1984

Metallacyclobutane Chemistry

John Thomas Burton

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METALLACYCLOBUTANE CHEMISTRY

by

John Thomas Burton

Department of Chemistry

Submitted in partial fulfillment of

the requirements for the degree of

Doctor of Philosophy

Faculty of Graduate Studies

The University of Western Ontario

London, Ontario

October, 1983

ABSTRACT

This thesis describes the preparation, characterisation, and reactivity of a new class of platinacyclobutane complexes, containing a hydroxyl or ester functionality. The monomeric compounds are prepared by the reaction of Zeise's dimer with the appropriate cyclopropane derivative and subsequent addition of pyridine.

Owing to the presence of the hydroxyl group, these complexes have been shown to interact with the shift reagent; $Eu(fod)_3$, so as to greatly simplify their ^1H-N.M.R. spectra. Using the results obtained from this study and the equation of Karplus, comparisons are drawn between ring conformations in the solid state and solution which indicate significant puckering of these complexes in solution.

A novel ring expansion reaction is presented by which platinacyclopentanes are prepared by solvolysis of the platinacyclobutylcarbinyl esters, under mild conditions. Platinacyclopentanes are the exclusive products, identified by their ^{13}C and ^1H N.M.R. spectra. The mechanism by which this rearrangement proceeds was studied by kinetics as well as suitable ^{13}C and ^2H labelling studies in the absence and presence of added pyridine. The results indicate one overall mechanism with a step dependent on pyridine concentration.

The reactions of Zeise's dimer with bicyclo[2.1.0]pentane and quadricyclane, in acetone, are shown to give cyclopentene and norbornadiene (NBD) and $[Pt_2Cl_2(\mu\text{-}Cl)_2(\text{cyclopentene})_2]$ and $[PtCl_2NBD]$ as the respective products.

1-Methylcyclopropyl carbinol and 2-cyclopropyl-2-propyl-p-nitrobenzoate react cleanly, in acetone, with $[Rh_2(CO)_4Cl_2]$ to give

1-methylcyclobutanol and 5-chloro-2-pentene, respectively. The mechanism of the first of these was investigated by kinetics and ^{2}H labelling studies while a novel carboxylate bridged rhodium dimer was obtained in the latter. Possible mechanisms for these rearrangements are presented which may involve metallacycle intermediates.

"And miles to go before I sleep,

And miles to go before I sleep."

Robert Frost

ACKNOWLEDGEMENTS

I would like to express my sincere admiration and appreciation to Dr. Richard J. Puddephatt for his immeasurable guidance and supervision throughout my graduate program.

I am also very grateful to Professor J.B. Stothers for his help in obtaining ^{13}C and ^{2}H N.M.R. spectra.

Thanks are also given to the rest of the chemistry faculty at the University of Western Ontario who were always available for helpful discussions. Special thanks are given to the other graduate students who made my stay so enjoyable. Also I would like to thank Terry Yanowski for her excellent typing of the manuscript.

Lastly, and above all, I would like to acknowledge my wife, Marilyn, whose unfaltering patience and understanding contributed greatly to the work of this thesis.

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Key Abbreviations

X = halogen

R = alkyl or aryl group

Me = methyl

Et = ethyl

Ph = phenyl

py = pyridine

bipy = 2,2'-bipyridine

THF = tetrahydrofuran

N.M.R. = nuclear magnetic resonance

Hz = Hertz

p.p.m. = parts per million

OMs = methanesulphonate

OPNB = *p*-nitrobenzoate

CHAPTER 1

INTRODUCTION

1. The chemistry of platinum

Historically, the first organometallic compound to be prepared was potassium trichloro(ethylene)platinate(II) monohydrate, commonly referred to as Zeise's salt in honour of its discoverer. The development seen in the organometallic chemistry of platinum can be attributed mainly to the fact that it forms a vast range of stable complexes which can be readily isolated and characterised.[1]

Although a few platinum systems are of catalytic interest, it is often this stability of the complexes which precludes the role of platinum complexes in much of the rich homogeneous catalysis exhibited by nickel and palladium. Often, however, investigation of the related platinum system can yield fruitful results owing to the isolation of complexes which could be envisioned, by analogy, as key intermediates in the catalytically active system.

Platinum coordination compounds are known for many oxidation states, 0, +1, +2, +3, +4 and higher. However the most common oxidation states for the organometallic complexes are 0, +2 and +4. Owing to this, two-electron reductive-elimination and oxidative-addition reactions between the divalent state and the 0 and +4 oxidation states are facile. These processes are made more favourable due to stable geometries of complexes in these oxidation states which allow for reductive-elimination and

oxidative-addition reactions to occur with loss of or addition of two ligands respectively. This is illustrated in figure 1.1.

1.1 Oxidation states.

The 0, +2 and +4 oxidation states of platinum and their usual stereochemistry are listed in Table 1.1. The chemistry of complexes of platinum in various oxidation states has been well reviewed,[1,2,3] and will only be discussed briefly here.

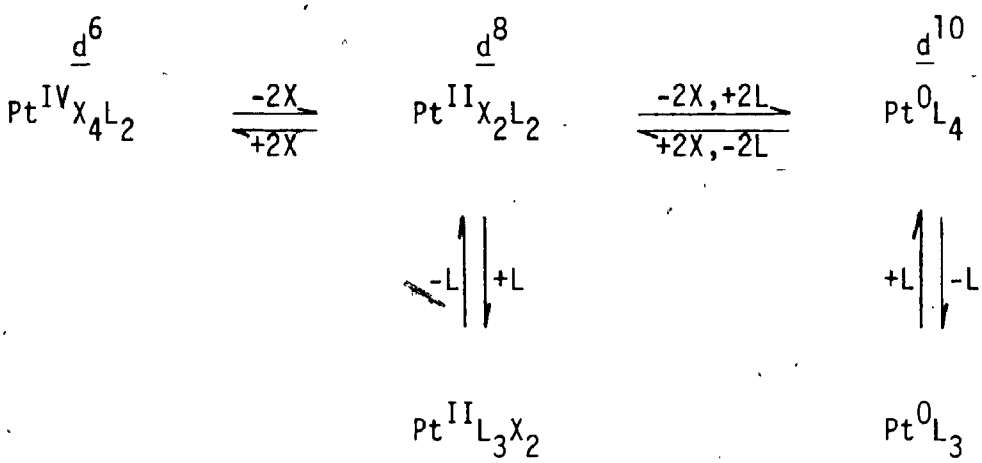
1.1.1 Platinum(0)

Platinum(0) has a $5\underline{d}^{10}$ electronic configuration. With four neutral ligands the normal geometry which results is tetrahedral, as expected for a $\underline{d}^{10}$ metal ion. This oxidation state is stabilised by tertiary phosphine ligands. An empirical observation is that stepwise replacement of carbon monoxide by phosphines in a series of complexes increases the stability in the order:[1]

$$[Pt(CO)_4] << [Pt(CO)_3(PR_3)] < [Pt(CO)_2(PR_3)_2], [Pt(CO)(PR_3)_3]$$

The dissociation of phosphine from $[Pt(PR_3)_4]$ type complexes to give $[Pt(PR_3)_3]$ and $[Pt(PR_3)_2]$ is well-known, the extent of which seems to depend on the steric bulk (cone-angle) of the phosphine. With extremely bulky phosphines only the coordinatively unsaturated $[PtL_2]$ can be isolated. For example when L = PPh^tBu_2 the complex $Pt(PPh^tBu_2)_2$ was isolated and its structure determined.[4] The stabilisation of the linear and trigonal coordinatively unsaturated compounds reflects the relief of steric strain seen in going to lower coordination numbers.

The reactions of $[Pt(PPh_3)_3]$ and $[Pt(PPh_3)_4]$ are numerous and generally fall into two catagories: oxidative addition and coordinative



(L = neutral ligand; X = anionic ligand)

Figure 1.1 The relationships between the common oxidation states of platinum

Table 1.1 Usual Coordination Number and Stereochemistries of Platinum Compounds in Common Oxidation States

Oxidation State	Coordination Number	Geometry	Examples	Ref.
0, $\underline{d}^{10}$	2	linear	$[Pt(PPh^tBu_2)_2]$	4
	3	trigonal planar	$[Pt(PPh_3)_3]$	2
	4	distorted tetrahedral	$[Pt(PPh_3)_3CO]$; one form	1
	4[a]	tetrahedral	$[Pt(PPh_3)_3CO]$, $[Pt(PPh_2Et)_2(CO)_2]$	1
+2, $\underline{d}^8$	4[a]	square planar	K_2PtCl_4	2
	5	trigonal bipyramidal	$[Pt(SnCl_3)_5]^{3-}$	2
	6	octahedral	$[Pt(NO)Cl_5]^{2-}$	2
+4, $\underline{d}^6$	6[a]	octahedral	K_2 fac-$[Pt(NO_2)_3Cl_3]$	3

a) most common

addition, each of which may involve initial generation of the $[Pt(PPh_3)_2]$ species. In the former, which involves oxidation to platinum(II), the incoming ligand (an alkyl halide or hydrohalic acid) is dissociated into two fragments which both coordinate to the metal, as in equation 1.1.

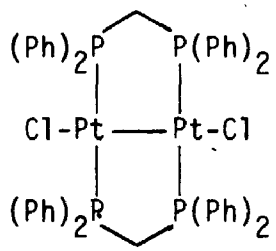
$$[Pt(PPh_3)_2] + CH_3I \longrightarrow [Pt(I)(CH_3)(PPh_3)_2] \quad ...(1.1)$$

In the latter, there is no change in the formal oxidation state of the metal as the incoming ligand (such as olefins, acetylenes or carbon monoxide), does not dissociate. The reaction proceeds as equation 1.2.

$$[Pt(PPh_3)_2] + \geq C{=}C \leq \longrightarrow [Pt(C_2H_4)(PPh_3)_2] \quad ...(1.2)$$

1.1.2 Platinum(I)

Platinum(I) compounds usually contain a Pt-Pt bond, which allows for the resulting species to be diamagnetic. An example of this type is the compound,[5] $Pt_2Cl_2(\mu\text{-dppm})_2$:



which has been shown to participate in many interesting reactions.

1.1.3 Platinum(II)

The complexes of platinum in the divalent state are extensive and varied, as is the chemistry of these compounds.[2] Platinum(II) has the $5d^8$ electronic configuration, the four-coordinate complexes being square-planar in geometry.

Platinum(II) shows a marked preference for nitrogen, halogens, cyanide and heavy donor atoms (P, As, S, Se) in formation of complexes, and exhibits only a small affinity for oxygen and fluorine donor groups.

Owing to their usual coordinative unsaturation, platinum(II) complexes show a diversity of reactions as they undergo oxidative-addition, reductive-elimination and ligand substitution reactions. Platinum(II) also shows an ease of formation of π-complexes, hydrido and Pt-C σ-bonded complexes.

1.1.4 Platinum(III)

The oxidation state +3 is very rare for platinum and complexes often occur only as shortlived intermediates. A few alkyl and aryl complexes of platinum(III) are known[1] and limited to binuclear carboxylate-bridged complexes. The preparation of a complex $[Pt_2(O_2CCH_3)_6]$ has been described,[6] as well as the complex $[Pt(\gamma\text{-picoline})(O_2CCF_3)(CH_3)_2]_2$[7] whose structure (figure 1.2) has been determined by X-ray diffraction methods. The number of platinum(III) dinuclear complexes which have been studied by X-ray

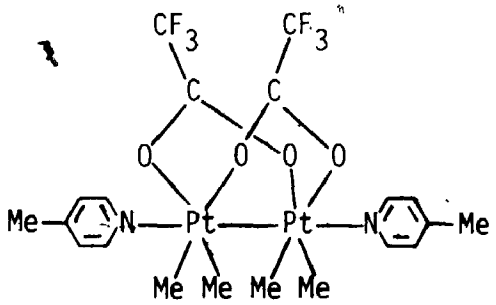


Figure 1.2 The structure of $[Pt(\gamma\text{-picoline})(O_2CCF_3)(CH_3)_2]_2$

crystallography is small[8] but has been extended recently by the X-ray structural determinations of the dinuclear compounds $K_2[Pt_2(SO_4)_4(OS(CH_3)_2)]\cdot 4H_2O$[9] and $Na_2[Pt_2(HPO_4)_4(H_2O)_2]$.[10]

1.1.5 Platinum(IV)

Platinum(IV) complexes are numerous. Many are able to undergo reductive elimination reactions as well as ligand substitution reactions. A characteristic of Pt(IV) alkyl complexes is the stability of the fac-$Pt(CH_3)_3$ unit. Typical of these are the complexes $[PtX(CH_3)_3]_4$ (X = iodide, chloride, hydroxide and azide) which are all tetrameric possessing the structure in figure 1.3 with platinum atoms located at opposite corners of a cube.

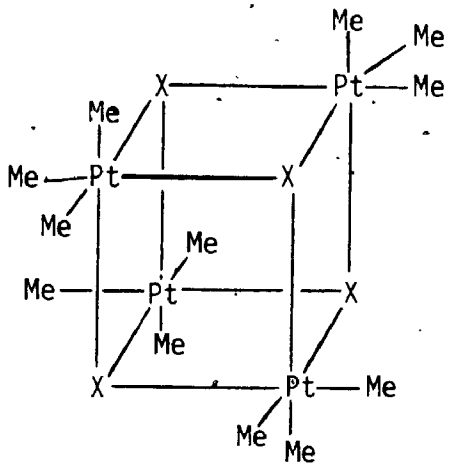


Figure 1.3 The tetrameric structure of $[PtX(CH_3)_3]_4$ complexes

1.1.6 Platinum in higher oxidation states[2]

The platinum(V) complexes which have been investigated are PtF_5, $PtOF_3$ and a series of hexafluoroplatinates(V). Most are octahedral, paramagnetic $\underline{d}^5$ systems with a single unpaired electron.

Complexes with platinum in the +6 oxidation state are known only with oxygen or fluorine ligands. PtF_6 is extremely reactive and believed to have octahedral symmetry.

1.2 Platinum-olefin complexes

Platinum, in both the 0 and +2 oxidation states forms olefin complexes. In fact they are the oldest class of organometallics known, $K[PtCl_3(C_2H_4)]\cdot H_2O$ being first reported in 1830.[11]

1.2.1 Preparation of platinum(II)-olefin complexes

The platinum(II)-olefin complexes may be prepared by:

a) Reaction of platinum(II) salts, $[PtCl_4]^{2-}$ with primary alcohols according to the reaction in equation 1.3.

$$Na_2[PtCl_4] + RCH_2CH_2OH \longrightarrow Na[Pt(RCH{=}CH_2)Cl_3] \qquad ...(1.3)$$

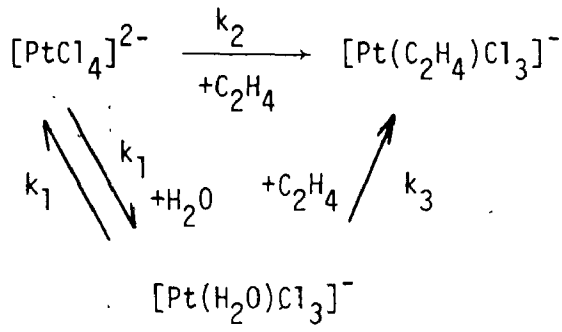
b) Treating a platinum(II) salt with olefin in aqueous solution. The mechanism for this reaction has been determined[1] (scheme 1.1). The reaction takes a number of days to go to completion, but addition of a trace of stannous chloride accelerates this reaction considerably (Scheme 1.2). A convenient route to Zeise's salt takes advantage of this rate enhancement and the mechanism of its formation by this method has been deduced by Belluco.[12] Dimerisation of $K[PtCl_3(C_2H_4)]$ is effected in ethanol by the addition of concentrated HCl to yield Zeise's dimer, $[Pt_2Cl_2(\mu\text{-}Cl)_2(C_2H_4)_2]$.[13]

c) Treatment of a chloroplatinate(II) salt with silver(I) and an olefin (equation 1.4).

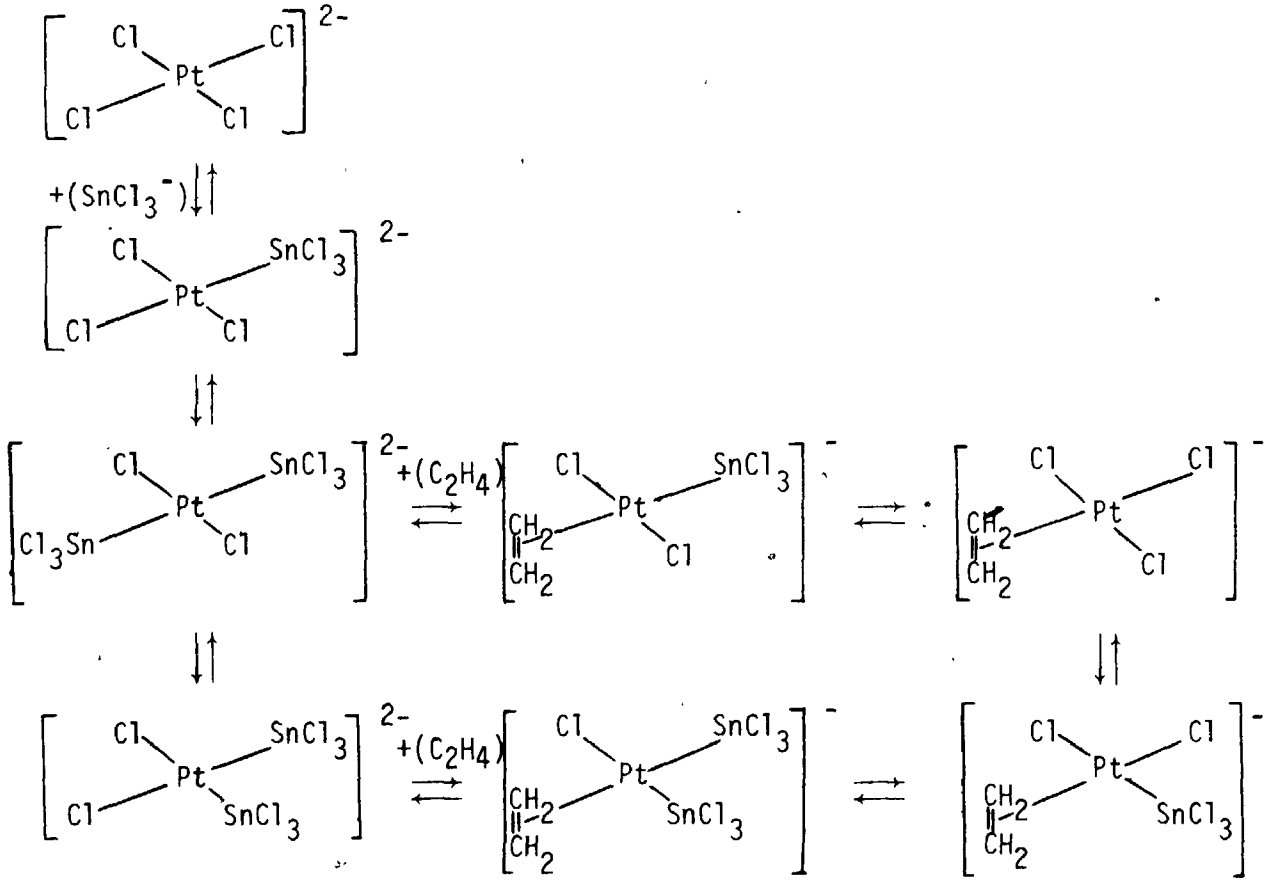
$$[PtCl(\eta^5\text{-}C_5H_5)PPh_3] + AgClO_4 + C_2H_4 \longrightarrow [Pt(C_2H_4)(\eta^5\text{-}C_5H_5)PPh_3]ClO_4 \qquad ...(1.4)$$

d) Cleavage of a halide bridge by olefins (equation 1.5).

$$[Pt_2Br_6]^{-2} + 2(olefin) \longrightarrow 2[PtBr_3(olefin)]^- \qquad ...(1.5)$$



Scheme 1.1 The mechanism for the reaction of ethylene with $[PtCl_4]^{2-}$



Scheme 1.2 The mechanism of the reaction of ethylene with $[PtCl_4]^{2-}$ in the presence of $[SnCl_3]^-$

e) Replacement of one olefin by another. An excess of one olefin is used to displace another olefin from its complex (equation 1.6). Ethylene complexes are often used as starting materials since removal of ethylene is rapid, owing to its volatility.

$$K[PtCl_3(C_2H_4)] + PhCH{=}CH_2 \longrightarrow K[PtCl_3(PhCH{=}CH_2)] + C_2H_4 \quad ...(1.6)$$

1.2.2 Bonding in platinum-olefin complexes

The nature of the platinum-olefin bond has been the subject of extensive investigation. The bonding is usually considered in terms of the Dewar-Chatt-Duncanson approach.[1] This approach considers the contribution from two components to the total bonding: a σ-bond involving donation of electrons from the filled π-molecular orbitals of the olefin to an empty dsp^2 hybrid orbital on the metal atom and a π-bond formed by the back-donation of electrons from a platinum dp hybrid orbital into the empty π*-antibonding orbital of the olefin, the olefin being oriented perpendicular to the $PtCl_3$ plane. This is illustrated in figure 1.4. The model can be used to explain all known properties of the complexes. Controversy only arises over the relative contribution of the σ and π-bonds in this scheme.

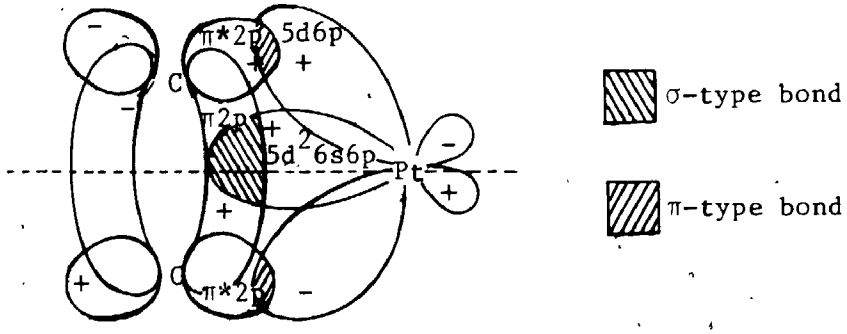
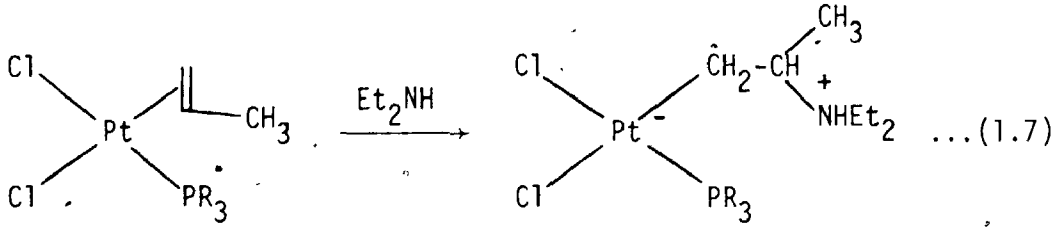


Figure 1.4 Bonding in platinum(II)-olefin complexes

Hoffmann[14] has addressed the bonding, rotational barriers and conformational preferences in ethylene complexes from a molecular orbital approach. He argues that the barrier to rotation of the ethylene about the Pt-ethylene axis in Zeise's salt type complexes is largely set by steric factors which favor the upright geometry. Essentially all of this barrier arises from the interaction of the cis-chlorines with the ethylene. This steric interaction is also shown to account for the observed bending back of the ethylene hydrogens away from the metal.

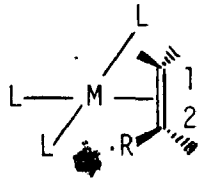
1.2.3 Nucleophilic attack on coordinated olefins

The bonding scheme for metal-olefin complexes, described in the previous section suggests that the electron density in the π-orbital of the olefin is greatly reduced upon coordination to the metal atom. This is supported not only by the observed increase in C=C bond length in the complexed olefin relative to that of the free olefin, but also by the increase in susceptibility towards nucleophilic attack in the former.[1] Nucleophiles which have been shown to attack olefin complexes to give σ-alkyl complexes include OH^-, CH_3COO^-, CH_3O^-, Cl^-, alcohols, amines and amides. In most of the cases studied, the process involved trans attack (from the face opposite the metal) by the nucleophile, without prior coordination. With substituted olefins this reaction usually proceeds yielding the product arising from attack at the more substituted carbon (equation 1.7).[3]



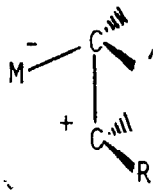
...(1.7)

This result has been rationalized by Eisenstein and Hoffman[15] in terms of a "slipping" motion of the alkene relative to the metal-alkene bond axis prior to bond formation between the nucleophile and the alkenic carbon. In asymmetrically substituted alkene complexes such as A, X-ray crystal structure determinations[14] reveal that the metal-carbon distance to the carbon atom carrying the substituent, C_2, is longer than that to the unsubstituted carbon, C_1.



A

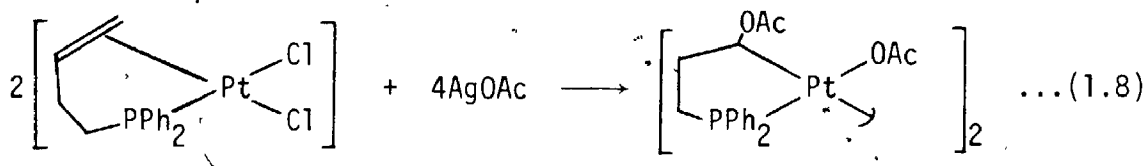
Frequently this bonding asymmetry is accompanied by a slipping of the olefin such that the center of the C_1-C_2 bond lies below the ML_3 coordination plane. For instance in A, when ML_3 = PtCl(acac) and R = OH[1] the Pt-C_1 distance is 2.222(9) Å. Also, the distance from the midpoint of the C_1-C_2 bond to the principal ML_3 coordination plane is 0.59 Å. Eisenstein and Hoffmann have extended this ground state observation to explain reactivity of olefins; symmetric or asymmetric. The asymmetric π-bonding to an olefin and the slipping of the olefin, when taken to their extreme, are signs of an easy transformation to a zwitterionic π-bonded form, complex B, which is effectively a metal-stabilised carbonium ion.



B

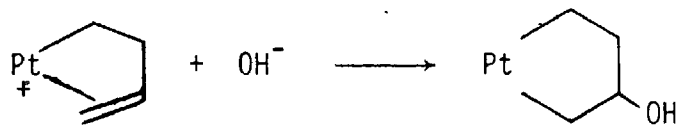
This resonance structure would account for the observed products of nucleophilic reactions as being those arising from attack at the more substituted carbon, in the absence of overriding steric effects.

Another example of nucleophilic attack on a platinum-olefin involves the preparation of platinum-carbon σ-bonded complexes from a π-bonded olefin, as in equation 1.8.[1] This type of reaction may give precedent for the preparation of substituted platinacyclopentane complexes from



...(1.8)

platinum but-3-enyl complexes according to equation 1.9. This aspect will be discussed further in a later chapter.



...(1.9)

1.3 Platinacyclobutane complexes

Interest in platinacyclobutane complexes has arisen owing to their possible relevance to several transition metal catalysed reactions, such as olefin metathesis and transition metal catalysed rearrangements of small rings. Each of these will be further explored separately in later sections.

The chemistry of platinacyclobutanes has been reviewed[17] and will not be repeated here. Discussion will be restricted to specific areas in the field required to introduce aspects brought up in later chapters.

1.3.1. Preparation

There exist in the literature several methods for the preparation of platinacyclobutanes of Pt(II) and Pt(IV). The first platinacyclobutane complex was prepared by the reaction of cyclopropane with hexachloroplatinic(IV) acid in acetic anhydride to give a brown solid of composition $PtCl_2(C_3H_6)$ which gave a white compound $[PtCl_2(C_3H_6)(py)_2]$ on treatment with pyridine.[18] This method can not be used to prepare substituted derivatives. The general method used is that discovered by McQuillin,[19] in which the cyclopropane derivative is reacted with Zeise's dimer, according to equation 1.10. The solvent of choice for this reaction is

$$\frac{n}{2}\ PtCl_2(C_2H_4)_2 + n\ R\text{-}\triangle \longrightarrow \text{(R-substituted cyclobutane)}PtCl_2\ _n + n\ C_2H_4 \qquad \ldots(1.10)$$

found to be tetrahydrofuran, as both the starting materials and product are soluble in it.[17] The reaction in equation 1.10 is accelerated by electron-releasing groups, R, and impeded when strongly electron-withdrawing groups are present, eg. R = CO_2CH_3, CN or $COCH_3$. The initially precipitated products are thought to be tetrameric in the solid state having the structure in figure 1.5, as determined from spectroscopic evidence. These products are insoluble in most organic solvents, however in solvents, S, containing a donor oxygen atom, such as tetrahydrofuran, the tetrameric species breaks up to give presumably $[PtCl_2(CH_2CH_2CH_2)S_2]$ in solution, though they are rarely seen upon isolation. On treatment with pyridine, or other good nitrogen donor ligands, the monomeric octahedral $[PtCl_2(CH_2CH_2CH_2)py_2]$ is formed. These types of complexes can be isolated and easily characterised owing to their enhanced solubilities compared to the tetrameric complexes. They have been shown to have the structure,

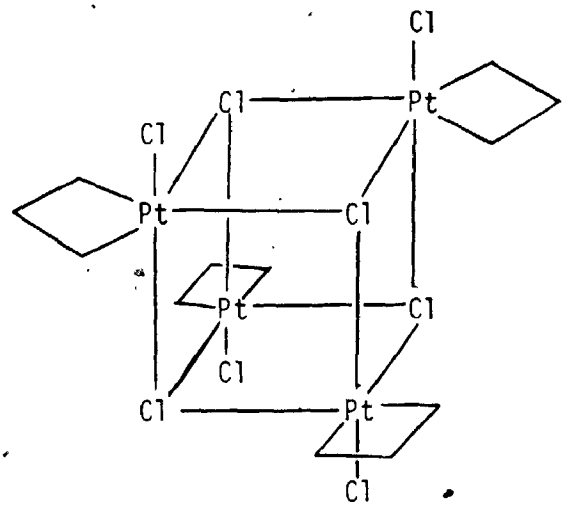


Figure 1.5 The tetrameric structure proposed for $[PtCl_2(C_3H_6)]_4$ complexes

shown in figure 1.6, with trans chloride and cis pyridine ligands.[20]

Reactions of soft ligands, L, such as trialkyl phosphines, carbon monoxide and alkenes with platinum(IV) metallacyclobutanes lead to reductive elimination of the cyclopropane derivative and formation of the platinum(II) complex, cis- $PtCl_2L_2$.

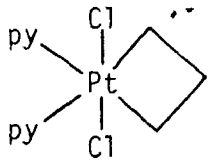
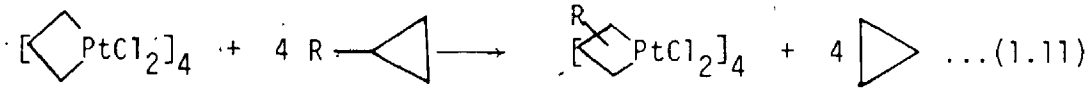


Figure 1.6 Octahedral arrangement of ligands in $[PtCl_2(CH_2CH_2CH_2)py_2]$ compounds

Ylide or alkene complexes are formed from decomposition of the platinum(IV) metallacyclobutanes upon addition of bulky nitrogen donor ligands or weakly coordinating ligands, such as methyl cyanide, or even

pyridine itself if the platinacyclobutane is heavily substituted as in $[\overline{PtCl_2(CHCH_3C(CH_3)_2CH_2}]py_2]$. α-elimination is strongly indicated in this mechanism.[21]

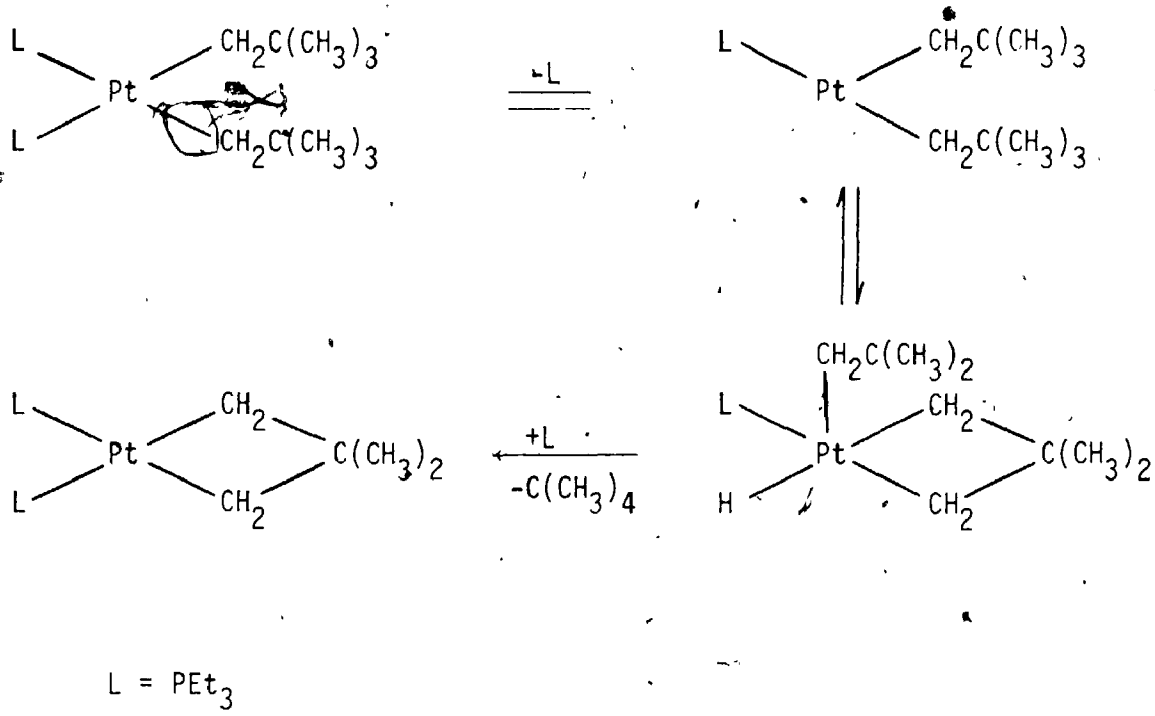
It has been demonstrated[22] that one cyclopropane can displace another in the tetrameric complex, but only slowly in the bis(pyridine) complex according to equation 1.11.



...(1.11)

Synthetic routes to platinum(II) metallacyclobutanes are known and have been presented elsewhere.[17] One of these, discovered by Whitesides,[23] involves γ-elimination of metal alkyls which lack a β-CH bond. The mechanism which has been deduced is shown in scheme 1.3. It involves three steps: creation of a vacant site on the platinum by dissociation of phosphine, oxidative addition of a methyl C-H bond from a neopentyl group to platinum(II), and reductive elimination of neopentane to yield the platinum(II) metallacyclobutane. An X-ray structural determination on one of these products has been performed.[23] This remarkable reaction may provide a general synthetic route to other metallacyclobutanes, as it has been extended so far to iridium[24] and thorium.[25]

Kochi[26] has recently reported the synthesis of some platinum(II) metallacyclobutanes by the electrochemical and chemical reduction of the corresponding platinum(IV) analogues. X-ray crystallography studies on $[\overline{PtCH_2CH_2CH_2}(bipy)]$ and $[\overline{PtCl_2(CH_2CH_2CH_2}](bipy)]$ reveal the essential identity of the platinacyclobutane moiety in both derivatives.



L = PEt_3

Scheme 1.3 Formation of platinum(II) metallacyclobutanes from a dialkylplatinum(II) complex

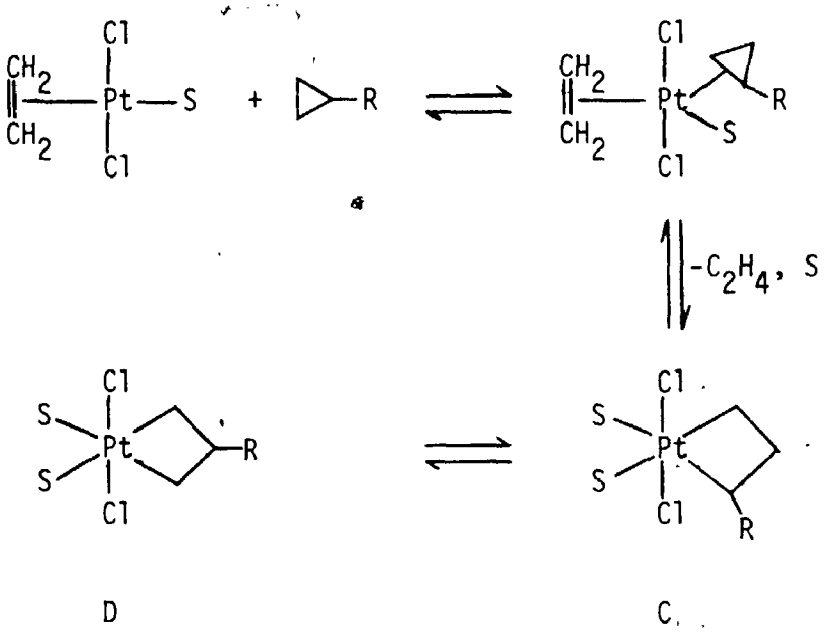
1.3.2 Mechanism of formation of platinacyclobutanes by the method of McQuillin[15]

In equation 1.10, when R = $n\text{-}C_6H_{13}$, $PhCH_2$, $o\text{-}O_2NC_6H_4$, or Ph, the product isolated after addition of pyridine is $[\overline{PtCl_2(CH_2CHRCH_2}]py_2]$, whereas when R = $CH_3C_6H_4$ the major product isolated is $[\overline{PtCl_2(CHRCH_2CH_2}]py_2]$.[22,27] These results indicate insertion of platinum into the least substituted and most substituted C-C bond of the cyclopropane, respectively. The mechanism which best explains the observed results from the reaction is illustrated in scheme 1.4.[28] In this mechanism, the platinum atom inserts into the most substituted bond to give compound C, $[\overline{PtCl_2(CHRCH_2CH_2}]S_2]$, which then undergoes an intramolecular isomerisation reaction to give compound D, $[\overline{PtCl_2(CH_2CHRCH_2}]S_2]$. Alternatively, insertion into the least substituted bond could occur to a minor degree, initially giving D. Either way, the skeletal isomerisation between the two products is rapid, leading to an equilibrium mixture of the two. Thus, it is not possible to determine the initial point of insertion into the cyclopropane ring.

This type of skeletal isomerisation has also been seen for the bis(pyridine) products[29] (S=py). The rate has been shown to be strongly dependent upon the concentration of added pyridine and the isomerization reaction does not occur for the analogous bipyridyl complexes. These results strongly indicate that reversible dissociation of pyridine from the platinacyclobutane giving a five-coordinate, 16-electron complex occurs prior to the skeletal rearrangement.

1.4 Metallacyclobutanes as intermediates

Metallacyclobutanes have been proposed as intermediates in several catalytic reactions, to explain the products from transformations. Two



D C

Scheme 1.4 Mechanism of formation of platinacyclobutanes

of these are the olefin metathesis reaction and the rearrangements of strained cycloalkanes.

1.4.1 The olefin metathesis reaction

Although the mechanism of olefin metathesis was once in doubt, most authors now accept the Herisson-Chauvin mechanism[30] illustrated in figure 1.7. The mechanism involves the generation of a metal-carbene which reacts with an olefin to give a metallacyclobutane intermediate,

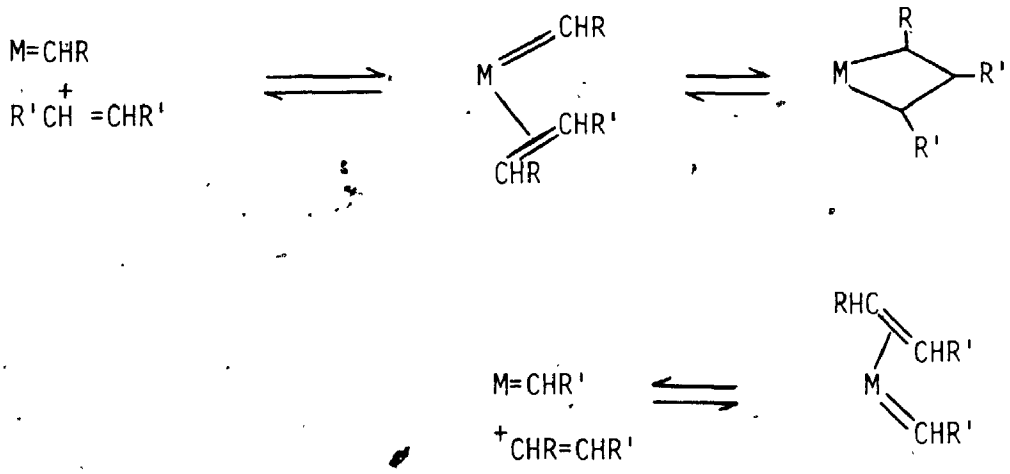


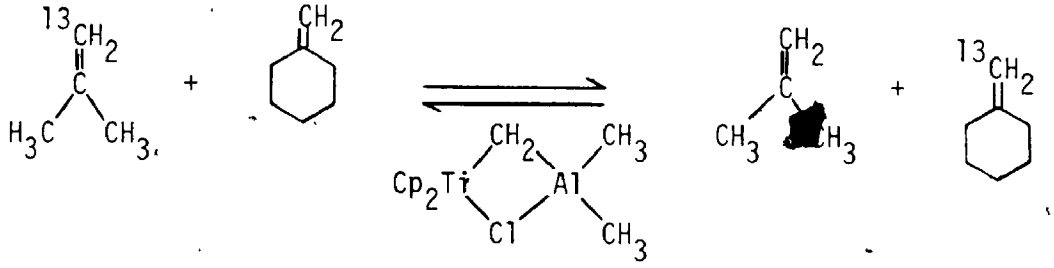
Figure 1.7 The nonpairwise mechanism for olefin metathesis

which can then break-up to give the original metal-carbene complex and olefin or different ones. This provides an explanation for the scrambling of alkylidene units observed experimentally. Evidence for this mechanism has been summarised elsewhere[31] and will not be elaborated upon here. Recent results will be discussed however, which firmly establish each of the major steps involved (figure 1.7).

The key steps which need to be demonstrated to lend credence to this mechanism are: (1) that a recoverable metal-carbene complex would

catalyse metathesis and (2) that metallacyclobutanes are intermediates in a catalytic reaction.

The first clear-cut case of catalysis by a carbene complex was reported by Parshall and Tebbe,[32] in which exchange of alkylidene units between metal carbene complexes and alkenes was shown (figure 1.8).

a) 

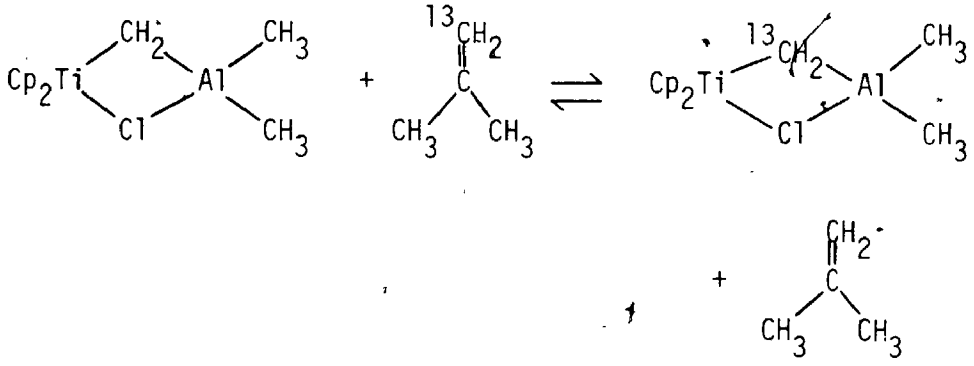
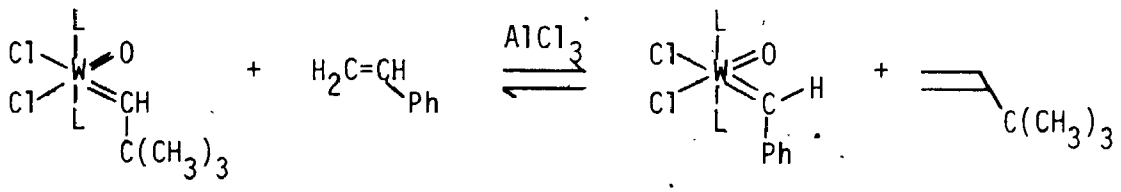
b) 

Figure 1.8 Examples of key steps in olefin metathesis:
a) scrambling of olefins
b) exchange between catalyst carbene and olefin

Another more recent result was reported by Schrock,[33] in which the exchanged carbene product could be isolated (equation 1.12).



L = PEt_3 ...(1.12)

The last of the major steps of the Chauvin mechanism to be modelled was the preparation of a metallacyclobutane complex from a metal carbene-olefin reaction. This has been demonstrated directly by Grubbs,[34] based on the Tebbe system according to figure 1.9. Several of the titanacyclobutane products of this reaction have been isolated and their X-ray crystallographic studies reported.[35]

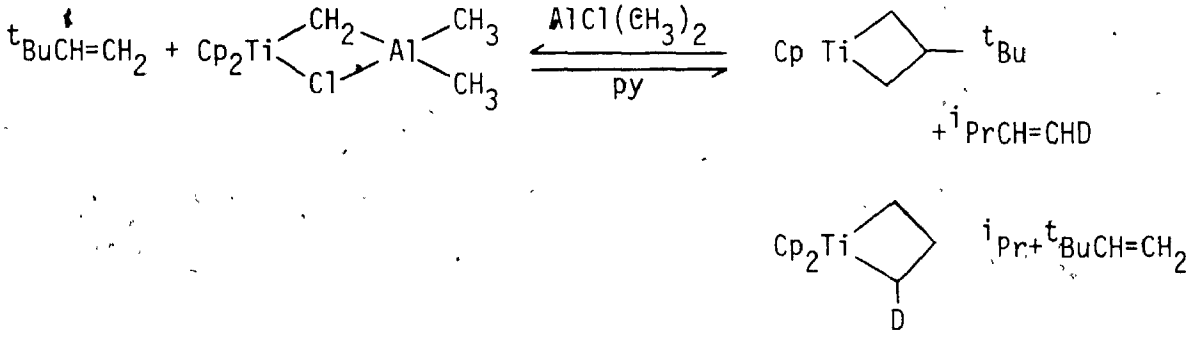


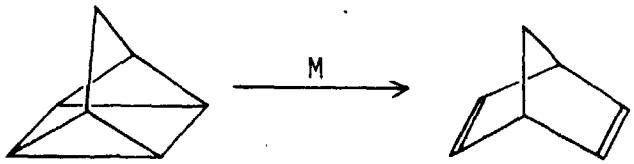
Figure 1.9 Preparation of a metallacyclobutane from a metal carbene-olefin reaction

Thus, the Chauvin mechanism is clearly supported by experimental results.

1.4.2 Rearrangement of strained cycloalkanes by transition metals

Transition metals are known to catalyse rearrangements of strained ring carbocyclic compounds. This topic has been a subject of reviews.[3] Metallacyclobutane-type intermediates are suggested for most of these reactions, although the evidence is usually indirect. Several of these reactions will be discussed briefly.

Quadricyclane (E) rearranges at room temperature to norbornadiene in the presence of many transition metal complexes according to the reaction (equation 1.13).



...(1.13)

E

If $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ is used as a catalyst however, a rhodiacyclobutane was trapped by CO insertion according to Figure 1.10. The product isolated, a rhodiacyclopentanone, supports the metallacyclobutane intermediate proposed. The formation of rhodiacyclopentanones has also

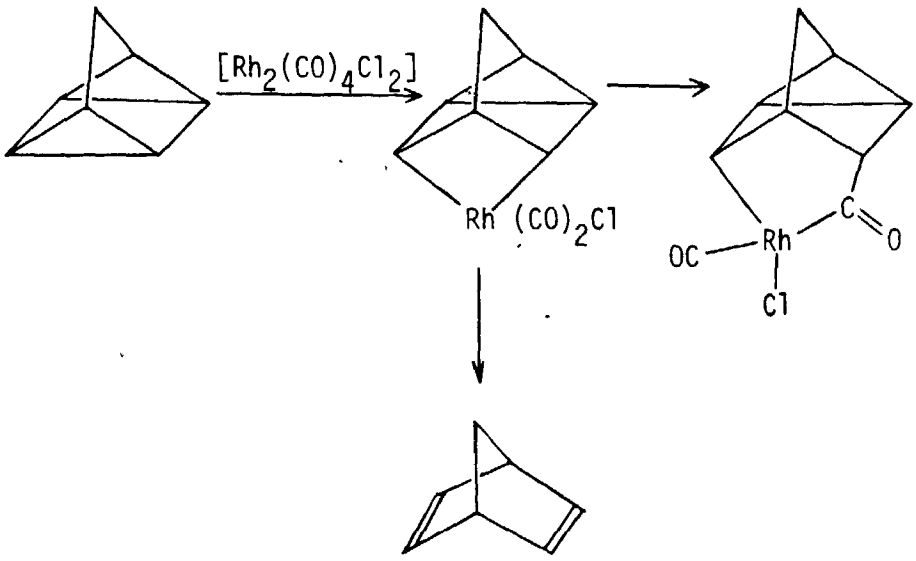
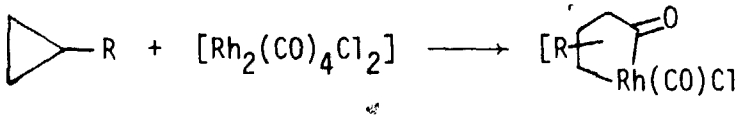


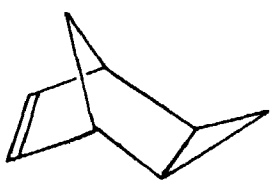
Figure 1.10 Reaction of $[Rh_2(CO)_4Cl_2]$ with quadricyclane

been seen in the reactions of cyclopropanes with $[Rh_2(CO)_4Cl_2]$ according to the reaction[37] in equation 1.14.

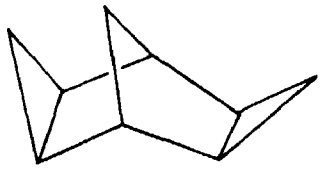


...(1.14)

The reaction of Zeise's dimer with the strained ring compounds F and G have recently been reinvestigated by Jennings.[38] The original work

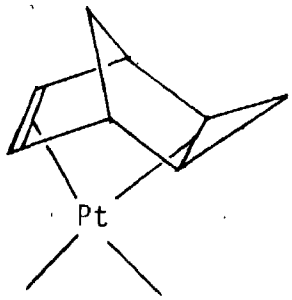


F

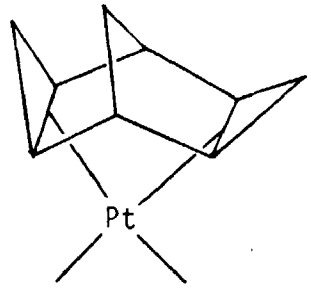


G

by Volger,[39] postulated the platinum complexes to contain bis-endo coordination to the edge of the cyclopropane as in H and I respectively. The latter of these complexes, I, was investigated subsequently by Johnson,[40]



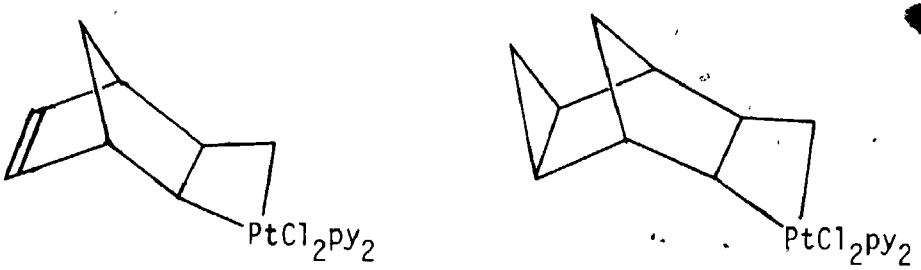
H



I

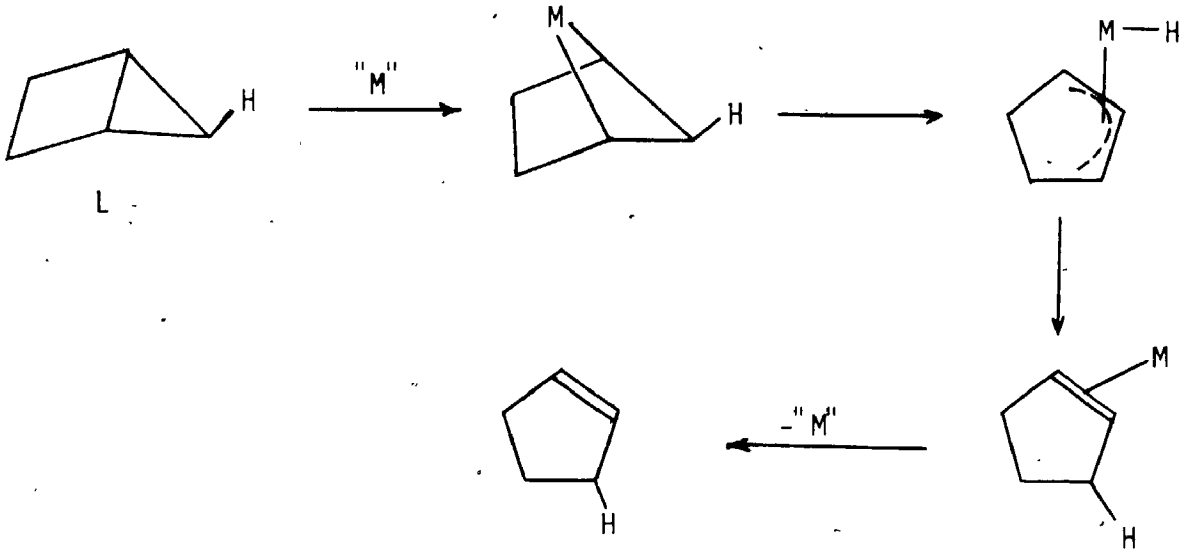
who concluded that the same structure, I, was present. Jennings,[38] however, has reported the products, more plausibly as the platinacyclobutane complexes J and K, respectively. These structures were supported by spectroscopic techniques which included solid-state ^{13}C-N.M.R.

