REACTIVITY OF SINGLY-BENT ARYLDIAZENIDO COMPLEXES OF RHENIUM

by

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"REACTIVITY OF SINGLY-BENT ARYLDIAZENIDO COMPLEXES OF RHENIUM"

ABSTRACT

This thesis describes an investigation of the reactions displayed by the 3 electron-donor, singly-bent aryldiazenido ligand $N_2C_6H_4R'$ (where R' is a substituent) in $[CpRe(CO)_2(N_2C_6H_4R')][BF_4]$, with anionic or neutral nucleophiles X = I^-, Br^-, Cl^-, OCH_3^-, H^-, CH_3^-, Ph^-, OH^-, NH_3, $HNMe_2$, NMe_3, NEt_3, PPh_3 and $Ph_2PCH_2PPh_2$. Products are dependent on the nucleophile and suggest attack at different sites in the complex cation, illustrated by the following:

i) Iodide produced $[CpRe(CO)_2(N_2)]$ plus $[CpRe(CO)_2I_2]$ possibly due to attack at the *ipso* carbon on the aromatic ring attached to the nitrogen atom N(2) and at the metal center, respectively.

ii) Ammonia and amines yielded the carbamoyl complexes $[CpRe(CO)(CONR''_2)(N_2C_6H_4R')]$ (R" = H or alkyl) (attack at the CO ligand).

iii) $NaBH_4$ yielded the diazenes $[CpRe(CO)_2(NHNC_6H_4R')]$, but CH_3Li gave the N(2)-methylated hydrazido (2-) species $[CpRe(CO)_2\{NN(CH_3)C_6H_4R'\}]$. Low temperature ^1H-NMR experiments indicate that for $NaBH_4$, H^- also initially attacks at N(2) to give the hydrazido (2-) species $[CpRe(CO)_2\{NN(H)C_6H_4R'\}]$ (the kinetic product), which rearranges to the diazene (the thermodynamic product).

iv) The product formed with OH^-, depends upon the reaction conditions used, and three different products, the dinitrogen complex $[CpRe(CO)_2(N_2)]$, the hydroxycarbonyl complex, $[CpRe(CO)(COOH)(N_2C_6H_4R')]$ and the hydrido complex $[CpReH(CO)(N_2C_6H_4R')]$, could be isolated.

The X-ray crystal structure of one of the hydrazido (2-) complexes $[CpRe(CO)_2\{NN(CH_3)C_6H_4R'\}]$ (R' = p-OCH_3) formed in iii) shows that the hydrazido (2-) ligand is bound to the metal in the highly unusual bent geometry, with Re-N(1)-N(2) = 138.1(6)°.

Both the diazene and hydrazido (2-) derivatives can be protonated with HBF_4 to give the corresponding hydrazido (1-) species $[CpRe(CO)_2\{NHN(H)C_6H_4R'\}][BF_4]$ and $[CpRe(CO)_2\{NHN(CH_3)C_6H_4R'\}][BF_4]$; these exist in solution ($CDCl_3$) as two stereoisomers and an NMR study of their stereoisomerism is discussed.

The synthesis and characterization of a dinuclear complex containing a bridging aryldiazo ligand $[CpMo(CO)_2(\mu-N_2C_6H_4R)Re(CO)_2Cp]$ and a brief ^{15}N- NMR study of several compounds containing an aryldiazo ligand, are also presented.

To Paola

ACKNOWLEDGEMENTS

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Table of Contents

Chapter I - Diazo Complexes of Transition Metals: Structure and Reactivity

Chapter II - Aryldiazenido Complexes of Manganese and Rhenium: Synthesis, Characterization and Selected Chemical Reactions.

Chapter III - Aryldiazene, Arylhydrazido(2-) and Arylhydrazido(1-) Complexes of Rhenium

Chapter IV - Hydrazido(1-) Complexes of Rhenium: A ^{1}H-NMR Study of their Stereoisomerism

Chapter V - Hydrido and Hydroxycarbonyl Complexes of Rhenium

Appendix I - Bimetallic Aryldiazenido Complexes.
Synthesis and Characterization of
$[Cp(CO)_2Mo(\mu\text{-}N_2C_6H_4CH_3)Re(CO)_2Cp]$ 33

Appendix II - ^{15}N-Nuclear Magnetic Resonance Spectra of
Some Diazo Compounds of Rhenium

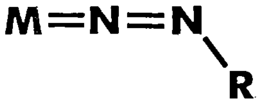
List of Tables

Table No. Page

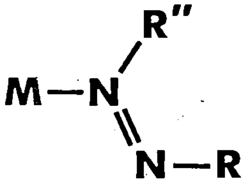
List of Figures

NOMENCLATURE AND STRUCTURE.

$M-N_2$ DINITROGEN



DIAZENIDO



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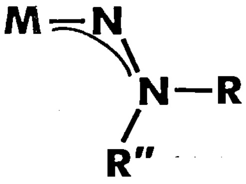
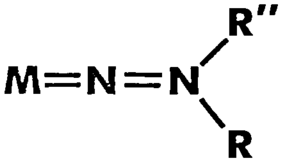


BENT HYDRAZIDO (2-)



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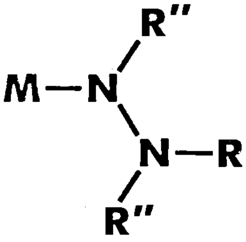
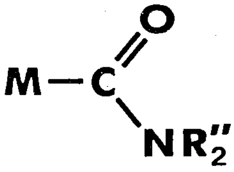


HYDRAZIDO (1-)



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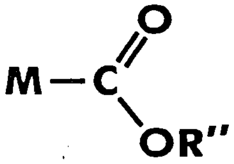
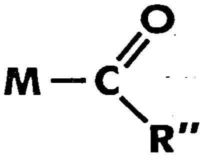


ALKOXYCARBONYL



ACYL

$\mathrm{M{-}COOH}$

HYDROXYCARBONYL

List of Abbreviations

bipy = 2,2'-bipyridyl

Bu^n = butyl, $C_4H_9^-$

Cp = η^5-cyclopentadienyl

das = ortho-phenylenebis(dimethylarsine)

diphos = bis(diphenylphosphine)methane ($Ph_2PCH_2PPh_2$)

dtc = dithiocarbamate (S_2CNMe_2)

dppe = 1,2-bis(diphenylphosphine)ethane ($Ph_2PCH_2CH_2PPh_2$)

dppm = bis(diphenylphosphine)methane

Et = ethyl, $C_2H_5^-$

Et_2O = diethyl ether

M = metal

Me = methyl, CH_3^-

NEt_2 = diethylamino

OMe = methoxy, OCH_3^-

Ph = phenyl, $C_6H_5^-$

PPP = $PhP(CH_2CH_2CH_2PPh_2)_2$

py = pyridine

pyz = pyrazolyl, cyclo-$C_3H_3N_2^-$

R = aryl

THF = tetrahydrofuran

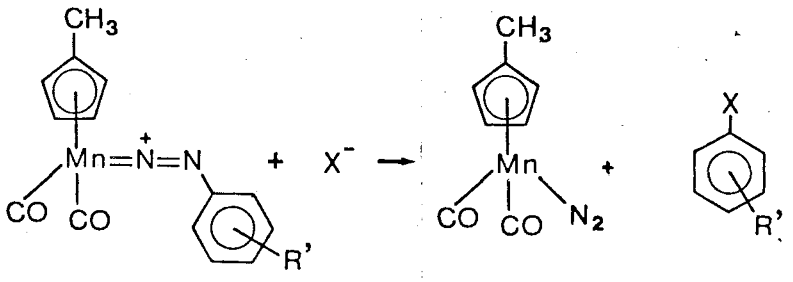
CHAPTER I

DIAZO COMPLEXES OF TRANSITION METALS: STRUCTURE AND REACTIVITY.

1.1 Introduction

A continuing theme in the research being carried out in our laboratory has been the investigation of the properties of protonated, arylated and alkylated derivatives of dinitrogen coordinated to transition metals. In the long term it is believed that this knowledge will contribute to our understanding of how molecular nitrogen may be transformed into ammonia, hydrazine or organonitrogen compounds using transition metals.[1-4] The focus of current work has been the synthesis and structural characterization of complexes containing the aryldiazenido ligand (N_2R). Results from this laboratory, and many others, have established that the N_2R ligand is capable of binding in a variety of structural modes and has a close relationship to nitrosyl and dinitrogen ligands. The reactions of the N_2R ligand have received much less attention than the structural aspects.

The work reported in this thesis was stimulated principally as a result of earlier findings during the author's M.Sc. program[5-7], where it was observed that $[MeCpMn(CO)_2(N_2R)]^+$ displayed reactions not hitherto observed in N_2R chemistry. For example, it reacts with a series of nucleophiles X^- (X = Cl, Br, I, CN, SCN) to yield the dinitrogen complex $[MeCpMn(CO)_2(N_2)]$ (eq. 1).



(1)

These results and the scarce number of reports concerning the reactivity of aryldiazenido complexes appeared to warrant a study of the reactivity of these types of ligands in order to gain a better understanding of their chemistry.

This stimulated us to design a program in which the potentially more easily studied congener $[CpRe(CO)_2(N_2R)]^+$ would be synthesized and studied in order to explore the variety of reactions available to the N_2R ligand in this complex.

In this chapter, a brief review is presented, surveying our present knowledge of the structures and reactivity of alkyl and aryldiazenido complexes and the previously known organodiazo chemistry of rhenium. This is followed by an outline of the work to be presented in the remainder of this thesis.

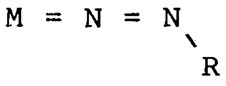
1.2 Structure of Alkyl and Aryldiazenido Ligands

Before any discussion of the different types of bonding found among N_2R ligands, it is necessary to explain the convention used in labelling the nitrogen atoms in this thesis. N^1 is the nitrogen atom bonded to the metal M and N^2 is the one bonded to the R group.

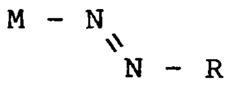
$$M - N^1 = N^2 - R$$

1.2.1 Terminal N_2R Ligands

Alkyl and aryldiazenido ligands can adopt several coordination geometries when attached to a transition-metal. Structural studies have shown that monodentate organodiazenido groups can adopt three basic structures called singly-bent (A), doubly-bent (B) and totally linear geometry (C).



(A)



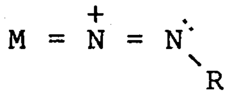
(B)

$$M - N \equiv N - R$$

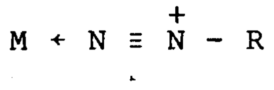
(C)

In the singly-bent case (A), the diazo ligand may be viewed as a three-electron donor terminal ligand and the bonding is described as σ-donation from an sp hybrid orbital on N^1 with strong π-back donation from filled d-orbitals on the metal into a p-orbital on N^1. Why?

A simple valence bond description of this type of complex is (1), where a $M - N^1 - N^2$ angle of approximately 180° and a $N^1 - N^2 - R$ angle close to 120°C are expected.[8]



(1)



$M \leftarrow N \equiv \overset{+}{N} - R$

(2)

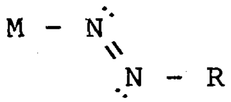
Examples of N^1 - N^2 - R angles intermediate between 180° and 120° may be expected depending upon the relative importance of the "singly-bent" (1) and the "linear" (2) formalisms to the electronic structure.[8]

This bonding mode is the more commonly found among terminal N_2R ligands and has been observed in numerous examples, such as $[Re(N_2Ph)Cl_2(PMe_2Ph)_3]$[9,36b] (ReNN = 173(2)°; NNR = 119(2)°), $[Fe(N_2Ph)(CO)_2(PPh_3)_2]^+$[10] (FeNN = 179.2(5)°; NNR = 124.2(6)°), $[MeCpMn(CO)_2(\underline{o}\text{-}N_2C_6H_4CF_3)]^+$[7] (MnNN = 171.8(8)°; NNR = 125.6(9)°) and $[CpW(CO)_2(N_2CH_3)]$[11] (WNN = 173.3(3)°; $NNCH_3$ = 116.5(4)°).

The experimental values for the NNR angles, close to 120° in these complexes, suggest the importance of backbonding in this type of geometry.

In the doubly-bent terminal structure (B), the aryldiazo ligand can be viewed as a one-electron donor (N_2R) radical or as a two-electron donor (N_2R^-) ligand, where the bonding is described as the overlap between a sp^2 orbital on N^1 with a hybrid orbital on the metal.

As a one-electron ligand, the aryldiazenido complex should posses an angle of 120° at both nitrogen atoms and the metal suffers a formal two-electron oxidation when this arises by bonding to the N_2R^+ ion (the N_2R^+ group acting as an electrophile).

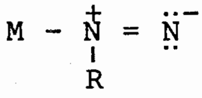


(3)

Although several complexes which are believed to contain the doubly-bent geometry (B) have been prepared, only three have been fully characterized by X-ray structural studies. These are $[Ru(N_2Ph)Cl(PPP)]^{+}$[12] (RuNN = 125.1(6)°; NNR = 118.9(8)°), $[IrCl_2(CO)(PPh_3)_2(\underline{o}\text{-}N_2C_6H_4NO_2)]$[13] (IrNN = 115(3)°; NNR = 115(3)°) and $[PtCl(PEt_3)_2(\underline{o}\text{-}N_2C_6H_4F)]$[14] (PtNN = 118(2)°; NNR = 118(2)°). A complex possessing an aryldiazo ligand coordinated to the mètal in a geometry intermediate between the singly (A) and doubly-bent (B) geometry, is also known. $[IrCl(N_2Ph)(PMePh_2)_3][PF_6]$[15] (IrNN = 155.2(7)°; NNR = 118.8(8)°).

The totally linear structure (C) has been observed only once, in a ruthenium diazo borane derivative $RuH_2(N_2B_{10}H_8SMe_2)(PPh_3)_3$[16] (RuNN = 175.9(6)°; NNB = 172.7(8)°).

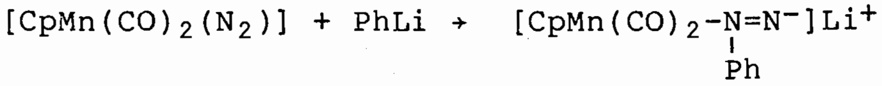
Very recently, Sellmann and Weiss[17] have prepared a monodentate aryldiazenido complex of a new type (D), from the



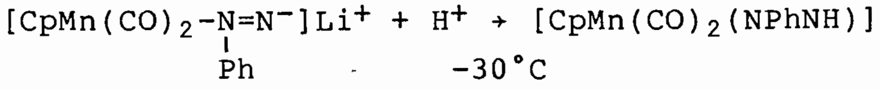
$$M-\overset{+}{\underset{R}{N}}=\ddot{\underset{\cdot\cdot}{N}}{}^{-}$$

(D)

reaction of the dinitrogen complex $CpMn(CO)_2(N_2)$ with organolithium reagents LiR (R = CH_3, Ph) (eq. 2); this ligand is susceptible to electrophilic attack at the terminal nitrogen atom, as in the reaction with protons at −30°C to give N^1-substituted diazene derivatives (eq. 3)



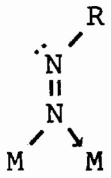
$$[CpMn(CO)_2(N_2)] + PhLi \rightarrow [CpMn(CO)_2-\underset{Ph}{N}=N^-]Li^+ \qquad (2)$$



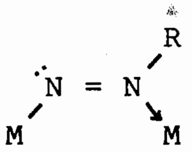
$$[CpMn(CO)_2-\underset{Ph}{N}=N^-]Li^+ + H^+ \xrightarrow[-30^\circ C]{} [CpMn(CO)_2(NPhNH)] \qquad (3)$$

1.2.2 Bridging N_2R Ligands

The aryldiazo ligand may, in principle, bridge two metal atoms in single-nitrogen (E) or double-nitrogen (F) bridged structures. In both cases, the ligand supplies three-electrons to the system.



(E)

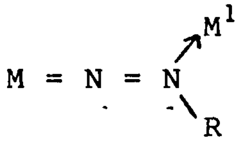


(F)

These types of complexes are extremely rare; only seven examples have been reported[18-24], of which but four have been fully characterized by X-ray structural analysis. These are $[Mn(N_2Ph)(CO)_4]_2$[18], $[Ir_2O(\underline{o}\text{-}N_2C_6H_4NO_2)(PPh_3)_2(NO)_2]^+$[20], $[Pd_2(dppm)_2(\underline{o}\text{-}N_2C_6H_4CF_3)Cl_2]^+$[21] and $[HOs_3(CO)_{10}(\underline{p}\text{-}N_2C_6H_4CH_3)]$[24].

In all cases, the aryldiazenido ligand adopts the single-nitrogen bridged mode (E). No example of mode (F) for an aryldiazo ligand has been found yet.

The bridging mode (G) found in the alkyldiazo complex $Cp(CO)_2W(NNCH_3)Cr(CO)_5$[25,26], has been found also to occur in the aryldiazo complex $Cp(CO)_2Mo(p\text{-}N_2C_6H_4CH_3)Re(CO)_2Cp$ and it will be discussed in detail in Appendix I.



(G)

1.3 Reactivity: A Literature Survey

In some instances, reagents which might have been expected to attack the organodiazo group are found not to. These reactions, together with those which lead to attack of the diazo group, are now reviewed.

1.3.1 Metathesis

This is simply an exchange of the counteranion and occurs,for example, when $[Fe(CO)_2(PPh_3)_2(N_2C_6H_4R')][BF_4]$ (R' = p-Br, o-CF_3) react with KI to give the products $[Fe(CO)_2(PPh_3)_2(N_2C_6H_4R')][I]$.[5,27]

1.3.2 Coordination of a donor at metal center (M) with no structural isomerism of MN_2Ar

This may be coordination of the donor to a vacant site, or replacement of another ligand.

The coordinatively unsaturated 16-electron complex $[IrCl(PPh_3)_2(N_2Ph)]^+$ reacts with one equivalent of LiCl to give the neutral 18-electron species $[IrCl_2(PPh_3)_2(N_2Ph)]$.[28]

The complexes $[M(das)(CO)_3(\underline{p}\text{-}N_2C_6H_4R')]^+$ (M = Mo, R' = F; M = W, R' = OMe) react with halide ions to give the neutral species $[M(das)(CO)_2X(\underline{p}\text{-}N_2C_6H_4R')]$.[29]

The cationic bridging species $\{[Ir(CO)_2(PPh_3)]_2\mu\text{-}(N_2C_6H_4R')\mu\text{-}(SO_2)\}^+$ reacts with X^- (X = Cl, Br, I) to yield the neutral bridging compound $\{[Ir(CO)(PPh_3)]_2\mu\text{-}(X)\mu\text{-}(N_2C_6H_4R')\mu\text{-}(SO_2)\}$.[23]

1.3.3. Coordination of a donor at M accompanied by isomerism of MN_2Ar

To compensate the further coordination of a two-electron donor at the metal center, the three-electron singly-bent MN_2R

group (A) converts to a doubly-bent one-electron ligand (B). The complexes $[M(CO)_2(PPh_3)_2(N_2Ph)]^+$ react with X^- (X = F, Cl, Br, I, NCO, N_3, HCO_3, CH_3COO; M = Os) and (X = Cl, Br, I, NCO; M = Ru) to give the neutral six-coordinated doubly-bent phenyldiazenido compounds $[MX(CO)_2(PPh_3)_2(N_2Ph)]$.[30]

The substance $[Mn(CO)_4(\mu\text{-}N_2Ph)]_2$, which contains a bridging aryldiazo group, reacts with $nPPh_3$ (n = 1 or 2) to give the complexes $[Mn(CO)_{4-n}(PPh_3)_n(N_2Ph)]$. In this case, the bridging diazo group converts to a three-electron donor terminal aryldiazenido ligand (singly-bent).[18]

1.3.4 Loss of the Organodiazo Group

A number of reactions are known which occur with the complete replacement of the organodiazo group. At this time, it is not clear what the likely mechanism is in each case, but possibilities include attack of the nucleophile at the metal (and the resulting doubly-bent aryldiazo ligand then dissociating) or attack at the diazo group (as in 1.3.7) to give a dinitrogen ligand which is easily dissociated.

$[RuCl(bipy)_2(\underline{p}\text{-}N_2C_6H_4OCH_3)]^{2+}$ was reported to react with excess of KI to give $[Ru(bipy)_2I_2]$, p-iodoanisole and N_2 gas.[31]

Reaction of $[Os(CO)_2(PPh_3)_2(N_2Ph)]^+$ with $NaBH_4$ gives $[OsH_2(CO)_2(PPh_3)_2]$. The ruthenium analog reacts with $NaBH_4$ forming an uncharacterized insoluble yellow residue, but when the same reaction was carried out in the presence of PPh_3, the complex $[RuH_2(CO)(PPh_3)_3]$ was isolated in good yield.[30]

The iridium complex $[IrCl(PPh_3)_2(N_2Ph)]^+$ reacts with $NaBH_4$ and Cl_2 to give the species $[IrH_3(PPh_3)_2]$ and $[IrCl_4(PPh_3)_2]$ respectively[28]; it also reacts with $[NO][PF_6]$ to give the complex $[IrCl(NO)(PPh_3)_2]^+$. This exchange reaction with NO^+ also has been observed with the aryldiazenido compound $[Fe(CO)_2(PPh_3)_2(N_2Ph)]^+$ to give the corresponding nitrosyl derivative $[Fe(CO)_2(PPh_3)_2(NO)]^+$[32], and with a related rhenium diazo compound $[ReCl_2(N_2COPh)(PPh_3)_2]$ which yielded $[ReCl_2(NO)(PPh_3)_2]$.[33]

The loss of a bridging aryldiazo group has also been observed. The "A-frame" complex $[Pd_2(dppm)_2Cl_2\mu\text{-}(N_2R)]^+$ reacts with HCl or Cl^- to give $[Pd(dppm)Cl_2]$.[21]

1.3.5 Attack at an Ancillary Ligand

Connelly *et al*[34], reported that the reaction of $[(C_6Me_6)Cr(CO)_2(\textit{p}\text{-}N_2C_6H_4R')]^+$ (R' = H, OMe, NO_2) with $NaBH_4$ in THF, afforded the neutral cyclohexadienyl derivatives $[(C_6Me_6H)Cr(CO)_2(\textit{p}\text{-}N_2C_6H_4R')]$; no nucleophilic attack at the diazo ligand was observed.

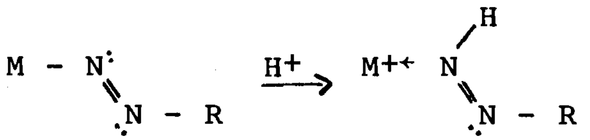
Other examples of this type of reactivity will be discussed in this thesis.

1.3.6 Electrophilic Attack at Nitrogen

This has been by far the most studied reaction, usually in connection with protonations (or alkylations).

Previous studies have shown that simple protonation or alkylation of organodiazo ligands can occur at N^1 or at N^2.

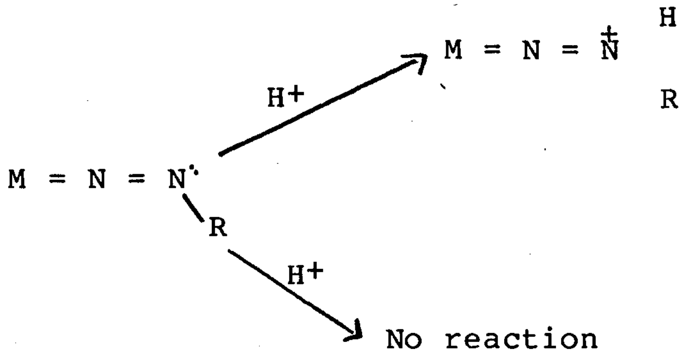
Doubly-bent diazo ligands so far always protonate at N^1, which seems to be the more basic nitrogen atom (this is supported by the ^{15}N chemical shift of this particular nitrogen atom; see Appendix II) (eq. 4). The ligand so formed is called an organodiazene.



(4)

This type of reactivity is exhibited by the complexes $[PtCl(PEt_3)_2(N_2Ph)]$[14], $[IrCl_2(CO)(PPh_3)_2(N_2Ph)]$[13] and $[RuCl(CO)_2(PPh_3)_2(N_2Ph)]$.[35]

Singly-bent diazenido ligands are expected to protonate (or alkylate) at N^2, due to the presence of a lone pair (more basic), but may not protonate at all, depending on the nature of the metal and co-ligands (eq. 5). The complexes $[ReCl_2(NH_3)(PMe_2Ph)(N_2Ph)]$[36], $[W(dtc)_3(N_2Ph)]$[37] and $[Mo(dtc)_3(\underline{p}\text{-}N_2C_6H_4R')]$[38] are examples of protonation at N^2.

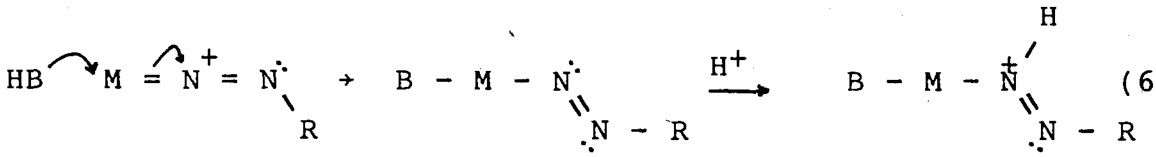


(5)

The molybdenum complexes $[Mo(dtc)_3(\underline{p}\text{-}N_2C_6H_4R')]$ can react with weakly coordinating acids like HBF_4 to yield the hydrazido (2-) species $[Mo(dtc)_3(\underline{p}\text{-}NNHC_6H_4R')][BF_4]$ or react with hydrohalic acids (HCl, HBr) to give $[Mo(dtc)_3(\underline{p}\text{-}NNHC_6H_4R')X]$ (X = Cl, Br). Also, they react with alkyl or arylhalides R"X (R"X = MeI, PhBr, etc.) to yield $[Mo(dtc)_3(\underline{p}\text{-}NNR''C_6H_4R')][X]$.[38] The X-ray structural analysis of $[Mo(dtc)_3(NNEtPh)][BPh_4]$ confirms that alkylation takes place on the nitrogen remote from the metal (N^2).[39]

The complexes $[ReCl_2(CO)(PMe_2Ph)_2(N_2Ph)]$ and $[OsCl_3(PPh_3)_2(N_2Ph)]$[30], do not protonate.

It has been observed, that certain singly-bent aryldiazenido complexes apparently protonate at N^1. These protonations were always accompanied by coordination of the counteranion even when weakly coordinating acids were used. Obviously, these are examples similar to those discussed in 1.3.3. In these reactions, coordination of the counteranion occurs first with concomitant isomerization of the singly-bent aryldiazo ligand to a doubly-bent one, and it is this ligand which is protonated (eq. 6).



(6)

Examples of complexes which show this type of reactivity are $[Re(CO)_2(PPh_3)_2(N_2Ph)]$[40], $[OsH(CO)(PPh_3)_2(N_2Ph)]$[30] and $[Os(CO)_2(PPh_3)_2(N_2Ph)]^+$.[30]

The ruthenium analog $[Ru(CO)_2(PPh_3)_2(N_2Ph)]^+$ reacts similarly with HI to give the monocationic diazene complex $[RuI(CO)_2(PPh_3)_2(NHNPh)]^+$.[41] It was claimed that the ruthenium aryldiazenido complex also reacts with HBF_4 to give the dicationic diazene derivative $[Ru(CO)_2(PPh_3)_2(NHNPh)]^{2+}$ (protonation at N^1), but no strong evidence (such as ^{15}N labelling) that protonation indeed had occurred at N^1 was provided.

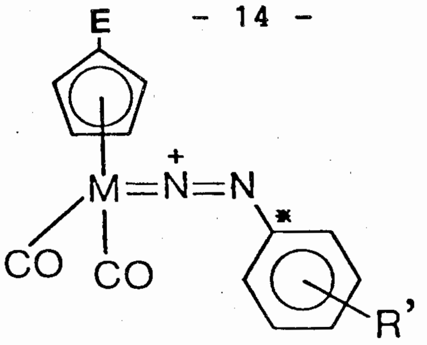
1.3.7 Nucleophilic Attack at Nitrogen

This is unknown in the literature, but we have been successful in observing this type of reactivity. It will be discussed in Chapter III.

1.3.8 Nucleophilic Attack at the ipso Carbon (C*)

No examples of this reaction are known except those discovered in our laboratory.[5-7]

Complexes of manganese (E = Me) and rhenium (E = H) of the type (4) show an extraordinary reactivity towards nucleophiles to yield the corresponding dinitrogen complexes $MeCpMn(CO)_2(N_2)$ and $CpRe(CO)_2(N_2)$ under very mild conditions.



(M=Mn,Re)
(E= Me,H)

(4)

Synthesis of these and similar dinitrogen compounds of manganese and rhenium have been described previously,[42-45] but they were prepared under very strong conditions, such as replacement of a labile ligand by dinitrogen under high pressure or by oxidation of a hydrazine ligand.

1.4 Diazo chemistry of Rhenium

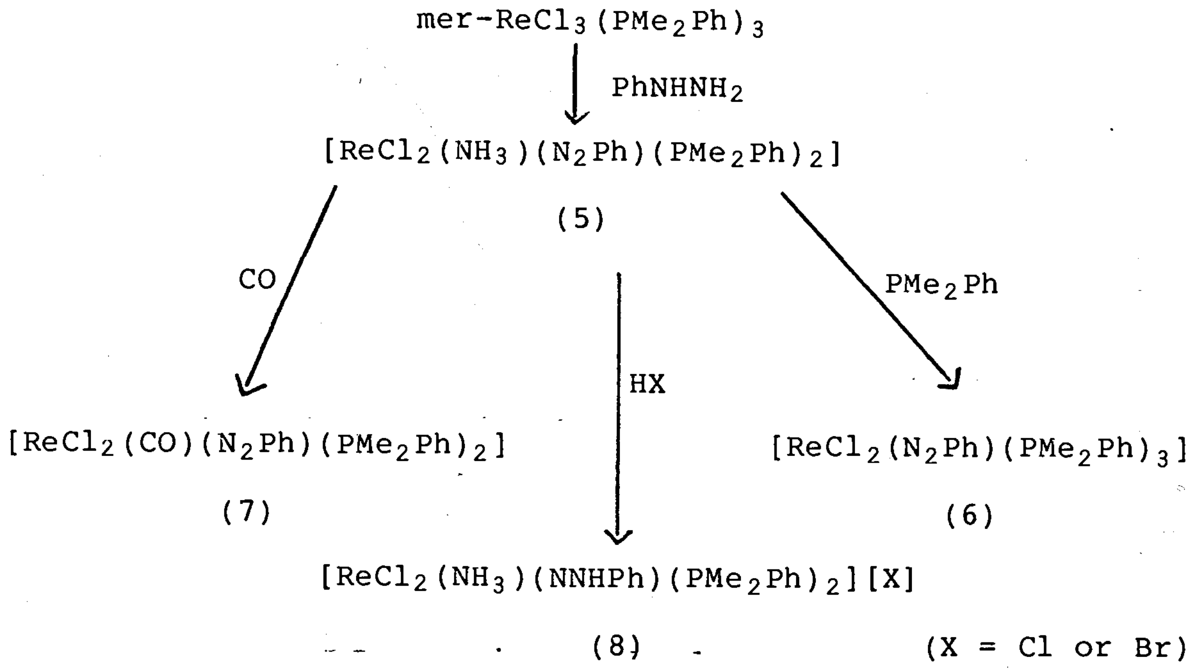
The previously reported diazo chemistry of this third-row transition-metal is confined to a few examples of aryldiazenido complexes, plus some other organometallic compounds containing diazo ligands other than aryldiazo ligands.

The complex mer-$[ReCl_3(PMe_2Ph)_3]$ reacts with phenylhydrazine to give two aryldiazenido derivatives, $[ReCl_2(NH_3)(N_2Ph)(PMe_2Ph)_2]$ (5) and $[ReCl_2(N_2Ph)(PMe_2Ph)_3]$ (6). X-ray structural studies reveal that the aryldiazo ligand adopts the singly-bent coordination mode.[9,36]

Compound (5) reacts with one mole of PMe_2Ph to yield (6) and reaction with carbon monoxide yielded the complex $[ReCl_2(CO)(N_2Ph)(PMe_2Ph_2)]$ (7), with the aryldiazo ligand presumed to be bonded in a singly-bent manner.

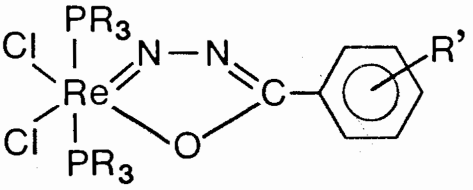
Compound (5) can be protonated with HCl or HBr to give the hydrazido (2-) complex $[ReCl_2(NH_3)(NNHPh)(PMe_2Ph)_2][X]$ (8); all these reactions are shown in Scheme I.

SCHEME I

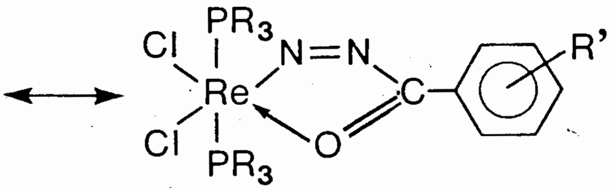


The hydride complex $ReH(CO)_2(PPh_3)_3$ reacts with benzenediazonium salt to give the aryldiazenido complex $[Re(CO)_2(PPh_3)_2(N_2Ph)]$.[40] This complex shows a ν(NN) frequency of 1536 cm^{-1}, which is the lowest yet recorded for a singly-bent aryldiazo ligand. The substances $[ReCl(CO)_2(NHNPh)(PPh_3)_2]$ and $[ReCl_2(NO)(NHNPh)(PPh_3)_2]$ are two other examples of diazo compounds of rhenium.[37]

Diazo derivatives, where the diazo moiety constitutes part of a five-membered ring (9), have been prepared from the reactions of $[ReOCl_3(PR_3)_2]$ with monoaroylhydrazine or 1,2-diaroylhydrazine.[33]

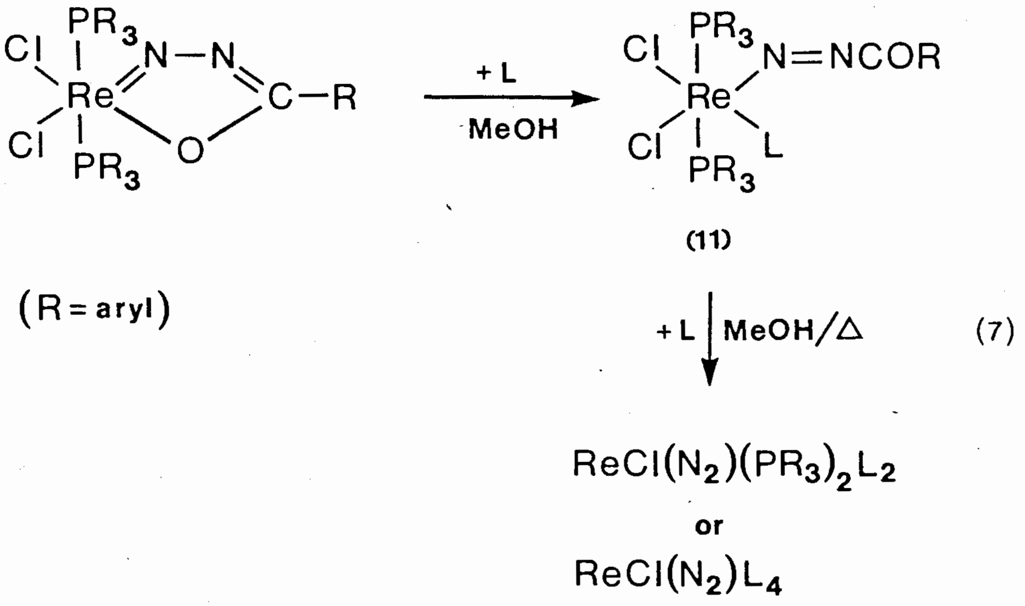


(9)



(10)

From spectroscopic evidence, these compounds have been described as aroylhydrazido (3-) complexes, (9), rather than compounds containing a chelating aroyldiazenido ligand (10).[33] The chelate ring is opened by a number of nucleophiles (L) to give aroyldiazenido complexes of general formula (11).[33] With certain ligands (L = CO[46], phosphines[47]) in boiling methanol, this reaction proceeds further to give neutral dinitrogen complexes (eq. 7).



Acetyldiazenido and benzoyldiazenido derivatives of rhenium can also be prepared by reaction of the dinitrogen complexes $[ReCl(N_2)(PMe_2Ph)_4]$ or $[ReCl(N_2)(PMe_2Ph)_3(py)]$ with acetyl or benzoyl chloride RCOCl (R = Me, Ph).[48]

1.5 Thesis

As mentioned in the introduction, this research project was stimulated principally by the extraordinary reactivity that had been observed to be exhibited by cyclopentadienyl dicarbonyl aryldiazenido complexes of manganese towards nucleophilic agents. This thesis extends these observations to include the more easily studied rhenium analogs, and represents an attempt to understand the factors which are important in determining the outcome of these types of reactions, and to examine their generality.

For example, we wanted to study the effect of changing the nature and position of the substituents in the benzene ring on the reactivity of these complexes towards different nucleophiles.

These reactions could, in principle, be visualized to occur at a choice of possible sites, including the metal center, N^1 (to give diazene species), N^2 (to give hydrazido (2-) derivatives), the aryl ring (to give dinitrogen complexes) or the CO ligands (to give formyl, acyl, ... etc.).

In Chapter II, a new synthetic route leading to the aryldiazenido complexes of rhenium $[CpRe(CO)_2(N_2R)][BF_4]$ will be described, together with their full characterization, and selected new chemical reactions exhibited by them. For example, it was found that they react with liquid ammonia to yield carbamoyl complexes (eq. 8).

$$[CpRe(CO)_2(N_2R)]^+ \xrightarrow{NH_3(\ell)} [CpRe(CO)(CONH_2)(N_2R)] \qquad (8)$$

The synthesis and characterization of aryldiazene, arylhydrazido (2-) and hydrazido (1-) complexes of rhenium derived from the aryldiazenido complexes will constitute Chapter III. This will include a description of the X-ray structures of two of these, the hydrazido (2-) complex $[CpRe(CO)_2(p\text{-}NN(CH_3)C_6H_4OCH_3)]$ and the hydrazido (1-) complex $[CpRe(CO)_2\{\underline{p}\text{-}N(H)N(CH_3)C_6H_4CH_3\}][BF_4]$, both determined for us in Professor F.W.B. Einstein's laboratory.

The ^{1}H-NMR of the hydrazido (1-) derivatives showed that these molecules are non-rigid and that two conformers are present in $CDCl_3$ solution at room temperature. A NMR study of their stereoisomerism will be presented in Chapter IV.

It was further discovered that the aryldiazenido complexes $[CpRe(CO)_2(N_2R)]^+$ react with OH^- to give stable hydroxycarbonyl and hydrido species. This work is covered in Chapter V.

In addition to the above mentioned work on the reactions of $[CpRe(CO)_2(N_2R)]^+$ and characterization of the products, two further studies were carried out, which are reported in appendices.

The synthesis and characterization of complexes containing a bridging aryldiazo ligand are discussed in Appendix I, together with the crystal structure of the complex $[CpMO(CO)_2(p\text{-}NNC_6H_4CH_3)Re(CO)_2Cp]$. Finally, a brief ^{15}N-NMR study of a series of aryldiazo complexes of rhenium is presented in Appendix II.

CHAPTER II

ARYLDIAZENIDO COMPLEXES OF MANGANESE AND RHENIUM: SYNTHESIS, CHARACTERIZATION AND SELECTED CHEMICAL REACTIONS

2.1 Introduction

As was mentioned in the introduction of Chapter I, aryldiazenido complexes of manganese $[(MeCp)Mn(CO)_2(N_2C_6H_4R')][BF_4]$ (R' = o-CF_3, o-F, H) showed an extraordinary reactivity towards nucleophiles (Cl^-, Br^-, I^-, CN^-, SCN^-) to give the dinitrogen complex $[(MeCp)Mn(CO)_2(N_2)]$.

These novel and interesting results stimulated us to explore the chemistry of these manganese systems, especially the reactivity concerning the N_2R ligand, towards a much larger number of nucleophiles. We also wanted to extend this study to the potentially more stable congener $[CpRe(CO)_2(N_2C_6H_4R')][BF_4]$ and compare its chemistry with the manganese system, as well as investigate the effect of changing the nature and position of the substituents on the aromatic ring in the N_2R ligand, on the chemistry of these systems.

In this chapter, the synthesis and characterization of some new aryldiazenido complexes of manganese and rhenium are described, together with their reactivity towards several nucleophiles (Cl^-, Br^-, I^-, OMe^-, NH_3, NH_2R, NHR_2, PPh_3 and diphos).

These reactions have been grouped together, since they do not directly involve the N_2R ligands, except in the halide cases.

2.2 Synthesis

The aryldiazenido complexes of manganese of general formula $[(MeCp)Mn(CO)_2(N_2R)][BF_4]$ (1: R = C_6H_4X with X = (a) o - CF_3, (b) p-CH_3; R = $C_6H_3X_2$ with X_2 = (c) 3,5 dimethyl, (d) 2,6 dichloro, (e) 2,6 dinitro) were prepared as reported previously[5-7] from the reaction of the corresponding arenediazonium tetrafluoroborate salt with $[(MeCp)MnH(CO)_2SiPh_3]$.[49]

Initially, the aryldiazenido complexes of rhenium were prepared by reaction of arenediazonium salts with the triphenylsilyl derivative $[CpReH(CO)_2SiPh_3]$.[50] This is a very lengthy synthesis, giving poor yields of the desired products and several derivatives could not be prepared by this route. A new method was developed for the synthesis of these complexes; reactions of arenediazonium salts with the THF derivative of rhenium $[CpRe(CO)_2THF]$[45,51] (which can be isolated as a crystalline solid) gave the complexes $[CpRe(CO)_2(N_2R)][BF_4]$ (2: R = C_6H_4X with X = (a) p-CH_3, (b) p-OCH_3, (c) o-OCH_3, (d) p-NEt_2, (e) o- CF_3, (f) H; R = $C_6H_3X_2$ with X_2 = (g) 2,6 dimethyl, (h) 3,5 dimethyl) in better than 95% yield in 10 minutes.

This method could not be used for manganese, because its THF derivative $[(MeCp)Mn(CO)_2THF]$ cannot be isolated as a solid and when this compound is reacted with diazonium salts *in situ*, instantaneous decompositon of the diazonium salt occurs. Probably this decomposition is catalyzed by secondary products produced during the photochemical generation of the THF adduct, since we now know the aryldiazenido complexes to be stable in THF.

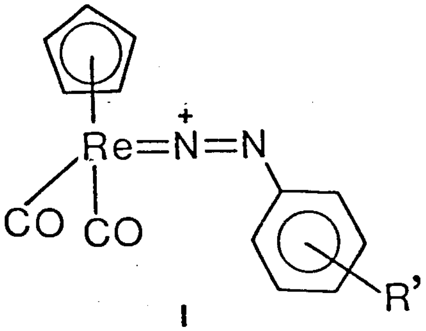
2.3 Characterization

All the above compounds were fully characterized by elemental analysis, IR and ^{1}H-NMR. The infrared spectra were taken in silver chloride or calcium fluoride cells, since some of these complexes reacted with KBr or NaCl windows to give the corresponding dinitrogen complexes $[(MeCp)Mn(CO)_2(N_2)]$[5-7] and $[CpRe(CO)_2(N_2)]$.

The IR spectra of these cationic complexes showed two strong ν(CO) bands and one strong and broad ν(NN) band (see Table I). A typical spectrum of this type of complex is shown in Figure 1.

The two ν(CO) absorptions that occur at 2090 and 2030 cm^{-1} (CH_2Cl_2) in the o-CF_3 derivative 2e are lowered when the benzene ring is substituted by more electron-releasing groups, to as much as 2058 and 1995 cm^{-1} (CH_2Cl_2) in the p-NEt_2 derivative 2d. The value of ν(NN), which is 1760 cm^{-1} (CH_2Cl_2) in 2e, is simultaneously raised in these other derivatives, becoming as high as 1836 cm^{-1} (CH_2Cl_2) in the 2,6 dimethyl derivative 2g. The assignment of ν(NN) has been confirmed by ^{15}N isotopic substitution at the metal-bound nitrogen position, N^1, in 1b, 1f,[52] 2a, 2b, 2d, which causes an observed lowering by 30-36 cm^{-1}. Steric, as well as electronic, effects evidently influence the increase in ν(NN) in 2,6-disubstituted derivatives as indicated by the high values (ca. 1824-1828 cm^{-1}) of the manganese compounds 1d and 1e having electron-withdrawing -Cl and $-NO_2$ groups in these positions.

From the similarities in spectroscopic (IR) and chemical properties, the rhenium aryldiazenido complexes are clearly structurally similar to the manganese ones and, in particular, possess aryldiazenido ligands coordinated in the singly-bent geometry I (cf. X-ray structure for 1a).[7]



I

^{1}H-NMR data gave additional confirmatory evidence of the formulation of 1 and 2 as aryldiazenido complexes. An example of the ^{1}H-NMR spectrum of an aryldiazenido complex of rhenium, 2b, is shown in Figure 2.

Table I. Infrared ν(CO) and ν(NN) Data for Rhenium and Manganese Aryldiazenido Complexes.

