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ORIENTATIONAL ISOMERS OF SOME RHENIUM ARYLDIAZENIDO COMPLEXES

by

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B.Sc., Universidad de La Habana, Cuba,1986

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ABSTRACT

Previous work from this laboratory has shown that two structural isomers are possible, resulting from different orientations of the aryldiazenide ligand in the cationic compounds $[(\eta^5\text{-}C_5Me_5)ReLL'(p\text{-}N_2C_6H_4OMe)][BF_4]$ and that these isomers interconvert on the NMR timescale. The isomerization process was interpreted as due to the change in the position that the aryl group occupies with respect to the plane that contains the ReNN unit and bisects the LReL' angle resulting from either inversion at the β nitrogen atom or by rotation about the ReN bond.

This thesis addresses the question as to whether or not this isomerization process can be observed in related neutral compounds. The synthesis and characterization of some new neutral pentamethylcyclopentadienyl rhenium aryldiazenido complexes of general formula $[Cp^*ReXL(p\text{-}N_2C_6H_4OMe)]$ [where $Cp^* = (\eta\text{-}C_5Me_5)$; L = CO and X = H, CH_3; X = Cl and L = PMe_3, $P(OMe)_3$, PPh_3] are reported. The isomerization process was investigated by using variable temperature ^1H and ^{31}P NMR spectroscopy. Both isomers were observed for $(\eta^5\text{-}C_5Me_5)ReCO(H)(p\text{-}N_2C_6H_4OMe)$ **(1)** and $(\eta^5\text{-}C_5Me_5)ReCO(CH_3)(p\text{-}N_2C_6H_4OMe)$ **(3)** in a ratio of approximately 1:1, as well as for $(\eta^5\text{-}C_5Me_5)RePMe_3(Cl)(p\text{-}N_2C_6H_4OMe)$ **(4)** and $(\eta^5\text{-}C_5Me_5)Re\{P(OMe)_3\}(Cl)(p\text{-}N_2C_6H_4OMe)$ **(5)** in ratios 4.3:1 and 4:1, respectively. Only one isomer was found for $(\eta^5\text{-}C_5Me_5)Re(PPh_3)(Cl)(p\text{-}N_2C_6H_4OMe)$ **(7)**. Line shape analyses were performed on the ^{31}P and ^1H NMR spectra of each of the compounds that exhibited isomerization and the rate constants and activation parameters ($\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$) were determined for each isomerization process.

ACKNOWLEDGMENTS

I would like to thank those who provided time and assistance in the production of this thesis. In particular, Ms. Marcy Tracey for the ^{1}H and ^{31}P variable temperature NMR experiments and the routine ^{1}H, ^{13}C, ^{31}P NMR spectra, and Mr. G. Owen for the mass spectra. It should be pointed out that Mr. Antonio Cusanelli carried two of the variable temperature NMR experiments described in this thesis.

I am grateful to Professors Roland Pomeroy and Saul Wolfe for discussions and invaluable suggestions.

I am indebted to those very good friends that day after day gave me the strength I needed to carry on with this work, especially to my T. S. F. for having so much faith in me.

Finally, I owe my thanks and appreciation to my senior supervisor, Professor Derek Sutton, for his enthusiastic support and guidance and for introducing me to the fascinating world of organometallic chemistry.

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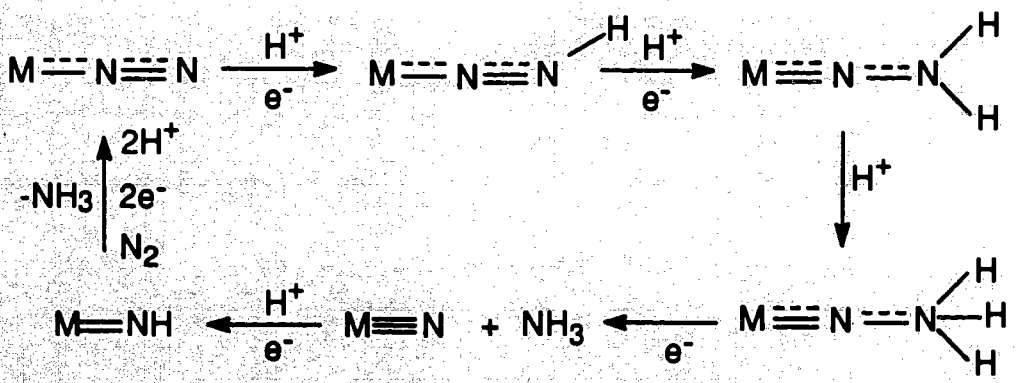
Chapter I: Introduction

I.1 General background

One of the fascinating problems in inorganic chemistry that has been the subject of intense research for some three decades is how bacteria can fix nitrogen under ambient conditions. The nitrogenase enzymes are able to take molecular nitrogen at atmospheric pressure and reduce it to ammonia at room temperature and moderate pH. It has been known for many years that the active site in the nitrogenases contain iron and molybdenum. This has been recently confirmed by a crystal structure determination of the FeMo protein of nitrogenase.[1]

Over the last 25 years, inorganic chemists have elucidated modes of bonding of dinitrogen and partially reduced dinitrogen (N_2H_x) ligands to transition metals and have been accumulating evidence to explain the mechanism by which dinitrogen can be reduced to ammonia. Based on the isolation of metal complexes of these nitrogen ligands and their reaction behavior in solution, a cyclic process (Scheme I) has been proposed as a model for the reduction of dinitrogen in nitrogenase.[2,3]



Examples of MNNH and $MNNH_2$ structures have been known for some time. Only recently, in 1987, has an example of the hydrazidium moiety (NNH_3) bonded to a transition metal been isolated and characterized, in the compound $[WCl(NNH_3)(PMe_3)_4]Cl_2$. This was formed in the reaction of the hydrazido (2-) ($MNNH_2$) complex $[WCl(NNH_2)(PMe_3)_4]Cl$ with anhydrous HCl in methanol.[3]

The reduction of hydrazine in complexes of Mo, W and Re to ammonia in the presence or absence of acid has been reported recently.[4,5] The cleavage of the N-N bond was proposed to occur in the hydrazine ($M\text{-}NH_2\text{-}NH_2$) species via a migration of hydrogen on the Nα atom to the Nβ atom in the absence of a proton source.

Few details are known about how the N-N bond of dinitrogen is cleaved by nitrogenase enzymes to give ammonia. Synthetic studies on the low oxidation state complexes, $M(N_2)_2L_4$ (M= Mo, W and L= phosphine) and their derivatives, however, suggest that a) dinitrogen can be stoichiometrically reduced to ammonia at a single metal center with an empty coordination site available, b) the key intermediate seems to be a hydrazido (2-) (NNH_2) complex; and finally c) ammonia is produced by the cleavage of the N-N bond in either $M{=}NNH_3$ or $M{=}NHNH_3$ intermediates to give ammonia and MN or M=NH, respectively.[6]

The challenge is to understand the inorganic chemistry at the metal centers in nitrogenases and hence to design a nonbiological system for the reduction of dinitrogen to ammonia.

The first intermediate in the cycle shown in Scheme I is that with the diazenido (MNNH) linkage. Only a few metal NNH diazenido complexes are known. Many more complexes with the aryldiazenido ligand (NNAr) have been

synthesized. The reasons for this are the easier synthetic methods available and the higher stability of aryldiazenido compounds compared with the diazenido complexes. The conjugated π system between the aryl group and the β nitrogen is believed to stabilize the aryldiazenido compounds.

Aryldiazenido compounds are usually obtained in good yields, from the reaction of the corresponding diazonium salt ($[N_2Ar]^+$) with a metal complex containing an easily displaced ligand. Diazenido compounds, on the other hand, are usually obtained by either the protonation of a dinitrogen ligand or deprotonation of hydrazine ligand (MN_2H_4) in a metal complex.[7]

I.2 Structure of aryldiazenido ligand

I.2.1 Conformational modes of the terminal aryldiazenido ligand and its protonated derivatives

A key ligand in the study of dinitrogen coordination chemistry is the diazenido ligand (i.e., NNH) since as mentioned above, this is the product of initial protonation of coordinated N_2. The Sutton group has made several important contributions to the synthesis and chemistry of stabilized metal complexes containing the diazenido ligand analogue, *aryldiazenido*, and related ligands. This thesis is concerned with the preparation and dynamic properties of some new rhenium complexes with the aryldiazenido ligand (i.e., N_2Ar).

In aryldiazenido ligands, M-N=NAr, the ß nitrogen (nitrogen furthest from the metal) exhibits sp^2 hybridization. This makes possible a number of structural conformations for the aryldiazenido ligand and its protonated derivatives, as

shown in Figs 1.1[8] and 1.2.[9] In the singly bent structure (I) the aryldiazenido unit is considered as a 2-electron donor (cationic) or as a 3-electron donor (neutral) ligand. In the doubly bent structure (II) it is thought to act as a 2-electron donor (anionic) ligand or 1-electron donor (neutral). Protonation at the ß nitrogen generates the arylhydrazido (2-) ligand that can have a MNN skeleton that is either linear (structure III) or bent (structure IV). Protonation at the α nitrogen forms the aryldiazene ligand (structure V). Protonation at both nitrogen atoms produces the arylhydrazido (1-) moiety which can also adopt different conformations. Structural studies show multiple bond character between N-N (as shown in VI) so that this may be considered a protonated form of the aryldiazene mode (structure V).[9]

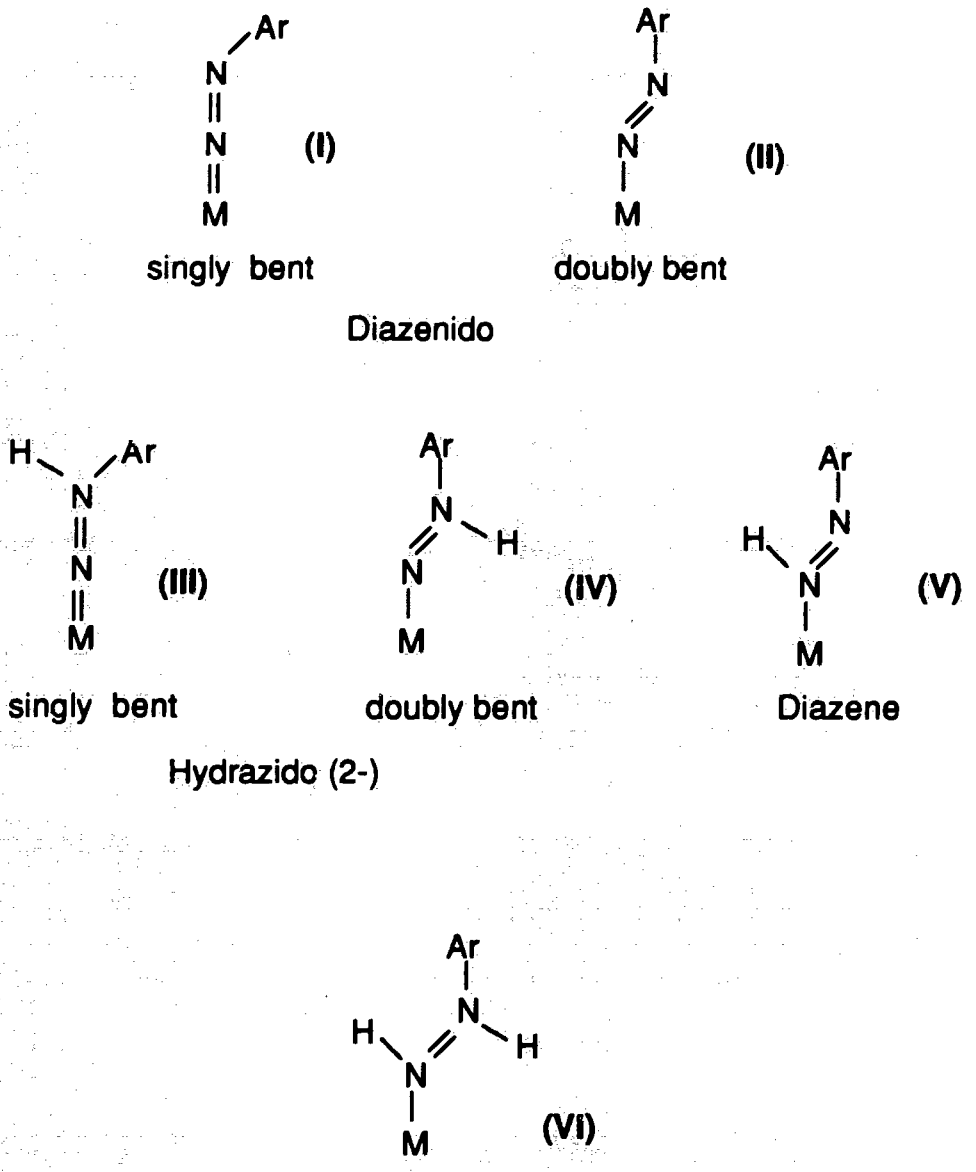


Fig 1.1 Conformation modes for the aryldiazenido ligand and protonated derivatives.

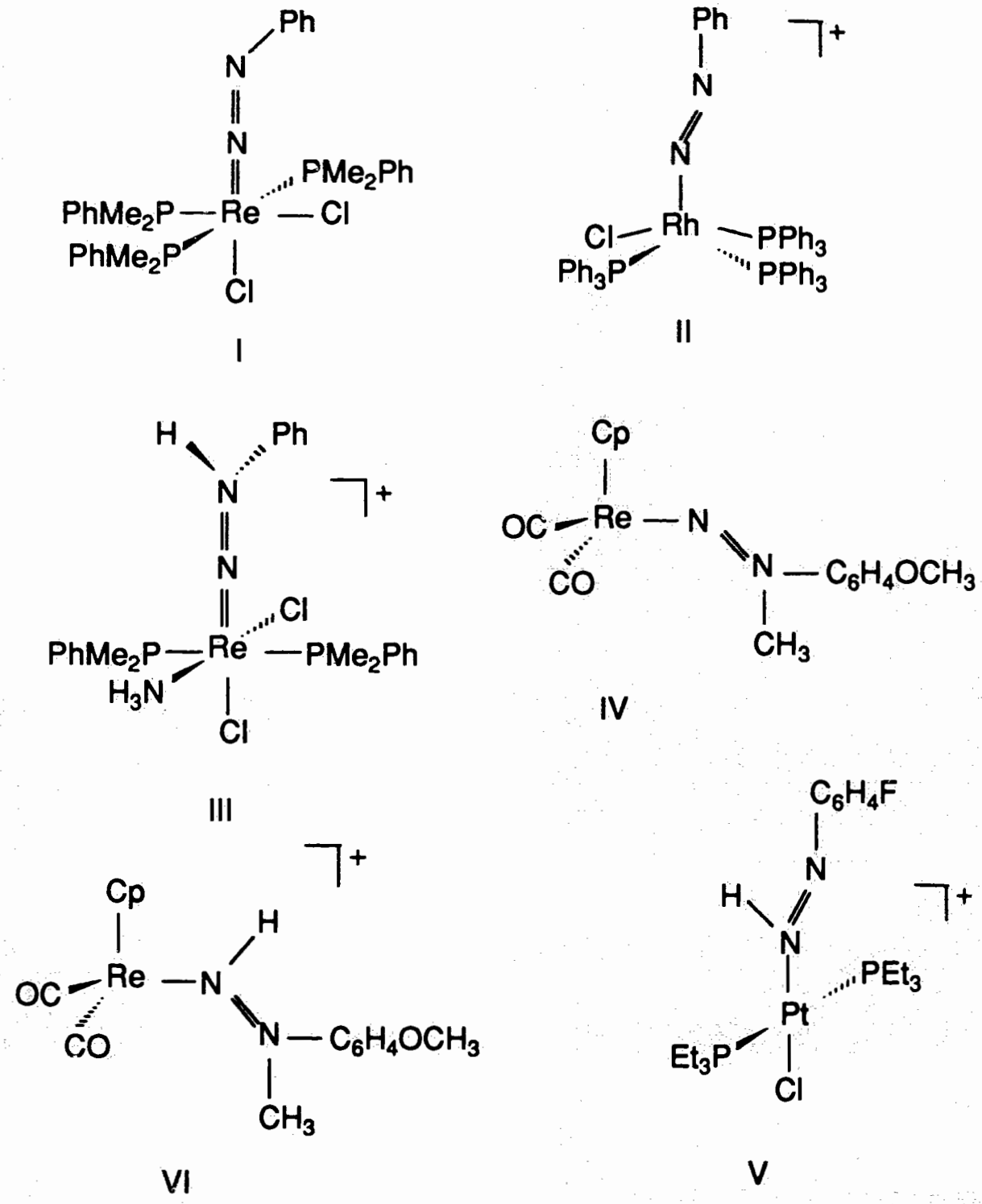


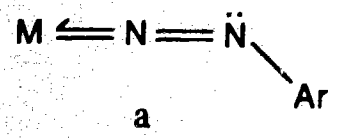
Fig. 1.2: Examples of metal complexes exhibiting various modes of coordination of the diazenido ligand

I.2.2 Geometries adopted by the aryldiazenido ligand

In section I.2.1 the singly bent and doubly bent geometries for the terminal aryldiazenido ligand were described. Variations in these two bonding modes can potentially occur, depending on the metal, ancillary ligands at the metal center, and the substituent at the outer nitrogen. Fig. 1.3 shows a number of these possibilities for monometallic (**a**-**e**) and polynuclear (**f**-**g**) compounds.[10] The singly bent structure **a** is by far the most common bonding mode observed for the N_2Ar ligand. The M-N-N angle is typically in the range 170°-180° with the N-N-C angle usually between 118°-125°; the N-N bond length is about 1.20 Å. There are numerous examples of structures with this type of aryldiazenido ligand reported in the literature. There are, however, no well-characterized examples of structure **b**. The complexes $RuCl_3(N_2Ar)(PPh_3)_2$ and $[IrCl(N_2Ar)(PPh_3)_2]^+$ were believed to be examples of structure **b** based on infrared evidence. Subsequent X-ray structure determinations on both compounds revealed the N-N bond length to be 1.16 Å for both, with the N-N-C angle 137° and 127°, for the Ru and Ir complexes, respectively. In other words, the complexes are intermediate in structure; the geometry is closer to **a** than to **b**. The singly bent geometry **c** is also very rare and no good examples have yet been synthesized. The doubly bent geometry **d** has been gaining importance lately.[11-14] In our laboratory several examples of iridium complexes with doubly bent diazenido ligands have been prepared with a general formula of $[Cp^*IrLL'(p\text{-}N_2C_6H_4OMe)]^+$ (where L = L' = PMe_3, $P(OMe)_3$ and L = PPh_3 and L' = PMe_3, $P(OMe)_3$, CO).[15] In such complexes, the angle between the N-N-C atoms is in the range 115-135°

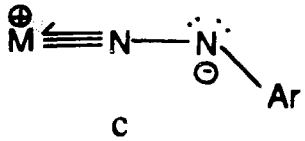
consistent with sp^2 hybridization at the β nitrogen. The M-N bond is lengthened by 0.15 Å -0.25 Å over that found for compounds with the geometry **a**. In the last mononuclear geometry (**e**) the diazenido ligand is bound by both nitrogen atoms to the metal, i.e., side on. This geometry is also rare; a well characterized example is the titanium complex $CpTiCl_2(N_2Ph)$.[10]

The presence of lone pairs on both nitrogen atoms of the aryldiazenido ligand allows it to act as a bridging ligand to two or more metal atoms as shown in structures **f**, **g** and **h** (Fig. 1.3). Just one structurally characterized example of structure **f** has been reported in the literature namely $Mn_3(CO)_{12}(N_2Me)$.[16] Similarly, only two examples of structure **g** have been synthesized and their structures determined by X-ray crystallography. These examples are $CpW(CO)_2(NNMe)Cr(CO)_5$[17] and $CpMo(CO)_3(p\text{-}NNC_6H_4Me)ReCp(CO)_2$[18]. Finally, structure **h** is more common and two examples are $Mn_2(CO)_8(N_2Ph)_2$[19] and $HOs_3(CO)_{10}(p\text{-}N_2C_6H_4Me)$.[20]



a

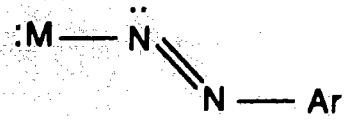
Singly bent



c

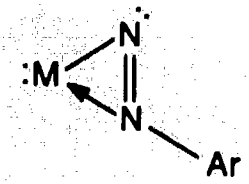
b

Linear



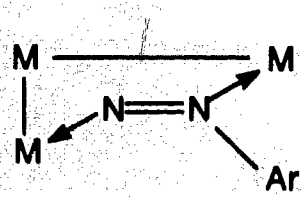
d

Doubly bent

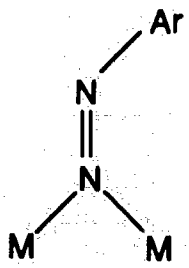


e

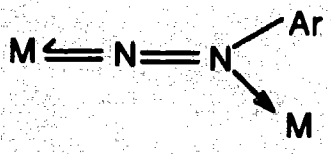
Side on



f



h



g

Fig 1.3 Structures adopted by the aryldiazenido ligand in organometallic compounds

I.2.3 Spectroscopic properties of the aryldiazenido ligand

IR spectroscopy is extremely useful in the characterization of compounds with dinitrogen and related NN ligands. The NN stretch (ν_{NN}) of the aryldiazenido ligand appears over a wide range of the infrared spectrum from 1400 to 2100 cm^{-1} with a medium to strong intensity. Sometimes the $\nu_{(NN)}$ is obscured by absorptions from other vibrations of the molecule, especially when these are in the lower 1400-1600 cm^{-1} region. The position of the NN stretch can often be diagnostic of the mode of coordination of the aryldiazenido ligand. In general higher values of ν_{NN} are identified with the singly bent and lower values with the doubly bent or bridging geometries. The charge on the complex, and the ancillary ligands, also affect this absorption.

Another very useful technique is ^{15}N NMR spectroscopy. Nitrogen-15 (spin 1/2) occurs in low natural abundance (0.37%) with a low, negative gyromagnetic ratio all of which combine to make ^{15}N difficult to observe by NMR techniques. For this reason, ^{15}N NMR studies are usually carried out on complexes that have been enriched in ^{15}N, even though nitrogen-15 compounds are expensive. It is relatively easy to enrich the aryldiazenido ligand at the α-nitrogen since the precursor aryldiazonium salt $[NNAr]^+$ can be prepared from the appropriate amine RNH_2 and the commercially available $Na^{15}NO_2$. ^{15}N NMR spectroscopy can readily distinguish the singly and doubly bent structures. The ^{15}N resonance for Nα appears between 290 to 220 ppm (i.e., downfield) for the doubly bent geometry, and from 0 to -90 ppm (i.e., upfield) for the singly bent mode relative to nitromethane.[10,21]

I.3 History and Proposal

As mentioned in I.1.1, the diazenido moiety (N_2H) has been proposed to be the first stage of production of ammonia from dinitrogen. The diazenido ligand has been identified in only a few compounds such as trans-[$W(N_2H)X(dppe)_2$] (X = F, Cl, Br, or I) by using ^{15}N NMR spectroscopy.[22] No crystal structure of the N_2H compounds has been obtained and so, the orientation of the hydrogen atom is not known yet. The study of the aryldiazenido compounds gives more information about the orientation of the phenyl group, but whether or not this is the same orientation for the hydrogen atom in the diazenido ligand is unknown.

