

ARENE RUTHENIUM CHEMISTRY

by

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Abstract

This thesis describes the synthesis and reactivity studies of new arene-ruthenium(II) and arene-ruthenium(0) complexes. Ultrasound has been investigated as an alternative energy source, with the overall aim of synthesising arene ruthenium clusters.

Chapter 1 gives an introduction and summary of the known arene ruthenium chemistry reported to date.

Chapter 2 reports the synthesis of $(C_6H_6)Ru(C_2H_4)_2$ and $(MeC_6H_4CHMe_2)Ru(C_2H_4)_2$. Low temperature protonation studies generated $(C_6H_6)Ru(H)(C_2H_4)_2^+$ and $(MeC_6H_4CHMe_2)Ru(H)(C_2H_4)_2^+$. These are observed by 1H nmr spectroscopy to undergo two dynamic processes, rotation of the ethylene ligands and an exchange between the hydride and the hydrogens of the ethylenes. On protonation with trifluoroacetic acid $(C_6H_6)Ru(O_2CCF_3)_2$ has been shown to be the final product. Nucleophilic substitution investigations of the bis(ethylene) complexes has determined that the arene is more labile than the coordinated ethylene.

Chapter 3 reports the generation of a reactive intermediate, $[(MeC_6H_4CHMe_2)Ru(THF)_2]^+$, and the reactions it undergoes. The synthesis and stereochemistry of the new complexes $[(MeC_6H_4CHMe_2)RuBr(C_3H_5)]$ and $\overline{Ru(H)[(C_6H_4O)P(OPh)_2][P(OPh)_3]_3}$ are reported.

Chapter 4 describes the successful synthesis of the project goal, with the formation of the trimer

$[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_3\text{Ru}_3\text{Se}_2]^{2+}$ and the tetra nuclear species $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_4\text{Ru}_4\text{H}_4]^{2+}$. Electrochemistry shows both complexes undergo two, one-electron reversible reductions to generate their neutral analogues. $\text{Ru}_3(\text{CO})_{12}$ was formed when arene ruthenium carbonyl clusters were sought.

Chapter 5 reports the formation and reactivity of arene ruthenium complexes containing nitrogen based ligands. The half sandwich complexes, $(\text{arene})\text{RuCl}_2(\text{NH}_2\text{R})$ (arene = C_6H_6 , R = Et, CMe_3 , $\text{C}_6\text{H}_4\text{Me}$; $\text{MeC}_6\text{H}_4\text{CHMe}_2$, R = CMe_3) and $(\text{C}_6\text{H}_6)\text{RuCl}(\text{NH}_2\text{C}_6\text{H}_4\text{Me})_2^+$ have been synthesised in good yield. However, these complexes are not synthetically useful as substrates for cluster synthesis, although $(\text{C}_6\text{H}_6)\text{RuCl}_2(\text{NH}_2\text{CMe}_3)$ can be converted to the mixed ethoxide-halide dimer, $[(\text{C}_6\text{H}_6)\text{Ru}(\text{OEt})]_2\text{Cl}^+$. Me_3SiN_3 on reaction with $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2$ affords $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)]_2$. An X-ray crystal structure determination of this complex showed the nitrogens bridging the two ruthenium atoms are pyramidal rather than the expected planar in geometry. $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)]_2$ undergoes chloride loss to form the triply bridged dimer, $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)_2]^+$, and bridge cleavage to form $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)\text{PPh}_3]$. The latter complex is believed to undergo disproportionation in solution.

Conclusions and future directions of the project are discussed in chapter 6.

The appendix provides a discussion of ultrasound.

* proposed structure.

Abbreviations

DMSO	dimethylsulfoxide
Pyz	pyrazine
THF	tetrahydrofuran
acac	acetylacetonate
COT	cyclooctatetraene
py	pyridine
cp	cyclopentadiene
cp*	pentamethylcyclopentadiene
HMB	hexamethylbenzene
CYM	cymene
Bz	benzene
TFA	trifluoroacetic acid
dppen	cis $\text{Ph}_2\text{PCH=CHPPh}_2$
)))	ultrasound
anal.	analysis
calc.	calculated
FAB	Fast Atom Bombardment
amu	atomic mass unit
*	postulated structure
COD	cyclooctadiene
solv	solvent
Me	methyl
Et	ethyl
Ph	phenyl
Bu	butyl

CHAPTER ONE

Chapter 1

1. Introduction

A more diverse group of arene complexes exists for ruthenium than any other metal. The diversity stems from the stability of the arene-metal bond and the ready availability of highly reactive arene containing starting materials.

Arene ruthenium complexes play an increasingly important role in organometallic chemistry. Along with osmium, these arene complexes appear to be good starting materials for access to reactive arene metal hydrides or 16 electron metal(0) intermediates that have been used for carbon-hydrogen bond activation.

From classic organometallic arene ruthenium chemistry an area relating to the search for "New Materials" has developed. Contributions to the chemistry of cyclophanes (compounds which are potential precursors of organometallic polymers) has occurred.

Cocondensation of arene with ruthenium vapours has recently allowed access to new types of arene ruthenium metal complexes and clusters.

In the world of catalysis, arene ruthenium

complexes appear to have their own niche. Apart from being specific catalyst precursors for classic hydrogenation, carbon-hydrogen bond activation and activation of alkynes, such complexes may become valuable reagents for organic synthesis.

This introduction will cover the different ways of preparing the arene ruthenium complexes and their properties, with emphasis on the reactions of the $[(\text{arene})\text{RuCl}_2]_2$ dimers and their derivatives.

1.1 Preparations of arene ruthenium complexes

The different methods of synthesising arene ruthenium complexes fall into three general classes.

- 1) Diene route
- 2) Fischer-Hafner method
- 3) Metal vapour

1.1.1 Diene route

The most general and useful method of access to arene ruthenium(II) complexes is based on the dehydrogenation of cyclohexadiene derivatives by ethanolic solutions of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, pioneered simultaneously by two groups, Zelonka and Baird¹ and Bennett and coworkers². The arene di- H - halo

ruthenium complexes $[(\text{arene})\text{RuX}_2]_2$ ($\text{X} = \text{Cl}$, arene = C_6H_6 , $\text{C}_6\text{H}_3\text{Me}_3$, $\text{MeC}_6\text{H}_4\text{CHMe}_2$, PhMe , $p\text{-C}_6\text{H}_4\text{Me}_2$) are prepared in high percentage yields as brown/red diamagnetic low solubility complexes via the above route. The chloride ligands can be exchanged with $\text{X} = \text{I}^-$, Br^- , SCN^- by treatment with the corresponding salt.

The complex $[(\text{C}_6\text{H}_5\text{OMe})\text{RuCl}_2]_2$ was prepared by treating a methanolic (but not ethanolic) solution of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ with 1-methoxycyclohexa-1,4-diene.²

The disadvantage of the diene route is the limited number of dienes available.

^1H nmr spectrum usually show the arene rings to be spinning quickly on the nmr time scale and far infrared spectroscopy indicates the terminal and bridging ruthenium halide stretches. The p-cymene complex was sufficiently soluble in chloroform for an osmometric determination of molecular weight, which showed the complex to be dimeric and this was assumed to be true for the other arene complexes.²

Recently an X-ray crystal structure determination has been carried out upon $[(\text{C}_6\text{Me}_6)\text{RuCl}_2]_2$. This confirmed the dimeric nature of the complex.⁸⁵

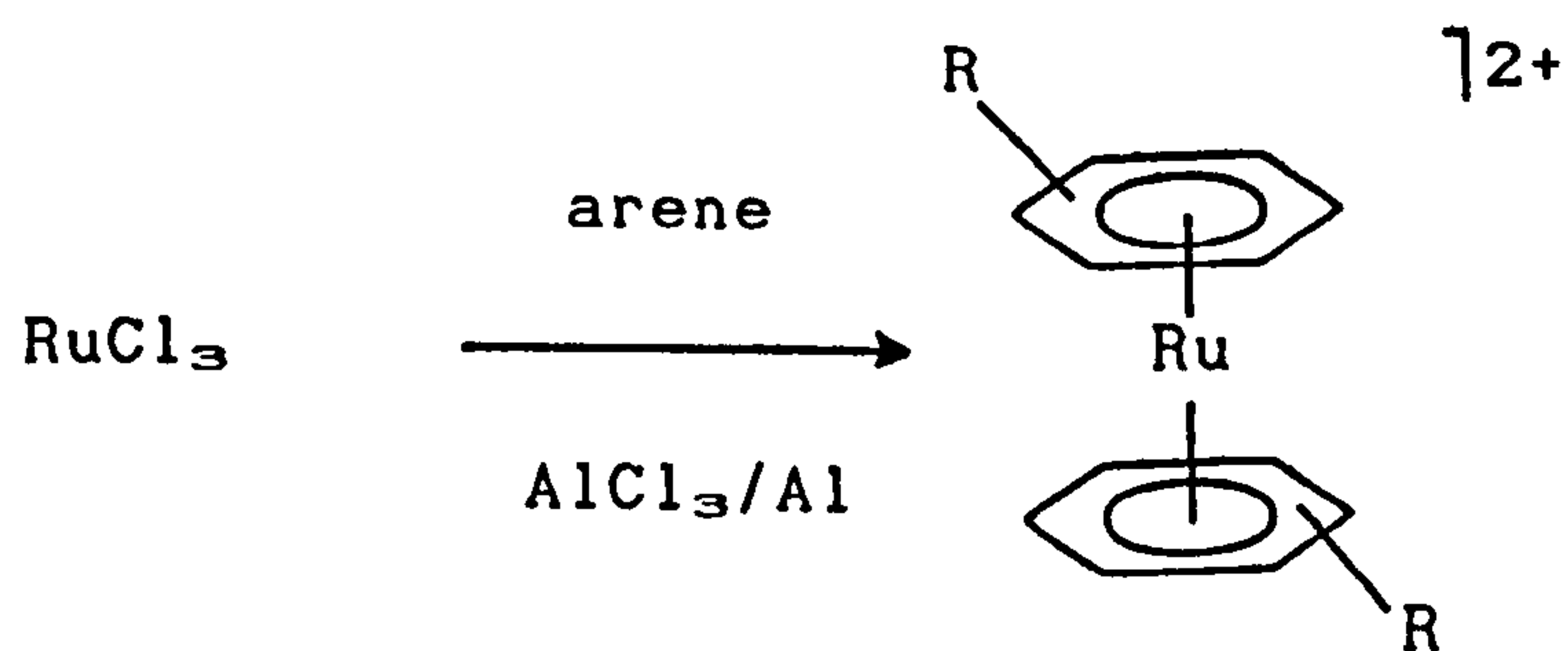
The activity of $[(\text{arene})\text{RuCl}_2]_2$ (arene = C_6H_6 , $\text{C}_6\text{H}_3\text{Me}_3$ and $\text{C}_6\text{H}_3\text{Ph}_3$) as a catalyst for the hydrogenation of alkenes has been investigated under a wide variety of conditions by Hinze³ and

Iwata and coworkers ^{4.5.6} and was found to be promoted by the presence of a small amount of pyrrolidine.

The above dimer system is ideal for substitution reactions due to the presence of the coordinatively unsaturated ruthenium centre, characteristic of bridging complexes. Simple substitution reactions are numerous along with the chemistry of their derivatives and will be discussed in detail in section 1.2.

1.1.2 Fischer-Hafner

The Fischer-Hafner approach can be used to synthesise bis arene ruthenium complexes, isolated as dications.⁷ This method involves the reaction of RuCl_3 with excess arene in the presence of AlCl_3 and Al dust.

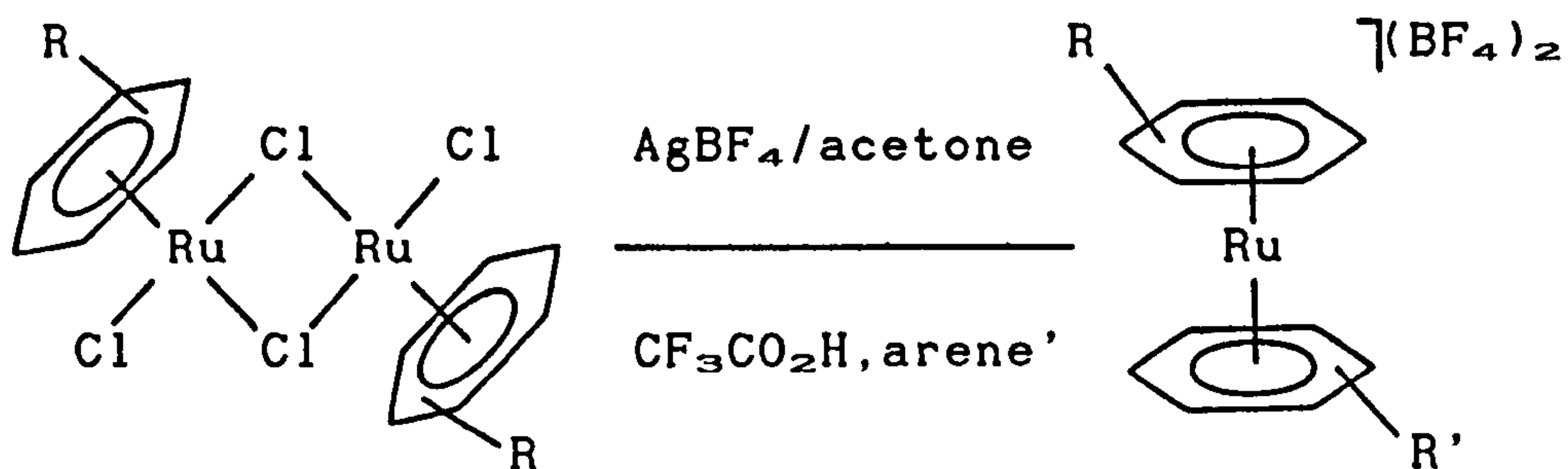


Although this is a relatively simple reaction, the yields are generally in the region of 10% and thus not economical.

Also this method cannot be applied to arenes bearing functional groups (e.g. Cl, Br, I, OCH₃, CO₂R, etc.) which are reactive under Friedel-Crafts conditions.

Another complication arises with alkylbenzenes where dealkylation^{7.8.9} often occurs. This problem has been partially overcome by modification of the original synthesis. For example, the use of Me₂AlCl as the reducing agent permits shorter reaction times and lower temperatures whilst limiting the rearrangement and fission of alkyl substituents in alkylbenzenes.¹⁰

More recently Bennett et al¹¹ have provided a straightforward general method for the preparation of both the symmetrical and unsymmetrical bis(arene) ruthenium(II) complexes.



(arene = arene' = C₆H₆, C₆H₃Me₃, C₆Me₆)

(arene = C₆H₆, arene' = C₆H₃Me₃, C₆H₅OMe, C₆H₅Cl, C₆H₅C(O)Me, C₆H₅C(O)OMe or C₆H₅Ph)

(arene = C₆H₃Me₃, arene' = C₆Me₆, C₆H₅OMe, C₆H₅Cl, C₆H₅Ph, C₆H₅NMe₂, C₆H₅OH, C₆H₅C(O)Me, C₆H₅C(O)OMe, C₆H₅C(O)OH, C₆H₅CF₃, naphthalene or anthracene)

(arene = C₆Me₆, arene' = C₆H₅OMe, C₆H₅Cl, C₆H₅NMe₂, C₆H₅C(O)Me, C₆H₅C(O)OMe or naphthalene)

Yields range from 20% to quantitative and are dependent upon the arene in the dimer in the order C₆Me₆ > C₆H₃Me₃ > C₆H₆.

Chemical Studies

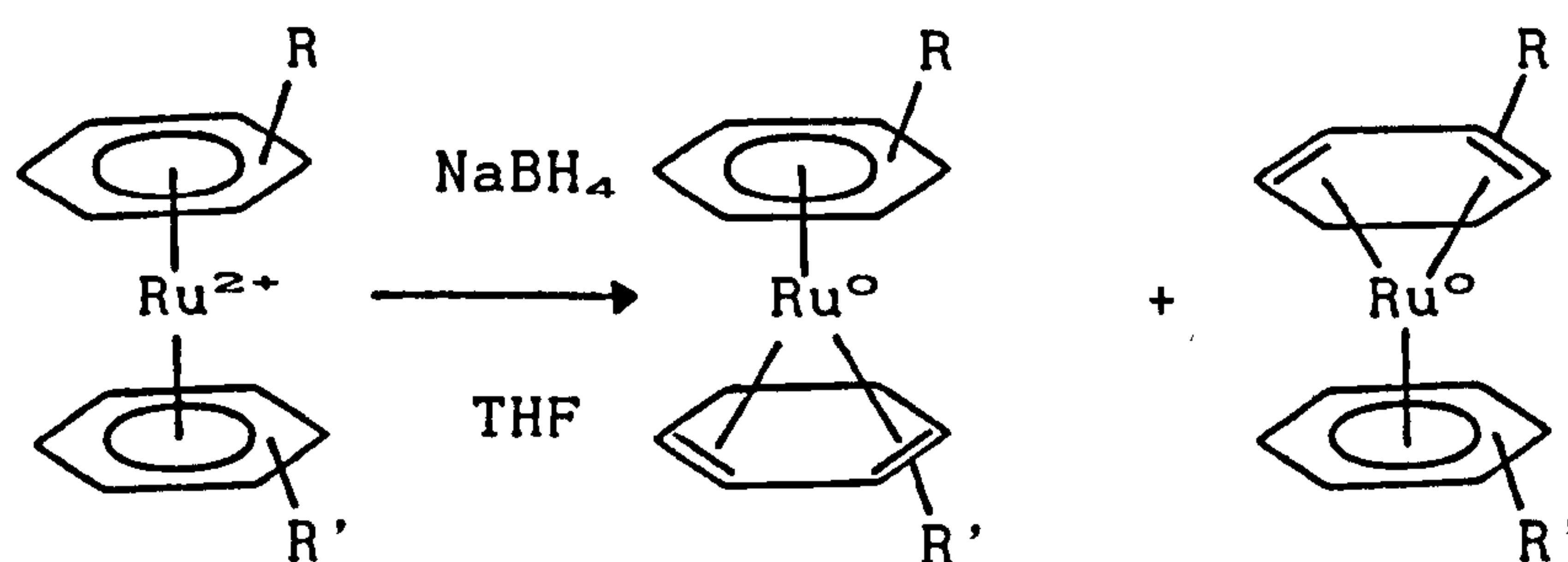
The dication species are only sparingly soluble in common organic solvents. They do dissolve in DMSO and were characterised in that solvent. These DMSO solutions are stable except in the case of the complex [(C₆H₃Me₃)Ru(anthracene)](BF₄)₂ which in DMSO changes from red to yellow in colouration. This colour change is assigned to the synthesis of

the complex $[(C_6H_3Me_3)Ru(DMSO)_3]^{2+}$ and the generation of free anthracene.¹¹

The complexes are also air-stable, diamagnetic and thermally unstable.

Reactions

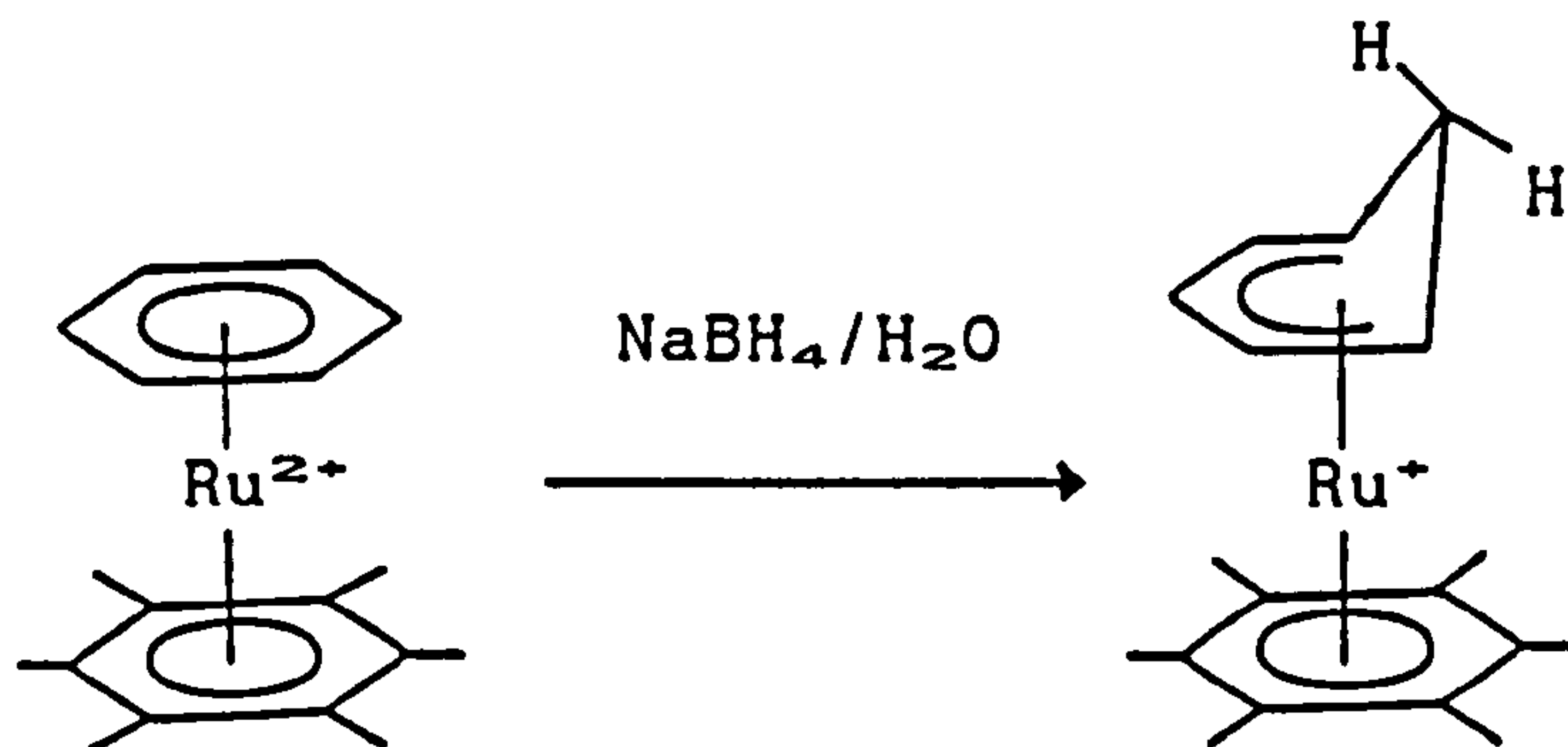
Some reactions of bis(arene) ruthenium(II) complexes with various nucleophiles have been investigated. Hydride additions using $NaBH_4$ or $LiAlH_4$ in tetrahydrofuran (THF) or a similar solvent have been reported for symmetrical as well as unsymmetrical bis(arene) ruthenium(II) complexes.^{8,12} Addition occurs preferentially to the less alkylated arene ring to yield new, zero-valent $(\eta^6\text{arene})(\eta^4\text{cyclohexadiene})\text{ruthenium}(0)$ complexes.¹²



When water is used as a solvent medium in the $NaBH_4$ reductions of dicationic complexes, an

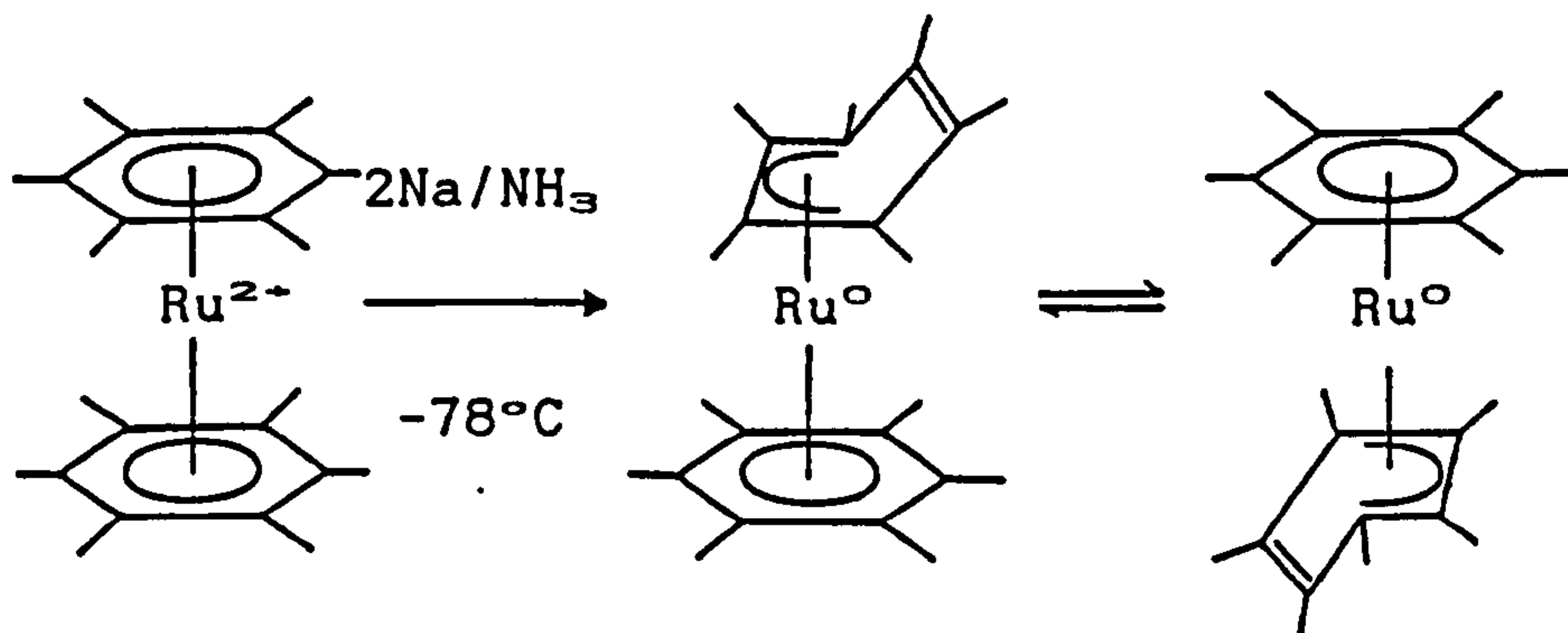
intermediate monocationic

(η^6 arene)(η^5 cyclohexadienyl)ruthenium(II) species can be obtained.¹²



A second hydride can be added to this under forcing conditions to yield the (η^6 hexamethylbenzene)(η^4 cyclohexadiene)ruthenium(0) complex.¹³

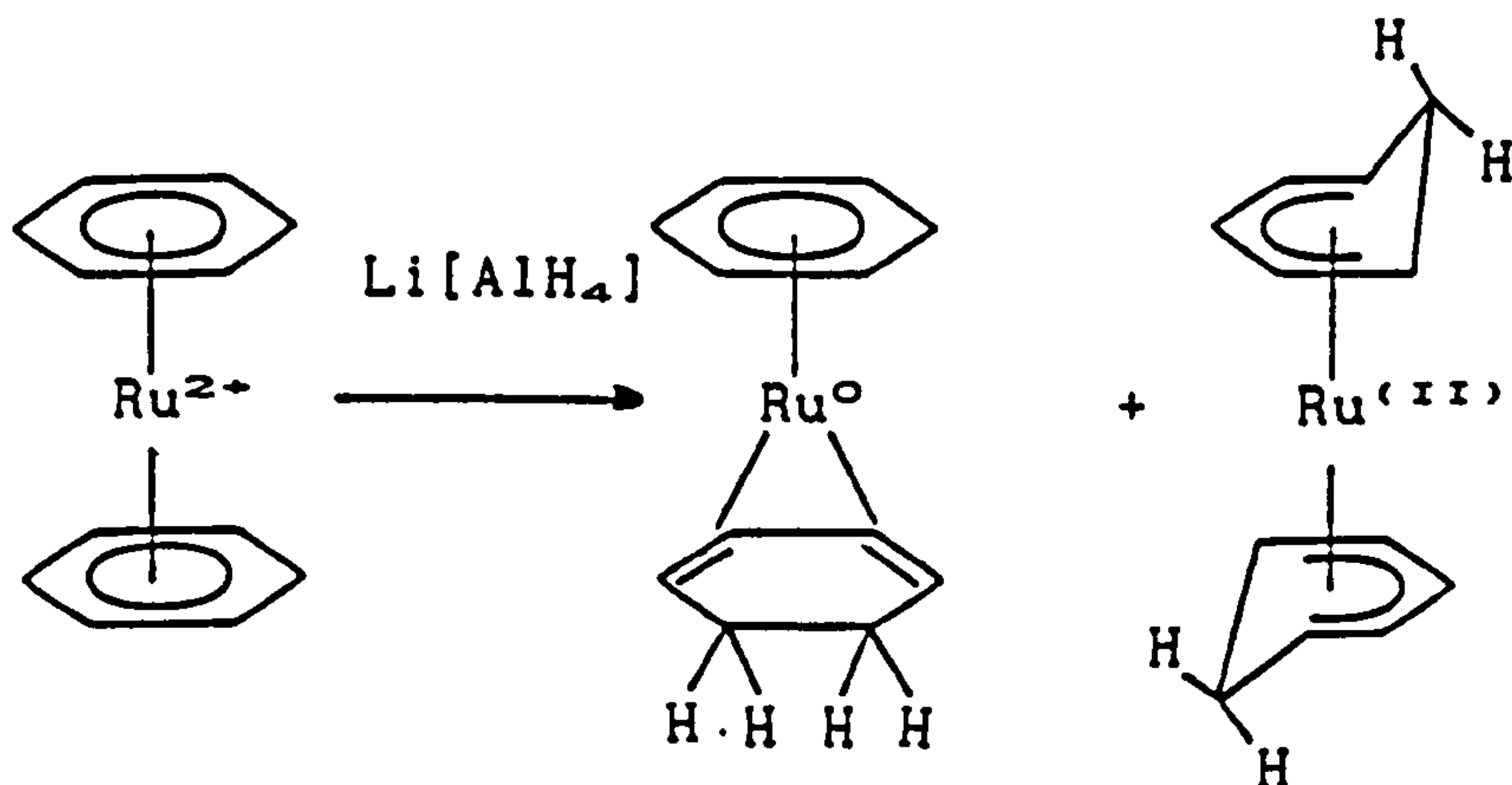
Fischer and Elschenbroich¹⁰ reported that the two-electron reduction of (η^6 C₆Me₆)₂Ru(II) complex by sodium-ammonia yielded (η^6 C₆Me₆)(η^4 C₆Me₆)Ru(0).



Variable temperature studies have shown that the zero-valent complex is highly fluxional. The ¹H nmr methyl resonances for the (η^6 C₆Me₆)₂Ru(0) complex

at -10°C in solution are consistent with the $(\eta^5\text{C}_6\text{Me}_6)(\eta^4\text{C}_6\text{Me}_6)\text{Ru}(\text{O})$ structure, whereas at approximately 50°C all the methyl ^1H nmr resonances are equivalent on the nmr time scale. Similarly, the complexes $[(\text{C}_6\text{H}_6)_2\text{Ru}(\text{II})]^{2+}$ and $[(\text{C}_6\text{H}_3\text{Me}_3)_2\text{Ru}(\text{II})]^{2+}$ are reduced to $[(\text{C}_6\text{H}_6)_2\text{Ru}(\text{O})]$ and $[(\text{C}_6\text{H}_3\text{Me}_3)_2\text{Ru}(\text{O})]$ respectively, by alkali metals.^{10,11}

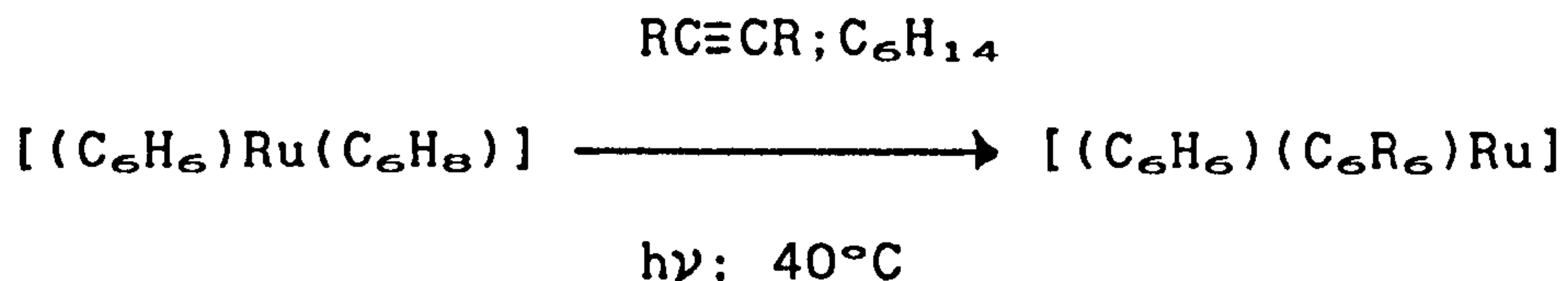
The bis(benzene) ruthenium(II) dication on reaction with $\text{Li}[\text{AlH}_4]$ yields a mixture of ruthenium zero- and two-valent complexes.⁸



Some other specific reactions reported are of $[(\text{C}_6\text{H}_3\text{Me}_3)(\text{C}_6\text{H}_5\text{OH})\text{Ru}](\text{BF}_4)_2$ with base to give $[(\text{C}_6\text{H}_3\text{Me}_3)(\text{C}_6\text{H}_5\text{OH})\text{Ru}](\text{BF}_4)$ and treatment of $[(\text{arene})(\text{C}_6\text{H}_5\text{Cl})\text{Ru}]^{2+}$ (arene = C_6H_6 , $\text{C}_6\text{H}_3\text{Me}_3$ and C_6Me_6) with methanol yielding

$[(\text{arene})(\text{C}_6\text{H}_5\text{OMe})\text{Ru}]^{2+}$.¹¹ Also the $[(\text{C}_6\text{H}_6)_2\text{Ru}]^{2+}$ complex reacts with LiPh in diethyl ether to yield the 1-endo- π -cyclohexadienyl derivative $[(\text{C}_6\text{H}_5.\text{C}_6\text{H}_6)_2\text{Ru}]$.⁸

The complexes $(\text{C}_6\text{H}_6)(\text{C}_6\text{R}_6)\text{Ru}$ ($\text{R} = \text{Ph}$ or COOMe) were prepared as below;¹⁴



However, if the alkyne is $\text{MeC}\equiv\text{CMe}$, the product is $[(\text{C}_6\text{Me}_6)_2\text{Ru}]$ and not the expected unsymmetrical $\text{bis}(\text{arene})(\text{arene}')\text{Ru}(\text{O})$.

The bis(hexamethylbenzene) ruthenium(0) complex forms thermally unstable, diamagnetic, orange monoclinic crystals. X-ray crystal determination has been carried out upon this complex and affords the information that one of the arene rings is planar with its methyl groups displaced by an angle greater than or equal to 4° . The second arene ring, in a position eclipsed with respect to the first, is non-planar and bonded to the ruthenium centre by only four carbon atoms which are coplanar by 42.8° ; ^{15, 16} (See Fig. 1.1.2.1)

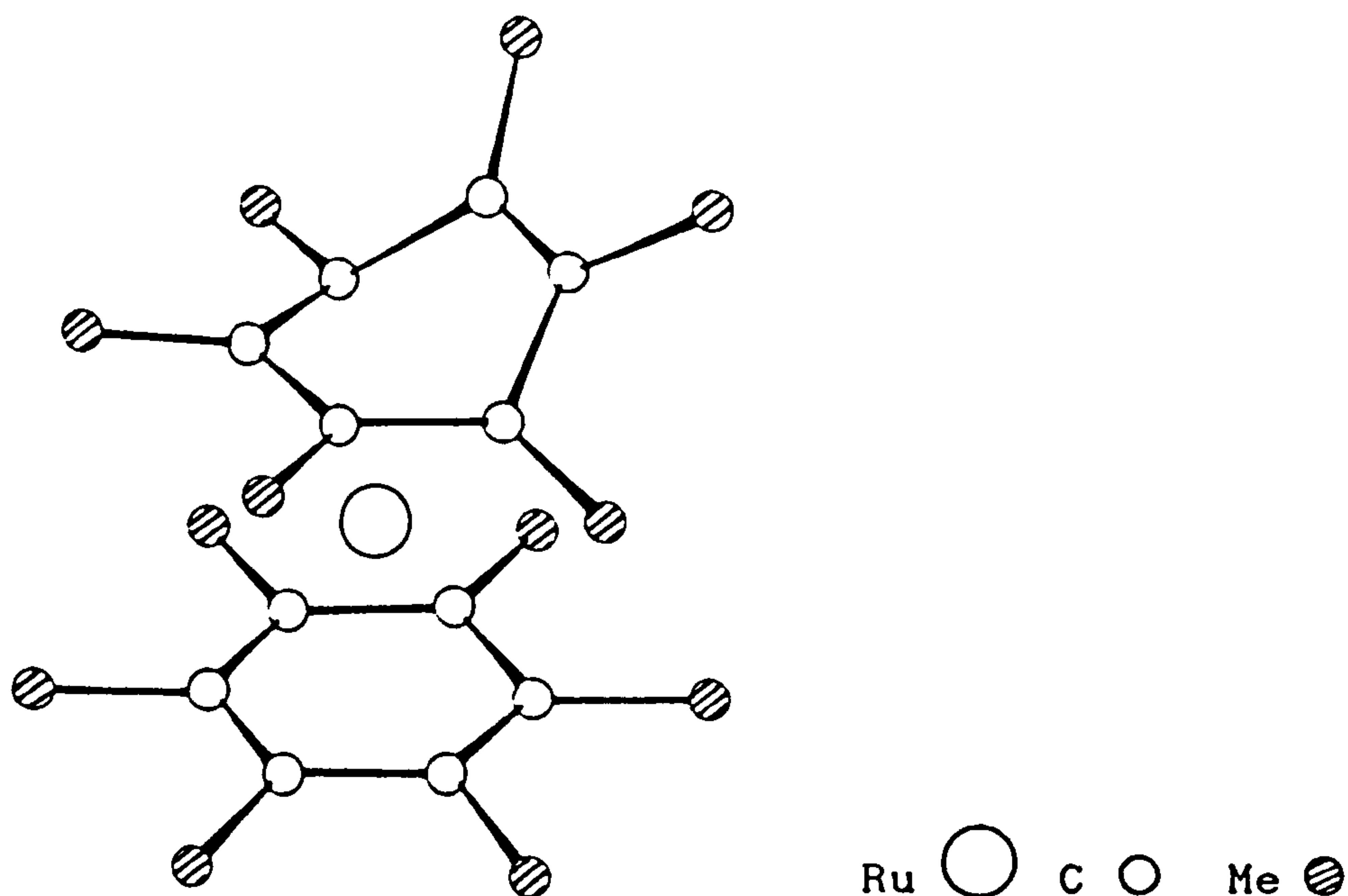
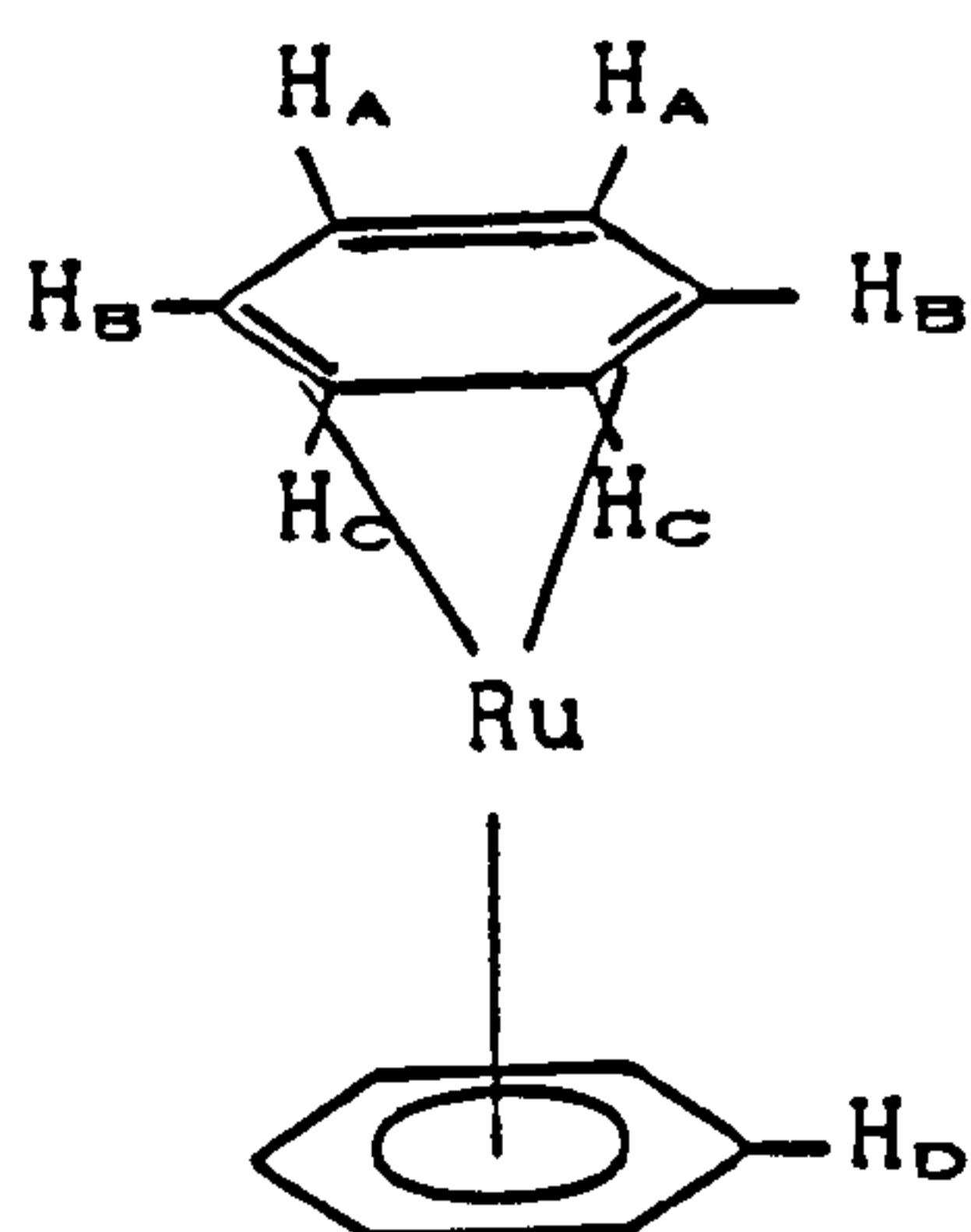


Fig. 1.1.2.1 Diagrammatical representation of the X-ray crystal structure determination of $[(C_6Me_6)_2Ru]$.

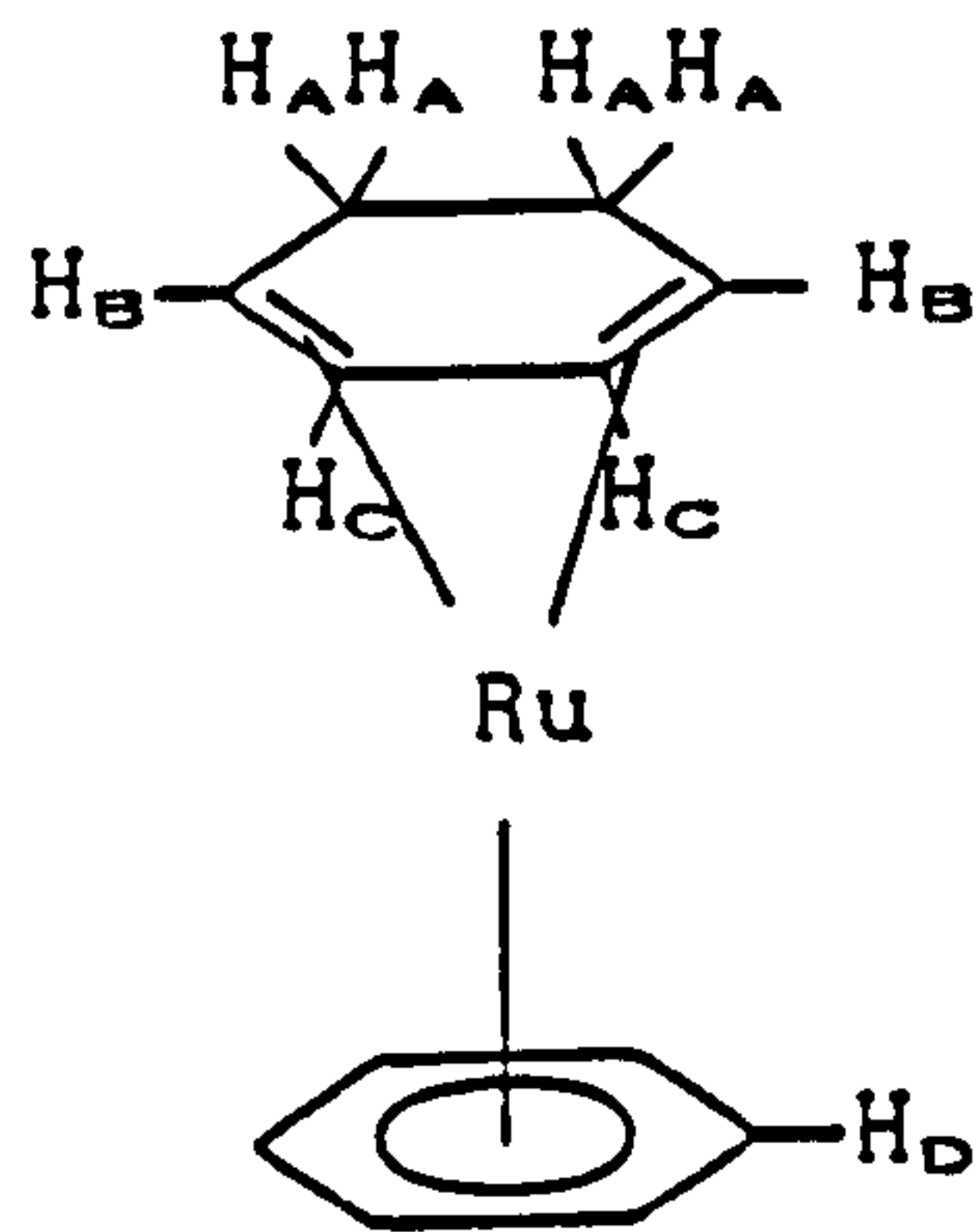
1.1.3 Metal vapour

The metal vapour method can be utilized to synthesise the thermally unstable $(C_6H_6)_2Ru$ neutral species. This involves the production of ruthenium vapour, by passing an electric current through tungsten filaments coated with a mixture of ruthenium powder and epoxy resin, and cocondensing the vapour with benzene.¹⁷ 1H nmr spectra exhibit resonances at $\delta = 5.78(2H)$, $5.16(6H)$, $4.90(2H)$ and $2.89(2H)$ ppm assigned to H_A , H_D , H_C and H_B respectively, in the 1-4 : 1-6 structure.

The assignment is aided by comparison of the proton resonances in the spectra of the $(C_6H_6)Ru(C_6H_6)$ complex.¹⁸



$[(C_6H_6)_2Ru]$



$[(C_6H_6)Ru(C_6H_5)]$

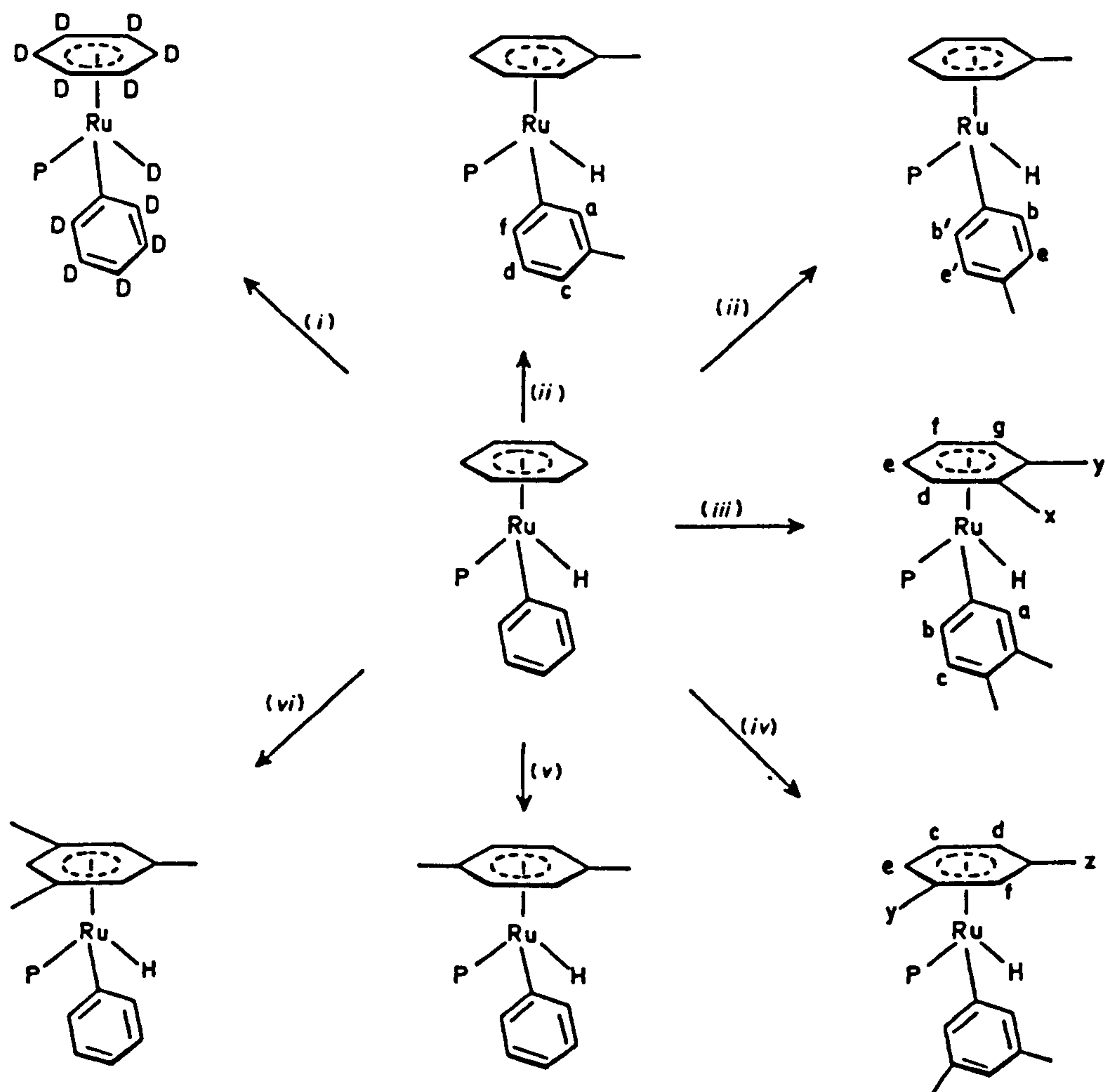
The proton signal positions are seen at $\delta = 5.00(6H)$, $4.92(2H)$, $3.72(2H)$, and $1.83(4H)$ ppm and are assigned to H_D , H_C , H_B and H_A respectively. The 1H nmr spectrum indicates that the molecule is not fluxional under conditions where it is stable.¹⁷

The hexamethylbenzene analogue is an active catalyst for the homogeneous hydrogenation of arenes.¹⁹

Cocondensation of metal atoms with a mixture of tertiary phosphines and arenes has proved to be a fruitful synthetic route to half sandwich transition metal arene tertiary phosphine derivatives (Re, Cr, W, Fe).^{20,21} Cocondensation of ruthenium atoms with a mixture of benzene and

trimethylphosphine affords crystals of
 $[(C_6H_6)RuH(PMe_3)(\sigma-C_6H_5)]$.

The chemistry carried out on this complex was
centred around arene exchange reactions. (See scheme
1.1.3.1²²



Scheme 1.1.3.1. $P=PMe_3$. (i) $[^2H_6]$ Benzene/ $80^\circ C$
/ 20hr. yield >80%; (ii) toluene/ $100^\circ C$ / 2weeks/ 60%;
(iii) o-xylene/ $100^\circ C$ / 4days/ 39%; (iv) m-xylene/
 $100^\circ C$ / 4days/ 30%; (v) p-xylene/ $100^\circ C$ / 4days/ 30%;
(vii) mesitylene/ $100^\circ C$ / 4days/ 89%.

1.2 Chemistry of $[(\text{arene})\text{RuCl}_2]_2$ and its derivatives

The substitution reactions of $[(\text{arene})\text{RuCl}_2]_2$ and the chemistry of its derivatives, will be divided into two general sections.

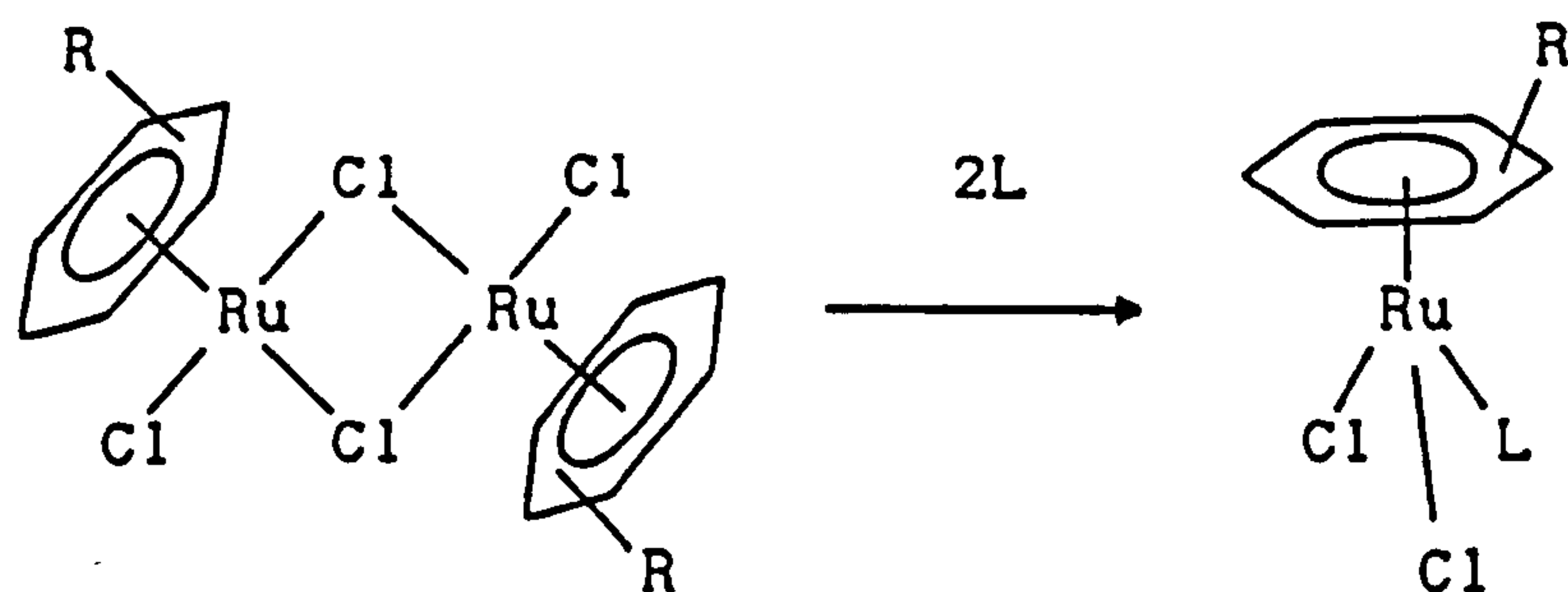
a) neutral derivatives.

b) ionic derivatives.

1.2.1 Neutral derivatives

1.2.1.1 Simple bridge cleavage

The simple cleavage reaction:

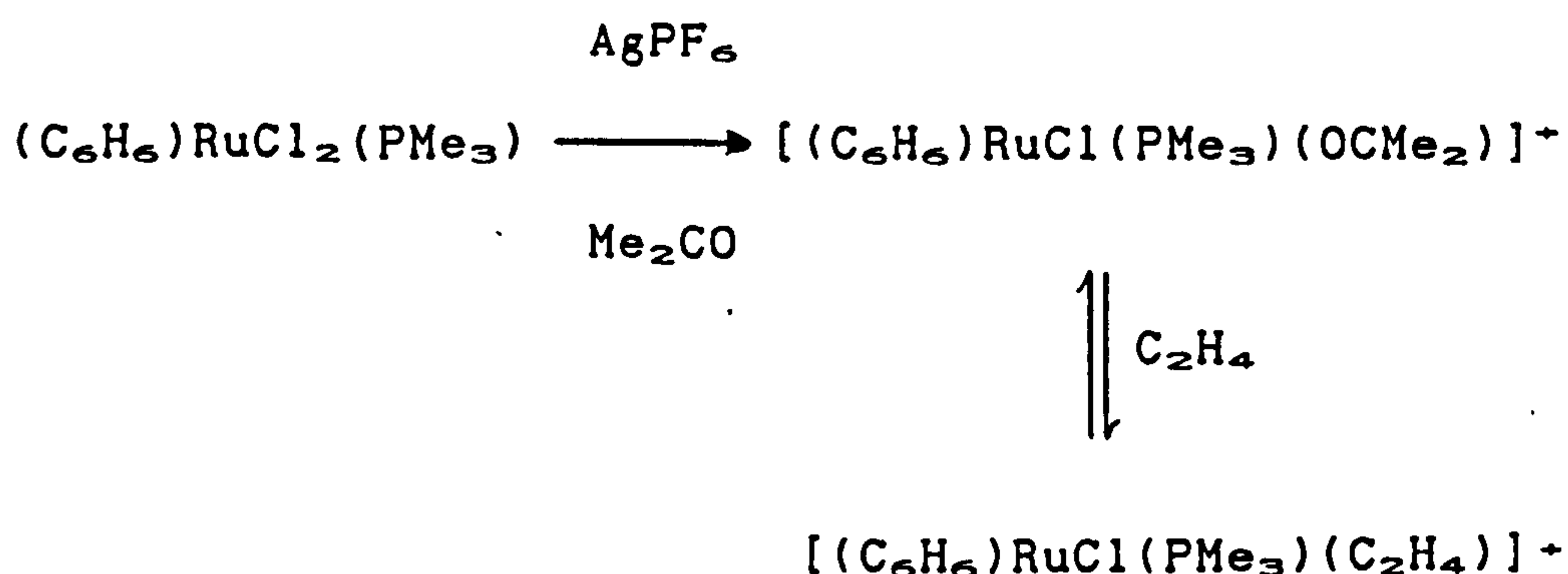


occurs on the addition of a variety of two electron ligands L, such as phosphine, phosphite, arsine, stilbene, pyridine,^{1,2} isonitrile,²³ carbon monoxide,²⁴ or dimethylsulfoxide²⁵ in a boiling solvent or as a neat ligand with the parent chloro dimer, affording mononuclear complexes in good yield.

These are monomeric in chloroform solution and a single crystal X-ray structural analysis of two of

the compounds $[(C_6H_6)RuCl_2(PMePh_2)]$ and $[(MeC_6H_4CHMe_2)RuCl_2(PMePh_2)]$ have been determined and show a slight tilting from planarity of the arene ligand.²⁶

Werner and coworkers²⁷ have investigated the reactivity of phosphine ligand substituted monomers. Primarily concerning the preparation and reactivity of an arene ethene Ru(II) complex which undergoes facile interconversion of the ethene / ethyl derivative.



1.2.1.2 Bidentate coordinated ligands

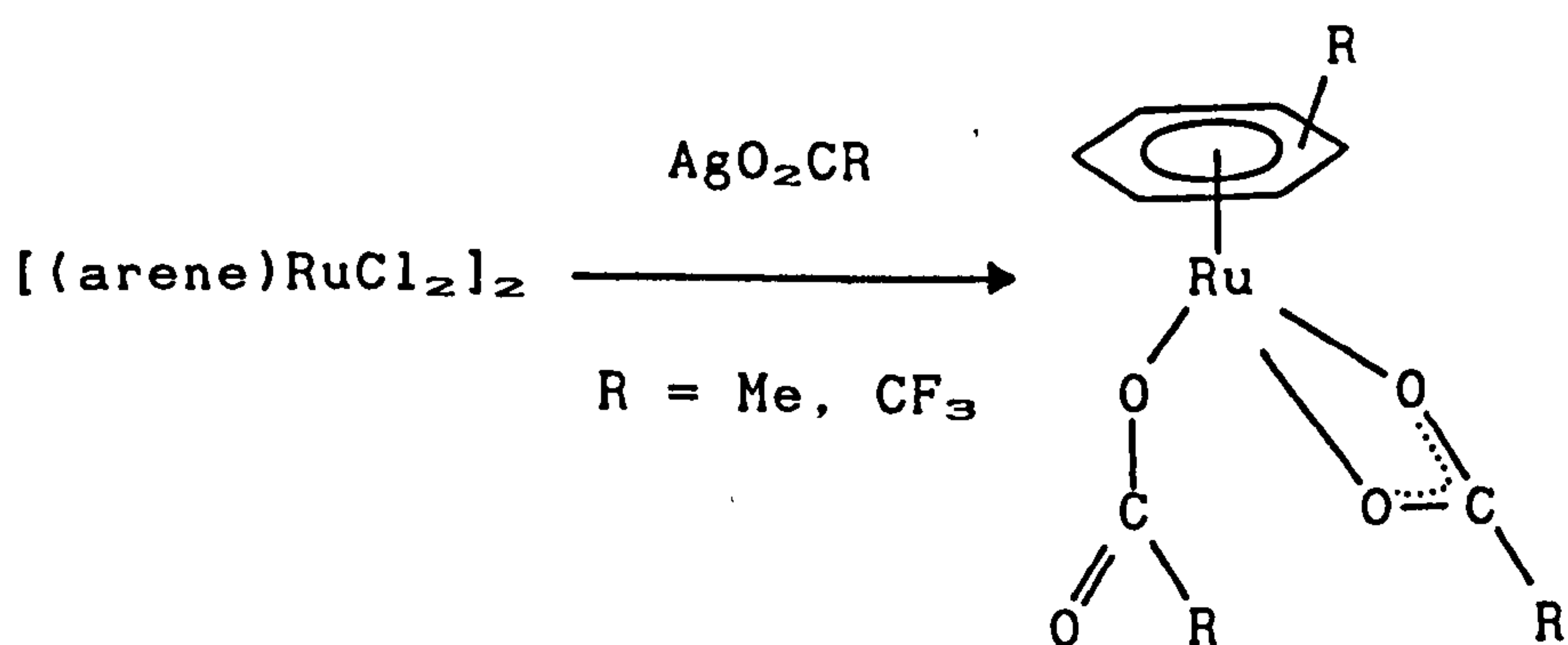
Various bidentate ligands L-L undergo reaction with the parent ruthenium chloro dimers to yield monomeric or bimetallic arene ruthenium species. (See scheme 1.2.1.2.1)

The parent chloro dimers and the half sandwich mononuclear (arene)RuCl₂(L) derivatives have been shown to be useful precursors for the synthesis of alkyl or hydrido arene ruthenium complexes. The hydrido compounds are utilised for the formation of arene ruthenium(0) intermediates capable of C-H bond activation leading to new hydrido and cyclometallated ruthenium arene derivatives.

Arene ruthenium carboxylates formed on reaction with the parent dimers also appear to be useful precursors of hydrido ruthenium complexes.

1.2.1.3 Arene ruthenium carboxylate complexes

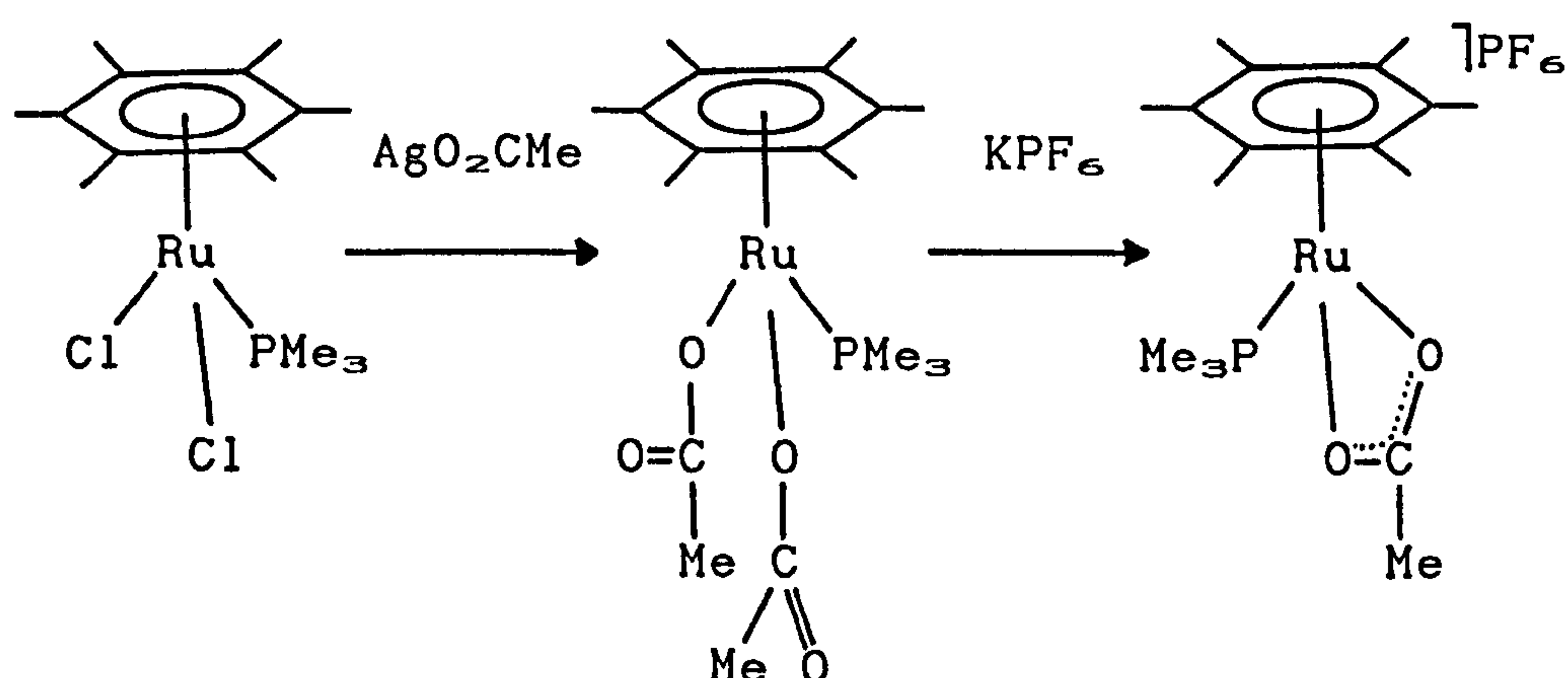
The bis(acetato) or bis(trifluoroacetato) ruthenium arene complexes are prepared by treatment of the parent dimers with a large excess of silver carboxylate for a variety of arenes;^{30,32}



(arene = C₆H₆, MeC₆H₄CHMe₂, C₆H₃Me₃, C₆H₂Me₄,
C₆Me₆)

One carboxylate group is unidentate and the other is bidentate, however, they appear equivalent on the nmr time scale.

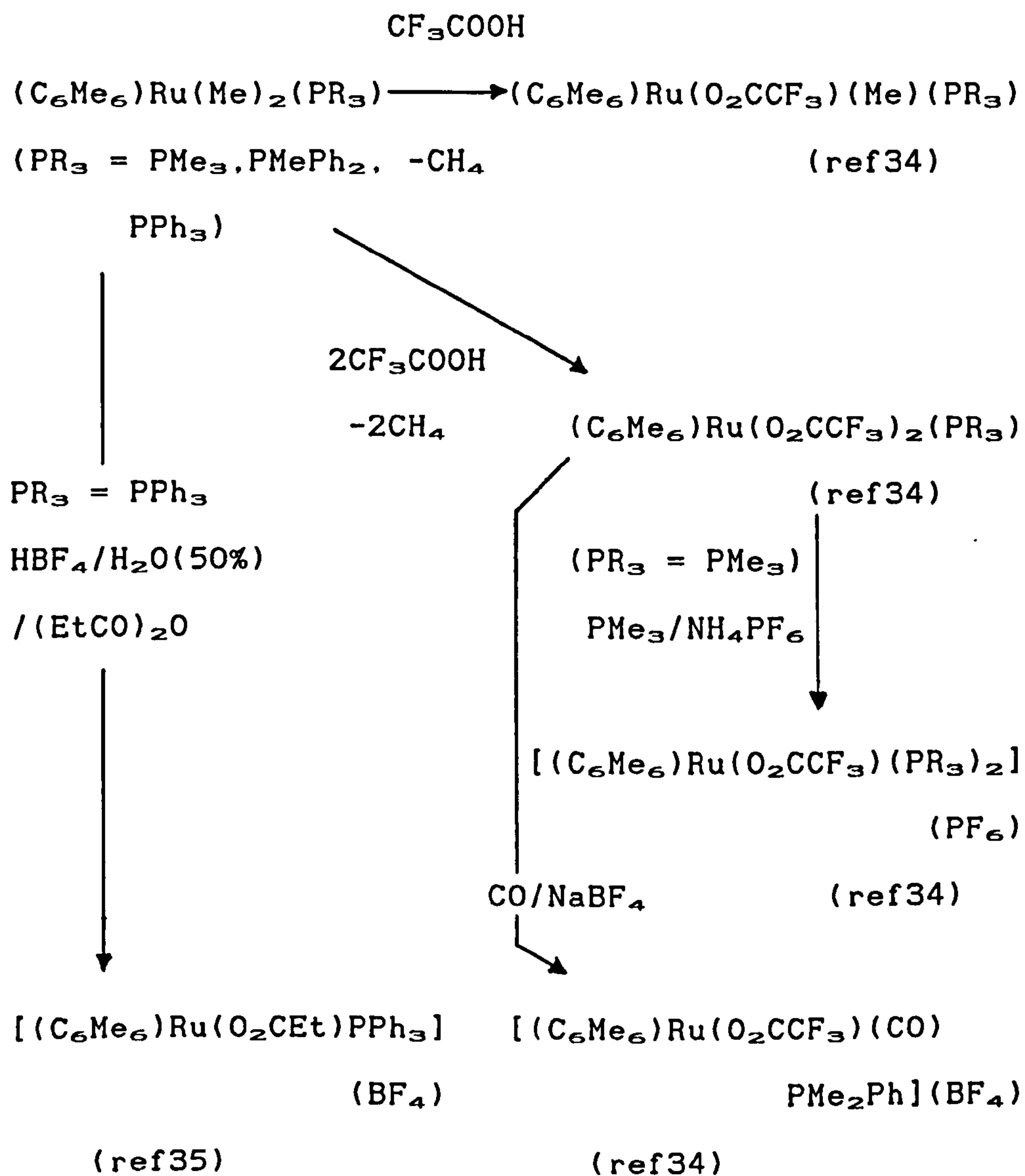
The mononuclear species $[(C_6Me_6)RuCl_2(PMe_3)]$ on reaction with silver carboxylate yields $[(C_6Me_6)Ru(O_2CMe)_2(PMe_3)]$ which, in turn, in the presence of KPF_6 , affords the cationic species $[(C_6Me_6)Ru(O_2CMe)(PMe_3)]PF_6$.³³



The triphenylphosphine analogue of the neutral trimethylphosphine acetato and trifluoroacetato complexes can be simply prepared by addition of PPh_3 to the $[(C_6Me_6)Ru(O_2CR)_2] \cdot H_2O$ complex ($R = Me, CF_3$).³⁰

The trifluoroacetato ruthenium(II) complexes $[(C_6Me_6)Ru(O_2CCF_3)(Me)(PR_3)]$ and $[(C_6Me_6)Ru(O_2CCF_3)_2(PR_3)]$ have been obtained by H. Werner and coworkers, by selective cleavage of

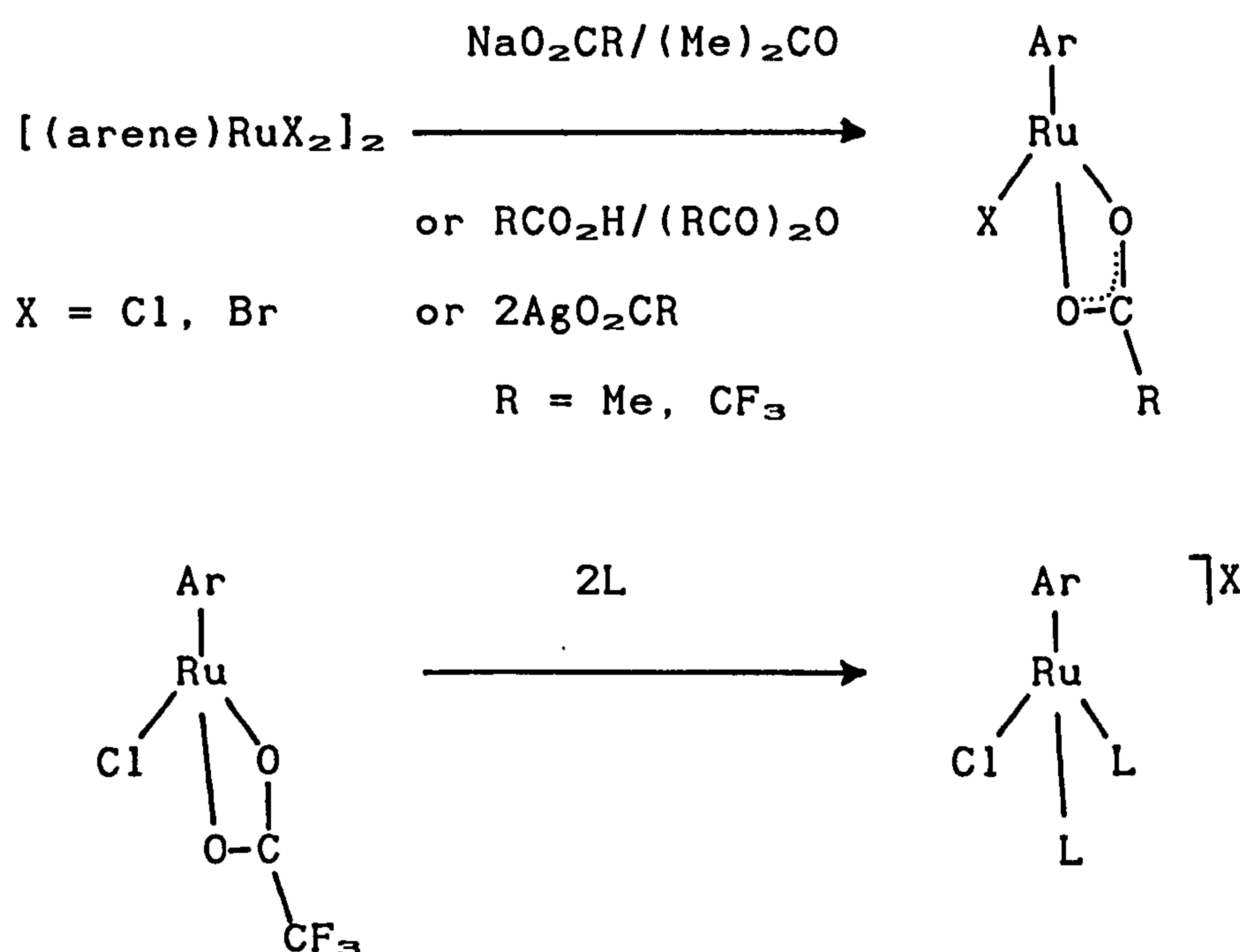
the Ru-CH₃ bonds of the dialkyl ruthenium(II) species [(C₆Me₆)Ru(Me)₂(PR₃)], the synthesis of which is outlined in section 1.2.1.4. The preparation and reactions of these complexes are summarised in scheme 1.2.1.3.1.



Scheme 1.2.1.3.1 Synthesis of the Trifluoroacetato complexes [(C₆Me₆)Ru(O₂CCF₃)(Me)(PR₃)] and [(C₆Me₆)Ru(O₂CCF₃)₂(PR₃)].

Reaction of the dialkyl ruthenium(II) species $[(C_6Me_6)Ru(Me)_2(PPH_3)]$ with HBf_4 in the presence of propionic anhydride yields the bidentate carboxylato ruthenium cation shown above.