Compound		Solvent[a]	ν(CO)[b]	ν(NN)[b]
$[\mathrm{MeCpMn(CO)_2}(\underline{o}\text{-}\mathrm{N_2C_6H_4CF_3})][\mathrm{BF_4}]$	(<u>1a</u>)	$CHCl_3$	2090vs, 2045vs	1795vs(br)
		Acetone	2083vs, 2041vs	c
$[\mathrm{MeCpMn(CO)_2}(\underline{p}\text{-}\mathrm{N_2C_6H_4CH_3})][\mathrm{BF_4}]$	(<u>1b</u>)	$CHCl_3$	2090vs, 2044vs	1794vs(br)
		Acetone	2085vs, 2040vs	c
$[\mathrm{MeCpMn(CO)_2}\{3,5\text{-}\mathrm{N_2C_6H_3(CH_3)_2}\}][\mathrm{BF_4}]$	(<u>1c</u>)	CH_2Cl_2	2086vs, 2042vs	1812vs(br)
		Acetone	2085vs, 2043vs	c
$[\mathrm{MeCpMn(CO)_2}\{2,6\text{-}\mathrm{N_2C_6H_3Cl_2}\}][\mathrm{BF_4}]$	(<u>1d</u>)	CH_2Cl_2	2095vs, 2048vs	1824vs(br)
		Acetone	2090vs, 2045vs	c
$[\mathrm{MeCpMn(CO)_2}\{2,6\text{-}\mathrm{N_2C_6H_3(NO_2)_2}\}][\mathrm{BF_4}]$	(<u>1e</u>)	CH_2Cl_2	2105vs, 2060vs	1828vs(br)
		Acetone	2104vs, 2062vs	c
$[\mathrm{CpRe(CO)_2}(\underline{p}\text{-}\mathrm{N_2C_6H_4CH_3})][\mathrm{BF_4}]$	(<u>2a</u>)	CH_2Cl_2	2080vs, 2021vs	1769vs(br) (1733vs)[d]
		Acetone	2075vs, 2018vs	c
$[\mathrm{CpRe(CO)_2}(\underline{p}\text{-}\mathrm{N_2C_6H_4OCH_3})][\mathrm{BF_4}]$	(<u>2b</u>)	CH_2Cl_2	2078vs, 2020vs	1770vs(br) (1735vs)[d]
		Acetone	2078vs, 2012vs	c
$[\mathrm{CpRe(CO)_2}(\underline{o}\text{-}\mathrm{N_2C_6H_4OCH_3})][\mathrm{BF_4}]$	(<u>2c</u>)	CH_2Cl_2	2070vs, 2010vs	1790vs(br)
		Acetone	2062vs, 2005vs	c

Table I, continued

Compound		Solvent[a]	ν(CO)[b]	ν(NN)[b]
$[CpRe(CO)_2\{p\text{-}N_2C_6H_4N(C_2H_5)_2\}][BF_4]$	(2d)	CH_2Cl_2	2058vs, 1995vs	1762vs(br) (1732vs)[d]
		Acetone	2060vs, 1990vs	c
$[CpRe(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$	(2e)	CH_2Cl_2	2090vs, 2030vs	1760vs(br)
		Acetone	2082vs, 2023vs	c
$[CpRe(CO)_2(N_2C_6H_5)][BF_4]$	(2f)	CH_2Cl_2	2075vs, 2016vs	1768vs(br) (1740vs)[e]
		Acetone	2073vs, 2015vs	c
$[CpRe(CO)_2\{2,6\text{-}N_2C_6H_3(CH_3)_2\}][BF_4]$	(2g)	CH_2Cl_2	2070vs, 2000vs	1836vs(br)
		Acetone	2068vs, 1995vs	c
$[CpRe(CO)_2\{3,5\text{-}N_2C_6H_3(CH_3)_2\}][BF_4]$	(2h)	CH_2Cl_2	2080vs, 2024vs	1775vs(br)
		Acetone	2082vs, 2022vs	c

a) Measured in CaF_2 cells; some of the solutions react with alkali halide windows (ref. 4).

b) Frequencies in cm^{-1}. Abbreviations: vs, very strong; br, broad; MeCp, $\eta^5\text{-}CH_3C_5H_4$; Cp, $\eta^5\text{-}C_5H_5$.

c) Band obscured by solvent.

d) $\nu\ (^{15}N^{14}N)$.

e) $\nu\ (^{14}N^{15}N)$.

Figure 1

IR spectrum (CH_2Cl_2) of the Aryldiazenido Complex $[CpRe(CO)_2(p\text{-}N_2C_6H_4CH_3)][BF_4]$ (2a)

——— $\nu(^{14}N^{14}N)$

----- $\nu(^{15}N^{14}N)$

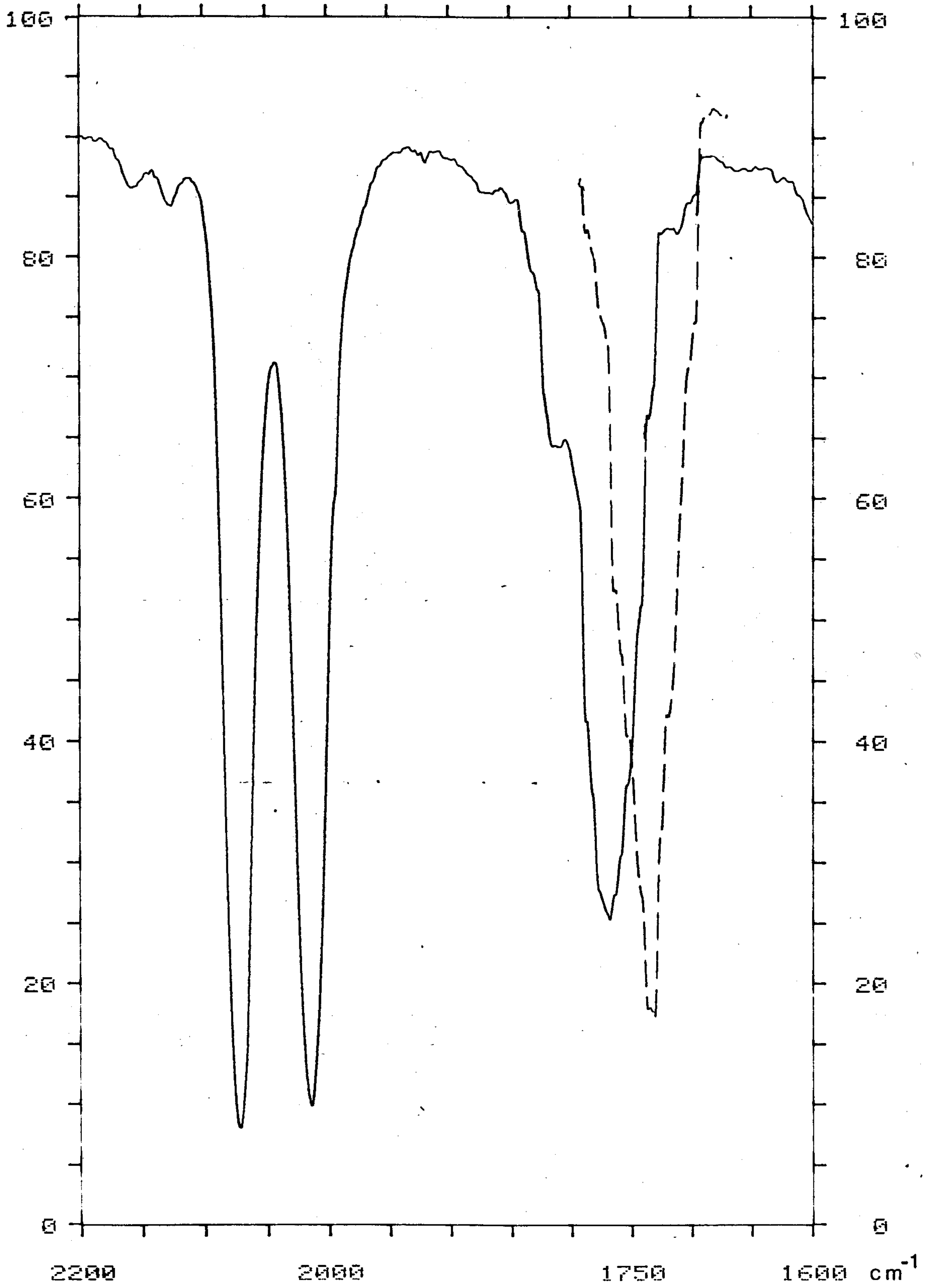
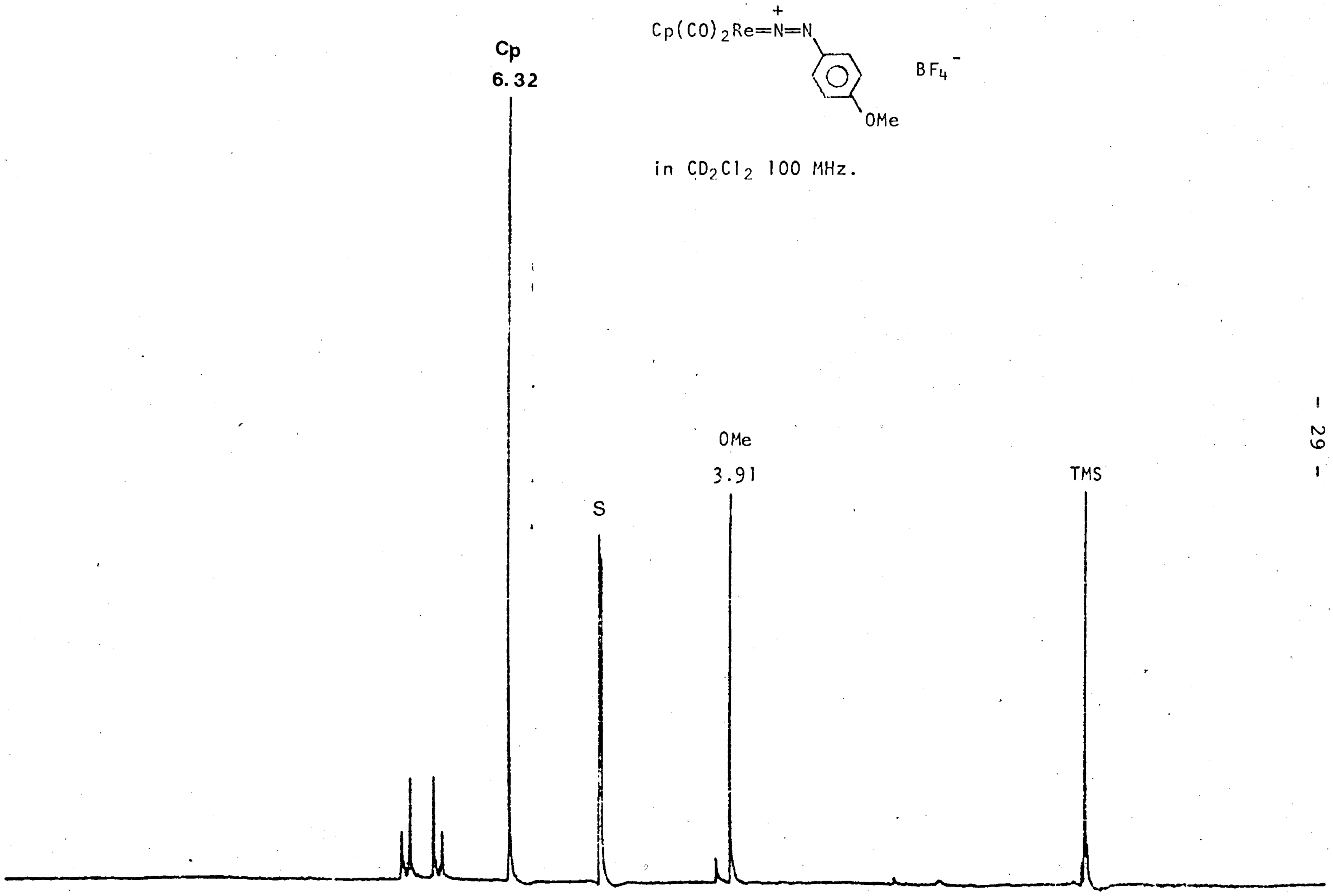

100
80
60
40
20
0
100
80
60
40
20
0
2200
2000
1750
1600 cm^{-1}

Figure 2

^{1}H-NMR (CD_2Cl_2) Spectrum of $[CpRe(CO)_2(\underline{p}\text{-}N_2C_6H_4OCH_3)][BF_4]$ (2b) (at 100 MHz).


Cp(CO)$_2$Re=N=N
+
OMe
BF$_4^-$
in CD$_2$Cl$_2$ 100 MHz.
Cp
6.32
S
OMe
3.91
TMS

2.4 Chemical Reactions

2.4.1 Reactions with Halides (X^-)

(a) Manganese: $[(MeCp)Mn(CO)_2(N_2R)][BF_4]$

It has been shown previously[5-7], that this type of aryldiazenido complex of manganese (R = o-CF_3, o-F, H) reacts with a series of nucleophiles X^- (X = Cl, Br, I, CN, SCN) in acetone to give $[\eta^5-(CH_3C_5H_4)Mn(CO)_2(N_2)]$, 3. These reactions occurred under extremely mild conditions (even in the solid state).

$$\underset{\underline{1}}{[(MeCp)Mn(CO)_2N_2R]^+} + X^- \rightarrow \underset{\underline{3}}{(MeCp)Mn(CO)_2N_2} + RX \qquad (9)$$

The sterically hindered 2,6-disubstituted derivatives (1d, dichloro, 1e, dinitro) reacted with NaI and KBr in solution (acetone) much faster as compared with 1a to give $[(MeCp)Mn(CO)_2(N_2)]$.

The presence of two electron-releasing groups in the 3 and 5 positions (1c, dimethyl) slowed the reaction, but the formation of 3 was still observed.

The para-methyl derivative (1b) did not react with NaI or KBr, and the starting materials were recovered unchanged after four hours.

The rate of the reaction therefore, seems to be very sensitive to the nature and position of the substituents in the benzene ring. Qualitatively speaking, these rates follow the order 2,6 dinitro ≈ 2,6 dichloro > o-CF_3 > 3,5 dimethyl >>> p-CH_3.

The only other product formed during each reaction was the corresponding iodo or bromo substituted arene IC_6H_4R', BrC_6H_4R', or $IC_6H_3R'_2$, $BrC_6H_3R'_2$. These were identified by GC-MS analysis and ^1H-NMR.

By comparison with the rhenium system, to be discussed next, the complexes $[(MeCp)Mn(CO)_2X_2]$ (X = I, Br) or the substituted benzene C_6H_5R', were not observed during these reactions.

(b) Rhenium $[CpRe(CO)_2(N_2R)][BF_4]$

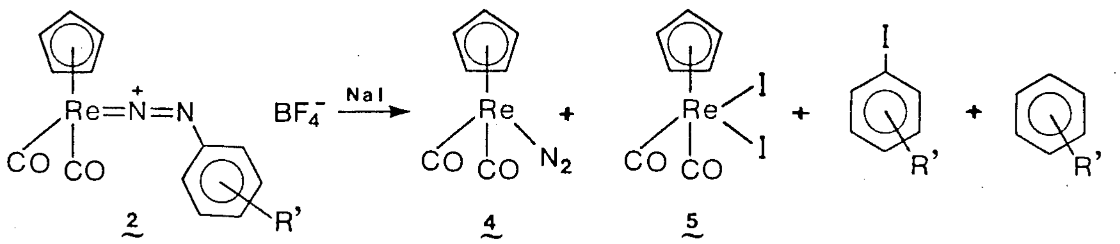
Reactions of the analogous aryldiazenido complexes of rhenium (2a, 2b, 2d, 2e and 2g) with NaI in acetone produced, in each case, the corresponding dinitrogen complex $[CpRe(CO)_2(N_2)]$, 4, plus the known diiodo complex $[CpRe(CO)_2I_2]$[50], 5. These compounds were fully characterized by IR, ^1H-NMR and MS.

The GC spectrum of the reaction mixture of the para-methoxy derivative (2b) showed four peaks. MS analysis of these peaks revealed the presence of complex 4 and the organic compounds $IC_6H_4OCH_3$ and $C_6H_5OCH_3$. The extra peak (m/e = 229), which was very small compared to the others, could not be identified. Compound 5 was not observed by this technique (GC-MS), but its MS was obtained, after it was isolated as a solid, by direct injection.

The iodo arene $IC_6H_4OCH_3$ was also identified by ^1H-NMR after being isolated by sublimation. Its ^1H-NMR spectrum clearly showed an AA'BB' pattern typical of 1,4-disubstituted benzene compounds.

GC-MS analysis of the reaction mixtures of other derivatives (2a, 2d, 2g) also showed the presence of complex 4, in addition to IC_6H_4R' (or $IC_6H_3R'_2$) and C_6H_5R' (or $C_6H_4R'_2$). Compound 5 was also formed in these reactions and its MS was obtained after isolation.

The general equation for these reactions is shown in eq. 10.



(10)

Although these final products in these reactions were not quantified, $[CpRe(CO)_2(N_2)]$ and the iodoarene were always the major products. Estimates from IR and GC indicate that the yield of these two compounds is approximately four times greater than that of the $[CpRe(CO)_2I_2]$ and the arene.

The rates of these reactions were indeed affected by the nature and position of the substituents, but in these cases, not so markedly as in the manganese system. The rates follow the order 2,6 dimethyl > o-CF_3 > p-CH_3 ≈ p-OCH_3 >> p-NEt_2. (For details of how these rates were compared, see the experimental section.)

The reaction with KBr (in acetone) was found to be more complex, but at the same time, more interesting. In general, this reaction was much slower compared with NaI. When the aryldiazenido complex 2b (R = p-OCH_3) was allowed to react with one equivalent of KBr in acetone at room temperature, a very slow reaction was observed; this is probably because of the near insolubility of KBr in acetone. Addition of excess of finely ground solid KBr speeded up the reaction to yield several carbonyl containing products (by IR). From an IR spectrum in CH_2Cl_2, it was possible to see clearly the formation of 4, the known dibromo derivative $[CpRe(CO)_2Br_2]$[53], 6, (ν(CO) 2055vs, 2004vs cm^{-1}) and the new complex $[CpRe(CO)Br(p\text{-}N_2C_6H_4OCH_3)]$, 7, (ν(CO) 1956vs; ν(NN) 1644vs, cm^{-1}). Each of these was separated and subsequently identified by MS. Compound 7 was identical to that formed in the solid state reaction (see below) from which it was isolated and fully characterized. The IR and MS data for complex 6 correlated well with those previously reported.[53,54]

GC-MS analysis of the reaction mixture directly, revealed the presence of $BrC_6H_4OCH_3$ (m/e = 188), $C_6H_5OCH_3$ (m/e = 108) and [CpRe(CO)$_2$(N$_2$)]. However, [CpRe(CO)$_2$Br$_2$] and [CpRe(CO)Br(p-$N_2C_6H_4OCH_3$)] were not observed by this technique. The gas chromatogram of the volatile products of this reaction collected after evacuation, was dominated by a peak due to anisole (identified by GC-MS). Three other peaks occurred, which exhibited parent peaks in the MS at m/e = 100, m/e = 98 and m/e = 229 respectively, and with an intensity of one-third relative to the anisole peak. No conclusive identification of these three peaks could be obtained.

The reaction of 2b with KCl in acetone at room temperature was extremely slow, and after 48 h. the formation of the new complex [CpRe(CO)Cl(p-$N_2C_6H_4OCH_3$)], 8, was clearly observed by IR. The dichloro derivative [CpRe(CO)$_2$Cl$_2$] and [CpRe(CO)$_2$(N$_2$)] were not formed under these conditions.

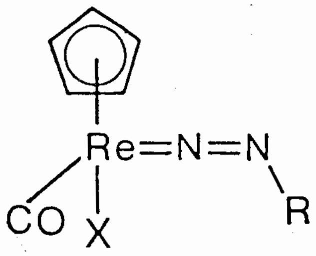
GC-MS analysis of this reaction mixture revealed the presence of anisole (m/e = 108) and [CpRe(CO)$_3$] (m/e = 336, 334); the latter was also identified by IR. The monohalide derivative [CpRe(CO)Cl(p-$N_2C_6H_4OCH_3$)] could not be observed by this technique, but it was fully identified by chemical analysis, IR, ^{1}H-NMR and MS after being isolated.

Following the completion of these solution experiments, it transpired that a new graduate student in our laboratory, Mr. Hugo Klahn, working with the related aryldiazenido complex $[(C_5Me_5)Re(CO)_2(p\text{-}N_2C_6H_4OCH_3)][BF_4]$, found that this reacted with potassium halides in the solid state at 95°C to give the novel monohalide derivatives $[(C_5Me_5)Re(CO)X(p\text{-}N_2C_6H_4OCH_3)]$ (X = Cl, Br, I). This provided a simpler method of isolating these new monohalide complexes.

Subsequently, therefore, similar experiments (in the solid state) with the cyclopentadienyl system were thus carried out in order to see if $[CpRe(CO)X(p\text{-}N_2C_6H_4OCH_3)]$ could be generated by this route. Indeed, reactions of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OCH_3)][BF_4]$ <u>2b</u>, with KBr and KCl at 95°C yielded the corresponding monohalide species $[CpRe(CO)Br(p\text{-}N_2C_6H_4OCH_3)]$ <u>7</u> and $[CpRe(CO)Cl(p\text{-}N_2C_6H_4OCH_3)]$ <u>8</u>, respectively, which were fully characterized by IR, ^{1}H-NMR and MS. These data confirm the identity with the monocarbonyl species formed in solution.

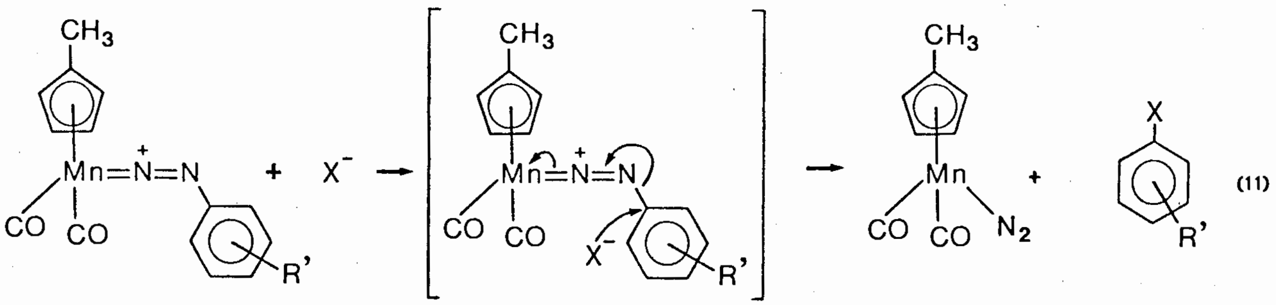
The reaction with KI did not produce the corresponding monoiodo derivative, but yielded the dinitrogen complex <u>4</u> as the major product, plus a small amount of $[CpRe(CO)_2I_2]$. These results are identical to those found in solution.

These neutral monohalide complexes show in the IR (CH_2Cl_2) a strong ν(CO) band (1956 cm^{-1} for <u>7</u>, 1949 cm^{-1} for <u>8</u>) and a strong band at about 1640-1630 cm^{-1}, which is tentatively assigned to ν(NN). This is consistent with the expected structure for these compounds (II) in which the diazo ligand is bound to the metal in a singly-bent, three-electron donor fashion, as expected for an 18-electron configuration.



II

What about the mechanism in these reactions? Obviously, the mechanism in the rhenium system is more complex as compared with the manganese analog in which apparently, a nucleophilic attack of the halide ion at the ipso carbon occurs[5-7] (eq. 11.).



(a) Radical Mechanism

In the rhenium case, the formation of the substituted benzene derivative C_6H_5R (or $C_6H_4R_2$) and the dihalide complexes

[$CpRe(CO)_2X_2$] could suggest the presence of some kind of radicals, together with the oxidation of X^- to X_2. If an organometallic radical is formed, of the type $Re{-}N_2Ar^\bullet$, this could decompose to give $Re{-}N_2$ + $Ar^\bullet$; the dinitrogen complex could react with I_2, for example, to give $Re{-}I_2$ + $N_2(g)$ (and experimentally it was observed that indeed, the dinitrogen complex does react with I_2 in this way, to give the diiodo complex [$CpRe(CO)_2I_2$]) and the new organic radical could abstract a hydrogen atom from the solvent (acetone in this case) to give C_6H_5R.

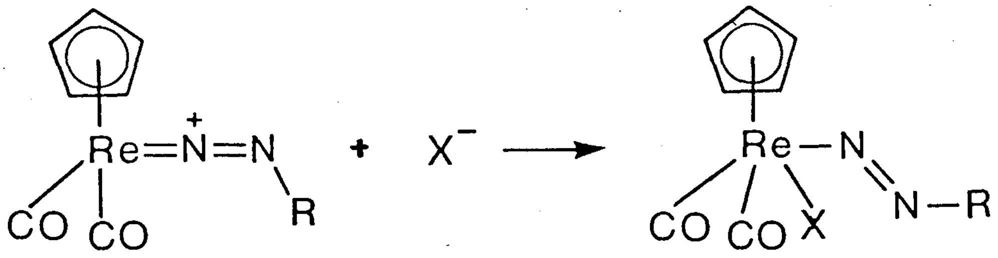
However, no ESR signal could be obtained when these reactions were carried out at low temperature in an ESR tube (similar ESR low temperature experiments were carried out by Drs. P.N. Preston and W.E. Lindsell at Heriot-Watt University, Scotland; they also could not observe any ESR signal.) No polymerization (polyacrylamide) or formation of blue ferrocinium ion were obtained when these reactions were performed in the presence of acrylamide or ferrocene, respectively.

These results are not conclusive, since these experiments would not detect radicals if they are very short lived. Probably special techniques, such as spin trapping ESR, could assist us in solving this question, but no such experiments were performed in this work.

Another possible explanation, which rationalizes reasonably well the formation of all the observed products is offered in Scheme II. What we are suggesting here is that two competitive reactions (with quite different mechanisms) are occurring at the same time.

First of all, a nucleophilic attack by the halide ion X^-, at the ipso carbon, to give the dinitrogen complex $[CpRe(CO)_2N_2]$ and the haloarene (pathway A). This, in general, is the more favorable reaction since these two compounds are always the major products in these reactions, especially when $X^- = I^-$.

The second reaction occurs via nucleophilic attack of the halide ion at the metal center to produce a neutral intermediate $[CpRe(CO)_2X(N_2C_6H_4R')]$ (III) with a doubly-bent N_2R group (pathway B). No evidence of the formation of intermediate III has been obtained.

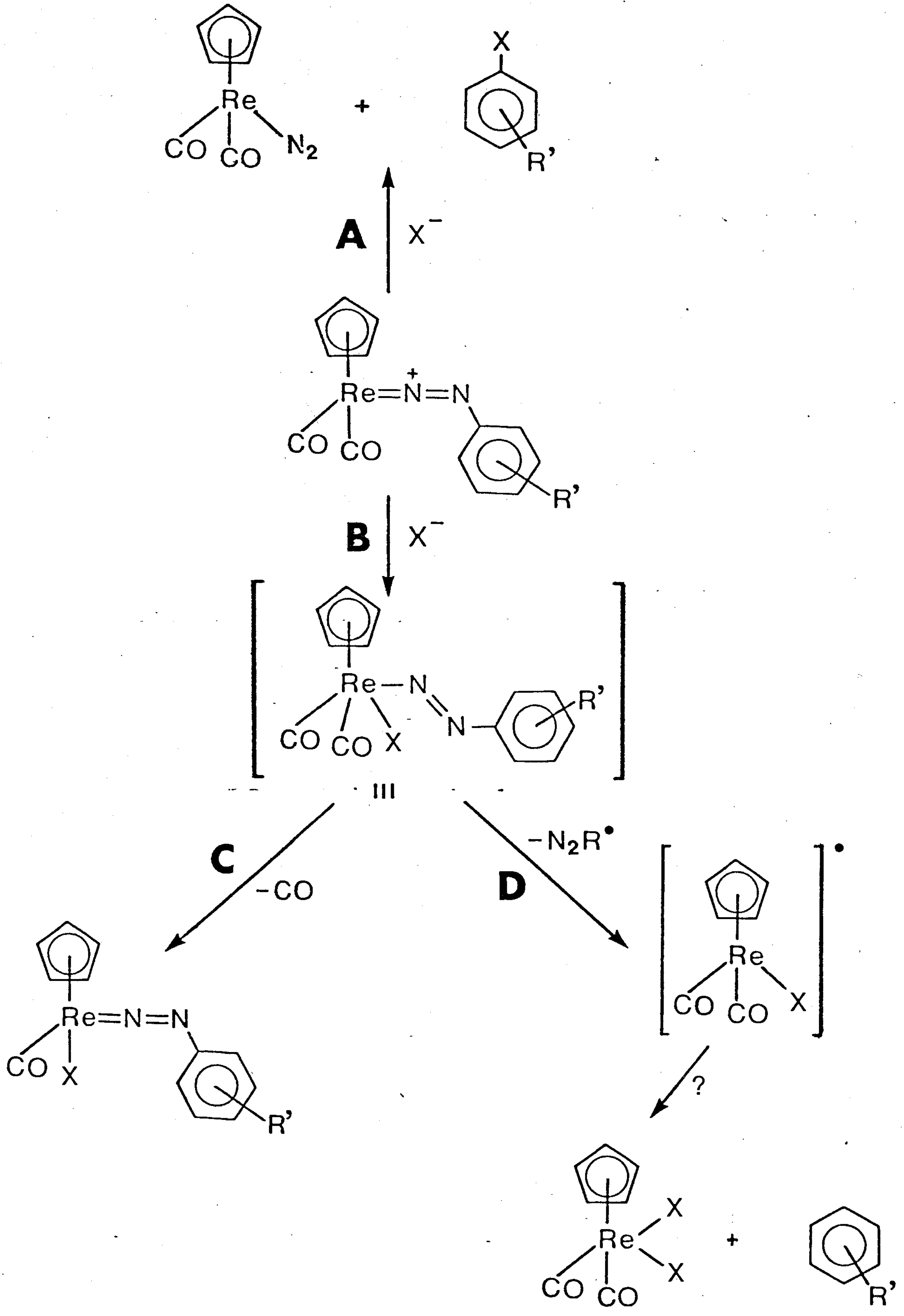


Isomerization of a singly-bent diazo group into a doubly-bent diazo ligand, induced by further coordination of a donor ligand, has been observed previously[27] in the reactions of $[M(CO)_2(PPh_3)_2(N_2Ph)]^+$ (M = Ru, Os) with several anionic nucleophiles, including halide ions. (See section 1.3.3.)

The intermediate III now has two "decomposition" routes, which apparently depend on the nature of the nucleophile. It could lose a CO ligand (pathway C) with concomitant rearrangement of the one-electron donor doubly-bent ligand back to the three-electron donor singly-bent ligand, to give the 18-electron monohalide derivative $[CpRe(CO)X(N_2C_6H_4R')]$, or could lose the N_2R group (pathway D) to generate the $N_2R^\bullet$ radical and the seventeen electron radical species $[CpRe(CO)_2X]^\bullet$. The radical $N_2R^\bullet$ would decompose to give $N_2 + R^\bullet$ which could lead, after abstraction of a hydrogen atom, to the formation of RH. The exact mechanism of formation of $[CpRe(CO)_2X_2]$ is not known at the present time.

In the reaction with I^- and Br^-, the two competitive reactions seem to occur to generate the expected products (according to Scheme II), except pathway C for the I^- reaction, since no evidence of the formation of the monoiodo derivative $[CpRe(CO)I(p\text{-}N_2C_6H_4OCH_3)]$ could be obtained.

In the Cl^- case, the only reaction observed was nucleophilic attack at the metal center (pathway B) to give finally the monochloro complex $[CpRe(CO)Cl(p\text{-}N_2C_6H_4OCH_3)]$ (pathway C). The formation of anisole in this reaction (identified by GC-MS) strongly suggests the involvement of radicals.


Re
CO
CO
N2
+
X
R'
A
X⁻
Re
N
N
+
CO
CO
R'
B
X⁻
Re
N
N
CO
CO
X
R'
III
C
−CO
D
−N2R•
Re
CO
CO
X
•
Re
N
N
CO
X
R'
?
Re
X
X
CO
CO
+
R'

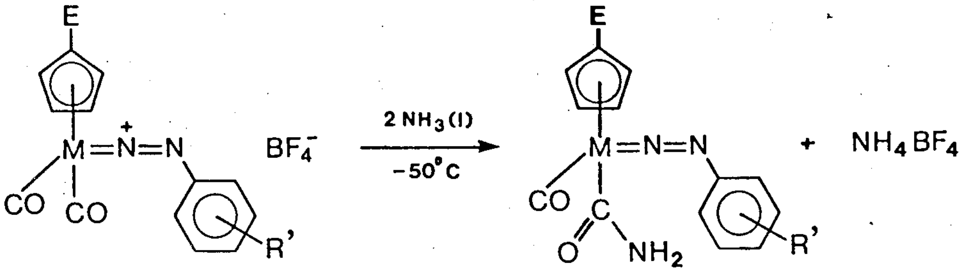
SCHEME II.

Because neither mechanism alone can explain the formation of all the products observed in these reactions, it is necessary to postulate that both mechanisms are involved. Thus the ionic one would seem to be involved in the formation of the monohalide [CpRe(CO)X($N_2C_6H_4R'$)], but cannot explain the formation of C_6H_5R' or $C_6H_4R'_2$. The latter would appear to result from a radical mechanism. The relative contribution of the two mechanisms to the final products apparently depends on the nature of the nucleophile.

2.4.2 Reactions with Ammonia and Amines

All the reactions which will be described in this section, were carried out by using the o-CF_3 derivative (1a) of manganese and the p-OCH_3 (2b) and o-CF_3 (2e) derivatives of rhenium.

It was noted that bubbling ammonia into an acetone solution of these aryldiazenido complexes produced very air-sensitive solutions containing monocarbonyl species, which were difficult to isolate pure. By carrying out these reactions in liquid ammonia, these substances could be isolated as solids which were less air-sensitive. These were characterized as the carbamoyl complexes 9 (Mn) and 10 (Re) (eq. 12.).



(12)

(M=Mn,Re)
(E=CH$_3$,H)

9a (Mn, R'= o-CF$_3$)
10b, 10e (Re, R'= p-OCH$_3$, o-CF$_3$)

Characterization of these complexes is based on chemical analysis, IR, ^{1}H-NMR and their reactions with acids. An acceptable ^{1}H-NMR spectrum of the manganese carbamoyl complex (9a) could not be obtained as it was very broad.

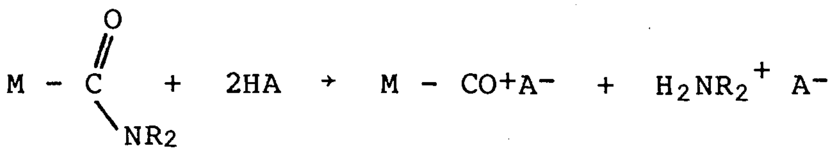
The IR spectra (CH_2Cl_2) of these carbamoyl complexes show a strong signal due to the terminal carbonyl ligand at 1980vs cm^{-1} (9a) and 1960vs cm^{-1} (10e); ν(NN) is tentatively assigned to a strong band at 1665 cm^{-1} in the manganese complex (9a), which decreased in the rhenium analog (10e) to 1632 cm^{-1}.

Three bands, with intensities medium to strong, are observed in the region 1600-1550 cm^{-1}, which could be assigned to [ν(C=O) + ν(C=N) + δ(NH_2)]. In the manganese complex (9a), these bands occur at 1600, 1578 and 1558 cm^{-1}, while in the rhenium case (10e), they are observed at 1595, 1574 and

1558 cm^{-1}. The band due to the CF_3 group is observed at 1320 cm^{-1} in both complexes. No band due to the N-H stretching mode was observed in either case. The IR spectrum (CH_2Cl_2) of the p-OCH_3 rhenium carbamoyl complex (<u>10b</u>), shows bands at 1945vs (ν(CO)), 1641vs (ν(NN)) and 1586vs and 1555s cm^{-1}.

These assignments correlate well with those reported for the isoelectronic nitrosyl complexes [(MeCp)Mn(CO)($CONH_2$)(NO)], [CpMn(CO)($CONH_2$)(NO)] and [CpRe(CO)($CONH_2$)(NO)][55] and with those for carbamoyl complexes of Rh[56], Fe, Ru Os[57] and other manganese carbamoyl derivatives.[58] (For a review on carbamoyl complexes, see ref. 57.)

It is known that carbamoyl species react with acids to regenerate metal carbonyl complexes as shown in eq. 13. When the acid is strong, such as HCl, the carbamoyl derivative always reacts in this way, making this reaction a useful chemical tool to establish the presence of these groups[59] (eq.13).



$$\mathrm{M - C(=O)NR_2 \;+\; 2HA \;\rightarrow\; M - CO^{+}A^{-} \;+\; H_2NR_2^{+}\,A^{-}} \qquad (13)$$

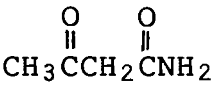
(R = H, alkyl)

In our examples, the carbamoyl complexes react with two moles of HCl to regenerate the aryldiazenido complexes $[CpM(CO)_2(N_2Ar)][A]$, (where A now is Cl^-) and NH_4Cl (the latter was identified by ordinary qualitative tests). They also react with HBF_4 to regenerate the original aryldiazenido derivatives (by IR).

Solutions of these carbamoyl complexes are chemically unstable (especially the manganese one). By monitoring an acetone solution by infrared, it was possible to observe their decomposition to generate the corresponding dinitrogen complexes <u>3</u> and <u>4</u>. This chemical transformation occurs much faster in the manganese case than in the rhenium one. GC-MS analysis of these acetone solutions (for manganese) showed the presence of the corresponding dinitrogen complex together with $\underline{o}$-$C_6H_5CF_3$, $CH_3COCH_2CONH_2$, a very small amount of the corresponding aromatic amine $H_2NC_6H_4CF_3$, and other organic derivatives which could not be identified.

ESR analysis (at room temperature) of an acetone solution (10^{-3} M) or a solid sample of $[(MeCp)Mn(CO)(CONH_2)(\underline{o}\text{-}N_2C_6H_4CF_3)]$, showed a broad, multiline resonance, which is indicative that the decomposition was accompanied by the formation of paramagnetic manganese species, probably of Mn(II).

The generation of α,α,α-trifluorotoluene suggests that th reaction probably involves radicals. No further studies to clarify the mechanism involved in these reactions were performed in this work.

The formation of the dinitrogen complexes in these reactions is not due to a nucleophilic attack at the ipso carbon on the aromatic ring by NH_2^- (which could have been generated in situ). Reaction of the aryldiazenido complex 1a with sodium amide ($NaNH_2$) under similar conditions (acetone, room temperature) indeed produced the dinitrogen manganese complex (the reaction is very fast and is completed in a few minutes), but GC-MS analysis of this solution shows the formation of the aromatic amine o-$H_2NC_6H_4CF_3$ as a very minor product, which should be a major product if the reaction proceeds in the manner of other nucleophilic agents, such as I^-.[5-7] The GC-MS profile of this solution is almost identical to the one generated by dissolving the carbamoyl complex $[(MeCp)Mn(CO)(CONH_2)(o\text{-}N_2C_6H_4CF_3)]$ 9a in acetone, except that the peak with m/e = 101, which corresponds to  $CH_3\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{O}{\|}}{C}NH_2$, is more intense in the reaction with $NaNH_2$.

When this reaction was carried out at low temperature, only the formation of the carbamoyl complex 9a was observed; no dinitrogen derivative was produced, except when the solution was warmed to room temperature.

Reaction of $NaNH_2$ with the analogous aryldiazenido rhenium derivative 2b in acetone at room temperature, gives only the corresponding carbamoyl complex $[CpRe(CO)(CONH_2)(p\text{-}N_2C_6H_4OCH_3)]$ 10b, which generates the dinitrogen complex 4 much slower than in the manganese case.

Aryldiazenido complexes of manganese and rhenium react with amines (primary and secondary) to give the corresponding carbamoyl complexes $[CpM(CO)(CONR^1R^2)(N_2C_6H_4R')]$.

Reaction of the complex 1a with neat $HNMe_2$ at low temperature, rapidly gave a brown-reddish microcrystalline solid, which was identified by chemical analysis and IR, as the dimethyl carbamoyl complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)(CONMe_2)(o\text{-}N_2C_6H_4CF_3)]$ 11a. Its IR spectrum (CH_2Cl_2) shows only one terminal carbonyl band at 1970 cm^{-1} (vs,br); $\nu(NN)$ is tentatively assigned to a strong and broad band at 1655 cm^{-1}. Two other bands, with intensities medium to strong, are observed at 1600 and 1580 cm^{-1}, which are assigned to $[\nu(C{=}O) + \nu(C{=}N)]$. The band due to $\nu(CF_3)$ is observed at 1320 cm^{-1}.

The rhenium analogue (2b) reacts with neat H_2NMe and $HNMe_2$, at low temperature, to give very rapidly, the carbamoyl species $[CpRe(CO)(CONHMe)(p\text{-}N_2C_6H_4OCH_3)]$ 12b and $[CpRe(CO)(CONMe_2)(p\text{-}N_2C_6H_4OCH_3)]$ 13b, respectively, as golden yellow solids. Their IR (CH_2Cl_2) show one terminal carbonyl band (1940vs and 1942vs cm^{-1}, respectively), and one strong band, which is tentatively assigned to ν(NN) (1640vs cm^{-1} in both complexes). The complex 12b, with a secondary carbamoyl group, CONHMe, also shows a strong and broad band at 1573 cm^{-1}; probably this band is a combination of ν(C=O), ν(C=N) and δ(NH). Two bands, with medium intensities, at 1592 and 1580 cm^{-1} are present in the N,N-dimethyl carbamoyl derivative 13b, which could be assigned to [ν(C=O) + ν(C=N)].

Both carbamoyl complexes 12b and 13b, react with HBF_4 very rapidly at room temperature to regenerate the original aryldiazenido complex 2b (by IR).

The room temperature ^{1}H-NMR spectrum ($CDCl_3$) of the complex [CpRe(CO)(CONHMe)(p-$N_2C_6H_4OCH_3$)] 12b, shows peaks at (ppm): 7.22d, 6.95d (4H, C_6H_4); 5.79s (5H, C_5H_5); 3.84s (3H, OCH_3); 2.84d (3H, CH_3; JHNCH = 4.8 Hz); 5.57s,br (1H, NH).

The N-H proton was assigned by comparison with previous reported values for monomethyl carbamoyl complexes [CpW(CO)$_3$(CONHCH$_3$)]^{58} (6.0); [Re(CO)$_5$(CONHCH$_3$)]^{59} (5.45); [Mn(CO)$_3$(PPh$_3$)$_2$(CONHCH$_3$)]^{60} (4.85) and [Re(CO)$_3$(PPh$_3$)$_2$(CONHCH$_3$)]^{60} (4.40). The coupling constants J(HNCH) in these compounds (5 Hz, 5.4 Hz, 4.2 Hz and 4.2 Hz, respectively) compare well with the one found in complex 12b, 4.8 Hz. The CH_3 resonance remains unchanged as a sharp doublet over the temperature range -40°C to +50°C.

The room temperature ^1H-NMR spectrum ($CDCl_3$) of the N,N-dimethyl carbamoyl complex [$CpRe(CO)(CONMe_2)(p\text{-}N_2C_6H_4OCH_3)$] 13b showed peaks at (ppm): 7.22d, 6.95d (4H, C_6H_4); 5.75s (5H, C_5H_5); 3.84s (3H, OCH_3) and 3.09s (6H, CH_3 groups). On cooling to -70°C, the methyl signal split into a doublet.

The nonequivalence of the two methyl groups has also been observed in other N,N-dimethyl carbamoyl couples of Mo, W, Pt and Pd[57a,58], and accounted for by restricted rotation around the C-N bond of the carbamoyl group. In complex 13b, which possesses a chiral center at the metal, the two methyl groups would become equivalent only if inversion at the nitrogen atom is occurring, as well as C-N bond rotation. The experimental evidence seems to indicate that this is the case.

The aryldiazenido complexes of rhenium 2 did not react with tertiary amines, such as pure NEt_3 (purified by distillation). With neat NMe_3 (condensed at -50°C) the complex 2b reacted very slowly to give a golden yellow solid which was fully characterized as the carbamoyl complex [$CpRe(CO)(CONHCH_3)(p\text{-}N_2C_6H_4OCH_3)$] 12b. In fact, it was found that the formation of this complex arose from the reaction of complex 2b with the primary amine H_2NCH_3, which was shown by GC-MS analysis, to be present as an impurity in NMe_3, and not from reaction with the tertiary amine NMe_3.

2.4.3 Reactions with $NaOCH_3$

The aryldiazenido complexes of manganese 1c (3,5 dimethyl), 1d (2,6 dichloro) and 1e (2,6 dinitro) react very rapidly with $NaOCH_3$ in acetone or methanol at room temperature to give the dinitrogen complex 3, as the only organometallic product. These reactions are identical with (only much faster than) those previously reported for the *o*-CF_3, *o*-F and H derivatives of manganese.[5-7]

The rhenium analogs do react with $NaOCH_3$, but in a different fashion. The complexes 2a, 2b and 2d react with one equivalent of $NaOCH_3$ in methanol to give the neutral alkoxycarbonyl derivatives $[CpRe(CO)(COOCH_3)(p\text{-}N_2C_6H_4CH_3)]$ 14a, $[CpRe(CO)(COOCH_3)(p\text{-}N_2C_6H_4OCH_3)]$ 14b and $[CpRe(CO)(COOCH_3)(p\text{-}N_2C_6H_4NEt_2)]$ 14e, respectively. The IR spectra (CH_2Cl_2) of these complexes show only one terminal $\nu(CO)$ band for each of them in the region 1952-1939 cm^{-1}, and a series of strong and broad bands in the region 1650-1550 cm^{-1}, which obviously contain the $\nu(NN)$ and $\nu(C{=}O)$ vibrational modes. Isotopic $^{15}N(N^1)$ substitutions indicate that the $\nu(NN)$ mode is strongly coupled to other vibrational modes, which makes very difficult any unambiguous assig ment of this particular mode. The IR spectra of these compounds with their corresponding ^{15}N labelling, are shown in Figure 3.