Although the chemistry of the aryldiazenido compounds has been studied for a number of years, it was only discovered quite recently by Sutton and coworkers[23] that in some complexes of this type there is an isomerization process taking place as detected by NMR spectroscopy in solution at low temperature. In singly bent cationic complexes of the type [$(\eta^5\text{-}C_5Me_5)ReLL'(p\text{-}N_2C_6H_4OMe)]BF_4$ (where L=L'= CO, PMe_3 or L= CO and L'= PMe_3), the aryl group of the aryldiazenido ligand occupies a position out of the plane that both contains the ReNN vector and bisects the LReL' angle.[24] There is therefore the possibility of isomers: one isomer in which the aryl group is cis to the L' ligand and the other one where it is cis to the L ligand. These isomers are shown in Fig. 1.4. When the ligands L and L' are identical, the two conformers are enantiomers, and chemically equivalent. In the locked conformation, the two L ligands are in different environments and hence an NMR-active nucleus would give rise to two different NMR signals (of equal intensity). The interconversion of the enantiomers can, in principle, be detected

by observing the behavior of these signals using variable temperature NMR, and the barrier to interconversion can be determined. The process cannot be detected by changes in signals due to the aryl moiety since when L = L' it is in an equivalent environment in either conformer. This process is more correctly called a fluxional process when L = L', whereas when the L and L' ligands are different the process is an isomerization.

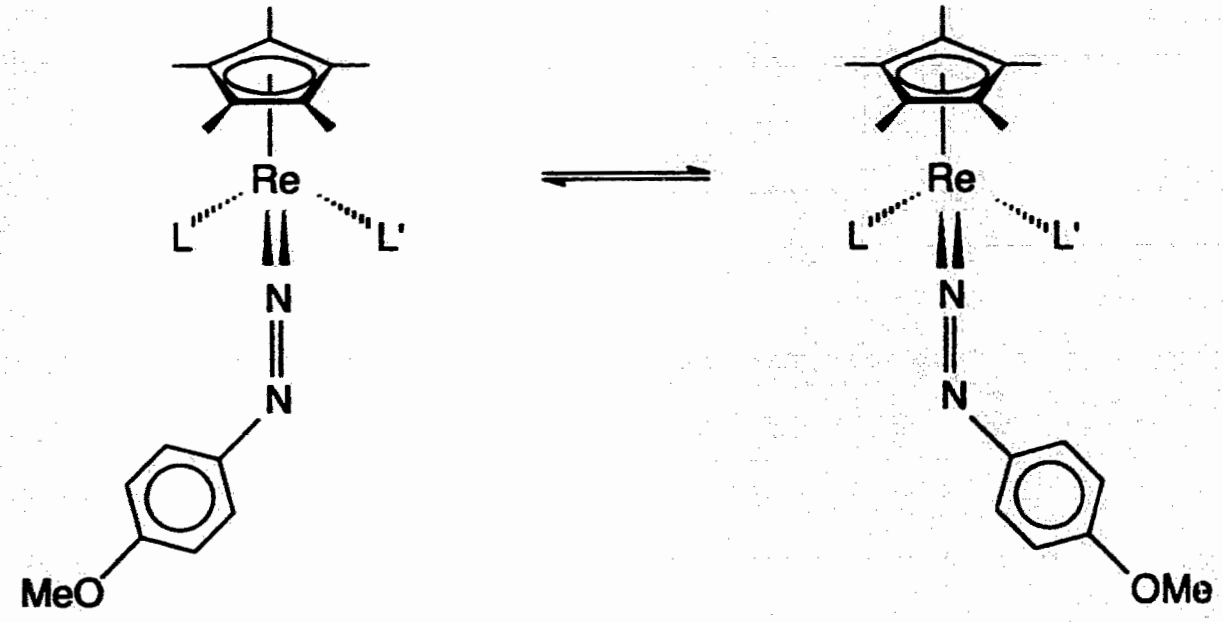


Fig 1.4: The two different isomers believed to be present in $[(\eta^5\text{-}C_5Me_5)ReLL'(p\text{-}N_2C_6H_4OMe)]^+$.

This discovery raised several questions. One is whether or not this isomerization process is also present in similar neutral compounds. Another important question is: does the barrier to isomerization arise from restricted rotation about the ReNN axis or an inversion at Nβ?. It was also of interest to study the effect of the ancillary ligands L and L' on both the barrier to

isomerization and on the isomer ratio. The work presented in this thesis attempts to address some of these questions. In order to answer the first question, we describe here the synthesis and characterization of some new neutral rhenium aryldiazenido compounds of general formula [$Cp^*ReXL(p\text{-}N_2C_6H_4OMe)$] [where $Cp^* = (\eta\text{-}C_5Me_5)$; L = CO and X = H, CH_3; L = PMe_3, $P(OMe)_3$, PPh_3 and X = Cl]. Furthermore, variable temperature NMR studies of some of these complexes have been carried out and isomerization has been detected in four cases.

On the basis of the limited amount of data available, some tentative proposals are made regarding the effect of the ancillary ligands on the barrier to isomerization as well as the isomer ratio observed.

Chapter II: Synthesis and characterization of novel neutral compounds of the type $(\eta^5\text{-}C_5Me_5)Re(X)(L)(p\text{-}N_2C_6H_4OMe)$

II.1 Introduction

In this chapter is reported the synthesis and characterization of the neutral rhenium complexes $(\eta^5\text{-}C_5Me_5)Re(H)(CO)(p\text{-}N_2C_6H_4OMe)$ (**1**), $(\eta^5\text{-}C_5Me_5)Re(CH_3)(CO)(p\text{-}N_2C_6H_4OMe)$ (**3**), $(\eta^5\text{-}C_5Me_5)Re(Cl)(PMe_3)(p\text{-}N_2C_6H_4OMe)$ (**4**), $(\eta^5\text{-}C_5Me_5)Re(Cl)\{P(OMe)_3\}(p\text{-}N_2C_6H_4OMe)$ (**5**), $(\eta^5\text{-}C_5Me_5)Re\{PO(OMe)_2\}(CO)(p\text{-}N_2C_6H_4OMe)$ (**6**) and $(\eta^5\text{-}C_5Me_5)Re(Cl)(PPh_3)(p\text{-}N_2C_6H_4OMe)$ (**7**). The hydrido carbonyl complex (**1**) was previously reported[25], but the remainder are new compounds. The phosphonate complex (**6**) was first obtained as a byproduct of the synthesis of compound **5**. The formation of compounds $(\eta^5\text{-}C_5Me_5)Re(Br)(PMe_3)(p\text{-}N_2C_6H_4OMe)$ (**8**) and $(\eta^5\text{-}C_5Me_5)Re(I)(PMe_3)(p\text{-}N_2C_6H_4OMe)$ (**9**) is also reported.

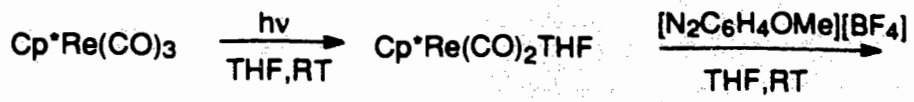
The neutral compounds obtained, with different ancillary ligands, were selected for this research to allow the possibility of observing the isomerization process. The presence of the hydrido or the methyl groups provides the possibility of studying these compounds by using ^1H NMR spectroscopy. On the other hand, the phosphine complexes can be studied by ^{31}P NMR spectroscopy.

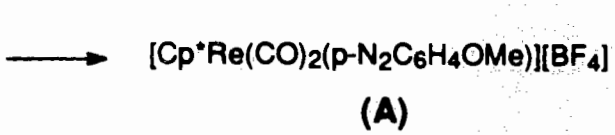
II.2 Results and Discussion

II.2.1 Preparation of the starting materials

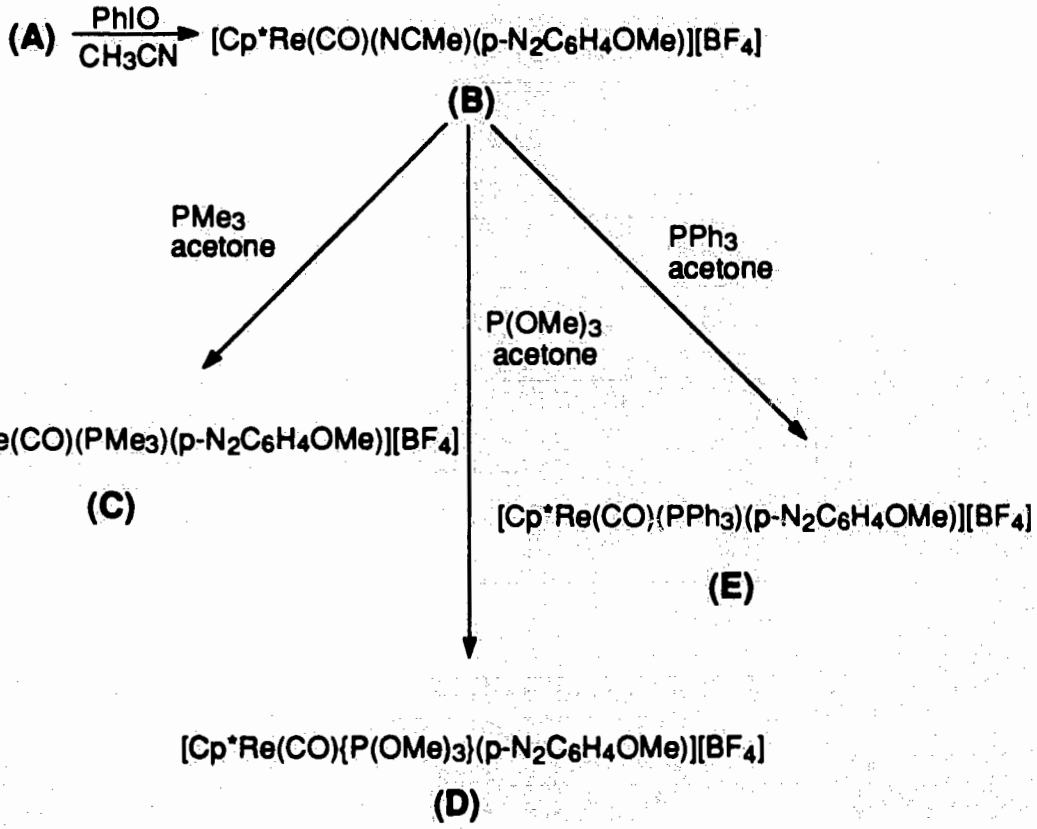
Previous synthetic strategies developed in this laboratory were used to prepare the starting materials $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(p\text{-}N_2C_6H_4OMe)][BF_4]$ **(A)** [25], and $(\eta^5\text{-}C_5Me_5)Re(CO)(L)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (L = PMe_3, $P(OMe)_3$, PPh_3).[26] The methods used are summarized in Scheme II.

The aryldiazenide derivative **A** was prepared from $(\eta^5\text{-}C_5Me_5)Re(CO)_2(THF)$, which in turn was prepared by the UV irradiation of $(\eta^5\text{-}C_5Me_5)Re(CO)_3$ in THF (Scheme II, equation 1). Reaction of **A** with iodosobenzene (PhIO) in acetonitrile gave $[(\eta^5\text{-}C_5Me_5)Re(CO)(NCMe)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **(B)**. The phosphine compounds $(\eta^5\text{-}C_5Me_5)Re(CO)(L)(p\text{-}N_2C_6H_4OMe)][BF_4]$ (L = PMe_3, $P(OMe)_3$, PPh_3) were prepared by addition of L to **B** in acetone (Scheme II,equations 2) as previously reported.[26]





equation 1



equations 2

Scheme II: Route of preparation of the starting materials A, C, D and E

II.2.2 Synthesis of complexes with general formula $(\eta^5\text{-}C_5Me_5)Re(X)(L)(p\text{-}N_2C_6H_4OMe)$ (X = H, CH_3, $PO(OMe)_2$, L = CO; X = Cl, L = PMe_3, $P(OMe)_3$, PPh_3)

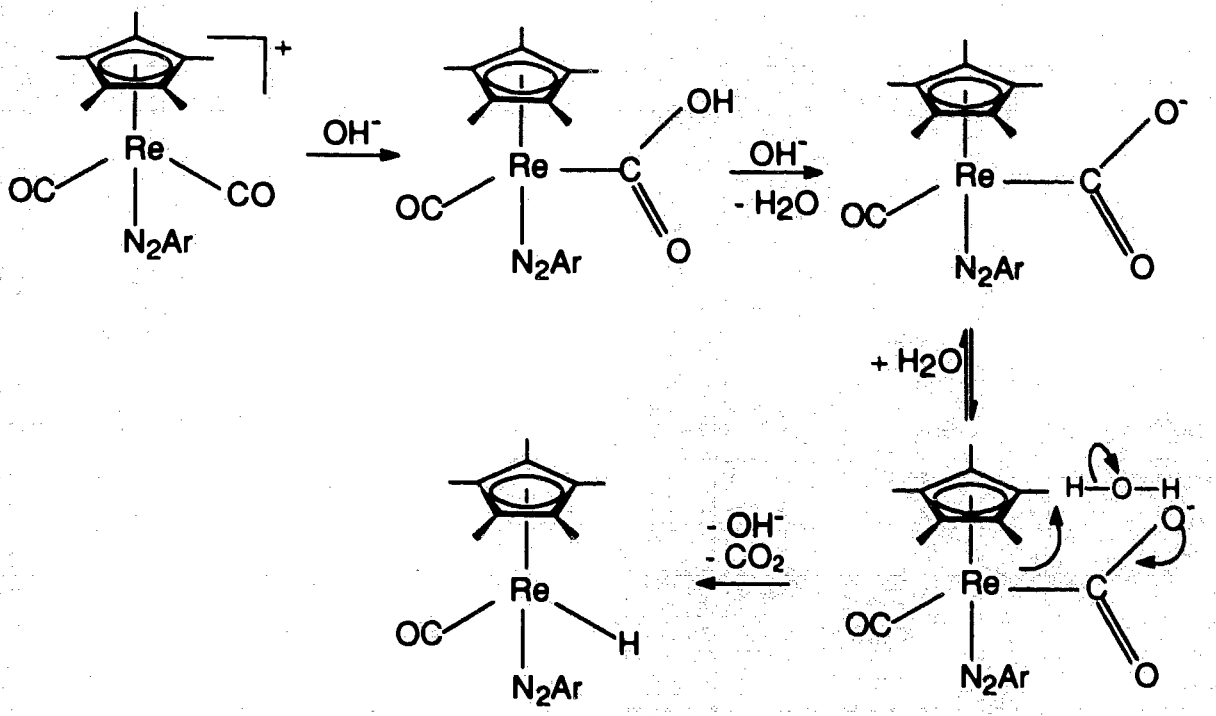
$(\eta^5\text{-}C_5Me_5)Re(H)(CO)(p\text{-}N_2C_6H_4OMe)$ (1) :

This compound was prepared according to equation 3 as a yellow air stable solid in yields of 52 % (method 1) and 62 % (method 2)

$$[Cp^*Re(CO)_2(N_2Ar)]^+ + 3\,OH^- \xrightarrow[RT]{\text{acetone}} \underset{\mathbf{1}}{Cp^*Re(H)(CO)(N_2Ar)} + CO_3^{2-} + H_2O$$

equation (3)

A mechanism of formation of compound **1** has been proposed by Sutton, et al.[25] The mechanism consists of the formation of the hydroxycarbonyl followed by nucleophilic attack of the Re center on the polar OH bond of a molecule of water, release of CO_2 and the formation of the hydride (Scheme III):



Scheme III: Nucleophilic attack mechanism of formation of the hydride from carbonyl in rhenium compounds

When the reaction was carried out in this study, the chloro compound **(η^5-C_5Me_5)Re(Cl)(CO)(*p*-$N_2C_6H_4OMe$) (2)** accompanied the formation of **1** and was removed by chromatography on a neutral alumina column with dichloromethane. The presence of **2** was confirmed by comparison of the ^1H NMR and IR spectra with those reported in the literature for **2**[27]. It is believed that **2** arose from an impurity in the sodium hydroxide used for the reaction. The NaOH (Fisher Scientific, A.R. grade) is stated to contain 1% NaCl. It has been suggested by Sutton et al [27], that the chloro compound is obtained from the reaction between the compound **A** and chloride anion. The formation of compound **2** therefore involves nucleophilic attack at the metal center by chloride, releasing CO.

The formation of **2** was originally thought to be due to reaction of the hydride complex **1** with the CH_2Cl_2 solvent through a radical substitution mechanism. Compound **2** was, however, also obtained by using acetone as a solvent, so that the source of chloride cannot be simply the halogenated solvent, thus implicating the chloride impurity in the NaOH that was used. When acetone was used as the solvent, the yield of the hydride **1** was 10% higher than when CH_2Cl_2 was employed. This was probably because of the greater solubility of NaOH and hence a higher concentration of hydroxide in the more polar solvent acetone.

Complex **1** exhibited a CO stretch at 1925 cm^{-1}, consistent with a single terminal carbonyl ligand in a neutral complex of rhenium, as well as an NN stretch at 1613 cm^{-1} in hexane. The ^1H NMR spectrum of **1** showed a singlet resonance at δ -6.55 ppm in acetone-d_6 (δ -5.85 ppm in C_6D_6) characteristic of the hydride ligand, along with resonances at δ 2.21 ppm (Cp*), 3.81 ppm (OMe) and doublets at 6.99 ppm and 7.29 ppm assigned to the protons of the phenyl group of the aryldiazenido ligand. The pattern for these last signals appeared as an AB pattern, although these protons are an AA'BB' system.

Compound **2** obtained in these preparations was used for the starting material in the synthesis of $(\eta^5\text{-}C_5Me_5)Re(CH_3)(CO)(p\text{-}N_2C_6H_4OMe)$ **(3)**. If, however, just compound **1** is required, it would probably be preferable to use either pure NaOH or KOH. The NaOH should also be dissolved in ethanol since the solubility of the sodium chloride in ethanol is small.

(η^5-C_5Me_5)Re(CH_3)(CO)(*p*-$N_2C_6H_4OMe$) (3):

The reaction between compound **2** and CH_3MgBr in ether was followed by infrared spectroscopy. There was disappearance of the $\nu_{(CO)}$ stretch of **2** at 1942 cm^{-1} in hexane concomintant with the appearance of a new $\nu_{(CO)}$ at 1915 cm^{-1} until there was complete conversion to product. This is presented in Fig 2.1. A large excess of the Grignard reagent was required in this reaction which may indicate that the solvent was not scrupulously anhydrous.

$$Cp^*Re(Cl)(CO)(N_2Ar) + CH_3MgBr \xrightarrow[RT]{ether} \underset{\mathbf{3}}{Cp^*Re(CH_3)(CO)(N_2Ar)} + MgBrCl$$

equation (4)

Compound **3** was obtained as a low melting yellow solid by crystallization at -78°C from hexane. The oily hexane supernatant solution was separated by pipette and the sample was dried under vacuum. It is worth noting that the compound melted below room temperature which made it difficult to isolate free from the solvent. The elemental analysis obtained for **3** was somewhat high in both carbon and hydrogen but lower in nitrogen. This was probably due to the presence of solvent in the sample. The single Cp* resonance in the ^1H NMR spectrum of the compound showed the absence of any Cp*-rhenium impurities. The ^1H NMR spectrum of **3** showed a broad resonance at δ 1.16 ppm ($CDCl_3$) due to the methyl ligand (the broadness is discussed in chapter III). The NMR spectrum also showed resonances at δ 1.98 ppm (s), 3.83 ppm (s), 6.89 ppm (d) and 7.19 ppm (d) attributable to the Cp*, OMe and aromatic protons

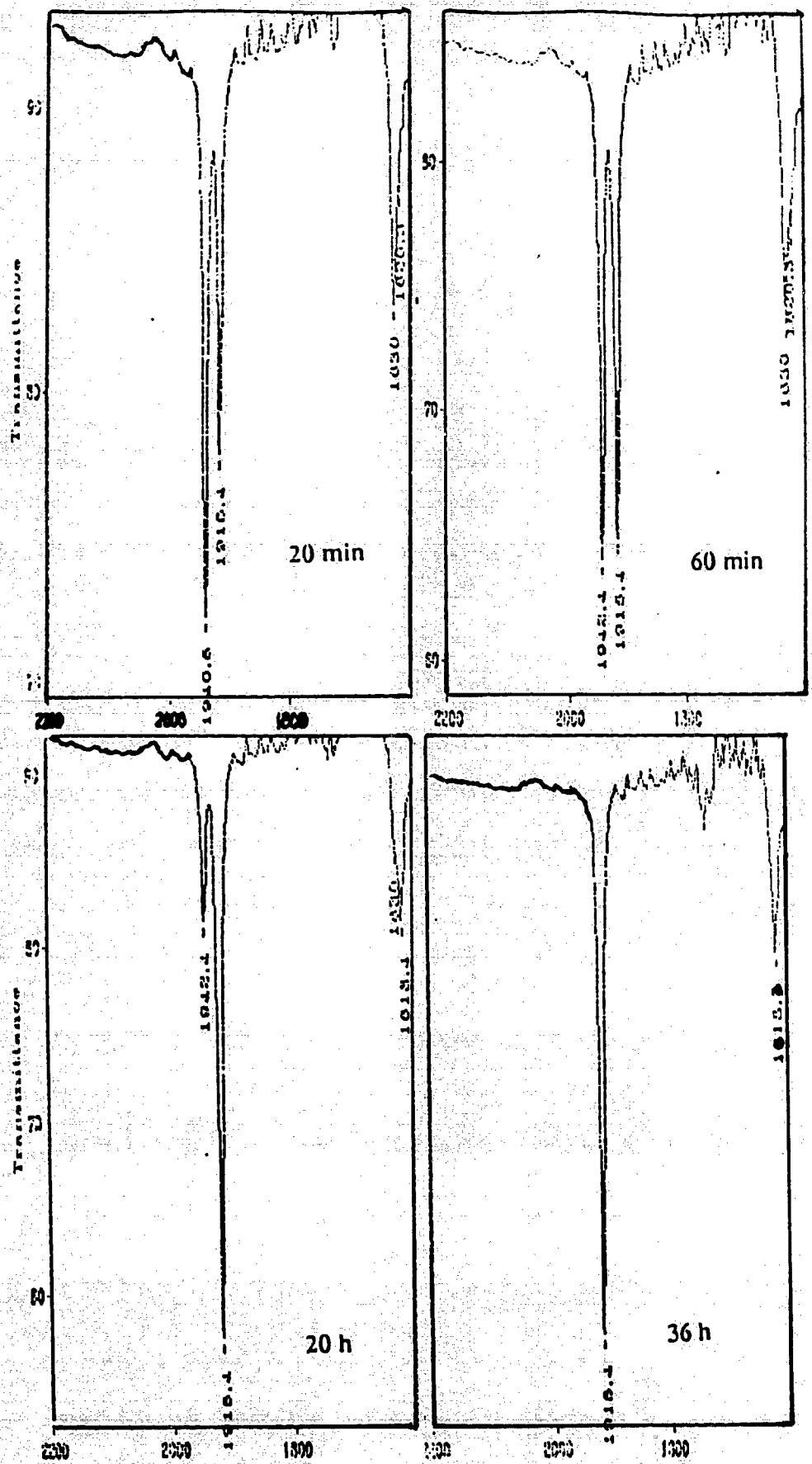


Fig. 2.1: IR spectra of the preparation of $(\eta^5\text{-}C_5Me_5)Re(CH_3)(CO)(p\text{-}N_2C_6H_4OMe)$ (3) ($\nu_{(CO)}$ = 1915 cm^{-1}) from the chloro compound 2 ($\nu_{(CO)}$ = 1940 cm^{-1}).

respectively. The mass spectrum of **3** (EI) showed a parent ion at m/z 500 with a pattern in agreement with that simulated by computer for $ReC_{19}H_{25}O_2N_2$. The mass spectrum also showed a peak at m/z 472 corresponding to $[M\text{-}CO]^+$. The strong absorption in the infrared spectrum of **3** in hexane at 1915 cm^{-1} was also consistent with the presence of a carbonyl ligand.