Bicycloalkanes are strained ring systems which generally rearrange to give olefinic products,[36] possibly via metallacyclobutane intermediates. Bicyclo[2.1.0]pentane, L, for example, when treated with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ reacts to give cyclopentene as the major product. The mechanism by which this reaction is thought to proceed is shown in figure 1.11. This



J K

mechanism is consistent with the results of studies performed on labelled bicyclopentanes.



L

Figure 1.11 Proposed mechanism for the rearrangement of bicyclo[2.1.0]-pentane in the presence of $[Rh_2(CO)_4Cl_2]$,"M".

Bicyclo[1.1.0]butane, M, is thermally stable but rearranges easily to 1,3-dienes in the presence of a variety of transition metal catalysts. An interesting reaction of M with Zeise's dimer has been reported recently to give a platinacyclobutane complex which was characterised as the more soluble bis(pyridine) adduct, N.[41] The reaction proceeds according to figure 1.12. The relevance of this reaction, and others, to the thesis work will be discussed in a later chapter.

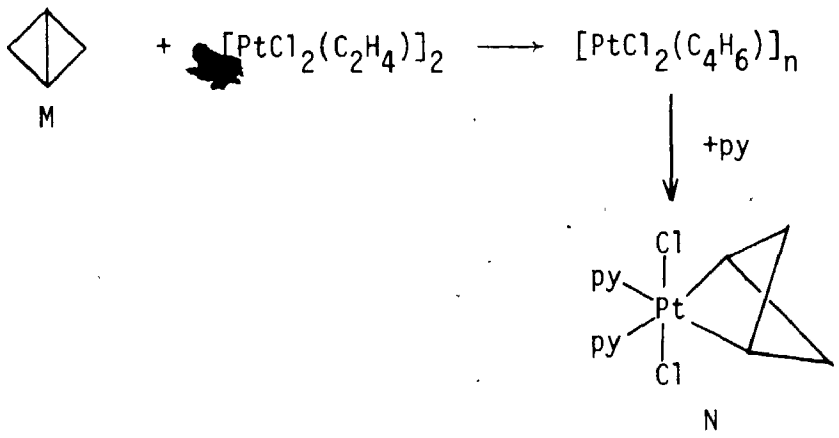


Figure 1.12 Reaction of bicyclo[1.1.0]butane with Zeise's dimer

1.5 Platinacyclopentanes

1.5.1 Preparation

There are at this time few general synthetic routes to platinacyclopentane complexes, though routes to other metallacyclopentanes are known. One method of preparation is by treatment of dihalogenoplatinum(II) complex with 1,4-dilithiobutane according to the reaction in figure 1.13.[42] The platinum(II) metallacyclopentanes are susceptible to oxidation by halogens to give the platinum(IV) metallacyclopentanes.

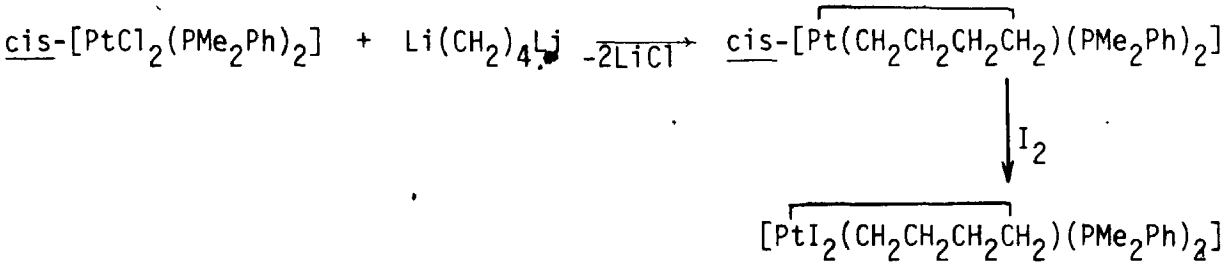


Figure 1.13 Preparation of platinum(II) and (IV) metallacyclopentanes

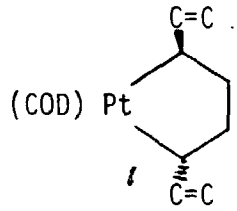
This method has not been used to prepare platinacyclopentanes with substituents on the rings.

A similar method[43] to the one above, involves the reaction of a di-Grignard reagent with dichloro(1,5-cyclooctadiene)platinum(II) followed by displacement of 1,5-cyclooctadiene, COD, with tertiary phosphines according to equation 1.15.

$$MgBr(CH_2)_4MgBr + (COD)PtCl_2 \longrightarrow (COD)Pt(CH_2)_4 \xrightarrow[-COD]{+PR_3} Pt(CH_2)_4(PR_3)_2 \quad \ldots(1.15)$$

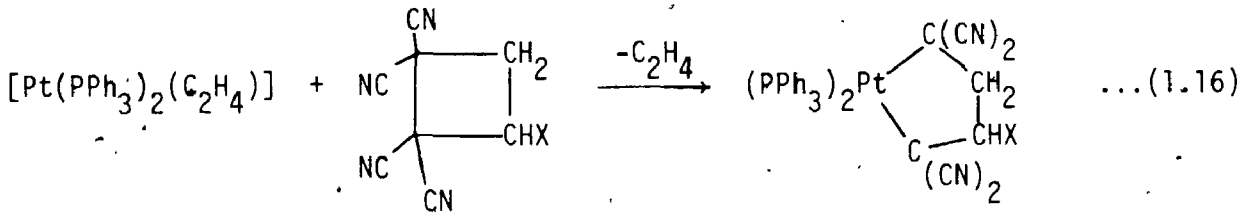
These products oxidatively add halogens to yield the corresponding platinum(IV) complex. This method has found utility in the preparation of substituted platinacyclopentanes such as $[\overline{Pt(CHCH_3CH_2CH_2CH_2)}(P\text{-}^tBu_3)_2]$

Another method,[44] though less general, involves the coupling of two butadiene units upon reaction with $(COD)_2Pt$ to give the $\underline{d}^8$ complex, O, having trans α,α'-vinyl groups as determined by X-ray diffraction methods.



O

A platinum(II) metallacyclopentane has also been prepared[45] by oxidative-addition of electronegatively substituted cyclobutanes to $[Pt(PPh_3)_2(C_2H_4)]$ according to the reaction (equation 1.16). The structure of the product (X = OEt) was determined by X-ray diffraction techniques.



...(1.16)

X = OEt, $C_6H_4OCH_3$

1.5.2 Metallacyclopentanes as intermediates

The role of metallacycloalkanes as catalytic intermediates has been a subject of a recent review.[46] Schrock[47] has noted a selective catalysis for the dimerisation of olefins via a tantalacyclopentane intermediate. The metallacyclopentane decomposes by ring contraction to give a metallacyclobutane followed by β-elimination-reductive elimination (figure 1.14). The reverse reaction, metallacyclobutane to metallacyclopentane ring-expansion will be presented in a later chapter for a novel platinum system.

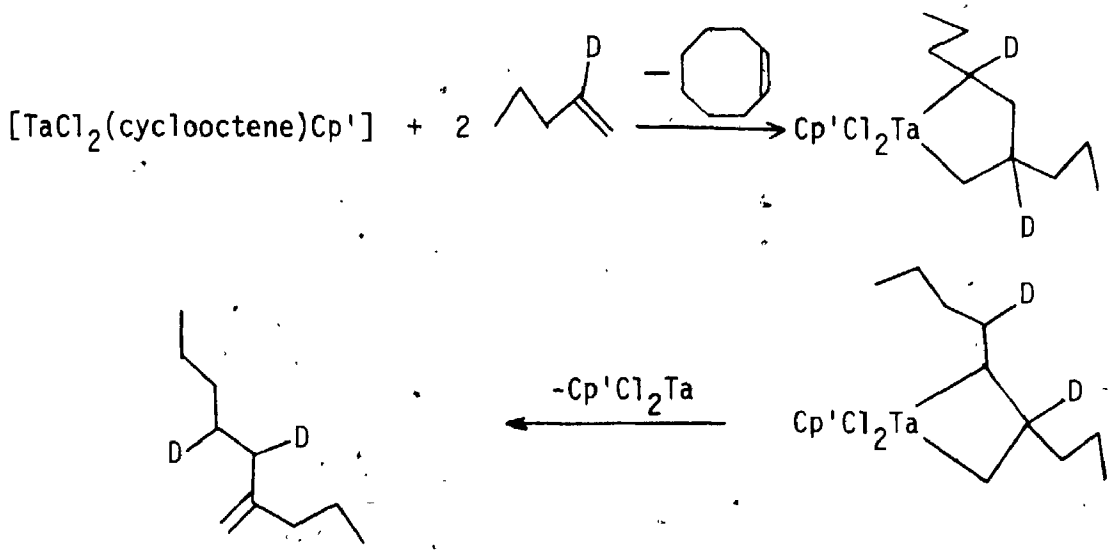


Figure 1.14 Dimerisation of 2-deuterio-1-pentene with $TaCl_2Cp'$. Cp'= $C_5(CH_3)_5$

CHAPTER 2

PREPARATION AND CHARACTERISATION OF PLATINACYCLOBUTANE COMPLEXES

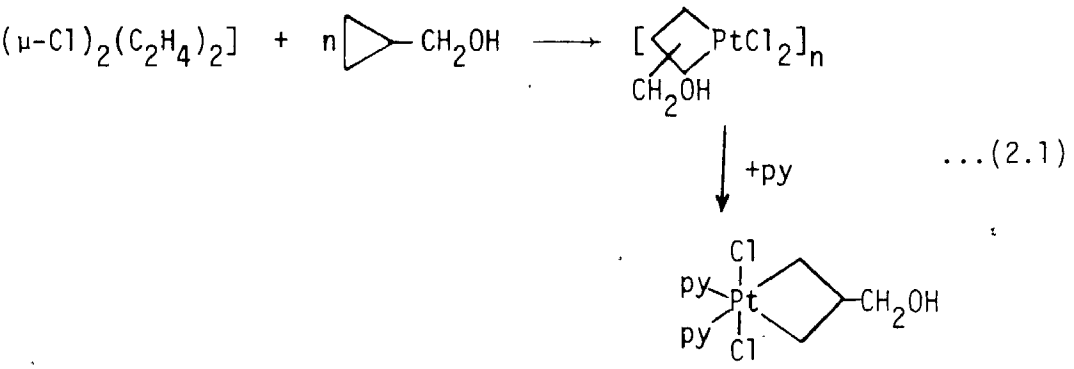
1. Introduction

Since the discovery of the first platinacyclobutane complex by Tipper,[18] in 1955, this area of research has received considerable attention.[17] The implication of metallacyclobutanes as key intermediates in such processes as olefin metathesis,[31] the transition metal catalysed rearrangements of small organic ring compounds[36] and the Ziegler-Natta polymerisation of olefins[48,49] has contributed greatly to the growth of this field. Not only have the preparation and reactivity of many platinacyclobutanes been reported, but investigations of the chemistry of metallacyclobutanes of other transition elements have also been undertaken.

Although the number of platinacyclobutanes which have been made is quite large, all previously known platinum(IV) metallacyclobutanes have either unsubstituted rings or have simple alkyl or aryl substituents on the ring.[17] Attempts to prepare derivatives with an amine functionality have failed since reaction of Zeise's dimer with either 2-cyclopropylpyridine or N,N-diethylcyclopropyl methylamine gave only the simple nitrogen bonded adducts, <u>trans</u>-$[PtCl_2(C_2H_4)(L)]$.[50]

The initial strategy of this thesis involves the preparation of platinacyclobutane complexes containing a hydroxyl functionality according to equation 2.1. The results of such studies not only extended the generality of this reaction (equation 1.10) but provided a route to ester derivatives containing a good leaving group. The significance of this aspect of the research will be dealt with in a later chapter.

This chapter reports the preparation and characterisation of all platinacyclobutanes prepared in this work, as well as the results for cyclopropane starting materials prepared.



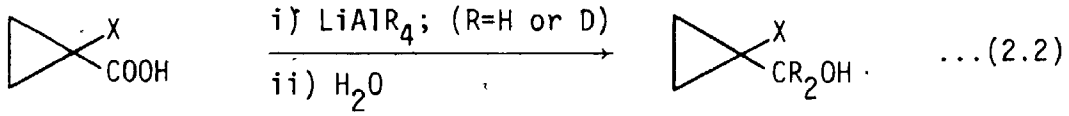
...(2.1)

2. Results and Discussion

2.1 Preparation of cyclopropane derivatives

The cyclopropanes used in this work consist of two types: those containing an alcohol group and those containing an ester linkage. The experimental details for the preparation of those cyclopropanes not obtained from commercial suppliers are described in Chapter 8.

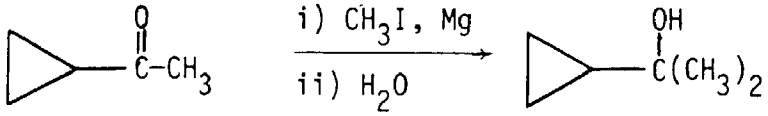
In general, the primary alcohols were prepared directly by reduction of the corresponding carboxylic acid in anhydrous ether, followed by hydrolysis, according to equation 2.2.[51] This route also provided a convenient method for deuterium incorporation at the carbinyl group through the use of lithium aluminum deuteride (R = D in equation 2.2).



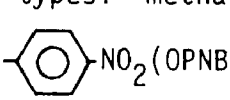
...(2.2)

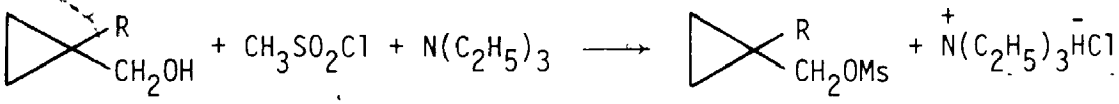
(X = H, CH_3 or Ph)

2-Cyclopropyl-2-propanol was prepared by the Grignard reaction of methylmagnesium iodide with cyclopropyl methyl ketone, according to equation 2.3.[52]



...(2.3)

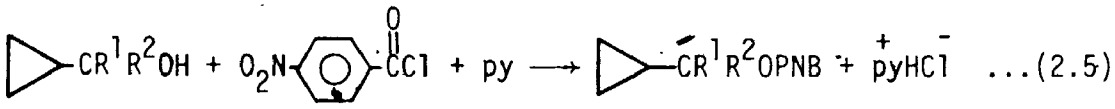
The ester-containing cyclopropane derivatives were prepared from the corresponding alcohol and were of two types: methanesulphonates; $-O-SO_2CH_3$(OMs) and *p*-nitrobenzoates;  (OPNB). The methanesulphonates of primary alcohols were prepared by the reaction of the alcohol with methanesulphonyl chloride, in triethylamine, at room temperature according to equation 2.4.[53] Attempts to prepare the methanesulphonate ester of the secondary alcohol, α-methylcyclopropyl methanol,



(R = H, CH_3, Ph) ...(2.4)

in good yield, were not successful. These reactions provided some of the desired product only at low temperature and prolonged reaction times.

p-Nitrobenzoate esters of the secondary and tertiary alcohols were prepared, according to equation 2.5, by the reaction of the alcohol with *p*-nitrobenzoyl chloride in dry pyridine at -5°C.



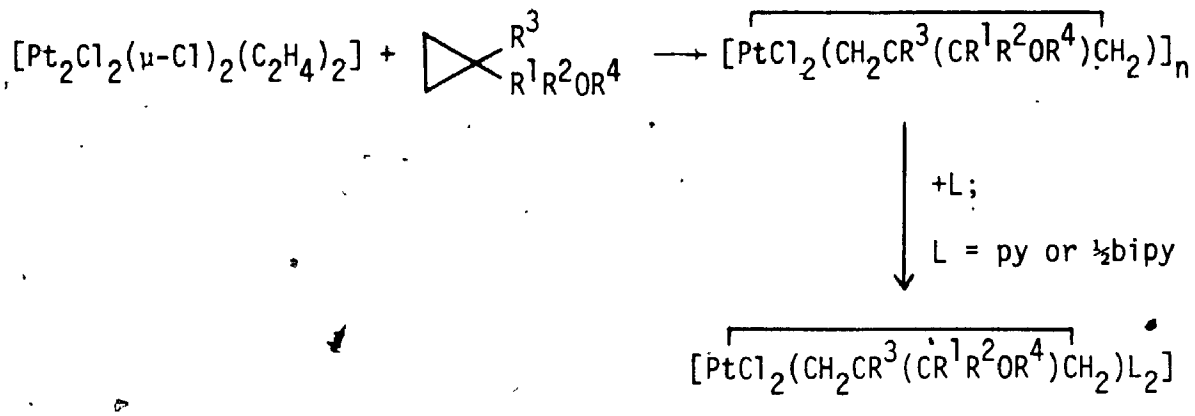
...(2.5)

The cyclopropanes prepared were characterised by ^1H and ^{13}C-N.M.R. spectroscopies as well as melting points or boiling points for the

solids or liquids respectively. This information is reported in the experimental section of Chapter 8.

2.2 Preparation of the platinacyclobutane complexes

The platinacyclobutane complexes (1→15) were prepared according to a revised method of McQuillin[19] using anhydrous tetrahydrofuran as solvent. A typical synthesis consisted of the reaction of a ten-fold molar excess of the cyclopropane derivative with Zeise's dimer for 10-20 hours at room temperature. This has been illustrated in scheme 1.4. Generally, the oxidative addition reaction is accompanied by a distinctive colour change from the characteristic orange of Zeise's dimer to a pale yellow. Upon removal of the solvent and unreacted cyclopropane, a solid residue remains which is probably tetrameric (figure 1.5). These insoluble products were then treated with pyridine or the chelating ligand, 2,2'-bipyridine to give the more soluble monomeric products. The 2,2'-bipyridine (bipy) complexes could also be produced directly from the pyridine complexes by addition of 2,2'-bipyridine. The bipy complexes were generally found to be less soluble than the analogous pyridine complexes and hence could be isolated by filtration. The exact details of each preparation has been outlined in chapter 8. The products were characterized by ^{1}H and ^{13}C N.M.R. spectroscopies, as well as elemental analyses and melting points. The product isolated, in all cases, was that depicted in scheme 2.1 which corresponds to compound D in scheme 1.4.



PRODUCTS

L = py	L = ½bipy
1: $R^1=R^2=R^3=R^4=H$	11: $R^1=R^2=R^3=R^4=H$
2: $R^1=R^3=R^4=H$; $R^2=CH_3$	12: $R^1=R^2=CH_3$; $R^3=R^4=H$
3: $R^1=R^2=CH_3$; $R^3=R^4=H$	13: $R^1=R^2=R^3=H$; $R^4=Ph$
4: $R^1=R^2=R^4=H$; $R^3=CH_3$	14: $R^1=R^2=R^3=H$; $R^4=Ms$
5: $R^1=R^2=R^4=H$; $R^3=Ph$	15: $R^1=R^2=H$; $R^3=Ph$; $R^4=Ms$
6: $R^1=R^2=R^3=H$; $R^4=Ms$	
7: $R^1=R^3=H$; $R^2=CH_3$; $R^4=PNB$	
8: $R^1=R^2=CH_3$; $R^3=H$; $R^4=PNB$	
9: $R^1=R^2=H$; $R^3=CH_3$; $R^4=Ms$	
10: $R^1=R^2=H$; $R^3=Ph$; $R^4=Ms$	

Scheme 2.1 Preparation and labelling code of platinacyclobutane products

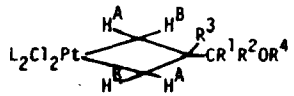
2.3 Characterisation of the platinacyclobutane complexes

2.3.1 ^{1}H-N.M.R. spectra

The proton N.M.R. spectra for complexes of the type $[PtCl_2CH_2CR^3(CR^1R^2OR^4)CH_2L_2]$ are often very complicated when R^3 = H owing to the plethora of couplings present, (both proton-proton, $J_{H,H}$ and platinum-proton, $J_{Pt,H}$) as well as very similar chemical shifts. A technique for simplification of these second-order spectra will be discussed in chapter 3. However, when R^3 is a methyl or phenyl group the complexity of the spectrum is greatly reduced and its interpretation is straightforward. The ^{1}H-N.M.R. spectral parameters for complexes 1-15 are given in Table 2.1. The solvent used was $CDCl_3$, except where indicated. The ^{1}H-N.M.R. spectrum for compound 9 will be discussed in more detail.

The ^{1}H-N.M.R. spectrum of $[PtCl_2(CH^AH^BC(CH_3)(CH_2OSO_2CH_3)CH^AH^B)py_2]$, 9, in figure 2.1 will be used to illustrate the assignment of the proton signals for these platinacyclobutane complexes. The spectrum in $CDCl_3$, consists of resonances in two distinct regions: the aromatic region containing the pyridine ligand resonances (7-10 ppm) and the aliphatic region containing the other resonances (1-5 ppm). The methyl group on the β-carbon appears as a broad singlet at 1.16 ppm. The observed broadening arises due to the small magnitude of $^4J_{Pt,H}$ coupling of the methyl protons to platinum-195. In contrast, the methyl group of the methanesulphonate ester appears as a sharp singlet at 2.98 ppm with no apparent coupling to platinum-195. This would require coupling across seven bonds and is expected to be negligible. The CH_2 carbinyl protons

Table 2.1 ^{1}H-N.M.R. Data for Platinum Complexes



Complex L=py	δH^A (ppm)	δH^B (ppm)	δR^1 (ppm)	δR^2 (ppm)	δR^3 (ppm)	δR^4 (ppm)
1: $R^1=R^2=R^3=R^4=H$ [a]	2.4-2.8	2.4-2.8	3.51	3.51	3.06	1.83
2: $R^1=R^3=R^4=H$; $R^2=CH_3$ [b]	2.3-3.1	2.3-3.1	3.66	1.03	2.3-3.1	1.87
3: $R^1=R^2=CH_3$; $R^3=R^4=H$	2.5-3.1	2.5-3.1	1.18	1.18	2.5-3.1	2.10
4: $R^1=R^2=R^4=H$; $R^3=CH_3$ [c]	2.39	2.74	3.45	3.45	1.16	1.64
5: $R^1=R^2=R^4=H$; $R^3=Ph$ [d]	3.00	3.22	3.70	3.70	7.39	1.53
6: $R^1=R^2=R=H$; $R=Ms$ [e]	2.36	2.58	4.12	4.12	3.04	2.94
7: $R^1=R^3=H$; $R^2=CH_3$; $R^4=PNB$ [f]	2.2-3.2	2.2-3.2	5.08	1.26	2.2-3.2	8.27
8: $R^1=R^2=CH_3$; $R^3=H$; $R^4=PNB$ [g]	2.54	3.02	1.54	1.54	3.02	8.33
9: $R^1=R^2=H$; $R^3=CH_3$; $R^4=Ms$ [h]	2.36	2.56	4.16	4.16	1.16	2.98
10: $R^1=R^2=H$; $R^3=Ph$; $R^4=Ms$ [i]	2.95	3.23	4.46	4.46	7.39	2.42
L= 1/2bipy						
11: $R^1=R^2=R^3=R^4=H$ [j]	2.37	2.61	3.52	3.52	3.06	1.54
12: $R^1=R^2=CH_3$; $R^3=R^4=H$	2.4-3.0	2.4-3.0	1.13	1.13	2.96	1.73
13: $R^1=R^2=R^4=H$; $R^3=Ph$ [k]	3.02	3.21	3.65	3.65	7.34	1.48
14: $R^1=R^2=R^3=H$; $R^4=Ms$ [l]	2.34	2.63	4.16	4.16	3.45	3.02
15: $R^1=R^2=H$; $R^3=Ph$; $R^4=Ms$ [m]	2.96	3.20	4.47	4.47	1.38	2.47

a) $^{2}J(Pt\text{-}H^{A})=83.3$ Hz; $^{2}J(Pt\text{-}H^{B})=83.3$ Hz; $^{2}J(R^{1}R^{2}\text{-}R^{3})=6.1$ Hz

b) $^{2}J(R^{1}\text{-}R^{2})=6.0$ Hz

c) $^{2}J(Pt\text{-}H^{A})=84.73$ Hz; $^{2}J(Pt\text{-}H^{B})=84.47$ Hz; $^{4}J(Pt\text{-}R^{3})=3.9$ Hz; $^{2}J(H^{A}\text{-}H^{B})=4.85$ Hz

d) $^{2}J(Pt\text{-}H^{A})=85.5$ Hz; $^{2}J(Pt\text{-}H^{B})=87.0$ Hz; $^{2}J(H^{A}\text{-}H^{B})=5$ Hz

e) $^{2}J(Pt\text{-}H^{A})=81.5$ Hz; $^{2}J(Pt\text{-}H^{A})=81.5$ Hz; $^{2}J(R^{1}R^{2}\text{-}R^{3})=7.4$ Hz; $^{2}J(H^{A}\text{-}H^{B})=4.8$ Hz; $^{2}J(R^{3}\text{-}H^{A})=9.0$ Hz; $^{2}J(R^{3}\text{-}H^{B})=7.1$ Hz

f) $^{2}J(R^{1}\text{-}R^{2})=5.8$ Hz

g) $^{2}J(Pt\text{-}H^{A})=80$ Hz; $^{2}J(Pt\text{-}H^{B})=77$ Hz

h) $^{2}J(Pt\text{-}H^{A})=84.6$ Hz; $^{2}J(Pt\text{-}H^{B})=86$ Hz; $^{2}J(H^{A}\text{-}H^{B})=5.4$ Hz

i) $^{2}J(Pt\text{-}H^{A})=85.5$ Hz; $^{2}J(Pt\text{-}H^{B})=87.0$ Hz; $^{2}J(H^{A}\text{-}H^{B})=6$ Hz

j) $^{2}J(Pt\text{-}H^{A})=81.5$ Hz; $^{2}J(Pt\text{-}H^{B})=85$ Hz; $^{2}J(R^{1}R^{2}\text{-}R^{3})=5.7$ Hz

k) $^{2}J(Pt\text{-}H^{A})=85.5$; $^{2}J(Pt\text{-}H^{B})=87.0$ Hz; $^{2}J(H^{A}\text{-}H^{B})=5$ Hz

l) $^{2}J(Pt\text{-}H^{A})=82.1$ Hz; $^{2}J(Pt\text{-}H^{B})=83.8$ Hz; $^{2}J(R^{1}R^{2}\text{-}R^{3})=6.1$ Hz; $^{4}J(Pt\text{-}R^{3})=3.5$ Hz

m) $^{2}J(Pt\text{-}H^{A})=86.5$ Hz; $^{2}J(Pt\text{-}H^{B})=87.3$ Hz; $^{2}J(H^{A}\text{-}H^{B})=5.2$ Hz

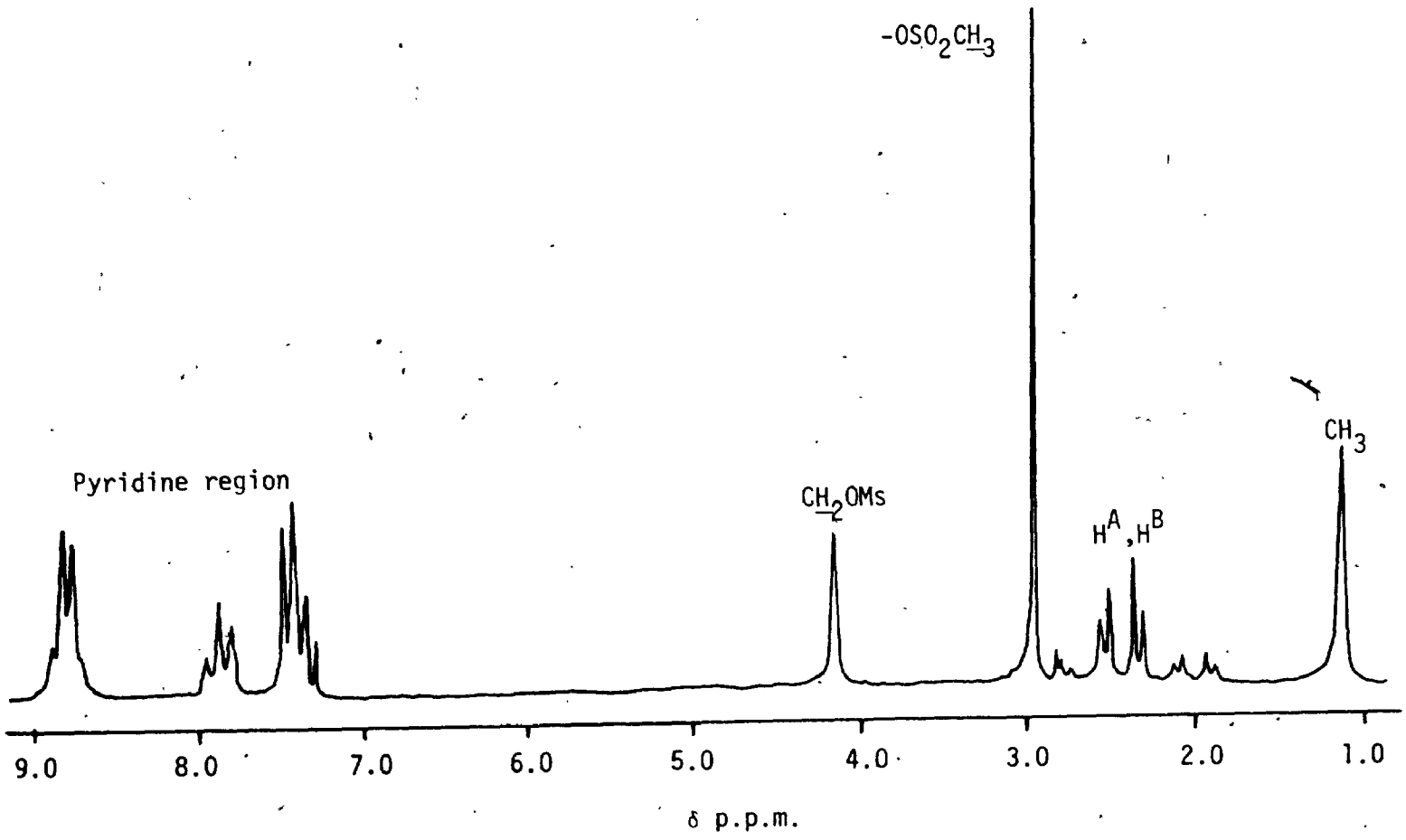


Figure 2.1 The ^{1}H-N.M.R. spectrum of $[PtCl_2(CH^AH^BC(CH_3)(CH_2OSO_2CH_3)CH^AH^B)py_2]$,9.

are highly deshielded by the oxygen atom and appear as a broad singlet at 4.16 ppm. The broadening can again be attributed to the magnitude of $^{4}J_{Pt,H}$ coupling. The ring methylene protons, H^{A} and H^{B}, appear as an AB pattern in the region 2.3-3.5 ppm with a large $^{2}J_{Pt-H}$ coupling of about 80 Hz producing satellites also of the same pattern. The satellite furthest downfield is masked by the methyl resonance of the methanesulphonate group, but its counterpart is clearly visible. The chemical shifts of the ring methylene protons, H^{A} and H^{B}, are shifted downfield by over 2 ppm relative to their chemical shifts in the free cyclopropane derivative as expected on going from a 3-membered to a 4-membered alicyclic compound.

The aromatic region of figure 2.1 contains the three separate proton resonances for the coordinated pyridine ligands centered at 7.37 ppm, 7.82 ppm and 8.74 ppm for the meta, para and ortho protons respectively. Platinum satellites can be seen on the ortho resonance which which arise through coupling to platinum-195.

2.3.2 ^{13}C-N.M.R. spectra

Carbon-13 N.M.R. spectroscopy has proven to be an invaluable tool for the investigation of platinacyclobutane complexes. The proton decoupled ^{13}C-N.M.R. spectra are, for the most part, readily interpretable. A single line appears for each of the different carbon environments in the molecule, the magnitude of the ^{13}C coupling to platinum being diagnostic for each ring position. The larger chemical shift range (~200 ppm) for the region of interest relative to that of ^{1}H-N.M.R. spectroscopy (~10 ppm) also makes for well-separated resonances. Off-resonance ^{1}H-decoupled spectra provide useful information as to the

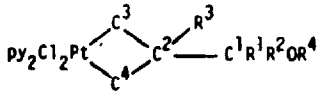
assignment of the carbon resonances as being either a tertiary, secondary, or primary carbon. This same information can be obtained through more sophisticated pulsing techniques such as INEPT sequence, which require less acquisition time than an off-resonance spectrum. By this technique CH_3 and CH carbons appear in the spectrum in a normal upright fashion, however, CH_2 carbons appear with negative intensities and tertiary carbons are quenched entirely.

The ^{13}C-N.M.R. data for the platinacyclobutane complexes 1-10 are presented in Tables 2.2 and 2.3. The chemical shifts are recorded relative to TMS using the central $^{13}CDCl_3$ peak, which is taken to be +77.0 ppm, as reference. The ^{13}C-N.M.R. spectra of the 2,2'-bipyridyl complexes 11-15 have not been attempted owing to their low solubility in $CDCl_3$.

A typical ^{13}C-N.M.R. spectrum for a bis(pyridine) platinacyclobutane complex consists of resonances in two distinct regions of interest. The aromatic region (120-170 ppm) contains the resonances of the ortho, meta and para pyridine carbons whereas the remaining carbons in the structure appear between -14 ppm and +90 ppm. The chemical shifts and coupling constants for the pyridine resonances are presented in Table 2.3.

The proton-decoupled ^{13}C-N.M.R. spectrum of compound 4, $[PtCl_2C^3H_2C^2(CH_3)(C^1H_2OH)C^4H_2py_2]$ in figure 2.2 will be taken as an example to illustrate the interpretation of the ^{13}C-N.M.R. spectra of these complexes. Figure 2.3 is an expansion of the aliphatic region of this spectrum. It contains both the normal $^{13}C\{^1H\}$ N.M.R. spectrum (figure 2.3b) as well as the spectrum resulting from use of the INEPT pulse sequence (figure 2.3a)

Table 2.2 ^{13}C-N.M.R. Data of Platinum Complexes[a]



Complex	δC^1 (ppm)	$^3J(^{195}Pt-^{13}C)$ (Hz)	δC^2 (ppm)	$^2J(^{195}Pt-^{13}C)$ (Hz)	δC^3 (ppm)	$^1J(^{195}Pt-^{13}C)$ (Hz)	δC^4 (ppm)	$^1J(^{195}Pt-^{13}C)$ (Hz)	Others
1: $R^1=R^2=R^3=R^4=H$	67.1	49.0	45.6	99.1	-11.3	350.1	-11.3	350.1	
2: $R^1=R^3=R^4=H$; $R^2=CH_3$	71.6	45.2	51.1	96.2	-11.1[a]	351.0	-10.5[a]	349.2	R^2=19.5ppm
3: $R^1=R^2=CH_3$; $R^3=R^4=H$	71.9	46.2	54.1	94.1	-10.5	352.3	-10.5	352.3	$R^1=R^2$=26.1ppm
4: $R^1=R^2=R^4=H$; $R^3=CH_3$	70.9	28.4	48.7	92.2	-3.0	355.7	-3.0	355.7	R^3=24.6ppm; $^3J(^{195}Pt-^{13}C)$=26.6Hz
5: $R^1=R^2=R^4=H$; $R^3=Ph$	71.2	21.5	58.5	88.4	-4.7	361.0	-4.7	361.0	b
6: $R^1=R^2=R^3=H$; $R^4=Ms$	73.8	54.1	42.1	103.9	-13.7	356.0	-13.7	356.0	R^4=37.1ppm
7: $R^1=R^3=H$; $R^2=CH_3$; $R^4=PNB$	77.2	60.6	48.5	100.9	-11.6[a]	357.8	-10.6[a]	355.0	R^2=16.5, c
8: $R^1=R^2=CH$; $R^3=H$; $R^4=PNB$	86.0	63.4	54.8	97.5	-9.8	361.3	-9.8	361.3	$R^1=R^2$=21.9ppm, d
9: $R^1=R^2=H$; $R^3=CH_3$; $R^4=Ms$	77.4	28.2	46.9	95.4	-4.9	361.3	-4.9	361.3	R^3=25.0ppm; R^4=36.7ppm $^3J=(^{195}Pt-^{13}C)$=30.2Hz
10: $R^1=R^2=H$; $R^3=Ph$; $R^4=Ms$	78.4	21.9	56.0	90.3	-6.7	367.5	-6.7	367.5	R^4=36.3, e

a) For the mono-methylated complexes assignments for C-3 and C-4 may be reversed.

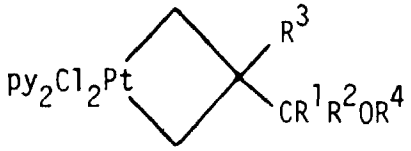
b) R^3 = 126.0, 126.1, 127.9, 147.7 [$^3J_{Pt-C}$ = 28.6 Hz]

c) R^4 = 123.2, 130.9, 136.3, 150.2, 164.7 ppm

d) R^4 = 124.1, 131.1, 137.3, 150.0, 164.2 ppm

e) R^3 = 126.3, 126.5, 128.0, 147.1 [$^3J(^{195}Pt-^{13}C)$ = 25 Hz]

Table 2.3 ^{13}C-N.M.R. Spectral Data For Pyridine Ligands Of Complexes:



Complex	δ ppm; ($J_{^{195}Pt-^{13}C}$)		
	meta	para	ortho
1: $R^1=R^2=R^3=R^4=H$	125;	138;	149
2: $R^1=R^3=R^4=H$; $R^2=CH_3$	125;	138;	149
3: $R^1=R^2=CH_3$; $R^3=R^4=H$	125.2 (11.2 Hz);	138.1;	149.2
4: $R^1=R^2=R^4=H$; $R^3=CH_3$	125;	138;	149
5: $R^1=R^2=R^4=H$; $R^3=Ph$	125.2 (11.4 Hz);	138.1;	149.2
6: $R^1=R^2=R^3=H$; $R^4=Ms$	125.3 (11.2 Hz);	138.3;	148.9
7: $R^1=R^3=H$; $R^2=CH_3$; $R^4=PNB$	125.2 (11.5 Hz);	138.1;	149.2
8: $R^1=R^2=CH_3$; $R^3=H$; $R^4=PNB$	125.2 (11.7 Hz);	138.1;	149.3
9: $R^1=R^2=H$; $R^3=CH_3$; $R^4=Ms$	125 (11.8 Hz);	138.2;	149.1
10: $R^1=R^2=H$; $R^3=Ph$; $R^4=Ms$	125.4 (11.8 Hz);	138.3;	149.3

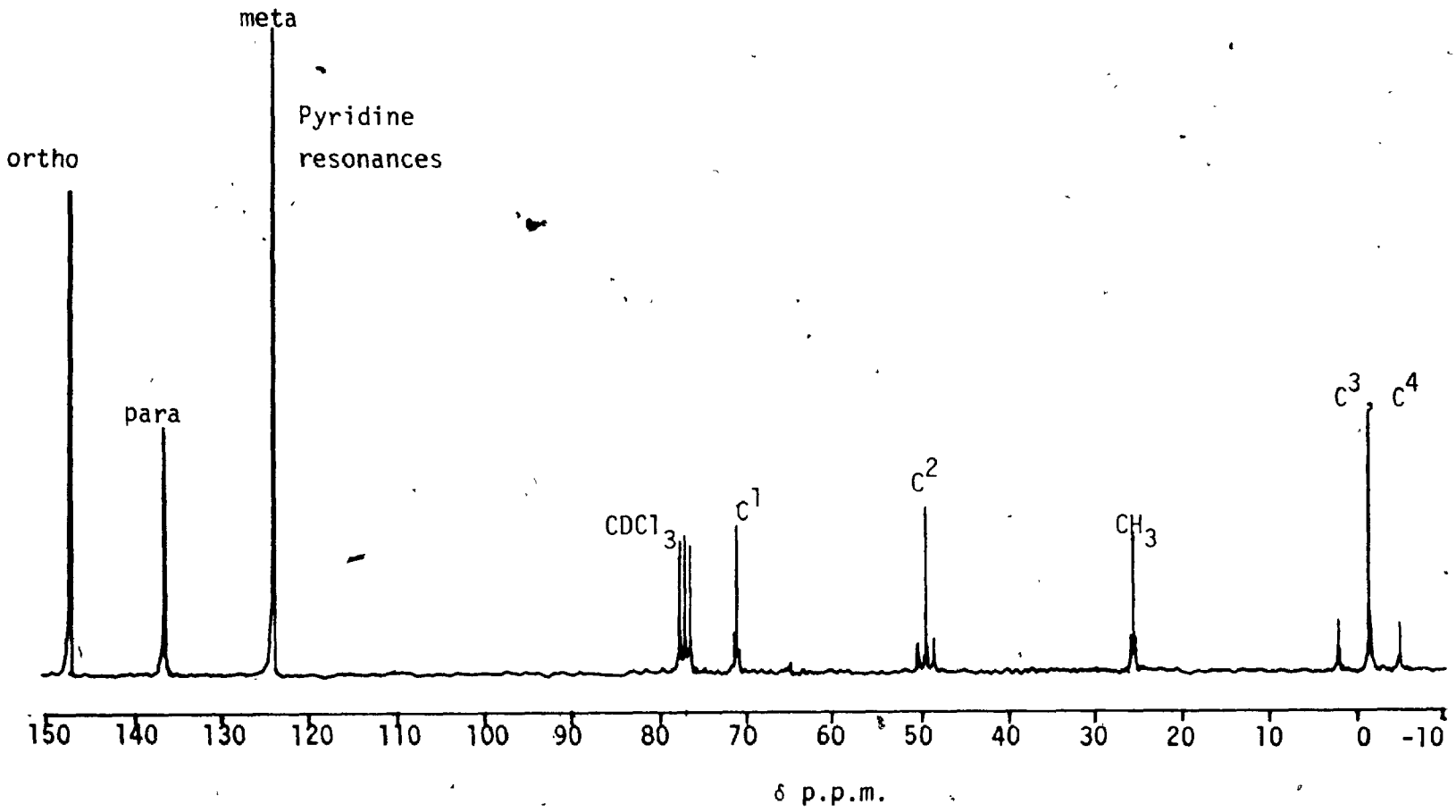


Figure 2.2 $^{13}C\{^{1}H\}$-N.M.R. spectrum of $[PtCl_2C^3H_2C^2(CH_3)(C^1H_2OH)C^4H_2py_2]$, 4, in $CDCl_3$.

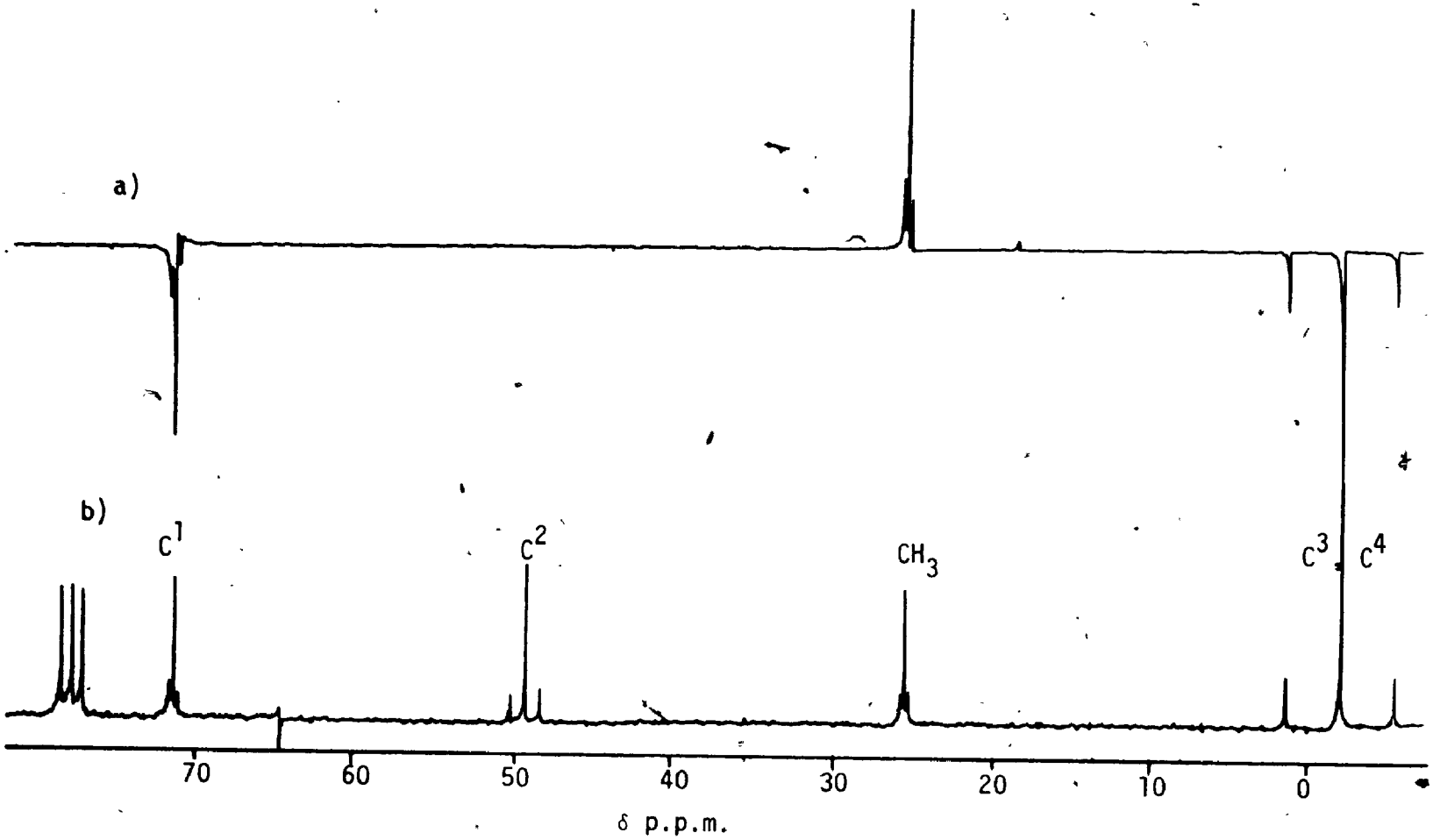


Figure 2.3 An expansion of the aliphatic region of the ^{13}C-N.M.R. spectrum of compound 4, $[PtCl_2C^3H_2C^2(CH_3)(C^1H_2OH)C^4H_2py_2]$. a) using INEPT pulse sequence. b) $^{13}C\{^1H\}$-N.M.R.

The pyridine carbon resonances are seen in figure 2.2 at 149.2 ppm, 125.2 ppm and 138.1 ppm for the ortho, meta and para carbons respectively. A small $J_{Pt,C}$ coupling of 11.2 Hz is seen for the meta carbon. Generally, the pyridine resonances are of little use in product identification, however, they do serve the purpose of establishing the presence of coordinated pyridine ligands.

The carbinyl carbon, C^1, is shifted the furthest downfield relative to the other aliphatic carbons owing to the deshielding effect of the hydroxyl group directly bonded to this carbon. The signal appears as a singlet at 70.9 ppm with a coupling to platinum $^3J_{Pt,C}$; of 28.3 Hz. From the INEPT spectrum, figure 2.3a, assignment of this signal to a CH_2 carbon is confirmed by the downward peak intensity.

The β-ring carbon, C^2, resonates upfield from C^1 at 48.7 ppm and has a coupling $^2J_{Pt,C}$ of 92.2 Hz. From the INEPT spectrum the absence of intensity confirms assignment of this resonance to a tertiary carbon.

The ring α-methylene carbons, C^3 and C^4, are equivalent and hence give rise to a single peak with satellites. The chemical shift of these carbon atoms is -3.0 ppm and the observable coupling, $^1J_{Pt,C}$, is 355.7 Hz. The INEPT spectrum supports this assignment as the resulting resonance points downward.

The range of $^1J_{Pt,C}$ coupling constants seen for compounds 1-10 is 349.2 Hz to 367.5 Hz and falls in the range observed previously for platinum(IV) metallacyclobutane complexes of this type.[17] The observed range of coupling constants, $^2J_{Pt,C}$, to the β-carbon (C^2) is 90.3 Hz to 103.9 Hz and is also consistent with previous reports.[17] In

comparison, the platinum(IV) alkyl complex,[55] $[PtI_2(C_2H_5)_2(4\text{-}CH_3C_5H_4N)_2]$ has a $^1J_{Pt,C}$ value of 507 Hz and a coupling to the β-methyl carbon of less than 8 Hz. These differences can be rationalized in terms of the degree of s-character in the bonds which is a contributing factor governing the coupling constants between directly bonded atoms. The smaller $^1J_{Pt,C}$ seen for platinacyclobutanes relative to those of platinum alkyl complexes has been attributed to ring strain[17] which necessitates a $C^3\text{-}Pt\text{-}C^4$ angle considerably less than the normal 90° and hence low s-character. In the platinum(IV) metallacyclobutane complexes there is expected to be a contribution to $^2J_{Pt,C}$ due to direct overlap between the β-carbon and the metal atom, based on structural data, a situation which is not possible in alkyl complexes. This overlap will be reflected in larger $^2J_{Pt,C}$ coupling constants.

These arguments are supported by the finding[56] that platinum(IV) metallacyclopentane complexes, in which the ring is expected to be opened up considerably relative to the four-membered rings, have $^1J_{Pt,C}$ values which fall into the range 0-43 Hz depending upon the substituents on the ring. This aspect serves to illustrate the effect of ring strain upon coupling in platinum complexes and will be discussed further in chapter 4 of this thesis.

CHAPTER 3

LANTHANIDE SHIFT REAGENT STUDIES ON SOME FUNCTIONALLY SUBSTITUTED PLATINACYCLOBUTANES AND THEIR PUCKERING IN SOLUTION

1. Introduction

1.1 The Lanthanide Shift Technique

Since the report by Hinckley[57] in 1969, that addition of tris-(dipivalomethanato)europium(III) dipyridinate, $Eu(dpm)_3py_2$, to a carbon tetrachloride solution of cholesterol produces a well-resolved spectrum of the latter, lanthanide shift reagents (LSRs) have proved to be a valuable development in the use of N.M.R. spectroscopy.[58] In favourable cases it is possible to simplify a very complex spectrum to a first-order analysis without loss of resolution.

In general, LSRs are six-coordinate metal complexes which can readily expand their coordination number in solution by binding to the heteroatoms of the substrate under study. Therefore, the LSR itself consists of a metal ion combined with its ligands. Metal ion complexes of the complete lanthanide series have been investigated,[58] the results indicating that the lanthanides of greatest interest for shifting experiments are europium, ytterbium and praseodymium. In the trivalent state europium has developed as the most widely used lanthanide for proton shift experiments and likewise, ytterbium is the lanthanide of choice for carbon-13 shift experiments. Praseodymium has been used for both proton and carbon-13 shift experiments.

Although it is possible to perform shift experiments in aqueous solution by use of the appropriate lanthanide salt, most work is done in

$CDCl_3$ or CCl_4, though other organic solvents have been used. It is necessary to have a shift reagent which is readily soluble in most organic solvents since a larger induced shift will be seen as the shift reagent concentration increases. This implies that conditions of fast-exchange on the N.M.R. time scale exist between the complex's substrate adduct and free substrate. 1,3-diketo type organic anions possess the qualities desirable in a good ligand as well as being readily adaptable to preparation of fluorinated analogues which show improved solubility and coordinating properties. Figure 3.1 shows the most frequently used metal ions and ligands seen in shift reagent studies.

The attributes of one LSR over another have been well established experimentally, making the technique amenable to many substrate types provided they possess a sufficiently polar and exposed functional group to form a complex with the LSR. The effectiveness of a functional group to form this shift reagent-substrate complex is a reflection of the dissociation constant and geometry and has been shown to be in the order:[58]

amine > hydroxyl > ketone > aldehyde > ether > ester > nitrile

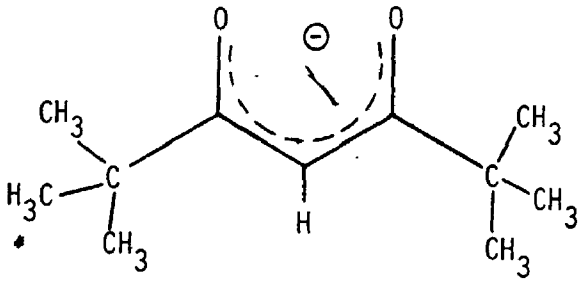
The addition of the LSR to the substrate leads to the equilibria:

$$L + S \overset{K_1}{\rightleftharpoons} LS \qquad \ldots(3.1)$$

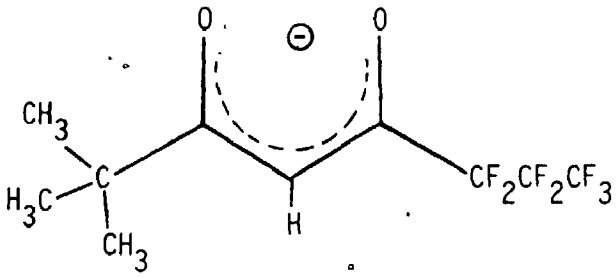
$$LS + S \overset{K_2}{\rightleftharpoons} LS_2 \qquad \ldots(3.2)$$

that is; formation of a 1:1 or 1:2 complex respectively. It is generally assumed that K_2 is negligible and only the 1:1 complex is formed. This assumption seems to be valid[58] when the concentration of added LSR is small relative to that of the substrate.

ANIONS:



dpm$^-$



fod$^-$

CATIONS: Eu^{+3}, Pr^{+3}, Yb^{+3}

Figure 3.1 Common anions and cations used in shift reagent studies

The observed lanthanide induced shift (LIS) is an average of the shifts for the complexed and uncomplexed substrate and is given by the equation:

$$LIS = \frac{[LS]}{[S_o]} \Delta_B \qquad \ldots(3.3)$$

where [LS] is the concentration of the lanthanide substrate adduct, $[S_o]$ is the total concentration of the substrate and Δ_B is the induced shift for the case when the substrate is completely bound to the LSR.