The ^{1}H-NMR data agree with the alkoxycarbonyl formulation of these complexes and are presented, together with the IR data, in Table II.

These alkoxycarbonyl complexes react with acids (HCl, HBF_4) to regenerate the starting aryldiazenido complexes <u>2</u> as shown schematically in eq. 14.

$$\text{Re-COOCH}_3 + \text{HA} \rightarrow \text{Re-CO}^+\text{A}^- + \text{CH}_3\text{OH} \qquad (14)$$

TABLE II

IR AND ^{1}H-NMR DATA OF ALKOXYCARBONYL COMPLEXES OF RHENIUM

$[CpRe(CO)(COOMe)(p\text{-}N_2C_6H_4R')]$ <u>14</u>

		^{1}H-NMR[b]			
<u>R'</u>	ν(CO)[a]	Aryl	Cp	-CO<u>OMe</u>	<u>R</u>
p-Me	1952vs	7.34s	5.99s	3.54s	2.45s (Me)
p-OMe	1948vs	7.44d 7.04d	5.97s	3.54s	3.86s (OMe)
$p\text{-}NEt_2$	1939vs	7.29d 6.78d	5.92s	3.52s	3.48q (CH_2) 1.17t (CH_3)

[a] In cm^{-1} for CH_2Cl_2 solution. [b] In acetone-d_6 at R.T.; all values in ppm. Abbreviations: s, singlet; d, doublet; t, triplet, q, quartet.

Figure 3

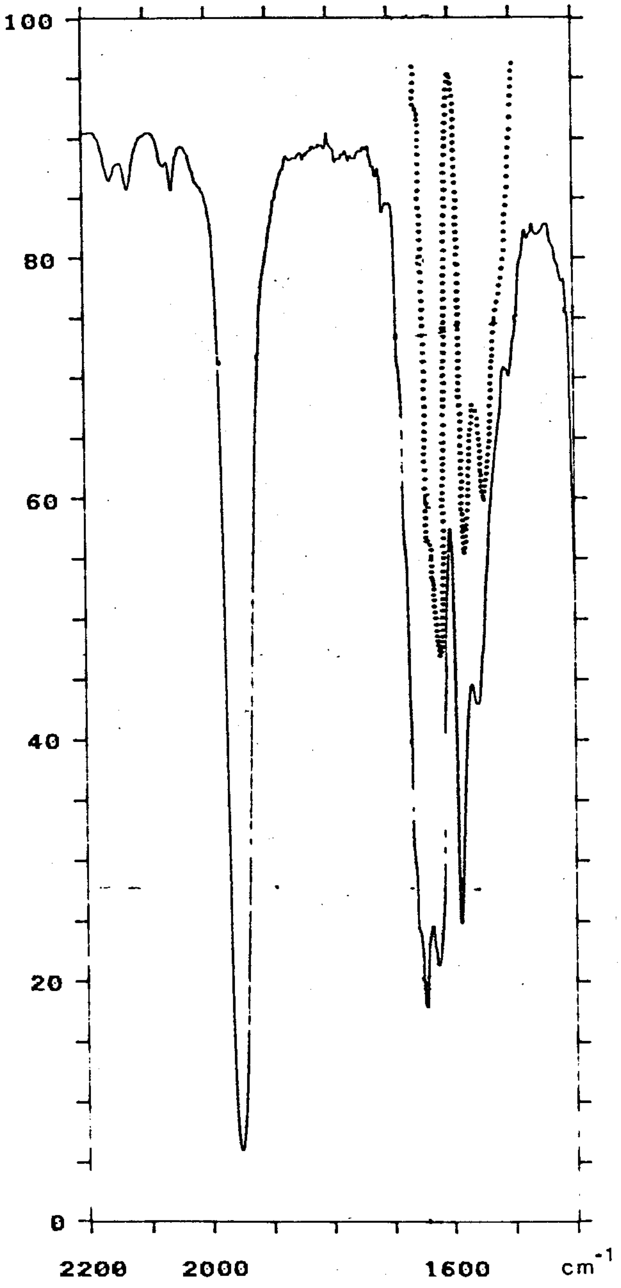
IR Spectra of Alkoxycarbonyl Complexes of Rhenium: $[CpRe(CO)(COOCH_3)(p\text{-}N_2C_6H_4R')]$ **14**.

Fig. 3A = R' = $p\text{-}CH_3$

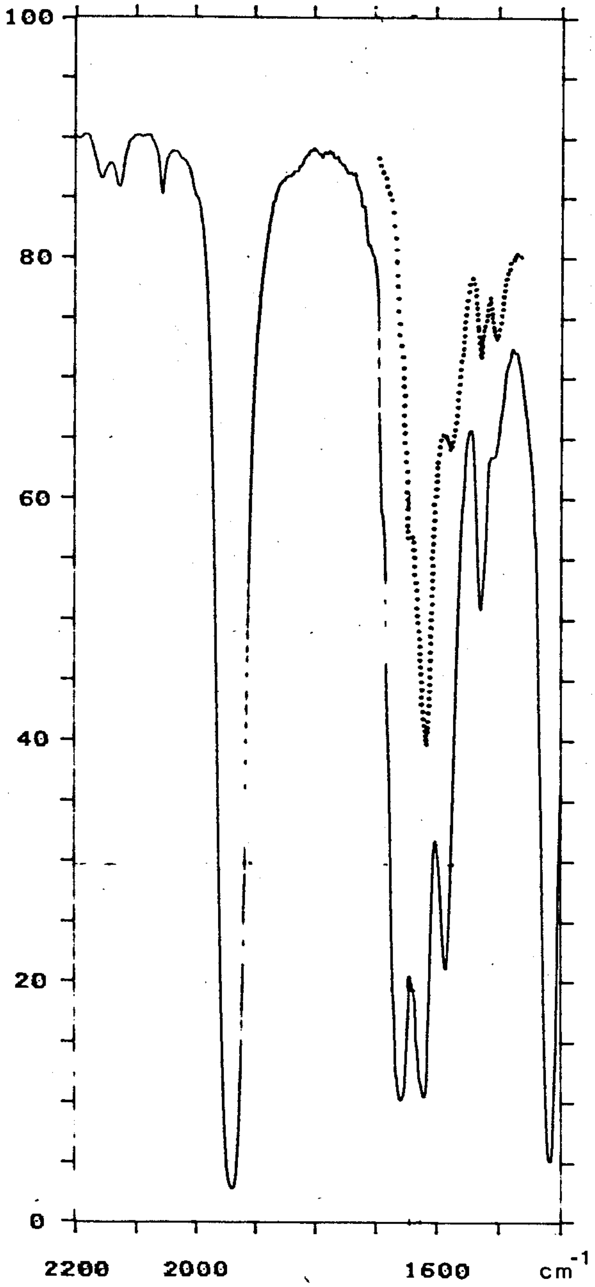
Fig. 3B = R' = $p\text{-}NEt_2$

______ $\nu(^{14}N^{14}N)$

----- $\nu(^{15}N^{14}N)$



3A



3B

2.4.4 Reactions with Phosphines

Aryldiazenido complexes of manganese $[(MeCp)Mn(CO)_2(N_2C_6H_4R')][BF_4]$ (R' = o-CF_3, o-F, H) react with one equivalent of triphenylphosphine to give $[(MeCp)Mn(CO)_2(PPh_3)]$. It was shown that these reactions proceed with the initial formation of the dinitrogen complex 3, which eventually is consumed during the reaction to give finally the known triphenylphosphine derivative $[(MeCp)Mn(CO)_2(PPh_3)]$[61] as the only organometallic product[5-7]. The mechanism of this reaction is not well understood.

The new derivatives of manganese 1b (p-CH_3), 1c (3,5 dimethyl), 1d (2,6 dichloro) and 1e (2,6 dinitro) reacted similarly as described above.

The analogous aryldiazenido complexes of rhenium also reacted with phosphines, but in this case, two equivalents of phosphine were required for complete reaction.

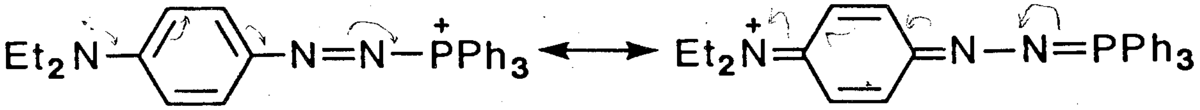
Reaction with two equivalents of PPh_3 in acetone at room temperature gave the known complex $[CpRe(CO)_2PPh_3]$[51]; this compound was fully characterized by chemical analysis, IR and ^1H-NMR. All of these analyses were identical with those obtained from a standard sample of this complex prepared by an alternative method[51], namely reaction of $[CpRe(CO)_2THF]$ with PPh_3.

Following the course of the reaction by IR, the formation of the corresponding dinitrogen complex 4 could not be observed even when the reaction was carried out at low temperatures.

When the substituents on the benzene ring were para-diethylamino (2d) or para-methoxy (2b), addition of diethyl ether or hexane to the reaction mixtures (at a point when reaction was completed by IR) precipitated out isolable red air-stable solids which were characterized as the diazo phosphonium salts [Ph_3P-p-$N_2C_6H_4NEt_2$][BF_4] and [Ph_3P-p-$N_2C_6H_4OCH_3$][BF_4], respectively. Chemical analysis and IR data agree well with those previously reported for these compounds.[32,62]

With other substituents (2a, p-CH_3, 2e, o-CF_3 and 2h, dimethyl) no diazophosphonium derivatives could be isolated, but a transient red color was noted, especially when these reactions were carried out at low temperatures, which might indicate that the reaction occurred via unstable, red diazo phosphines [Ph_3P-$N_2C_6H_4R$][BF_4].

The reaction of triphenyl phosphine with arenediazonium salts has been previously investigated.[63,64] It was found that these reactions are strongly affected by change of solvent, pH and aryl substitution. The presence of an electron-releasing substituent in the para-position, able to delocalize electron density via π-electron donation, seems to be required for the synthesis of stable diazophosphines. The contribution of a delocalized electronic structure to the stabilization of these compounds has been demonstrated for the para-diethylamino derivative.[65]



Interaction of arenediazonium salts and triphenylphosphine also seems to be involved in the reaction of $IrH(CO)(PPh_3)_3$ with $[\underline{o}\text{-}N_2C_6H_4NO_2][BF_4]$[66], where two equivalents of diazonium salt were required for a complete reaction to give the orthometallated species $[Ir(\underline{o}\text{-}NHNHC_6H_3NO_2)(CO)(PPh_3)_2][BF_4]$. Although the fate of the second mole of diazonium salt was not known, its reaction with the dissociated PPh_3 ligand to give the unstable diazophosphine $[Ph_3P\text{-}\underline{o}\text{-}N_2C_6H_4NO_2]^+$ is clearly a possibility.

The reactions of <u>2b</u> and <u>2d</u> with bis(diphenylphosphino)-methane ($Ph_2PCH_2PPh_2$) also required two equivalents of phosphine for complete reaction. Following the course of the reactions (which were carried out in acetone at room or low temperatures) by IR, no formation of the dinitrogen complex <u>4</u> was observed; the two ν(CO) bands of the starting aryldiazenido complexes smoothly decreased in intensity as two new ν(CO) bands, at lower wavenumber (1927vs, 1859vs cm^{-1}) increased, which correspond to the diphosphine derivative $[CpRe(CO)_2(Ph_2PCH_2PPh_2)]$. By ^{31}P-NMR, it was found that the diphosphine ligand is acting as a two-electron donor monodentate ligand, since two distinctive phosphorus resonances were observed (22.17s, 11.58s, ppm).

Addition of diethyl ether, after the reactions were completed, precipitated out an orange-brown solid (in the p-OCH_3 case) and a brown-greenish solid (in the p-NEt_2 case). Chemical analysis of these solids (after attempted purification) did not correlate well with the formulation of diazophosphonium salts (which was expected), although they showed a high content of nitrogen.

An independent reaction of diphosphine with para-diethylamino diazonium salt (ratio 1:1) in acetone at room temperature gave instantaneously a strong bright orange-red color which slowly disappeared with continued stirring of the mixture at room temperature. Although no attempt to identify the orange-red compound was made, it seems reasonable to assume that the coloration corresponds to the diazophosphine $[Ph_2PCH_2Ph_2P-N_2C_6H_4NEt_2][BF_4]$, which decomposes under the reaction conditions.

A transient red coloration was also observed during the rhenium reactions, especially with the p-NEt_2 derivative, which suggests to us that these diazophosphine compounds are also formed in these reactions, but they are unstable.

2.4.5 Reactions with Acids

As was described in Chapter I (1.3.6), many diazenido complexes can be protonated to give diazene (protonation at N^1) or hydrazido (2-) ligands (protonation at N^2) depending on the coordination mode of the diazenido ligand (singly or doubly bent).

In general, we found that $[MeCpMn(CO)_2(N_2R)][BF_4]$ and $[CpRe(CO)_2(N_2R)][BF_4]$ complexes do not react at all with acids (even if they are strong acids), except in one particular case.

The complex $[CpRe(CO)_2(p\text{-}N_2C_6H_4NEt_2)][BF_4]$ 2d, reacts with HCl gas (and presumably it reacts with any acid) in CH_2Cl_2 at room temperature to give a new complex $[CpRe(CO)_2(p\text{-}N_2C_6H_4NEt_2)][BF_4]\cdot HCl$. Its IR spectrum ($CH_2Cl_2$) showed two ν(CO) bands at higher wavenumbers compared with 2d (2095vs, 2038vs, cm^{-1}) and ν(NN) at 1752 cm^{-1}, which shifted to 1725 cm^{-1} under ^{15}N isotopic substitution, thus, confirming its assignment.

It was observed that acetone solutions (orange-reddish) of this new complex slowly regenerated the original aryldiazenido complex 2d (dark green-yellow). Its solution also gave a positive Cl^- test with $AgNO_3$.

In this case, it is obvious that protonation has occurred at the nitrogen atom of the diethylamino group to give the dicationic adduct $[CpRe(CO)_2(p\text{-}N_2C_6H_4NHEt_2)][BF_4][Cl]$.

2.5 EXPERIMENTAL

Substituted anilines were available commercially (Aldrich) and were converted to diazonium tetrafluoroborate salts by diazotization with $NaNO_2$; these were then recrystallized from acetone/diethyl ether. The ^{15}N isotopic label was introduced at N(1) with $Na^{15}NO_2$ (96% ^{15}N).

Methylcyclopentadienyl tricarbonylmanganese (Ventron, Alfa products), decacarbonyldirhenium (Strem chemicals) and triphenylsilane (Matheson, Coleman and Bell) were used directly as purchased. $[(\eta^5\text{-}C_5H_5)Re(CO)_3]$ was synthesized by the published method.[67]

All solvents were dried and purified by standard methods (tetrahydrofuran by reflux with sodium strips and benzophenone) and distilled under nitrogen.

Reactions and manipulations were carried out in standard Schlenkware, connected to a switchable inert-atmosphere/vacuum supply, and were conducted under nitrogen or argon.

All photochemical reactions were carried out at atmospheric pressure in a Pyrex vessel (250 mL) equipped with a water cooled quartz finger joined to the vessel by a 60/50 standard taper joint. A 200 watt ultraviolet source (Hanovia high-pressure mercury N°654A36) was placed inside the quartz finger. Nitrogen was passed through the reaction vessel prior to the addition of the solvent and starting materials, and slow passage of nitrogen was maintained during the reaction.

Infrared spectra were recorded on Perkin-Elmer Models 599B and 983 calibrated against polystyrene. ^{1}H and ^{31}P-NMR spectra were recorded at 100 MHz with a Varian XL-100 spectrometer modified for Fourier-transform spectroscopy and are reported in ppm downfield relative to internal $SiMe_4$. Gas chromatograph-mass spectra were obtained with a Hewlett-Packard Model 5985 GC-MS system operating at 70 eV. GC analyses were carried out with a SE-30 capillary column in the temperature range 60-240°C with a heating rate of 10°C per min.

Microanalyses were performed by Mr. M.K. Yang and Mr. J. Hewitt of the microanalytical laboratory of Simon Fraser University. There was occasional difficulty in obtaining carbon analysis acceptably close to theoretical values for some of the aryldiazenido complexes 2 and their derivatives, even though these samples were crystalline and spectroscopically pure (by IR, NMR).

The method used to evaluate the rate of reaction for the reactions of the aryldiazenido complexes 1 and 2 with NaI was quite qualitative. The two reagents were mixed in acetone and immediately, an IR spectrum was recorded in the region 2200-1800 cm^{-1}; a new spectrum was recorded every two minutes until the reaction was completed.

$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(p\text{-}N_2C_6H_4CF_3)][BF_4]$ (1a). This was synthesized as described previously.[7]

[(η^5-$CH_3C_5H_4$)Mn(CO)$_2$(p-$N_2C_6H_4CH_3$)][BF_4] (1b). To a solution of [(η^5-$CH_3C_5H_4$)MnH(CO)$_2$SiPh$_3$][49] (300 mg, 0.67 mmol) in acetone (15 mL) was slowly added solid [p-$CH_3C_6H_4N_2$][BF_4] (137.3 mg, 0.68 mmol), and the mixture was stirred for 3 h. at room temperature. The color changed from yellow to red-brownish. The solution was evaporated in vacuo at room temperature to ca. 2 mL, Et_2O added carefully so as to precipitate only unreacted diazonium salt, and the mixture filtered. Excess of Et_2O was added now to precipitate the aryldiazenido complex; a brown-reddish oil was obtained, which was stirred with several portions of Et_2O until the ether solution was clear. Addition of hexane gave the product (20%) as a dark brown solid, which gives a deep red solution in acetone.

[(η^5-$CH_3C_5H_4$)Mn(CO)$_2${3,5-$N_2C_6H_3(CH_3)_2$}][BF_4] (1c). This was synthesized analogously with 1b by using [3,5-$(CH_3)_2C_6H_3N_2$][BF_4] (66 mg, 0.30 mmol) and stirring for 2h. at 35°C. The solution changed from yellow to dark reddish-brown. No solid could be isolated, only a brown-reddish oil being obtained in low yield. This was identified by a comparison of its properties and IR spectrum with those of 1a and 1b.

[(η^5-$CH_3C_5H_4$)Mn(CO)$_2$(2,6-$N_2C_6H_3Cl_2$)][BF_4] (1d). This was prepared similarly in 43% yield, m.p. 124-125°C, as a brown-orange microcrystalline solid. Anal. Calcd. for

$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(2,6\text{-}N_2C_6H_3Cl_2)][BF_4]$: C, 37.25; H, 2.22; N, 6.21. Found: C, 37.16; H, 2.40; N, 6.15.

$[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2\{2,6\text{-}N_2C_6H_3(NO_2)_3[BF_4]$ (1e). This was prepared similarly in 20% yield, m.p. 104-105°C as a brown microcrystalline solid, and characterized by IR.

$CpRe(CO)_2THF$. This was synthesized by a modification of the published method.[45] A solution of $[(\eta^5\text{-}C_5H_5)Re(CO)_3]$ (1 g, 3 mmol) in freshly distilled, pure tetrahydrofuran (250 mL) was irradiated for 45 min. to give a deep yellow-brownish solution. Evaporation of the solvent to ca. 20 mL and cooling to -78°C afforded $CpRe(CO)_2THF$ as a golden-yellow solid. Yield: ≈50%. IR (THF) : ν(CO) 1910vs, 1836vs.

$[CpRe(CO)_2(p\text{-}N_2C_6H_4CH_3)][BF_4]$ (2a). To a solution of $[CpRe(CO)_2THF]$ (200 mg, 0.53 mmol) in 20 mL of acetone was slowly added solid $[p\text{-}CH_3C_6H_4N_2][BF_4]$ (108.7 mg, 0.53 mmol), and the mixture was stirred for 15 min. at room temperature. The reaction was instantaneous and the color changed from yellow to orange. The solution was evaporated in vacuo at room temperature to ca. 2 mL and excess diethyl ether was carefully added to precipitate the aryldiazenido complex as a microcrystalline orange solid. This was washed by stirring with several portions of ether until the ether solution was clear. Yield 97%, m.p. 130°C.

Anal. Calcd. for $[(\eta^5\text{-}C_5H_5)Re(CO)_2(p\text{-}N_2C_6H_4CH_3)][BF_4]$: C, 32.75; H, 2.34; N, 5.46; Found: C, 32.99; H, 2.35; N, 5.55. ^1H-NMR ($CDCl_3$): δ7.40s (4H, C_6H_4); 6.37s (5H, C_5H_5); 2.52s (3H, CH_3).

$[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (2b). A similar procedure to that used for 2a gave this as a pink-red microcrystalline solid, m.p. 114°C in 95% yield.

Anal. Calcd. for $[(\eta^5\text{-}C_5H_5)Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$: C, 31.76; H, 2.27; N, 5.29. Found: C, 31.90; H, 2.29; N, 5.40. ^1H-NMR (Acetone-d_6): δ7.55d, 7.18d (4H, C_6H_4); 6.65s (5H, C_5H_5); 3.91s (3H, OCH_3)

$[CpRe(CO)_2(o\text{-}N_2C_6H_4OMe)][BF_4]$ (2c). A similar procedure to that used for 2a gave this as a red microcrystalline solid, m.p. 108°C, in 93% yield.

Anal. Calcd. for $[(\eta^5\text{-}C_5H_5)Re(CO)_2(o\text{-}N_2C_6H_4OCH_3)][BF_4]$: C, 31.76; H, 2.27; N, 5.29. Found: C, 31.43; H, 2.27; N, 5.01.

$[CpRe(CO)_2(p\text{-}N_2C_6H_4NEt_2)][BF_4]$ (2d). A similar procedure to that used for 2a gave this as a dark green microcrystalline solid, m.p. 141-142°C, 95% yield.

Anal. Calcd. for $[(\eta^5\text{-}C_5H_5)Re(CO)_2\{p\text{-}N_2C_6H_4N(C_2H_5)_2\}][BF_4]$: C, 35.79; H, 3.33; N, 7.37. Found: C, 35.63; H, 3.45; N, 7.49. ^{1}H-NMR (CD_2Cl_2) δ7.62d, 7.23d (4H, C_6H_4); 6.24s (5H, C_5H_5); 3.85q (4H, CH_2); 1.20t (6H, CH_3).

$[CpRe(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ (2e). A similar procedure to that used for 2a gave this as a brown-orange microcrystalline solid, m.p. 132°C, in 93% yield.
Anal. Calcd. for $[(\eta^5\text{-}C_5H_5)Re(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$: C, 29.63; H, 1.59; N, 4.94. Found: C, 28.98; H, 1.65; N, 4.90.

$[CpRe(CO)_2(N_2C_6H_5)][BF_4]$ (2f). A similar procedure to that used for 2a gave this as an orange-reddish oil. ^{1}H-NMR (acetone-d_6): δ7.71s (5H, C_6H_5); 6.72s (5H, C_5H_5).

$[CpRe(CO)_2(2,6\text{-}N_2C_6H_3Me_2)][BF_4]$ (2g). A similar procedure to that used for 2a gave this as an orange microcrystalline solid, m.p. 118°C in 95% yield.
Anal. Calcd. for $[(\eta^5\text{-}C_5H_5)Re(CO)_2\{2,6\text{-}N_2C_6H_3(CH_3)_2\}][BF_4]$: C, 34.16; H, 2.66; N, 5.31. Found: C, 34.15; H, 2.56; N, 5.19.

$[CpRe(CO)_2(3,5\text{-}N_2C_6H_3Me_2)][BF_4]$ (2h). A similar procedure to that used for 2a gave this as a brown-reddish microcrystalline solid, m.p. 133-134°C in 93% yield.
Anal. Calcd. for $[(\eta^5\text{-}C_5H_5)Re(CO)_2\{3,5\text{-}N_2C_6H_3(CH_3)_2\}][BF_4]$:

C, 34.16; H, 2.66; N, 5.31. Found: C, 32.75; H, 2.54; N, 5.03.

Reactions of $[(MeCp)Mn(CO)_2(N_2C_6H_3R'_2)][BF_4]$. ($R_2$ = 3,5 dimethyl, 1c; 2,6 dichloro, 1d; 2,6 dinitro, 1e) with NaI (or KBr).

These reactions were carried out as described previously for the o-CF_3 derivative.[7]

To an acetone solution of the aryldiazenido compound, an excess of solid NaI (or KBr) was added and the mixture stirred at room temperature. The IR spectrum of this solution (after the reaction was completed, t<5 min) showed the presence of $[(MeCp)Mn(CO)_2(N_2)]$ as the only organometallic product. GC-MS analysis of the reaction mixture showed the presence of the corresponding iodo substituted benzene derivatives $IC_6H_3(CH_3)_2$ (m/e = 232); $IC_6H_3(Cl)_2$ (m/e = 272) and $IC_6H_3(NO_2)_2$ (m/e = 294), respectively.

No reaction was observed when the para-methyl (1b) derivative was used.

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OCH_3)][BF_4]$ 2b with NaI (solution).

To 2b (50 mg) dissolved in acetone (10 mL) was added an excess of solid NaI and the mixture was stirred at room temperature. The IR spectrum of this solution (after the reaction was completed, t = 15-20 min) showed the presence of [$CpRe(CO)_2(N_2)$] 4 (ν(CO) = 1960vs, 1898vs, cm^{-1}; ν(NN) = 2142s, cm^{-1}) and the diiodo complex [$CpRe(CO)_2I_2$] 5 (ν(CO) = 2041vs, 1980vs, cm^{-1}). GC-MS analysis of this solution showed the presence of three compounds, anisole p-iodoanisole and 4; complex 5 was not detected in this analysis.

Separation and characterization of the compounds resulting from this reaction was carried out as follows. After the reaction was completed, hexane was added to the reaction mixture to precipitate the excess of NaI, which was separated by filtration. The acetone/hexane solution was pumped down to dryness under vacuum and a dark brown-red solid residue was obtained. Sublimation of this residue under vacuum at room temperature afforded the p-iodoanisole as a white solid which was identified by ^1H-NMR and MS. ^1H-NMR ($CDCl_3$): δ7.56d, 6.68d (4H, C_6H_4); 3.77s (3H, OCH_3). MS, M^+ = 234. By increasing the vacuum ($\approx 10^{-6}$ mm Hg), a second solid (yellow) was obtained which was identified as [$CpRe(CO)_2N_2$], ^1H-NMR ($CDCl_3$) = δ5.23 (5H, C_5H_5); MS, M^+ = 336, 334. Finally, the dark red-brown residue (which did not sublime under these conditions) was identified as [$CpRe(CO)_2I_2$] by IR and MS. IR (acetone) ν(CO) = 2041vs, 1980vs cm^{-1}; (CH_2Cl_2) ν(CO) = 2049vs, 1988vs, cm^{-1}. MS: M^+, $(M-CO)^+$, $(M-2CO)^+$, $(M-I)^+$, $(M-CO-I)^+$, $(M-2CO-I)^+$.

Reaction of [CpRe(CO)$_2$(p-N$_2$C$_6$H$_4$OCH$_3$)][BF$_4$] 2b with KBr (Solution).

To a solution of 2b (40 mg) in acetone (10 mL) was added a stoichoimetric amount of solid KBr and the mixture stirred at room temperature. An IR spectrum of this solution (after 1 h.) showed very little reaction, probably due to the insolubility of KBr in acetone. Only after addition of excess of finely ground solid KBr and stirring another 12 additional hours, the reaction was completed.

GC-MS analysis of this reaction mixture revealed the presence of $BrC_6H_4OCH_3$ (m/e = 188), $C_6H_5OCH_3$ (m/e = 108) and 4 (m/e = 336, 334).

The IR spectrum of this solution was complicated, indicating the presence of several compounds. Evaporation of the acetone under vacuum yielded a red-brownish residue which was extracted with hexane. The IR spectrum of the yellow hexane extract showed only the presence of complex 4 (ν(CO) = 1974vs, 1920vs; ν(NN) = 2145vs, cm^{-1}). The remaining residue was dissolved in CH_2Cl_2 (deep red color) and its IR spectrum showed that this solution was essentially a mixture of two compounds; [CpRe(CO)$_2$Br$_2$] 6 (ν(CO) = 2055vs, 2004vs, cm^{-1}) and [CpRe(CO)Br(p-N$_2$C$_6$H$_4$OCH$_3$)] 7 (ν(CO) = 1956vs, ν(NN) = 1644vs, cm^{-1}).

The mass spectrum of this residue also confirmed the presence of 6 and 7.

MS of 6, M^+, $(M-CO)^+$, $(M-2CO)^+$, $(M-Br)^+$, $(M-CO-Br)^+$, $(M-2CO-Br)^+$.

This mass spectrum agrees perfectly with the one previously reported.[54] The MS of complex 7 is reported later on (page 71).

Reaction of $[CpRe(CO)_2(p-N_2C_6H_4OCH_3)][BF_4]$ 2b with KCl (Solution).

To a solution of 2b (50 mg) in acetone (10 mL) was added in excess of finely ground solid KCl and the mixture stirred at room temperature for 48 hs.

An IR spectrum of this solution showed clearly the formation of $[CpRe(CO)Cl(p-N_2C_6H_4OCH_3)]$ 8 plus a small amount of the tricarbonyl complex $[CpRe(CO)_3]$. A large amount of unreacted 2b was also observed. $[CpRe(CO)_2(N_2)]$ and $[CpRe(CO)_2Cl_2]$ were not formed under these conditions. The isolation and characterization of complex 8 are described on page 72 (solid state reaction).

Reactions of $[CpRe(CO)_2(N_2C_6H_4R')][BF_4]$ (R' = $p-CH_3$, 2a; $p-NEt_2$, 2d; $o-CF_3$, 2e; 2,6 dimethyl, 2g) with NaI or KBr.

These reactions were carried out similarly to those described for 2b.

From reactions with NaI, the compounds 4, 5, C_6H_5R' (or $C_6H_4R'_2$) and IC_6H_4R' (or $IC_6H_3R'_2$) were clearly observed and identified.

From reactions with KBr, the compounds 4, 6, C_6H_5R' (or $C_6H_4R'_2$) and BrC_6H_4R' (or $BrC_6H_3R'_2$) were observed and identified.

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OCH_3)][BF_4]$ 2b with KI (Solid State Reaction).

A solid sample of the aryldiazenido derivative 2b was finely ground with solid KI in a mortar. This mixture was heated in the oven (95°C) for 5 min. A strong odor of iodoanisole was produced. An IR spectrum of a KI pellet of this heated mixture showed the presence of a large amount of $[CpRe(CO)_2(N_2)]$ and a small amount of $[CpRe(CO)_2I_2]$.

The reaction was completed in 15 min. No production of the monocarbonyl derivative $[CpRe(CO)I(p\text{-}N_2C_6H_4OCH_3)]$ was observed.

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OCH_3)][BR_4]$ 2b with KBr (Solid State Reaction).

A similar procedure as described above was used. This reaction is much slower compared with the KI one, and it required 24 h. for completion. Following the reaction by IR (KBr pellet) showed the formation of $[CpRe(CO)Br(p\text{-}N_2C_6H_4OCH_3)]$ 7 as the major product. $[CpRe(CO)_2(N_2)]$ was not formed under these conditions.

Compound 7 was extracted from the solid reaction mixture by CH_2Cl_2 and chromatographed on a silica gel column prepared in hexane and eluted with CH_2Cl_2/hexane (70/30). Evaporation of the solvent afforded 7 as an analytically pure red-orange microcrystalline air-stable solid. IR (KBr): ν(CO) 1939vs, ν(NN) 1642vs, cm^{-1}; (CH_2Cl_2) ν(CO): 1956vs, ν(NN) 1644vs, cm^{-1}. ^1H-NMR (acetone-d_6): δ7.26d, 7.04d (4H, C_6H_4); 6.05s (5H, C_5H_5); 3.84s (3H, OCH_3). MS: M^+, $(M-CO)^+$, $(M-N_2R)^+$, $(M-CO-N_2R)^+$, $(M-CO-N_2R-Br)^+$.

Anal. Calcd. for $[CpRe(CO)Br(p-N_2C_6H_4OCH_3)]$: C, 31.58, H, 2.43; N, 5.67. Found: C, 31.60; H, 2.46; N, 5.61.

Reaction of $[CpRe(CO)_2(p-N_2C_6H_4CH_3)][BF_4]$ 2a with KBr (Solid State Reaction).

A similar procedure as described above was used and the monobromo complex $[CpRe(CO)Br(p-N_2C_6H_4CH_3)]$ was obtained as a red-orange microcrystalline air-stable solid. IR (KBr): ν(CO) 1945vs, ν(NN) 1643vs, cm^{-1}. (hexane): ν(CO) 1967vs, ν(NN) 1644vs, cm^{-1}. MS: M^+, $(M-CO)^+$, $(M-N_2R)^+$, $(M-CO-N_2R)^+$, $(M-CO-N_2R-Br)^+$.

Anal. Calcd. for $[CpRe(CO)Br(p-N_2C_6H_4CH_3)]$: C, 32.64; H, 2.51; N, 5.86. Found: C, 32.66; H, 2.53, N, 5.81.

Reaction of [$CpRe(CO)_2(p-N_2C_6H_4OCH_3)$][$BF_4$] 2b with KCl (Solid State Reaction).

A similar procedure as described above was used . This reaction was even slower compared with KBr. After 24 h. heating at 95°C, a significant amount of 2b remained. Again [$CpRe(CO)Cl(p-N_2C_6H_4OCH_3)$] 8 was the major product; no formation of [$CpRe(CO)_2(N_2)$] was observed.

Complex 8 was extracted from the solid reaction mixture by CH_2Cl_2 and this solution chromatographed on a silica gel column prepared in hexane.

Elution with CH_2Cl_2/hexane (70/30) moved an orange band which corresponded to compound 8. Evaporation of the solvent afforded 8 as a red-orange microcrystalline air-stable solid. Complex 8 was obtained as red crystals from an hexane solution at -12°C (freezer). m.p. 107-109°C. IR (KBr): ν(CO) 1936vs, ν(NN) 1642vs cm^{-1}. (CH_2Cl_2): ν(CO) 1949vs, ν(NN) 1643vs cm^{-1}. (hexane): ν(CO) 1963vs, ν(NN) 1642vs cm^{-1}. ^{1}H-NMR (acetone-d_6): δ7.27d, 7.07d (4H, C_6H_4); 6.07s (5H, C_5H_5); 3.88s (3H, OCH_3). MS: M^+, $(M-CO)^+$, $(M-N_2R)^+$, $(M-CO-N_2R)^+$, $(M-CO-N_2R-Cl)^+$.

Anal. Calcd. for [$CpRe(CO)Cl(p-N_2C_6H_4OCH_3)$]: C, 34.71; H, 2.67; N, 6.23. Found: C, 34.69; H, 2.64; N, 6.22.

Reaction of [(MeCp)Mn(CO)$_2$(o-$N_2C_6H_4CF_3$)][BF_4] 1a with NH_3(ℓ)

Liquid ammonia (*ca.* 5 mL) was condensed at -50°C. Solid 1a (50 mg) was added and the mixture stirred at this temperature for 15 min. A fast reaction took place and a brown-orange solid precipitated out of the solution, and was isolated by decanting the excess of ammonia and then washed twice with *ca.* 2 mL of liquid ammonia (NH_4BF_4, which was the side product of this reaction, is soluble in liquid ammonia). The solid was dried, first with a stream of N_2 (g) and then vacuum. The solid can be handled in air for about 30 min. without deterioration, but with longer exposure it decomposes. Solutions in organic solvents were extremely air sensitive. Yield 96%. IR (CH_2Cl_2) = ν(CO) 1980vs, ν(NN) 1665vs, cm^{-1}.

Anal. Calcd. for [(MeCp)Mn(CO)($CONH_2$)(*o*-$N_2C_6H_4CF_3$)]: C, 47.49; H, 3.43; N, 11.08. Found: C,47.21; H, 3.46; N, 11.25.

Reaction of [(MeCp)Mn(CO)$_2$(o-$N_2C_6H_4CF_3$)][BF_4] 1a with $HN(CH_3)_2$

This reaction was carried out in neat $HN(CH_3)_2$; the secondary amine was condensed at -50°C to a volume *ca.* 5 mL. Solid 1a (50 mg) was added and the mixture stirred at this temperature for 15 min. A fast reaction took place and a brown-reddish solid precipitated out of the solution. The excess of amine was evaporated under vacuum and the brown-reddish residue obtained was dissolved in CH_2Cl_2. Addition of diethyl ether precipitated a white solid which was filtered off. This solid was analyzed, after purification, as the ammonium salt $[H_2N(CH_3)_2][BF_4]$.

The brown-reddish dichloromethane solution was pumped down to dryness affording an oily product which was washed twice with hexane to give a brown-reddish microcrystalline solid. Yield 95%.

Anal. Calcd. for $[(MeCp)Mn(CO)(CONMe_2)(o\text{-}N_2C_6H_4CF_3)]$: C, 50.12; H, 4.18; N, 10.32. Found: C, 49.89; H, 4.20; N, 10.28.

Reaction of $[(MeCp)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ 1a with $NaNH_2$

To a solution of 1a in acetone (10 mL) was added a stoichoimetric amount of solid $NaNH_2$ and the mixture was stirred at room temperature for 15 min. The IR spectrum of the red solution showed the presence of $[(MeCp)Mn(CO)_2(N_2)]$ 3, as the only carbonyl containing product. When the reaction was carried out at -30°C, the carbamoyl complex $[(MeCp)Mn(CO)(CONH_2)(o\text{-}N_2C_6H_4CF_3)]$ was obtained instead (by IR).

Reaction of $[CpRe(CO)_2(o\text{-}N_2C_6H_4CF_3)][BF_4]$ 2e with $NH_3(\ell)$

A procedure similar to that used for the o-CF_3 derivative of manganese 1a gave the rhenium carbamoyl complex

$[CpRe(CO)(CONH_2)(o\text{-}N_2C_6H_4CF_3)]$ 10e, as a golden-yellow microcrystalline solid in 97% yield.

Anal. Calcd. for $[CpRe(CO)(CONH_2)(o\text{-}N_2C_6H_4CF_3)]$: C, 33.87; H, 2.22; N, 8.47. Found: C,31.92; H, 2.28; N, 8.45.

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OCH_3)][BF_4]$ 2b with $NH_3(\ell)$

A procedure similar to that used for 1a gave the carbamoyl complex $[CpRe(CO)(CONH_2)(p\text{-}N_2C_6H_4OCH_3)]$ 10b, as a golden-yellow microcrystalline solid in 96% yield. ^1H-NMR ($CDCl_3$): δ7.19d, 6.92d (4H, C_6H_4); 5.78s (5H, C_5H_5); 3.81s (3H, OCH_3).

Anal. Calcd. for $[CpRe(CO)(CONH_2)(p\text{-}N_2C_6H_4OCH_3)]$: C, 36.68; H, 3.06; N, 9.17. Found: C, 35.02; H, 3.11; N, 9.20.

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OCH_3)][BF_4]$ 2b with H_2NCH_3

A procedure similar to that used for the reactions with liquid ammonia, gave the carbamoyl complex $[CpRe(CO)(CONHCH_3)(p\text{-}N_2C_6H_4OCH_3)]$ 12b, as a golden-yellow microcrystalline solid in 96% yield. ^1H-NMR ($CDCl_3$): δ7.22d, 6.95d (4H, C_6H_4); 5.79s (5H, C_5H_5); 3.84s (3H, OCH_3); 2.84d (3H, CH_3; JHNCH = 4.8 Hz); 5.57s, br (1H, NH).

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OCH_3)][BF_4]$ 2b with $HN(CH_3)_2$

A procedure similar to that used for the reactions with liquid ammonia, gave the carbamoyl complex $[CpRe(CO)(CONMe_2)(p\text{-}N_2C_6H_4OCH_3)]$ 13b, as a golden-yellow microcrystalline solid in 98% yield. ^1H-NMR ($CDCl_3$): δ7.22d, 6.95d

(4H, C_6H_4); 5,75s (5H, C_5H_5); 3.84s (3H, OCH_3); 3.09s (6H, CH_3).

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OCH_3)][BF_4]$ 2b with $NaNH_2$

To a solution of 2b in CH_2Cl_2 (10 mL) was added a stoichoimetric amount of solid $NaNH_2$ and the mixture was stirred at room temperature for 5 min. The color changed from red to yellow-orange. The IR spectrum of this solution showed only the presence of the carbamoyl complex $[CpRe(CO)(CONH_2)(p\text{-}N_2C_6H_4OCH_3)]$ 10b.

Reactions of Carbamoyl Complexes 9a, 11a, 10b, 10e, 12b and 13b with Acids

To an acetone or CH_2Cl_2 solution of the carbamoyl complex 9a, 11a, 10b, 10e, 12b or 13b, was added aqueous HCl or HBF_4 and the mixture stirred at room temperature for 5 min. An IR spectrum of the reaction mixture showed the regeneration of the corresponding aryldiazenido complex in each case.

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OCH_3)][BF_4]$ 2b with PPh_3

To a solution of 2b (70 mg) in acetone (10 mL) was added a stoichoimetric amount of solid PPh_3 (34.7 mg) and the mixture was stirred at room temperature for 2 h. An IR spectrum of this solution showed the presence of the starting aryldiazenido complex 2b and the known triphenylphosphine derivative

[$CpRe(CO)_2PPh_3$] in approximately equal amount. The mixture was stirred for another 6 h. and the new IR spectrum showed that the ratio of both compounds had not changed. A second equivalent of PPh_3 was added and the mixture stirred for 4 h. An IR spectrum showed now that the reaction had been completed.

Addition of diethylether induced the precipitation of a red-orange microcrystalline solid which was identified (after recrystallization from acetone/CH_2Cl_2) as the diazophosphonium salt [Ph_3P-$N_2C_6H_4OCH_3$][BF_4].

The light yellow ether solution was pumped down to dryness under vacuum to give a white-yellowish microcrystalline solid, which corresponded to [$CpRe(CO)_2PPh_3$]. Light yellow crystals for microanalysis were obtained from a hexane solution at -12°C (freezer). IR (acetone): ν(CO) 1929vs, 1861vs, cm^{-1}.
Anal. Calcd. for [$CpRe(CO)_2(PPh_3)$]: C, 52.72; H, 3.52. Found: C, 52.73; H, 3.57.
Anal. Calcd. for [Ph_3P-$N_2C_6H_4OCH_3$][BF_4]: C, 61.98; H, 4.55; N, 5.79. Found: C, 60.80; H, 4.60; N, 5.80.

Reaction of [$CpRe(CO)_2(p$-$N_2C_6H_4NEt_2)$][BF_4] 2d with PPh_3

This reaction was carried out as described above for 2b. The color changed from dark green to red. The products obtained from this reaction were [$CpRe(CO)_2PPh_3$] and the corresponding diazophosphonium salt [Ph_3P-$N_2C_6H_4NEt_2$][BF_4], which was obtained as a ruby-red microcrystalline solid.

Anal. Calcd. for $[Ph_3P\text{-}N_2C_6H_4NEt_2][BF_4]$: C, 64.00; H, 5.52; N, 8.00. Found: C, 63.16; H, 5.52; N, 7.84.

Its IR spectrum (KBr) was identical to the one previously reported.[32]

Reactions of other Aryldiazenido Complexes of Rhenium (2a, p-CH_3; 2e, o-CF_3; 2g, 3,5 dimethyl) with PPh_3

These reactions were carried out as described above for 2b. The product obtained from these was $[CpRe(CO)_2PPh_3]$, but in these cases, the corresponding diazophosphine could not be obtained.

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OCH_3)][BF_4]$ 2b with $Ph_2PCH_2PPh_2$

A procedure similar to that used for the reactions with PPh_3, gave the new diphosphine derivative $[CpRe(CO)_2(Ph_2PCH_2PPh_2)]$ as a pale yellow microcrystalline air-stable solid. IR (acetone) ν(CO) 1927vs, 1858vs, cm^{-1}. (hexane): ν(CO)1938vs, 1872vs, cm^{-1}. ^{1}H-NMR (acetone-d_6): δ7.96-7.25 m, br, (20H, C_6H_5); 5.06s (5H, C_5H_5); 4.37dd (2H, CH_2). ^{31}P-NMR (acetone-d_6; calibrated against external H_3PO_4): δ22.17; 11.58.

The free ligand ($Ph_2PCH_2PPh_2$) showed only one phosphorus signal at -23.43 ppm.

An orange-brown solid precipitated out of the solution after addition of diethyl ether, but its chemical analysis did not fit its formulation as a diazophosphonium salt, even though it showed a high content of nitrogen.

Anal. Calcd. for [CpRe(CO)$_2$(Ph$_2$PCH$_2$PPh$_2$)]: C, 55.57; H, 3.91. Found: C, 55.88; H, 4.02.

Reaction of [CpRe(CO)$_2$(p-N$_2$C$_6$H$_4$NEt$_2$)][BF$_4$] 2d with Ph$_2$PCH$_2$PPh$_2$

A procedure similar to that used for the reactions with PPh$_3$, gave the diphosphine derivative [CpRe(CO)$_2$(Ph$_2$PCh$_2$PPh$_2$)]. A brown-greenish solid was obtained by addition of diethyl ether, but again, its chemical analysis did not fit its formulation as a diazophosphonium salt, even though it showed a high content of nitrogen.

Reaction of [CpRe(CO)$_2$(p-N$_2$C$_6$H$_4$CH$_3$)][BF$_4$] 2a with NaOCH$_3$

To a solution of 2a (30 mg) in methanol (5 mL) was added a stoichoimetric amount of solid NaOCH$_3$ (3.2 mg) and the mixture 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 [CpRe(CO)(COOCH$_3$)(p-N$_2$C$_6$H$_4$CH$_3$)] 14a. Evaporation of the solvent under vacuum and extraction by CH$_2$Cl$_2$ afforded 14a as a microcrystalline yellow solid. Spectroscopic data are given in the text.