$(\eta^5\text{-}C_5Me_5)Re(Cl)(L)(p\text{-}N_2C_6H_4OMe)]$ (L = PMe_3 (4), $P(OMe)_3$ (5), PPh_3 (7)) and $(\eta^5\text{-}C_5Me_5)Re(CO)\{PO(OMe)_2\}(p\text{-}N_2C_6H_4OMe)]$ (6):

Compounds **4**, **5** and **7** were prepared according to equation 5. Individual preparations are given below. Compound **4** was obtained as a brown solid in 78 % yield. It is not particularly air stable and decomposed under nitrogen after one week at 0°C. Compound **5** was obtained pure by careful chromatography as a brown solid in 43 % yield. Compound **7** was also obtained as a brown solid, in 83 % yield.

$$[Cp^*Re(L)(CO)(N_2Ar)]^+ + Cl^- \xrightarrow[NaOH\ /\ EtOH]{CHCl_3} Cp^*Re(L)(Cl)(N_2Ar) + CO$$

equation (5)

It is proposed that the mechanism of formation of the chloride compounds **4, 5** and **7** takes place by the nucleophilic attack of chloride to the metal center in the starting material **C,D** or **E** releasing carbon monoxide. This mechanism was proposed earlier in the case of the production of halide complexes

$Cp^*Re(X)(CO)(N_2Ar)$ from reactions of the dicarbonyl cation **A** with X^- in THF / H_2O.[27] We observed no reaction in $CHCl_3$ alone. It is possible that the presence of the ethanolic solution of NaOH is necessary to increase the concentration of Cl^- in the system. Further syntheses must be performed in aqueous solution or H_2O/THF to confirm this. In all of the syntheses a large excess of KCl was necessary in order to obtain high yields. Lower yields were obtained when a small excess (20%) of KCl was used. Due to the low solubility of KCl in $CHCl_3$, these reactions appeared very dependent on both the amount of chloride added, as well as the concentration of NaOH used.

$(\eta^5\text{-}C_5Me_5)Re(Cl)(PMe_3)(p\text{-}N_2C_6H_4OMe)$ (4):

The ^1H NMR spectrum of compound **4** showed a doublet at δ 1.54 ppm ($CDCl_3$) assigned to the protons of the trimethylphosphine ligand. The coupling constant of this resonance ($^3J_{PH}$ = 9.3 Hz) is somewhat lower than that for most PMe_3 ligands reported in the literature, but is still in the range for coordinated PMe_3 ligands. The doublet resonance at δ 16.68 ppm in the ^{13}C NMR spectrum of **4** with a $^2J_{PC}$ = 34 Hz is also typical for a coordinated PMe_3 ligand. Other good evidence for the formation of compound **4** was the position of the phosphine resonance in the ^{31}P NMR spectrum at δ 35.64 ppm ($CDCl_3$) indicative of the coordinated PMe_3.[26] The presence of the chloride ligand was detected by mass spectroscopy: a set of peaks centred at m/z 568 was observed, with a distinctive pattern due to the two isotopes ^{35}Cl and ^{37}Cl and those of ^{185}Re and ^{187}Re. The pattern observed matched that simulated by computer for compound **4**.

(η^5-C_5Me_5)Re(Cl){P(OMe)$_3$}(p-$N_2C_6H_4$OMe) (5):

In the synthesis of compound **5**, two Cp* signals together with a multiplet around 3.5-3.6 ppm and ~ 7 ppm (phenyl region) were observed in the ^{1}H NMR spectrum of the reaction products ($CDCl_3$ solvent), which suggested the presence of two compounds. IR spectroscopy was invaluable in understanding the processes that were taking place. A carbonyl stretch at 1940 cm^{-1} in CH_2Cl_2 was observed after completion of the reaction (the carbonyl stretch for the starting material **D** (Scheme I) occurs at 1964 cm^{-1} in CH_2Cl_2), together with $\nu_{(NN)}$ absorptions at 1641 cm^{-1} and 1609 cm^{-1}. The observation of the two N-N stretches indicated the presence of a second compound (which subsequently was identified as compound **6**, see below). As mentioned above, compound **5** was obtained pure by careful chromatography as a brown solid in a 43 % yield. The ^{1}H NMR spectrum of pure **5** showed a doublet at 3.62 ppm corresponding to a P(OMe)$_3$ ligand. The coupling constant of 11.5 Hz is typical for a coordinated phosphite ligand.[26,28] The ^{13}C NMR spectrum showed a singlet for the methyl groups in the phosphite ligand at δ 52.54 ppm. It is not surprising that no coupling between carbon and phosphorus atoms was observed, as the ^{13}C NMR spectra of compounds with phosphite ligands have been reported with and without P-C coupling for this ligand.[28] The ^{31}P NMR spectrum showed a resonance at δ 119.75 ppm (acetone-d_6) due to the phosphite. This resonance is in the range for a coordinated phosphite.[26,28]

(η^5-C_5Me_5)Re(Cl)(PPh_3)(*p*-$N_2C_6H_4OMe$) (7):

The preparation of compound **7** was performed by using the same method as that for compounds **4** and **5**. Compound **7** was obtained as a brown solid in 83 % yield. The IR spectrum exhibited a ν_{NN} absorption in CH_2Cl_2 at 1607 cm^{-1}. The ^1H NMR spectrum of compound **7** showed resonances at δ 1.65 ppm (for the Cp* ligand), δ 3.80 ppm (for the methoxy group), the characteristic AB pattern for the protons of the phenyl ring of the diazenide ligand and a multiplet at δ 7.30-7.58 ppm due to the PPh_3 ligand. The ^{13}C NMR spectrum in the 120-140 ppm region exhibited resonances corresponding to the ipso, ortho, meta and para carbon atoms of the PPh_3 group together with some of the resonances of the phenyl ring of the diazenide ligand; other resonances due to the latter ligand occurred at δ 114.04 ppm and δ 167.71 ppm. Signals corresponding to the methyl groups of the Cp*, (at 10.00 ppm), the methoxy (at 55.49 ppm) and the Cp* ring (at 100.92 ppm) were also observed in this spectrum. The ^{31}P NMR spectrum of **7** showed a signal at δ 17.11 ppm characteristic for PPh_3 coordinated to rhenium.[26] The mass spectrum showed a parent ion centered at m/z 754 and peaks centered at 492 corresponding to the loss of the PPh_3 ligand.

The synthesis of compound **E**, (the starting material for **7**) occurs at a very slow rate and a large excess of triphenylphosphine was therefore employed. At the end of the synthesis of **7**, the product was washed several times with diethyl ether in order to remove free PPh_3. The elemental analysis of compound **7** however, was high in both carbon and hydrogen and this is attributed to the presence of trace amounts of unreacted PPh_3.

$(\eta^5\text{-}C_5Me_5)Re(CO)\{PO(OMe)_2\}(p\text{-}N_2C_6H_4OMe)$ (6):

The formation of phosphonates from phosphites in rhenium compounds has been proposed recently [28]. The Arbuzov reaction was found to occur in phosphite compounds such as $[(\eta^5\text{-}C_5Me_5)Re(X)(CO)_2\{P(OR)_3\}]^+$ (where R = Me, Et; X = Cl, Br, I) in the presence of nucleophiles such as Cl^- , Br^- , I^-; when the trihalide anions (eg. I_3^-)were present, the reaction took place faster and in a higher yield. In order to identify the second product formed in the synthesis of **5**, compound **D** was placed together with KI in tetrahydrofuran. The presence of the phosphonate compound **6** was rapidly detected and after 3 h at 40°C, the IR showed absence of **D**. The reaction with KCl takes longer and the yield is about 50%. The ^1H NMR of compound **6** (Fig.2.2) shows two doublets at 3.56 ppm and 3.59 ppm in $CDCl_3$ corresponding to the non-equivalent methoxy groups of the $PO(OMe_2)$ ligand,with a coupling constant J_{PH} of 11.8 Hz. The inequivalence of the two diastereotopic methoxy groups in 6 can be visualized in Fig 2.3(a). In the synthesis of **5**, the formation of the phosphonate compound **6** by the Arbuzov reaction occurs by the nucleophilic attack of either chloride or the hydroxide anion on the phosphite compound **5**. This process is represented in Fig 2.3(b).

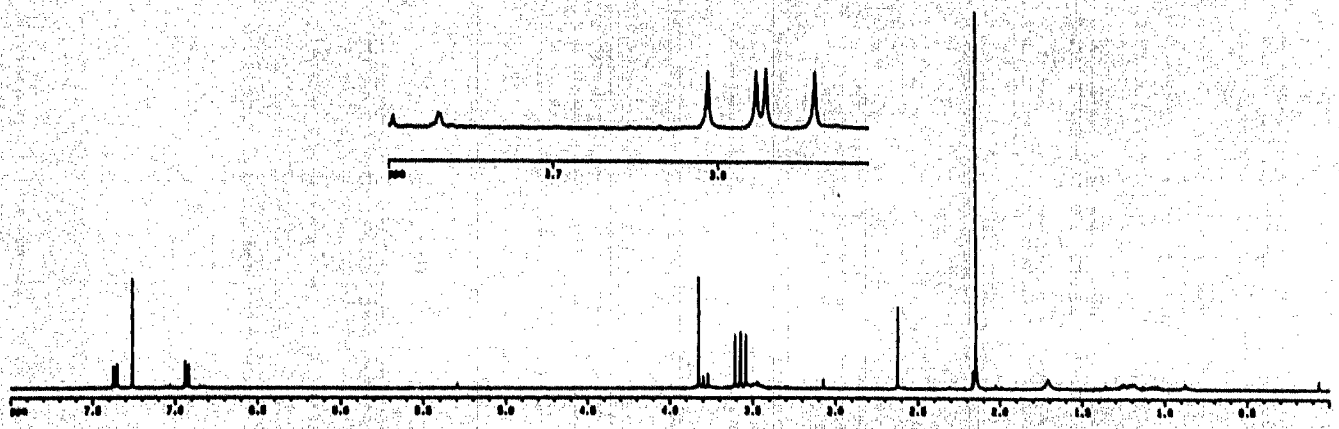
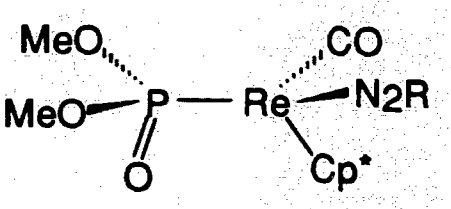
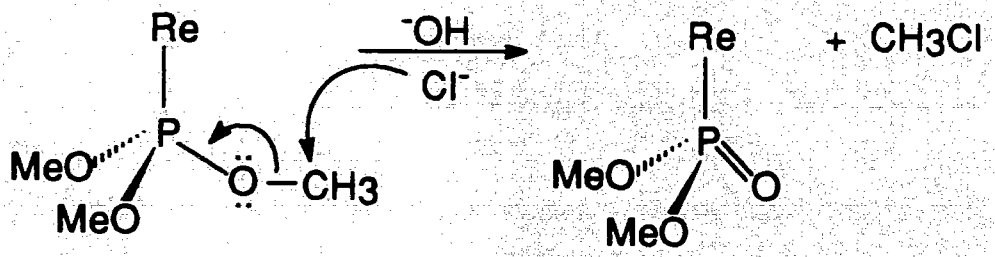


Fig 2.2: ^{1}H NMR spectrum of $(\eta^{5}\text{-}C_5Me_5)Re(CO)\{PO(OMe)_2\}(p\text{-}N_2C_6H_4OMe)$ **(6)**

Assignments of the peaks: δ 2.15 (Cp*); δ 3.56 (d) $\{PO(OMe)_2\}$; δ 3.59 (d) $\{PO(OMe)_2\}$; δ 3.82 (OMe); δ 6.93 (d) (C_6H_4); δ 7.36 (d) (C_6H_4)



a



b

Fig 2.3 : a- Diastereotopic methyl groups in compound **6**. b- Arbuzov nucleophilic attack for the formation of compound **6**.

The ^{13}C NMR spectrum for compound **6**, at the operating frequency of 100.6 MHz, shows two resonances at 50.33 ppm and 50.39 ppm. These are assigned to the two diastereotopic methoxy groups in **6** with no significant coupling to the phosphorus. (Another alternative assignment could be that the resonance corresponds to two equivalent methoxy groups appearing as a doublet with J_{PC} = 6.5 Hz. One easy way to distinguish between these two possibilities would be to record the spectrum at a different frequency. If the second assignment is correct, the coupling constant would not change upon change in the frequency.) The ^{31}P NMR was also a helpful technique to identify compound **6**. The signal at 68.7 ppm is in a position upfield of the corresponding phosphite complex, in agreement with the phosphonates reported in the literature.[28]

The compound **6** is obtained as a yellow oil in a 97 % yield by direct preparation reported above, and in 51 % yield as a byproduct of the preparation of **5**. Crystallization from hexane at -78°C was tried in order to obtain the compound as a pure solid, but the solid so obtained melted as soon as the Schlenk tube was removed from the dry ice bath.

When compound **6** was prepared by the nucleophilic attack of the iodide (KI) to the $O\text{-}CH_3$ bond of the phosphite ligand in compound **D**, another compound was obtained in a very small amount as a byproduct. This compound was identified as $(\eta^5\text{-}C_5Me_5)Re(I)(CO)(p\text{-}N_2C_6H_4OMe)$ by comparison with the data reported in the literature.[27] This iodide compound gave ν_{CO} absorption at 1929 cm^{-1} and ν_{NN} absorption at 1630 cm^{-1} in CH_2Cl_2, as well as resonances in the ^1H NMR spectrum ($CDCl_3$) at 2.14 ppm (s,15H, Cp*), 3.82 ppm (s, 3H, OMe), 6.91 ppm (d, 2H, $^3J_{HH}$ = 9 Hz) and 7.29 ppm (d, 2H, $^3J_{HH}$ = 9 Hz). The formation of this compound could be explained by nucleophilic attack of the iodide at the metal center, with loss of the phosphite ligand.

The proportions of the phosphite **5** and the phosphonate **6** produced in the reaction are very dependent on the concentration of KCl and the order of addition of the reactants. We already described that an excess of the potassium chloride was necessary in order to get higher yields of the chloride compounds **4**, **5** and **7**, but in this specific reaction, because of the collateral formation of the phosphonate, the excess also affects the yield of compound **5**. On the other hand, if the order of addition of the NaOH and KCl is reversed, more phosphonate compound **6** is produced since the KCl can freely attack the methoxy group. A compromise between these two factors is necessary in order to obtain good yields of **5**.

The three chloride compounds **(4 , 5** and **7)** are soluble in hexane and they were recrystallized from cold hexane. However, the phosphonate **6** is not very soluble in hexane which makes it easy to separate from the phosphite on a neutral alumina column by elution with hexane.

A comparison of the compounds **(4 , 5** and **7)** can be made by looking at the $\nu_{(NN)}$ stretch in the IR spectra. The $\nu_{(NN)}$ value does not vary significantly for the three compounds in CH_2Cl_2 (see table below). This suggests that the aryldiazenido ligand is receiving almost the same electronic density from the Re metal through the back bond in each case. Therefore it appears that the influence of the difference in basicity of these phosphines on the NN bond is very small.

Compound	$\nu_{(NN)}$ (cm^{-1},CH_2Cl_2)
$(\eta^5\text{-}C_5Me_5)Re(Cl)(PMe_3)(p\text{-}N_2C_6H_4OMe)$ **(4)**	1605
$(\eta^5\text{-}C_5Me_5)Re(Cl)\{P(OMe)_3\}(p\text{-}N_2C_6H_4OMe)$ **(5)**	1609
$(\eta^5\text{-}C_5Me_5)Re(Cl)(PPh_3)(p\text{-}N_2C_6H_4OMe)$ **(7)**	1607

$(\eta^5\text{-}C_5Me_5)Re(I)(PMe_3)(p\text{-}N_2C_6H_4OMe)$ (9):

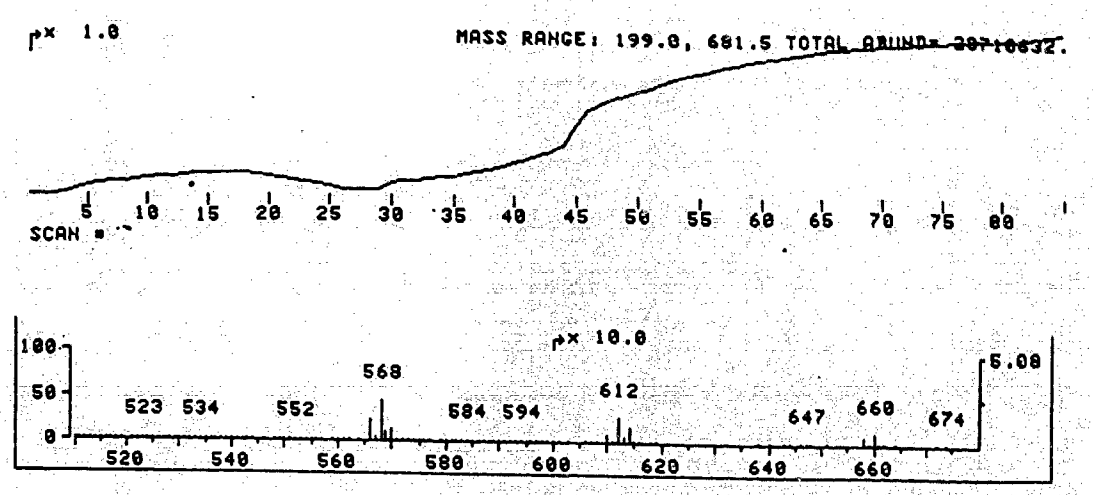
The hydride derivative $(\eta^5\text{-}C_5Me_5)Re(H)(PMe_3)(p\text{-}N_2C_6H_4OMe)$ was not observed in the reaction between **C** and NaOH carried out in acetone in the absence of KCl. Under these conditions, the iodide derivative **(9)** was obtained instead. It is believed that iodide was present as the counterion in **C** in place of $[BF_4]^-$ to some extent because the precursor $[(\eta^5\text{-}C_5Me_5)Re(NCMe)(CO)(p\text{-}N_2C_6H_4OMe)]BF_4$ **(B)** was obtained from the reaction between $[(\eta^5\text{-}$

$C_5Me_5)Re(CO)_2(p\text{-}N_2C_6H_4OMe)]BF_4$ **(A)** and iodosobenzene (C_6H_5IO) in MeCN. (Subsequently, compound **B** was reacted with the phosphine to give **C** by replacement of the NCMe ligand by L) The iodide present as a counterion could therefore attack the metal center, in a mechanism similar to that proposed for the formation of the chloride, **2**.

Compound **9** exhibited an IR absorption at 1604 cm^{-1} assigned to ν_{NN}. The ^1H NMR spectrum in acetone-d_6 showed a doublet at 1.59 ppm attributable to the protons of the PMe_3 ligand with a coupling constant of 10.0 Hz, singlets at 2.05 (Cp^*) and 3.72 ppm (OMe), and doublets at 6.80 and 6.96 ppm (with a $^3J_{HH}$ = 9 Hz) corresponding to the protons in the phenyl group.

(η^5-C_5Me_5)Re(Br)(PMe_3)(*p*-$N_2C_6H_4OMe$) (8):

Compound **8** was obtained in a small amount when compound **4** was placed together with KBr in acetone. The substitution of the chloride ligand in compound **4** by the bromide to a very limited extent can be explained as due to the higher crystal lattice energy for NaCl than NaBr driving the reaction to produce Re-Br and NaCl. Although the presence of the bromide compound was not detected by ^1H NMR (probably due to the positions of the signals being similar to the ones for compound **4**), the presence of peaks in the mass spectrum attributable to the parent ion of **8** was definitive, due to the similarity of the peaks with the computer simulated ones (Fig 2.4).



ReC20H31ON2PBr

610	36.97	**********
611	8.74	*****
612	100.00	**********
613	23.48	**********
614	64.27	**********
615	14.75	*********
616	1.77	*
617	0.14	

Fig. 2.4: Mass spectrum (EI) of the bromo compound 8 and the chloro compound 4 and the simulated peaks

With the purpose of preparing (η^5-C_5Me_5)Re(CH_3)(PMe_3)(*p*-$N_2C_6H_4OMe$) by methyl substitution of the chloride ligand in compound **4**, it was reacted together with CH_3MgBr. Instead, the bromide compound **8** was obtained. To explain this, the crystal lattice energy should be taken in account again. The Mg-Cl ionic interaction is stronger than Mg-Br driving the reaction to the formation of the Re-Br product. The Hard and Soft Acids and Bases theory (HSABT) can also be used to explain this metathesis reaction. The bromide anion is softer than chloride, therefore the bromide would bind the rhenium metal preferentially to Mg due to the hardness of the latter one with respect to Re.