Alternatively, this type of bidentate acetato complex can be prepared by a variety of methods from the arene ruthenium halide dimers;³⁰



(arene = C_6H_6 , $MeC_6H_4CHMe_2$, $C_6H_3Me_3$, $C_6H_2Me_4$, C_6Me_6)

(L = $PEtPh_2$, py, pyrazine, 1,3 dithiane,

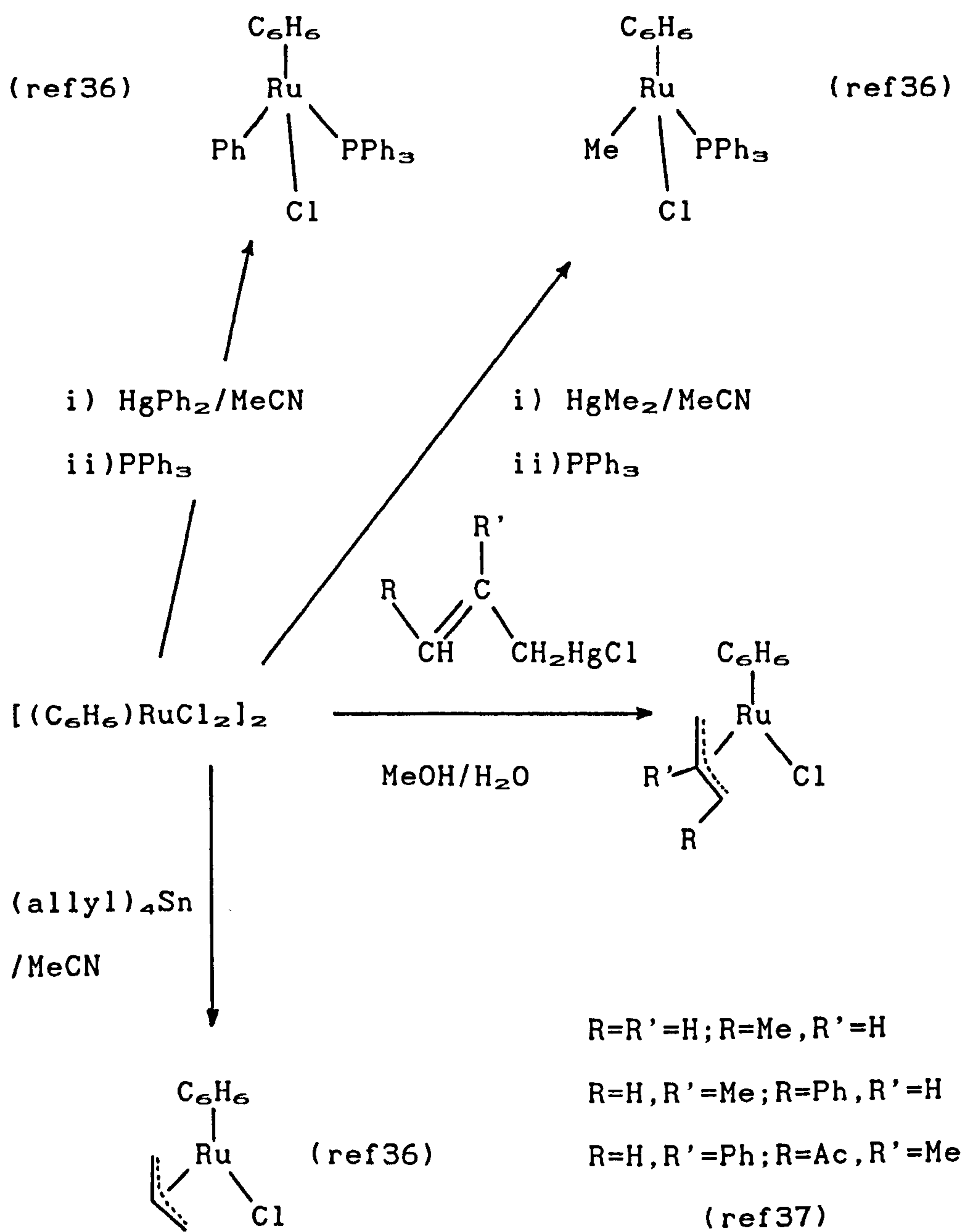
4,4'-bipyridine; L_2 = 2,2'-bipyridine)

Scheme 1.2.1.3.2 Synthesis and reaction of $[(\text{arene})RuCl(O_2CR)]$.

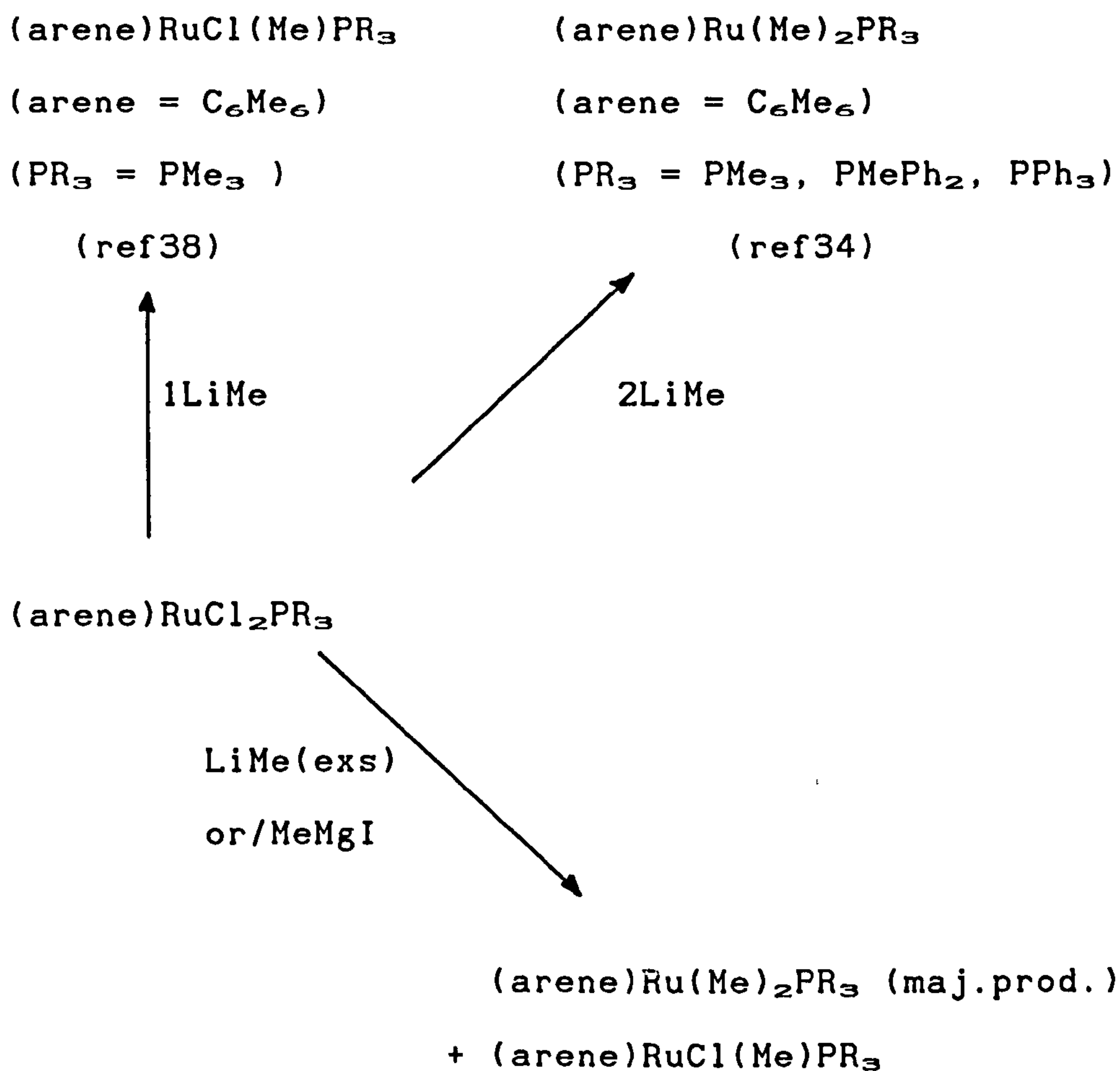
The trifluoroacetic chloro ruthenium complex is a good starting material for the preparation of cations, by displacement of the trifluoroacetic acid ligand by two equivalents of ligand. The potentially binucleating ligands pyrazine (pyz), 4,4'-bipyridyl and 1,3-dithine form the $[(\text{arene})\text{RuClL}_2]^+$ salts in which only one donor atom of the ligand is coordinated. However, when pyrazine and $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2$ react in tetrahydrofuran, the pyrazine bridged species $\{[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2(\mu\text{-pyz})\}$ is formed. The structure of the complex $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{pyz})_2]\text{PF}_6$ has been verified by X-ray analysis.³⁰

1.2.1.4 Arene ruthenium alkyl derivatives

The $[(\text{C}_6\text{H}_6)\text{RuCl}_2]_2$ dimer and the half sandwich $[(\text{arene})\text{RuCl}_2(\text{PR}_3)]$ complexes have been shown to be suitable substrates for the formation of alkyl and allyl arene ruthenium derivatives. A selection of the preparations are shown in scheme 1.2.1.4.1.



Scheme 1.2.1.4.1 Preparation of alkyl species from $[(\text{C}_6\text{H}_6)\text{RuCl}_2]_2$.



$(\text{arene} = \text{C}_6\text{H}_6, \text{MeC}_6\text{H}_4\text{CHMe}_2, \text{C}_6\text{H}_3\text{Me}_3; \text{PR}_3 = \text{PMe}_2\text{Ph})$

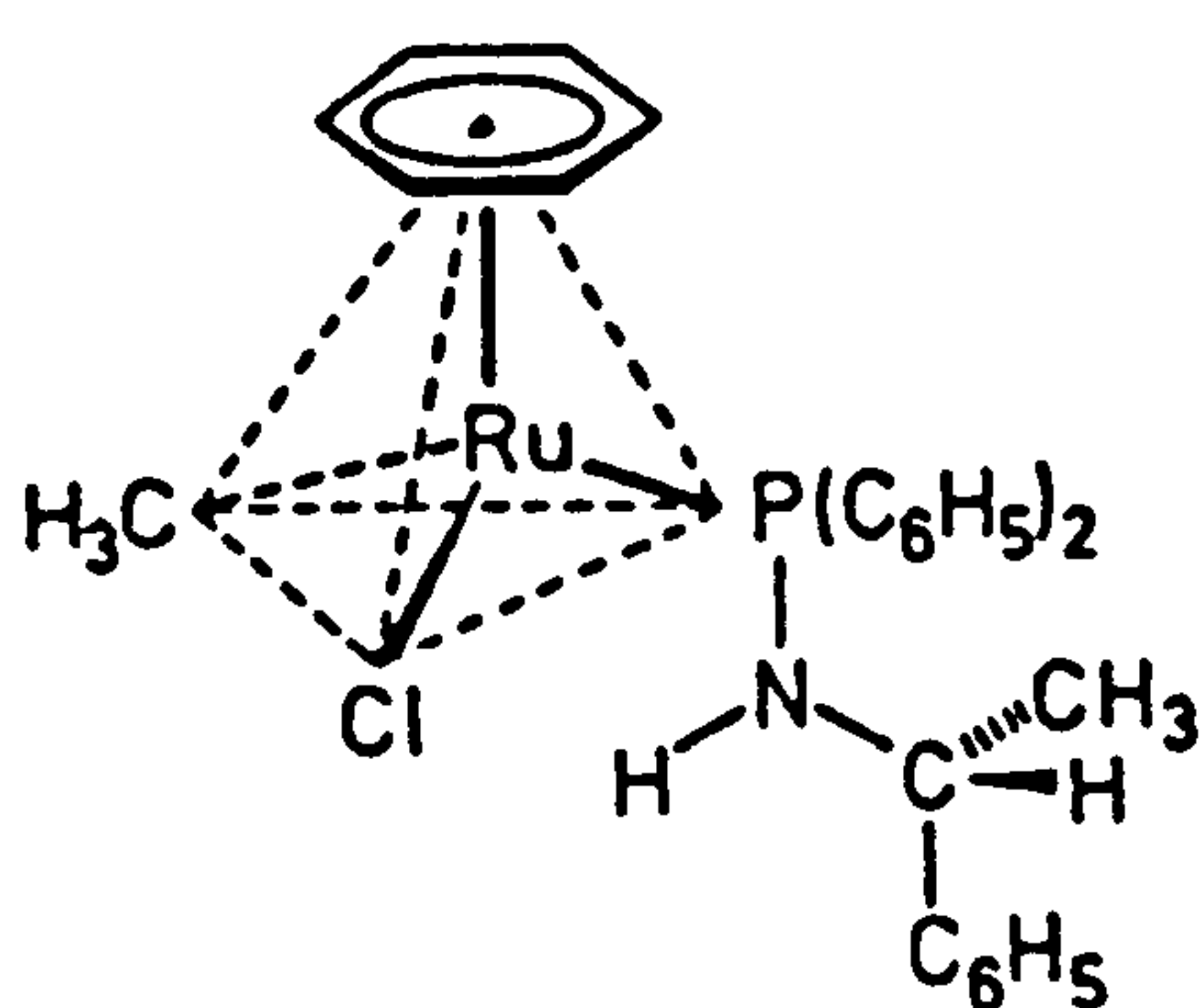
$(\text{arene} = \text{C}_6\text{H}_6; \text{PR}_3 = \text{PPh}_3)$

$(\text{ref}2)$

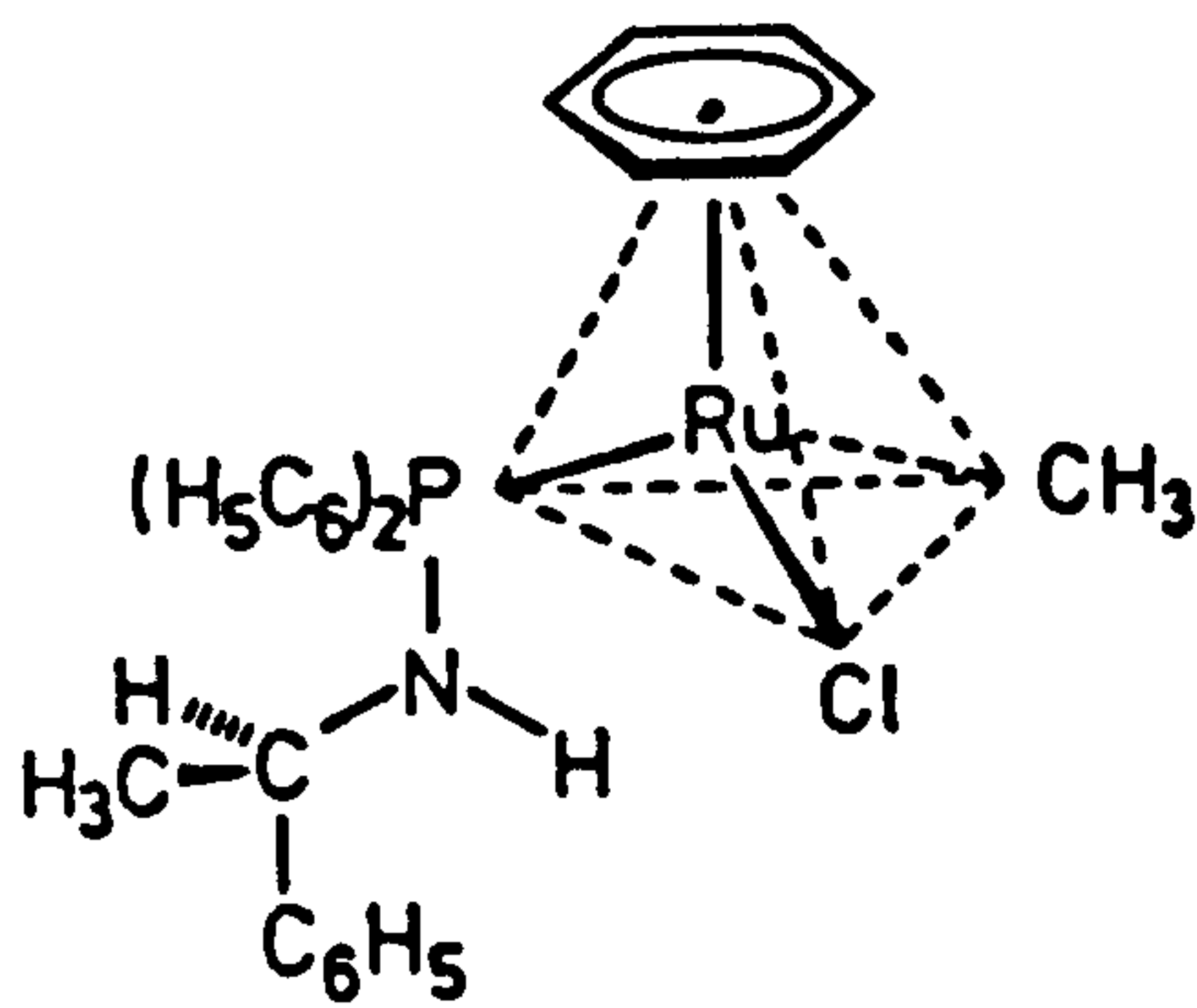
Scheme 1.2.1.4.2 Preparation of alkyl species from half sandwich complexes.

The dimethyl mercury reaction has been utilised to prepare an optically active benzene ruthenium complex.³⁹ When the tertiary phosphine R-(+)-Ph₂PNHCHMePh is added to a reaction mixture

of $[(C_6H_6)RuCl_2]_2$ in acetonitrile with $HgMe_2$, the product is $[(C_6H_6)RuCl(Me)(PPh_2NHCHMePh)]$ as a pair of diastereoisomers.



85

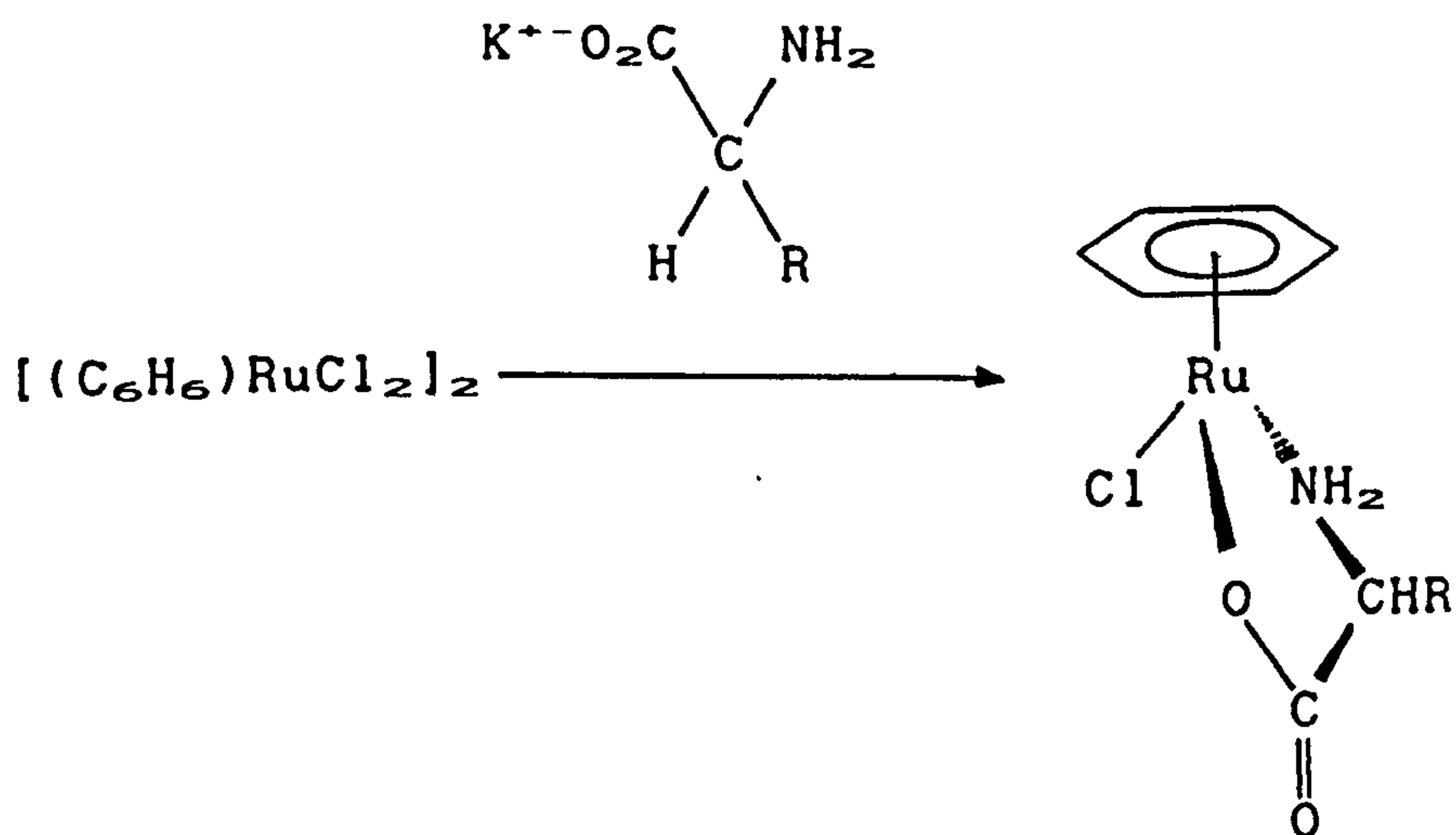


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$(+)_578^-$ and $(-)_578^--(C_6H_6)RuCl(Me)[Ph_2PNHCH(Me)(Ph)]$

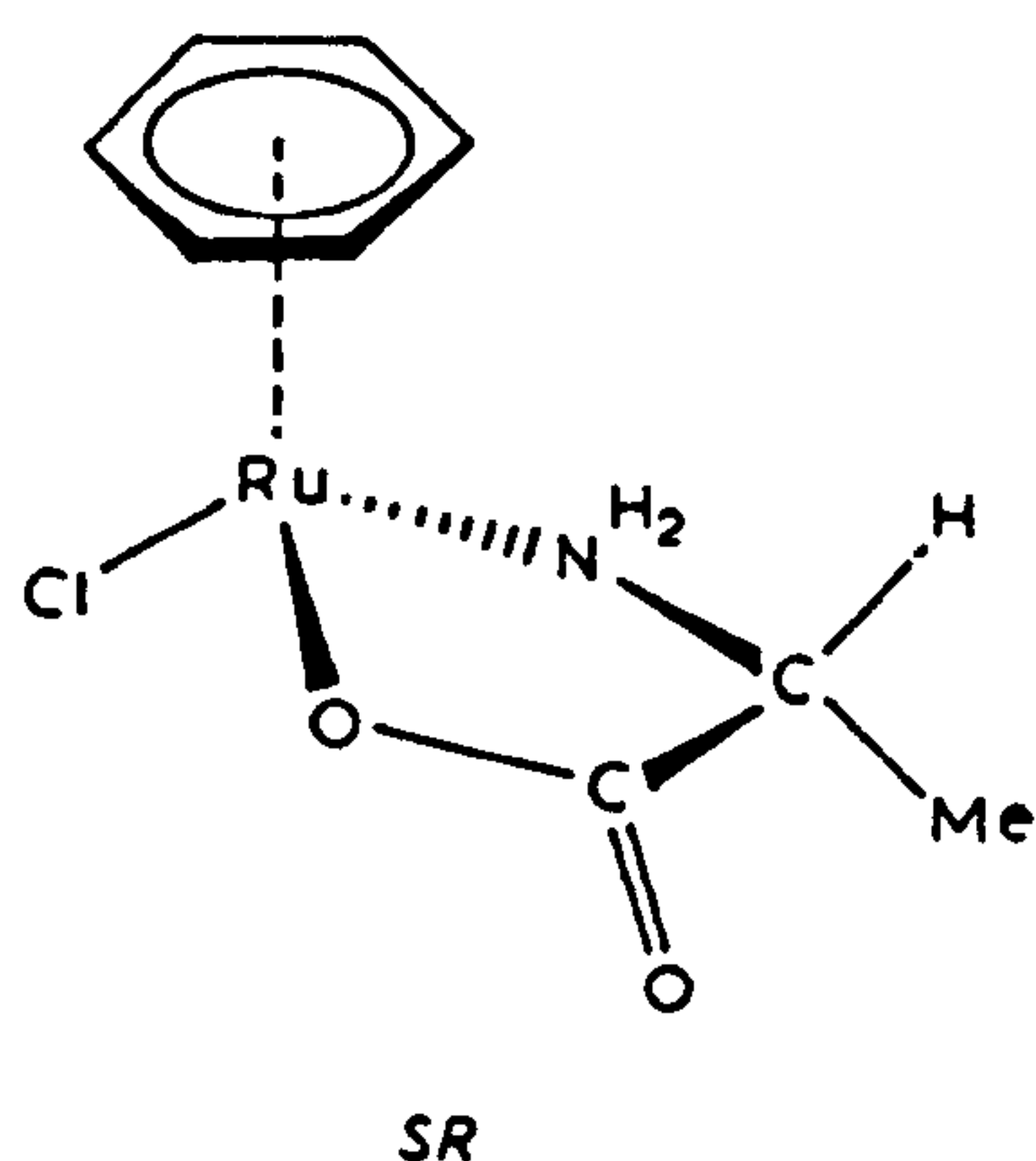
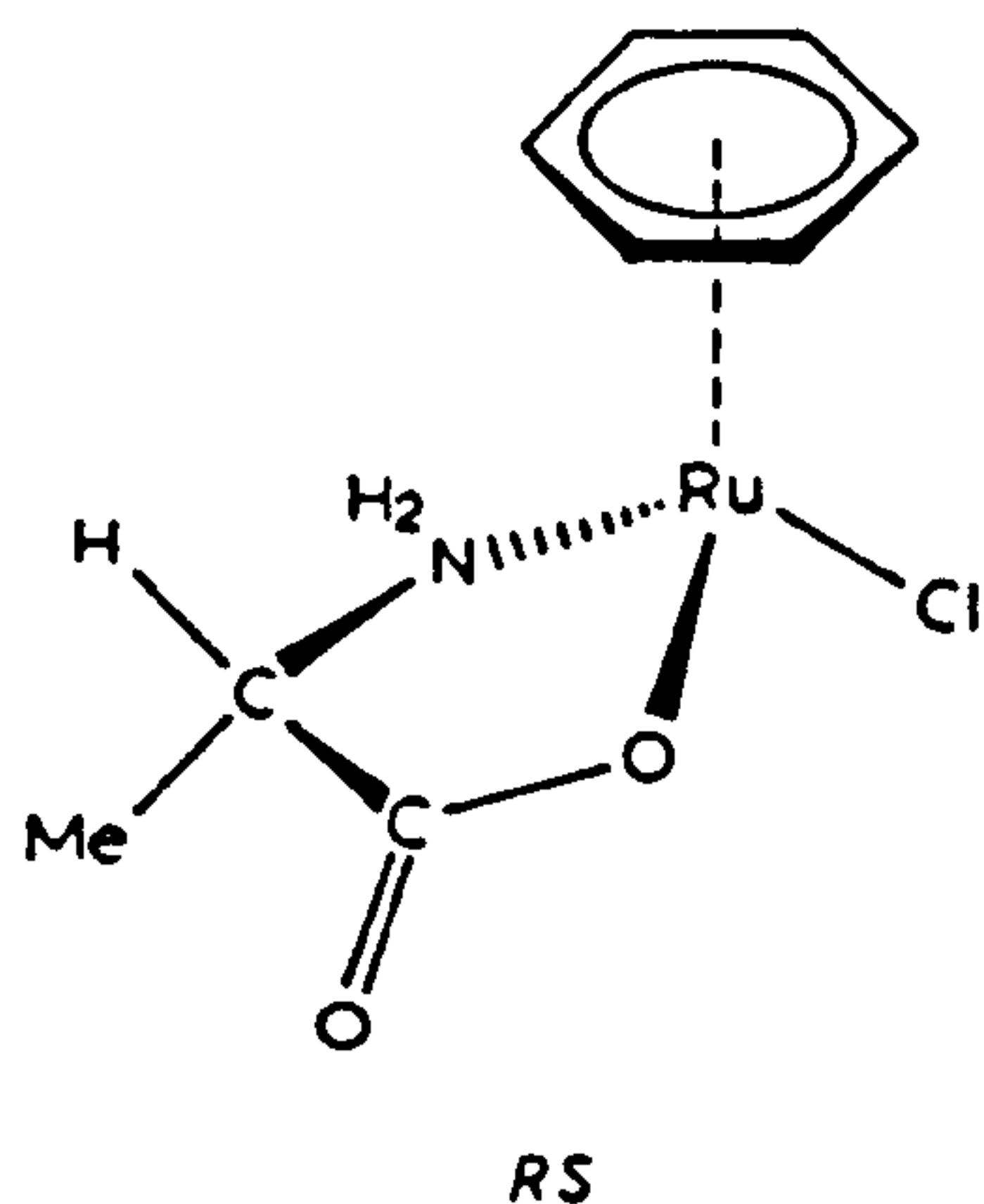
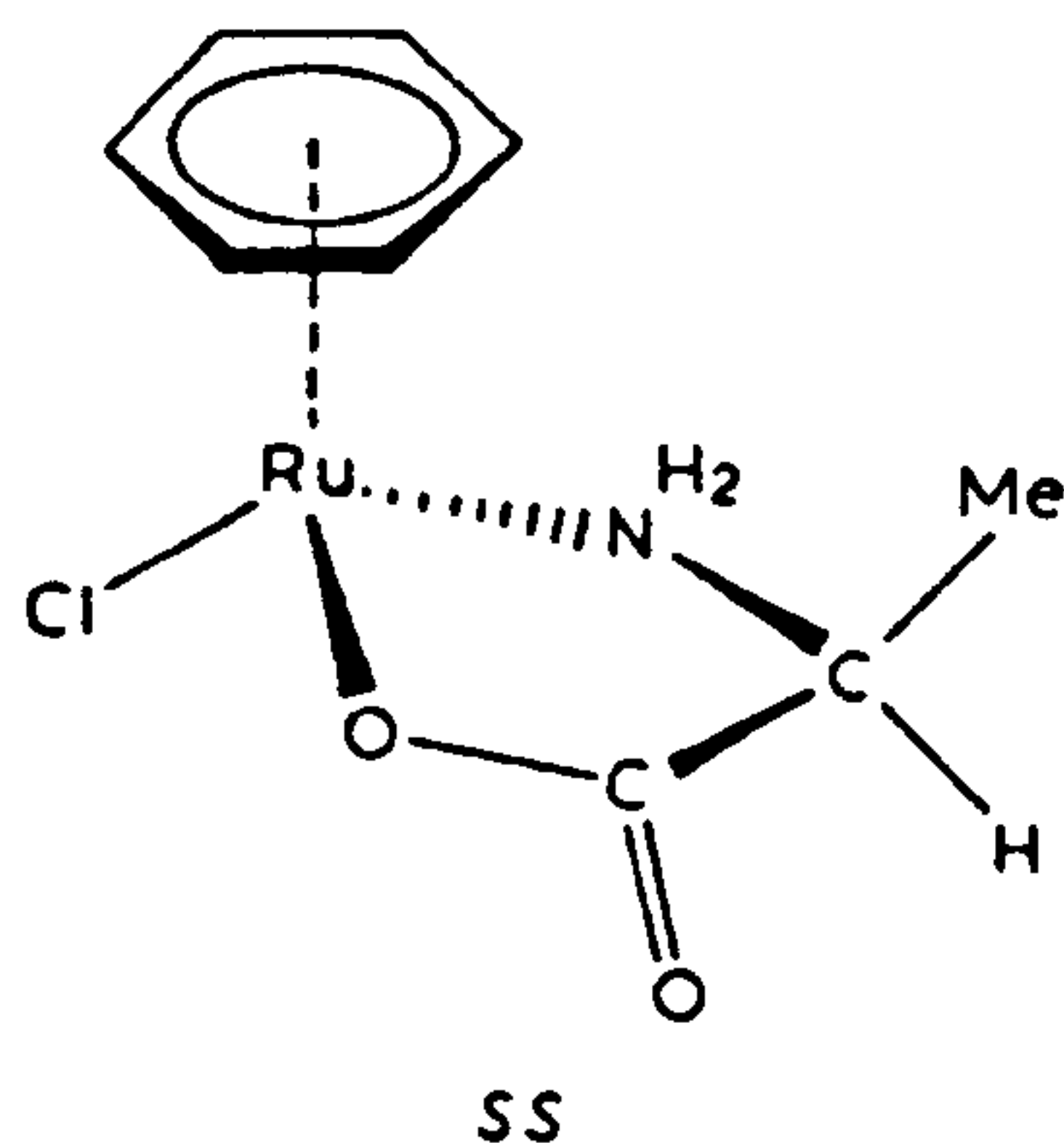
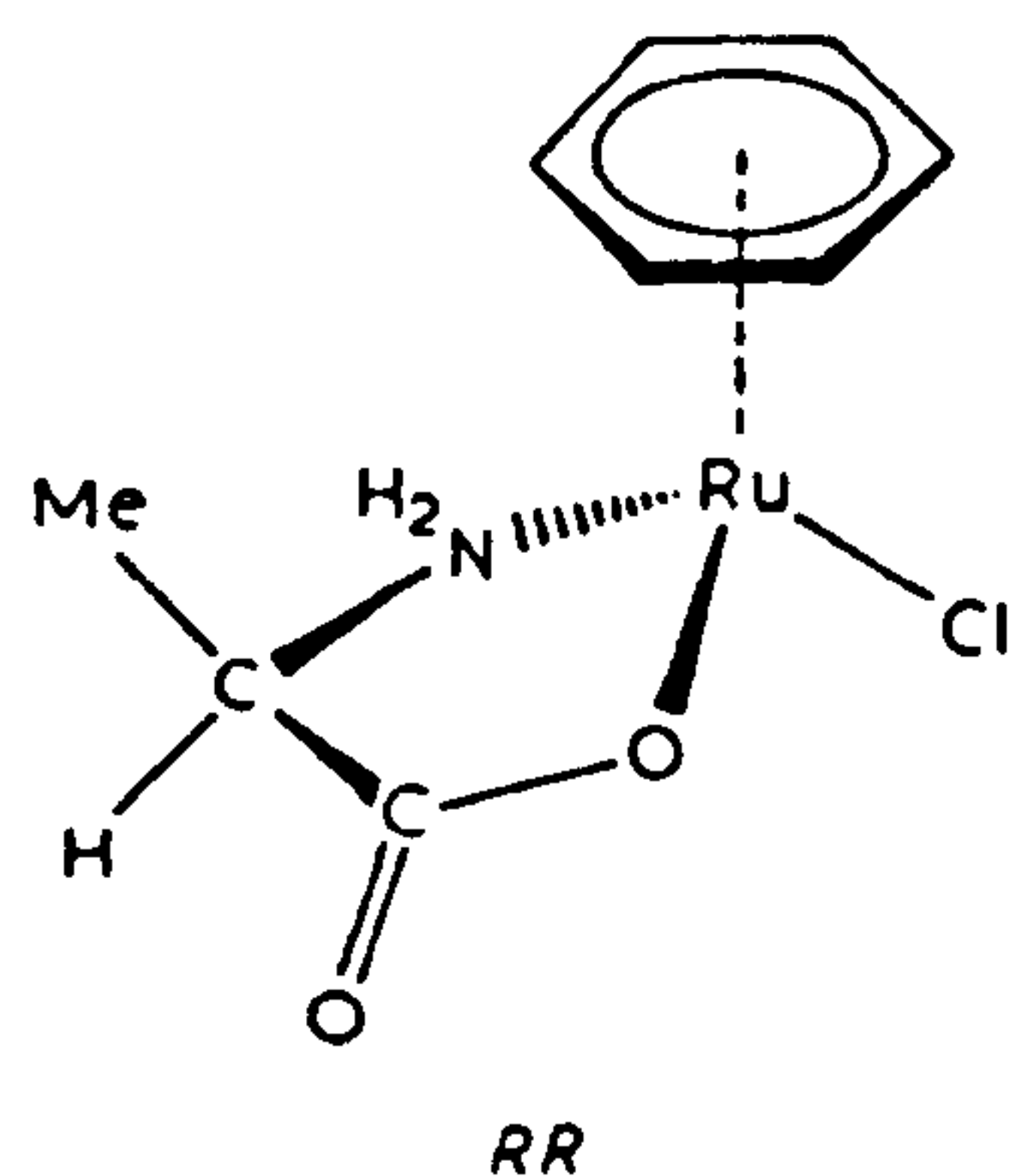
Addition of $SnCl_2$ to this product forms the $SnCl_3$ complex $[(C_6H_6)Ru(SnCl_3)(Me)(PPh_2NHCHMePh)]$.³⁹

As shown in scheme 1.2.1.2.1, another route to form chiral eta 6 arene ruthenium complexes is possible by the treatment of $[(C_6H_6)RuCl_2]_2$ with aminoacid anions, potassium glycinate or alanate.³¹



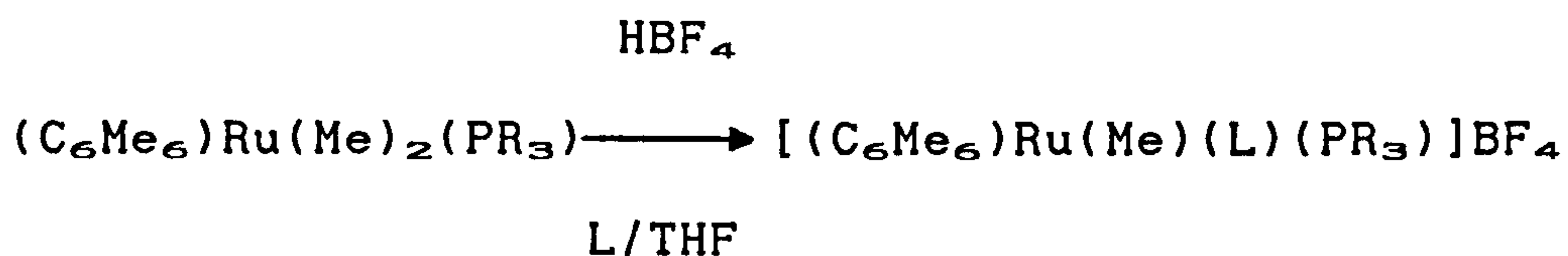
$R = H, Me.$

^1H and ^{13}C nmr spectroscopy readily distinguishes between the two diastereomerically related pairs of enantiomers, *RR*, *SS* and *RS*, *SR* of the alanto complex ($R = \text{Me}$).



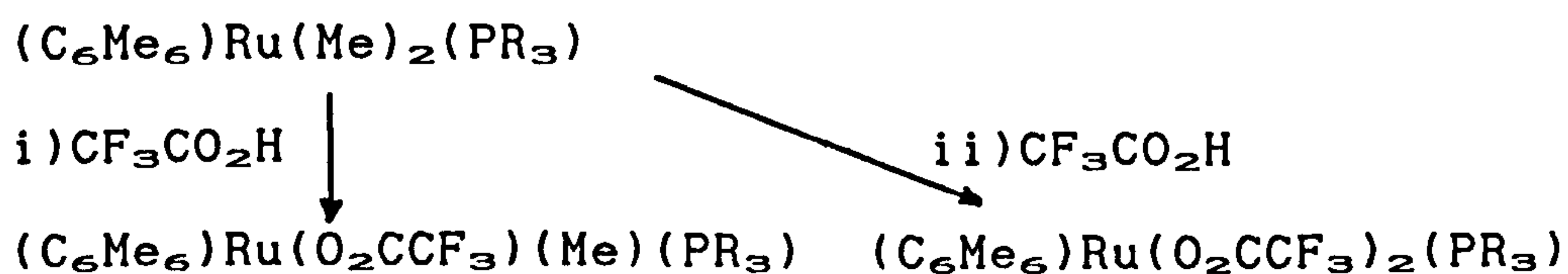
Werner et al have utilised methyl ruthenium complexes, via cleavage of Ru-Me bonds by acids, for the selective introduction of small molecules at the ruthenium centre.

On addition of HBF_4 to $(\text{C}_6\text{Me}_6)\text{Ru}(\text{Me})_2(\text{PR}_3)$, carbon monoxide or ethylene can be incorporated into the ruthenium coordination sphere;³⁵

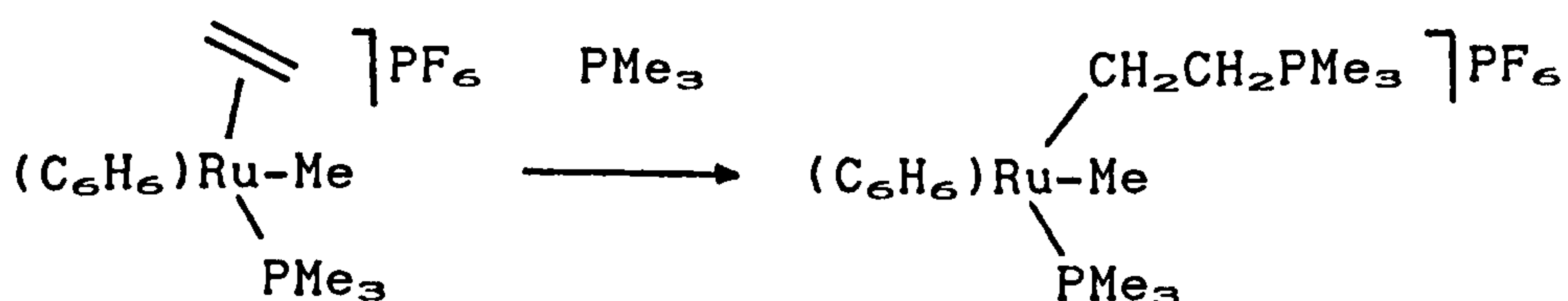


L	PR ₃
CO	PPh ₃
C ₂ H ₄	PPh ₃
C ₂ H ₄	PMe ₃

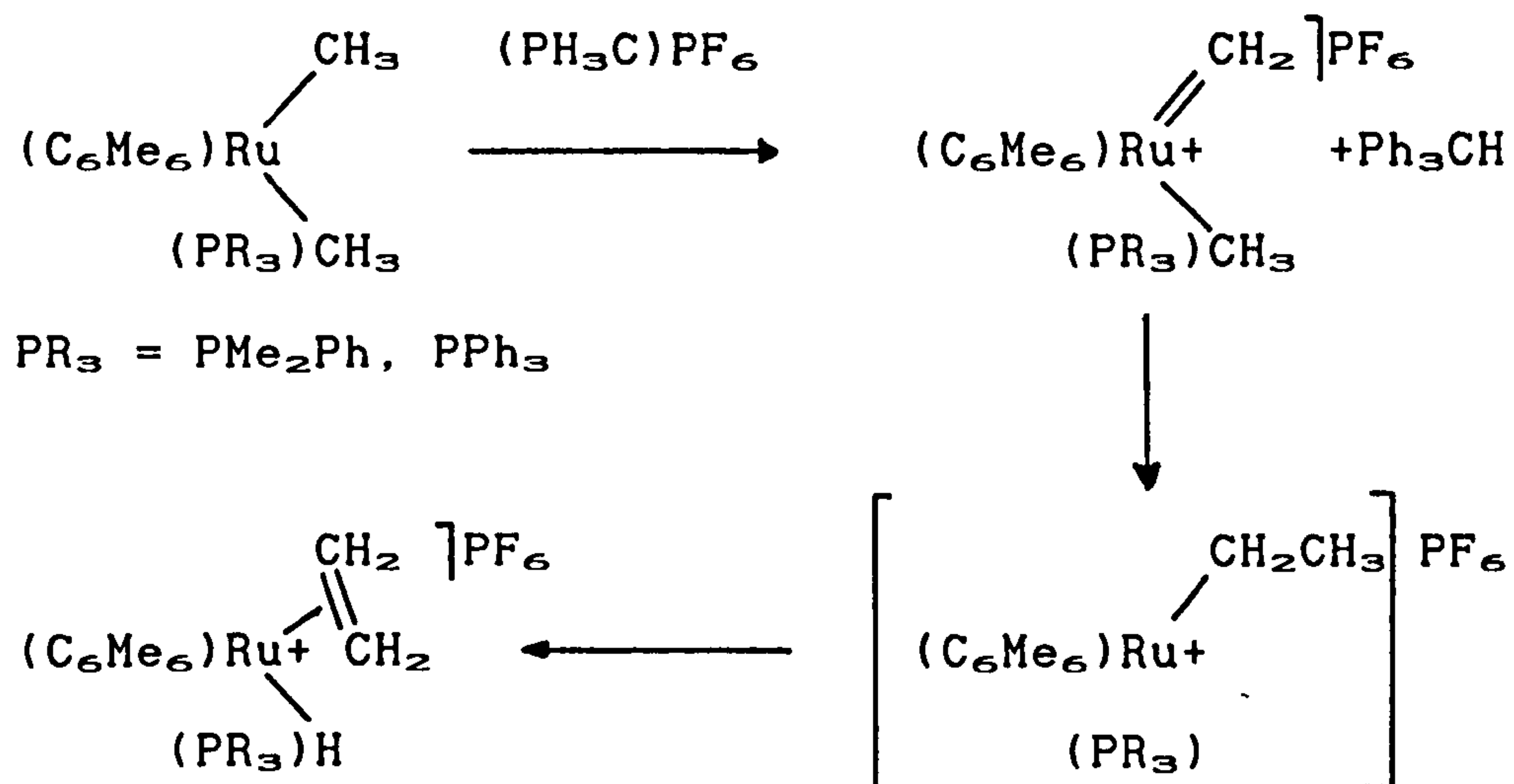
As shown above, on treatment with carboxylic acids the dimethyl ruthenium complexes will convert to a mono or bis acetato compound;^{34.35}



An alternative route to a bis(alkyl) ruthenium(II) complex is by the addition of PMe₃ to the ethylene compound $[(\text{C}_6\text{H}_6)\text{Ru}(\text{Me})(\text{C}_2\text{H}_4)(\text{PR}_3)]\text{PF}_6$.²⁷



A reaction carried out upon the bis(alkyl) complexes, was hydride abstraction affording ethylene complexes. Summarised below are the reactions and proposed pathway.^{38,40}



The above scheme is proposed as a model reaction of an elementary step in the Fischer-Tropsch synthesis.⁴⁰ Studies of the mechanism of the heterogeneous Fischer-Tropsch synthesis have established that the chain forming step, ie the coupling of C-C bonds on the surface of the catalyst proceeds via successive insertion of the methylene groups into the metal-alkyl bonds.⁴¹

The X-ray structure has been determined for the ethylene hydride triphenylphosphine cation and shows bond distances of 1.50Å° for Ru-H and

1.41(1) Å for the ethylene ligand C-C bond, significantly longer than in the free olefin.^{38,40}

Addition of $(\text{Ph}_3\text{C})\text{PF}_6$ to the mono alkyl species $[(\text{C}_6\text{Me}_6)\text{RuCl}(\text{Me})(\text{PMe}_3)]$, results in abstraction of the methyl group to yield $[(\text{C}_6\text{Me}_6)\text{RuCl}(\text{PMe}_2\text{Ph})(\text{PMe}_3)]\text{PF}_6$, in the presence of PMe_2Ph .³⁸

1.2.1.5 Hydrido arene ruthenium complexes

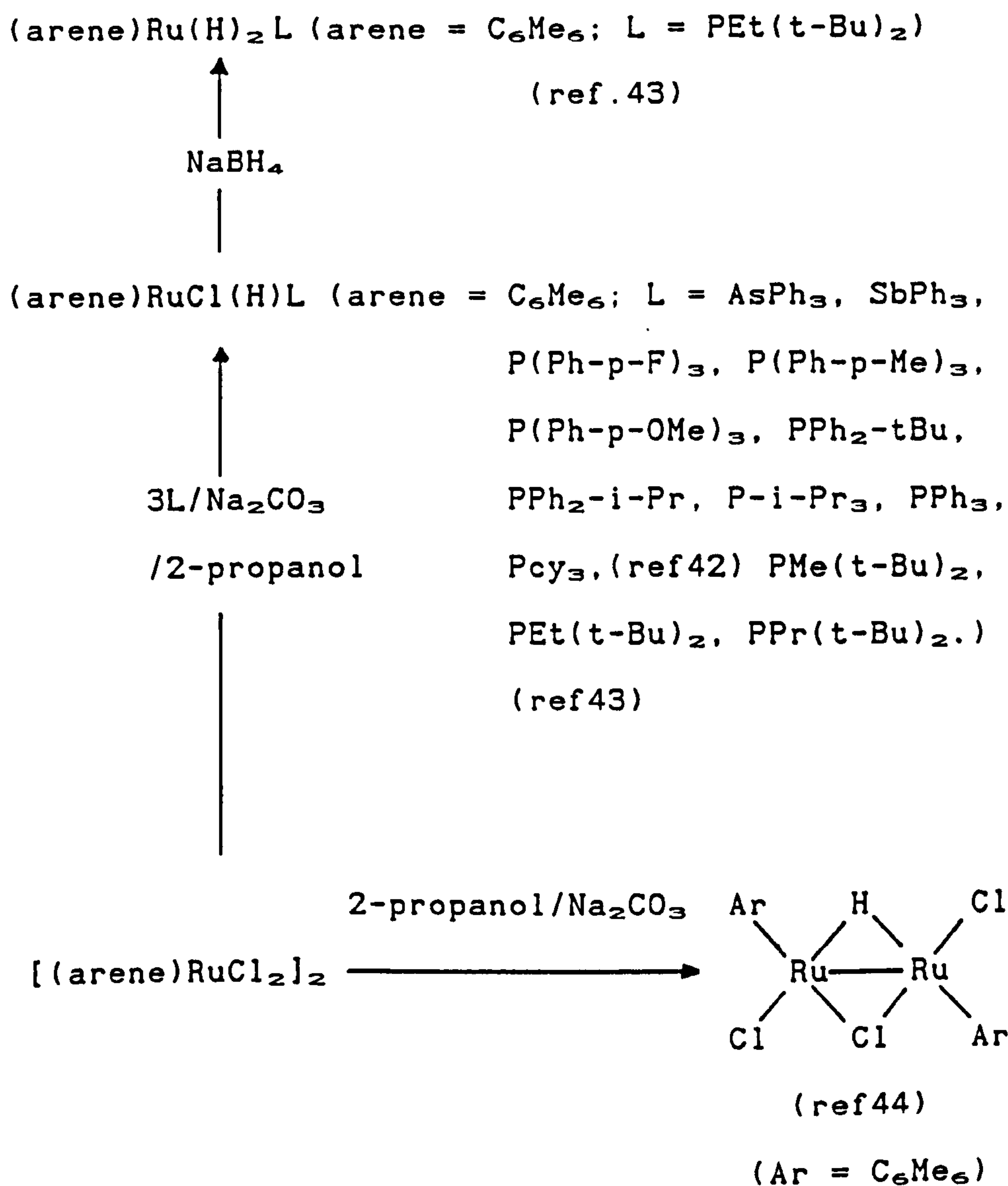
As stated earlier, investigation of these types of complexes demonstrated their usefulness as an entry to arene ruthenium(0) intermediates and C-H bond activation.

Two general routes utilised to prepare hydrido arene ruthenium complexes are;

- i) selective reduction of the arene ruthenium(II) compounds.
- or ii) protonation of arene ruthenium(0) compounds.

A wide variety of ruthenium arene substrates can be utilised to prepare hydride complexes including chloro dimers, half sandwich, acetato, trifluoroacetato, bis L, L' Ru(0) and alkyl arene complexes. Metal vapour synthesis has also recently been applied to this field.

Shown schematically below are the reactions of these substrates;

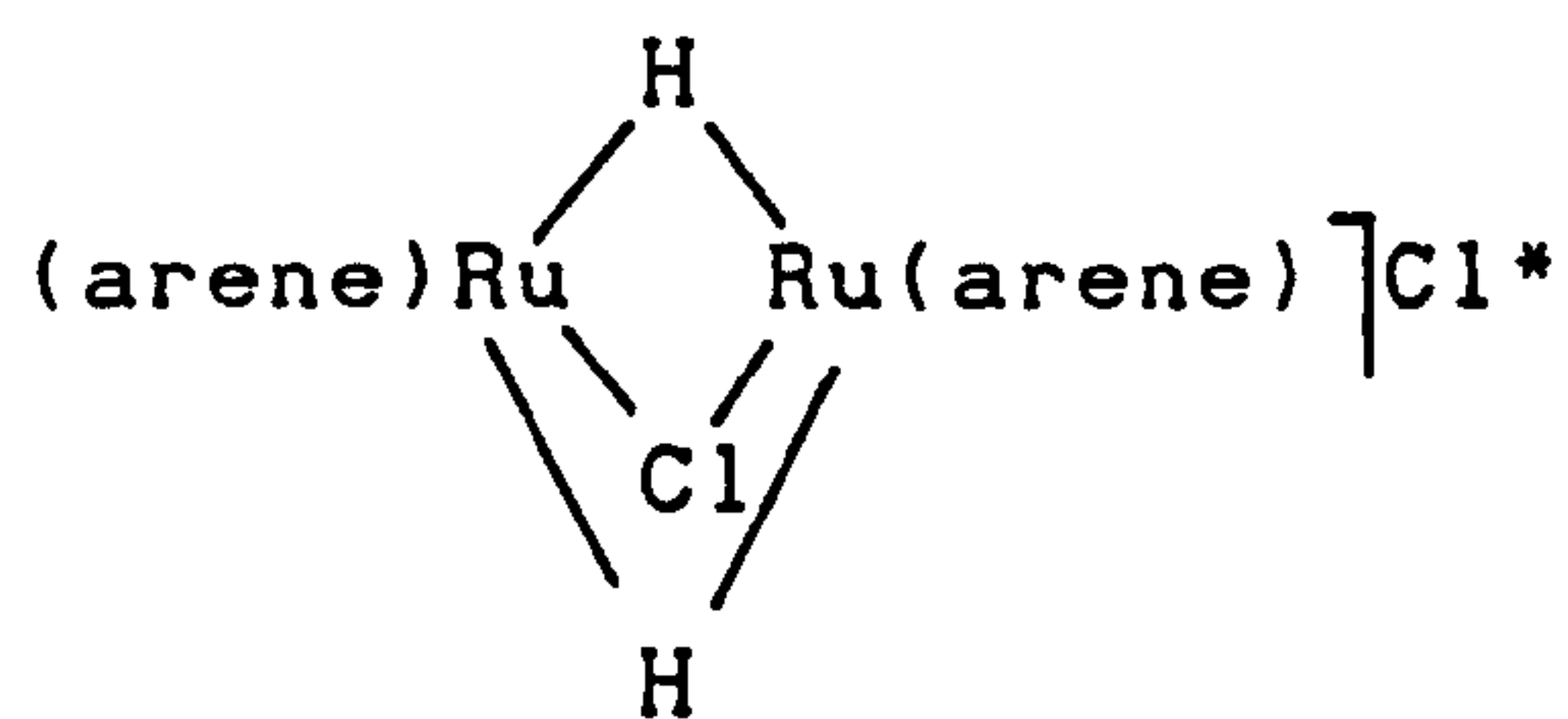


Scheme 1.2.1.5.1 Preparation of hydrido complexes
 from $[(\text{arene})\text{RuCl}_2]_2$.



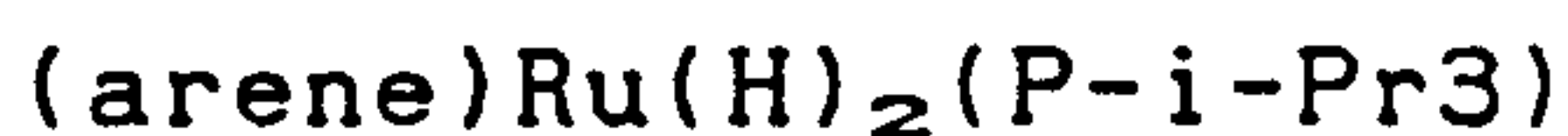
(ref45)

(arene = C_6H_6) (ref46)



(arene = C_6Me_6 , $\text{C}_6\text{H}_3\text{Me}_3$)

*Not reproducible

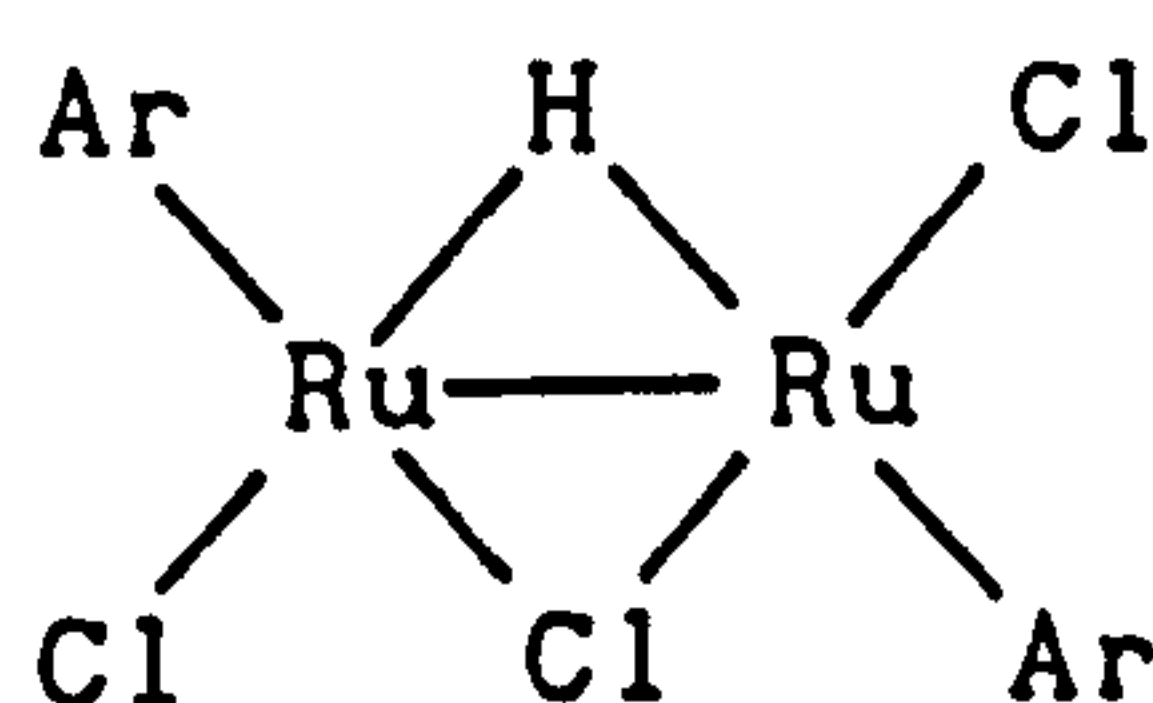


(arene = C_6H_6) (ref46)

i) P-Pr_3

ii) Red-Al

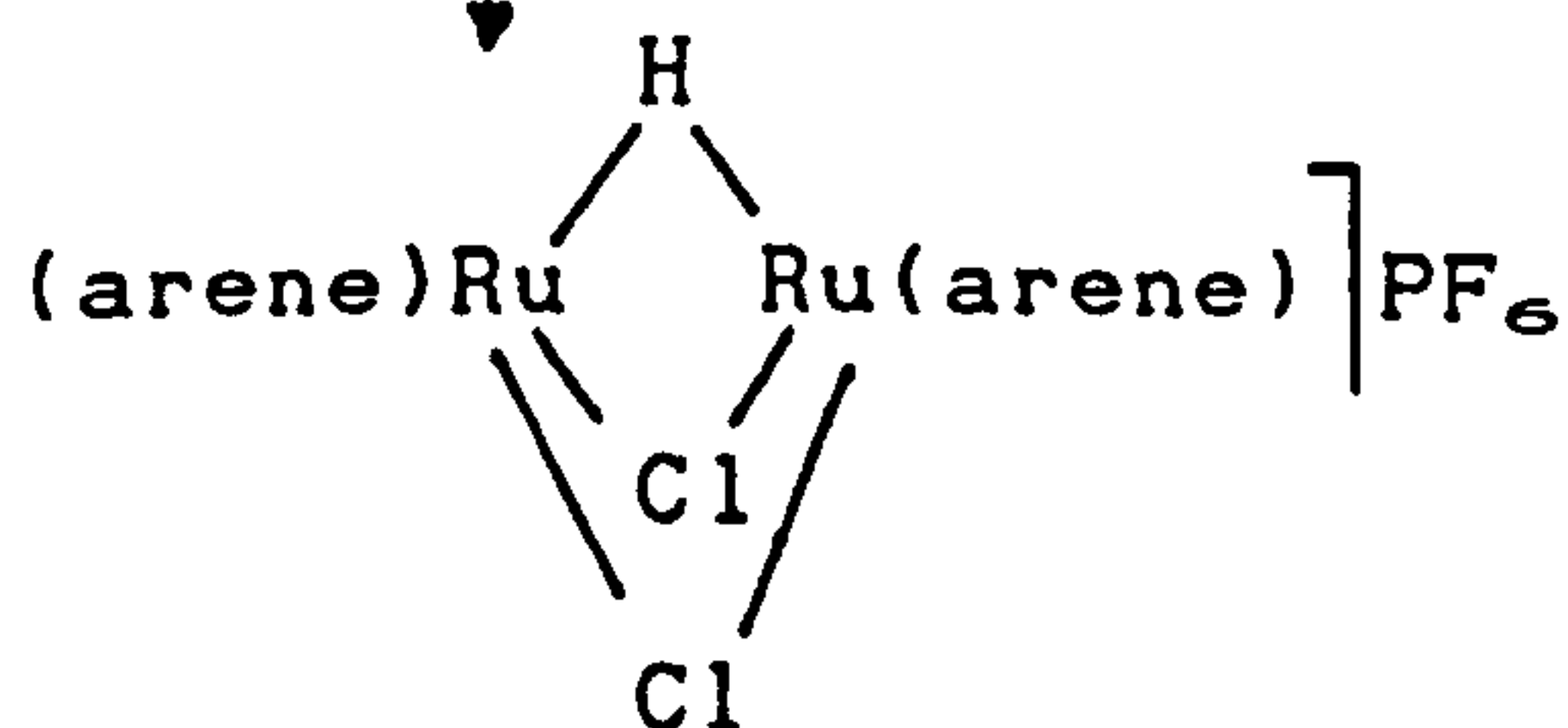
2-propanol/ Na_2CO_3



X = Cl, Br; Ar = C_6Me_6 , $\text{C}_6\text{H}_2\text{Me}_4$,
 $\text{C}_6\text{H}_3\text{Me}_3$.

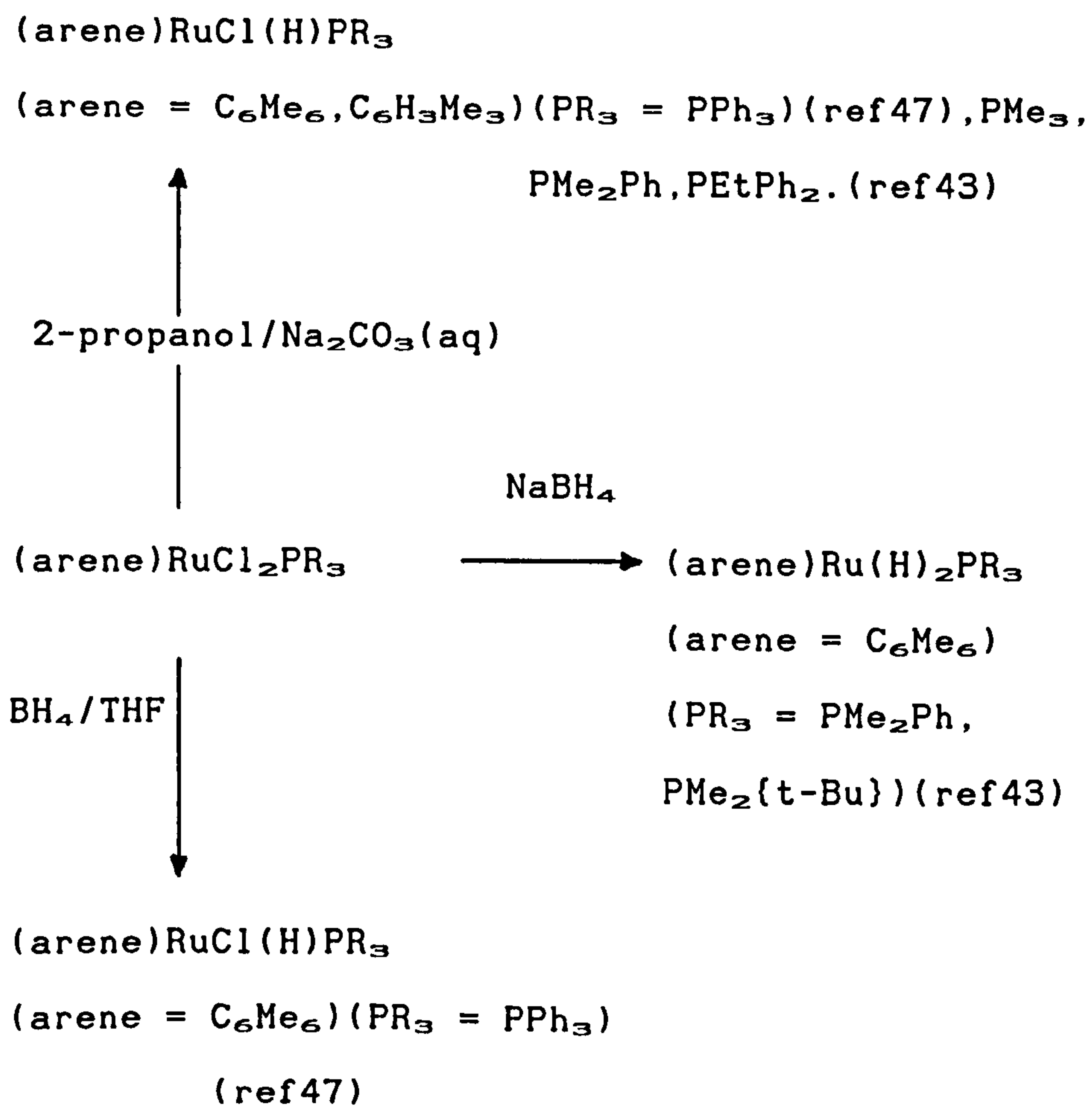
X = Cl; Ar = C_6H_6 , $\text{MeC}_6\text{H}_4\text{CHMe}_2$ (arene = $\text{C}_6\text{H}_3\text{Me}_3$) (ref45)

(ref44)

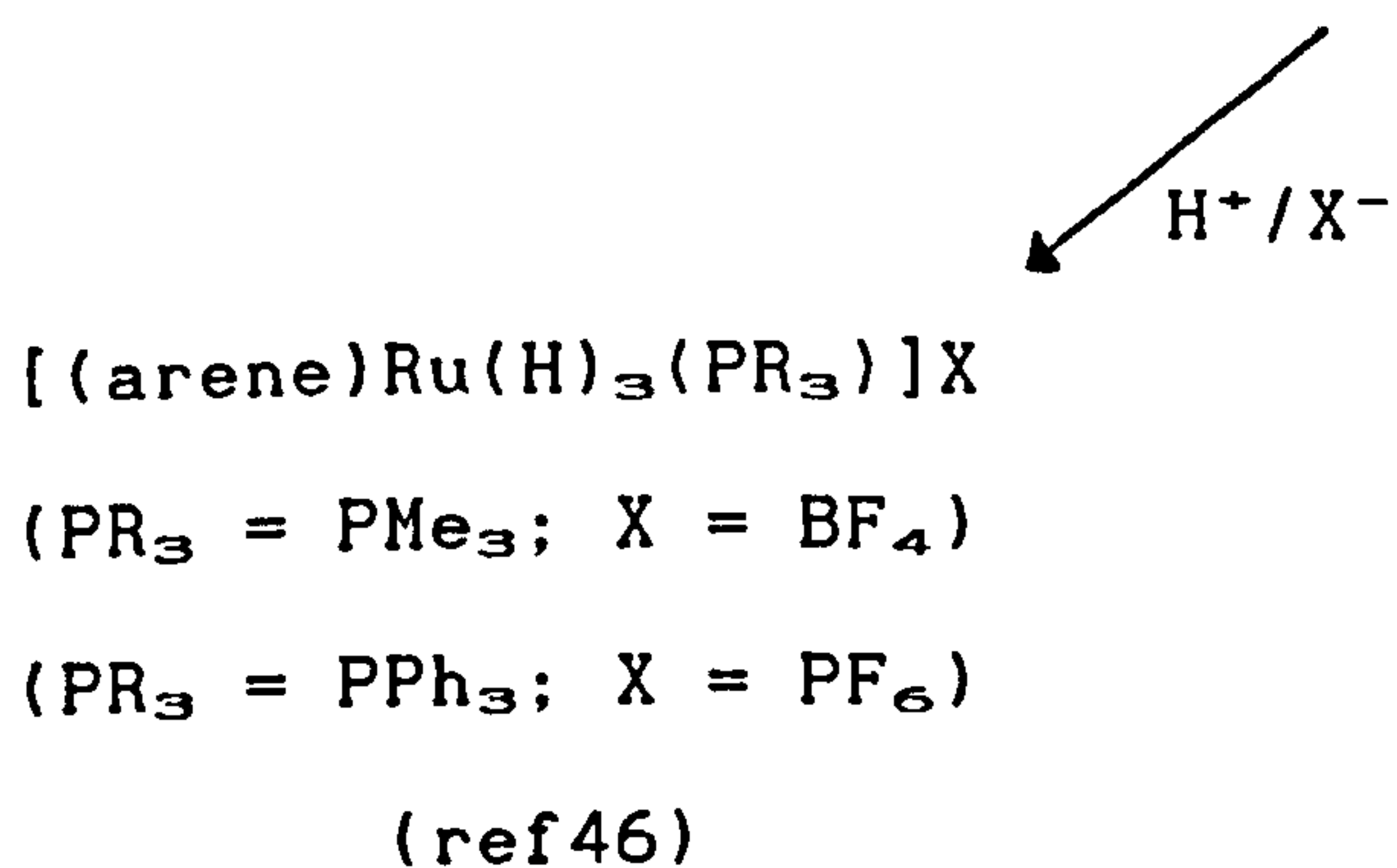
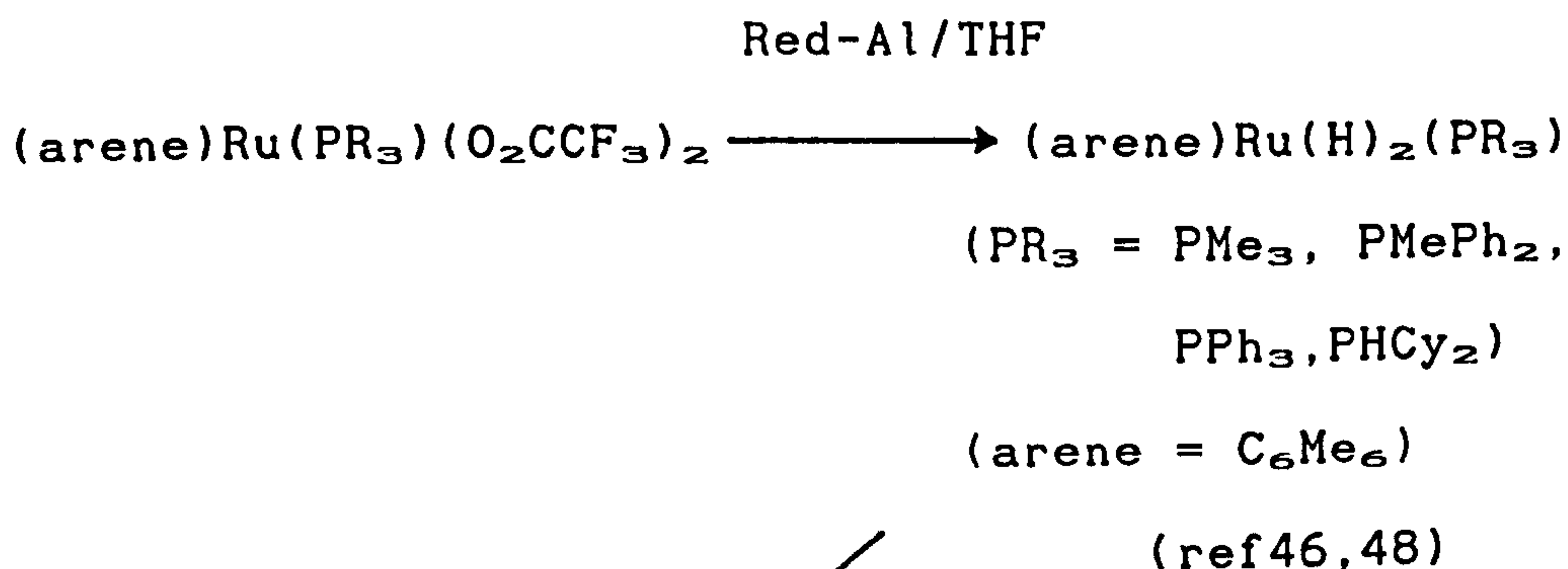
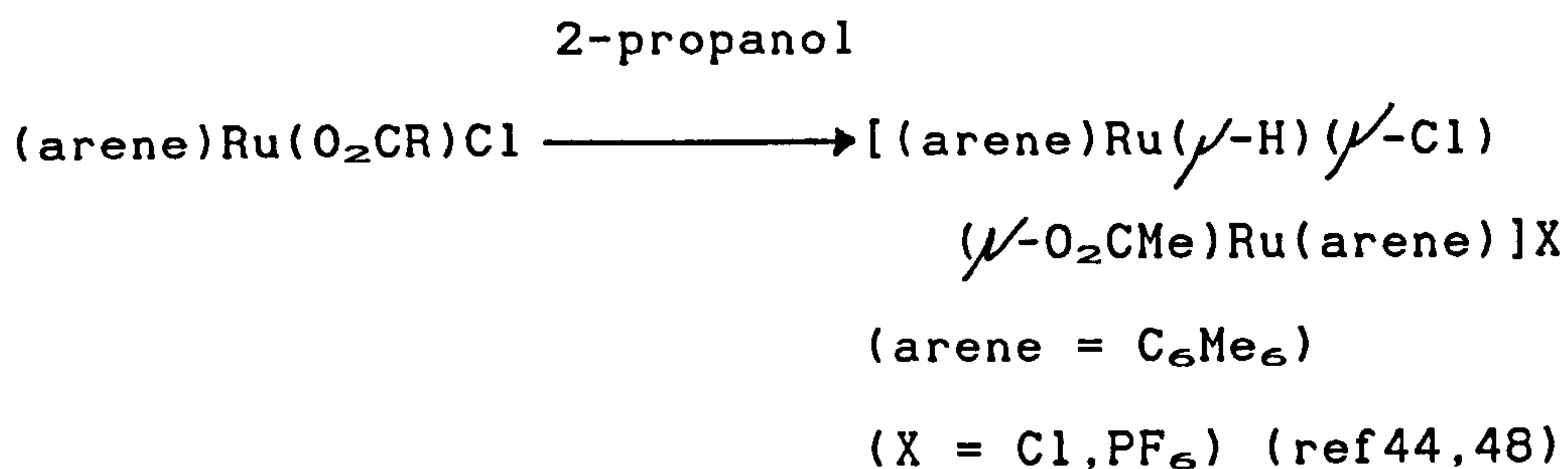
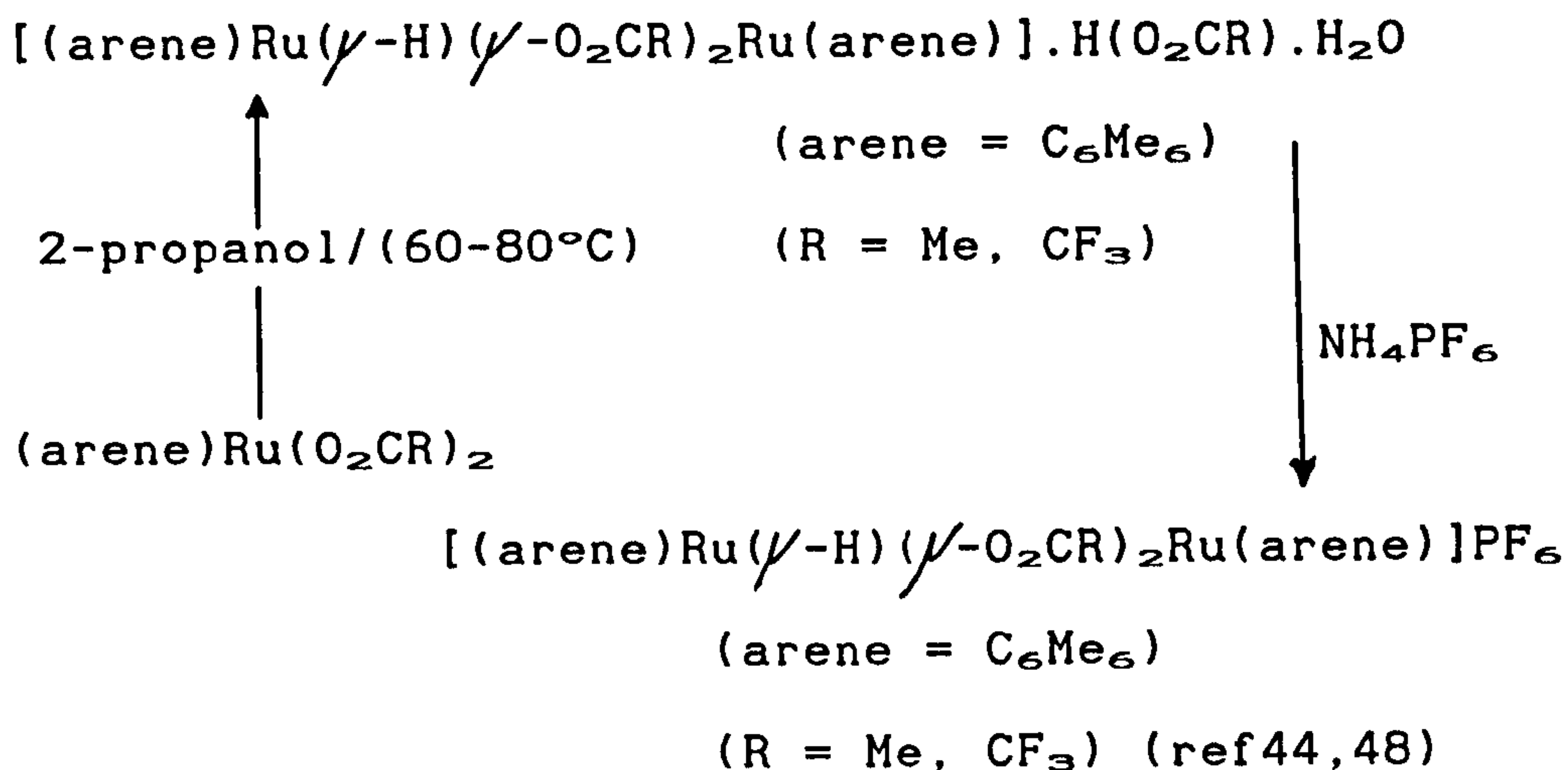


(arene = C_6Me_6 , $\text{C}_6\text{H}_2\text{Me}_4$,
 $\text{C}_6\text{H}_3\text{Me}_3$, C_6H_6 ,
 $\text{MeC}_6\text{H}_4\text{CHMe}_2$)
(ref44)

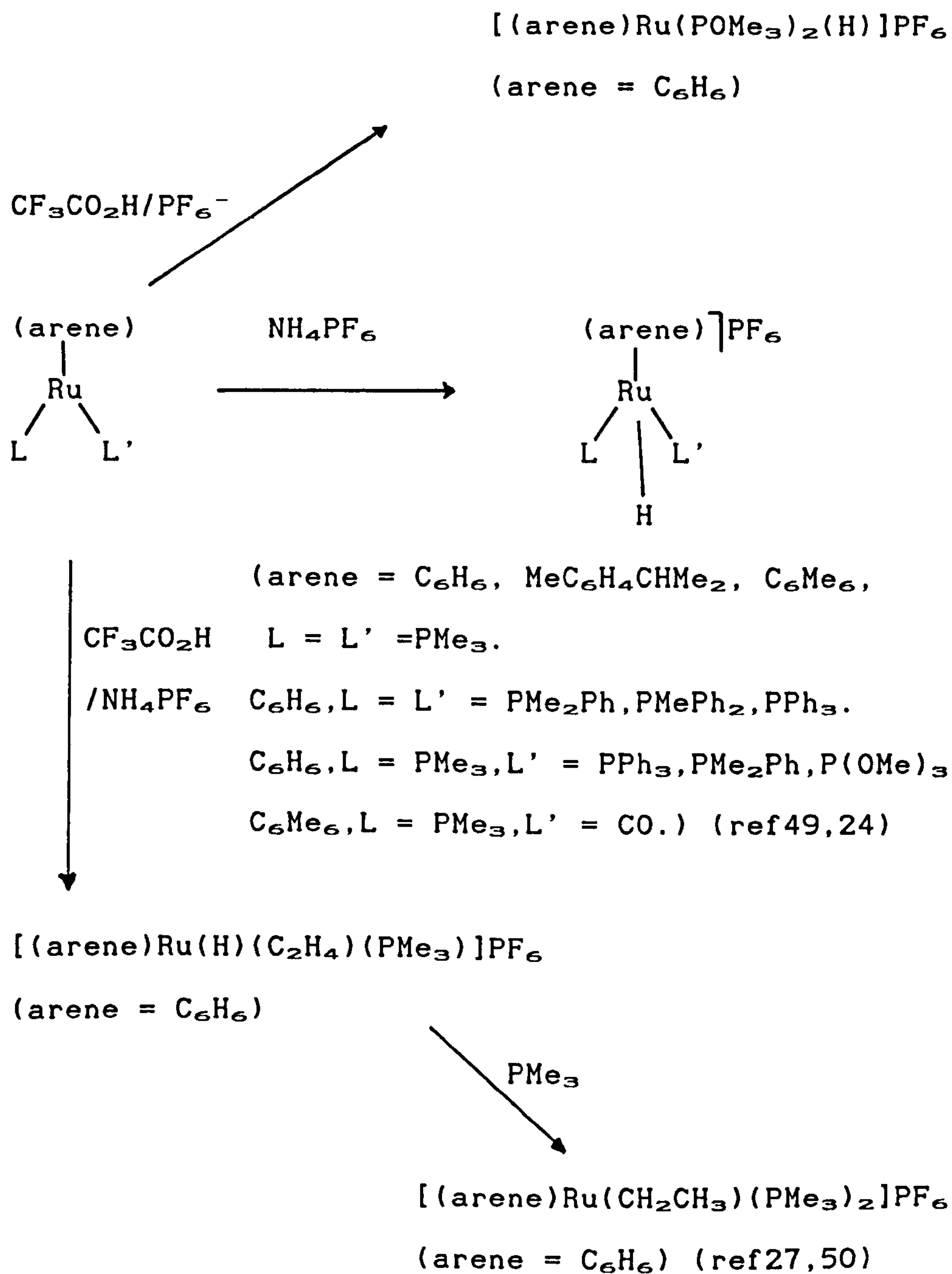
Scheme 1.2.1.5.1 (continued)



Scheme 1.2.1.5.2 Preparation of hydrido complexes from half sandwich complexes.