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OCH_3][BF_4]$ 2b with $NaOCH_3$

A procedure similar to that used for 2a gave the alkoxycarbonyl complex $[CpRe(CO)(COOCH_3)(p\text{-}N_2C_6H_4OCH_3)]$ 14b as a microcrystalline orange-yellow solid.

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4NEt_2)][BF_4]$ 2d with $NaOCH_3$

A procedure similar to that used for 2a gave the alkoxycarbonyl complex $[CpRe(CO)(COOCH_3)(p\text{-}N_2C_6H_4NEt_2)]$ 14d, as a microcrystalline red-orange solid.

Reactions of Alkoxycarbonyl Complexes 14a, 14b and 14d with Acids

These reactions were carried out as described for the carbamoyl complexes, with similar results.

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4NEt_2)][BF_4]$ 2d with HCl(g)

Dry HCl(g) was bubbled into a solution of 2d (60 mg, 0.105 mmol) in CH_2Cl_2 (10 mL) for a few minutes at room temperature. An instantaneous reaction took place and the color changed from dark green to reddish-brown and a reddish-brown oil precipitated out. An orange-brown solid was isolated by washing the oil with hexane at least two times and identified as the adduct $[CpRe(CO)_2(p\text{-}N_2C_6H_4NEt_2)][BF_4]\cdot HCl$.IR ($CH_2Cl_2$) 2095vs, 2038vs ($\nu(CO)$), 1752vs, br ($\nu(NN)$); [1725vs, br $\nu(^{15}N^{14}N)$].

Anal. Calcd. for $[CpRe(CO)_2(\underline{p}\text{-}N_2C_6H_4NEt_2)][BF_4]\cdot HCl$ C, 33.64; H, 3.30; N, 6.92. Found: C, 32.25; H, 3.57; N, 6.58. This adduct readily loses HCl to regenerate the aryldiazenido complex. None of the other rhenium aryldiazenido complexes 2 reacts with HCl(g).

CHAPTER III

Aryldiazene, Arylhydrazido(2-) and Arylhydrazido(1-) Complexes of Rhenium

3.1 Introduction

Catalytic reduction of molecular nitrogen under mild conditions via dinitrogen complexes and other nitrogen hydride intermediates, such as diazenido or hydrazido(2-) complexes, to give hydrazine and ammonia, is one of the more important goals in homogeneous catalysis today. Although it has been demonstrated that well defined complexes containing the dinitrogen ligand are reduced to NH_3 and N_2H_4 under mild conditions[68], the detailed mechanism for the reduction of dinitrogen is not well understood.

Several mechanisms for this process have been postulated[69],[70] and they involve diazene and hydrazido(2-) complexes, among others.

There is a large number of diazene complexes known, which have been reviewed recently.[71] They are available by different synthetic approaches; complexes of the more stable disubstituted diazenes are formed directly from the free ligand, which is not possible with monosubstituted diazenes since they are very unstable and very difficult to handle. Complexes of diazene and its monosubstituted derivatives are therefore usually made from an already metal-bound precursor so that interaction with the transition metal stabilizes the diazene ligand so synthesized.

Bridging diazene complexes have been synthesized by oxidation of species containing substituted or unsubstituted hydrazine ligands.[72-74] Sellman and co-workers[17], using a completely different approach, were able to reduce the ligating dinitrogen in the complex $[CpMn(CO)_2(N_2)]$ to a diazene ligand by consecutive nucleophilic (at N^1) and electrophilic attack (at N^2) to give the complexes $[CpMn(CO)_2(NPhNH)]$ and $[CpMn(CO)_2(NCH_3NCH_3)]$. The complex containing the phenyldiazene ligand can react further with $[CpMn(CO)_2THF]$ to give the dinuclear species containing a bridging phenyldiazene group, $[\{CpMn(CO)_2\}_2\mu\text{-}(NPhNH)]$.[17]

Monoaryldiazene complexes of the type M-NHNR are most commonly synthesized by protonation of doubly-bent aryldiazenido derivatives[13,14,35] or insertion of aryldiazonium cations into a metal hydride bond.[75] Examples of these reactions are shown in eq. 15

$$\begin{tikzcd}
PtCl(NNPh)(PEt_3)_2 + H^+ \arrow[dr] & \\
& {[PtCl(NHNPh)(PEt_3)_2]^+} \qquad (15) \\
PtCl(H)(PEt_3)_2 + PhNN^+ \arrow[ur] &
\end{tikzcd}$$

The synthesis of diazene complexes by a new reaction is described in this chapter. It has been found that the aryldiazenido complexes of rhenium of the type $[CpRe(CO)_2(N_2C_6H_4R')][BF_4]$ 2, described in the previous chapter, react with $NaBH_4$ in THF/H_2O or methanol near 0°C instantaneously to give bright coloured solutions from which the new aryldiazene complexes $[CpRe(CO)_2(NHNC_6H_4R')]$ easily can be isolated.

The hydrazido(2-) ligand, NNR^1R^2, is an isomer of diazene and it is frequently found in Mo, W and Re chemistry. Hydrazido(2-) complexes are intermediates frequently observed in the formation of ammonia or amines from protonation or alkylation reactions of molybdenum and tungsten dinitrogen complexes containing tertiary phosphines as co-ligands.[68,76,77] They are also available by attack of an electrophile, e.g. H^+, Me_3O^+ or Et_3O^+, at an 18-electron singly-bent aryldiazenido complex[78], as shown in eq. 16.

$$Mo(NNPh)(S_2CNR_2)_3 + HBF_4 \rightarrow [Mo(NNHPh)(S_2CNR_2)_3][BF_4] \quad (16)$$

Recently, several papers dealing with hydrazido(2-) complexes have been published which include synthesis[77,79-81], protonation reactions[82,83,76], mechanism of their formation[84], reactivity[85-87] and theoretical studies.[88]

The synthesis of hydrazido(2-) complexes by a new approach will be described in this chapter. It was found that the complexes $[CpRe(CO)_2(N_2C_6H_4R')][BF_4]$ 2, react with R"- (R" = CH_3, Ph, Bu^n) to yield the new hydrazido(2-) derivatives $[CpRe(CO)_2(NNR"C_6H_4R')]$.

Hydrazido(1-) complexes of transition metals are relatively rare and only very few have been characterized by X-ray structural studies. This type of complex has been obtained by different synthetic approaches, for example, reaction of a metal dihydrido complex with RN=NR (R = Ph, CO_2Me) (eg. $Cp_2MoH(RNNHR)$)[89] or with diazonium salt (eg. $Cp_2W(NH_2NR)$)[90], reaction of a metal-monohydride species with diazonium salt (eg. $[Ir(CO)(NHNHC_6H_3R)(PPh_3)_2][BF_4]$)[91], protonation of a hydrazido(2-) complex (eg. $[Mo(NNMePh)(NHNMePh)(dtc)_2][BF_4]$)[79] and by reaction of metal nitrosyl derivatives of molybdenum with alkyl or aryl-hydrazines (eg. CpMo(NO)(NHNHMe)I).[92]

In this chapter, the synthesis of hydrazido(1-) complexes of rhenium of general formula $[CpRe(CO)_2(NHNR"C_6H_4R')][BF_4]$ from protonation of hydrazido(2-) complexes will also be discussed.

The reactions of $[CpRe(CO)_2(N_2C_6H_4R')][BF_4]$ 2 with $NaBH_4$, $LiCH_3$, LiPh and $LiBu^n$ to give these diazene and hydrazido(2-) complexes, therefore, warrant a separate chapter in this thesis.

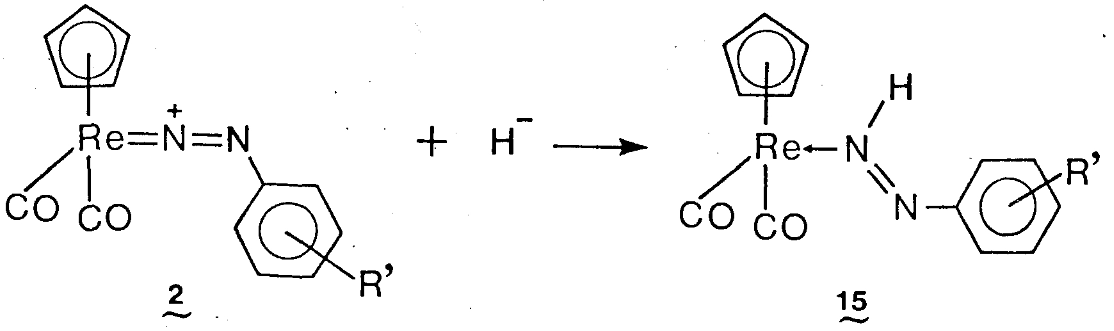
3.2 Chemical Reactions

3.2.1 Reaction with $NaBH_4$

Our interest in the possibility of obtaining interesting products by reaction of $[CpRe(CO)_2(N_2R)][BF_4]$ and $[(MeCp)Mn(CO)_2(N_2R)][BF_4]$ with $NaBH_4$ was directly stimulated by reports that the related and isoelectronic cationic nitrosyl complex $[CpRe(CO)_2(NO)]^+$ and particulary its phosphine derivative $[CpRe(CO)(PPh_3)(NO)]^+$ reacted with hydride ion (attack at a carbonyl group) to yield rare examples of stable formyl complexes.[93-95] On the other hand, as described in Chapter II, we had already found that these aryldiazenido complexes reacted with several nucleophiles to give different types of compounds, depending on the site of nucleophilic attack.

Therefore, the reaction of H^- with these complexes could, in principle, be visualized to occur at a choice of possible sites, including the metal center (to give a metal hydrido derivative), CO (to give a formyl ligand), the aryl ring (to give the dinitrogen complex) or even at the diazo ligand.

We found that the rhenium complexes <u>2</u> reacted instantaneously in 1:1 THF-water solution or in methanol near 0°C with a stoichoimetric amount of $NaBH_4$ to give very bright coloured solutions, shown by IR to contain a dicarbonyl species. These new substances were easy to isolate as pure microcrystalline solids, which were highly soluble in non-polar solvents, such as hexane, which suggested to us that they were neutral compounds. They have been unambiguously identified by ^{1}H-NMR to contain the aryldiazene ligand HNNR, 15 (with the hydrogen bound at N^1). (eq. 17). $[CpRe(CO)_2(N_2)]$ was not formed in these reactions.



(17)

The aryldiazenido complexes of manganese 1 also reacted with $NaBH_4$ to give deep-coloured solutions, which contained two dicarbonyl species by IR. $[(MeCp)Mn(CO)_2(N_2)]$ 3 was positively identified as one of them and the second one was tentatively assigned to the corresponding aryldiazene $[(MeCp)Mn(CO)_2(NHNR)]$ 16.

This is, to our knowledge, the first instance in which an aryldiazenido ligand has been found capable of conversion to an identifiable aryldiazene ligand by hydride attack. In all those cases that we know of, where aryldiazenido compounds have been reacted with borohydride, reduction to a hydrido complex[30] or attack at an ancillary ligand[34] tends to have occurred instead.

The rhenium aryldiazene complexes were fully characterized by IR and ^{1}H-NMR. IR and ^{1}H-NMR data are presented in Table III. The IR spectra of these complexes showed two ν(CO) bands, which are lowered substantially from the corresponding positions in the aryldiazenido complexes. For example, the original ν(CO) bands: 2058vs, 1995vs (in CH_2Cl_2) in the p-NEt_2 derivative 2d are lowered to 1920vs, 1851vs, cm^{-1} in 15d. The position of ν(NN) has not been unambiguously identified. No absorption due to ν(NH) was observed either in solution or KBr pellets.

The ^{1}H-NMR spectra of these diazene complexes 15 showed that the N-H resonance occurs well downfield (ca. δ15), at the lower end of the range (ca. 11-15 ppm) observed for many other aryldiazenes[96,97], and the resonance was split into a sharp doublet ($^1J(^{15}NH)$ = 69 Hz) in the spectrum of the $^{15}N^1$ derivative $[CpRe(CO)_2(p\text{-}^{15}NHNC_6H_4NEt_2)]$ 15d.

This coupling constant compares well with $^1J(^{15}NH)$ values observed for a number of other aryldiazene complexes, such as $RhCl_3(p\text{-}^{15}NHNC_6H_4OCH_3)(PPh_3)_2$ (65 Hz)[97], $OsCl_2(p\text{-}^{15}NHNC_6H_4CH_3)(CO)(PPh_3)_2$ (67 Hz)[97] and $[RuCl(^{15}NHNPh)(CO)_2(PPh_3)_2][ClO_4]$ (65 Hz)[35].

Table III. IR and ^{1}H-NMR Data for Rhenium and Manganese Aryldiazene Complexes

Compound		ν(CO)^a	^{1}H-NMR^b			
			Cp	Aryl	NH	Other
$[CpRe(CO)_2(\underline{p}\text{-}NHNC_6H_4CH_3)]$	**15a**	1938, 1876	5.61s	7.24d 7.39d	15.70s	2.26s (CH_3)
$[CpRe(CO)_2(\underline{p}\text{-}NHNC_6H_4OCH_3)]$	**15b**	1938, 1874	5.61s	6.95d 7.46d	15.46s	3.86s (OCH_3)
$[CpRe(CO)_2\{\underline{p}\text{-}NHNC_6H_4NEt_2\}]$	**15d**	1932, 1869	5.40s	6.60d 7.31d	14.80^{c}s	1.09t (CH_3) 3.40q (CH_2)
$[CpRe(CO)_2(NHNC_6H_5)]$	**15f**	1952, 1893	5.49s	7.37s	15.81s	
$[CpRe(CO)_2(3,5\text{-}NHNC_6H_3Me_2)]$	**15h**	1940, 1877				
$[MeCpMn(CO)_2(\underline{o}\text{-}NHNC_6H_4CF_3)]$	**16a**	1958, 1900	d	d	13.70s(br)	d
$[MeCpMn(CO)_2(3,5\text{-}NHNC_6H_3Me_2)]$	**16c**	1957, 1901				

a In cm^{-1} for hexane solution; all bands are very strong.

b In acetone-d_6 at -30°C; abbreviations: s, singlet; d, doublet; q, quartet.

c 14.82d in ^{15}N(1)H derivative, $^1J(^{15}NH)$ 69 Hz.

d Very broad.

The dinitrogen complex $[CpRe(CO)_2(N_2)]$ 4 and the corresponding substituted arene C_6H_5R' (or $C_6H_4R'_2$) were the only products observed during MS analysis of complexes 15, presumably as a result of thermal decomposition of the aryldiazene complex. This has been shown to occur by monitoring a heated KBr disk of 15b by IR, where the ν(CO) bands of 15b become smoothly replaced by those of complex 4, and an odor of anisole was produced. (eq. 18).

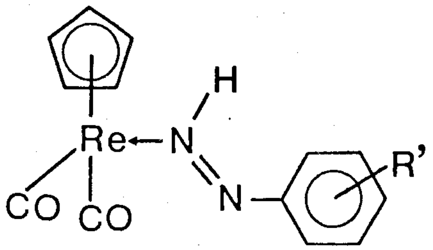
$$\underset{\underline{15}}{[CpRe(CO)_2(NHNR)]} \xrightarrow{\Delta} \underset{\underline{4}}{[CpRe(CO)_2(N_2)]} + RH \qquad (18)$$

The thermal stability of these aryldiazene complexes seems to increase in the order p-NEt_2 > p-OCH_3 ≈ p-CH_3 >> H

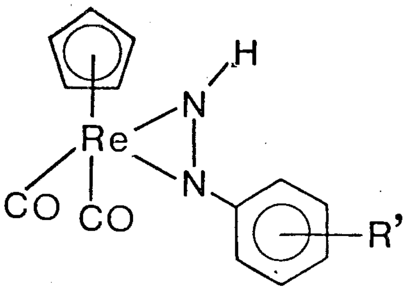
The IR spectrum of the reaction mixture of the manganese complex 1a with $NaBH_4$ showed the presence of the dinitrogen complex 3 and an additional dicarbonyl species with ν(CO) bands at 1958vs, 1900vs, cm^{-1}. We tentatively suggest that these may be correlated with a lowfield NMR signal at δ13.70 as indicating the formation of the analogous diazene complex $[(MeCp)Mn(CO)_2(o\text{-}NHNC_6H_4CF_3)]$ 16a. Furthermore, the broadness of the ^{1}H-NMR and the presence of a broad, multiline ESR resonance showed that the reaction was accompanied by the formation of paramagnetic species. We were not able to obtain the manganese aryldiazene complex, which appeared to be extremely air and temperature sensitive, pure and free from paramagnetic contamination for further studies.

Returning to the rhenium compounds, IR and ^{1}H-NMR evidently support the formulation of complexes <u>15</u> as aryldiazene complexes, but the actual bonding mode (η^1 or η^2) of the ligand could not be deduced from these data. All previously reported aryldiazene complexes have been shown, or are believed to be η_1-bonded[98,35] and on this basis <u>15</u> has structure IV. However ^{15}N-NMR (see Appendix II) and ^{1}H-NMR experiments carried out with the hydrazido(1-) complex [CpRe(CO)$_2$(p-NHNHC$_6$H$_4$OCH$_3$)]-[BF$_4$] formed by protonating this diazene complex (which will be discussed in Chapter IV). suggest the possibility of an η^2 (cyclic) structure V for the diazene complexes. This η^2-bonding mode is known to occur in a number of <u>bis</u>aryl or <u>bis</u>alkyl diazene complexes.[99,100]

In absence of specific experiments, such as NOE and obviously X-ray structural studies, this problem cannot be resolved at the present time; therefore, complexes <u>15</u> will be represented in this thesis as IV.



IV



V

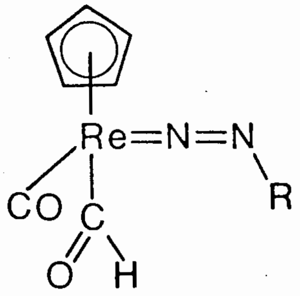
An examination by IR and NMR of the extracted solutions of the diazene complexes quickly after synthesis (THF/H_2O solvent), particularly when maintained at low temperature, gave evidence of the presence of a second compound which seemed quite likely to be an intermediate in the synthesis of the diazene.

By changing the solvent to methanol, the course of the reaction could be followed by ^{1}H-NMR (see Figure 4). Addition of $NaBH_4$ to $[CpRe(CO)_2(p\text{-}N_2C_6H_4OCH_3)][BF_4]$ 2b in methanol-d_4 at -40°C gave spectrum Fig. 4B-II (t = 5 min.) which exhibits signals due to the intermediate at δ16.60 (NH), 5.94 (C_5H_5) and 3.86 (OCH_3) and to the diazene complex 15b, at 5.56 (C_5H_5) and 3.82 (OCH_3). The signals corresponding to the intermediate species smoothly disappeared with concomitant increase of the resonances due to the diazene complex 15b, which was the final product. (See Fig. 4B-III and IV.)

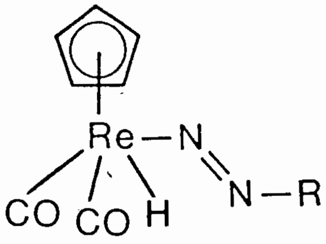
No NH resonance due to the diazene complex 15b was observed at the end of the reaction, probably because of exchange with deuterium. By now replacing methanol-d_4 by acetone-d_6, we were able to observe this resonance, ca. δ15 (presumed exchange back to NH from H_2O present in the acetone), which split into a sharp doublet with ^{15}N-isotopic labelling at N^1. This NH resonance disappeared again immediately after addition of one drop of methanol-d_4 (see Fig. 4C).

Identical experiments at -70°C (in methanol-d_4) showed that the reaction was instantaneous to give the intermediate species as the only product, which was stabilized at this temperature. Above -45°C, identical transformations from the intermediate species to the diazene complex 15b, exactly as described above, were observed.

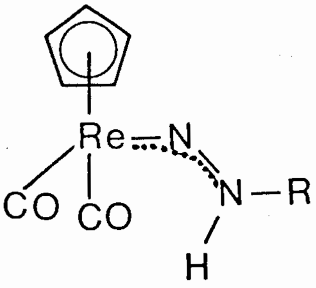
Three plausible intermediates that could lead to a diazene complex are: (i) the formyl complex VI (attack at CO), (ii) a metal-hydrido derivative VII (attack at metal center) or (iii) a hydrazido(2-) species VIII (attack at N^2).



VI



VII



VIII

Figure 4

Low Temperature ^{1}H-NMR Experiments (100 MHz): Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ (2b) with $NaBH_4$ in Methanol-d_4 (-40°C).

Figure 4A: ^{1}H-NMR spectrum of 2b in Methanol-d_4.

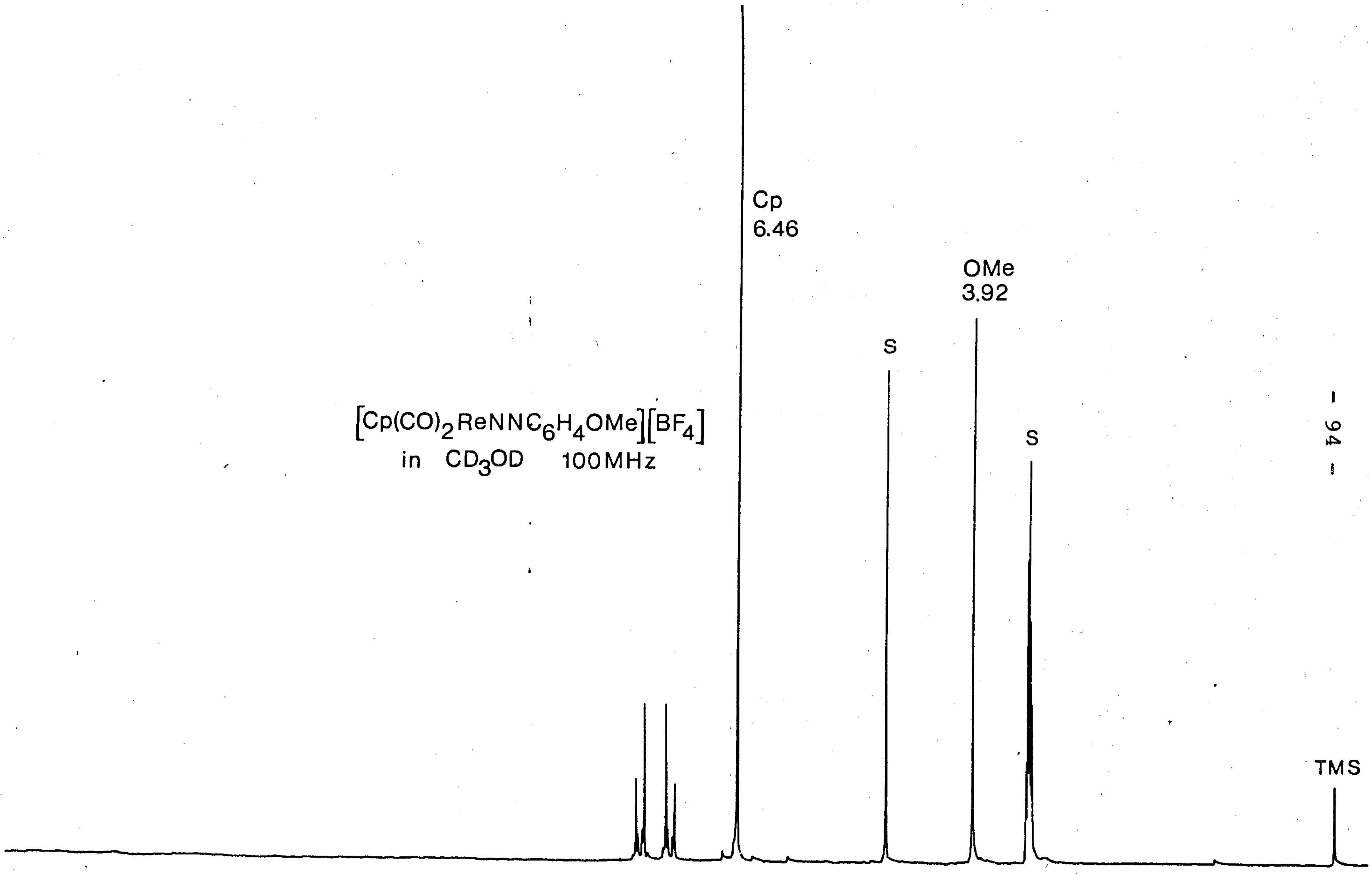
Figure 4B: I → Time = 0 min (spectrum of 2b).

II → Time = 5 min.

III → Time = 15 min.

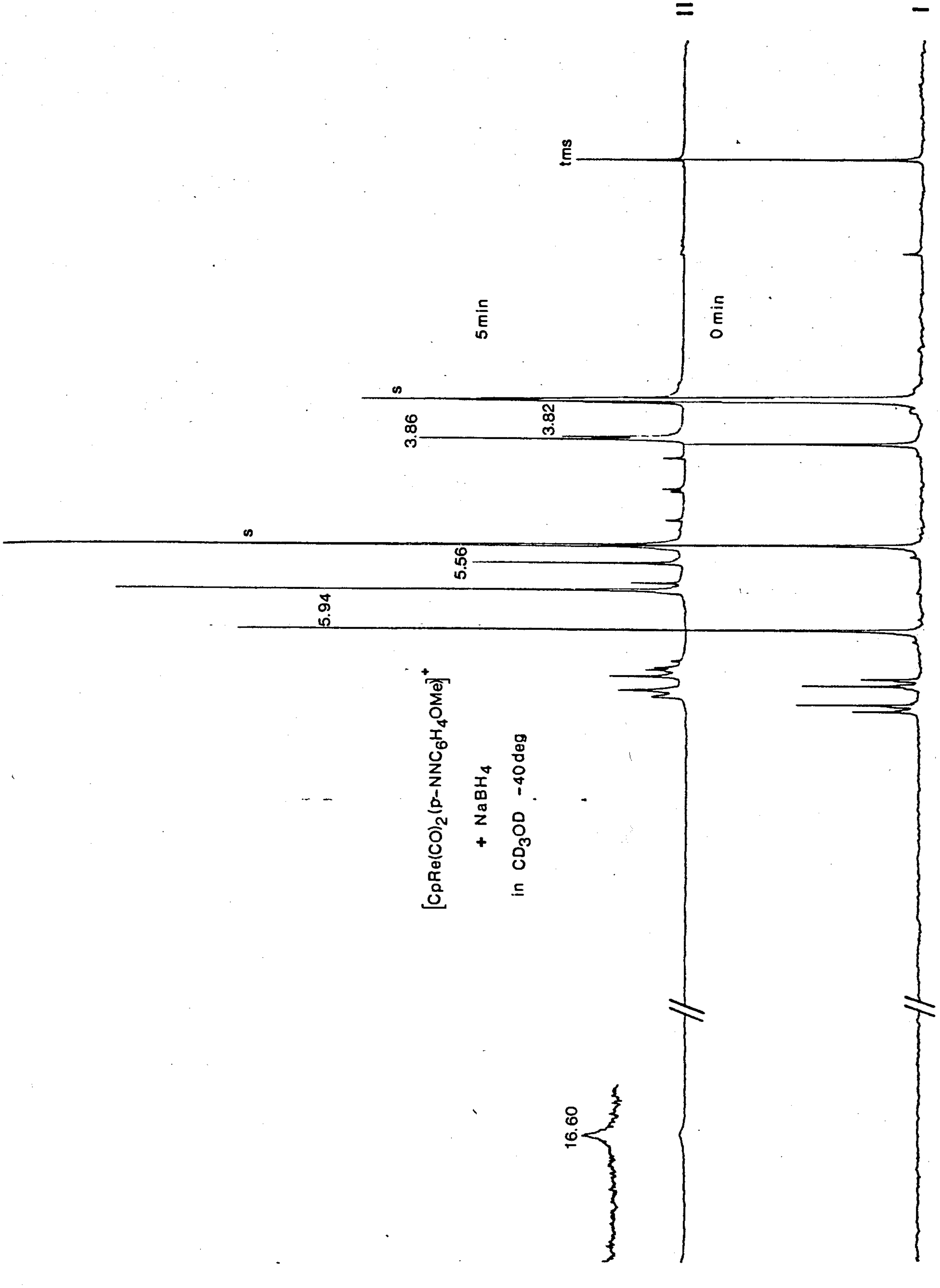
IV → Time = 40 min (spectrum of 15b).

Figure 4C: ^{1}H-NMR spectrum of 15b in Acetone-d_6.

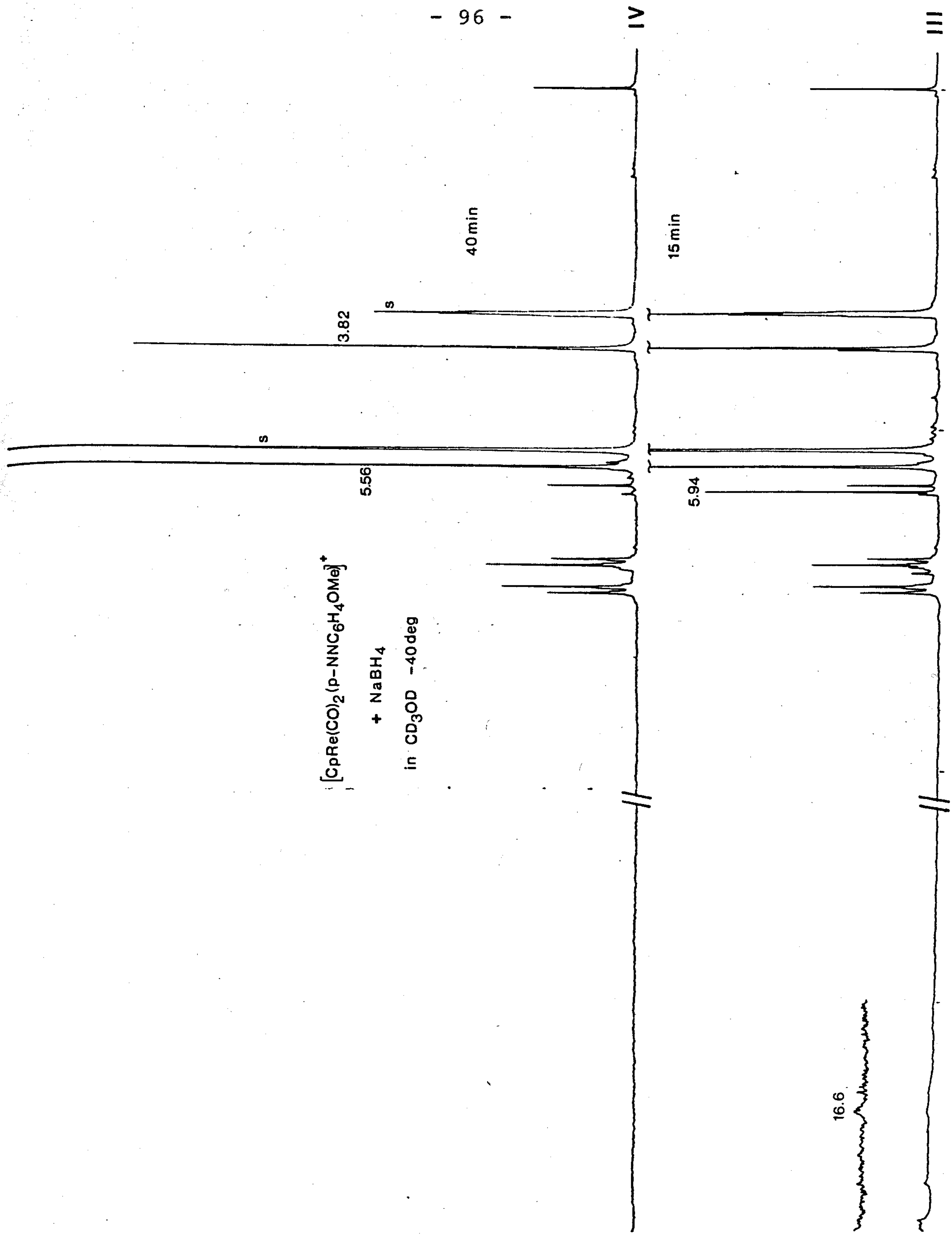


$[Cp(CO)_2ReNNC_6H_4OMe][BF_4]$
in CD_3OD 100MHz

4A


II
I
tms
5 min
0 min
s
3.86
3.82
s
5.56
5.94
16.60
$[CpRe(CO)_2(p\text{-}NNC_6H_4OMe)]^+$
+ $NaBH_4$
in CD_3OD -40 deg

4B

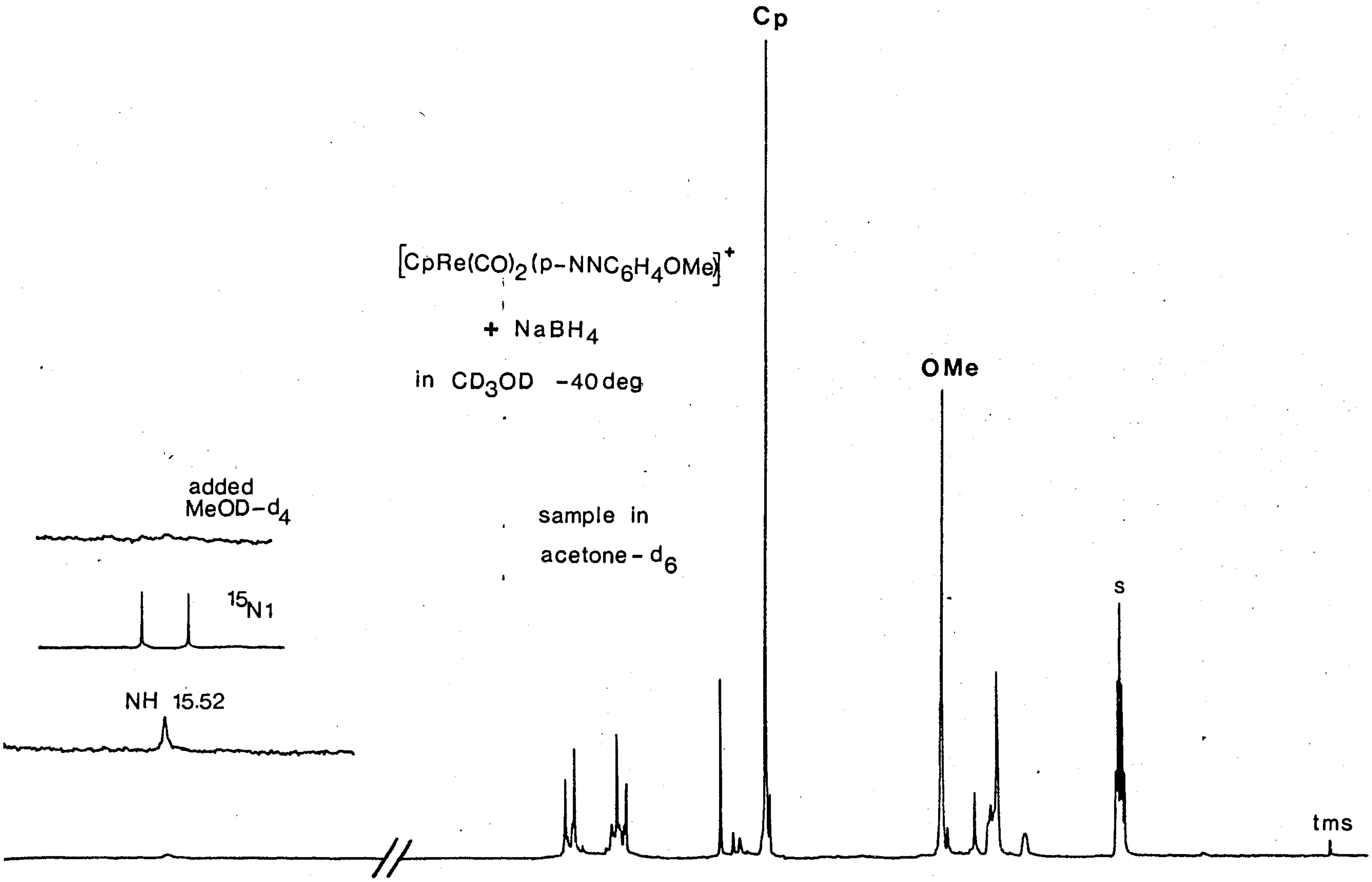


$[CpRe(CO)_2(p\text{-}NNC_6H_4OMe)]^+$

$+ NaBH_4$

in CD_3OD -40 deg

4B


Cp
$[CpRe(CO)_2(p\text{-}NNC_6H_4OMe)]^+$
$+ NaBH_4$
in CD_3OD -40 deg
OMe
added
MeOD-d_4
$^{15}N1$
NH 15.52
sample in
acetone-d_6
s
tms

4C

The downfield proton signal (ca. δ16) observed in the low-temperature ^{1}H-NMR spectrum eliminates the metal-hydrido derivative VII as a possibility, since this region is not a very realistic position for a Re-H resonance. No signal upfield from TMS was observed.

This signal could correspond to the hydrogen atom of a formyl ligand since δ12-17 ppm is the normal region where these formyl resonances are found (eg. CpRe(CO)(HCO)(NO) δ = 16.2-16.5[93,95]; CpRe(PPh$_3$)(HCO)(NO) δ = 16.48[93,95]; for other examples, see ref. 101), but the presence of two terminal ν(CO) bands in the IR spectrum (-78°C) is not consistent with a monocarbonyl species.

Formulation of the intermediate as VIII, containing the hydrazido(2-), is the only one which seems to fit all our data. Attempts to prove unambiguously that this is the case by observing ^{15}NH coupling in the NMR of an intermediate labelled with ^{15}N at N^2 in the unsubstituted derivative [CpRe(CO)$_2$(N^{15}NC$_6$H$_5$)][BF$_4$] 2f (^{15}N-aniline is the only ^{15}N-primary amine commercially available) failed due to the poor solubility of this derivative in methanol-d$_4$ at low temperature.

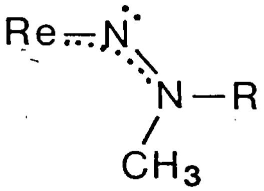
In summary, the evidence suggests that these reactions proceed by H$^-$ attack first at N^2 to give the neutral hydrazido(2-) complexes [CpRe(CO)$_2$(p-NNHC$_6$H$_4$R')] VIII (which are the kinetic products), which then rearrange to yield the more stable diazene complexes [$CpRe(CO)_2(p\text{-}NHNC_6H_4R')$] <u>15</u> (which are the thermodynamic products).

3.2.2 Reaction with CH_3Li.

Contrasting with the reaction of H-, which gives the N^1H product, the rhenium aryldiazenido complexes <u>2</u> reacted with CH_3^- in hexane at room temperature to give N(2)-methylated derivatives, the N(2)-aryl-N(2)-methylhydrazido(2-)-N(1) complexes [$CpRe(CO)_2(p\text{-}NN(CH_3)C_6H_4R')$] <u>17</u>. Competing reactions also occur, resulting in formation of the dinitrogen complex <u>4</u> (presumed to be formed via nucleophilic displacement at the benzene ring) and precipitation of a very air sensitive brown solid, which was a monocarbonyl compound (by IR). This was tentatively identified as the acetyl complex [$CpRe(CO)(COCH_3)(p\text{-}N_2C_6H_4R')$] <u>18</u> (due to attack at a CO group). The latter type seems to be formed also in reactions with PhLi and n-BuLi (see section 3.2.3). Qualitatively, the proportion of <u>4</u> increased in the order of benzene substituents: $o\text{-}CF_3 \geq p\text{-}CH_3 \approx p\text{-}OCH_3 > p\text{-}NEt_2$.

The hydrazido(2-) complexes <u>17</u> are dark red, air-stable solids, all soluble in organic solvents and have ν(CO) values <u>ca</u>. 1950vs and 1880vs, cm^{-1} (hexane), which have been lowered substantially from the corresponding positions in the aryldiazenido complexes <u>2</u>, typical of neutral compounds. They have been completely characterized by IR, ^{1}H-NMR and mass spectral data (Table IV) and by an X-ray crystal structure determination on 17b, which was kindly performed by Dr. Terry Jones and Prof. F.W.B. Einstein (Simon Fraser University) (see Figure 5).

The principal chemical features elucidated by the structure are that methylation of the aryldiazenido ligand in 2b has occurred at N^2 to generate a hydrazido(2-) ligand and, furthermore, that this ligand is coordinated to the metal through N^1 in an "end-on" fashion in the highly unusual bent geometry IX, with a $Re\text{-}N^1\text{-}N^2$ angle of 138.1(6)°.



IX

This is only the third example of a hydrazido(2-) complex known to have this geometry, and the metrical details closely parallel those of $[Cp_2WH(p\text{-}NN(H)C_6H_4F)][PF_6]$[102] ($W\text{-}N^1\text{-}N^2$ = 146.4(5)°) and $[MoO(NNMe_2)(C_9H_6NO)_2]$[83] ($Mo\text{-}N^1\text{-}N^2$ = 155.5(9)°). Thus, the Re-N(1) distance (1.937(7) Å) in 17b is probably lengthened over that in the aryldiazenido compound 2b[103], whereas the N(1)-N(2) length (1.28(1) Å) is intermediate between typical single

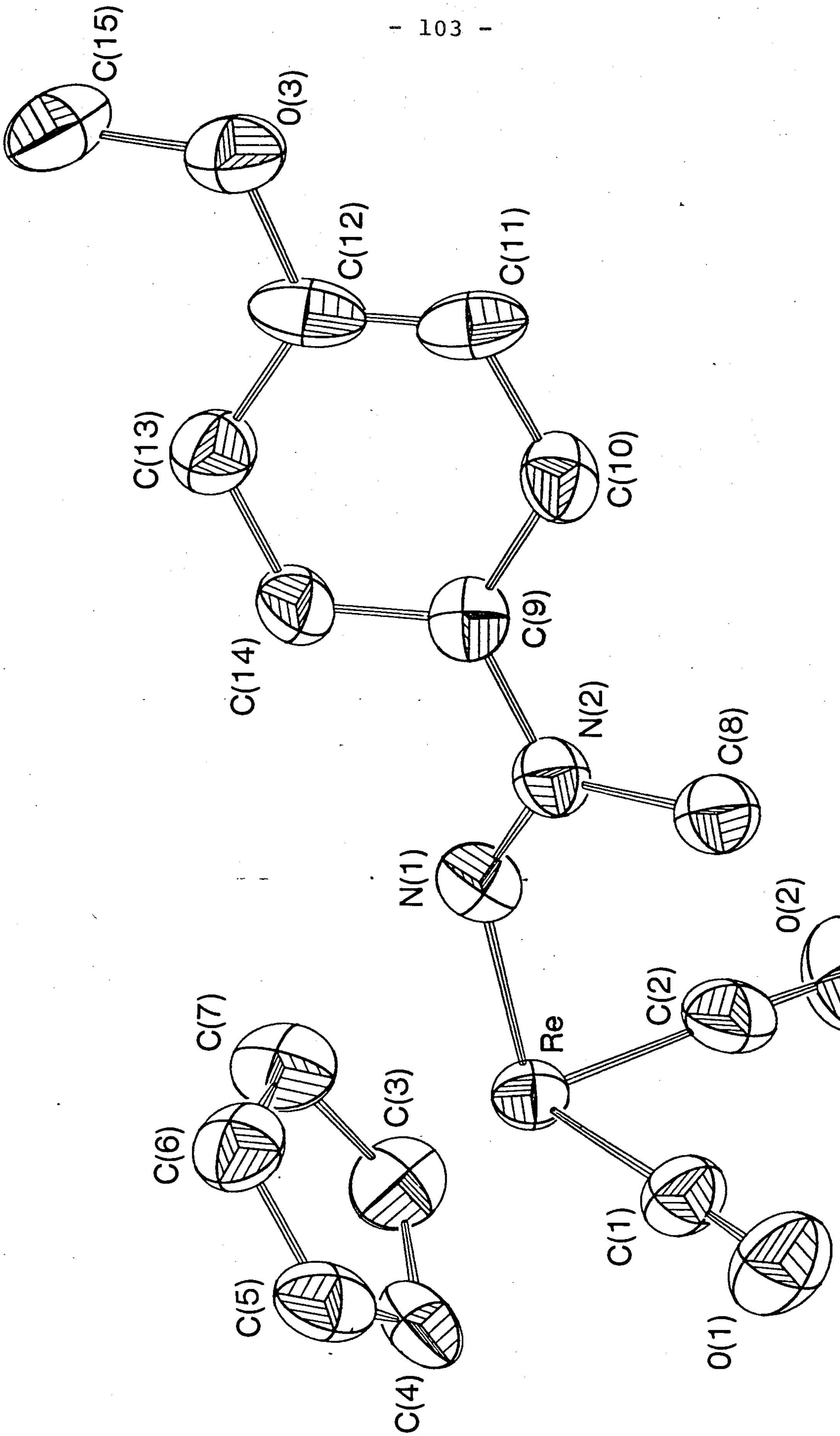
Table IV. Analytical, MS, IR and NMR Data for the Hydrazido(2-) Complexes.