The ^1H NMR for compound **8** exhibits a doublet resonance at 1.61 ppm assigned to the PMe_3 ligand with a coupling constant of 9.3 Hz, a singlet at 1.97 ppm due to the Cp* and the 3.80 ppm signal corresponding to the OMe, as well as the typical AB pattern for the protons on the phenyl ring at 6.88 ppm and 7.28 ppm. The mass spectrum also indicated the formation of compound **8** by the observation of the parent ion at m/z 612 together with a pattern at m/z 475 assigned to the loss of the fragment $N_2C_6H_4OMe$ and 2H (137 units)

Reaction of (η^5-C_5Me_5)Re(COOMe)(CO)(*p*-$N_2C_6H_4OMe$) (10) with NaOH:

The formation of compound **10** has been proposed to be by a nucleophilic attack of OMe^- (using NaOMe) on the carbon atom of the carbonyl group in **A**[27]. The compound **10** reacted with NaOH to produce the hydride derivative **(1)**. Compound **1** was identified as a product in this reaction by the characteristic singlet in the ^1H NMR at -6.55 ppm assigned to the hydride ligand and the other resonances reported above (see discussion of compound **1**). It is worth noting

that this reaction occurs with the formation of $Cp^*Re(CO)_3$ as a byproduct as evidenced by the strong absorptions at 1910 cm^{-1} and 2006 cm^{-1} in acetone assigned to the asymmetric and symmetric carbonyl stretches. The mechanism proposed for this reaction is the attack of the hydroxide ion on the carbonyl carbon of the methoxycarbonyl group to give the hydroxycarbonyl complex which then reacts with further hydroxide as shown previously in Scheme III to give the hydride **1**.

Experimental Section

General

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

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

Infrared spectra were measured by using a Bomem Michelson 120 FTIR instrument, calibrated against polystyrene or carbon monoxide. CaF_2 cells (0.1 mm) were used to measure the IR spectra in solution using the solvent as an internal reference and substracting this from the spectra of the sample. NMR spectra were recorded by Mrs. M. Tracey on a Bruker AMX-400 instrument at 400.13 and 100.6 (referred to TMS) for ^1H and ^{13}C and at 161.92 MHz for ^{31}P (referred to 85 % phosphoric acid). A Bruker SY-100 instrument was used to record some of the ^1H NMR spectra. Mass spectra were obtained by Mr. G. Owen on a Hewlett-Packard Model 5985 GC mass spectrometer capable of providing both electron impact (EI) and chemical ionization (CI) methods. The m/z values reported are referred to ^{187}Re. Microanalyses were performed by Mr. M. K. Yang of the Microanalytical Laboratory of S.F.U.

The p-methoxybenzenediazonium tetrafluoroborate salt [*p*-$N_2C_6H_4OMe$][BF_4] was prepared by diazotization of *p*-anisidine (Aldrich) with $NaNO_2$ and was recrystallized from acetone/diethyl ether. Pentamethylcyclopentadiene (Cp*H) was prepared by the method 1 reported by Whitesides.[29] The decacarbonyldirhenium (Strem Chemicals) and sodium hydroxide (Fisher Scientific., AR, chloride ≤ 1%) were used directly as purchased. The $Cp^*Re(CO)_3$ was synthesized by the method of Gladysz.[30]

Preparation of (η^5-C_5Me_5)Re(H)(CO)(*p*-$N_2C_6H_4OMe$) (1)

Method 1

This synthesis used the method reported by Sutton and Klahn[25] which involves the reaction of [(η^5-C_5Me_5)$Re(CO)_2$(*p*-$N_2C_6H_4OMe$)][BF_4] **(A)** with an aqueous solution of NaOH (6M) in CH_2Cl_2 followed by extraction of the hydride **(1)** into tetrahydrofuran (THF) and then hexane in two sequential steps to give a reported yield of **(1)** of 80 %.

In our hands the IR spectrum of the THF extract showed two $\nu_{(CO)}$ absorptions at 1911 and 1925 cm^{-1} in a ratio 1/0.8 rather than the one expected if only **(1)** were present. After extraction into hexane, a solid remained, which was identified as (η^5-C_5Me_5)Re(Cl)(CO)(*p*-$N_2C_6H_4OMe$) **(2)** (see below) by comparison with the spectroscopic data reported in the literature.[27] The hexane extract showed the presence of both compounds. They were separated on a neutral alumina column prepared in hexane and with benzene as the initial eluant. Compound **(1)** was eluted as a yellow solution (yield 52%, 21 mg, 0.043mmol with respect to 50 mg (0.083 mmol) of compound **A**). Compound **2**

eluted with dichloromethane as a red solution (yield 41.6%, 18.1 mg, 0.035 mmol).

Data for compound **1**: IR (hexane, cm^{-1}): $\nu_{(CO)}$ 1925, $\nu_{(NN)}$ 1613; (THF, cm^{-1}): $\nu_{(CO)}$ 1911, $\nu_{(NN)}$ 1618; (benzene, cm^{-1}): $\nu_{(CO)}$ 1912, $\nu_{(NN)}$ 1609; (acetone, cm^{-1}): $\nu_{(CO)}$ 1910, $\nu_{(NN)}$ 1618. Literature[25]: R (hexane, cm^{-1}): $\nu_{(CO)}$ 1925, $\nu_{(NN)}$ 1619; (THF, cm^{-1}): $\nu_{(CO)}$ 1910, $\nu_{(NN)}$ 1615. ^1H NMR (100 MHz, C_6D_6): δ 1.92 (s, 15H, C_5Me_5), 3.29 (s, 3H, OMe), 6.79 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz), 7.63 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz), -5.86 (s, 1H). ^1H NMR (100 MHz, acetone-d_6): δ 2.21 (s, 15H, C_5Me_5), 3.81 (s, 3H, OMe), 6.99 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz), 7.29 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz), -6.55 (s, 1H). Literature[25] ^1H NMR (100 MHz, C_6D_6): δ 1.90 (s, 15H, C_5Me_5), 3.27 (s, 3H, OMe), 6.78 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz), 7.61 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz), -5.88 (s, 1H).

Data for compound **2**: IR (hexane, cm^{-1}): $\nu_{(CO)}$ 1940, $\nu_{(NN)}$ 1630; (benzene, cm^{-1}): $\nu_{(CO)}$ 1927, $\nu_{(NN)}$ 1628; (THF, cm^{-1}): $\nu_{(CO)}$ 1925, $\nu_{(NN)}$ 1628; (CH_2Cl_2, cm^{-1}): $\nu_{(CO)}$ 1925, $\nu_{(NN)}$ 1626; (diethyl ether, cm^{-1}): $\nu_{(CO)}$ 1933, $\nu_{(NN)}$ 1628. Literature[27]: IR (CH_2Cl_2, cm^{-1}): $\nu_{(CO)}$ 1924, $\nu_{(NN)}$ 1624. ^1H NMR (C_6D_6, 100 MHz): δ 1.74 (s, 15H, C_5Me_5), 3.20 (s, 3H, OMe), 6.67 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz), 7.60 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz). ^1H NMR (acetone-d_6, 100 MHz): δ 2.03 (s, 15H, C_5Me_5), 3.83 (s, 3H, OMe), 7.00 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz), 7.27 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz). ^1H NMR ($CDCl_3$, 100 MHz): δ 2.03 (s, 15H, C_5Me_5), 3.82 (s, 3H, OMe), 6.91 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz), 7.28 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz). Literature[27] ^1H NMR (100 MHz, $CDCl_3$): δ 2.00 (s, 15H, C_5Me_5), 3.81 (s, 3H, OMe), 6.92 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz), 7.29 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz). M.S. (EI): m/z 520 $(M)^+$: 492 $(M-(CO))^+$.

Method 2:

This method avoids the use of chlorinated solvents. The dicarbonyl complex **A** (50 mg, 0.083 mmol) was dissolved in acetone (ca 4 mL) and 2 mL of aqueous NaOH (6M) was added. The solution was stirred for about 1 h and then allowed to separate into two layers. The aqueous (bottom) layer was removed and discarded. The acetone was removed under vacuum from the remaining organic solvent layer. The product was extracted into hexane and filtered through Celite to give a yellow solution. This extract was checked by IR spectroscopy and two $\nu_{(CO)}$ absorptions were also observed corresponding to compounds **(1)** and **(2)**. The solvent was removed under vacuum and the hydride was purified by chromatography on neutral alumina column as has been reported above. When the acetone was used as a solvent it was found that the % of the hydride increased by 10 % (62%, 25 mg, 0.052 mmol for **1** and 34%, 15 mg, 0.028 mmol for **2**).

Preparation of (η^5-C_5Me_5)Re(CH_3)(CO)(*p*-$N_2C_6H_4OMe$) (3)

An excess of CH_3MgBr (ca. 3 mL of 3.0 M in Et_2O, Aldrich) was added to a stirred solution of compound **2** (50 mg, 0.010 mmol) in diethyl ether (ca. 3 mL) that had been freshly distilled. The reaction was followed by IR spectroscopy and was complete in 36 h (Fig 2.1). Two drops of water were added to destroy the excess Grignard reagent, and the desired product was extracted into hexane/ether (1/1) and the solution filtered through Celite. The solvent was removed under vacuum to give an oily orange-yellow solid which was recrystallized by dissolving it in cold hexane and keeping it for 6-7 h at -78 °C.

The yellow solid was washed with cold hexane and dried on the vacuum line: Yield 38.9 mg (0.078 mmol), 81%. IR (CH_2Cl_2, cm^{-1}): $\nu_{(CO)}$ 1896, $\nu_{(NN)}$ 1613 IR (hexane, cm^{-1}): $\nu_{(CO)}$1915, $\nu_{(NN)}$ 1618 ; IR (ether. cm^{-1}): $\nu_{(CO)}$ 1910, $\nu_{(NN)}$1618. ^1H NMR ($CDCl_3$, 400MHz): δ 1.16 (s, 3H, CH_3), 1.98 (s, 15H, Cp*), 3.83 (s, 3H, OMe), 6.89 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz); 7.19 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz). MS (EI): m/z 500 $(M)^+$, 472 $(M-(CO))^+$. Elemental Analysis: Calculated: C, 45.68; H, 5.04; N, 5.61. Found C, 46.04; H, 5.23; N, 5.47.

Preparation of $(\eta^5\text{-}C_5Me_5)Re(Cl)(PMe_3)(p\text{-}N_2C_6H_4OMe)$ (4)

A large excess of KCl was added as a finely ground solid to a stirred solution of $[(\eta^5\text{-}C_5Me_5)Re(PMe_3)(CO)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **(C)** (50 mg, 0.080 mmol) in $CHCl_3$ (5 mL). Subsequently, NaOH in ethanol (4M, 3 mL) was added slowly with stirring. The solution was stirred overnight and then the excess KCl was removed by filtration through Celite. The solvent was removed on the vacuum line and the remaining solid extracted with hexane; removal of the hexane from the extract yielded a yellow oily product. This was recrystallized from hexane to give a brown solid in 78% yield (38.2 mg, 0.067 mmol). IR (CH_2Cl_2 or $CHCl_3$, cm^{-1}): $\nu_{(NN)}$ 1605. ^1H NMR ($CDCl_3$): δ 1.54 (d, 9H, PMe_3 , $^3J_{PH}$ = 9.3 Hz), 1.93 (s, 15H, Cp*), 3.79 (s, 3H, OMe), 6.87 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz), 7.26 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz). $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz): δ 10.96 (s, C_5Me_5), 16.68 (d, PMe_3, $^2J_{PC}$ = 34 Hz), 55.52 (s, OMe), 100.76 (s, C_5Me_5), 114.34, 120.85, 123.61, 156.93 (s, C_6H_4). $^{31}P\{^1H\}$NMR (acetone d_6): δ 29.00 (s, PMe_3); ($CDCl_3$): 35.64 (s, PMe_3). MS (EI) m/z: 568 $(M)^+$, 492 $(M\text{-}PMe_3)^+$.

Elemental Analysis: Calculated : C, 42.28 ; H, 5.50 ; N, 4.93 ; Found: C, 42.44 ; H, 5.56 ; N, 5.10.

Together with compound **4** a small amount of $(\eta^5\text{-}C_5Me_5)Re(I)(PMe_3)(p\text{-}N_2C_6H_4OMe)$ was found to be produced. Although its concentration was not enough for full characterization, its presence was detected by MS giving rise to peaks at 660 $(M)^+$ and 584 $(M\text{-}PMe_3)^+$.

Preparation of $(\eta^5\text{-}C_5Me_5)Re(Cl)\{P(OMe)_3\}(p\text{-}N_2C_6H_4OMe)$ (5)

A solution of $[(\eta^5\text{-}C_5Me_5)Re\{P(OMe)_3\}(CO)(p\text{-}N_2C_6H_4OMe)][BF_4]$ **(D)** (50 mg, 0.070 mmol) and NaOH (4M in ethanol, 2 mL) in ca. 5 mL of chloroform was stirred for about 2 min at room temperature followed by addition of KCl (21 mg, 0.28 mmol) and the mixture was stirred for 60 min. The solution was filtered through Celite to remove the excess of the inorganic salt. The solvent was removed under vacuum and the residual yellow oil was dissolved in hexane and chromatographed on a neutral alumina column prepared in hexane. Elution with hexane-diethylether (2/1) eluted the desired product in 43% yield (19 mg, 0.031 mmol). A second product **(6)** was eluted from the column by using chloroform as eluant and was identified as $(\eta^5\text{-}C_5Me_5)Re(CO)\{PO(OMe)_2\}(p\text{-}N_2C_6H_4OMe)$ by comparison with a sample prepared by a different method (see below). It was purified by chromatography on a neutral alumina column prepared in hexane and washed with hexane (3 mL) and ether (3 mL). Acetone failed to remove the compound from the column, but chloroform did so. The solvent was removed to give **6** as a yellow oil in 51% yield (i.e., the major product of this reaction, 22 mg, 0.037 mmol).

Note: The amount of the phosphonate compound **6** produced in this reaction was found to be dependent on the amount of KCl used and the order of addition of the NaOH and KCl. It is, therefore, recommended to add the NaOH before the KCl (see Discussion).

Data for compound **5**: IR ($CHCl_3$ or CH_2Cl_2, cm^{-1}): $\nu_{(NN)}$ 1609. ^1H NMR ($CDCl_3$): δ 1.93 (s, 15H, Cp*), 3.62 (d, 9H, $P(OMe)_3$, $^3J_{PH}$ = 11.5 Hz), 3.79 (s, 3H, OMe), 6.87 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz); 7.27 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz). $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz): δ 10.17 (s, C_5Me_5), 52.54 (s, $P(OMe)_3$), 55.48 (s, OMe), 101.86 (s, C_5Me_5), 114.86, 121.99, 157.52 (s, C_6H_4). $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 119.75 (s, $P(OMe)_3$). MS (EI) m/z: 616 $(M)^+$, 492 $[M\text{-}P(OMe)_3]^+$. Elemental analysis : Calculated : C, 38.99 ; H, 5.07 ; N, 4.55. Found: C, 39.21 ; H, 5.26 ; N, 4.45.

Preparation of $(\eta^5\text{-}C_5Me_5)Re(CO)\{PO(OMe)_2\}(p\text{-}N_2C_6H_4OMe)$ (6)

A solution of **D** (50 mg, 0.070 mmol) in tetrahydrofuran (5 mL) was heated at 40 °C for 3 h with a 20% - 30% excess of KI. When almost all the KI had dissolved, the IR spectrum of the reaction solution showed the absence of starting material. The solution was filtered through Celite to remove the undissolved KI and the solvent removed under vacuum. The oily product was extracted with diethyl ether and the solution filtered through Celite. The solvent was again removed and the remaining compound dissolved in acetone and placed onto a short neutral alumina column prepared in hexane. The column was eluted in order with hexane (3 mL), hexane/acetone 1/1 (3 mL), acetone (2 mL) and finally, chloroform; the last fraction contained the product. After the

chloroform was removed under vacuum, the yellow oily product was obtained in 97% yield (41 mg, 0.070 mmol). IR (CH_2Cl_2, cm^{-1}): $\nu_{(CO)}$ 1940 ,$\nu_{(NN)}$ 1641 . ^1H NMR ($CDCl_3$): δ 2.15 (s, 15H, Cp*), 3.56 (d, 3H, $PO(OMe)_2$, $^3J_{PH}$ = 11.8 Hz), 3.59 (d, 3H, $PO(OMe)_2$, $^3J_{PH}$ = 11.8 Hz), 3.82 (s, 3H, OMe), 6.93 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz); 7.36 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz). $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz): δ 10.4 (s, C_5Me_5), 50.33 (s, OMe from $PO(OMe)_2$), 50.39 (s, OMe from $PO(OMe)_2$), 55.6 (s, OMe), 105.0 (s, C_5Me_5), 114.7, 122.8, 124.0, 160.3 (s, C_6H_4), 203.6 (d, (CO), $^2J_{PC}$ = 19 Hz). $^{31}P\{^1H\}$NMR ($CDCl_3$): δ 68.7 (s, $PO(OMe)_2$). MS (EI) m/z: 594 $(M)^+$.

Preparation of (η^5-C_5Me_5)Re(Cl)(PPh_3)(*p*-$N_2C_6H_4OMe$) (7)

A large excess of KCl was added as a finely ground solid to **E** (50 mg) in chloroform (ca. 5mL) followed by ethanolic solution of NaOH (4M, 3mL). The mixture was stirred overnight. After the excess NaOH and KCl were separated by filtration through Celite, the solvent was removed under vacuum and the residue extracted into hexane to give a yellow-orange solution. Compound **7** was obtained by recrystallization from hexane as a brown solid in 83% yield (36 mg, 0.048 mmol). IR (CH_2Cl_2, cm^{-1}): $\nu_{(NN)}$ 1607 . ^1H NMR ($CDCl_3$):δ 1.65 (s, 15H, Cp*), 3.80 (s, 3H, OMe), 6.84 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz), 7.21 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz), 7.30-7.58 (m, 15H, PPh_3). $^{13}C\{^1H\}$NMR ($CDCl_3$, 100 MHz): δ 10.00 (s, C_5Me_5), 55.49 (s, OMe), 100.92 (s, C_5Me_5), 114.04 (s, C_6H_4), 121.75-134.34 (C_6H_4 and C_6H_5), 167.71 (s, C_6H_4). $^{31}P\{^1H\}$NMR (acetone-d_6): δ 17.11 (s, PPh_3). MS (EI) m/z: 754 $(M)^+$; 492 $(M\text{-}PPh_3)^+$.

Reaction of 4 with KBr.

A solution of **4** (10 mg, 0.018 mmol) in acetone was stirred for 12 h in the presence of an excess of KBr. After this time, the solution was filtered through Celite to separate the undissolved KBr and the solvent was removed under vacuum. Extraction of the remaining solid in hexane and subsequent removal of solvent gave a yellow oily product. The ^{1}H NMR spectrum of this product in $CDCl_3$ was identical to that of the starting material **4**. The mass spectrum, however, showed, in addition to those for **4**, peaks consistent with the formation of (η^5-C_5Me_5)Re(Br)(PMe_3)(*p*-$N_2C_6H_4OMe$) **(8)**. The patterns of these peaks were in good agreement with those simulated by computer for **8**. The parent ions $\mathbf{4}^+$ and $\mathbf{8}^+$ were observed in 14/9 intensity ratio (Fig. 2.4). MS (EI): m/z 568 $(\mathbf{4})^+$ and 612 $(\mathbf{8})^+$.

Reaction of 4 with CH_3MgBr.

Compound **4** (10 mg, 0.018 mmol) was dissolved in freshly distilled ether (5 mL) and methyl magnesium bromide, CH_3MgBr, (20 % excess, 3M in ether) was added slowly with stirring. After 12 h, 3 mL of hexane were added and after that a drop of water to destroy the excess CH_3MgBr. The hexane/ether supernatant was filtered through Celite. The solvent was removed under vacuum and the remaining yellow oily product extracted into hexane. After several attempted chromatographic separations on neutral alumina, the product was always contaminated with the starting material **4**. The ^{1}H NMR spectrum of the mixture showed no signal corresponding to a methyl group, but a new Cp*

signal, as well as a new doublet attributed to the protons of a PMe_3 group. This product was identified as the bromo compound **8** as shown by its mass spectrum. ^1H NMR ($CDCl_3$):δ 1.61 (d, 9H, PMe_3 , $^3J_{PH}$ = 9.3 Hz), 1.97 (s, 15H, Cp*), 3.80 (s, 3H, OMe), 6.88 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz), 7.28 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz). MS (EI): m/z 612 $(M)^+$, 475 $(M - N_2C_6H_4OMe - 2H)^+$.

Reaction of C with NaOH

The complex **C** (ca.10 mg) was dissolved in acetone (3 mL), and NaOH in water (6M) (ca. 1 mL) was added. The mixture was stirred for 2 h at room temperature. After that time, the aqueous solution was separated and the solvent was removed under vacuum. The oily product was extracted into hexane and filtered through Celite. The expected hydride $(\eta^5\text{-}C_5Me_5)Re(H)(PMe_3)(p\text{-}N_2C_6H_4OMe)$ was not obtained. The product obtained was identified as $(\eta^5\text{-}C_5Me_5)Re(I)(PMe_3)(p\text{-}N_2C_6H_4OMe)$ **(9)** and is presumed to be formed through iodide impurities from previous steps in the preparation of **C** (see discussion). IR (acetone, cm^{-1}): $\nu_{(NN)}$ 1604. ^1H NMR ($CDCl_3$): δ 1.59 (d, 9H, PMe_3 , $^3J_{PH}$ = 10 Hz), 2.05 (s, 15H, Cp*), 3.72 (s, 3H, OMe), 6.80 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz), 6.96 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz). $^{13}C\{^1H\}$NMR, (acetone-d_6, 100 MHz): δ 11.7 (s, C_5Me_5), 24.1 (d, PMe_3, $^2J_{PC}$ = 38.1 Hz), 55.7 (s, OMe), 100.1 (s, C_5Me_5), 114.8, 122.0, 124.4, 158.3 (s, C_6H_4). $^{31}P\{^1H\}$NMR (acetone- d_6): δ 37.6 (s, PMe_3); ($CDCl_3$) δ 43.1 (s, PMe_3). MS (EI) m/z: 660 $(M)^+$, 584 $(M\text{-}PMe_3)^+$, 523 $(M\text{-}N_2C_6H_4OMe - 2H)^+$.

Reaction of (η^5-C_5Me_5)Re(COOMe)(CO)(*p*-$N_2C_6H_4OMe$) (10) with NaOH.