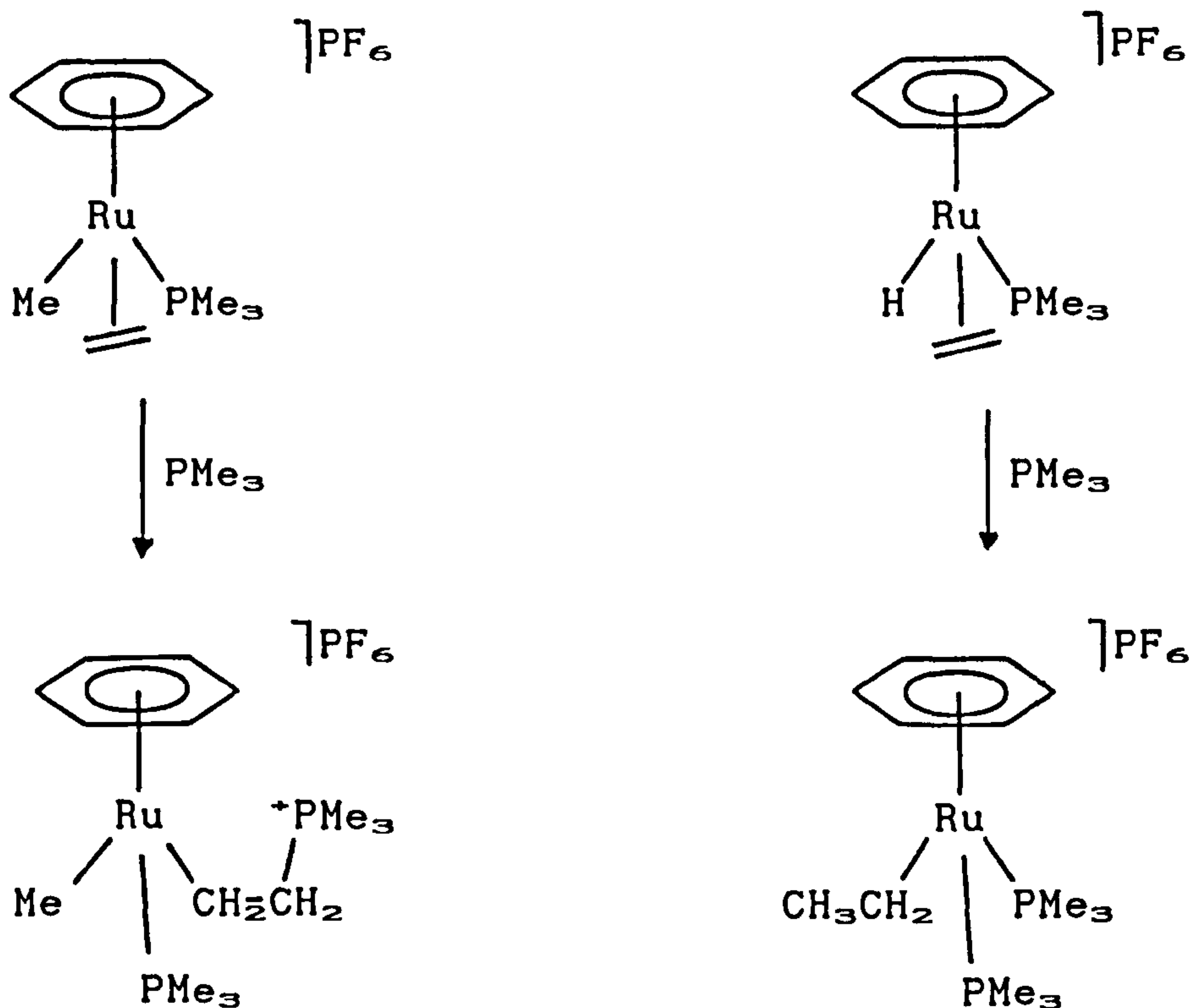


Scheme 1.2.1.5.3 Preparation of hydrido complexes from arene ruthenium acetato and trifluoroacetato compounds.



Scheme 1.2.1.5.4 Preparation of hydrido complexes from bis L,L' ruthenium(0) compounds.

Comparison of the complexes'
 $(C_6H_6)Ru(R)(C_2H_4)(PMe_3)$ ($R = Me, H$) reactions with
 PMe_3 shows that two types of products are
 afforded.²⁷

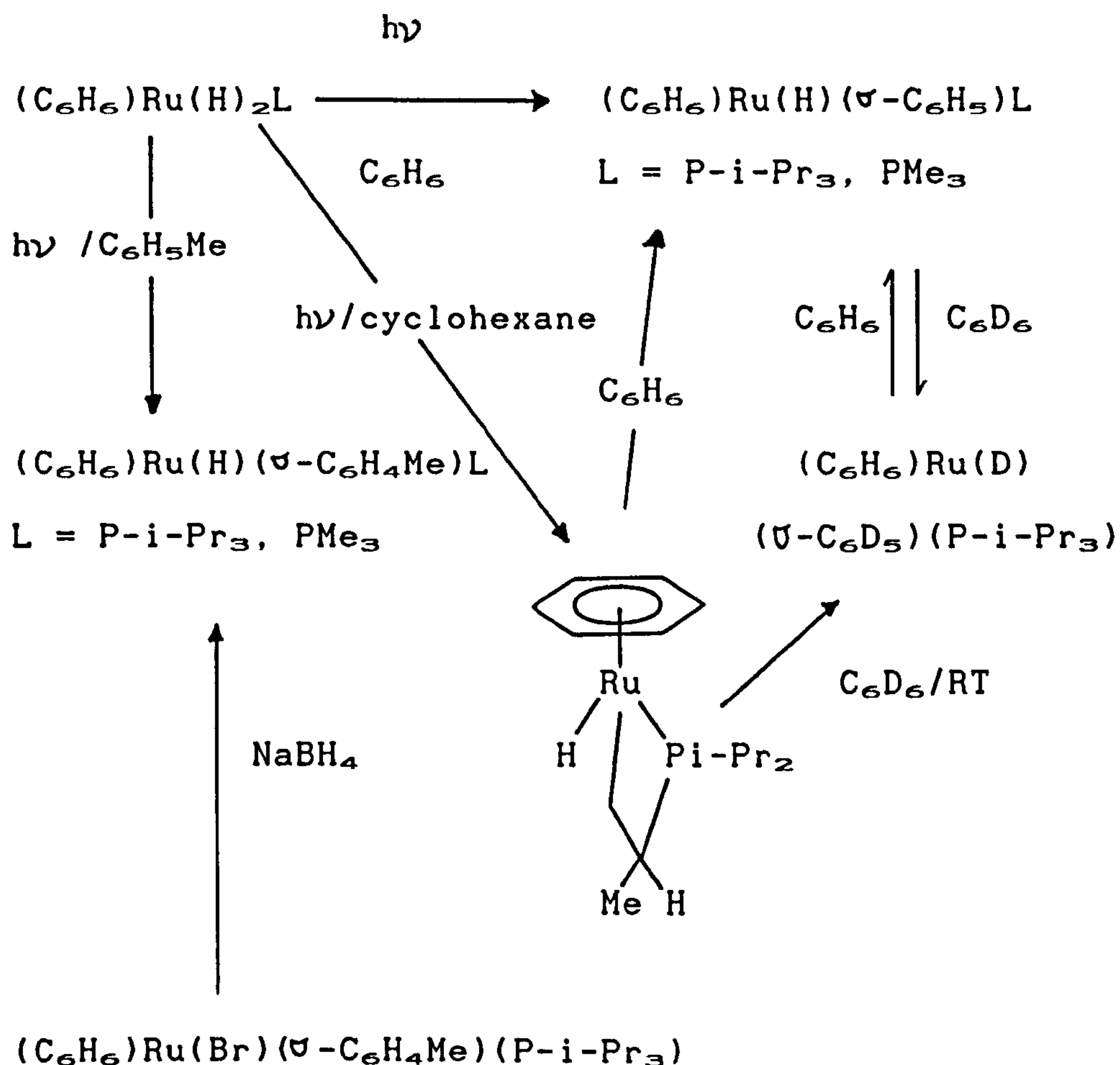


1.2.1.6 C-H bond activation and cyclometallated arene ruthenium complexes.

A range of methods have been applied to the synthesis of these complexes: photolysis, reduction (borohydride, methyllithium, phenyllithium and red-aluminium) and metal vapour.

Photolysis of the dihydrido species
 $[(arene)Ru(H)_2(L)]$ in an arene source causes H_2

elimination and C-H bond activation;⁵¹

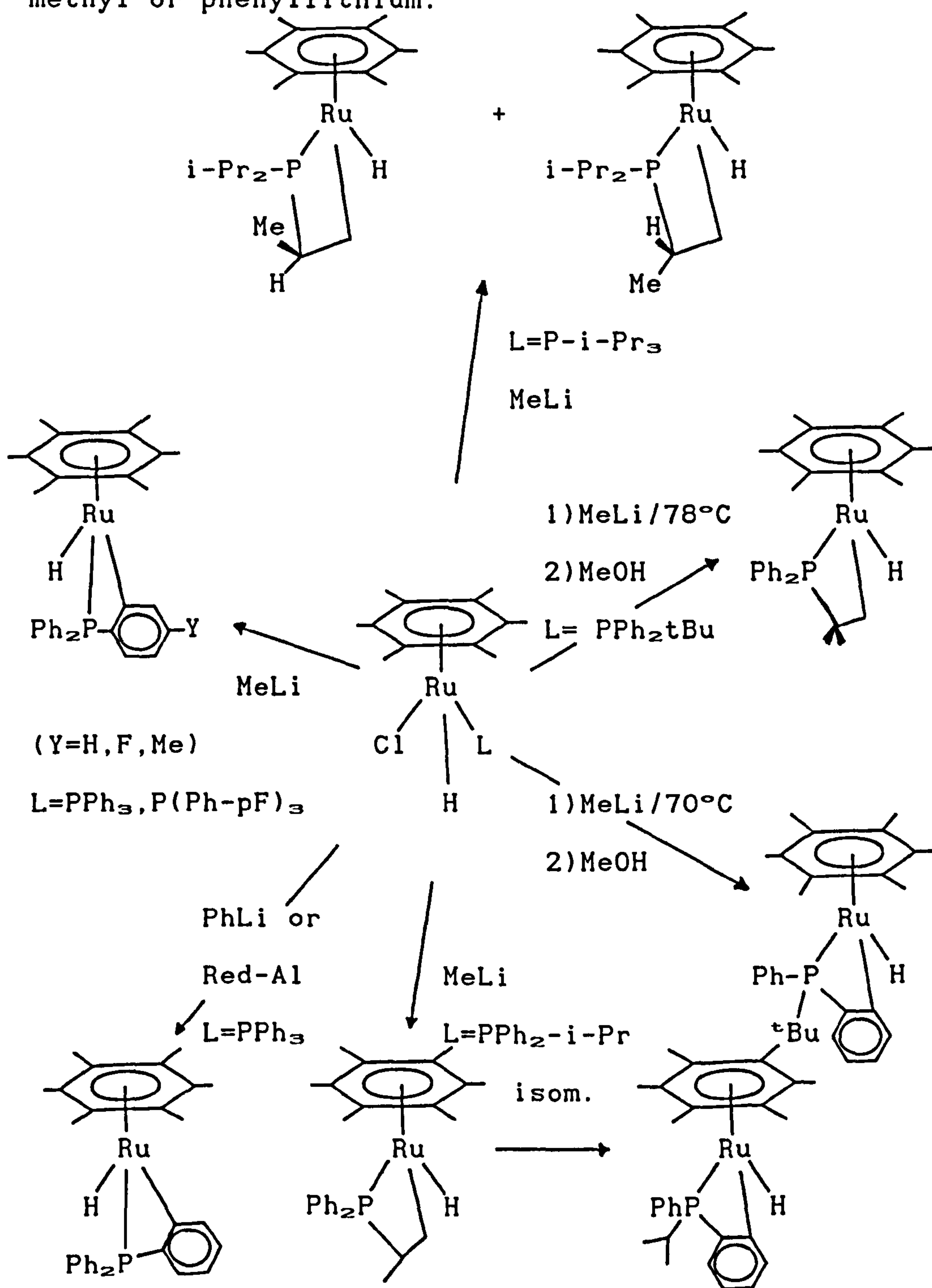


Scheme 1.2.1.6.1 C-H bond activation via photolysis

An interesting observation shown in scheme 1.2.1.6.1 is the contrast in products when photolysis of the dihydrido ruthenium complex occurs in cyclohexane and not an arene source. The cyclometallated complex shown arises from intramolecular C-H bond activation.⁵¹

A useful access to orthometallated complexes is

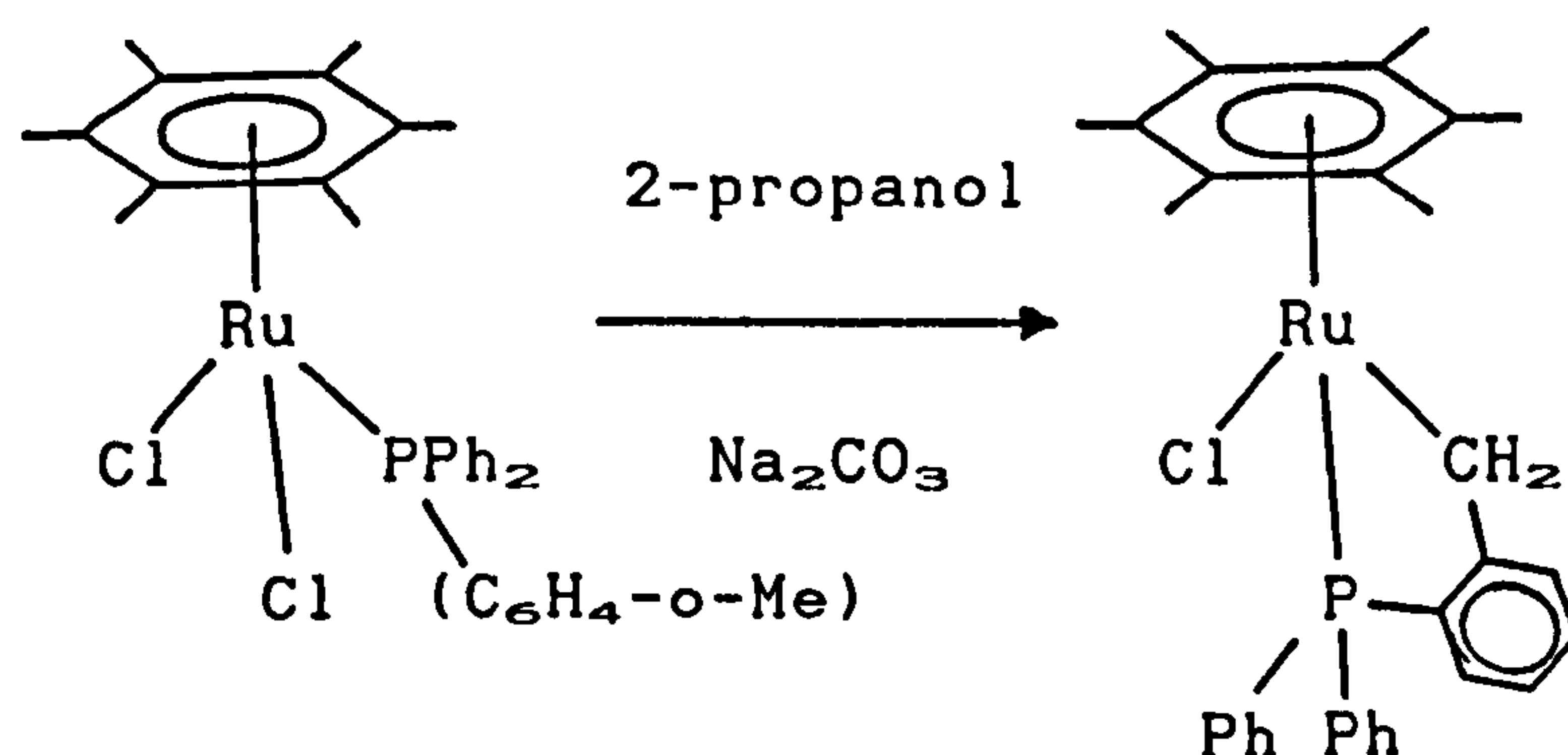
the reaction of $(C_6Me_6)Ru(H)(Cl)(L)$ complexes with methyl or phenyllithium.⁴²



Scheme 1.2.1.6.2 Utilisation of $(arene)RuCl(H)L$ to afford orthometallated complexes.

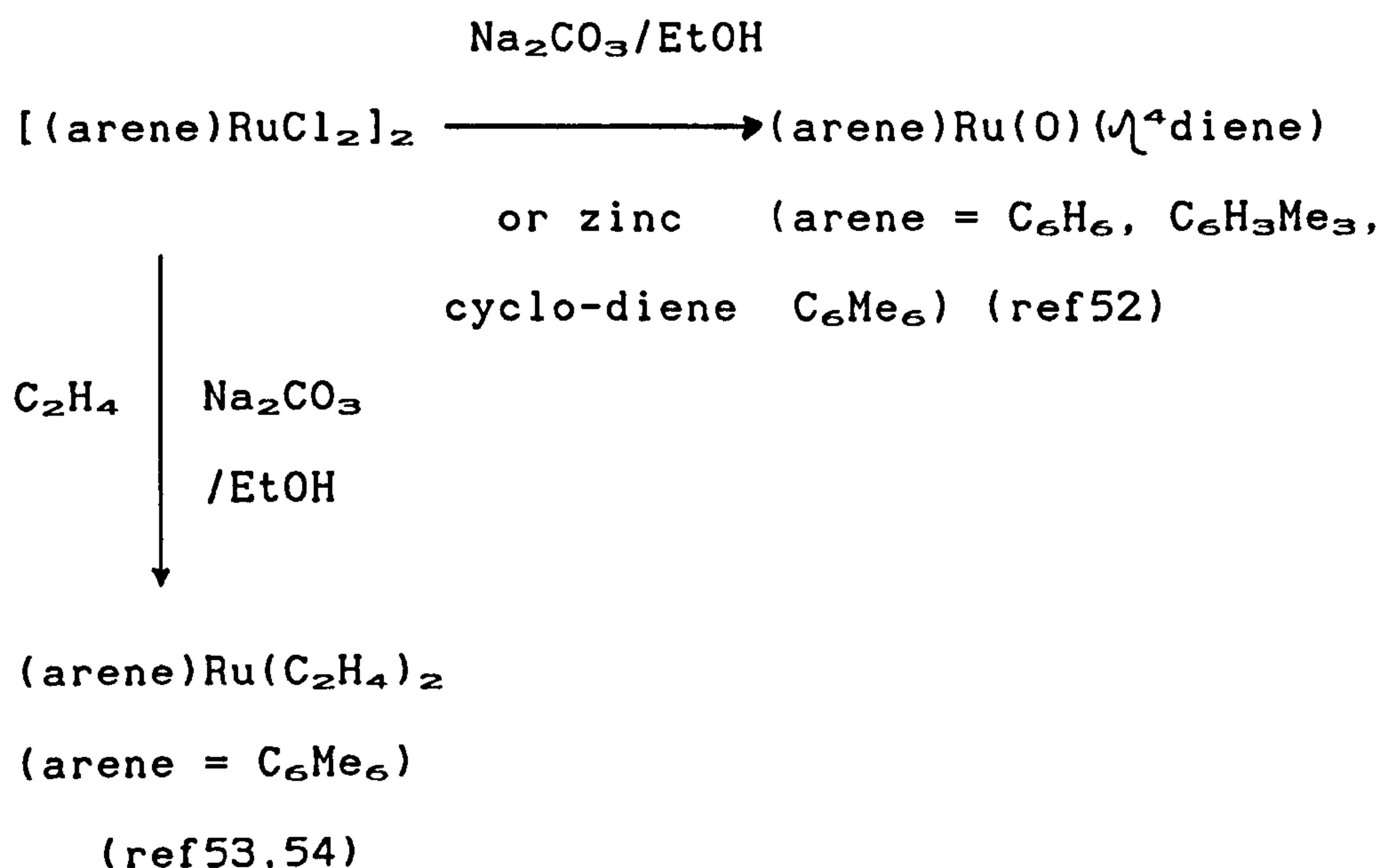
The formation of $[(C_6Me_6)Ru(H)(PC_6H_xR_{5-x}C_6H_{x-1}R_{4-x})]$ from $[(C_6Me_6)Ru(H)(Cl)(PC_6H_xR_{5-x})_3]$ occurs most likely through an initial reduction to a 16 electron ruthenium(0) intermediate followed by C-H activation, as for the transformation of the dihydrido complexes $(arene)Ru(H)_2L$ to $(arene)Ru(H)(\eta-C_6H_5)L$.

An alternative C-H bond activation is that which occurs when the half sandwich complex $(C_6Me_6)RuCl_2PPh_2(C_6H_4-o-Me)$ is reacted using the conditions leading to $(arene)Ru(H)(Cl)(L)$ [2-propanol/ Na_2CO_3] the following cyclometallated compound is formed;⁴³



1.2.1.7 Preparation of arene ruthenium(0) complexes from [(arene)RuCl₂]₂.

The [(arene)RuCl₂]₂ complexes react with 1,5-cyclooctadiene and 1,3 or 1,4 cyclohexadiene in the presence of ethanol and Na₂CO₃ or zinc dust to yield (arene)Ru(0)(η^4 diene) compounds in 60% yield.

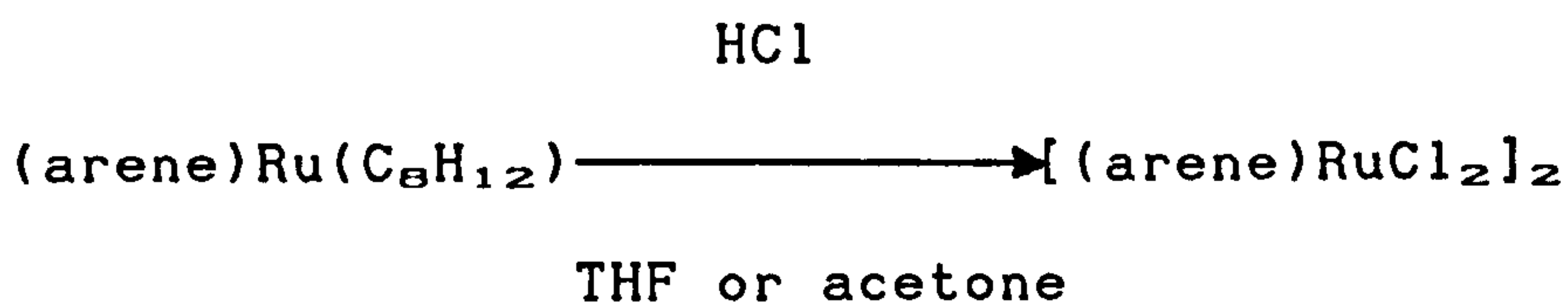


Scheme 1.2.1.7.1 Preparation of arene ruthenium(0) complexes from [(arene)RuCl₂]₂.

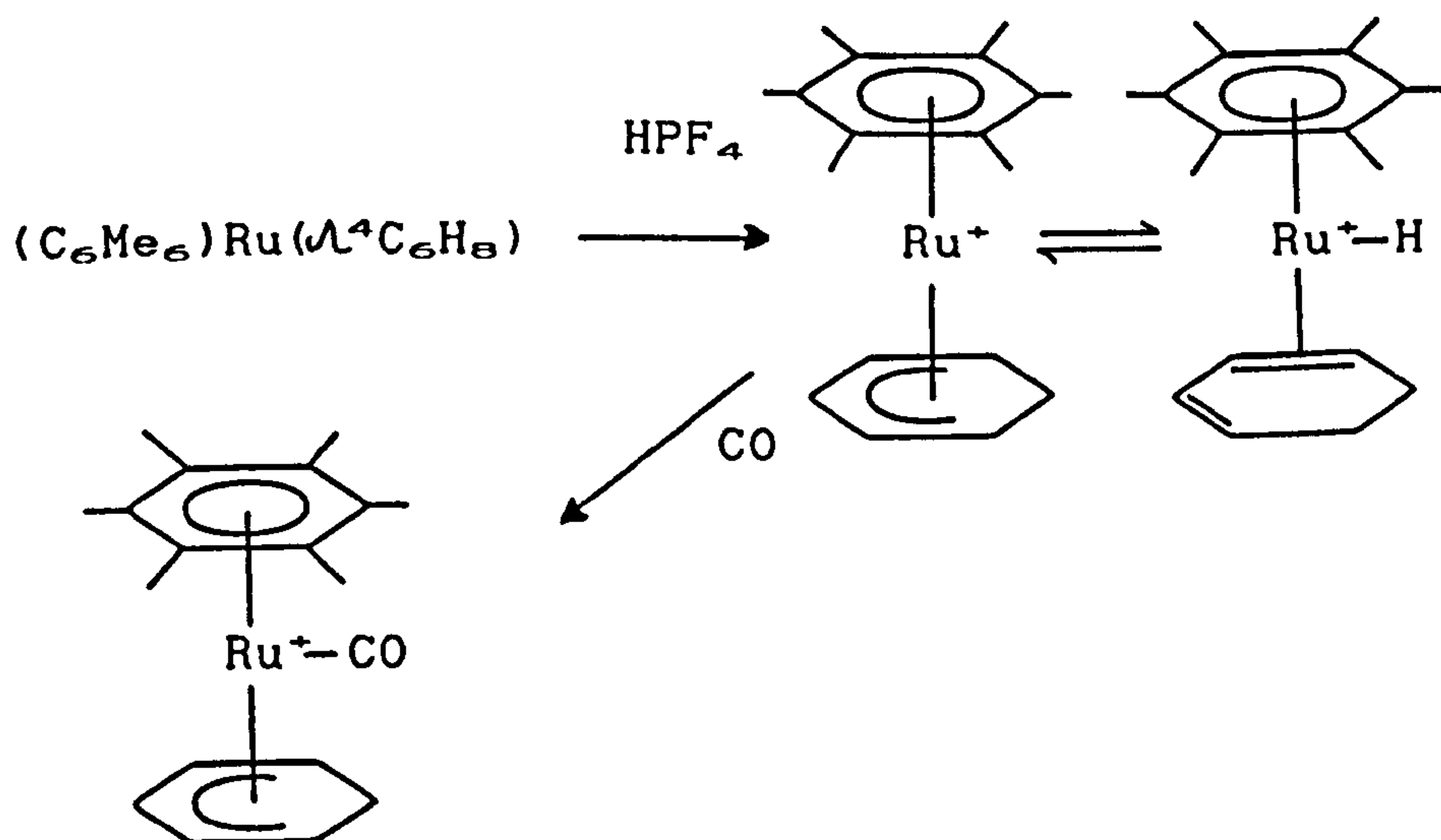
As could be expected, utilising these reaction conditions with ethylene replacing the cyclo-diene ligand, the bis(ethylene) ruthenium(0) complex is yielded (as shown above).

A synthetically useful reaction that (arene)

ruthenium (1,5-cyclooctadiene) complexes undergo, is the conversion to parent chloro dimer on treatment with aqueous HCl.⁵⁵



Protonation of the $(\text{C}_6\text{Me}_6)\text{Ru}(\text{O})(\eta^4\text{C}_6\text{H}_8)$ complex has been investigated. In solution it was determined that there was an equilibrium between an eta 4 diene ruthenium hydride species and a simple protonated diene. The protonated species adds carbon monoxide to afford the cationic carbonyl complex as shown below.³³



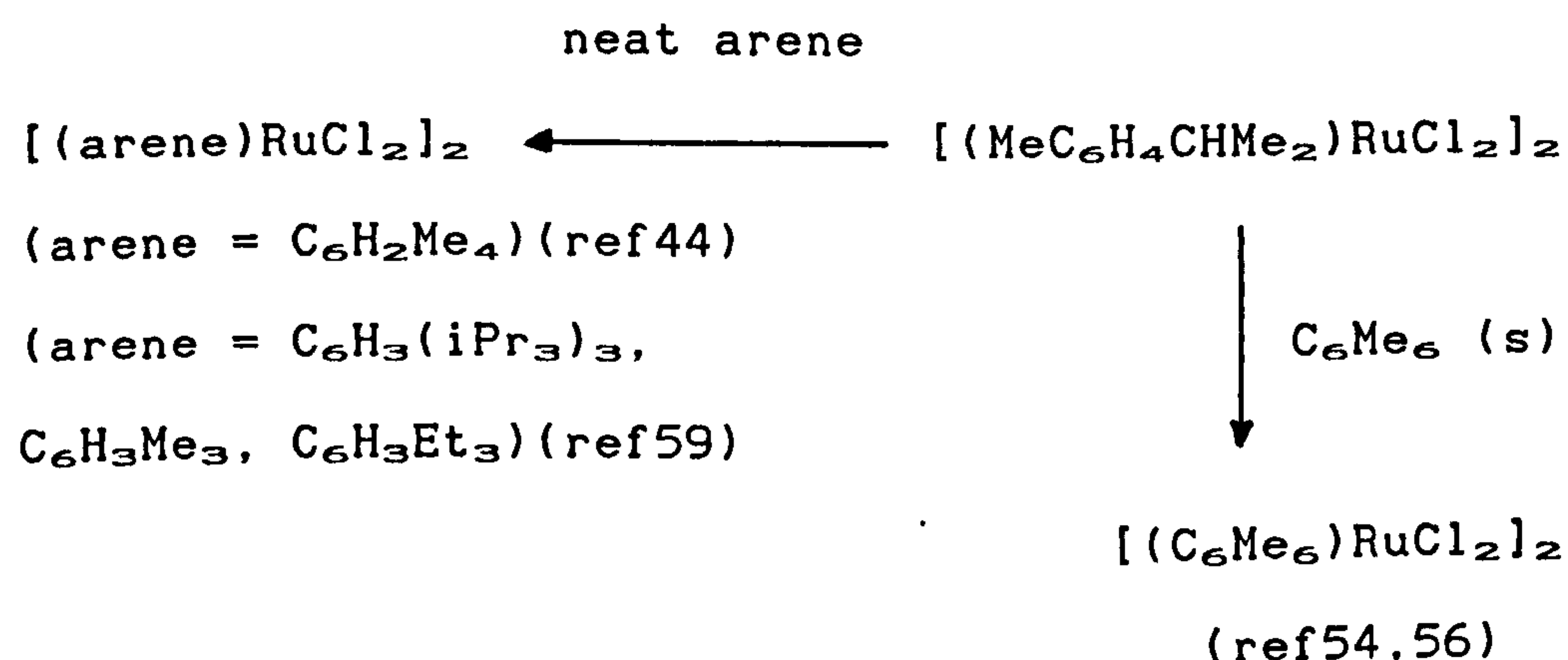
The $(\text{arene})\text{Ru}(1,4\text{-n-cyclooctatetraene})$

The isomerisation shown for the (arene)Ru(COT) cation is incomplete when the acid utilised is $\text{CF}_3\text{CO}_2\text{H}$. Nmr studies show an equilibrium process between the two complexes.

The hexamethylbenzene ruthenium(0) complex has been characterised using X-ray crystal structure determination. This shows the 1-4 coordination for the (COT) ligand.⁵⁷

1.2.1.8 Arene ligand exchange

An extensively utilised arene exchange reaction is applied in the synthesis of the $[(\text{C}_6\text{Me}_6)\text{RuCl}_2]_2$ complex. It is readily obtained not via a diene route but from an arene exchange reaction by displacement of the labile p-cymene ligand of the (cymene) ruthenium chloro dimer. Other arene dimers have also been prepared via this route;



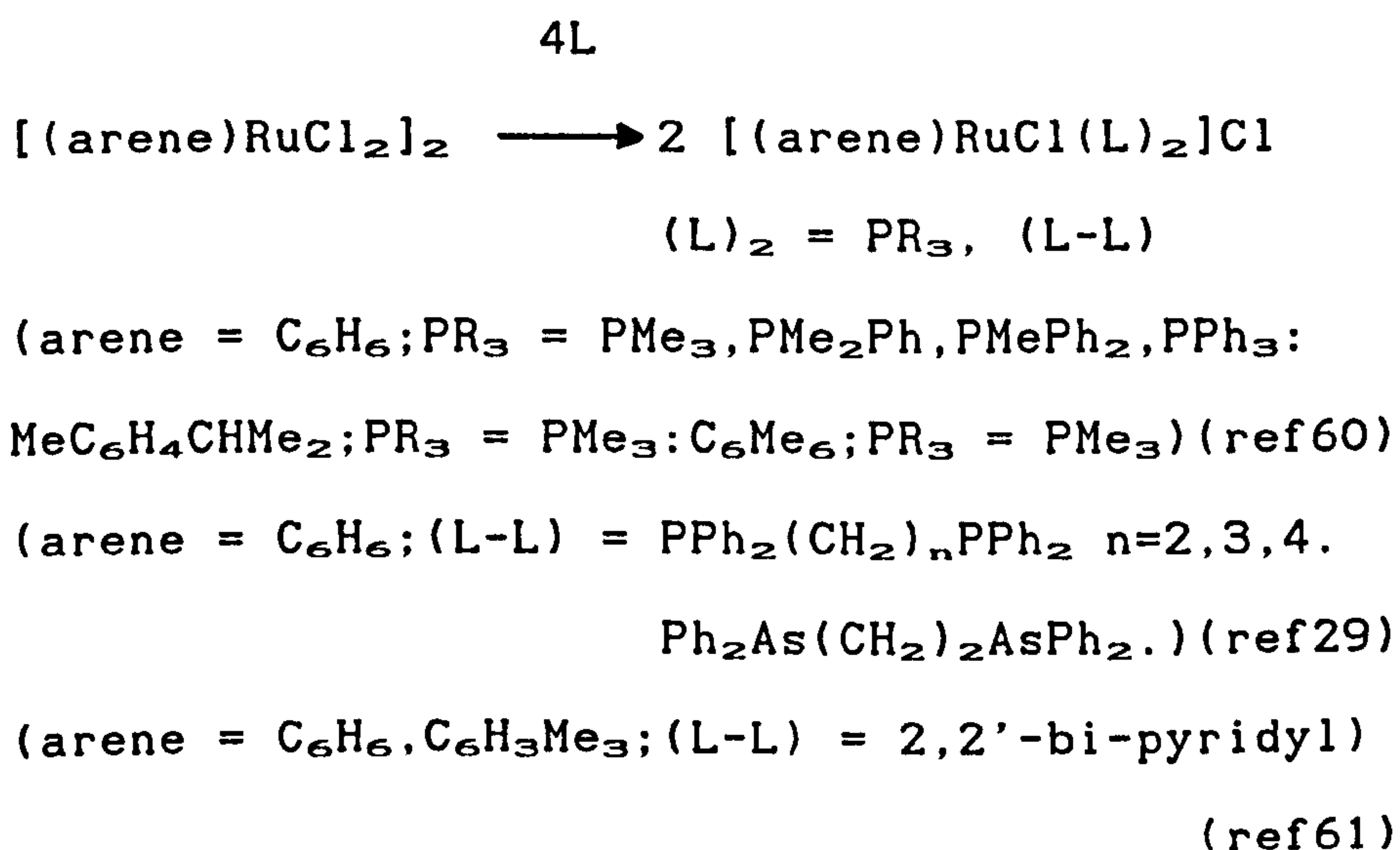
The half sandwich ruthenium complex $(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2(\text{PBU}_3)$ has also been shown to undergo arene exchange, photochemically and

thermally, with benzene and hexamethylbenzene in moderate yields.²

1.2.2 Ionic derivatives

1.2.2.1 Simple bridge cleavage

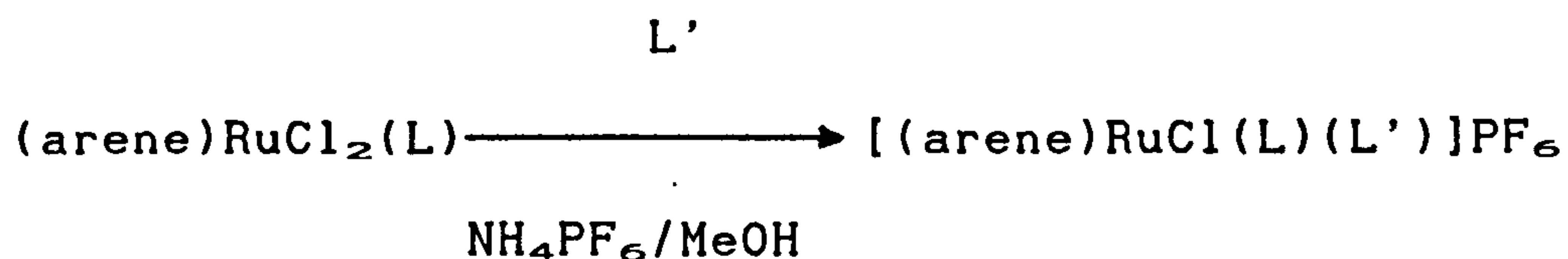
In polar solvents the arene ruthenium chloro dimers can be substituted at the ruthenium metal centre by two basic ligands to afford cationic species.



1.2.2.2 Conversion of half sandwich complexes

The half sandwich complexes $[(\text{arene})\text{RuCl}(\text{L})(\text{L}')]\text{X}$ can be generated by the reaction of the monosubstituted dichloro arene ruthenium complexes in the presence of a second

ligand with NH_4PF_6 in methanol.^{60.62}



(arene = C_6H_6 ; $\text{L} = \text{L}' = \text{PMe}_3$ or $\text{P}(\text{OMe})_3$)

$\text{L} = \text{PMe}_2\text{Ph}$, $\text{L}' = \text{PMe}_3$

$\text{L} = \text{PPh}_3$, $\text{L}' = \text{PMe}_3, \text{PMe}_2\text{Ph}, \text{PMePh}_2$

$\text{L} = \text{P}(\text{OMe})_3$, $\text{L}' = \text{PMe}_3$

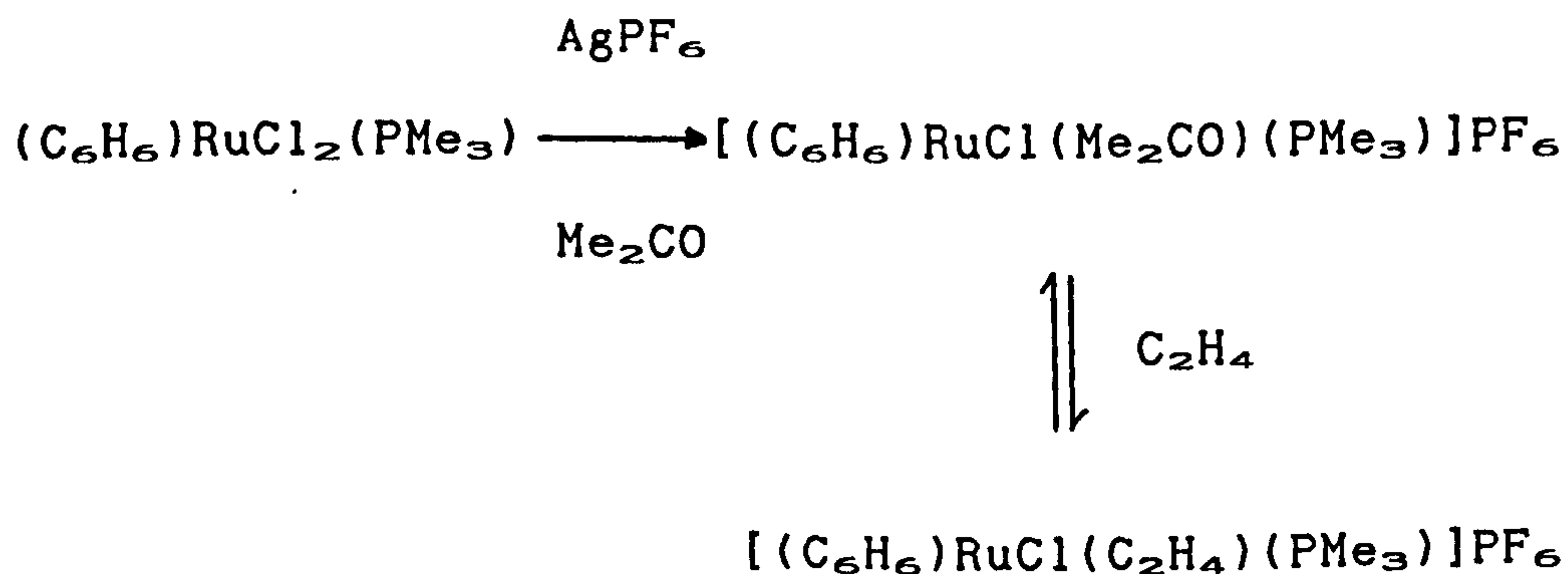
$\text{MeC}_6\text{H}_4\text{CHMe}_2$; $\text{L} = \text{PMe}_2\text{Ph}$, $\text{L}' = \text{PMe}_3$

$\text{L} = \text{CO}$, $\text{L}' = \text{PMe}_3$

C_6Me_6 ; $\text{L} = \text{P}(\text{OMe})_3$, $\text{L}' = \text{PMe}_3$

$\text{L} = \text{CO}$, $\text{L}' = \text{PMe}_3$

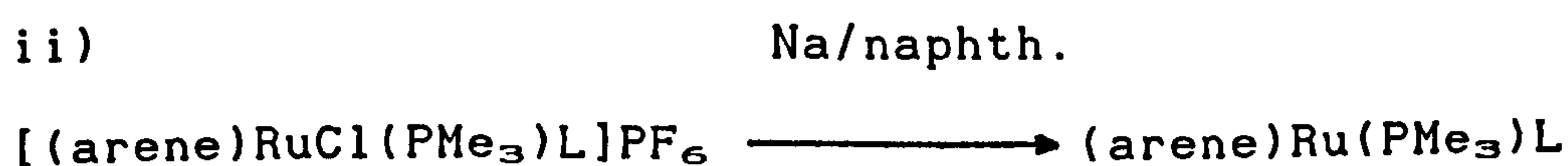
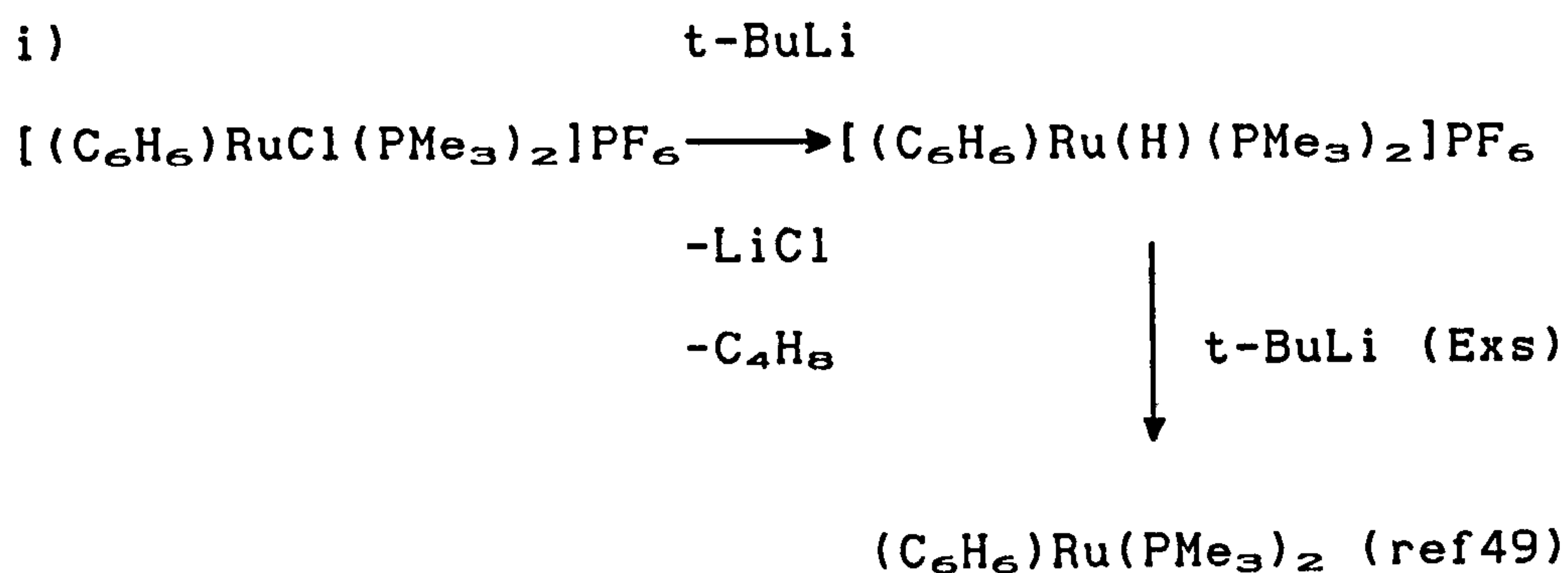
As described in section 1.2.1.1 Werner utilised this mixed ligand preparation (ligand and solvent being one and the same) to show the facile interconversion of acetone and ethylene.²⁷



These half sandwich cationic complexes are utilised to form neutral (arene)Ru(0)(L)(L') complexes via two routes:

i) Conversion to a Ru(II) hydride and then deprotonation.

ii) Reduction using sodium naphthalene.



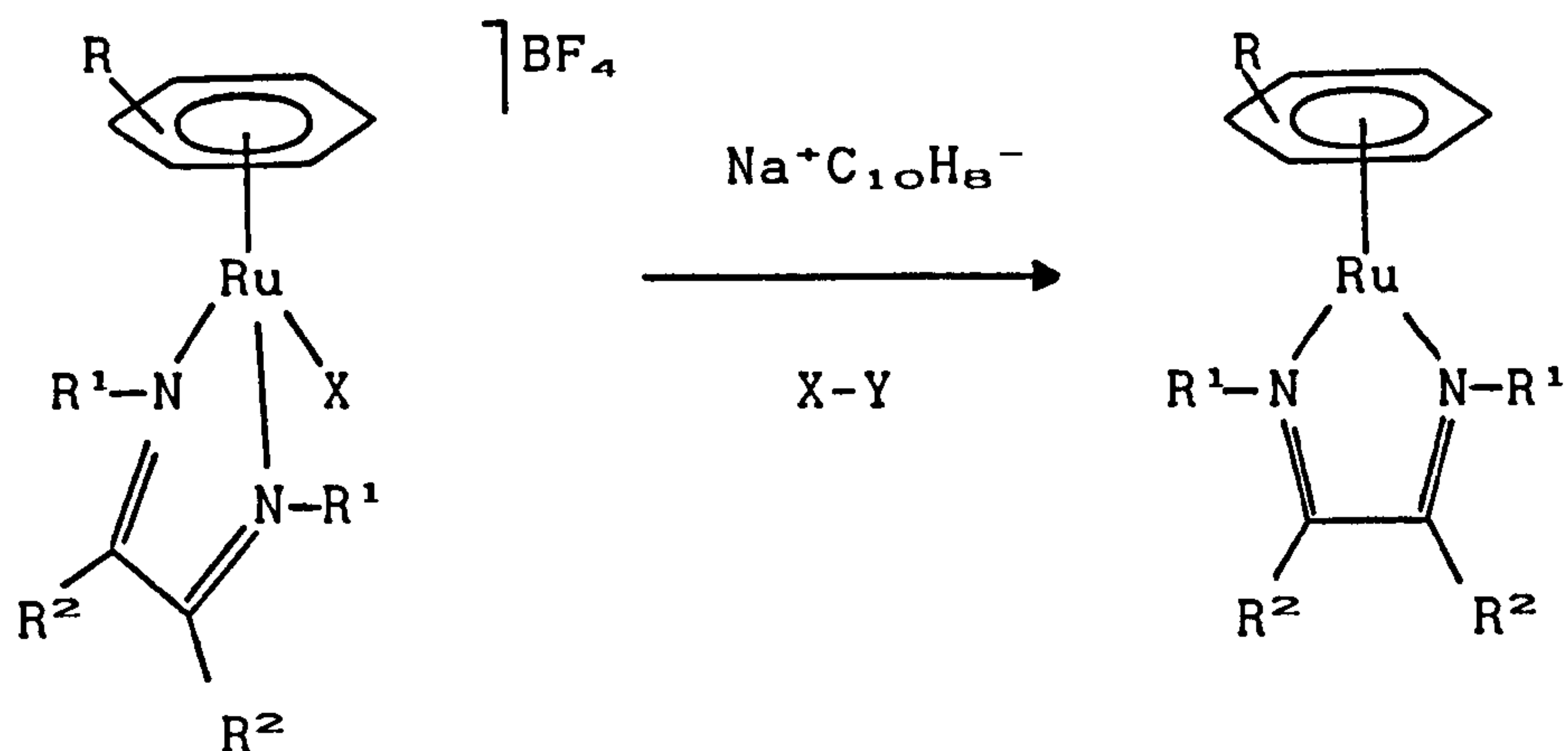
(arene = C_6H_6 , $\text{MeC}_6\text{H}_4\text{CHMe}_2$, C_6Me_6 ; L = PMe_3)

(arene = C_6H_6 ; L = C_2H_4) (ref 27, 50)

(arene = C_6Me_6 ; L = CO) (ref 62, 49)

The reduction with sodium naphthalene is general for the L-L bidentate diazadiene ruthenium

complexes shown below;⁶⁴

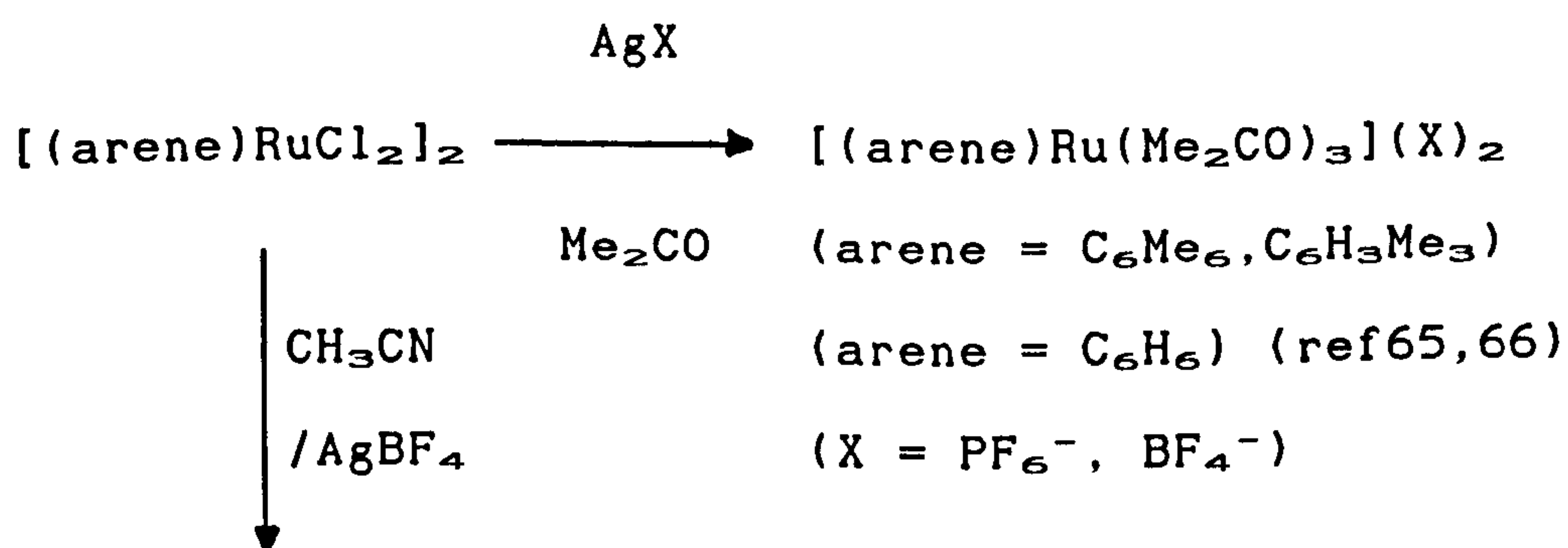


(arene = C_6H_6 , $\text{C}_6\text{H}_3\text{-1,2-Et-4-Me}$.)

R^2 ; H or Me; R^1 ; i-Pr, t-Bu, $\text{C}_6\text{H}_5\text{-}_n\text{R}_n$)

1.2.2.3.Preparation of tris ligated dications and cyclophane chemistry

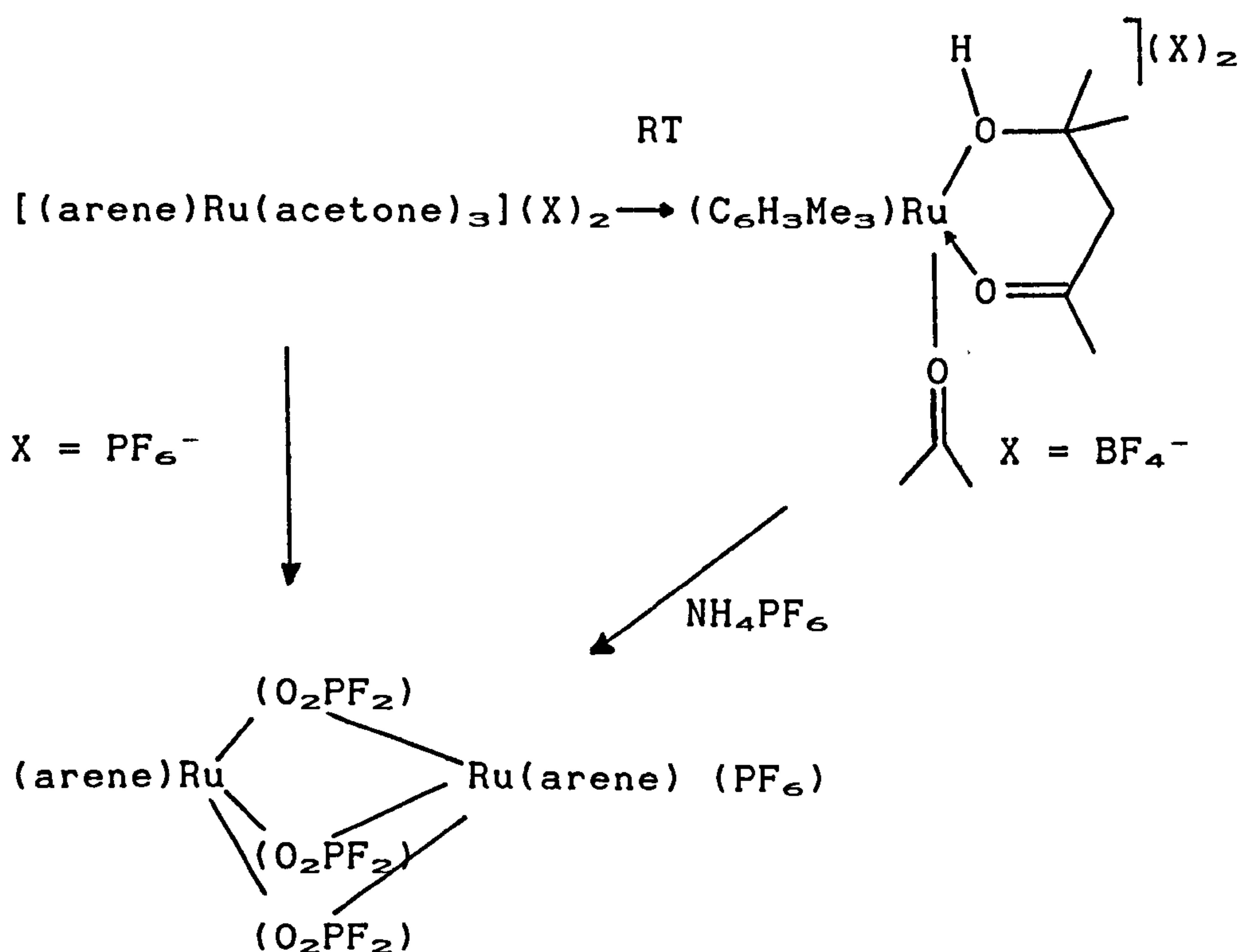
Treatment of the complexes $[(\text{arene})\text{RuCl}_2]_2$ with silver salts in the presence of coordinating solvents such as acetone and acetonitrile yield useful half sandwich dicationic complexes.



(arene = C_6H_6 , $\text{MeC}_6\text{H}_4\text{CHMe}_2$)

(ref2)

The tris acetone dicationic species above 0°C converts to a dimeric species, according to the nature of X^- (PF_6^- or BF_4^-) via an intermediate cation (for which an X-ray crystal structure has been determined for the mesitylene analogue).

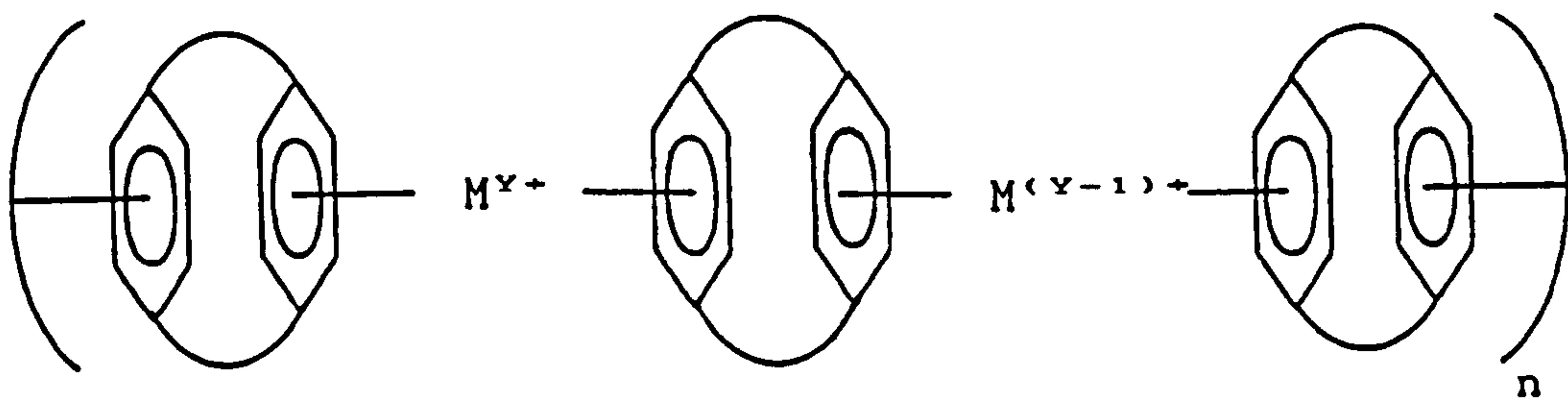


The normally inert anion in the $[(\text{arene})\text{Ru}(\text{acetone})_3](\text{PF}_6)_2$ salts undergo partial hydrolysis at room temperature to give the tri- μ -difluorophosphato complexes $[(\text{arene})_2\text{Ru}_2(\mu\text{-O}_2\text{PF}_2)_3](\text{PF}_6)$. $[(\text{C}_6\text{H}_3\text{Me}_3)\text{Ru}(\text{acetone})_3](\text{BF}_4)_2$ isomerises rapidly at room temperature to give the complex

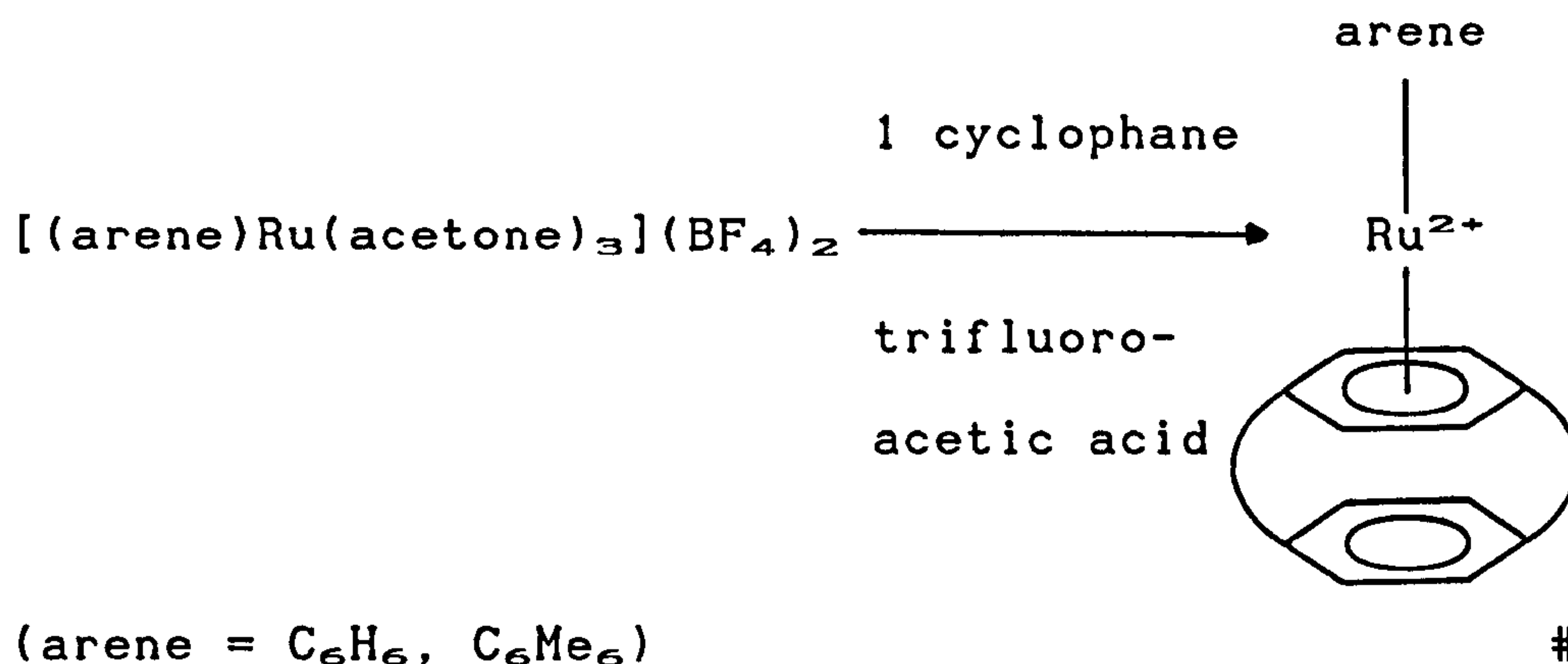
$[(C_6H_3Me_3)Ru(OCMe_2)\{MeC(OH)CH_2COMe\}](BF_4)_2$,

containing bidentate 4-hydroxy-4-methylpentan-2-one (probably evolved via an aldol condensation between two acetone molecules), which reacts with NH_4PF_6 to give the tri- μ -difluorophosphato complex shown above.⁶⁵

The tris acetone dicationic species has been investigated as a substrate for industrial application in the field of cyclophane chemistry. $[2_n]$ cyclophane ruthenium complexes are of interest as possible monomeric components in the construction of multilayered organometallic polymers which might show extended π - electron delocalisation.^{67.68.69.70}

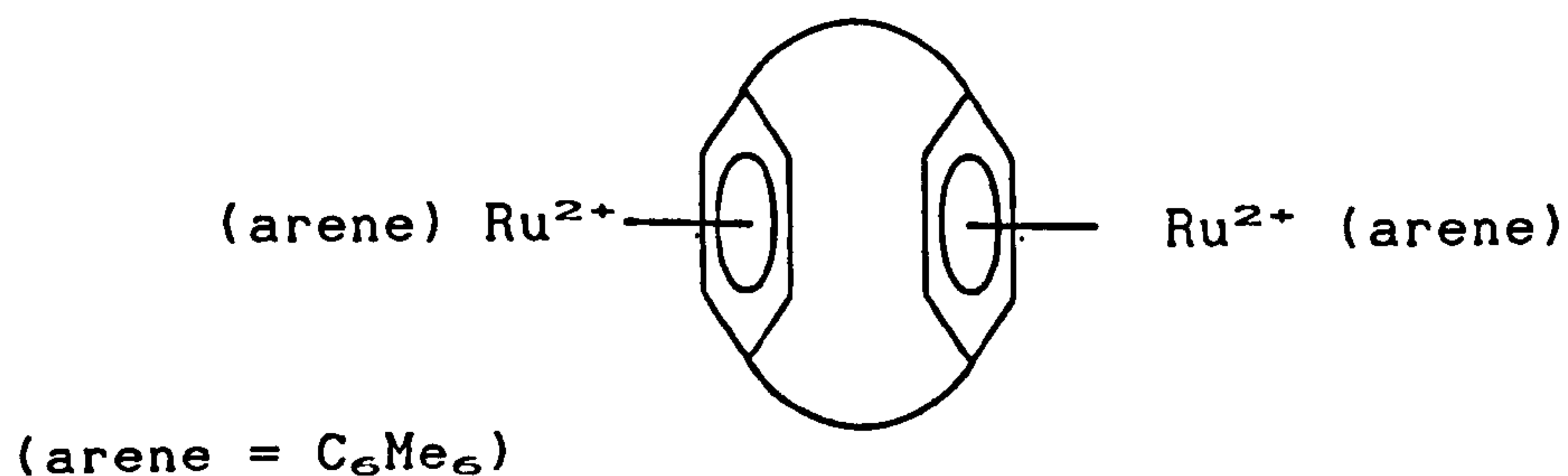


Cyclophane ruthenium complexes have been prepared utilising the tris acetone complex for a range of cyclophanes in good yield.

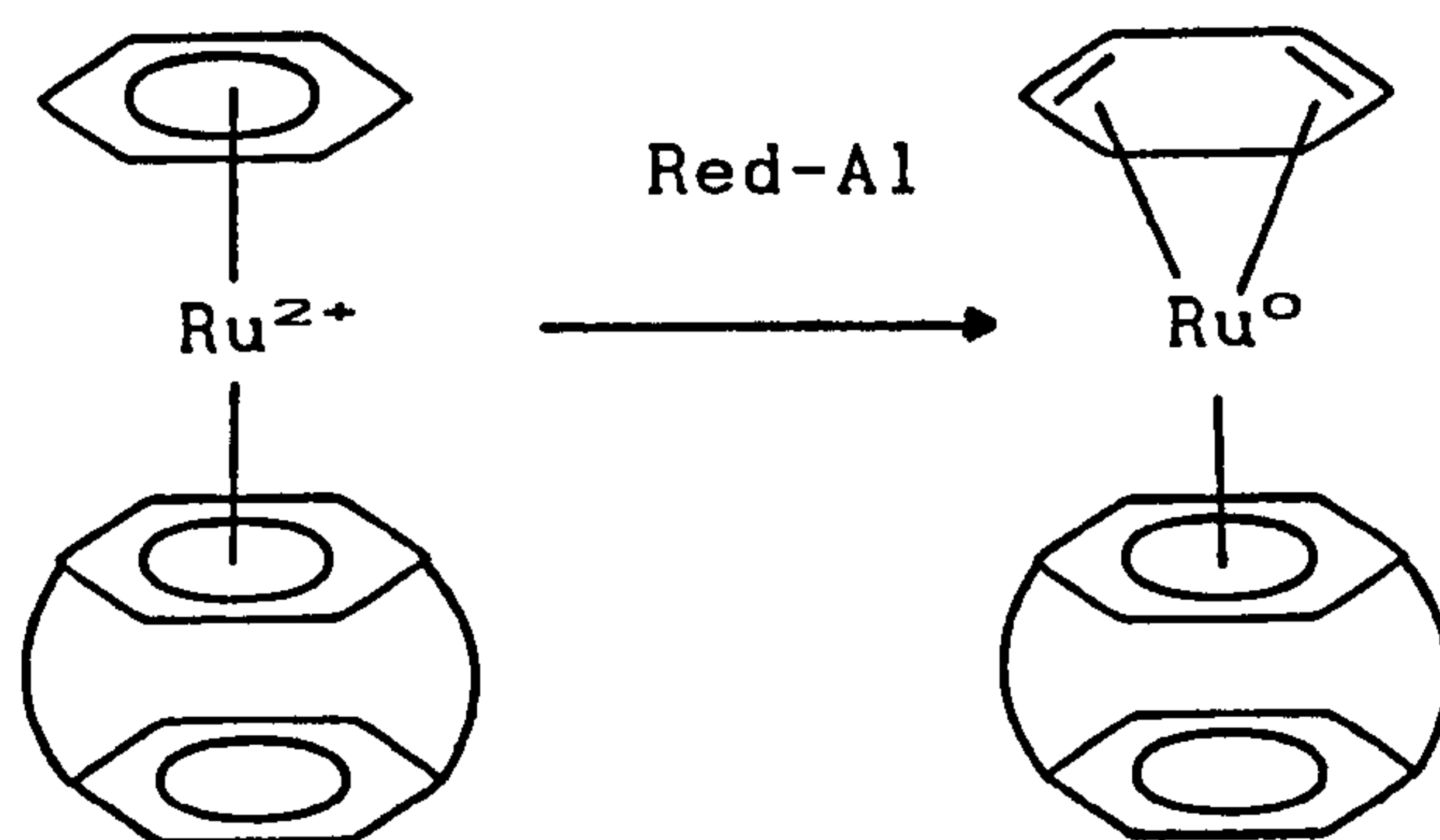


Generalised structure representing any one of the possible $[2_n]$ cyclophanes.

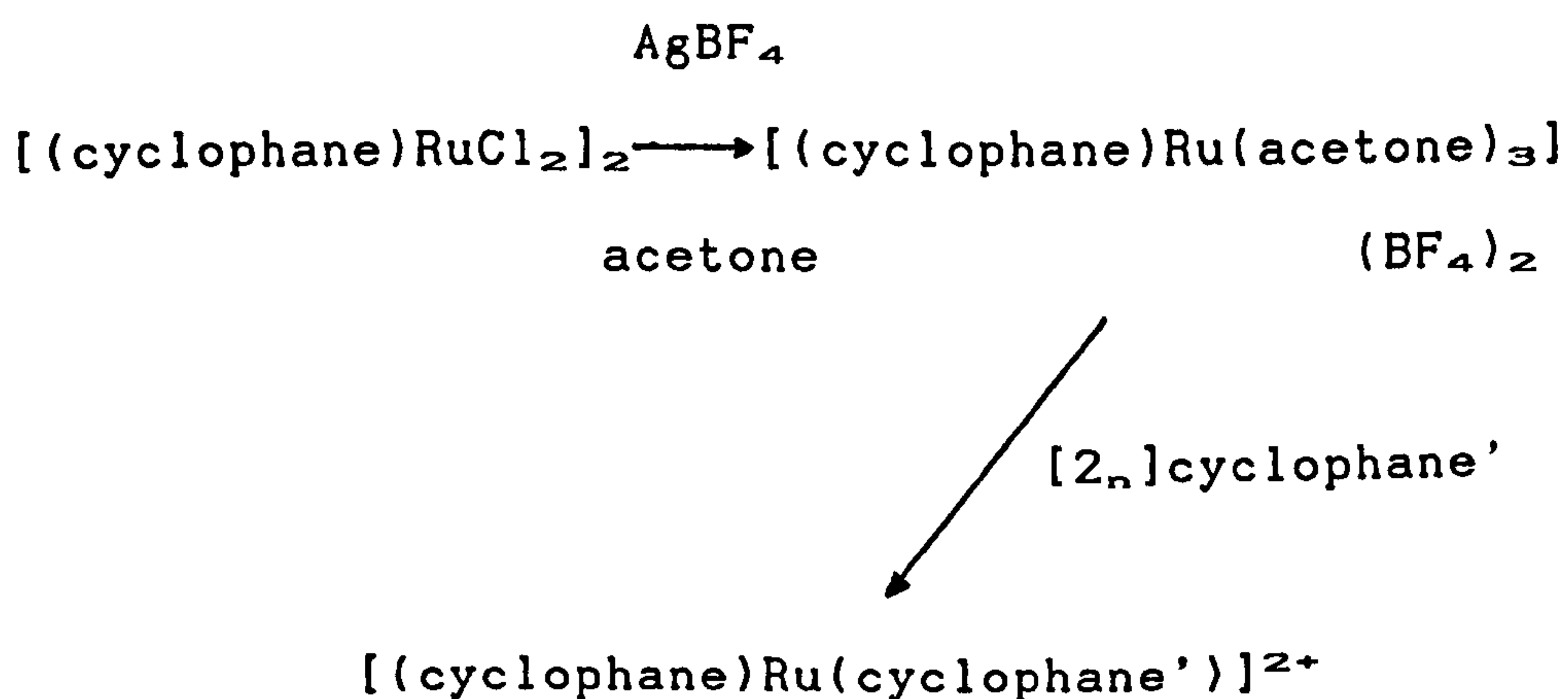
If the tris acetone cation is used in excess, the triple layered complex shown below is afforded.