K_1, from reaction 3.1 is given by the equation:

$$K_1 = \frac{[LS]}{[L][S]} = \frac{[LS]}{([L_o]-[LS])([S_o]-[LS])} \qquad \ldots(3.4)$$

If one assumes that $S_o >> L_o$ (i.e. low LSR concentrations), equation 3.4 becomes:

$$K_1 = \frac{[LS]}{([L_o]-[LS])[S_o]}$$

extracting [LS],

$$[LS] = \frac{K_1[L_o][S_o]}{1+[S_o]K_1}$$

and substituting [LS] into equation 3.3 yields:

$$LIS = \frac{K_1[L_o]\Delta_B}{1+[S_o]K_1} \qquad \ldots(3.5)$$

There are two experimental approaches which are frequently used, both of which give a graphical representation of the LIS experiment. The first is to make standard additions to the substrate (vary S_o) keeping L_o constant. The second is to make standard additions of the

shift reagent (vary L_o) keeping S_o constant. Since it is the latter technique which was used in this study, the mathematical expressions used in this approach will be developed.

In the case of strong binding of the substrate (i.e. amines and alcohols), $K_1[S_o]>>1$, which when substituted into equation 3.5 gives, upon simplification:

$$LIS = \frac{[L_o]\Delta_B}{[S_o]} \qquad \ldots(3.6)$$

When LIS is plotted vs $[L_o]/[S_o]$ it corresponds to a straight line passing through the origin with a slope equal to Δ_B.

For the case of weak binding of the substrate to the reagent $K_1[S_o]>>1$ which simplifies equation 3.5 to:

$$LIS = K_1[L_o]\Delta_B$$

or

$$LIS = K_1[S_o]\Delta_B \frac{[L_o]}{[S_o]} \qquad \ldots(3.7)$$

Since the functional group of the substrate in this study is a hydroxyl it is the first of these cases which is applicable.

1.2 The Shift Mechanism

The shift which results from the interaction between the paramagnetic metal ion and the nuclei of the substrate is said to be highly dominated by a paramagnetic component, Δpara (the diamagnetic component has been found to be essentially negligible[59]) which can be expressed as the sum of the two terms; contact (Δ_c) and pseudocontact (Δ_p) where:

$$\Delta para = \Delta_c + \Delta_p \qquad \ldots(3.8)$$

For lanthanides, the contact shift component, Δ_c, occurs by direct electron-nucleus magnetic interaction, the so-called "through-bond" interaction. It is restricted to atoms close to the coordination site (up to three or four bonds) and falls off rapidly with increasing distance. The hydrogen atoms of the substrate are usually located at peripheral positions and aren't directly involved in the bonding. For this reason it has been determined[58b] that contact contributions are relatively small, though for all other nuclei, both pseudocontact and contact shifts are to be expected.

With lanthanides, the predominent magnetic interaction is pseudo-contact in nature and given, in its most general form[58] as:

$$\Delta_p = K_{axial}\left[\frac{3\cos^2\theta-1}{r^3}\right] + K_{nonaxial}\left[\frac{\sin^2\theta\cos 2\theta}{r^3}\right] \qquad \ldots(3.9)$$

where the position of the lanthanide ion is given by the coordinates (0,0,0) in figure 3.2.

For the special case of an axially symmetrical field, equation 3.9 reduces to the familiar McConnell-Robertson equation:[60]

$$\Delta_p = K\frac{(3\cos^2\theta-1)}{r^3} \qquad \ldots(3.10)$$

which shows the pseudocontact shift to be independent of the nucleus but very strongly dependent on the geometry of the complex. The McConnell-Robertson equation has been used with great success in the study of the shift-distance relationships, namely that the magnitude

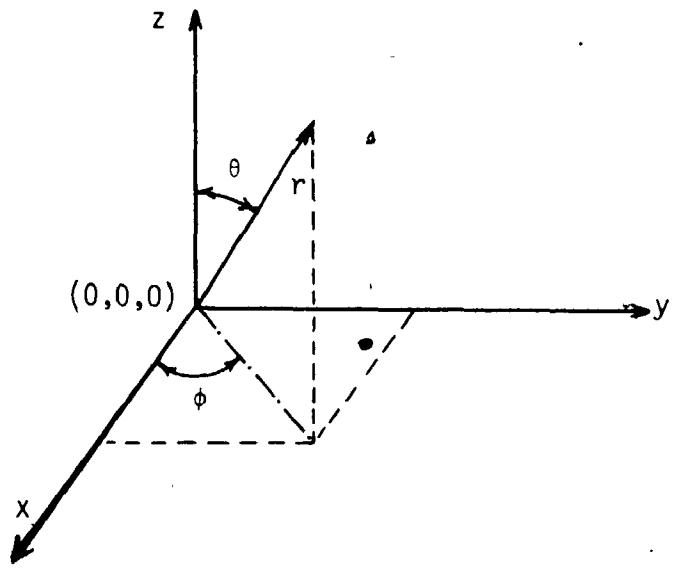


Figure 3.2 Definition of the parameters for equation 3.9

of the lanthanide induced shift is inversely proportional to the cube of the average distance from the metal ion.

1.3 Scope of this chapter

Although LSRs have been used routinely to simplify the N.M.R. of organic compounds, they have received much less attention for co-ordination and organometallic compounds.[58] Most studies of this latter type have dealt with the interaction of LSRs with functionalized metallocene complexes. There have been no reports to date of the use of LSRs to simplify the N.M.R. of metallacycloalkane complexes. It is the results of such a study which will be discussed in this chapter.

The preparation of some platinacyclobutane derivatives with hydroxymethyl substituents have been discussed in chapter 2 of this thesis. As might be expected, the ^{1}H-N.M.R. spectra of these compounds are often complex owing to second-order effects. The presence of the donor hydroxyl group, however, has made simplification possible by the use of the lanthanide shift reagent, $Eu(fod)_3$. Simplification has enabled the extraction of certain N.M.R. parameters which are unattainable from the unshifted spectrum. These parameters have been used to make predictions of ring puckering in solution.

The complexes studies are $[PtCl_2(CH_2CH(CH_2OH)CH_2)py_2]$ (1), $[PtCl_2(CH_2CH(CHCH_3OH)CH_2py_2]$ (2), $[PtCl_2(CH_2CH(C(CH_3)_2OH)CH_2)py_2]$ (3).

2. Results and Discussion

2.1 The lanthanide shift experiments

The ^{1}H-N.M.R. spectra were recorded with a Varian XL-100

spectrometer. Lanthanide shift studies were carried out by adding portions of a weighed sample $Eu(fod)_3$ shift reagent to a solution of a known weight of the platinacyclobutane in $CDCl_3$ solution. Molar ratios were calculated from each spectrum by comparison of the integration for the tertiary butyl group of $Eu(fod)_3$ and the integration of an appropriate signal corresponding to the platinacyclobutane.

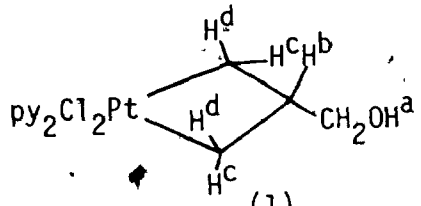
Tables 3.1, 3.2 and 3.3 show the observed proton spectral parameters of the three platinacyclobutanes with varied $Eu(fod)_3$/substrate ratios. The shift data are presented graphically in figures 3.3, 3.4 and 3.5 which show the effect of added $Eu(fod)_3$ on the individual proton resonances of the complexes. As expected, based on the $1/r^3$ dependence in the McConnell-Robertson equation (equation 3.10) the shifting parameter, S, which is defined by equation 3.11, is largest for those protons closest to the OH group.

$$\delta_{complexed} = \delta_{uncomplexed} + \frac{S\ Eu(fod)_3}{substrate} \qquad \ldots(3.11)$$

Several consistencies within the data bear mentioning. The hydroxyl protons H^a, is seen to show the largest magnitude of the change in the chemical shift all being in the range 40.5±2. From the data for compounds 1 and 2 the carbinol protons, as expected, have the next largest shifting parameter: 12.0±.4. Methyl groups directly bound to the carbinol carbon as in 2 and 3 show a shifting parameter of 6.4±.2. H^b is the next highest shifted proton with a S value of 5.9±.5. The assignments for the ring methylene protons H^c and H^d are based on the expected larger shift for the protons in cyclopropylcarbinol except that in this study[61] the shifting reagent used was $Pr(dpm)_3$ which

Table 3.1 ^{1}H-N.M.R. Spectral Data and Lanthanide Shift Parameters for Compound 1

(i)



(1)

Molar Ratio[a]	δ ppm; description				
$\frac{Eu(fod)_3}{substrate}$	H^a	H^b	H^c ($^2J[^{195}Pt-^1H^c]_{\pm\sigma}$)[c] Hz	H^d ($^2J[^{195}Pt-^1H^d]_{\pm\sigma}$) Hz	CH_2OH
0.0	1.83; s	3.06; m	2.4-2.8; m (83.3±1.3)	2.4-2.8; m (83.3±1.3)	3.51; d
0.190	9.45; brs	4.37; m	3.60; dd (81.0±.5)	3.31; dd (84.1±.8)	5.74; brd
0.494	—	6.25; br	5.36; dd (81.7±.5)	4.37; dd (84.5±.4)	—
0.737	—	—	6.97; dd (82)	5.19; dd (84)	12.1; brd
0.824	36.7; brs	8.36; br	7.3; br —	5.33; dd (88)	13.1; brd
S[d]	42.5	6.4	5.9	3.7	11.6
Correlation	0.99999	0.9999	0.99997	0.997	0.999999
Calculated Inter.	1.83	3.06	2.47	2.61	3.51

a) Calculated by integration of the t-butyl group of $Eu(fod)_3$ and a suitable substrate peak

b) Calculated from residual $CHCl_3$ peak in deuterated solvent; where the peak could not be identified no shift value has been given

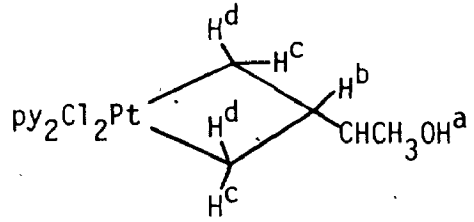
c) Where it was not possible to see the individual satellites, no σ value has been given

d) Where S is defined by $\delta_{complexed} = \delta_{uncomplexed} + S \frac{Eu(fod)_3}{substrate}$.

The assignment for H^c and H^d are made on the basis of the expected larger S for H^c. For poorly resolved signals the value $\delta_{complex}$ is taken as the average value.

Table 3.2 ^{1}H-N.M.R. Spectral Data and Lanthanide Shift Parameters for Compound 2

(ii)

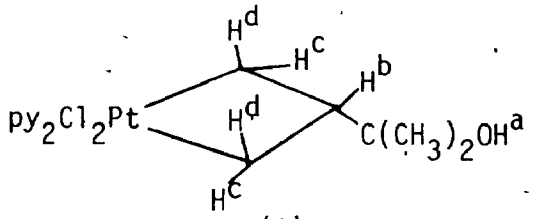


(2)

Molar Ratio	δ ppm; description					
$\frac{Eu(fod)_3}{substrate}$	H^a	H^b	($^2J[^{195}Pt-^1H]_{\pm\sigma}$) Hz	($^2J[^{195}Pt-^1H^c]_{\pm\sigma}$) Hz	$CHCH_3OH$	$CHCH_3OH$
0.0	1.87; s	2.3-3.1; m	2.3-3.1; m	2.3-3.1; m	3.66; m	1.03; d
0.110	6.40; brs	3.37; brm	—	2.98; dd (84)	4.84; m	1.67; d
0.347	—	4.56; brm	4.14; m	3.73; dd (84.4±1.1)	8.08; brm	3.47; d
0.639	—	6.20; brm	5.26; dd (84.9±.4)	4.60; dd (85.0±.1)	11.36;brm	5.26; d
0.840	—	—	6.12; dd	5.26; dd (85.5±.6)	13.94;brm	6.57; d

Table 3.3 ^{1}H-N.M.R. Spectral Data and Lanthanide Shift Parameters for Compound 3

(iii)



(3)

Molar Ratio	δ ppm; description				
$\frac{Eu(fod)_3}{substrate}$	H^a	H^b	H^c ($^2J[^{195}Pt-^1H^c]\pm\sigma$) Hz	H^d ($^2J[^{195}Pt-^1H^d]\pm\sigma$) Hz	CH_3
0.0	2.10; s	2.5-3.1; m	2.5-3.1; m	2.5-3.1; m	1.18; s
0.167	8.55; s	3.60-3.65; m	3.97; m (87.2±6.2)	3.18; dd (84.1±1.2)	2.18; s
0.229	—	4.15-4.20; m	4.54; dd (79.1±.1)	3.45; dd (83.6±.4)	265; s
0.495	—	5.56; quint	6.30; dd (80.8±.3)	4.42; dd (84.6±.1)	4.25; s
S	38.3	5.69	6.96	3.74	6.22
Correlation	—	0.995	0.998	0.9996	0.9996
Calculated Intercept	2.10	2.75	2.87	2.57	1.18

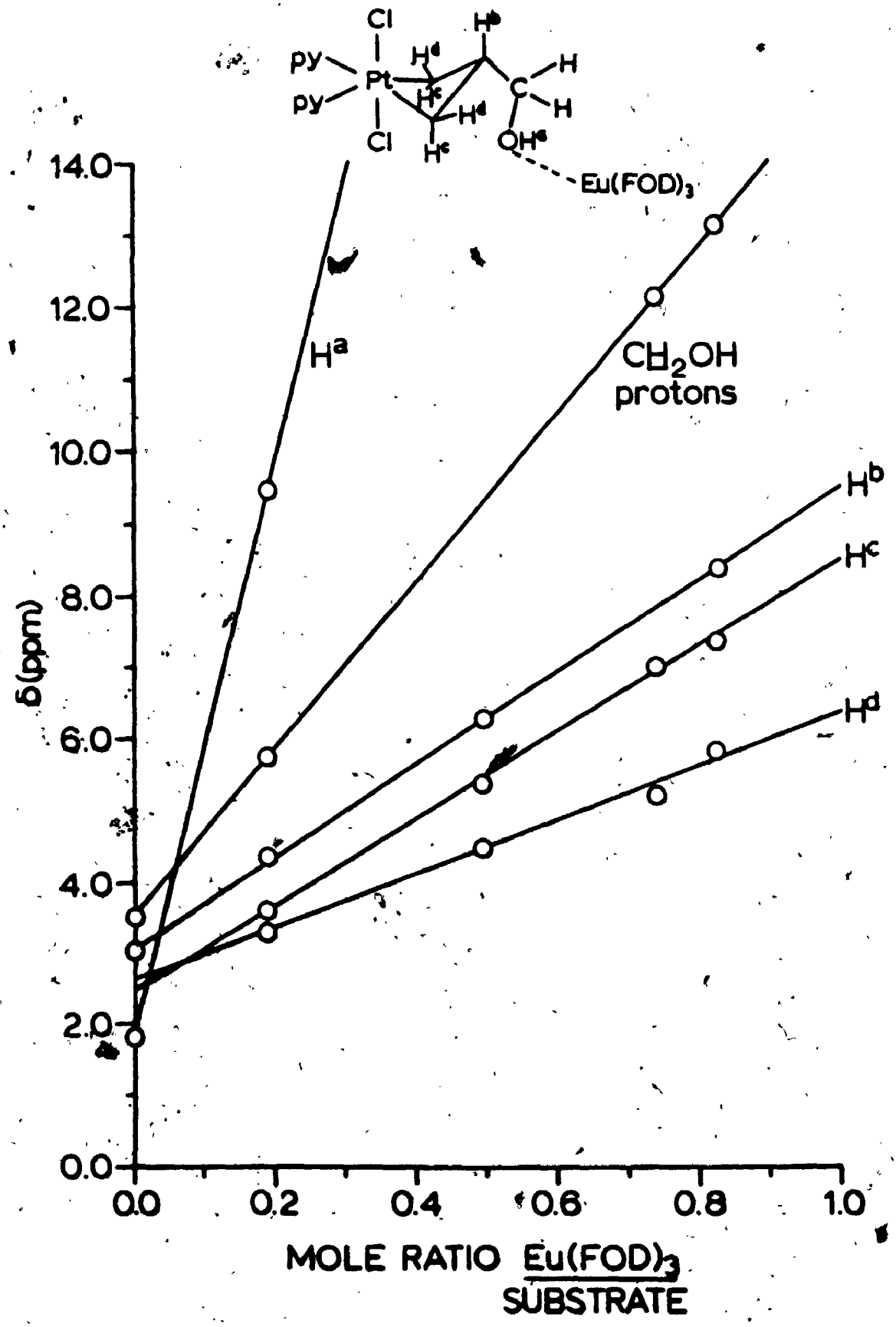


Figure 3.3 δ p.p.m. plot for compound 1 with varying additions of shift reagent.

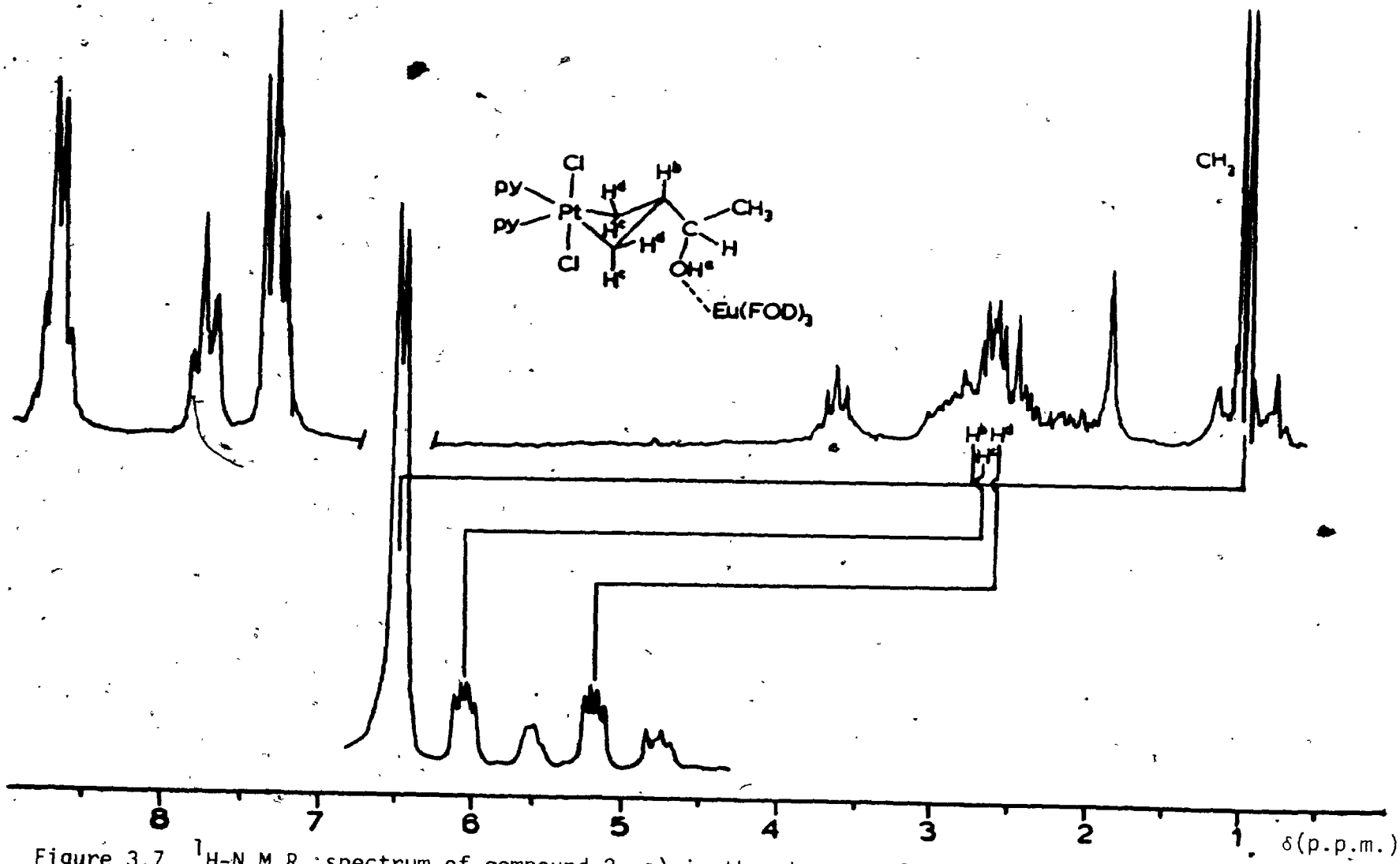


Figure 3.7 ^{1}H-N.M.R. spectrum of compound 2, a) in the absence of added shift reagent and b) at a $\frac{Eu(fod)_3}{substrate}$ ratio of 0.840.

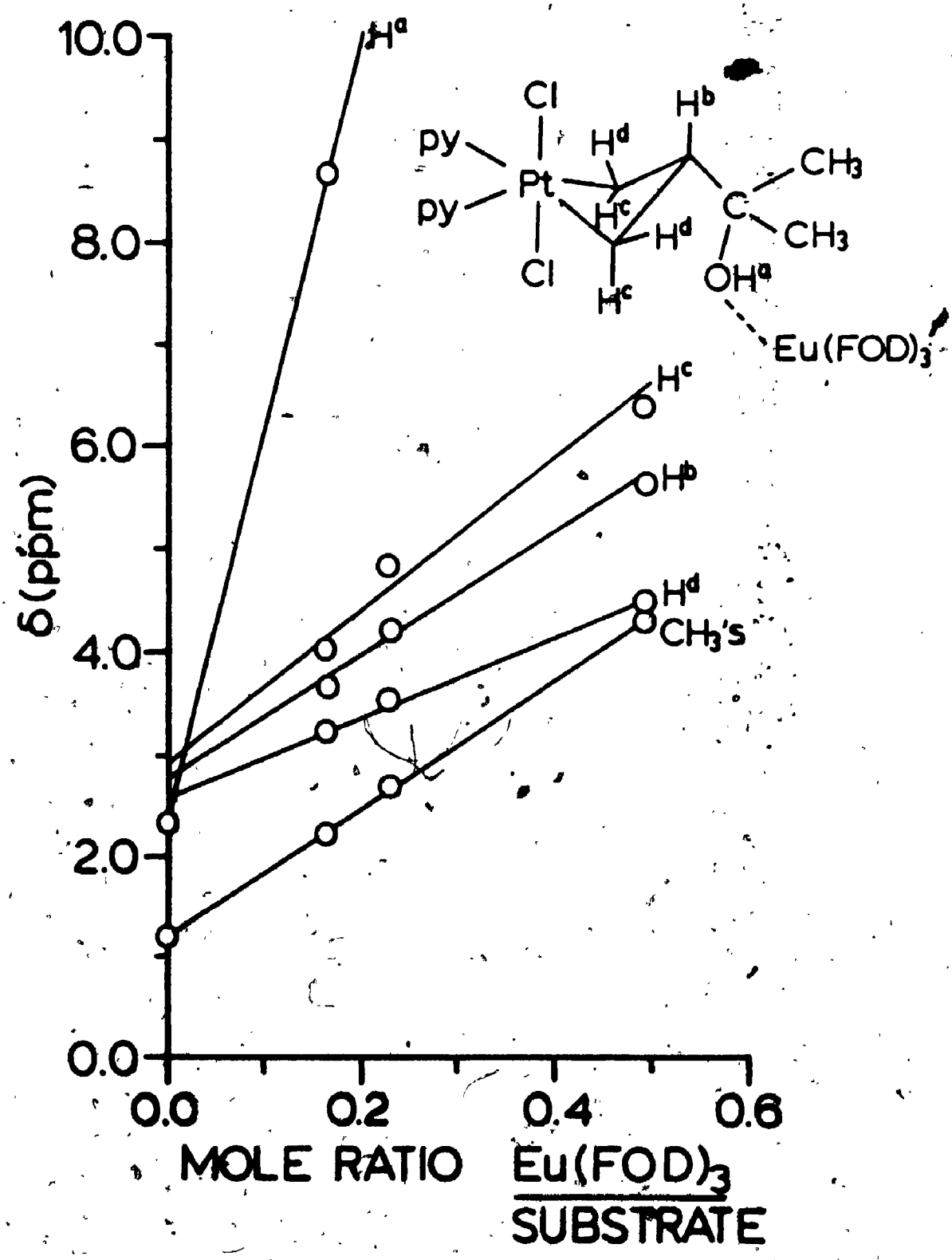
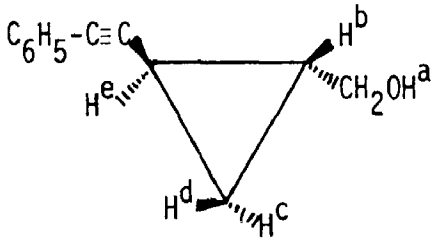


Figure 3.5 δ p.p.m. plot for compound 3 with varying additions of shift reagent.

causes an induced shift negative to that seen using europium shift reagents. The study[62] of the effect of addition of $Eu(dpm)_3$ on trans-1-phenylethynyl-2-hydroxymethylcyclopropane allows a more direct comparison to be made. Using these authors' data for $Eu(dpm)_3$/substrate ratios $\leq .75$, shifting parameters for protons a through e can be calculated. These S values for this cyclopropane are shown in Table 3.4 and indicate a trend in good agreement with the data for the platinacyclobutanes.

Figures 3.6, 3.7 and 3.8 show the spectra exhibited for each of the platinacyclobutanes studies (1→3), in the absence of shift reagent and with an appropriate $Eu(fod)_3$/substrate ratio such that a first-order analysis results. The gross difference between the two spectra for each of the complexes reflects the utility of the technique. Not only do the multiplicities of the resonances become apparent with the corresponding proton-proton couplings, but also, in most cases, the platinum-proton couplings become readily discernible. The magnitudes of these are not obvious from the unshifted spectra. For compound 1 the ^{1}H-N.M.R. spectrum was simulated by means of the parameters obtained from extrapolation in figure 3.3 to a $Eu(fod)_3$/substrate ratio of zero. The chemical shifts, obtained in this manner as well as the proton-proton coupling constants obtained from the first-order analysis were refined using the program LAOCN III. A comparison between the observed and calculated spectra in the region H^c and H^d is shown in figure 3.9. The coupling constants and chemical shifts obtained by direct measurement from the first-order spectrum are in good agreement with those for the N.M.R. simulation. Thus, it would appear that coordination of the hydroxyl function to the shift reagent does not appear to change to

Table 3.4 Calculated Shifting Parameters, S, for trans-1-phenylethynyl-2-hydroxymethyl-cyclopropane, Based on Data from Reference 62



Proton	S
H^a	62.2
CH_2OH	17.4
H^b	10.6
H^c	7.1
H^d	4.2
H^e	7.8

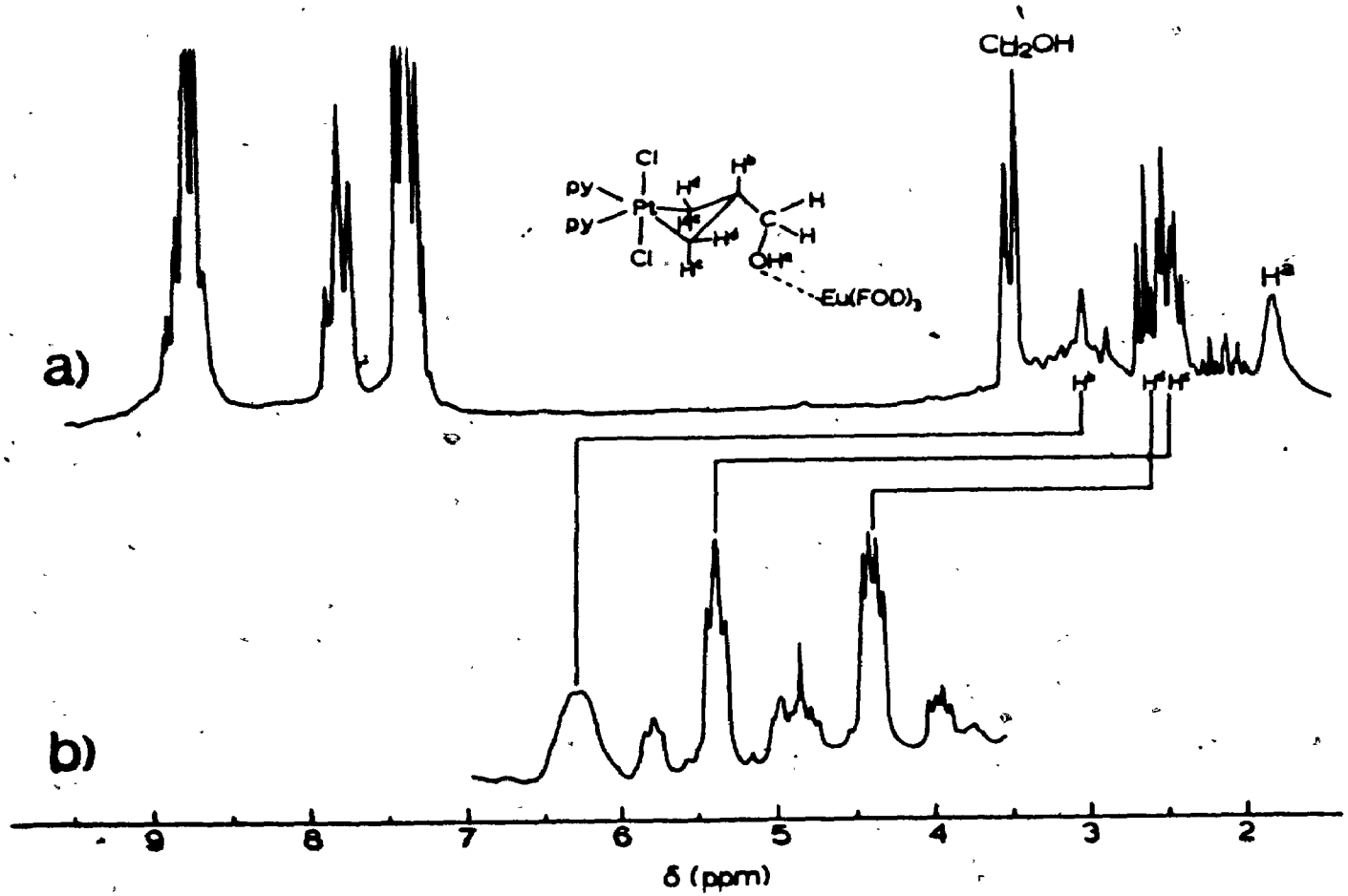


Figure 3.6 ^{1}H-N.M.R. spectrum of compound 1, a) in the absence of added shift reagent and b) at a $\frac{Eu(fod)_3}{substrate}$ ratio of 0.494.

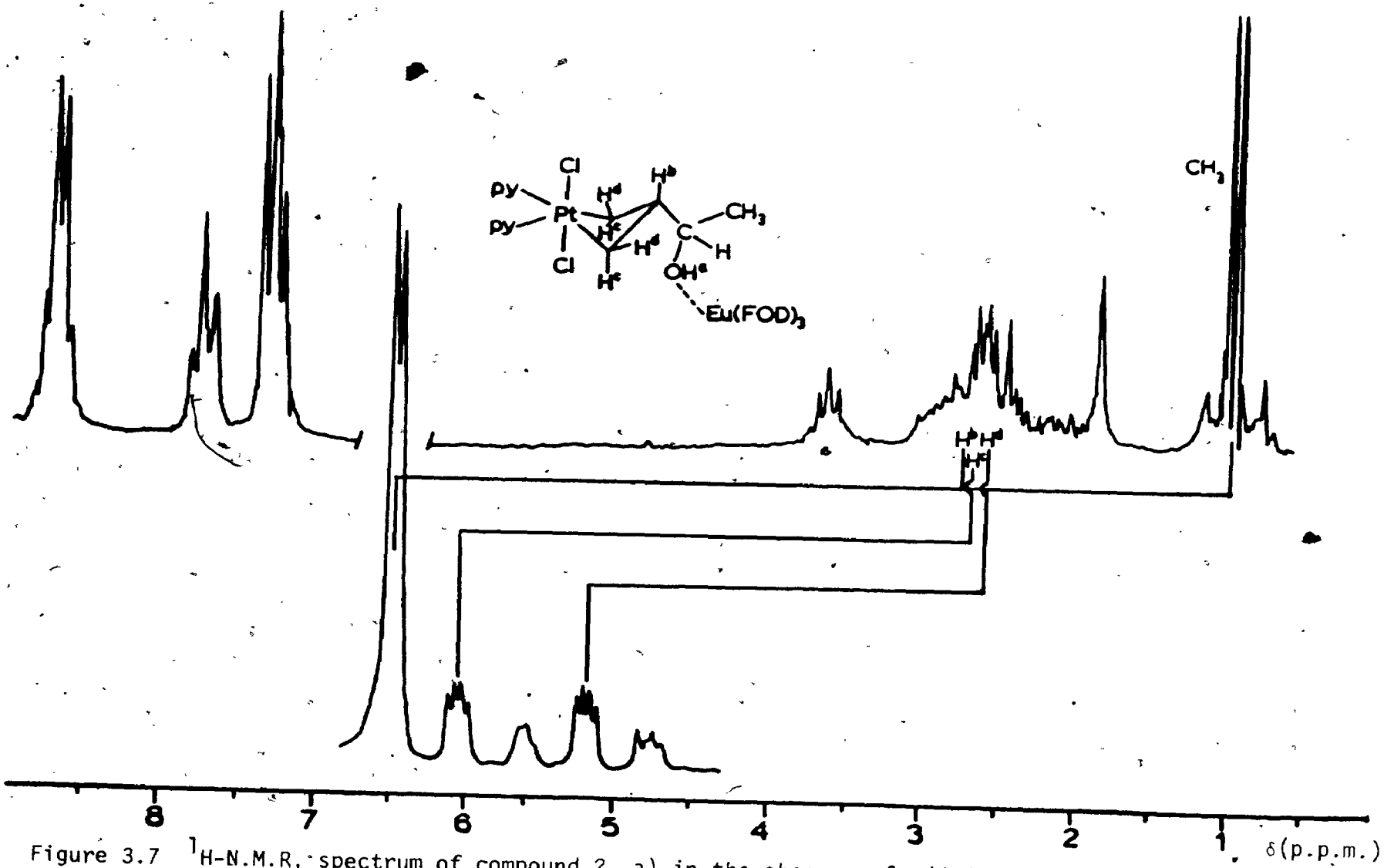


Figure 3.7 ^{1}H-N.M.R. spectrum of compound 2, a) in the absence of added shift reagent and b) at a $\frac{Eu(fod)_3}{substrate}$ ratio of 0.840.

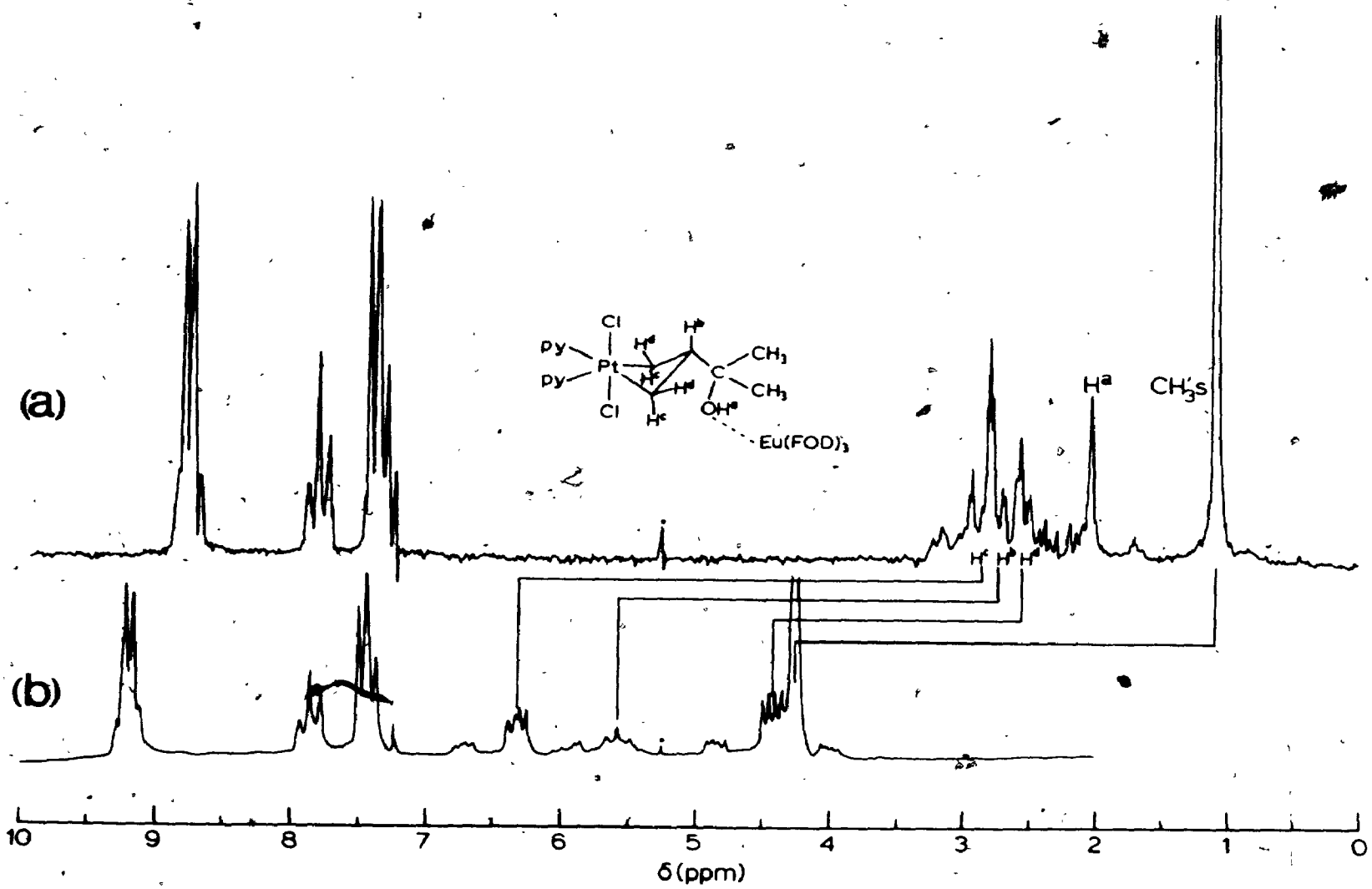


Figure 3.8 ^{1}H-N.M.R. spectrum of compound 3, a) in the absence of added shift reagent and b) at a $\frac{\text{Eu(fod)}_3}{\text{substrate}}$ ratio of 0.495.

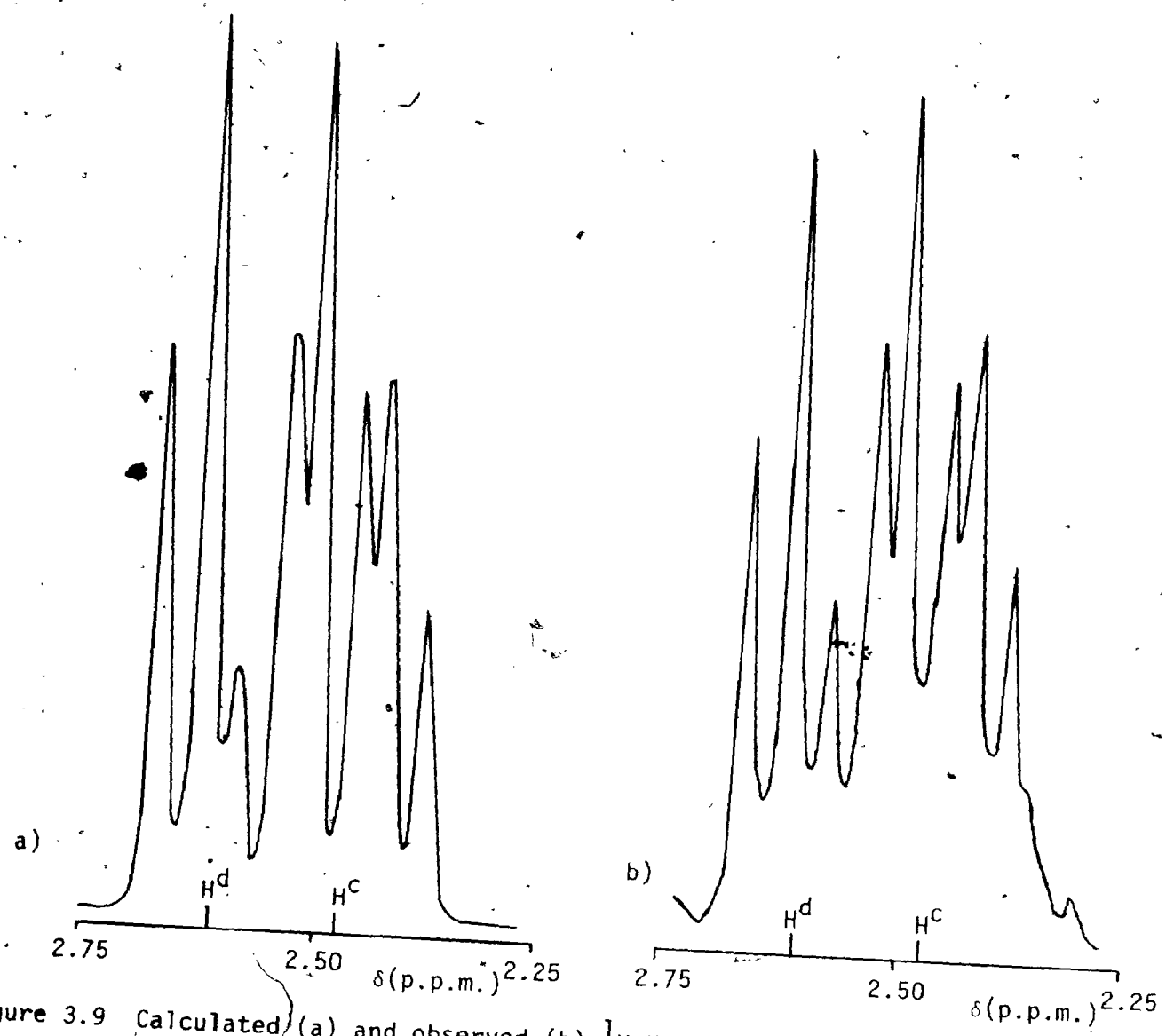


Figure 3.9 Calculated (a) and observed (b) ^{1}H-N.M.R. spectrum of compound 1 in the region H^d , H^c.

any significant degree, the geometry of the complex. This fact, combined with the ability to measure vicinal and geminal couplings for the platinacyclobutane ring protons from the first-order analysis has enabled predictions to be made as to the puckering of these metallacycles in solution.

2.2 Puckering of the platinacyclobutanes in solution

There is general agreement by workers in this field that there is a low activation towards puckering of the metallacyclobutane ring.[17] Both ring puckering in solution and lack of appreciable ring strain energy may contribute to the importance of metallacycles as intermediates in transition metal-catalyzed reactions. The pucker angle found in an X-ray structure determination may depend on steric effects or crystal packing forces. Thus, the degree of puckering of a metallacyclobutane ring in the solid state and in solution may differ.

It has been shown by X-ray crystallographic analysis that the degree of puckering in platinacyclobutanes varies widely.[63] The minimum pucker angle yet determined is 0° for the complex $[\overline{PtCl_2(CH_2CH_2CH_2)}(bipy)]$,[64] whereas the maximum value is 50°, obtained for the complex $[\overline{PtCH(CO_2CH_3)C(O)CH(CO_2CH_3)}(PPh_3)_2]$.[65] Although facile puckering in solution and hence shorter Pt-H contacts have been used to interpret large $^3J(^{195}Pt\text{-}^1H)$ to the β-CH_2 protons of $[\overline{Pt(CH_2CH_2CH_2)}(bipy)]$, a complex which is essentially planar in the solid state,[64] there have been no attempts to estimate equilibrium pucker angles of metallacyclobutanes in solution. Furthermore, it is also possible to make comparisons between pucker angles in solution and those in the solid state since X-ray crystallographic studies have been performed by Ibers,

Jones and Sabat[66] on compound 3 as well as [$PtCl_2(CH_2C(CH_3)(CH_2OH)CH_2)py_2$] 4.[67] A comparison between the structural parameters for the two metallacyclobutanes is given in Table 3.5. ORTEP plots of these structures are given in figures 3.10 and 3.11 for compounds 3 and 4 respectively. Although the crystallographers are unable at this time to account for the difference in C(1)-C(2) and C(2)-C(3) bond lengths found in the structure of compound 3, all other aspects of the determination are normal. They are also confident that the pucker angle in 3 is 5°±1°.

The equation of Karplus[68] (equation 3.12) relates the magnitude of the vicinal $^3J(^1H\text{-}^1H)$ coupling constant to the H-CC-H torsion angle. From empirical studies the set of parameters which is most

$$^3J = A + B\cos\Phi + C\cos 2\Phi \qquad \ldots(3.12)$$

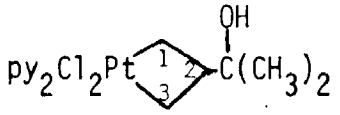
reliable is A = 7, B = -1 and C = 5. Thus, substitution into equation 3.12 produces equation 3.13.[69] Inherent in this relationship are

$$^3J = 7 - \cos\Phi + 5\cos 2\Phi \qquad \ldots(3.13)$$

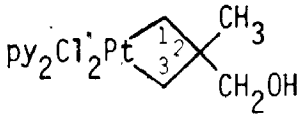
certain limitations, however it has been used successfully to determine the pucker angles in cyclobutanol, which can invert, as well as rigid bicyclic derivatives which cannot invert.[70] From the analysis of the first-order ^1H-N.M.R. spectral parameters of the platinacyclobutanes 1-3 it should be possible to calculate a torsion angle from equation 3.13 and hence the extent of puckering in these metallacycles.

Figure 3.12 is a view looking down the β-carbon towards one of the α-carbons of the platinacyclobutanes. The angles Φ^{bd} and Φ^{bc} which

Table 3.5 Structural parameters for metallacyclobutanes 3 and 4



3



4

Space Group	$P2_1/c$	Pbca
	Intramolecular Distances (Å)	
Pt-C(1)	2.064(10)	2.042(7)
Pt-C(2)	2.670(9)	2.676(7)
Pt-C(3)	2.061(9)	2.039(6)
C(1)-C(2)	1.597(12)	1.542(10)
C(2)-C(3)	1.492(14)	1.548(10)
C(1)-C(3)	2.375(12)	2.345(10)
	Bond Angles (Degrees)	
C(1)-Pt-C(3)	70.50(36)	70.15(28)
C(1)-C(2)-C(3)	100.42(64)	98.75(55)
Pt-C(1)-C(2)	92.71(54)	95.55(46)
Pt-C(3)-C(2)	96.15(53)	95.54(44)
	Pucker Angle (Degrees)	
[C(1)-Pt-C(3)] - [C(1)-C(2)-C(3)]	5	1

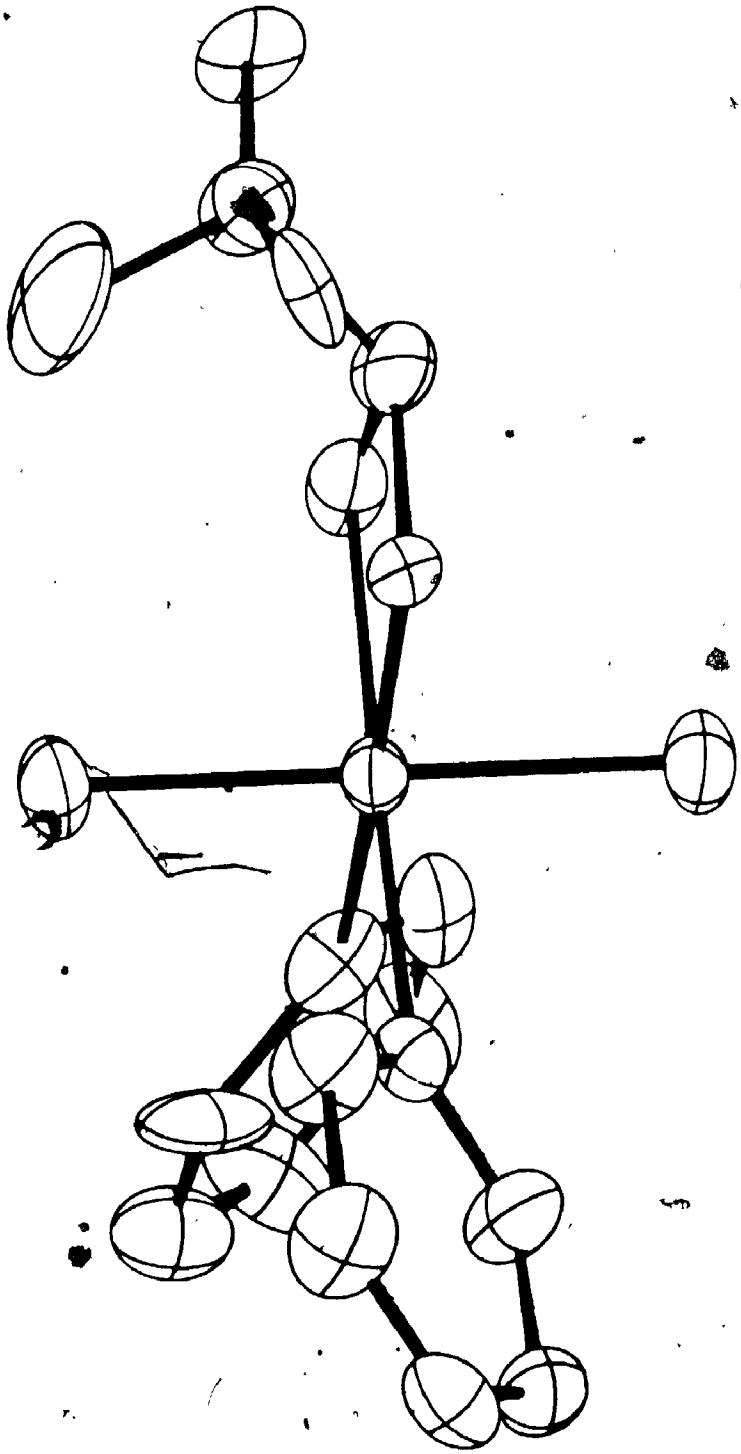


Figure 3.10 ORTEP drawing of the molecule: $[PtCl_2CH_2CH(C(CH_3)_2OH)CH_2py_2]$; 3.

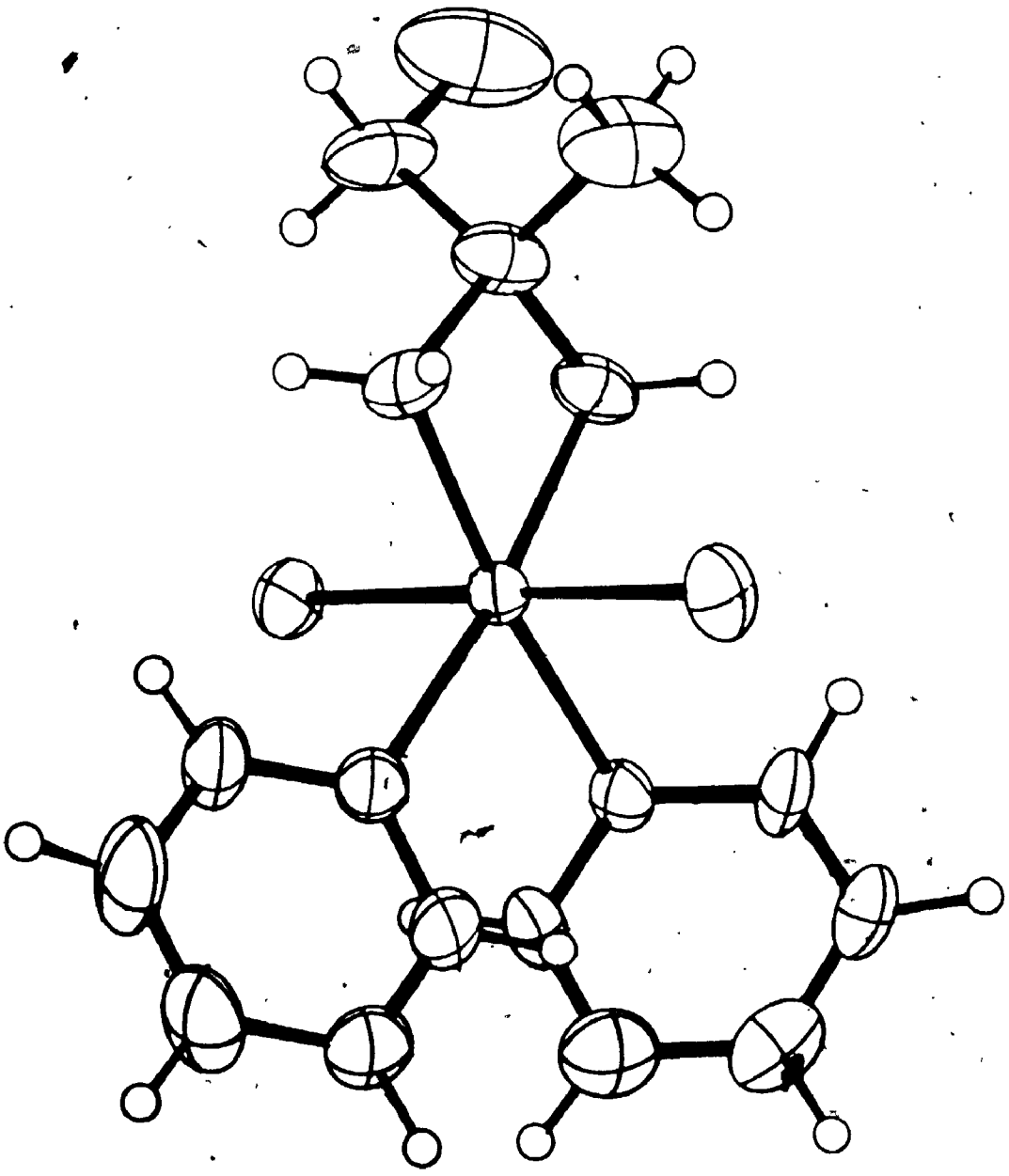


Figure 3.11 ORTEP drawing of the molecule: $[PtCl_2CH_2C(CH_3)(CH_2OH)CH_2py_2]$; 4.