Compound	Color	Analysis[a]			m/e[b]	IR	^{1}H-NMR[h]			
	m.p.(°C)	%C	%H	%N		ν(CO)[d]	Cp	C_6H_4	$N(CH_3)$	Other
[CpRe(CO)$_2${p-NN(CH$_3$)C$_6$H$_4$Me}] 17a	dk.red	40.82	3.40	6.40	440,442	1953, 1881[e]	5.85s	7.12s	3.79s	2.28s(Me)
	132-135 (dec)	(38.92)	(3.36)	(6.17)		1936, 1855[f]				
						1937, 1855[g]				
[CpRe(CO)$_2${p-NN(CH$_3$)C$_6$H$_4$OMe}] 17b	dk. red	39.39	3.28	6.13	456, 458[c]	1952, 1877[e]	5.86s,	6.84d	3.78[i]s	3.81[i]s (OMe)
	148	(39.17)	(3.24)	(5.90)		1938, 1857[f]		7.20d		
						1942, 1859[g]				
[CpRe(CO)$_2${p-NN(CH$_3$)C$_6$H$_4$NEt$_2$}] 17d	dk. red	43.37	4.43	8.43	497, 499	1946, 1875[e]	5.79s	6.56d	3.80s	3.34q (CH$_2$)
	89	(42.56)	(4.34)	(8.22)		1930, 1850[f]		7.12d		1.15t (CH$_3$)

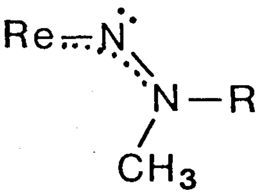
[a] Calculated values in parentheses. [b] Re isotopes 185 (37.07%), 187 (62.93%. [c] High resolution spectrum yielded exact mass values 456.0611, 458.0638, (Calcd. 456.0607, 458.0637). [d] In cm^{-1}; all bands very strong. [e] Hexane soln. [f] CH_2Cl_2 soln. [g] $CHCl_3$ soln. [h] 100 MHz; solvents are $CDCl_3$ (for 17a, 17d) and CD_2Cl_2 (for 17b); s, singlet; d, doublet; t, triplet; q, quartet. [i] $N(CH_3)$ and OMe assignments could be reversed.

Figure 5

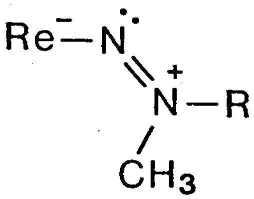
Perspective view of the complex $[CpRe(CO)_2\{\underline{p}\text{-}NN(CH_3)C_6H_4OCH_3\}]$ (17b). Re-N(1) = 1.937(7) Å; N(1)-N(2) = 1.28(1) Å; Re-N(1)-N(2) = 138.1(6)°


C(15)
0(3)
C(12)
C(11)
C(13)
C(10)
C(14)
C(9)
N(2)
C(8)
N(1)
0(2)
C(7)
C(2)
Re
C(3)
C(6)
C(1)
C(5)
0(1)
C(4)

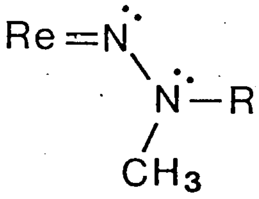
(1.40 Å)[104,105] and double (1.23 Å) [106] bonds. The structure seems to be best described in valence terms by IX, intermediate between the formal structures X and XI.



IX



X



XI

The observed bent geometry contrasts with the totally linear (or nearly so) M-N-N skeleton more frequently observed in hydrazido(2-) complexes of Mo[107,108], W[109,82] and Re[36b]. The reason for the nonlinearity in the present case is clear. As in the W example[102], the metal thereby acquires an 18-electron count, which would be exceeded if the lone pair on N^1 were to donate to Re also, to make the ReNN skeleton linear. By contrast, such a donation is required to establish the 18-electron count in the Mo, W and Re complexes cited above possessing a linear MNN skeleton.

It is instructive to compare the dimensions of the rhenium-hydrazido(2-) group in the two determined structures possessing linear and nonlinear geometries. In

$[ReCl_2(NH_3)(N_2HPh)(PMe_2Ph)_2]Br$[36b], the values observed for the linear Re-N-N system are Re-N = 1.75(1) Å, N-N = 1.28(2) Å, and Re-N-N = 172(1)°. Thus, the Re-N distance is considerably shorter than in the present case, consistent with this notion that the linearity is due to the nitrogen atom donating to Re the (otherwise) lone pair of electrons, thus increasing the multiple bonding to the Re atom. In both cases, however, the N-N bonds are not significantly different in length (and are slightly longer than a typical double-bond length). If the Re-N distance to the NH_3 ligand in ref. 36b (2.200(13) Å) can be taken as representative of a single-bond, then it appears that a considerable degree of Re-N multiple bonding exists in the aryldiazenido complex and in both the linear and the bent arylhydrazido(2-) complexes.

3.2.3 Reactions with PhLi and n-BuLi

The complexes $[CpRe(CO)_2(N_2C_6H_4R')][BF_4]$ (R' = p-OCH_3, 2b; p-NEt_2, 2d) reacted with an excess of PhLi and n-BuLi at room temperature to give the hydrazido(2-) derivatives $[CpRe(CO)_2(p\text{-}NN(Ph)C_6H_4R')]$ 19 and $[CpRe(CO)_2(p\text{-}NN(Bu^n)C_6H_4R')]$ 20, respectively, and in some cases, monocarbonyl complexes which were tentatively identified as the benzoyl complexes $[CpRe(CO)(COPh)(p\text{-}N_2C_6H_4R')]$ 21 and the n-butyryl complexes $[CpRe(CO)(COBu^n)(p\text{-}N_2C_6H_4R')]$ 22; $[CpRe(CO)_2(N_2)]$ 4 was always observed in variable amounts.

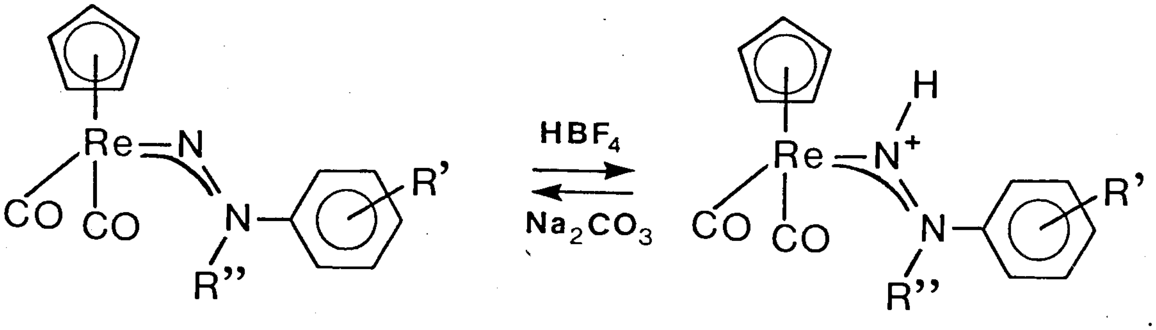
It was found that the course of the reaction leading to the hydrazido(2-) and Re-COR" derivatives (R" = Ph, n-Bu) depends markedly on the solvent used; thus, PhLi reacted in CH_2Cl_2 with complex 2b to give a mixture of both compounds 19 and 21, the benzoyl derivative 21 being the major product (approximately 2:1 ratio), but in hexane/acetone or hexane/-CH_2Cl_2 mixtures, the benzoyl derivative 21 and the dinitrogen complex 4, were the only products formed.

On the other hand, n-BuLi reacted with the aryldiazenido complexes 2b and 2d , in CH_2Cl_2 to give exclusively the hydrazido (2-) derivatives $[CpRe(CO)_2(p\text{-}NN(Bu^n)C_6H_4R')]$ 20 (R' = p-OCH_3, 20b; p-NEt_2, 20d), plus a very small amount of $[CpRe(CO)_2(N_2)]$, whereas in hexane/acetone (50:50) it reacted vigorously to give exclusively the butyryl complexes $[CpRe(CO)(COBu^n)(p\text{-}N_2C_6H_4R')]$ 22 (R' = p-OCH_3, 22b; p-NEt_2, 22d).

These new hydrazido(2-) complexes 19 and 20 are expected to have a bent hydrazido(2-) ligand, as in the methyl case, since their spectroscopic and chemical properties are similar. They are all dark red air-stable solids and were fully characterized by ^{1}H-NMR, IR and MS. The monocarbonyl species Re-COR" (R" = CH_3, Ph, n-Bu), which seem to be very air sensitive, could not be isolated as pure substances preventing a full characterization of them.

3.2.4 Protonation Reactions of Diazenes and Hydrazido(2-) Complexes

The crystal structure of the hydrazido(2-) complex $[CpRe(CO)_2(p\text{-}NN(CH_3)C_6H_4OCH_3)]$ 17b, which shows the hydrazido(2-) ligand to be bent (Fig. 5) suggests a lone pair of electrons to be present on N^1. This is entirely consistent with the reactivity exhibited by these complexes, since protonation at N^1 occurred on addition of HBF_4 to yield the cationic hydrazido(1-) complexes $[CpRe(CO)_2(p\text{-}NHN(CH_3)C_6H_4R')][BF_4]$ 23 (R' = $p\text{-}CH_3$, 23a; $p\text{-}OCH_3$, 23b), $[CpRe(CO)_2(p\text{-}NHN(Ph)C_6H_4R')]$-$[BF_4]$ 24 (R' = $p\text{-}OCH_3$, 24b) and $[CpRe(CO)_2(p\text{-}NHN(Bu^n)C_6H_4R)'][BF_4]$ 25 (R' = $p\text{-}OCH_3$, 25b) respectively, as air-stable dark red solids (eq. 19). These hydrazido(1-) complexes can be easily deprotonated by Na_2CO_3 or other bases, regenerating the corresponding hydrazido(2-) complex.

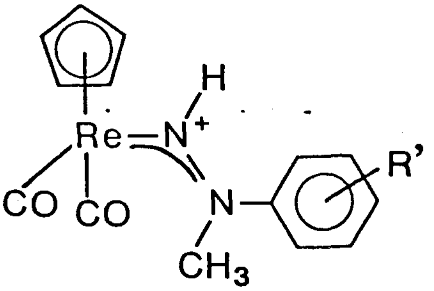


(19)

$(R''=CH_3, Ph, Bu^n)$

The protonation is accompanied by an increase in the ν(CO) positions (eg. to near 2000vs and 1935vs, cm^{-1} in the p-CH_3 and p-OCH_3 derivatives 23a and 23b), and δ(NH) occurs near 16 ppm in the ^{1}H-NMR (Table V). The site of protonation has been confirmed by $^{15}N^1$ isotopic substitution in [$^{15}N^1$] 23b with the observed coupling constant $^1J(^{15}NH) = 78$ Hz and by an X-ray crystal structure determination of 23a (Figure 6), kindly done by Dr. Terry Jones, Prof. F.W.B. Einstein (SFU) and Dr. Charles F. Campana (Nicolet XRD Corporation, California).

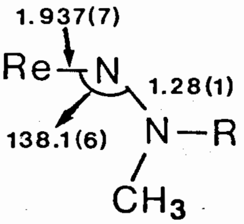
The X-ray structure showed that protonation has occurred at N^1 to generate a hydrazido(1-) ligand and, furthermore, that this ligand is coordinated to the metal through N^1 in an "end-on" fashion XII with a Re-N(1)-N(2) angle of 139.1(7)°.



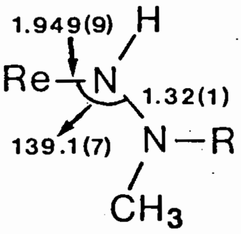
XII

This is the third example of a hydrazido(1-) complex known to have this geometry; the other two examples are Mo{HB(Me_2pyz)$_3$}(NO)I(HNNMePh)[110] and Mo{HB(Me_2pyz)$_3$}(NO)I($HNNMe_2$).[110] All the other hydrazido(1-)

complexes for which structures have been determined, show that the hydrazido(1-) ligand is bounded in a "side-on" fashion (η^2).[89–92,79] In this case, protonation did not introduce significant metrical changes in the diazo moeity, since the dimensions around the hydrazido(1-) ligand in 23a are not much different from those observed for the hydrazido(2-) complex 17b.

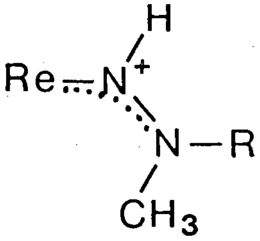


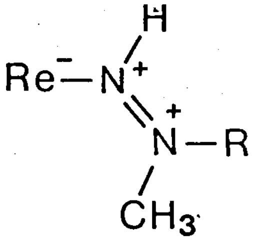
17b

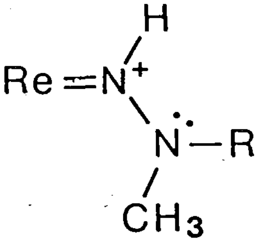


23a

The N(1)-N(2) distance (1.32(1) Å) has been lengthened compared to the hydrazido(2-) complex (1.28(1) Å), but still has a considerable double bond character, since this value is intermediate between typical single (1.40 Å)[104,105] and double (1.23 Å)[106] bonds. The Re-N(1) distance (1.949(9) Å) is not significantly different to that observed in the hydrazido(2-) complex; thus, the structure again seems to be best described in valence terms by XII, intermediate between the formal structures XIII and XIV.


XII


XIII


XIV

It was found that all these hydrazido(1-) complexes are non-rigid molecules and that they exist as two stereoisomers in solution in $CDCl_3$ (but not in $(CD_3)_2CO$) at room temperature; each resonance in the ^{1}H-NMR of, for example, 23b occurs as two unequal sets of signals of consistent relative intensity (see Figure 7). A NMR study of their stereoisomerism and calculation of thermodynamic parameters of this process is discussed in Chapter IV.

The presence of the two isomers was observed only in $CDCl_3$ or CD_2Cl_2, but not in solvents such as $(CD_3)_2CO$ or CD_3CN. The reason for this is not well understood, but it is reasonable to suggest either that acetone and acetonitrile could stabilize only one of these isomers by hydrogen bonding or that the energy gap (ΔE) between both isomers is greater in this type of solvent.

The protonation of the p-NEt_2 derivative $[CpRe(CO)_2(p\text{-}NN(CH_3)C_6H_4NEt_2)]$ 17d needs a special mention, since three compounds were formed. Careful addition of HBF_4 in Et_2O to a CH_2Cl_2 solution of the hydrazido(2-) complex 17d, first afforded a deep-blue species ($\nu(CO)$: 1988vs, 1925vs, cm^{-1} in CH_2Cl_2) which remained in solution, and a red oil ($\nu(CO)$: 1999vs, 1937vs, cm^{-1} in acetone) which precipitated out; further addition of HBF_4 produced a red-brownish solution (the blue color disappeared) with $\nu(CO)$ bands (in CH_2Cl_2) at 2030vs and 1943vs, cm^{-1}. Although no isolation and characterization of each particular compound was attempted, compounds 23d, 26d and 27d are suggested as the species formed in this reaction. (Compare with the reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4NEt_2)][BF_4]$ 2d with HCl in Chapter II.)

Table V. IR and ^{1}H-NMR Data for Rhenium Arylhydrazido(1-) Complexes.

Compound		$\nu(CO)^a$		^{1}H-NMR^b				
			Isomer^c	Cp	Aryl	NH	N-R^d	Other
$[CpRe(CO)_2\{p\text{-}N(H)N(CH_3)C_6H_4CH_3\}][BF_4]$	23a	2002, 1936	1^e	6.21s	7.28d 7.43d	15.79s	3.09s (CH_3)	2.30s (CH_3)
			2^e	6.03s	f	16.06s	3.19s (CH_3)	2.44s (CH_3)
$[CpRe(CO)_2\{p\text{-}N(H)N(CH_3)C_6H_4OCH_3\}][BF_4]$	23b	2003, 1935	1	6.17s	6.94d 7.45d	15.72s	3.09s (CH_3)	3.83s (OCH_3)
			2	6.04s	7.08d 7.42d	16.11s	3.21s (CH_3)	3.91s (OCH_3)
$[CpRe(CO)_2\{p\text{-}N(H)N(Ph)C_6H_4OCH_3\}][BF_4]$	24b	2010, 1943	1	6.18s	f	16.25s	7.30m,br^g	3.82s (OCH_3)
			2	6.15s	f	16.52s	f	3.92s (OCH_3)
$[CpRe(CO)_2\{p\text{-}N(H)N(Bu^n)C_6H_4OCH_3\}][BF_4]$	25b	2007, 1937	1	6.04s	7.10d	16.12s	3.74t ($N\text{-}CH_2^-$)	3.92s (OMe)
					7.36d		1.16m,br ($-(CH_2)_2$)^g 0.90 t ($-CH_3$)	
			2	6.16s	f	15.62s	f	3.88s (OMe)
$[CpRe(CO)_2\{p\text{-}N(H)N(H)C_6H_4OCH_3\}][BF_4]$	28b	2022, 1945	1			16.36d^{h,j}		
						12.90d^{i,j}		
			2			15.57d^{h,k}		
						13.68d^{i,k}		

---

[a] In cm^{-1} for CH_2Cl_2 solutions; all bands are very strong. [b] In $CDCl_3$ at -30°C; all values in ppm. [c] Isomer 1: more concentrated isomer; Isomer 2: less concentrated isomer. [d] R = CH_3, phenyl or n-butyl groups . [e] In CD_2Cl_2. [f] Resonances obscured by other signals. [g] Broad multiplet centered at the values given. [h] $\delta N(1)H$. [i] $\delta N(2)H$. [j] $^1J(HH)$ = 8Hz. [k] $^1J(HH)$ = 18Hz.

Figure 6

Perspective View of the Complex

$[CpRe(CO)_2\{p\text{-}N(H)N(CH_3^{-})C_6H_4CH_3\}][BF_4]$ (23a)

Re-N(1) = 1.949(9) Å; N(1)-N(2) = 1.32(1) Å; Re-N(1)-N(2) = 139.1(7)°.

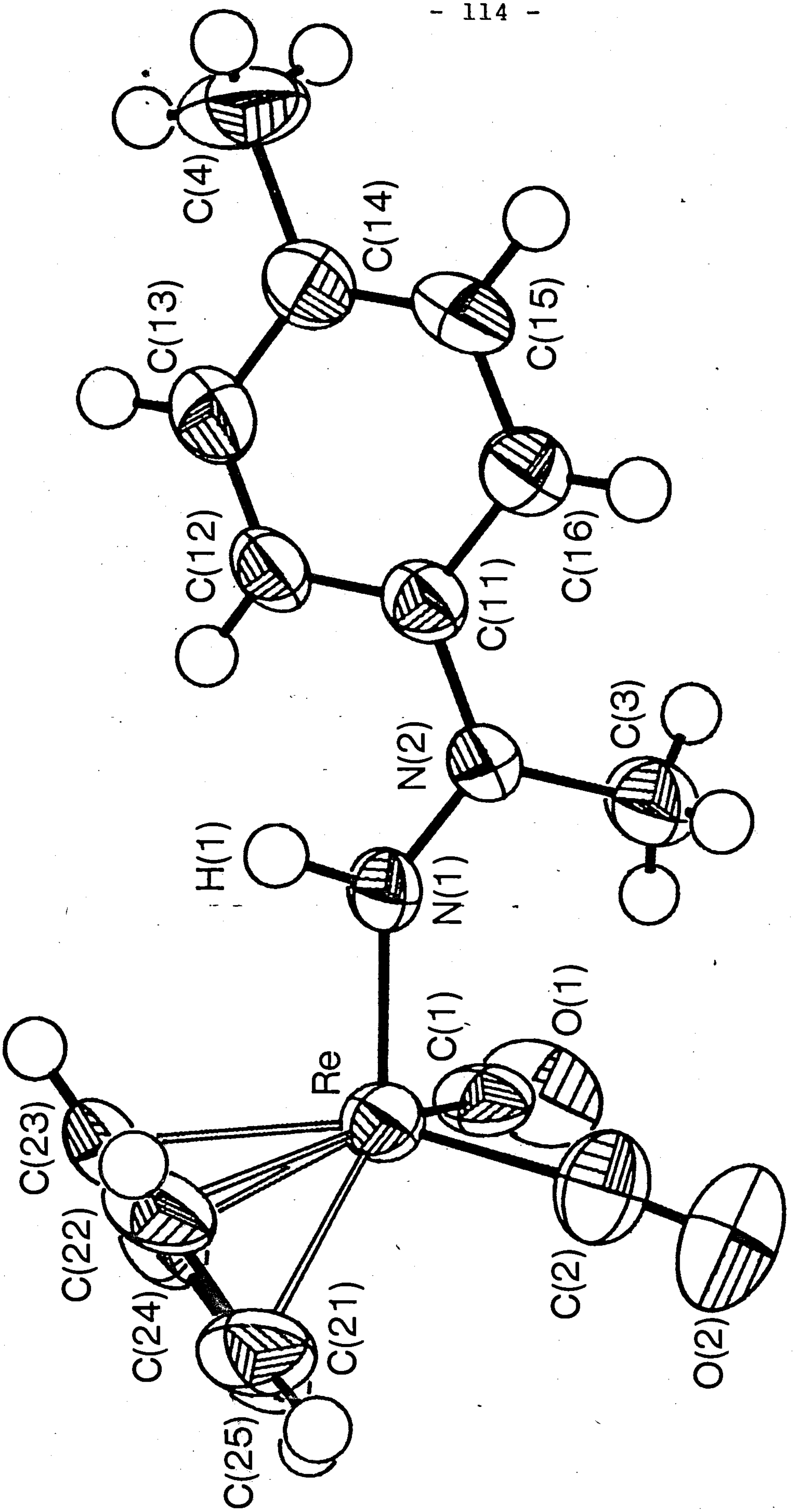
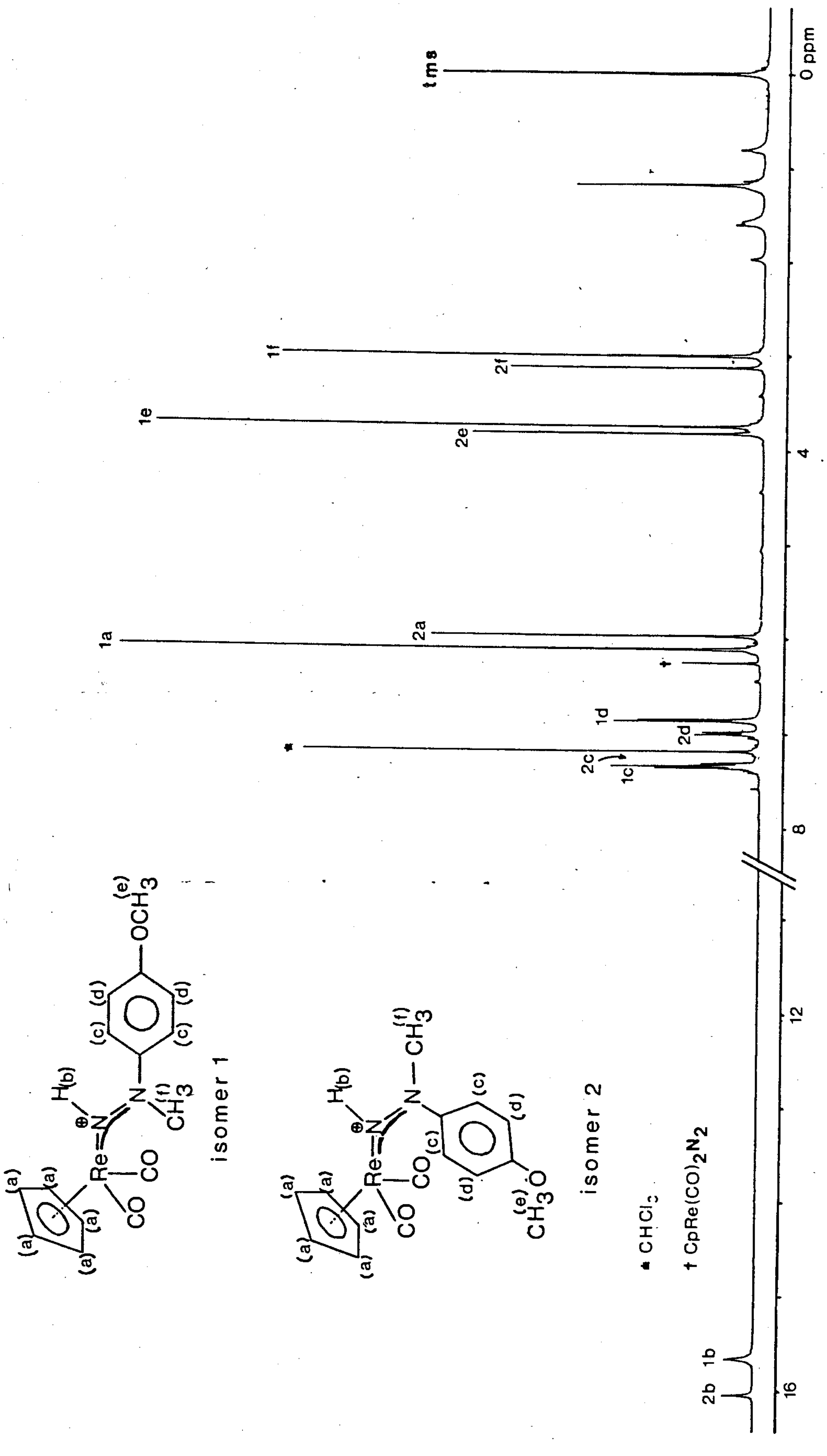
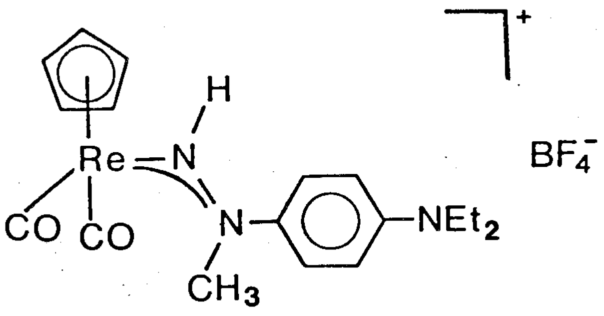

C(4)
C(14)
C(13)
C(15)
C(12)
C(16)
C(11)
H(1)
N(2)
C(3)
N(1)
Re
C(1)
O(1)
C(23)
C(22)
C(24)
C(21)
C(25)
C(2)
O(2)

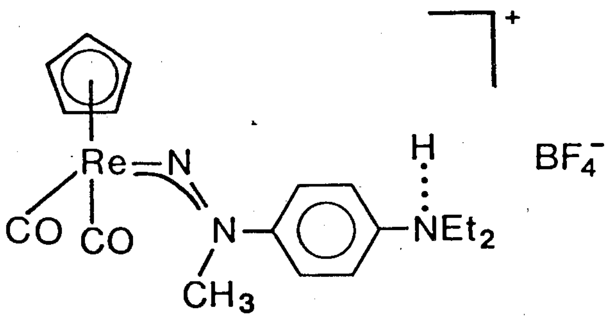
Figure 7

Room Temperature ^{1}H-NMR Spectrum ($CDCl_3$) of the Hydrazido(1-) Complex $[CpRe(CO)_2\{\underline{p}\text{-}N(H)N(CH_3)C_6H_4OCH_3\}][BF_4]$ <u>23b</u> (at 400 MHz).

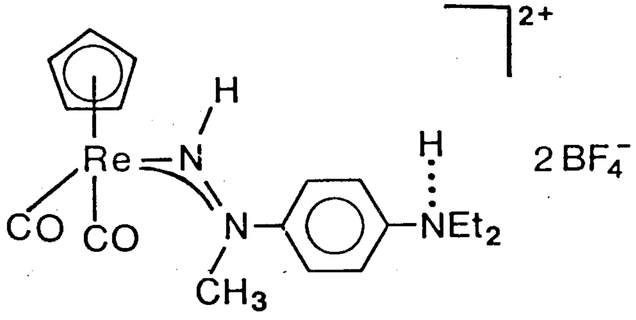

tms
0 ppm
4
8
12
16
1f
2f
1e
2e
1a
2a
†
1d
2d
*
2c
1c
2b 1b
(a)
(b)
(c)
(d)
(e)
(f)
Re
CO
H
N
CH_3
OCH_3
CH_3O
⊕
isomer 1
isomer 2
* $CHCl_3$
† $CpRe(CO)_2N_2$



23d



26d

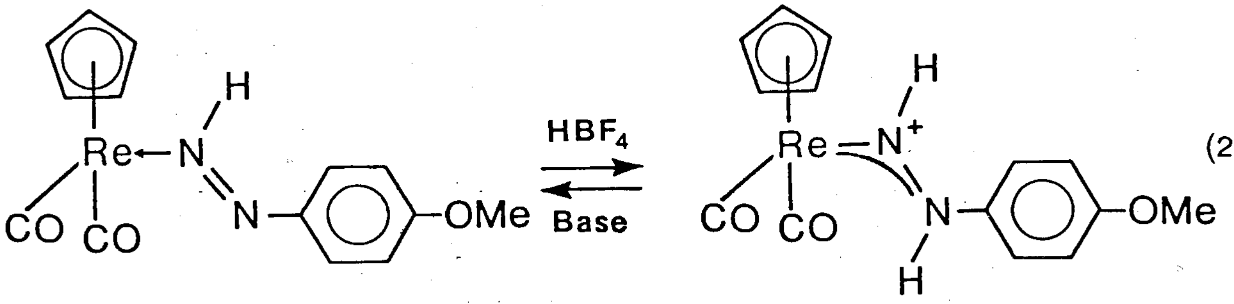


27d

Compound 27d can be assigned, almost certainly, to the red-brownish complex formed last, since its dicationic nature should show the ν(CO) bands at higher wavenumbers in the IR.

The assignment of the other two compounds is more ambiguous. From their different solubilities in CH_2Cl_2, it seems reasonable to suggest that the blue soluble complex corresponds to compound 23d (other hydrazido(1-) complexes of rhenium described in this work are soluble) and that the red-oil is compound 26d; the presence of an ammonium group in this complex probably is responsible for its insolubility in CH_2Cl_2.

The diazene complexes (Re-NHNR) 15 can also be protonated (in this case at N^2) to give hydrazido(1-) complexes. Indeed, addition of HBF_4 in Et_2O to a CH_2Cl_2 solution of the diazene complex 15b (p-OCH_3) yielded the hydrazido(1-) complex $[CpRe(CO)_2(p\text{-}NHN(H)C_6H_4OCH_3)][BF_4]$ 28b as a very dark-red, air-stable solid (eq. 20). This complex can be easily deprotonated by base (even weak bases such as Et_2O) to regenerate the diazene complex.



15b

28b

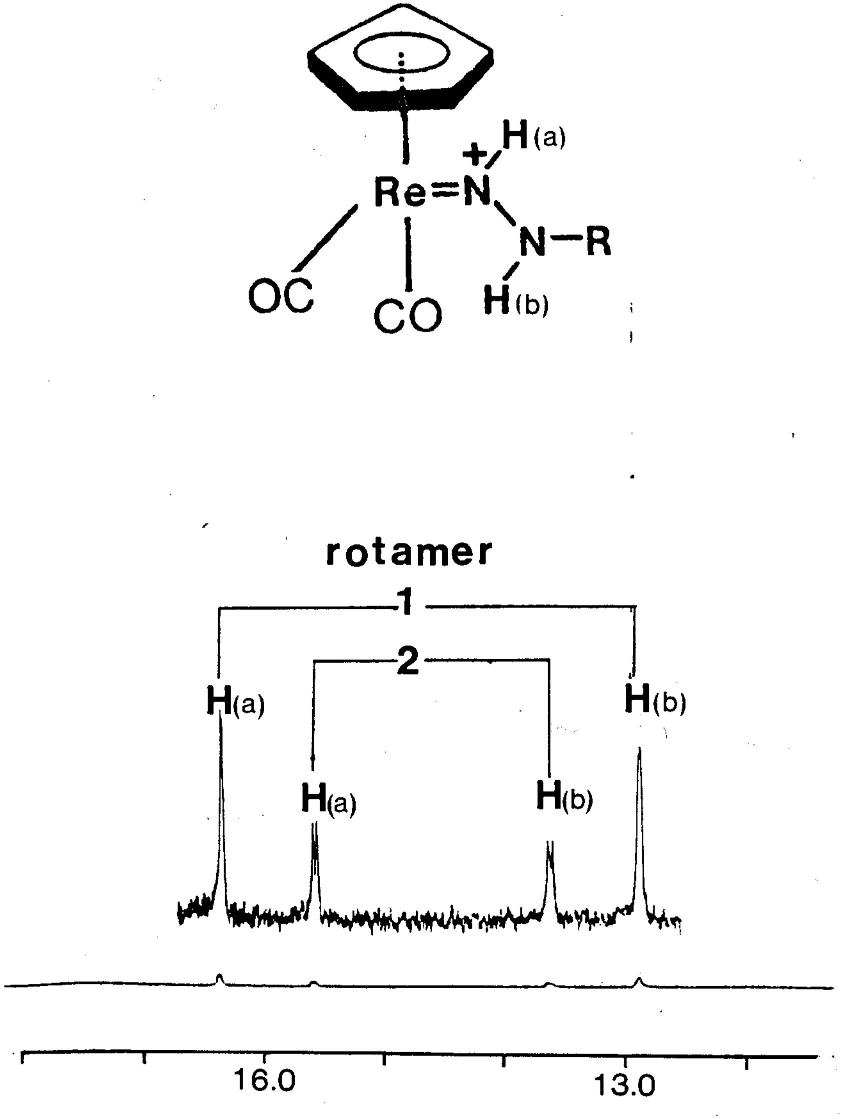
(20)

Again, the protonation is accompanied by an increase in the ν(CO) position to 2003vs and 1935vs, cm^{-1} in the p-OCH_3 derivative 28b. The room temperature ^1H-NMR spectrum ($CDCl_3$) of 28b showed the presence of not just the expected two N-H resonances, but also showed that this hydrazido(1-) complex exists as two stereoisomers in solution (see Figure 8A); assignment of the N^1H and N^2H resonances were carried out by $^{15}N^1$ isotopic substitution in $[^{15}N^1]$ 28b (see Figure 8B). Further work on the characterization of this hydrazido(1-)

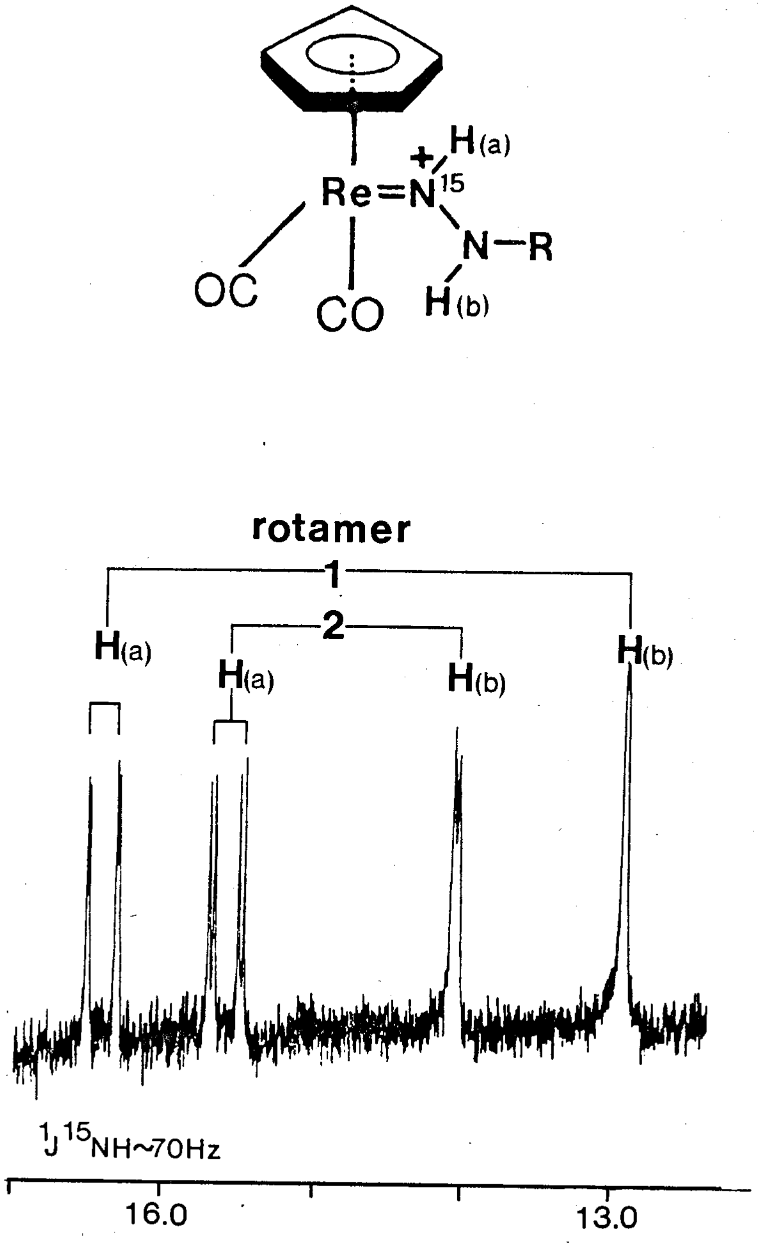
Figure 8

A) Room temperature ^{1}H-NMR ($CDCl_3$) spectrum (at 400 MHz) showing the N-H resonances of the hydrazido(1-) complex $[CpRe(CO)_2\{p\text{-}N(H)N(H)C_6H_4OCH_3\}][BF_4]$ (28b).

B) $^{15}N(1)$ Isotopic substitution in $[^{15}N^1]$ 28b.


H(a)
Re=N
+
N−R
H(b)
OC
CO
rotamer
1
2
H(a)
H(a)
H(b)
H(b)
16.0
13.0

8A.


H(a)
Re=N15
+
N−R
H(b)
OC
CO
rotamer
1
2
H(a)
H(a)
H(b)
H(b)
$^1J\,^{15}{}_{NH}$~70Hz
16.0
13.0

8B.

complex and a NMR study of its stereoisomerism is discussed in Chapter IV.

The presence of the two isomers in the ^{1}H-NMR spectrum is also affected by the solvent; acetone and acetonitrile again stabilize only one particular isomer.

3.2.5 Reactions of Diazenes and Hydrazido(2-) Complexes with $(CH_3)_3O^+$ and CH_3I

The diazene complex $[CpRe(CO)_2(p\text{-}NHNC_6H_4OCH_3)]$ 15b reacted with $(CH_3)_3O^+BF_4^-$ (or FSO_2OCH_3) to give several compounds, one of them being the hydrazido(1-) complex $[CpRe(CO)_2\{p\text{-}N(H)N(CH_3)C_6H_4OCH_3\}][BF_4]$ 23b, which was identified by IR and ^{1}H-NMR. The complex $[CpRe(CO)_2\{p\text{-}N(H)N(H)C_6H_4OCH_3\}][BF_4]$ 28b was also observed and this probably was formed by reacting with HBF_4 produced from hydrolysis of the $(CH_3)_3O^+BF_4^-$.

Similar methylation reactions were attempted in the case of the hydrazido(2-) complex $[CpRe(CO)_2(p\text{-}NN(CH_3)C_6H_4OCH_3)]$ 17b. The reaction was quite complicated giving several compounds where the complex $[CpRe(CO)_2\{p\text{-}N(H)N(CH_3)C_6H_4OCH_3\}][BF_4]$ 23b was always the major product. Although the species $[CpRe(CO)_2\{p\text{-}N(CH_3)N(CH_3)C_6H_4OCH_3\}][BF_4]$ might have been expected to be formed and may be responsible for some of the observed ν(CO) bands in the IR spectrum or the extra δCH_3, as well as Cp and aryl resonances observed in the ^{1}H-NMR, no conclusive proof of its formation could be obtained.

No reaction of the hydrazido(2-) or the diazene complexes with CH_3I was observed.

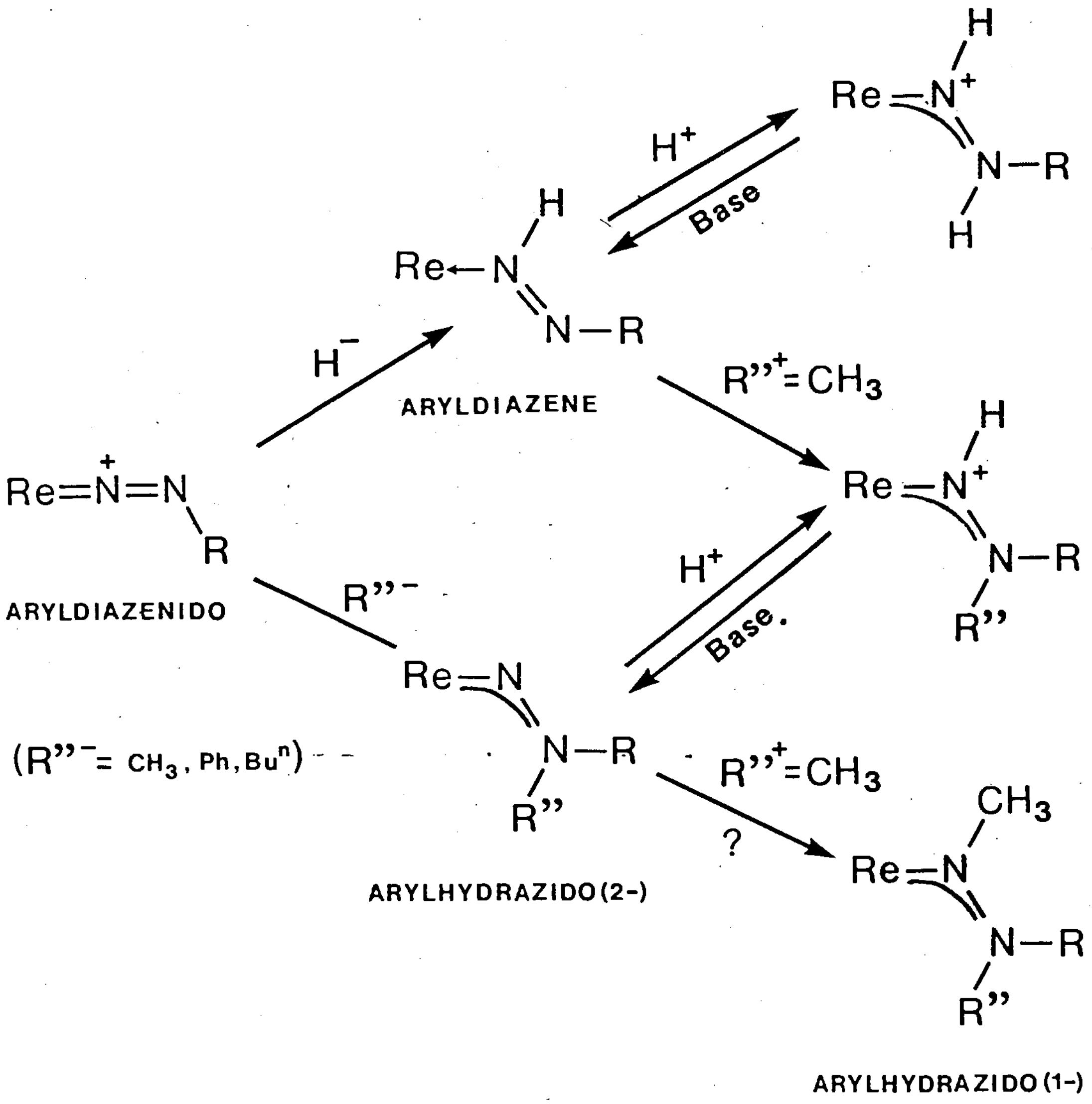
3.2.6 Miscellaneous

Attempts to prepare the hydrazido(1-) complex $[CpRe(CO)_2\{p\text{-}N(Ph)N(CH_3)C_6H_4OCH_3\}][BF_4]$ failed since the hydrazido(2-) derivative $[CpRe(CO)_2(p\text{-}NN(CH_3)C_6H_4OCH_3)]$ 17b did not react with the phenylating agent $Ph_2I^+BF_4^-$; both reagents were recovered unchanged after stirring for several hours at room temperature in CH_2Cl_2.

Reactions of the hydrazido(1-) complex $[CpRe(CO)_2\{p\text{-}N(H)N(CH_3)C_6H_4OCH_3\}][BF_4]$ 23b with NaI and $NaBH_4$ were carried out with the idea to synthesize the alkyl-diazene complex $[CpRe(CO)_2\{N(H)N(CH_3)\}]$ (attack at the ipso carbon) or the formyl derivative $[CpRe(CO)(HCO)\{p\text{-}N(H)N(CH_3)C_6H_4OCH_3\}]$ (attack at CO). Both reactions failed to produce the desired products since I^- and H^- reacted only as bases, deprotonating the hydrazido(1-) complex to regenerate the hydrazido(2-) derivative 17b.

A resumé of the reactions described in this chapter is presented in Scheme III.

SCHEME III


ARYLDIAZENIDO
ARYLDIAZENE
ARYLHYDRAZIDO(2-)
ARYLHYDRAZIDO(1-)
H⁻
H⁺
Base
R''⁺=CH₃
R''⁻
H⁺
Base.
R''⁺=CH₃
?
(R''⁻= CH₃, Ph, Buⁿ)

3.3 Experimental

As described in Chapter II. Dry HBF_4 was prepared by drying HBF_4 (48% solution, Fisher Scientific) with molecular sieve and extracting with diethyl ether; the ether solution was stored and dried over $CaSO_4$. $(CH_3)_3O^+BF_4^-$ (Aldrich) and FSO_2OCH_3 (>95%, Fluka) were used directly as purchased. Some ^1H-NMR spectra were recorded at 400 MHz with a Bruker WM-400 instrument.

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OCH_3)][BF_4]$ (2b) with $NaBH_4$

Method A: To 2b (100 mg) dissolved in a 1:1 mixture of THF and water (3 mL) was added a stoichiometric amount of solid $NaBH_4$, and the mixture was stirred at 0°C for 15 min. under N_2. An instantaneous reaction occurred, with considerable gas evolution, and the color changed from red-orange to a bright, deep orange. The solution was cooled to -50°C and the viscous mass so formed was extracted with cold hexane and filtered. The IR spectrum of the hexane extract showed the presence of the diazene complex $[CpRe(CO)_2(p\text{-}NHNC_6H_4OCH_3)]$ 15b, and a very small amount of the dinitrogen complex $[CpRe(CO)_2(N_2)]$. By cooling the very air and thermally sensitive solution, the diazene complex was isolated as a dark red solid, m.p. 73°C (darkens), 83°C (dec.). The GC-MS analysis showed only two GC peaks in addition to solvent, having parent ions at m/e 108 (anisole) and 334, 336 $[CpRe(CO)_2(N_2)]$.