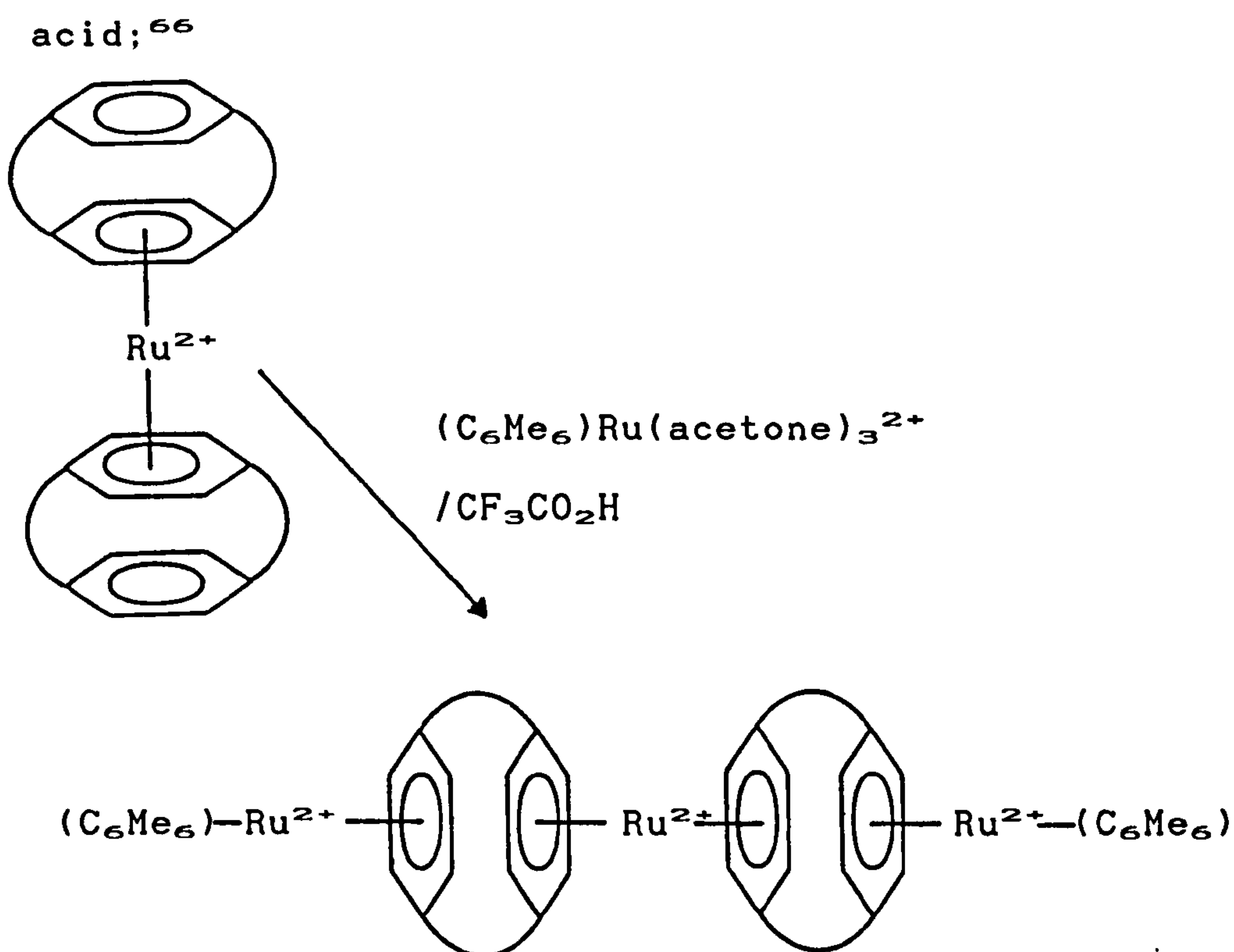
A general route utilised to synthesise bis(cyclophane) ruthenium(II) complexes involves a reduction of the double layered (benzene) $\text{Ru}(\text{cyclophane})^{2+}$ complexes;⁶⁶



On treatment with HCl these yield the chloro dimer, $[(\text{cyclophane})\text{RuCl}_2]_2$. Using the procedure to form the tris acetone arene ruthenium dicationic species, the cyclophane analogue can be prepared which will react with $[2_n]$ cyclophane to afford the desired bis($[2_n]$ cyclophane) ruthenium(II) complexes.



Synthesis of a cyclophane complex containing three ruthenium centres is achieved by heating the bis(cyclophane) complex with $[(\text{C}_6\text{Me}_6)\text{Ru}(\text{acetone})_3]^{2+}$ in neat trifluoroacetic



A requirement for an electrically conducting polymer is that it have a partially filled conduction band, and this in turn requires that a subunit of the organometallic polymer have mixed valence properties. Preliminary studies of double and triple layered arene ruthenium (cyclophane) complexes has been carried out to examine the electrochemical behaviour of mixed valence species.^{68,69} The double layered hexamethylbenzene species in acetonitrile showed an overall two electron reduction appearing as two closely spaced, overlapping one electron waves rather than a single, two electron wave. The waves may be separated, if two exist, by a CH_3CN to CH_2Cl_2

solvent change, thereby decreasing the relative Ru^{2+} vs Ru^+ reduction.

The chemical reversibility of the redox process;



is a function of the cyclophane ligand structure (dependent upon ring strain of the cyclophane).

The triple layered species (A) (see below), when investigated using cyclic voltammetry in acetone, shows a reversible net two electron reduction wave giving the mixed valence complex (B) and a second net two electron wave reducing (B) to (C). Both reduction steps are completely reversible.

The observation of two processes indicates that the two ruthenium centres are interacting due to the presence of the cyclophane. This indicates the suitability of this type of complex as a unit of an electric conducting polymer.

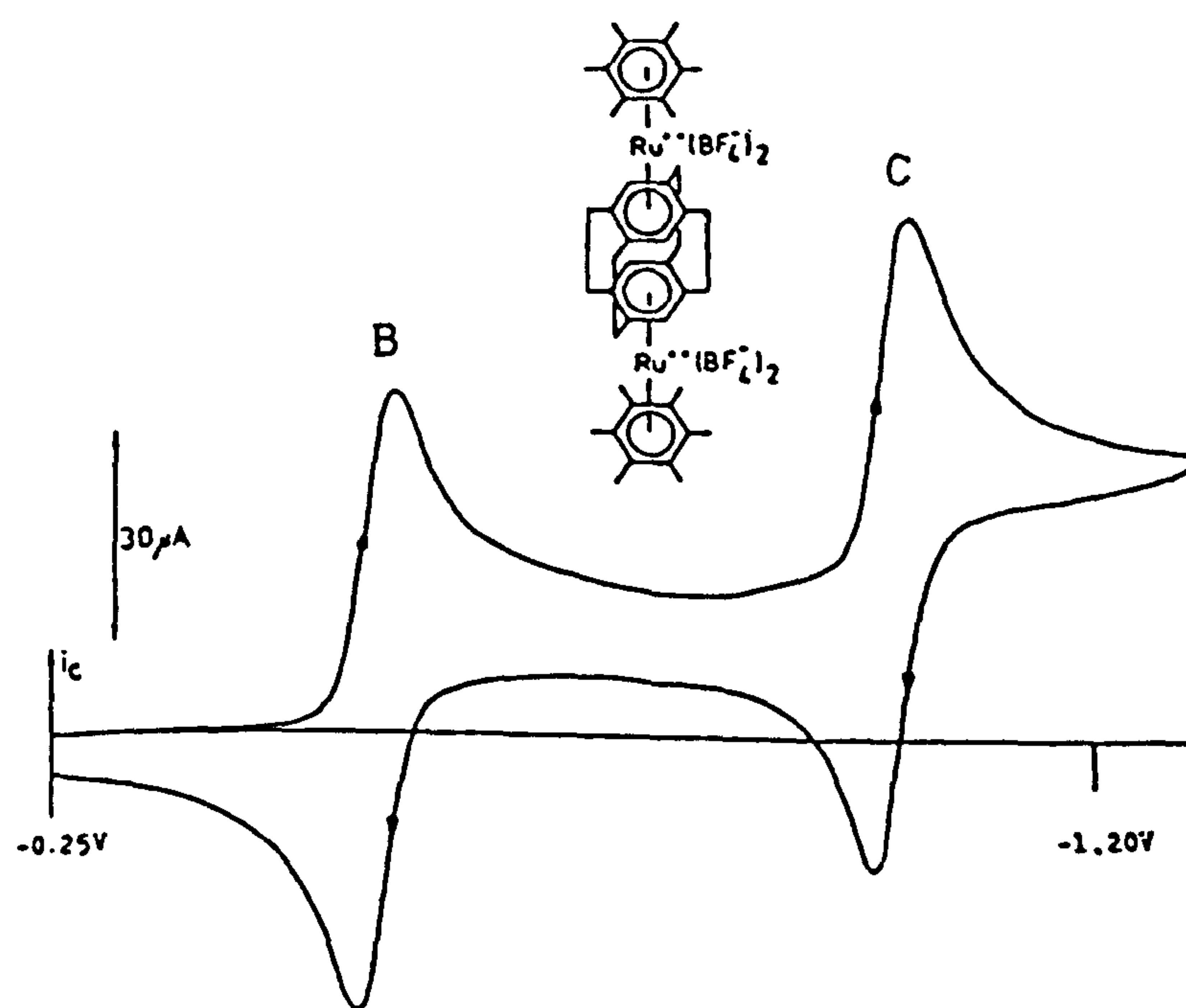
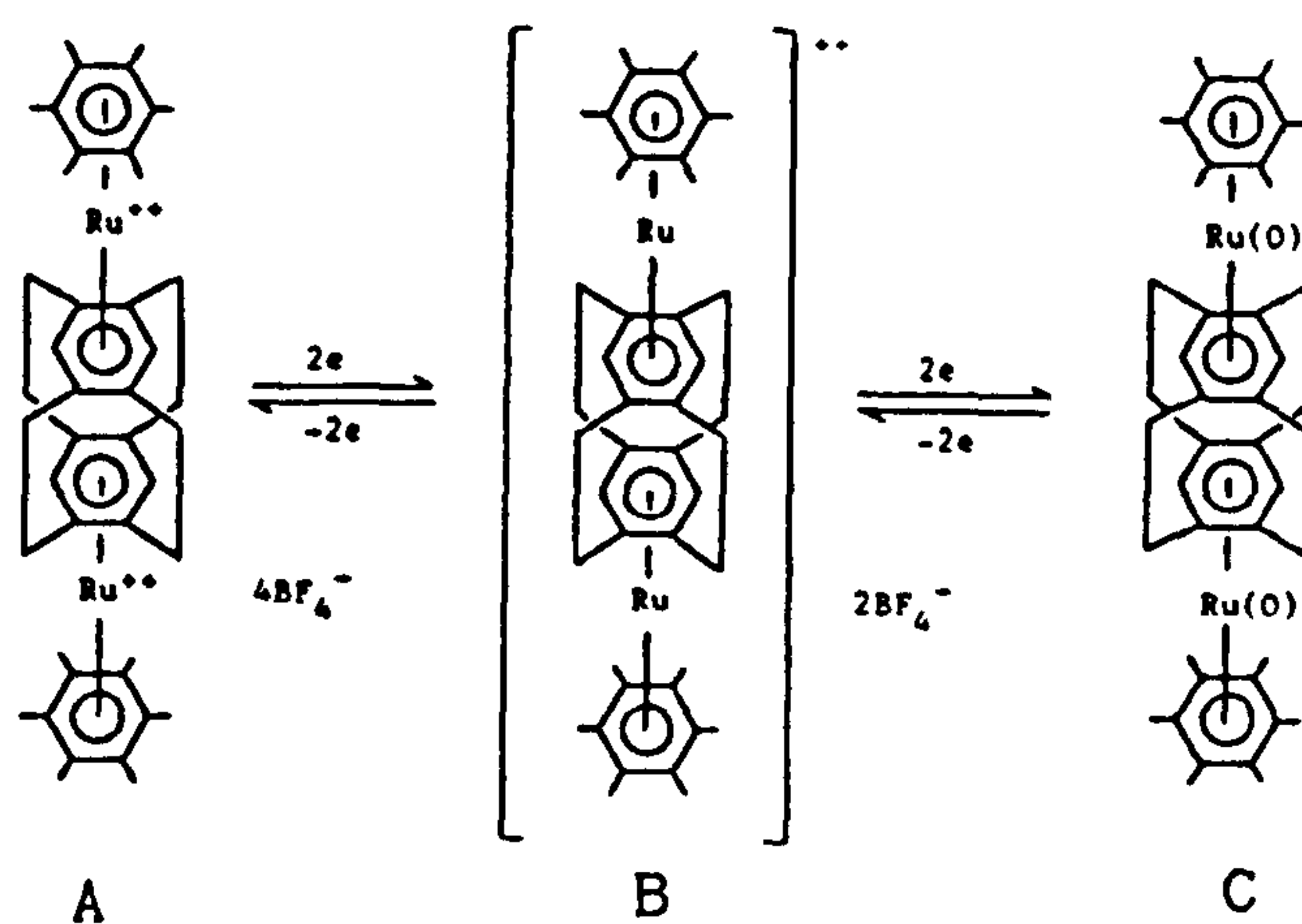
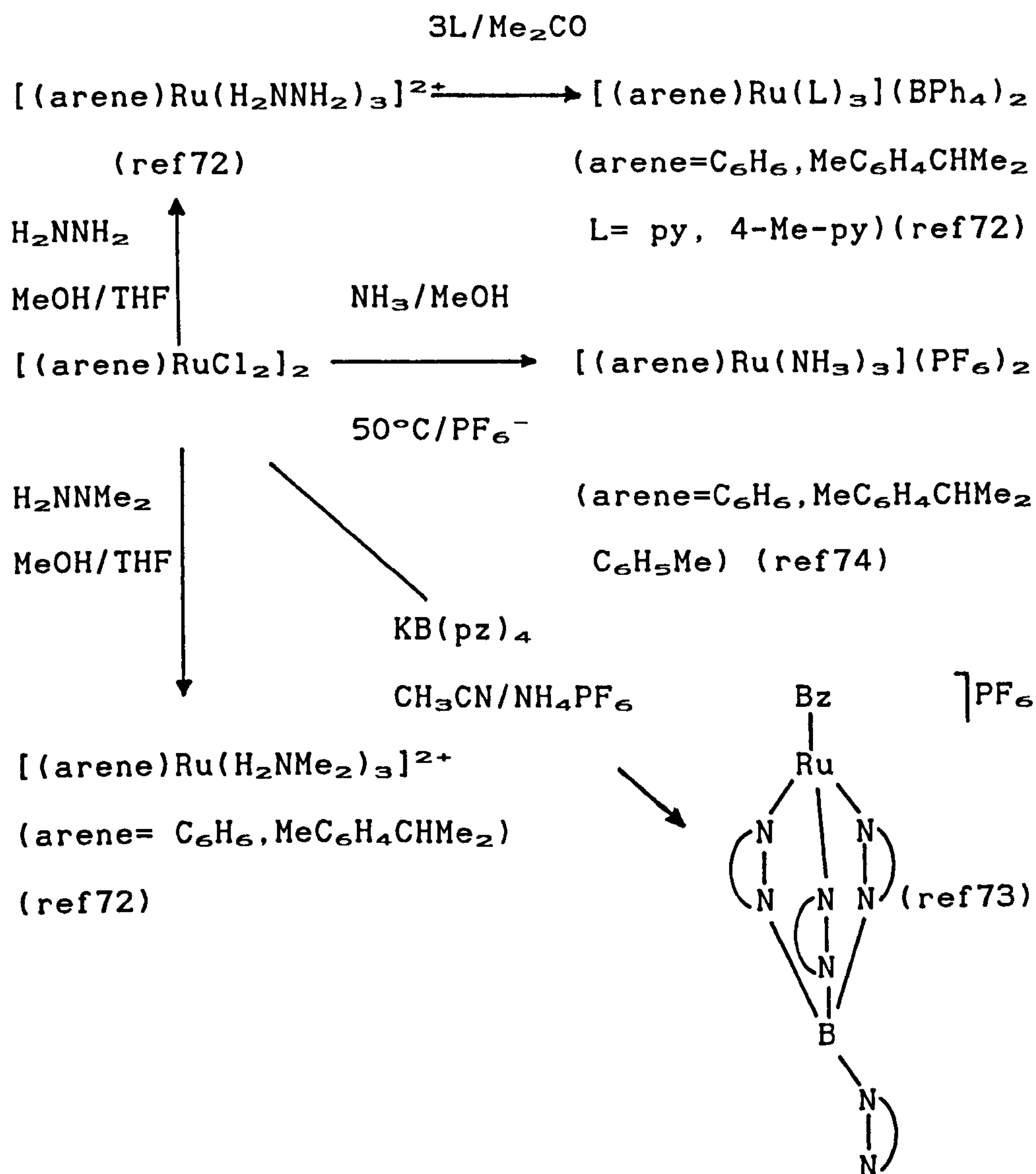


Fig. 1.2.2.3.1 Cyclic voltammogram of (A) in Me_2CO

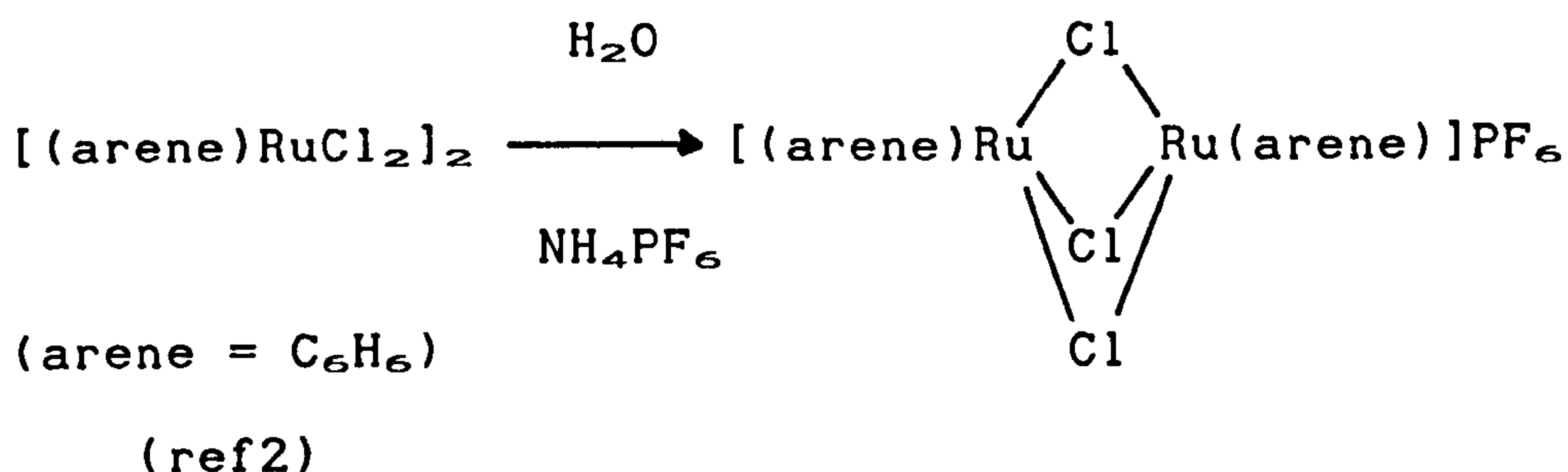
A variety of tris ligated dicationic species involving nitrogen based ligands have been prepared. A summary of their syntheses and chemistry is shown below.



Scheme 1.2.2.3.1 preparation of tris ligated cations.

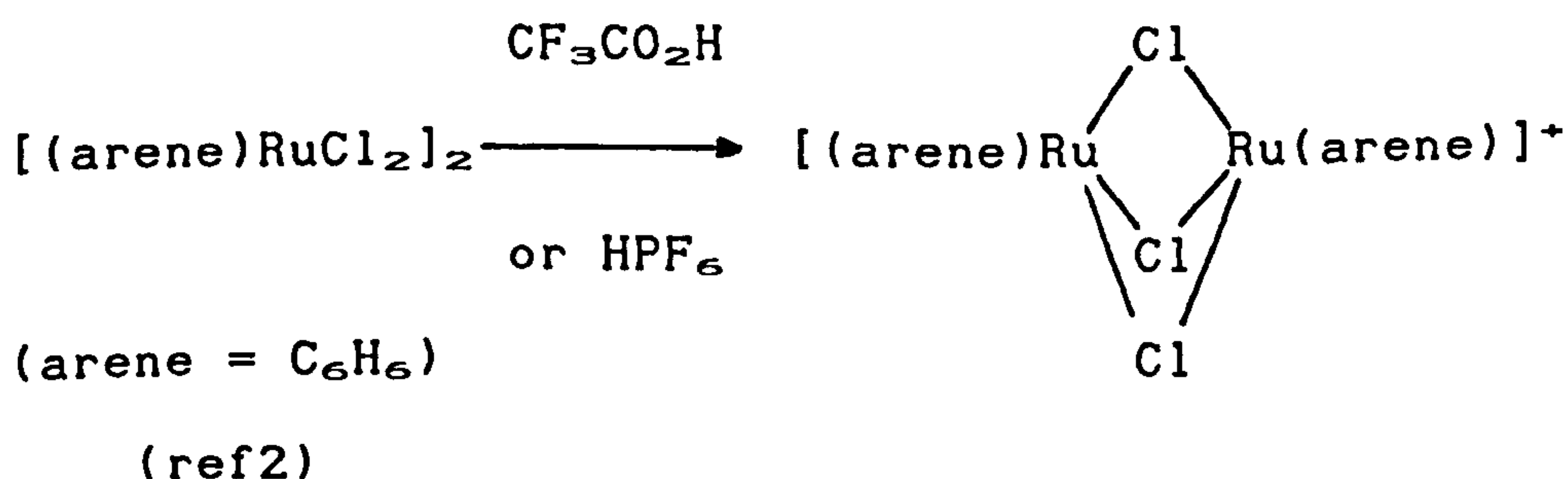
1.2.2.4 The $[(\text{arene})\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\text{arene})]^+$ system

Reaction of the $[(\text{arene})\text{RuCl}_2]_2$ compounds with hot water and NH_4PF_6 yields the triply chloro bridged ruthenium dimer.



This complex can be prepared in almost quantitative yield (>90%) by shaking the parent chloro dimer with an excess of NH_4PF_6 in methanol.²⁵

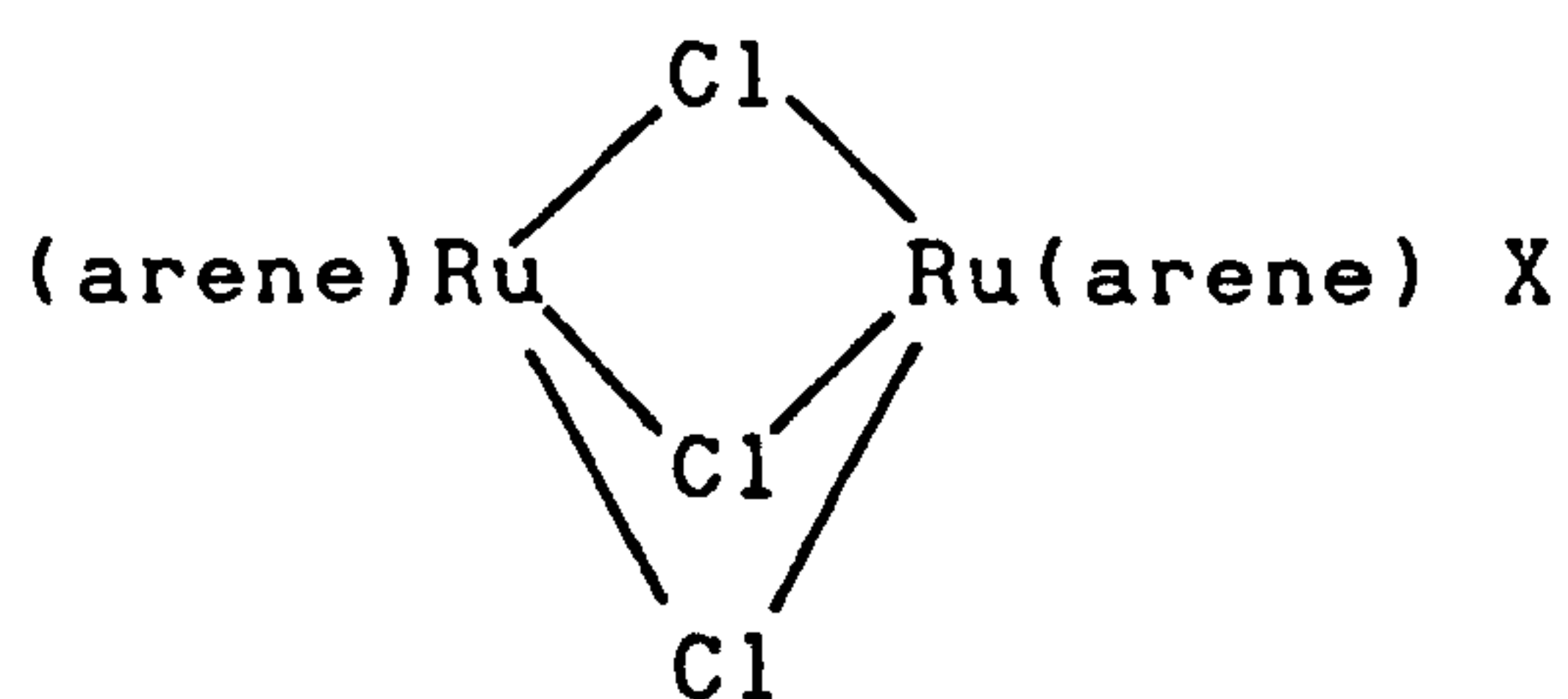
An alternative route, which affords the benzene triply bridged species in good yield, involves reaction of the parent chloro dimer with an acid.⁷⁵



However, Stephenson and coworkers have developed a novel and convenient synthesis for a series of arene triply chloro bridged ruthenium dimers.^{76,77}



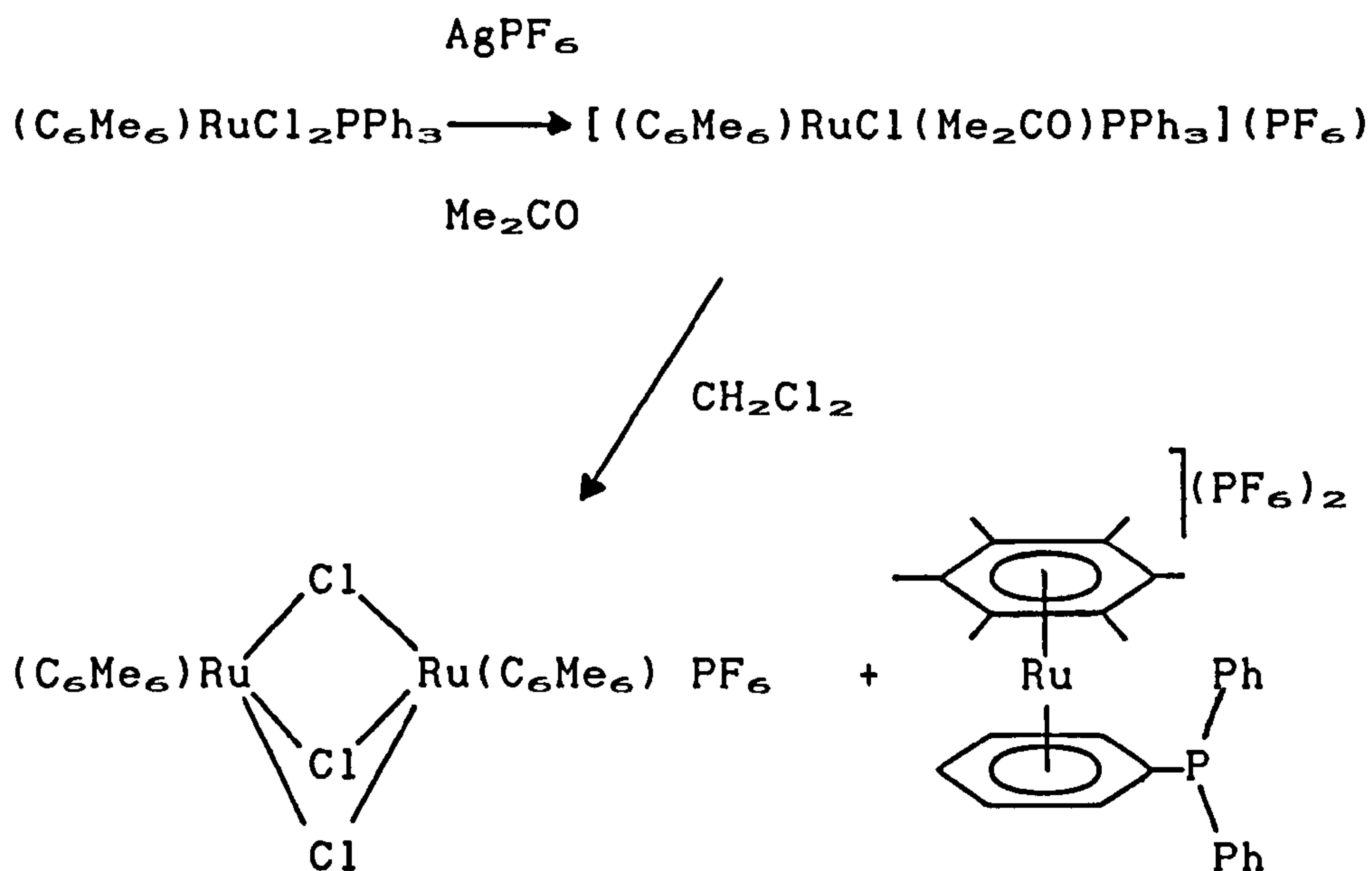
HX/MeOH



(arene = C₆H₆, MeC₆H₄CHMe₂, C₆H₃Me₃)

(X = BF₄, PF₆)

The hexamethylbenzene analogue has been prepared as a low yield by-product in a novel preparation of a bis(arene) ruthenium complex;⁷⁸



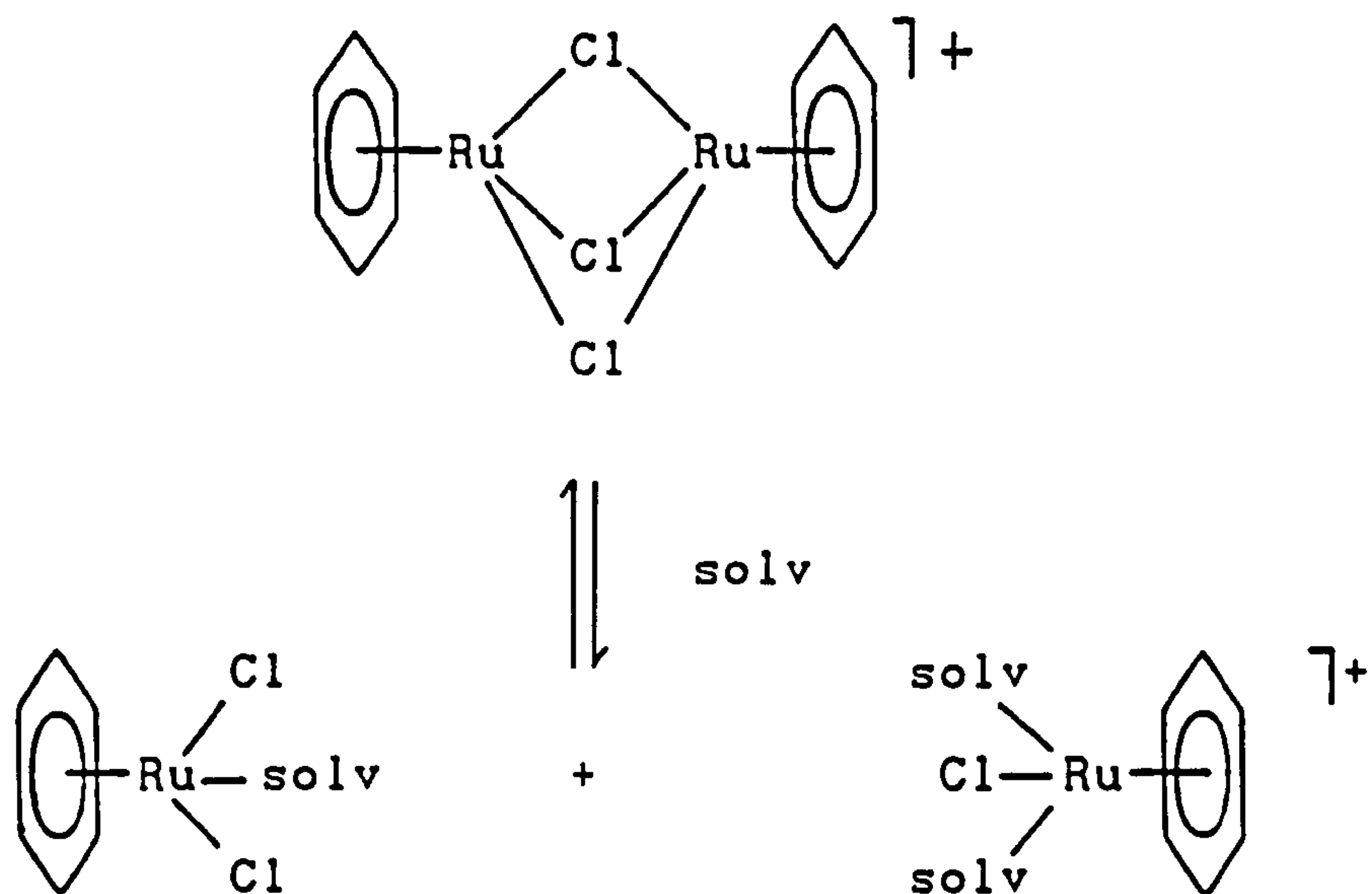
X-ray determination shows the eta 6 bonding mode of one of the phenyl rings of the triphenylphosphine.

1.2.2.5 Reactivity of the $[(\text{arene})\text{Ru}(\mu\text{-Cl})_3\text{Ru}(\text{arene})]^+$ system

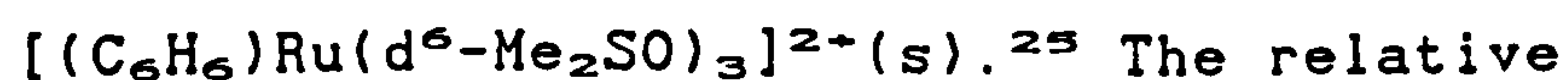
Stephenson and coworkers, when characterising the benzene analogue using ^1H nmr, discovered the presence of more than one eta 6 C_6H_6 resonance in solvents such as D_2O and $d^6\text{-Me}_2\text{SO}$.

In D_2O the ^1H nmr spectrum contained two eta 6 C_6H_6 resonances of comparable intensity. These chemical shift positions were virtually identical to those found for $[(\text{C}_6\text{H}_6)\text{RuCl}_2]_2$ dissolved in D_2O ,

indicating facile bridge cleavage has occurred as shown in the equation.



In d^6 -Me₂SO three singlets were observed in the ¹H nmr spectrum corresponding closely to the quoted positions of the eta 6 resonances for the species (relative intensities in brackets):

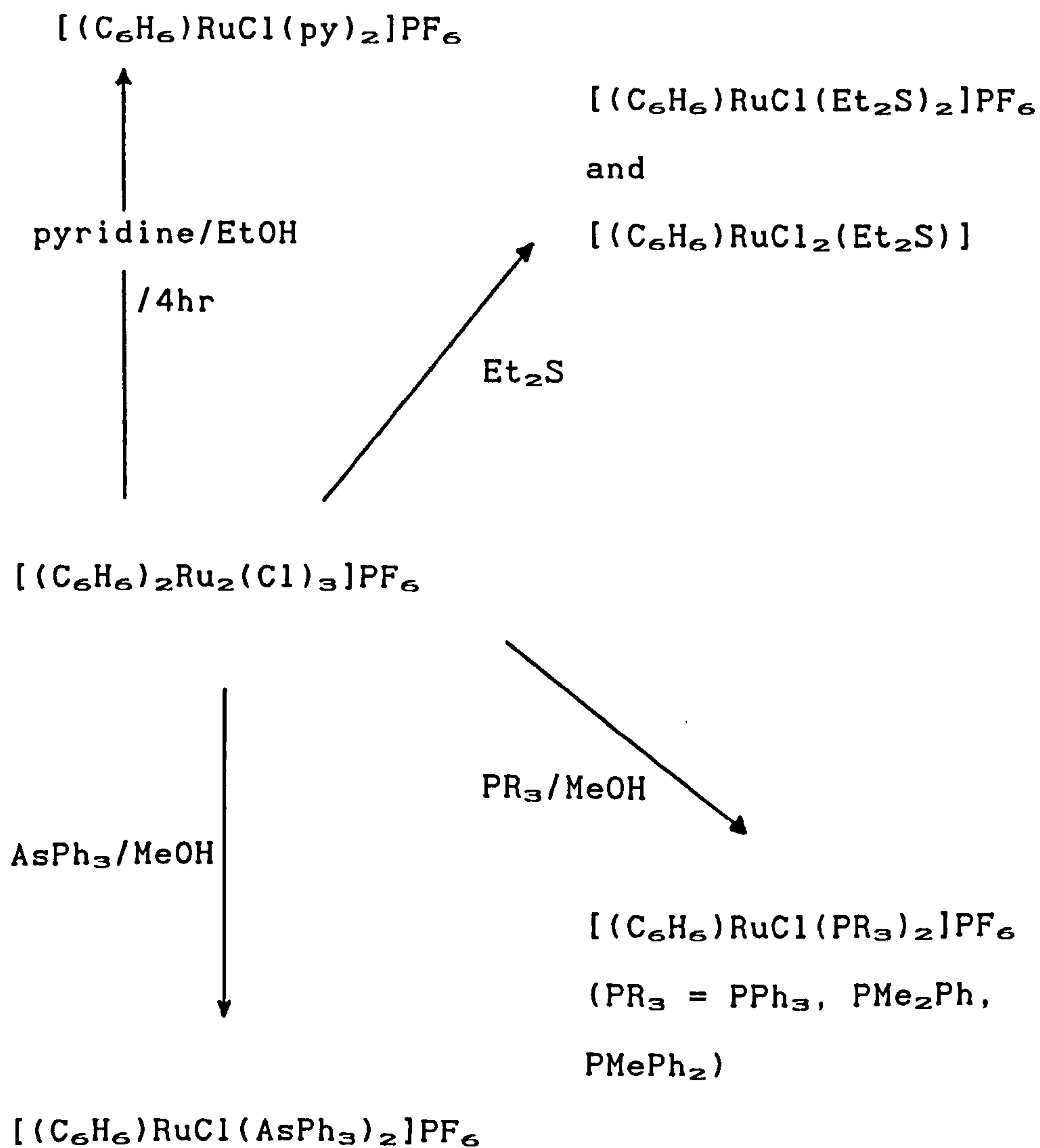


The relative intensities of these signals suggested that the monocation reacted further with d^6 -Me₂SO to give the dication.

Stephenson and coworkers proposed that the most likely mechanism of formation of $[(C_6H_6)_2Ru_2(Cl)_3]^+$ was by intermolecular coupling of the weakly solvated monomers $[(C_6H_6)RuCl_2(solv)]$ and $[(C_6H_6)RuCl(solv)_2]^+.$ ²⁵ At a later date they

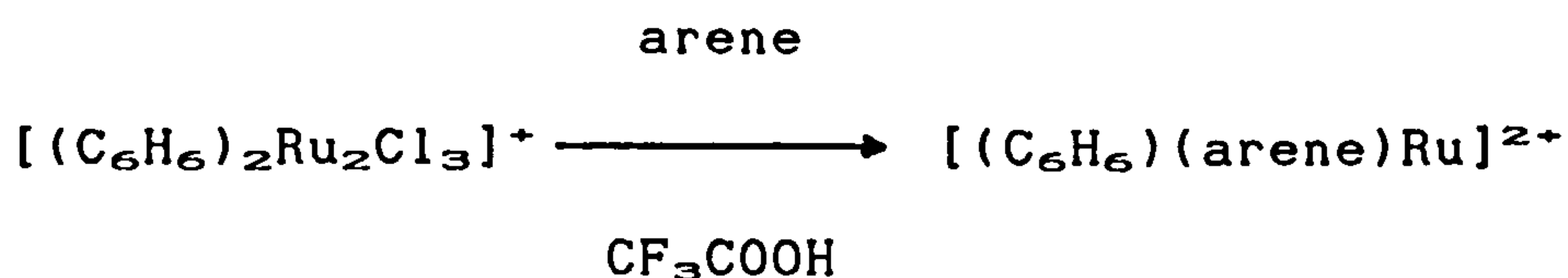
elegantly supported this claim by their synthesis of the $[(\text{arene})_2\text{Ru}_2(\text{Cl})_3]^+$ system via coupling of the mono and disubstituted pyridine complexes, $[(\text{arene})\text{RuCl}_2(\text{py})]$ and $[(\text{arene})\text{RuCl}(\text{py})_2]^+$.^{76,77}

The triply bridged cation species undergoes bridge cleavage with a variety of ligands.²⁵



Scheme 1.2.2.5.1 Bridge cleavage of triply bridged cation $[(\text{C}_6\text{H}_6)_2\text{Ru}_2(\text{Cl})_3]\text{PF}_6$

The triply bridged chloro species can be utilised as an intermediate for the preparation of bis(arene) ruthenium complexes.⁷⁵



(arene = C₆H₅Me, C₆H₃Me₃, C₆H₅NH₂, C₆H₅OEt, C₆H₆, 1-4-C₆H₄Me₂, C₆Me₆)

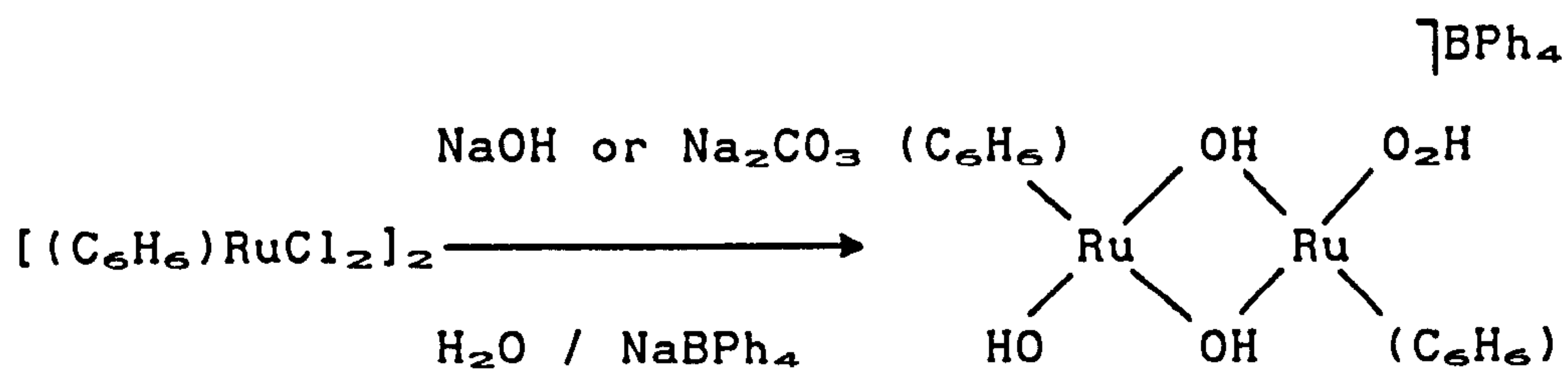
Also the bis(mesitylene) ruthenium dication can be prepared via this route.

1.2.2.6 Hydroxy and alkoxide arene ruthenium complexes

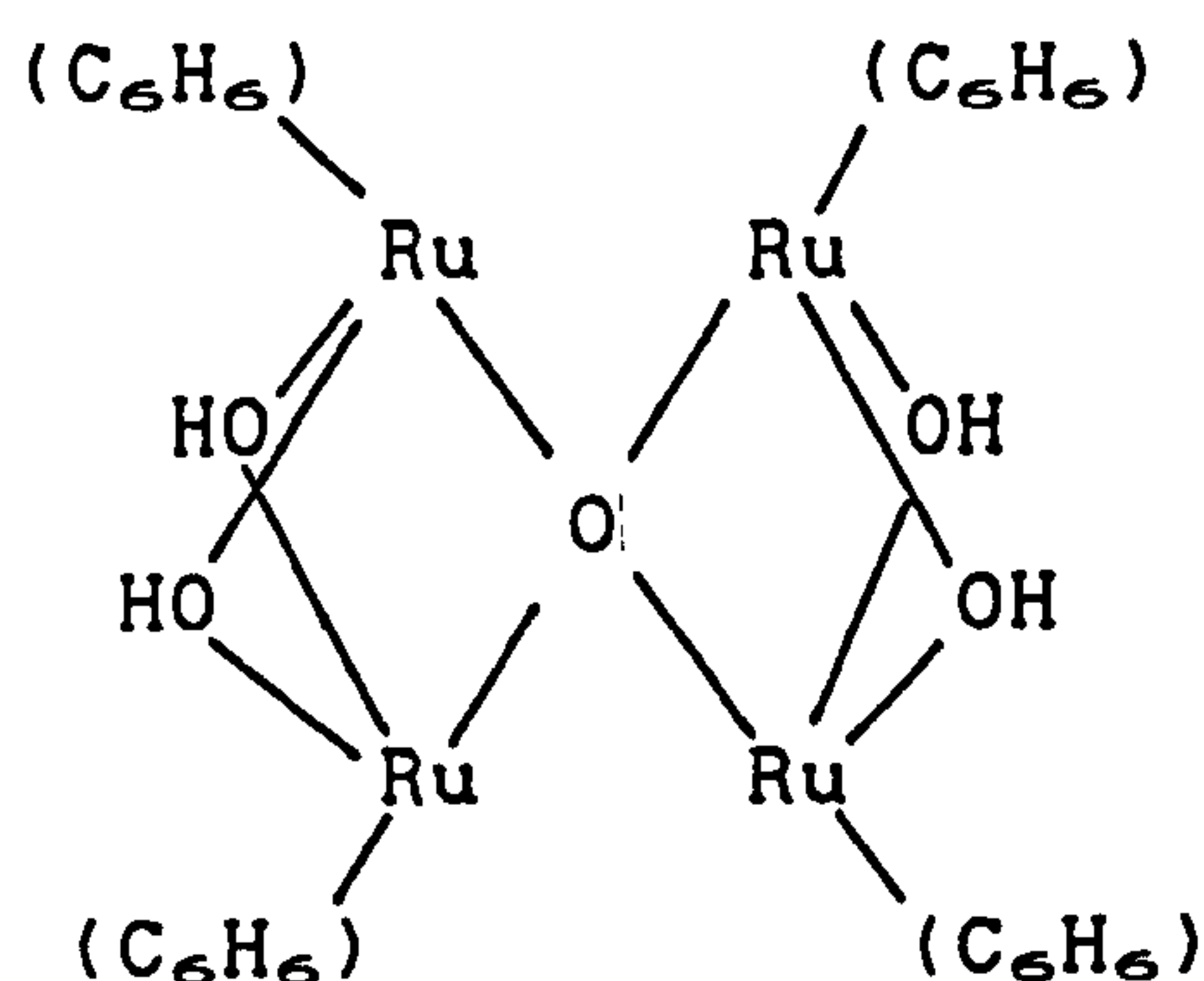
The arene ruthenium chloro dimers have been reacted with a variety of hydroxide and alkoxide ligands under a range of conditions to afford a number of arene ruthenium complexes.

1.2.2.6.1 Hydroxide complexes

Reaction of [(C₆H₆)RuCl₂]₂ in water with an excess of NaOH or Na₂CO₃ yields two cationic hydroxy compounds.⁷⁹

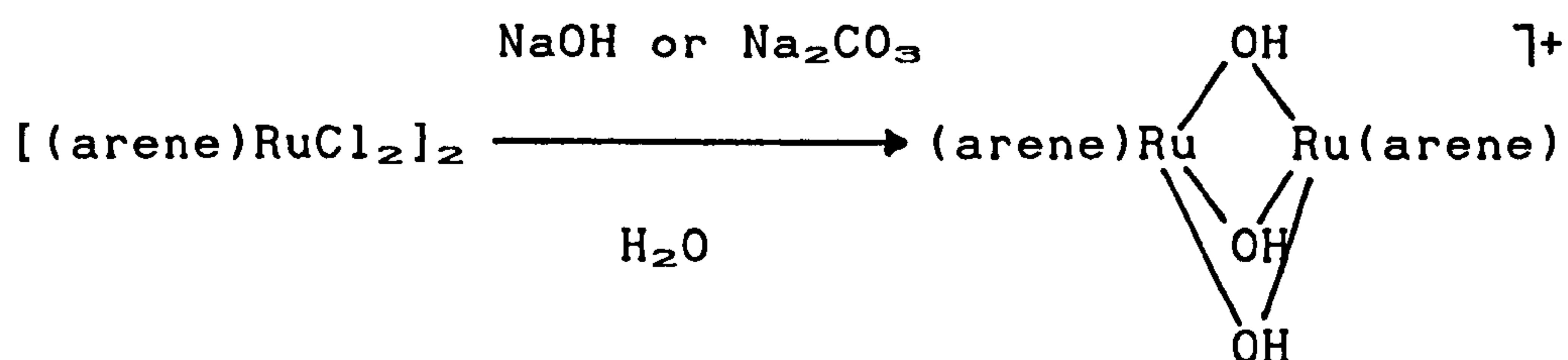


+



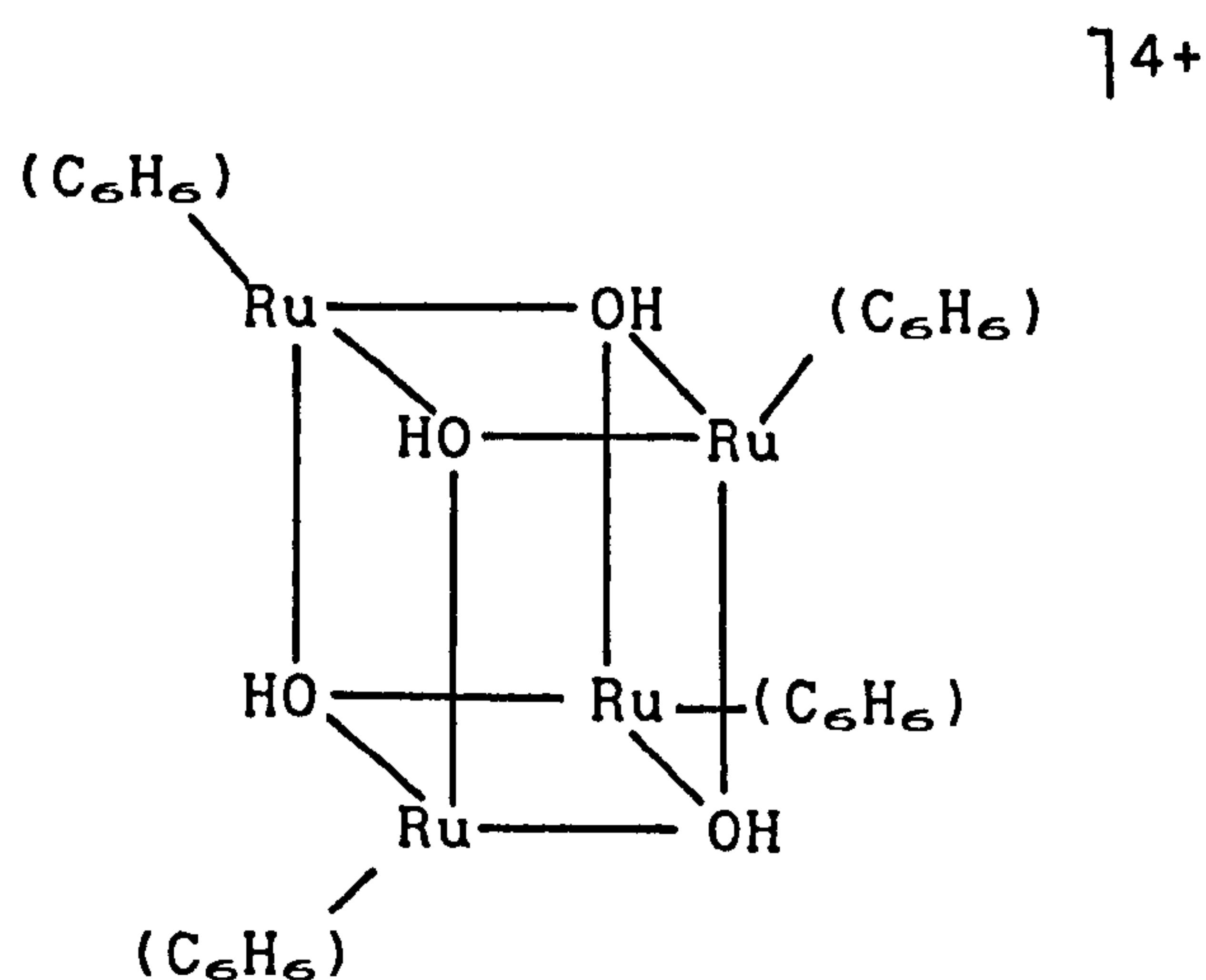
The tetranuclear μ_4 bridging O^{2-} ion complex is the minor of the two products but, on recrystallisation of the reaction mixture in acetone, it is the only product afforded.⁷⁸

Reaction of an aqueous solution of the mesitylene, cymene and hexamethylbenzene chloro dimers, with an excess of NaOH or Na_2CO_3 , gives a single product characterised by an X-ray crystal structure determination to be triply bridged by hydroxy ligands.^{79,80}



(arene = $\text{C}_6\text{H}_3\text{Me}_3$, $\text{MeC}_6\text{H}_4\text{CHMe}_2$, C_6Me_6)

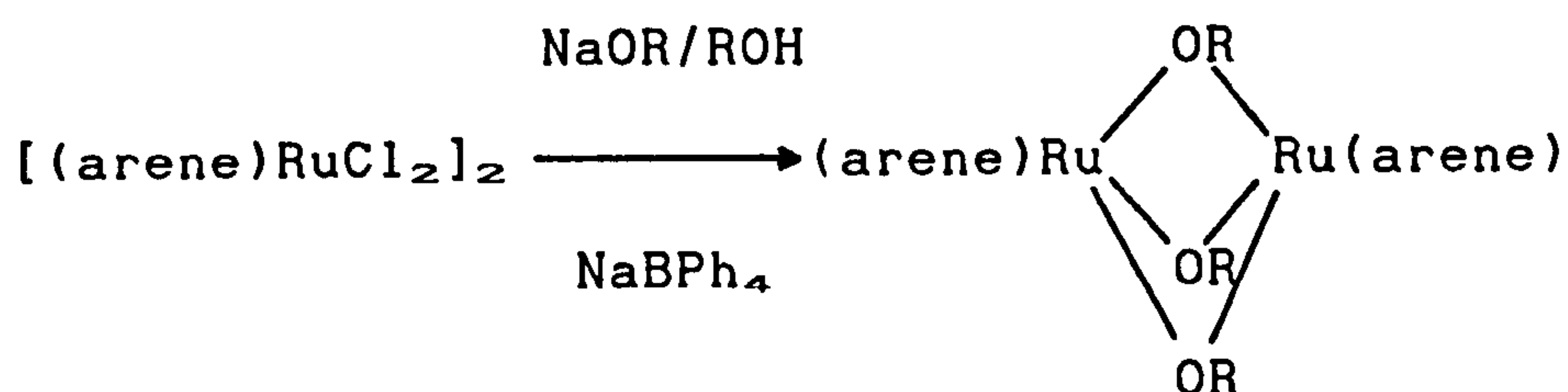
Reaction of $[(\text{C}_6\text{H}_6)\text{RuCl}_2]_2$ with aqueous Na_2CO_3 in the presence of an excess of Na_2SO_4 gives the cubane-like complex $[(\text{C}_6\text{H}_6)_4\text{Ru}_4(\text{OH})_4](\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, whose structure has been determined by an X-ray crystal structure analysis.⁸¹



1.2.2.6.2 Alkoxide complexes

Reaction of the $[(\text{arene})\text{RuCl}_2]_2$ dimers with NaOR/ROH and NaBPh_4 gives triply alkoxo bridged complexes analogous to the hydroxy ruthenium dimers above.⁸²

7BPh₄



(arene = C₆H₃Me₃, R = Me, Et, Ph)

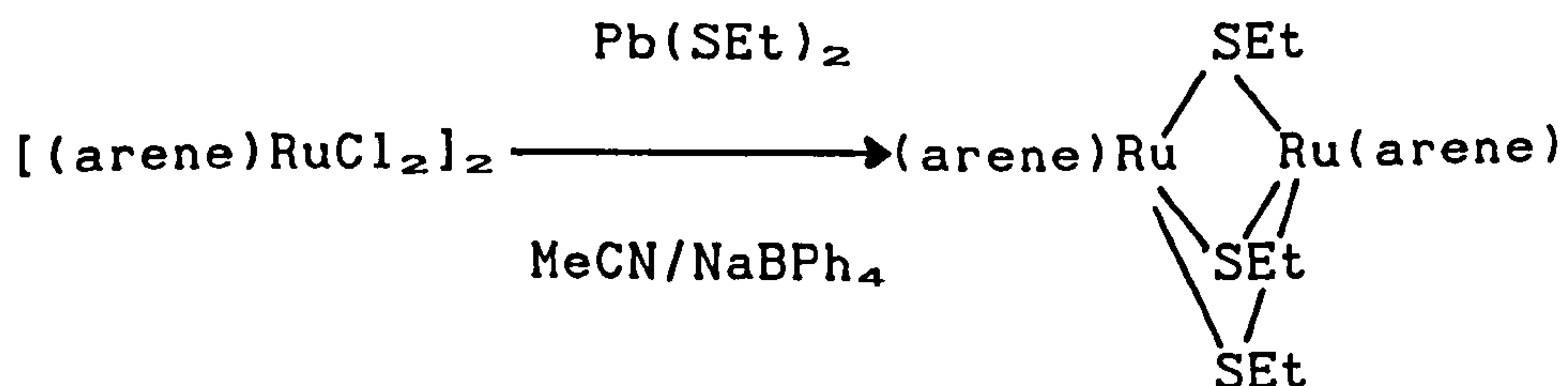
(arene = C₆H₆, C₆Me₆, R = Me)

The benzene and cymene complexes can be prepared from their tris hydroxy complexes by refluxing the respective complex in methanol or ethanol.⁸² The benzene analogue's structure has been confirmed by X-ray crystallography.⁸⁰

Another alternative route for the synthesis of the benzene and cymene triply alkoxo bridged complexes is the reaction of the parent chloro dimers with NaNH₂ in MeCN followed by treatment with an ethanolic or methanolic solution of NaBPh₄.⁸⁰

The thioata analogues of the triply alkoxide bridged dimers have been synthesised.⁸⁰

7BPh₄

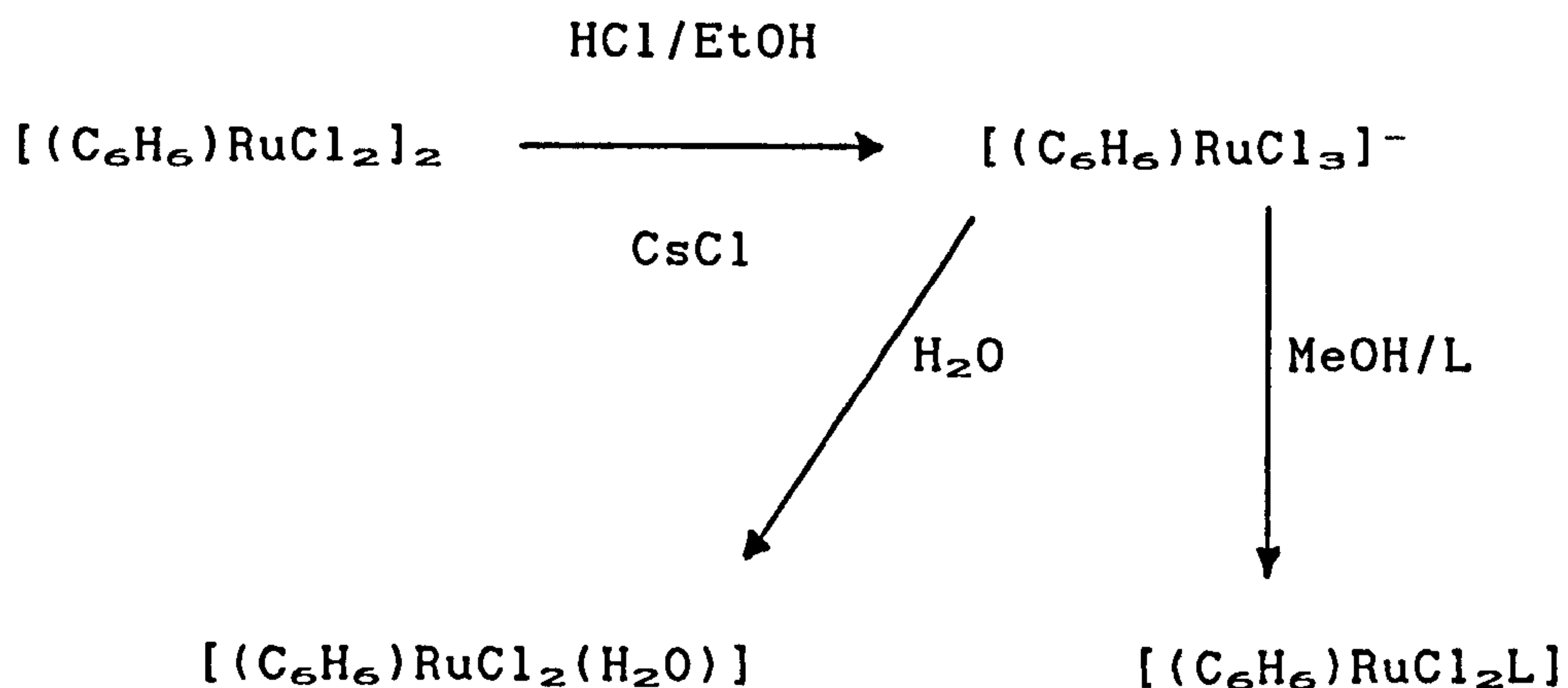


(arene = MeC₆H₄CHMe₂, C₆H₆)

1.2.2.7 The anionic arene ruthenium chloro complex



The benzene ruthenium chloro dimer when shaken with HCl in ethanol in the presence of excess CsCl affords the monomeric $[(C_6H_6)RuCl_3]^-$.²⁵



L = PPh_3 , PMe_2Ph ,
 $PMePh_2$, $SbPh_3$, py

This can be utilised as an alternative substrate to the neutral half sandwich $(C_6H_6)RuCl_2L$ system, as shown above.

1.3 X-ray crystal structure data

In table 1.3.1 are examples of neutral and ionic ruthenium(0) and ruthenium(II) arene complexes. Comparison of Ru-L, Ru-Cl and

Ru-C(arene) bond lengths is given and shows that these dimensions vary minimally, irrespective of the oxidation state or charge of the complex. The comparison of phosphorus and nitrogen based ligands is made and the ruthenium ligand bond length is shorter in the nitrogen case, as expected.

Table 1.3.1 X-ray crystal structure data of a range of ruthenium(0) and ruthenium(II) complexes

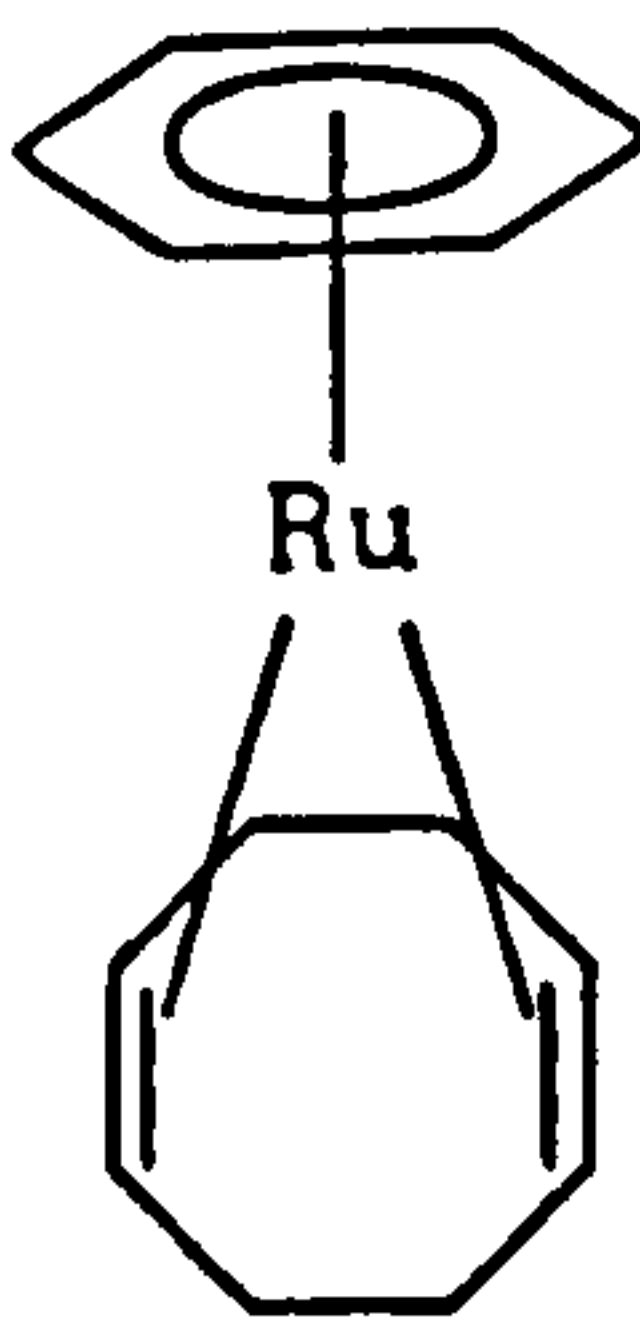
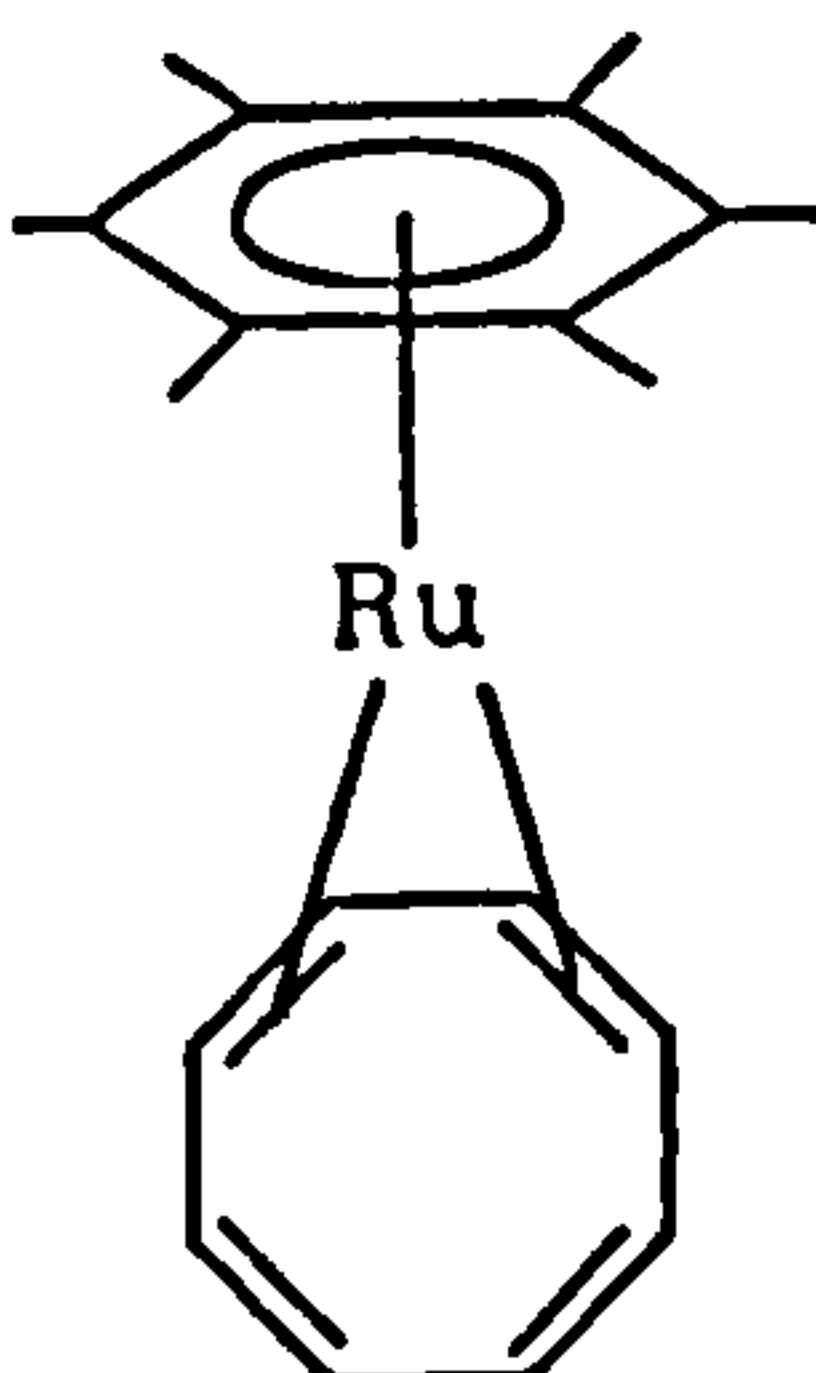
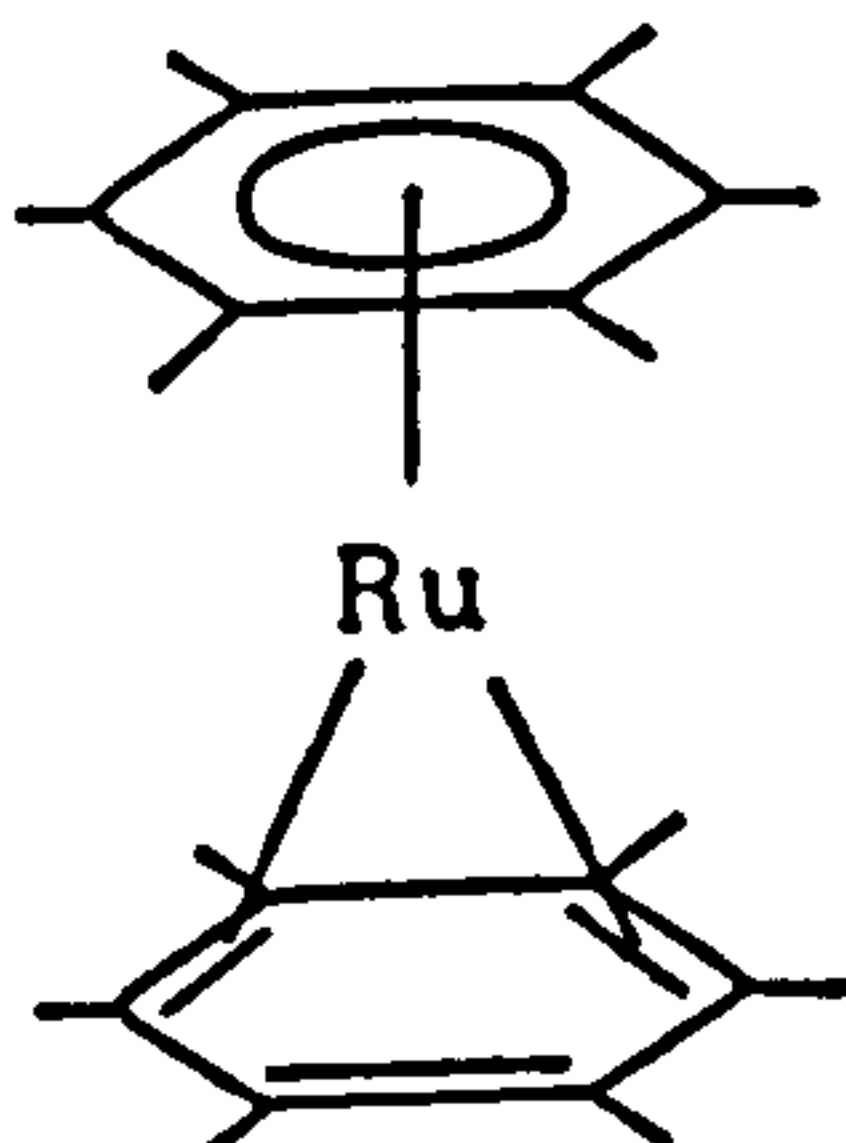
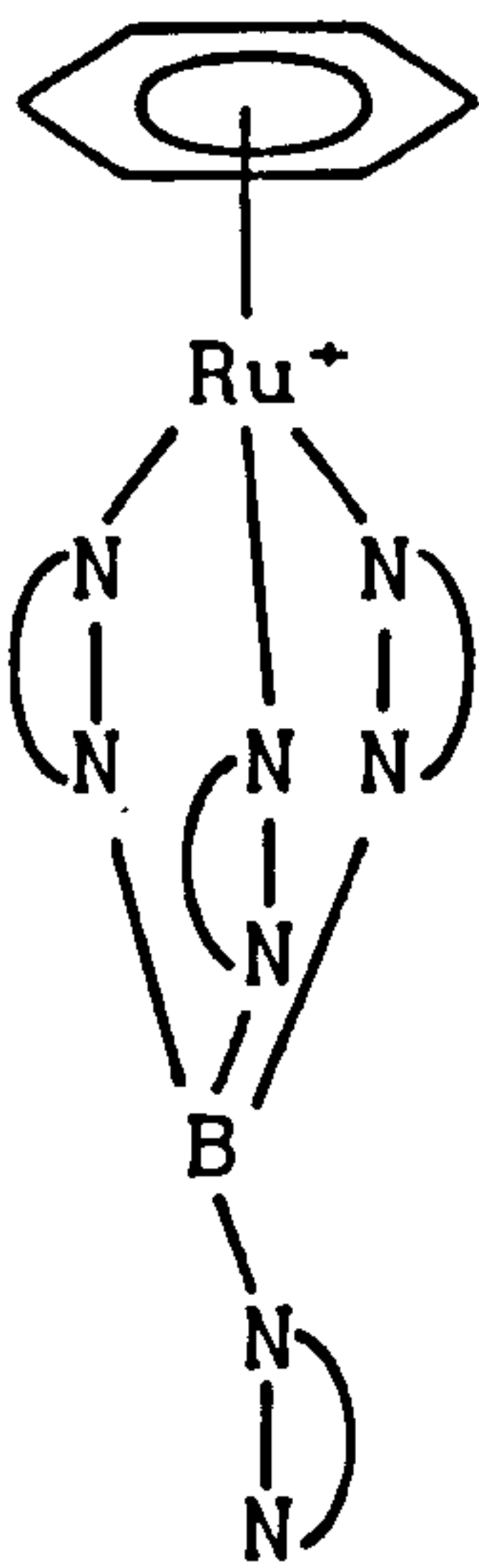
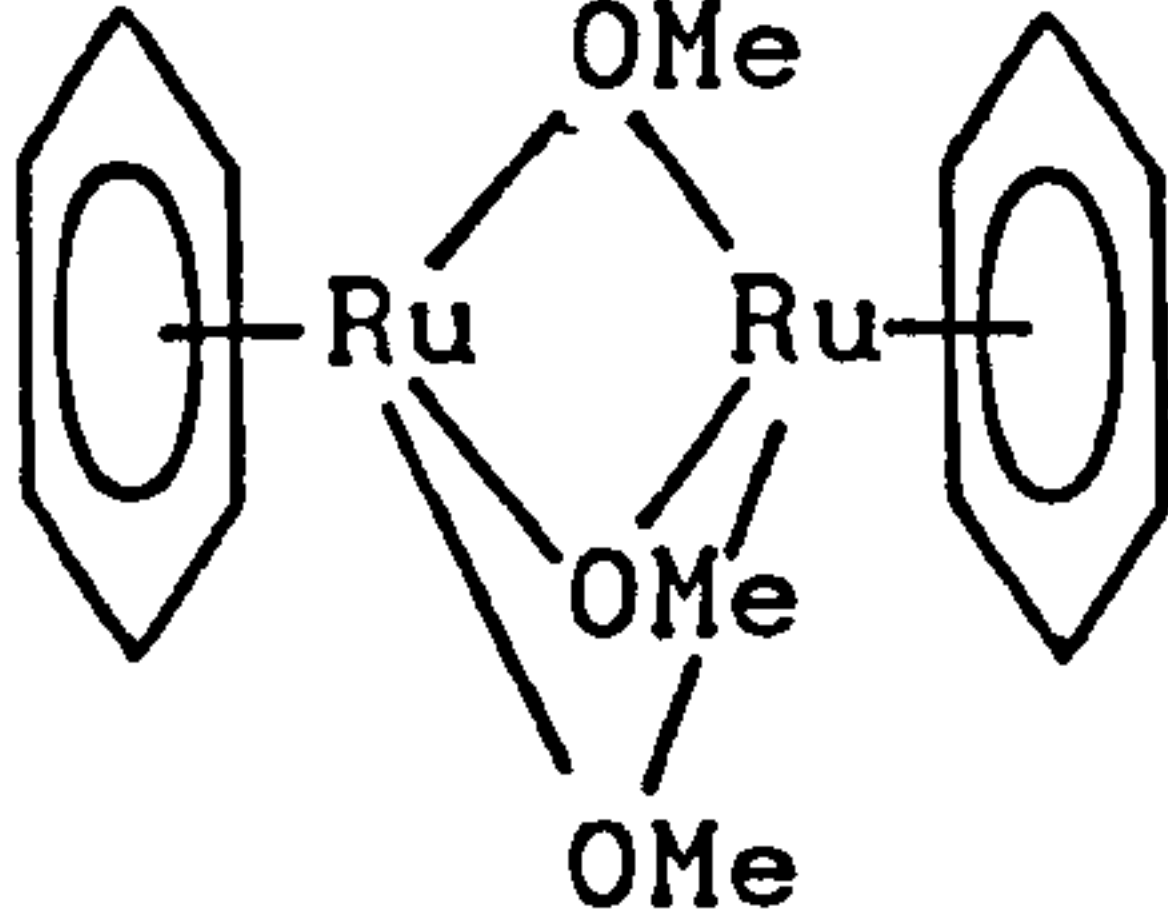
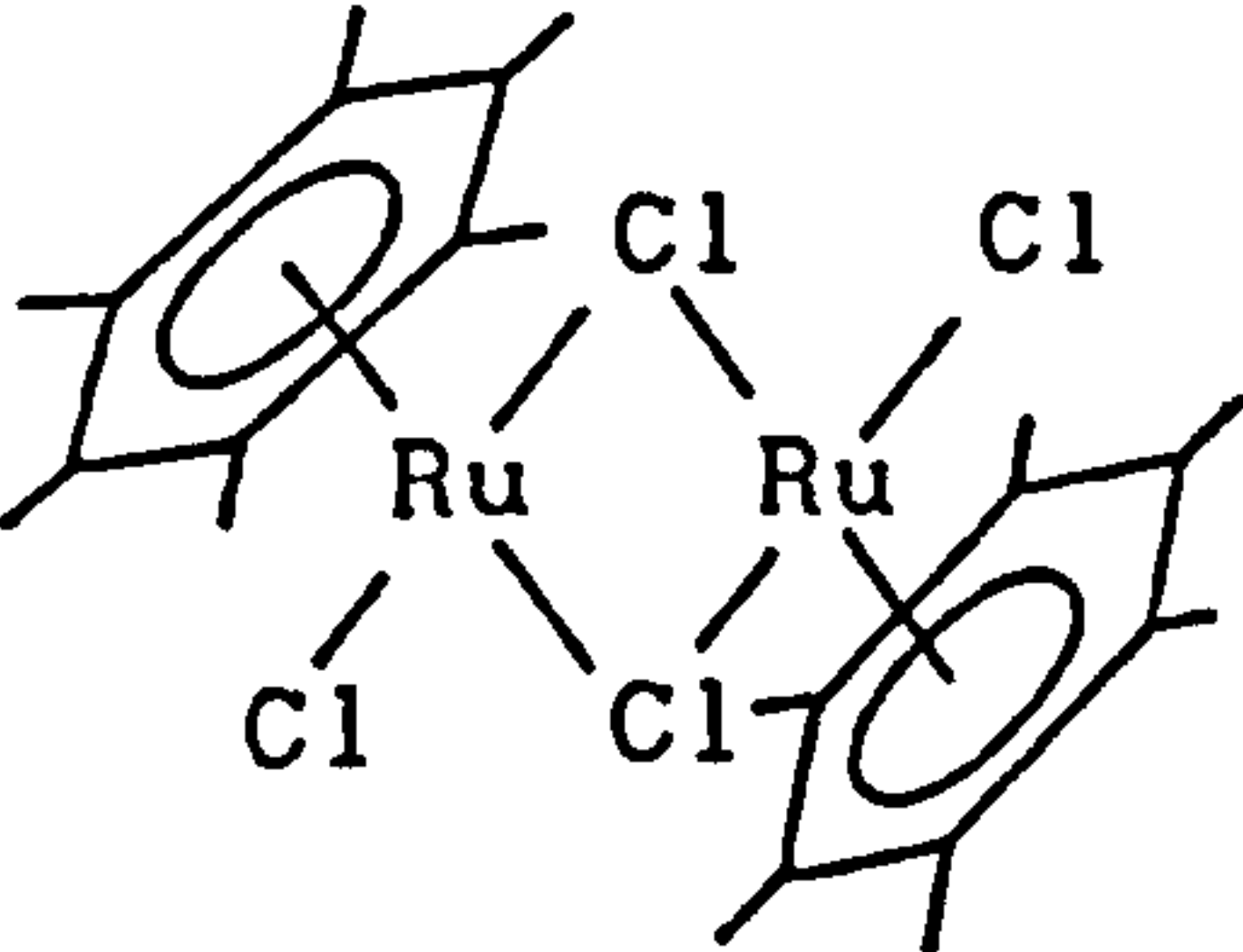
A°				
Complex	O.S.	Ru-C	Ru-L	Ru-Cl ref
	0	2.261(7)- 2.252(7)	2.135(5)- 2.148(5)	83
	0	2.220(30) (mean)	2.14- 2.25	56
	0	2.221(6) 2.283(6)	2.082(7) 2.185(6)	16