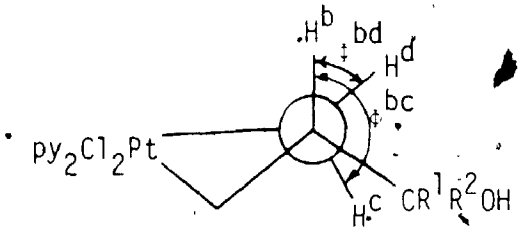


Figure 3.12 A view down the C^2-$C^{3,4}$ bond

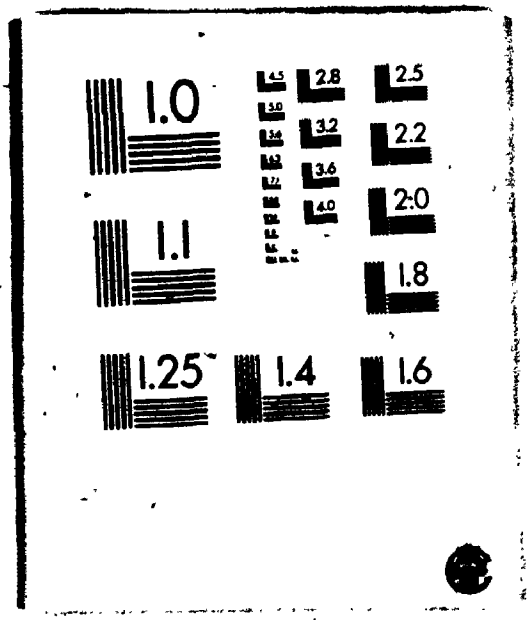
are shown correspond to the two torsion angles expected, between H^bH^d and H^bH^c respectively. The labelling of the diagram is such that H^c has been assigned to the proton cis to the CR_1R_2OH group whereas H^d is trans to the CR_1R_2OH group. These are the same assignments as previously made in Chapter 2, being based upon the expected larger shifting parameter for H^c. If however, a reversal of the assignments is made there is little change in the resulting pucker angle.

The results are shown in Table 3.6 where Φ_1 corresponds to the torsion angle for the assignments of figure 3.12 and Φ_2 corresponds to a reversal of assignments for H^c and H^d. The pucker angle has been determined from figure 3.12 which is based on an idealized platinacycle having Pt-C bond lengths of 2.040 Å, metallacyclic C-C bond lengths of 1.545 Å, a C(1)-C(2)-C(3) bond angle of 98.68°, and at planarity (pucker angle = 0°) a Pt-C-C bond angle of 95.60°. These values were based upon those obtained in the crystallographic study of compound 4.[67] The hydrogen atom positions of the methylene groups were idealized so that the H-C-H angle is 109.5 and the CH_2 plane is perpendicular to the CXY plane where X and Y are the atoms attached to C.

Table 3.6 Torsion and Pucker Angles For Complexes 1-3

Compound	^3J(Hz)	Φ_1	Pucker Angle	Φ_2	Pucker Angle
(1) $R^1=R^2=H$;	$^3J(H^bH^c)=7.6$	134°	15°	37°	53°
	$^3J(H^bH^d)=8.9$	28°	39°	141°	22°
(2) $R^1=H$;	$^3J(H^bH^c)=8.9$	141°	23°	28°	39°
$R^2=CH_3$;	$^3J(H^bH^d)=9.3$	25°	34°	144°	25°
(3) $R^1=R^2=CH_3$;	$^3J(H^bH^c)=8.3$	138°	19°	32°	45°
	$^3J(H^bH^d)=9.3$	24°	33°	144°	25°

2



solvolysis mixture but also their solvolysis rate was slowed, presumably due to OPNB being a much poorer leaving group in solvolysis, so that reductive elimination of the cyclopropane derivative from the metal became competitive. This had the effect of reducing yields to such an extent that when $R^1 = R^2 = CH_3$, $R^3 = H$, $R^4 = PNB$, (8), no platinacycle could be isolated, the products of the reaction being $[PtCl_2py_2]$ and 2-cyclopropyl-2-propyl - *p*-nitrobenzoate.

A typical solvolysis experiment was performed by dissolving the platinacyclobutane in a 60% or higher aqueous acetone mixture and allowing the reaction to proceed, with stirring at slightly elevated temperatures. Addition of equimolar amounts of $CaCO_3$ to the solution to react with the acid formed had no effect on the rate of solvolysis nor product ratios or yields and in most cases it was omitted. After completion of the reaction the solution was worked up by addition of K_2CO_3 until a saturated aqueous layer separated out. The solvents were then evaporated and the residue was taken up in CH_2Cl_2. The organic layer was filtered, dried over anhydrous K_2CO_3 and evaporated to about one millilitre. Addition of n-pentane to this solution caused precipitation of the products.

Table 4.1 lists the products of solvolysis from these reactions. One observation becomes apparent, being that in no case was the unexpanded platinacyclobutane derivative $[PtCl_2(CH_2CR^3(CR^1R^2OR^4)CH_2)L_2]$ formed in detectable quantity and hence solvolysis occurs with essentially complete ring expansion. These unrearranged platinacyclobutanes have been prepared independently and fully characterized as described in chapter 2. They would have been detected if present in 1-2% yield, in favourable cases. Also it is seen that on introduction

nearly planar ring should result from solution studies. This however is not the case as the conformation with the CR^1R^2OH group in the endo position, figure 3.13(c), is not only destabilized by two gauche-butane type interactions between the CR^1R^2OH group and the platinum atom, but also upon investigation of space-filling models this conformation is much less likely due to severe steric interaction with the axial chloride. Thus, a rapid equilibrium between structures a and b in figure 3.13 results and should yield N.M.R. parameters intermediate between those for the extremes but naturally weighted towards the more stable conformer.

It would also be expected that substitution of a hydrogen by a methyl group on the β-carbon as in compound 4 should alter the equilibrium conformations in figure 3.13 so as to allow both the methyl and CR^1R^2OH substituents to occupy a position in which each substituent is symmetrically disposed. This would indicate that for 4 the equilibrium would be closer to 3.13(b) than for 1-3 which could adopt a conformation closer to 3.13(a) relative to that of 4. Supportive to this are the magnitude of the $^3J(^{195}Pt-^{13}C)$ couplings between the platinum atom and the carbinol carbon which is in the range 47±2 Hz for 1-3 and only 28±4 Hz for compound 4 (see Table 2.2). This does not appear to be mere coincidence as similar results were seen in Chapter 2 for the methanesulphonate esters of compounds 1 and 4 which show $^3J(^{195}Pt-^{13}C)$ couplings of 54.1 and 28.2 Hz respectively. Furthermore, similar results were obtained by Puddephatt et al.[71] for the mono- and di-methyl substituted platinacyclobutanes $[\overline{PtCl_2(CH_2CH(CH_3)CH_2py_2}]$ and $[\overline{PtCl_2(CH_2C(CH_3)_2CH_2)py_2}]$ which have $^3J(^{195}Pt-^{13}C)$ couplings to the

methyl carbons of 54.0 and 29.0 Hz respectively, though no interpretation for this difference was given. These results are summarized in Table 3.7.

Qualitatively, the large difference in coupling constants can be rationalized with the Karplus relationship although the parameters A, B and C in equation 3.12 are unknown. In a planar platinacyclobutane, 3.14(a), and a puckered platinacyclobutane, 3.14(b), one would expect a small $^3J(^{195}Pt-^{13}C)$ and a large $^3J(^{195}Pt-^{13}C)$ respectively based upon

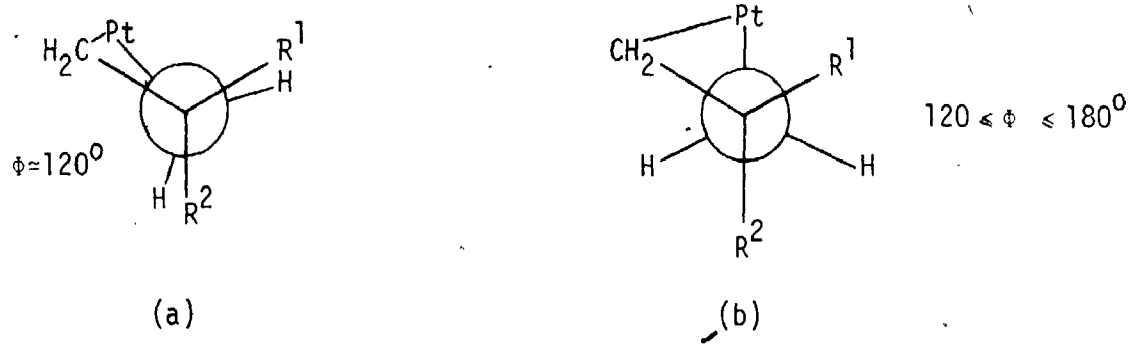
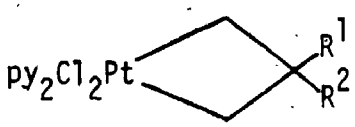


Figure 3.14 Newman projections of a non-puckered (a) and a puckered (b) platinacyclobutane

equation 3.12. Table 3.7 illustrates this point as large $^3J(^{195}Pt-^{13}C)$ couplings are seen for the complexes where R^1 = H which are expected to have equilibrium conformations more highly puckered than the disubstituted complexes which show smaller coupling constants corresponding to a more planar equilibrium conformation.

The validity of the conclusions drawn from the proton work is based upon the reliability of the Karplus equation and the constants of Bothner-By used in equation 3.13. Strong support for self-consistency of the data is seen from consideration of the platinacyclobutanes $[PtCl_2CH^aPhCH^bPhCH^cH^dL_2]$; where L = pyridine or 4-tertbutyl pyridine,

Table 3.7 Comparison of $^{3}J(^{195}Pt-^{13}C)$ values for mono- and di-methyl substituted platinacyclobutanes



Compound	$^{3}J(^{195}Pt-^{13}C)$; (Hz)	Reference
R^1=H; R^2=CH_2OH	49.0	a
R^1=H; R^2=$CH_2OSO_2CH_3$	54.1	a
R^1=H; R^2=$CH(CH_3)OH$	45.2	a
R^1=H; R^2=$C(CH_3)_2OH$	46.2	a
R^1=H; R^2=CH_3	54.0	71
R^1=CH_3; R^2=CH_2OH	28.4	a
R^1=CH ; R^2=$CH_2OSO_2CH_3$	28.2	a
R^1=R^2=CH_3	29.0	71

a) this work

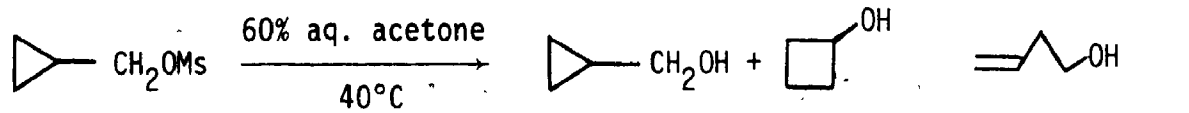
for which $^3J(H^bH^c) \simeq {}^3J(H^bH^d)$ = 9.0±1.0 Hz or 8.6±1.0 Hz respectively[72,73] similar to those seen for complexes 1-3, indicating very similar conformations in solution. An X-ray crystal structure determination on $[\overline{PtCl_2CHPhCHPhCH_2py_2}]$, reveals the presence of two conformers in the solid state with pucker angles of 22° and 28°.[74] These are consistent with the range calculated for compounds 1-3 of 27±8° indicating that it has very similar conformations in both solid state and solution. If one argues that equation 3.13 is so unreliable for platinacyclobutanes that equal vicinal couplings of 8.5±1 Hz corresponds to a planar ring in 1-3, then these 1,2-diphenyl substituted analogues must be approximately planar in solution as well. This is highly improbable based upon examination of space-filling models which indicate very significant steric hindrance to a planar platinacyclobutane.

CHAPTER 4

RING-EXPANSION REACTIONS OF PLATINACYCLOBUTANES: THEIR SCOPE AND LIMITATIONS

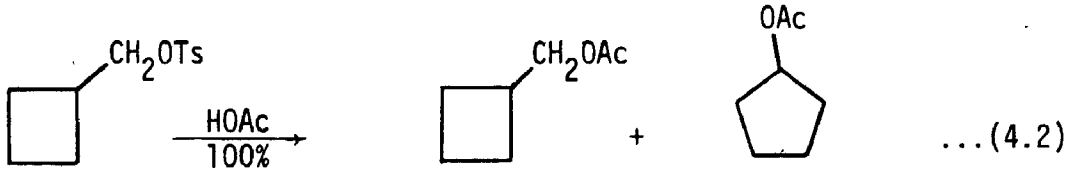
1. Introduction

The observation that cyclopropylcarbinyl derivatives give mixtures of products upon solvolysis (equation 4.1) has been well established in organic chemistry and often used as a synthetic tool.[75]



53% 44% 3% ...(4.1)

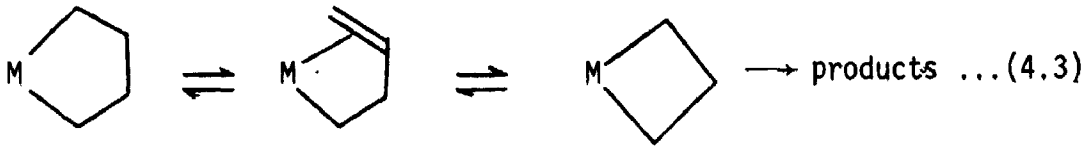
Much less studied experimentally however, are cyclobutylcarbinyl derivatives which also give a mixture of products upon solvolysis, formation of ring expanded products though are often much more favoured in this case compared with the cyclopropylcarbinyl system (equation 4.2)[76].



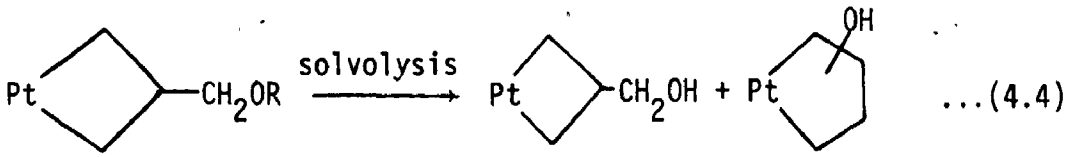
1% 99% ...(4.2)

It is this preference for ring expansion in the cyclobutylcarbinyl systems which made the possibility for similar reactions in the platinacyclobutylcarbinyl system seem attractive.

Schrock has proposed that short-lived tantalacyclobutane intermediates are formed from tantalacyclopentanes during some catalytic alkene dimerization reactions (equation 4.3)[77] but the reverse reaction, which should be favoured thermodynamically[78] has not been observed.



This chapter will discuss such a reaction and its scope and limitations, the synthetic strategy stemming from the analogy with the organic systems (equation 4.4).

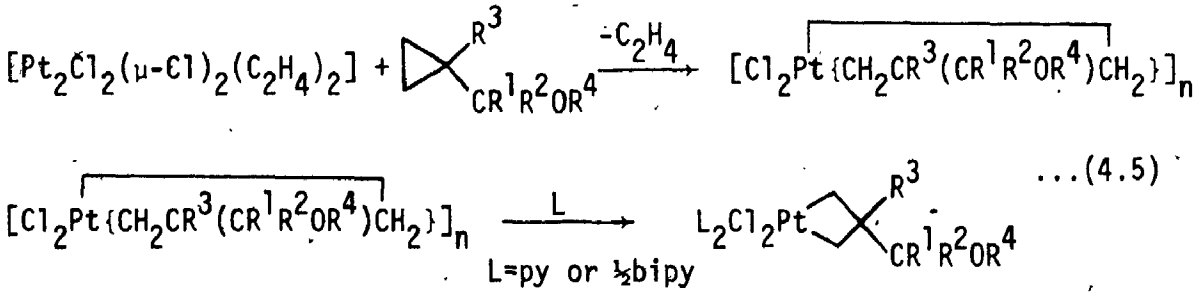


OR=a leaving group

2. Results and Discussion

2.1 Preparation of Platinacyclobutane Complexes

The preparation of the platinacyclobutanes containing a leaving group suitable for solvolysis involved the oxidative addition of the required cyclopropane derivative with Zeise's dimer (equation 4.5) as described in chapter 2.



It was not known "a priori" whether platinacyclobutanes would be products of such a reaction owing to the high reactivity of the starting

cyclopropane derivatives (especially when OR^4 = methanesulphonate (OMs)) and the expected reactivity of the platinacyclobutane complex thus formed. It was discovered that these reactions proceed cleanly and in good yield, presenting few synthetic difficulties. The products were stable crystalline solids.

2.2 Solvolysis of Platinacyclobutane Complexes

The solvolysis of the platinacyclobutanes in equation 4.5 proceeded smoothly for the methanesulphonate esters (R^4 = Ms) in, for the most part, 60% aqueous acetone mixtures at 36°C. The solvent was chosen so as to parallel as closely as possible the studies of the organic derivatives keeping the conditions mild enough such that the platinacyclobutanes would be stable against reductive elimination processes but would still be reactive towards solvolysis. It was found that the platinacyclobutanes were generally much more soluble at higher acetone:water ratios. However, solvolysis rates were typically reduced in these less polar solvent mixtures. Solubility was not a concern except during the kinetic runs for the bipy derivatives which are very much less soluble than their pyridine counterparts and are just sparingly soluble in a 60% aqueous acetone medium. Qualitatively it was observed that these bipy complexes reacted much more slowly than the pyridine ones, indicating that ligand dissociation might be involved at some stage. The significance of this result will be discussed further in chapter 5.

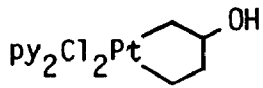
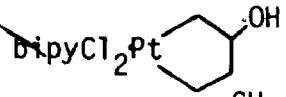
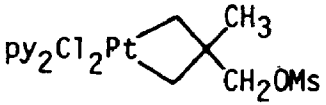
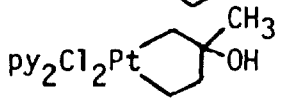
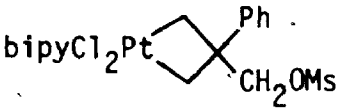
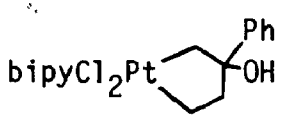
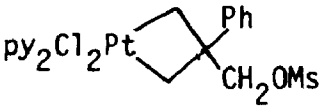
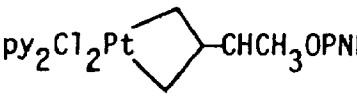
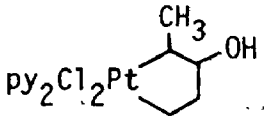
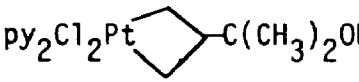
Less success was seen for the *p*-nitrobenzoate derivatives, (R^4 = PNB), of the secondary and tertiary alcohols. Not only were they less soluble than the methanesulphonates (R^4 = Ms) in the

solvolysis mixture but also their solvolysis rate was slowed, presumably due to OPNB being a much poorer leaving group in solvolysis, so that reductive elimination of the cyclopropane derivative from the metal became competitive. This had the effect of reducing yields to such an extent that when $R^1 = R^2 = CH_3$, $R^3 = H$, $R^4 = PNB$, (8), no platinacycle could be isolated, the products of the reaction being $[PtCl_2py_2]$ and 2-cyclopropyl-2-propyl - *p*-nitrobenzoate.

A typical solvolysis experiment was performed by dissolving the platinacyclobutane in a 60% or higher aqueous acetone mixture and allowing the reaction to proceed, with stirring at slightly elevated temperatures. Addition of equimolar amounts of $CaCO_3$ to the solution to react with the acid formed had no effect on the rate of solvolysis nor product ratios or yields and in most cases it was omitted. After completion of the reaction the solution was worked up by addition of K_2CO_3 until a saturated aqueous layer separated out. The solvents were then evaporated and the residue was taken up in CH_2Cl_2. The organic layer was filtered, dried over anhydrous K_2CO_3 and evaporated to about one millilitre. Addition of n-pentane to this solution caused precipitation of the products.

Table 4.1 lists the products of solvolysis from these reactions. One observation becomes apparent, being that in no case was the unexpanded platinacyclobutane derivative $[PtCl_2(CH_2CR^3(CR^1R^2OR^4)CH_2)L_2]$ formed in detectable quantity and hence solvolysis occurs with essentially complete ring expansion. These unrearranged platinacyclobutanes have been prepared independently and fully characterized as described in chapter 2. They would have been detected if present in 1-2% yield, in favourable cases. Also it is seen that on introduction

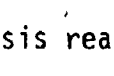
Table 4.1 Solvolysis Products From Platinacyclobutanes

Starting Material		Product		Yield (%)	Conditions
	(6)		(16)	(81-85)	a; 24 hrs.
	(14)		(17)	(83)	a; 100 hrs.
	(9)		(18)	(86-90)	a; 30 hrs.
	(15)		(19)	(46)	45°C; 80% aq. acetone; 170 hrs.
	(10)	——		(0(b))	a; 100 hrs.
	(7)		(20)	(51-65)	40°C; 70% aq. acetone; 120 hrs.
				(20)	54°C, 70% aq. acetone; 120 hrs.
	(8)	——		(0(b))	40°C; 70% aq. acetone; 120 hrs.

a) 36°C, 60% aqueous acetone

b) only $[PtCl_2py_2]$ could be isolated from solution

of a phenyl substituent on the β-carbon no ring expansion products were isolated for the bis(pyridine) adduct, 10, yet when L = bipy, 15, compound 19 could be isolated though in a reduced yield compared to most of the other reactions presented. This reflects the stabilising effect that the chelating bipy ring has on the intermediate of the reaction.

Only in an isolated case was more than one platinacyclopentane product isolated. In a single solvolysis reaction of py_2Cl_2Pt  CH_2OMs, 6, to give 16, three geometrical isomers were produced as identified by their ^{13}C-N.M.R. spectra. They differed only in the orientation of the chloride and pyridine ligands with respect to the platinacyclopentane ring. The predominant isomer in this case was the one isolated all other times, presumably with <u>trans</u> chloride and <u>cis</u> pyridine ligands. This aspect of formation of other isomers was not pursued further due to non-reproducibility in the system, but has been observed previously in related platinacyclopentanes.[79]

2.3 Characterisation of Platinacyclopentane complexes

The platinacyclopentane products 16-20 were characterised most easily by their ^{13}C-N.M.R. spectra. ^{1}H-N.M.R. spectra were less useful owing to their complexity. Mass spectra and elemental analyses were also helpful in several of the cases.

2.3.1 Mass spectra

The mass spectra for compounds 16 and 17 run at 230°C and 70 eV show no parent ion. However the first ion observed corresponded to a

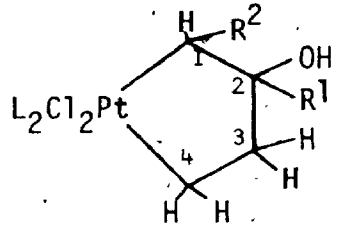
loss of ethylene (m/e = 28) with the most intense peak of the isotope pattern at 496 and 494 respectively. The next observable ions at 424 and 422 respectively correspond to loss of the fragment CH_2CHOH (m/e = 44) leaving behind the bare $[PtCl_2L_2]$ fragment which underwent further fragmentation. All peaks had the correct isotope pattern. The results support the structural assignments in Table 5.1 and are consistent with the pyrolysis and photolysis studies of other platinacyclopentanes[79,80] which show ready loss of ethylene from the metallacycle or loss of the entire organic moiety to give the longer-chain olefin with no formation of cyclobutane products. In the mass spectral analysis for compounds 16 and 17 there was no evidence for loss of the CH_2CHOH unit prior to the loss of ethylene as the mass spectra in the region m/e = 440-460 were devoid of peaks.

2. .2 ^{1}H-N.M.R. Analysis of the Platinacyclopentane Products

The ^{1}H-N.M.R. data obtained for the complexes 16-20 are presented in Table 4.2. In all cases the spectra were very complex and often second-order. The spectra were simplified somewhat using decoupling techniques and deuterium labelling studies (see chapter 5), which allowed for clear assignments of the chemical shift ranges for the protons, yet few homonuclear ^{1}H-^{1}H couplings or heteronuclear ^{195}Pt-^{1}H couplings could be readily discerned.

Several features of the chemical shifts deserve mention. It is apparent that the spectra for these complexes are much different than those seen for other platinacyclopentanes with an unsubstituted five-membered ring. For example, $[PtI_2(CH_2CH_2CH_2CH_2)(PPh(CH_3)_2)_2]$ exhibits a ^{1}H-N.M.R. spectrum consisting of a broad unresolved

Table 4.2 Proton N.M.R. Data for The Platinacyclopentane Complexes 16-20

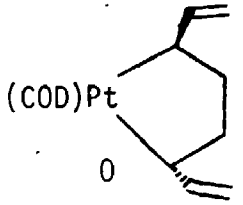


Complex	δ(α-1) ppm 1	δ(α-1) ppm R^2	δ(β-3) ppm 1	δ(β-3) ppm 2	δ(α-4) ppm 1	δ(α-4) ppm 2	δR^1 ppm	Solvent
16; $R^1=R^2=H$ L = py	2.29-3.1	3.70 J=8.6 & 4.8 Hz	0.92-1.16	~1.52-1.78	2.66-2.92	3.16-3.40	3.40-3.54	$CDCl_3$
17; $R^1=R^2=H$ L=1/2bipy	3.05-3.6	2.80 J=7.5 & 4.8 Hz	0.98-1.24	1.4-1.78	2.92-3.05	3.28-3.61	3.28-3.61	CD_2Cl_2
18; $R^1=CH_3$ $R^2=H$, L=py	2.60	3.95 J_{gem}=9.2Hz	0.61	1.92-2.17	2.49-2.70	3.45-3.74	1.36	CD_2Cl_2
19; $R^1=Ph$, $R^2=H$ L=1/2bipy	2.98	4.47 J_{gem}=9.1Hz	0.79-1.05	___ a	2.52-2.90	3.76-4.12	7.2-7.6	CD_2Cl_2
20; $R^1=H$, $R^2=CH_3$ L=py	3.62-4.05	0.66 $^3J_{PtH}$= 20.5Hz $^3J_{HH}$= 6.5Hz	0.78-1.05	1.44-1.72	2.78-3.00	3.14-3.48	a	CD_2Cl_2

a) assignments uncertain due to masking

multiplet at δ4.48 ppm.[79] Substitution on the ring by a methyl group, as in the platinum(II) complex $[\overline{Pt(CHCH_3CH_2CH_2CH_2)}(P\text{-}^nBu_3)_2]$,[43] causes a shift such that the methine proton can be distinguished yet the methylene protons remain unresolved.

The maximum chemical shift difference between the protons on the α and β-carbons for complexes 16-20 is in all cases greater than 2.5 ppm. The downfield shift of the α-protons relative to the β-protons is a similar result as that seen in the substituted platinum(II) platinacyclopentane, complex 0,[44] in which the α-protons were found to



COD = 1,5-cyclooctadiene

resonate downfield from the β-protons in the ranges 3.4-3.1 and 2.2-1.2 ppm respectively. This difference is less than that seen for complexes 16-20 but certainly lends credence to the assignments of the α and β-protons.

Due to the unsymmetrical nature of the ring in these complexes arising from the β-hydroxyl group it is possible to distinguish in almost every case each of the inequivalent protons. Unambiguous assignment between geminal methylene protons is not possible.

It is seen, in Table 4.2, that generally the α-1 proton(s) and the α-4 protons alternate in chemical shifts. That is, the hydroxyl group causes the α-1 proton to resonate furthest downfield followed next by an α-4 proton, then the other α-1 proton while the remaining α-4 proton resonates the furthest upfield.

In 20 the ^{1}H-N.M.R. spectrum was helpful in assignment of the structure owing to the appearance of the methyl group as a doublet

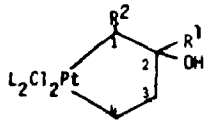
with a large coupling to platinum indicating that it is coupled to a single hydrogen and is on the α-carbon. The chemical shift of 0.66 ppm, the coupling to H-α_1 and the magnitude of the coupling to platinum of 20.5 Hz are close to the parameters seen in $[\overline{PtCl_2(CHCH_3CH_2CH_2)py_2}]$[50] whose methyl resonance occurs at 0.84 ppm with a $^3J(CH_3\text{-}H^a)$ = 8 Hz and $^3J(Pt\text{-}CH_3)$ = 22 Hz. This data supports the structure of 20, as that shown in Table 4.1.

2.3.3 ^{13}C-N.M.R. Spectra of the Platinacyclopentane Complexes

Of particular value in the unequivocal characterisation of the platinacyclopentane products were ^{13}C chemical shifts, the multiplicities observed in the off-resonance decoupled ^{13}C-N.M.R. spectra (for 20 this same information was obtained from an INEPT experiment) and the magnitudes of the couplings $^1J_{Pt\text{-}C}$ which differ markedly in platinacyclobutanes and platinacyclopentanes. Table 4.3 lists the observed spectral parameters for the complexes 16-20. One of these will be discussed more fully.

One would expect from the structure of 18 two resonances for each of the α-carbons which should have large $^2J(^{195}Pt\text{-}^{13}C)$ couplings. Also it would be expected that the hydroxyl should shift the α-carbon closest to it (C-1) some 8-13 ppm downfield of the other α-carbon (C-4) based on analogy to trends found in similar organic compounds.[81] Also one would expect two more resonances, one for each of the β-carbons. The magnitudes of the couplings $^2J(^{195}Pt\text{-}^{13}C)$ to platinum-195 should be quite small reflecting the relief in ring strain relative to the platinacyclobutanes which show quite large (≈100 Hz) $^2J_{Pt\text{-}C}$ couplings to the β-carbons. The presence of the hydroxyl directly

Table 4.3 ^{13}C-N.M.R. Data for Platinacyclopentane Complexes[a]



Complex	δC^1 ppm	$^1J(^{195}Pt-^{13}C^1)$ Hz	δC^2 ppm	$^2J(^{195}Pt-^{13}C^2)$ Hz	δC^3 ppm	$^2J(^{195}Pt-^{13}C^3)$ Hz	δC^4 ppm	$^1J(^{195}Pt-^{13}C^4)$ Hz	Other
L=py 16 $R^1=R^2=H$	29.0, t	537.7	77.0, d	19.5	41.2, t	7.4	17.2, t	495.7	
L=1/2bipy 17 $R^1=R^2=H$	33.1	540.2	77.2	___	40.7	___	20.9	494.4	
L=py 18 $R^1=CH_3$, $R^2=H$	34.0, t	540.9	81.0, s	14.7	46.9, t	5.7	18.4, t	493	R^1=25.7 ppm $^3J(^{195}Pt-^{13}CR^1)$ =34.5 Hz
L=bipy 19 $R^1=Ph$, $R^2=H$	38.8	549.3	84.4	___	46.6	___	21.0	492	
L=py 20[b] $R^1=H$, $R^2=CH_3$	38.8 (CH)	546.2	80.8 (CH)	43.3	39.1 (CH_2)	7.8	10.7 (CH_3)	487.1	R^2=19.3 $^2J(^{195}Pt-^{13}CR^2)$ =17.9 Hz

a) Solvent $CDCl_3$, Multiplicities from off-resonance decoupled spectra due to $^1J(CH)$ couplings are indicated by s = singlet, d = doublet, t = triplet, q = quartet

b) Solvent $CDCl_3$, Assignments of methylene (CH_2) or methine (CH) carbons from INEPT ^{13}C spectrum

bonded to the β-carbon (C-2) should cause a pronounced downfield shift (36-51 ppm) of this carbon relative to the other β-carbon (C-3). Also the α-carbons should be shielded relative to the β-carbons as seen in platinacyclobutane complexes.[17] The methyl group should fall in the typical region δ19-30 ppm and should deshield the resonances of the α- and β-carbons somewhat, similar to the shift induced by the hydroxyl but much smaller in magnitude.. In summary then one would expect a total of five resonances, one for each of the four ring carbons and one for the methyl group.

This is exactly what is observed in the ^{13}C-N.M.R. spectrum of compound 18. Figure 4.1 is the 50.309 MHz $^{13}C\{^{1}H\}$ N.M.R. spectrum of 18 in CD_2Cl_2 (the quintet at 53.8 ppm due to the solvent has been removed for clarity) in the ring carbon and methyl regions. The α-carbons are located at δ18.4 ppm; $^{1}J(^{195}Pt-^{13}C)$ = 493.9 Hz and δ34.0 ppm; $^{1}J(^{195}Pt-^{13}C)$ = 540.9 Hz for carbons 4 and 1 respectively. Although the chemical shift difference between these two, 15.6 ppm, does not fall within the predicted range, this can be attributed to the methyl group deshielding C-1 more than C-4. The β-carbons are located downfield of the α-carbons at δ81.0 ppm; $^{2}J(^{195}Pt-^{13}C)$ = 14.7 Hz and δ46.9 ppm; $^{2}J(^{195}Pt-^{13}C)$ = 5.7 Hz for carbons 2 and 3 respectively. The hydroxyl causes the 34 ppm downfield shift of carbon-2 relative to carbon-3, as predicted above. The magnitudes of the platinum-carbon coupling constants are dramatically less than those of the α-carbons, though non-zero. The methyl group is readily assigned to the peak at 25.7 ppm; $^{3}J(^{195}Pt-^{13}C)$ = 34.5 Hz. The off-resonance decoupled spectrum (Table 4.3, not shown) also confirms these assignments.

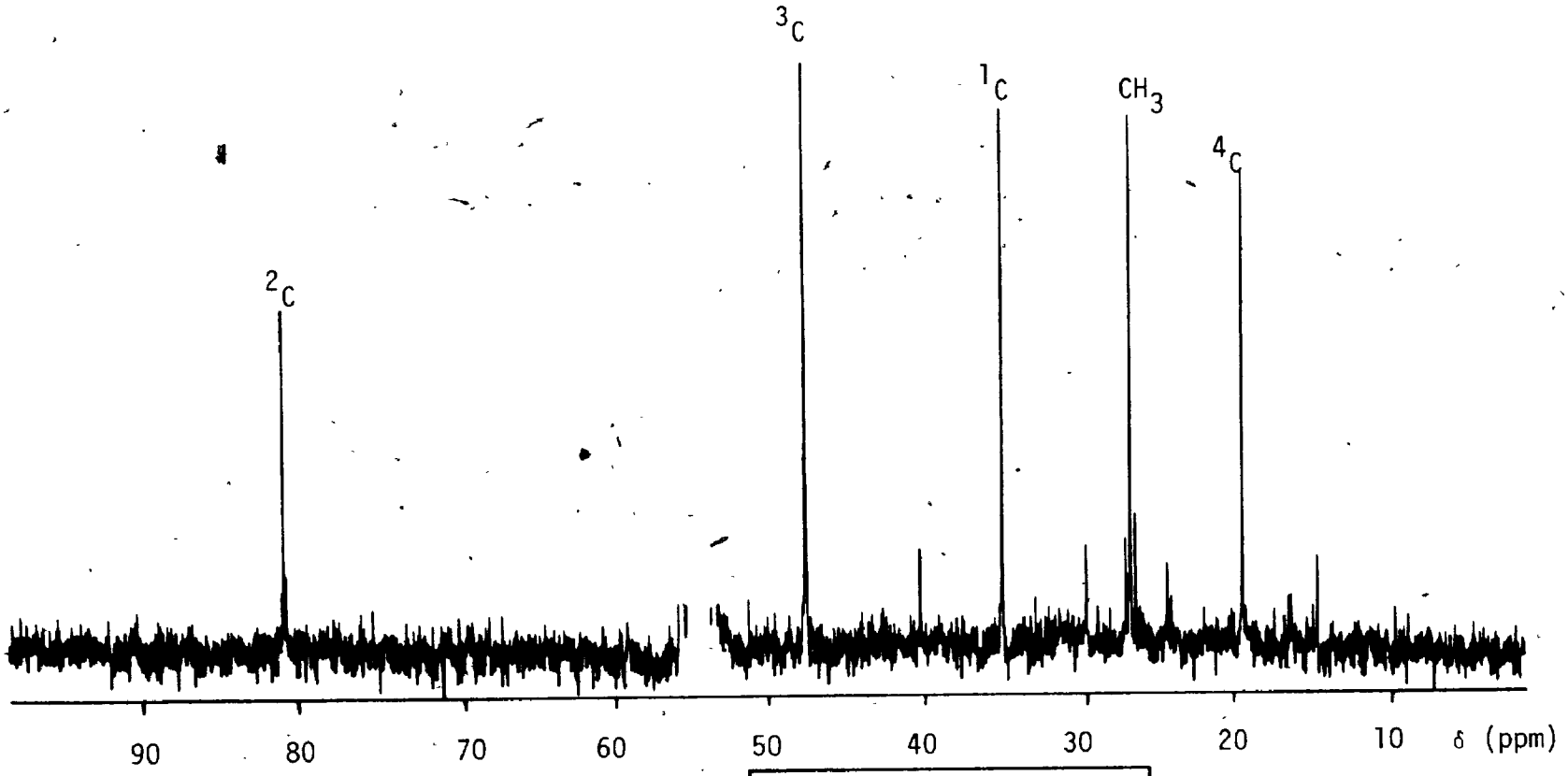


Figure 4.1 $^{13}C\{^{1}H\}$ N.M.R. spectrum of $[PtCl_2\{^{1}CH_2{}^{2}C(CH_3)(OH){}^{3}CH_2{}^{4}CH_2\}py_2]$: 18, in CD_2Cl_2.

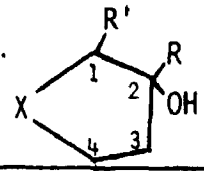
The data in Table 4.3 are self-consistent. Chemical shifts and coupling constants of the individual carbon resonances within the series of complexes fall for the most part within quite a narrow range. Substitution of pyridine by 2,2'-bipyridyl (cf. 16 and 17) seems to alter only the magnitude of the coupling to carbon-2 which is estimated to be less than 5 Hz in the bipy complex. The substitution of a methyl group (as in 18) or a phenyl group (as in 19) on carbon-2 relative to the unsubstituted rings (as in 16 and 17) has little marked effect on the spectral parameters. The coupling of platinum to carbon-2 in 19 was not observed due to a lesser solubility and the fact that it is a tertiary carbon and thereby of low intensity. Hence, the absence of satellites in this case does not imply the coupling is less than 5 Hz but instead is undetermined. The most striking difference among the data set occurs in complex 20 for which the magnitude of the $^{2}J(^{195}Pt-^{13}C)$ coupling to C-2 is rather high; 43.3 Hz. This anomalously high coupling may indicate that this position is the most sensitive to ring conformation, although the magnitude of the coupling is expected to be dominated by through-bond components. The conformation of the ring in 20 is expected to differ from the others as the α-methyl group would prefer to occupy an equatorial position in the five-membered ring, based on conformational studies of substituted five-membered rings.[82] This should lead to a puckering of the platinacyclopentane ring regardless of the geometry of the methyl group relative to the hydroxyl. In 18 and 19 the substituent, now on carbon-2, will prefer to be equatorial. The ring conformation of 20 compared to 18 and 19 need not be the same and is probably different. Puckering of the five-membered ring in the solid state is a common observation from X-ray structural investigations.

In $[PtI_2(CH_2CH_2CH_2CH_2)(PPh(CH_3)_2)_2]$,[83] for example, the puckering in the butanediyl ligand was attributed to relief of crowding of the hydrogen atoms on adjacent carbon atoms. Substitution on the ring is expected to favour puckering.[44] Steric hindrance between the α-methyl group in 20 and the pyridine and chloride ligands may be the dominant factor in the determination of the magnitude of the coupling constant. This steric crowding may also account for the thermal instability of 20, which shows accelerated decomposition in solution relative to the other platinacyclopentanes prepared. A solution allowed to remain at room temperature overnight in methylene chloride became distinctly brown in colour. These steric and conformational differences may also account for the upfield shift of carbon-4 in 20 relative to the other complexes in Table 4.3.

The product arising from solvolysis of 7 was assigned structure 20 with the methyl group on carbon 1 and the hydroxyl group on carbon 2 but we note that this would have similar $^{13}C\{^1H\}$ and INEPT ^{13}C-spectra as that of its C-4 epimer, with the methyl group on carbon-4 and the hydroxyl group on carbon-2. This apparent ambiguity is resolved upon inspection of the chemical shift positions of each of the carbons in the structure relative to those of the other platinacyclopentanes 16-19 in Table 4.3. Clearly, structure 20 is much more consistent with the trends. Also, as will be shown in chapter 5, structure 20 is more consistent with the available mechanistic data.

The geometry of 20, as being the cis or trans isomer, with respect to orientation of the methyl and hydroxyl substituents, is not readily determined even when comparison is made between the ^{13}C-chemical

Table 4.4 ^{13}C-Data For Complexes of the Type:

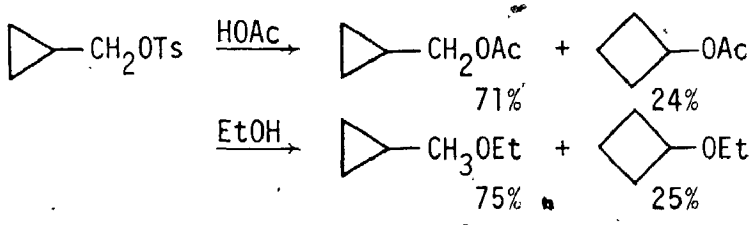


R, R'	X=CH_2 Carbon Position	X=CH_2 Chemical Shift δ(ppm)	X=CH_2 Reference	X=$PtCl_2py_2$ Compound Number	X=$PtCl_2py_2$ Chemical Shift δ(ppm)	Chemical Shift Difference Δ_{CH_2-Pt} (ppm)
R=R'=H	C-1	35.3	81	16	28.8	+6.5
	C-2	73.6			77.0	-3.4
	C-3	35.3			41.1	-5.8
	C-4	23.7			17.0	+6.7
R=CH_3, R'=H	C-1	41.2	84	18	34.0	+7.2
	C-2	79.7			81.0	-1.3
	C-3	41.2			46.9	-5.7
	C-4	24.3			18.5	+5.8
	CH_3	28.3			25.8	+2.5
R=Ph, R'=H	C-1	41.8	85	19	38.8	+3.0
	C-2	83.3			84.4	-1.1
	C-3	41.8			46.6	-4.8
	C-4	23.8			21.0	+2.8
		cis / trans				if cis / if trans
R=H, R'=CH_3	C-1	40.1 / 42.2	86	20	38.8	+1.3 / +3.4
	C-2	75.5 / 80.1			80.8	-5.3 / -0.7
	C-3	34.6 / 34.1			39.1	-4.4 / -5.0
	C-4	22.3 / 21.7			10.7	+11.6 / +11.0
	CH_3	14.0 / 18.6			19.3	-5.3 / -0.70

shifts of the parent cyclopentanols and the platinacyclopentane complexes. This comparison is shown in Table 4.4. Based upon the trends seen it appears as if assignment of a trans geometry to compound 20 more closely fits the data. As will be illustrated in chapter 5, this is also the isomer expected mechanistically.

2.4 Other reactions of platinacyclobutane complexes

Cyclopropylcarbinyl complexes are known to undergo reactions with acids and alcohols of the type illustrated in equation 4.6. It has

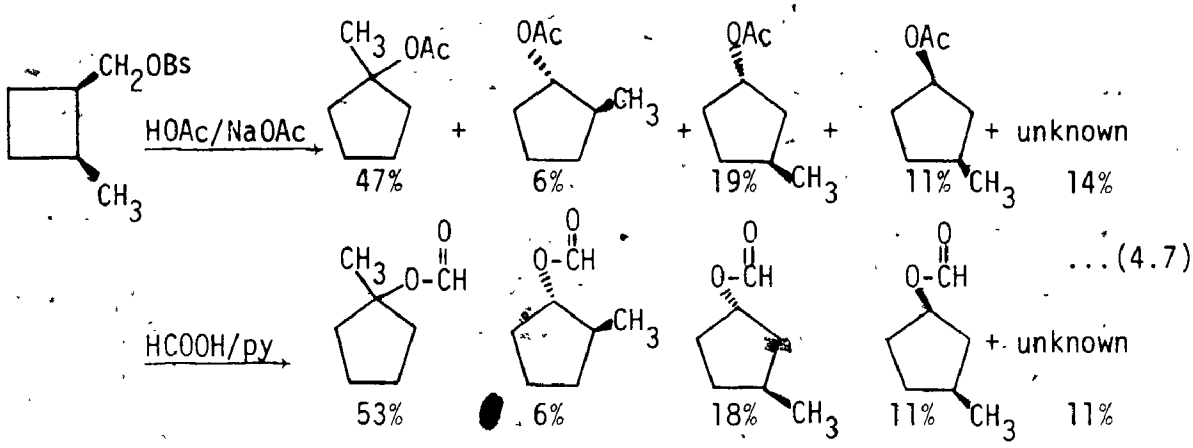


...(4.6)

been known since 1960 that treatment of cyclopropylcarbinol with dilute HCl is a good method for the preparation of cyclobutanol.[87] Acid catalysis of the cyclopropylcarbinyl systems is not restricted to only the unsubstituted cyclopropylcarbinol but 1-methylcyclobutanol is also prepared in 95% yield by the action of HCl on 1-methylcyclopropylcarbinol at 100°C in water.

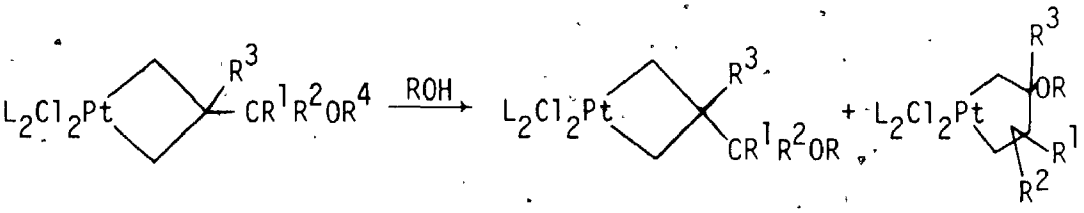
Cyclobutylcarbinyl derivatives have been studied to a far lesser degree but are known to readily undergo acetolysis and formolysis reactions (equations 4.2 and 4.7).[76b]

It was anticipated at the onset of this study that the platinacyclobutylcarbinol complexes and their esters might undergo alcoholysis and acid catalysed reactions to give, to a certain extent, platinacyclopentane derivatives according to equation 4.8.



...(4.7)

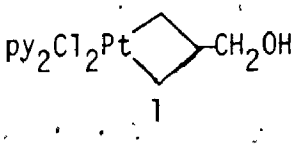
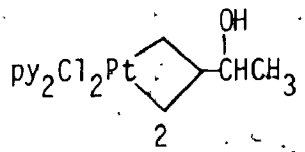
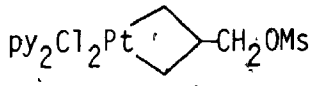
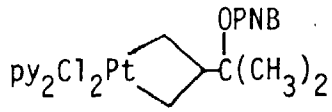
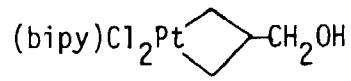
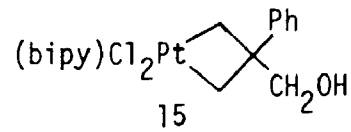
OBs = *p*-bromobenzenesulphonate



...(4.8)

Table 4.5 lists the reactions attempted and the results obtained for the platinacyclobutanes underconsideration. There are several trends which are apparent from the data. Firstly, the platinacyclobutane-carbinol derivatives were robust to reactions in the neat alcohols (with EtOH, $CHCl_3$ had to be added to facilitate dissolution of the starting material). Addition of HCl, generated "in situ" by addition of 2-3 equivalents of acetylchloride caused a dramatic change in these results for the bis(pyridine) adducts. The starting materials decomposed to $[PtCl_2py_2]$ and unidentified products. The bipy complexes survived these conditions with few spectral changes. Dioxane/water mixtures with HCl added were as unsuccessful as the alcoholysis reactions. In no case could a stable product other than starting material or $[PtCl_2L_2]$, (L = py or 1/2bipy) be isolated from these reaction mixtures.

Table 4.5 Solvolysis and Alcoholysis Reactions Performed and Products Isolated

Complex	Reaction Conditions (4-5 days)	Product
 1	i) EtOH; 40°C	SM
	ii) EtOH/$CHCl_3$+AcCl; 40°C	SM + (b)
	iii) dioxane/H_2O; 40°C	(d)
	iv) dioxane/H_2O+$HClO_4$; 40°C	(d)
 2	i) CH_3OH; 40°C	SM
	ii) CH_3OH+AcCl; 40°C	SM + (a)
 6	i) MeOH	(d)
	ii) EtOH	(d)
	iii) $LiB(C_2H_5)_3H$	Pt
	iv) $Sn(CH_3)_4$/acetone	SM + (d)
	v) $HN(CH_3)_2$; 40°C	
 8	i) H_2O; 40°C	(d)
	ii) H_2O+AcCl; 40°C	(d)
	iii) EtOH/$CHCl_3$; 40°C	SM
	iv) EtOH+AcCl; 40°C	(d)
 11	i) CH_3OH+AcCl	SM
	ii) dioxane/H_2O+HCl	(d)
 15	i) CH_3OH+AcCl; 40°C	SM
	ii) dioxane/H_2O+HCl; 40°C	SM
	iii) acetone/H_2O+HCl; 40°C	(d)

Legend:

a) possibly [$\overline{PtCl_2(CHCH_3CHOCH_3CH_2CH_2)}py_2$], see text.

b) possibly [$\overline{PtCl_2(CH_2CHOEtCH_2CH_2)}py_2$] or [$\overline{PtCl_2(CH_2CH(CH_2OEt)CH_2)}py_2$], see text.

SM = only the platinacyclobutane starting material recovered.

d) general decomposition, the solution darkening to unidentifiable insoluble products.

AcCl = acetyl chloride

In only two of the cases were complexes isolated which resembled the desired ring-expansion products. The reaction of $[PtCl_2(CH_2CH(CHCH_3OH)CH_2)py_2]$, 2, with acetyl chloride produced a new product, other than starting material, in very low yield. The ^{1}H-N.M.R. spectrum, in CD_2Cl_2, showed not only a methoxy resonance at δ3.55 ppm but also the presence of a methyl doublet at δ0.64 ppm with a proton-platinum coupling constant of 20 Hz. These results are consistent with the presence of an α-methyl substituted ring similar to that seen for the platinacyclopentane 20 except that no methoxy resonance is present in the latter compound.

Likewise, the reaction of $[PtCl_2(CH_2CH(CH_2OH)CH_2)py_2]$, 1, in $EtOH/CHCl_3$ solution in the presence of acetyl chloride produced another new product. The ^{1}H-N.M.R. spectrum exhibited a triplet at δ1.13 ppm ($^3J_{H,H}$ = 6.8 Hz) and a quartet at δ3.87 ppm ($^3J_{H,H}$ = 6.8 Hz) corresponding to the CH_3 and CH_2 groups respectively of the ethoxide product, expected. The rest of the ^{1}H-N.M.R. spectrum was very complex, though not like the starting material, 1. Purification of the product was unsuccessful.

In both of the above cases the results were of variable reproducibility. The products were formed in low yield and poor purity, thereby thwarting full characterisation. These results, therefore, only support the conclusion that this type of alcoholysis reaction may be possible for platinacyclobutanes. The ideal reaction conditions for such a transformation have not yet been fully realised.

In another experiment $[PtCl_2CH_2CH(CH_2OMs)CH_2py_2]$, 6, was solvolyzed in 60% acetone/H_2O (v/v) solution saturated with lithium chloride. The reaction was allowed to proceed as described before

(section 2.2), for two days, after which time it was worked up and the product analysed. The only product was identified to be $[\overline{PtCl_2CH_2CHOHCH_2CH_2py_2}]$, 16, by its ^1H and ^{13}C-N.M.R. spectra which matched exactly those previously obtained (Tables 4.2 and 4.3) for the same complex. This experiment shows that although ring expansion occurs completely under these conditions, the absence of any ring-substituted chloro product, $[\overline{PtCl_2CH_2CHClCH_2CH_2py_2}]$, must reflect that hydroxide is a much better nucleophile than chloride in these solvolysis reactions.

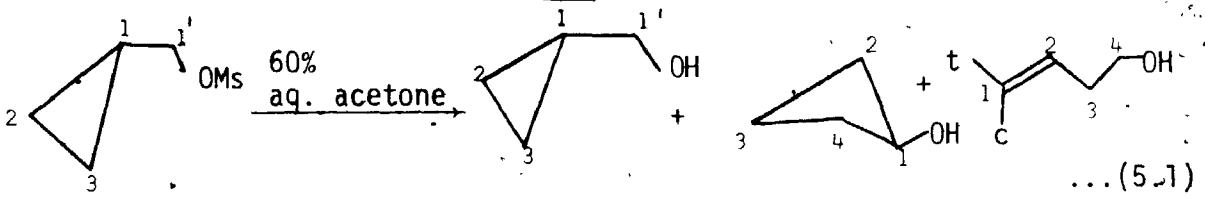
CHAPTER 5

MECHANISTIC STUDIES ON THE RING EXPANSION REACTIONS

The scope and limitations of the ring expansion reactions discovered have been presented in the previous chapter. This chapter will deal with the investigation of the mechanism by which this novel rearrangement proceeds. First, however, some comments on the ring expansion reactions in the organic systems warrant mentioning. Points raised will be used later to rationalise some of the observed features of the platinacyclobutylcarbinyl ring expansion reactions.

1.1 The organic precedents

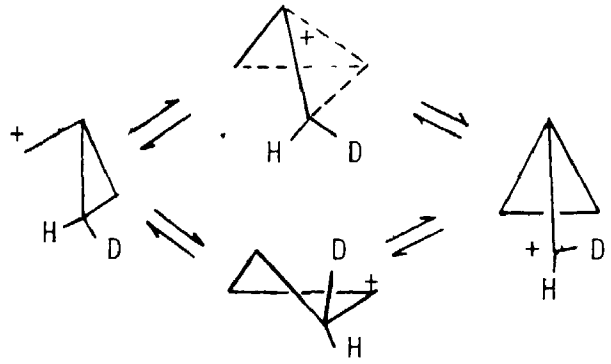
As previously mentioned in Chapter 4, the solvolysis of cyclopropylcarbinyl derivatives has been the subject of considerable research.[75] A particularly elegant study[88] (equation 5.1) involves the solvolysis of cyclopropylcarbinyl methanesulphonate deuterated except for one position (mostly cis-2 or -3).