Aqueous NaOH (6M, ca. 2 mL) was added to a stirred solution of compound 10[27] (20 mg, 0.037 mmol) in acetone (ca. 3 mL). After 30 min, the aqueous layer was separated by pipet and the solvent was removed from the organic phase under vacuum. The residue was dissolved in hexane and filtered through Celite. The IR spectrum of the product showed the presence of the hydride derivative **1** together with the tricarbonyl compound (η^5-C_5Me_5)Re$(CO)_3$. The ^{1}H NMR and mass spectra corroborated these results. IR (acetone, cm^{-1}): $\nu_{(CO)}$ 1910; $\nu_{(NN)}$ 1618 for **1** ; $\nu_{(CO)}$ 2006 , 1910 for the tricarbonyl compound. ^{1}H NMR (100 MHz, acetone-d_6): δ 2.21 (s, 15H, C_5Me_5), 3.81 (s, 3H, OMe), 6.99 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz); 7.29 (d, 2H, C_6H_4, $^3J_{HH}$ = 9 Hz); -6.55 (s, 1H). MS (EI) m/z for (η^5-C_5Me_5)Re$(CO)_3$: 406 $(M)^+$, 378 $(M-(CO))^+$; for **1**: 485 $(M-H)^+$.

Chapter III: Dynamic ^{31}P and ^{1}H NMR spectroscopy

III.1 Introduction

The study of diazenido compounds has increased dramatically in the last few years.[31] A major reason for this is that these studies may help in the understanding of the nitrogen fixation process. This research area, however, has been dominated by synthesis and characterization of novel compounds with diazenido ligands. To our knowledge, there have been no studies on the structure and dynamics of the diazenido complexes in solution.

In complexes of the type $[(\eta^5\text{-}C_5Me_5)ReLL'(p\text{-}N_2C_6H_4OMe)]^+$ the position that the aryl group occupies (as demonstrated by a crystal structure[24]) with respect to the plane that contains the ReNN unit and bisects the LReL' angle was shown in Fig1.2. Related structures have been observed in different diazenido compounds.[15,32,33] Based on this fact, two conformational isomers are possible. Such isomers were first detected at low temperature in the rhenium cationic complexes of general formula $[(\eta^5\text{-}C_5Me_5)ReLL'(p\text{-}N_2C_6H_4OMe)][BF_4]$ in this laboratory.[23] These isomers were observed to be in dynamic equilibrium on the NMR time scale such that coalescence of the signals from each isomer is observed for the complexes in solution at ambient temperature. The barrier to isomerization could be interpreted as resulting from either i) restricted rotation about the ReNN axis or ii) inversion at the β nitrogen or a combination of them as presented in Fig. 3.1.

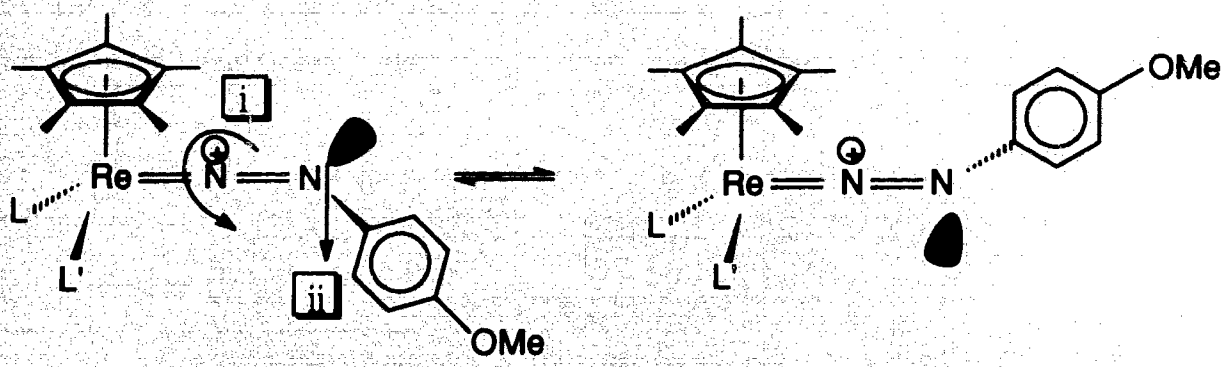


Fig 3.1 Possible mechanism of isomerization of aryldiazenido ligand in Re complexes.

The $\nu_{(NN)}$ stretches for these cationic compounds[26] showed no correlation with the $\Delta G^{\neq}$ obtained for the barriers.[23] For instance, when L = CO and L' = PMe_3, the complex has $\nu_{(NN)}$ absorption at 1677 cm^{-1} and for L' = $P(OMe)_3$ the absorption appears at 1689 cm^{-1}but the barrier is lower. The NN bond in the first example would appear to be weaker than in the trimethyl phosphite complex and, therefore, a faster NN bond rotation might be expected, and hence a lower activation barrier, if rotation about the NN bond is the dominant mechanism.

The different population in these isomers is another observation to be explained. The steric effect that the L and L' ligands produce could give rise to the different populations. The electronic effect of these ligands, donating or withdrawing electronic density from the metal center and thus affecting the back bonding of the Re atom to the N_2Ar ligand could also influence the distribution of isomers.

In order to further understand this interesting isomerization, we have carried out low temperature NMR studies on some of the compounds reported in

Chapter II namely $(\eta^5\text{-}C_5Me_5)Re(H)(CO)(p\text{-}N_2C_6H_4OMe)$ **(1)**, $(\eta^5\text{-}C_5Me_5)Re(CH_3)(CO)(p\text{-}N_2C_6H_4OMe)$ **(3)**, $(\eta^5\text{-}C_5Me_5)Re(Cl)(PMe_3)(p\text{-}N_2C_6H_4OMe)$ **(4)**, $(\eta^5\text{-}C_5Me_5)Re(Cl)\{P(OMe)_3\}(p\text{-}N_2C_6H_4OMe)$ **(5)** and $(\eta^5\text{-}C_5Me_5)Re(Cl)(PPh_3)(p\text{-}N_2C_6H_4OMe)$ **(7)**. In all cases, except **7**, two isomers were detected at low temperature that were in rapid equilibrium on the NMR time scale at room temperature. Each of these complexes is neutral, compared with the cationic rhenium complexes described above which are concurrently being studied in our laboratory.[23] They have significantly lower values of $\nu_{(NN)}$ so that they provide additional cases in which to test whether or not there is any correlation of $\Delta G^{\neq}$ with $\nu_{(NN)}$ for these isomerizations.

The results of this study including line shape analyses of some of the variable temperature NMR spectra form the basis of this chapter.

III.2 Results and Discussion

III.2.1 Dynamic ^1H and ^{31}P NMR experiments

As mentioned in the Introduction (III.1), the isomerization of the cations $[(\eta^5\text{-}C_5Me_5)Re(CO)(PMe_3)(p\text{-}N_2C_6H_4OMe)]^+$ has been interpreted[23] as the interconversion of the conformers I and II of the aryldiazenido ligand as shown the Newman projection in Fig. 3.2. If this occurs by an inversion at Nβ the isomers interconvert via a linear Re-NNC skeletal transition state, not shown. If this occurs by a rotation about the ReNN axis, the transition state is the conformer III. When L = L' (eg., PMe_3) two equal intensity PMe_3 ^{31}P resonances were observed at low temperature which coalesced to a single resonance on increasing the temperature. The two resonances are interpreted to arise from the inequivalent phosphorus ligands in the ground state conformer I (and in its enantiomer II), and the exchange results from the rapid interconversion of the enantiomers. The population of the symmetrical conformer III must be small, consistent with it being a higher energy state, since no additional resonance corresponding to the equivalent phosphorus atoms in III is observable in the low temperature spectrum.

When L and L' are different ligands, or as in this case, the ligands are L and X, the conformers I and II may have significantly different ground state energies. In the rotation model, the observation of (say) two phosphorus resonances at low temperature that coalesce at higher temperature could again be interpreted as I ↔ II interconversion via unobserved III. However, the steric or electronic properties of L and X could be such as to preclude conformer II and significantly populate III. In this case, the low temperature resonances would

originate in I and III and would again coalesce if interconversion of I and III by rotation is rapid.

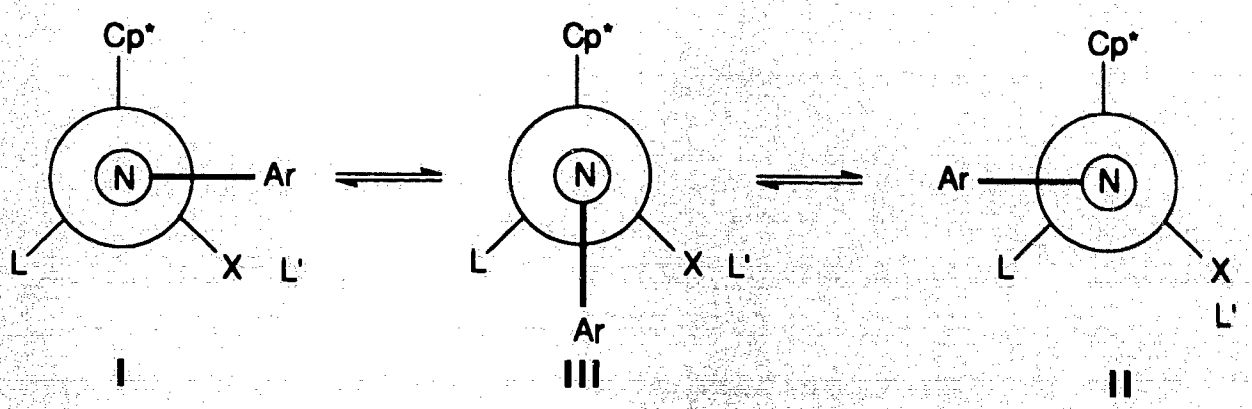


Fig 3.2: The idealized Newman projections for the two conformers of the Re aryldiazenido complexes looking down the NNRe axis.

Because this latter situation cannot be responsible for the behaviour of the complexes with L = L', we are inclined to think that it is not responsible when L ≠ L' or when L' = X (as here). Therefore the NMR behaviour will be interpreted as the interconversion of the conformers I and II in all cases where coalescence is observed.

The variable temperature ^{1}H or ^{31}P NMR spectra of $(\eta^5\text{-}C_5Me_5)Re(H)(CO)(p\text{-}N_2C_6H_4OMe)$ **(1)**, $(\eta^5\text{-}C_5Me_5)Re(CH_3)(CO)(p\text{-}N_2C_6H_4OMe)$ **(3)**, $(\eta^5\text{-}C_5Me_5)Re(Cl)(PMe_3)(p\text{-}N_2C_6H_4OMe)$ **(4)** and $(\eta^5\text{-}C_5Me_5)Re(Cl)\{P(OMe)_3\}(p\text{-}N_2C_6H_4OMe)$ **(5)** were consistent with the presence of two isomers in solution that were in dynamic equilibrium on the NMR time scale. For example, the singlet resonance due to the OMe group in the ^{1}H NMR spectrum of **3** at room temperature decoalesced such that at temperatures of ~ -40 °C two sharp singlets were observed. For the methyl

derivative **3** and the hydride **1** there was similar decoalescence of the methyl and hydride singlet resonances, respectively. This is shown in Fig 3.3. Likewise, the singlet resonance observed in the ^{31}P NMR spectra of **4** and **5** at room temperature, decoalesced to two unequal signals at ~ -50 °C. This is illustrated in Fig 3.4.

The ratio of isomers for **1** and **3** was approximately 1:1 whereas for the PMe_3 compound **4** it was 4.5:1 and for the $P(OMe)_3$ derivative **5** it was 3.5:1. Interestingly, for $(\eta^5\text{-}C_5Me_5)Re(Cl)(PPh_3)(p\text{-}N_2C_6H_4OMe)$ **(7)** there was no evidence for a second isomer in the low temperature ^{31}P NMR spectra of this complex.

The differences in the isomer ratios is tentatively attributed to steric factors. In compound **7** steric interactions between the phenyl substituents and the aryl group of the diazenido ligand are presumably large such that conformer II (Fig. 3.2) is not significantly populated (the cone angles of $P(OMe)_3$, PMe_3 and PPh_3 are 107°, 118° and 145°, respectively).

In compounds **1** and **3**, steric interactions between the hydride or methyl group with the aryl substituent on the aryldiazenido ligand are probably small and comparable to the interaction between the aryl and the carbonyl ligand. For this reason, the populations of conformers I and II are approximately the same. In **4** and **5** the steric interactions between the L and aryl groups are probably intermediate such that conformer II (Fig. 3.2) is populated, but not to the same extent as I.

In order to determine the activation parameters for the rearrangement, complete lineshape analyses of the variable temperature NMR spectra for **(1)**, **(3)**, **(4)** and **(5)** were carried out by using the program DNMR3.[34] The calculation of the rate constants for the isomerization were achieved by trial and

error: a series of simulated spectra at different rates were plotted until the best possible fit between the calculated and the experimental bandshape was obtained. This method of evaluation of the rate constants is called the complete bandshape method (CBS) or complete lineshape method (CLS). The rate constants were evaluated from the higher to the less populated isomer in all cases.

There was a significant variation in the chemical shifts with the temperature in the NMR spectra for all the compounds reported here. This was especially the case for the $^{31}P\{H\}$ NMR spectra of **4** and **5**. It was also assumed that the ratio of isomers did not change significantly over the temperature range at which coalescence occurred.

$(\eta^5\text{-}C_5Me_5)Re(H)(CO)(p\text{-}N_2C_6H_4OMe)$ (1):

The experimental and calculated ^1H NMR spectra at several temperatures are shown in Fig 3.5 and 3.6 for compound **1**. The two hydride resonances at δ 6.60 and δ 6.68 at 220 K (in an approximate 1:1 ratio) broaden at ~ 256 K and at room temperature coalesce to give a single peak at δ -6.55. The rate constants for **1** at the different temperatures are given in Table 3.1.

Table 3.1: Rate constants for conformer exchange in **1**

Temperature (K)	Rate constant (s^{-1})
235	3.5 ± 0.5
251	35 ± 5
254	40 ± 5
258	70 ± 5
293	2000 ± 50

• **(η^5-C_5Me_5)Re(CH_3)(CO)(*p*-$N_2C_6H_4OMe$) (3):**

The ^1H NMR spectrum of **3** at 231 K (Fig 3.8) showed two resonances at δ 1.13 and δ 0.93 in a ratio of about 1:1 due to the methyl protons and two singlets at δ 3.81 and δ 3.78 assigned to the methoxy groups. These methoxy resonances coalesced to a sharp singlet at a lower temperature (the signal is already sharp at 261 K) than that for the methyl resonances. This is due to the larger chemical shift difference between the two resonances for the methyl ligand. At ~275 K, the two methyl resonances coalesced, and at room temperature (291 K) gave a single peak (Fig. 3.9).

The apparent triplet (together with the two doublets) observed for the signal due to the aryl protons at low temperature is interpreted as two overlapping AB patterns. In the fast exchange limit, these AB patterns should collapse to a single AB pattern. This was not reached in the ^1H NMR spectrum at room temperature (Fig 3.9) at an operating frequency of 400 MHz. It was, however, seen in the corresponding spectrum at an operating frequency of 100 MHz. The signal corresponding to the Cp* ligand did not split even at the lowest

temperature studied (231 K). This is attributed to near degeneracy of the Cp* resonances of the two isomers because the site of isomerization is too far removed from the Cp* ligand to affect the chemical shift of the Cp* resonance.

A preliminary calculation was carried out by using the equation $k = 2.22 \bullet \Delta\nu_{AB}$ where k is the rate constant at the temperature at which coalescence occurs and $\Delta\nu_{AB}$ is the chemical shift difference between the two signals due to the sites undergoing exchange as obtained from the low temperature limit spectrum. (This equation only applies to a system where there are equal population of the two sites undergoing exchange). The calculations were carried out for the resonances of the methyl and the methoxy groups at their respective coalescence temperatures. The $\Delta G^{\neq}$ values so obtained were $\Delta G^{\neq} = 55$ kJmol^{-1} at 275 K as calculated from the methyl resonances and $\Delta G^{\neq} = 56$ kJmol^{-1} at 261 K from the methoxy resonances.

The detailed kinetics of isomerization were studied by using the methyl signal at δ 1.07 (in acetone-d_6) in the VT ^{1}H NMR spectra of **3**. Since not enough sets of temperatures were available for the methoxy resonance (due to the lower coalescence temperature) this resonance was not taken into account for the calculations of the activation parameters. The rate constants obtained by using the line shape simulation analyses are reported in Table 3.2.

Table 3.2: Rate constants for conformer exchange in **3**

Temperature (K)	Rate constant (s^{-1}) Me	Rate constant (s^{-1}) OMe
241	2 ± 0.5	2.5 ± 0.5
261	20 ± 2.5	25 ± 2.5
271	70 ± 5	
273	90 ± 5	
275	100 ± 10	
281	200 ± 10	
291	500 ± 10	

• **(η^5-C_5Me_5)Re(Cl)(PMe_3)(*p*-$N_2C_6H_4OMe$) (4):**

The line shape analysis for compound **4** was carried out by comparing the experimental $^{31}P\{^1H\}$ NMR spectra with the simulated spectra at specific temperatures. Fig 3.10 and 3.11 show the two resonances corresponding to the phosphine ligand of the two isomers in the experimental and calculated $^{31}P\{^1H\}$ NMR spectra. These signals appear at δ 25.8 ppm and δ 32.0 ppm at 213 K. The experimental spectra indicated an isomer population of 82 % and 18 % (~4.5:1) of the two isomers. The resonances broaden with an increase in temperature and at ~ 243 K, just one broad signal was detected. At 293K (i.e. room temperature) a sharp resonance at approximately the weighted average value of δ 29.0 ppm was observed.

The variation of the rate constant with the temperature for **4** is presented in Table 3.3.

Table 3.3 : Rate constants for conformer exchange in **4**

Temperature (K)	Rate constant (s^{-1})
223	80 ± 5
233	290 ± 10
236	600 ± 50
243	900 ± 50
273	15000 ± 100
293	90000 ± 100

• (η^5-C_5Me_5)Re(Cl){P(OMe)$_3$}(*p*-$N_2C_6H_4OMe$) (5):

Compound **5** was also studied by variable temperature $^{31}P\{^1H\}$ NMR spectroscopy (Fig 3.12). At the lowest temperature investigated (203 K) the spectrum exhibited two sharp peaks corresponding to the resonances of the two isomers at δ 122.2 ppm and δ 121.2 ppm in a ratio of 78 % and 22 % (3.5:1). The signals began to broaden as soon as the temperature was increased above 203 K and at ~ 233 K the signals had coalesced into one broad signal centered at ~δ 121.5 ppm. At 293 K a sharp signal at δ 119.7 ppm was observed indicative of rapid interconversion of the isomers at this temperature. That the signal in the high temperature spectrum is significantly different from to the weighted average of the two low temperature signals is attributed to a marked temperature dependence of the ^{31}P NMR resonances.

The rate constants derived from the line shape analysis are tabulated in 3.4.

Table 3.4: Rate constants for conformer exchange in **5**

Temperature (K)	Rate constant (s^{-1})
213	6 ± 0.5
225	30 ± 2
230	60 ± 5
253	820 ± 20
273	5700 ± 100
293	30000 ± 1000

• **(η^5-C_5Me_5)Re(Cl)(PPh_3)(*p*-$N_2C_6H_4OMe$) (7):**

The $^{31}P\{^1H\}$ NMR signal of compound **7** in acetone-d_6 at δ 17.11 ppm was used to check for isomerization. Spectra were recorded from 293 K to 213 K, but no change in the signal was observed. This may be interpreted in at least three ways. The first is that isomerization between conformer I and II (Fig. 3.2) is still rapid on the ^{31}P NMR time scale. The second is that the ^{31}P NMR resonances for the two conformers are accidentally degenerate. The third explanation is that there is slowed isomerization but the population of one of the isomers is too small to detect. Given the similarities in the size of the barriers in compounds **4** and **5** and related cationic compounds the first explanation can probably be ruled out. The second is unlikely. From a comparison of the other phosphorus derivatives (i.e. **4** and **5**) it is believed that the last explanation is probably the most likely one.

III.2.2 Activation parameters

III.2.2.1 Comparison of activation parameters

By using the modified Eyring equation and the linear least-square polynomial program, the values of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were obtained from the slope and intercept respectively of the plot of ln (k_r / T) versus (1 / T). From these values the appropriate $\Delta G^{\neq}$ at 298 K was calculated. These values are presented in Table 3.5.

Table 3.5: Activation parameters for **1**, **3**, **4** and **5**.

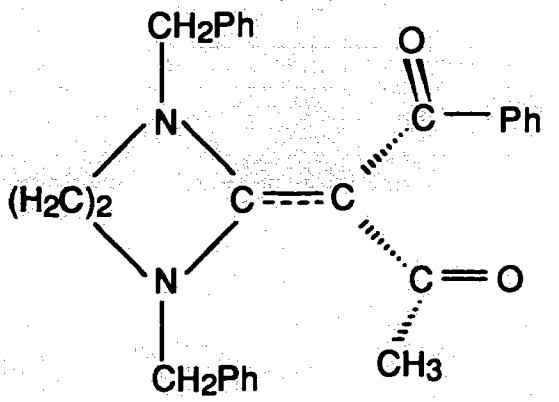
Compounds		$\Delta G^{\neq}$(298K)	$\Delta H^{\neq}$	$\Delta S^{\neq}$
		kJ mol^{-1}	kJ mol^{-1}	J mol^{-1}K^{-1}
(η^5-C_5Me_5)Re(H)(CO)(*p*-$N_2C_6H_4OMe$)	(1)	53 ± 5	58 ± 5	17 ± 2
(η^5-C_5Me_5)Re(CH_3)(CO)(*p*-$N_2C_6H_4OMe$)	(3)	56 ± 6	62 ± 6	20 ± 2
(η^5-C_5Me_5)Re(Cl)(PMe_3)(*p*-$N_2C_6H_4OMe$)	(4)	44 ± 4	52 ± 4	27 ± 2
(η^5-C_5Me_5)Re(Cl){$P(OMe)_3$}(*p*-$N_2C_6H_4OMe$)	(5)	47 ± 3	53 ± 3	23 ± 1

III.2.2.2 The entropy of activation term

As we can see from Table 3.5 the $\Delta S^{\neq}$ values for the isomerization are in the same range for the comparable compounds **1** with **3** and **4** with **5**. Entropy of

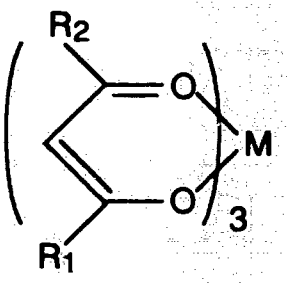
activation ($\Delta S^{\neq}$) parameters for intramolecular exchange processes are usually small and negative. Large negative or positive values for this term for an intramolecular process should therefore be regarded with suspicion, especially as $\Delta S^{\neq}$ values are notorious for being subject to large errors. Nevertheless, several examples of positive values for $\Delta S^{\neq}$ have been reported in the literature for intramolecular processes in organic and organometallic compounds. This has been explained as due to different interactions with the solvent in the ground and transition states.[35] If the transition state is significantly more or less polar than the ground state then interactions with polar solvent molecules will be different and this will, in turn, significantly affect the $\Delta S^{\neq}$ either in a positive sense (less association of solvent in the transition state) or negative sense (more association of solvent in the transition state).