Table 1.3.1 (continued)

Å°				
Complex	O.S.	Ru-C	Ru-L	Ru-Cl ref
	II	2.212(8) - 2.253(10)	2.215(9) 2.251(10)	78
	II	2.190(10) - 2.270(10)	2.335(3)	2.410(3) 26
	II	2.220(10) - 2.250(10)	2.341(3)	2.414(3) 26
	II	2.174(20) - 2.195(20)	2.129(10)	2.383 84

Table 1.3.1 (continued)

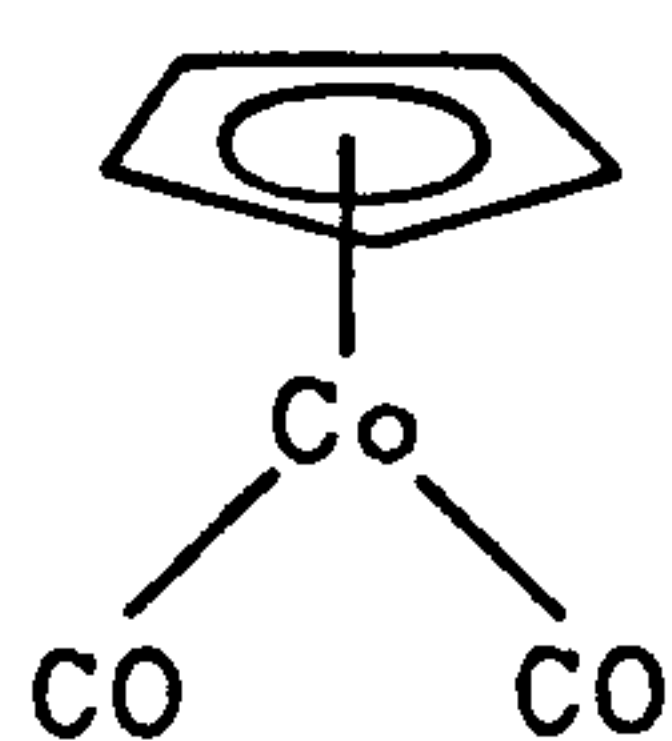
Complex	O.S. Ru-C	Ru-L	Ru-Cl	ref
	II 2.20(3) (mean)	2.105(7)		73
+				
	II 2.133(14) - 2.177(14) -	2.046(8) - 2.078(7)		80
	II 2.179(2) - 2.209(2)		2.394 (term) 2.460 (bridge)	85

CHAPTER TWO

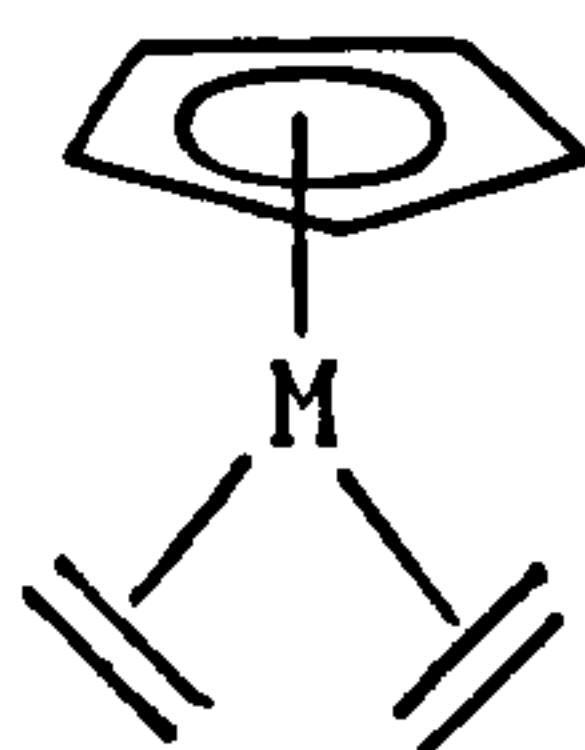
Chapter 2

2.1 Arene ruthenium zero valent complexes

This chapter concentrates on the preparation and chemistry of arene ruthenium bis(ethylene) complexes, which are members of the cyclic aromatic metal L_2 system. (see scheme 2.1)

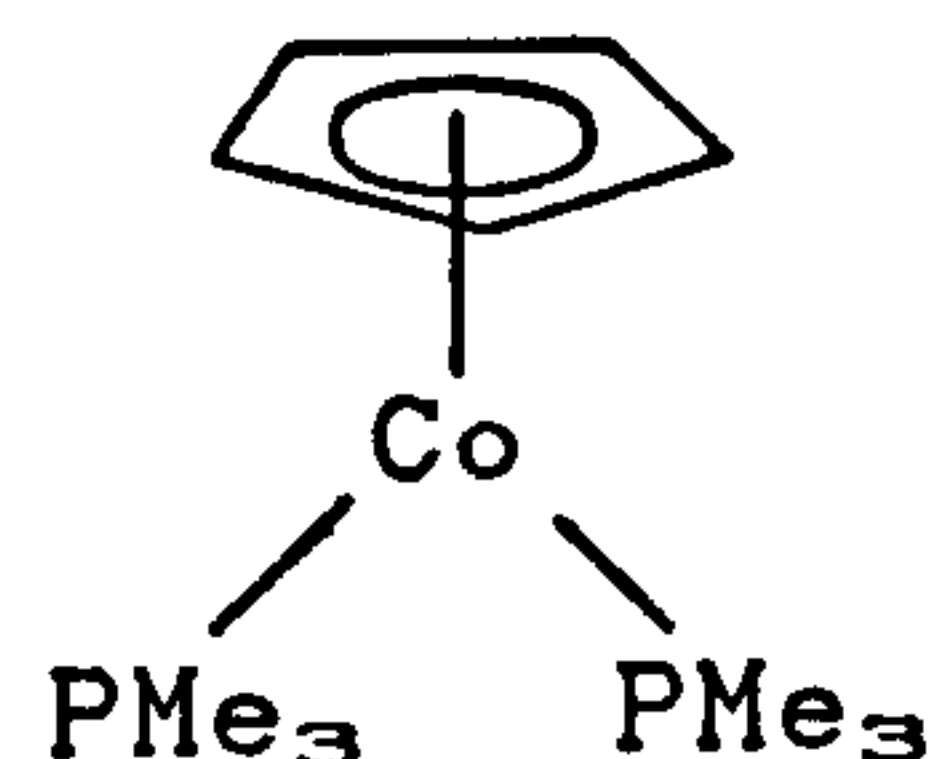


(ref86)

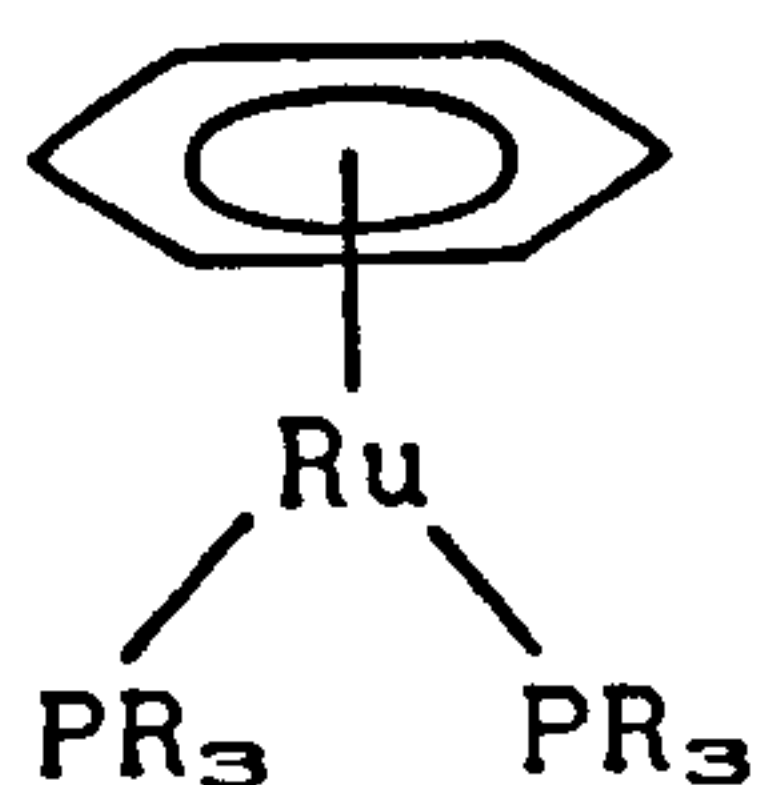


M=Co, Rh, Ir

(ref87,88,89)



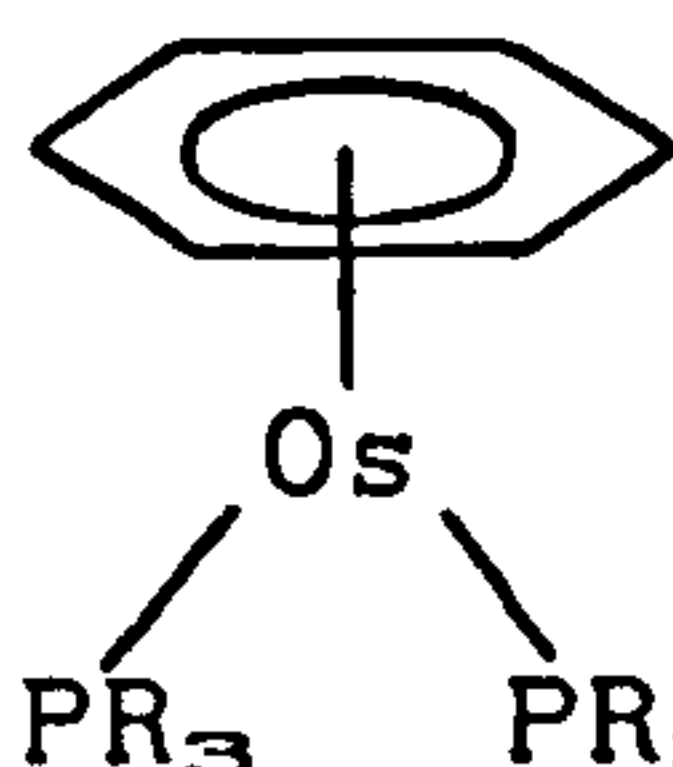
(ref90)



(ref49)

$PR_3 = PMe_3, PPh_3$

$PMe_2Ph, PMePh_2$



(ref49)

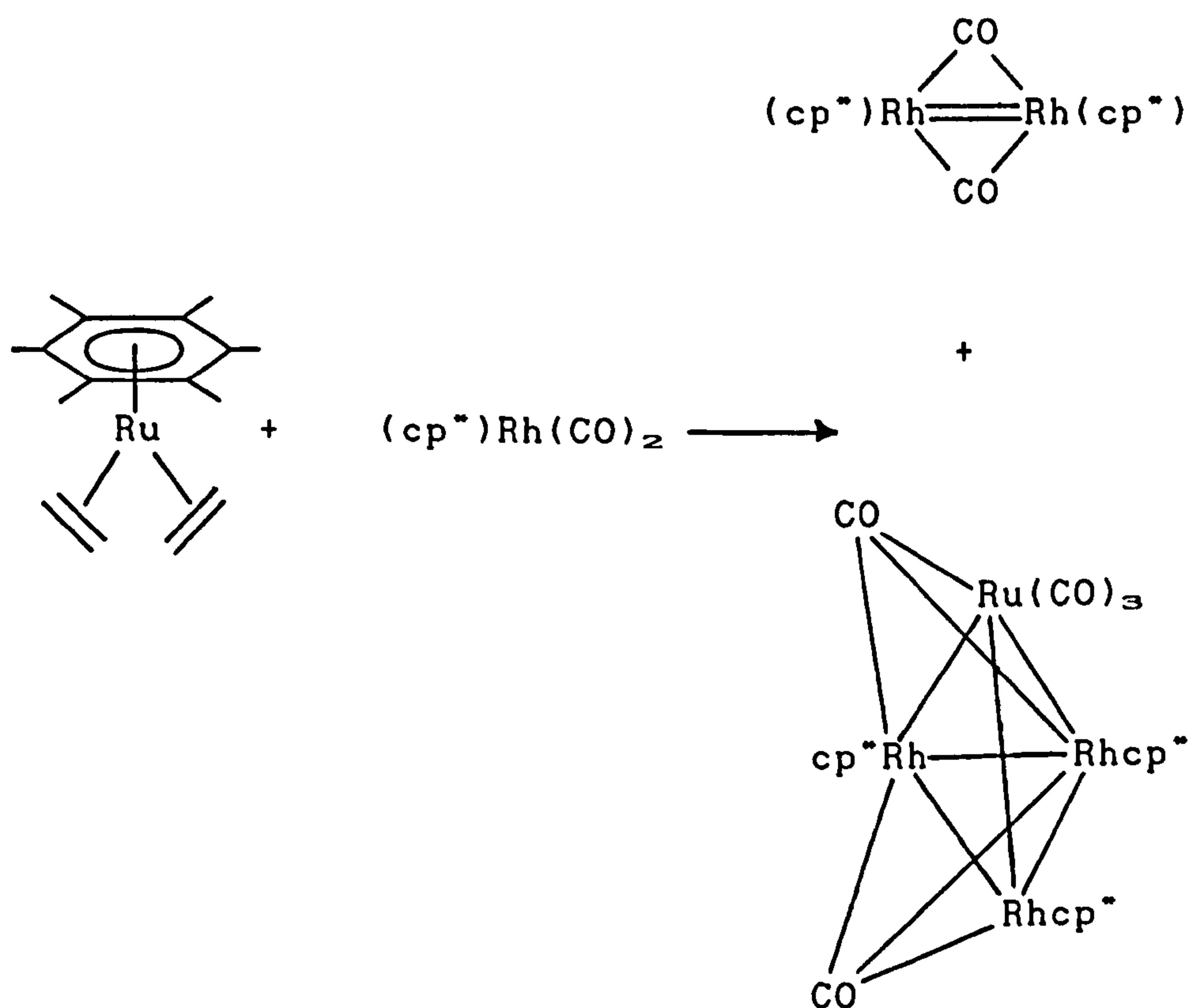
$PR_3 = PPh_3,$

$P(OMe)$

Scheme 2.1. Members of the cyclic aromatic metal L_2 system.

As mentioned in chapter 1, the preparation of one member of this class of compounds has been described, the ethylene complex $[(C_6Me_6)Ru(C_2H_4)_2]$.^{53,54} The chemistry of the group 8 and 9 bis(ethylene) derivatives is summarised below.

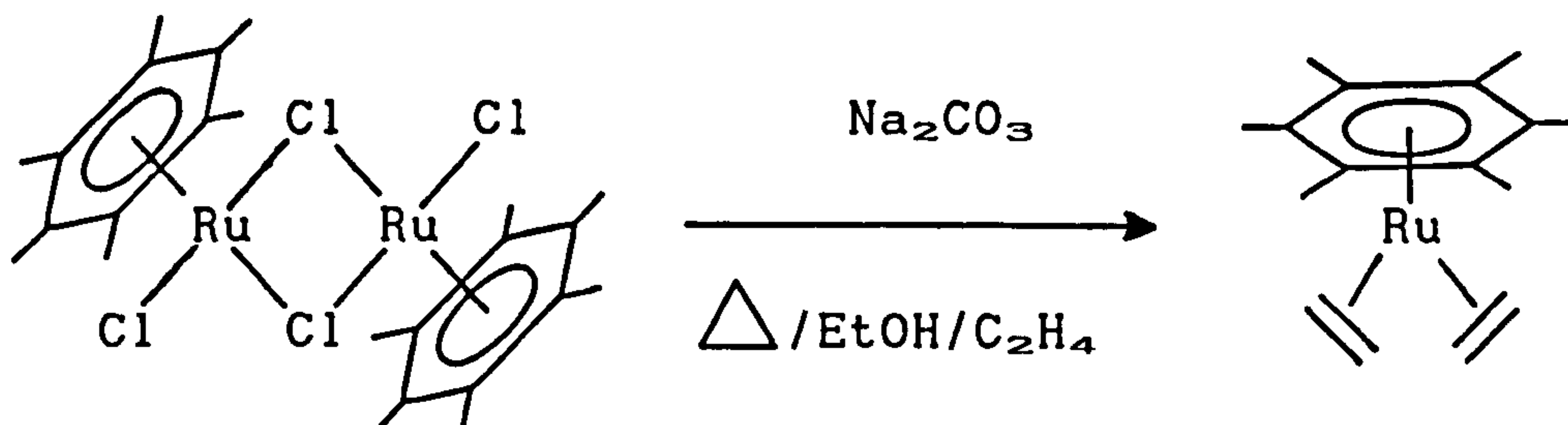
The hexamethylbenzene ruthenium bis(ethylene) complex has been utilised as a source of ruthenium in a mixed metal cluster synthesis.⁹¹



This is the only reference in the literature that refers to the chemistry of this complex. Also no arene analogues have successfully been

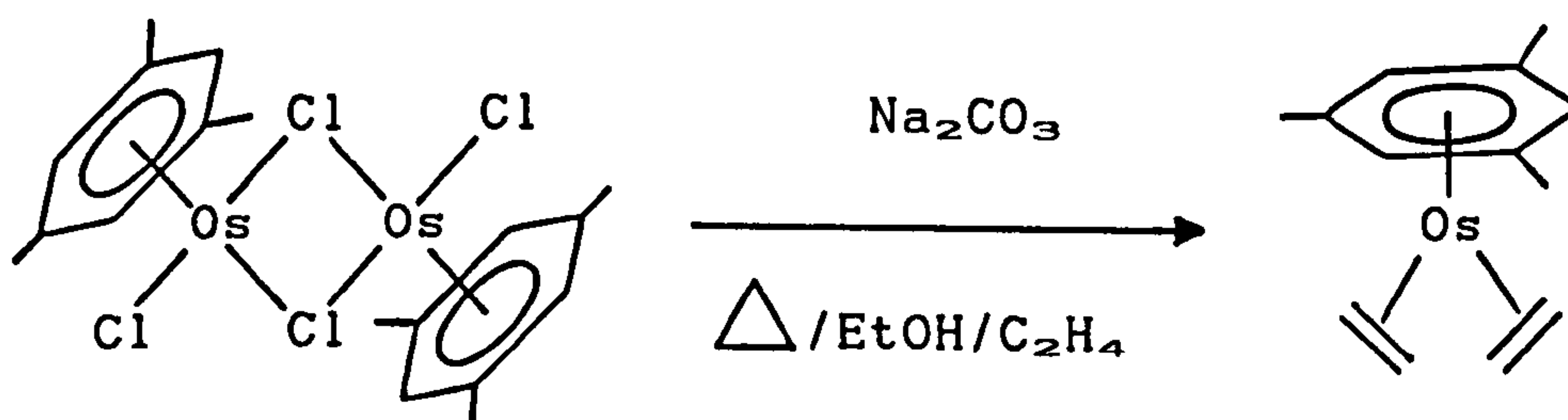
synthesised.

The preparation of the hexamethylbenzene ruthenium bis(ethylene) complex is synthetically crude but very successful. However, if other arene analogues are desired, a more subtle route is required.



In the Group 8 triad, iron and osmium arene bis(ethylene) systems have also been synthesised.

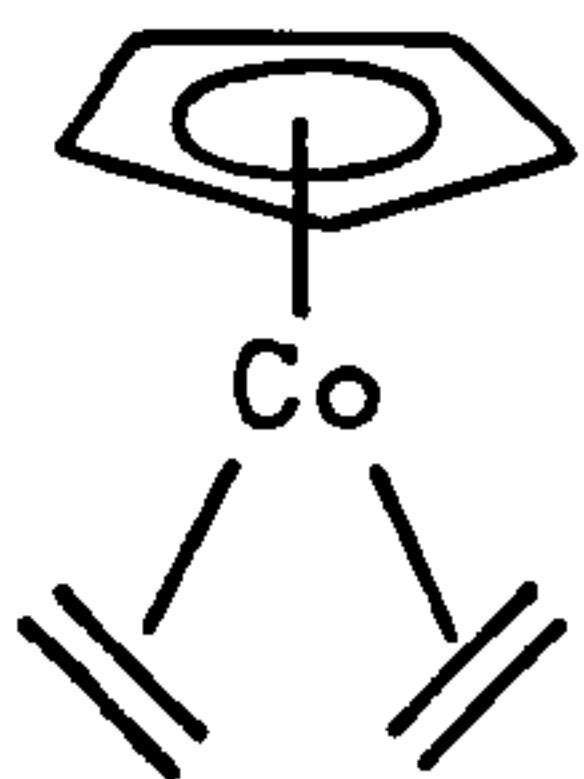
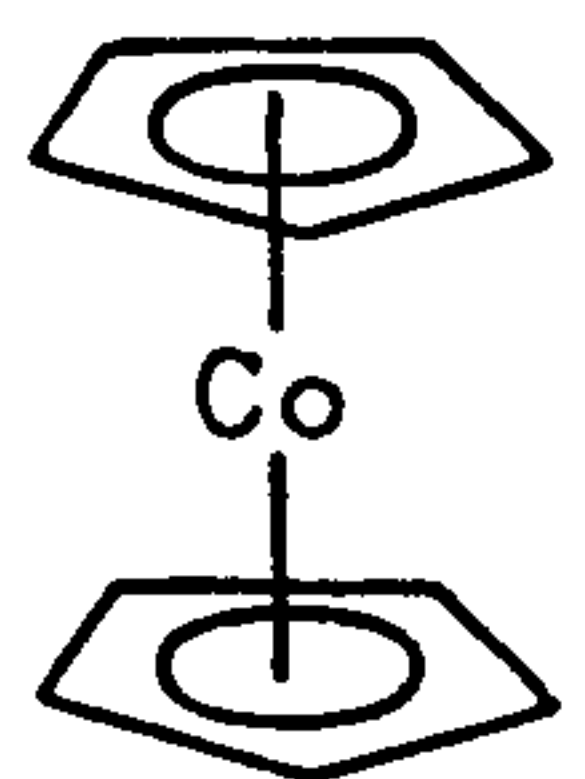
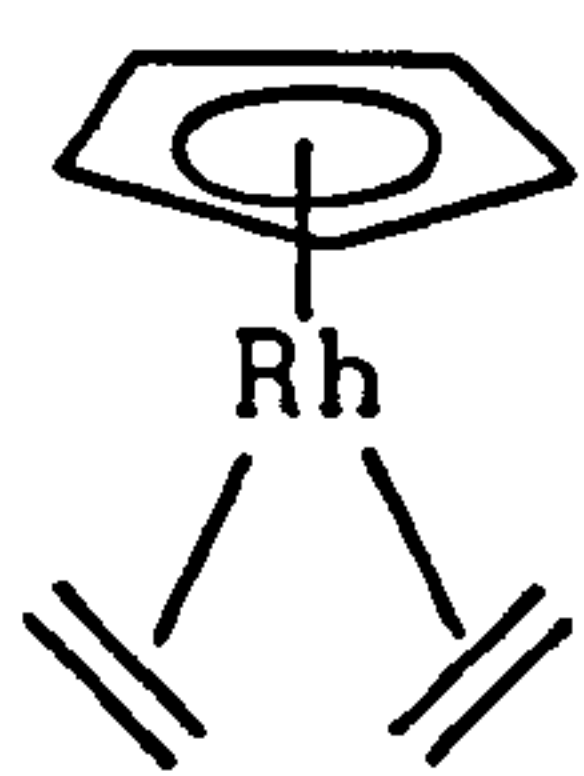
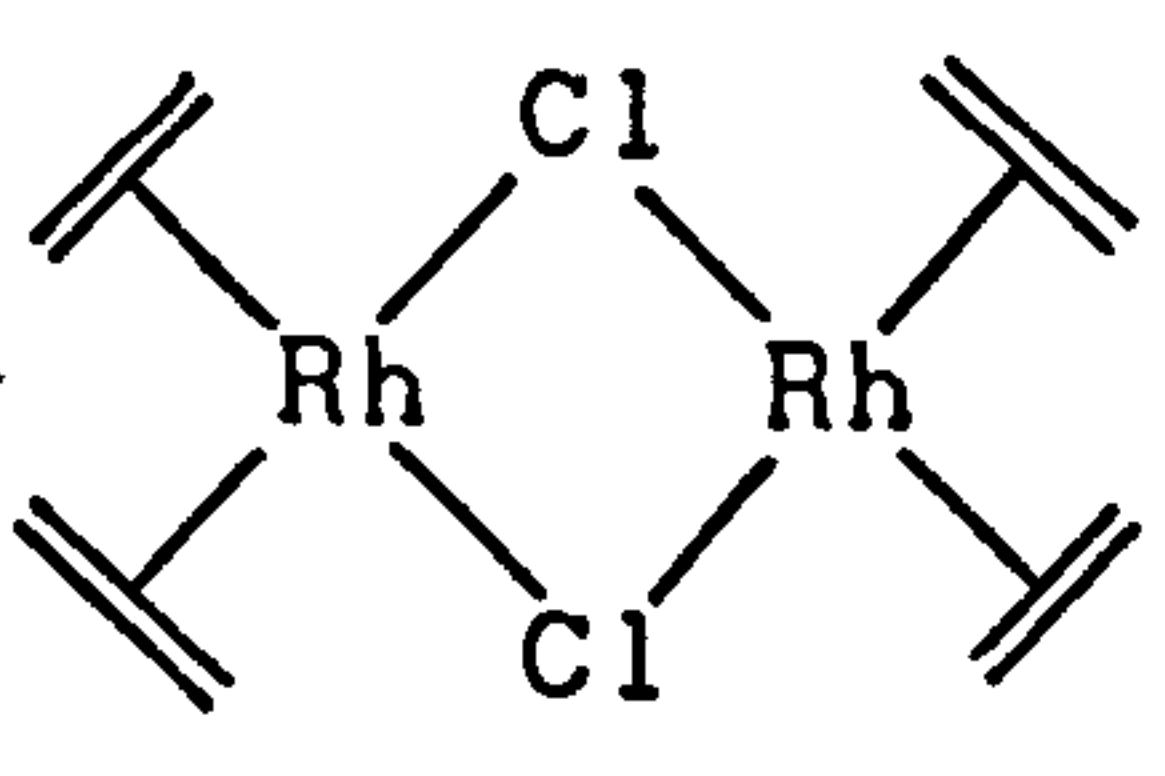
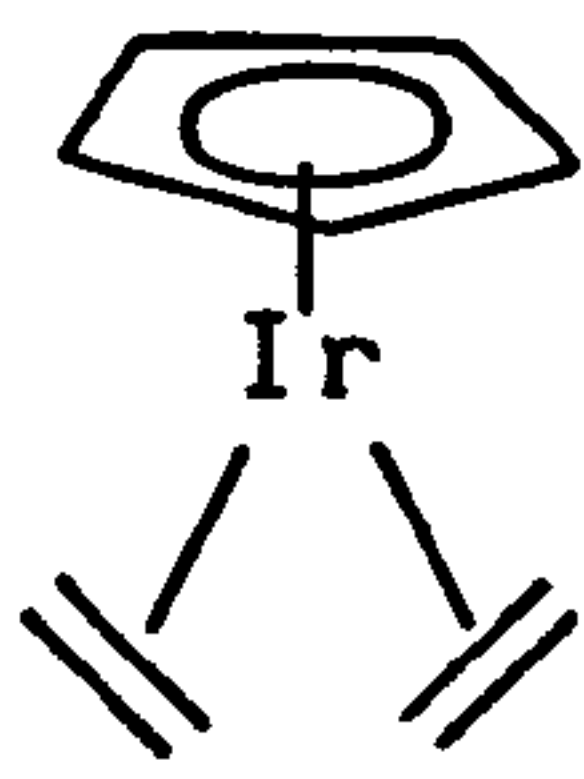
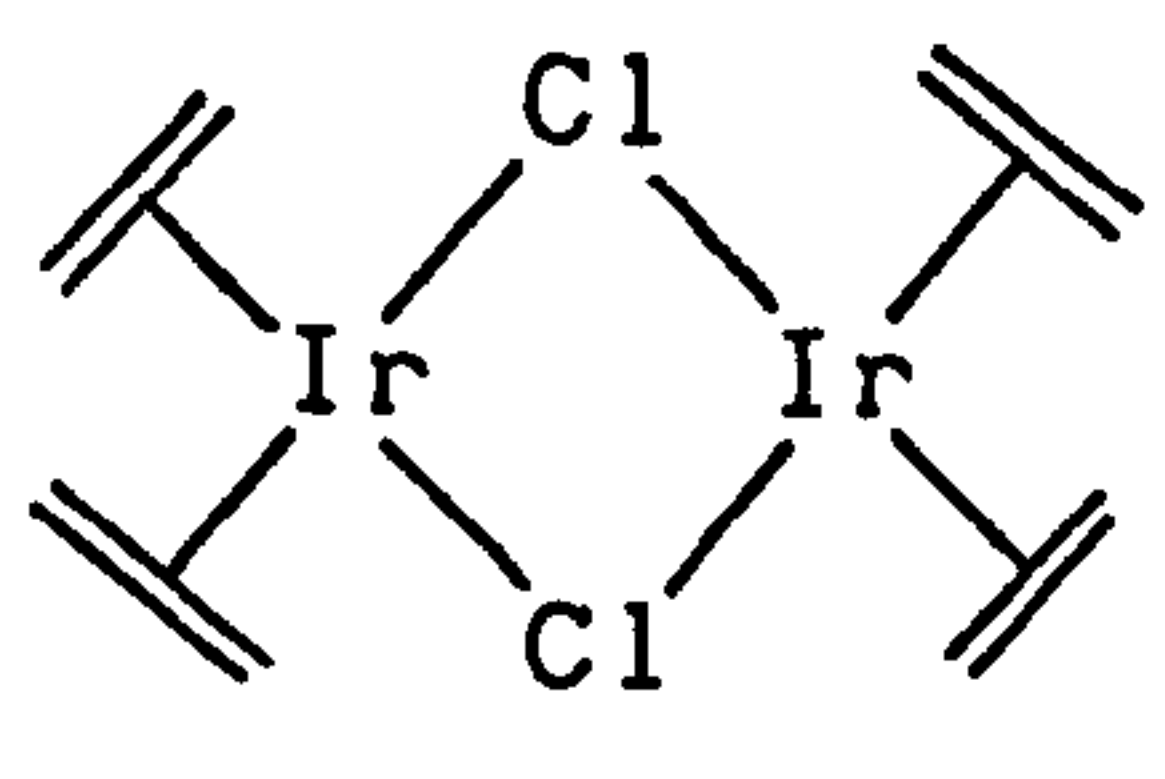
The osmium mesitylene complex has only very recently been prepared utilising Bennet's reflux route.⁹²



Complexes of the first member of the triad, iron, are prepared via the metal vapour synthesis of the bis(arene) system $(\eta^6\text{arene})\text{Fe}(\eta^4\text{arene})$ (arene = $\text{C}_6\text{H}_3\text{Me}_3$, C_6H_6 , $p\text{-MeC}_6\text{H}_4\text{CHMe}_2$), which, in turn, at low temperature react with ethylene to yield highly reactive and relatively unstable

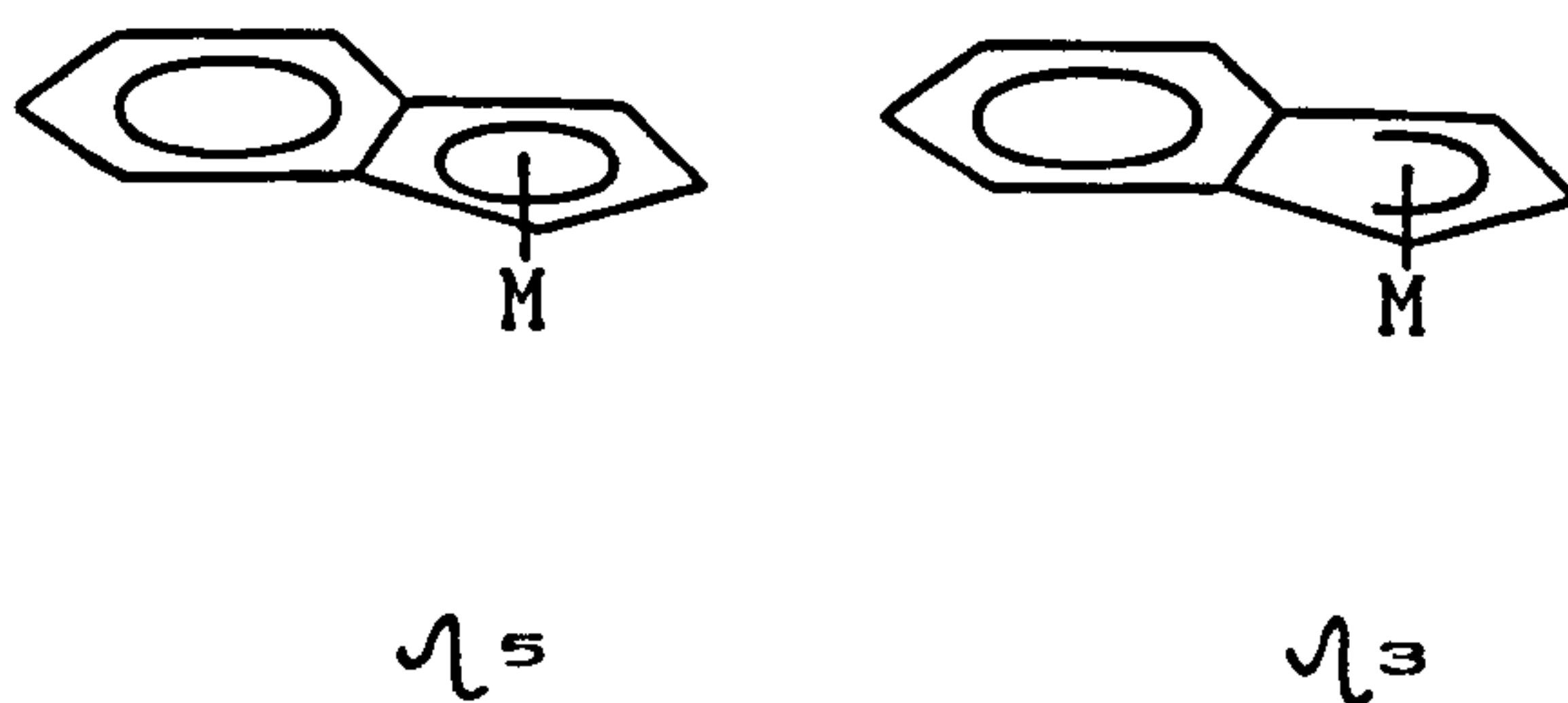
(arene)Fe(C₂H₄)₂ compounds.⁹³ These readily undergo ethylene exchange reactions in the presence of phosphites, phosphanes and diolefins, to yield neutral (arene)Fe(L)₂ complexes.⁹³

The isoelectronic system (cp)M(C₂H₄)₂ of the Group 9 triad, M = Co, Rh and Ir, has been studied extensively and summarised below are their respective preparations.

Complex	Preparation	Yield	Ref
	 K/C ₂ H ₄ /Et ₂ O ← -20°C	85%	87
	 2Nacp/THF ←	90%	88
	 Tlcp/THF ←	95%	89

All three complexes are relatively stable, the second and third members of the triad being non-reactive with respect to ethylene displacement at ambient temperature by nucleophiles such as PPh_3 , CN^- , and CO .¹¹⁵

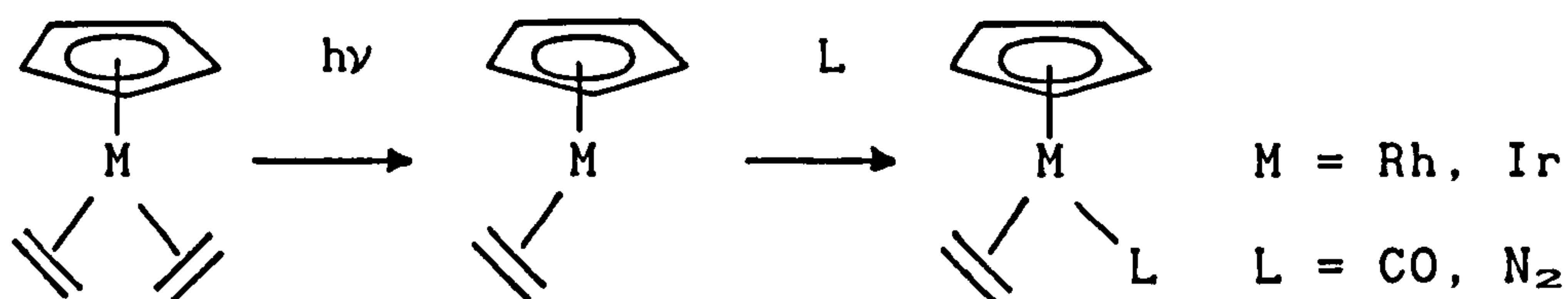
However, their reactivity is increased when the cp analogue indenyl is the cyclic aromatic. This effect can be rationalised in terms of ring slippage.



The cp part of the fused aromatic can be eta 5 or eta 3; ie when the indenyl is present in the eta 3 mode the metal is coordinatively unsaturated, allowing nucleophilic attack to occur. Thus ethylene displacement with diolefins, cyclooctatetraene and carbon monoxide is achieved, forming neutral indenyl $\text{M}(\text{L})_2$ complexes.¹¹⁵

As for the arene iron bis(ethylene) complexes, the isoelectronic cobalt analogue is highly reactive and readily undergoes ethylene displacement and can be utilised as a (cp)Co moiety in a large variety of reactions.⁸⁷

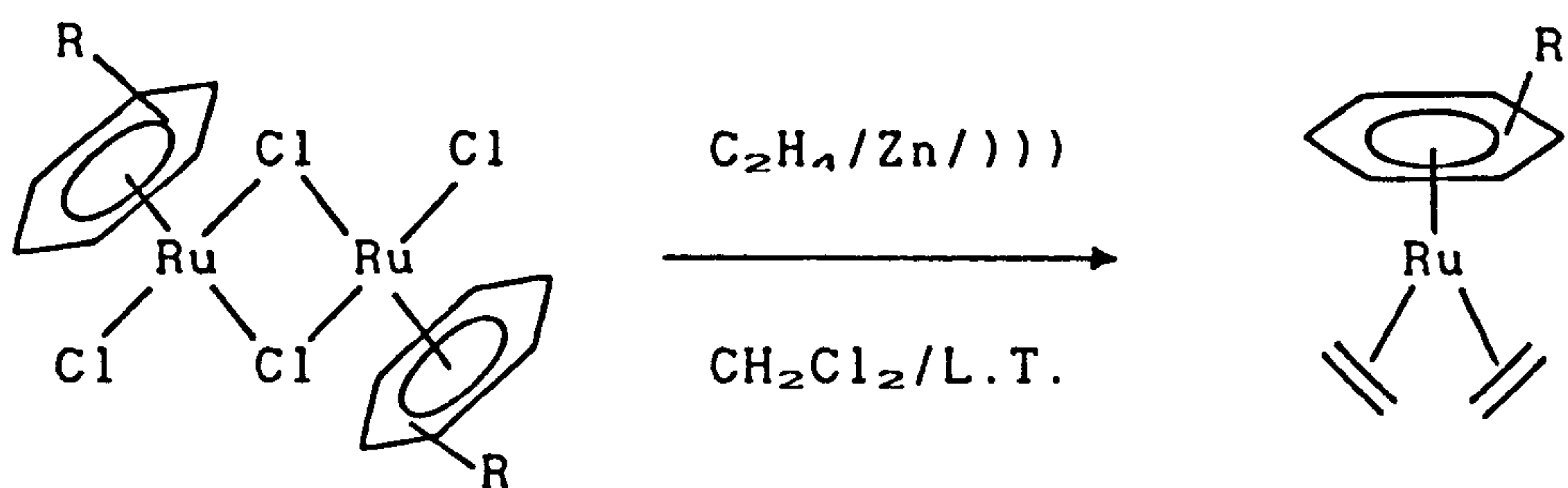
Matrix photochemistry of the rhodium and iridium (cp)M(C₂H₄)₂ complexes has been carried out and reported. In both cases 16 electron intermediates are generated which can react with N₂ and CO to yield 18 electron complexes.^{94,95}



2.2 Arene ruthenium bis(ethylene) system

Conventional chemical reductions failed to afford the arene ruthenium bis(ethylene) system. Ultrasound was investigated as an alternative energy source in the presence of zinc to carry out the desired reduction.

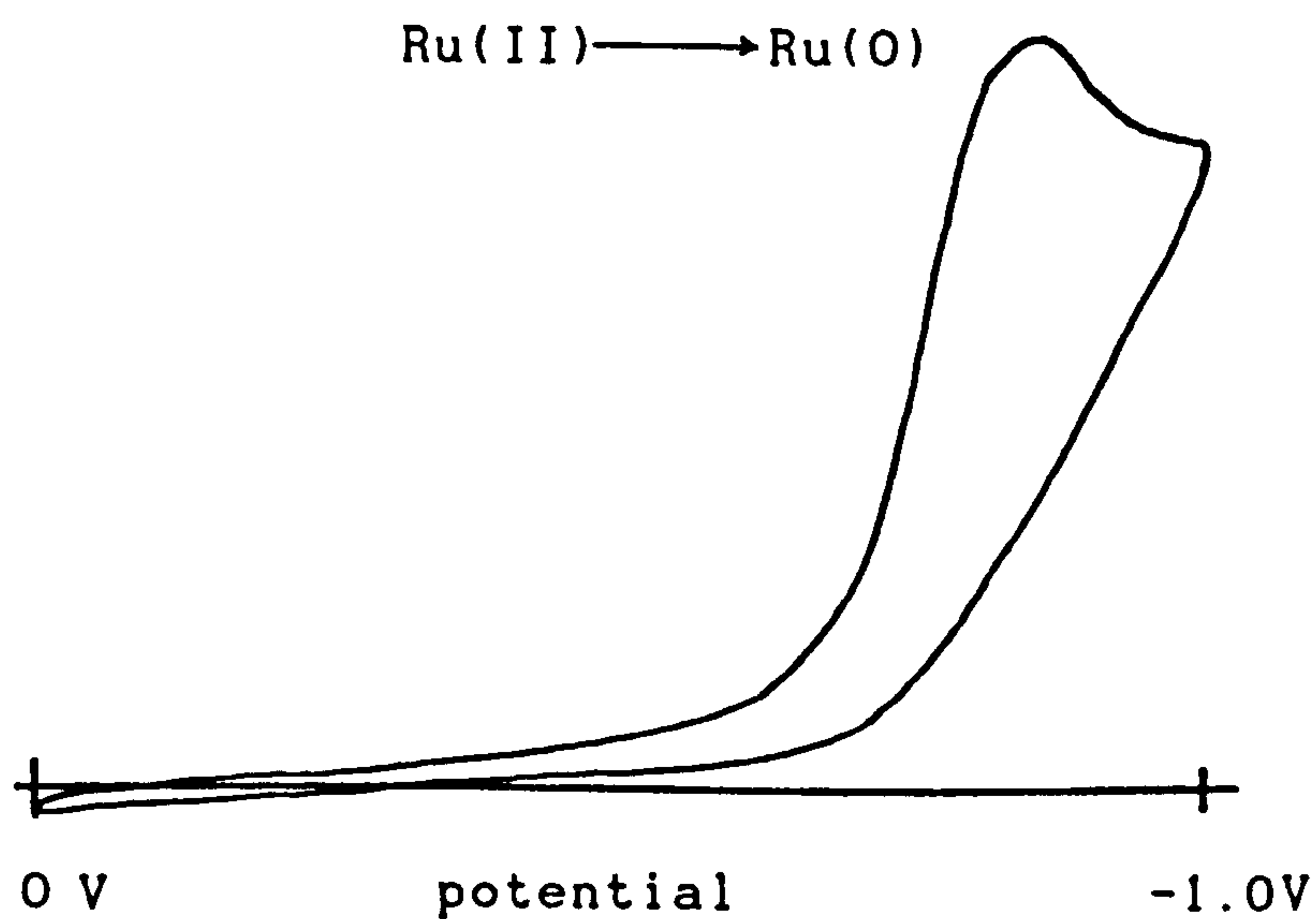
Low temperature sonication of a dichloromethane solution of the benzene or cymene [(arene)RuCl₂]₂ dimers, in the presence of zinc and ethylene affords a purple solution. This solution when taken to dryness and sublimed, yields the respective arene ruthenium bis(ethylene) derivatives as white crystalline solids.



The variables of the reaction were investigated to obtain the optimum yield.

Reducing agent

Cyclic voltammetry was utilised to determine the reduction potential of the process;



Cyclic voltammogram of $[(MeC_6H_4CHMe_2)RuCl_2]_2$ in CH_2Cl_2 , electrolyte NEt_4BF_4 , conc. $0.002 mol cm^{-3}$, reference ferrocene as internal standard.

From the cyclic voltammogram of the

$[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2$ dimer in dichloromethane, (shown above) it can be seen that an irreversible reduction occurs in the region -0.65 to -1.0V. Thus the redox potential of the reducing agent should be within this working range. Also a reducing agent which undergoes a two electron process would be preferred. Zinc has a redox potential of -0.76V⁹⁶ and manganese a value of -1.03V.⁹⁶ Both reducing agents were utilised to afford the desired product, but the ultrasound reaction was more efficient with zinc, in terms of yield (50%:<10%, Zn:Mn). Stronger reducing agents such as aluminium (-1.7V)⁹⁶ and magnesium (-2.4V)⁹⁶ reduced the desired product further before isolation could take place.

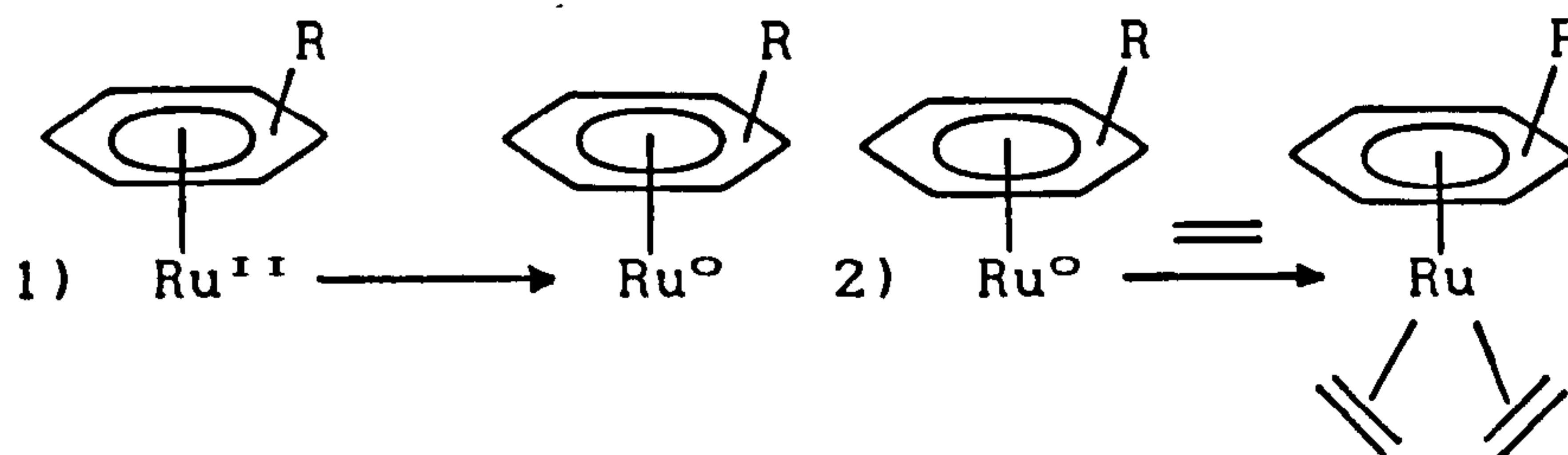
Temperature

Variation of the temperature at which the reaction was carried out, affected the yield dramatically. (see table 2.2.1)

Table 2.2.1 Yield of (arene)Ru(C₂H₄)₂ v temperature

Yield /%	Temperature / °C
0	24
45 - 55	-10
40 - 45	-20
trace amounts	-50

A possible mechanism involves the reaction occurring in two stages.



As temperature decreases, the concentration of ethylene in solution will increase, favouring process 2). Also cavity collapse will be more dramatic because of decreasing solvent vapour pressure. However, low temperature decreases the solubility of the $[(\text{arene})\text{RuCl}_2]_2$ dimers, probably affecting the success of the reduction reaction 1).

To fully understand the effect of temperature on the yield of this reaction, more detailed experiments would have to be executed.

Solvent system

Investigation of the solvent system resulted in the discovery of a competing process occurred when tetrahydrofuran was used (see chapter 3). Solvents such as acetonitrile or methanol could not be utilised to afford the desired products. It was determined that the polar non-coordinating chlorinated solvents, dichloromethane and dichloroethane, were suitable for the reaction.

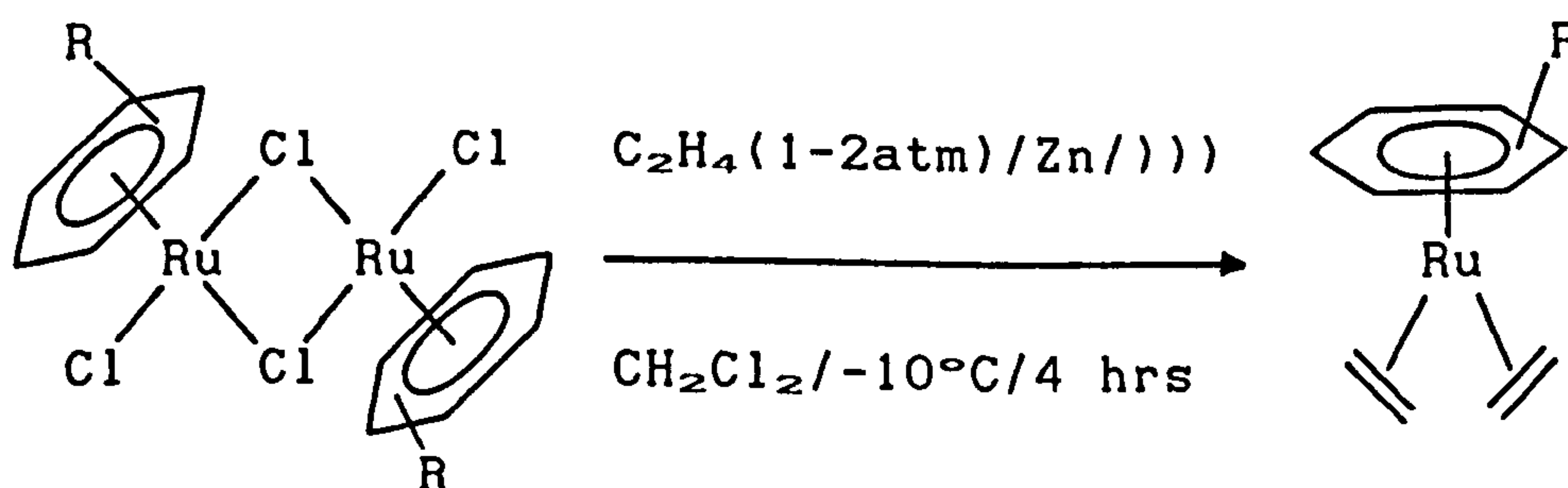
Ethylene

The reaction was found to proceed more cleanly, once the apparatus involved a continuous head pressure of ethylene, and not ethylene being bubbled into solution throughout the reaction. This was a reflection on ultrasound's use for degassing solvents. Yields varied minimally, whether the head pressure of the ethylene was 1, 2 or 3 atmospheres.

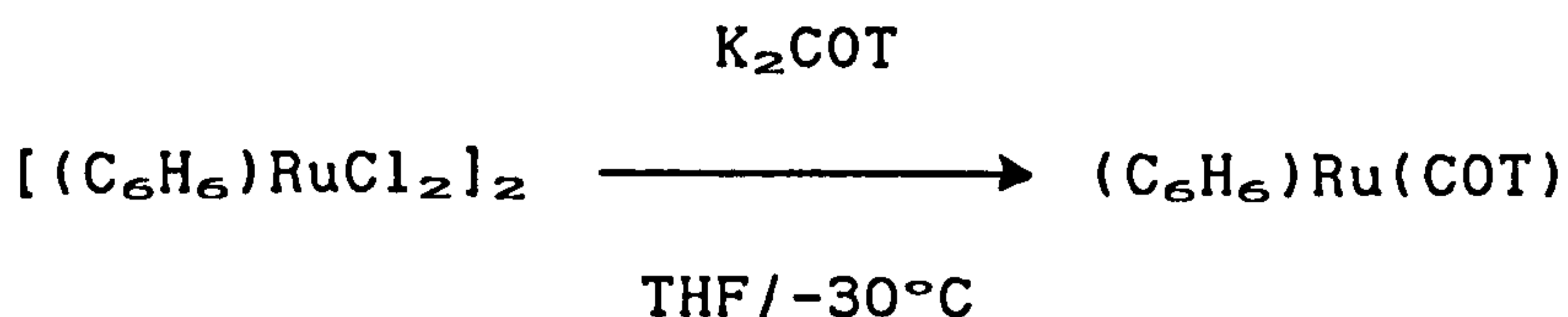
Time

Generally the optimum reaction time was 4 hours. No trace of starting material was detected by ^1H nmr after this length of time. However, extended reaction times did not enhance or decrease the yield. The reaction time could not be well defined, this appeared to be associated with the ultrasound being pulsed and altering slightly in intensity from experiment to experiment.

Thus the ideal conditions were surmised to be;



Alternative olefin ligands, cyclohexadiene, cyclooctadiene and cyclooctatetraene, when reacted under similar conditions, do not form analogues of the arene ruthenium bis(ethylene) complexes. These findings indicate that the reaction intermediate may not be a simple arene ruthenium solvated species, as the reaction conditions to form the benzene ruthenium (η^4 -cyclooctatetraene) complex are related to the ones attempted above.⁵⁶

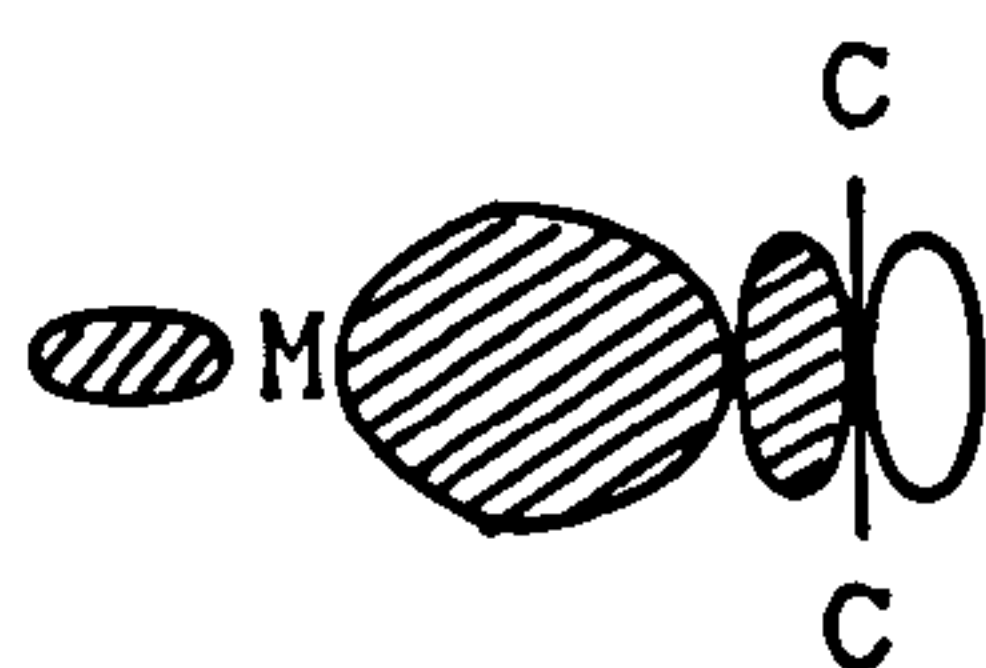


This will be discussed further in chapter 3.

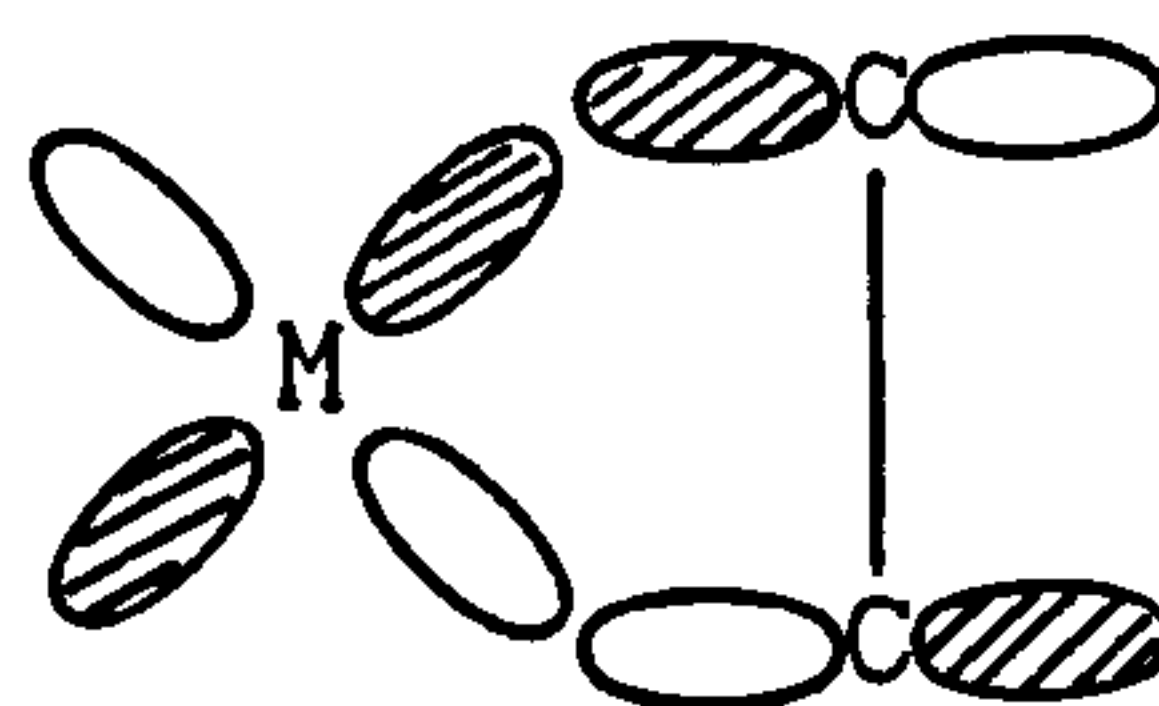
To interpret the ^1H nmr spectra of the bis(ethylene) complexes, a simple understanding of the bonding of the ethylene ligand is required.

The ruthenium ethylene bonding is a combination of σ - and π - bonding. The simple Dewar - Chatt-Duncanson model⁹⁷ is a widely accepted theoretical model for describing the bonding between a transition metal and an alkene. This model describes the bonding as a two-way donor-acceptor mechanism involving the frontier orbitals of both the metal fragment and the alkene. The HOMO of an

alkene is the π -bonding orbital and this donates electron density to the metal centre via a σ -bond with an empty directional metal based molecular orbital of appropriate symmetry.



σ -bond



π -bond

The LUMO of an alkene is an empty π -anti bonding orbital that can accept electron density to form a π -bond, from a full metal based orbital, again of appropriate symmetry.

The ^1H nmr spectra of the neutral cymene and benzene ruthenium bis(ethylene) species have distinct characteristic features, as does the hexamethylbenzene analogue. A relationship between the arene and the position of the ethylene multiplets was determined. The information from the spectra is summarised in table 2.2.3.

On the nmr time scale, the ethylenes bound to the metal are not freely rotating. Thus the non equivalence of the ethylene hydrogens H_a and H_b and two multiplets is observed.

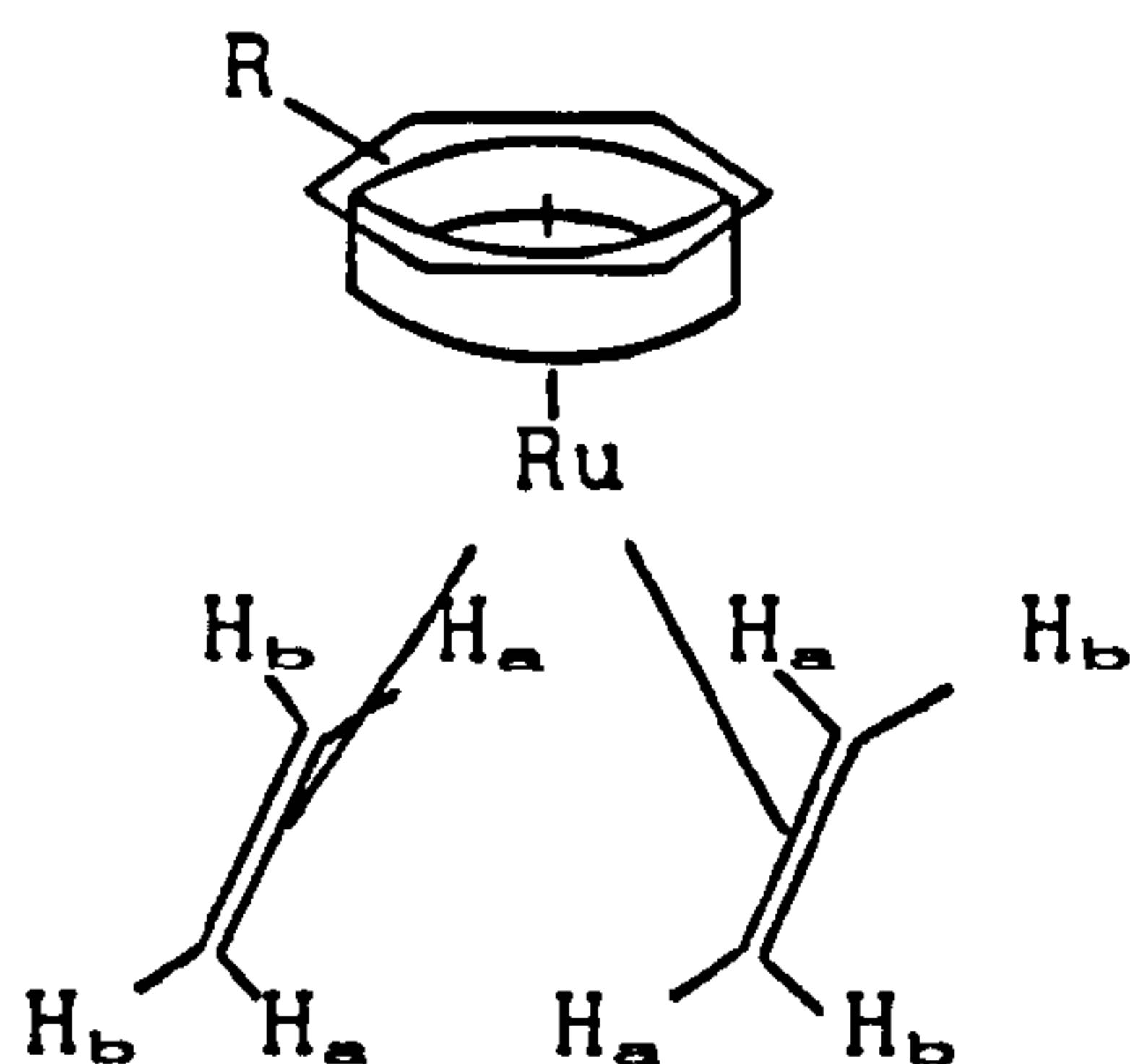


Table 2.2.3 ^1H nmr data of (arene) $\text{Ru}(\text{C}_2\text{H}_4)_2$
complexes #

Complex	Position of C_2H_4 multiplets /ppm	Δ /ppm	Mean position /ppm
(Hmb)	1.22, 0.62	0.6	0.92
(Cym)	1.87, 0.57	1.3	1.22
(Bz)	2.30, 0.54	1.76	1.42

solvent CDCl_3 .

chem. shift values quoted in terms of δ .

The variation in position of the ethylene multiplets, Δ , reflects directly the degree of equivalence or non equivalence of H_a and H_b .

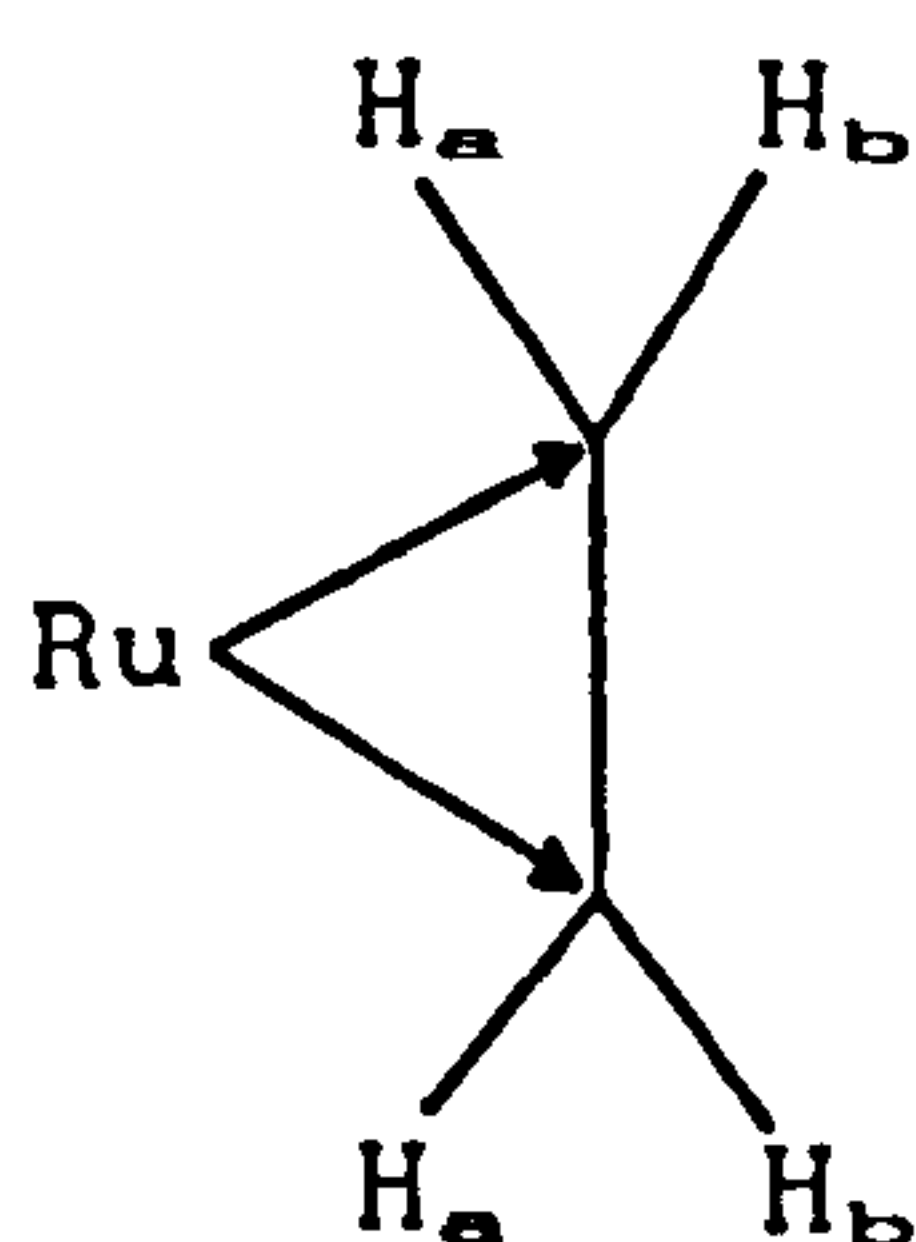
The difference can be largely attributed to the relatively close proximity of H_b and the arene ring current.

If there

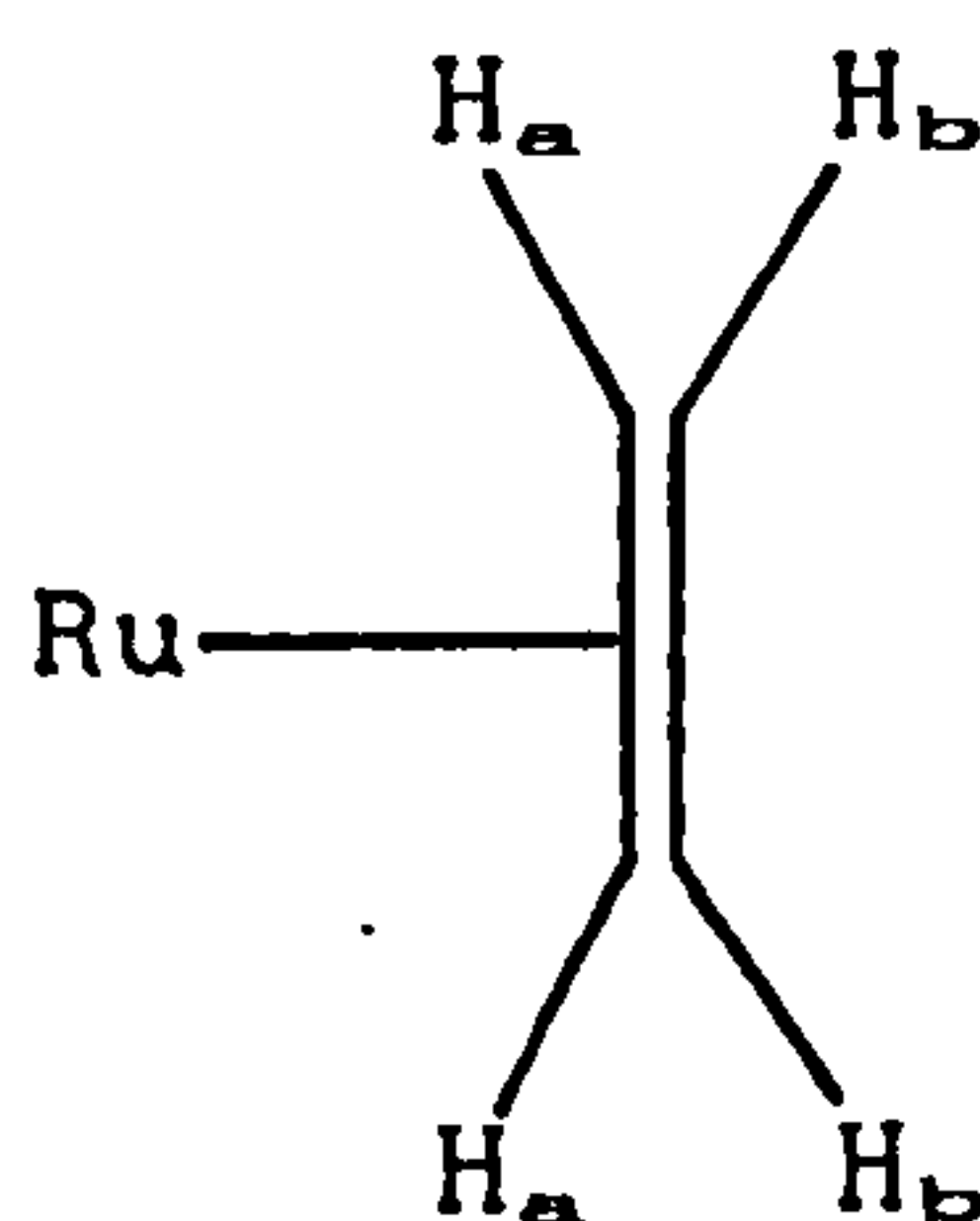
is no steric hindrance (cf benzene), the interaction between the ring current and H_a causes a large variation in the environments of H_a and H_b , and thus large Δ . The reverse is true in a sterically hindered arene case (cf hexamethylbenzene), where the substituents of the arene act as a barrier to interaction between the ring current and H_a . Thus Δ is relatively small.

As would be expected, an arene with partial substitution (cf cymene), the value of Δ is intermediate with respect to the benzene and hexamethylbenzene complexes.

The mean position of the multiplets is dependent upon how unsaturated in character the ethylene hydrogens H_a and H_b are. Case 1 and 2 can be used as models of the two extremes of π -back bonding.



Case 1



Case 2

As shown in table 2.2.3, the trend as the arene

changes from hexamethylbenzene, to cymene to benzene, the mean position of H_a and H_b shift to low field. This is explained by the amount of π -back bonding occurring for each complex.

The hexamethylbenzene arene is electron rich and in turn so is the ruthenium metal centre it is bound to. This leads to π -back bonding similar to that represented by case 1. The bonding of the metal and the ethylene ligand can be assumed to be similar to a metallocyclopropane. The hydrogens H_a and H_b can be termed as near saturated, thus their relative high field mean chemical shift position.

The benzene arene is a poorer electron donator to the ruthenium metal centre than hexamethylbenzene, and thus the π -back bonding that occurs can be represented by case 2. The hydrogens H_a and H_b can be termed unsaturated, thus the relative low field mean chemical shift position of the ethylene ligands for this complex.

With respect to electron donation to the ruthenium metal centre, cymene is intermediate compared to the benzene and the hexamethylbenzene arene complexes. This reflects on the π -back bonding and as expected the mean position should be, and is, between those represented by case 1 and 2.

These two proposed explanations for the difference in the position, Δ , and the mean

position of the ethylene multiplets is supported by comparison of the analogous complexes $(cp^*)Co(C_2H_4)_2$ and $(cp)Co(C_2H_4)_2$. They represent direct analogies to the hexamethylbenzene and benzene ruthenium bis(ethylene) complexes respectively. The same trend occurs for the difference in how electron rich or methyl substituted the cyclic aromatic ligand is, as occurs for the arene ruthenium bis(ethylene) system. (see table 2.4.4)

Table 2.2.4 1H nmr data of (cp) and (cp^*) cobalt bis(ethylene) complexes. #⁹⁸

Complex	Position of C_2H_4 multiplets/ ppm	Δ /ppm	Mean position / ppm
cp^*	1.60, 0.86	0.74	1.23
cp	2.55, 0.68	1.87	1.62

solvent C_6D_6 , chem. shift values quoted in terms of δ .

The barrier to rotation of the ethylenes in the arene ruthenium system was investigated. A 1H nmr experiment was performed, where the arene ruthenium bis(ethylene) complexes were heated in deuterated

benzene to 343K in 10K steps. It was determined that over this temperature range, on the nmr time scale, the multiplets assigned to the ethylene ligands remained unaltered (except for changes in resolution). Thus it appears on the nmr time scale the ethylenes do not rotate freely, even on warming. In contrast, the cp rhodium bis(ethylene) system when investigated by R. Cramer⁹⁹, was shown to undergo ethylene rotation on warming. The consequence of this process is that the hydrogens H_a and H_b become fluxional and interchange, thus the observation that the ethylene multiplets coalesce.