Method B: An improved synthesis of the diazene complex 15b (yield near quantitative) was carried out by using methanol as the solvent. To 2b dissolved in methanol was added a stoichiometric amount of solid $NaBH_4$ and the mixture was stirred at 0°C for 15 min. under N_2. An instantaneous reaction took place, with considerable gas evolution, and the color changed from red-orange to a bright, deep-orange. The solvent was distilled off under vacuum and the deep-orange residue was carefully dissolved in diethyl ether without stirring (the procedure of adding diethyl ether along the wall of the Schlenk-tube very slowly and without stirring left behind most, if not all, the $NaBF_4$ produced during the reaction and other insoluble decomposition products). Filtration and evaporation of the ether, afforded the desired product 15b as a microcrystalline deep red solid in high yield.

NOTE: The ether solution of complex 15b was much more air and temperature stable compared to the hexane extract of 15b in method A.

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4CH_3)][BF_4]$ (2a) with $NaBH_4$. This reaction was carried out similar to the reaction of 2b described above in method A. The color changed from red-brown to a bright, deep orange-red and the IR spectrum of the hexane extract showed the presence of the new diazene complex $[CpRe(CO)_2(p\text{-}NHNC_6H_4CH_3)]$ 15a together with a significant amount of the dinitrogen complex $[CpRe(CO)_2(N_2)]$. The solution is very air and thermally labile and a GC-MS analysis showed only two GC peaks in addition to solvent, having parent ions at m/e 92 (toluene) and 334, 336 $[CpRe(CO)_2(N_2)]$.

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4NEt_2)][BF_4]$ (2d) with $NaBH_4$. This was carried out as described above for 2b (Method A). The color changed from dark green to blood-red, and the IR of the blood-red hexane extract showed the presence of the new diazene complex $[CpRe(CO)_2(p\text{-}NHNC_6H_4NEt_2)]$ 15d, plus a very small amount of the dinitrogen complex.

Evaporation of the solvent under reduced pressure afforded a blood-red microcrystalline solid, m.p. 55°C (darkens), 82°C (dec.).

Anal. Calcd. for $[(\eta^5\text{-}C_5H_5)Re(CO)_2\{p\text{-}NHNC_6H_4N(C_2H_5)_2\}]$: C, 42.15; H, 4.13; N, 8.68. Found: C, 39.11; H, 4.12; N, 8.49. The GC-MS of the solution showed only two components, having parent ions at m/e 149 $(C_6H_5NEt_2)$ and 334, 336 $[CpRe(CO)_2(N_2)]$. A direct injection MS of the solid 15d similarly showed only these two components, and no parent peak for 15d even when the spectrum was obtained at 15 ev and a low inlet temperature (90°C).

Reaction of $[CpRe(CO)_2(N_2C_6H_5)][BF_4]$ (2f) with $NaBH_4$. This reaction was carried out as described above for 2b in method

B. The color changed from reddish-brown to bright, deep orange red. Evaporation of the diethyl ether afforded the diazene complex [CpRe$(CO)_2(NHNC_6H_5)$] 15f as a very air and temperature sensitive dark red-orange microcrystalline solid.

Reaction of [CpRe$(CO)_2(3,5\text{-}N_2C_6H_3Me_2)$][$BF_4$] (15h) with $NaBH_4$. This reaction was carried out as described above for 2b in method A. The color changed from reddish-brown to bright deep orange-red. The IR spectrum of the hexane extract showed the presence of the new diazene complex [$(\eta^5\text{-}C_5H_5)Re(CO)_2(3,5\text{-}NHNC_6H_3Me_2)$] 15h and a significant amount of the dinitrogen complex (4). The GC-MS spectrum of this solution showed only two components with parent ions at m/e: 106 and m/e: 334, 336, which correspond to 1,3-$(CH_3)_2C_6H_4$ and the dinitrogen complex (4).

Reaction of [$(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(o\text{-}N_2C_6H_4CF_3)$][$BF_4$] (1a) with $NaBH_4$. To 1a (100 mg) dissolved in a mixture of 1:1 THF/H_2O (3 mL) was added to 1:1 stoichiometric amount of solid $NaBH_4$, and the mixture was stirred at 0° for 15 min. under N_2. The reaction took place instantaneously, with considerable gas evolution and the color of the solution changed from red-orange to dark red-violet. After 15 min. the solution was cooled to -50°C and a viscous mass was obtained. The products were extracted with cool hexane, and the IR spectrum of this dark red-violet solution showed the presence of the dinitrogen complex $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2(N_2)]$ 3 (ν(CO): 1975vs, 1920vs; ν(NN): 2170vs)[4] and a new complex with strong carbonyl bands at 1958 and 1900 cm^{-1}. Evaporation of the deep red-violet hexane solution to dryness under vacuum at -30°C gave a deep red-violet, very air and temperature sensitive solid which decomposes at about -20°C. The low temperature ^1H-NMR spectrum (in $CDCl_3$) of this solid was very broad, but showed a band at δ 13.70 ppm which tentatively is assigned as the N-H resonance of a diazene complex 16a analogous to those of the rhenium series.

The broadening of the NMR is ascribed to the presence of Mn(II) species formed in the reaction. The ESR spectrum exhibited a multiline resonance identical with the ESR of aqueous $MnCl_2$.

Reaction of $[(\eta^5\text{-}CH_3C_5H_4)Mn(CO)_2\{3,5\text{-}N_2C_6H_3(CH_3)_2\}][BF_4]$ (1c) with $NaBH_4$. This reaction was carried out as described for compound 1a. The color changed from orange-red to a much deeper orange-red, and the IR spectrum of the orange-red hexane solution showed the presence of the dinitrogen complex 3, plus a new complex with ν(CO) bands at 1957 and 1901 cm^{-1}. This very air and temperature sensitive complex, which could not be isolated, is tentatively suggested to be the diazene complex

16c. No resonance assignable to δ(NH) could be discerned in the extremely paramagnetically-broadened ^{1}H-NMR. The ESR spectrum was identical with that for the reaction of 1a.

Reaction of [CpRe(CO)$_2$(p-N$_2$C$_6$H$_4$OCH$_3$)][BF$_4$] 2b with NaBH$_4$: Low Temperature ^{1}H-NMR Experiments. Solid NaBH$_4$ (2 mg, 0.05 mmol) was put in a 5 mm NMR tube which was evacuated and sealed under nitrogen with a septum cap. The tube was cooled down to liquid nitrogen temperature and a solution of 2b (28 mg, 0.05 mmol) in methanol-d$_4$ was injected through the septum with a syringe; the solution immediately solidified at that temperature. The NMR tube was removed from the liquid nitrogen bath and placed in the XL-100 NMR spectrometer, which had been previously adjusted for homogenity, and set at -40°C. Once the NMR tube was in the probe, the solidified methanol-d$_4$ solution melted, since the temperature of the probe was -40°C, and the first spectrum was recorded (t = 5 min.). A new spectrum was recorded every 5 min. until the reaction was over.

An identical procedure was used when the reaction was carried out at -70°C.

Reaction of [CpRe(CO)$_2$(p-N$_2$C$_6$H$_4$Me)][BF$_4$] (2a) with CH$_3$Li. To a suspension of 2a in hexane (20 mL) excess methyllithium (1.3 M in Et$_2$O) was added by syringe, and the mixture was stirred for

30 min. at room temperature under N_2. A fast reaction took place, and the hexane solution became red, while a light brown solid precipitated out of the solution.

The IR spectrum of the hexane solution showed the presence of the new hydrazido(2-) complex [CpRe(CO)$_2$(p-NN(CH$_3$)C$_6$H$_4$CH$_3$)] (17a) plus the dinitrogen complex (4). The hexane solution was separated and concentrated *in vacuo* to *ca*. 4 mL. Dark red air-stable crystals of the hydrazido(2-) complex 17a were obtained by cooling this solution to -12°C in the freezer. The dinitrogen complex 4 remained in solution.

The precipitate was a mixture of LiBF$_4$ and a monocarbonyl complex (by IR) which has been tentatively identified as the acetyl complex [CpRe(CO)(COCH$_3$)(p-N$_2$C$_6$H$_4$Me)] (18a), and obtained in impure form by repeated crystallization from CH$_2$Cl$_2$-hexane. IR (CH$_2$Cl$_2$): 1952s (ν(CO)); 1640s,br (acyl).

Reactions of [CpRe(CO)$_2$(p-N$_2$C$_6$H$_4$OMe)][BF$_4$] (2b), [CpRe(CO)$_2$(p-N$_2$C$_6$H$_4$NEt$_2$)][BF$_4$] (2d), and [CpRe(CO)$_2$(o-N$_2$C$_6$H$_4$CF$_3$)][BF$_4$] (2e) with CH$_3$Li. These reactions were carried out under identical conditions to those described above, to give the new hydrazido(2-) complexes [CpRe(CO)$_2${p-NN(CH$_3$)C$_6$H$_4$OMe}] 17b, [CpRe(CO)$_2${p-NN(CH$_3$)C$_6$H$_4$NEt$_2$}] (17d) and [CpRe(CO)$_2${o-NN(CH$_3$)C$_6$H$_4$CF$_3$}] (17e) as dark red, air-stable solids, and the corresponding acetyl complexes (18b), (18d) and (18e) as impure light brown air sensitive solids.

Reaction of [CpRe(CO)$_2$(p-N$_2$C$_6$H$_4$OCH$_3$)][BF$_4$] 2b with PhLi. To a solution of 2b (60 mg, 0.11 mmol) in CH$_2$Cl$_2$ (5 mL) was added by syringe an excess of PhLi (1.95 M in cyclohexane/Et$_2$O, 70/30), and the mixture was stirred at room temperature for 30 min. under nitrogen. A fast reaction took place and the solution became dark red-orange. The IR spectrum of the solution showed the presence of a monocarbonyl species as the major product (presumed to be [CpRe(CO)(COPh)(p-N$_2$C$_6$H$_4$OCH$_3$)] 21b), the new hydrazido(2-) complex [CpRe(CO)$_2$(p-NN(Ph)C$_6$H$_4$OCH$_3$)] 19b and a small amount of [CpRe(CO)$_2$(N$_2$)] 4. The solution was chromatographed on a Florisil column prepared in hexane. Elution with hexane removed the dinitrogen complex 4. Elution with CH$_2$Cl$_2$ afforded a yellow-orange band which corresponded to the monocarbonyl species 21b and finally, elution with acetone yielded the hydrazido(2-) complex 19b as a dark red band.

21b: IR (CH$_2$Cl$_2$): 1949vs (ν(CO)); 1644s,br (acyl and probably ν(NN)).

^{1}H-NMR (acetone-d$_6$, R.T.): δ7.32s,br (5H, Ph); 7.26d, 7.04d (4H, C$_6$H$_4$); 6.05s (5H, C$_5$H$_5$); 3.87s (3H, OCH$_3$).

19b: IR (CH$_2$Cl$_2$): ν(CO): 1948vs, 1867vs, cm^{-1}.

^{1}H-NMR (acetone-d$_6$, R.T.): δ7.65-6.90m,br (5H, Ph); 7.27d, 7.01d (4H, C$_6$H$_4$); 5.97s (5H, C$_5$H$_5$); 3.86s (3H, OCH$_3$).

MS: M$^+$, (M-CO)$^+$, (M-2CO)$^+$.

A similar reaction, but carried out in a mixture of 1:1 hexane/CH_2Cl_2 as the solvent, gave different results. To a solution of 2b in hexane/CH_2Cl_2 was added by syringe an excess of PhLi and the mixture stirred at room temperature for 30 min. A fast reaction took place and the solution became orange. An IR spectrum of this solution showed the presence of complexes 21b and 4. The hydrazido(2-) complex 19b was not formed under these conditions.

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OCH_3)][BF_4]$ 2b with n-BuLi. To a solution of 2b (60 mg, 0.11 mmol) in CH_2Cl_2 (5 mL) was added by syringe an excess of n-BuLi (2.4 M in hexane), and the mixture was stirred at room temperature for 30 min. under nitrogen. A fast reaction took place and the solution became deep red. The IR spectrum of this solution showed the presence of the hydrazido(2-) complex $[CpRe(CO)_2(p\text{-}NN(Bu^n)C_6H_4OCH_3)]$ 20b and a small amount of $[CpRe(CO)_2(N_2)]$ 4. No formation of any monocarbonyl species was observed. Addition of hexane produced precipitation of $LiBF_4$ generated during the reaction. Filtration and evaporation of the hexane, yielded complex 20b as a dark red microcrystalline solid in nearly quantitative yield.

IR (CH_2Cl_2): ν(CO): 1935vs, 1855vs, cm^{-1}.

^{1}H-NMR ($CDCl_3$, -30°C): δ7.18d, 6.85d (4H, C_6H_4); 5.87s (5H, C_5H_5); 4.34t (2H, $N(CH_2)$); 3.83s (3H, OCH_3); 1.16-1.92m,br (4H, $-(CH_2)-$); 0.98t (3H, CH_3).

MS: M^+, $(M-CO)^+$, $(M-2CO)^+$.

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4NEt_2)][BF_4]$ 2d with n-BuLi. This was carried out as described above for 2b. The color changed from dark green to dark red-orange, and the IR of the solution showed the presence of the new hydrazido(2-) complex $[CpRe(CO)_2(p\text{-}NN(Bu^n)C_6H_4NEt_2)]$ 20d and a very small amount of complex 4. Evaporation of the hexane under reduced pressure afforded complex 20d as a dark red microcrystalline solid in nearly quantitative yield.

IR (CH_2Cl_2): ν(CO): 1933vs, 1852vs cm^{-1}.

^{1}H-NMR ($CDCl_3$, -30°C): δ7.11d, 6.57d (4H, C_6H_4); 5.82s (5H, C_5H_5); 4.34t (2H, $N(CH_2)$); 3.35q (4H, CH_2(Et)); 1.15t (6H, CH_3(Et)); 1.04-1.92m,br (4H, $CH_2(Bu^n)$); 0.97t (3H, $CH_3(Bu^n)$).

MS: M^+, $(M-CO)^+$, $(M-2CO)^+$.

When the reaction was carried out in a mixture of 1:1 hexane/acetone, n-BuLi reacted vigorously with 2d to give a monocarbonyl complex as the only product, which was tentatively identified as the butyryl complex $[CpRe(CO)(COBu^n)(p\text{-}N_2C_6H_4NEt_2)]$ 22d. This compound can be precipitated as an orange-yellow air sensitive solid by addition of excess of hexane to the reaction mixture.

IR (CH_2Cl_2): ν(CO) 1938vs cm^{-1}; strong and broad bands at 1660-1600 cm^{-1}.

Reaction of [CpRe(CO)$_2${p-NN(CH$_3$)C$_6$H$_4$Me}] (17a) with HBF$_4$. To a solution of 17a in CH$_2$Cl$_2$ or CHCl$_3$ (10 mL) was added dry HBF$_4$ in Et$_2$O and the mixture stirred at room temperature for 20-30 min. under N$_2$. A fast reaction took place, the color changed from red-orange to deep red, and precipitation of an air-stable dark red solid was completed by the addition of diethyl ether. It was easily recrystallized as dark red diamond-shaped crystals from CHCl$_3$-Et$_2$O, m.p. 155-158°C (dec.).

Anal. Calcd. for [CpRe(CO)$_2${p-NHN(CH$_3$)C$_6$H$_4$Me}][BF$_4$] 23a: C, 34.03; H, 3.02; N, 5.29. Found: C, 33.85; H, 3.11; N, 4.95. IR [CH$_2$Cl$_2$] 2002vs, 1936vs (νCO). ^{1}H-NMR [(CD$_3$)$_2$CO] 16.5s,br (NH); 7.26d, 7.58d (C$_6$H$_4$); 6.41s (Cp); 3.24s (NCH$_3$); 2.26s (CH$_3$).

Reaction of [CpRe(CO)$_2${p-NN(CH$_3$)C$_6$H$_4$OMe}] (17b) with HBF$_4$. To a solution of 17b in CH$_2$Cl$_2$ or CHCl$_3$ (10 mL) was added dry HBF$_4$ in Et$_2$O, and the mixture was stirred at room temperature for 20-30 min. under nitrogen. The color rapidly changed from red-orange to deep red and a dark red solid precipitated. Ether was added, the supernatant liquid removed, and the precipitate washed several times with ether, then dried in a stream of N$_2$. It was recrystallized from chloroform-ether, m.p. 158-159° (dec.).

Anal. Calcd. for [(η^5-C$_5$H$_5$)Re(CO)$_2${p-NHN(CH$_3$)C$_6$H$_4$OMe}][BF$_4$] 23b: C, 33.03; H, 2.94; N, 5.14. Found: C, 31.04; H, 2.80;

N, 5.03. IR ($CHCl_3$) 2001vs, 1933vs (νCO).

Reactions of [$CpRe(CO)_2(p\text{-}NN(Ph)C_6H_4OCH_3)$] 19b, [$CpRe(CO)_2(p\text{-}NN(Bu^n)C_6H_4OCH_3)$] 20d, and [$CpRe(CO)_2(p\text{-}N(H)NC_6H_4OCH_3)$] 15b with HBF_4. These reactions were carried out under conditions identical to those described above, to give the new hydrazido(1-) complexes [$CpRe(CO)_2\{p\text{-}N(H)N(Ph)C_6H_4OCH_3\}$][$BF_4$] 24b, [$CpRe(CO)_2\{p\text{-}N(H)N(Bu^n)C_6H_4OCH_3\}$][$BF_4$] 25b, and [$CpRe(CO)_2\{p\text{-}N(H)N(H)C_6H_4OCH_3\}$][$BF_4$] 28b. *Anal.* Calcd. for 28b: C, 31.64; H, 2.64; N, 5.27. Found: C, 30.76; H, 2.60; N, 5.08.

Reaction of [$CpRe(CO)_2(p\text{-}NN(CH_3)C_6H_4OCH_3)$] 17b with $Ph_2I^+BF_4^-$. A solution of 17b in CH_2Cl_2 was stirred with $Ph_2I^+BF_4^-$ at room temperature for 12 h. The IR spectrum of this solution showed that no reaction had occurred. The starting materials were recovered unchanged.

Reaction of [$CpRe(CO)_2\{p\text{-}N(H)N(CH_3)C_6H_4OCH_3\}$][$BF_4$] 23b with NaI. A solution of 23b in acetone (5 mL) was stirred with solid NaI at room temperature for 1h. The IR spectrum of this solution showed the presence of the hydrazido(2-) complex [$CpRe(CO)_2(p\text{-}NN(CH_3)C_6H_4OCH_3)$] 17b as the major product.

Evaporation of the acetone and extraction with hexane afforded 17b which was fully characterized by IR, NMR and MS (see Table IV). The dark red-brown residue was then extracted with CH_2Cl_2, which IR spectrum indicated the presence of the diiodo complex $[CpRe(CO)_2(I_2)]$ 5 (identified by IR, MS).

Reaction of $[CpRe(CO)_2\{p\text{-}N(H)N(CH_3)C_6H_4CH_3\}][BF_4]$ 23a with NaI. This reaction was carried out under conditions identical to those described above for 23b. The complexes $[CpRe(CO)_2(p\text{-}NN(CH_3)C_6H_4CH_3)]$ 17a and $[CpRe(CO)_2I_2]$ 5 were fully identified from this reaction.

Reaction of $[CpRe(CO)_2(p\text{-}NHNC_6H_4OCH_3)]$ 15b with $(CH_3)_3O^+BF_4^-$. To a solution of 15b in CH_2Cl_2 (5 mL) was added a stoichiometric amount of $(CH_3)_3O^+BF_4^-$ dissolved in CH_2Cl_2 and the mixture stirred at room temperature. An instantaneous reaction took place and the color changed from bright orange to deep red. An IR spectrum of this solution showed the presence of the hydrazido(1-) complexes $[CpRe(CO)_2\{p\text{-}N(H)N(CH_3)C_6H_4OCH_3\}]$-$[BF_4]$ 23b and $[CpRe(CO)_2\{p\text{-}N(H)N(H)C_6H_4OCH_3\}][BF_4]$ 28b, among other unidentified compounds.

Evaporation of the solvent and extraction of the residue by $CHCl_3$ afforded essentially complex 23b, which was identified by IR and ^1H-NMR. Complex 28b was identified by IR only.

Reaction of [$CpRe(CO)_2(p\text{-}NN(CH_3)C_6H_4OCH_3)$] 17b with $(CH_3)_3O^+BF_4^-$. This reaction was carried out under conditions identical to those described above. A very fast reaction took place and the IR spectrum of this solution was quite complicated. It showed very broad ν(CO) bands at about 1990 and 1930 cm^{-1}, but they seem to correspond to a mixture of different compounds.

Addition of hexane to the reaction mixture produced a dark red precipitate which was stirred with hexane (3 × 10 mL) and dried under vacuum. The ^1H-NMR (acetone-d_6) of this solid indeed showed that this was a mixture; the hydrazido(1-) complex [$CpRe(CO)_2\{p\text{-}N(H)N(CH_3)C_6H_4OCH_3\}$][$BF_4$] 23b was clearly identified (major product), but additional aryl, Cp, OCH_3 and CH_3 resonances were also observed.

Reactions of [$CpRe(CO)_2(p\text{-}NHNC_6H_4OCH_3)$] 15b and [$CpRe(CO)_2(p\text{-}NN(CH_3)C_6H_4OCH_3)$] 17b with CH_3I. Solid 15b or 17b was dissolved in CH_3I and the solution stirred at room temperature for 24 h. The IR spectrum of the solution showed that no reaction had occurred.

CHAPTER IV

Hydrazido(1-) Complexes of Rhenium: A ^{1}H-NMR Study of their Stereoisomerism in Solution.

4.1 Introduction

As was discussed in Chapter III, the arylhydrazido(1-) complexes [CpRe(CO)$_2$(NHNRR")][BF$_4$] (where R = C_6H_4X with X = p-CH$_3$, p-OCH$_3$ or p-NEt$_2$, and R" = H, CH$_3$, Ph or Bu^n) have been synthesized either by protonation of the corresponding arylhydrazido(2-) complex [CpRe(CO)$_2$(NNRR")] or by methylation or protonation of the corresponding aryldiazene complex [CpRe(CO)$_2$(NHNR)].

It was found that these hydrazido(1-) complexes are non-rigid molecules and that they exist as two stereoisomers in solution (CDCl$_3$) at room temperature.

In order to understand the mechanism operating in this fluxional process, we have examined the NMR of these hydrazido(1-) complexes in some detail. This study was done in collaboration with Dr. Alan Tracey whose help is gratefully acknowledged.

4.2 ^{1}H-NMR Spectroscopy.

This NMR study was carried out with two of these hydrazido(1-) complexes, [CpRe(CO)$_2${p-N(H)N(CH$_3$)C$_6$H$_4$OCH$_3$}][BF$_4$] 23b and [CpRe(CO)$_2${p-N(H)N(H)C$_6$H$_4$OCH$_3$}][BF$_4$] 28b.

a) $[CpRe(CO)_2\{p\text{-}N(H)N(CH_3)C_6H_4OCH_3\}][BF_4]$ 23b.

The ^{1}H-NMR spectrum of this hydrazido(1-) complex in $CDCl_3$ at ambient temperature exhibits two sets of resonances, due to the presence of two stereoisomers (see Fig. 7). The pairs of lines due to corresponding protons in each stereoisomer coalesce as the temperature is increased.

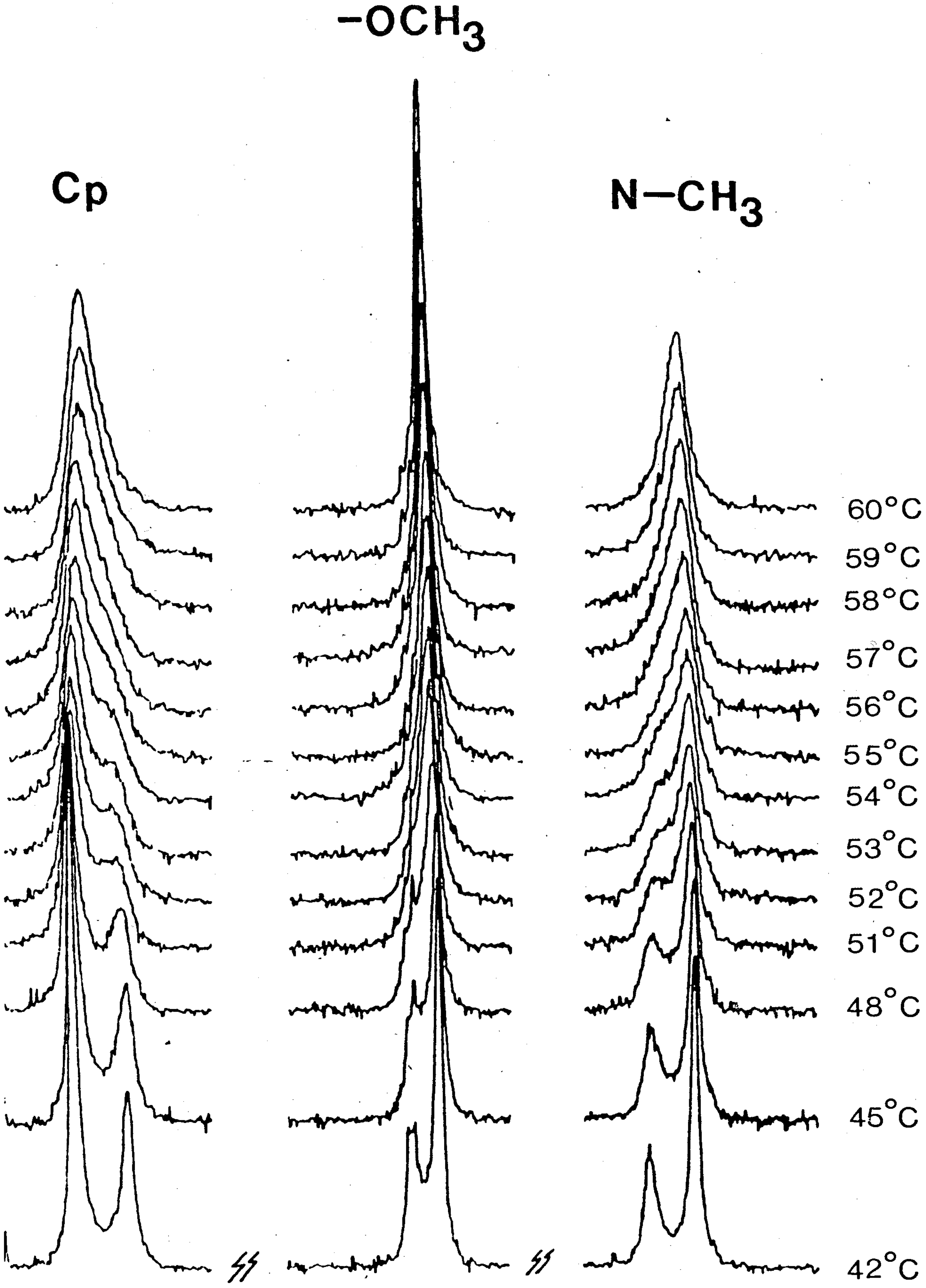
The activation energy $\Delta G^\dagger$ was obtained from coalescence temperature experiments (see Fig. 9). The value of $\Delta G^\dagger$ was obtained by using the Eyring equation and the coalescence temperature T_C (328°K) and k_C calculated from the equation $k_C = \pi/\sqrt{2}(\bar{\Delta}\nu_\infty)^{112}$ ($\nu_\infty = 7.55$ Hz) for the Cp resonances; $\Delta G^\dagger = 17.4 \pm 0.2$ kcal mol^{-1} (72.9 kJ mol^{-1}). For examples of calculation, see the end of this chapter.

From the proportion of the two components at room and lower temperatures (290, 273, 256 and 239 K), the ground-state energy difference, ΔE, between the two isomers was calculated to be 0.39 ± 0.03 kcal mol^{-1}.

Since, in determining the activation energy, the coalescence point was estimated from transitions of unequal intensity, it was decided also to measure interconversion rates directly from a saturation transfer experiment. Briefly, this is a useful consequence of the NOE experiment (described below) in that if the site of irradiation is involved in chemical exchange, saturation can be transferred as exchange occurs.

Figure 9

100 MHz ^{1}H-NMR Spectra ($CDCl_3$) of the Hydrazido(1-) Complex $[CpRe(CO)_2\{p\text{-}N(H)N(CH_3)C_6H_4OCH_3\}][BF_4]$ 23b at increasing temperatures, showing only the Cp, OCH_3 and NCH_3 resonances (coalescence temperature experiment).


$-OCH_3$
Cp
$N-CH_3$
60°C
59°C
58°C
57°C
56°C
55°C
54°C
53°C
52°C
51°C
48°C
45°C
42°C

This is the basis of the saturation transfer experiment described by Forsén and Hoffman[113] from which exchange kinetics are obtained. This procedure has recently been reviewed.[114] In this case, the resonance corresponding to the Cp group in one stereoisomer was irradiated and the intensity of the Cp peak of the second stereoisomer was determined as a function of time. The rate of interconversion was determined at four temperatures (273, 290, 297 and 305 K) and the results gave an activation energy $\Delta G^{\dagger} = 17.5 \pm 0.3$ kcal mol^{-1} in very good agreement with the value obtained from the coalescence temperature.

In order to try to determine the identity of each stereoisomer, a particularly useful NMR experiment is Nuclear Overhauser Effect (NOE) difference spectroscopy. One spectrum is accumulated while simultaneous saturating irradiation is applied at the transition of interest. This spectrum is subtracted from a second spectrum for which the irradiation frequency is moved to a region free from any transitions. The resultant spectrum shows a large resonance corresponding to the first irradiation frequency, plus any resonances which are enhanced by the NOE. The magnitude of the NOE provides information concerning internuclear distances, and in the present case, is only expected to be significant for protons with reasonably short intramolecular non-bonded contacts.[115]

Interpretation of the NOE results is complicated by the fact that chemical NH-exchange between the stereoisomers (and with trace of water) occurs during the irradiation period required for NOE build-up (10 sec.). Thus, irradiation at NH (isomer 1) results in magnetization transfer to NH (isomer 2) and, therefore, corresponding NOE enhancement of appropriate protons in isomer (1) and isomer (2). Fortunately an internal referencing is available; the NH intensities for isomer (1) and isomer (2) can be individually compared to the intensities of the NOE enhanced peaks which are zero in the absence of NOE.

Let isomer (1) be the dominant isomer at ambient temperature. Each isomer is associated with the Cp, NH, aromatic, NCH_3 and OCH_3 resonances as shown in Figure 7. Irradiation at the separate NH(1) and NH(2) positions results in NOE enhancement of Cp, aromatic (*ortho*-positions) and NCH_3 resonances only. The relative intensities observed (normalized with respect to the aromatic resonances) are given in Table VI, and a typical difference spectrum is shown in Figure 10.

Table VI. Relative Intensity of NOE Enhanced Peaks.[a]

Irradiation Position	NH(2)	NH(1)	*o*-Arom[b]	Cp(1)	Cp(2)	MMe(2)	NMe(1)
NH isomer (2)	4.76	1.33	1	1.01	0.67	0.60	0.33
NH isomer (1)	2.33	1.45	1	0.81	0.52	0.33	0.17

[a] All listed in order of increasing field. [b] Orthoaromatic resonances from isomers 1 and 2 are superimposed.

The results are analysed by comparing the NOE enhancements for these protons with the magnitude of the NH(2) intensity observed for (a) irradiation at NH(2) directly and (b) irradiation at NH(1) (which also gives rise to NH(2) intensity from magnetization transfer). This is repeated for the NH(1), and the presence or absence of correlation is examined. First, we notice that the NH(1) intensity is roughly the same for irradiation at NH(1) directly and for irradiation at NH(2). Of the NOE enhanced resonances, only the ortho aromatic protons show a similar *ca.* 1:1 ratio, indicating that aromatic protons enhancement arises only from NH(1) irradiation.

Figure 10

^{1}H-NMR difference spectrum ($CDCl_3$ at 400 MHz) of the hydrazido(1-) complex $[CpRe(CO)_2\{p\text{-}N(H)N(CH_3)C_6H_4OCH_3\}][BF_4]$ 23b obtaining by irradiating (↓) the NH resonance of isomer (1).

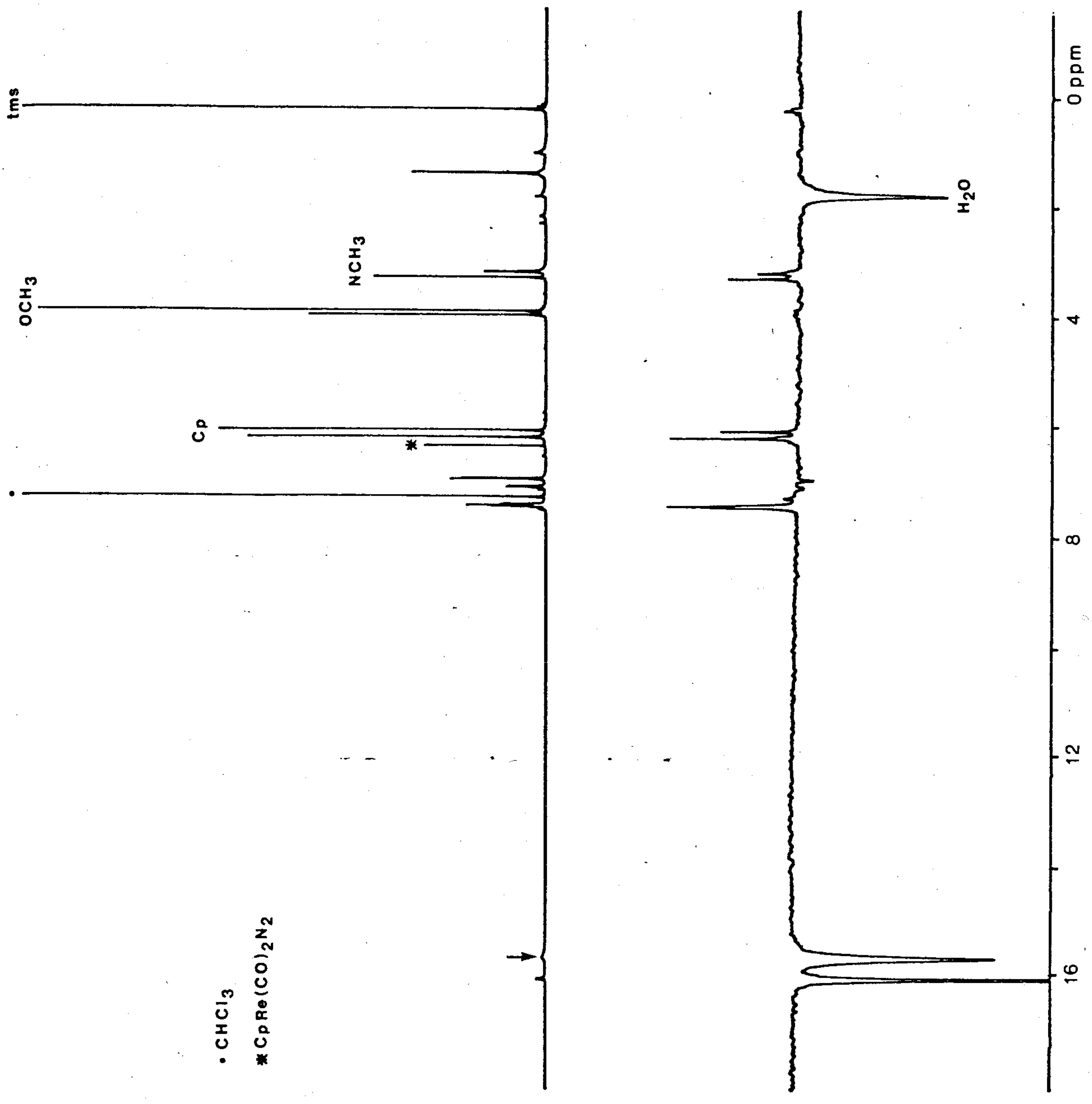
I → Normal spectrum.

II → NOE difference spectrum.

† = $CpRe(CO)_2(N_2)$

* = impurities

x = water


tms
OCH$_3$
NCH$_3$
Cp
*
•
H$_2$O
0 ppm
4
8
12
16
• CHCl$_3$
* CpRe(CO)$_2$N$_2$

Second, we observe that the NH(2) intensity for irradiation at NH(2) directly is roughly twice the NH(2) intensity for irradiation at NH(1). Of the NOE enhanced resonances, only NMe(2) and NMe(1) exhibit similar ratios, indicating that NMe enhancement arises solely from NH(2) irradiation. Since the major enhancement is between NH(2) and NMe(2), these protons are in the more effective NOE positions and the weaker enhancement of NMe(1) arises from enhancement transferred to this position by the interconversion process. A similar situation probably also is occurring for the aromatic protons but cannot be distinguished because of their near superposition in the NMR spectrum.

There is no simple correlation of the NOE of Cp resonances with either NH(1) or NH(2) alone, which indicates that Cp enhancements occur from both NH(1) and NH(2) directly.

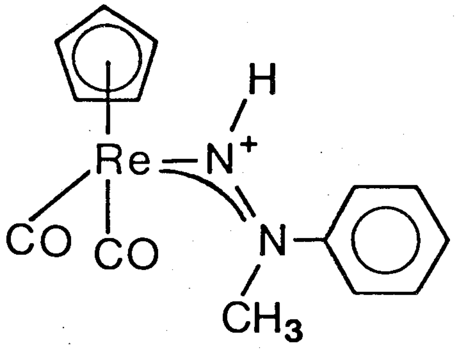
Calculation[116] of the contributions to the enhancements of Cp(1) and Cp(2) from NH(1) and NH(2) indicate that the enhancement of each Cp resonance has an equal contribution from NH(1) and NH(2).

If we restrict consideration only to the monohapto structures XV-XVIII, these NOE results conclusively indicate that isomer 1 has structure XV (which is also the solid state structure and thermodynamically the more stable in $CDCl_3$ and acetone solution), whilst isomer 2 has structure XVI related to XV by rotation about the NN bond. The $\Delta G^{\dagger}$ value (17.5 kcal mol^{-1}), which falls in the range observed for restricted-rotation about a partial double bond[90,117] supports the relationship between both structures, i.e., rotation about a NN double bond. In acetone, where only one set of signals is observed, irradiation of the NH resonance resulted only in enhancement of the Cp and ortho aromatic resonances, but not the NCH_3. This conclusively shows that only the more stable isomer 1 (structure XV) is present.

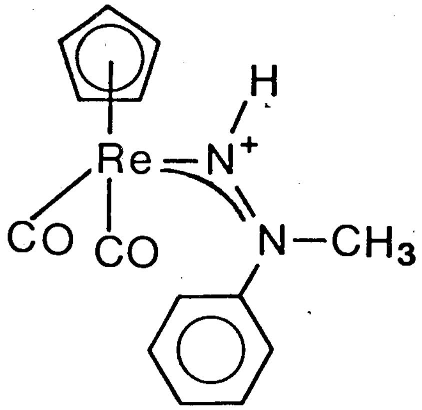
The tentative proposal made previously[118] that "interconversion" involved rotation about the Re-N bond is ruled out by the NOE results.

Further NOE experiments allow us to rule out of consideration a dihapto (cyclic) structure such as XIX, since irradiation of the Cp resonances produced no NOE enhancement of either the NMe or aromatic resonances, or vice versa. Since it has already been established that an NOE occurs between the Cp and the bound (α) NH group, an NOE would also be expected between the Cp and one or other of these groups if the β-nitrogen atom were also coordinated to the metal.

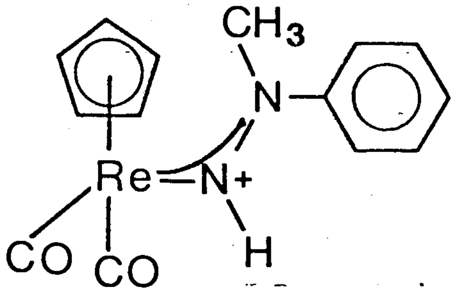
In summary, then, the NOE experiments conclusively establish that the interconverting stereoisomers in $CDCl_3$ solution are XV and XVI.



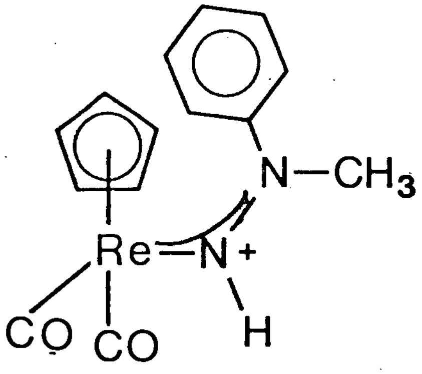
XV



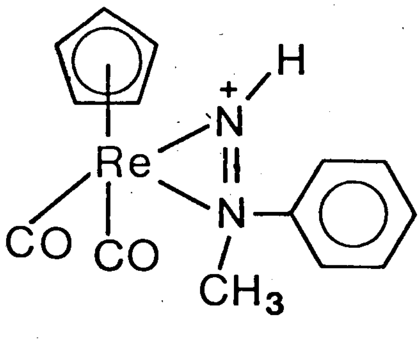
XVI



XVII



XVIII



XIX

b) [CpRe(CO)$_2${p-N(H)N(H)C$_6$H$_4$OCH$_3$}][BF$_4$] 28b.

The ^{1}H-NMR spectrum (CDCl$_3$) of this hydrazido(1-) complex shows that this compound also exists as two stereoisomers at ambient temperature (see Fig. 8). Similar NOE experiments to those described above, were carried out in this case, in order to try to determine the identity of each stereoisomer.[111]

As was indicated in Chapter III, the four NH resonances observed in the ^{1}H-NMR spectrum of this complex were unambiguously identified (by ^{15}N isotopic substitution at N^1), the two signals at lower field corresponding to the protons attached to N(1) or N$_\alpha$ atom (in both stereoisomers) and the two signals at higher field corresponding to the protons attached to N(2) or N$_\beta$. These four resonances will be named as NH$_\alpha$(1), NH$_\alpha$(2), NH$_\beta$(2) and NH$_\beta$(1) in order of increasing field respectively; this is shown in Figure 11.

From these NOE experiments, the following observations were obtained:

i) Irradiation of NH$_\alpha$(1) or NH$_\alpha$(2) enhanced NH$_\beta$(1) and NH$_\beta$(2) respectively and vice-versa.

ii) Irradiation of NH$_\beta$(1) enhanced the Cp(1) resonance.

iii) Irradiation of NH$_\alpha$(1) enhanced Cp(1).

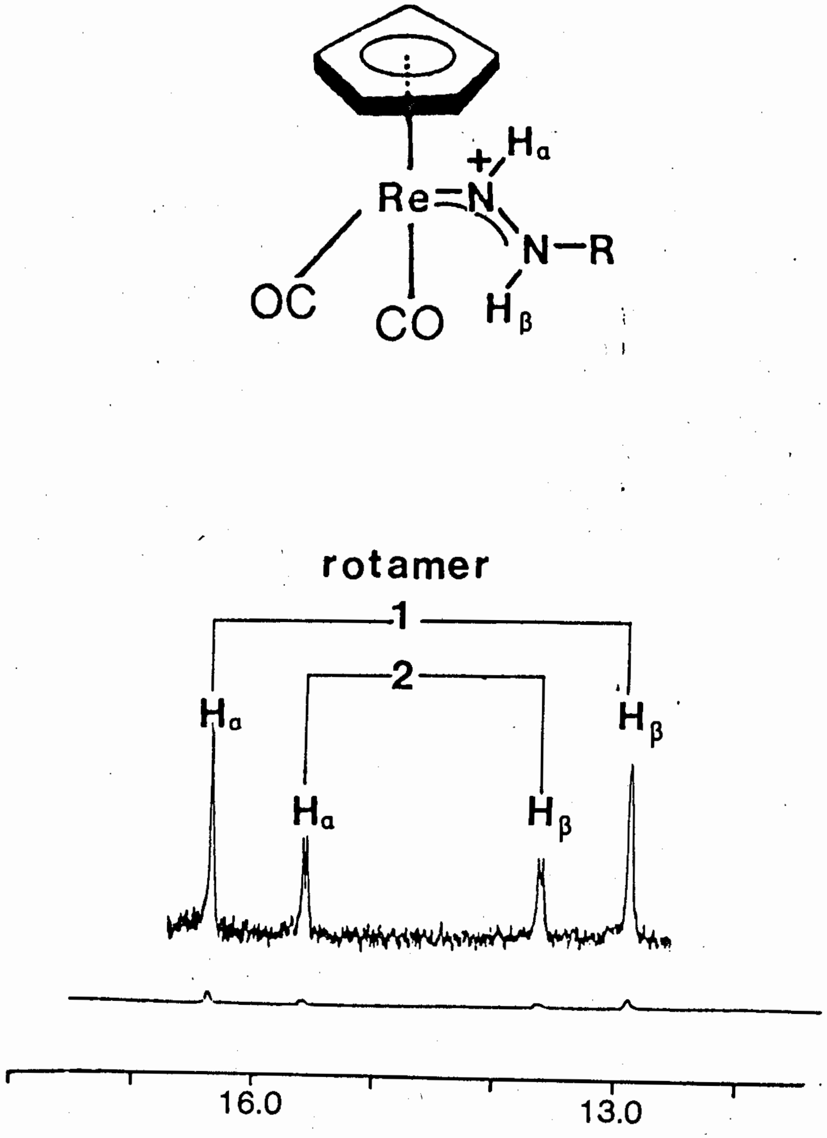
iv) Irradiation of NH$_\beta$(2) gave no Cp enhancement.

v) Irradiation of NH$_\alpha$(2) gave no Cp enhancement.