For example, positive values of $\Delta S^{\neq}$ (32.2 and 42.7 J $mol^{-1}K^{-1}$ in o-dichlorobenzene) are found in compounds like those shown below in the passage from a twisted to a planar form in the transition state.[36]



Other examples of positive $\Delta S^{\neq}$ values are the chair to twist inversion system in cyclohexane derivatives[37-39], cyclopentadienyl-β-diketonate Zr(IV)

and Hf(IV) complexes[40,41] and in complexes with the M-O_6 core shown below:[42-44]



The variation of the chemical shift in ^1H and ^{31}P NMR of complexes **1**, **3**, **4** and **5** with the temperature was mentioned before. Marked temperature dependence of chemical shifts have been previously explained as due to changes in fast rotamer equilibria and in solute-solute and/or solute-solvent interactions.[35] The positive values for $\Delta S^{\neq}$ and the considerable change in the chemical shift of the resonances with the temperature are therefore consistent with strong solvent (acetone-d_6) interactions with these molecules and the positive $\Delta S^{\neq}$ values observed are indicative of fewer solvent-molecule interactions in the transition state. Further studies in this field should be performed in order to fully understand these processes. First of all the similar studies should be carried out using less polar solvents, and this can be done since the solubility of these neutral compounds in non polar solvents is not a problem unlike the cationic complexes previously investigated.[23]

III.2.2.3 The free energy of activation term

The free energy of activation for the isomerization determined for compounds **1**, **3**, **4** and **5** was found to be 53 ± 5, 56 ± 6, 44 ± 4, and 47 ± 3 kJ

mol^{-1} respectively at 298 K. These values are essentially the same order of magnitude as in the cationic compounds $[(\eta^5\text{-}C_5Me_5)ReLL'(p\text{-}N_2C_6H_4OMe)][BF_4]$ (where L= CO and L'= PMe_3, $P(OMe)_3$).[23] That the $\Delta G^{\neq}$ parameters are similar suggests the barrier to isomerization arises from restricted rotation about the NN rather than the ReN bond. If barrier to isomerization was due to rotation about the ReN bond, then it would be expected that the barrier would show more variation with a change in the ancillary ligands bonded to the rhenium atom.

It might be expected that if the barrier to isomerization was due mainly to restricted rotation about the NN bond, then there might be a correlation of the NN stretch (a measure of double bond character) with the $\Delta G^{\neq}$ to isomerization.

The NN stretch and $\Delta G^{\neq}$ of activation are presented in Table 3.6.

Compound	$\nu_{(NN)}$ (cm^{-1})		$\Delta G^{\neq}$ ($kJmol^{-1}$)
$(\eta^5\text{-}C_5Me_5)Re(H)(CO)(p\text{-}N_2C_6H_4OMe)$ **(1)**	1613	(hexane)	53 ± 5
$(\eta^5\text{-}C_5Me_5)Re(CH_3)(CO)(p\text{-}N_2C_6H_4OMe)$ **(3)**	1618	(hexane)	56 ± 6
$(\eta^5\text{-}C_5Me_5)Re(Cl)(PMe_3)(p\text{-}N_2C_6H_4OMe)$ **(4)**	1605	(CH_2Cl_2)	44 ± 4
$(\eta^5\text{-}C_5Me_5)Re(Cl)\{P(OMe)_3\}(p\text{-}N_2C_6H_4OMe)$ **(5)**	1609	(CH_2Cl_2)	47 ± 3
$(\eta^5\text{-}C_5Me_5)Re(Cl)(PPh_3)(p\text{-}N_2C_6H_4OMe)$ **(7)**	1607	(CH_2Cl_2)	-

As we can see, the difference in basicity of the phosphorus ligand does not affect significantly the NN stretch. This might be expected, based on electronic reasons. The *p* orbital from the coordinated nitrogen involved in the back bonding to the metal is orthogonal with respect to the *p* orbital involved in the double bond with the ß nitrogen.[15a] A change in the electron density on the

metal resulting from a change in the ancillary ligands should affect the Re-N bond, but not significantly affect the N-N bond. Therefore if the barrier to isomerization is due to rotation about ReN, compound **4** would exhibit a higher barrier than compound **5** since the PMe_3 ligand donates more electron density to the metal, favoring back bonding to the α nitrogen and enhancing the Re-N multiple bond. The values obtained for $\Delta G^{\neq}$ for compounds **4** and **5** are not consistent with this view, as they show no significant difference at the precision of these experiments

The NN stretches for the cationic compounds[25] are, however, significantly higher than those for the neutral complexes and yet the barriers to isomerization that are being obtained in this parallel study[23] are not greatly different from those of the neutral complexes being studied here. This may indicate there is no relationship between the barriers and NN bond strength and that the mechanism of interconversion does not involve rotation about the NN bond. Having said this, it should be remembered that the NN and Re-N bond strengths are ground state properties, whereas $\Delta G^{\neq}$ is the difference in free energy between the ground state and the transition state. The latter term need not show any relationship to such ground state property.

III.2.2.4 Proposal for future work

In order to more fully understand the isomerization process occurring in these neutral compounds, values for $\Delta G^{\neq}$ of more compounds should be obtained to compare with values reported in this thesis. Compounds such as

$(\eta^5\text{-}C_5Me_5)Re(Cl)(CO)(p\text{-}N_2C_6H_4OMe)$ (**2**), $(\eta^5\text{-}C_5Me_5)Re(Br)(CO)(p\text{-}N_2C_6H_4OMe)$ and $(\eta^5\text{-}C_5Me_5)Re(I)(CO)(p\text{-}N_2C_6H_4OMe)$[27] could be studied by variable temperature ^1H NMR by using the methoxy signal to see if they exhibit isomerization and if so, their $\Delta G^{\neq}$ values should be determined and compared with those of **1** and **3**.

A VT ^{31}P NMR study could be carried out for compounds like $(\eta^5\text{-}C_5Me_5)Re(Cl)\{P(Me_2Ph)\}(p\text{-}N_2C_6H_4OMe)$, $(\eta^5\text{-}C_5Me_5)Re(Cl)\{P(MePh_2)\}(p\text{-}N_2C_6H_4OMe)$, as well as other phosphine analogues in which the steric and electronic properties of the phosphine are altered. A comparison of the $\Delta G^{\neq}$ values obtained for these compounds (if isomerization is detected) with the $\Delta G^{\neq}$ for compounds **4** and **5** reported in this thesis could enlighten the understanding of this isomerization process. Another study that should be performed is the investigation of the barriers to ReNNAr rearrangement in the analogous C_5H_5 (Cp) derivatives. It is well known that Cp and Cp* have very different steric and electronic properties and the comparison of the $\Delta G^{\neq}$ values for the Cp with the Cp* analogues could help to rationalize the process.

Linear inversion of an sp^2 hybridized nitrogen atom has been proposed previously to account for isomerization in some organic systems.[45-48] Such a process could also account for the isomerization of the complexes studied here. A possible experimental way to distinguish between rotation about the ReNN axis or inversion at the β nitrogen atom is to investigate aryldiazenido compounds with bulky groups at the ortho position. The inversion process would not be significantly affected by such a substitution and thus the barrier to isomerization should be approximately the same as in the unsubstituted aryldiazenido analogues. If the isomerization is due to rotation, the $\Delta G^{\neq}$

parameters for the isomerization should be much higher for steric reasons than those for the unsubstituted derivatives.

An alternative experimental way to study this process may be to complex the lone pair of electrons at the β nitrogen atom by protonation or Lewis acid addition. If the isomerization process is due to inversion, this should block the isomerization but it should still be allowed by a rotation mechanism.

All of the protonation reactions performed in our laboratory have been unsuccessful due to the preferential attack of the anion from the acid to the metal center forming a relative stable compound with a general formula $(\eta^5\text{-}C_5Me_5)Re(X)(CO)(p\text{-}N_2C_6H_4OMe)$ where X is the anion of the acid used.

The reaction of aryldiazenido compounds with Lewis acids has not been reported very much in the literature. The two better known compounds are the bimetallic tungsten-chromium[17] and manganese-rhenium[18] compounds already mentioned in the introduction of this thesis. In the latter, the $CpRe(CO)_2THF$ compound reacts to coordinate to the β nitrogen releasing the THF ligand. The reaction of this THF compound with the neutral compounds reported here and the study of them at variable temperature should give more information about this mechanism of isomerization. $AlCl_3$ can also be used as a Lewis acid in order to coordinate to the β nitrogen. The reaction of $AlCl_3$ with compounds **3**, **4** and **5** was performed in this study but the short time available did not allow us to analyze the resulting compounds. However, preliminary results showed the possibility that coordination of the Lewis acid had been achieved. For example, in the case of the reaction with **3** a change in the color from yellow to red-orange was immediately observed after adding the $AlCl_3$. The IR spectrum in CH_2Cl_2 of the product showed a carbonyl stretch at 1989 cm^{-1} indicative of a shift in 93 cm^{-1} from the starting material ($\nu_{(CO)}$ 1896 cm^{-1} in

CH_2Cl_2). The increase in the wavelength of the carbonyl stretch upon protonation has been reported for a series of hydrazido (2-) ruthenium compounds.[49] This can be explained as due to the decreased back bonding donation from the metal to the carbonyl ligand because of the formation of a cationic species. The same behavior has been seen in the bimetallic $(Cp)(CO)_2W(NNCH_3)Cr(CO)_5$ and $(Cp)(CO)_2Mo(p\text{-}NNC_6H_4CH_3)Re(CO)_2(Cp)$ compounds. [18,19] In both compounds the carbonyl stretches move up upon coordination of the Lewis acid. This indicates the effective removal of electron density by the Cr and Re atoms from W and Mo through the diazenido ligand. The crystal structure of the W-Cr compound showed shortening in the W-C (Cp) and C-O (carbonyl) bonds and lengthening in W-C (CO) bond. This was explained as a partial rehybridization (Fig 3.13) that makes the tungsten atom more electropositive and less able to back donate electron density to the carbonyl as before coordination.

Fig 3.13 Rehybridization process upon coordination of a Lewis acid to the outer nitrogen in diazenido compounds.[18,50]

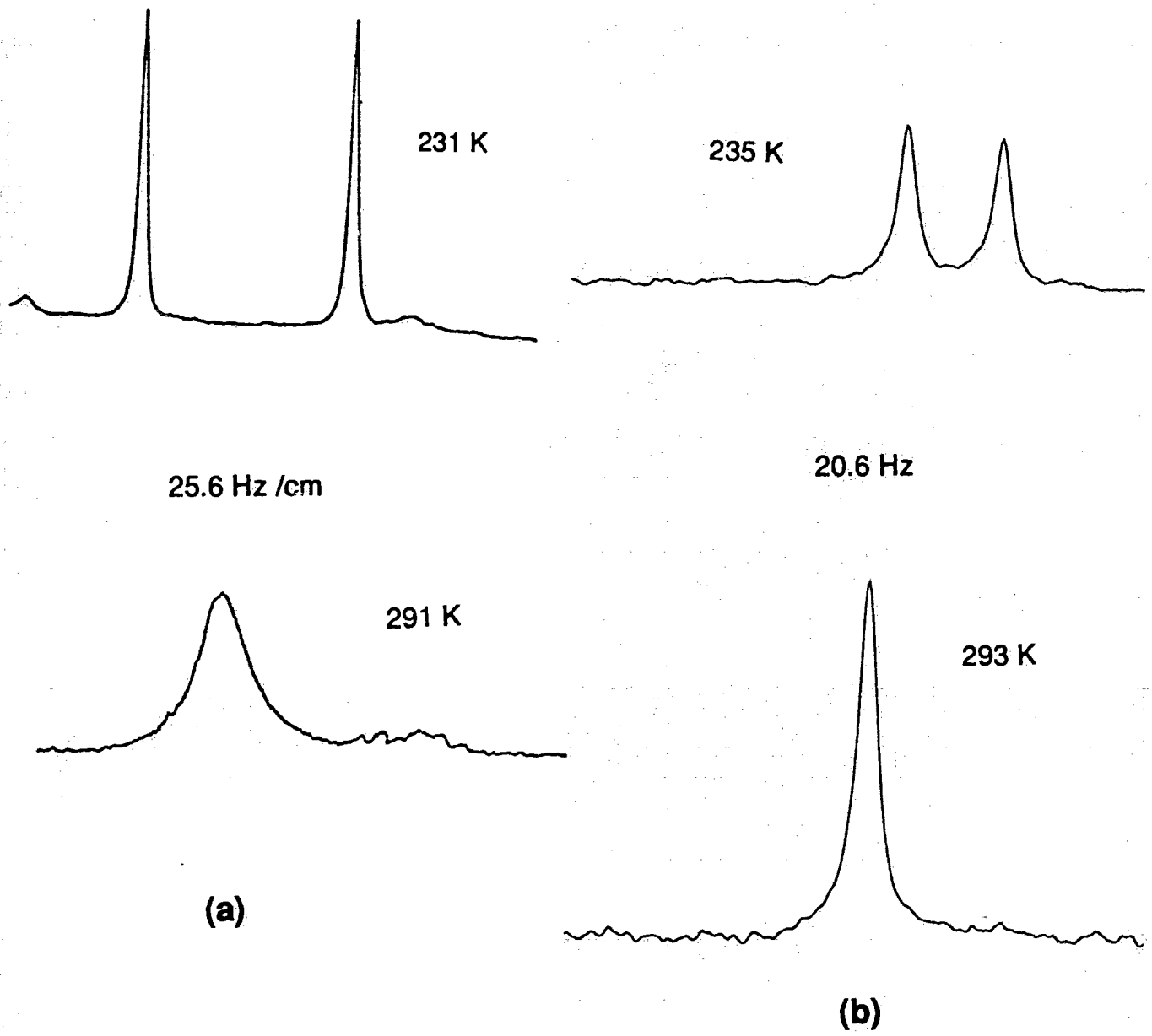


Fig 3.3: ^{1}H NMR spectra of a) (η^5-C_5Me_5)Re(CH_3)(CO)(*p*-$N_2C_6H_4OMe$) **(3)** (methyl signal)

b) (η^5-C_5Me_5)Re(H)(CO)(*p*-$N_2C_6H_4OMe$) **(1)** (hydride signal) at the low and high limit temperatures observed.

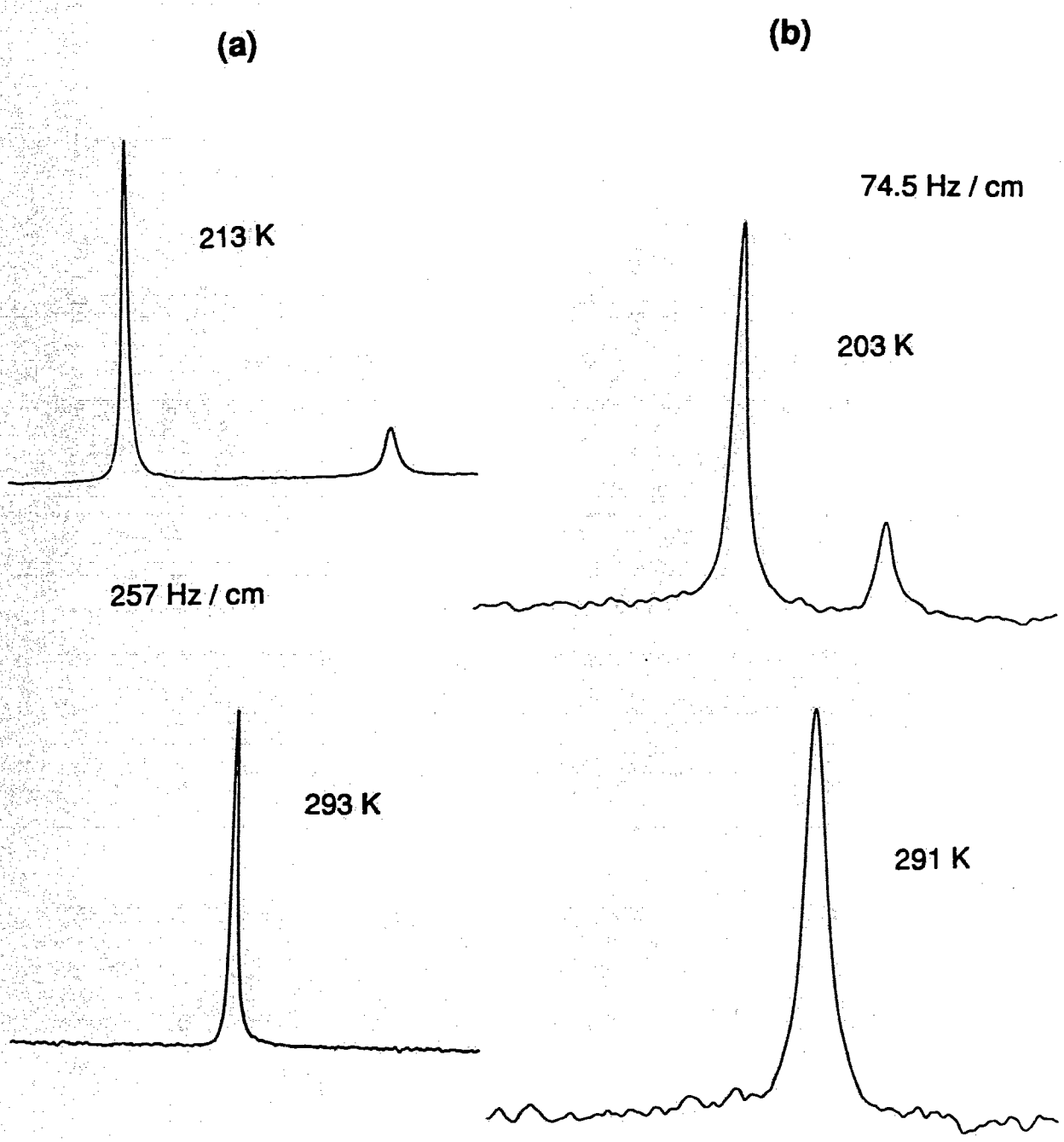


Fig 3.4: $^{31}P\{^{1}H\}$ NMR spectra of

a) $(\eta^5\text{-}C_5Me_5)Re(Cl)(PMe_3)(p\text{-}N_2C_6H_4OMe)$ **(4)**

b) $(\eta^5\text{-}C_5Me_5)Re(Cl)\{P(OMe)_3\}(p\text{-}N_2C_6H_4OMe)$ **(5)** at the low and high limit temperature observed.

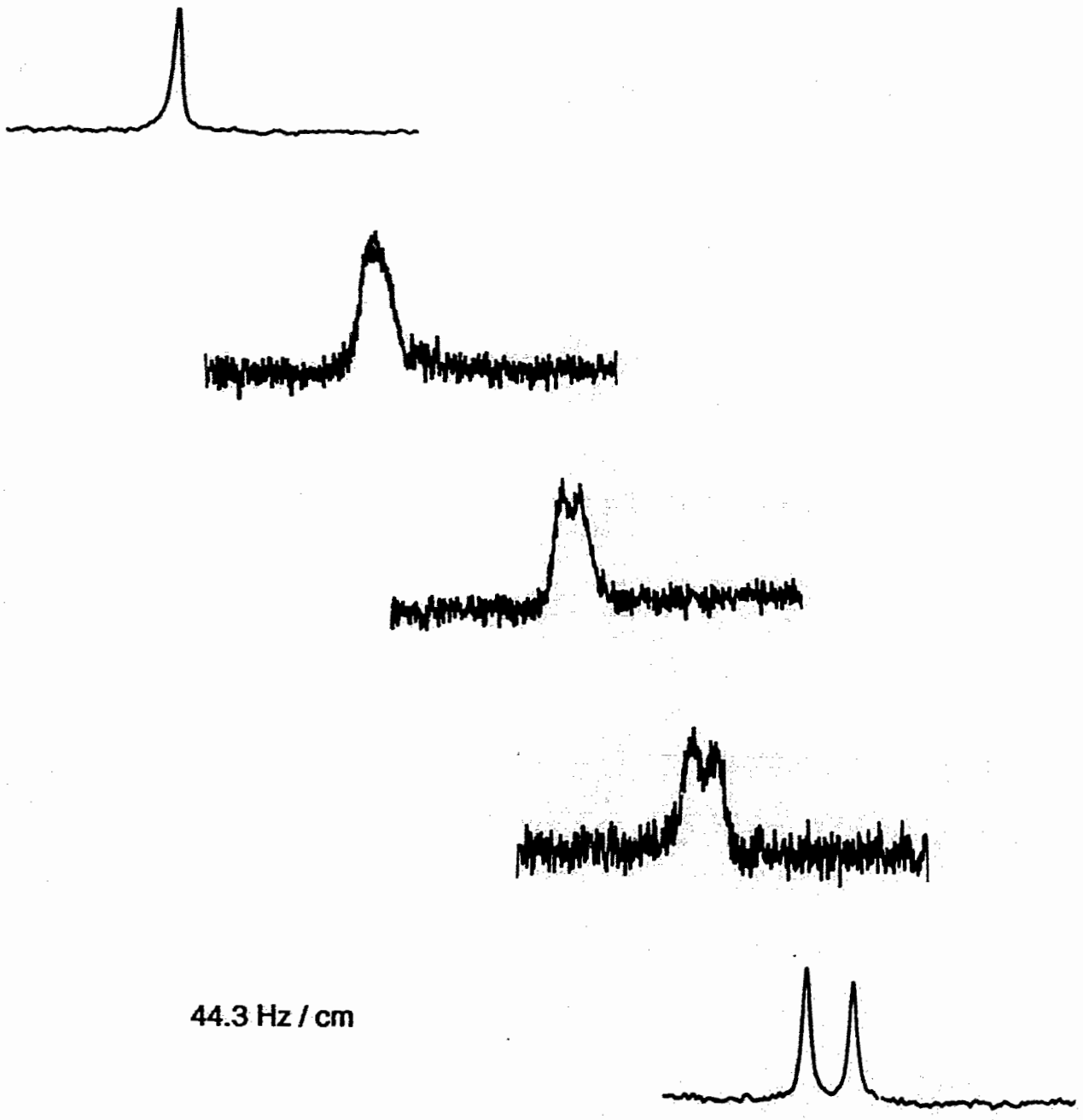


Fig 3.5: VT ^{1}H NMR spectra of the hydride resonance of (η^5-C_5Me_5)Re(H)(CO)(*p*-$N_2C_6H_4OMe$) (**1**). The temperatures are the same as given in the simulation (Fig. 3.6)