The explanation for the difference in the analogous systems can be rationalised in terms of the strength of the π -bond between the metal and the ethylene. With the ruthenium system, the metal is more electron rich than the rhodium analogue and the π -bond much stronger, as an arene is more electron rich than a cyclopentadienyl ligand. This argument is supported by the investigations carried out by R. Cramer on substituted cyclopentadienyl rhodium bis(ethylene) complexes. He found substitution with electronegative groups (-CN or -COOCH₃) weakens the π -bond, while substitution with methyl groups strengthened the bond. Thus the barriers to rotation and the coalescence temperatures were lower and higher respectively, in

comparison to the unsubstituted cyclopentadienyl ligand.⁹⁹

Interpretation of the infrared data of the benzene ruthenium bis(ethylene) complex gave support to the arguments put forward to explain the ¹H nmr trends observed.

G. Davidson and J. A. Crayston^{100,101} investigated the infrared and raman spectra of metal ethene complexes. Using group theory, they predicted for a metal-ethylene unit of symmetry C_{2v} four $\nu(\text{CH})$ modes ($a_1 + a_2 + b_1 + b_2$) should be observed. However, the a_2 mode is ir-inactive and when investigating the Pt(C₂H₄)(PPh₃)₂ complex, the b_2 mode is masked by strong aromatic $\nu(\text{CH})$ bands of PPh₃ at approximately 3060cm⁻¹. This mode is also not observable for either the rhodium bis(ethylene)⁸⁸ or the benzene ruthenium bis(ethylene) complex. (see table 2.2.5)

Table 2.2.5 IR of metal ethylene complexes

Complex	Aryl $\nu(\text{C-H})$ / cm ⁻¹	Ethene $\nu(\text{C-H})$ / cm ⁻¹
(C ₆ H ₆)Ru(C ₂ H ₄) ₂	3080	2965 (a_1) , 2925 (b_1)
(C ₅ H ₅)Rh(C ₂ H ₄) ₂	3090	3010 (a_1) , 2950 (b_1)
Pt(C ₂ H ₄)(PPh ₃) ₂	3060	2971 (a_1) , 2958 (b_1)

The ethene $\nu(\text{C-H})$ stretches for the above complexes have absorptions which lie in what is normally regarded as the saturated $\nu(\text{C-H})$ stretching region. This characteristic of metal ethylene complexes has caused spectroscopists to argue whether metal-alkene complexes are better described as metallocyclopropanes.^{102.103.104}

If the overall σ and π donor contributions are best described as a metallocyclopropane, the $\nu(\text{C-H})$ stretches of the ethylene would be expected to absorb at a lower frequency than classic unsaturated $\nu(\text{C-H})$ stretches.

This evidence gives support to the use of the metallocyclopropane bonding model, applied to explain the trend observed in the mean position of the ethylene multiplets, for a series of various arene ruthenium bis(ethylene) complexes in the ^1H nmr studies carried out.

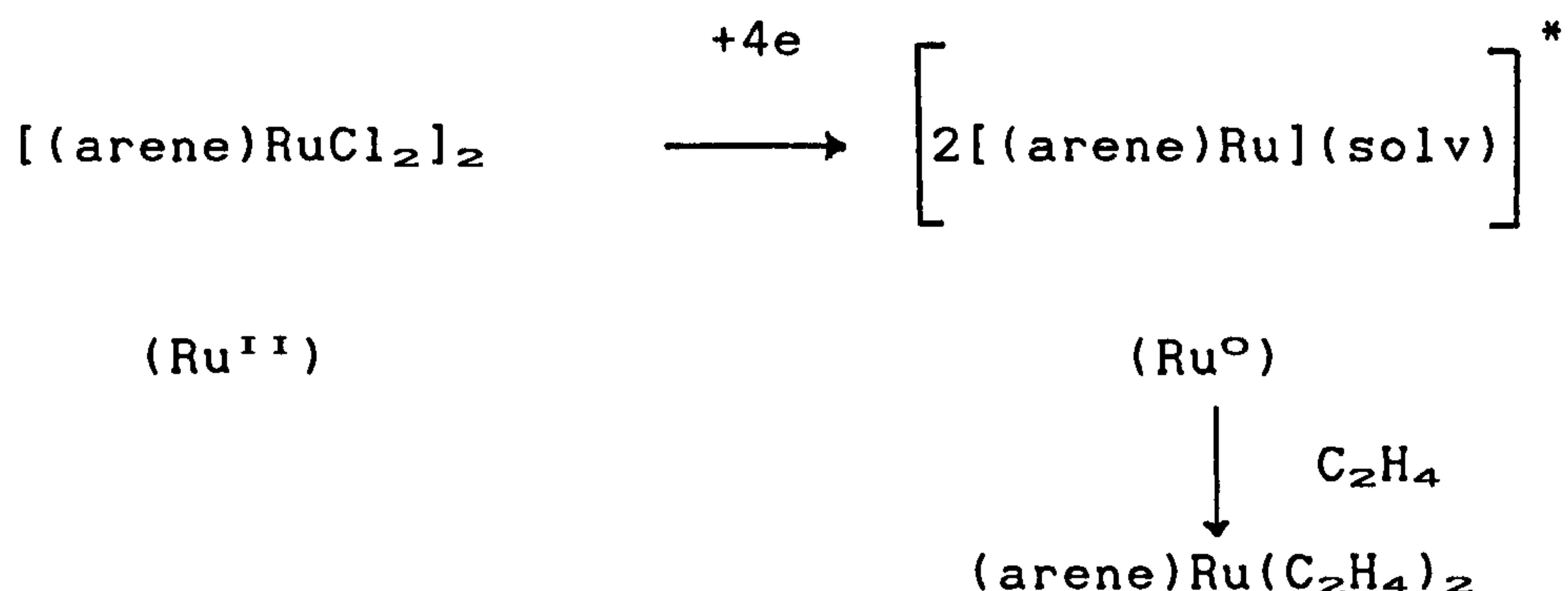
An arene ligand is more electron rich than a cyclopentadienyl ligand and thus the metal will be more electron rich with consequent increased π -back bonding to the ethylene ligand. This will reflect in the position of the ethylene $\nu(\text{C-H})$ stretches. The ruthenium bis(ethylene) complex would be expected and in fact does have ethylene $\nu(\text{C-H})$ stretches at a lower frequency than the rhodium analogue. (see table 2.2.5)

2.3 Mechanism

Removal of zinc from the reaction yields no conversion of starting material via chloro bridge cleavage to a half sandwich complex of form (arene)RuCl₂L. This implies for the bis(ethylene) preparation that the initial step involves chloride abstraction from the coordination sphere, affording ZnCl₂ and a coordinatively unsaturated arene ruthenium complex.

Of all the common solvents available to the synthetic chemist, dichloromethane is perhaps the only one that is commonly thought of as polar but non-coordinating. However, the structure Ag₂(CH₂Cl₂)₄Pd(OTeF₅)₄ has recently been reported.¹⁰⁵ The structural results leave no doubt that dichloromethane can coordinate to metal ions, that both chlorine atoms form four membered chelate rings and if a metal ion is unsaturated enough, that more than one dichloromethane molecule can coordinate to it.

Despite this reported interaction between metal ions and the chlorine atom lone pairs of the chlorocarbon solvent, ethylene can be assumed to enter the coordination sphere in preference to the solvent. Further ethylene substitution and chloride abstraction would afford the desired bis(ethylene) species.



From the chemistry carried out in chapter 3, the intermediate is believed to be more complex than a simple solvated arene ruthenium moiety, this will be discussed further in section 3.3.

2.4 Reaction studies of the arene ruthenium bis(ethylene) system

Complexes of this system are electron rich and are commonly termed as metal bases. Thus reaction with electrophiles was investigated. The simplest electrophile is a proton, H^+ , so some protonation studies were carried out. However, at room temperature or subambient temperatures (0°C to -30°C), hydride complexes could not be isolated. To overcome this problem, some low temperature protonation experiments were carried out in a nmr tube, and the effect of heat investigated upon any simple protonated species afforded.

The benzene system was the simplest complex to monitor protonation experiments by ^1H nmr, as there

are no substituents of the arene ring which could mask important new signals in the ethyl region. A range of acids were utilised; triflic ($\text{CF}_3\text{SO}_3\text{H}$), which has a relatively non-coordinating counteranion, trifluoroacetic ($\text{CF}_3\text{CO}_2\text{H}$), which has a relatively good coordinating counteranion, and deuterated trifluoroacetic acid ($\text{CF}_3\text{CO}_2\text{D}$), a source of D^+ .

In general the complex being investigated would be in CD_2Cl_2 and the selected acid added when the temperature was 193K to 203K.

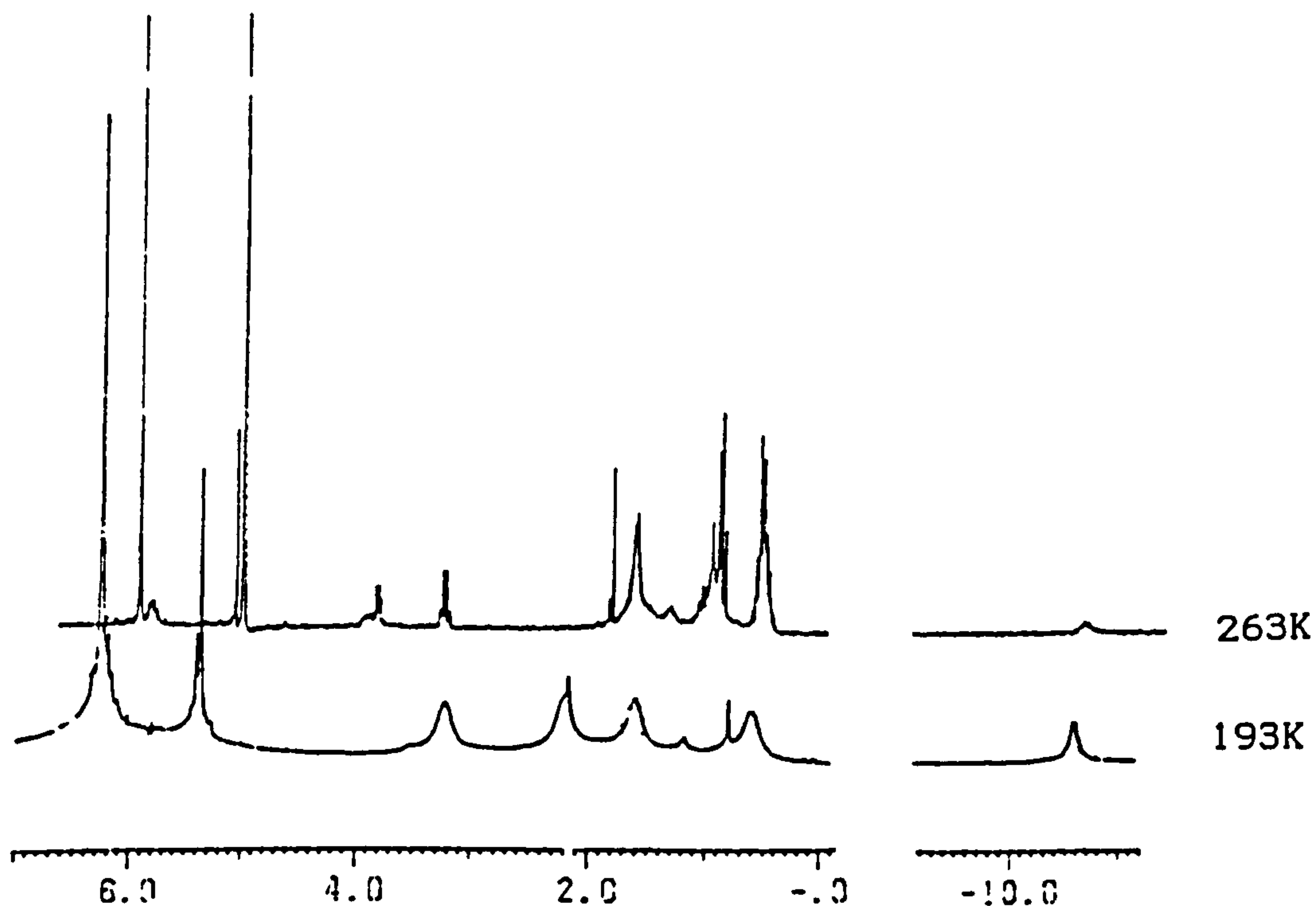
2.4.1 Protonation studies of the arene ruthenium bis(ethylene) system

2.4.1.1 Protonation of $(\text{C}_6\text{H}_6)\text{Ru}(\text{C}_2\text{H}_4)_2$ followed by ^1H nmr spectroscopy

I) Triflic acid

On addition of triflic acid to a solution of benzene ruthenium bis(ethylene), new proton signals assignable to C_6H_6 , C_2H_4 and a metal hydride were observed. On protonation of the ruthenium metal centre, the electron density upon it changes sufficiently to allow rotation of the ethylene ligands. At 193K, the complex was observed towards the low temperature limit of ethylene rotation. Thus the presence of four broad signals, assignable

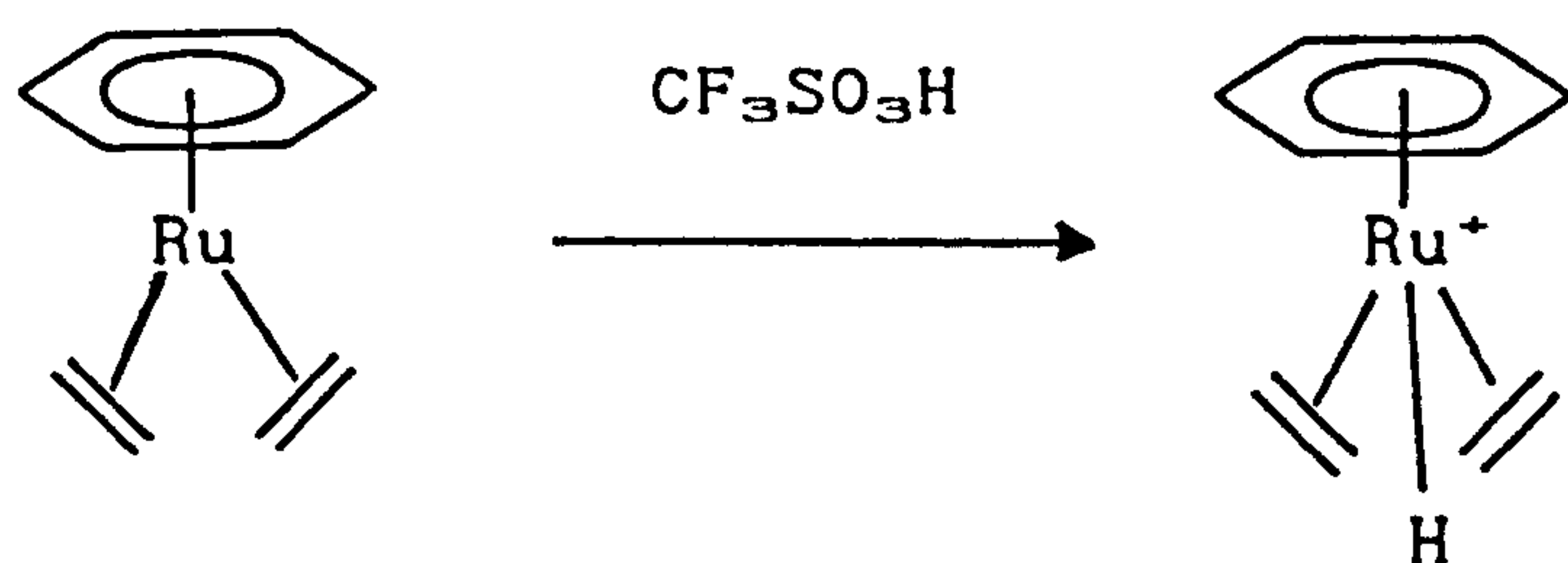
to four hydrogen environments. On protonation of the neutral species the H_a , H_b system becomes split to H_a , H_a' , H_b , H_b' due to the presence of the metal hydride.



Stackplot I. Protonation experiment of $(C_6H_6)Ru(C_2H_4)_2$ with triflic acid exhibiting extremes in ethylene rotation.

When the temperature was raised in 10K jumps, a dynamic process was observed where the ethylene signals coalesced to an ultimate chemical shift position (δ) of 1.95ppm (263K) (Integrals of C_6H_6 : C_2H_4 : H were 6: 7.47: 0.99). However, at higher temperatures, the hydride and ethylene proton signals collapsed although the benzene signal remained unaltered, implying that an exchange

process occurs between the hydride and the hydrogens of the ethylene ligands.

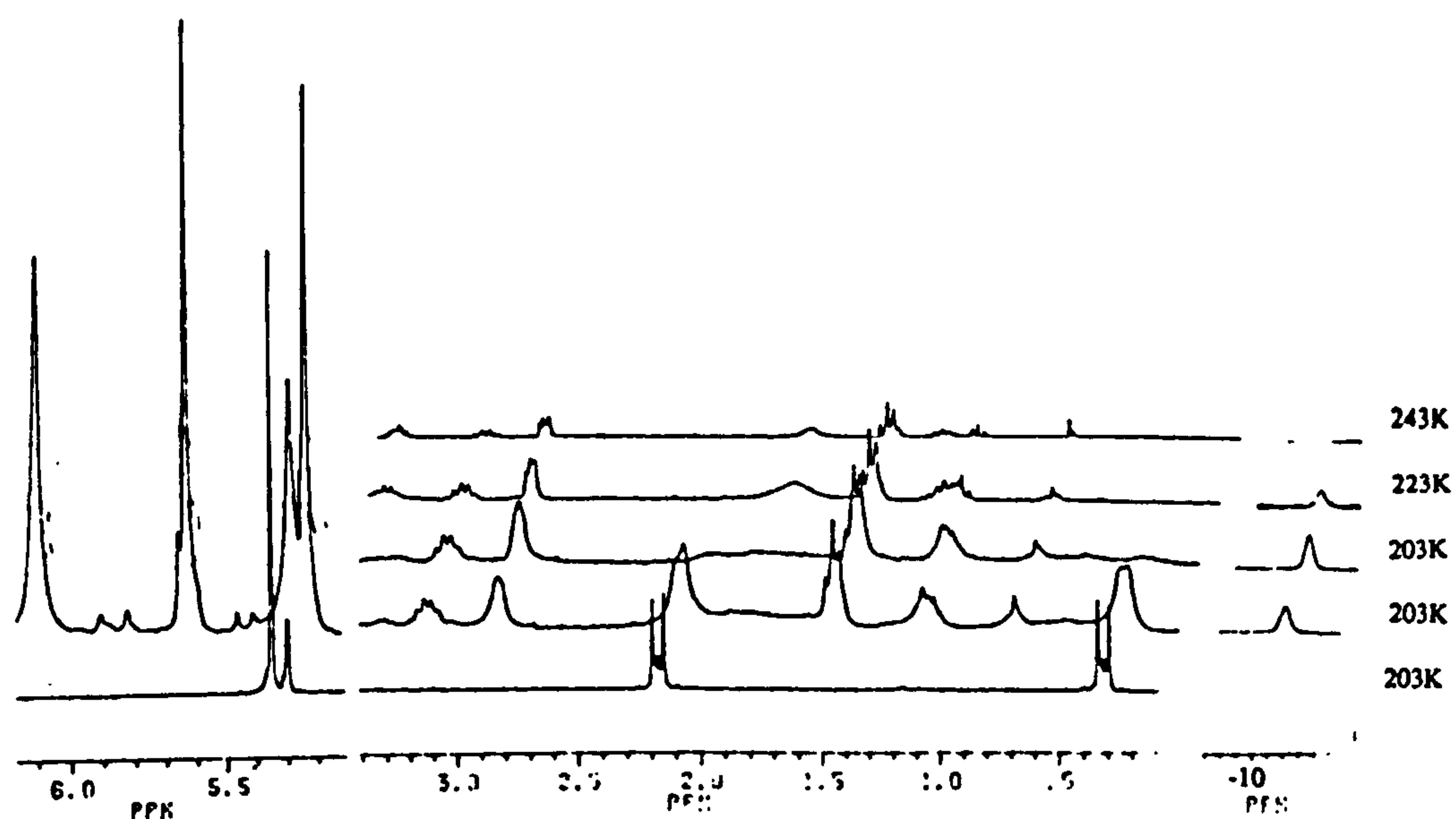


II) Trifluoroacetic acid

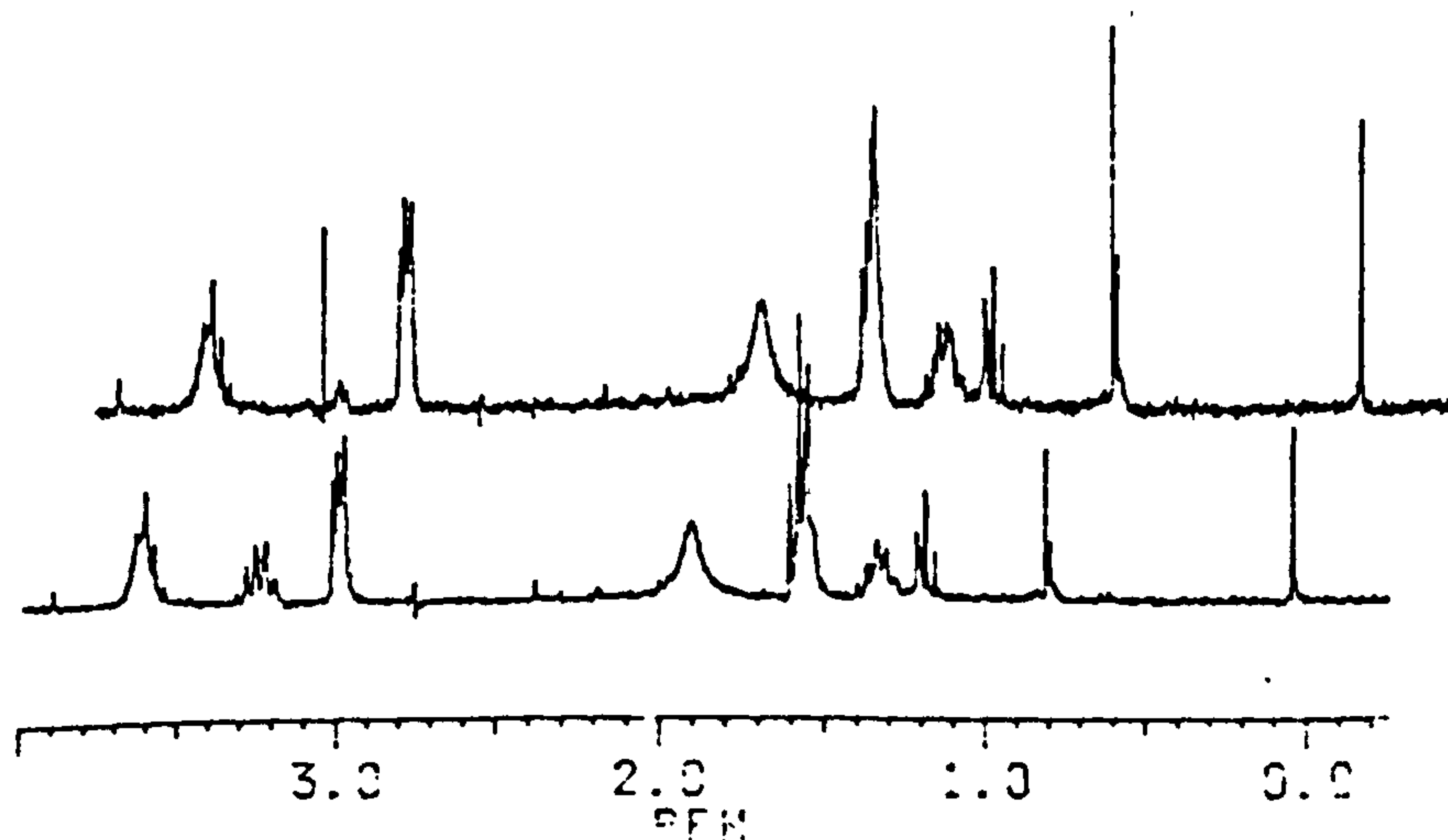
Protonation using trifluoroacetic acid (203K to 243K), initially afforded two new products confirmed by the presence of two new arene signals. With one species having approximately the same chemical shift as that present in the triflic acid protonation experiment, a hydride and some broad signals in the ethyl region, one of the complexes was assigned to be the simple protonated species $(C_6H_6)Ru(H)(C_2H_4)_2^+$.

The remaining signals in the ethyl region were made up of a quartet, a triplet and an unresolved multiplet. Homonuclear decoupling confirmed the relationship between the triplet and the quartet, indicating the presence of an ethyl group, and referring to Cramer's $(cp)RhCl(C_2H_4)(CH_2CH_3)$ complex¹⁰⁶, the unresolved multiplet could be

assigned as a single coordinated ethylene. The second product was confidently assigned as $[(C_6H_6)Ru(O_2CCF_3)(C_2H_4)(CH_2CH_3)]$.



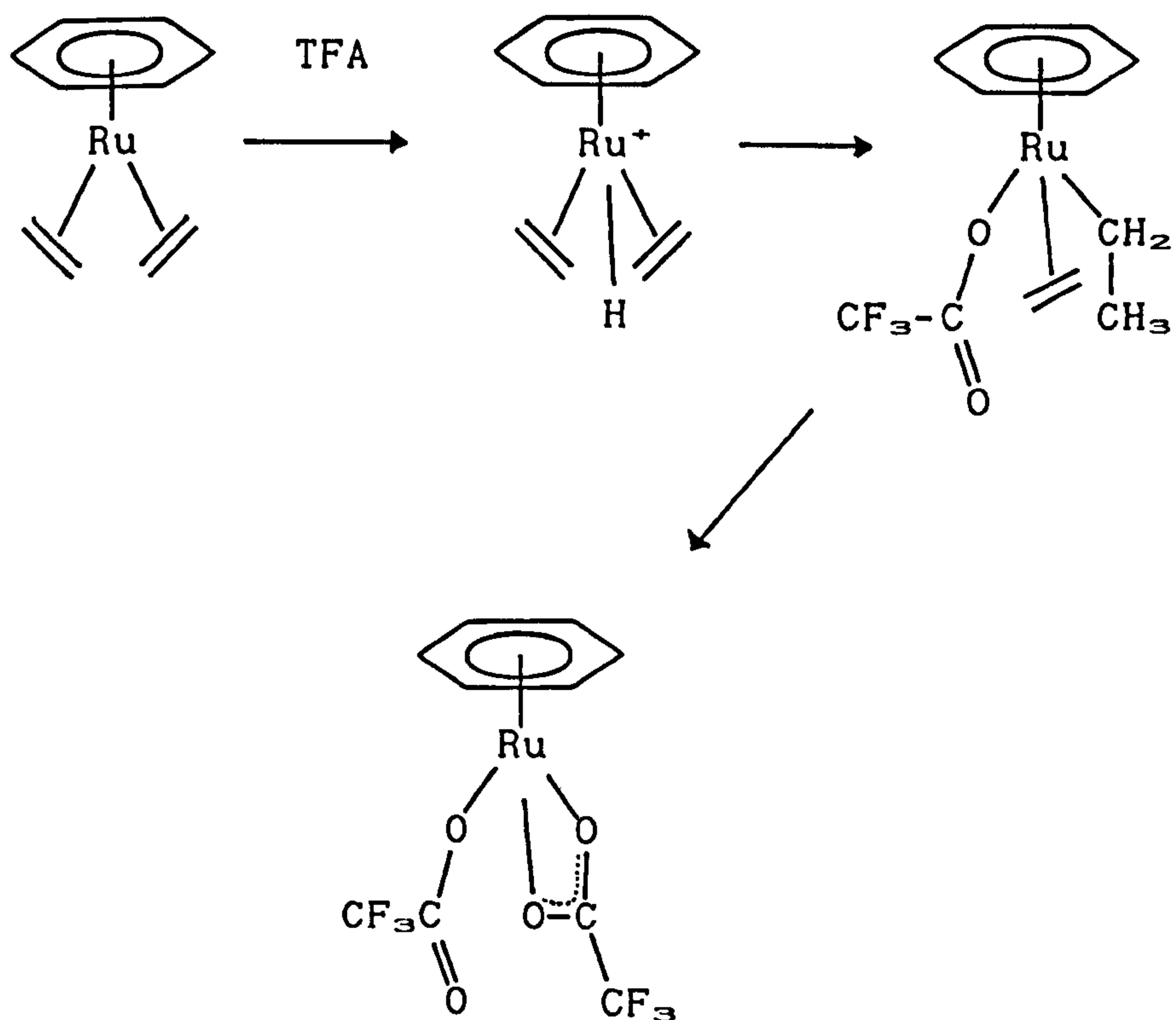
Stackplot II. Protonation experiment of $(C_6H_6)Ru(C_2H_4)_2$ with trifluoroacetic acid over the temperature range 203K to 243K.



Spectra of homonuclear decoupling of quartet at 3.25ppm. (243K)

On bringing the solution to room temperature, a new arene signal grew in, as did free ethylene and ethane signals. The thermodynamically favoured product benzene ruthenium bis(trifluoroacetate) was formed, and characterised utilising infrared and mass spectrometry.

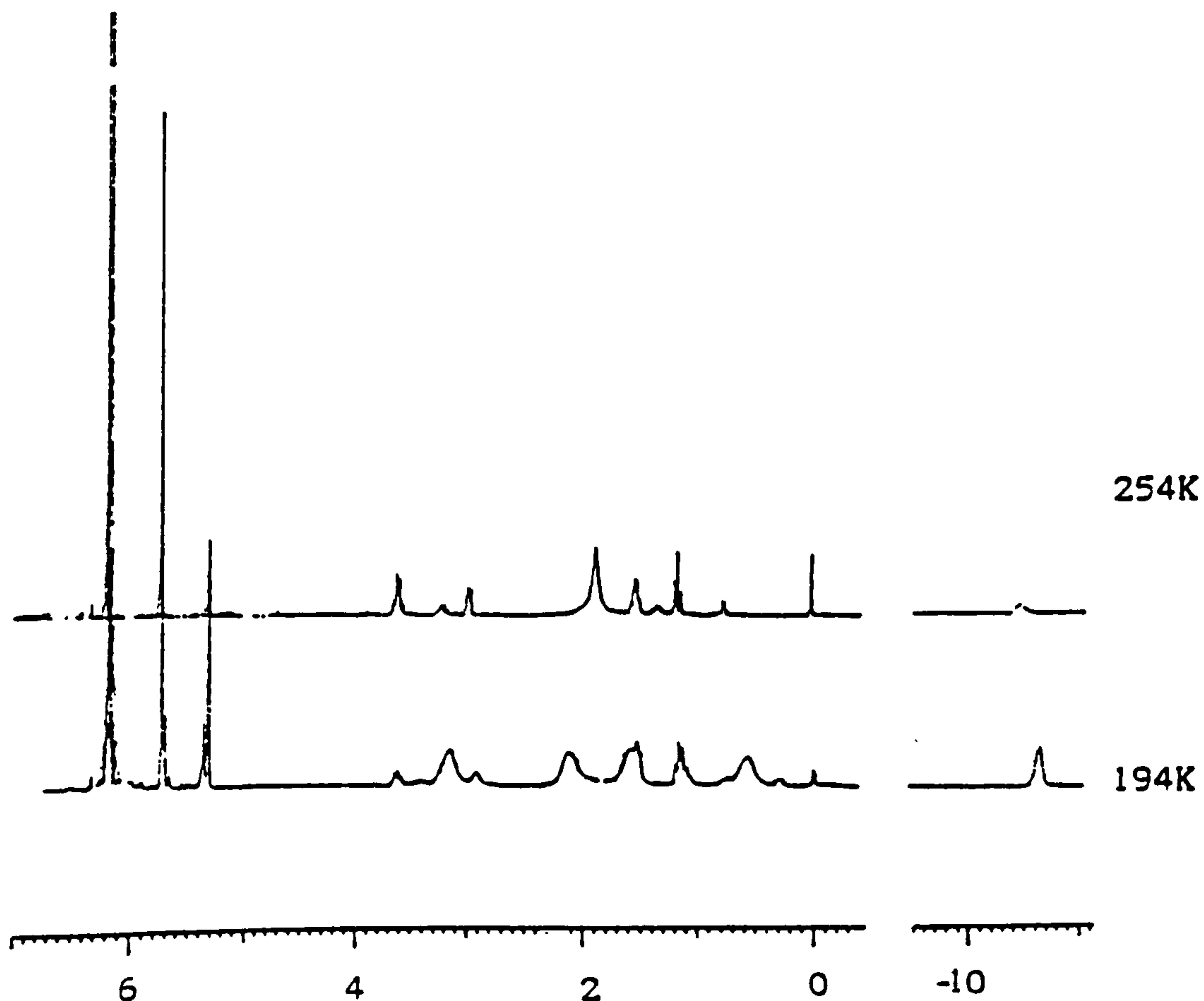
From the complexes characterised in this protonation experiment, a reaction scheme is proposed for a step wise conversion of benzene ruthenium bis(ethylene) to the benzene ruthenium bis(trifluoroacetate) complex using trifluoroacetic acid. The difference in protonation experiments (I) and (II) arises from the relative nucleophilicity of the counteranions, and the stability of the complexes they form.



(III) Deuterated trifluoroacetic acid

Addition of deuterated trifluoroacetic acid to a solution of benzene ruthenium bis(ethylene) at 193K. yields the proton nmr signals obtained from the protonation experiment (II).

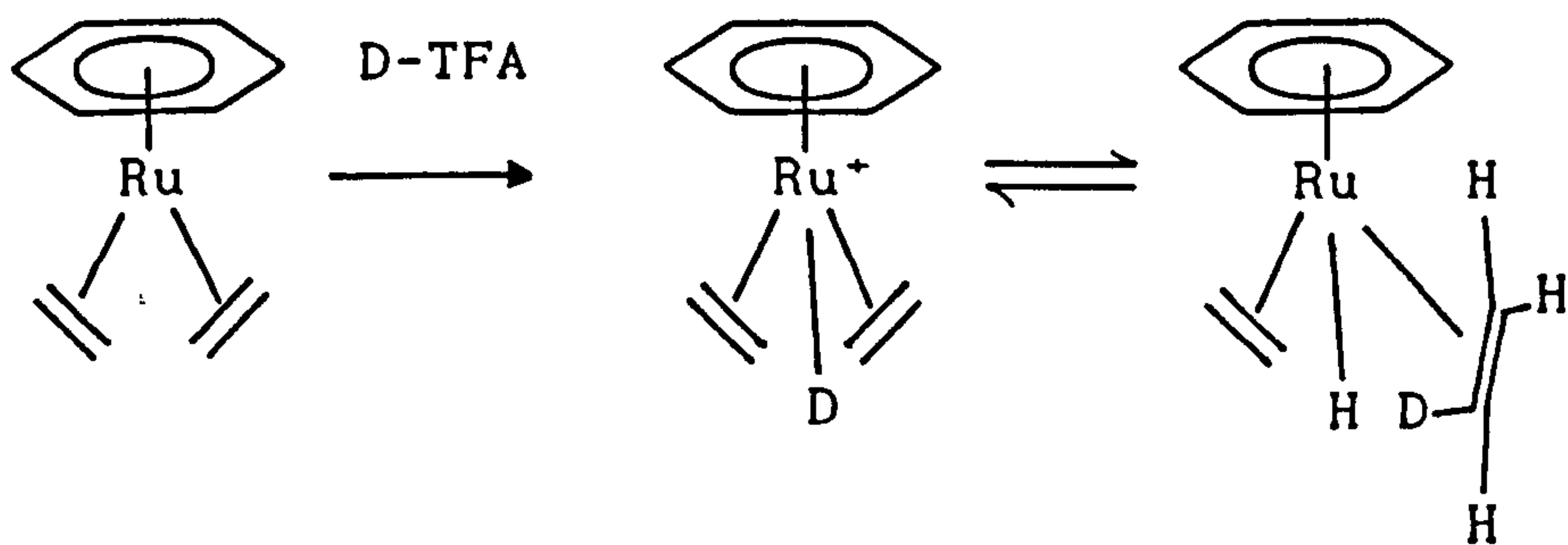
The presence of a metal hydride signal, signifies that an exchange process occurs in the protonated benzene ruthenium bis(ethylene) complex, between the protons of the ethylene ligands and the hydride.



Stackplot III. Protonation experiment of $(C_6H_6)Ru(C_2H_4)_2$ with deuterated trifluoroacetic acid exhibiting extremes of ethylene rotation.

At the low temperature limit, the integrals of C_6H_6 : C_2H_4 : H were 6: 6.7: 0.92. Allowing for accumulative error of the four integrals of the broad ethylene proton absorptions, the make up of this complex was confidently assigned as a system containing eight protons and one deuterium, undergoing continuous exchange about two ethylene and one hydride ligands. Confirmation of this was obtained by following the dynamic process to 253K, where the ethylene proton absorptions coalesced to an ultimate chemical shift position (δ) of 1.95ppm. The integrals of C_6H_6 : C_2H_4 : H at 253K were 6: 7.04: 0.98.

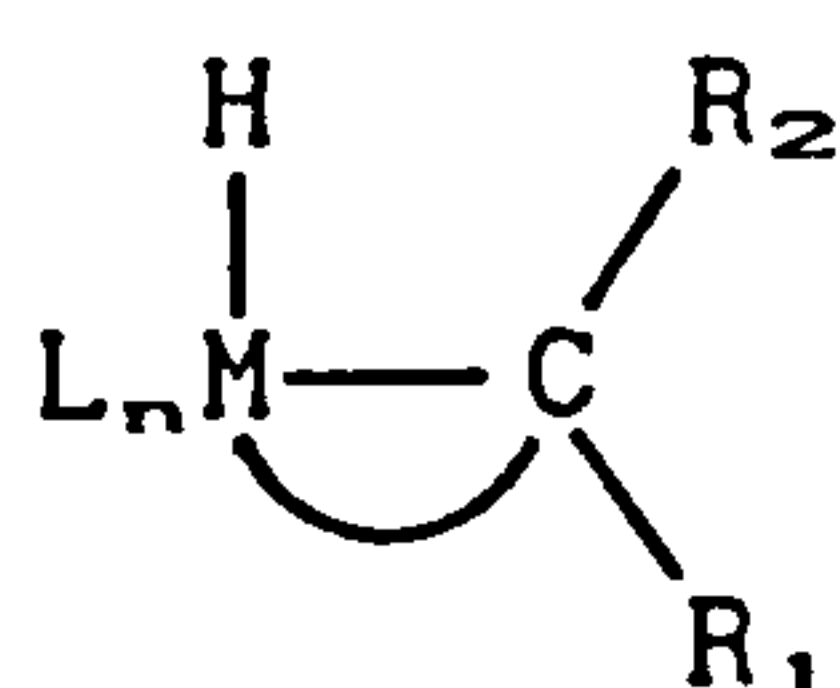
This supports the conclusion of an exchange process occurring between the hydride and the ethylene hydrogens from the protonation experiment I. It can be assumed that this exchange process occurs for the simple protonated species afforded in all the protonation studies.



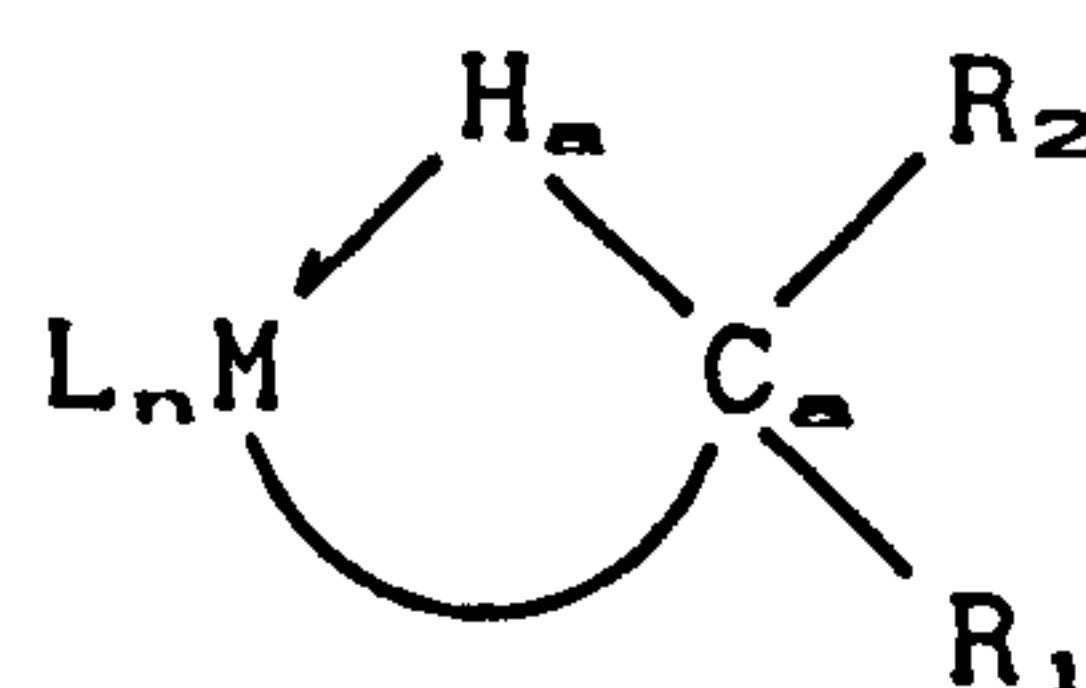
2.4.1.2 Protonation of $(C_6H_6)Ru(C_2H_4)_2$ followed by
 ^{13}C nmr spectroscopy

IV) Triflic acid

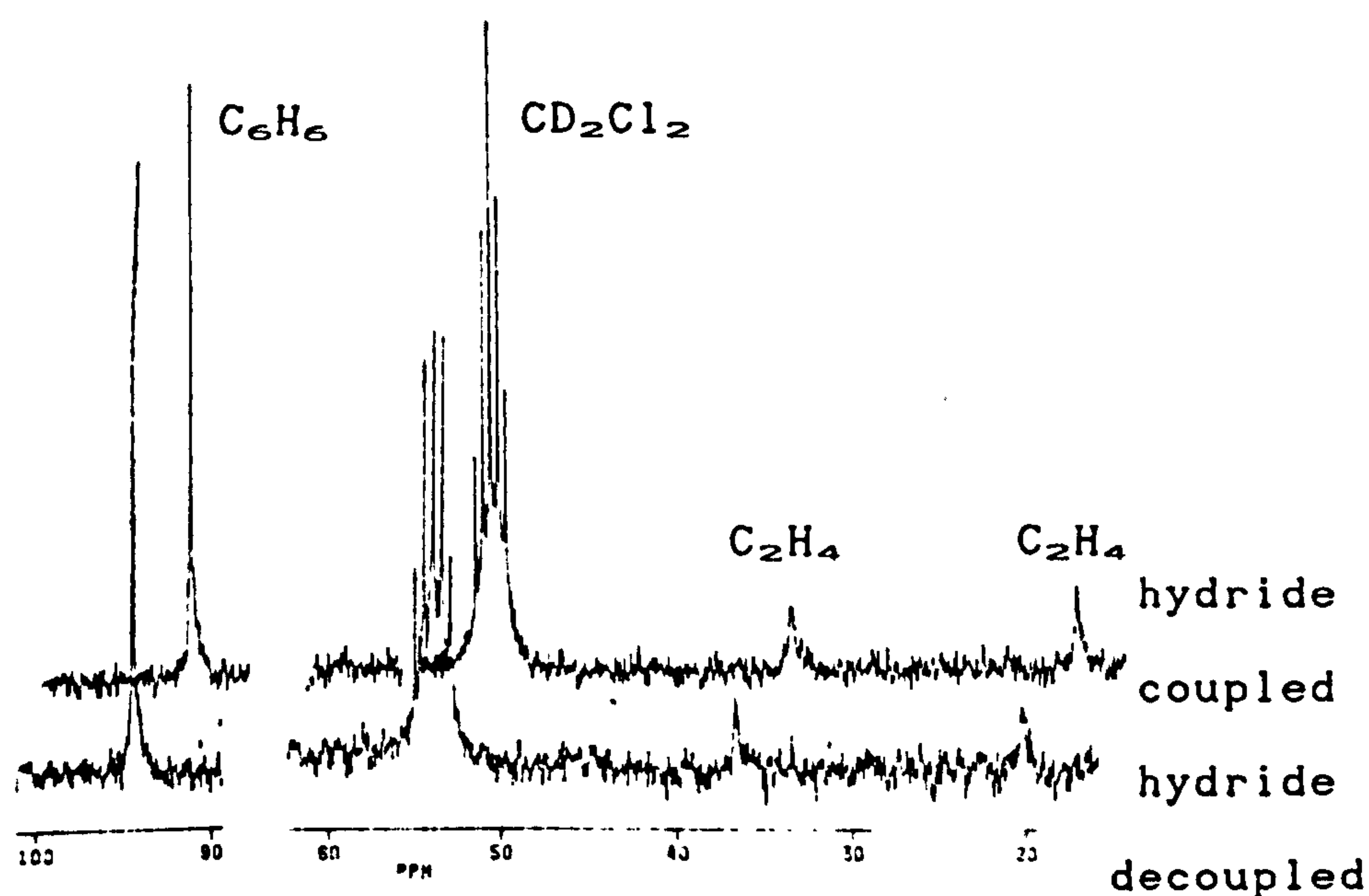
To distinguish whether the protonated species afforded in the above protonation studies was a classical C-M-H alkyl hydride system (A) or had a M-H-C agostic structure (B), the protonation with triflic acid was monitored by ^{13}C nmr.



(A)



(B)



Stackplot IV. Protonation experiment of
 $(C_6H_6)Ru(C_2H_4)_2$ with triflic acid followed by ^{13}C
nmr. (194K)

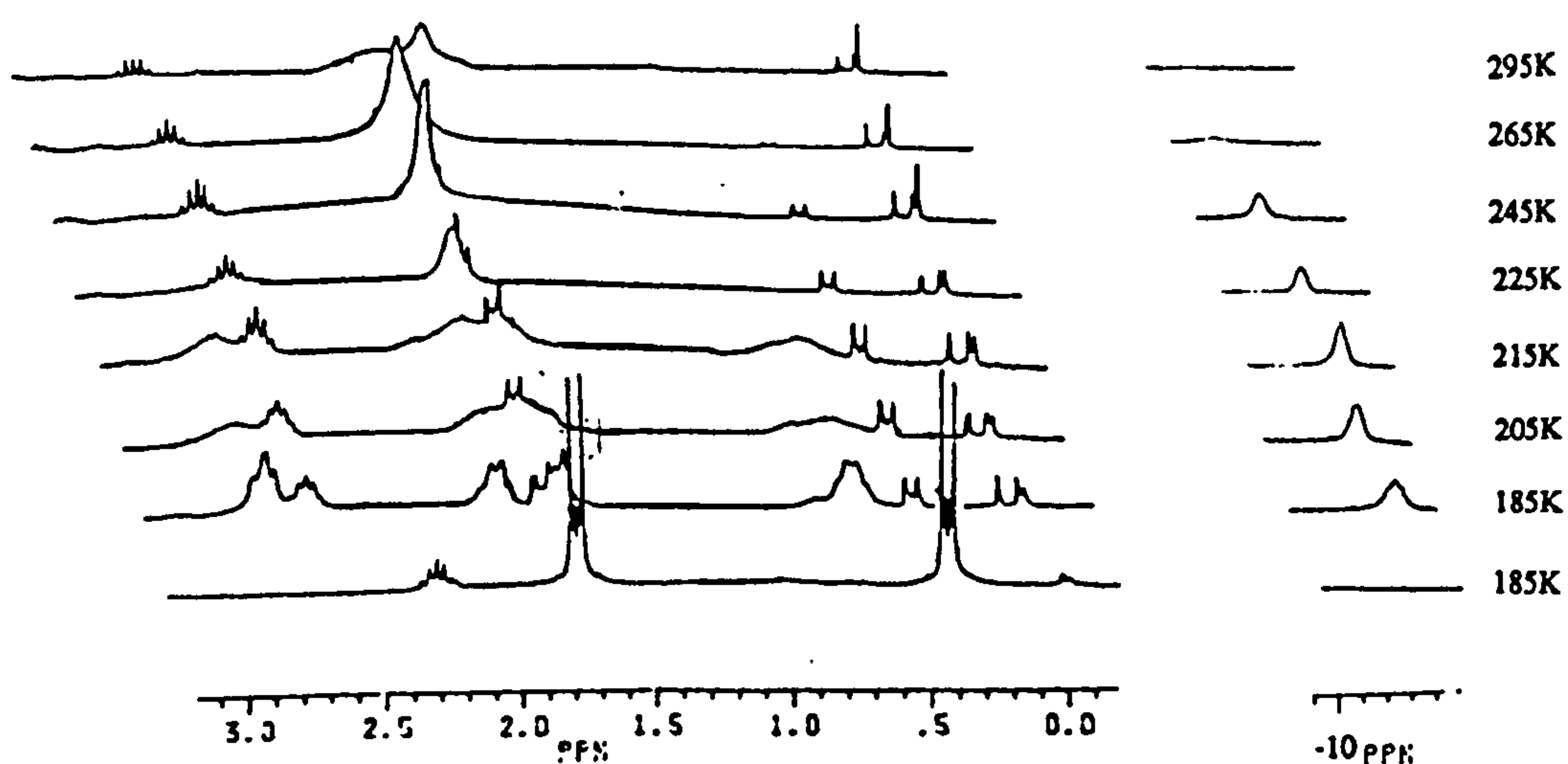
The most characteristic feature of a M-H-C agostic interaction is the value of $J(C_{\alpha}-H_{\alpha})$ due to the reduced $C_{\alpha}-H_{\alpha}$ bond order in the $(3c-2e)$ system and the resultant C-H bond. Typical values for $J(C_{\alpha}-H_{\alpha})$ are in the range of 60-90 Hz.¹⁰⁷ These values are significantly higher than expected for a classical C-M-H alkyl hydride system [$J(C-H) < 10$ Hz] and are thus a reliable indicator of an agostic interaction. Comparison of spectra, showed that the variation in the hydride decoupled and coupled ^{13}C nmr spectra is minimal and thus the coupling $J(C-H)$ is small. This suggested that the $(C_6H_6)Ru(H)(C_2H_4)_2^+$ complex is a classical C-M-H alkyl hydride system. The significance of two ^{13}C signals in the alkyl region of the spectra is due to the non equivalence of the two carbons of the bound ethylene ligand. This is supported by the signal at the chemical shift value 36.67ppm being slightly broader than that of the signal at 20.31ppm. This is explained by the carbon in question being closer in proximity to the hydride, relative to the other and thus broader due to increased coupling. On raising the temperature in 10K steps the two carbon signals assigned to the ethylene ligand coalesced at 264K to a chemical shift position of 26.0ppm.

2.4.1.3 Protonation of $(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{Ru}(\text{C}_2\text{H}_4)_2$

followed by ^1H nmr spectroscopy

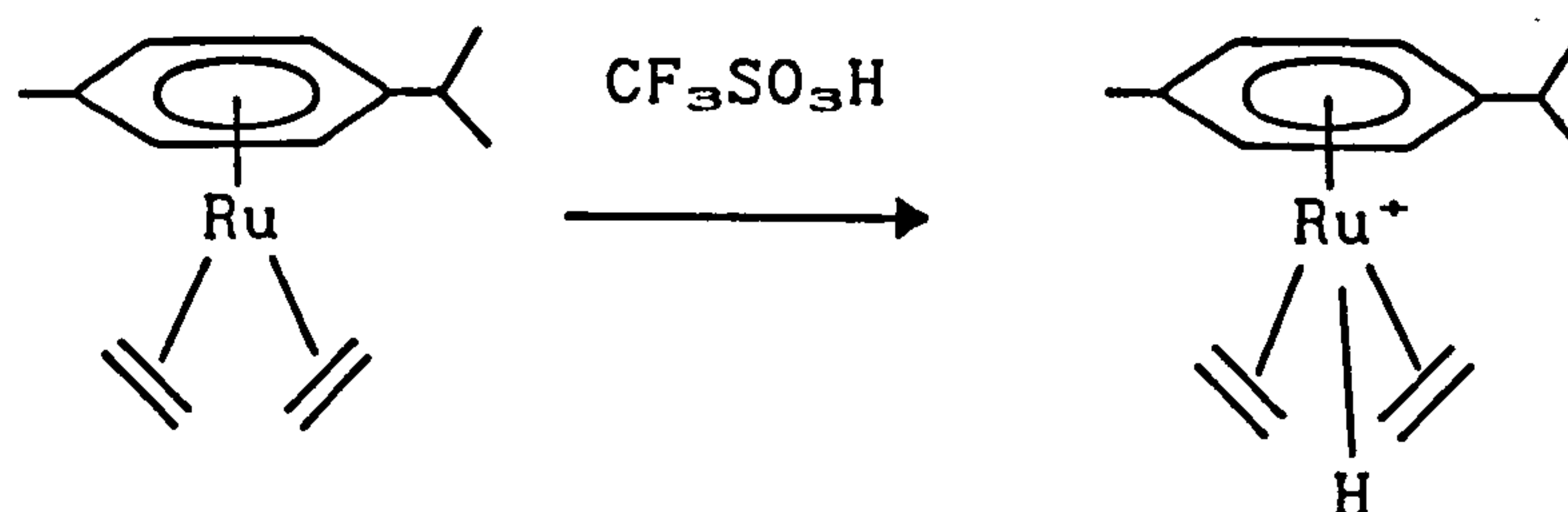
V) Triflic acid

Similar results were obtained for the protonation experiment of $(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{Ru}(\text{C}_2\text{H}_4)_2$ with triflic acid, to the benzene analogue. At 185K the protonated species, $(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{Ru}(\text{H})(\text{C}_2\text{H}_4)_2^+$, was observed towards the low temperature limit of ethylene rotation. Thus the presence of four broad signals, assignable to the four hydrogen environments of the ethylene ligands, were visible at this temperature. (The arene methyl and doublet have been removed for clarity)



Stackplot V. Protonation experiment of $(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{Ru}(\text{C}_2\text{H}_4)_2$ with triflic acid over the temperature range 185K to 295K.

As with the benzene analogue, when the temperature was raised in 10K steps, a dynamic process was observed with the coalescence of the ethylene signals to a single peak. ($\delta = 1.89\text{ppm}$, 265K). Also, as above, at higher temperatures the exchange process between the hydride and ethylene hydrogens was observed.

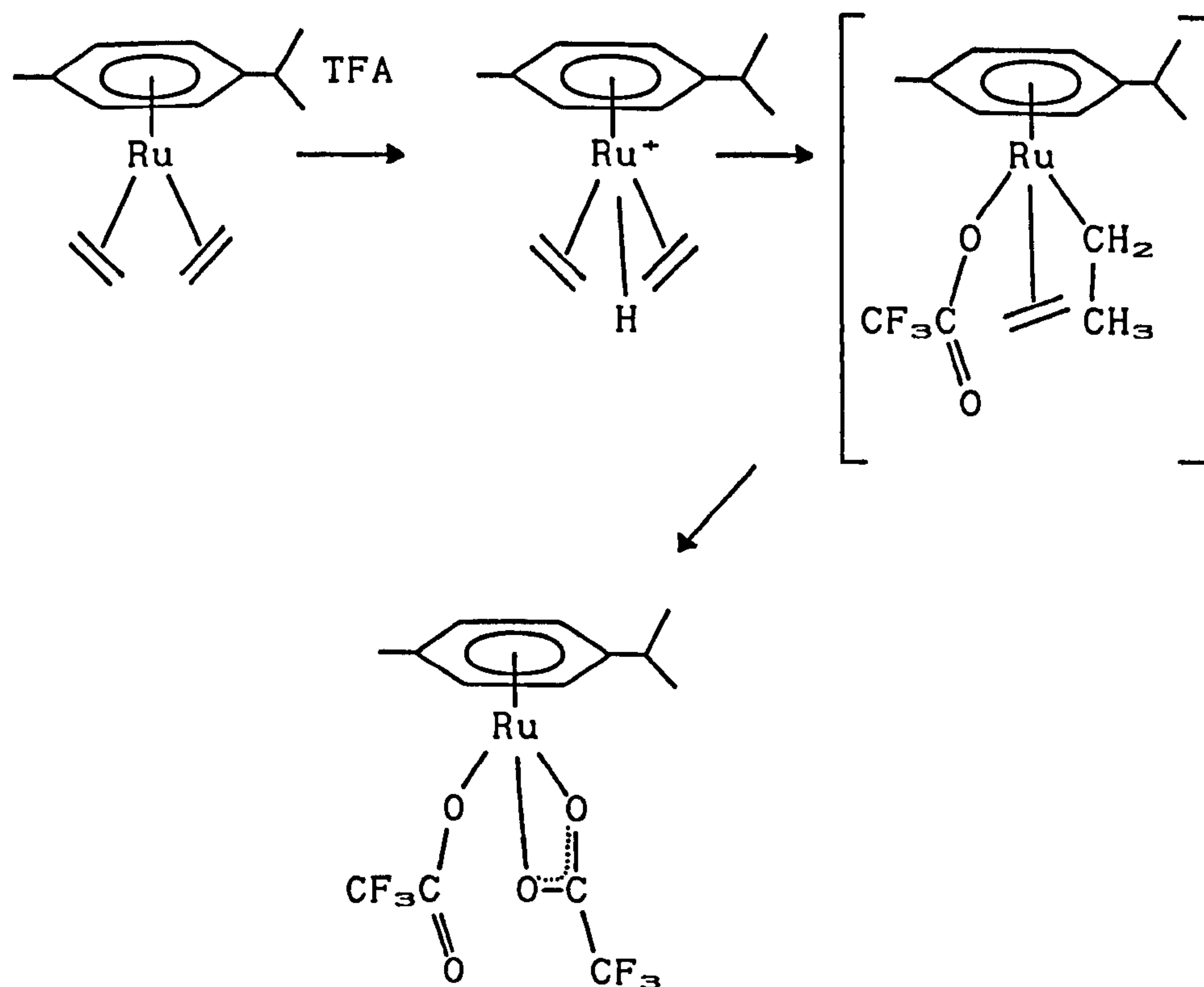


The temperature at which coalescence of the ethylene multiplets occurred for the protonated benzene and cymene ruthenium bis(ethylene) species could be expected to vary due to the different substituents on the arene ligand. However, in the protonation experiments carried out, no marked difference was observed. The coalescence temperature was determined by means of integration and evaluated to be approximately 265K in both cases.

VI) Trifluoroacetic acid

The protonation study with trifluoroacetic acid was also investigated, affording the simple

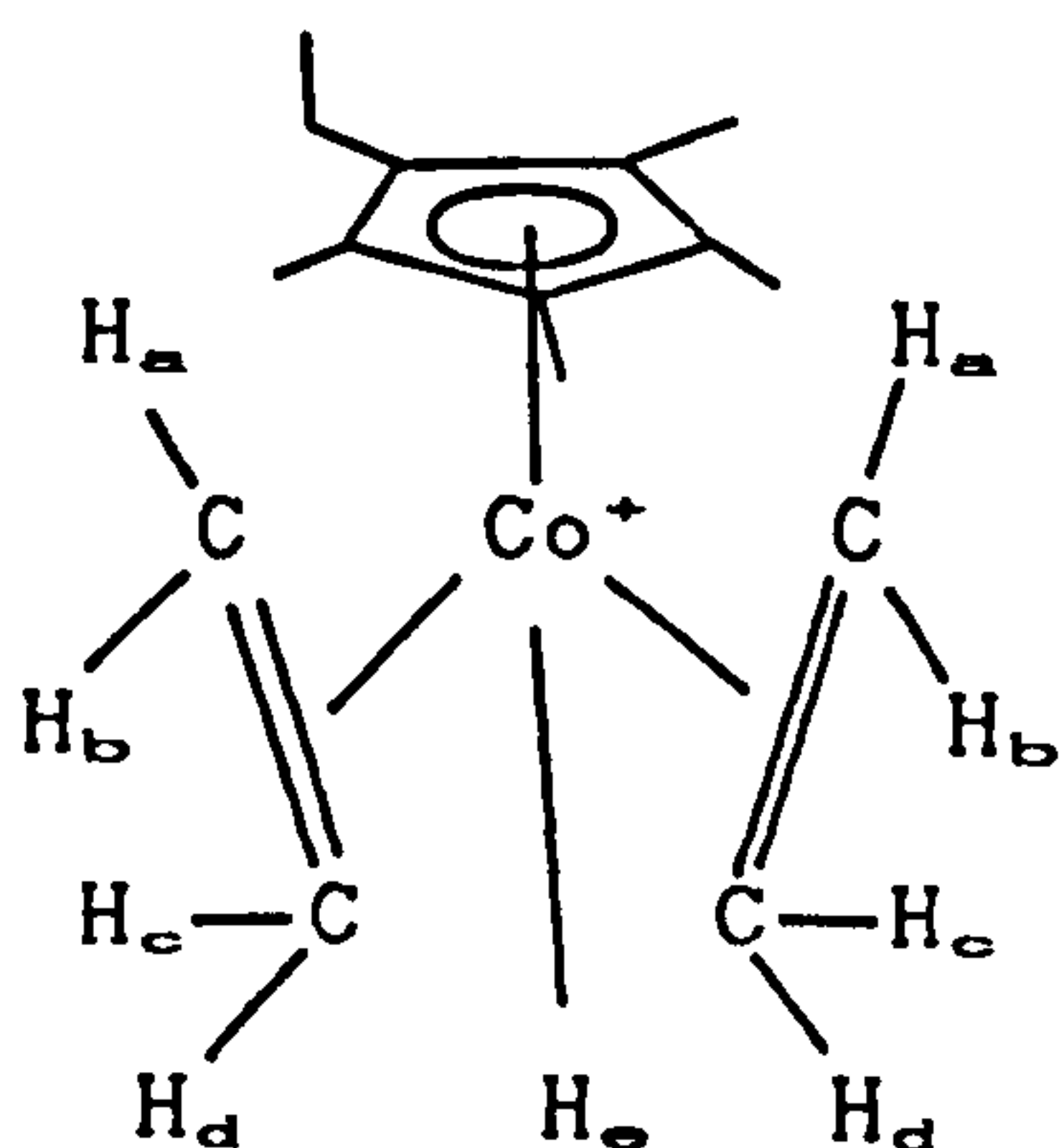
protonated species $(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{Ru}(\text{H})(\text{C}_2\text{H}_4)_2^+$ (assigned by straight comparison with the triflic protonation experimental data - see experimental section). On warming to room temperature, the thermodynamically favoured product, $(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{Ru}(\text{O}_2\text{CCF}_3)_2$, was afforded. However, the substituents of the arene masked the ethyl region and so confirmation of analogous intermediates of the benzene protonation could not be obtained. It is highly likely that the same sequential ethylene displacement reaction occurred.



2.4.2 Related experiments

The analogous metal bases, (cyclicaromatic) $M(C_2H_4)_2$ ($M = Co, Rh, Ir$), have been extensively investigated and a number of protonation studies reported.

The bis(ethylene) derivative $(C_5Me_4Et)Co(C_2H_4)_2$ can be protonated by tetrafluoroboric acid forming a cation $[(C_5Me_4Et)Co(C_4H_9)]^+$. On the basis of variable temperature 1H nmr studies, it was proposed that at low temperatures ($-85^\circ C$) the spectrum was most consistent with the bis(ethylene)-hydride structure (A);¹⁰⁸



(A)

However, unusual features were noted in the 1H nmr spectrum of the presumed bis(ethylene)-hydride cation.

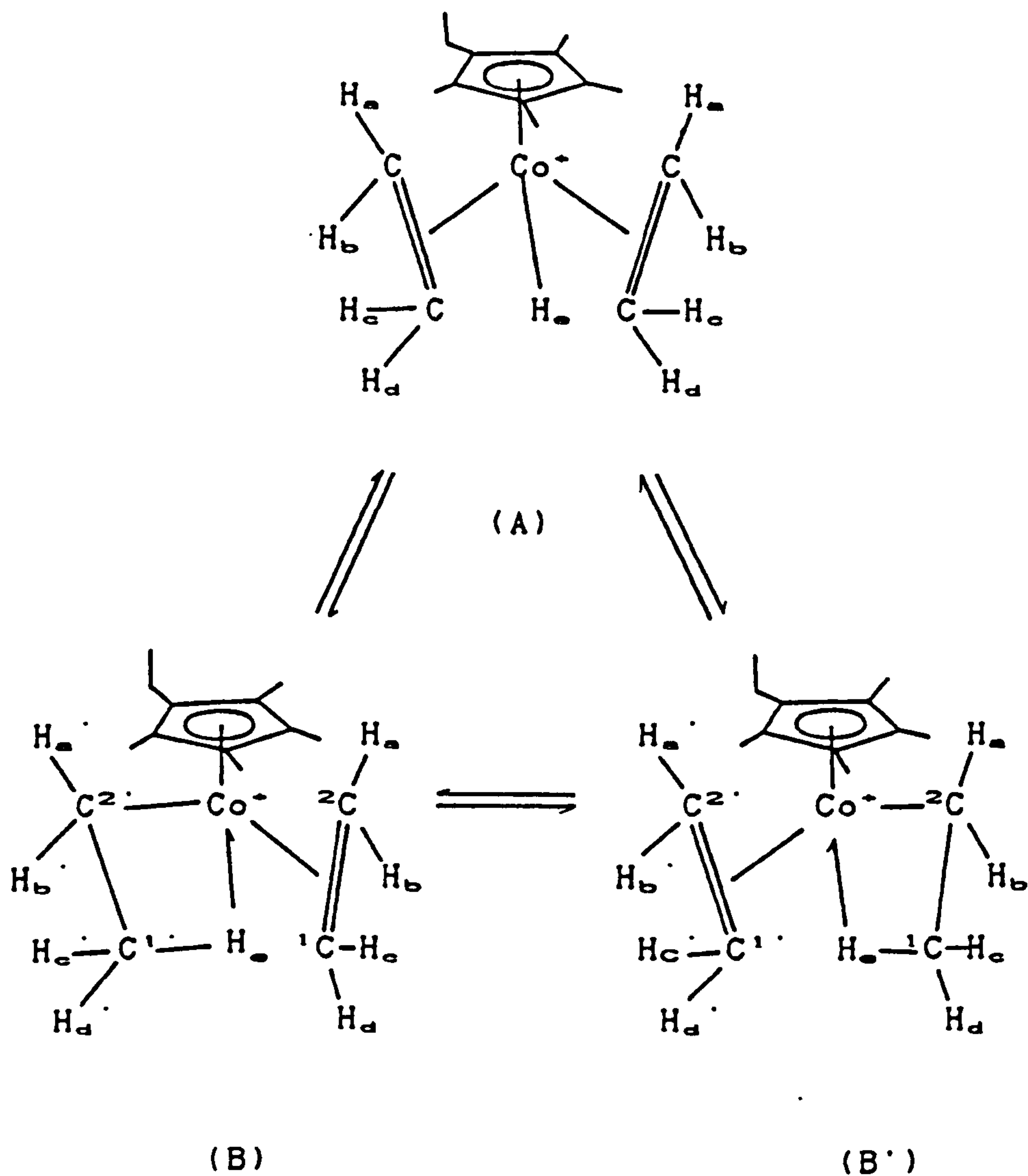
i) Substantial coupling (9.3Hz) between the $Co-H_e$ and H_c , H_d but no coupling between $Co-H_e$ and

H_a and H_b .

ii) Appearance of H_a and H_b as symmetrical triplets, implying the cis olefinic couplings J_{ac} and J_{bd} were approximately equal in magnitude to the trans olefinic couplings J_{ad} and J_{bc} .

iii) Remarkable high field shifts for the olefinic hydrogens H_a (1.48ppm) and H_b (0.46ppm).

An alternative interpretation of the spectrum incorporates a C-H \rightarrow Co bond: the new structure proposed is shown below as (B).¹⁰⁹



The observed ^1H nmr spectrum at -85°C requires a rapid degenerate equilibrium between (B) and (B') via transfer of the bridging H_a from one ethylene unit to the other. The transfer may be via the bis(ethylene)-hydride species denoted as (A) or possibly by direct exchange.

The unusual spectral features mentioned above are explained completely by the agostic structure (B).

i) Substantial coupling (up to 22Hz) between bridged hydrogens and the hydrogens attached to the bridged carbon has been previously verified.

ii) The H_a and H_b resonances would be expected at high field positions based on similar agostic systems.

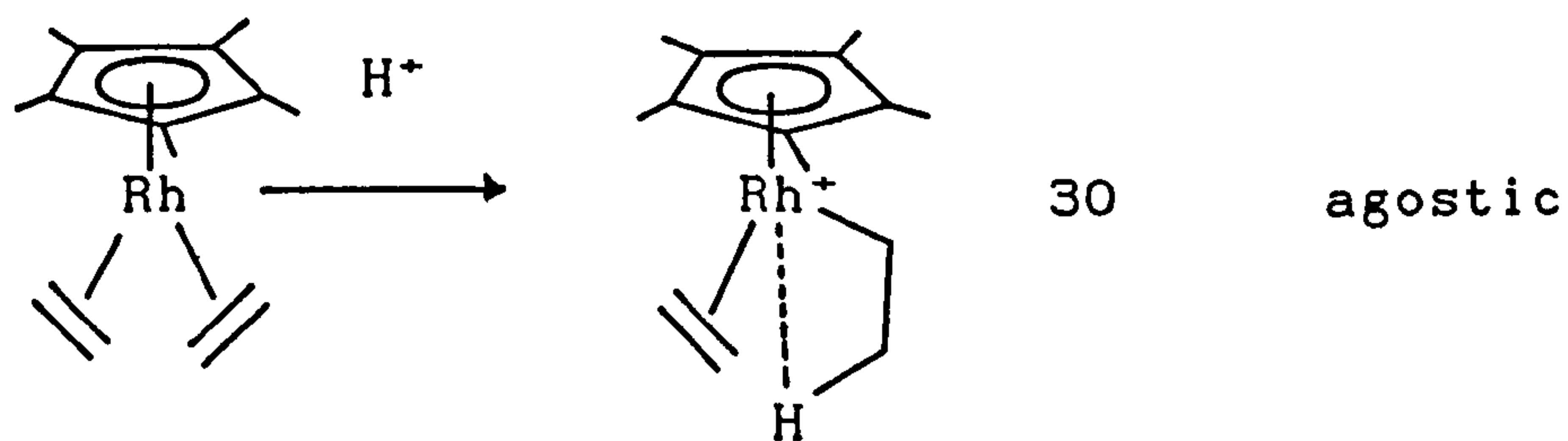
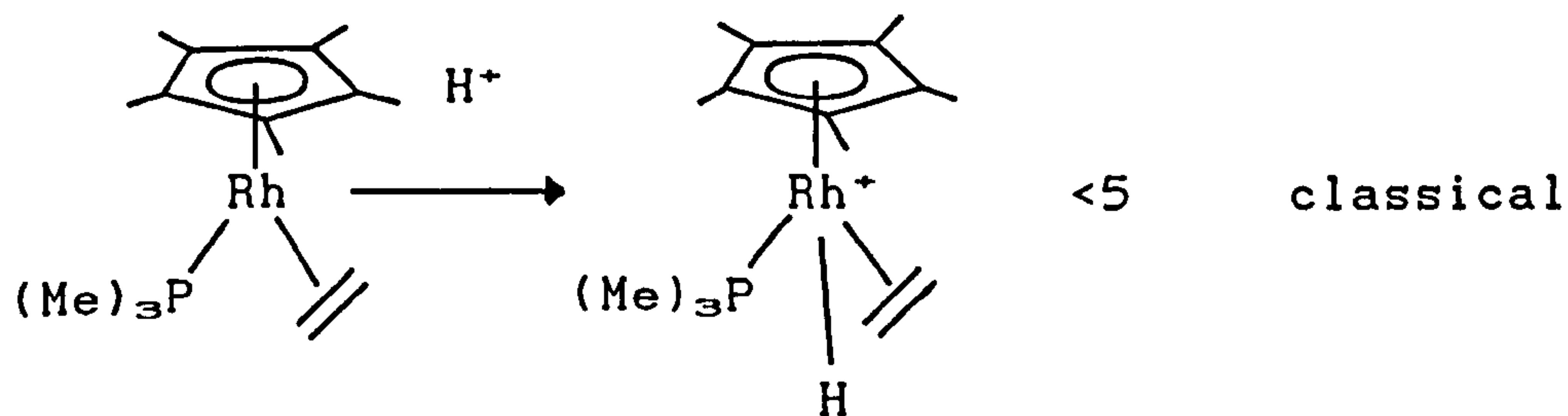
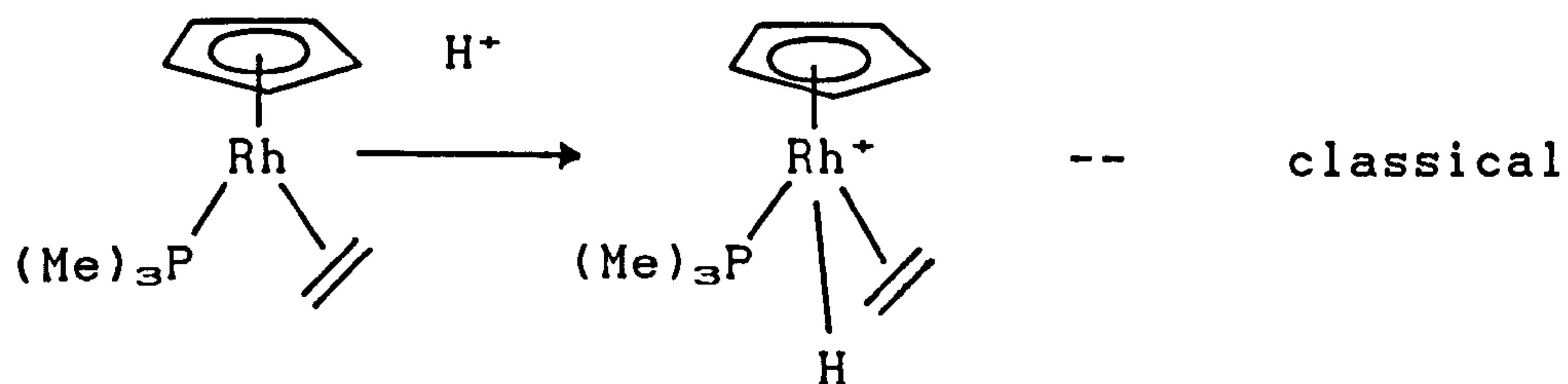
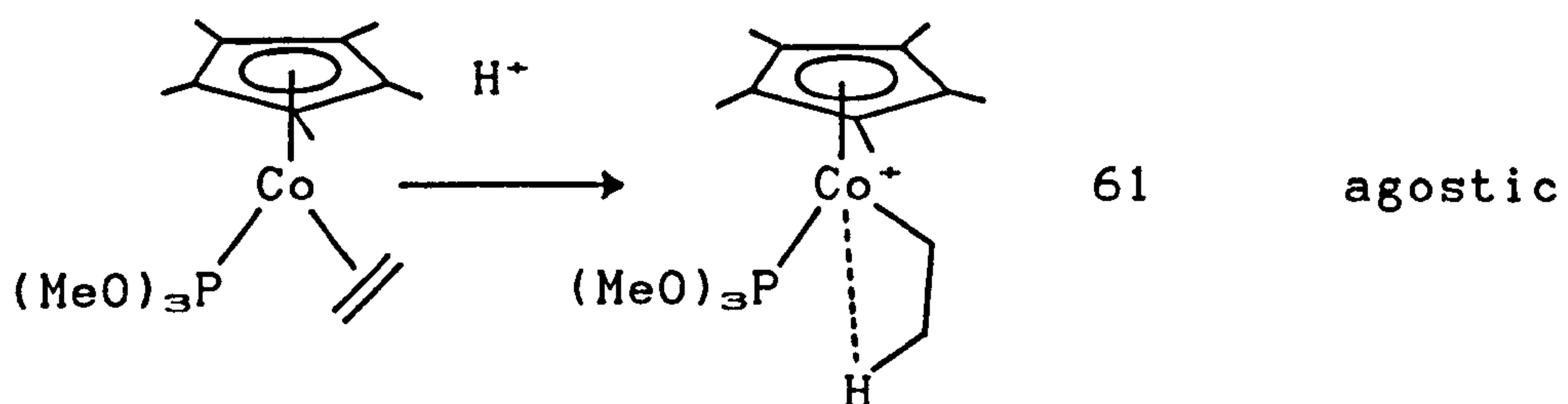
iii) The near equivalence of J_{bd} with J_{be} and J_{ac} with J_{ad} represents an averaged coupling involving one ethylene unit and one agostic ethyl moiety.

Also the high field shift of the hydrogen H_a (-12.1ppm) is in the region expected for bridged hydrogens.¹⁰⁹

Recently, Brookhart¹¹⁰ has investigated the cobalt and rhodium bis(ethylene) and ethylene phosphite / phosphine simple protonated species to determine which have agostic structures. His findings are tabulated in table 2.4.1

Table 2.4.1 Brookhart's determinations of agostic or classical structures of simple protonated ethylene complexes

Protonation experiment	J_{CH}/Hz	agostic/ classical
------------------------	--------------------	-----------------------



M.L.H. Green has also determined that the complex $[(\text{cp}^*)\text{Fe}(\text{PMe}_3)(\text{C}_2\text{H}_4)\text{H}]$ is a classical system and not agostic.¹¹¹

All these findings can be rationalised in terms of π -bonding of the ethylene and metal centre.

A good example of the effect of altering the electron density at the metal centre is the $[(\text{cp}^*)\text{Rh}(\text{PMe}_3)(\text{C}_2\text{H}_4)]$ complex. On protonation the complex forms a classical C-M-H system, whereas the bis(ethylene) derivative forms an agostic structure. The PMe_3 ligand is a better donor than an ethylene and pushes electron density onto the rhodium metal centre, allowing the rhodium ethylene π -bond to become stronger and not take part in an agostic interaction.