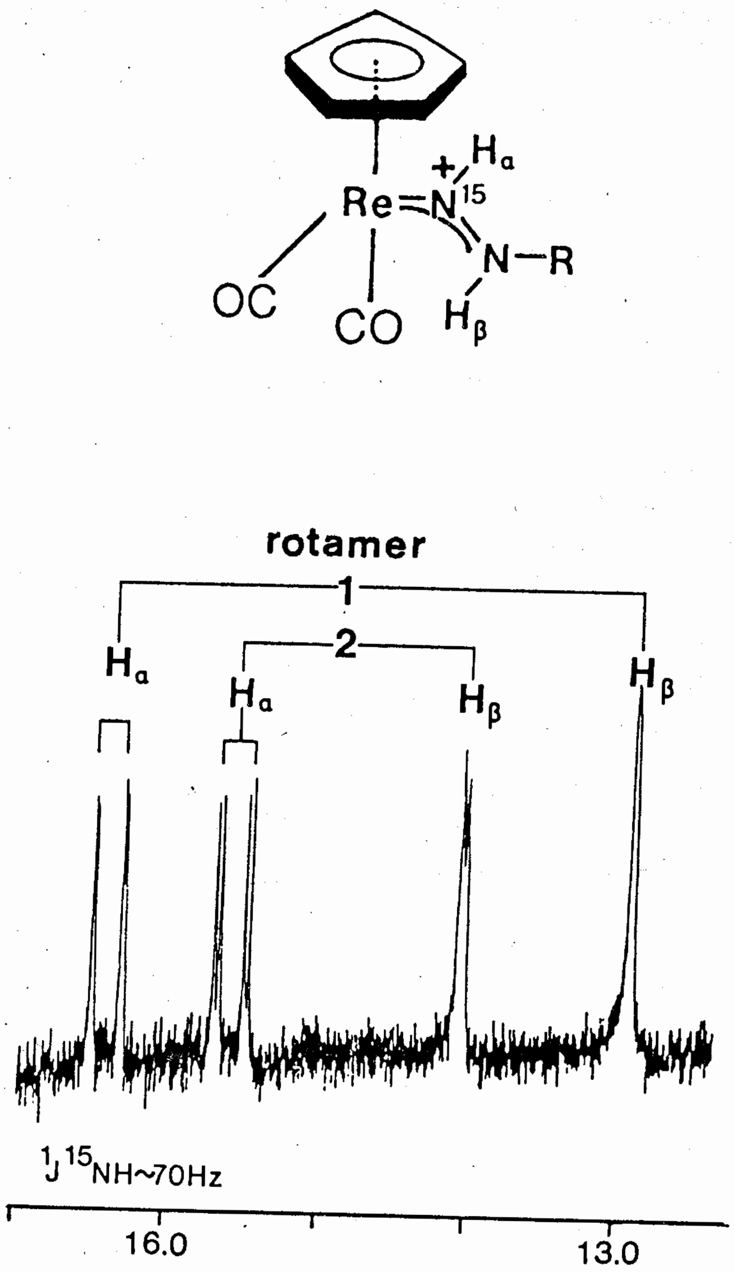
vi) The aromatic resonances were enhanced from both NH$_\alpha$ and NH$_\beta$.

Figure 11

^{1}H-NMR spectrum ($CDCl_3$, at 400 MHz) showing the NH resonances of the two stereoisomers, of the hydrazido(1-) complex $[CpRe(CO)_2\{p\text{-}N(H)N(H)C_6H_4OCH_3\}][BF_4]$ 28b.


Re
OC
CO
N
N−R
+
H_α
H_β
rotamer
1
2
H_α
H_α
H_β
H_β
16.0
13.0

11A.


Re
OC
CO
N^{15}
N−R
+
H_α
H_β
rotamer
1
2
H_α
H_α
H_β
H_β
$^{1}J_{^{15}NH} \sim 70Hz$
16.0
13.0

11B.

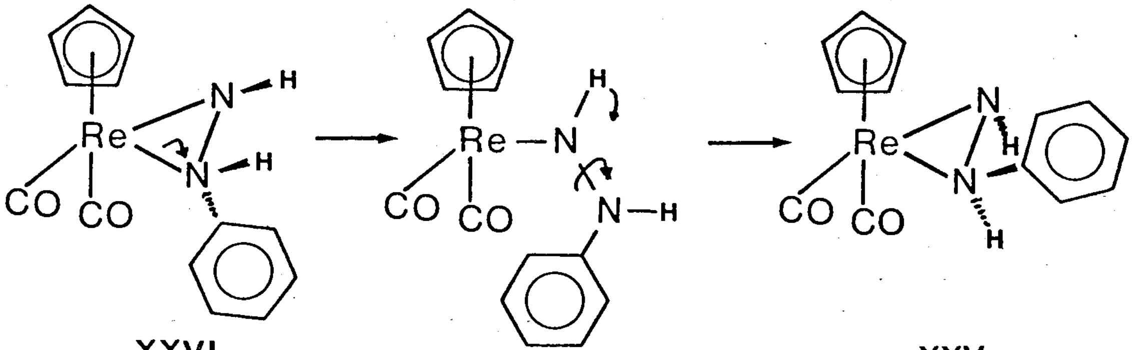
Combination of ii) and iii) indicate that NH$_\alpha$ and NH$_\beta$ in isomer (1) must be *cis* to Cp. Combination of iv) and v) indicate that NH$_\alpha$ and NH$_\beta$ in isomer (2) must be *trans* to Cp. The observation i) indicates that the two H must be *cis* (or *syn*) to each other in both isomers.

It is possible to draw eight structures for these isomers, four in which the hydrazido(1-) ligand is coordinated to the metal in an "end-on" fashion (XX-XXIII) and four in which the diazo ligand adopts a "side-on" geometry (XXIV-XXVII).

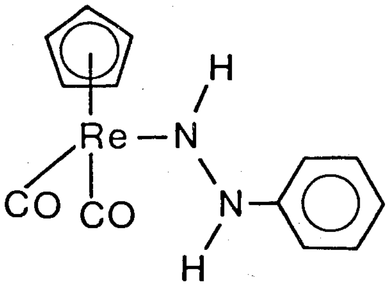
Isomer 1 must satisfy observations i), ii) and iii) which means that its structure must have the two H *cis* to Cp and *cis* (or *syn*) to each other. Among the eight possible structures, XXVI is the only one which satisfies these requirements and possibly observation vi) also.

Isomer 2 must satisfy observations i), iii) and iv); the only two structures which agree with this are structure XXIII and XXV. Between these two, XXV seems to be more reasonable, since an enhancement of the aromatic protons will indeed be expected from NH$_\beta$ and probably from NH$_\alpha$ (observation vi)) while from structure XXIII enhancement of these protons (ortho-protons) from NH$_\alpha$ is not to be expected since they are *trans* to each other.

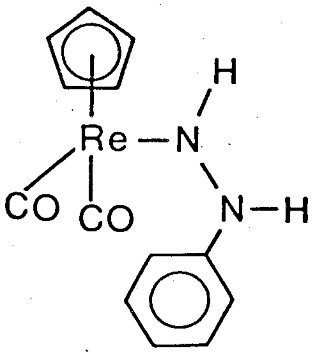
If structures XXV and XXVI are the actual structures of these two stereoisomers, how do they interconvert? A possible mechanism is shown in eq. 20. This involves an opening of the ring and rotation about the N-N bond with simultaneous inversion at Nα and Nβ and closing again.



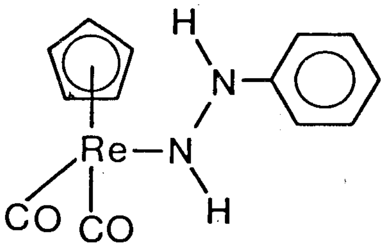
(20)



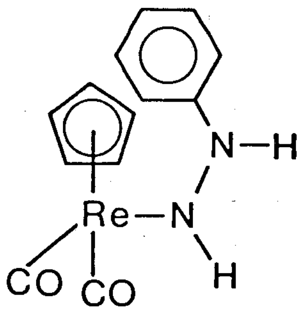
XX



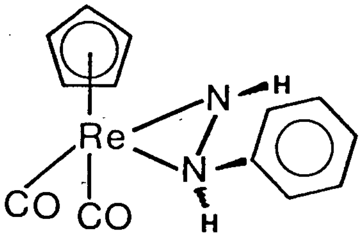
XXI



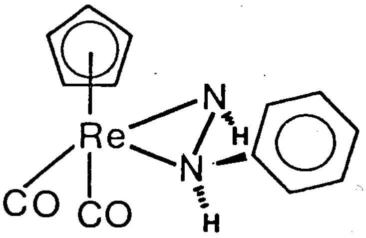
XXII



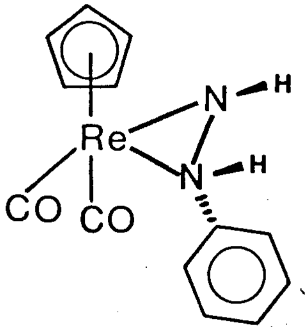
XXIII



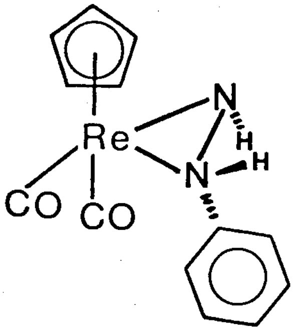
XXIV



XXV



XXVI



XXVII

Arguments against these structures, are the observed $^1J(HH)$ coupling constants; the $^1J(HH)$ for one isomer is 8 Hz (isomer 1) and 18 Hz (isomer 2) for the other one. At the present time, it is difficult to rationalize this difference especially when the two suggested structures both have the two protons <u>syn</u> to each other. It is also not well understood why these two structures should have chemical shifts of the NH_α and NH_β in one isomer, at lower and higher field respectively, when compared to the NH_α and NH_β of the other isomer (see Fig. 11). The ^{15}N-NMR chemical shifts for this hydrazido(1-) complex (see Appendix II) also seem to support a cyclic structure, at least for one of the two isomers, since the ^{15}N-NMR spectrum was taken in acetone-d_6 where only one isomer is present, but in absence of more conclusive experiments, it is not possible to go further than this.

4.3 Examples of Calculation of $\Delta G^\dagger$ and ΔE

a) Calculation of $\Delta G^\dagger$ from Coalescence Temperature Experiments.

From the plot of T(K) vs. $\Delta\nu$(Hz) ($\Delta\nu$ is the difference in chemical shift of the signals which coalesce), the $\Delta\nu^\infty$ value can be obtained and the rate constant k_c can be calculated. In our example, the following data was obtained.

Coalescence temperature (T_C) = 328 ± 1°K

$\Delta\nu_\infty$ = 7.55 ± 0.7 Hz

$$k_c = \frac{\pi}{\sqrt{2}} \Delta\nu_\infty = \underline{16.8 \pm 1.6 \text{ sec}^{-1}}$$

By using the Eyring equation, the $\Delta G^\dagger$ value can be calculated.

$$k_c = \frac{kT}{h} e^{-\Delta G^\dagger/RT_c}$$

k = Boltzmann constant (1.3807×10^{-16} ergs. K^{-1})

h = Planck's constant (6.63×10^{-27} erg. sec.)

R = Gas constant (1.987 cal.K^{-1}.mol^{-1})

$$\underline{\Delta G^\dagger = 17.4 \pm 0.2 \text{ kcal.mol}^{-1}}$$

b) Calculation of ΔE.

In this experiment, the ^{1}H-NMR spectrum is obtained at different temperatures. From the population ratio of the two isomers at each particular temperature and by using the Boltzmann distribution equation, the ΔE value can be obtained.

$$\frac{N-}{N+} = e^{-\frac{\Delta E}{KT}} \quad \text{Boltzmann distribution.}$$

k = Boltzmann constant

T = Temperature (K)

$\frac{N-}{N+}$ = ratio of both isomers

At each particular temperature, the N-value is given by the integral of the resonance under study (eg. Cp, NMe) of the less dominant isomer, and N+ by the integral of the corresponding resonance of the dominant isomer.

For example, at T = 273 K, the ratio

$$\frac{N-}{N+} = \frac{35}{75} \quad \text{(Cp resonances)}$$

then

$$\Delta E = -k\ (273)\ \ln \frac{35}{75} \times N$$

$k = 3.30 \times 10^{-27}$ kcal K^{-1}

N = Avogadro's number = 6.023×10^{23}

$$\underline{\Delta E = 0.41 \text{ kcal mol}^{-1}}$$

For each temperature, a value of ΔE is obtained from the Cp resonances and the same can be done for other resonances. The average of these values will give a more realistic value of ΔE.

c) <u>Calculation of the Activation Energy from Saturation Transfer Experiments.</u>

The description to follow, of how the activation energy ($\Delta G^{\dagger}$) value was obtained, is presented from a practical point of view; for the theoretical aspects of this technique, see ref. 113.

From a purely qualitative point of view, the observation of an intensity decrease for a given signal (A) in species (1), upon strong irradiation of the corresponding signal (B) in species (2), is a good indication of the existence of an exchange process between A and B.

Saturation of B makes the B magnetization zero ($M_B = o$) and the A magnetization at time t is given by eq. 21. At $t = o$, $M_{A_t} = M_oA$.

$$M_t = M_oA \left[\frac{\tau_{1A}}{T_{1A}} + \frac{\tau_{1A}}{T_{1A}} \exp \quad -t/T_{1A} \right] \tag{21}$$

M_{A_t}: magnetization of A at time t.

M_oA : equilibrium magnetization of A.

τ_{1A} = time constant.

T_{1A} = spin-lattice relaxation time.

Thus, from the moment at which we start to irradiate B, we observe an exponential decay of the A magnetization which decreases until a new equilibrium magnetization $M_{A(t\to\infty)}$ is reached:

$$M_{A(t\to\infty)} = \frac{\tau_{1A}}{T_{1A}} \quad M_oA$$

According to eq. 21, a semilogarithmic plot of ln

$(M_{A_t} - M_{A(t\to\infty)})$ against time (t) is a straight line of slope $- 1/\tau_{1A}$ from which the value of τ_{1A} is obtained. This value is related to the lifetime of species (1) (τ_A) and T_{1A} by

$$\frac{1}{\tau_{1A}} = \frac{1}{\tau_A} + \frac{1}{T_{1A}}$$

and the ratio between the initial and final values of M_A ($M_{A_t}/M_{A(t\to\infty)}$) gives the quotient T_{1A}/τ_{1A}. From the known values of T_{1A}/τ_{1A} and τ_{1A}, the values of τ_A and T_{1A} are obtained.

A plot of $\ln\tau$ against $\frac{1}{T}$ K^{-1} gives a straight line of slope $- \Delta G^{\dagger}/1.987$ from which the value of $\Delta G^{\dagger}$ is obtained.

In our particular example, the Cp resonance position in one isomer was irradiated and the integral, I, of the Cp signal of the second stereoisomer was determined as a function of time. In each spectrum, the integral I of the Cp signal under study was normalized to the total integral of the NMe or OCH_3 signals of both isomers, which were used as internal references.

As time t increases, the error in determining the value of I also increases, therefore, a "weight" to each measurement was given and a least-squares analysis was applied to the set of points at each particular temperature.

A Numerical Example

First of all, let us define some parameters.

$I_o = M_{A_{t=o}}$ = integral of the Cp signal at t=o

$I_\infty = M_{A_{t\to\infty}}$ = integral of the Cp signal at $t\to\infty$

$I_t = M_{A_t}$ = integral of the Cp signal at anytime t

When T = 273 K

$I_o = 60.2$

$I\infty = 33.4$

The plot ln $[I_t - I\infty]$ vs t gave a slope value of -0.48

$$\therefore \quad -\frac{1}{\tau_1} = -0.48$$

$$\underline{\tau_1 = 2.08 \text{ sec.}}$$

$$\frac{T_1}{\tau_1} = \frac{I_o}{I_\infty} = \frac{60.2}{33.4} = 1.80$$

$$\therefore \underline{T_1 = 3.74 \text{ sec.}}$$

then

$$\frac{1}{\tau_1} = \frac{1}{\tau} + \frac{1}{T_1}$$

$$\underline{\tau = 4.67 \text{ sec.}}$$

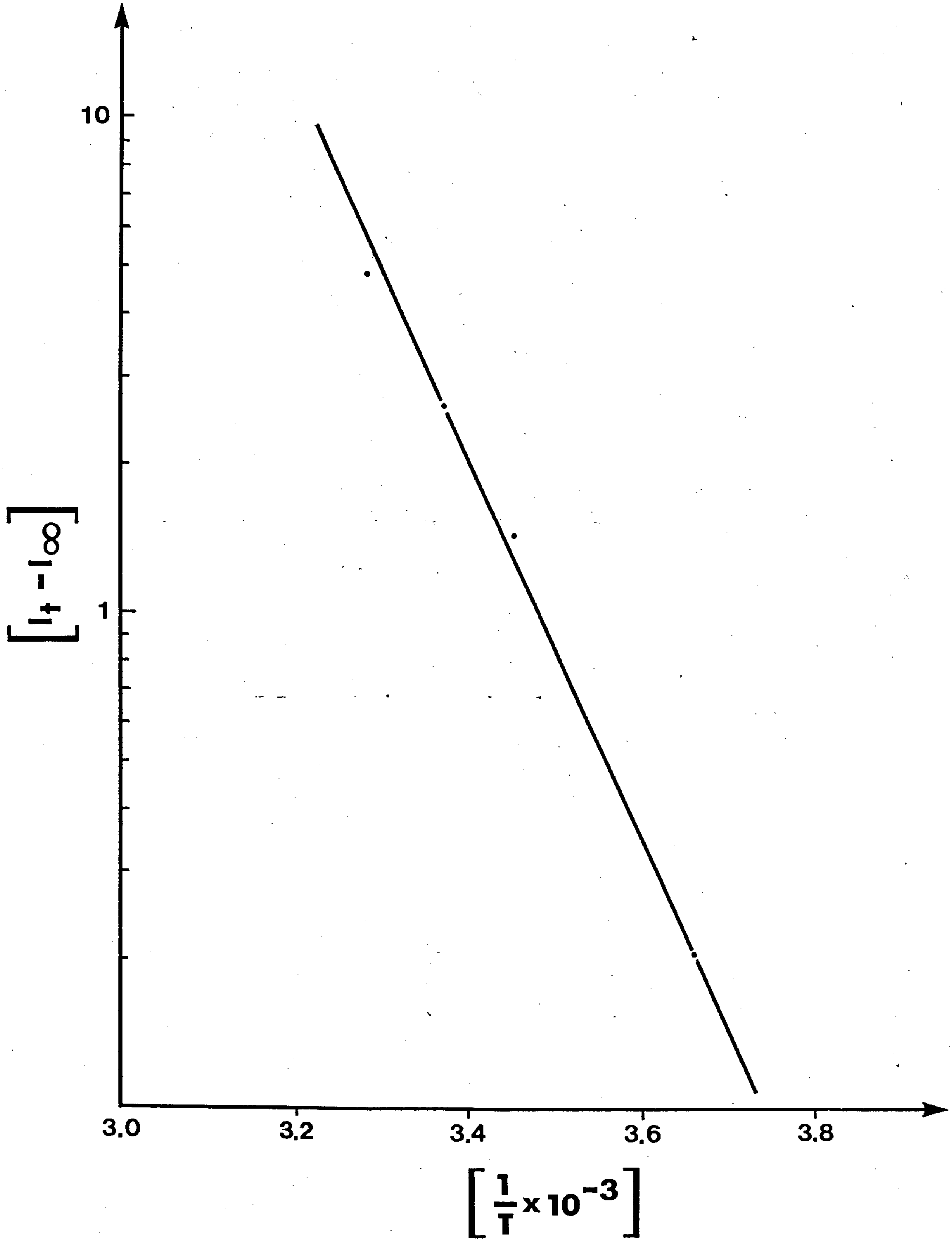
The exchange rate constant (k) for the magnetization transfer process is $k = \frac{1}{\tau}$ (at $T = 273$ K, k - 0.21 sec.).

The plot of $\ln\tau$ vs $\frac{1}{T}$ k^{-1} (Figure 12) gives a straight line of slope $- \frac{\Delta G^{\dagger}}{1.987} = -8.83$

$$\therefore \Delta G^{\dagger} = 17.5 \pm 0.3 \text{ kcal/mol.}$$

Figure 12

Determination of Activation Energy ($\Delta G^{\dagger}$) by Saturation Transfer Experiments. Plot of $\ln\tau$ vs $\frac{1}{T}$ K^{-1}.


10
1
$\left[I_t - I_\infty\right]$
3.0
3.2
3.4
3.6
3.8
$\left[\frac{1}{T} \times 10^{-3}\right]$

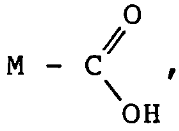
4.4 Experimental

Spectra were obtained for solutions in $CDCl_3$ using either a Varian XL-100 operating at 100 MHz in the FT mode (coalescence temperature experiments), or a Bruker WM-400 FT instrument operating at 400 MHz. Nuclear Overhauser Effect (NOE) experiments on $[CpRe(CO)_2\{p\text{-}N(H)N(CH_3)C_6H_4OCH_3\}][BF_4]$ 23b and $[CpRe(CO)_2\{p\text{-}N(H)N(H)C_6H_4OCH_3\}][BF_4]$ 28b were done at ambient temperature, and saturation transfer experiments (only for 23b) at 273, 290, 297 and 305 K, using the Bruker instrument. Since both are well known experiments[119] they will not be discussed further, except to state that the time used for NOE build-up was 10 sec. and the delays used to obtain the rates of saturation transfer were 0.05, 0.10, 0.25, 0.50, 0.75, 1.00, 2.00, 3.00, 5.00 and 7.50 sec. All spectra were obtained using an 8 KHz spectral width. Four hundred difference spectra (i.e., 800 total spectra) were obtained in the NOE experiments and 36 spectra for the saturation transfer experiments. The coalescence temperature was measured using the XL-100 since the smaller (by × 4) proton chemical shift range (in Hz) for this instrument compared to the Bruker allowed coalescence to be observed within the usable temperature range of $CDCl_3$. The range of temperatures observed was -60 to +60°C and in the range +40 to +60 a spectrum was taken every one degree increment.

CHAPTER V

Hydrido and Hydroxycarbonyl Complexes of Rhenium

5.1 Introduction

Metallocarboxylic acids (or hydroxycarbonyls),  $\mathrm{M-C(=O)OH}$, are usually regarded as key intermediates in a variety of important reactions. For example, they have been postulated as intermediates in the oxidation of CO by metal ions,[120-122] in the homogeneous catalysis of the water-gas shift reaction,[123-125] in the isotopic oxygen exchange of metal carbonyls with water[126,127], in ligand substitution reaction of Group VI metal carbonyls under phase transfer conditions,[128,129] and in reactions of metal carbonyls with water or base to form the corresponding hydrides[130-131] (among others).

Although these species have been postulated to be involved in these and other processes, only very few have been isolated or even partially characterized.[93b,94b,124,132-136]

In this chapter are reported the synthesis and characterization of some new hydroxycarbonyl and hydrido complexes of rhenium of general formula [CpRe(CO)(COOH)(p-$N_2C_6H_4R'$)] and [CpReH(CO)(p-$N_2C_6H_4R'$)], respectively.

5.2 Synthesis and Characterization[137]

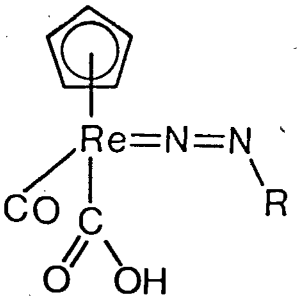
The aryldiazenido complexes of rhenium, $[CpRe(CO)_2(p\text{-}N_2C_6H_4R')][BF_4]$ 2 (R' = a) CH_3, b) OCH_3, d) NEt_2), are found to react with OH^- to give hydroxycarbonyls $[CpRe(CO)(COOH)(p\text{-}N_2C_6H_4R')]$ 29, or hydrido compounds $[CpReH(CO)(p\text{-}N_2C_6H_4R')]$ 30 and the dinitrogen complex $[CpRe(CO)_2(N_2)]$. The nature and ratio of the products obtained in these reactions are strongly dependent upon the reaction conditions.

Thus, compounds 2 reacted with NaOH (5 N) in CH_2Cl_2 at room temperature to give the hydrido species 30 and a large amount of $CpRe(CO)_2(N_2)$. A similar reaction, but under phase transfer conditions[138,139] gave identical results, but the amount of $CpRe(CO)_2N_2$ produced seemed to be less. By carrying out these reactions in CH_2Cl_2 with solid KOH or NaOH (pellets), it was possible to observe (by IR) the initial formation of a monocarbonyl species which then disappeared and was replaced by the hydrido complex 30. Continuous and increasing formation of $CpRe(CO)_2(N_2)$ was also observed under these conditions apparently by a competing reaction. The monocarbonyl intermediate was believed to be the hydroxycarbonyl complex $[CpRe(CO)(COOH)(p\text{-}N_2C_6H_4R')]$ 29, and this was confirmed later on by comparing its IR with that of a pure sample of 29, which could be obtained in high yield by a slightly different method.

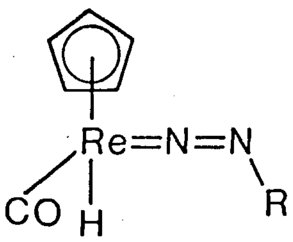
The hydroxycarbonyls 29 were obtained as analytically pure golden-yellow microcrystalline solids by reaction of 2 with an equimolar amount of NaOH in water[140].

High yields of the hydrido complexes 30 were obtained by carrying out the reactions in diethyl ether with excess of aqueous KOH (5 N) (preferred over NaOH; see later for details). They were isolated as air-stable orange oils.

The hydroxycarbonyl complexes 29 were fully characterized by analysis, IR and ^{1}H-NMR (see Table VII). All exhibit in the IR spectrum a strong terminal ν(CO) band at about 1950 cm^{-1} and two or three strong and broad bands in the region 1660-1550 cm^{-1}. These bands should correspond to the ν(CO) stretching and δ(COH) bending modes of the -COOH group and to ν(NN), since from electron counting arguments, these hydroxycarbonyl complexes should possess a three-electron donor singly-bent aryldiazo ligand and have structure (XXVIII). This is precisely the region observed for ν(NN) in neutral complexes containing a singly-bent aryldiazenido ligand.



XXVIII



XXIX

Table VII. IR and ^{1}H-NMR data of hydroxycarbonyl complexes of rhenium.

Compound		ν(CO)^a	Others		^{1}H-NMR^b			
					-COOH	Aryl	Cp	Others
[CpRe(CO)(COOH)(p-$N_2C_6H_4CH_3$)]	29a	1954vs	1643vs,	1596vs	8.9br,s	7.25s	5.83s	2.45s (CH_3)
[CpRe(CO)(COOH)(p-$N_2C_6H_4OCH_3$)]	29b	1954vs	1646br,vs	1584 br,s	8.4br,s	7.36d 6.93d	5.81s	3.82s (OCH_3)
[CpRe(CO)(COOH)(p-$N_2C_6H_4NEt_2$)]	29d	1945vs	1662br,s 1632br,s 1596s		7.8br,s	7.25d 6.66d	5.80s	3.41q (CH_2) 1.17t (CH_3)

^{a} In cm^{-1} for CH_2Cl_2 solutions. Abbreviations: vs, very strong; s, strong; br, broad. ^{b} In $CDCl_3$ at room temperature: All values in ppm, relative to internal TMS. Abbreviations: s, singlet; d, doublet; t, triplet, q, quadruplet.

Attempts to identify unambigously a particular band corresponding to ν(NN) failed, since several bands shifted under ^{15}N-isotopic substitution at N^1 in the complex 29a (see Figure 13), confirming that ν(NN) is strongly coupled to other vibrational modes in this region.

^{1}H-NMR data give additional confirmatory evidence of the formulation of 29 as hydroxycarbonyl complexes. They show a broad band at δ = 8-9 ppm, which integrates as 1H and is assigned to the carboxylic proton. These values agree well with those reported for other hydroxycarbonyl complexes CpRe(CO)(NO)(COOH)[136] (9.5); $PtCl(PEt_3)_2(COOH)$[135] (8.5) and $IrCl_2(CO)(PMe_2Ph)_2(COOH)$[132] (≈8). An unusual value of δ = 1.62 ppm in $CDCl_3$ was reported for $CpRe(NO)(PPh_3)(COOH)$[94b]; this seems to be in error, since such a large upfield shift of ca. 7.9 ppm would not be expected to arise simply from substitution of a CO ligand by PPh_3 as compared to the value for CpRe(CO)(NO)(COOH). A reasonable explanation is that this particular band corresponds to H_2O in $CDCl_3$.

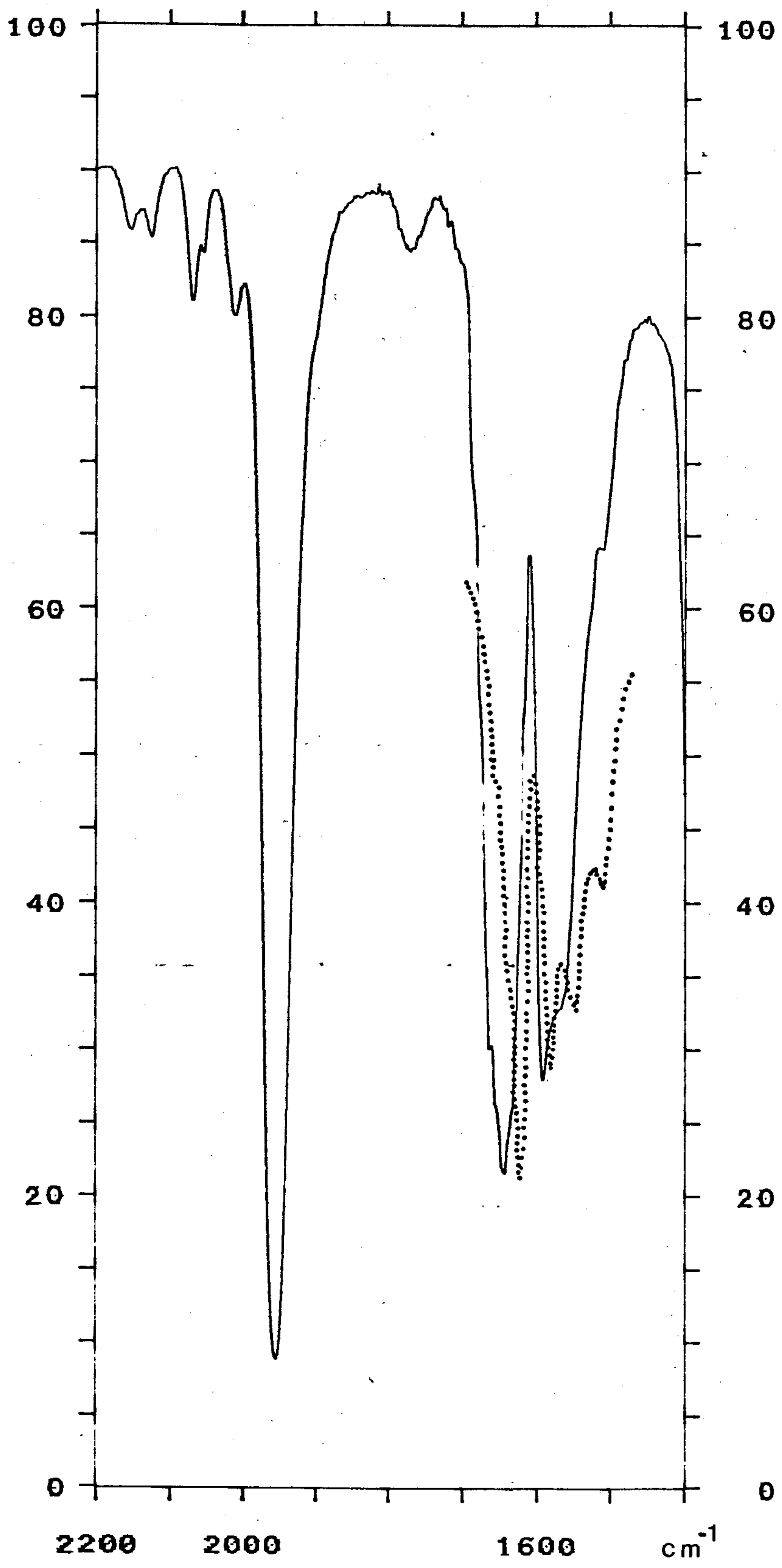
Mass spectral analysis did not give the molecular peak for the hydroxycarbonyl complexes 29, even when a low electron voltage (12 eV) and lower temperatures (ion source = 40°C) were used. Decomposition occurs during the analysis to give the corresponding hydrido complexes 30. This was clearly observed by recording the peak profile of their volatilization as shown in Figure 14 for the complex 29a.

Figure 13

IR spectrum (CH_2Cl_2) of the hydroxycarbonyl complex $[CpRe(CO)(COOH)(\underline{p}\text{-}N_2C_6H_4CH_3)]$ 29a.

—— N^1 (^{14}N)

--- N^1 (^{15}N)


100
80
60
40
20
0
100
80
60
40
20
0
2200
2000
1600
cm⁻¹

Curve A corresponds to the thermal decomposition of compound 29a. Simultaneously to the recording of this decomposition curve, the liberation of CO_2 (m/e = 44; curve B) and the generation of the ion with m/e = 400 (which corresponds to the molecular peak of the hydrido complex 30a; curve C) also were monitored. These curves, which are similar in shape, show that the maximum concentration of the hydrido complex 30a generated, was obtained when the maximum concentration of CO_2 liberated was reached.

The hydrido complexes 30, also were fully characterized by IR, ^{1}H-NMR and MS (see Table VIII). All show in the IR (CH_2Cl_2), a strong terminal ν(CO) band at about 1925 cm^{-1} and a strong band at ca. 1630 cm^{-1}, which was unambiguously assigned to ν(NN) by ^{15}N-isotopic substitution at N^1 in the complex 30d; a shift of 17 cm^{-1} to a lower wavenumber was observed.

The occurrence of ν(NN) in this region is evidence that these hydrido complexes 30 also contain a three-electron donor diazo ligand bonded to the metal in a singly-bent fashion, and have structure XXIX.

A weak band at 2025, 2030 and 2033 cm^{-1} (for 30a, 30b and 30d, respectively) is tentatively assigned to ν(Re-H) by comparison with the ν(Re-H) value (2011 cm^{-1}) reported for the isoelectronic hydrido species [CpRe(CO)(NO)(H)][136]. No confirmatory evidence for this assignment was attempted.

Figure 14

Mass Spectrum Display for the Hydroxy-Carbonyl Complex $[CpRe(CO)(COOH)(\underline{p}\text{-}N_2C_6H_4CH_3)]$ 29a.

Curve A: Thermal Decomposition Curve of Complex 29a.

Curve B: Liberation of CO_2 (m/e = 44).

Curve C: Generation of $CpReH(CO)(\underline{p}\text{-}N_2C_6H_4CH_3)$ 30a (m/e = 400).

* In practice, Curve A is the total ion current and Curve B and C are the ion current of peak with m/e = 44 and m/e = 400, respectively.

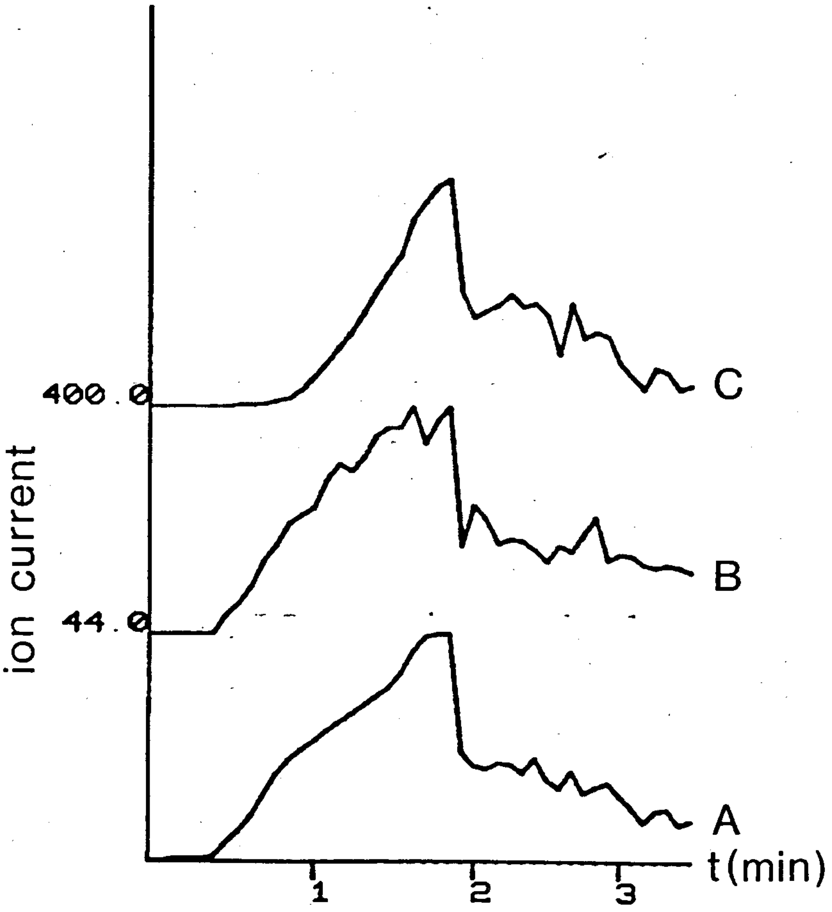
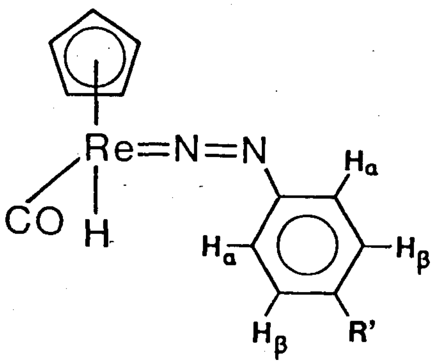

400.0
44.0
ion current
C
B
A
1
2
3
t(min)

Table VIII. IR and ^1H-NMR Data of Hydrido Complexes of Rhenium.

Compound		IR[a]		^1H-NMR[c]			
		ν(CO)	ν(NN)	Re-H	Aryl	Cp	Others
$[CpRe(H)(CO)(p\text{-}N_2C_6H_4CH_3)]$	<u>30a</u>	1928	1629	-7.26s,br	7.52d 6.95d	4.75s	2.10s (CH_3)
$[CpRe(H)(CO)(p\text{-}N_2C_6H_4OCH_3)]$	<u>30b</u>	1925	1630	-6.8s,br	7.59d,br 6.79d	4.80s	3.27s (OCH_3)
$[CpRe(H)(CO)(p\text{-}N_2C_6H_4NEt_2)]$	<u>30d</u>	1914	1627 (1610)[b]	-6.7s,br	7.68s,br 6.53d	4.87s	2.94q ($-CH_2-$) 0.85t ($-CH_3$)

[a] In cm^{-1} for CH_2Cl_2 solutions. All are very strong bands. [b] ^{15}N-isotopic substitution at N^1: $\nu(N^{15}N^{14})$. [c] In C_6D_6 at room temperature: all values in ppm relative to internal TMS. Abbreviation: s, singlet; d, doublet; t, triplet; q, quartet; br, broad.

The ^{1}H-NMR spectra of these hydrido complexes 30 show the hydride signal at ca. δ-7.0 ppm, as a broad singlet, much more so in 30b and 30d than in 30a. The aryl proton resonance for complexes 30b and 30d is not the usual AA'BB' pattern expected for 1,4 disubstituted benzene compounds. The Hα protons (i.e., the protons α to the carbon attached to the nitrogen atom) appear as a broad doublet in 30b and as a very broad singlet in 30d.



The broadening of these particular protons is not due to coupling with the hydride, since irradiation of the hydride resonance does not remove this broadening. At the present time, it is not clear the reason for this.

Mass spectral analysis showed indeed the molecular ions as the base peaks at m/e = 400, 416 and 457 (based on Re^{187}) for the hydrido complexes 30a, 30b and 30d, respectively.

5.3 Discussion

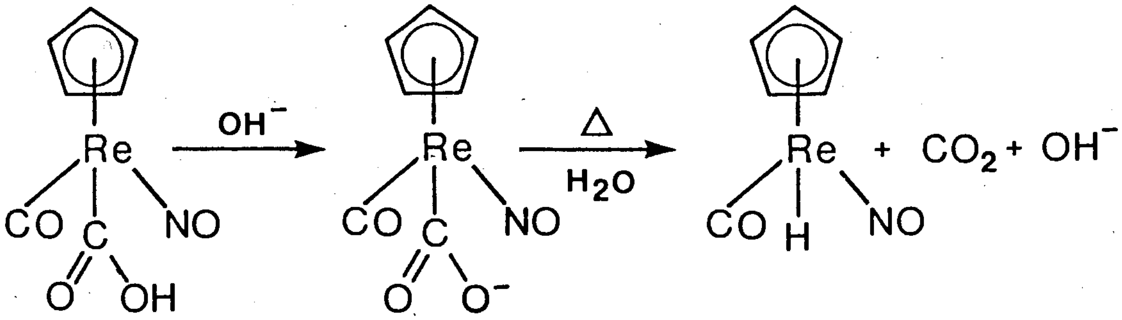
Although a detailed study on the properties of the metallocarboxylic acids 29 and their intermediate role in the synthesis of hydrido complexes, was not carried out, it is worthwhile to mention some interesting experimental observations, and to draw a comparison with the work of Sweet and Graham[136] on the closely related compounds derived from $[CpRe(CO)_2(NO)]^+$.

Hydroxycarbonyl complexes have been postulated as intermediates in the reactions of metal carbonyls with water or base to give the corresponding metal-hydrides[130,131] (eq. 22).

$$M - CO \xrightarrow{OH^-} [M - COOH]^- \xrightarrow[-CO_2]{H^+} [M - H]^- \text{ or } M - H_2 \qquad (22)$$

Sweet and Graham[136] have provided good evidence that this is the case in the $[CpRe(CO)_2(NO)]^+$ system. They found that the complex $[CpRe(CO)_2(NO)]^+$ reacted with excess of base (Et_3N-H_2O) in acetone at 50°C to give the hydrido complex [CpReH(CO)(NO)]. When the reaction was carried out with an equimolar amount of Et_3N or NaOH in water, the hydroxycarbonyl [CpRe(CO)(NO)(COOH)] was obtained instead. The hydroxycarbonyl complex was transformed into the hydrido derivative in >90% yield with excess of base: Et_3N-H_2O in acetone at 50°C for 1 h.

They suggested that the decarboxylation mechanism, to give the hydrido species [CpReH(CO)(NO)], involves first deprotonation of the acid by OH$^-$ to give the carboxylate anion [CpRe(CO)(NO)(COO)]$^-$ from which CO$_2$ loss readily occurs; the anion [CpRe(CO)(NO)]$^-$ thus generated is a strong base, and rapidly acquires a proton to generate the hydrido complex (eq. 23). In their case, the carboxylate anion could not be isolated, but strong indirect evidence for its formation was provided.



(23)

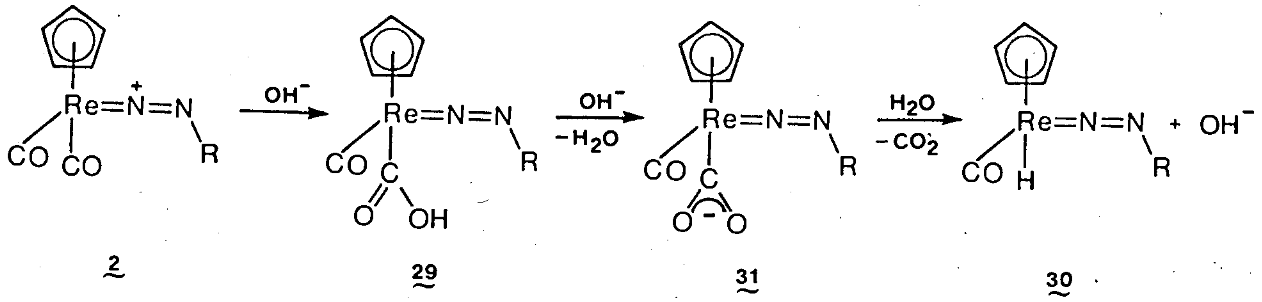
In the aryldiazenido systems 2, the hydroxycarbonyl complexes 29, could not be isolated or even detected (by IR) when the reaction was carried out in acetone or CH$_2$Cl$_2$ with an excess of aqueous base (KOH or NaOH); the hydrido species 30 were the major final products. But the hydroxycarbonyl complexes 29 were clearly first identified by IR when the reactions were carried out with an excess of KOH (or NaOH) pellets;

obviously here, the instantaneous base concentration in solution was low, slowing down considerably the reaction. Also the deprotonation of the acid is probably not so fast under these conditions, thus allowing us to monitor the formation and disappearance of the hydroxycarbonyl 29 to give finally the hydrido species 30.

By using similar conditions to those described for the nitrosyl system,[136] the hydroxycarbonyls 29 were successfully synthesized and isolated by reacting complexes 2 with an equimolar amount of NaOH (1 N) in water. They are slightly soluble in water giving bright yellow solutions. Addition of excess of base to a suspension of 29 in water produced a rapid dissolution to give orange-yellow solutions; as in the nitrosyl case,[136] no complex could be extracted from these solutions with CH_2Cl_2 (into which complexes 29 are extractable) or Et_2O (into which complexes 30 are extractable), so it seems likely that these orange solutions contain the anionic carboxylate complexes $[CpRe(CO)(N_2C_6H_4R)(COO)]^-$ 31.