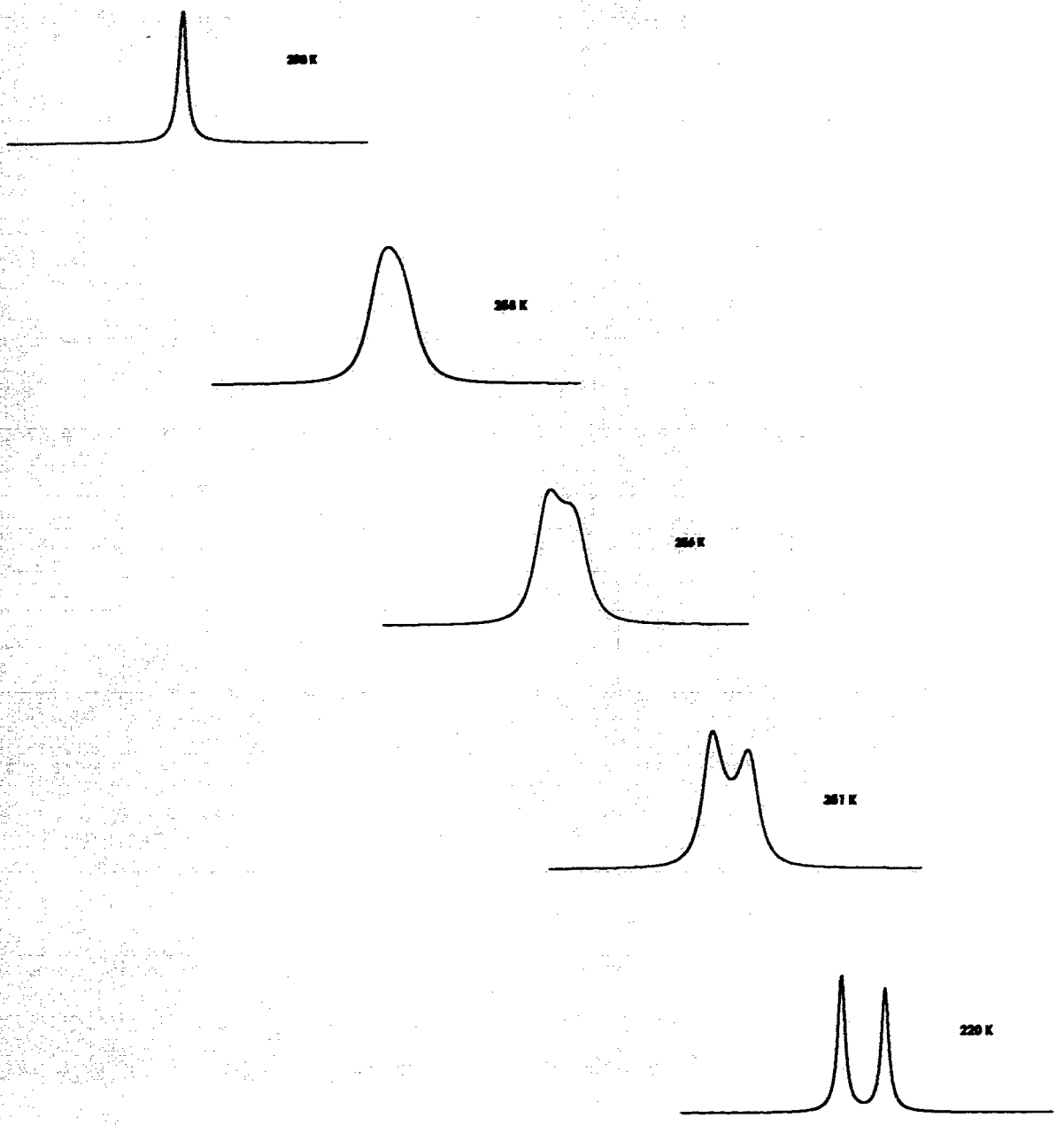


Fig 3.6: Calculated ^{1}H NMR spectra for the spectra shown in Fig. 3.5

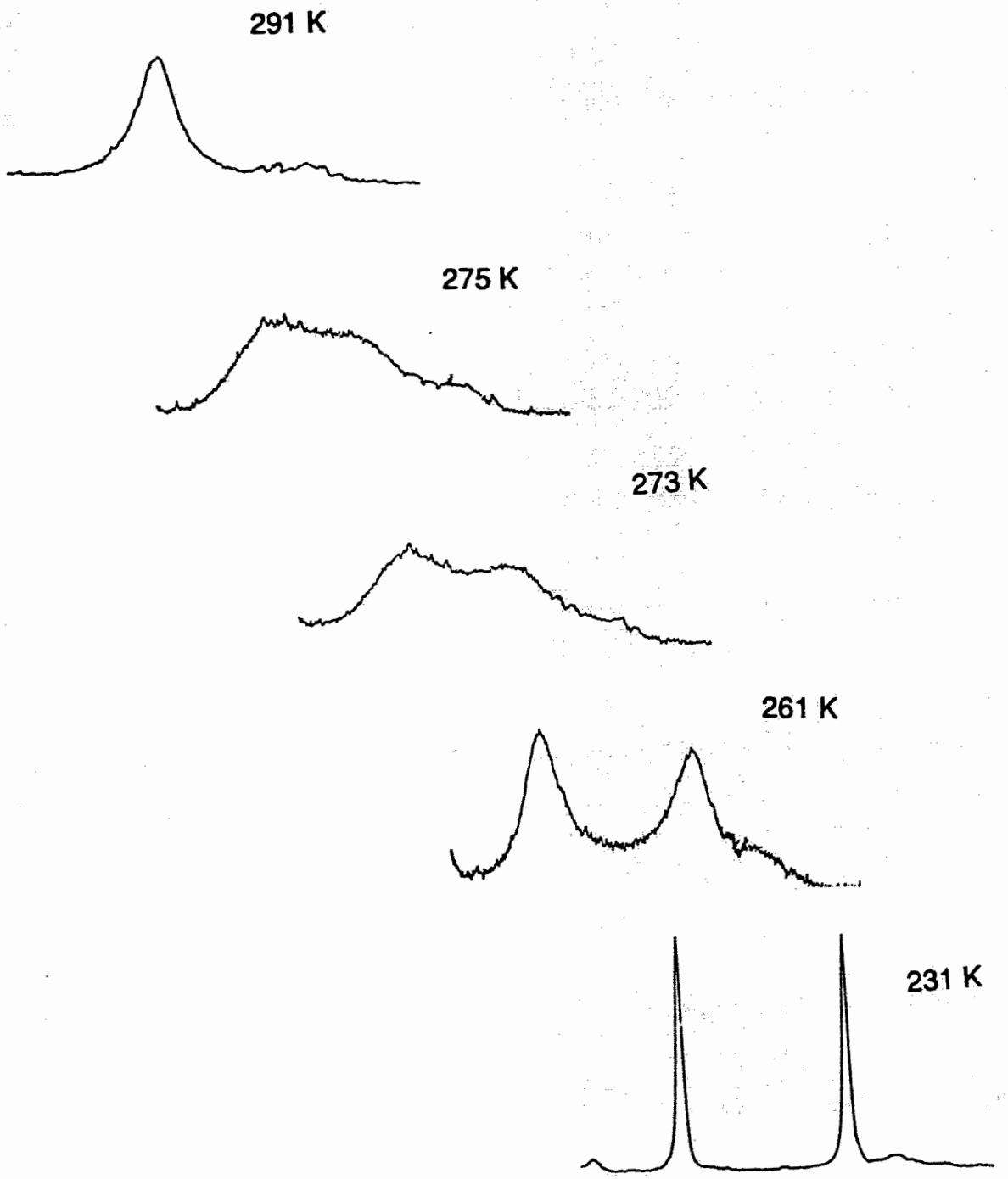


Fig 3.7: VT ^1H NMR spectra of the methyl resonance of $(\eta^5\text{-}C_5Me_5)Re(CH_3)(CO)(p\text{-}N_2C_6H_4OMe)$ **(3)**.

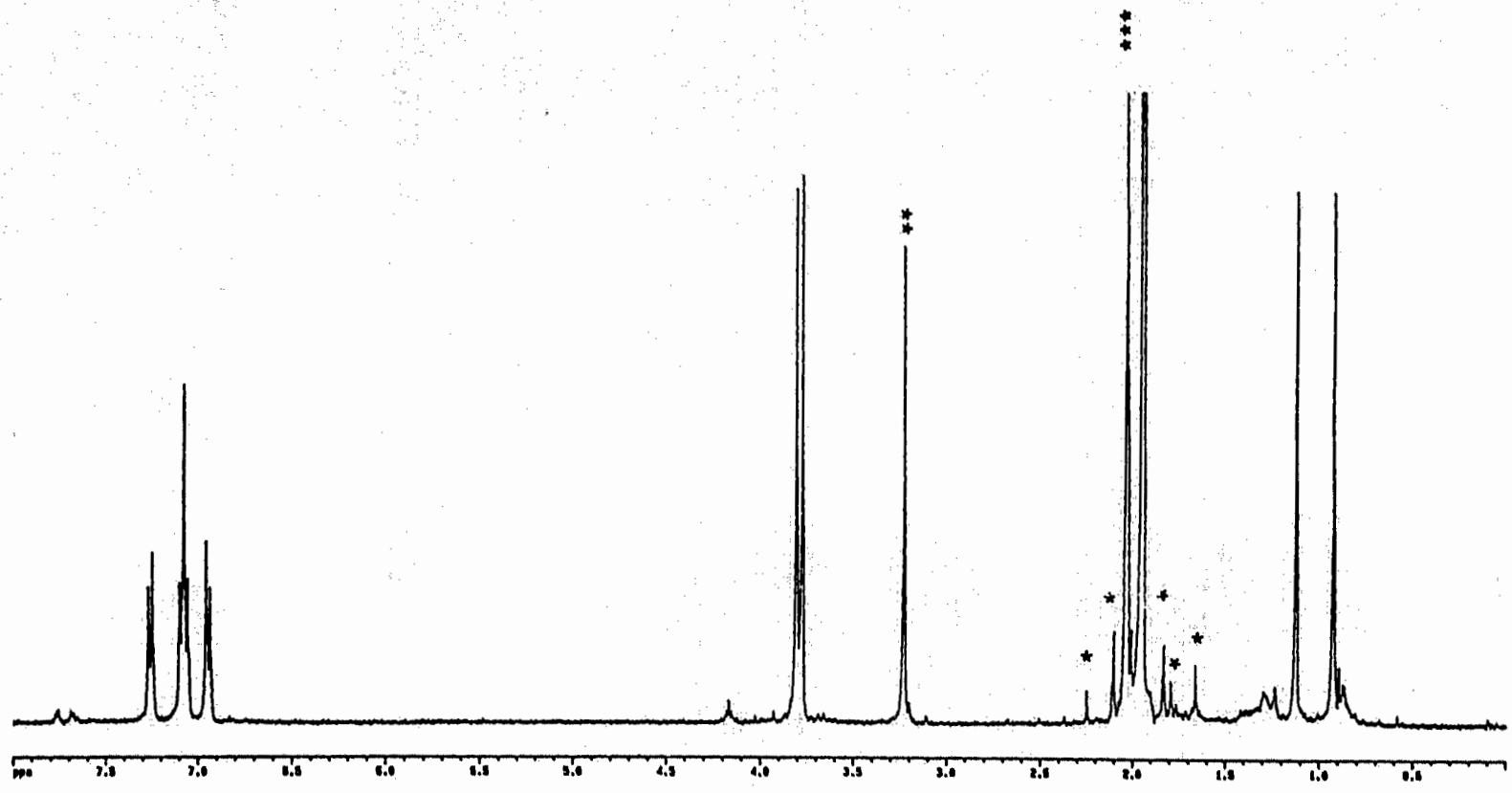


Fig. 3.8;^{1}H NMR spectrum (400 MHz, acetone-d_6) of

(η^5-C_5Me_5)Re(CH_3)(CO)(*p*-$N_2C_6H_4OMe$) **(3)** at 231 K.

* impurities in the sample ** water signal δ3.23 ppm *** acetone-d_6

Assignment of the peaks: δ0.93, 1.13 (Me) ; δ1.96 (Cp*) ; δ3.78, 3.81 (OMe) ; δ 6.95 (d), 7.06 (d), 7.09 (d), 7.25 (d) (C_6H_4)

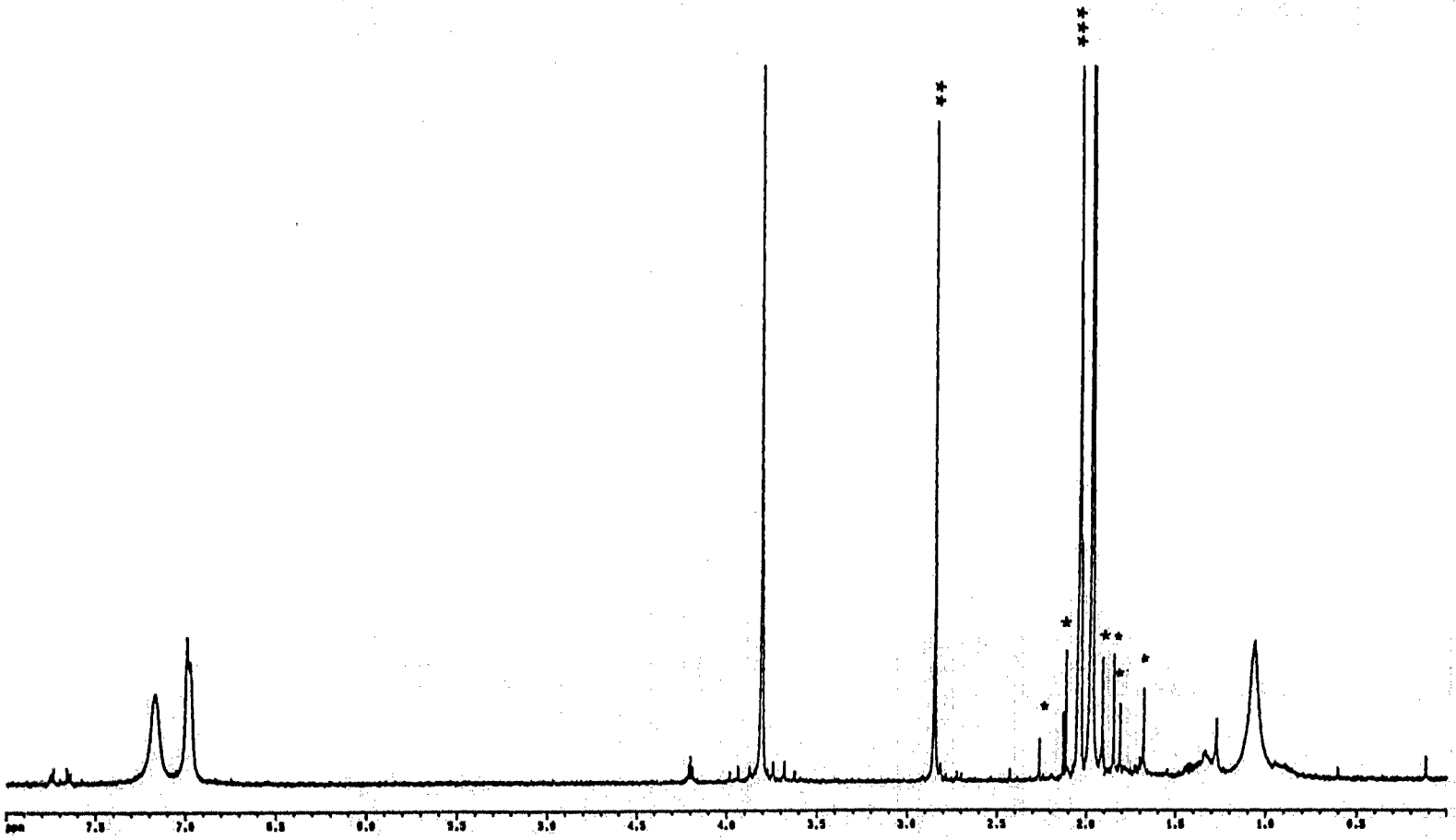


Fig. 3.9: ^{1}H NMR spectrum of (η^5-C_5Me_5)Re(CH_3)(CO)(*p*-$N_2C_6H_4OMe$) **(3)** at 291 K.

* impurities in the sample ** water signal δ2.85 ppm *** acetone-d_6

Assignment of the peaks: δ1.07 (Me) ; δ1.97 (Cp*) ; δ 3.81 (OMe) ;

δ 6.98 (d), 7.17 (d) (C_6H_4)

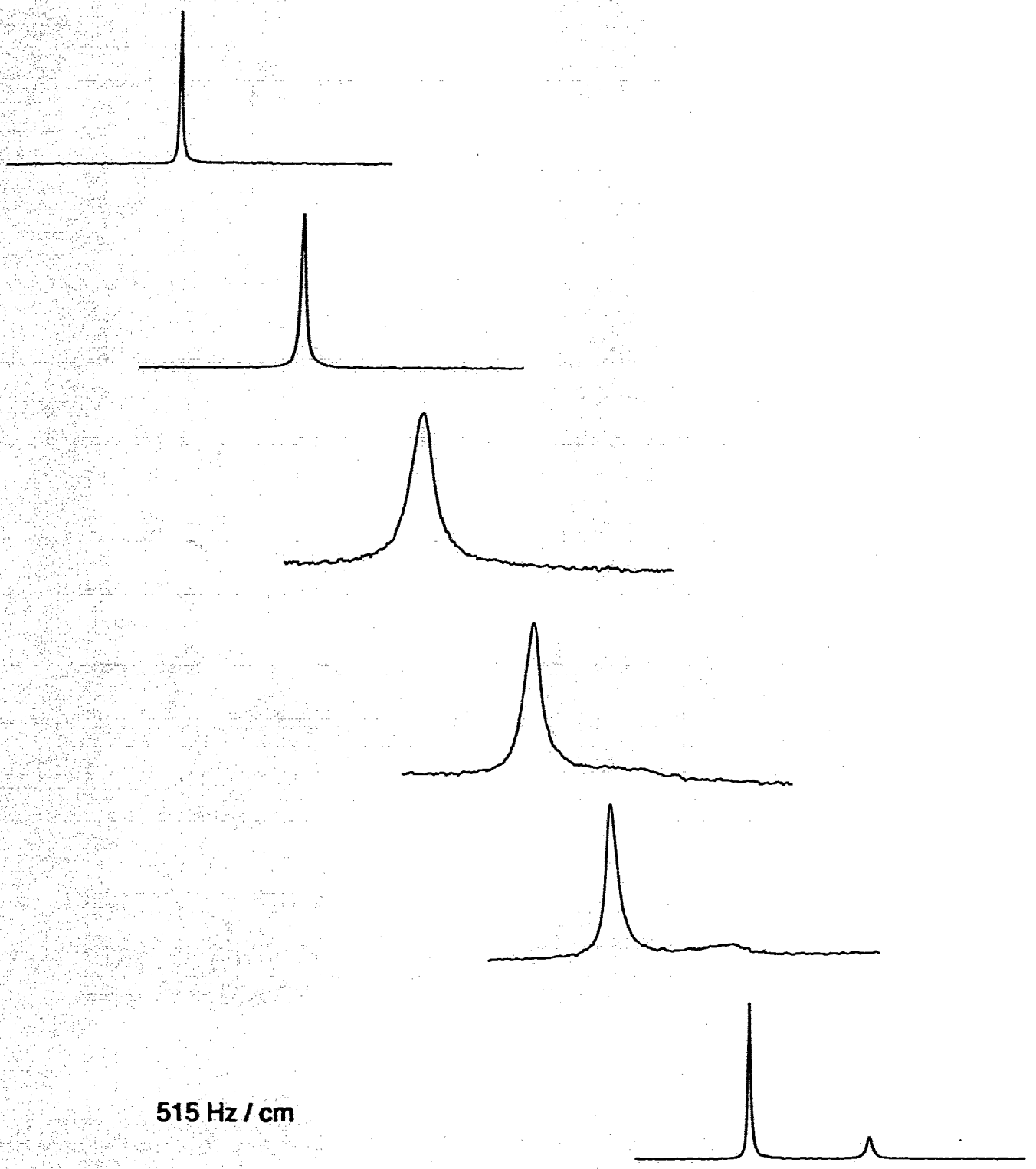


Fig 3.10: VT ^{31}P NMR spectra of $(\eta^5\text{-}C_5Me_5)Re(Cl)(PMe_3)(p\text{-}N_2C_6H_4OMe)$ (4)

The temperatures are the same as given in the simulation (Fig. 3.11)