...(5.1)

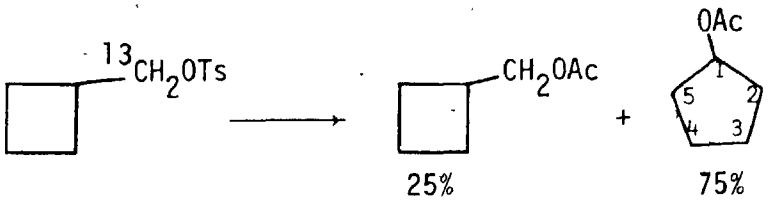
1, 10%	1, 10.2%	1, 9.8%	cis-1, 26%
1', 1.9%	1', 21.1%	cis-2 and -4, 48.8%	trans-1, 3%
cis-2 or -3, 80.6%	cis-2 and -3, 62.2%	trans-2 and -4, 5.0%	2, 10%
trans-2 or -3, 7.5%	trans-2 and -3, 6.5%	cis-3, 32.8% trans-3, 3.6%	3, 27% 4, 34%

The product analysis reveals that scrambling of methylene units in this reaction is extensive, but is not complete. Hydride shifts are known[89] not to occur and all processes take place with high stereo selectivity (no cis⇌trans). The exact mechanism of this reaction is still an area of controversy[90] but may involve rapidly equilibrating structures as those in scheme 5.1.[75]



Scheme 5.1 Possible route to rearrangement of methylene groups in the cyclopropylcarbinyl system

Studies of similar reactions of cyclobutylcarbinyl derivatives are much more rare, especially those containing suitable labels. A study of the acetolysis of ^{13}C-labelled cyclobutyl-*p*-toluenesulphonate[91] as well as product distribution is given in equation 5.2. It is clear



25% 75%

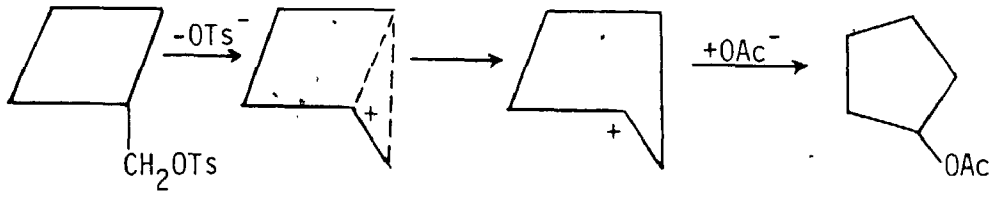
C_1, 20%

C_2+C_5, 64%

C_3+C_4, 16%

...(5.2)

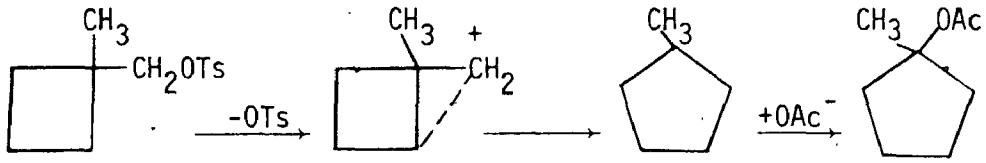
from the data that methylene scrambling has occurred to some degree as the label is located not only in the 2 and 5 positions (the position expected mechanistically by equation 5.3) but in all other positions as well. A mechanism for scrambling of the methylene units has not been presented. In the simple cyclopentyl cation of equation 5.3 no second



...(5.3)

rearrangement (in the absence of reversibility) save for a hydride shift appears possible. Such a process has not been observed in a similar system.[76b]

There is general agreement by workers in this field that the extent of ring expansion depends on the ring strain difference between n and (n+1) membered carbocycles. The relative stabilities of the carbonium ions in the order 3°>2°>1° is also a contributing factor in equation 5.3. In 1-methylcyclobutylcarbinyl tosylate, relief of ring strain together with the conversion of a primary to a tertiary carbonium ion (equation 5.4) in the intermediate provides the driving



...(5.4)

force for ring-expansion.[92] Table 5.1 lists the strain energies (relative to cyclohexane = 0) and heats of combustion of cycloalkanes n = 3, 4 and 5.[93] As can be seen by this data that there is considerably

Table 5.1 Some Properties of Cycloalkanes

Cycloalkane	Heat of Combustion ΔH (kcal mol^{-1})	ΔH/n (kcal)	Total Strain (kcal mol^{-1})
cyclopropane	499.83	166.6	27.6
cyclobutane	655.86	164.0	26.4
cyclopentane	793.52	158.7	6.5

more relief of ring strain associated with expansion of a four to a five-membered ring (19.9 kcal mol^{-1}) than expansion of a three to a four-membered ring (1.2 kcal mol^{-1}). All things being equal, one would predict that in a reaction which can proceed via a route involving ring expansion that more of the ring expanded product (n+1) will be seen when n = 4 than when n = 3. Empirically this is what is observed.

1.2 Kinetic studies of the platinacyclobutylcarbinyl ring expansion reactions

The solvolyses of three methanesulphonate platinacyclobutane complexes: $[PtCl_2(CH_2CH(CH_2OMs)CH_2)py_2]$, 6, $[PtCl_2(CH_2CH(CH_2OMs)CH_2)(bipy)]$, 14, and $[PtCl_2(CH_2C(CH_3)(CH_2OMs)CH_2)py_2]$, 9, were conducted in 60% (v/v) acetone-d_6/D_2O mixtures at 36°C in a constant temperature bath. The reactions were conveniently monitored by ^{1}H-N.M.R. on a Varian T-60 N.M.R. spectrometer by observing the rate of disappearance of the singlet due to the methyl group of the methanesulphonate on the complex and the appearance of the methyl singlet due to the methanesulphonic acid-d_1 produced. The instrument was tuned to achieve the maximum possible resolution before each spectrum. As both of the

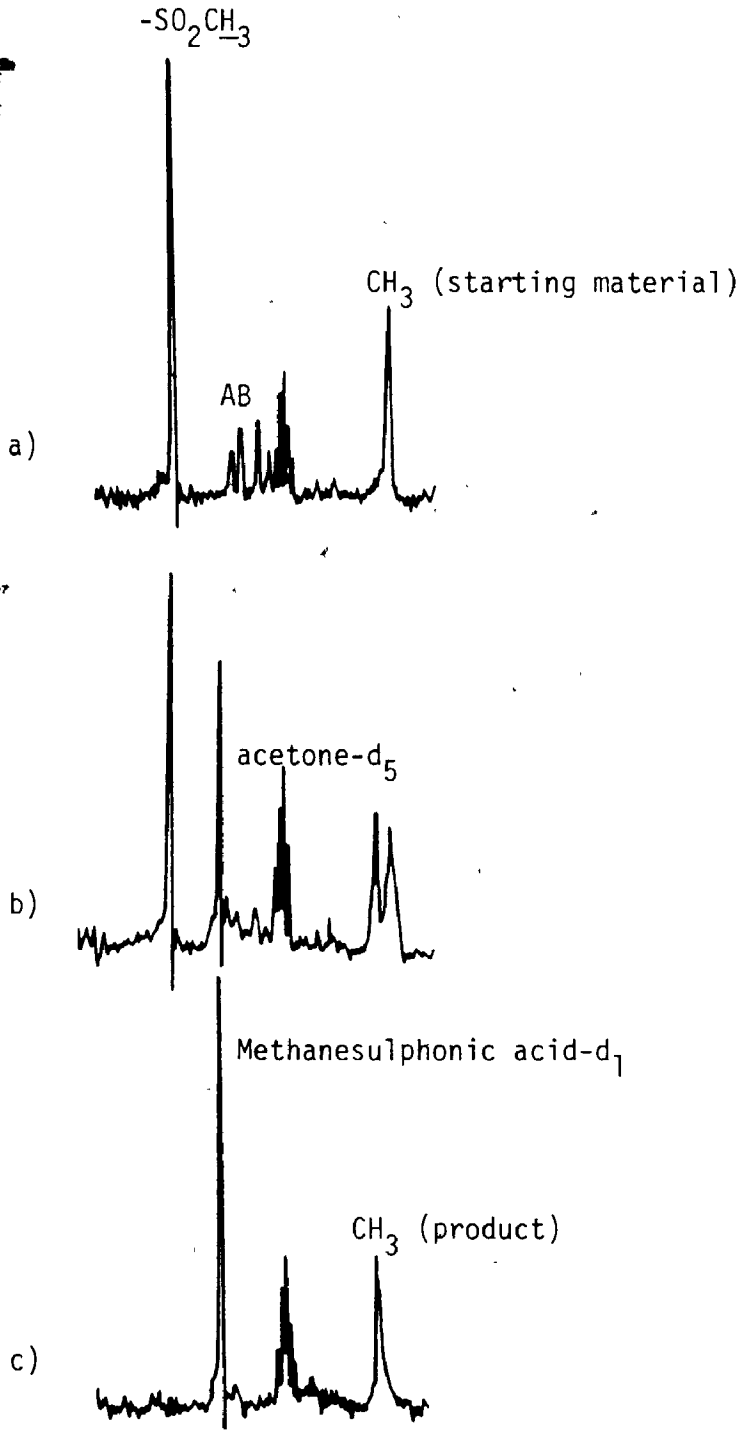


Figure 5.1 ^{1}H-N.M.R. spectrum during the solvolysis of 8, $[PtCl_2(CH_2C(CH_3)(CH_2OMs)CH_2)py_2]$ at time intervals of a) t=5 minutes b) t= 500 minutes c) t= 1680 minutes

observed signals were a sharp methyl singlet and the separation between 0.4-0.5 ppm ($\underline{CH_3}SO_3D$ resonates upfield from the $-OSO_2\underline{CH_3}$ signal for the complex) quantitative information could be obtained from the measurement of their relative peak heights. The deuterated acetone-d_5 peak was used as an internal standard.

Figure 5.1 illustrates the differences observed in the ^{1}H-N.M.R. spectrum during the solvolysis of $[\overline{PtCl_2(CH_2C(CH_3)(CH_2OMs)CH_2}py_2]$, 8, as the reaction proceeds. At t = 5 minutes (figure 5.1a) the spectrum is dominated by the methyl peak of the methanesulphonate peak of the complex 0.9 ppm downfield from the acetone-d_5 quintet and the broad upfield singlet due to the methyl peak on the β-carbon. Also present is the AB pattern of the methylene ring protons just downfield from the acetone-d_5 quintet. As the reaction proceeds the methanesulphonic acid-d_1 peak appears (just displaced from interference by the AB pattern of the starting material) 0.4 ppm downfield from the acetone-d_5 quintet. Also the methyl peak of the ring expanded product $[\overline{PtCl_2(CH_2C(CH_3)(OD)CH_2CH_2}py_2]$ becomes present ~0.15 ppm downfield from the methyl group of the starting material. This is most readily seen when the reaction approaches one half-life (figure 5.1b) and the product and starting material are of comparable concentrations in solution. When the reaction is complete the AB pattern of the ring protons is no longer present and only the methanesulphonic acid-d_1 peak and the methyl of the platinacyclopentane product remain clearly visible.

The kinetic plots obtained in this manner are shown in figures 5.2, 5.3 and 5.4 for compounds 6, 14 and 9 respectively. The data

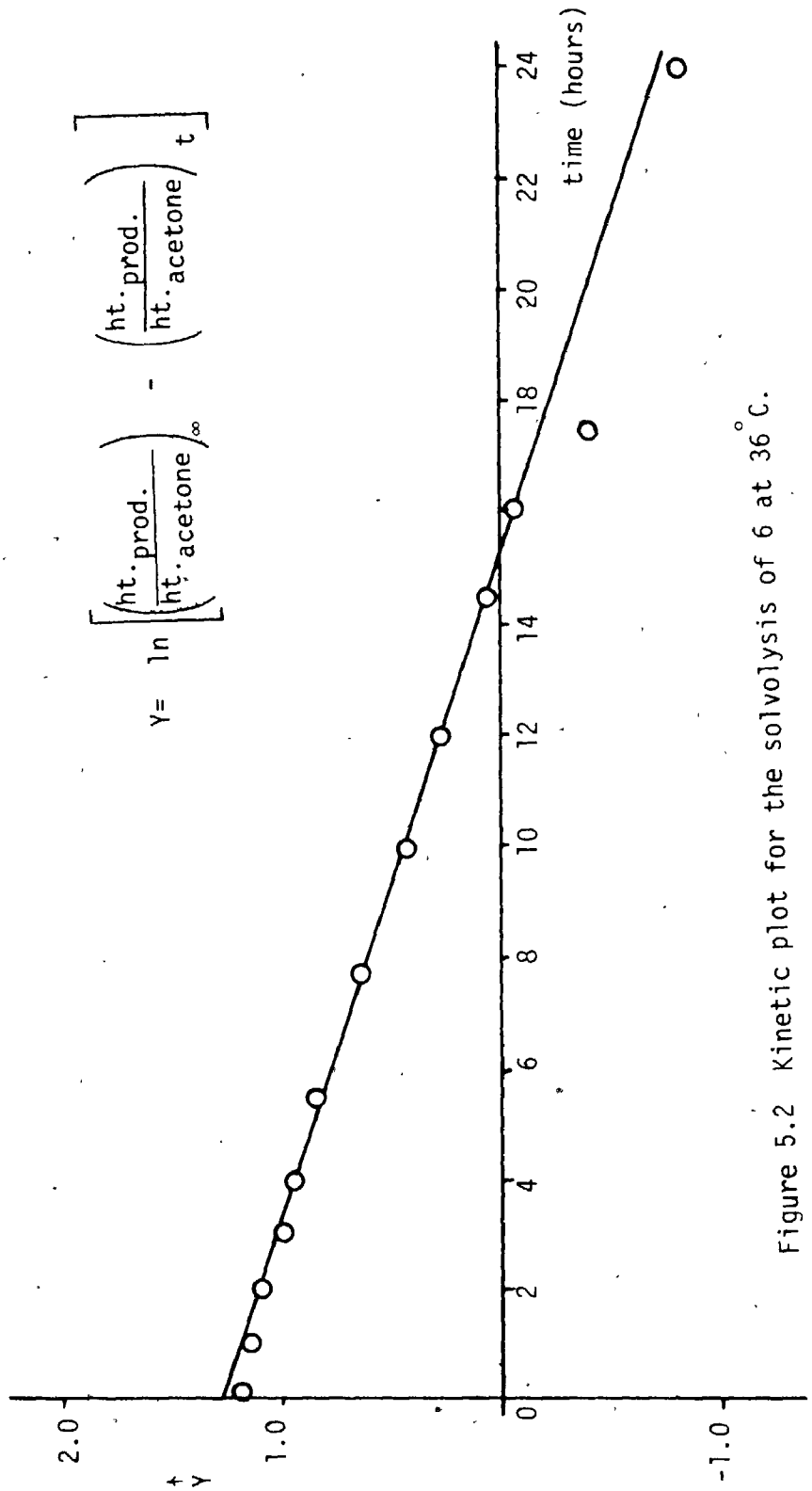


Figure 5.2 Kinetic plot for the solvolysis of 6 at 36°C.

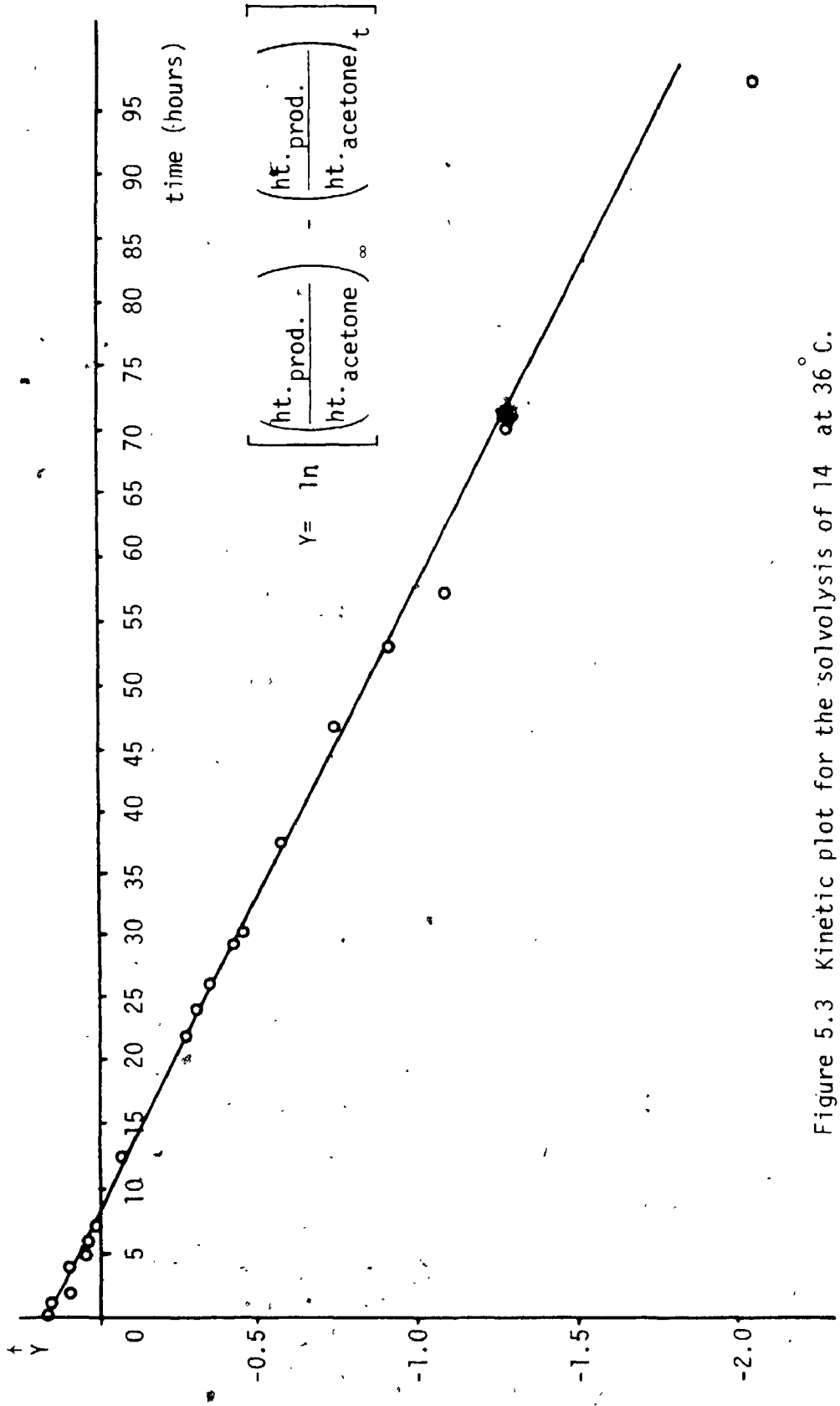


Figure 5.3 Kinetic plot for the solvolysis of 14 at 36°C.

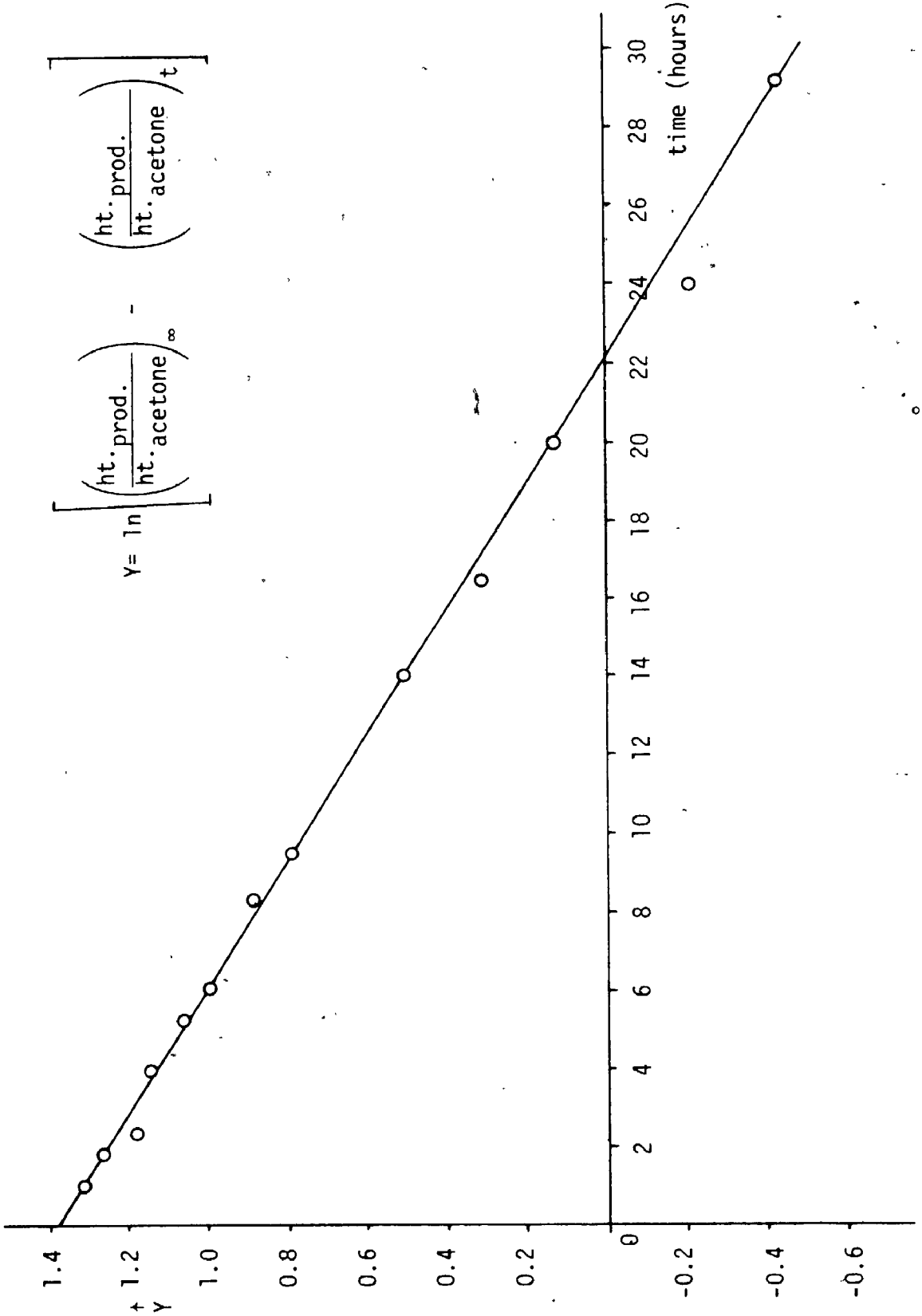


Figure 5.4 Kinetic plot for the solvolysis of 9 at 36°C.

indicates a first-order dependence for each of the three complexes. The rate constants obtained from the slopes of these graphs are presented in Table 5.2. The first observation upon comparison of

Table 5.2 Pseudo-first Order Rate Constants for the Solvolysis of $[PtCl_2(CH_2CR(CH_2OMs)CH_2)L_2]$ in 60% acetone-d_6/D_2O at 36°C

Compound	k_{obs} (s^{-1})
6; R=H; L=py	2.40×10^{-5}
14; R=H; L=1/2bipy	5.86×10^{-6}
9; R=CH_3; L=py	1.81×10^{-5}

the rates is that the chelating group 2,2'-bipyridyl has slowed down the solvolysis by a factor of four compared to the bis(pyridine) complex. This is a highly significant finding indicating that dissociation of a pyridine ligand may in fact be necessary at some step during the mechanism. In 14, bipy would not be expected to dissociate to any significant degree and hence the rate would be retarded if dissociation is important.

A second feature of this data is that the presence of the methyl group on the β-carbon of the platinacyclobutane ring (as in 9) has slowed the solvolysis reaction to a small extent. This finding is contrary to analogous organic systems in which such a substitution causes a significant rate increase (see Table 5.3). This apparent lack of a rate enhancement in solvolysis of 9 relative to 6 will be rationalized in a later section of this chapter by the existence of two competing mechanisms which produce this result. As will be seen, a

a) The ancilliary ligands of the platinum system have been removed for clarity

b) this work

c) exclusively

small rate enhancement is observed when only one of these routes is considered.

The rates in Table 5.2 are intermediate between those found for the cyclopropylcarbinyl and the cyclobutylcarbinyl systems. In the solvolysis of cycloalkylcarbinyl esters, the rate of reaction is largely influenced by the degree of strain in adjacent C-C bonds. The rate constant for hydrolysis of $\overline{CH_2CH_2}CHCH_2OMs$ in 60% aqueous diglyme at 40°C is 2.607×10^{-3} s^{-1} [53] and by extrapolation from rates at higher temperatures, that for acetolysis of cyclobutylcarbinyl tosylate at 36°C is expected to be 3×10^{-7} s^{-1}. 1-Methylcyclobutylcarbinyl brosylate solvolyzes 42 times faster than 1-methylcyclopentylcarbinyl brosylate under identical conditions for each.[95] It would appear as if the rates for solvolysis of complexes 6, 9 and 14 are actually faster than those based on strain arguments. Platinacyclobutanes are less strained than cyclobutanes and hence should have slower relative rates if mechanisms similar to those of equations 5.3 or 5.4 are evoked for each of the two systems. The results indicate the possibility of neighbouring group participation by the platinum atom and/or the possibility of different mechanisms operating in each of the two systems.

The evidence from the work of this thesis indicates that ring strain in platinacyclobutanes, as was the case in the organic systems, is a significant factor leading to ring expansion. This statement is supported by the observation that in none of the solvolyses was the unexpanded product (equation 4.4) detected. This appears to be contrary to results of Whitesides[23,96] whose evidence points to only a 5 kcal mol^{-1} difference in ring strain between his platinum(II)

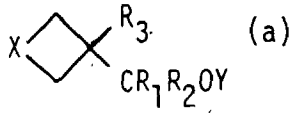
metallacyclobutane and metallacyclopentane complexes depicted in scheme 1.3 of chapter 1. Of course, the systems are not completely analogous, differing in oxidation state of the platinum, ancillary ligands, substituents on the rings, and method of ring formation. A difference of only 5 kcal mol^{-1} is not expected to be sufficient to cause preferential formation of only the ring expanded products as was observed in this study.

The products obtained from solvolysis in the platinum system are not unlike those obtained from studies of the corresponding cycloalkylcarbinyl systems as seen in Table 5.4. The only complex which does not fit the organic results well is the 1-phenyl derivative 15 which gives the ring expanded product whereas in the 1-phenylcyclobutylcarbinyl derivative studied, solvolysis is accompanied by 1,2-phenyl rearrangement rather than ring expansion to give exclusively rearranged products. Also it is seen that complex 9 does give a similar product to that of the organic system, however, with no evidence for olefin formation. Both 1-phenyl and 1-methyl cyclopropylcarbinyl derivatives, on the other hand give 1-substituted cyclobutanol as the only products.[75] Clearly, in these cases, 9 and 17, the platinum system is behaving more like the cyclopropylcarbinyl derivatives.

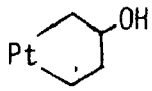
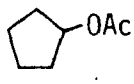
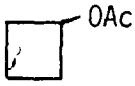
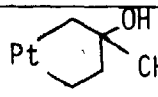
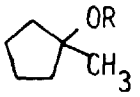
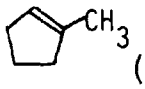
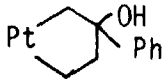
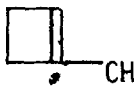
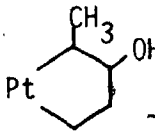
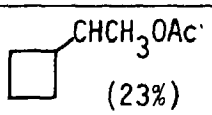
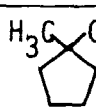
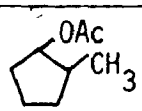
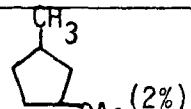
Certainly the two systems in Table 5.4 are not identical and a mechanism would then have to account for the observed differences in rates and products obtained.

The effect of added pyridine upon the solvolysis rate was investigated in order to study the implications of the rate differences

Table 5.4 Comparison of Products from Solvolysis of Complexes of the type



(a)

Complex	Observed Product(s)	ref
$R_1=R_2=R_2=H$		
X=Pt; Y=Ms; (6,14)	 (c)	b
$X=CH_2$; Y=Ts	 (99%)  (1%)	76
$R_1=R_2=H$; $R_3=CH_3$		
X=Pt; Y=Ms; (9)	 (c)	b
$X=CH_2$; Y=Bs	 (59%)  (41%)	95
$R_1=R_2=H$; $R_3=Ph$		
X=Pt; Y=Ms; (15)	 (c)	b
$X=CH_2$; Y=Ts	 (95%)  (5%)	94, 97
$R_1=R_3=H$; $R_2=CH_3$		
X=Pt; Y=PNB; (7)	 (c)	b
$X=CH_2$; Y=Ts	 (23%)  (22%)  (53%) (20% cis; 33% trans)  (2%)	98

a) The ancilliary ligands of the platinum system have been removed for clarity

b) this work

c) exclusively

observed between complexes 6 and 14. As well a quantitative result was measured for the effect of added pyridine on the rate of solvolysis of 9.

1.3 Effect of added pyridine on the observed solvolysis rates

The rate of solvolysis in 60% acetone-d_6/D_2O at 36°C was measured as described in the previous section for complex 6 at various pyridine concentrations. The results are summarized in Table 5.5 and presented graphically in figure 5.5. These results illustrate the dramatic influence added pyridine has upon the solvolysis rate, further supporting the idea that ligand dissociation might be involved at some stage in the mechanism.

Plots of $\frac{1}{k_{obs}-k_\infty}$ vs. [py]; where k_∞ is the limiting rate seen by extrapolation of the curve in figure 5.5 to infinite [py] values were constructed for various k_∞ values. The best result was obtained for $k_\infty = 5.90 \times 10^{-6}$ sec^{-1} though small changes in the k_∞ value had little effect on the slope obtained. The only exception to this was the final point, at highest [py] ([py] = 3.23×10^{-1} M), which was influenced the most by this k_∞ value as expected based upon the value $(k_{obs}-k_\infty)$ for this point being very small and hence the most sensitive. Table 5.6 summarizes the $\frac{1}{k_{obs}-k_\infty}$ value at various pyridine concentrations, the results being shown graphically in figure 5.6 for $k_\infty = 5.90 \times 10^{-6}$ sec^{-1}. This data leads to the two-term rate expression for the first-order rate constants, after simplification of $k_{obs} \approx 5.90 \times 10^{-6} + \frac{1.81 \times 10^{-5}}{1+275\ [py]}$. An interesting result of the influence of added pyridine in this study is that the k_∞ value is identical, within

Table 5.5 Solvolysis Rates of $[\overline{PtCl_2(CH_2CH(CH_2OMs)CH_2)}py_2]$, 6, ($7.0 \times 10^{-2}$ M) at Various Pyridine Concentrations

[py] (M)	k_{obs} (s^{-1})
0	2.40×10^{-5}
1.29×10^{-2}	9.73×10^{-6}
2.58×10^{-2}	7.99×10^{-6}
6.45×10^{-2}	6.85×10^{-6}
3.23×10^{-1}	6.10×10^{-6}

Table 5.6 $(k_{obs} - k_{\infty})^{-1}$ Values at Various Pyridine Concentrations Where $k_{\infty} = 5.90 \times 10^{-6} s^{-1}$

[py]	$(k_{obs} - 5.90 \times 10^{-6})^{-1}$
0	5.5×10^4 s
1.29×10^{-2}	26×10^4 s
2.58×10^{-2}	48×10^4 s
6.45×10^{-2}	105×10^4 s
3.23×10^{-1}	500×10^4 s

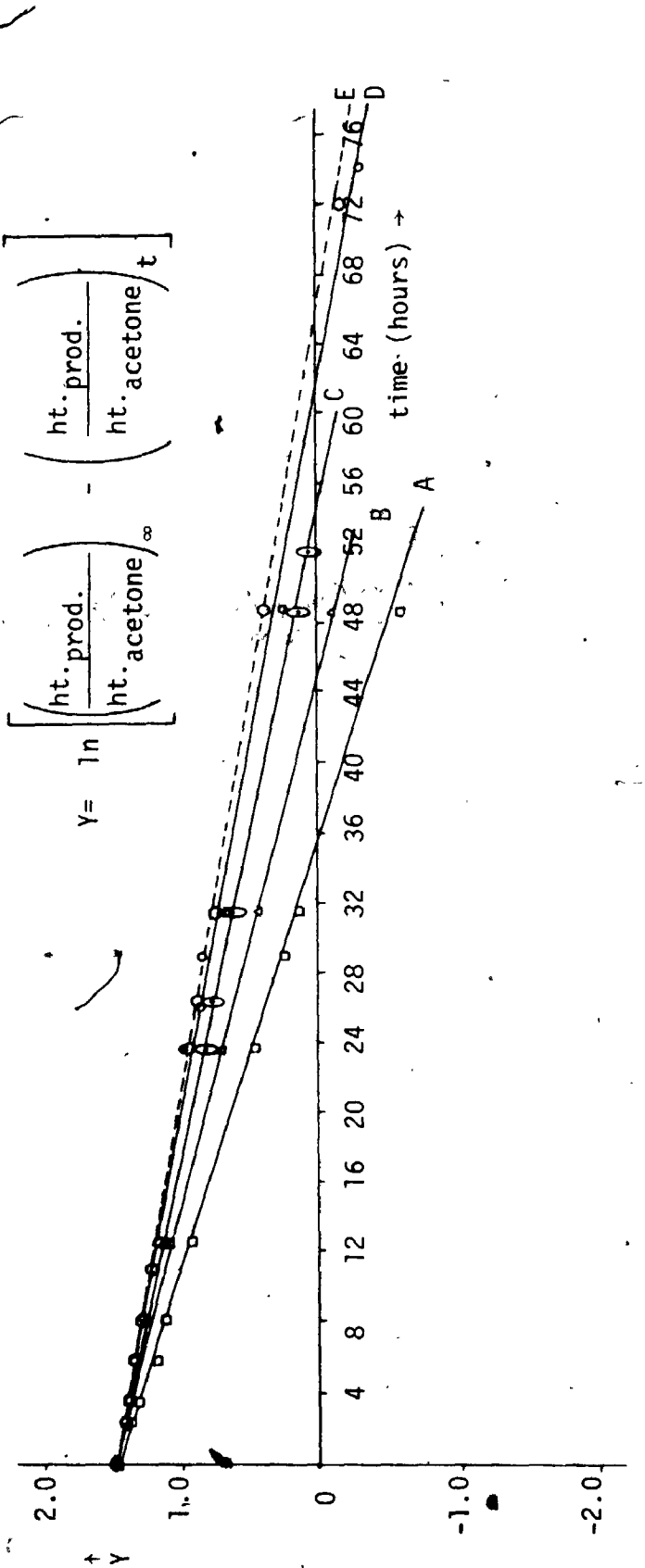


Figure 5.5 Kinetic plots for the solvolysis of $[PtCl_2(CH_2CH(CH_2OMs)CH_2)py_2]$, 6, at various concentrations of added pyridine A= 0 M, B= 1.29×10^{-2} M, C= 2.58×10^{-2} M, D= 6.45×10^{-2} M and E= 3.23×10^{-1} M.

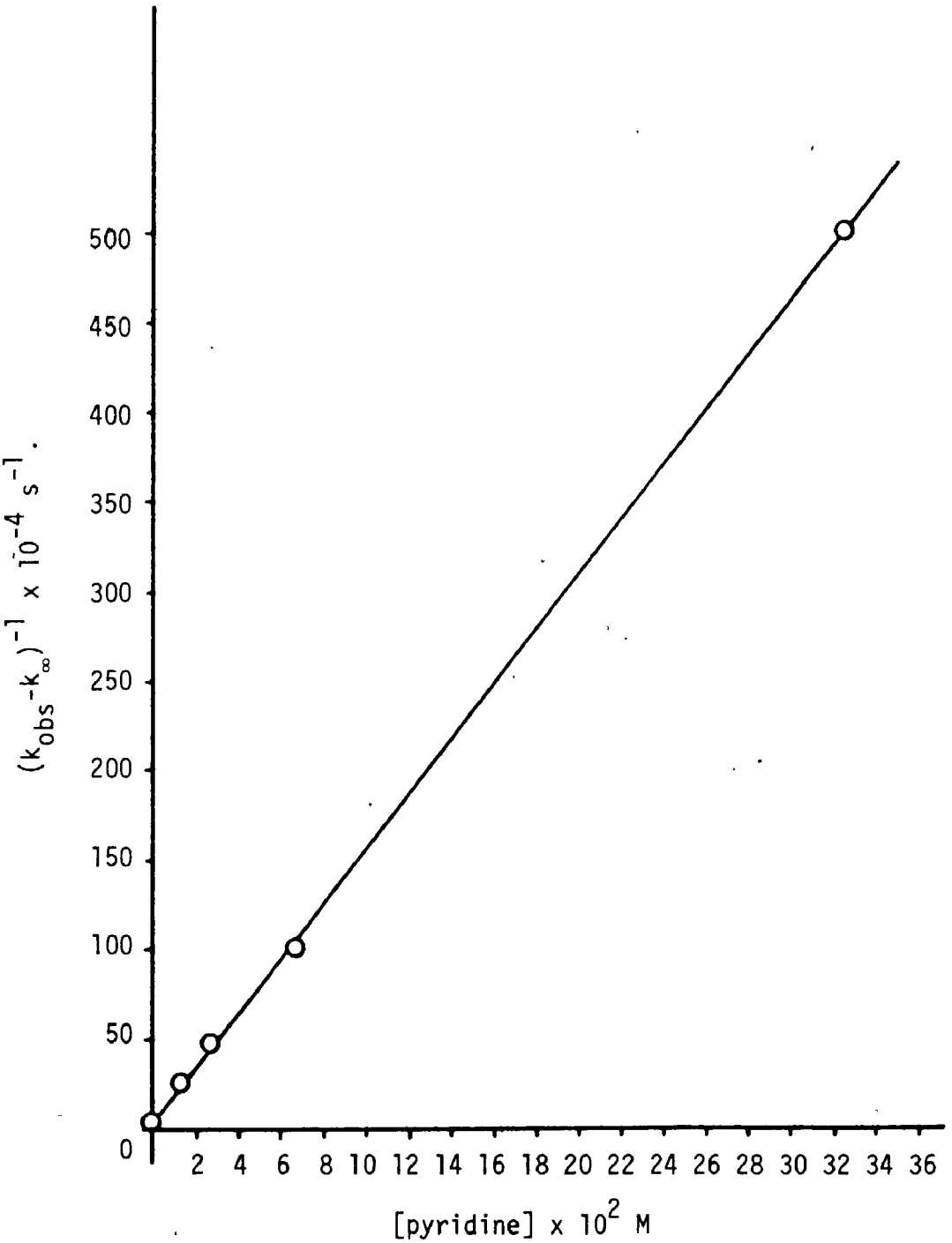


Figure 5.6 Graphical representation of the data from Table 5.6, $k_\infty = 5.90 \times 10^{-6}\ s^{-1}$.

experimental error, to the rate observed for the solvolysis of the 2,2'-bipyridyl complex 14 of 5.86 x 10^{-6} sec^{-1} (Table 5.2). Although this similarity could be merely fortuitous it is more likely that these results do indicate a similar mechanism for the solvolysis reaction of 6, at high pyridine concentrations and that of 14.

A similar study to the one above was undertaken on the complex $[PtCl_2(CH_2C(CH_3)(CH_2OMs)CH_2)py_2]$, 9. A detailed quantitative result similar to that done for 6 above, was not undertaken owing to the observation that at an added pyridine concentration of 1.032 M (over three times the concentration required to quench the solvolysis of 6 to 97% of the limiting value) the solvolysis rate of 9 was still 1.66 x 10^{-5} sec^{-1}. Thus, pyridine had little effect on this solvolysis rate. Most certainly a different mechanism, one not involving significant ligand dissociation is being observed in the solvolysis of 9.

In order to further elucidate the mechanism, ^{13}C and ^{2}H labelling studies were undertaken.

2. Labelling Studies

2.1 ^{13}C Labelling Studies

Labelling experiments were carried out using the complexes: $[PtCl_2(CH_2CH(*CH_2OMs)CH_2)L_2]$, L = py:(6-$^{13}C^{1}$), bipy:(14-$^{13}C^{1}$) where *C denotes a carbon enriched to 7.5% ^{13}C. These complexes were prepared from ^{13}C cyclopropylcarbinyl methanesulphonate, as described in chapter 2 for the unlabelled complexes. The cyclopropane derivative was prepared by literature procedures and enriched to 7.5% ^{13}C as determined by ^{1}H-N.M.R. The ligand showed no evidence of scrambling of

the label prior to its use and the platinacyclobutanes formed from it showed enrichment only on the carbinyl carbon as expected in the absence of rearrangement processes.

The solvolyses for these complexes were run at 36°C in 60% (v/v) acetone/water mixtures as previously described, for greater than three half-lives. The ^{13}C-N.M.R. spectra of the platinacyclopentane products formed from these reactions are shown in figures 5.7 and 5.8 for the labelled complexes 16-*C and 17-*C respectively. The method of assignments of chemical shifts for each of the carbon atoms was described in chapter 4. The carbon ring positions have been numbered as described in this earlier discussion. The numbers above the signals in figures 5.7 and 5.8 correspond to these ring assignments.

Figure 5.7 indicates that for complex 16-*C the ^{13}C label is located primarily at the C-1 position with a lesser, though significant amount of enrichment occurring at the C-3 position. The C-2 and C-4 carbons of the ring show no evidence for enrichment at these positions.

Figure 5.8 shows that the extent of enrichment at the ring positions in complex 17-*C is a reversal of that seen in figure 5.7 for the bis(pyridine) analoque (16-*C). Figure 5.8 shows primary label incorporation at the C-3 position with a lesser amount of enrichment at the C-1 position. As in the bis(pyridine) case the C-2 and C-4 position in the platinacyclopentane ring show no detectable amounts of enrichment.

Clearly the two results show selective label incorporation has occurred in the same two ring positions, C-1 and C-3, yet the relative amounts of label at each position are reversed in the two cases. This

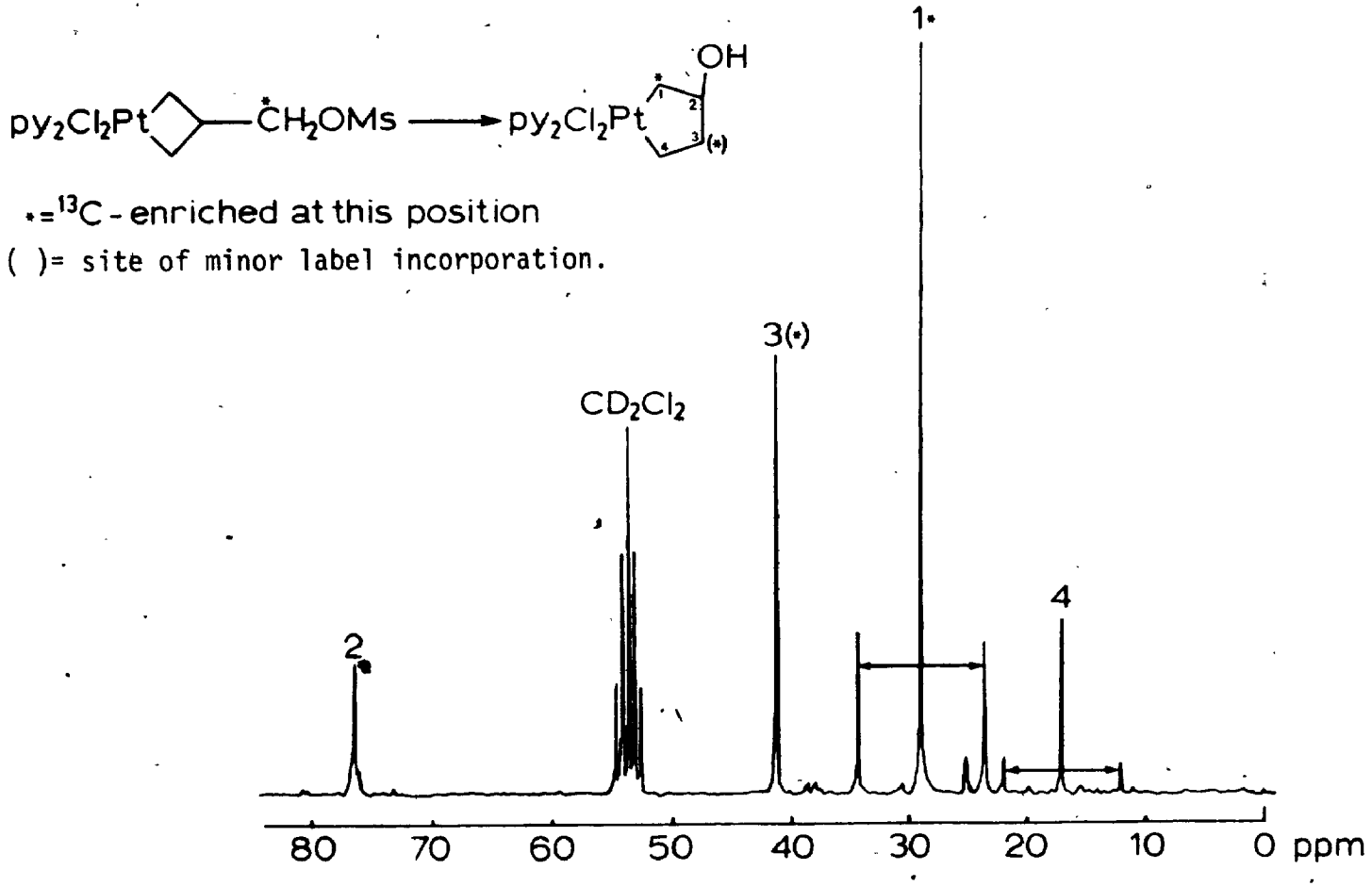
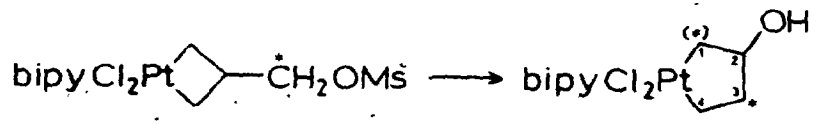


Figure 5.7 $^{13}C\{^{1}H\}$-N.M.R. of the product from the solvolysis of 6-$^{13}C^{1}$: 16-*C.



• = ^{13}C-enriched at this position
( ) = site of minor incorporation

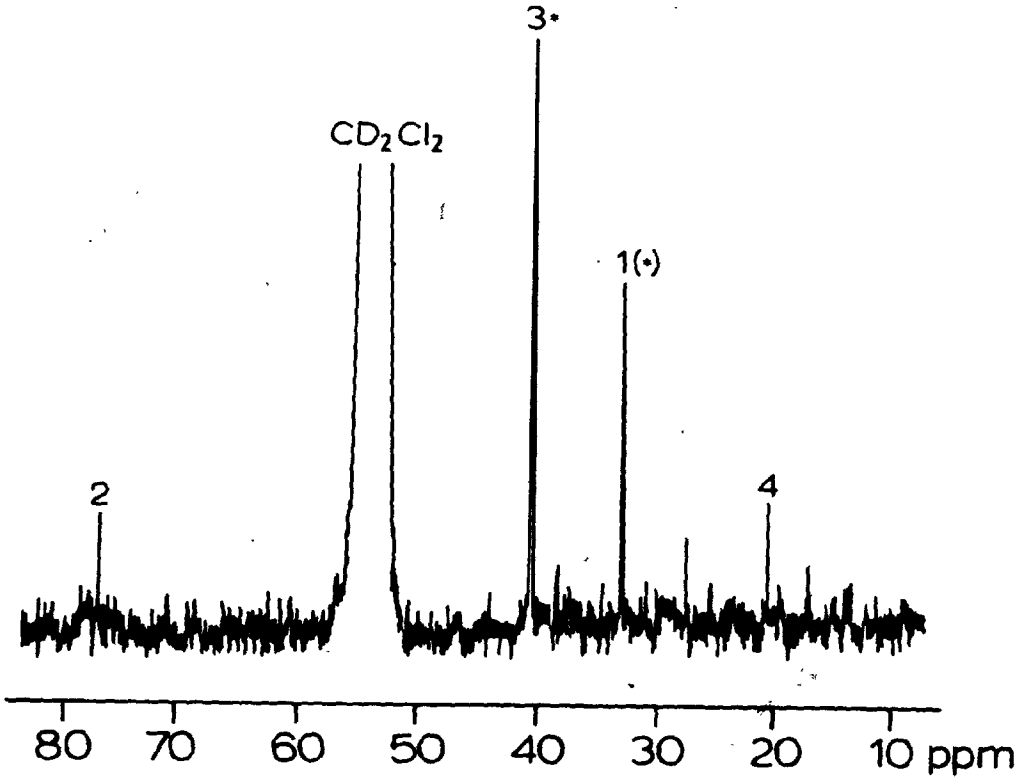


Figure 5.8 $^{13}C\{^1H\}$-N.M.R. of the product from the solvolysis of 14-^{13}C : 17-*C.

is a significant finding and indicates the possible presence of two competing pathways.

Carbon-13 N.M.R. spectroscopy as performed in this section is not a quantitative method. The results however are certainly different enough that the conclusions drawn from them are justified. In order to quantify these results, as well as to further investigate the mechanism, deuterium labelling was performed.

2.2 Deuterium Labelling Studies

The results of the ^{13}C labelling studies described above prompted further investigation of the mechanism with another label. The ease of preparation of the α,α-dideuterio-cyclopropylcarbinyl ligands, from the ^{1}H labelled alcohols, prepared by reduction of the corresponding acid with $LiAlD_4$, (equation 2.2; R = D), made this method seem very promising.

This deuterium labelling will give evidence to two important aspects of the mechanism. A check of hydride migrations is possible since in the $^{13}C\{^{1}H\}$ N.M.R. spectrum a CHD group will appear as a triplet. As ^{2}H-N.M.R. is a quantitative technique, a measure of the deuterium incorporation at each of the ring sites is possible. Together with the ^{13}C-N.M.R. spectral results the exact ring assignment could be made. These assignments were supported by both homonuclear decoupling studies on the ^{2}H-labelled and unlabelled complexes as well as previous assignments (Table 4.2).

Three deuterium labelled platinacyclobutane complexes were prepared: $[\overline{PtCl_2(CH_2CH(CD_2OMs)CH_2}py_2]$, 6-$D_2$, $[\overline{PtCl_2(CH_2CH(CD_2OMs)CH_2}(bipy)]$, 14-$D_2$, and $[\overline{PtCl_2(CH_2C(CH_3)(CD_2OMs)CH_2}py_2]$, 9-$D_2$. These

complexes were solvolyzed under the same conditions as described in chapter 4. In the cases of both bis(pyridine) complexes 6-D_2 and 9-D_2 simultaneous reactions were run in the absence and presence of large amounts of added pyridine in an effort to decipher the kinetic and ^{13}C labelling results previously described. The results for each of these complexes will be discussed.

Figure 5.9a,b shows the ^{13}C-N.M.R. spectra of the platinacyclopentane products from the solvolysis of $[PtCl_2(CH_2CH(CD_2OMs)CH_2)py_2]$, 6-$D_2$, in the absence of added pyridine and in the presence of a .32 M concentration of pyridine respectively, as compared to the ^{13}C-N.M.R. spectrum of the fully protiated product. The most dramatic effect seen upon deuteration for the reaction in the absence of pyridine (figure 5.9a) is that the signal for C-1 at δ29.0 ppm is reduced in intensity to such an extent that it is just visible above the baseline (see arrow). This is consistent with the majority of the label being incorporated at the C-1 carbon as a methylene CD_2 unit, with no evidence for hydride migrations (deuterium scrambling). In the presence of added pyridine (figure 5.9b) the peak at 29.0 ppm due to C-1 reappears, though not to its full extent, whereas the peak at 41.2 ppm has now been greatly reduced. These results indicate the majority of the label has been incorporated as a methylene-CD_2 unit at C-3 with some still at C-1. Although no quantitative information could be obtained from the ^{13}C-N.M.R. spectra described in section 2.1 an estimate of the ratios of the two products in figure 5.9b is possible in so far as the central peak for C-4 appears as two resonances (in an approximate ratio of 3:1) separated by 1.5 Hz. The upfield resonance corresponds to the C-4 carbon of the isomer in highest abundance, the

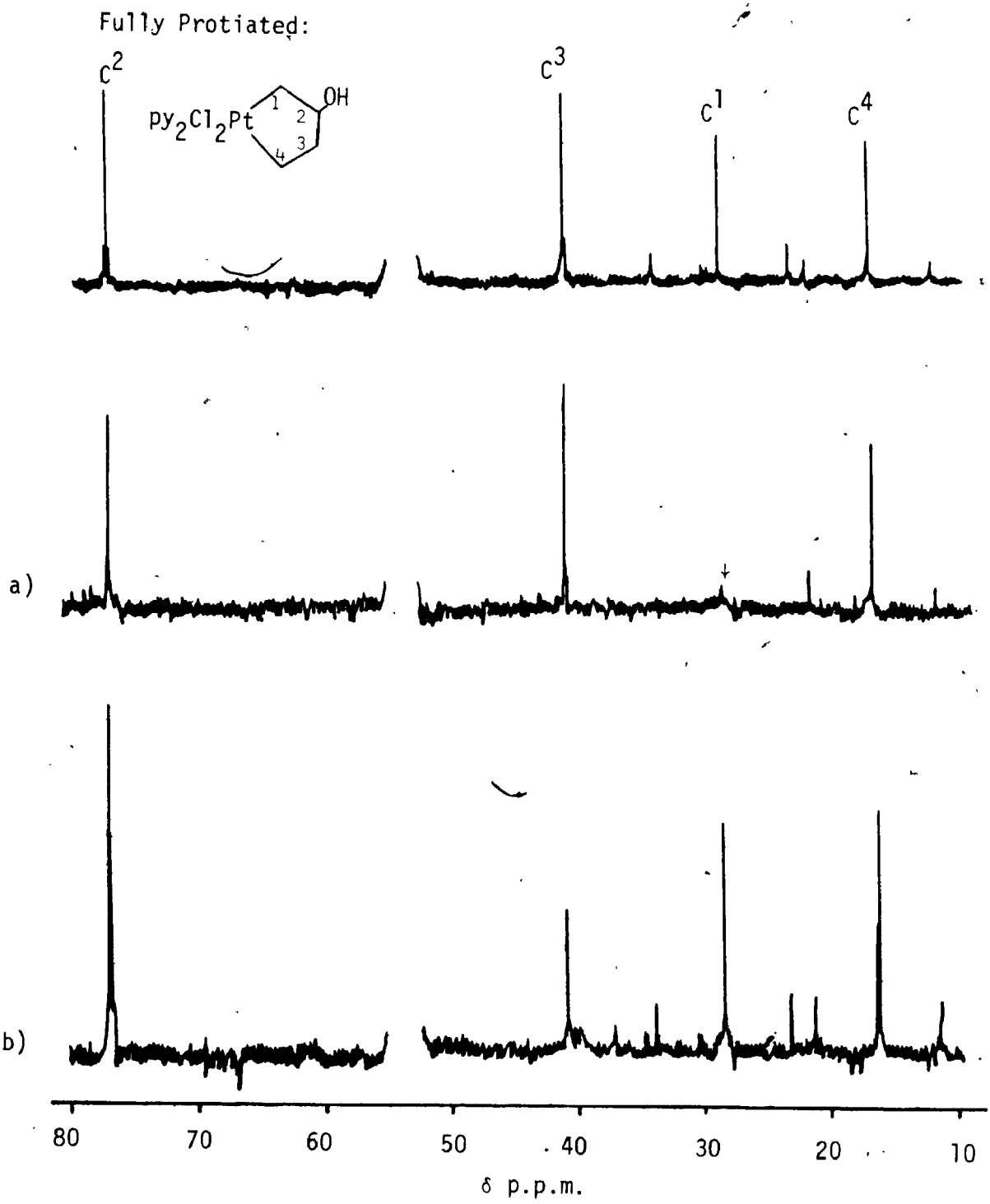


Figure 5.9 $^{13}C\{^{1}H\}$-N.M.R. spectrum of the solvolysis product(s) from $[PtCl_2(CH_2CH(CD_2OMs)CH_2)py_2]$,(6-$D_2$):16-$D_2$, a) in the absence of added pyridine. b) in the presence of added pyridine ([0.32M]), relative to fully protiated spectrum.

one with the D_2 on C-3. The resonance just downfield from that corresponds to the C-4 of the less abundant isomer, that with the D_2 label on C-1. The deuterium isotope effect on ^{13}C-chemical shifts that is observed here is well known[95] but had not been reported before in platinacycles.