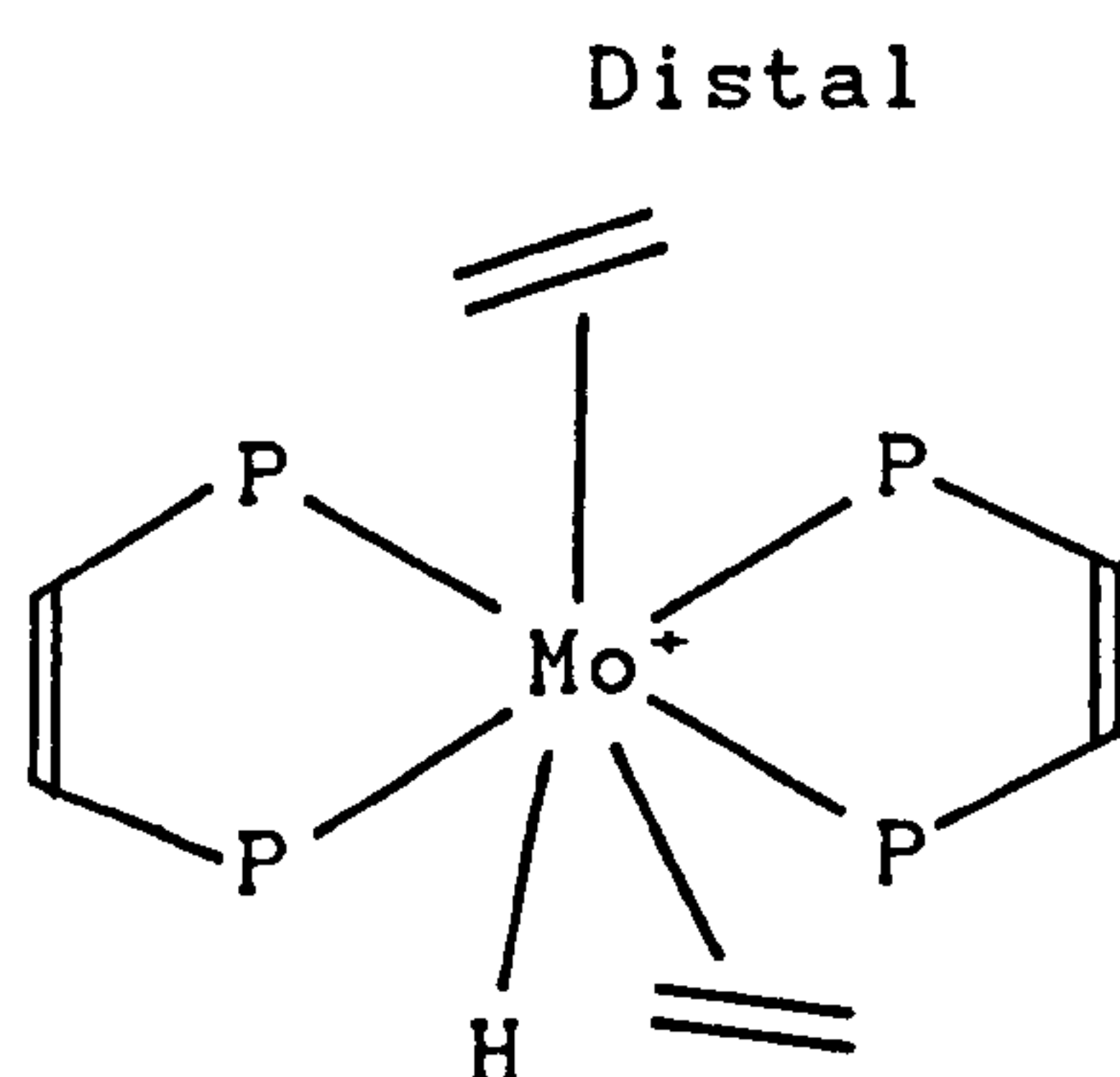
In terms of electron density, the arene ruthenium bis(ethylene) complexes are more analogous to the $[(\text{cp}^*)\text{Rh}(\text{PMe}_3)(\text{C}_2\text{H}_4)]$ complex than the $[(\text{cp}^*)\text{Rh}(\text{C}_2\text{H}_4)_2]$ complex. This supports the evidence from the protonation experiment IV, where the findings suggested a classical C-M-H alkyl hydride system, when $[(\text{C}_6\text{H}_6)\text{Ru}(\text{C}_2\text{H}_4)_2]$ was protonated.

From the simple protonation experiments of the arene ruthenium bis(ethylene) system, it has been shown that ethylene hydride scrambling occurs. The mechanism of this process can not be deduced using this simple system. However, M.L.H. Green and

Luet-Lok Wong have recently investigated the mechanism of hydrogen scrambling in ethylene-hydride complexes,¹¹² along with an earlier proposal by Osborn¹¹³. Their findings can be applied to the more simple bis(ethylene) system.

In 1977, Osborn and coworkers reported the crystal structure determination and dynamic nmr studies of the molybdenum bis(ethylene)-hydride complex $[\text{Mo}(\text{dppen})_2(\text{C}_2\text{H}_4)_2\text{H}]\text{CF}_3\text{CO}_2$ (C) (dppen = *cis* $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$). They proposed the mechanism of hydrogen scrambling involved coupled pseudorotation to include end to end exchange of the ethylene ligand. (see Fig. 2.4.2.1)

The 62.89 MHz gated decoupled ^{13}C nmr spectrum of (C) at 173K showed four triplets for the ethylene carbons, thus conclusively establishing the compound as an ethylene-hydride.



(C)

In the variable temperature ^1H nmr spectrum of (C), the ethylene-hydride exchange process is the first to be frozen-out on the nmr time scale (slow exchange at $T < \text{ca. } 233\text{K}$, $\Delta G^\ddagger = 44 \pm 1 \text{ kJ mol}^{-1}$) and the hydride exchanges exclusively with the proximal ethylene. The spectra at $T < 233\text{K}$ show that

the proximal ethylene undergoes end to end exchange ($\Delta G^\ddagger = 38.1 \text{ kJ mol}^{-1}$). M.L.H. Green modified Osborn's proposed coupled pseudorotation mechanism (Fig. 2.4.2.1). to include net end to end exchange of the distal ethylene by changing its sense of rotation with respect to the coupled rotation of the proximal ethylene and hydride ligands from conrotatory (Fig. 2.4.2.1.c) to disrotatory (Fig. 2.4.2.1.d).

Another modification he proposed was the stringent requirement of simultaneous and coupled rotation of the ethylene ligands by 90° to be unnecessary. Their dynamic behaviour after proximal ethylene-hydride exchange has been frozen out can be rationalised more simply by rapid rotation of the ethylene ligands about the metal ethylene centroid axes.

Since ethylene-hydride exchange is fast at 298K, the observation of exclusive exchange of mutually cis phosphorus nuclei in (C) (determined by $^{31}\text{P}\{-^1\text{H}\}$ nmr) has significant implications on the mechanism of the ethylene-hydride exchange process. This process is expected to proceed via reversible ethylene insertion into the molybdenum-hydride bond and thus the initial formation of an unobserved agostic η^2 -ethyl intermediate. It is normally proposed that the agostic hydrogen in this η^2 -ethyl intermediate then

dissociates to form an unobserved

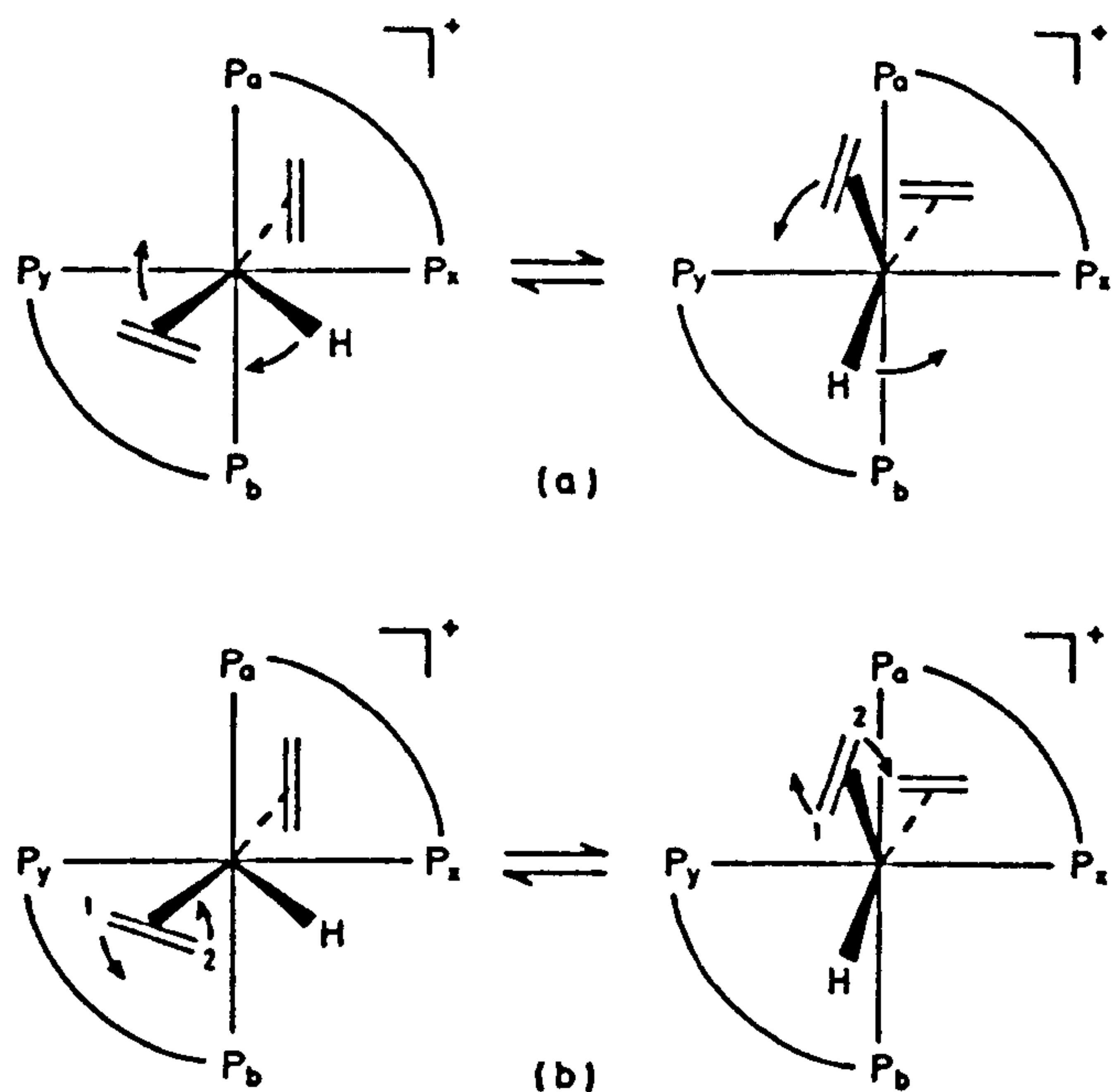


Figure 2.4.2.1. The pseudorotation mechanism proposed by Osborn for the dynamic processes in (C). For clarity the rotation processes are shown separately, the mechanism is a combination of processes in (a), (b), and (c). The process shown in (d) is the modified version of the proposed mechanism. The arrows donate the direction of the 90° rotations. (a) Coupled rotation of the proximal ethylene and the hydride ligands giving rise to scrambling of the cis phosphorus nuclei only. (b) Rotation of the proximal ethylene about the metal-ethylene-centroid axis. This rotation is disrotatory with respect to the process shown in (a) and results in end-to-end rotation of the ethylene ligand.

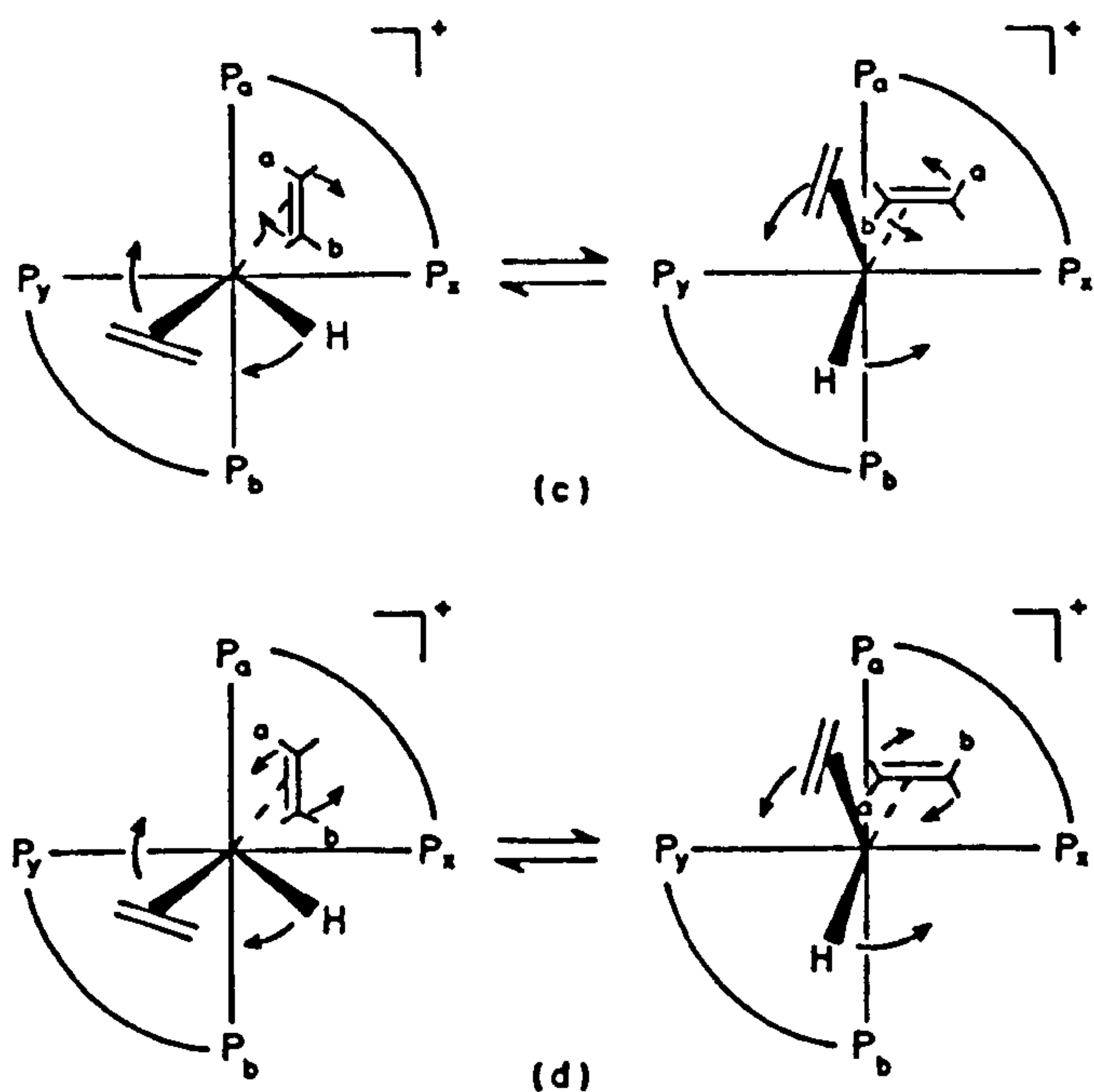


Figure 2.4.2.1. cont. (c) Conrotatory motion of the distal ethylene with respect to the coupled rotation shown in (a), does not result in end-to-end exchange. (d) Disrotatory motion of the distal ethylene which may account for the observed end-to-end exchange.

16 electron σ -ethyl intermediate. Rotation about the $C_\alpha-C_\beta$ bond followed by β -elimination would lead to the observed ethylene-hydride exchange. However, if this mechanism is operating in (C), random exchange of the phosphorus nuclei at the fast exchange limit will result unless there is restricted rotation about the Mo- C_α bond. This is unlikely because the ethylene ligands, which are sterically more demanding than a σ -ethyl group, in

the precursor to (C), $[\text{trans-Mo(dppen)}_2(\text{C}_2\text{H}_4)_2]$, are observed to undergo free rotation.¹¹⁴ These arguments suggest that the 18 electron agostic ethyl intermediate occurs "in-plane" without dissociation of the agostic hydrogen and thus the proposal of a new mechanism of hydrogen scrambling in ethylene-hydride complexes is put forward. (Fig. 2.4.2.2)

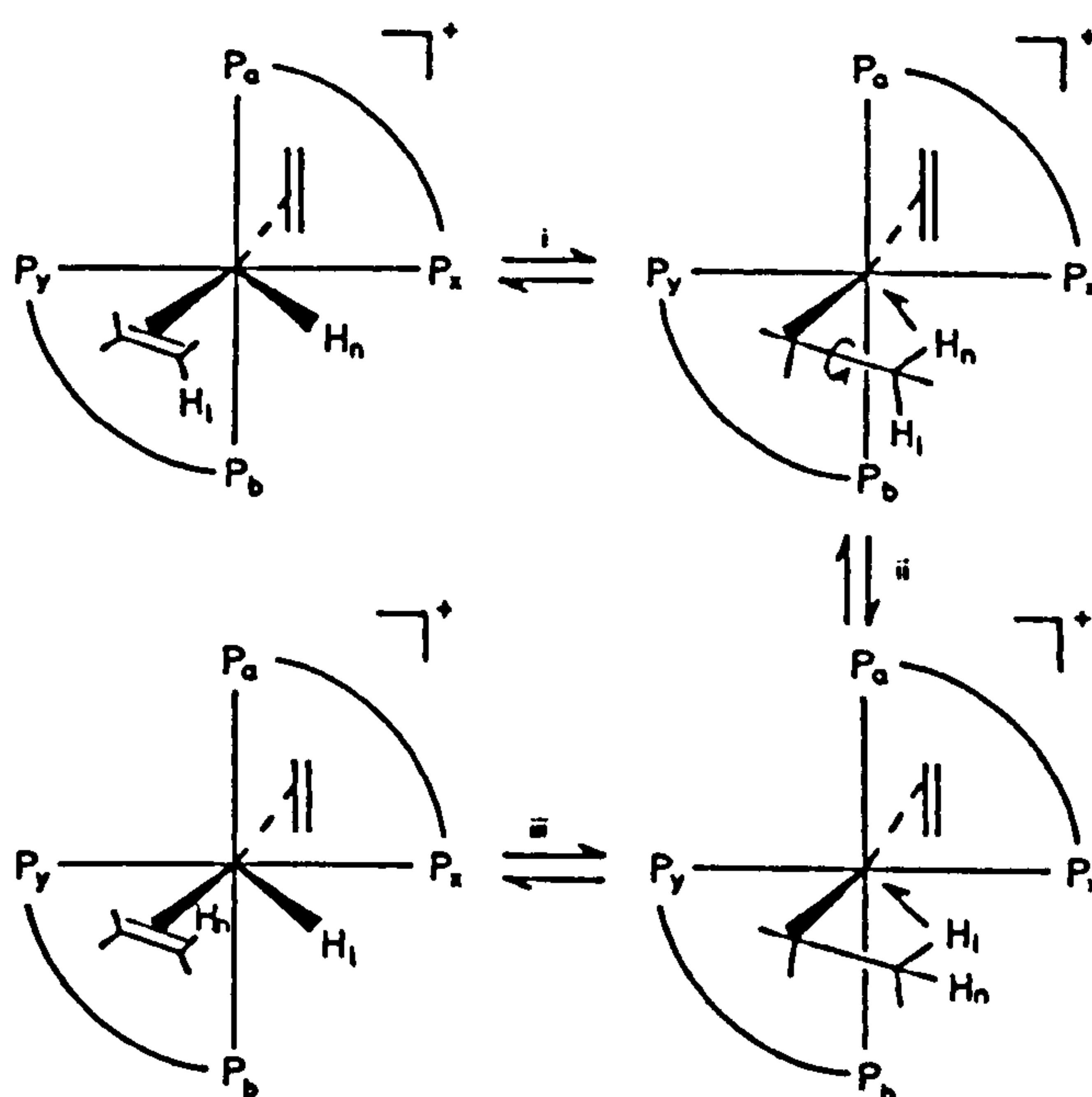


Figure 2.4.2.2. The in-place rotation mechanism via an associative step proposed for intramolecular hydrogen scrambling in the ethylene-hydride complex (C).

The differences in the two mechanisms are depicted in Fig 2.4.2.3.

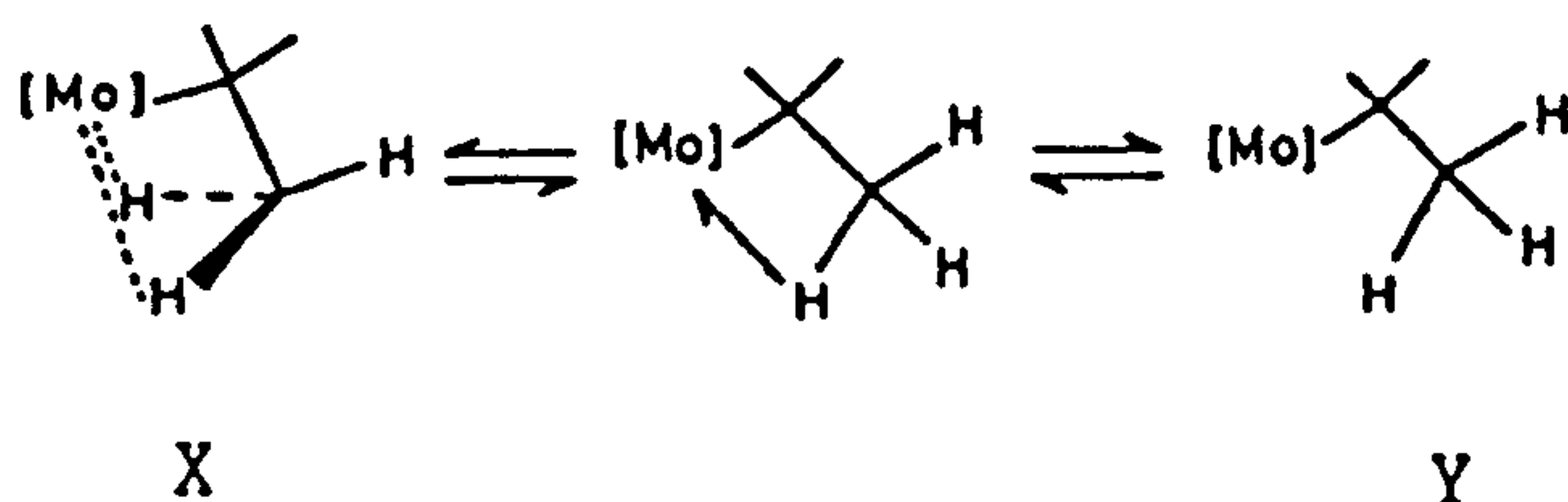


Figure 2.4.2.3. Associative and dissociative intermediates of ethylene-hydride exchange.

The key step in the new mechanism of intramolecular ethylene-hydride exchange processes involves an associative pathway and the transition state X, which has an η^3 -ethyl group. In the normally proposed mechanism, which proceeds via the 16 electron σ -ethyl intermediate Y, a dissociative pathway is followed.

In the case of the arene ruthenium bis(ethylene) complexes (arene = benzene, cymene), on protonation, the simple ethylene-hydride complexes $[(\text{arene})\text{Ru}(\text{C}_2\text{H}_4)_2\text{H}]^+$ were formed, which undergo hydrogen scrambling.

Both mechanisms can be applied to the simple system under investigation, as there are no other nuclei involved such as the dppe ligands in complex (C).

However, M.L.H. Green's proposal of an associative pathway which has a η^3 -ethyl group as a transition state is attractive as the mechanism involves 18 electron species throughout the proposed pathway. One adaptation to the in-plane

rotation mechanism would be the involvement of both the ethylene ligands, each with equal opportunity to undergo hydrogen scrambling.

Summarised below, (Fig. 2.4.2.4) is a proposed associative pathway mechanism for the hydrogen scrambling process occurring in the $[(\text{arene})\text{Ru}(\text{C}_2\text{H}_4)_2\text{H}]^+$ complexes (arene = benzene or cymene). Rotation of the individual ethylenes can be assumed to be as in Osborn's model.

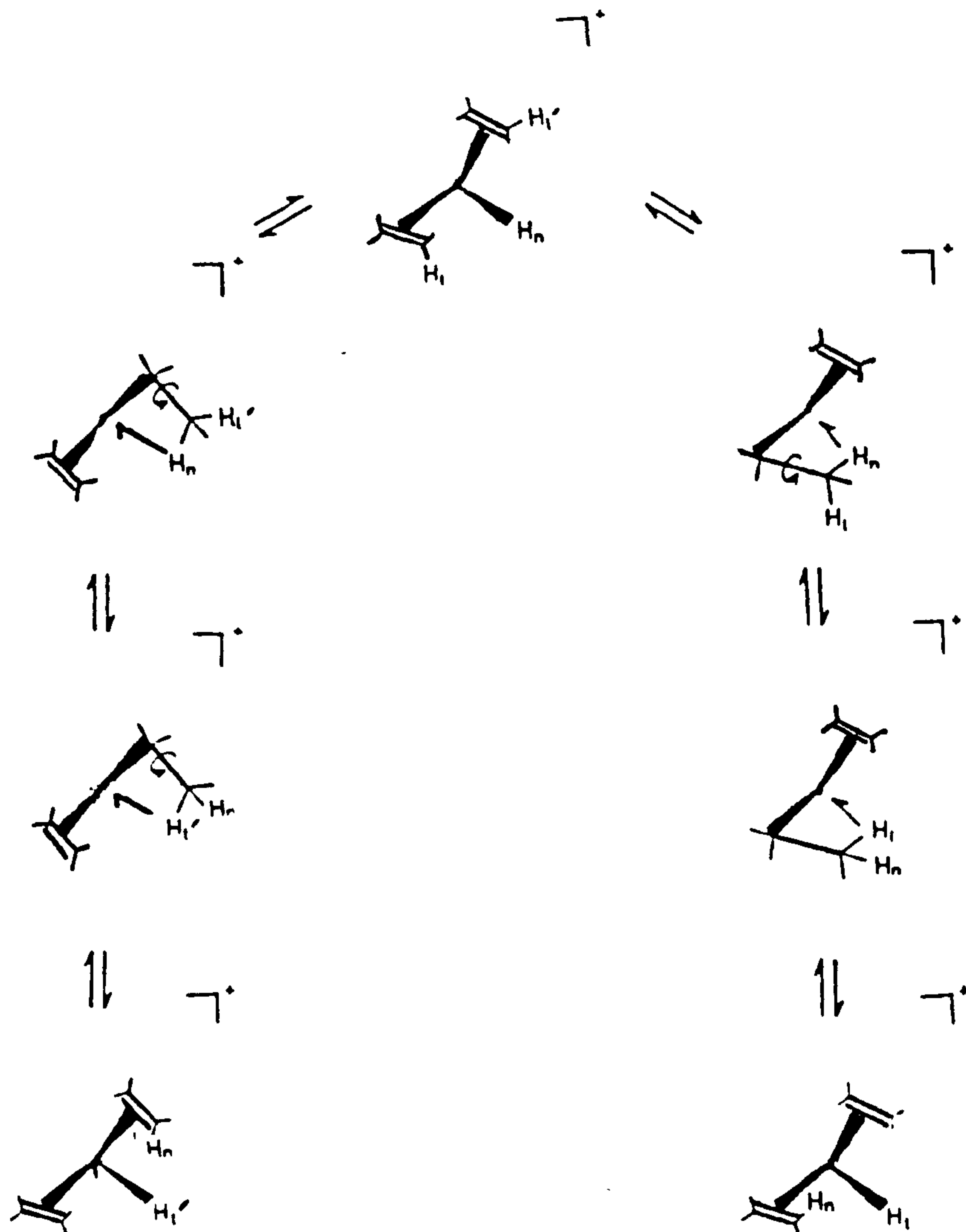
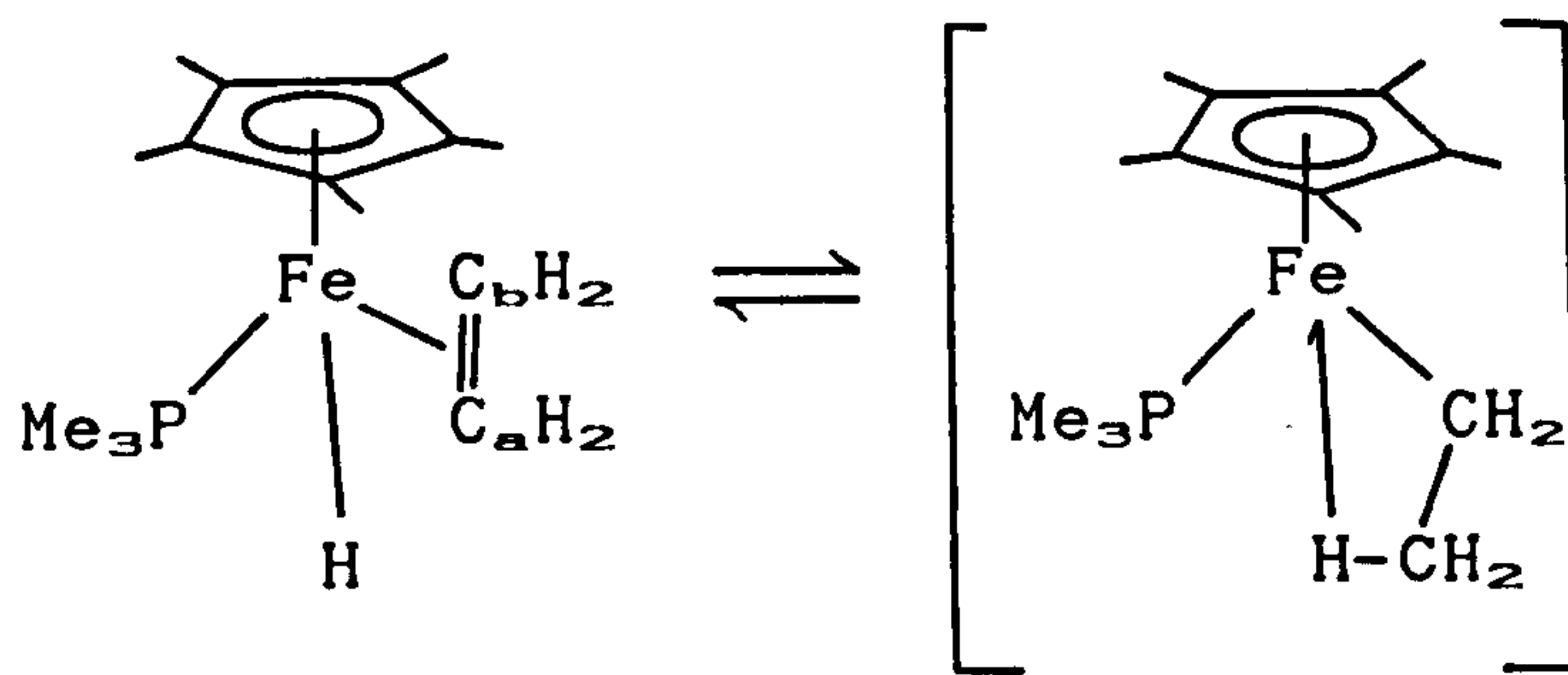


Figure 2.4.2.4. Proposed associative mechanism for the hydrogen scrambling process occurring in the $(\text{arene})\text{Ru}(\text{H})(\text{C}_2\text{H}_4)_2^+$ species. (arene=cymene, benzene)

Previously M.L.H. Green studied the compounds $[(C_5R_5)Fe(PMe_3)(C_2H_4)H]$, which have the ethylene-hydride structure, to examine whether there was an equilibrium between the ethylene-hydride structure and one with an agostic ethyl, ie $[(C_5R_5)Fe(\overline{C_2H_4-H})(PMe_3)]$.¹¹¹

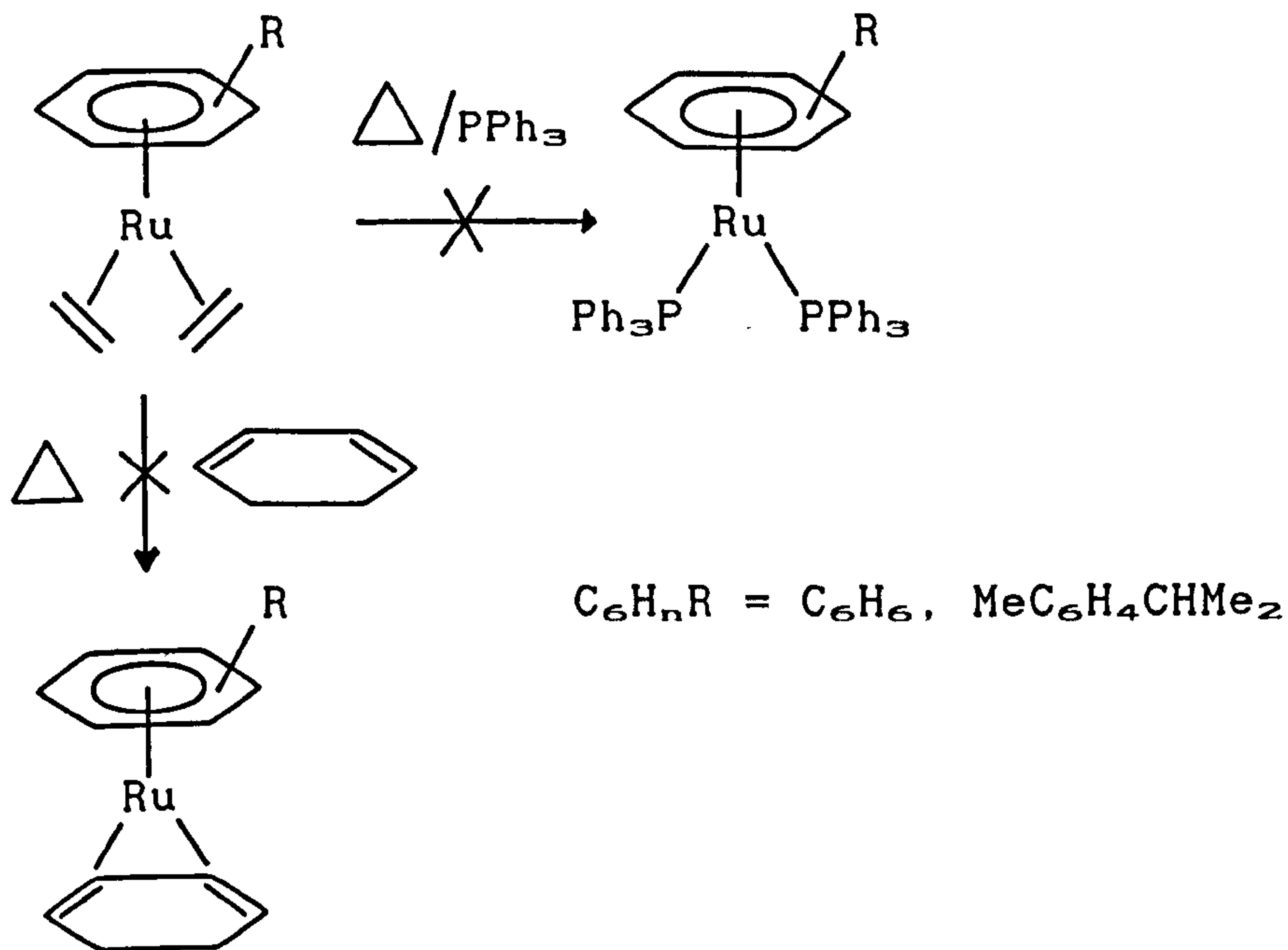
The dynamic behaviour of $[(C_5R_5)Fe(PMe_3)(C_2H_4)H]$ was investigated by variable-temperature 1H and ^{13}C nmr spectroscopy. The ^{13}C nmr spectrum at 236K strongly supports a static ethylene-hydride structure, with a triplet at 27.2ppm and a triplet of doublets at 30.4 ppm for the carbons of the ethylene ligand, (no quoted carbon-hydride coupling - thus small and indicates ethylene-hydride structure).

He was also able to conclude that there was exchange between the Fe-H hydrogen and the two hydrogens attached to one carbon, C_a , of the ethylene ligand at $T > 253K$. The carbon, C_b , retains coupling to the phosphorus atom of PMe_3 at 353K, ruling out any rapid rotation of the coordinated ethylene. It can be envisaged that this rapid exchange proceeds via an equilibrium between the static ethylene-hydride structure and an unobserved intermediate with an agostic $Fe-H-C_a$ structure for the Fe-Et group.



2.4.3 Nucleophilic substitution

The arene ruthenium bis(ethylene) complexes were investigated with respect to nucleophilic displacement of ethylene. It was determined that on warming in benzene with PPh_3 or 1,3-cyclohexadiene, neither complex underwent reaction to form simple displacement products.



However, arene and ethylene loss occurs at higher temperatures, possibly affording non-arene

organometallic complexes, although no such species were observed by ^1H nmr spectroscopy.

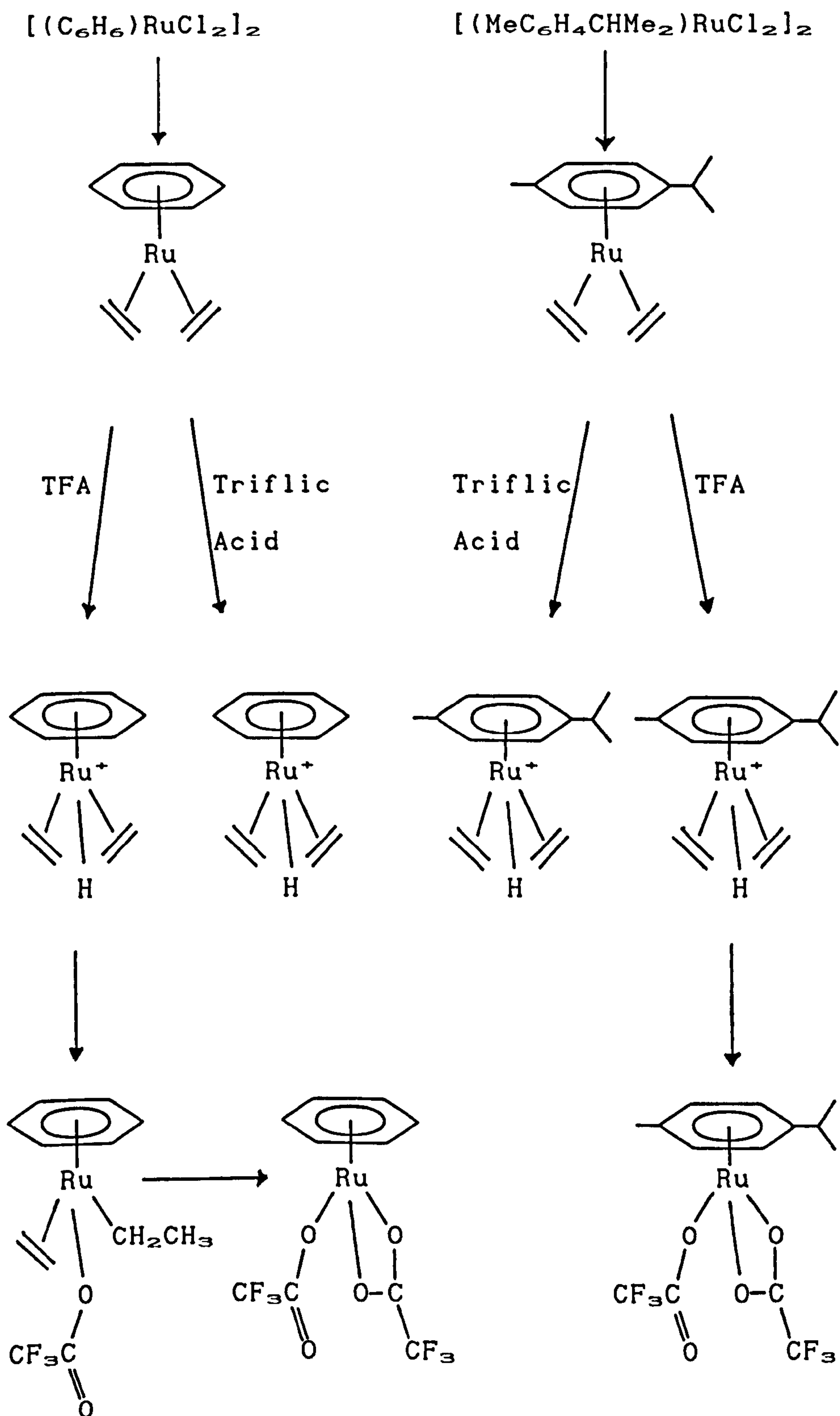
This chemical study confirms the similarity in stability of the second row complex, $(\text{cp})\text{Rh}(\text{C}_2\text{H}_4)_2$ which has been shown to be non-reactive with respect to ethylene displacement at ambient temperatures by nucleophiles.¹¹⁵

R. Cramer and L.P. Seiwel¹¹⁶ in earlier studies were able to monitor nucleophilic displacement of ethylene from $(\text{cp})\text{Rh}(\text{C}_2\text{H}_4)_2$, by observing changing nmr spectrum, when the bis(ethylene) complex was heated at 100°C to 130°C with the desired phosphine or phosphite in a sealed nmr tube. (see table 2.4.2)

Table 2.4.2 Summary of nucleophilic displacement products of $(\text{cp})\text{Rh}(\text{C}_2\text{H}_4)_2$ at various temperatures

L	Temp / $^\circ\text{C}$	Product composition / %		
		$(\text{cp})\text{RhE}_2$	$(\text{Cp})\text{RhEL}$	$(\text{Cp})\text{RhL}_2$
$\text{P}(\text{OEt})_3$	25	100	0	0
	100	87	13	trace
	130	0	0	100
PMe_3	25	80	0	20
	100	0	0	100
$\text{P}(\text{OMe})_3$	25	100	0	0
	100	37	17	45

2.5 Scheme of compounds in chapter 2



2.6 General Experimental

The procedures outlined below relate to all the experimental work in this thesis. Standard Schlenk tube techniques¹⁸³ were utilised for all manipulations involving air sensitive complexes.

Solvents used were purified by distillation: tetrahydrofuran, diethyl ether, isopropyl ether and n-hexane from sodium/benzophenone; dichloromethane and acetonitrile from calcium hydride.

When the procedure did not involve materials that were air sensitive, solvent was removed under reduced pressure using a rotary evaporator.

Routine recrystallisations were achieved by dissolving the sample in a low boiling point solvent, then adding a higher boiling point solvent, in which the complex was virtually insoluble. Evaporation at reduced pressure effected gradual crystallisation.

However, single crystals suitable for X-ray diffraction studies were obtained by dissolving the compound in a low boiling point solvent, filtering the solution into a 1/2 dram vial and then surrounding this vessel by a larger one (4 dram) containing a higher boiling point solvent, in which the compound was virtually insoluble.

Slow diffusion within the system and evaporation through vents in the top of the vial

effected gradual crystal growth over a period of 1-3 days.

New compounds, where possible, were characterised by means of chemical analysis, mass spectrometry, infrared, ^1H nmr and ^{13}C nmr spectral data. Analytical data was obtained from the Microanalysis Services of the University of Nottingham and mass spectral data from the Mass Spectrometry Unit at the University of Nottingham.

Infrared spectra were recorded as nujol mulls between caesium iodide discs, unless otherwise stated. They were recorded on a Perkin Elmer model 983 G spectrometer.

A Bruker 250 MHz spectrometer was used to record nmr spectra, in deuterated solvents calibrated to TMS (or 85% phosphoric acid for ^{31}P spectra).

Johnson Matthey kindly loaned us the ruthenium(III) chloride, and all other reagents were purchased from Aldrich unless otherwise stated. The starting materials, $[(\text{arene})\text{RuCl}_2]_2$ (arene = cymene and benzene) were prepared as in the literature,^{1,2} although in the preparation of the former the alternative diene α -terpinene was utilised.

2.6.1 Experimental

Preparation of $[(C_6H_6)Ru(C_2H_4)_2] \cdot 0.5H_2O$

$[(C_6H_6)RuCl_2]_2$ (250mg; 0.5mmol) was placed in the reaction jacket (appendix Fig. 5) with Zn dust (500mg; 7.6mmol). Under a flow of ethylene CH_2Cl_2 (40ml) was added and the sonic probe secured in place. The reaction vessel was cooled ($-10^\circ C$), the ethylene head pressure increased (1 to 2 atm.) and sonics applied (4 hrs). The solution was filtered away from the excess unreacted zinc and taken to dryness. The residue was sublimed onto a cold finger ($35^\circ C / -20^\circ C$) to afford $[(C_6H_6)Ru(C_2H_4)_2 \cdot 0.5H_2O]$ (110mg; 47%, anal. Found: C 49.59, H 6.19%), (formula $RuC_{10}H_{15}O_{0.5}$ calc. C 49.17, H 6.19%).

Characterisation. 1H nmr shows proton signals assignable to coordinated benzene, $\delta = 5.35ppm$, (s, 6H, C_6H_6) and ethylene multiplets 2.39 and 0.54ppm, (8H). ($CDCl_3$). FAB mass spectrometry observed the presence of the molecular ion $(C_6H_6)Ru(C_2H_4)_2^+$, 236 amu, and the expected fragmentation ions. (see table 2.6.1) Infrared spectroscopy indicated the presence of H_2O , $\nu(OH)$ 3452 cm^{-1} (br).

Preparation of (MeC₆H₄CHMe₂)Ru(C₂H₄)₂

The above procedure was utilised.

[(MeC₆H₄CHMe₂)RuCl₂]₂ (250mg; 0.4mmol) was reacted to afford [(MeC₆H₄CHMe₂)Ru(C₂H₄)₂] (128mg; 54%).

Characterisation. ¹H nmr shows proton signals assignable to coordinated cymene, δ = 5.30ppm (m, 4H, C₆H₄), 2.39ppm (spt, 1H, CHMe₂), 2.08ppm (s, 3H, MeC₆H₄) and 1.23ppm (d, 6H, CHMe₂) and ethylene multiplets, 1.87 and 0.57ppm, (8H). (CDCl₃). FAB mass spectrometry observed the presence of the molecular ion (MeC₆H₄CHMe₂)Ru(C₂H₄)₂⁺, 291 amu, and the expected fragmentation ions. (see table 2.6.1)

Experimental details of nmr protonation studies

I Protonation of (C₆H₆)Ru(C₂H₄)₂ with triflic acid

(C₆H₆)Ru(C₂H₄)₂ (ca. 50mg; ca. 0.1mmol) was dissolved in degassed CD₂Cl₂ (0.5ml) and filtered into a 5mm nmr tube. This tube was placed into the nmr spectrometer with the variable temperature system linked up with it. The temperature was decreased in 10K steps to 185K and the spectrum of the starting material recorded and stored on disk for later reference, retrieval and manipulation.

The nmr tube was brought out of the spectrometer and quickly placed in a slush bath at

185K. One drop of triflic acid (one drop of neat triflic acid in 0.25ml CD_2Cl_2) was syringed into the nmr tube, then the tube was wiped clean, placed in the spectrometer and the temperature allowed to equilibrate before a spectrum was recorded and stored on disk. (If starting material was still present, the last procedure was repeated adding a further drop of triflic acid until the signals due to starting material were minimal or not present). The temperature was then raised in 10K steps to 295K. The system was allowed to come to equilibrium at each temperature before a spectrum was recorded and stored. See stackplot I. (chem. shift values δ /ppm) 193K. 6.25, (s, 6H, C_6H_6); 3.21, 2.19, 1.61, 0.63, (m, 8H, C_2H_4), -10.59, (s, 1H, Ru-H).

263K. 6.21, (s, 6H, C_6H_6); 1.95, (s, 8H, C_2H_4), -10.41, (s, 1H, Ru-H).

II Protonation of $(\text{C}_6\text{H}_6)\text{Ru}(\text{C}_2\text{H}_4)_2$ with trifluoroacetic acid

The procedure used in I was applied. See stackplot II.

203K. δ = 6.21, (s, 6H, C_6H_6), 5.73, (s, 6H, C_6H_6); 3.25, (q, 2H, CH_2CH_3), 2.93, (m, 4H, C_2H_4), 1.56, (t, 3H, CH_2CH_3), -10.63, (s, 1H, Ru-H).

III Protonation of $(C_6H_6)Ru(C_2H_4)_2$ with
D-trifluoroacetic acid

The procedure used in I was applied. See stackplot III.

194K. $\delta = 6.18$, (s, 6H, C_6H_6), 5.75, (s, 6H, C_6H_6), 3.16, 2.13, 1.60, 0.60, (m, 8H, C_2H_4), -10.70, (s, 1H, Ru-H).

254K. $\delta = 6.20$, (s, 6H, C_6H_6), 5.72, (s, 6H, C_6H_6), 3.23, (q, 2H, $\underline{CH_2}CH_3$), 2.95, (m, 4H, C_2H_4), 1.56, (t, 3H, $CH_2\underline{CH_3}$), -10.54, (s, 1H, Ru-H)

IV Protonation of $(C_6H_6)Ru(C_2H_4)_2$ with triflic acid
followed by ^{13}C nmr.

The procedure in I was applied, but the protonation was monitored using hydride coupled and decoupled ^{13}C nmr. See stackplot IV.

194K. (Hydride decoupled). $\delta = C_6H_6$, 94.47; CH_2 , 36.67 and 20.31 ppm.

194K. (Hydride coupled). $\delta = C_6H_6$, 94.48; CH_2 , 36.52 and 20.24 ppm.

V Protonation of $(MeC_6H_4CHMe_2)Ru(C_2H_4)_2$ with
triflic acid

The procedure in I was applied. See stackplot V
185K. $\delta = 5.77$, (m, 4H, C_6H_4), 2.65, (spt, 1H, $\underline{CH}Me_2$),

2.45, (s, 3H, MeC₆H₄), 1.33, (d, 6H, CHMe₂), 2.78, 1.96, 1.6, 0.63, (m, 8H, C₂H₄), -10.82 (s, 1H, Ru-H). 265K. δ = 5.90, (m, 4H, C₆H₄), 2.74, (spt, 1H, CHMe₂), 2.45, (s, 3H, MeC₆H₄), 1.39, (d, 6H, CHMe₂), 1.89, (br.s, 8H, C₂H₄), -10.55, (s, 1H, Ru-H).

VI Protonation of (MeC₆H₄CHMe₂)Ru(C₂H₄)₂ with trifluoroacetic acid

The procedure in I was applied.

263K. δ = 5.78, (m, 4H, C₆H₄), 2.69, (spt, 1H, CHMe₂), 2.45, (s, 3H, MeC₆H₄), 1.37, (d, 6H, CHMe₂), 1.86, (br.s, 8H, C₂H₄), -10.62 (s, 1H, Ru-H).

Preparation of [(C₆H₆)Ru(O₂CCF₃)₂].H₂O

(C₆H₆)Ru(C₂H₄)₂ (50mg; 0.2mmol) was dissolved in CH₂Cl₂ (1ml) and cooled (203K). Trifluoroacetic acid (0.1ml of 0.41 in 1ml CH₂Cl₂, 0.53mmol) was added and the reaction mixture allowed to come up to room temperature slowly. On standing overnight the orange crystalline material was filtered away from the solution to afford [(C₆H₆)Ru(O₂CCF₃)₂].H₂O] (53mg; 63%, anal. Found C 28.17, H 1.81%), (formula RuC₁₀H₈F₆O₅, calc. 28.38, H 1.91%).

Characterisation. The infrared spectrum of the complex was compared to spectroscopic data of a genuine sample.³⁰

$\nu_{\text{asym}}(\text{OCO}), 1679 \text{ cm}^{-1} \text{ (s)}, 1580 \text{ cm}^{-1} \text{ (w)};$
 $\nu_{\text{sym}}(\text{OCO}), 1429 \text{ cm}^{-1} \text{ (s)}, 1407 \text{ cm}^{-1} \text{ (s)}.$
 $\nu(\text{OH}), 3422 \text{ cm}^{-1} \text{ (br)}.$ FAB mass spectrometry
 showed the presence of the expected fragment
 $(\text{C}_6\text{H}_6)\text{Ru}(\text{O}_2\text{CCF}_3)^+.$ (See table 2.6.1)

Table 2.6.1 FAB mass spectrometry characterisation
of complexes in chapter 2.

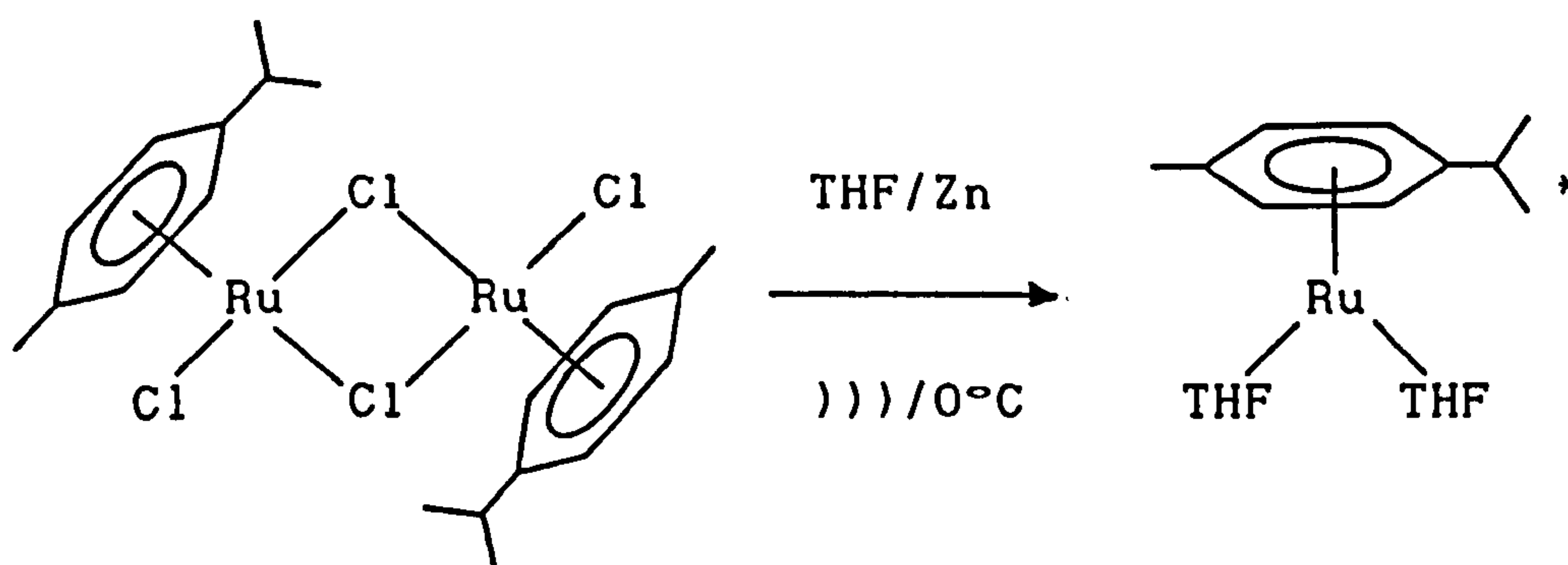
Complex	MW/amu	Fragmentation
$(\text{benzene})\text{Ru}(\text{C}_2\text{H}_4)_2$	236	$236 (\text{benzene})\text{Ru}(\text{C}_2\text{H}_4)_2^+$ $208 (236 - \text{C}_2\text{H}_4)$ $180 (236 - 2 \text{ C}_2\text{H}_4)$
$(\text{cymene})\text{Ru}(\text{C}_2\text{H}_4)_2$	292	$292 (\text{cymene})\text{Ru}(\text{C}_2\text{H}_4)_2^+$ $264 (292 - \text{C}_2\text{H}_4)$ $236 (292 - 2 \text{ C}_2\text{H}_4)$
$(\text{benzene})\text{Ru}(\text{O}_2\text{CCF}_3)_2$	406	$293 (406 - \text{O}_2\text{CCF}_3)$

CHAPTER THREE

Chapter 3.

3.1 Synthesis of a reactive arene ruthenium intermediate

As described in Chapter 2, the neutral arene ruthenium bis(ethylene) complexes prepared were unreactive with respect to simple nucleophilic attack. When the ultrasonic reduction was carried out using tetrahydrofuran as a solvent, a competing process was observed, with the generation of a reactive arene ruthenium species.



Sonication of the cymene ruthenium chlorodimer, in the presence of zinc, yields a reactive arene moiety when the solvent system used is tetrahydrofuran. Failure with the solvent systems, dichloromethane, dichloroethane, acetonitrile or methanol, when utilising the above conditions, implies tetrahydrofuran plays a significant role in the make up of the reactive species proposed above.

However, on removal of solvent, the complex was

unstable and decomposition occurred. Thus no positive characterisation was possible.

^1H nmr spectroscopy was utilised to confirm the total conversion of the starting material to the reactive intermediate, but this technique could not be applied to monitor new proton absorptions assignable to coordinated arene or tetrahydrofuran.

An attractive possible structure for the intermediate is the simple tetrahydrofuran solvated species as shown above. Investigation of the reactions this tetrahydrofuran complex undergoes may provide more information on the make up of the arene ruthenium moiety.

Quantifying the yield of the reactive tetrahydrofuran complex was difficult, as it was not possible to isolate the complex in a pure form. ^1H nmr analysis of an aliquot of the reaction mixture taken to dryness showed that free arene was present - this could be possible due to free arene being generated during the synthesis, or the instability of the tetrahydrofuran complex when taken to dryness. Subsequent reactions indicate that the tetrahydrofuran solvated arene ruthenium moiety was afforded in approximately 50% yield, by comparison of the yield of the desired products with respect to the initial amount of cymene ruthenium chlorodimer reacted.

Application of ultrasound to a tetrahydrofuran

solution of the benzene ruthenium chlorodimer in the presence of zinc, fails to afford an arene ruthenium moiety that can be utilised. The explanation for this may be a combination of insolubility and reactivity factors.

3.2 Investigation of the reactivity of the tetrahydrofuran complex

Although the complex could not be fully characterised, the synthesis was reproducible. The reactivity of the tetrahydrofuran complex was investigated to determine whether the reactions the complex undergoes would give any information on the intermediate's structure, and its use as a new arene ruthenium substrate.

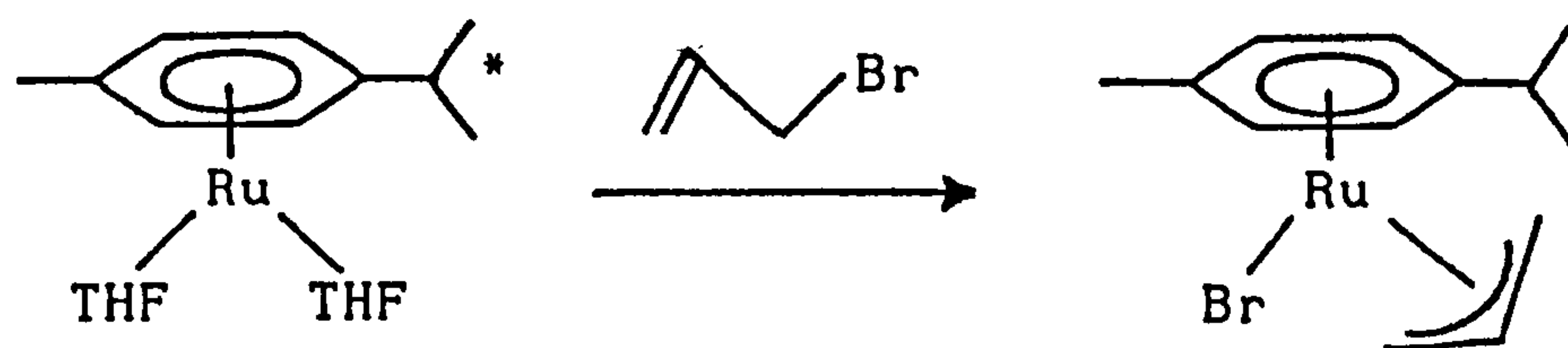
As reported in chapter 1 (1.2.2.3), two synthetically useful Ru(II) half sandwich complexes are the tris ligated dicationic species $[(\text{arene})\text{Ru}(\text{acetone})_3]^{2+}$ ^{65,66} and $[(\text{arene})\text{Ru}(\text{CH}_3\text{CN})_3]^{2+}$ ². The acetone complexes have been utilised extensively in cyclophane chemistry, the desired arene complex being prepared in situ and reacted with the required cyclophane under various reaction conditions.

The tetrahydrofuran complex was proposed to be zero valent and was investigated to determine its synthetic usefulness. As for the acetone complexes,

the tetrahydrofuran complex was prepared in situ and then reacted with the desired ligand.

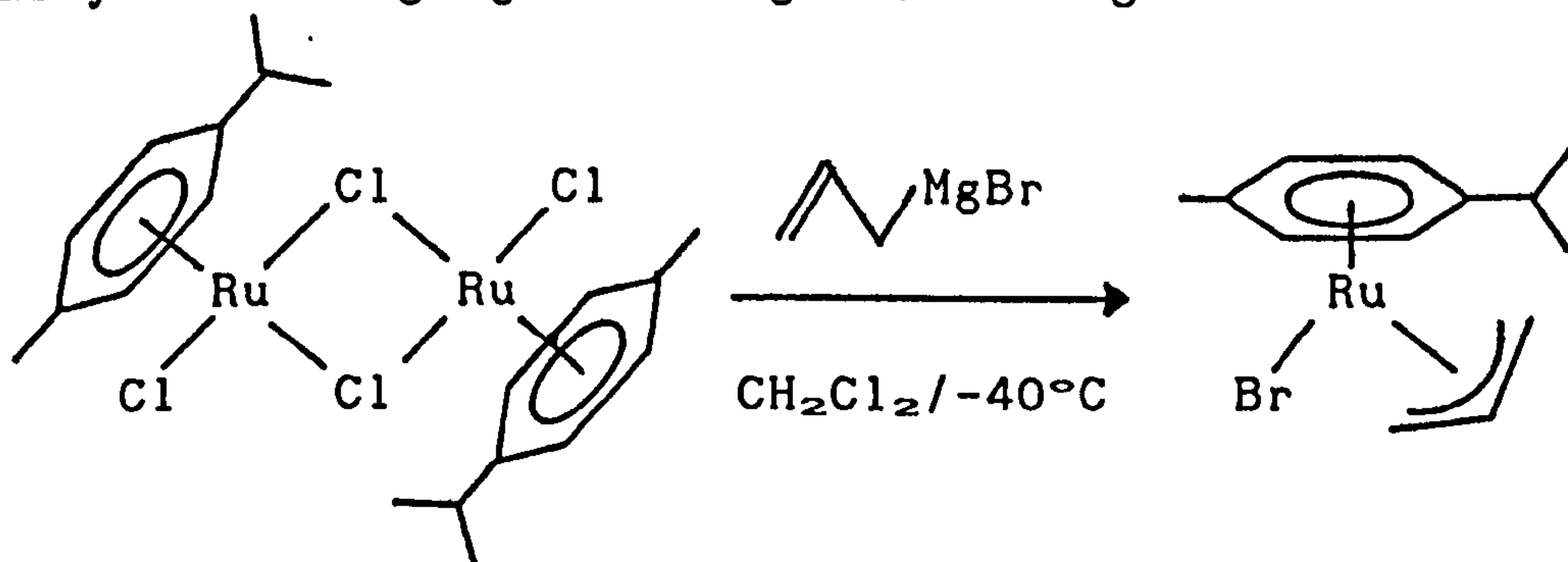
3.2.1 Oxidative addition

The tetrahydrofuran complex was prepared in situ, the excess unreacted zinc dust removed, and allylbromide added.



An eta 3 allyl complex was isolated from the reaction mixture as a deep red brown oil.

This complex was also prepared on reaction of the cymene ruthenium chlorodimer with the allylbromide grignard reagent, $\text{CH}_2=\text{CH}-\text{CH}_2\text{MgBr}$.



The preparation of arene ruthenium halide allyl complexes has previously been reported utilising tetraallyltin³⁶ and allyl mercury halides.³⁷

¹H nmr spectroscopy was utilised to fully assign the stereochemistry of the complex afforded.

Also fast atom bombardment mass spectrometry confirmed the proposed product. (see experimental 3.5)

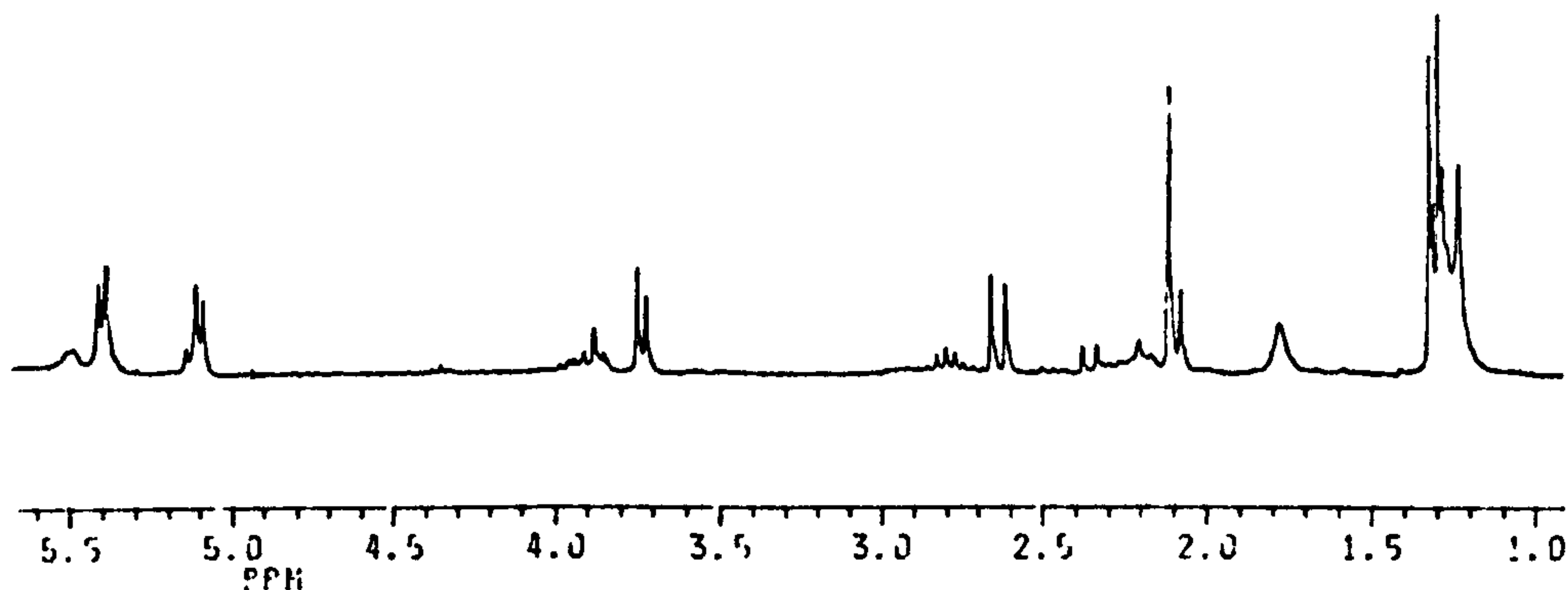


Fig 3.1 ^1H nmr spectrum of $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuBr}(\eta^3\text{C}_3\text{H}_5)]$ in CDCl_3 .

The eta 3 allyl group has three different proton environments as shown in figure 3.2, when linked with a transition metal: H_m (meso) attached to the central carbon, H_{syn} (syn) and H_{anti} (anti).

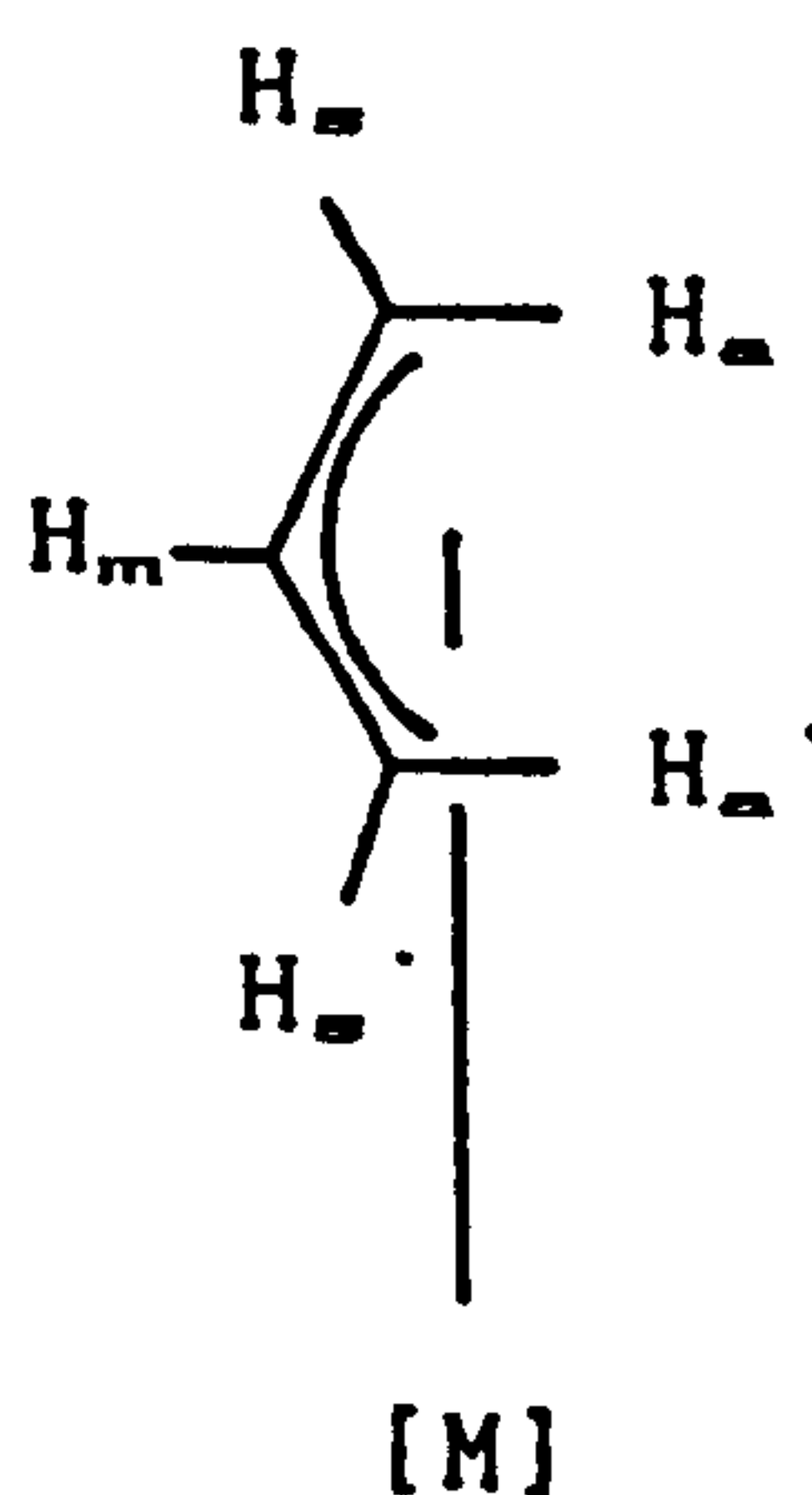


Fig 3.2 Proton assignment of an eta 3 allyl group

The anti protons are nearer to the metal centre than the syn protons and hence are more strongly shielded. The signal to highest field is therefore assigned to H_a (doublet). This is confirmed from the coupling constants. The trans coupling $^3J(H_a H_m)$ is greater than the cis coupling $^3J(H_a H_m)$. H_m appears at low field as a multiplet.¹¹⁷

The 1H nmr spectrum of the allyl complex can be assigned; $\delta = 5.28$ (m, C_6H_4), 2.8 (spt, $\underline{CHMe_2}$), 2.12 (s, $\underline{MeC_6H_4}$), 1.33 (d, $\underline{CHMe_2}$), 3.9 (m, H_m), 3.75 (d, H_a) and 2.64 ppm, (d, H_a).

However, under close inspection the nmr spectrum appears to have proton absorptions assignable to a species with similar arene chemical shift positions and a possible doublet shifted slightly up field with the same coupling as the proton assigned as H_a . The explanation for these findings is that the allyl can be coordinated with the central carbon exo or endo with respect to the arene. (Fig.3.3)

Conformational equilibria between conformers of π -allyl derivatives of molybdenum and tungsten complexes have been widely noted; nevertheless, convincing evidence for assigning given configurations was lacking until W. Faller et al surveyed a series of substituted allyl complexes, assessing the importance of steric factors in

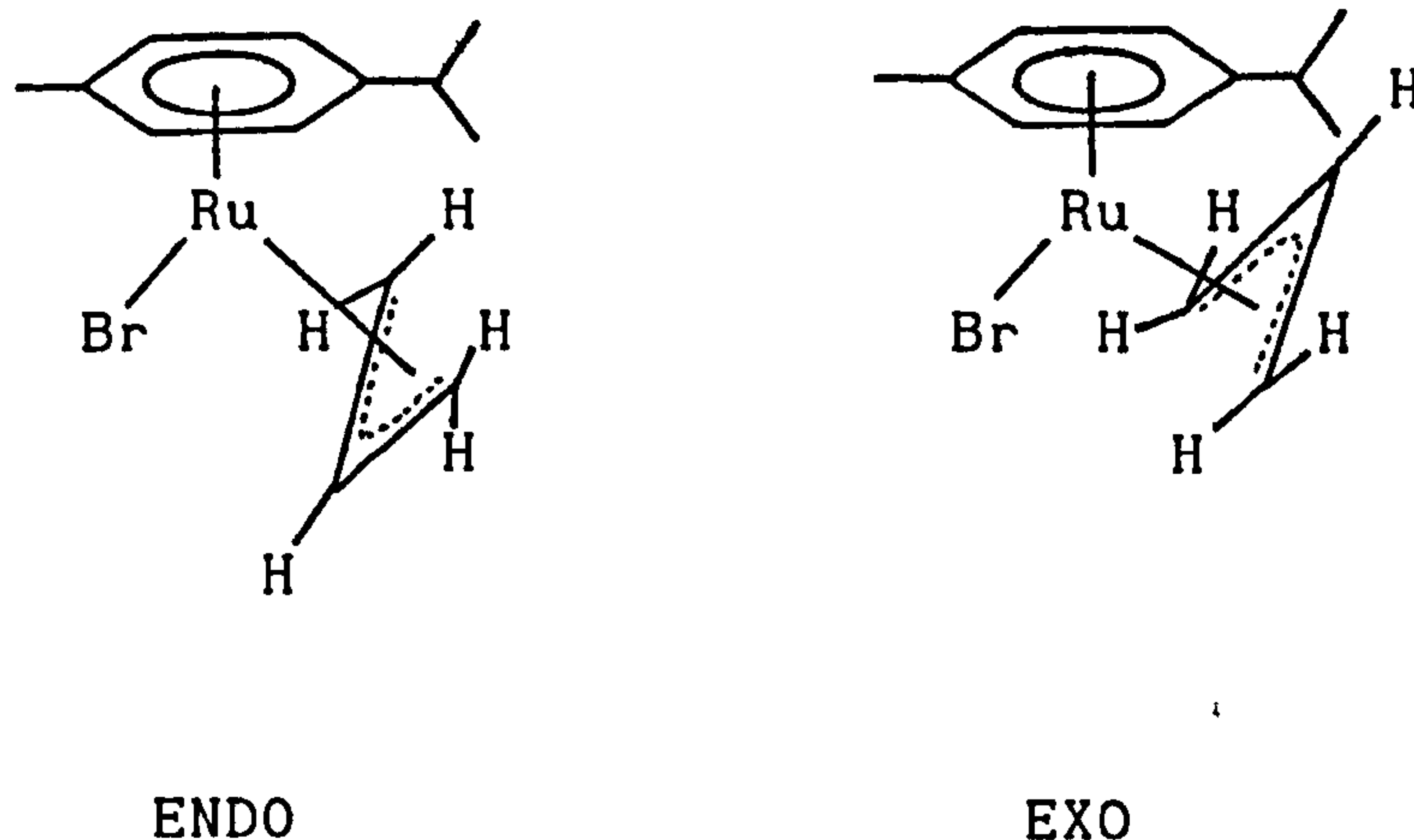


Fig 3.3 Diagrammatical representation of the coordination of an allyl ligand

determining the orientation of the allyl moiety for π -cyclopentadienyl and π -indenyl- π allyl metal dicarbonyl species (metal=Mo,W).¹¹⁸ Infrared and ¹H nmr spectra confirmed the presence of two isomers in solution and general rules could be applied to determine between the endo and exo isomers.

i) The most reliable characteristic for exo is the higher field shift of the anti protons in the cyclopentadienyl derivatives.

ii) A fairly reliable characteristic property of the isomers is an upfield shift of the syn protons in the exo configuration.

Application of i) indicates in solution the $[(\text{MeC}_6\text{HCHMe}_2)\text{RuBr}(\eta^3\text{C}_3\text{H}_5)]$ complex is present predominantly in an endo configuration with reference to the allyl ligand and has proton

absorptions as defined above.