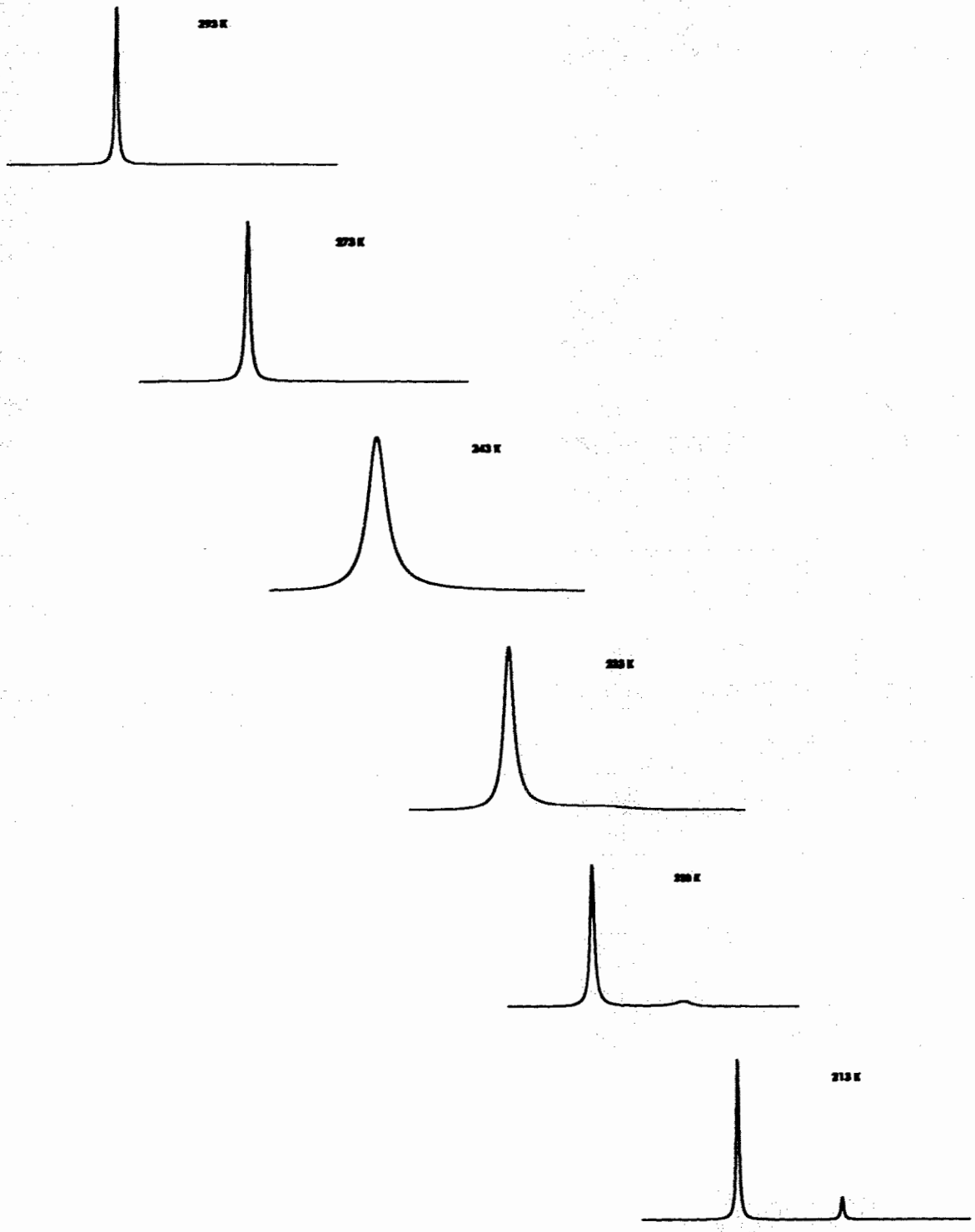


Fig 3.11: Calculated ^{31}P NMR spectra for the spectra shown in Fig. 3.10

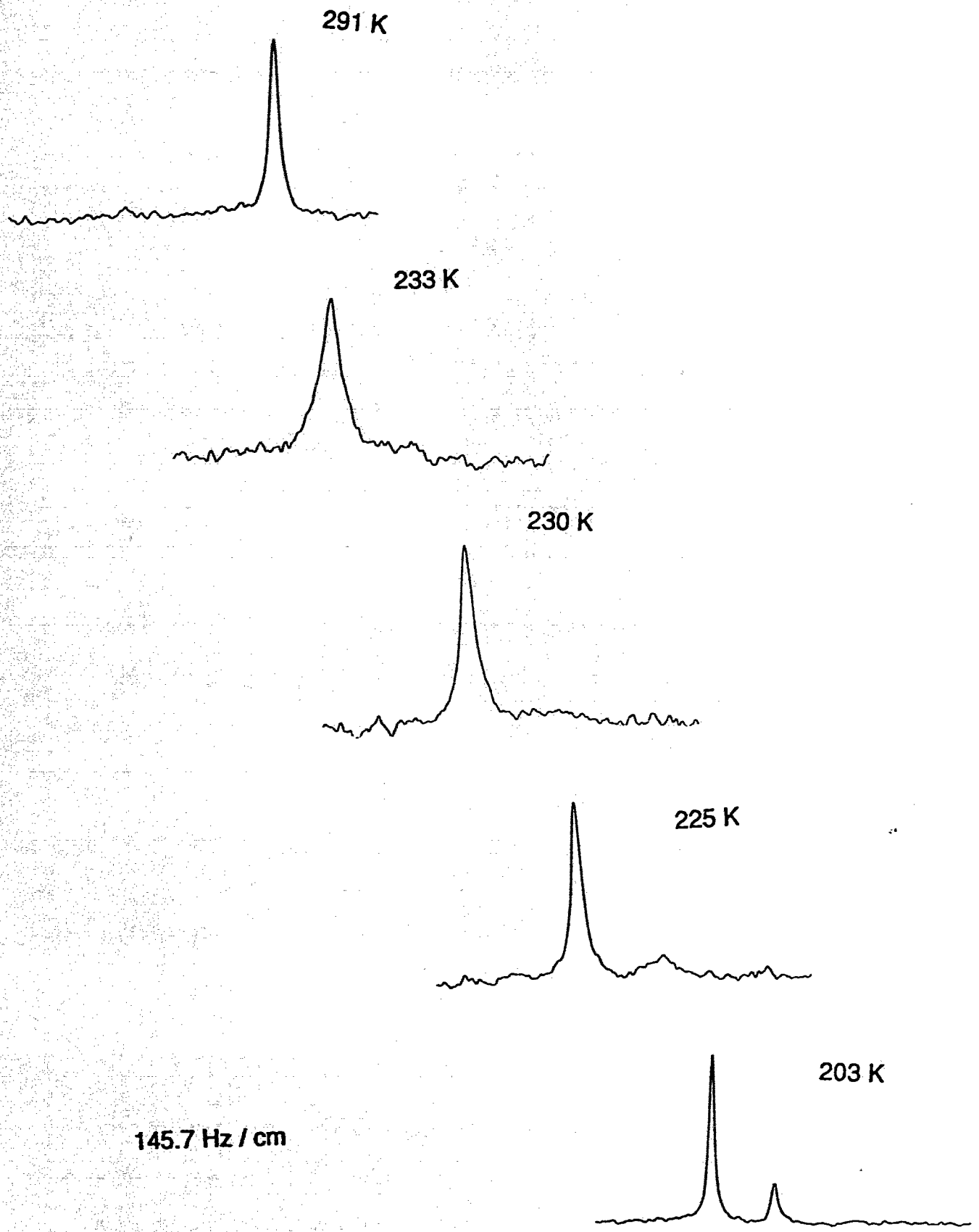


Fig 3.12: VT ^{31}P NMR spectra of $(\eta^5\text{-}C_5Me_5)Re(Cl)\{P(OMe)_3\}(p\text{-}N_2C_6H_4OMe)$ (5)

III.3 Experimental Section

III.3.1 General

The variable temperature NMR experiments were performed on a Bruker AMX-400 instrument at operating frequencies 400 and 162 MHz for ^{1}H and ^{31}P, respectively. The samples were prepared immediately before carrying out the experiments. The solvent used was acetone-d_6; the samples were degassed and then placed under nitrogen. The temperature of the spectrometer had previously been calibrated with a thermocouple and temperatures quoted for the samples are believed accurate to ± 1 K. Calculation of simulated line shapes was performed by use of a slightly modified version of the DNMR3 program.[34] The rate constants at each temperature were obtained by visual comparison of the spectra simulated by the program with the spectra obtained from the NMR instrument at a given temperatures. The temperature was measured with a precision of 0.1 K. The error in the temperature settle on the NMR instrument and the temperature the solution actually present in the NMR tube was obtained by calibration. The experimental errors given for the rate constants (see tables in Results and Discussion) were estimated from the ranges in rates over which it was impossible to distinguish between the experimental and calculated spectra.

III.3.2 Calculation of activation parameters:

The values of $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ were calculated by using the Eyring equation that relates the rate constant with the equilibrium constant at the

transition state (equation 1), together with the other thermodynamic equations applied to the transition state.

$$k_r = (k_B \bullet T / h)K^{\neq}_{eq} \qquad (1)$$

k_B: Boltzmann's constant

h: Planck's constant

T: temperature

$K^{\neq}_{eq}$: Equilibrium constant at the transition state

Rearranging:

$$\ln (k_r / T) = (- \Delta H^{\neq} / R) \bullet (1 / T) + \{(\Delta S^{\neq} / R) + \ln (k_B / h)\} \qquad (2)$$

Once the rate constants were found by the line shape analysis, activation parameters and errors were calculated by the use of a linear least-squares program, plotting $\ln (k_r / T)$ versus $(1 / T)$. It is worth noting that the errors in the rate constant were introduced in the program and taken in account for the calculation of the error in the slope and intercept. The slope $\{(- \Delta H^{\neq} / R)\}$ and the intercept $\{(\Delta S^{\neq} / R) + \ln (k_B / h)\}$ were obtained and the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values were calculated, as well as the $\Delta G^{\neq}$ for any temperature can be obtained. The errors quoted for the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values are the standard deviations given by the least squares plot. The errors in the $\Delta G^{\neq}$ parameter was estimated from the errors in $\Delta H^{\neq}$ and $\Delta S^{\neq}$.

III.3.3 Analysis of errors

Tables 3.1-3.4 report the rate constants along with an estimation of their errors. The errors were obtained by finding the slower and faster rates which gave a detectable difference in the simulated spectrum at the rate in question. Another source of error is the error in the temperature of the determinations. As mentioned above, the instrument had been previously calibrated with a thermocouple inside an NMR sample tube and temperatures are believed to be correct to ± 1 K (or better). The temperature is therefore, not believed to be the main source of error.

In order to obtain the best possible activation parameters, the experimental errors should be minimized. An ideal system would be one that gives a wide range in the temperature and where the spectra are sensitive to changes in the rate constants. A relatively wide temperature range of about 80 K was employed in the complexes studied here and the spectra at the different temperatures were also quite sensitive to changes in the rate constant. Two sources of error that were not corrected for were the possible change in the chemical shift difference between the two sites and the population of the two sites in the region of coalescence. These changes could have been estimated from extrapolation of plots of chemical shift difference versus temperature, and isomer ratio versus temperature from studies of the systems at temperatures below coalescence. Time constraints did not allow for these studies.

The standard deviation in the slope and the intercept from the least-square program are quoted as the errors in the $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values and these errors are used to calculate the error in the $\Delta G^{\neq}$. For reasons mentioned above the errors maybe somewhat underestimated.

IV Conclusions

1) The synthesis and characterization of five new neutral aryldiazenido Re compounds of general formula [Cp*ReXL(p-$N_2C_6H_4OMe$)] [where Cp* = (η^5-C_5Me_5); L = CO and X = CH_3 (**3**), $PO(OMe)_2$ (**6**); L = PMe_3 (**4**), $P(OMe)_3$ (**5**), PPh_3 (**7**) and X = Cl] have been carried out. The syntheses involved the substitution of a CO ligand by chloride anion (compounds **4**, **5** and **7**), replacement of the chloride by the methyl group for compound **3**; and by nucleophilic attack of the chloride anion on the methoxy group in an Arbuzov reaction (to give **6**). A different method of preparation for the known compound (Cp*)Re(H)(CO)(*p*-$N_2C_6H_4OMe$) (**1**) has also been discovered.

2) Variable temperature ^{31}P and ^{1}H NMR experiments for compounds **1**, **3**, **4** and **5** showed the presence of two isomers. Compound **7**, however, showed no evidence of isomerization. The difference in population of the isomers of compounds **4** and **5** was interpreted as mainly due to steric effects, although more studies should be carried out in order to support this preliminary conclusion.

3) Line shape analyses of the VT NMR spectra were performed and the activation parameters $\Delta G^{\neq}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ calculated for the isomerizations. The results did not favor either the ReNN rotation or the β nitrogen inversion mechanism. That the $\Delta G^{\neq}$ values for **1**, **3**, **4** and **5** were similar and similar to the cationic compounds studied in a parallel research, indicate the isomerization is insensitive to changes in the metal centre. Further studies of analogous compounds should give more information about the mechanism of isomerization.

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Appendix

In this appendix are related the plotting of ln (k_r / T) versus (1 / T) for each of the compounds that have been studied by VT NMR spectroscopy:

(η^5-C_5Me_5)Re(H)(CO)(*p*-$N_2C_6H_4OMe$) (1)

(η^5-C_5Me_5)Re(CH_3)(CO)(*p*-$N_2C_6H_4OMe$) (3)

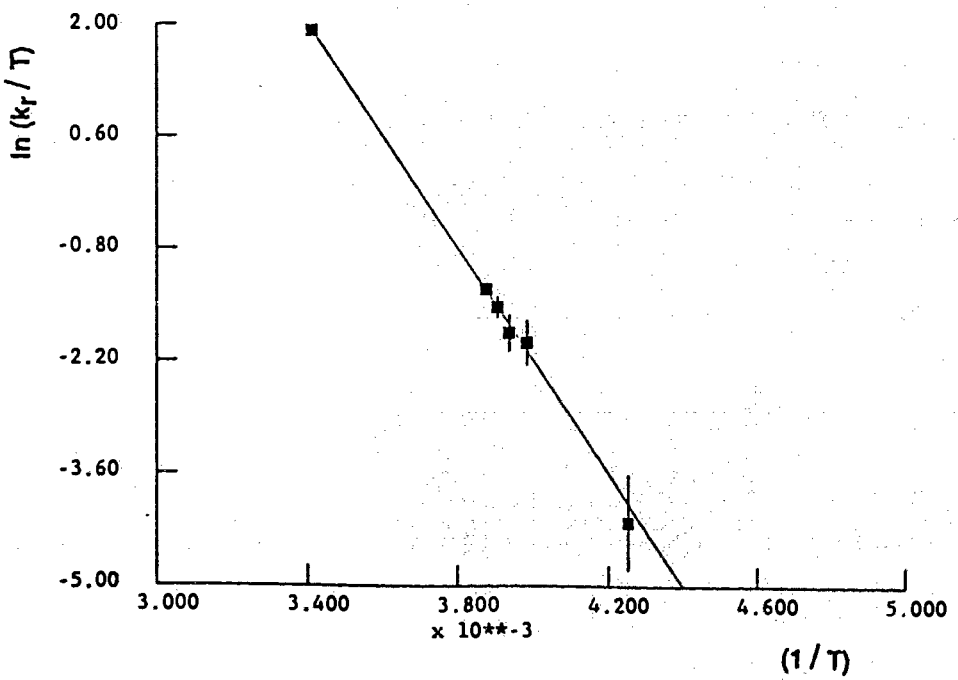
(η^5-C_5Me_5)Re(Cl)(PMe_3)(*p*-$N_2C_6H_4OMe$) (4)

(η^5-C_5Me_5)Re(Cl){$P(OMe)_3$}(*p*-$N_2C_6H_4OMe$) (5)

POWER	0	1
COEFFICIENTS	25.820	-7002.2
STD DEVNS	.22125	61.890

WEIGHTED STD DEVN OF FIT =3.471E-02

X	Y EXP	Y CALC	DEVN	ERR EST
4.2550E-03	-4.2070	-3.9738	.233	.601
3.9840E-03	-1.9700	-2.0762	-.106	.282
3.9370E-03	-1.8480	-1.7471	.101	.231
3.9060E-03	-1.5310	-1.5300	1.008E-03	.139
3.8760E-03	-1.3050	-1.3199	-1.493E-02	9.320E-02
3.4130E-03	1.9210	1.9221	1.080E-03	4.800E-02

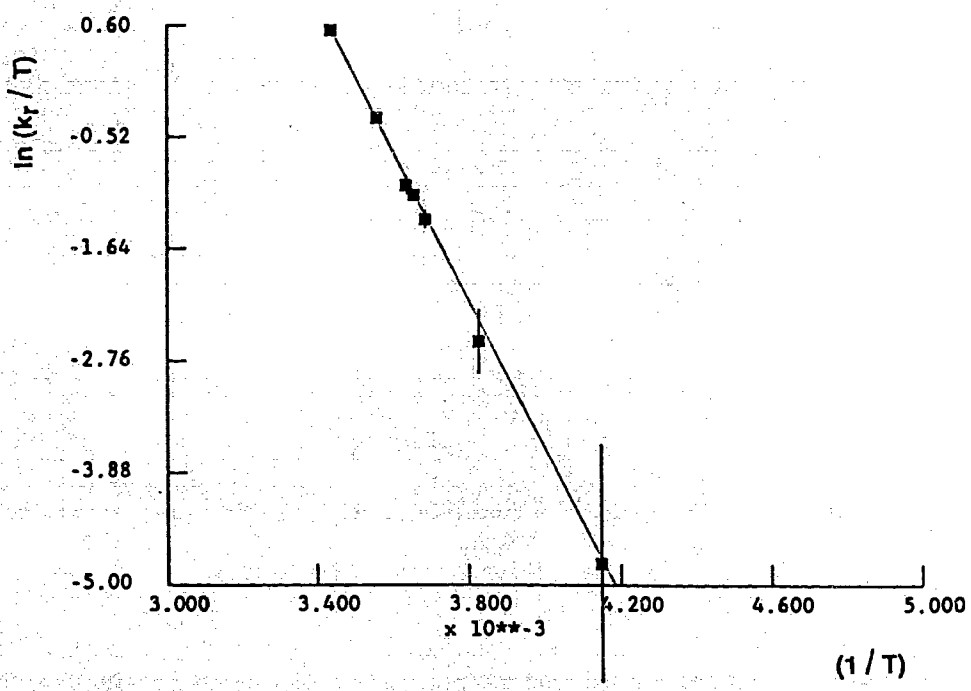


$(\eta^5\text{-}C_5Me_5)Re(H)(CO)(p\text{-}N_2C_6H_4OMe)$ (1)

POWER	0	1
COEFFICIENTS	26.142	-7441.6
STD DEVNS	.25635	73.611

WEIGHTED STD DEVN OF FIT -1.268E-02

X	Y EXP	Y CALC	DEVN	ERR EST
4.1500E-03	-4.7920	-4.7402	5.175E-02	1.20
3.8300E-03	-2.5690	-2.3589	.210	.321
3.6900E-03	-1.3540	-1.3171	3.688E-02	9.670E-02
3.6600E-03	-1.1100	-1.0939	1.612E-02	6.160E-02
3.6400E-03	-1.0120	-.94505	6.695E-02	.102
3.5600E-03	-.34000	-.34972	-9.719E-03	1.700E-02
3.4400E-03	.54130	.54327	1.970E-03	1.080E-02

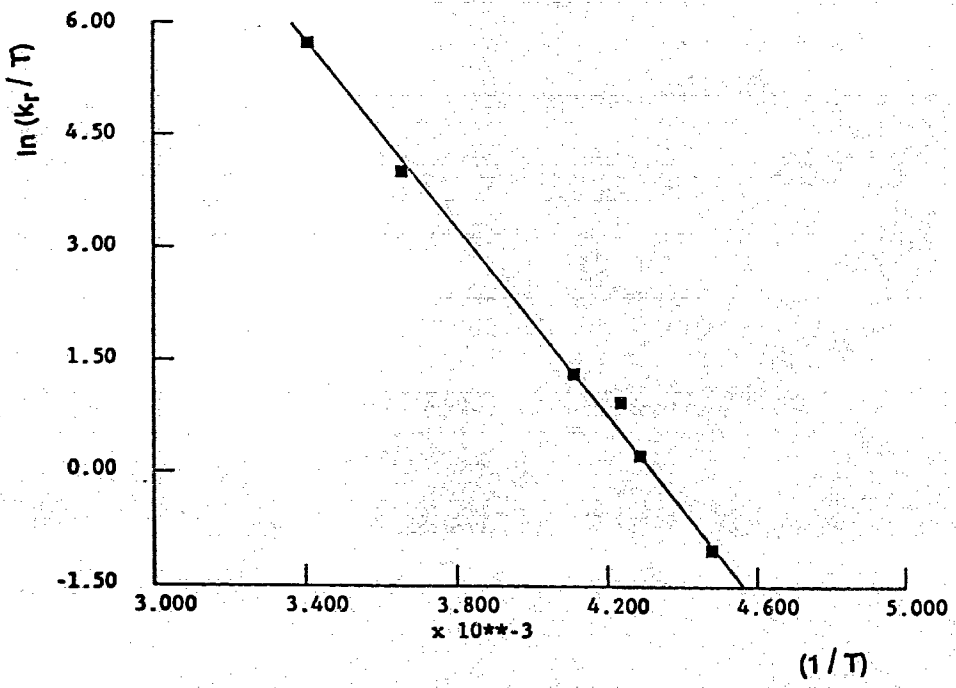


$(\eta^5\text{-}C_5Me_5)Re(CH_3)(CO)(p\text{-}N_2C_6H_4OMe)$ (3)

POWER	0	1
COEFFICIENTS	27.045	-6253.4
STD DEVNS	.16423	43.123

WEIGHTED STD DEVN OF FIT =4.539E-02

X	Y EXP	Y CALC	DEVN	ERR EST	
4.4800E-03	-1.0250	-.97016	5.484E-02	6.410E-02	
4.2900E-03	.21880	.21800	-8.023E-04	7.500E-03	
4.2400E-03	.93310	.53067	-.402	7.770E-02	**
4.1150E-03	1.3093	1.3124	3.051E-03	7.270E-02	
3.6600E-03	4.0060	4.1577	.152	2.670E-02	**
3.4100E-03	5.7270	5.7210	-5.970E-03	6.400E-03	

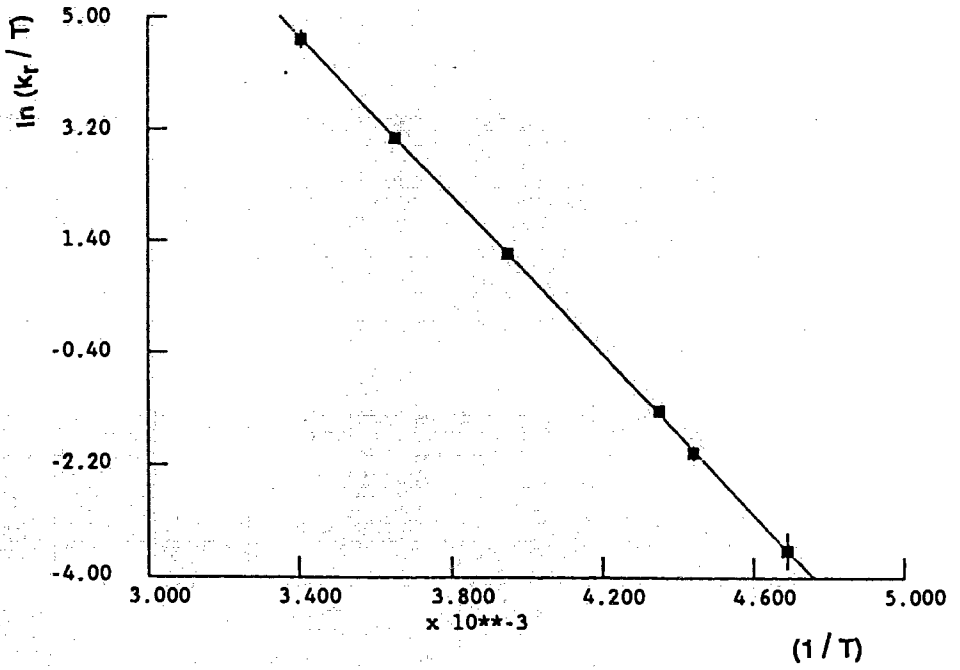


$(\eta^5\text{-}C_5Me_5)Re(Cl)(PMe_3)(p\text{-}N_2C_6H_4OMe)$ (4)

POWER	0	1
COEFFICIENTS	26.505	-6412.1
STD DEVNS	.12646	32.239

WEIGHTED STD DEVN OF FIT =1.602E-02

X	Y EXP	Y CALC	DEVN	ERR EST
4.6900E-03	-3.5700	-3.5680	2.024E-03	.297
4.4400E-03	-2.0150	-1.9650	5.004E-02	.134
4.3500E-03	-1.3440	-1.3879	-4.387E-02	.112
3.9500E-03	1.1760	1.1770	9.532E-04	2.870E-02
3.6600E-03	3.0390	3.0365	-2.548E-03	5.330E-02
3.4100E-03	4.6290	4.6395	1.047E-02	.154



$(\eta^5\text{-}C_5Me_5)Re(Cl)\{P(OMe)_3\}(p\text{-}N_2C_6H_4OMe)$ (5)