From these observations and a comparison with the results of Sweet and Graham[136] for the $[CpRe(CO)_2(NO)]^+$ system, it is reasonable to suggest that the reactions proceed as in Scheme IV.

SCHEME IV



Thus, restricting the OH⁻ concentration by using an equimolar [OH⁻] allows isolation of 29, whereas the presence of an excess of base (but limited by its solubility in an organic solvent) allows the formation of 29 and its subsequent transformation to 30 to be observed. Similarly, previously isolated samples of 29 could be smoothly transformed to 30 by treatment with excess of base and simultaneous extraction of the product into ether.

Other variations in the reaction conditions were employed in an attempt to observe the postulated anionic carboxylate complex intermediate in the following way.

When a suspension of the aryldiazenido complex 2a (R' = p-Me) in Et_2O was reacted with excess aqueous NaOH (5 N) at room temperature, a fast reaction took place, the aqueous layer became orange (this is believed to contain 31) and the Et_2O layer slightly yellow. Gradually, under rapid stirring, the

Et_2O solution became much darker while the aqueous layer became less orange. After approximately 2 h., the transformation was complete (the aqueous layer now being colorless) and identification of the product in the Et_2O layer revealed it to be the hydrido complex 30a.

When the complex 2b (p-OMe) was used instead, the aqueous orange solution, believed to contain 31, was much more stable and after 4 h. of rapid stirring, the Et_2O layer appeared just slightly yellow due to the presence of 30b. Evaporation of the water under vacuum afforded an impure orange solid which could not be purified, since it decomposed rapidly to the hydride 30b when dissolved in any of several solvents (by IR). An IR spectrum of this orange solid (CH_2Cl_2) after 16 h. of storage under N_2 at room temperature, showed no terminal carbonyl bands.

More interesting was the reaction of the p-diethylamino derivative 12d[141] under similar conditions. Addition of NaOH produced an instantaneous yellow-orange precipitate and the Et_2O layer appeared quite yellow (due to 30d). After 1h. of rapid stirring, no major change was noted except that the yellow-orange solid seemed to dissolve slightly in water to give an orange-yellow solution. An IR spectrum of the solid in CH_2Cl_2 (only slightly soluble in CH_2Cl_2) showed a terminal $\nu(CO)$ band at 1900 cm^{-1} and several broad bands in the region

1700-1550 cm^{-1}; a strong and sharp band at 1605 cm^{-1} was easily distinguished from the rest.

This IR spectrum strongly suggests that the solid could indeed be the carboxylate complex 31d; the ν(CO) band occurs at 45 wavenumbers lower than the ν(CO) band of the corresponding acid 29d. Shifts to lower wavenumbers are expected going from a neutral to an anionic species.

This yellow-orange solid also decomposed after storage under N_2 (16 h.) and now its IR (CH_2Cl_2) showed no terminal carbonyl bands.

These unstable solids generated the corresponding hydrido complexes 30b and 30d when they were heated (≈35°C) with NaOH in a H_2O/Et_2O mixture (strong gas evolution was observed).

All the evidence suggests that these orange solutions could, in fact, contain the anionic carboxylate complexes $[CpRe(CO)(N_2C_6H_4R)(COO)]^-$ 31 and the solids be the corresponding sodium salts.

An interesting and curious result was obtained by reacting a suspension of any of the aryldiazenido complexes 2 in Et_2O with KOH (5 N) (rather than NaOH reported above). In this case, a fast reaction took place and the hydrido complex 30 was obtained in high yield (from the Et_2O layer). $CpRe(CO)_2N_2$ was also produced in varied amount, depending on the substituent, R', in the aromatic ring (with R' = p-Me > p-OMe >> $pNEt_2$); the reaction was accompanied by strong gas evolution.

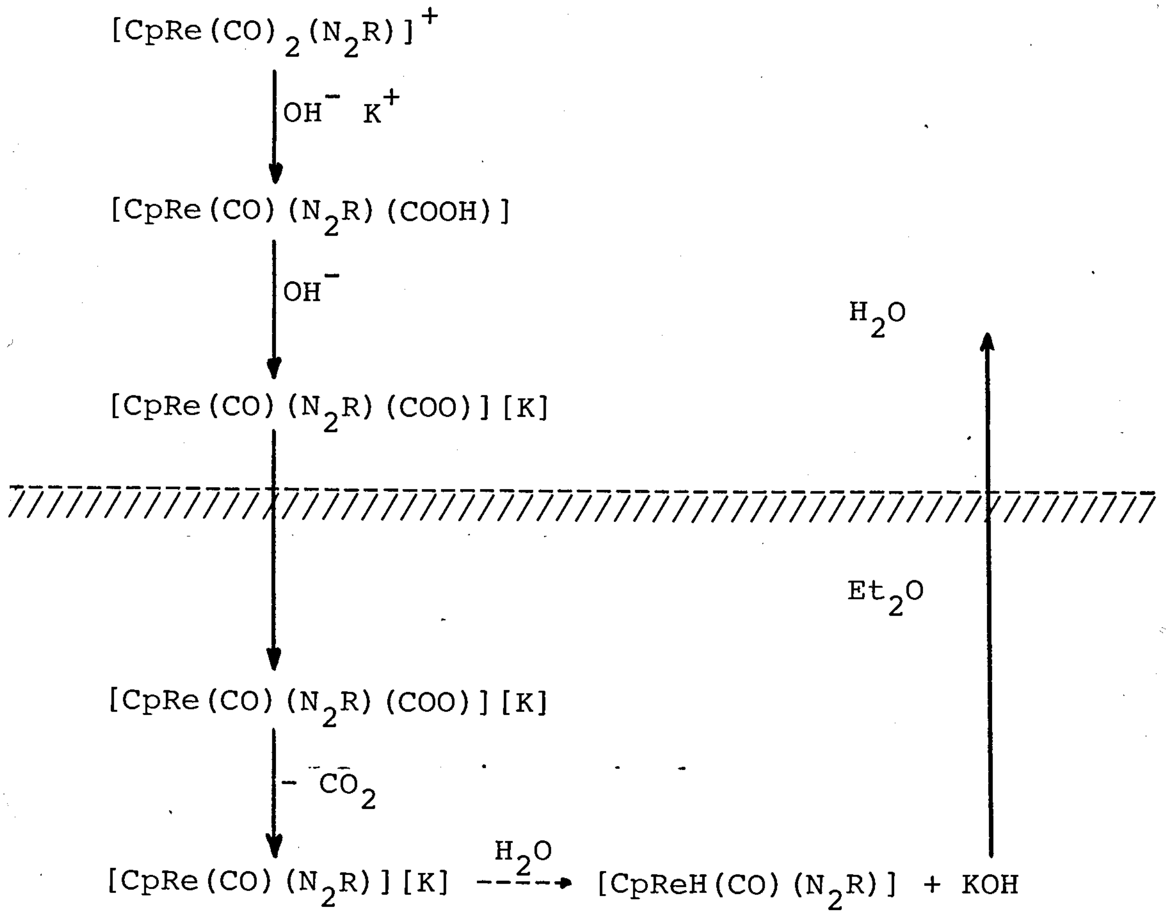
When R' = p-NEt_2, 2d, a yellow-orange solid was also obtained, but could not be identified, since it decomposed to give the hydride 30d, under dissolution.

At the present time, we do not know for sure the reason for the different results observed upon changing the base from NaOH to KOH, but a plausible explanation might be related to the transfer into the organic phase of the anionic carboxylate complexes 31.

In the presence of excess of base, the metallocarboxylic acids 29 seem to exist as the anionic carboxylate species 31 in water, in which, as it has been suggested,[136] they are stabilized by hydrogen bonding. Under the reaction conditions employed, which are really phase transfer conditions, the K^+ ion might be acting as a phase transfer catalyst (better than Na^+), facilitating the transfer of the anionic carboxylate 31 into the organic phase.

There, because the absence in this medium of the stabilization forces (hydrogen bonding), rapid decarboxylation can occur. Subsequent proton abstraction, probably from water, generates the corresponding hydrido complexes 30 (see Scheme V).

SCHEME V


[CpRe(CO)$_2$(N$_2$R)]$^+$
OH$^-$ K$^+$
[CpRe(CO)(N$_2$R)(COOH)]
OH$^-$
[CpRe(CO)(N$_2$R)(COO)][K]
H$_2$O
Et$_2$O
[CpRe(CO)(N$_2$R)(COO)][K]
- CO$_2$
[CpRe(CO)(N$_2$R)][K]
H$_2$O
[CpReH(CO)(N$_2$R)] + KOH

5.4 Experimental

Synthesis of [CpRe(CO)(COOH)(p-$N_2C_6H_4CH_3$)] 29a. A stoichiometric amount of aqueous sodium hydroxide (1 N) was added dropwise to a suspension of [CpRe$(CO)_2$(p-$N_2C_6H_4CH_3$)][BF_4] 2a (100 mg, 0.195 mmol) in water (ca. 10 mL) under continuous stirring, at room temperature. The solution turned yellow-orange from which a yellow solid precipitated. The supernatant solution was pipetted off and the yellow solid washed with 2 × 3 mL of water and dried under vacuum yielding complex 29a (82 mg, 95%) as analytically pure, air-stable, golden yellow microcrystals. Anal. Calcd. for [(η^5-C_5H_5)Re(CO)(COOH)(p-$N_2C_6H_4CH_3$)]: C, 37.92; H, 2.93; N, 6.32. Found: C, 37.77; H, 2.89; N, 6.27%.

Synthesis of [CpRe(CO)(COOH)(p-$N_2C_6H_4OCH_3$)] 29b. This was prepared similarly in 95% yield, as a golden yellow, air-stable, microcrystalline solid.
Anal. Calcd. for [(η^5-C_5H_5)Re(CO)(COOH)(p-$N_2C_6H_4OCH_3$)]: C, 36.60; H, 2.83; N, 6.10. Found: C, 36.65; H, 2.84; N, 6.12%.

Synthesis of [CpRe(CO)(COOH)(p-$N_2C_6H_4NEt_2$)] 29d. This was prepared similarly in 96% yield, as a golden yellow, air-stable microcrystalline solid.
Anal. Calcd. for [(η^5-C_5H_5)Re(CO)(COOH)(p-$N_2C_6H_4NEt_2$)]: C, 40.80; H, 4.00; N, 8.40. Found: C, 40.72; H, 3.96; N, 8.32%.

Synthesis of [$CpRe(H)(CO)(p\text{-}N_2C_6H_4CH_3)$] 30a. To a suspension of 2a (100 mg, 0.195 mmol) in diethyl ether (10 mL) an excess of aqueous KOH (5 mL, 5 N) was added and the mixture was stirred vigorously at room temperature. The Et_2O layer became yellow and strong gas evolution was observed.

The ether solution was separated and dried over $CaSO_4$. Filtration and evaporation of the solvent under vacuum afforded an orange oil. An IR spectrum (CH_2Cl_2) of this oil showed that it was a mixture, complex 30a being the major component, but a significant amount of $CpRe(CO)_2N_2$ was also present. Sublimation of the oily material at room temperature afforded the dinitrogen complex in an estimated yield of 20-30%. When the temperature was increased to 80°C, an orange-yellow oil sublimed, which was characterized (see Table VIII) as the hydrido complex 30a. (Estimated yield ≈70%.)

Synthesis of [$CpRe(H)(CO)(p\text{-}N_2C_6H_4OCH_3)$] 30b. This was prepared similarly in an estimated yield of 80-90% as an orange-yellow air-stable oil. The yield of $CpRe(CO)_2(N_2)$ by-product was much less than in the previous case. Its characterization was carried out by IR, ^{1}H-NMR and MS (see Table VIII).

Synthesis of [CpRe(H)(CO)(p-$N_2C_6H_4NEt_2$)] 30d. This was prepared similarly in an estimated yield of 70% as an orange-yellow oil. Its spectroscopic properties (IR, ^{1}H-NMR and MS) are listed in Table VIII.

During this reaction, an orange-yellow solid precipitated off, which was isolated by centrifugation. This could not be purified since it decomposed to give the hydrido 30d when it was dissolved in several solvents (acetone, methanol, CH_2Cl_2). It is slightly soluble in water, giving an orange solution, but insoluble in Et_2O. Although it was not characterized at this time, it is believed to be the anionic carboxylate complex [CpRe(CO)(p-$N_2C_6H_4NEt_2$)(COO)][K] 31d.

Reactions with NaOH (5 N)

[CpRe$(CO)_2$(p-$N_2C_6H_4Me$)][BF_4] 2a suspended in diethyl ether was reacted with an excess of NaOH (5 N) at room temperature and the mixture was stirred vigorously. A fast reaction took place and the aqueous layer became orange and the ether layer slightly yellow. Gradually, the ether solution became more orange-yellow in color while the aqueous solution less intense. After 2 h. of stirring, the aqueous layer was almost colorless.

The orange-yellow ether solution was separated out and dried over $CaSO_4$. After filtration and evaporation of the solvent under vacuum, an orange-yellow oil was obtained which was identified by IR, ^{1}H-NMR and MS as the hydrido complex 30a (see Table VIII). $CpRe(CO)_2(N_2)$ was formed only in a very small amount.

$[CpRe(CO)_2(p\text{-}N_2C_6H_4OCH_3)][BF_4]$ 2b suspended in diethyl ether was reacted with an excess of NaOH (5 N) at room temperature. The aqueous solution rapidly became orange in color and the Et_2O layer only very slightly yellow. No change was observed after 4 h.

The ether solution was worked up as described for the p-Me derivative and showed to contain the hydrido complex 30b.

The orange aqueous solution was pumped down to approximately 1 mL and an orange solid precipitated off, which was separated. This impure solid could not be purified since it decomposed to the hydride 30b when dissolved. It also decomposed to a product having no ν(CO) bands in the IR, after being stored under N_2 at room temperature for 16 h. This orange solid was not further characterized at this time.

$[CpRe(CO)_2(p\text{-}N_2C_6H_4NEt_2)][BF_4]$ 2d suspended in diethyl ether was reacted with an excess of NaOH (5 N) at room temperature. A fast reaction took place and a yellow-orange solid precipitated off immediately after addition of NaOH and the Et_2O layer became yellow. After 1 h. of strong stirring, no major change was noted, except that the solid slightly dissolved in water to give an orange solution.

The ether solution was separated and showed to contain the hydrido complex 30d.

The yellow-orange solid was centrifuged off and its IR spectrum in CH_2Cl_2 (only slightly soluble in CH_2Cl_2) showed a strong ν(CO) band at 1900 cm^{-1} and several broad bands in the region 1700-1550 cm^{-1}. This solid decomposed to a product having no ν(CO) bands in the IR, after being stored under N_2 at room temperature for 16 h.

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4OCH_3)][BF_4]$ 2b with Solid NaOH.

To a solution of 2b (100 mg, 0.19 mmol) in CH_2Cl_2 (10 mL) an excess of solid NaOH (pellets) was added and the mixture stirred at room temperature.

The color of the solution gradually changed from red-orange to dark red. An IR spectrum of this solution after 15 min. showed the presence of a monocarbonyl species (ν(CO) = 1954vs, other bands at 1646vs,br; 1584s,br cm^{-1}, which was identified as the hydroxycarbonyl complex $[CpRe(CO)(p\text{-}N_2C_6H_4OCH_3)(COOH)]$ 29b), together with $[CpRe(CO)_2(N_2)]$ and some unreacted starting material 2b. At 30 min., a new IR spectrum revealed the presence of a new monocarbonyl complex (ν(CO) = 1925vs, ν(NN) = 1630vs, cm^{-1}, which was identified as the hydrido species [$CpRe(H)(CO)(p\text{-}N_2C_6H_4OCH_3)$] 30b); the hydroxycarbonyl complex 29b was not observed at this stage and the concentration of $CpRe(CO)_2N_2$ increased.

Isolation of the hydrido complex 30b was carried out similarly as described above.

Reaction of [$CpRe(CO)_2(p\text{-}N_2C_6H_4NEt_2)$][$BF_4$] 2d with Aqueous NaOH under Phase Transfer Conditions.

To a solution of 2d (100 mg, 0.175 mmol) in CH_2Cl_2 (20 mL), finely ground $Et_4N^+Br^-$ (10 mg, 0.05 mmol; phase transfer catalyst) followed by aqueous NaOH (5 mL, 5 N) were added and the mixture stirred vigorously at room temperature.

The color rapidly changed from dark green to dark red and an IR spectrum of the solution (after 5 min.) revealed the presence of a monocarbonyl species; which was identified as the hydrido complex [$CpRe(H)(CO)(p\text{-}N_2C_6H_4NEt_2)$] 30b, and a significant amount of $CpRe(CO)_2N_2$. At this time, the reaction was already over, since no unreacted starting material, 2d, was detected.

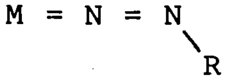
The CH_2Cl_2 solution was separated and stirred with water (3 × 10 mL) and dried afterwards over $CaSO_4$. Filtration and evaporation of the solvent yielded a red oily residue, from which the hydrido complex 30b was isolated as described before.

APPENDIX I

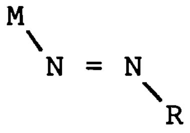
Bimetallic Aryldiazenido Complexes. Synthesis and Characterization of $(\eta^5\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}NNC_6H_4CH_3)Re(CO)_2(\eta^5\text{-}C_5H_5)$, Possessing a μ-Aryldiazenido-N^1,N^2 Bridge.

A.I.1 Introduction

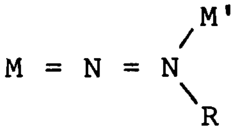
In mononuclear complexes, organodiazenido ligands (N_2R) (R = alkyl or aryl) have been found to exhibit two common structural types: the "singly-bent" structure (A) where N_2R is formally a three-electron donor and the "doubly-bent" structure (B) where N_2R is formally a one-electron donor.



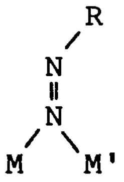
A



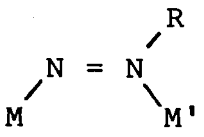
B



G



E



F

Using these as a basis, a number of potential structures for bimetallic organodiazenido complexes can be visualized, such as E, F and G. Structure E has been found to occur in the aryldiazenido complexes $Mn_2(CO)_8(N_2Ph)_2$[18], $HOs_3(CO)_{10}(\underline{p}\text{-}N_2C_6H_4CH_3)$[24], $[\{IrNO(PPh_3)\}_2O(\underline{o}\text{-}N_2C_6H_4NO_2)]^+$ [20]

and $Pd_2Cl_2(dppm)_2$(p-$N_2C_6H_4F$).[21] Structure F is presently not known. In this section, are reported the synthesis and characterization of a bimetallic aryldiazenido complex conforming to structure G. A similar structure has been proposed for related alkyldiazenido complexes and was subsequently verified crystallographically.[25,26]

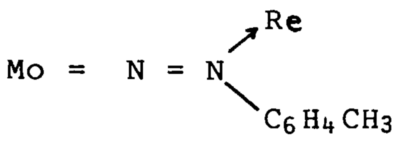
A.I.2 Synthesis and Characterization

A theoretical approach to the synthesis of a bridging aryldiazenido complex of type G is the following. Compounds containing singly-bent aryldiazo ligands (A) possess an unshared electron pair in formally a sp^2-hybrid orbital on N^2. Provided this electron pair is sufficiently basic, it could bind to a second transition metal to yield bimetallic complexes (G) containing a bridging aryldiazenido ligand.

The rhenium complex $CpRe(CO)_2THF$, which can (by facile loss of THF) be regarded as furnishing the 16-electron intermediate $CpRe(CO)_2$, does indeed, react with the neutral molybdenum aryldiazenido complex $CpMo(CO)_2$(p-$N_2C_6H_4CH_3$) 32 under mild conditions to generate the bimetallic title complex (η^5-C_5H_5)$(CO)_2$Mo(μ-$NNC_6H_4CH_3$)Re$(CO)_2$(η^5-C_5H_5) (33), which was fully characterized by IR, ^{1}H-NMR and its structure determined by X-ray crystallography (kindly carried out by Dr. F.W.B. Einstein and Dr. T. Jones).

An alkyldiazenido complex of tungsten structurally related to 32, which might, if anything, be expected to be more basic than 32, gives related bimetallic alkyldiazenido complexes in a similar fashion.[25,26] This was not the case, however, when a cationic aryldiazenido complex was used instead. The rhenium complex $[CpRe(CO)_2(p\text{-}N_2C_6H_4CH_3)][BF_4]$ 2a did not react with $CpRe(CO)_2THF$ and after 24 h., the starting materials were recovered unchanged. ($CpRe(CO)_3$ is formed during this reaction, from partial decomposition of the adduct $CpRe(CO)_2THF$).

A perspective view of compound 33 (Figure 15) illustrates the relative disposition of the carbonyl and Cp groups and the environment of the aryldiazenido ligand. The latter spans the metals in the form of a μ-N^1,N^2 bridge of the type shown in structure G, and acts as a three-electron donor to Mo and a two-electron donor to Re as shown in Structure XXX.



$$\mathrm{Mo} = \mathrm{N} = \mathrm{N}\begin{matrix}\nearrow \mathrm{Re} \\ \searrow \mathrm{C_6H_4CH_3}\end{matrix}$$

XXX

Consistent with this, the Mo-N(2) distance is 1.822(4) Å, identical with the Mo-N_2Ph distance (1.825(4) Å) in $(HBpz_3)Mo(CO)_2(N_2Ph)$[142] (which contains a three-electron donor singly-bent N_2Ph ligand), whereas the Re-N(1) length is

2.152(4) Å. The Mo-N(2)-N(1) skeleton is essentially linear (178°) and the N(2)-N(1) distance is 1.256(6) Å. This is marginally longer than the N-N distance in $(HBpz_3)Mo(CO)_2(N_2Ph)$ (1.211(6) Å), but whether or not binding of the lone pair of electrons on N^2 in 32 actually results in a lengthening of the N-N bond cannot be determined at this time without the structure of 32 for comparison.

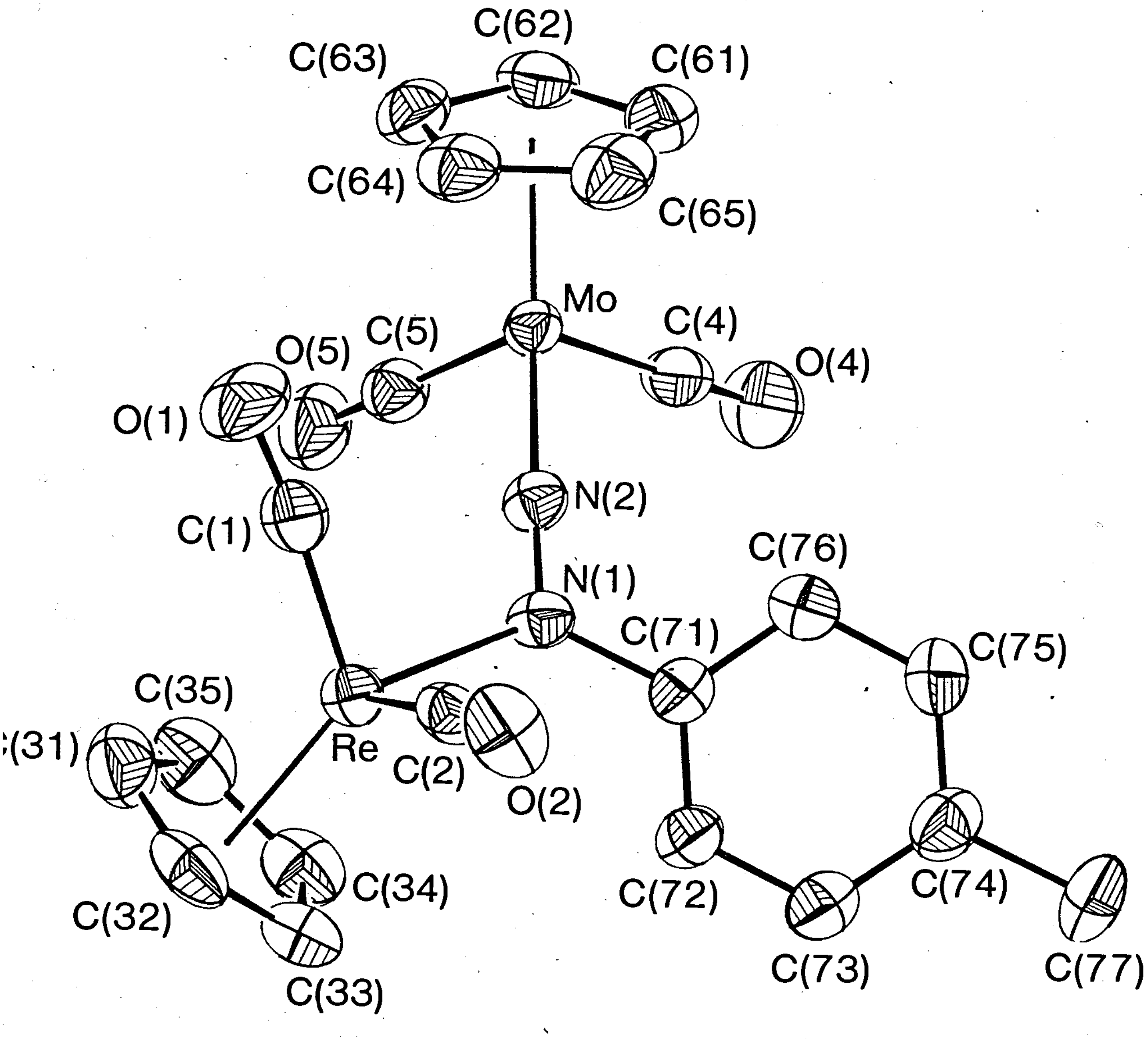
A comparison of the IR and ^{1}H-NMR parameters of the bimetallic complex 33 with those of the mononuclear molybdenum precursor 32 and $CpRe(CO)_2(THF)$ provides some evidence for the electronic changes that result from the substitution of THF by 32 in the formation of 33. The two μ(CO) modes of 32 move up from 1991 and 1921 cm^{-1} to 2008 and 1945 cm^{-1} in 33 and the Cp resonance moves downfield from δ5.91 in 32 to δ6.15 in 33. Both effects are those expected as a result of withdrawal of electron density from the molybdenum atom in the process of N' coordinating to the rhenium atom. Furthermore, N' appears to be marginally a better donor to Re than is THF, since the ν(CO) positions in $CpRe(CO)_2(THF)$ at 1927 and 1859 cm^{-1} are lowered to 1920 and 1858 cm^{-1} in 33; the Cp resonance is virtually unaffected, changing from δ5.11 to δ5.10 in 33.

Figure 15

Perspective View of the complex.

[Cp(Co)$_2$Mo(μ-NNC$_6$H$_4$CH$_3$)Re(CO)$_2$Cp] 33.

Mo-N(2) = 1.822(4) Å; Re-N(1) = 2.152(4) Å; N(2)-N(1) = 1.256(6) Å; Mo-N(2)-N(1) = 177.7(4)°; Re-N(1)-N(2) = 118.9(3)°; N(2)-N(1)-C(71) = 113.5(4)°. The numbering scheme is that used in ref. 160.


C(62)
C(63)
C(61)
C(64)
C(65)
Mo
C(4)
O(4)
C(5)
O(5)
O(1)
N(2)
C(1)
C(76)
N(1)
C(71)
C(75)
C(35)
(31)
Re
C(2)
O(2)
C(34)
C(72)
C(74)
C(32)
C(73)
C(77)
C(33)

A.I.3 Experimental

Preparation of $(\eta^5\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}NNC_6H_4CH_3)Re(CO)_2(\eta^5\text{-}C_5H_5)$

To a solution of $CpMo(CO)_2(p\text{-}N_2C_6H_4CH_3)$ 32 (75 mg, 0.22 mmol) in THF (20 mL) was slowly added solid $CpRe(CO)_2(THF)$ (85 mg, 0.22 mmol), and the mixture was stirred for 24 h. at room temperature. An IR spectrum of the solution at this stage showed the presence of unreacted molybdenum complex, some $CpRe(CO)_3$ (from decomposition of the THF adduct ($CpRe(CO)_2(THF)$) and the desired product. The solution was evaporated to dryness under vacuum at room temperature to yield a dark red oil, which was dissolved in benzene (1 mL) and passed through a silica gel column prepared in benzene. Elution with benzene afforded first a dark red band which was identified as the molybdenum aryldiazenido complex 32. The second band (yellow) was $CpRe(CO)_3$. The final band (dark red), which was the desired product 33, was collected under nitrogen and evaporated *in vacuo* to dryness to give a dark red oil. Dissolving this in hexane and cooling to -12°C (freezer), gave the product as dark red crystals (yield 40% based on $CpMo(CO)_2(p\text{-}N_2C_6H_4CH_3)$) m.p. 133°C.

Anal. Calcd. for $(\eta^5\text{-}C_5H_5)(CO)_2Mo(\mu\text{-}N_2C_6H_4CH_3)Re(CO)_2(\eta^5\text{-}C_5H_5)$: C, 39.19; H, 2.64; N, 4.35%. Found: C, 39.49; H, 2.50; N, 4.34%. IR (hexane) $\nu(CO)$ 2008s, 1945vs, 1920vs, 1858vs cm^{-1}. ^1H-NMR (acetone-d_6): 7.48d, 7.17d (4H, C_6H_4), 6.15s (5H, $Mo[C_5H_5]$), 5.10s (5H, $Re[C_5H_5]$), 2.34s (3H, CH_3).

Reaction of $[CpRe(CO)_2(p\text{-}N_2C_6H_4CH_3)][BF_4]$ 2a with $CpRe(CO)_2THF$.

To a solution of 2a (77 mg, 0.15 mmol) in THF or acetone (20 mL) was slowly added solid $CpRe(CO)_2THF$ (57 mg, 0.15 mmol), and the mixture was stirred for 24 h. at room temperature. An IR spectrum of the solution at this stage showed only the presence of the starting materials and some $CpRe(CO)_3$ formed from partial decomposition of the THF adduct $CpRe(CO)_2THF$. Evaporation of the solvent under reduced pressure, gave a red-orange oil, which was extracted with hexane. The IR spectrum of the yellow hexane extract showed the presence of $CpRe(CO)_3$ and $CpRe(CO)_2THF$. The red-orange oil was washed with hexane until solidification occurred and the hexane extract was clear. The IR spectrum (CH_2Cl_2) of the red-orange solid was identical of the starting aryldiazenido complex 2a.

APPENDIX II

^{15}N Nuclear Magnetic Resonance Spectra of Some Diazo Compounds of Rhenium

A.II.1 Introduction

The nuclear magnetic resonance spectrosopy of nitrogen in inorganic, organic and biochemistry is an area of considerable potential interest. Nitrogen is a constituent of many compounds which are important in these areas, and its spectroscopy can be expected to be a sensitive probe of bonding, coordination geometry and electronic structure. The range of chemical shifts for nitrogen (^{15}N and ^{14}N) is very large, ca. 1100 ppm for diamagnetic compounds, which makes the identification of different types of nitrogen in compounds relatively easy. The use of the particularly useful ($I = 1/2$) ^{15}N nucleus in ^{15}N-NMR has been limited by problems of its low natural abundance (0.365%), low sensitivity (10^{-3} for ^{14}N and ^{15}N relative to ^{1}H; cf. 10^{-2} for ^{13}C)[143] and long relaxation times.

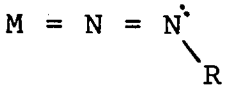
The low natural abundance problem has been overcome in the past by expensive ^{15}N isotopic enrichment.

At the present time, availability of wide-bore high-field F.T. spectrometers and new techniques, such as the pulse-Fourier transform method with ^{1}H noise decoupling,[144-146] makes this technique more accessible for natural-abundance work with

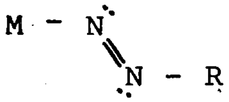
^{15}N. But, it is still far from being a routine technique, as compared, for example, to ^{13}C-NMR. (For recent reviews on nitrogen-NMR spectrocopy, see references 143 and 147.)

As an example of its use in structure determination, ^{15}N-NMR proved to be a powerful technique in settling the actual coordination mode of the dinitrogen ligand in the square-planar dinitrogen complex trans-[RhCl(N$_2$)(P-i-Pr$_3$)$_2$], which was earlier claimed to possess the N$_2$ ligand coordinated "side on" (η^2) to rhodium.[148] The ^{15}N-NMR spectrum showed two ^{15}N resonances, incompatible with an η^2-mode, but consistent with coordination in an "end-on" (η^1) fashion, which was confirmed by a redetermination of the X-ray structure.[149]

Several other dinitrogen complexes (of Re[150,151], Fe[151], Rh[151], Mo[152], W[152], Ti[152,153] and Zr[152,153]), as well as diazenido complexes (of W[151,154], Mo[154], Rh[154], Re[154]) and hydrazido(2-) complexes (of Mo and W)[155] have been investigated by ^{15}N-NMR spectroscopy. Although the ^{15}N-NMR data for these types of diazo complexes are still scarce, results suggest that this technique is indeed a powerful tool in their identification and chracterization since their chemical shifts seem to differ greatly. For example, ^{15}N chemical shifts seem to provide a simple distinction between singly-bent (A) and doubly-bent (B) diazenido complexes; a dramatic downfield shift of about 350 ppm is associated with bending at N^1.[155] It has been suggested that this dramatic shift is associated with the deshielding effect of the high lone pair character at N^1 (low lying (n → π*) state).[143]



A



B

In this work, we were interested to measure the ^{15}N-NMR spectra of some of the complexes synthesized during this thesis, in order to begin to assemble ^{15}N-NMR parameters for organonitrogen complexes of interest in this and related work in this laboratory.

A.II.2 Results and Discussion

In Table IX, the ^{15}N-NMR data for some aryldiazo complexes of rhenium, together with ^{15}N chemical shifts of some related compounds previously reported, are listed. All the compounds studied were singly-labelled at N^1.

The chemical shift of N^1 of the aryldiazenido complexes 2a (-12.3) and 2d (-2.9) compare well with those found in related diazenido complexes $[WF(^{15}N_2H)(dppe)_2]$[151] (-24.6); $[WBr(^{15}N_2H)(dppe)_2]$[151] (-25.9); $[RuCl_3(\underline{p}\text{-}^{15}NNC_6H_4NO_2)(PPh_3)_2]$[154] (-46.8);

Table IX. ^{15}N-NMR Data for Diazo Complexes and Free Aryldiazonium Salts[a]

Compound	$\delta(N^1)$[b]	$\delta(N^2)$[b]	Solvent	Reference
1. Free Aryl Diazonium Salt				
$[^{15}NNC_6H_5][BF_4]$	-63.4	-156.4	$CHCl_3$	147
$[p\text{-}^{15}NNC_6H_4CH_3][BF_4]$	-59.0	--	Acetone-d_6	h
$[p\text{-}^{15}NNC_6H_4OCH_3][BF_4]$	-59.4	-154.7	$CHCl_3$	147
$[p\text{-}^{15}NNC_6H_4NEt_2][BF_4]$	-20.7	--	Acetone-d_6	h
2. Diazenido Complexes ($M\text{-}N_2R$)				
2.1 Singly-bent (A)				
$[CpRe(CO)_2(p\text{-}^{15}NNC_6H_4CH_3)][BF_4]$ 2a	-12.3	--	Acetone-d_6	h
$[CpRe(CO)_2(p\text{-}^{15}NNC_6H_4NEt_2)][BF_4]$ 2d	- 2.9	--	Acetone-d_6	h
$[t\text{-}WF(^{15}N_2H)(dppe)_2]$	-24.6	-182.6	THF	151
$[t\text{-}WBr(^{15}N_2H)(dppe)_2]$	-25.9	-187.1	THF	151
$[MoBr(^{15}N_2Et)(dppe)_2]$	-29.0	-146.8	THF	154
$[WBr(^{15}N_2Et)(dppe)_2]$	-28.2	-164.7	THF	154
$[MoCl(^{15}N_2COCH_3)(dppe)_2]$	-35.4	-123.7	THF	154

Table IX, continued

Compound	$\delta(N^1)^b$	$\delta(N^2)^b$	Solvent	Reference
$[WCl(^{15}N_2COCH_3)(dppe)_2]$	-32.2	-134.5	THF	154
$[ReCl_2(^{15}N_2COCH_3)(py)(PPh_3)_2]$	-55.9	-148.6	Toluene	154
$[RuCl_3(^{15}NNPh)(PPh_3)_2]$	-46.8	--	CH_2Cl_2	154
2.2 Doubly-Bent (B)				
$[RhCl_2(^{15}NNPh)(PPh_3)_2]$	+298.4	--	CH_2Cl_2	154
$[RhCl_2(\underline{p}\text{-}^{15}NNC_6H_4NO_2)(PPh_3)_2]$	+327.1	--	CH_3Cl_2	154
3. Diazene Complexes (M-NHNR)				
$[CpRe(CO)_2(p\text{-}^{15}N(H)NC_6H_4CH_3)]^c$ 15a	-34.4^f	--	Acetone-d_6	h
$[Ir(CO)Cl(p\text{-}^{15}N(H)NC_6H_3Br)(PPh_3)_2][BF_4]^d$	-32.1	--		158
$[RhCl_3(\underline{p}\text{-}^{15}N(H)NC_6H_4NO_2)(PPh_3)_2]$	+200.1	--	CH_2Cl_2	154
4. Hydrazido(2-) Complexes $(M\text{-}NNR^1R^2)$				
4.1 Linear				
$[MoF(^{15}N^{15}NH_2)(dppe)_2][BF_4]$	-83.3	-243.9	CH_2Cl_2	155
$[WF(^{15}N^{15}NH_2)(dppe)_2][BF_4]$	-101.4	-255.1	CH_2Cl_2	155

Table IX, continued

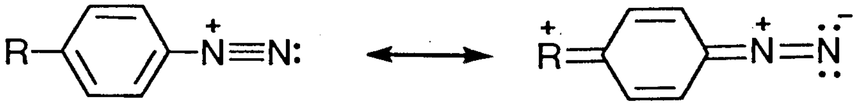
Compound	$\delta(N^1)$[b]	$\delta(N^2)$[b]	Solvent	Reference
$[Mo(^{15}N^{15}NH_2)(8\text{-quin})(PMe_2Ph)_3]Cl$	-64.3	-220.8	CH_2Cl_2	155
$[W(^{15}N^{15}NH_2)(8\text{-quin})(PMe_2Ph)_3]Cl$	-82.1	-241.6	CH_2Cl_2	155
$[MoCl(^{15}N^{15}NH_2)(py)(PMe_2Ph)_3]Cl$	-72.8	-227.0	CH_2Cl_2	155
$[WCl(^{15}N^{15}NH_2)(py)(PMe_2Ph)_3]Cl$	-90.6	-240.6	CH_2Cl_2	155
4.2 <u>Bent</u>				
$[CpRe(CO)_2(\underline{p}\text{-}^{15}NN(CH_3)C_6H_4CH_3)]$ <u>17a</u>	+324.6	--	Acetone-d_6	h
$[Cp_2WH(p\text{-}^{15}NN(H)C_6H_4F)][PF_6]$[e]	+147.9[f,g]	--	Acetone-d_6	h
5. <u>Hydrazido(1-) Complexes $(M\text{-}N(R^3)NR^1R^2)$</u>				
$[CpRe(CO)_2(\underline{p}\text{-}^{15}N(H)N(CH_3)C_6H_4CH_3)][BF_4]$ <u>23a</u>	-54.4	--	Acetone-d_6	h
$[CpRe(CO)_2(\underline{p}\text{-}^{15}N(H)N(H)C_6H_4CH_3)][BF_4]$[c] <u>28a</u>	-176.6	--	Acetone-d_6	h

[a] Chemical shifts relative to external $C^2H_3NO_2$ ± 0.1 ppm. [b] For explanation of the signs + or -, see ref. 15b. [c] In these complexes, an η^2 coordination mode for the diazo ligand is suspected. [d] This complex is an orthometallated species. [e] This compound was prepared as described in ref. 102 and kindly provided by Dr. L. Hanlan. [f] $T° = -37°C$. [g] $^1J(^{15}N\text{-}^{183}W = 3.2$ Hz). [h] This work.

$[MoBr(^{15}N_2Et)(dppe)_2]$[154] (-29.0); $[MoCl(^{15}N_2Et)(dppe)_2]$[154] (-35.4); $[ReCl_2(^{15}N_2COPh)(py)(PPh_3)_2]$[154] (-55.9).

In all these diazenido compounds, it has been suggested or confirmed that the diazo ligand is bonded in a singly-bent manner (A).

The difference in chemical shift between 2a and 2d can be simply accounted for, by the different electron-releasing properties of the para-substituents, where the diethyl-amino group (in 2d) is the better donor, and in accord with this, related differences in chemical shifts are found in the parent para-substituted benezediazonium cations.[150,157] Electron-release by substituents at the four position leads to a larger contribution from resonance structures, such as XXXII; therefore, a downfield shift of the nitrogens will be observed.



XXXI XXXII

The diazene complex 15a shows a chemical shift of -34.4 ppm; this value compares well with δ = -32.1 ppm found in the orthometallated diazene complex $[Ir(CO)Cl(p\text{-}^{15}N(H)NC_6H_3Br)(PPh_3)_2][BF_4]$[158], but differs greatly from δ = +200.1 ppm reported for the rhodium diazene complex $[RhCl_3(\underline{p}\text{-}^{15}N(H)NC_6H_4NO_2)(PPh_3)_2]$.[154] At the present time, it is difficult to rationalize these differences in chemical shifts, because the limited number of examples known, but the value δ = -34.4 ppm observed for the diazene complex 15a may indicate that in this complex, the diazo ligand is bonded in different fashion, perhaps as an η^2-ligand, as suggested in Chapter III and IV; in the Rh diazene derivative, the diazo ligand is bonded in a η^1-fashion.

Dramatic differences in chemical shifts also have been observed in organodiazenes (RN=NR), where usually the nitrogen nuclei are strongly deshielded (δ ca. +150 ppm).[147] However, $Me_3SiN{=}NSiMe_3$ with δ = +618 ppm, exhibits the greatest nitrogen deshielding that has so far been observed in diamagnetic compounds. Conversely, a strong shielding effect is observed in compounds where one, or both, lone pairs on the nitrogen atoms form a $N\rightarrow O$ dative bond (azoxy compounds, $RN = N(R)\rightarrow O$ δ ca. -40 ppm), or a $N\rightarrow N$ dative bond (azimines $RN = N(R)\rightarrow N\text{-}NR_2$ δ ca. -60 ppm).[147]

All the hydrazido(2-) complexes, for which ^{15}-NMR spectra have been measured previously, have a linear MNN skeleton and the range of $^{15}N^{1}$ shifts is δ -60 to -100 ppm,[155] which is comparable to that observed (-20 to -60 ppm) for singly-bent diazenido complexes[151,154] and for diazonium salts (-14 to -70 ppm).[157]

The hydrazido(2-) complexes $[CpRe(CO)_2(\underline{p}\text{-}^{15}NN(CH_3)C_6H_4CH_3)]$ 17a and $[Cp_2WH(\underline{p}\text{-}^{15}NN(H)C_6H_4F)][PF_6]$ constitute a unique class among hydrazido(2-) compounds, since they possess a "bent" hydrazido(2-) ligand[118,102] with a high lone pair character at N^1. As expected, these exhibit $^{15}N^{1}$ chemical shifts (Re ± +324.6 ppm; W = +147.9 ppm) which strongly differ from those of "linear" hydrazido(2-) complexes, revealing strongly deshielded nitrogen atoms associated with the lone pair of electrons. The chemical shift of the Re complex matches the region observed for "doubly-bent" diazenido complexes: $[RhCl_2(\underline{p}\text{-}^{15}NNC_6H_4NO_2)(PPh_3)_2]$[154] ($\delta$ = +327.1) and $[RhCl_2(^{15}NNPh)(PPh_3)_2]$[154] ($\delta$ = +298.4).

The difference in chemical shift between the Re and the W complexes is not yet well understood, but we suggest the cationic nature of the W complex might be partially responsible for the increased shielding observed.

Protonation of complex 17a gives the hydrazido(1-) complex 23a and an observable upfield shift of 379 ppm. An upfield protonation shift of 127 ppm from $[RhCl_2(p\text{-}^{15}NNC_6H_4NO_2)(PPh_3)_2]$ (doubly-bent) to $[RhCl_3(\underline{p}\text{-}^{15}N(H)NC_6H_4NO_2)(PPh_3)_2]$ has been reported.[154] Protonation of azobenzene causes an upfield shift of 150 ppm.[159]

The hydrazido(1-) complex <u>28a</u> shows a chemical shift at -176.6 ppm, which represents an upfield shift of 142 ppm from the parent diazene complex <u>15a</u>.

As illustrated by these limited examples, ^{15}N-NMR spectroscopy can be an important technique in distinguishing among different types of diazo compounds, and could be especially valuable in identifying intermediates formed during reactions.

A.II.3 Experimental

The ^{15}N spectra were obtained for solutions in acetone-d_6 using a Bruker WM-400 FT instrument at a frequency of 40.431 MHz. The normal operating conditions employed a pulse width of 15.0 μs (30° pulse) with no relaxation delay. With these conditions, useful spectra could usually be obtained with accumulation time of 1-3 h. The samples were run at ambient temperature and no decoupling was used except for <u>23b</u> and <u>28b</u> where inverse gated decoupling was employed. A saturated aqueous solution of $^{15}NH_4Cl$ locked on ^{2}H (acetone-d_6) contained in a coaxial 2 mm tube, was used as external standard, but the chemical shifts in the text are referred to neat CH_3NO_2. All the compounds studied were 40% enriched in ^{15}N.

All the spectra were obtained by Mrs. Marcy Tracey, which is gratefully acknowledged.

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