The $^2H\{^1H\}$ N.M.R. spectra of the products obtained from solvolysis of 6-D_2 in the absence and presence of pyridine were run in CH_2Cl_2 with a trace of $CDCl_3$ as a reference. The results are shown in figure 10a and 10b respectively. The peak marked with an asterisk is due to OD in the residual water. The two broad upfield peaks (without platinum satellites) in 10a correspond to the two inequivalent deuterium methylene atoms on C-3 (labelled as 3-D_2). The two large downfield peaks correspond to the two inequivalent deuterium atoms on the C-1 position (labelled as 1-D_2). These both have large observable platinum-deuterium couplings, the magnitude of which is 13.2 Hz for the downfield resonance and about the same for the other, though one satellite is masked by the water impurity. In figure 10b the peak intensities for the α and β deuteriums have now been reversed. Integration of the signals yields the results shown in Table 5.7.

Solvolysis of $[\overline{PtCl_2(CH_2CH(CD_2OMs)CH_2}](bipy)]$, 14-$D_2$, was performed as previously described. The ^{13}C N.M.R. of the product was attempted but, owing to poor solubility, the spectral quality was poor and hence it is not illustrated here. It does however support the $^2H\{^1H\}$ N.M.R. data. The $^2H\{^1H\}$ N.M.R. spectrum obtained, is shown in figure 5.11 and indicates very similar results to those obtained in the solvolysis of 6 in the presence of added pyridine. That is,

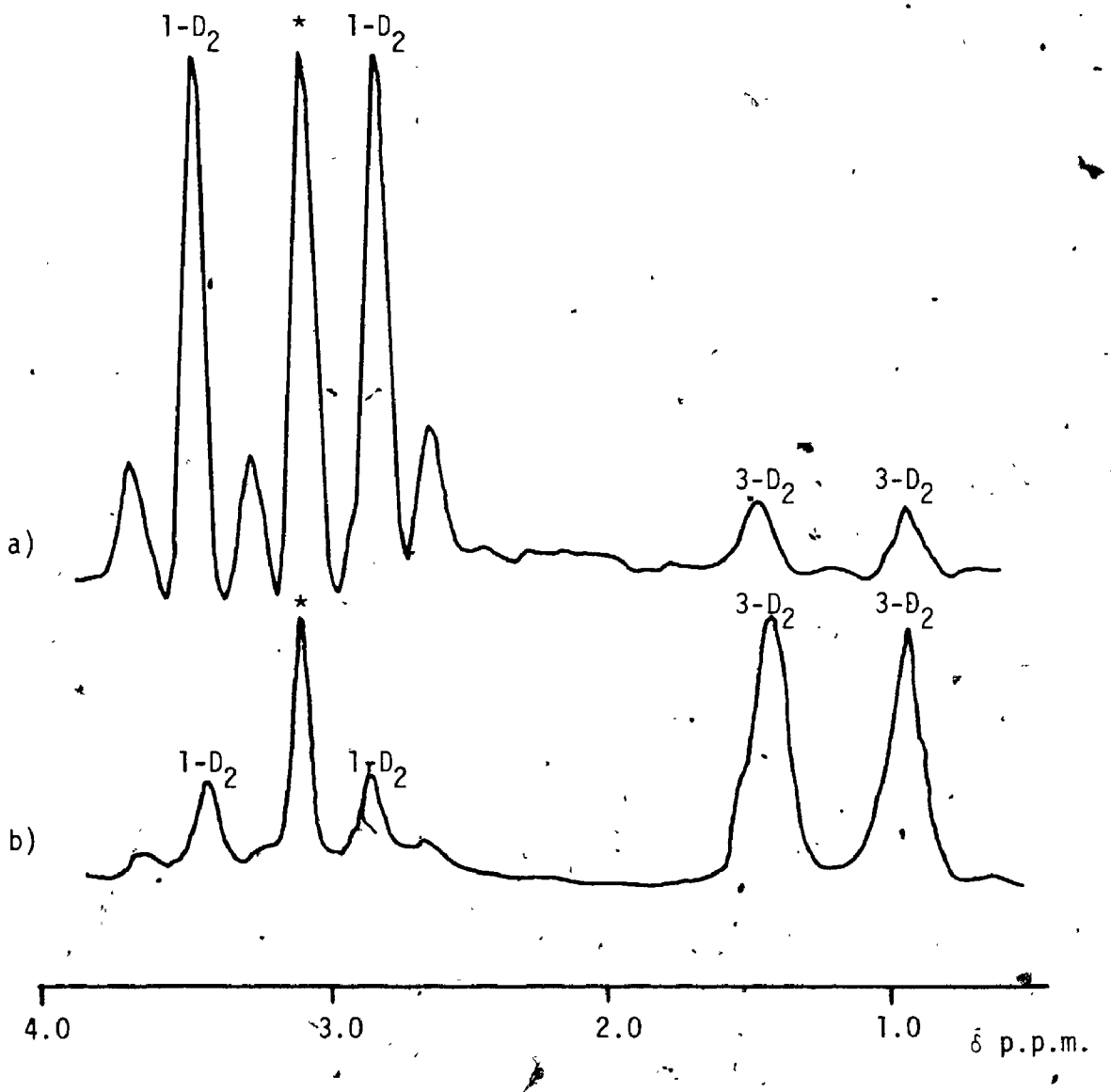


Figure 5.10 $^{2}H\{^{1}H\}$-N.M.R. spectrum of the product(s) from the solvolysis of 6-D_2, a) in the absence of added pyridine and b) in the presence of added pyridine ([0.32 M]).

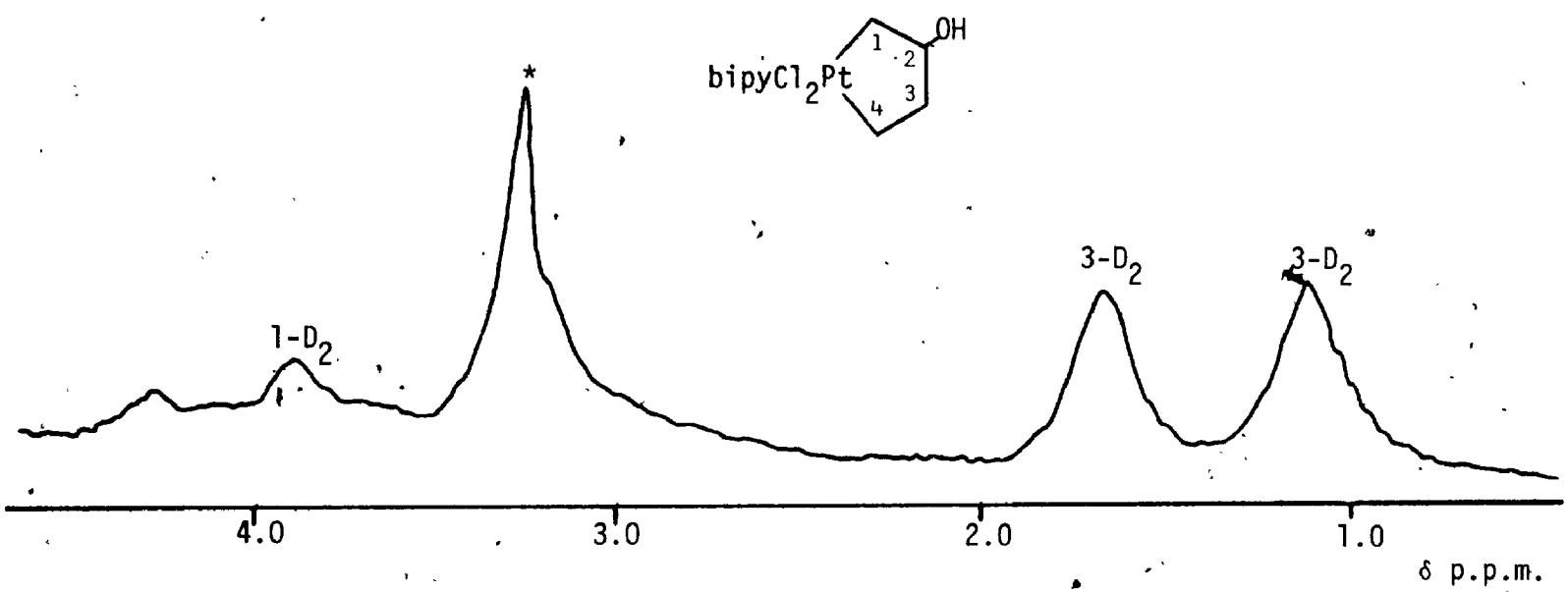


Figure 5.11 $^{2}H\{^{1}H\}$-N.M.R. spectrum of the solvolysis product(s) from 14-D_2: $[PtCl_2(CH_2CH(CD_2OMs)CH_2)(bipy)]$

predominant formation of the 3-D_2 isomer and to a lesser extent the 1-D_2 isomer is established. The results are summarized in Table 5.7.

The solvolysis studies of the deuterium labelled complex, $[PtCl_2(CH_2C(CH_3)(CD_2OMs)CH_2)py_2]$, 9-$D_2$, showed much less effect of added pyridine on the product ratios obtained. Based on the previous kinetic results, which showed little effect of added pyridine on the solvolysis rate, this was to be expected. Figure 5.12a and 5.12b show the ^{13}C N.M.R. spectra of the products from solvolysis of 9-D_2 in the absence of added pyridine and the presence of a 0.78 M concentration of pyridine, respectively, compared with the ^{13}C-N.M.R. of the fully protiated product. In both of the deuterium labelled cases the most striking difference seen from the protiated result is the great reduction in intensity for the C-3 signal at 46.9 ppm with little effect upon the rest of the spectrum. This is consistent with predominent formation of the isomer with the methylene-d_2 unit on the C-3 position (3-D_2) with very little of the 1-D_2 isomer. The $^2H\{^1H\}$ N.M.R. spectra confirm these results as seen in figure 5.13. The chemical shifts and absence of observable platinum-deuterium coupling confirm the assignment of the two major peaks at δ0.44 ppm and δ1.91 ppm as being due to the two inequivalent deuterium atoms on the β-position (3-D_2). These assignments are also consistent with those obtained from the ^1H-N.M.R. assignments determined previously. The quantitative results from the $^2H\{^1H\}$ N.M.R. spectra are shown in Table 5.7.

Upon investigation of Table 5.7 one can make certain vital conclusions. Firstly, the product ratio for the solvolysis of 6-D_2 in the absence of pyridine is much different than that for the reaction

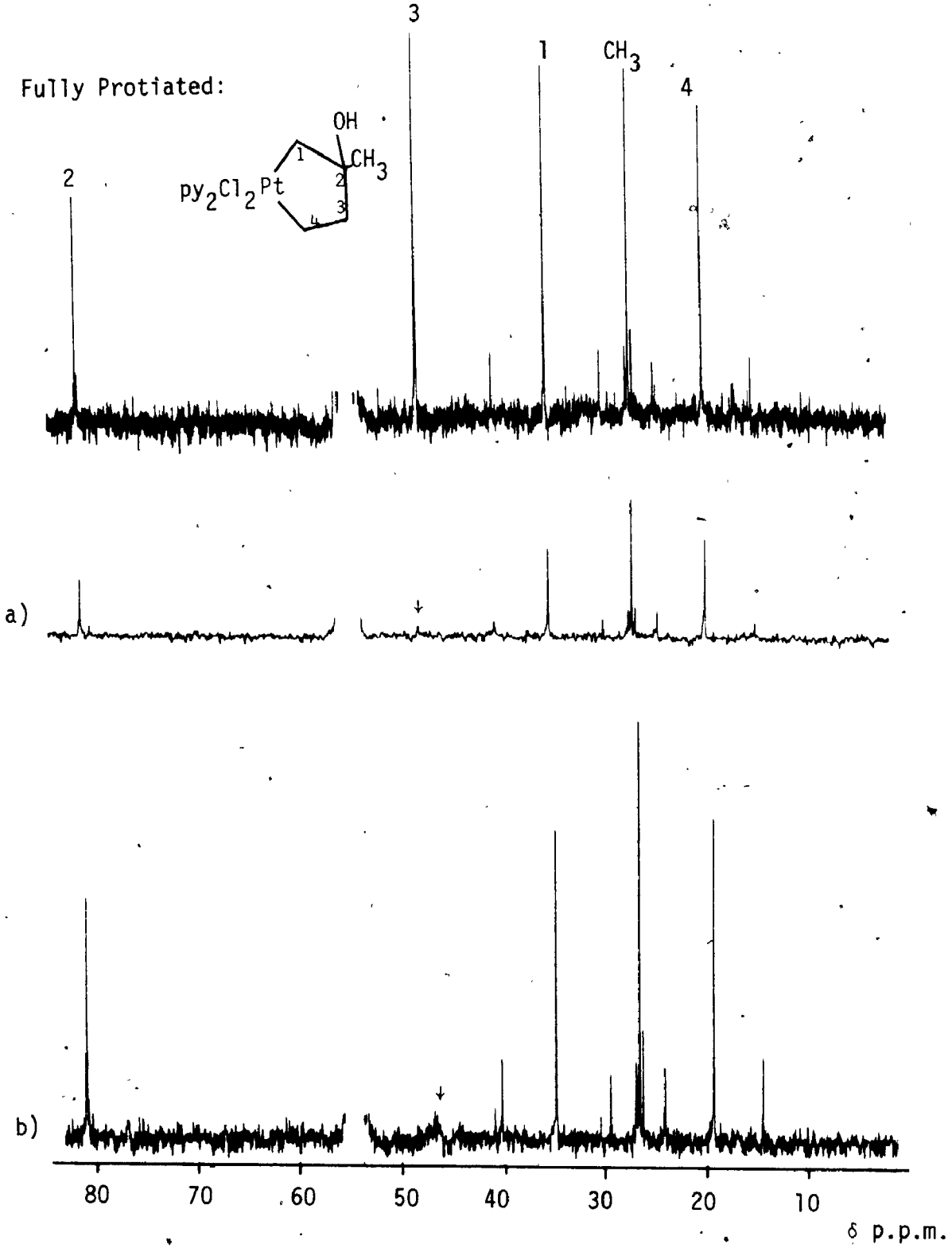


Figure 5.12 $^{13}C\{^{1}H\}$-N.M.R. spectrum of the solvolysis product(s) from $[PtCl_2(CH_2C(CH_3)(CD_2OMs)CH_2)py_2]$, 9-$D_2$, a) in the absence of added pyridine. b) in the presence of added pyridine ([0.78 M]), relative to the fully protiated sample.

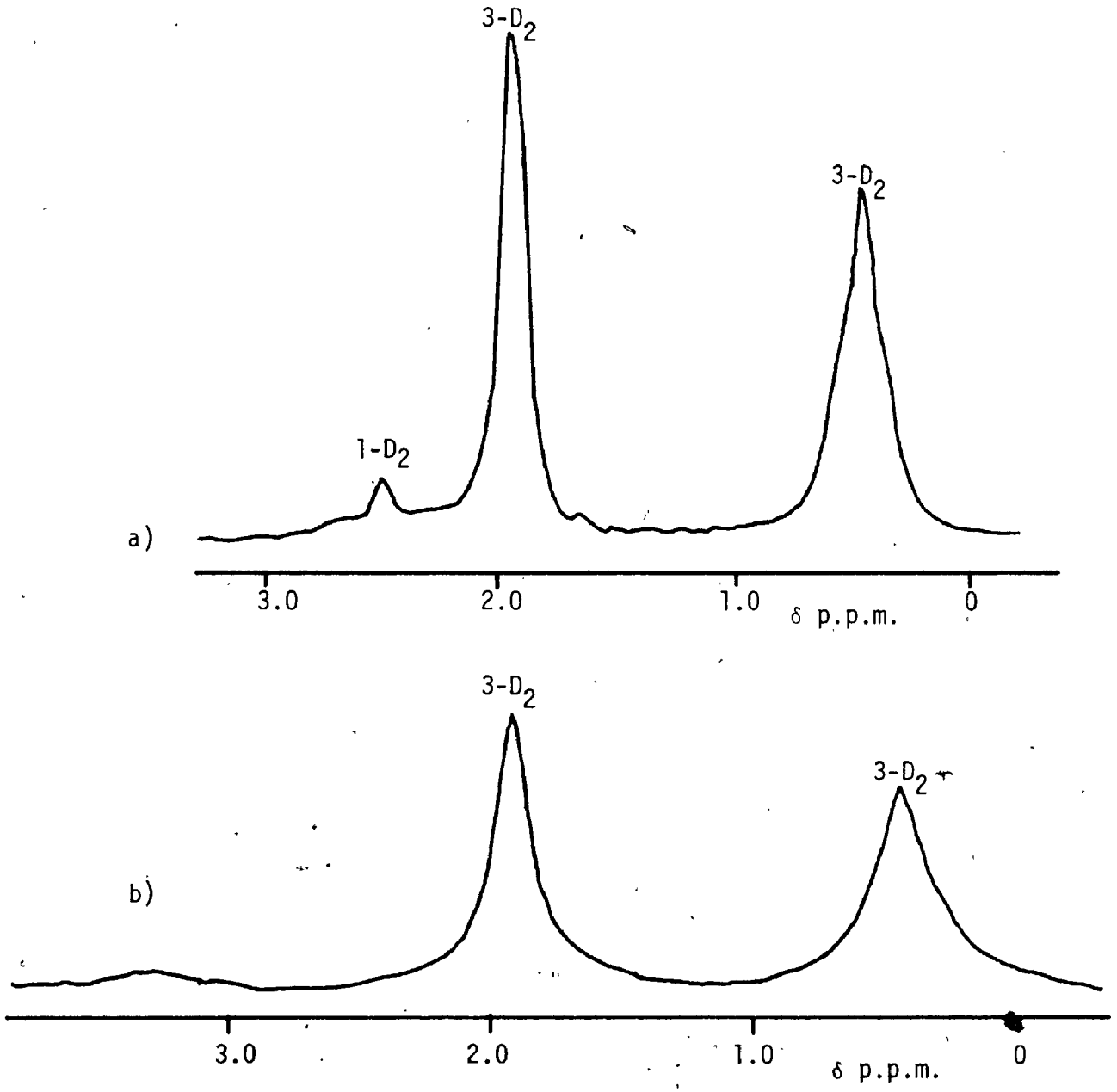


Figure 5.13 $^{2}H\{^{1}H\}$-N.M.R. spectrum of the product(s) from the solvolysis of 9-D_2 a) in the absence of added pyridine and b) in the presence of added pyridine ([0.78 M]).

Table 5.7 Product Distributions From Solvolyses of Deuterium Labelled Platinacyclopentanes

Complex	[py], M	% Product $1\text{-}D_2$	% Product $3\text{-}D_2$
$6\text{-}D_2$	0	86	14
$6\text{-}D_2$	0.32	32	68
$14\text{-}D_2$	0	27	73
$9\text{-}D_2$	0	10	90
$9\text{-}D_2$	0.78	<5	>95

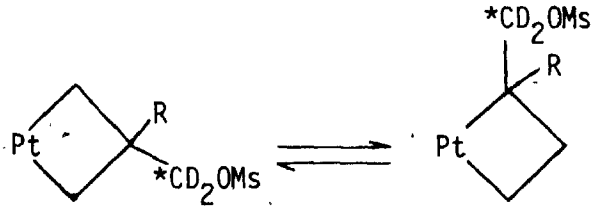
of the same complex in the presence of pyridine. Furthermore, the latter of these behaves almost identically to that for the bipy complex, 14-D_2. These results strongly support both the kinetic results and the ^{13}C-N.M.R. labelling results. Also the same can be said for complex 9-D_2 which shows a different product ratio from either 6-D_2 or 14-D_2, as well as showing little influence of isomer ratio or added pyridine.

With these results so far discussed in this chapter, a reaction scheme can now be presented.

3. Mechanisms of the Solvolyses Reactions

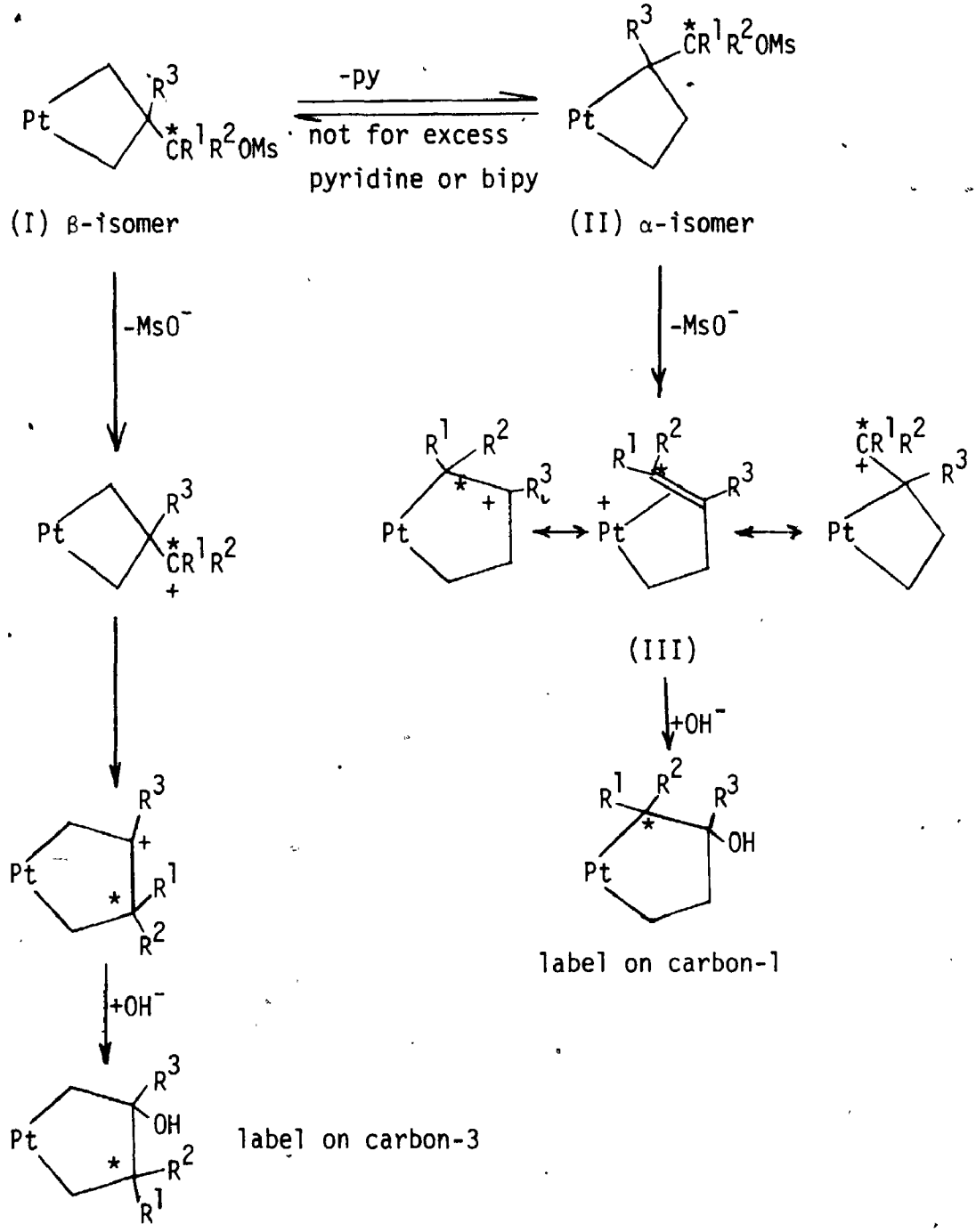
The results of the solvolysis studies, thus far discussed, strongly support the mechanism shown in scheme 5.2, in which there are two separate pathways; one which gives the labels on the 1-C position and the other on the 3-C ring position.

For 6, 6-^{13}C and 6-D_2 it is likely that the major reaction pathway involves initial skeletal isomerisation from the β-isomer(I) to the α-isomer(II) followed by rapid solvolysis of II to give the label

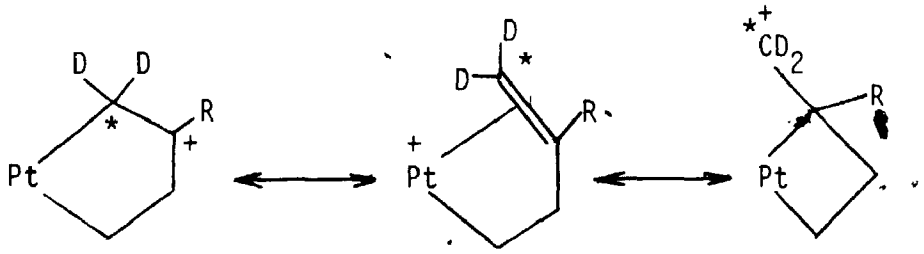


(I) (II)

in the 1-C position. This solvolysis is strongly metal-assisted since the intermediate carbonium ion is stabilized by the metal-alkene resonance form, III. The platinacyclobutane resonance form of III is expected to be destabilised relative to the other two owing to it



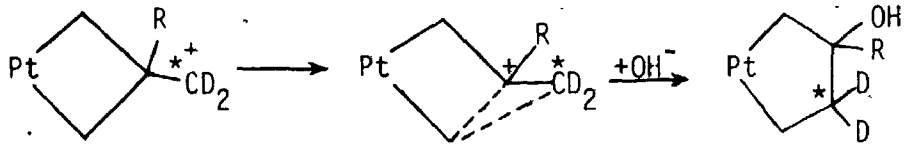
Scheme 5.2 Mechanism for the rearrangement.



(III)

being more strained as well as a primary carbonium ion (see section 1.1 of this chapter).

The skeletal isomerisation, I→II is expected to be retarded by free pyridine[17] and cannot occur[29] in 14,14-^{13}C or 14-D_2 when the ligand is 2,2'-bipyridyl. Hence, under these conditions the reaction occurs by direct solvolysis of the β-isomer, (I), giving largely the label on the 3 position of the ring. The mechanism of this solvolysis is expected to be very similar to that seen in the organic systems (equations 5.3 and 5.4). This is illustrated by equation 5.5 (R = H). However, the actual product formed under these conditions is still about



...(5.5)

30% of the 1-C isomer. Either there is a route to skeletal isomerisation which can occur without ligand dissociation or else solvolysis of isomer I can give 30% of the 1-C isomer.

This aspect of the mechanism, that of formation of the α-D_2 isomer directly from the β-isomer is not easy to explain. A mechanism, for skeletal isomerisation, involving formation of a platinum-carbene-

olefin complex would require ligand dissociation. In the absence of ligand dissociation a "20-electron" intermediate would be involved; such complexes are unknown in platinum chemistry. A more likely route would involve a concerted process in which C-C and Pt-C bond cleavage and formation occur in a concerted manner. Two such mechanisms can be envisioned. The first, depicted in Figure 5.14 involves β→α isomerisation, similar to that seen in other platinacyclobutanes,[17] followed by formation of a metal-alkene resonance structure (see III in scheme 5.2). Another route, also involving a concerted process is shown in

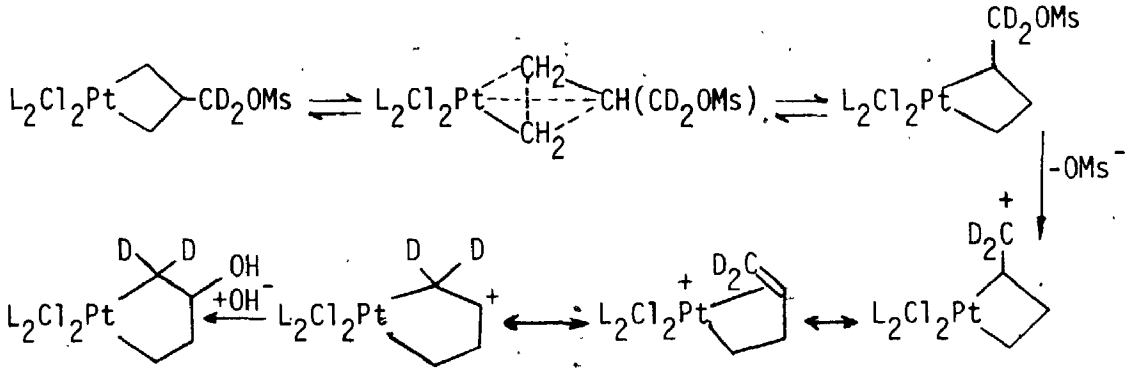


Figure 5.14 A proposed concerted route to the platinacyclopentane product with the labels ending up on carbon 1, in the absence of ligand dissociation

figure 5.15. This proposed mechanism does not involve an isomerisation step prior to ring-expansion.

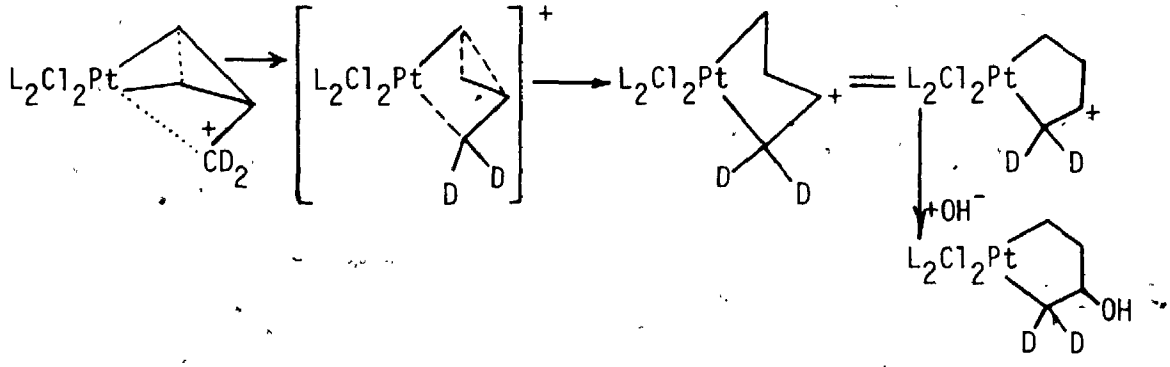


Figure 5.15 Another proposed concerted route

Now when I in scheme 5.2 is the methyl-substituted species, 9, 9-^{13}C or 9-D_2, steric hindrance is expected to hinder the isomerisation I to II. It is probably for this reason that solvolysis proceeds through the isomer I directly according to equation 5.5 (R = CH_3). The product ratios would not be expected to differ greatly in the presence or absence of added pyridine, in this case, since ligand dissociation is now not important. The product will be mainly the 3-C isomer. Although the rate of solvolysis of 9 is slower than 6, there has actually been a rate enhancement of the solvolysis of structure (I) for 9 compared to that of 6 in the presence of added pyridine or 14 by a factor of 3; $[\frac{1.81 \times 10^{-5}}{5.9 \times 10^{-6}}]$. As this route, direct solvolysis of the β-isomer, more closely resembles that of the organic system one would expect such an anchimeric assistance from the methyl group.[75]

From the observed product of the solvolysis of 15, it is reasonable to assume that this reaction also proceeds by direct solvolysis of (I) similar to that seen in the other bipy complex, 14.

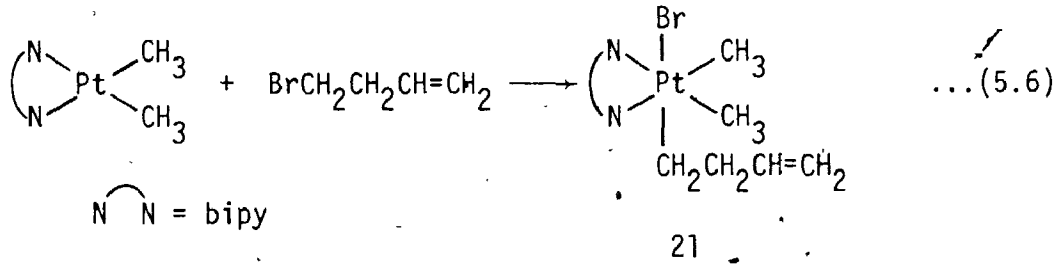
For complex 7, in which a methyl group is now on the carbinyl carbon the isolated product, 20, strongly suggests that the isomerisation I to II of the platinacyclobutane occurs prior to formation of the carbonium ion if scheme 5.2 is considered to operate in this case. As this complex is the only one with steric crowding at the carbinyl carbon, direct comparisons to the other systems is not possible.

4. Attempts to prepare but-3-enylplatinum(IV) complexes of the type III in scheme 5.1

Further support for the overall mechanism of the ring-expanion

reactions (Scheme 5.2) would involve the preparation of a but-3-enylplatinum(IV) complex and conversion of it to a platinacyclopentane product. A review of complexes containing σ-bonded organic ligands linked by a π-bond with the metal has been presented elsewhere.[99] But-3-enylplatinum complexes have been proposed as intermediates in the decomposition of platinacyclopentanes, to explain high yields of 1-butene in such reactions.[80]

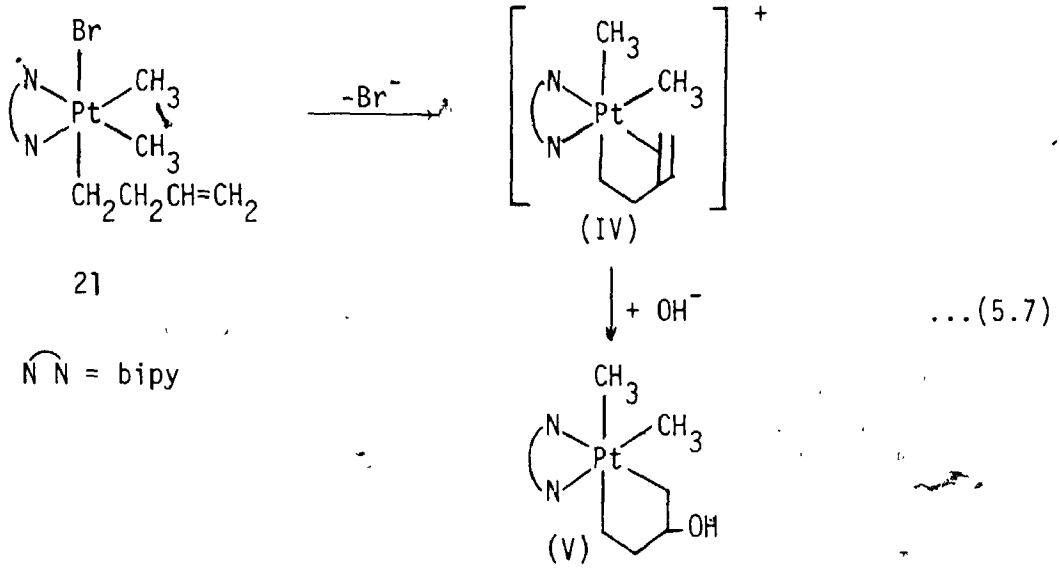
The initial strategy followed was to oxidatively add 4-bromo-1-butene to $[Pt(CH_3)_2bipy]$ as shown in equation 5.6. Once isolated it was thought that treatment of the oxidative addition product, 21, in acetone, with aqueous $AgBF_4$ would cause abstraction of the bromide (as AgBr) followed by formation of the desired platinacyclopentane, $[Pt(CH_3)_2(CHCHOHCH_2CH_2)(bipy)]$.



...(5.6)

21

The reaction hoped for is shown in equation 5.7. This reaction was not observed. However, it is much less favourable than that proposed in scheme 5.2, because both complexes IV and V contain mutually <u>trans</u> Pt-C σ-bonds. Such complexes are very rare and usually highly reactive, eg. $[Pt(CH_3)_4(bipy)]$,[100] and it seems that simple substitution of Br^- by OH_2 is preferred in this reaction. The product has been identified as $[Pt(CH_3)_2(CH_2CH_2CH=CH_2)(OH_2)(bipy)][BF_4]$.

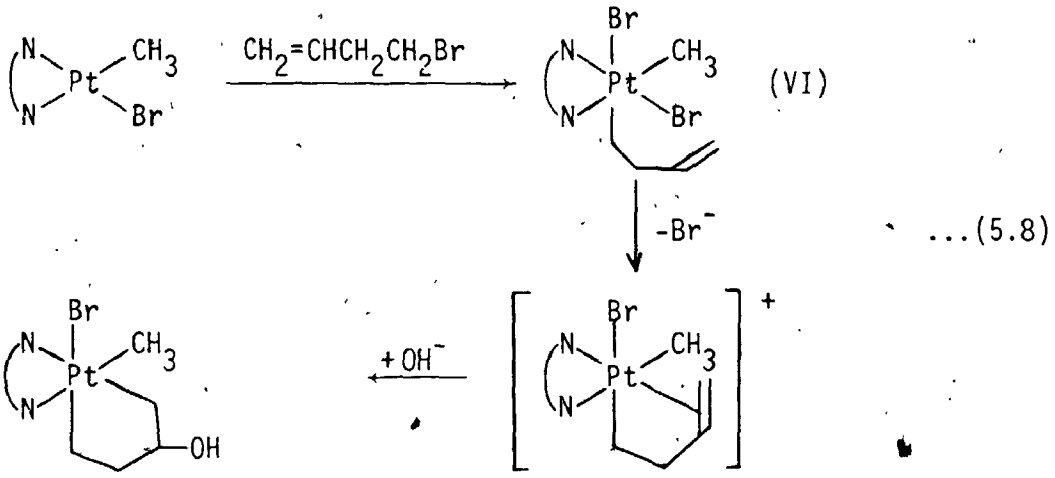


21

N N = bipy

...(5.7)

A better analogy to the reaction proposed in scheme 5.2 could be realized by the reaction shown in equation 5.8. However, in this



...(5.8)

case the oxidative addition step of butenyl bromide was very slow and gave the desired species VI in only very low yield.

Attempts to prepare butenylplatinum complexes from reactions of butenyl Grignard reagents with $[PtCl_2(SMe_2)_2]$ were also unsuccessful.

5. Conclusions

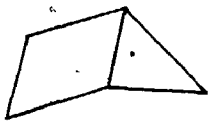
This chapter has described mechanistic studies of the ring expansion reaction presented in chapter 4. These studies have been

varied, yet the results are all consistent with one overall scheme (5.2). Comparisons have been made, wherever possible, to the organic systems upon which this reaction is based. The two systems actually have quite similar mechanisms and products, the major difference being that in the platinacyclobutylcarbinyl systems a route involving a but-3-enylplatinum(IV) intermediate is proposed. Although attempts to prepare such intermediates were not entirely successful, the difficulty seems to be a preparative one and does not preclude their role as intermediates in these processes.

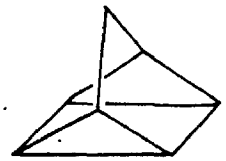
CHAPTER 6

REACTIONS OF ZEISE'S DIMER WITH STRAINED ORGANIC COMPOUNDS

The reaction of transition metal complexes with small ring organic compounds has been introduced in Chapter 1. This chapter will describe the reactions of bicyclo[2.1.0.]pentane and quadricyclane with Zeise's dimer, $[Pt_2Cl_2(\mu\text{-}Cl)_2(C_2H_4)_2]$. The reactions hoped for



Bicyclo[2.1.0.]pentane



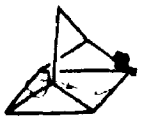
Quadricyclane

in each case are illustrated in equations 6.1 and 6.2 respectively. The preparation of platinacyclobutanes by reaction of cyclopropanes with Zeise's dimer has been discussed at length (see Chapter 2). As will be seen these reactions do not give isolable platinacycles as products, even at low temperature, but instead undergo skeletal isomerisation.

$+ [Pt_2Cl_2(\mu\text{-}Cl)_2(C_2H_4)_2] \xrightarrow{-C_2H_4} [PtCl_2(C_5H_8)]_n$

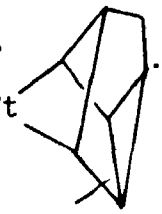
$\downarrow$ py

py_2Cl_2Pt  ...(6.1)



$+ [Pt_2Cl_2(\mu\text{-}Cl)_2(C_2H_4)] \xrightarrow{-C_2H_4} [PtCl_2(C_7H_8)]_n$

$\downarrow$ py

py_2Cl_2Pt  ...(6.2)

Also, the preparation of bicyclo[2.1.0]pentane will be described.

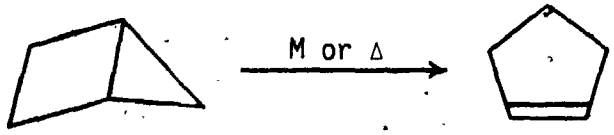
1. Bicyclo[2.1.0]pentane

1.1 Preparation of bicyclo[2.1.0]pentane

The method used for the preparation of this compound was that of Gassman and Mansfield[101] and is illustrated in scheme 6.1. The procedure used was essentially that of the literature and is described fully in the experimental section with references to alterations. The products were characterised at each isolation stage by boiling points and H^1-N.M.R. spectroscopy.

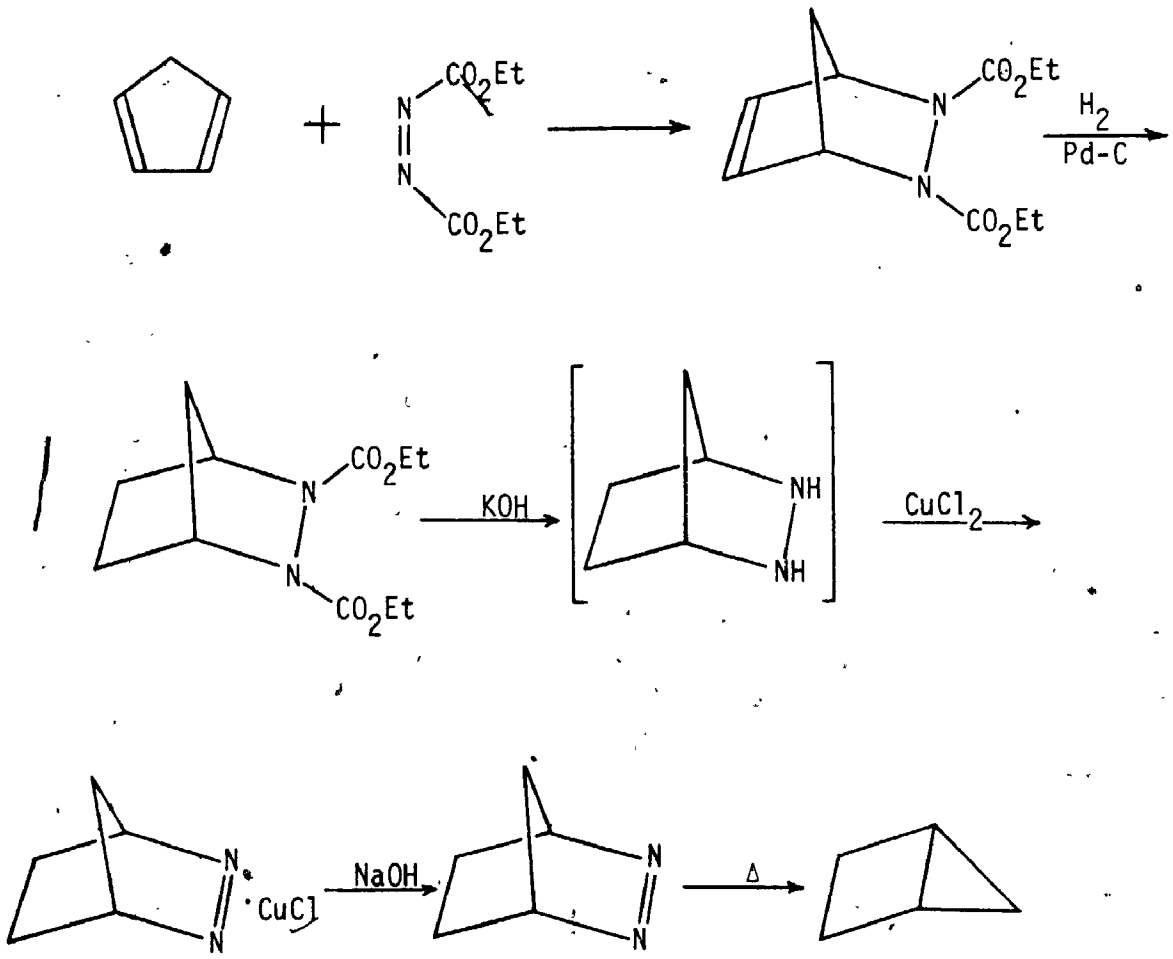
1.2 Reaction of bicyclo[2.1.0]pentane with Zeise's dimer

Although the reaction sought was that shown in equation 6.1, it is also known[36] that exposure of bicyclo[2.1.0]pentane to several transition metal complexes causes the rearrangement shown in equation 6.3. Thermally, a temperature of 330°C is required to bring about this reaction[36]. As the total strain energy in bicyclo[2.1.0]pentane is



...(6.3)

about 57 kcal mol^{-1}[102] a process, such as that depicted in equation 6.3 is likely. However, with a transition metal species, such as $[Pt_2Cl_2(\mu\text{-}Cl)_2(C_2H_4)_2]$ which is known to react in benzene with cyclopentene[103] as well as other olefins (ol) to yield dimeric analogues of Zeise's dimer, $[Pt_2Cl_2(\mu\text{-}Cl)_2(ol)_2]$, olefin complexes must be considered



Scheme 6.1 Preparative route to bicyclo[2.1.0]pentane

as possible reaction products. Zeise's dimer has been found to be monomeric in acetone[104,105] and present as the species $[PtCl_2(C_2H_4)(acetone)]$ (owing to the high trans-effect of olefinic ligands, this species is expected to have the trans geometry).

When freshly prepared bicyclo[2.1.0]pentane is added to a solution of Zeise's dimer in acetone-d_6 an orange precipitate is formed within an hour. Although this product is only sparingly soluble in chloroform-d_1, a ^{1}H-N.M.R. spectrum run overnight revealed a broad peak at δ5.6 ppm together with another broad signal at δ1.8 ppm, the noise level of the spectrum being rather high. When a similar reaction is performed with cyclopentene a similar orange precipitate is formed which is also sparingly soluble in chloroform-d_1. A ^{1}H-N.M.R. spectrum run overnight exhibited a broad peak at δ5.70 ppm and another at δ1.90 ppm. A small amount of cyclopentene was also present in this dilute sample.

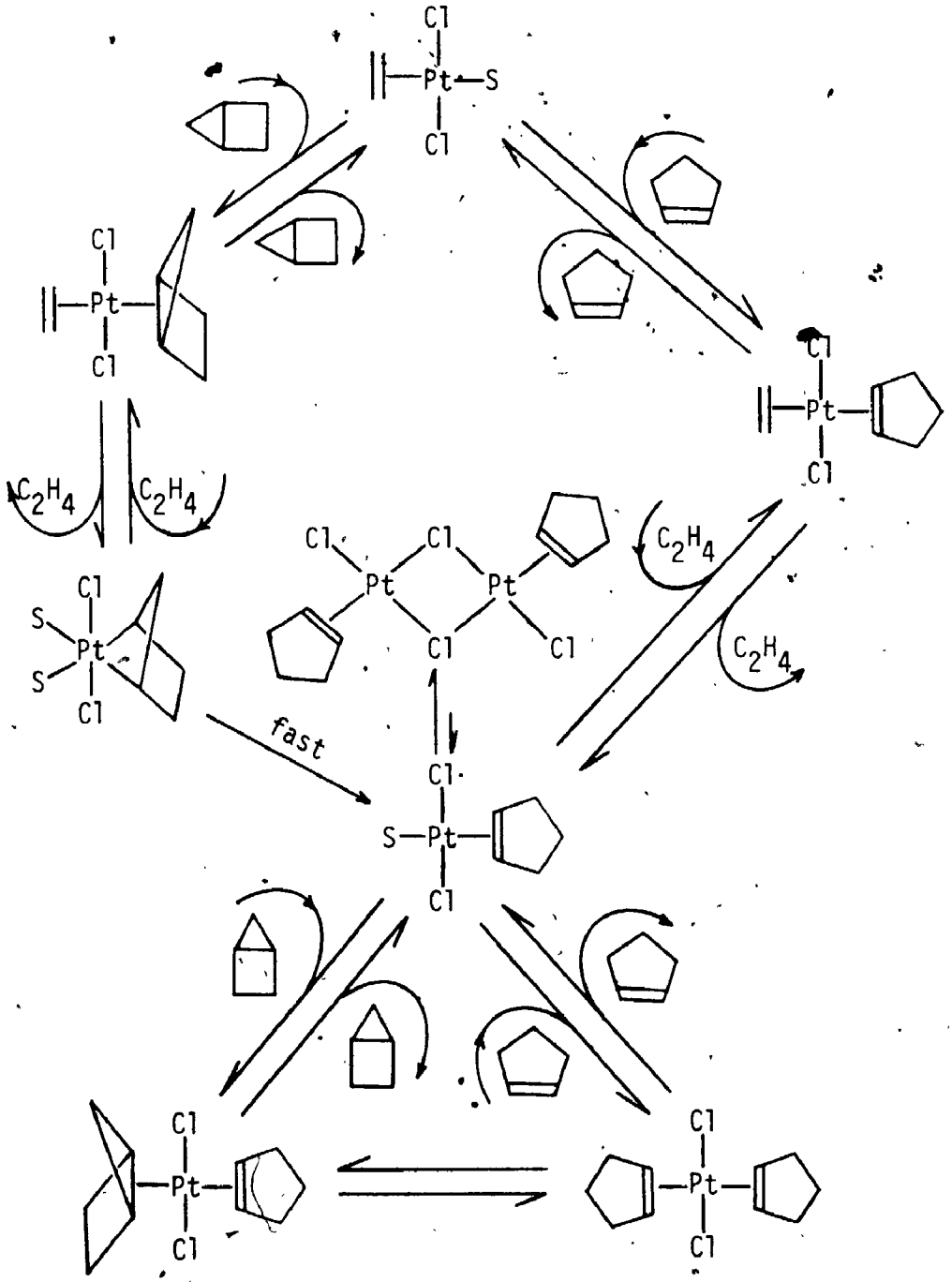
The above results indicate that the two precipitates are likely the same compound in both cases. $[Pt_2Cl_2(\mu\text{-}Cl)_2(cyclopentene)_2]$, prepared by the reaction of cyclopentene with Zeise's dimer in benzene, is also an orange complex which is fairly insoluble in chloroform but gives ^{1}H-N.M.R. data (=CH, 2, 6.05 ppm and CH_2, 6, 2.1 ppm)[106] close to those obtained for the isolated precipitates. These results suggest that the initially formed precipitates are $[Pt_2Cl_2(\mu\text{-}Cl)_2(cyclopentene)]$.

When bicyclo[2.1.0]pentane is added to an acetone-d_6 solution of Zeise's dimer at -80°C and the reaction followed by ^{1}H-N.M.R. spectroscopy no reaction occurs until -35°C. At this temperature an orange precipitate starts to form. The species identified to be in

solution are Zeise's dimer (as $[PtCl_2(C_2H_4)(acetone\text{-}d_6)]$), in equilibrium with free ethylene, bicyclo[2.1.0]pentane and cyclopentene. As the solution is warmed further, more precipitate is formed as well as cyclopentene whose signals in the ^{1}H-N.M.R. grow relative to those corresponding to the two starting reagents. Upon complete conversion of the initial Zeise's dimer, the products seen in solution are cyclopentene, ethylene and some bicyclo[2.1.0]pentane. At no time was a platinacycle seen.

A similar variable temperature study to the reaction above was performed using cyclopentene in place of bicyclo[2.1.0]pentane. A precipitate formed around -10°C and no new peaks were observed in the ^{1}H-N.M.R. spectrum.

These results are consistent with the pathways shown in scheme 6.2. Cyclopentene reacts with $[PtCl_2(C_2H_4)(acetone)]$ to give $[PtCl_2(cyclopentene)(acetone)]$ (presumably via the mixed bis(olefin) intermediate: $[PtCl_2(C_2H_4)(cyclopentene)]$). This is in equilibrium with the dimer, $[Pt_2Cl_2(\mu\text{-}Cl)_2(cyclopentene)_2]$ which is insoluble. Precipitation of this dimeric product drives the reaction to completion. The concentration of $[PtCl_2(cyclopentene)(acetone)]$ in solution is probably small. Even so, detection of it in the ^{1}H-N.M.R. spectrum would be doubtful due to overlap of signals from uncomplexed cyclopentene, and probable rapid exchange between free and coordinated cyclopentene. This type of reaction has been seen before.[107] A complex "$[PtCl_2(C_2H_4)(ol)]$", where ol = propene or 1-butene, is produced by the splitting of Zeise's dimer in acetone as solvent at -78°C. On warming, this complex decomposes to give principally $[PtCl_2(ol)]_2$.



Scheme 6.2 Conversions and interconversions in the bicyclo[2.1.0]-pentane and cyclopentene reactions with Zeise's dimer in acetone (=S). Alkene for alkene exchanges will be fast.

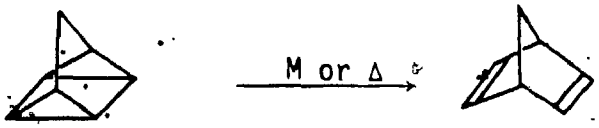
Now, when bicyclo[2.1.0]pentane is used in place of cyclopentene, generation of the species $[PtCl_2(cyclopentene)(acetone)]$ is also possible in solution, presumably via an undetectable platinacycle. $[PtCl_2(cyclopentene)(acetone)]$ can then react as before, eventually giving $[Pt_2Cl_2(\mu\text{-}Cl)_2(cyclopentene)_2]$ which is insoluble. Since C_2H_4 is a better ligand than cyclopentene, the equilibria will probably favour $[PtCl_2(C_2H_4)(acetone)]$ at first until a very high concentration of cyclopentene is formed. All exchange steps will be fast. This, of course, accounts for the presence of free cyclopentene in solution.

The salient features of this study are that upon treatment with Zeise's dimer in acetone, bicyclo[2.1.0]pentane is converted to $[Pt_2Cl_2(\mu\text{-}Cl)_2(cyclopentene)_2]$, with free cyclopentene being generated. At no step, even at low temperatures, is a platinacycle detected in solution. However, such a species is postulated as an intermediate.

2. Quadricyclane

2.1 Reaction of Quadricyclane with Zeise's dimer

Although the reaction sought was that shown in equation 6.2 it is known[36] that exposure of quadricyclane to several transition metal complexes causes the rearrangement to norbornadiene (NBD), shown in equation 6.4. Thermally, this same reaction is known to proceed



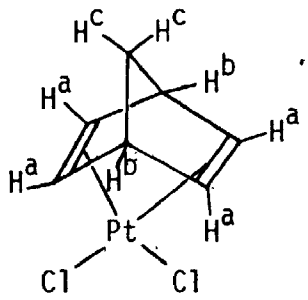
...(6.4)

slowly ($t_{1/2}$ > 14 hr at 140°C).[108] One of the complexes which is known to catalyse the reaction in equation 6.4 is $[PtCl_2(NBD)]$ itself.[109]

Although this complex can be prepared from Zeise's dimer by reaction with norbornadiene,[110] the direct reaction of Zeise's dimer with quadricyclane has not been studied previously.

When quadricyclane is added to an acetone solution of Zeise's dimer at room temperature, a fluffy pale-yellow complex immediately precipitates out of solution. The reaction proceeds until the orange colour of Zeise's dimer is no longer detectable. The product, which is only slightly soluble in $CDCl_3$, was identified to be $[PtCl_2(NBD)]$ by ^{1}H-N.M.R. spectroscopy (see Table 6.1).

Table 6.1 ^{1}H-N.M.R. Spectral Data For The Complex $[PtCl_2(NBD)]$, in $CDCl_3$

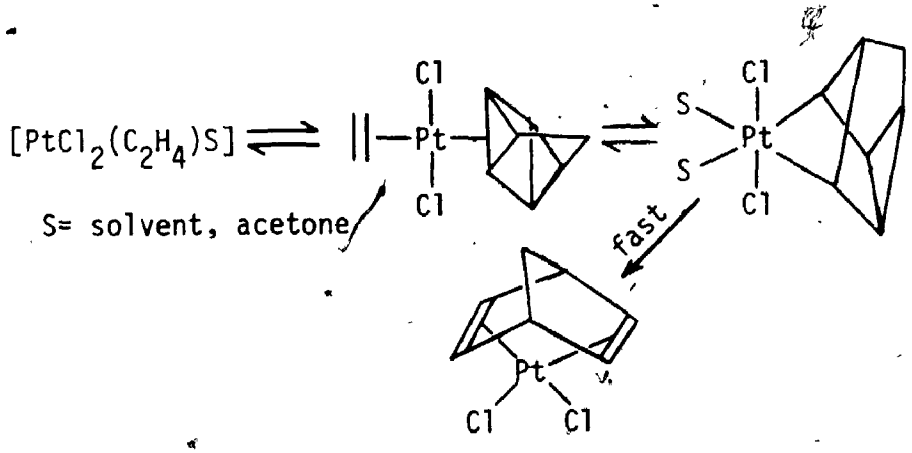


Proton	Chemical Shifts in $CDCl_3$ Complex	NBD[111]	Comments
H^a	5.30 ppm	6.72	$J_{Pt,H}$ = 67.5 Hz
H^b	1.70 ppm	1.97	
H^c	4.34 ppm	3.52	

When quadricyclane is added to an acetone-d_6 solution of Zeise's dimer at -75°C a precipitate forms immediately as before. There is no evidence for quadricyclane in solution, as checked by ^{1}H-N.M.R. spectroscopy, the principle species being readily identified

as NBD (in acetone-d_6 H^a, δ6.77 ppm; H^b, δ1.71 ppm; H^c, δ3.56 ppm, c.f. Table 6.1). The only other species detected in solution was $[PtCl_2(C_2H_4)(\text{acetone-}d_6)]$ in equilibrium with free ethylene. The reaction was determined to be catalytic as a 10-fold excess of quadricyclane was converted immediately to NBD even at this temperature. This solution was warmed slowly and the ^{1}H-N.M.R. spectrum was analysed at incremental temperatures. The ^{1}H-N.M.R. spectrum remained unchanged. At ambient temperature the cap was removed from the N.M.R. tube. After 2 hours no ethylene peak could be observed in the ^{1}H-N.M.R. spectrum.

This study shows that Zeise's dimer can effect the conversion in equation 6.4, catalytically, even at -75°C. The active catalytic species is presumed to be $[PtCl_2(NBD)]$. This species is most likely formed according to the mechanism in equation 6.5. Once formed, the catalytic conversion of quadricyclane to NBD may involve coordination of quadricyclane to $[PtCl_2(NBD)]$ via an exchange with the originally coordinated olefin, or by extension of the coordination around the metal. Either of these processes may be thought of as involving platinacycle intermediates. However, no such intermediates or complexes were detected even at -75°C.



...(6.5)

$[PtCl_2(NBD)]$

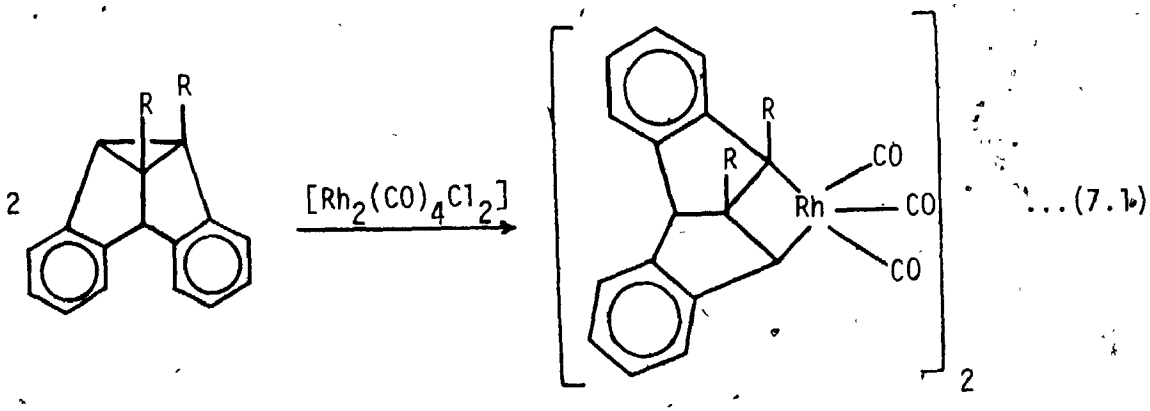
CHAPTER 7

REACTIONS OF SOME CYCLOPROPANES WITH $[Rh_2(CO)_4Cl_2]$

7.1 Preamble

Dichlorotetracarbonyldirhodium(I), $[Rh_2(CO)_4Cl_2]$, obtained by the reduction of $[RhCl_3 \cdot 3H_2O]$ with CO,[112] is perhaps the most important starting material for rhodium(I) chemistry. Rhodium metallacycles have been prepared using this complex.[113]

As discussed in chapter 1, rhodiacycles have been proposed as intermediates in the reaction of $[Rh_2(CO)_4Cl_2]$ with cyclopropanes (equation 1.14) and quadricyclane (figure 1.10). These reactions do not give isolable rhodiacyclobutanes but instead undergo insertion of a terminal CO, from the starting material, to give a rhodiacyclopentanone product. Support for the rhodiacyclobutane intermediate is seen in the reactions of dibenzosemibullvalenes with $[Rh_2(CO)_4Cl_2]$[113] (equation 7.1) in which the products isolated appear to be rhodiacyclobutane complexes.



...(7.1)

The aim of the work in this section of the thesis was to determine the products of the reactions between $[Rh_2(CO)_4Cl_2]$ and the

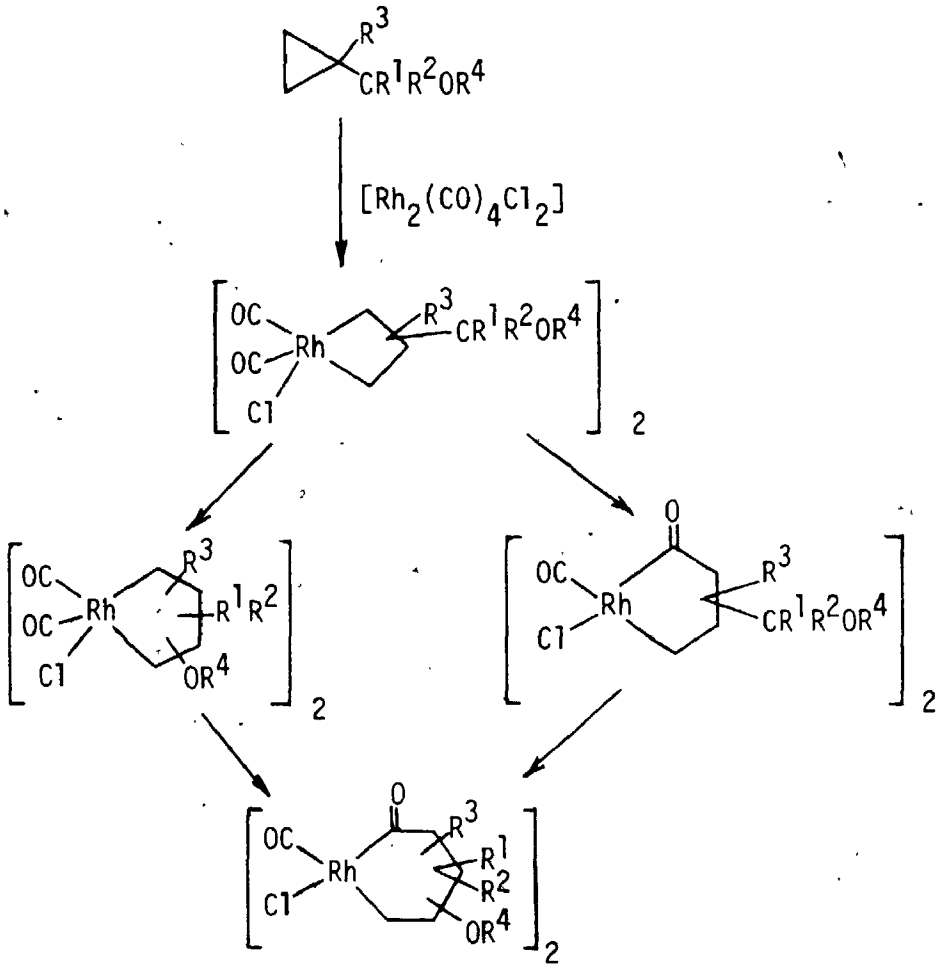
various cyclopropanes used in the preparation of the platinacyclobutanes of chapter 2. The reactions hoped for are illustrated in scheme 7.1. They are based, by analogy, on those previously known in the rhodium systems studied to date and those of the platinum systems discussed in this thesis. By such processes rhodiacycles containing three, four, or five carbon atoms in the cyclic array can be envisioned. In this study, however, no stable rhodiacycles could be isolated. The products, where reactions occurred were organic compounds derived from rearrangement of the starting cyclopropanes. These reactions were not general for all the cyclopropanes studied but are novel in their own right and will be discussed in separate sections.

7.2 Reactions attempted

The reactions of $[Rh_2(CO)_4Cl_2]$ which have been attempted are summarised in Table 7.1. In general two methods were tried: reaction was carried out in the neat cyclopropane and in organic solvents such as tetrahydrofuran, chloroform, or acetone. Two of these latter reactions proved to be interesting and involved rearrangement of the cyclopropane. These are marked by asterisks in Table 7.1.

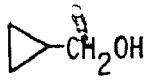
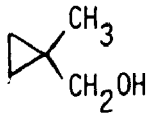
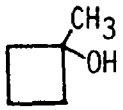
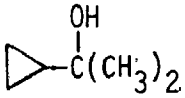
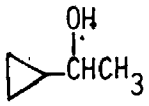
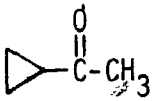
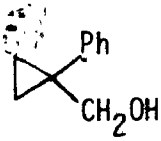
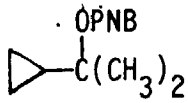
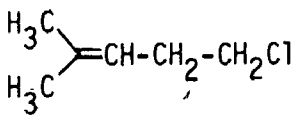
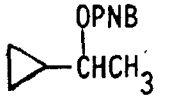
7.2.1 Reaction of $[Rh_2(CO)_4Cl_2]$ with the neat cyclopropane

McQuillin[35] has prepared stable rhodiacycles by the reactions of $[Rh_2(CO)_4Cl_2]$ in neat cyclopropane derivatives, under mild conditions, the products precipitating from solution (equation 1.14). This method, however, proved unsuccessful for the reaction of $[Rh_2(CO)_4Cl_2]$ with the cyclopropanes used in this study (see Table 7.1).



Scheme 7.1 Possible Metallacycles in the Reaction of $[Rh_2(CO)_4Cl_2]$ With Some Cyclopropanes

Table 7.1 Reactions Attempted Between Cyclopropanes And $[Rh_2(CO)_4Cl_2]$ In Various Solvents At 40°C

Cyclopropane	Solvent	Result
	i) neat	no reaction
	ii) THF	no reaction
	iii) $CHCl_3$	no reaction
	iv) acetone	very slow; decomp.
	i) neat	no reaction
	ii) THF	no reaction
	iii) $CDCl_3$	very slow; decomp.
	* iv) acetone-d_6	
	i) neat	no reaction
	ii) THF	no reaction
	iii) acetone-d_6	no reaction
	i) neat	no reaction
	ii) THF	no reaction
	iii) $CDCl_3$	no reaction
	iv) acetone-d_6	
	i) neat	no reaction
	i) neat	no reaction
	ii) THF	no reaction
	iii) acetone-d_6	very slow; decomp.
	* i) acetone-d_6	
	i) acetone-d_6	no reaction

* - denotes a reaction which was studied in detail

In a typical experiment, $[Rh_2(CO)_4Cl_2]$ was dissolved in the cyclopropane and the resulting solution was either kept in a nitrogen atmosphere or placed in a sealed tube. In both of these cases the same result was obtained. The solution gradually (within six hours) darkened owing to the formation of rhodium metal. Upon work-up, by evaporation of the cyclopropane and filtration of the metal, the orange residue was identified by infrared spectroscopy to be the starting material $[Rh_2(CO)_4Cl_2]$.

Many of these same reactions were followed by ^{1}H-N.M.R. spectroscopy which showed no noticeable spectral changes. In every case studied prolonged reaction time or reaction at slightly elevated temperatures served only to increase the extent of decomposition.

7.2.2 Reactions of $[Rh_2(CO)_4Cl_2]$ with Cyclopropanes in Organic Solvents

Reactions of $[Rh_2(CO)_4Cl_2]$ with cyclopropanes in sealed tubes containing tetrahydrofuran or chloroform (or $CDCl_3$) as solvent gave results similar, for the most part, to those described in section 7.2.1 above. That is, no reaction was observed except for gradual reduction of $[Rh_2(CO)_4Cl_2]$ to elemental rhodium. The reaction was allowed to proceed until this decomposition made further study impossible. The use of $CDCl_3$ as solvent allowed these reactions to be conveniently monitored by ^{1}H-N.M.R. spectroscopy. In only one case was a reaction observed in $CDCl_3$ which involved more than just decomposition of the rhodium starting material. The reaction of 1-methylcyclopropyl carbinol (5% mole excess) with $[Rh_2(CO)_4Cl_2]$ was very slow at 40°C, going to ~80% completion after ten days. The product of this reaction

was determined by ^{1}H-N.M.R. spectroscopy to be 1-methylcyclobutanol, identified by comparison to an authentic sample.[87] However, the reaction was thought to be too slow to conveniently study further and decomposition to rhodium metal was fairly extensive as well.

In acetone as solvent, reactions of the various cyclopropanes proved to be more fruitful. Predictions as to reactivity could not be made a priori with any degree of certainty.

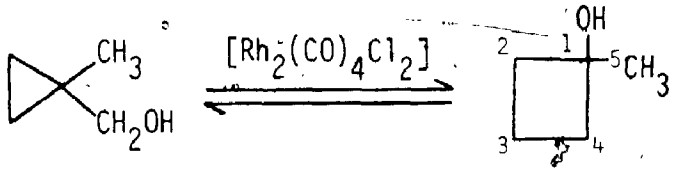
Both $\overline{CH_2CH(CH_2OH)CH_2}$ and $\overline{CH_2C(C_6H_5)(CH_2OH)CH_2}$ reacted very slowly with $[Rh_2Cl_2(CO)_4]$ in acetone-d_6 as followed by ^{1}H-N.M.R. spectroscopy. Product identification, however, was not possible owing to decomposition of the catalyst to rhodium metal, prior to sufficient reaction.

The reactions which yielded good results were those involving $\overline{CH_2C(CH_3)(CH_2OH)CH_2}$ and $\overline{CH_2CH\{C(CH_3)_2OPNB\}CH_2}$, in separate experiments with $[Rh_2(CO)_4Cl_2]$. The first of these was determined to be catalytic giving 1-methylcyclobutanol exclusively. The second gave $(CH_3)_2C{=}CHCH_2CH_2Cl$ by a non-catalytic route.

7.3 Reaction of 1-methylcyclopropyl carbinol with $[Rh_2(CO)_4Cl_2]$ in acetone-d_6

7.3.1 General results

It was found that $[Rh_2(CO)_4Cl_2]$ could catalyse the rearrangement of 1-methylcyclopropyl carbinol to 1-methylcyclobutanol, according to the equilibrium in equation 7.2. This reaction does not proceed in the absence of added catalyst nor in the presence of added acids (such as trifluoroacetic), under the mild conditions employed. The presence



...(7.2)

of an equilibrium was established empirically based upon the observation that all the 1-methylcyclopropyl carbinol could never be converted. Integration of the methyl signals, using a 100 MHz ^{1}H-N.M.R. spectrometer yielded an equilibrium constant of 21 at 40°C. Using equation 7.3, this equilibrium constant converts into a free energy of -1.9 kcal mol^{-1}. This may represent the difference in ring-strain between

$$\Delta G = -RT\ln K = -1.9 \text{ kcal mol}^{-1} \quad \ldots(7.3)$$

the three and four membered rings. From Table 5.1 this value is 1.2 kcal mol^{-1} for the parent cycloalkanes. This is consistent with a similar determination of an equilibrium mixture of cyclobutyl chloride and cyclopropylmethyl chloride which claims a ratio of 36:1 for these isomers at 25°C[75] ($\Delta G = -2.1$ kcal mol^{-1}).

The reaction was most easily studied by following it with ^{1}H-N.M.R. spectroscopy. In acetone-d_6 the methyl resonance of the initial 1-methylcyclopropyl carbinol occurs 0.18 ppm upfield from that of the 1-methylcyclobutanol produced. The cyclopropyl protons diminish accordingly and resonances appear some 2 ppm downfield from this position, consistent with the product being a cyclobutane. These facts are clearly illustrated in figure 7.1 which shows a typical run at 40°C for time intervals of t = 0 mins, t = 370 mins and t = 900 mins. As can be seen from the final spectrum, the reaction goes essentially to completion. In figure 7.1b the reaction has almost

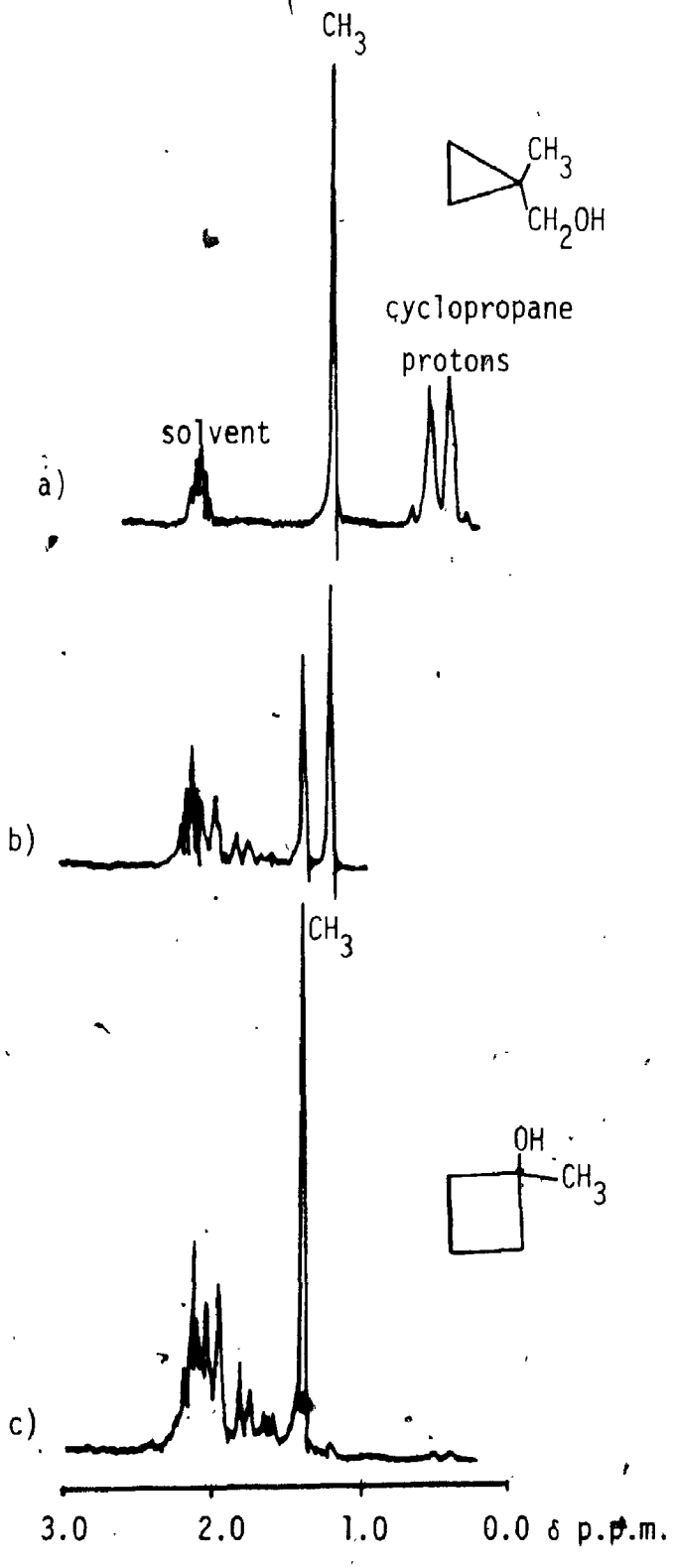


Figure 7.1 ^{1}H N.M.R. spectrum during the solvolysis of 1-methyl-cyclopropyl carbinol at time intervals of a) 0 minutes b) 370 minutes and c) 900 minutes in acetone-d_6 at 40 ^{o}C.

reached one half-life as estimated from the heights of the two methyl resonances. The concentration of $[Rh_2(CO)_4Cl_2]$ for this experiment was 8.57×10^{-2} M and the concentration of 1-methylcyclopropyl carbinol was twice this: 1.71×10^{-1} M. The product formed is most readily identified by its $^{13}C\{^1H\}$ and ^{13}C-INEPT N.M.R. spectra. The results in Table 7.2 are consistent with those in the literature for the same compound.[114] Identical spectra were obtained whether or not the sample was separated from the catalyst prior to running the spectrum. Upon evaporation of the volatile products, the residue which remained contained only $[Rh_2(CO)_4Cl_2]$. This was established by infrared spectroscopy in $CDCl_3$ which showed only those peaks consistent with the starting dimer and ^1H-N.M.R. spectroscopy which confirmed the absence of proton containing materials. Thus, the catalytic nature of this reaction was supported. Likewise, the conversion of greater than stoichiometric amounts of 1-methylcyclopropyl carbinol and kinetic studies showed similar results.

The results of kinetic studies to determine the order of the reaction with respect to the reactants will now be discussed.

7.3.2 Kinetic studies

The dependence of the catalysed rearrangement of 1-methylcyclopropyl carbinol with respect to $[Rh_2(CO)_4Cl_2]$ was determined by the incremental additions of catalyst to a standard solution of cyclopropane and observing the rate of 40°C. Plots of $C-C_\infty$ versus time; where C = the concentration of 1-methylcyclopropyl carbinol and C_∞ = the concentration of this cyclopropane after infinite reaction, for

Table 7.2 ^{13}C-N.M.R. Results of 1-Methylcyclobutanol

Carbon Atom	δ ppm	
	Found[a]	Literature[b,114]
1	72.5 (tertiary)	72.1
2, 4	38.4 (CH_2)	37.1
3	12.2 (CH_2)	11.4
5	27.2 (CH_3)	26.5

a) in acetone-d_6, reference:center of acetone-d_6 septet at 29.8 ppm downfield from TMS

b) in $CDCl_3$ relative to TMS

each of these experiments are shown in figure 7.2. C_∞ was determined by accurate integration (at 100 MHz) of the methyl proton signals after the reactions had reached equilibrium at 40°C. The value of C_∞ was determined to be 0.0082 M by this method. The near linearity of these plots indicates that the dependence of this reaction with respect to 1-methylcyclopropyl carbinol is small and probably close to zero. Now, a plot of the initial slopes of the graphs in figure 7.2 versus the square of the concentration of $[Rh_2(CO)_4Cl_2]$ gives a straight line (figure 7.3). This indicates a second-order dependence with respect to catalyst.

In solvents containing oxygen donor atoms, such as dioxane, the equilibrium of equation 7.4 has been found, by infrared spectroscopy, to lie well to the right.[115] The predominant species in solution being: $[Rh(CO)_2ClS]$; S = solvent. The infrared spectrum of

$$[Rh_2(CO)_4Cl_2] + 2S \rightleftharpoons 2[Rh(CO)_2ClS] \qquad \ldots(7.4)$$

$[Rh_2(CO)_4Cl_2]$ in acetone exhibits two strong bands in the carbonyl region at 1987 cm^{-1} and 2055 cm^{-1}. This is consistent, by analogy to the dioxane study, with the species in solution being the monomer cis-$[RhCl(CO)_2S]$; S = acetone. Therefore, the squared dependence observed is actually with respect to $[RhCl(CO)_2S]$ which indicates that dimerisation of $[RhCl(CO)_2S]$ to an active species is rate-limiting. A mechanism which supports the available data will be presented in section 7.3.3.

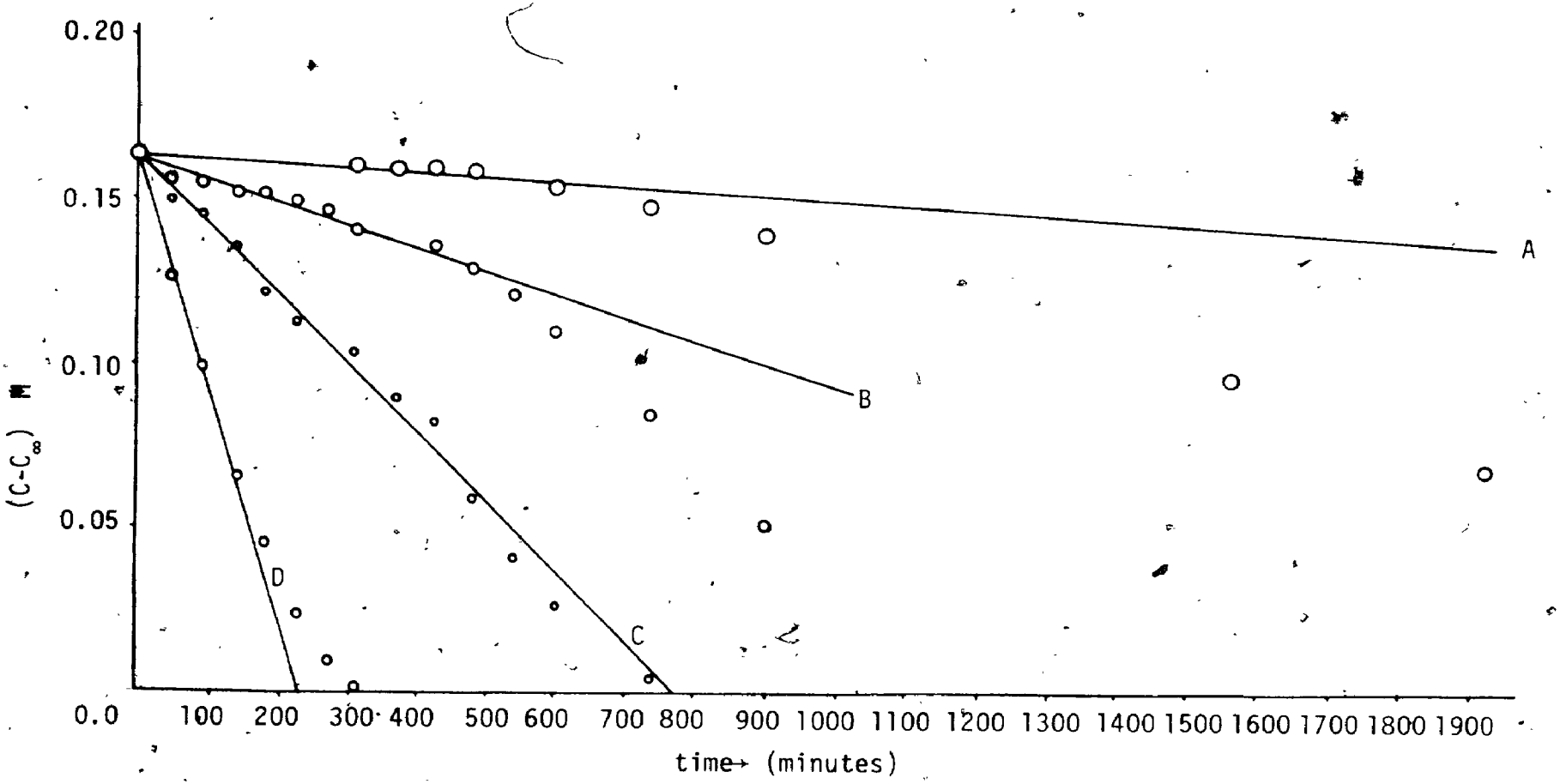


Figure 7.2 Kinetic plots for the rearrangement of 1-methylcyclopropyl carbinol ($C=1.71 \times 10^{-1}$ M) to 1-methylcyclobutanol under the influence of the catalyst: $[Rh_2(CO)_4Cl_2]$ A) 1.71×10^{-1} M B) 8.57×10^{-2} M C) 3.43×10^{-2} M D) 1.71×10^{-2} M, where C and C_∞ are as defined in the text.

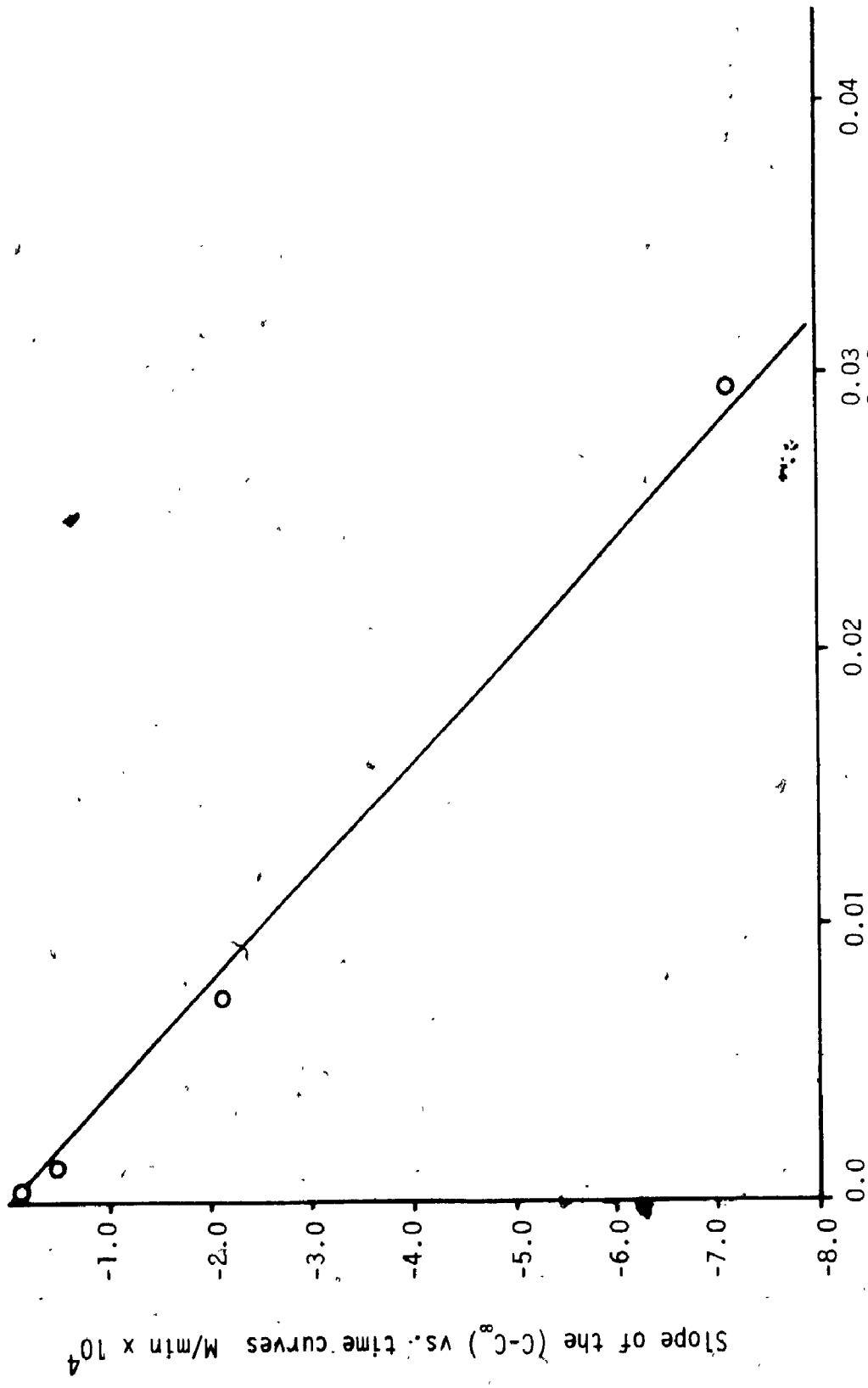


Figure 7.3 Graph of the initial slopes of the curves in figure 7.2 versus the square of the $[Rh_2(CO)_4Cl_2]$ concentration to show the second-order dependence on catalyst concentration.

7.3.3 Mechanism involving $[Rh(CO)_2ClS]$ acting as a Lewis acid or a Rhodiacycle

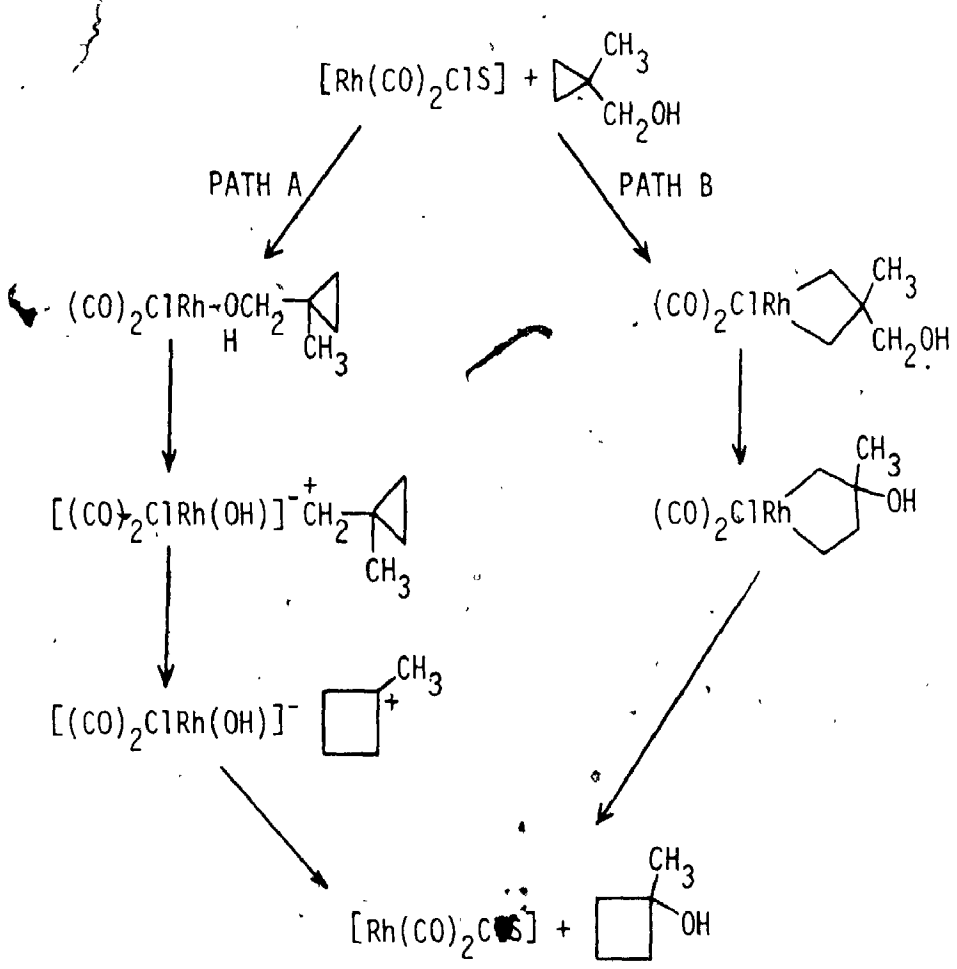
At this stage in the study it was not possible to discern between a Lewis acid mechanism or one involving a rhodiacycle. The two likely routes are illustrated in Scheme 7.2.

The evidence against the Lewis acid mechanism is:

1. H^+ does not effect the isomerisation.
2. No 1-chloro-1-methylcyclobutane was detected as compared to an authentic sample.
3. No catalysis in $CHCl_3$, where the catalyst exists as the dimer $[Rh_2(CO)_4Cl_2]$,[114] was observed.
4. Kinetic studies in acetone show rate α $[Rh(CO)_2ClS]^2$ indicating a binuclear catalyst and 0 order with respect to the cyclopropane derivative.

In order to gain further insight into the mechanism of rearrangement the reaction of $\overline{CH_2C(CH_3)(CD_2OH)CH_2}$ with $[Rh_2(CO)_4Cl_2]$ in acetone-d_6 at 40°C was attempted. For comparative purposes the solvolysis of the methanesulphonate analogue, $\overline{CH_2C(CH_3)(CD_2OMs)CH_2}$ in 60% acetone/H_2O at 40°C was also performed. It was anticipated that if a rhodiacyclobutane intermediate is operating then a different label distribution should be seen in the products of the two reactions. If, however, the same label distribution is observed for these two reactions then evidence would point to the existence of the same carbonium ion intermediate in both cases.

The products of the two reactions described above were analysed by their ^{13}C-N.M.R. spectra in acetone-d_6. The conditions of data collection and spectral display were identical for each as was the



Scheme 7.2 Two Likely Routes For The Rearrangement

1) One Involving Lewis Acid (Path A) and

2) One Involving A Rhodiacycle

concentration of 1-methylcyclobutanol in each sample, thereby making comparisons between the results possible. The results of this experiment were conclusive in that the same product mixture of deuterium labelled 1-methylcyclobutanol was obtained in each of these cases (see figure 7.4). This result supports the role of similar carbonium ion intermediates in both cases. The result can also be rationalised by a mechanism involving a rhodiacyclobutane which gives

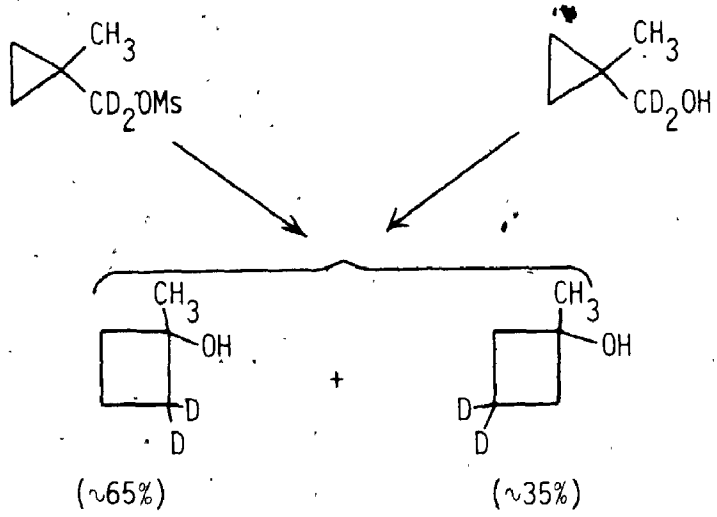


Figure 7.4 Same product mixtures obtained in the two labelling studies

the same label distribution as that of the solvolysis case. However, this is much less likely than the other possibility.

The available evidence just presented for the catalysed rearrangement of 1-methylcyclopropyl carbinol by $[Rh_2(CO)_4Cl_2]$ suggests a process similar to that outlined in scheme 7.3. This mechanism accounts for the second-order dependence on $[Rh(CO)_2ClS]$ as the dimer with one solvent molecule must be formed before reaction can occur. Displacement of the solvent molecule by the alcohol is

expected to be rapid. Now, interaction of the cyclopropyl end of the molecule with the other rhodium atom can activate the ring to expand. The precise mechanism of this is not yet known but involves generation of the carbonium ion which can then rearrange.

The fact that this reaction is not general for all the cyclopropanes studied may well be dependent upon the geometry of the cyclopropane and its ability to interact with the other rhodium atom while in the spanning position. However, a more important factor may well be linked to the rate enhancement seen in methyl substituted cyclopropanes in normal solvolysis[75] as well as the formation of a secondary

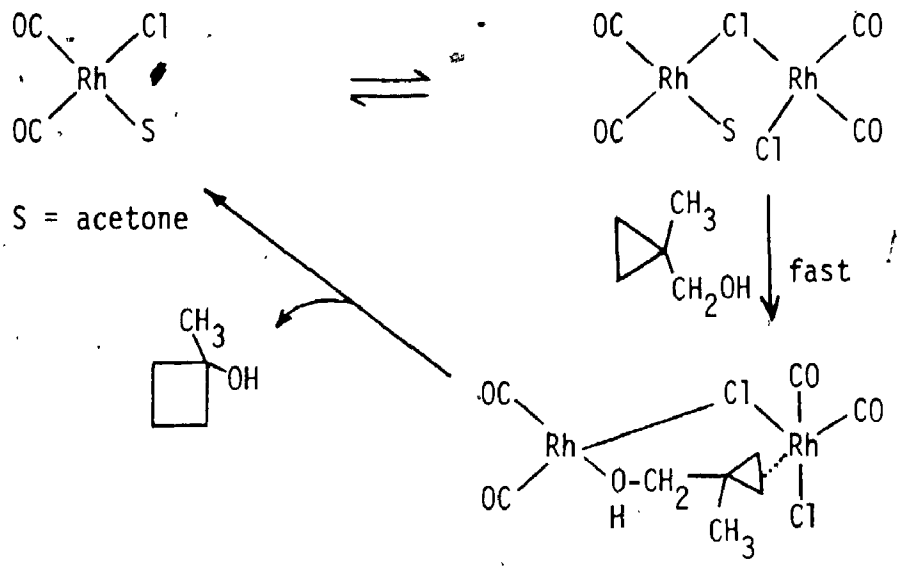
...(7.5)

carbonium ion from a primary one, as depicted in equation 7.5

7.3.4 Reaction of 1-methylcyclopropyl carbinol with $[Rh_2(CO)_4Cl_2]$ in acetone-d_6 under carbon monoxide pressure at 40°C

Although the evidence presented in the previous sections seems to rule out a rhodiacyclic intermediate it was thought that, if present, one could be trapped by CO insertion to give a more stable rhodiacycle, as in scheme 7.1. Therefore, a reaction was set up under identical conditions as before except that the reaction was performed in a bomb under 150 psi of CO. Before discussing these results, the possible interactions of CO with each of the starting materials will be discussed briefly with reference to results from the literature.

Under a carbon monoxide pressure of 50 kg/cm^2 and a temperature of 200°C cyclopropane itself has been shown to be converted catalytically



Scheme 7.3 The Probable Mechanism For Rearrangement of 1-Methylcyclopropyl carbinol by $[Rh_2(CO)_4Cl_2]$ in Acetone

to a mixture of mainly propylene, dipropyl ketone, cyclobutanone and isopropyl propyl ketone by either $[Rh_2(CO)_4Cl_2]$ or the rhodiacyclopentanone: $[\overline{RhCl(COCH_2CH_2CH_2)(CO)}]_2$.[116] These conditions are very severe and comparison to results at 40°C may not be possible.

It has been found[117] that carbon monoxide is capable of bridge-splitting reactions with $[Rh_2(CO)_4Cl_2]$ at elevated pressures (200 psi) according to equation 7.6. The extent of the equilibrium at 25°C is

$$[Rh_2(CO)_4Cl_2] + 2CO \rightleftharpoons 2Rh(CO)_3Cl \qquad ...(7.6)$$

dependent upon the partial pressure of CO and the solvent employed. The conversion to $[Rh(CO)_3Cl]$ is approximately ten times larger in 1,2-dichloroethane than in hexane.[117]

When a catalytic amount of 1-methylcyclopropyl carbinol is reacted with $[Rh_2(CO)_4Cl_2]$ at 40°C in acetone-d_6 under CO (150 psi) for 12 hours and the resultant solution allowed to equilibrate to atmospheric pressure the organic product is only 1-methylcyclobutanol, as identified by ^{1}H-N.M.R. spectroscopy. The rhodium complex in solution is still $[Rh(CO)_2Cl(acetone)]$. However, precipitating out of the original solution were several large black crystals. Infrared spectra of these crystals in the carbonyl region (nujol (cm^{-1}): 2070s, 2015m, 1800s; $CDCl_3$ (cm^{-1}): 2070s, 2040m, 1800s) and their colour confirm them as being the cluster $Rh_6(CO)_{16}$. This known compound is black and air stable and has carbonyl stretching frequencies of 2073 cm^{-1}, 2026 cm^{-1} and 1800 cm^{-1} in KBr.[118] Previous reports[119] have indicated that both $[Rh_4(CO)_{12}]$ and $[Rh_6(CO)_{16}]$ can be formed from reactions of $[Rh_2(CO)_4Cl_2]$ with CO depending upon the solvent

system. It would appear that the insolubility of $[Rh_6(CO)_{16}]$ in acetone facilitates its identification in this case.

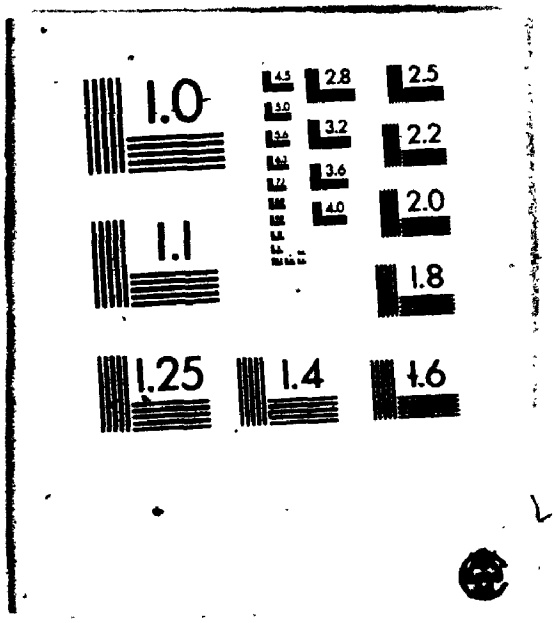
7.4 Reaction of $[Rh_2(CO)_4Cl_2]$ with 2-cyclopropyl-2-propyl - *p*-nitrobenzoate

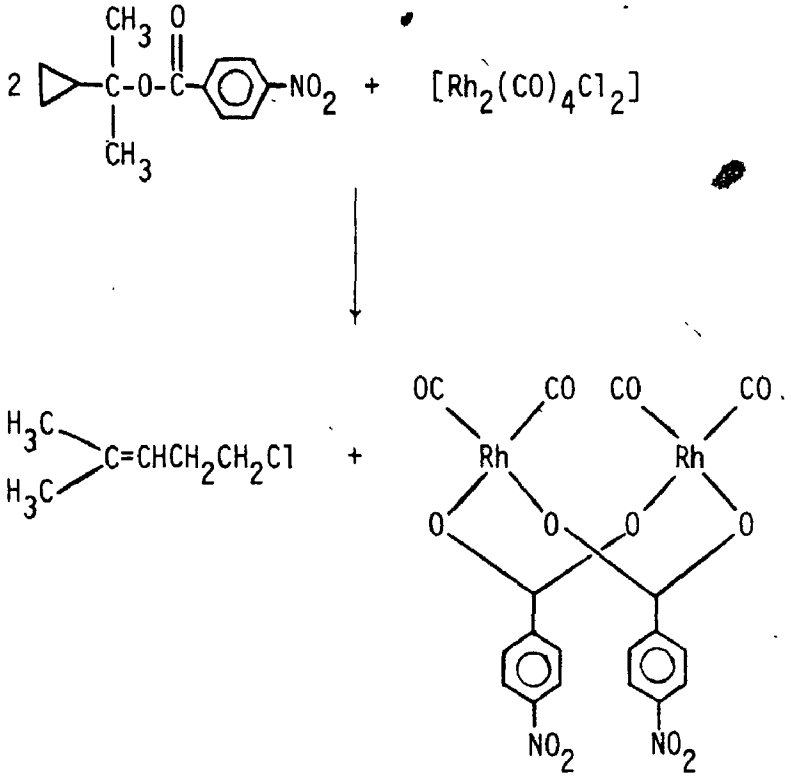
When 2-cyclopropyl-2-propyl - *p*-nitrobenzoate is added to an acetone solution of $[Rh_2(CO)_4Cl_2]$ the solution turns a deep red colour within half an hour and a dark precipitate comes out of solution. The reaction has been shown to give the products in scheme 7.4. The organic product, derived from rearrangement of the starting cyclopropane is 5-chloro-2-methyl-2-pentene. The chloride is derived from the $[Rh_2(CO)_4Cl_2]$ starting material. The fate of the rhodium employed is generation of the novel carboxylate complex $[Rh_2(\mu\text{-}O_2C\text{-}C_6H_4\text{-}p\text{-}NO_2)_2(CO)_4]$. These two products account for the lack of catalysis observed in this reaction.

7.4.1 Product identification

5-Chloro-2-methyl-2-pentene is formed in 95% yield from this reaction. The product is most easily characterised by its ^{1}H-N.M.R. spectrum, as well as by its $^{13}C\{^1H\}$ and INEPT ^{13}C-N.M.R. spectra. The spectral data and comparison to that of the literature is summarised in Table 7.3.

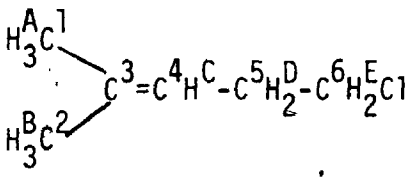
The rhodium complex: $[Rh_2(\mu\text{-}O_2C\text{-}C_6H_4\text{-}p\text{-}NO_2)_2(CO)_4]$ is readily characterised by its infrared spectra (Table 7.4), ^{1}H-N.M.R. spectrum (multiplet at δ8.34 ppm in acetone-d_6) and elemental analysis. Its purity is supported by a sharp melting point (209-210°C). The compound is blue-black in the solid state and is soluble in common





Scheme 7.4 Products of the reaction of $[Rh_2(CO)_4Cl_2]$ with 2-Cyclopropyl-2-propyl - *p*-nitrobenzoate

Table 7.3 ^{1}H and ^{13}C-N.M.R. Spectral Parameters For 5-Chloro-2-methyl-2-pentene



Proton	δ (ppm) Found[a]	Literature[b]
H^A, H^B	1.63, s	1.63, s
	1.69, d; J=1.2 Hz	1.71, s
H^C	5.17, m; J=1.2 Hz, 7.02 Hz	5.12; J=7 Hz
H^D	2.44, quart; J=7.02 Hz	2.20-2.70; J=7 Hz
H^E	3.53, t; J=7.02 Hz	3.45; J=7 Hz

Carbon	δ (ppm)[c] Found	
C^1, C^2	25.8, 17.8	(CH_3's)
C^3	135.1	(tertiary)
C^4	121.2	(methine)
C^5	32.2	(methylene)
C^6	45.1	(methylene)

a) in acetone-d_6 solvent, using acetone quintet as reference, δ2.04 ppm from TMS

b) in $CDCl_3$, relative to TMS from reference 120

c) in acetone-d_6 solvent, using acetone septet as reference δ29.8 ppm relative to TMS

organic solvents; giving an orange solution in acetone. The dichroic nature of carboxylate bridged rhodium complexes has been observed before[113] and has been rationalised in terms of different Rh-Rh interactions in the solid state and solution. Similar type complexes, prepared by the reaction in equation 7.7, have been shown to be dimeric in acetone or benzene solutions based on molecular weight determination in these solvents.[121] A comparison of the infrared

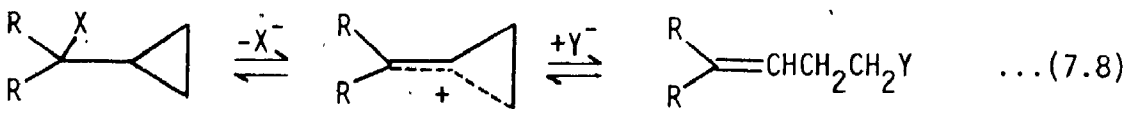
$$[Rh_2(CO)_4Cl_2] \xrightarrow{2AgO_2CR} [Rh_2(\mu\text{-}O_2CR)_2(CO)_4] + 2AgCl \qquad \ldots(7.7)$$

$$R = CH_3,\ CF_3,\ Ph,\ p\text{-}FC_6H_4$$

spectral data for the complex isolated and a very similar complex ($R = p\text{-}FC_6H_4$ in equation 7.7) is given in Table 7.4.

7.4.2 Discussion of the reaction

The formation of 5-chloro-2-methyl-2-pentene from 2-cyclopropyl-2-propyl - *p*-nitrobenzoate is not totally unexpected based upon similar organic systems which undergo the process in equation 7.8.[75] However, 2-cyclopropyl-2-propyl - *p*-nitrobenzoate under solvolysis conditions gives only unrearranged 2-cyclopropyl-2-propanol and no olefin products.[122] The reaction observed is most closely related to a study



...(7.8)

of the conversion of cyclopropylmethanols into homoallylic halides using Lewis acids such as MgX_2 (X = Cl, Br or I) as shown in

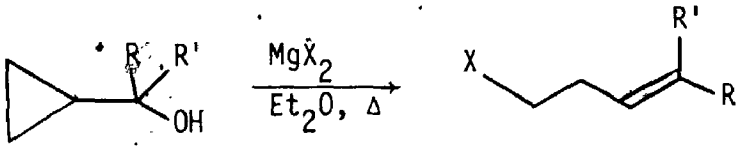
Table 7.4 Infrared Bands (in cm^{-1}) of Bridged Carboxylate Complexes of the Type: $[Rh_2(\mu\text{-}O_2CR)_2(CO)_4]$ (Nujol and Halocarbon Oils)

Compound	CO stretch	Asym COO	Sym COO	Other strong bands
R=p-$NO_2C_6H_4$ [a] Blue Black m.p. 209-210°C	2076 vs, 2021 vs	1605	1555	1530 m, 1430 s 1345 s
R=p-FC_6H_4 [b] Blue m.p. 144°C	2079 vs, 2024 vs 1984 w	1603	1546	1508 s, 1408 s, 1403 s

a) this work

b) reference 121

equation 7.9. 5-Chloro-2-methyl-2-pentene itself was prepared from

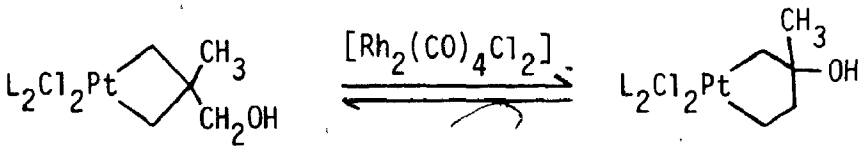


...(7.9)

2-cyclopropyl-2-propanol by this reaction. Cyclopropyl carbinol, however, did not react at an appreciable rate. These authors also found that substitution of an alkoxy functionality for hydroxy did not preclude reaction, it only slowed the rate. Unfortunately no ester functionalities were attempted which could be used in comparison to work done in this thesis.

7.5 Reactions of $[Rh_2(CO)_4Cl_2]$ with some platinacyclobutanes

As seen in section 7.3, $[Rh_2(CO)_4Cl_2]$ is able to effect the transformation of 1-methylcyclopropyl carbinol to 1-methylcyclobutanol in good yield (equation 7.2). Also, an estimate was obtained for the difference in ring strain in the three and four membered carbocycles. It was hoped that $[Rh_2(CO)_4Cl_2]$ might also catalyse the ring expansion reaction of a platinacyclobutane to a platinacyclopentane complex as seen in equation 7.10.



...(7.10)

If such a reaction could be observed then an equilibrium mixture of the two metallacycles would give a direct estimate of their relative ring strains. This value has been estimated to be ≤ 5 kcal mol^{-1}, by some authors, for a similar Pt(II) system,[23,96] though work in this

thesis suggests a larger value in this Pt(IV) system studied. Unfortunately, as will be discussed, $[Rh_2(CO)_4Cl_2]$ does not catalyse the reaction in equation 7.10.

When a catalytic amount of the bis(pyridine) adduct: $[PtCl_2(CH_2C(CH_3)(CH_2OH)CH_2)py_2]$, 4, was dissolved in acetone and allowed to react with $[Rh_2(CO)_4Cl_2]$ for several days at room temperature, the solution blackened somewhat. The starting platinacyclobutane, however, was recovered unchanged indicating the black insoluble species was rhodium metal.

The bipy complex, $[PtCl_2(CH_2C(CH_3)(CH_2OH)CH_2)bipy]$ was prepared directly from the pyridine analogue by addition of 2-2'-bipyridine and filtration of the insoluble product. When this complex was dissolved in acetone and, likewise, allowed to react with $[Rh_2(CO)_4Cl_2]$ the starting platinacyclobutane was again recovered unchanged (as identified by its ^{1}H-N.M.R. spectrum), though some rhodium metal was also present.

The above results clearly show that $[Rh_2(CO)_4Cl_2]$ does not catalyse the reaction in equation 7.10. However, they do not preclude the possibility that such an equilibrium might exist if a suitable catalyst could be found.

CHAPTER 8

EXPERIMENTAL

8.1 General

^{1}H-N.M.R. spectra were recorded using a Varian T60 N.M.R. Spectrometer at 60 MHz or a Varian XL100 Spectrometer at 100 MHz. ^{13}C-N.M.R. spectra were recorded using a Varian XL100 instrument operating at 25.2 MHz, a Varian XL200 instrument at 50.309 MHz or a Bruker WH-400 spectrometer at 100.618 MHz. ^{2}H-N.M.R. spectra were recorded using a Varian XL200 instrument operating at 30.710 MHz.

The infrared spectra of solid compounds were recorded as nujol or halocarbon oil mulls. Solution infrared spectra were run in either methylene chloride, chloroform or acetone using 1.0 mm NaCl cells. The spectra were all recorded on a Beckman 4250 instrument.

Mass spectra were recorded on a Varian MAT 311A instrument operating under conditions specified in the text.

Microanalyses were performed by Guelph Chemical Laboratories, Guelph, Ontario, Canada.

Cyclopropanes, not synthesised, were obtained from Aldrich and were used without further purification. Ethylene and carbon monoxide were obtained from Linde. K_2PtCl_4 and $RhCl_3 \cdot 3H_2O$ were obtained from Strem Chemicals Inc. All deuterated solvents were obtained from MSD Isotopes whereas all protiated solvents were obtained from Fischer Scientific Company. Pyridine and methanesulphonyl chloride were supplied by Eastman Kodak Co. $[Pt(CH_3)_2(bipy)]$ was kindly supplied by Mr. P.K. Monaghan. ^{13}C-labelled cyclopropyl carbinol was prepared

by the method of Golding et al[123] with experimental assistance from Mr. T. McLean. Most other chemicals were obtained from Aldrich.

Solvents were generally used as is except for anhydrous tetrahydrofuran and methylene chloride which were distilled from CaH_2.

8.2 Preparation of Transition Metal Starting Materials

8.2.1 Zeise's Salt, $K[PtCl_3(C_2H_4)]\cdot H_2O$

Potassium tetrachloroplatinate(II), K_2PtCl_4, (4.5g, 10.8 mmol) was added to 45 mL of 5 M aqueous hydrochloric acid in a 125 mL two necked flask equipped with a magnetic stirrer. The flask was sealed with a rubber septum fitted with two needles, one of which extended into the solution and used as an inert gas inlet and another used as a gas outlet. The other opening is fitted with a thermometer couple through which is placed a disposable Pasteur pipette which extends into the solution and is attached to a cylinder of ethylene. The flask is then flushed with nitrogen for thirty minutes during which time ethylene is intermittently bubbled to aid flushing. With a hypodermic syringe 5 mL of distilled water was added to hydrated tin(II) chloride, $SnCl_2\cdot 2H_2O$, (.04 g, 0.2 mmol) and the resulting suspension was quickly transferred, also by means of a hypodermic syringe, to the flask containing the K_2PtCl_4. A stream of ethylene was slowly bubbled through the resulting stirred reaction mixture. During the course of the reaction, the initial red-brown suspension turns yellow and all the solid dissolves as the reaction proceeds. After 12 hrs the reaction mixture was warmed to 45°C and clarified through a sintered glass funnel. The solution was evaporated on a rotary evaporator

until yellow crystals initially formed. The flask was then cooled in a salt-ice mixture yielding a yellow precipitate of needle shaped crystals of Zeise's salt. The $K[PtCl_3(C_2H_4)]\cdot H_2O$ was filtered and then washed with a small amount of ice water. The product was dried in vacuo giving 3.2 g (76%). The filtrate was then allowed to evaporate at room temperature and the resulting solids were extracted with methanol (3 x 10 mL). KCl and other impurities were filtered off and the methanol was evaporated to give a further yield of Zeise's salt. Total yield was 82%.

8.2.2 Zeise's Dimer: $[Pt_2Cl_2(\mu\text{-}Cl)_2(C_2H_4)_2]$[13]

Zeise's salt (1 g, 2.6 mmols) was added to 15 mL of absolute ethanol. 0.5 mL of concentrated HCl was added dropwise with stirring. Potassium chloride was precipitated immediately. The mixture was clarified by filtering through a fine sintered glass filter. The solvent was pumped off to give a bright orange product which was washed with a little cold ethanol and dried under vacuum overnight. The yield was 0.73 g, 97%.

8.2.3 $[PtCl_2(SMe_2)_2]$

K_2PtCl_4 (5 g, 12.0 mmol) was dissolved in 30 mL of water and the resulting solution was filtered. Dimethyl sulphide (2.5 mL) was added to the stirred solution. The reaction was allowed to proceed at room temperature for 2 1/2 hrs and for a further hour at 80°C. The aqueous solution was evaporated to dryness and the residue extracted with CH_2Cl_2 (3 x 30 mL). The organic layer was filtered and dried

over Na_2SO_4 then filtered again and evaporated. The yield of yellow product was 4.14 g (88%). m.p. 157-158°C.

8.2.4 $[PtBr_2(SMe_2)_2]$

This was prepared in an identical fashion as that for the dichloro analogue, $[PtCl_2(SMe_2)_2]$ (8.2.3) except that the K_2PtCl_4 was dissolved in 85 mL of saturated aqueous KBr prior to addition of the dimethyl sulphide. Yield = 4.57 g, (79%) of orange product m.p. = 165-167°C.

8.2.5 $[Pt_2(CH_3)_4(\mu\text{-}SMe_2)_2]$

$[PtCl_2(SMe_2)_2]$, (1 g, 2.78 mmol), was suspended in 75 mL anhydrous ether cooled in an ice-saltwater bath. $LiCH_3$, (12 mL of 1.5 M solution in ether) is added dropwise to the stirred suspension. The reaction is performed under N_2 for one hour. The mixture is transferred to a separatory funnel and 25 mL of saturated aqueous NH_4Cl solution is added. The ether layer is obtained, washed with water (1 x 10 mL) and dried over $MgSO_4$. The ether was removed on a rotary evaporater giving a light brown residue (.65 g, 81%).

8.2.6 $[PtBrCH_3(SMe_2)_2]$

$[Pt_2(CH_3)_4(\mu\text{-}SMe_2)_2]$, (182 mg, 0.32 mmol) was dissolved in CH_2Cl_2 (2 mL) and SMe_2 (47 µL, 0.64 mmol) was added. The mixture was stirred for 30 minutes at room temperature after which time $[PtBr_2(SMe_2)_2]$ (303 mg, 0.64 mmol), dissolved in CH_2Cl_2 (6 mL), was added dropwise with stirring. The reaction flask was covered in foil and allowed to stir at room temperature for 21 hrs. The clear

light yellow solution was filtered and hexanes (5 mL) was added to drive off the dimethyl sulphide. After evaporation of the solvent the residue was dried on high vacuum to give a light brown residue (447 mg, 92%).

8.2.7 $[PtBrCH_3(bipy)]$

$[PtBrCH_3(SMe_2)_2]$, (201 mg, 0.485 mmol), was dissolved in 2 mL of dry benzene and the solution filtered. A 5% mole excess of 2,2'-bipyridine (80 mg) was also dissolved in 1 mL of dry benzene and the solution filtered. These two solutions were combined in the dark and allowed to react at 0°C for 3 hours. Orange needles of the desired product precipitated and were filtered, washed with n-pentane (2 x 3 mL) and anhydrous ether (1 x 2 mL). The yield of the product was 202 mg (93%). ^{1}H-N.M.R. in CD_2Cl_2 CH_3 at δ1.10 ppm, $^2J(^{195}Pt-^1H)$=78 Hz. m.p. 180°C (d).

8.2.8 $[Rh_2(CO)_4Cl_2]$[112]

Carbon monoxide is passed through a finely divided sample of $[RhCl_3 \cdot 3H_2O]$, (3.0 g, 11.5 mmol), at 100°C so as to maintain a convenient rate of sublimation of the product. At regular intervals the water is removed with absorbent cotton and the red-orange product isolated. After six hours the reaction is complete and only a small amount of starting material (presumably as the inert $[RhCl_3]$) remains unreacted. The product was sublimed under vacuum at 80°C to give 2.05 g (87%) of the desired red-orange product. The product was stored in a desiccator.

8.3 Preparation of Cyclopropanes (see Tables 8.1 and 8.2 for ^1H and ^{13}C-N.M.R. data)

8.3.1 Cyclopropyl carbinol

Cyclopropanecarboxylic acid (5.0 g, 58.1 mmol) in 10 mL of anhydrous ether was reduced with 1.05 equivalents of lithium aluminum hydride in 75 mL of anhydrous ether. The acid was added dropwise to the suspension at a rate to maintain gentle reflux. The top of the condenser was fitted with a $CaCl_2$ drying tube. After addition (30 mins.), the mixture was allowed to react at reflux for an additional three hours. Distilled water was then added dropwise with caution until there was no further effervescing and the precipitate was a pure white colour. The suspension was allowed to settle and then decanted and filtered through Celite. The Celite and precipitate were washed with ether (2 x 50 mL). The ether extracts were combined, dried over K_2CO_3 and evaporated at 0°C on a rotary evaporater. The residue was fractionally distilled under reduced pressure to give 3.23 g (77% yield) of the product. b.p. 35-37°C/16 mm Hg.

8.3.2 Cyclopropyl-α,α-d_2 carbinol

The procedure used was the same as that for the preparation of cyclopropyl carbinol (8.3.1) except that lithium aluminum deuteride, containing 99 atom % deuterium, was used to reduce the acid. The yield of the product was 2.68 g (62%).

8.3.3 Cyclopropylcarbinyl methanesulphonate

To a stirred solution of cyclopropyl carbinol (1 g, 13.9 mmol)

in CH_2Cl_2 (1 mL) and triethylamine (2.8 g, 27.8 mmol), at 0°C, was added methanesulphonyl chloride (1.59 g, 13.9 mmol) in CH_2Cl_2 (1 mL). After stirring for an additional 2 hours at 0°C 2 mL of cold CH_2Cl_2 was added and the organic phase washed sequentially with ice water (3 x 4 mL), 2% Na_2CO_3 at 0°C (1 x 4 mL) and again with 4 mL of ice water. After drying over K_2CO_3 the solvent was removed in vacuo at 0°C over a period of five hours. The residue obtained (1.51 g, 72%) was used without further purification.

8.3.4 Cyclopropylcarbinyl-α,α-d_2 methanesulphonate

The procedure was the same as for the preparation of cyclopropylcarbinyl methanesulphonate (8.3.3) except that the ester was prepared from cyclopropyl-α,α-d_2 carbinol. The yield of product was 1.33 g (65%).

8.3.5 1-Methylcyclopropyl carbinol

1-Methylcyclopropanecarboxylic acid (10.0 g, 0.1 mol) was reduced in 150 mL of anhydrous ether with 1.05 equivalents of lithium aluminum hydride. The acid in 25 mL of anhydrous ether was added dropwise with stirring to the suspension at a rate to maintain a gentle reflux. The suspension was allowed to reflux for an additional 3 hours after which time distilled water was added with caution until there was no more effervescing and the precipitate was a pure white. The suspension was allowed to settle and the solution and suspension were filtered through a Celite pad. The Celite was washed with ether (3 x 25 mL) and the ethereal solution was dried over K_2CO_3. The ether was removed under reduced pressure at 0°C. The residue was dried

again over K_2CO_3 prior to distillation which gave one main fraction of the title compound (6.63 g, 77%). b.p. 37-39°C/15 mm Hg.

8.3.6 1-Methylcyclopropyl-α,α-d_2 carbinol

The procedure was the same as for the preparation of 1-methylcyclopropyl carbinol (8.3.5) except that lithium aluminum deuteride, containing 99 atom % deuterium, was used to reduce the acid, (5.0 g, .05 mol). The yield of product was 2.5 g (57%).

8.3.7 1-Methylcyclopropylcarbinyl methanesulphonate

To a stirred solution of 1-methylcyclopropyl carbinol (1 g, 11.6 mmol) in CH_2Cl_2 (1 mL) and triethylamine (2.35 g, 23.2 mmol), at 0°C, was added dropwise methanesulphonyl chloride (1.33 g, 11.6 mmol) in CH_2Cl_2 (1 mL). After stirring for an additional 2 hours at 0°C, cold CH Cl (2 mL) was added and the organic phase washed sequentially with ice water (3 x 4 mL), 2% aqueous Na_2CO_3 solution at 0°C (1 x 4 mL) and again with ice water (1 x 4 mL). After evaporation under high vacuum for four hours at 0°C there remained a light yellow oil (0.98 g, 52% yield) which was used without further purification.

8.3.8 1-Methylcyclopropylcarbinyl-α,α-d_2 methanesulphonate

The procedure used was the same as that for the preparation of 1-methylcyclopropylcarbinyl methanesulphonate (8.3.7) except that lithium aluminum deuteride, containing 99 atom % deuterium was used to reduce the acid. The yield of produce was 1.16 g (62%).

8.3.9 2-Cyclopropyl-2-propanol[52]

Cyclopropyl methyl ketone (8.4 g, 0.1 mol) in anhydrous ether (25 mL) was added over a period of forty-five minutes to a solution of methyl iodide (17.04 g, 0.12 mol) and magnesium turnings (2.92 g, 0.12 mol) in anhydrous ether (100 mL) at 0°C. After the addition was completed, the reaction mixture was refluxed for thirty minutes, poured onto ice and filtered through a Celite pad. The organic layer was separated and the aqueous layer was extracted with ether (2 x 75 mL). The combined organic layers were washed once with water (50 mL) and dried with K_2CO_3. The solvent was removed and the residue distilled under a reduced pressure of 16 mm Hg to give a single fraction (41-44°C) of the desired product (8.2 g, 82%).

8.3.10 2-Cyclopropyl-2-propyl - *p*-nitrobenzoate

2-Cyclopropyl-2-propanol (1 g, 0.01 mol) was reacted with *p*-nitrobenzoyl chloride (1.94 g, 0.0105 mol) in dry pyridine (10 mL) at -5°C for 72 hours. Cold CH_2Cl_2 (30 mL) was added and the organic phase was washed with ice water (3 x 30 mL), cold 5% aqueous Na_2CO_3 solution (1 x 30 mL) and again with ice water (1 x 30 mL). The organic layer was dried over K_2CO_3, filtered and evaporated to give an oily solid which was recrystallised from hexanes to give a white crystalline product (2.0 g, 70%). m.p. = 88-89°C.

8.3.11 α-Methylcyclopropylcarbinyl-*p*-nitrobenzoate

α-Methylcyclopropyl carbinol (1 g, 11.6 mmol) was reacted with *p*-nitrobenzoyl chloride (2.26 g, 12.2 mmol) in dry pyridine (10 mL) at

-5°C for 72 hours. Cold CH_2Cl_2 (30 mL) was added and the organic phase was washed with ice water (3 x 30 mL), cold aqueous 5% Na_2CO_3 solution (1 x 30 mL) and again with ice water (1 x 30 mL). The organic layer was dried over K_2CO_3, filtered and evaporated to yield an orange oil which crystallised upon standing. The product was recrystallised twice from hexanes to give 1.9 g (70%) of white crystals. m.p. = 55-56°C.

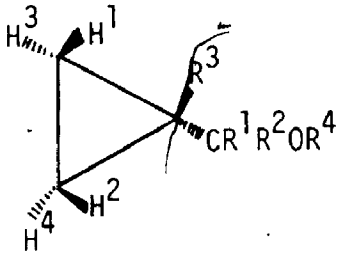
8.4 Preparation of Platinacyclobutane Complexes

8.4.1 $[PtCl_2(CH_2CH(CH_2OH)CH_2)py_2]$, 1.

Zeise's dimer (100 mg, 0.172 mmol) was placed in a round bottom flask fitted with a condenser, drying tube and stirring bar. The dimer was dissolved in dry THF (5 mL) and cyclopropyl carbinol (125 mg, 1.72 mmol) was added dropwise to the stirring solution. The reaction was allowed to proceed overnight at room temperature after which time the solution was filtered through a K_2CO_3 plug and evaporated to dryness under high vacuum. To the solid tetrameric complex was added CH_2Cl_2 (5 mL) and then pyridine was added to the stirred suspension, kept at 0°C, until the solution cleared. This solution was then evaporated to dryness and the residue washed with anhydrous ether (1 x 1 mL). The last traces of ether and residual pyridine were removed under high vacuum to give an amorphous pale yellow compound. This was then recrystallised from CH_2Cl_2 solution by the addition of n-pentane to give a pale yellow product which was identified by its ^1H and ^{13}C-N.M.R. spectra (Chapter 2). Yield 86 mg (50%); m.p. 93-95°C (dec.).

Analysis found: C, 32.26; H, 3.60; N, 5.08. Calculated for

Table 8.1 ^{1}H-N.M.R. Date For Synthesized Cyclopropanes



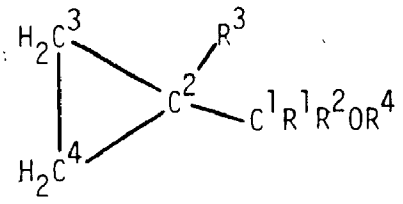
Compound	H^1, H^2	H^3, H^4	R^1 R^2	R^3	R^4
$R^1=R^2=R^3=R^4=H$[b]	0.54.m	0.24,m	3.35,d	1.02,m	4.00,s
$R^1=R^2=R^3=H$; R^4=Ms	0.70,m	0.42,m	4.09,d	1.23,m	3.04,s
$R^1=R^2=R^4=H$; $R^3=CH_3$	0.42,m	0.31,m	3,37,s	1.13,s	3.47,s
$R^1=R^2=H$; $R^3=CH_3$; R^4;Ms	0.57,m	0.48,m	4.02,s	1.20,s	3.04,s
$R^1=R^2=CH_3$; $R^3=R^4=H$	0.36,m	0.26,m	1.18,s	0.92,m	1.81,s
$R^1=R^2=CH_3$; $R^3=H$; R^4=PNB	0.58,m	0.52,m	1.57,s	1.56,m	8.21,m
$R^1=R^3=H$; $R^2=CH_3$; R^4=PNB[c]	0.55,m	0.55,m	4.36,m/ 1.46,d	1.12,m	8.25,m
$R^1=R^2=H$; R^3=Ph; R^4=Ms	0.96,m	0.96,m	4.08,s	6.96,m	2.61,s

a) in $CDCl_3$ relative to residual $CHCl_3$ at 7.24 ppm relative to TMS

b) $J_{1,2\text{-}3} = 6.7$ Hz

c) $J_{1,2} = 6.3$ Hz

Table 8.2 ^{13}C-N.M.R. Data For Some Synthesized Cyclopropanes



Compound	C^1	C^2	C^3	C^4	Others
$R^1=R^2=R^3=H$; R^4=Ms	75.8	10.2	3.8	3.8	R^4=37.1
$R^1=R^2=R^4=H$; $R^3=CH_3$	70.4	17.9	10.8	10.8	R^3=20.6
$R^1=R^2$=H; R^3;CH_3;R^4;Ms	78.8	15.4	11.7	11.7	R^3=20.4; R^4=37.3
$R^1=R^2=CH_3$; R^3=H; R^4=PNB	84.7	20.6	2.1	2.1	R^1,R^2=24.8[b]
$R^1=R^3$=H; $R^2=CH_3$; R^4=PNB[c]	77.4	16.4	2.7	3.9	R^2=19.9,d
$R^1=R^2$=H; R^3=Ph; R^4=Ms	78.2	25.0	12.2	12.2	R^4=37.3,e

a) in $CDCl_3$ relative to central $^{13}CDCl_3$ peak at +77.0 ppm relative to TMS

b) R^4 = 123.9, 130.5, 137.5, 150.3, 163.6

c) assignments for C-3 and C-4 may be reversed

d) R^4 = 123.5, 130.7, 136.4, 150.4, 164.3

e) R^3 = 127.1, 128.5, 129.0, 141.2

$C_{14}H_{18}Cl_2N_2OPt$: C, 33.89; H, 3.66; N, 5.65.

8.4.2 $[PtCl_2\{CH_2CH(CH(CH_3)OH)CH_2\}py_2]$, 2

This compound was prepared by the same procedure as for $[PtCl_2(CH_2CH(CH_2OH)CH_2)py_2]$, (8.4.1), employing α-methylcyclopropyl carbinol (150 mg, 1.73 mmol). The light yellow product was recrystallised from CH_2Cl_2/n-pentane: yield 81 mg (46%), m.p. 120-127°C (dec.). Analysis found: C, 34.15; H, 3.53; N, 5.74. Calculated for $C_{15}H_{20}Cl_2N_2OPt$: C, 35.31; H, 3.95; N, 5.49.

8.4.3 $[PtCl_2\{CH_2CH(C(CH_3)_2OH)CH_2\}py_2]$, 3.

This compound was prepared by the same procedure as for $[PtCl_2(CH_2CH(CH_2OH)CH_2)py_2]$ (section 8.4.1), employing 2-cyclopropyl-2-propanol (125 mg, 1.24 mmol). The light yellow product was recrystallised from CH_2Cl_2/n-pentane = yield 124 mg (69%), m.p. 119-120°C.

Analysis found: C, 36.37; H, 4.26; N, 5.20. Calculated for $C_{16}H_{22}Cl_2N_2OPt$: C, 36.65; H, 4.23; N, 5.34.

8.4.4 $[PtCl_2(CH_2C(CH_3)(CH_2OH)CH_2)py_2]$; 4.

This compound was prepared by the same procedure as for $[PtCl_2(CH_2CH(CH_2OH)CH_2)py_2]$, (8.4.1), employing 1-methylcyclopropyl carbinol (150 mg, 1.91 mmol). The white product was recrystallised from CH_2Cl_2/n-pentane: yield 111 mg (63%), m.p. 116-117°C (dec.).

Analysis found: C, 35.24; H, 3.92; N, 5.41. Calculated for $C_{15}H_{20}Cl_2N_2OPt$: C, 35.31; H, 3.95; N, 5.49.

8.4.5 $[\overline{PtCl_2(CH_2C(Ph)(CH_2OH)CH_2)}py_2]$; 5.

This compound was prepared by the same procedure as for $[\overline{PtCl_2(CH_2CH(CH_2OH)CH_2)}py_2]$, (8.4.1), employing 1-phenylcyclopropyl carbinol (250 mg, 1.72 mmol) except that owing to the involatile nature of the cyclopropane derivative the tetramer was washed with anhydrous ether (3 x 1 mL) prior to pyridine addition. The white product was recrystallised from CH_2Cl_2/n-pentane: yield 138 mg (70%), m.p. 121-123°C (dec.).

Analysis found: C, 41.90; H, 3.64; N, 5.30. Calculated for $C_{20}H_{22}Cl_2N_2OPt$: C, 41.96; H, 3.88; N, 4.89.

8.4.6 $[\overline{PtCl_2(CH_2CH(CH_2OMs)CH_2)}py_2]$; 6.

This compound was prepared by the same procedure as for $[\overline{PtCl_2(CH_2CH(CH_2OH)CH_2)}py_2]$, (8.4.1), employing cyclopropylcarbinyl methanesulphonate (104 mg, 0.69 mmol), except that owing to the involatile nature of the cyclopropane derivative the tetramer was washed well with anhydrous ether (6 x 0.5 ml) prior to pyridine addition. The product from pyridine addition was passed down a short column of Florisil, eluting with CH_2Cl_2. The solvent was then removed and the product washed to give a pale yellow residue. This light yellow product was recrystallised from CH_2Cl_2/n-pentane: yield 113 mg (57%), m.p. 56-59°C (dec.).

Analysis found: C, 31.71; H, 3.79; N, 4.94. Calculated for $C_{15}H_{20}Cl_2N_2O_3PtS$: C, 31.37; H, 3.51; N, 4.88.

8.4.7 $[PtCl_2(CH_2CH(CHCH_3OPNB)CH_2)py_2]$; 7.

This compound was prepared by the same procedure as for $[PtCl_2(CH_2CH(CH_2OH)CH_2)py_2]$, (8.4.1), employing α-methylcyclopropylcarbinyl-*p*-nitrobenzoate (250 mg, 1.06 mmol), except that the tetramer was washed well with anhydrous ether (5 x 1 mL) prior to pyridine addition. The white product was recrystallised from CH_2Cl_2/n-pentane: yield 125 mg (55%), m.p. 151-153°C.

Analysis found: C, 39.95; H, 3.60; N, 6.20. Calculated for $C_{22}H_{23}Cl_2N_3O_4Pt$: C, 40.07; H, 3.52; N, 6.37.

8.4.8 $[PtCl_2\{CH_2CH(C(CH_3)_2OPNB)CH_2\}py_2]$; 8.

This compound was prepared by the same procedure as for $[PtCl_2(CH_2CH(CH_2OH)CH_2)py_2]$, (8.4.1), employing 2-cyclopropyl-2-propyl - *p*-nitrobenzoate (250 mg, 1.00 mmol), except that the tetramer was washed with anhydrous ether (4 x 1 mL) prior to pyridine addition. The white product was recrystallised from CH_2Cl_2/n-pentane: yield 156 mg (67%), m.p. 92-96°C (dec.).

Analysis found: C, 39.20; H, 3.72; N, 5.83. Calculated for $C_{23}H_{25}Cl_2N_3O_4Pt$: C, 41.02; H, 3.74; N, 6.24.

8.4.9 $[PtCl_2(CH_2C(CH_3)(CH_2OMs)CH_2)py_2]$; 9.

This compound was prepared by the same procedure as for $[PtCl_2(CH_2CH(CH_2OH)CH_2)py_2]$, (8.4.1), employing 1-methylcyclopropylcarbinyl methanesulphonate (210 mg, 1.28 mmol), except that the tetramer was washed with anhydrous ether (2 x 2 mL) prior to pyridine addition. The light yellow product was recrystallised from

CH_2Cl_2/n-pentane: yield 98 mg (48%), m.p. 86-91°C (dec.): Analysis found: C, 32.72; H, 3.88; N, 4.76. Calculated for $C_{16}H_{22}Cl_2N_2O_3PtS$: C, 32.66, H, 3.77; N, 4.76.

8.4.10 $[PtCl_2\{CH_2C(Ph)(CH_2OMs)CH_2\}py_2]$; 10.

This compound was prepared by the same procedure as for $[PtCl_2(CH_2CH(CH_2OH)CH_2)py_2]$, (8.4.1), employing 1-phenylcyclopropyl-carbinyl methanesulphonate (150 mg, 0.66 mmol), except that the tetramer was washed with anhydrous ether (1 x 1 mL) prior to pyridine addition. The light yellow product was recrystallised from CH_2Cl_2/n-pentane: Yield 63 mg (28%), m.p. 132-135 (dec.). A satisfactory analysis could not be obtained for this compound owing to $[PtCl_2py_2]$ impurities.

8.4.11 $[Pt(CH_2CH(CH_2OH)CH_2)(bipy)]$; 11.

$[PtCl_2(CH_2CH(CH_2OH)CH_2)py_2]$, 1, (100 mg, 0.20 mmol) was dissolved in CH_2Cl_2 (2 mL) and the solution filtered into a round bottom flask wrapped in aluminum foil. 5% molar excess of 2,2'-bipyridine was added to this solution and the reaction flask swirled. The solution was placed in the fridge for three hours after which time yellow crystals of the product had formed. The solvent was removed by pipette and the crystals washed with anhydrous ether. The crystals were dried in vacuo to give 82 mg (82%) of the title compound. The compound was identified by its ^{1}H-N.M.R. spectrum (Table 2.1), m.p. 196-200°C (dec.).

8.4.12 $[PtCl_2\{CH_2CH(C(CH_3)_2OH)CH_2\}(bipy)]$; 12.

This compound was prepared by the same method as for

$[PtCl_2(CH_2CH(CH_2OH)CH_2)bipy]$,(8.4.11), employing the bis(pyridine) complex, 3 (75 mg, 0.14 mmol). The yield was 64 mg (85%) of the title compound, m.p. >210°C (dec.).

8.4.13 $[PtCl_2\{CH_2C(Ph)(CH_2OH)CH_2\}(bipy)]$; 13.

This compound was prepared by the same method as for $[PtCl_2(CH_2CH(CH_2OH)CH_2)(bipy)]$, (8.4.11), employing the bis(pyridine) complex, 5 (125 mg, 0.22 mmol). The yield was 110 mg (88%) of the title compound. m.p. >260°C (dec.).

8.4.14 $[PtCl_2(CH_2CH(CH_2OMs)CH_2)(bipy)]$; 14.

This compound was prepared by the same method as for $[PtCl_2(CH_2CH(CH_2OH)CH_2)(bipy)]$, (8.4.11), employing the bis(pyridine) complex, 6 (110 mg, 0.19 mmol). The yield was 78 mg (71%) of the title compound, m.p. >195°C (dec.).

8.4.15 $[PtCl_2\{CH_2C(Ph)(CH_2OMs)CH_2\}(bipy)]$; 15.

This compound was prepared by the same method as for $[PtCl_2(CH_2CH(CH_2OH)CH_2)(bipy)]$, (8.4.11), employing the bis(pyridine) complex, 10 (60 mg, 0.09 mmol). The yield was 50 mg (83%) of the title compound, m.p. >235°C (dec.).

8.5 Experimental details for chapter 4

8.5.1 Solvolysis of $[PtCl_2(CH_2CH(CH_2OMs)CH_2)py_2]$; 6.

$[PtCl_2(CH_2CH(CH_2OMs)CH_2)py_2]$ (95 mg, 0.17 mmol) was dissolved in a 60% acetone-d_6/D_2O (V/V) solvent mixture and allowed to react at

36°C for twenty four hours. The reaction was monitored by ^{1}H-N.M.R. spectroscopy to make sure it had gone to completion. The solvent was removed under high vacuum to give a pale yellow residue. This product was redissolved in acetone and K_2CO_3 (0.200 g) was added. Water was then added dropwise to this suspension until a saturated aqueous phase resulted. The layers were stirred intimately for fifteen minutes after which time the solution was evaporated to dryness. The residue was extracted with CH_2Cl_2 (5 x 2 mL) until there was no more colour in the extractions. The methylene chloride solution was filtered and evaporated until the total solvent volume was approximately 1 mL. n-Pentane was added which caused precipitation of the product. The solvent was decanted and the residue dried to give pale yellow [$\overline{PtCl_2(CH_2CHOHCH_2CH_2)}py_2$], 16, (70 mg, 84%). m.p. 135-140°C (dec.).

Analysis found: C, 33.97; H, 3.88; N, 5.58. Calculated for $C_{14}H_{18}Cl_2N_2OPt$: C, 33.88; H, 3.60; N, 5.64.

8.5.2 Solvolysis of [$\overline{PtCl_2(CH_2CH(CHCH_3OPNB)CH_2)}py_2$]; 7

[$\overline{PtCl_2(CH_2CH(CHCH_3OPNB)CH_2)}py_2$] (145 mg, 0.22 mmol) was solvolysed by the procedure described above (section 8.5.1) in 70% aqueous acetone at 40°C for 120 hours. Upon purification, as before, light brown [$\overline{PtCl_2(CHCH_3CHOHCH_2CH_2)}py_2$], 20, (73 mg, 65%) remained. m.p. 125°C (dec.).

8.5.3 Solvolysis of [$\overline{PtCl_2\{CH_2CH(C(CH_3)_2OPNB)CH_2\}}py$]; 8

[$\overline{PtCl_2\{CH_2CH(C(CH_3)_2OPNB)CH_2\}}py_2$], 8, was solvolysed by the same method as described above (section 8.5.1) and by varying the reaction conditions. The product isolated, however, was always

$[PtCl_2py_2]$ as identified by its m.p., solubility and ^{1}H-N.M.R. spectrum.

8.5.4 Solvolysis of $[\overline{PtCl_2(CH_2C(CH_3)(CH_2OMs)CH_2)}py_2]$; 9

$[\overline{PtCl_2(CH_2C(CH_3)(CH_2OMs)CH_2)}py_2]$, 9, (125 mg, 0.21 mmol) was solvolysed by the procedure described above (section 8.5.1) for 30 hours. Upon purification, as before, light yellow $[\overline{PtCl_2(CH_2C(CH_3)OHCH_2CH_2)}py_2]$, 18, (95 mg, 88%) was isolated. m.p. 105-110°C (dec.).

Analysis found: C, 35.29; H, 3.97; N, 5.46. Calculated for $C_{15}H_{20}Cl_2N_2OPt$: C, 35.31; H, 3.95; N, 5.49.

8.5.5 Solvolysis of $[\overline{PtCl_2\{CH_2C(Ph)(CH_2OMs)CH_2\}}py_2]$; 10

$[\overline{PtCl_2\{CH_2C(Ph)(CH_2OMs)CH_2\}}py_2]$, 10, was solvolysed by the same method as described above, (8.5.1), and by the reaction conditions. The product isolated, however, was always $[PtCl_2py_2]$ as identified by its m.p., solubility and ^{1}H-N.M.R. spectrum.

8.5.6 Solvolysis of $[\overline{PtCl_2(CH_2CH(CH_2OMs)CH_2)}(bipy)]$; 14

$[\overline{PtCl_2(CH_2CH_2(CH_2OMs)CH_2)}(bipy)]$, 14, (80 mg, 0.14 mmol) was solvolysed for 100 hours according to the procedure outlined above, (8.5.1). Upon purification, as before, light yellow $[\overline{PtCl_2(CH_2CHOHCH_2CH_2)}(bipy)]$, 17, (57 mg, 83%) remained.

8.5.7 Solvolysis of $[\overline{PtCl_2\{CH_2C(Ph)(CH_2OMs)CH_2\}}(bipy)]$; 15

$[\overline{PtCl_2\{CH_2C(Ph)(CH_2OMs)CH_2\}}(bipy)]$, 15, (50 mg, 0.076 mmol) was solvolysed in 80% aqueous acetone at 40°C for 120 hours. The reaction mixture was worked up as described above, (8.5.1) to give 20 mg (46%)

of $[\overline{PtCl_2(CH_2C(Ph)(OH)CH_2CH_2)}(bipy)]$; 19. m.p. >175°C (dec.).

8.5.8. Kinetics of the solvolysis of 6, in the absence of and presence of pyridine

A stock solution was prepared containing compound 6 (100 mg, 1.74×10^{-4} mol) dissolved in 2.5 mL of a 60% (V/V) acetone-d_6/D_2O mixture. Five N.M.R. samples of 0.5 mL each were prepared from this solution. Pyridine was added to these solutions, by syringe, so as to have a range of pyridine concentrations from 0 M to .32 M. The solvolysis of these samples was followed at 36°C by observing the ^{1}H-N.M.R. at various time intervals.

8.6 Experimental details for chapter 5

Solvolyses of the ^{13}C and ^2H-labelled complexes

These complexes were solvolysed according to the procedures outlined in section 8.5 for the unlabelled platinacyclobutanes. In every reaction the yield was approximately the same as for the unlabelled case.

8.6.1 Preparation of $[PtBr(CH_3)_2(CH_2CH_2CH{=}CH_2)(bipy)]$; 21

$[Pt(CH_3)_2(bipy)]$ (200 mg, 0.53 mmol) was dissolved in dry acetone (25 mL) and 4-bromo-1-butene (354 mg, 2.62 mmol) was added to this solution with stirring. The mixture was allowed to react for 24 hours, after which time the intense red colour had been dispersed leaving a pale yellow solution. The solution was filtered and taken to dryness. The residue was washed with anhydrous ether (2 x 1 mL) and evaporated again. The solid residue was taken up in CH_2Cl_2 and precipitated with

n-pentane to give 250 mg (92% yield) of the light yellow product. m.p. 202-204°C.

Analysis found: C, 36.97; H, 3.70; N, 5.48; Br, 15:00. Calculated for $C_{16}H_{21}BrN_2Pt$: C, 37.22; H, 4.10; N, 5.43; Br, 15.47.

^{13}C-N.M.R., spectrum in $CDCl_3$: δ-3.8 ppm (CH_3, $^1J_{PtC}$=695Hz); δ17.9 ppm (CH_2, $^1J_{PtC}$=696Hz); δ34.4 ppm (CH_2, $^2J_{PtC}$=20Hz); δ138.5 ppm (CH=); δ113.2 ppm (=CH_2, $^4J_{PtC}$=6Hz). bipy resonances at δ123.5, 126.8, 138.8, 146.9 and 154.9 ppm. This compound decolorizes $KMnO_4$ and CCl_4 solutions of Br_2.

8.6.2 Reaction of 21 with $AgBF_4$

$[PtBr(CH_3)_2(CH_2CH_2CH=CH_2)(bipy)]$, 21, (80 mg, 0.16 mmol) was dissolved in 10 mL of acetone. $AgBF_4$ (29.3 mg, 0.15 mmol) in 2 mL of water, was added with stirring and a precipitate immediately formed. The solution was stirred in the dark for one hour after which time it was filtered to give a light yellow solution which was evaporated to dryness on a high vacuum. The residue was dried in a desiccator, over P_2O_5. The residue was taken up in CH_2Cl_2 and precipitated by the addition of n-pentane to give 65 mg (92% yield) of $[Pt(CH_3)_2(CH_2CH_2CH=CH_2)(OH_2)(bipy)][BF_4]$. m.p. 124-127°C. I.R. CsI pellet BF_4^- (1060 cm^{-1}). Analysis found: C, 36.67; H, 4.29; N, 5.36. Calculated for $C_{16}H_{23}BF_4NOPt$: C, 35.5; H, 4.3; N, 5.2.

8.6.3 Attempted preparation of $[PtBr_2CH_3(CH_2CH_2CH=CH_2)(bipy)]$

This reaction was the same as for the preparation of $[PtBr(CH_3)_2(CH_2CH_2CH=CH_2)(bipy)]$, 21, (8.6.1), employing $[PtBrCH_3(bipy)]$

(102 mg, 0.23 mmol). The solution was allowed to react for four days, after which time it was evaporated to dryness. The light yellow product was very insoluble. The mass spectrum of this compound gave identifiable peaks at m/e = 511 ($PtBr_2$bipy), 446($PtBrCH_3$bipy), 431(PtBrbipy) and 351(Ptbipy), all with the correct isotope pattern. The product is most likely [$PtBr_3CH_3$(bipy)].

8.7 Experimental details for chapter 6

8.7.1 Preparation of bicyclo[2.1.0]pentane

Bicyclo[2.1.0]pentane was prepared by the method of Gassman and Mansfield[101] (scheme 6.1).

i) Diethyl 2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate

Diethyl azodicarboxylate (50 g, 0.287 mol) in 100 mL anhydrous ether, is placed in a 500 ml 2-necked flask equipped with a pressure equalizing dropping funnel and a condenser. Freshly prepared cyclopentadiene (21.3 g, 0.304 mol) is added dropwise over a one hour period to the stirred solution. The reaction is cooled as necessary to maintain a gentle reflux. After addition, the reaction mixture is allowed to stand for an additional two hours. The ether and unreacted cyclopentadiene are distilled off and the residue is fractionally distilled to give a colourless liquid (62.1 g, 91% yield). b.p. 125-130°C (.5 mm Hg). ^{1}H-N.M.R. in $CDCl_3$/TMS δ1.29 (CH_3, t, J=7Hz), 1.75(CH, m) 4.22($\underline{CH_2}CH_3$, quart., J=7Hz), 5.15(CH_2 bridgehead, brs), 652(=CH, m).

ii) Diethyl 2,3-diazabicyclo[2.2.1]heptane

Diethyl 2,3-diazabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (30 g, 0.125 mol) in absolute ethanol (40 mL) is placed in a Parr

pressure reactor along with 100 mg of 10% palladium on carbon catalyst. The bomb is pressurized to 200 psi and stirring is begun. The reaction proceeds with some evolution of heat as the temperature reached 50°C. After 45 minutes the reaction is complete and the procedure is repeated on a second batch. The combined solutions are filtered and the ethanol removed on a rotary evaporator. The residue is fractionally distilled to give 46 g (76%) of the desired product. ^{1}H-N.M.R. in $CDCl_3$/TMS: δ1.29 (CH_3, t, J=7.1Hz), 1.4-1.8 (CH_2+CH, m), 4.22 ($\underline{CH_2}CH_3$, quart., J=7.1Hz), 4.58 (CH_2 bridgehead, brs).

iii) 2,3-Diazabicyclo[2.2.1]hept-2-ene

A stream of N_2 is bubbled through 350 mL of ethylene glycol for 30 minutes with stirring and mild heating (40°C). The gas inlet is replaced with a thermometer, which reaches into the solution and 85% KOH pellets (68 g, 1.21 mol) are added in four portions. Diethyl 2,3-diazabicyclo[2.2.1]heptane-2,3-dicarboxylate (45 g, 0.196 mol) is added rapidly under N_2 to the solution at 125°C. The reaction mixture is kept below 130°C during the addition and allowed to stir for 2 hours at 125°C. The reaction mixture is cooled and then poured slowly into a 2-L beaker containing ice (250 g), water (250 mL) and concentrated HCl (120 mL). When the acidification is complete the reaction mixture is warmed to about 40°C and neutralized with 5N NH_4OH solution. Half of this neutral solution is transferred to a second 2-L beaker and subsequent operations are carried out on both batches.

The solution is stirred slowly and 2N $CuCl_2$ solution (15 mL) is added slowly. The blue-green color is rapidly discharged and a brick red coloration occurs followed by precipitation of the bright red

cuprous chelate. The pH is adjusted to 5-6 by the addition of SN ammonium hydroxide. The solution is heated to 40°C to cause coagulation of the precipitate which is then filtered. The combined precipitate is washed with 20% NH_4Cl (100 mL) 95% ethanol (2 x 100 mL) and cold water (2 x 75 mL).

The damp product is broken up and transferred to a 1-L flask containing a magnetic stirrer and water (100 mL). A cold solution of NaOH (15 g) in water (25 mL) is added slowly with stirring. The stirred yellow orange suspension is then continuously extracted with pentane (350 mL) for three days. The pentane extract is dried over K_2CO_3 and removed on a rotary evaporator at 0°C. A white crystalline residue (11.1 g, 62% yield) of the desired product reamins. ^{1}H-N.M.R. in $CDCl_3$/TMS: δ0.8-2.0 (6 H), 5.20 (2 H; bridgehead).

iv) Bicyclo[2.1.0]pentane

2,3-diazabicyclo[2.2.1]hept-2-ene (3 g, 0.031 mol) is placed in a 10 mL round bottom flask. The flask is heated at 130-140°C to completely remove any traces of pentane. A 15-cm unpacked Hempel column is installed and connected to a receiver flask, fitted with a drying tube, cooled in a dry ice-acetone bath. The complex is pyrolysed by heating to 180-195°C. The bicyclo[2.1.0]pentane is filtered through a plug of $MgSO_4$ to give 1.5 g (71%) yield). ^{1}H-N.M.R. in $CDCl_3$/TMS: δ0.56 (2 H, cyclopropane), 1.45 (4 H), 2.12 (2 H).

8.7.2 Reactions of Zeise's dimer with bicyclo[2.1.0]pentane

Zeise's dimer (100 mg, 0.172 mmol) was dissolved in acetone and bicyclo[2.1.0]pentane (100 mg, 1.47 mmol) was added with stirring. The reaction is allowed to stir for four hours at room temperature,

after which time an orange precipitate product had formed which was insoluble in acetone. This compound was filtered, washed with a little acetone and dried under high vacuum to give 70 mg (61% yield based on $[Pt_2Cl_2(\mu\text{-}Cl)_2(cyclopentene)_2]$). ^{1}H-N.M.R. run in $CDCl_3$: δ1.8 (6 H), 5.6 (2 H).

A low temperature reaction was attempted using Zeise's dimer (25 mg, .043 mmol) and bicyclo[2.1.0]pentane (16 µL) in acetone-d_6 (0.75 mL). The mixture was slowly warmed from -80°C to room temperature. The product was identified by ^{1}H-N.M.R. spectroscopy to be the same as that above.

8.7.3 Reactions of Zeise's dimer with quadricyclane

Zeise's dimer (100 mg, .172 mmol) was dissolved in acetone. When quadricyclane (125 mg, 1.36 mmol) was added dropwise the orange colour of the Zeise's dimer was rapidly discharged and a white insoluble complex formed. This product was filtered to give 110 mg (89% yield) of $[PtCl_2NBD]$ as identified by its ^{1}H-N.M.R. (Table 6.1). A low temperature reaction was also performed using Zeise's dimer (25 mg, .043 mmol) and quadricyclane (10 µL) in acetone-d_6 (0.75 mL). At -80°C the quadricyclane was completely digested yielding a white precipitate so more quadricyclane (0.5 mL) was added and immediately digested. The species in solution was identified to be norbornadiene by its ^{1}H-N.M.R. spectrum (Table 6.1).

8.8 Experimental details for chapter 7

8.8.1 Reactions of cyclopropanes with $[Rh_2(CO)_4Cl_2]$

i) in neat cyclopropane derivatives

$[Rh_2(CO)_4Cl_2]$ (60 mg, 0.154 mmol) is dissolved in each of the cyclopropane derivatives (1 mL) listed in Table 7.1. The reaction vessel is then sealed or kept under N_2. The mixture is allowed to react at 40°C (the temperature was also varied with no success) for 48 hours after which time the cyclopropane was removed by evaporation to give a black residue containing rhodium metal and $[Rh_2(CO)_4Cl_2]$. In the case of the involatile 1-phenylcyclopropyl carbinol the same result was observed from infrared and ^{1}H-N.M.R. spectroscopy on the reaction mixture. Several of the other reactions were also followed by ^{1}H-N.M.R. spectroscopy.

ii) in tetrahydrofuran, acetone or chloroform

$[Rh_2(CO)_4Cl_2]$ (50 mg, 0.129 mmol) is dissolved 5 mL of tetrahydrofuran, acetone or chloroform. 50 mg (0.20 0.69 mmol) of the cyclopropanes in Table 7.1 and the solution kept in a sealed vessel or under N_2 for 48 hours at 40°C. The solutions were also followed by ^{1}H-N.M.R. spectroscopy. Decomposition to rhodium metal was prevalent in all cases and only two reactions proved to give definite reaction. 1-Methylcyclopropyl carbinol gave 1-methylcyclobutanol and $[Rh_2(CO)_4Cl_2]$ as the products (see section 7.3). 2-Cyclopropyl-2-propyl - *p*-nitrobenzoate gave 5-chloro-2-pentene as the organic product and $[Rh_2(\mu\text{-}CO_2\text{-}C_6H_4\text{-}p\text{-}NO_2)(CO)_4]$ as the rhodium complex (see section 7.4).

Analysis found: C, 33.46; H, 1.95; N, 4.20. Calculated for $C_{18}H_8N_2O_{12}Rh$: C, 33.25; H, 1.23; N, 4.31.

iii) Reaction of 1-Methylcyclopropyl carbinol with $[Rh_2(CO)_4Cl_2]$ and carbon monoxide

1-Methylcyclopropyl carbinol (74 mg, 0.86 mmol) is added to a solution of $[Rh_2(CO)_4Cl_2]$ (50 mg, 0.129 mmol) in acetone-d_6 (5 mL). The mixture is quickly transferred to a Parr bomb and the CO pressure set to 150 psi. The temperature was maintained at 40°C for twelve hours after which time the bomb was opened. There were several black crystals of $Rh_6(CO)_{16}$ present on the bottom of the vessel. The solution contained only 1-methylcyclobutyl carbinol and an equilibrium amount of 1-methylcyclopropyl carbinol.

iv) Reaction with 1-methylcyclopropyl-α-α-d_2 carbinol

$[Rh_2(CO)_4Cl_2]$ (40 mg, 0.103 mmol) is added to a solution of 1-methylcyclopropyl-α-α-d_2 carbinol (50 mg, 0.556 mmol) in acetone-d_6 (0.6 mL) and the reaction vessel (containing an N.M.R. tube) is degassed and sealed under vacuum. The reaction is allowed to proceed for 48 hours at 40°C after which time the volatiles are distilled over into the N.M.R. tube which is then sealed and the ^{13}C-N.M.R. spectrum run and compared with that from section 8.8.2. See chapter 7.

8.8.2 Solvolysis of 1-methylcyclopropylcarbinyl-α,α-d_2 methanesulphonate[53]

1-Methylcyclopropylcarbinyl-α,α-d_2 methanesulphonate (566 mg, 3.41 mmol) was solvolysed in a vigorously stirred suspension of $CaCO_3$ (.341 g, 34.1 mmol) in 15 mL of 60% aqueous acetone at 40°C. After 90 minutes 10 mL of pentane was added followed by anhydrous K_2CO_3 until a saturated water solution separated out. The aqueous layer was extracted with a 1:1 pentane-ether mixture (3 x 3 mL). The solvent was removed carefully on a water aspirator vacuum connected in series

to dry ice-acetone trap until no more solvent came off and then for a further 10 minutes under high vacuum at 0°C. The product was shown by ^{1}H-N.M.R. to be clean and free from solvent impurities. 50 mg of this product was sealed in an N.M.R. tube containing 0.6 mL of acetone-d_6 solvent. See chapter 7.

8.8.3 Reactions of $[Rh_2(CO)_4Cl_2]$ with the platinacyclobutanes: $[PtCl_2(CH_2C(CH_3)(CH_2OH)CH_2)py_2]$ (20 mg, 0.040 mmol) or $[PtCl_2(CH_2C(CH_3)(CH_2OH)CH_2)(bipy)]$ (20 mg, 0.040 mmol) are reacted under N_2 with $[Rh_2(CO)_4Cl_2]$ (10 mg, 0.051 mmol) in acetone-d_6 for 48 hours at room temperature the starting platinacyclobutane is recovered unchanged. Some elemental rhodium (or platinum) is present but this is removed by filtration prior to running the ^{1}H-N.M.R. spectrum.

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