The ^1H nmr data for the exo configuration is; $\delta =$ 5.33 (m, C_6H_4), 2.07 (s, MeC_6H_4), 1.25 (d, CHMe_2), 3.9 (d, H_m) and 2.35 ppm, (d, H_a). This information is summarised below. (Fig.3.4)

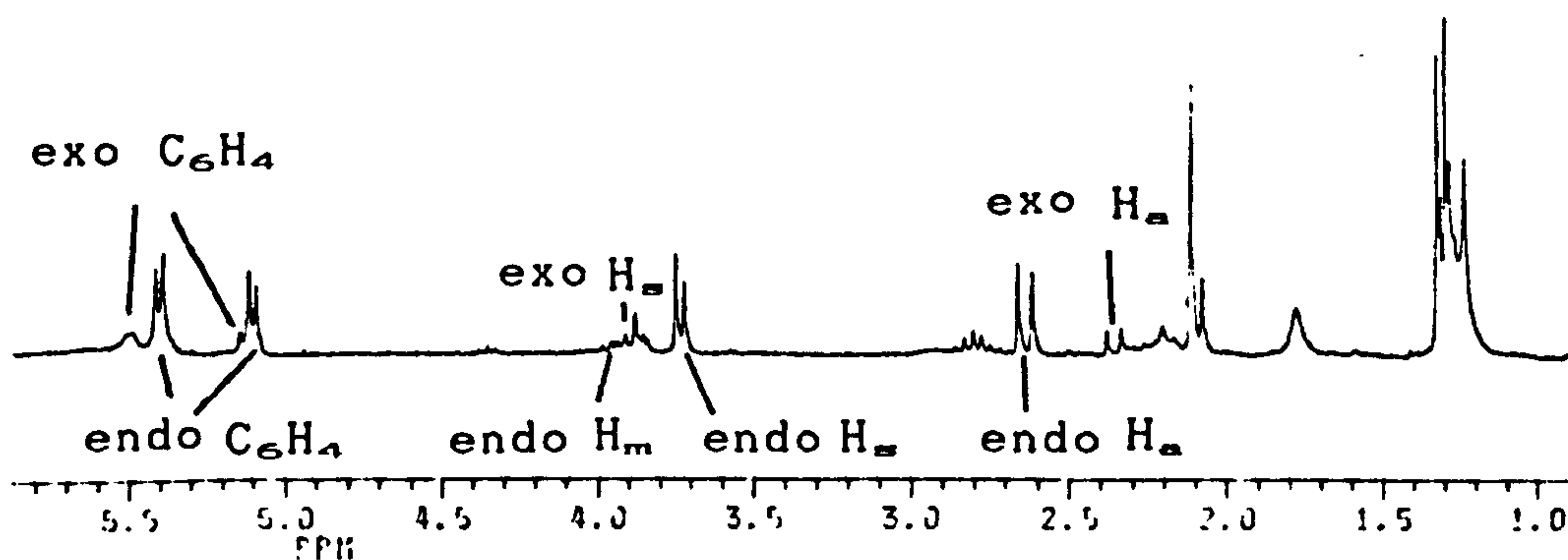
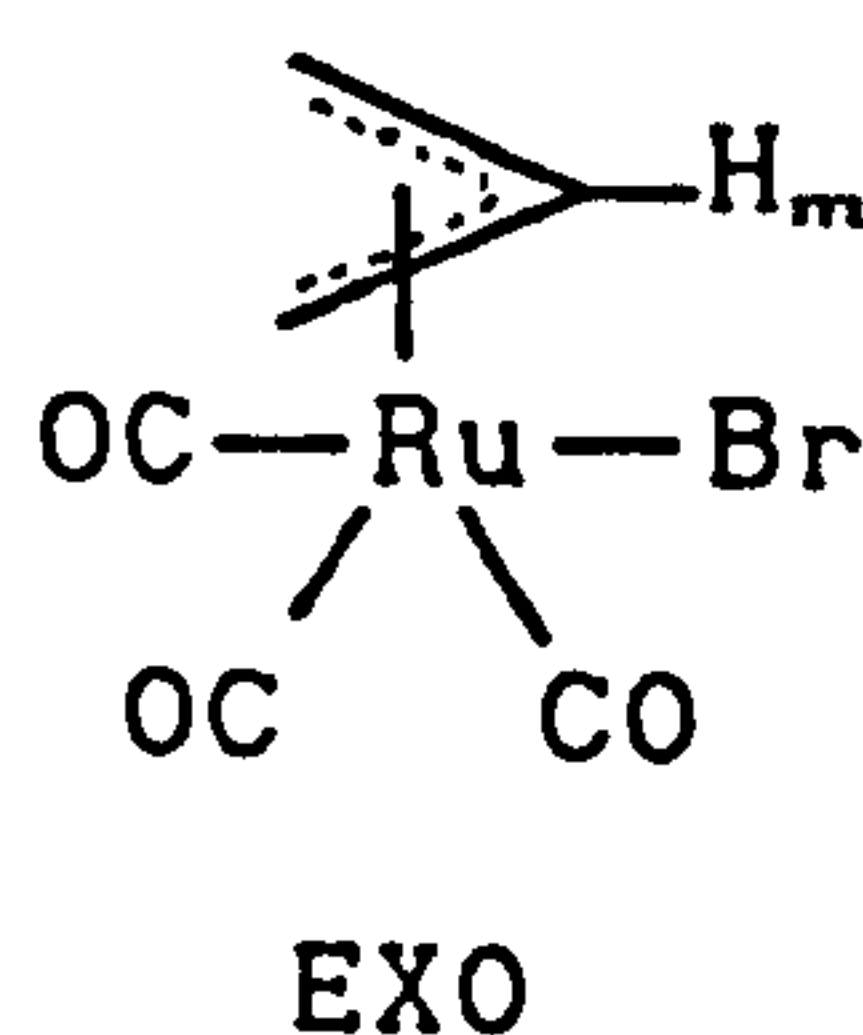
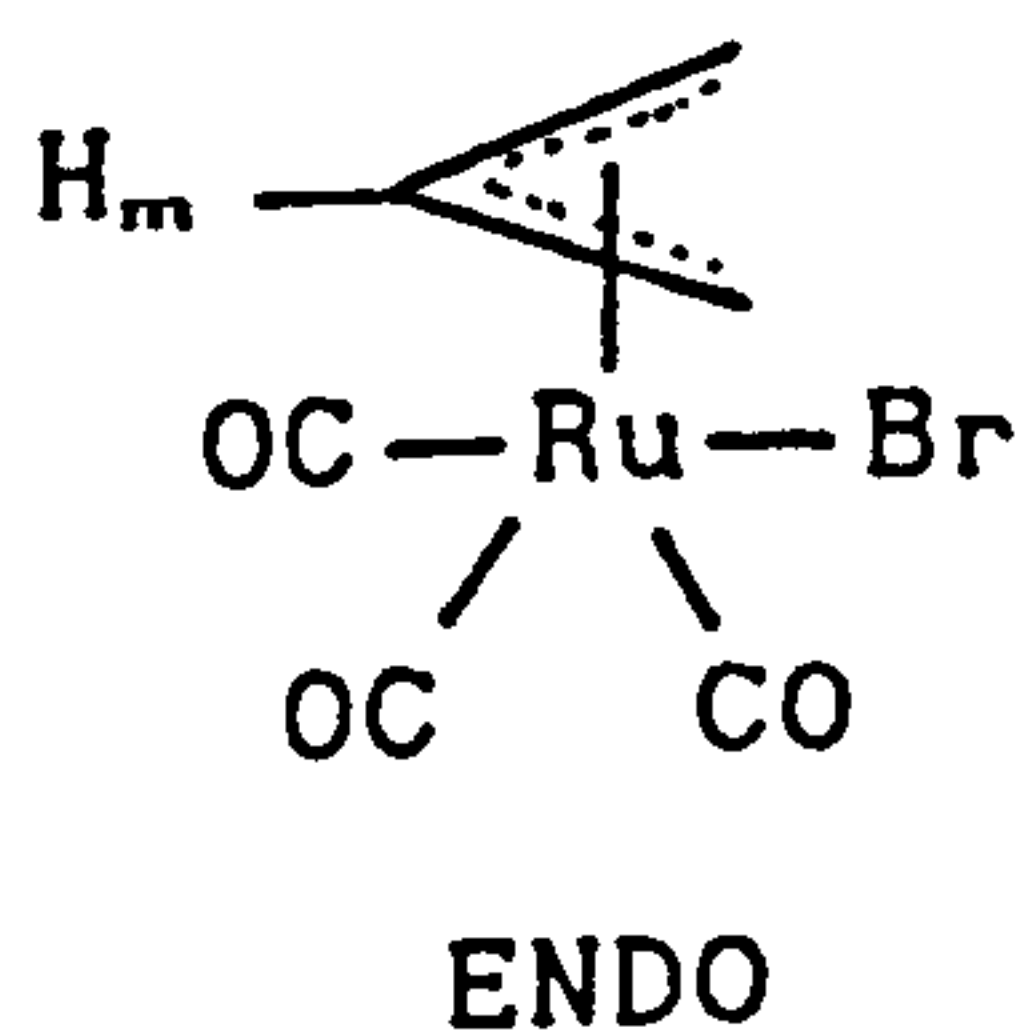


Fig 3.4 Full ^1H nmr spectrum assignment of $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuBr}(\eta^3\text{C}_3\text{H}_5)]$ in solution.

The isoelectronic complex $\text{Ru}(\text{CO})_3\text{Br}(\text{C}_3\text{H}_5)^{119}$ exists in solution in a conformational equilibrium between endo and exo isomers.



At room temperature the two isomers

interconvert slowly ($t_{1/2} > 10$ mins) and the endo isomer predominates (>95%). This can be compared to the analogous complexes $\text{Fe}(\text{CO})_3\text{X}(\text{C}_3\text{H}_5)$ ($\text{X} = \text{Br}$ and I), which are also present in solution predominantly in the endo form.¹²⁰ (It should be noted that these complexes are all predominantly in solution as the endo isomer with respect to the most electronegative group bound to the ruthenium metal centre. However, the carbonyl and arene complexes are opposite stereochemically, if the bonding of the allyl ligand is compared with respect to the halogen in both complexes.)

Comparison of the solution behaviour with the solid state allyl configurations can be made, since the $(\text{C}_6\text{H}_6)\text{RuI}(\text{C}_3\text{H}_5)^{121}$, $(\text{C}_6\text{H}_6)\text{Ru}(\text{CN})(\text{C}_3\text{H}_5)^{121}$, $\text{Fe}(\text{CO})_3\text{Br}(\text{C}_3\text{H}_5)^{122}$, and $\text{Fe}(\text{CO})_3\text{I}(\text{C}_3\text{H}_5)^{123}$ complexes have been verified by X-ray analysis. The latter two complexes have the allyl moiety in an endo configuration, thus agreeing with the stereochemical behaviour of the complexes in solution.

However, the analogous arene ruthenium complexes $(\text{C}_6\text{H}_6)\text{RuI}(\text{C}_3\text{H}_5)$ and $(\text{C}_6\text{H}_6)\text{Ru}(\text{CN})(\text{C}_3\text{H}_5)$ have been shown in the solid state to have the exo isomer present. (Fig.3.5)

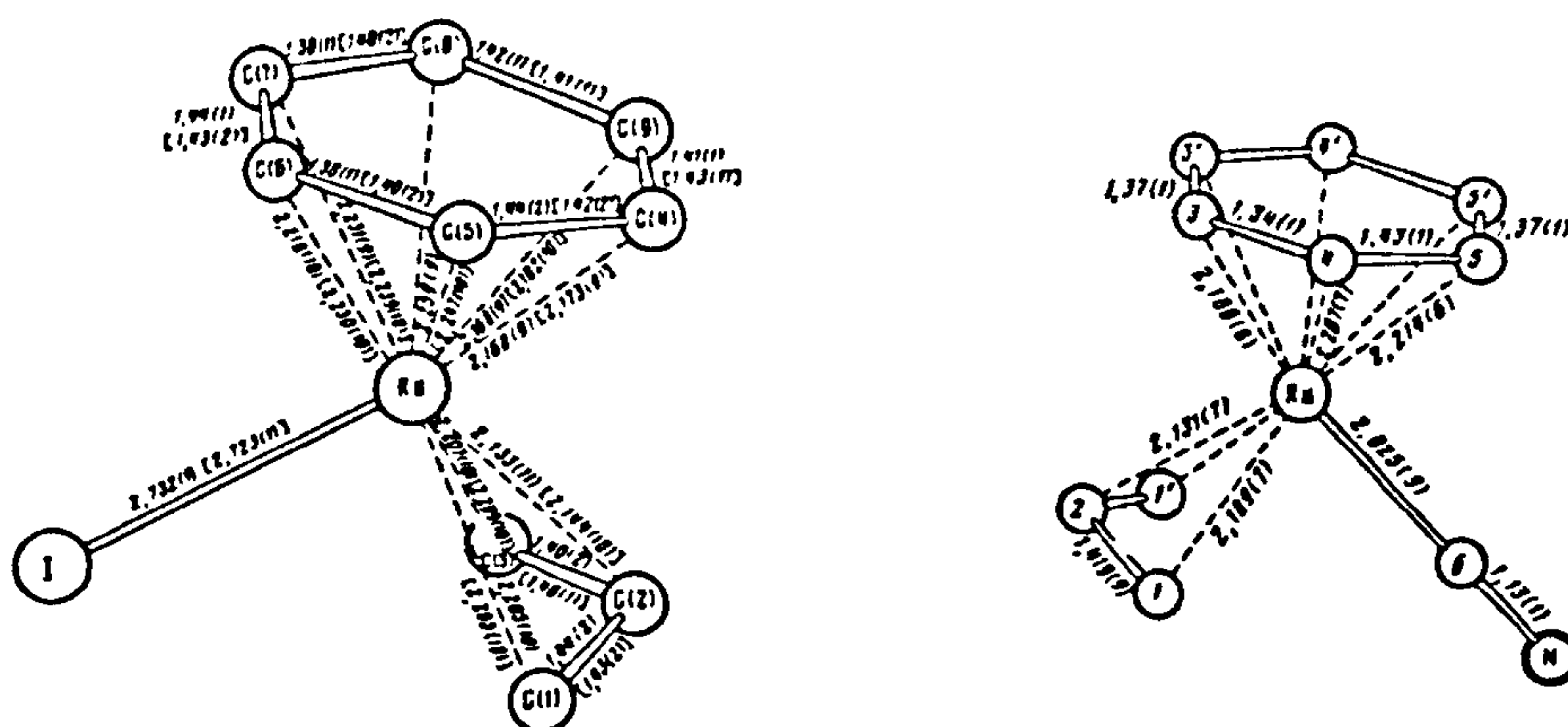
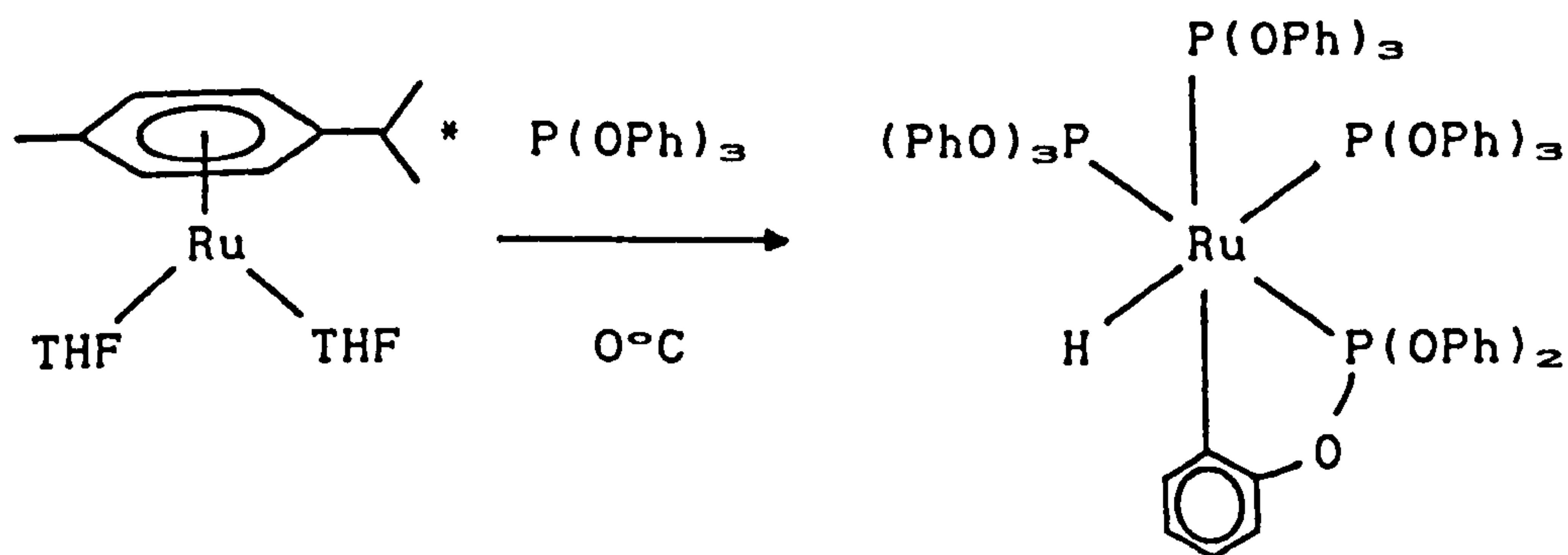


Fig.3.5 X-ray structures of $(C_6H_6)RuI(C_3H_5)$ and $(C_6H_6)Ru(CN)(C_3H_5)$.

3.2.2 Source of naked ruthenium

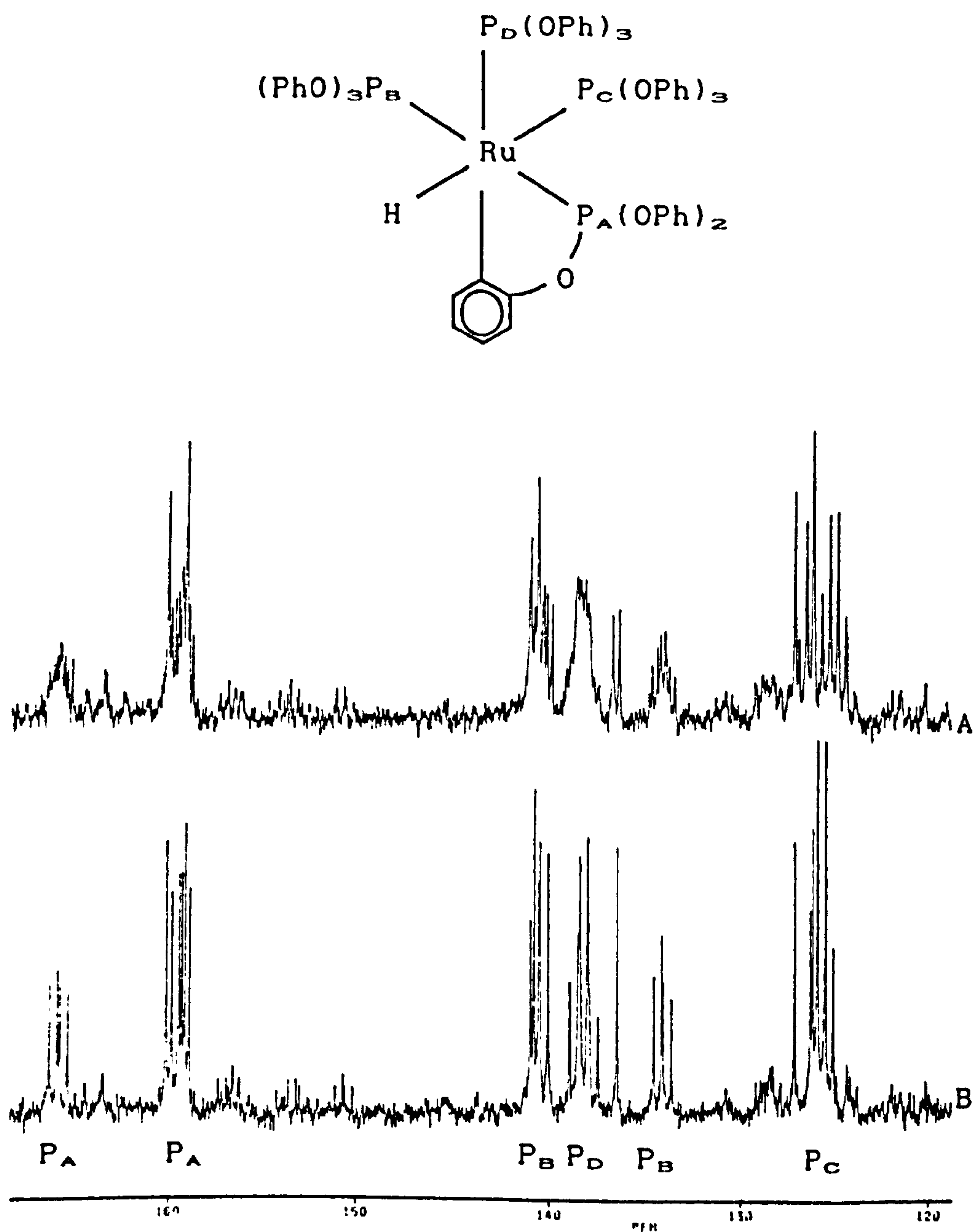
The tetrahydrofuran complex was investigated to determine whether it would undergo nucleophilic substitution.

Triphenylphosphite was stirred with the intermediate at $0^\circ C$ for 4 hours. From the reaction mixture was isolated a red oil.



Characterisation of the product and

determination of the stereochemistry was assigned utilising ^1H and ^{31}P nmr spectroscopy. The phosphorus environments can be fully assigned;



A = $^{31}\text{P}(^1\text{H}$ coupled), B = $^{31}\text{P}(^1\text{H}$ decoupled).

Fig.3.6 $^{31}\text{P}(^1\text{H}$ coupled and decoupled) nmr spectra of $(\text{H})\text{Ru}[(\text{C}_6\text{H}_4\text{O})\text{P}(\text{OPh})_2][\text{P}(\text{OPh})_3]_3$.

Two fundamental rules allow P_A and P_B to be assigned.

i) Orthometallated triphenylphosphite phosphorus absorptions appear at low field.¹²⁴

ii) Large couplings are associated with trans geometries.¹²⁵

If the multiplets of the proton decoupled phosphorus nmr are thought of as doublets of doublets of doublets, when a trans coupling is available to the phosphorus nuclei under investigation, the absorptions due to this phosphorus environment appear as two separate doublets of doublets. Comparison of the coupling of these doublets of doublets show they are related, confirmation from 2D COSY ^{31}P spectra was also obtained.

P_A and P_B are trans to each other and thus their signals appear as two separate doublets of doublets. Also, it is possible to distinguish between the two, since P_A appears at low field as the ligand has undergone orthometallation. (See Fig.3.6)

Assignment of P_C and P_D is afforded by comparison of the proton coupled and decoupled phosphorus nmr spectra. P_C is the only trans phosphorus environment to the hydride and only one phosphorus environment has markedly different coupling. As no trans geometry is possible for P_C

and P_D , the three couplings are very similar and a broadened quartet is observed for both environments.

As would be expected, the hydride signal should be a multiplet made up of a doublet of doublet of doublet of doublets, due to four non equivalent phosphorus environments. (See Fig.3.7)

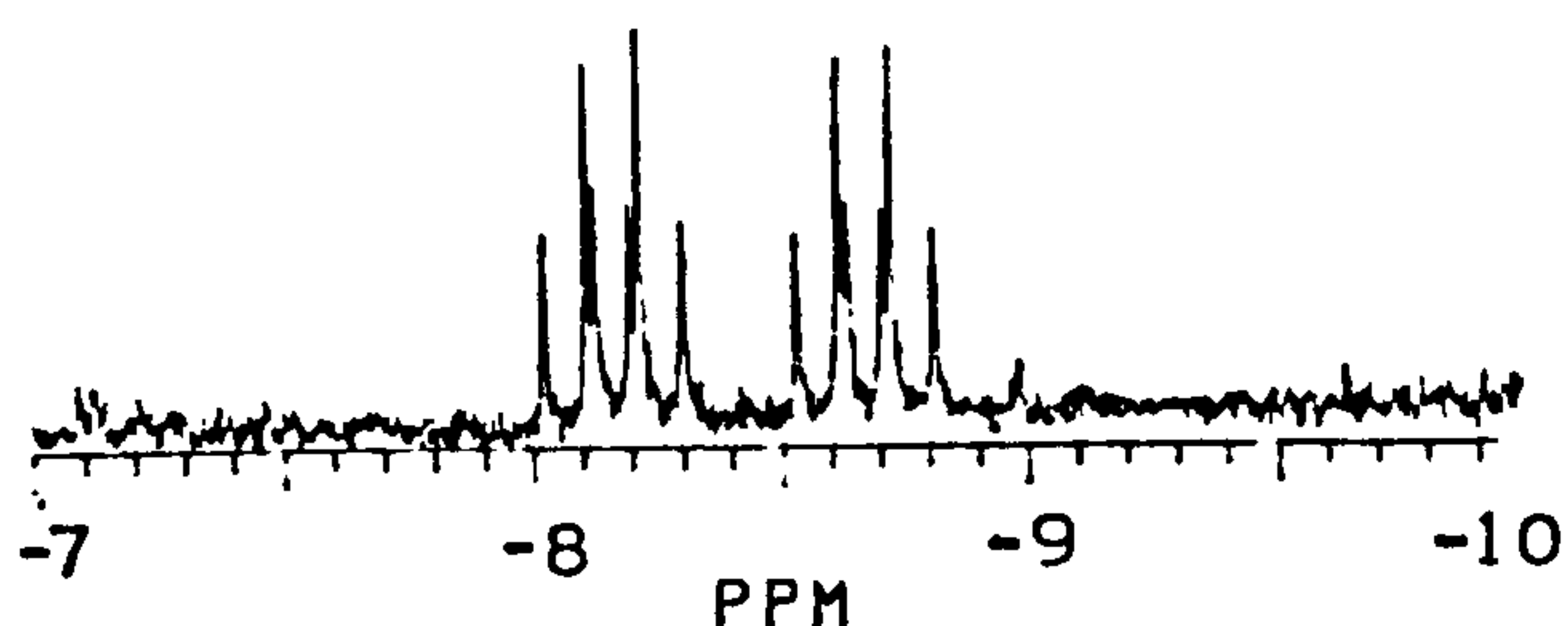
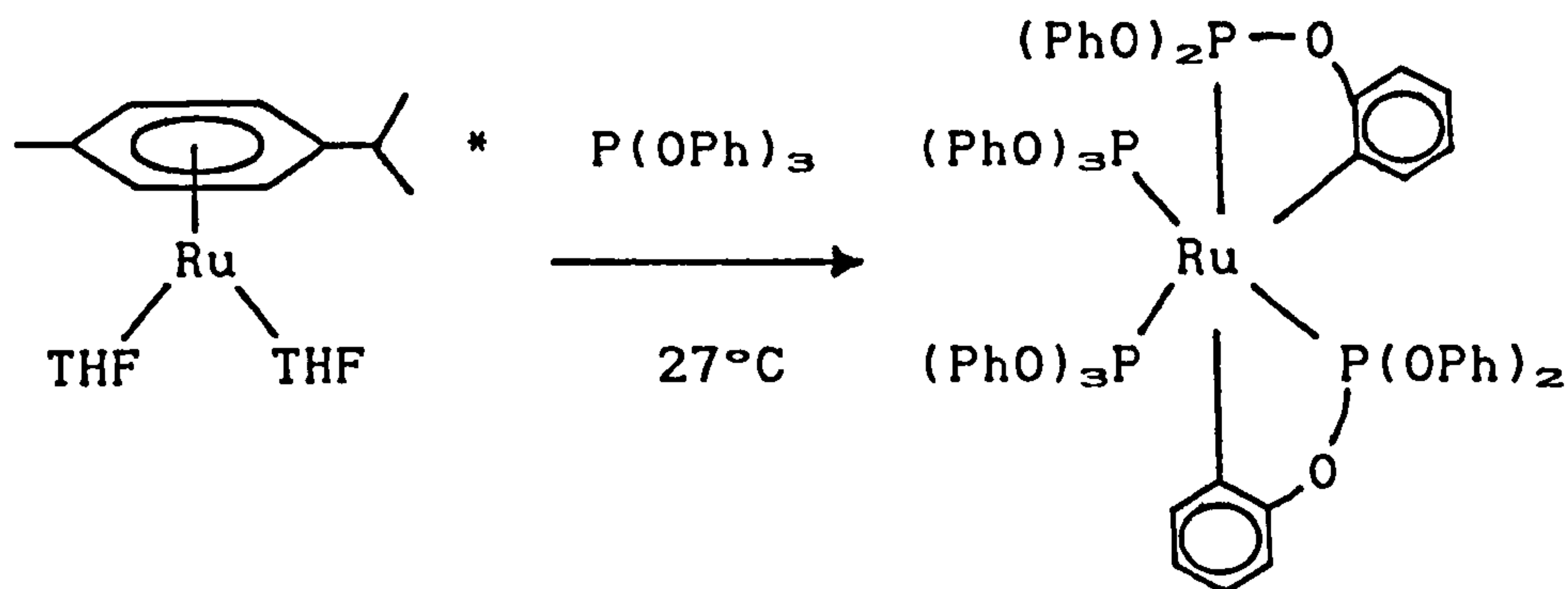


Fig 3.7 ^1H nmr spectrum of high field region of $(\text{H})\text{Ru}[(\text{C}_6\text{H}_4\text{O})\text{P}(\text{OPh})_2][\text{P}(\text{OPh})_3]_3$

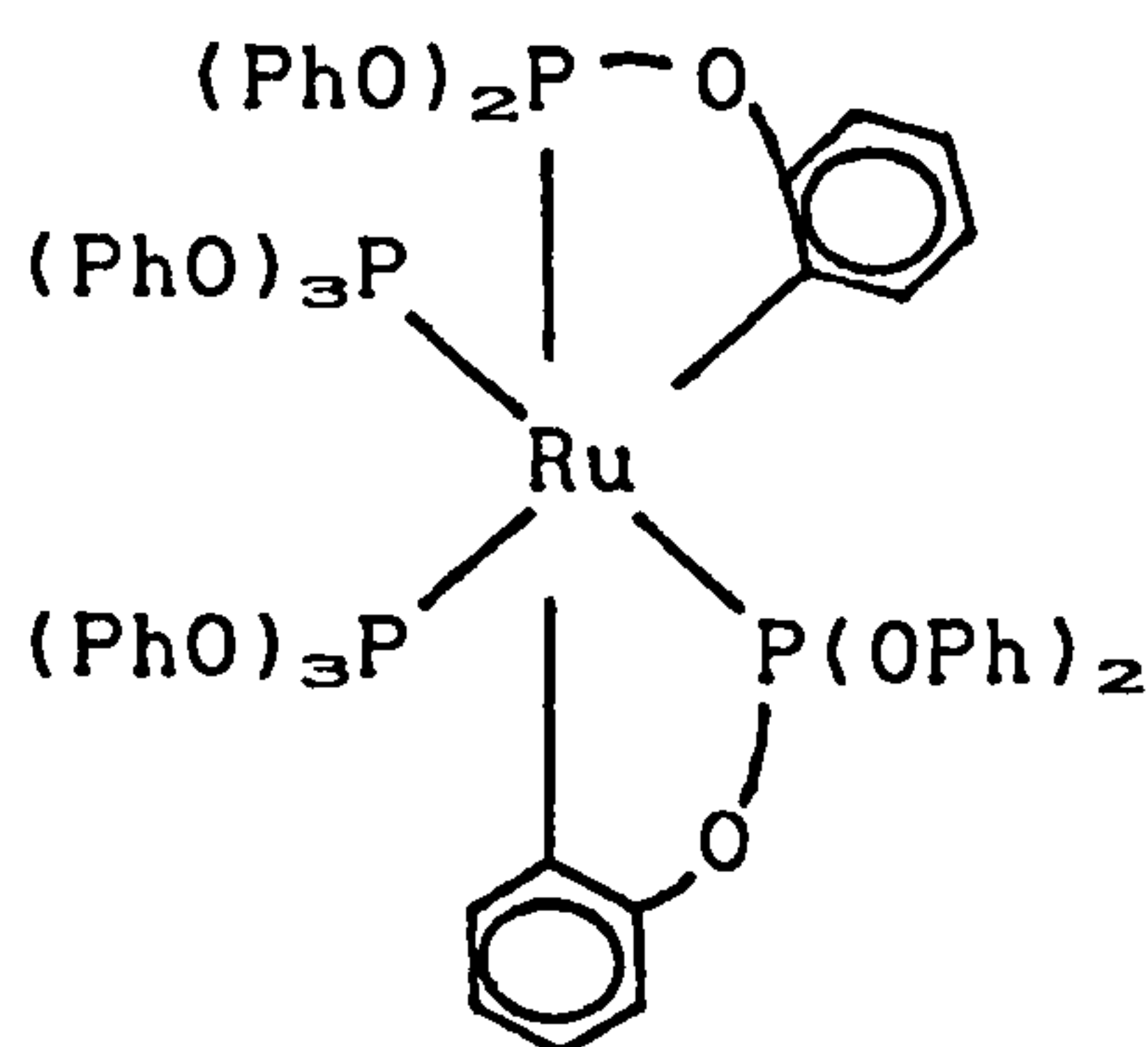
As can be seen from figure 3.7, the hydride signal is made up of 16 signals, or 8 doublets, as would be expected from this system. This confirms that the stereochemistry of the complex involves four non equivalent phosphorus environments.

However, if the reaction occurs at room temperature, or the above hydride complex is recrystallised at ambient temperatures, a different non arene complex is afforded. A white microcrystalline solid determined to be the bis orthometallated species was obtained.



The bis orthometallated species was characterised using 1H and ^{31}P nmr spectroscopy. FAB mass spectrometry showed the presence of the parent ion of the complex (1340 amu.) and an isotope pattern associated with the parent ion minus one triphenylphosphite ligand (1029). 1H nmr spectroscopy was used to determine that no hydride species was afforded, and that only proton signals assignable to phenyl groups were present. ^{31}P nmr spectroscopy was used to investigate whether the stereochemistry of the complex could be completely assigned.

The stereochemistry of the bis orthometallated species, determined from ^{31}P nmr spectra for the previous reactions was; ^{125.126}



This was confirmed more recently by X-ray crystal structure determination.¹²⁷ The complex was determined to have two aryl carbon ruthenium bonds, cis to each other.

However, it is possible to visualise a number of chemically different environments for the individual ligands of the bis orthometallated species. A selection of which are shown schematically below. (Fig3.9)

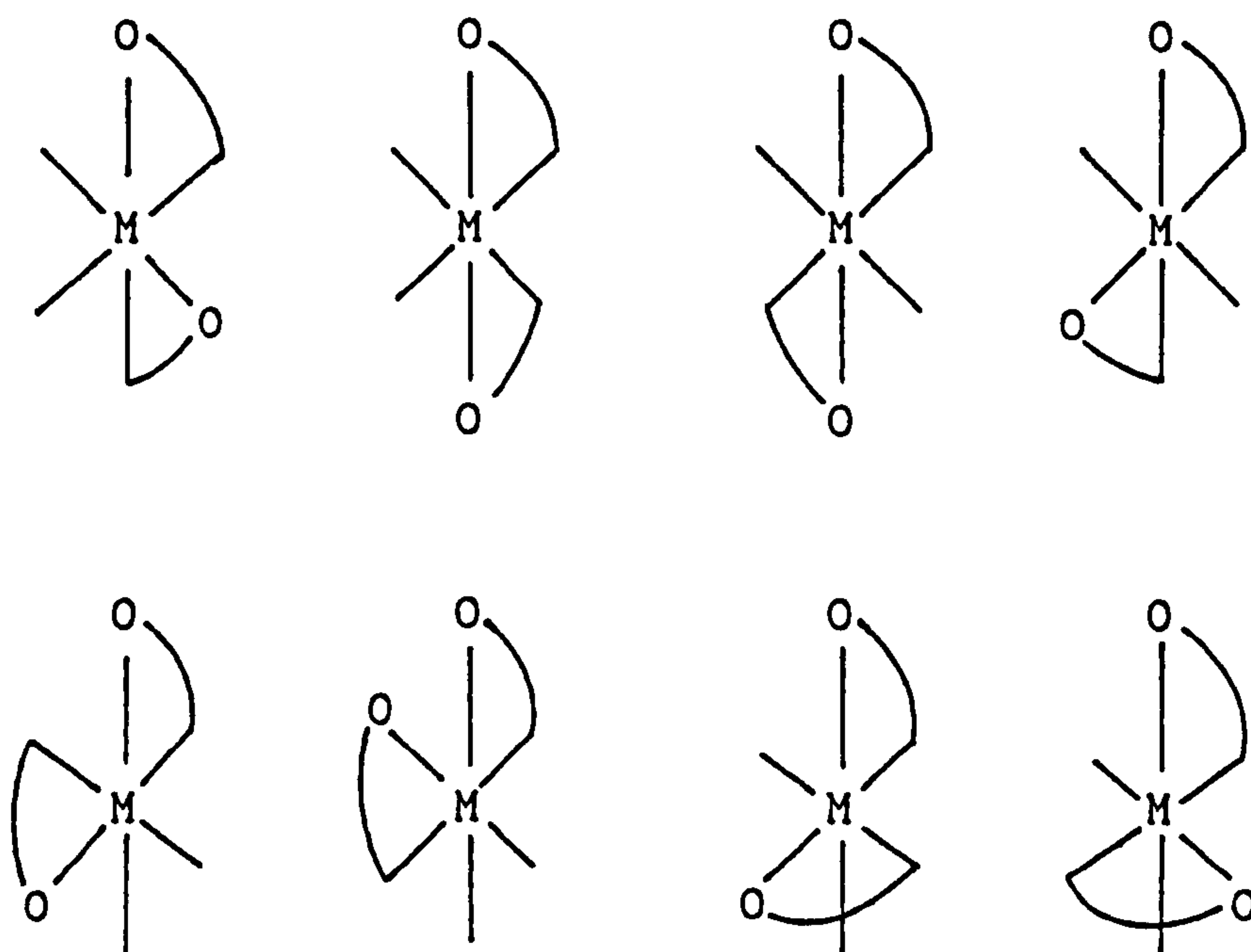
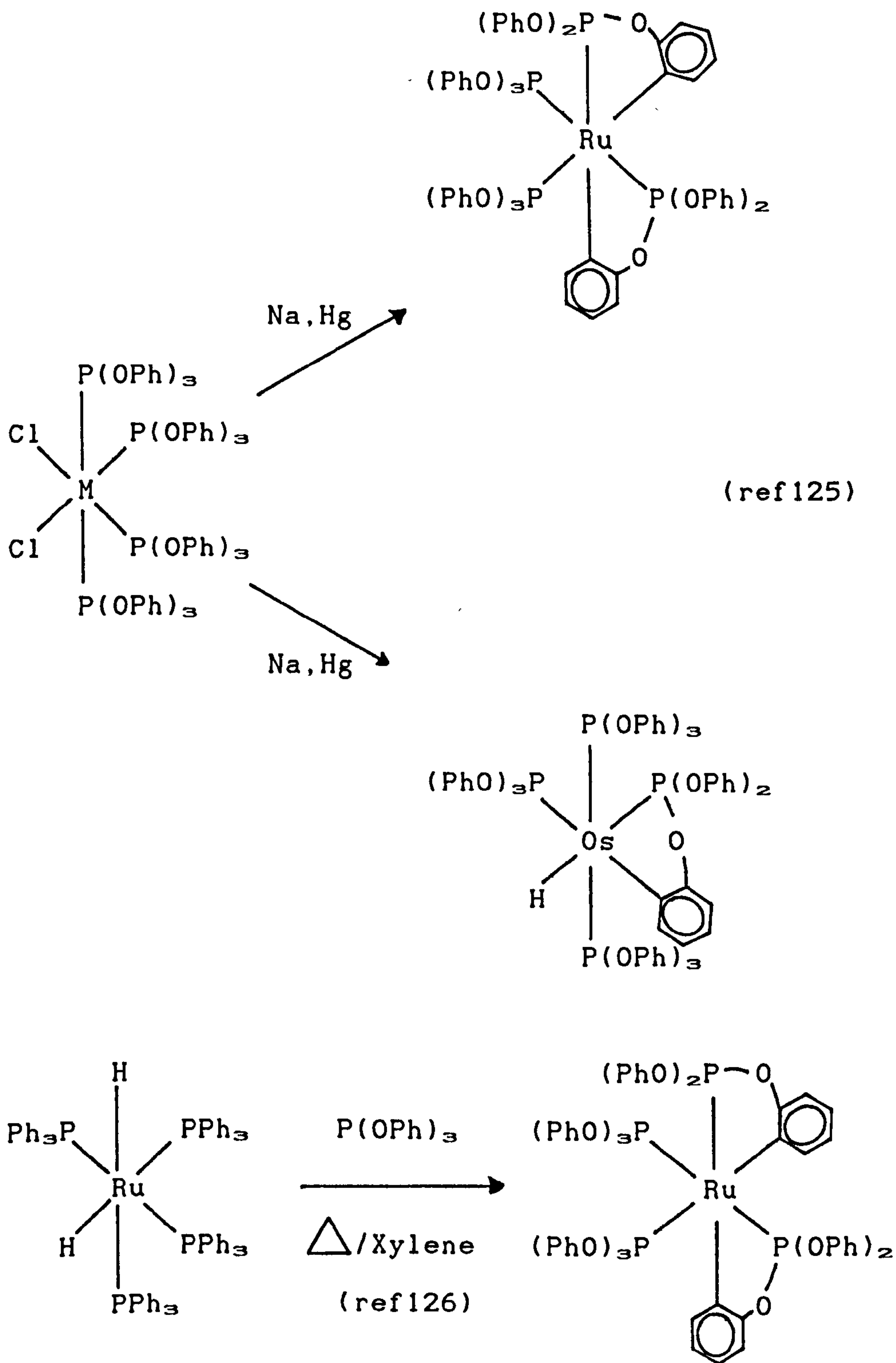


Fig.3.9 Some possible chemically different environments for $\overline{\text{Ru}[(\text{C}_6\text{H}_4\text{O})\text{P}(\text{OPh})_2]_2[\text{P}(\text{OPh})_3]_2}$

From the reaction conditions used, a mixture of isomers appears to have been afforded. Thus a complex ^{31}P nmr spectra was obtained. For convenience though, the complex will be drawn as by

previous workers.

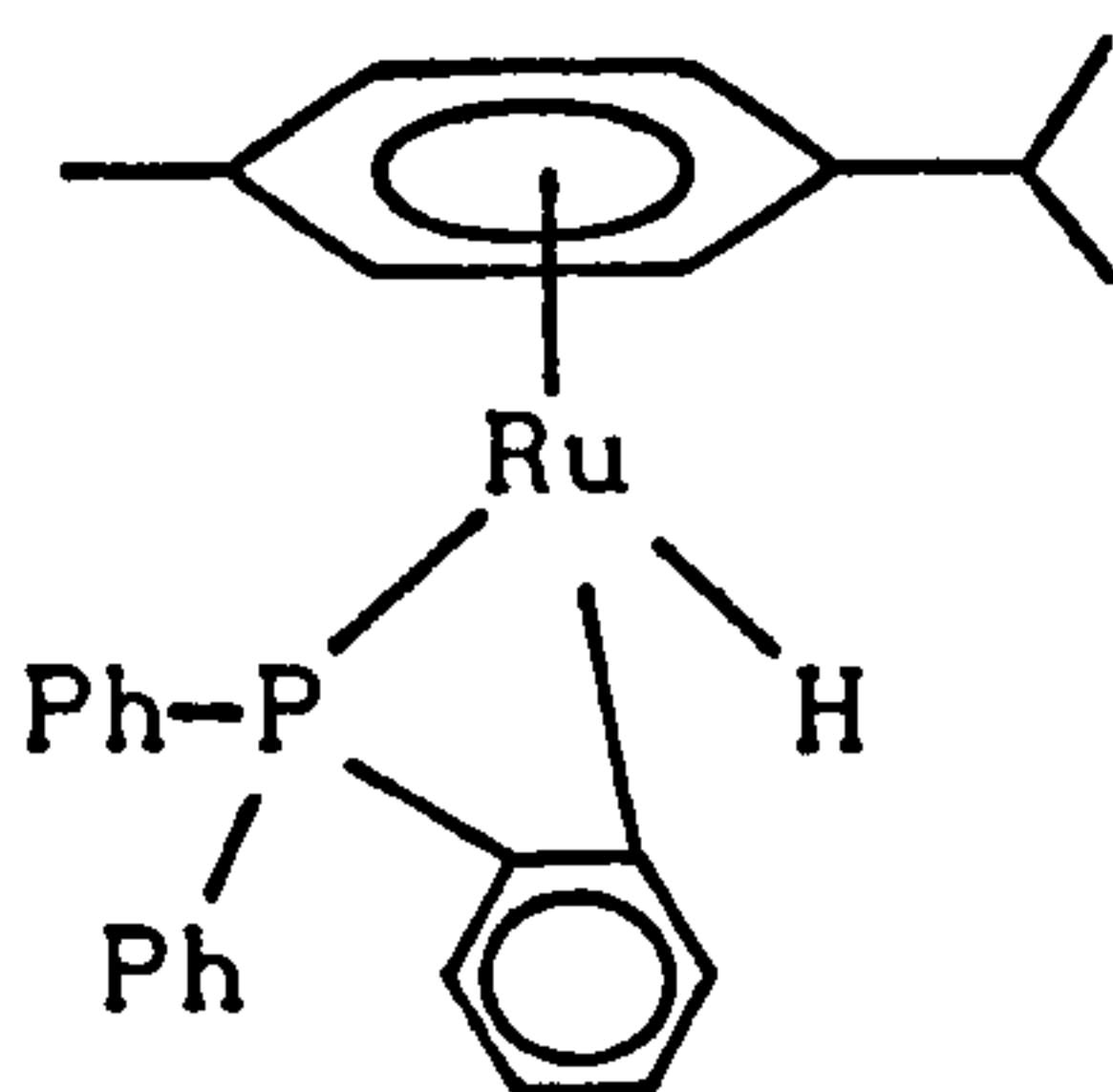
Related orthometallated complexes have previously been prepared, although the hydride species was afforded in a different stereochemical form.



3.2.3 Reaction with PPh₃

The product obtained from the reaction of PPh₃ with the tetrahydrofuran complex, unlike the P(OPh)₃ ligand reaction, had coordinated arene present. ¹H nmr spectroscopy inferred orthometallation had occurred. (A range of complex phenyl signals and a hydride doublet were present).

Initially, the simple product (shown below) was proposed.



However, on comparison of the ¹H nmr data of the above complex, to a fully characterised member of the orthometallated class, [(C₆Me₆)Ru(o-C₆H₄PPh₂)H]⁴²⁺, a large high field shift for the hydride signal was noted. The complex was confirmed as cationic in nature and afforded as a [PF₆]⁻ salt.

At present, full characterisation of the product from this reaction has not been achieved. However, the information obtained from various sources, allows a proposed structure to be put forward. This needs to be tested, by an X-ray

crystal structure determination at a later date.
(See table 3.1).

Table 3.1 Summary of the information known about
the product afforded from the PPh_3 reaction

Characterisation technique	Conclusion
^1H nmr spectros.	The presence of one hydride as a doublet, implies the complex has one phosphine ligand.
^{13}C nmr spectros.	Analysis of DEPT sequence implied one type of arene (cym), which was not free rotating.
FAB mass spectros.	Dimeric structure implied with isotope patterns for structures with molecular weight > 600 amu.
IR spectros.	Presence of $[\text{PF}_6]^-$ counteranion confirms cationic nature.
Microanalysis.	C 43.21 ; H 4.46%.

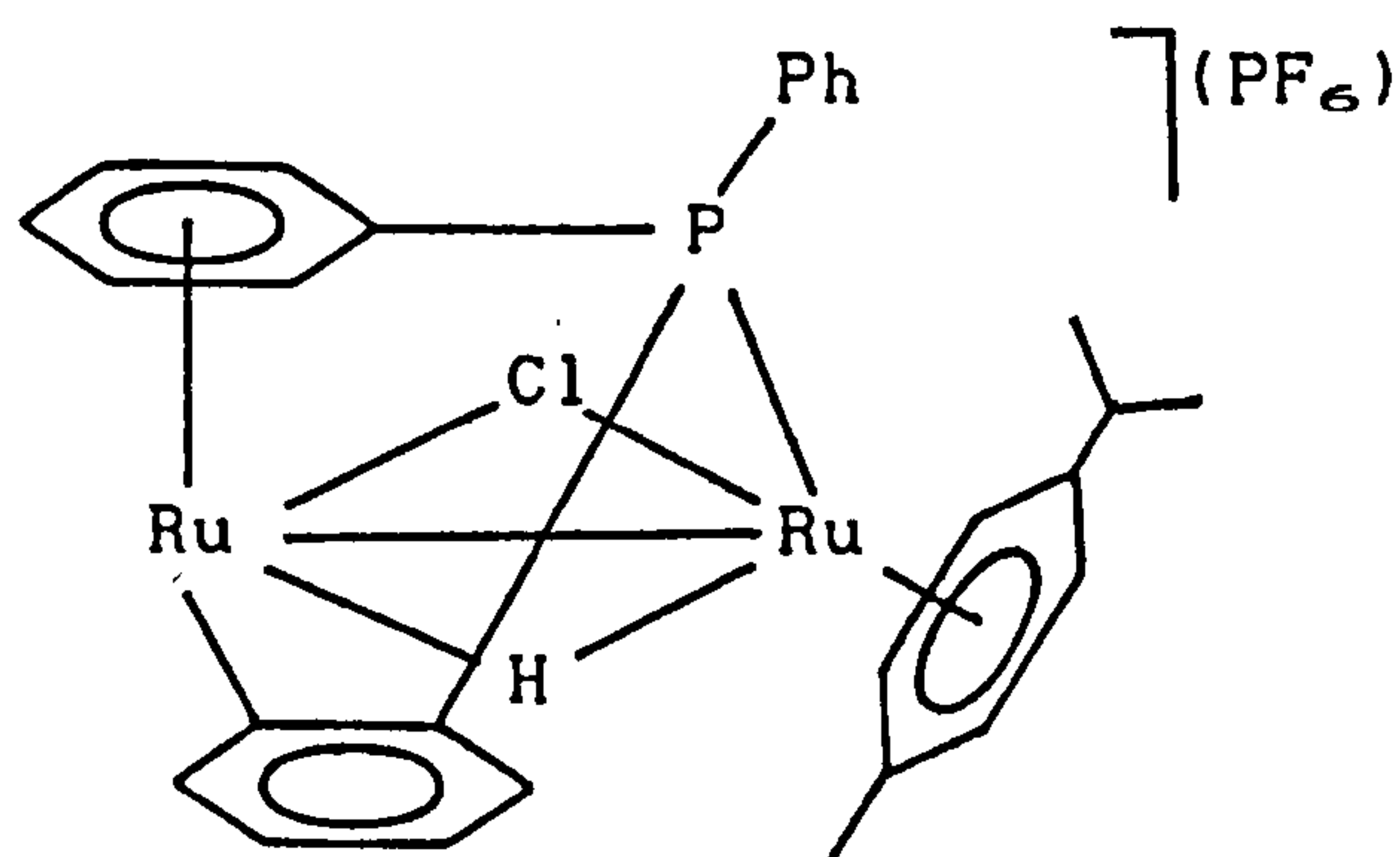


Fig.3.10 Proposed structure of product from the PPh_3 reaction.

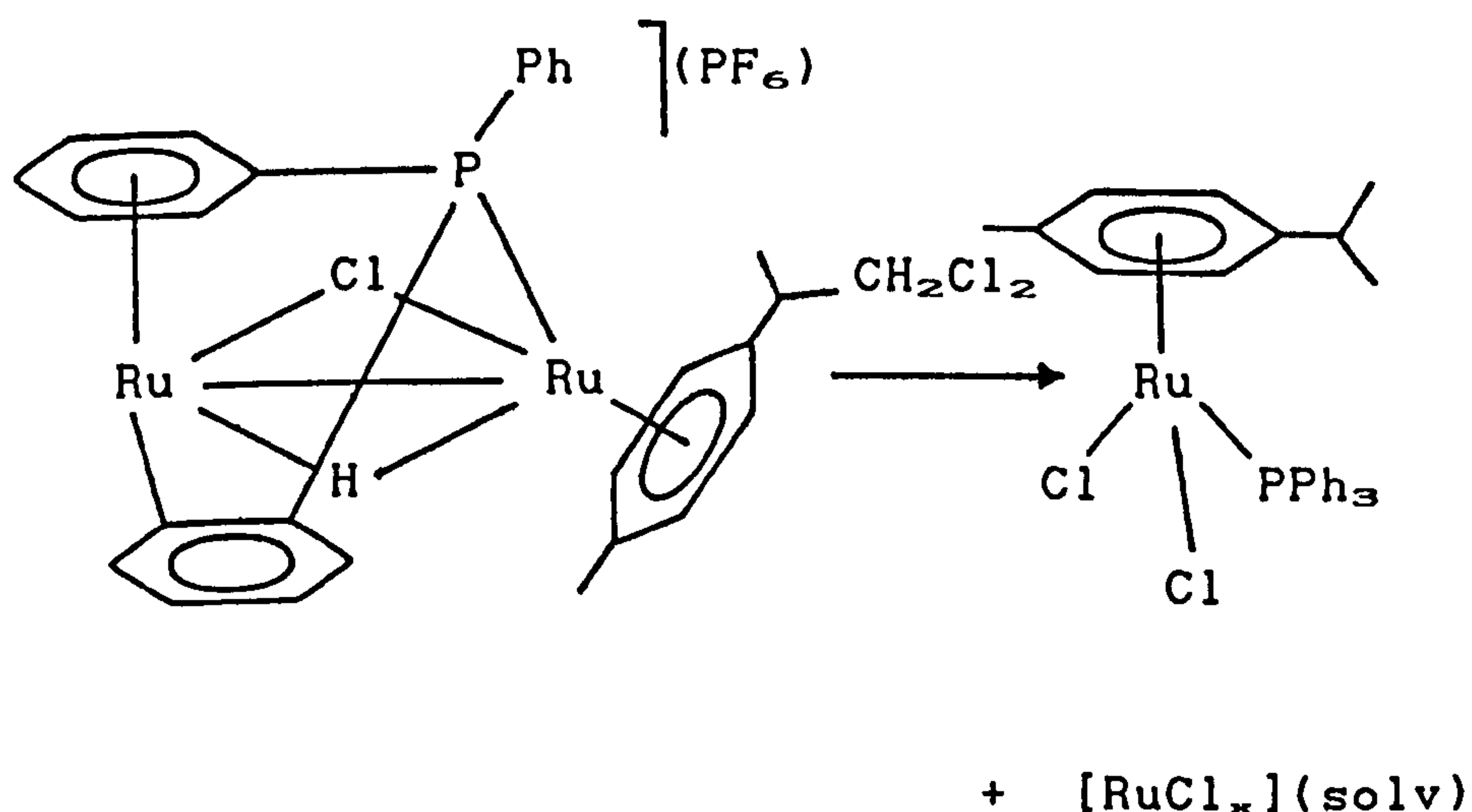
FAB mass spectrometry indicates the presence of the molecular ion (633amu), the structure is cationic, and microanalysis shows agreement (Found, C 43.19: H 3.73%). ^1H nmr and ^{13}C nmr spectra imply one type of arene present. Referring to the characterisation of the novel bis(arene) complex $[(\text{C}_6\text{Me}_6)\text{Ru}(\eta^6\text{C}_6\text{H}_5)\text{PPh}_2]^2+$, the eta 6 phenyl group was determined to have signals at low field, with respect to arene protons ($\delta = 6.52, \text{m}, (2\text{H})$ and $7.07, \text{m}, (3\text{H})$).⁷⁸ These signals would thus fall within the accepted orthometallated region (8.1 to 6.7)⁴². It can be assumed that if the structure has a similar eta 6 phenyl structure, that ^1H nmr and ^{13}C nmr spectroscopy would indicate the presence of one coordinated arene (cymene), and a complex phenyl region. All this is so.

Assuming the structure of the complex is that drawn in figure 3.10, the yield of pure crystalline product is relatively good (37%), considering the

reaction product is afforded via two major steps. Firstly the preparation of the tetrahydrofuran complex is unlikely to be quantitative and the major workup step is dissolving the phosphine product in water before obtaining the $[\text{PF}_6]^-$ salt.

3.2.3.1 Reactivity of the PPh_3 complex

When the proposed cationic complex is stirred in a chlorinated solvent, the robust cymene ruthenium dichloro triphenylphosphine complex was generated. Simple rearrangement of the proposed reaction product, in the presence of chloride ions, could explain the generation of the half sandwich mononuclear species.

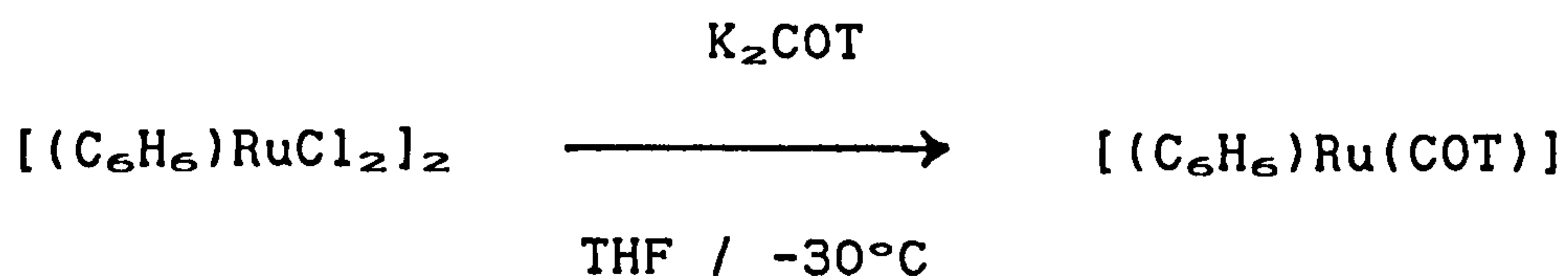


$(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2\text{PPh}_3$ was characterised by comparison to spectroscopic data of a genuine sample.

3.3 Structure of arene ruthenium moiety complexes of chapter 2 and 3

From the reaction studies of the tetrahydrofuran complex and the successful synthesis of the bis(ethylene) complexes, but not alternative olefin complexes (chapter 2), further assumptions of the arene ruthenium moiety may be postulated.

As reported in chapter 2, the reaction conditions utilised yielded the simple ethylene derivatives but not other olefinic alternatives, although relatively similar reaction conditions afford the benzene ruthenium (η^4 cyclooctatetraene) complex;⁵⁶



This could be due to a number of factors. The nucleophilicity of the cyclooctatetraene ligand in the above reaction may be the driving force and overcome any steric hindrance that occurs. Whereas the conditions that generate the ethylene complex may have steric hindrance about the ruthenium metal centre that the neutral cyclooctatetraene, cyclooctadiene and cyclohexadiene ligands cannot overcome.

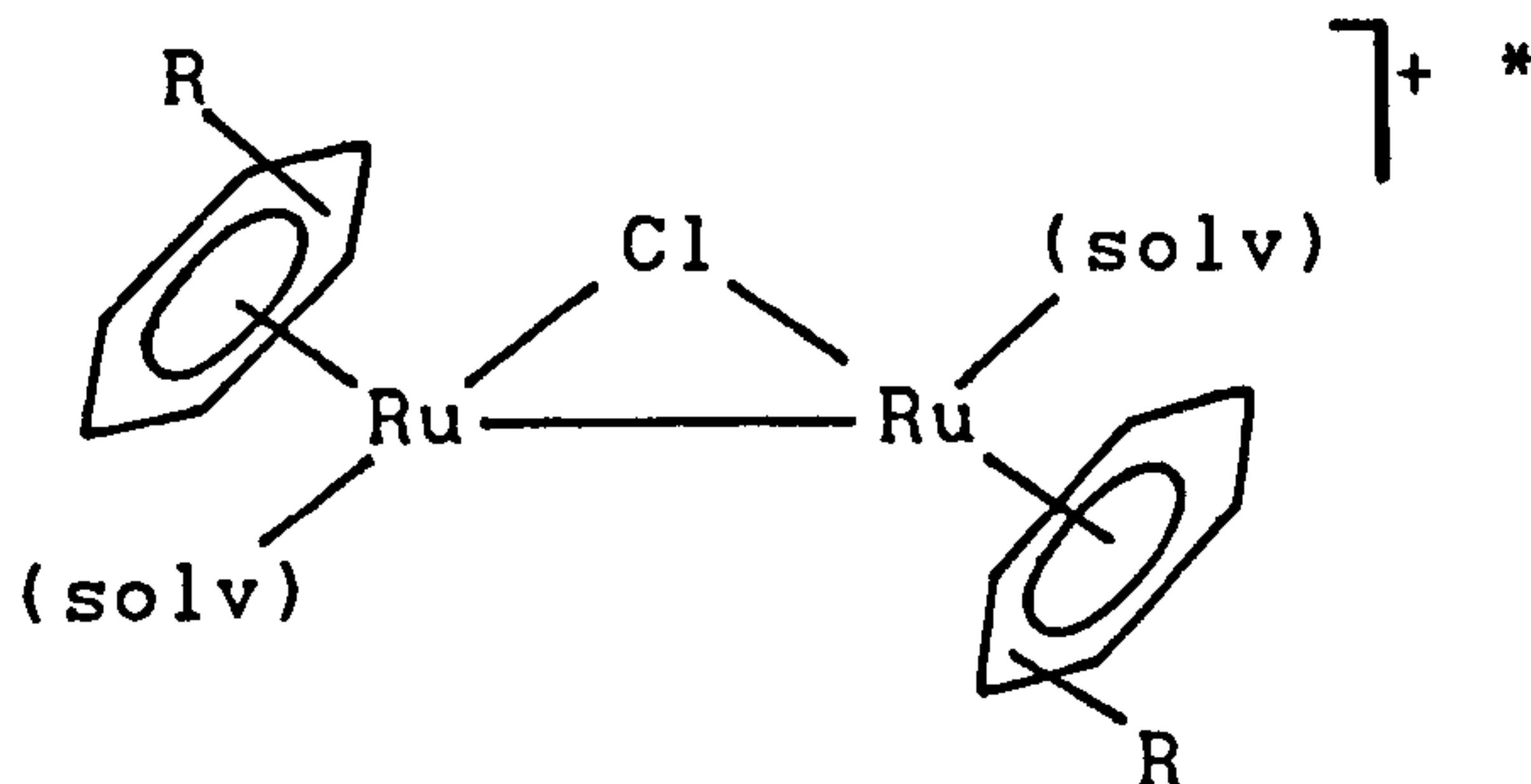
It is postulated that the arene ruthenium moiety is not a simple solvated substrate and that steric hindrance to the ruthenium coordination sphere would explain why ethylene can coordinate whilst cyclooctatetraene, cyclooctadiene and cyclohexadiene cannot.

The reaction of the tetrahydrofuran complex with allyl bromide and triphenylphosphite, imply that the intermediate is a source of Ru(0). Although the preparation of the tetrahydrofuran complex was not quantitative, the yield of the respective products were not ideal. Isolation problems could explain this, but the proposal that the intermediate may also have a Ru(II) centre could help explain the moderate yields obtained.

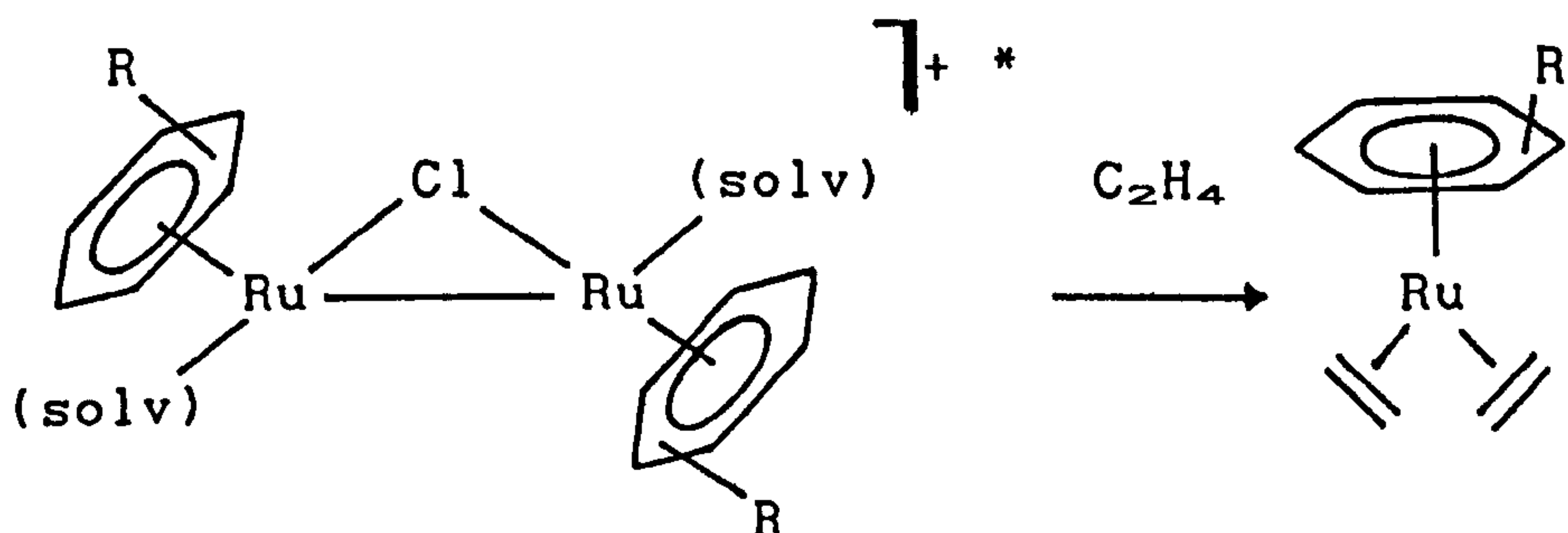
The proposed reaction product from the reaction of the tetrahydrofuran complex with triphenylphosphine gives support to a complicated structure for the arene ruthenium moieties. The reaction product was reproducibly formed and appears to contain a bridging chloride between two ruthenium metal centres. This chloride bond can be assumed to be present in the arene ruthenium moiety complex structures. Solvation appears to play an important role, as the reactive intermediate can only be obtained and used in situ when tetrahydrofuran is present. Relative solvation strengths should be noted, reaction of the

tetrahydrofuran complex with ethylene did not afford the bis(ethylene) complexes.

It is postulated, that the arene ruthenium moiety complexes can be considered to be dimeric, solvated, chloride bridged and possibly cationic.

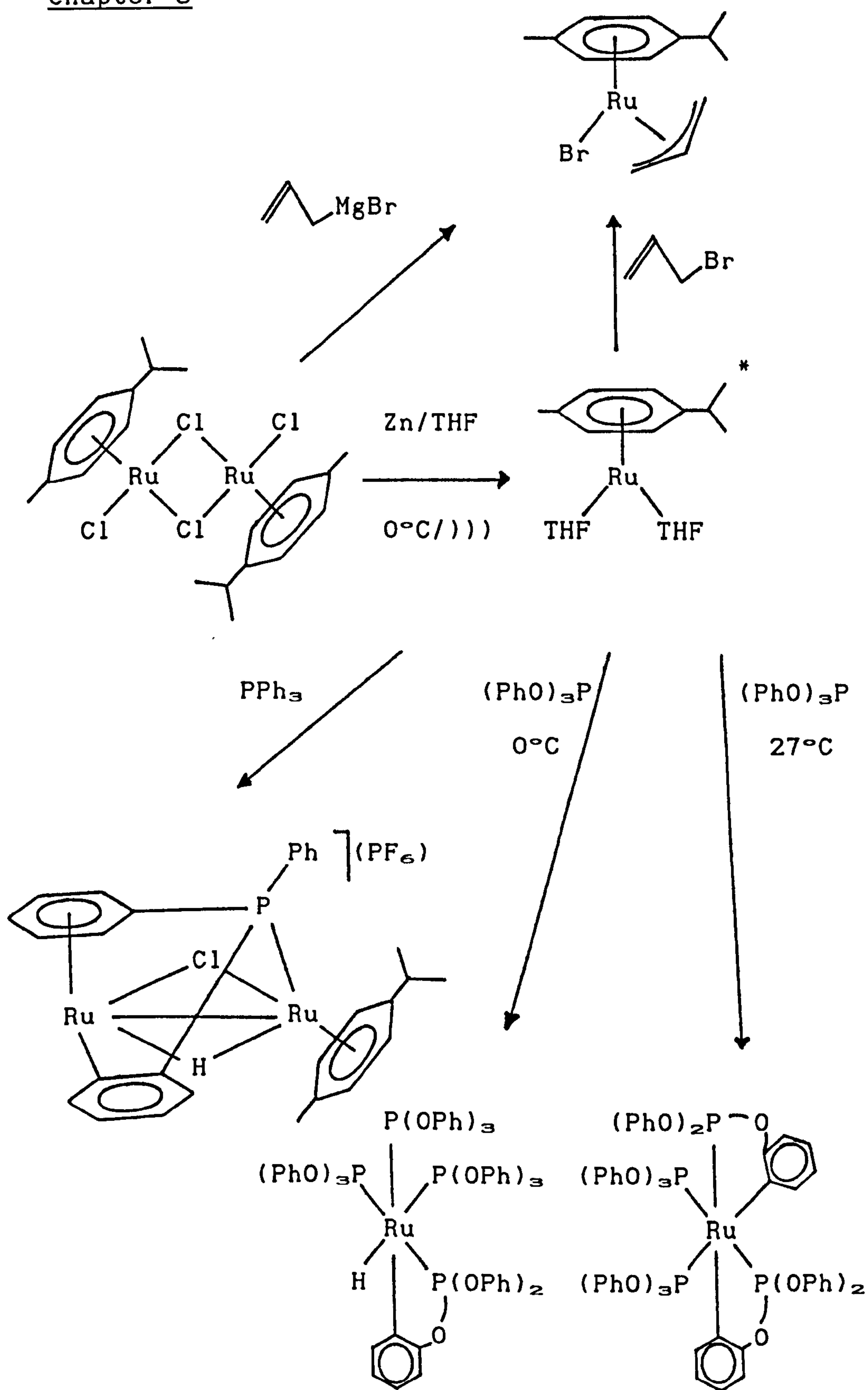


For the ethylene reactions, CH_2Cl_2 is a poor solvent, ethylene readily enters the coordination sphere and further ethylene reacts to afford the arene ruthenium bis(ethylene) complexes.



However, if the solvent is tetrahydrofuran, the "dimer" is less susceptible to ethylene attack and formation of the desired complex.

3.4 Reaction scheme of complexes prepared in chapter 3



3.5 Experimental

Preparation of $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{Ru}(\text{THF})_2]^*$

The reaction vessel utilised in the preparation of the above complex, depends upon the source of ultrasound. The same set up as for the arene ruthenium bis(ethylene) complexes (chapter 2) can be used. However, a simple sonic bath can be the sonic source and a Schlenk tube the reaction vessel.

$[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2$ (250mg;0.4mmol), zinc (500mg;7.6mmol) and THF (40ml) were placed in the reaction vessel (See appendix Fig. 5) under an inert atmosphere (N_2), cooled (0°C) and sonics applied (4 hours). The intense purple solution was allowed to stand (15 mins.), cannulated away from the unreacted zinc into a Schlenk tube and used in situ.

Preparation of $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{Ru}(\text{C}_3\text{H}_5)\text{Br}]$

Allylbromide (145mg;0.1ml;1.2mmol) was added to a previously prepared solution containing $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{Ru}(\text{THF})_2]$ (see above) and stirred (4 hours, 27°C). The reaction mixture was taken to dryness, redissolved in chloroform, any solid remaining was filtered away from the mother liquor

and the filtrate taken to dryness. The deep red brown oil afforded could not be obtained in a crystalline form, but was pumped upon to remove any tetrahydrofuran or excess allyl bromide present. Yield (64mg;22%).

Characterisation. ^1H nmr (see section 3.2.1). FAB mass spectrometry shows the fragmentation isotope pattern for $[\text{Ru}(\text{C}_3\text{H}_5)\text{Br}]^+$ (224amu).

Preparation of $\text{HRu}[(\text{C}_6\text{H}_4\text{O})\text{P}(\text{OPh})_2][\text{P}(\text{OPh})_3]_3$

Triphenylphosphite (1.24g;1.0ml;4.0mmol) was added to a previously prepared solution containing $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{Ru}(\text{THF})_2]$ (see above) and stirred (4 hours, 0°C). The reaction mixture was taken to dryness. A slight impurity of arene containing species was present (<10%) which could not be removed without the conversion of the mono orthometallated to the bis orthometallated species. Yield (290mg;27%).

Characterisation. See section 3.2.2 for specific assignment. ^1H nmr. (CDCl_3), $\delta = 7.5-6.5$, (m, 59H, phenyl), -8.42 (m, 1H, Ru-H). $^{31}\text{P}\{-^1\text{H}\}$ nmr. (CDCl_3), 162.6, 138.2, 137.4, 125.8ppm, $J_{\text{P-Ptrans}}$ 630Hz, $J_{\text{P-Pcis}}$ 51, 50, 43, 41Hz.

Preparation of $\text{Ru}[(\text{C}_6\text{H}_4\text{O})\text{P}(\text{OPh})_2]_2[\text{P}(\text{OPh})_3]_2$

Triphenylphosphite (2.48g; 2.0ml; 8.0ml) was added to a previously prepared solution containing $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{Ru}(\text{THF})_2]$ (see above) and stirred (4 hours, 27°C). The reaction mixture was taken to dryness and abstracted into ether. The ether soluble fraction was reduced in volume and on addition of pentane a buff white solid was afforded. Yield (514mg; 48%).

Characterisation. See section 3.2.2 for ^1H and ^{31}P nmr spectroscopic evidence. FAB mass spectrometry confirmed the presence of the parent ion $\text{Ru}[(\text{C}_6\text{H}_4\text{O})\text{P}(\text{OPh})_2]_2[\text{P}(\text{OPh})_3]_2^+$ (1340amu) and a fragmentation pattern related to a species with the loss of one triphenylphosphite ligand (1029amu).

Preparation of $(\text{cym})\text{Ru}(\mu\text{H})(\mu\text{Cl})\text{PPh}(\text{C}_6\text{H}_4)(\text{C}_6\text{H}_5)\text{Ru}$

PPh_3 (536mg; 2.0ml) was added to a previously prepared solution containing $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{Ru}(\text{THF})_2]$ (see above) and stirred (4 hours, 27°C). The reaction mixture was reduced in volume (5ml) and a pale purple solid crashed out with hexane. The product was purified by dissolving the solid in water, filtering off the insoluble matter, bringing out a light purple floccular solid on addition of NH_4PF_6 (aq) and recrystallising this

solid from acetone and ether. Yield. (115mg;37%).

Characterisation. See section 3.2.3.

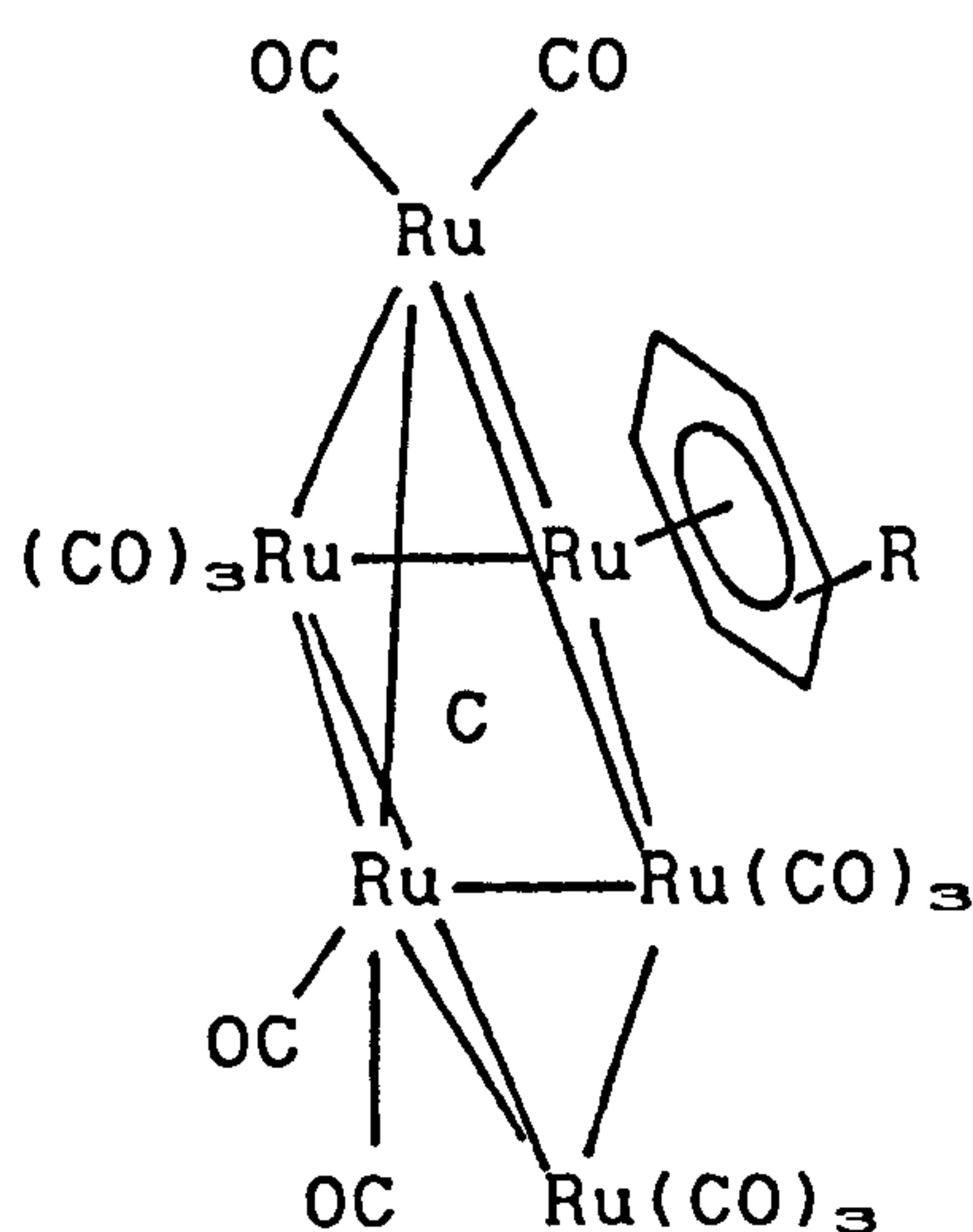
CHAPTER FOUR

Chapter 4.

4.1 Ruthenium clusters

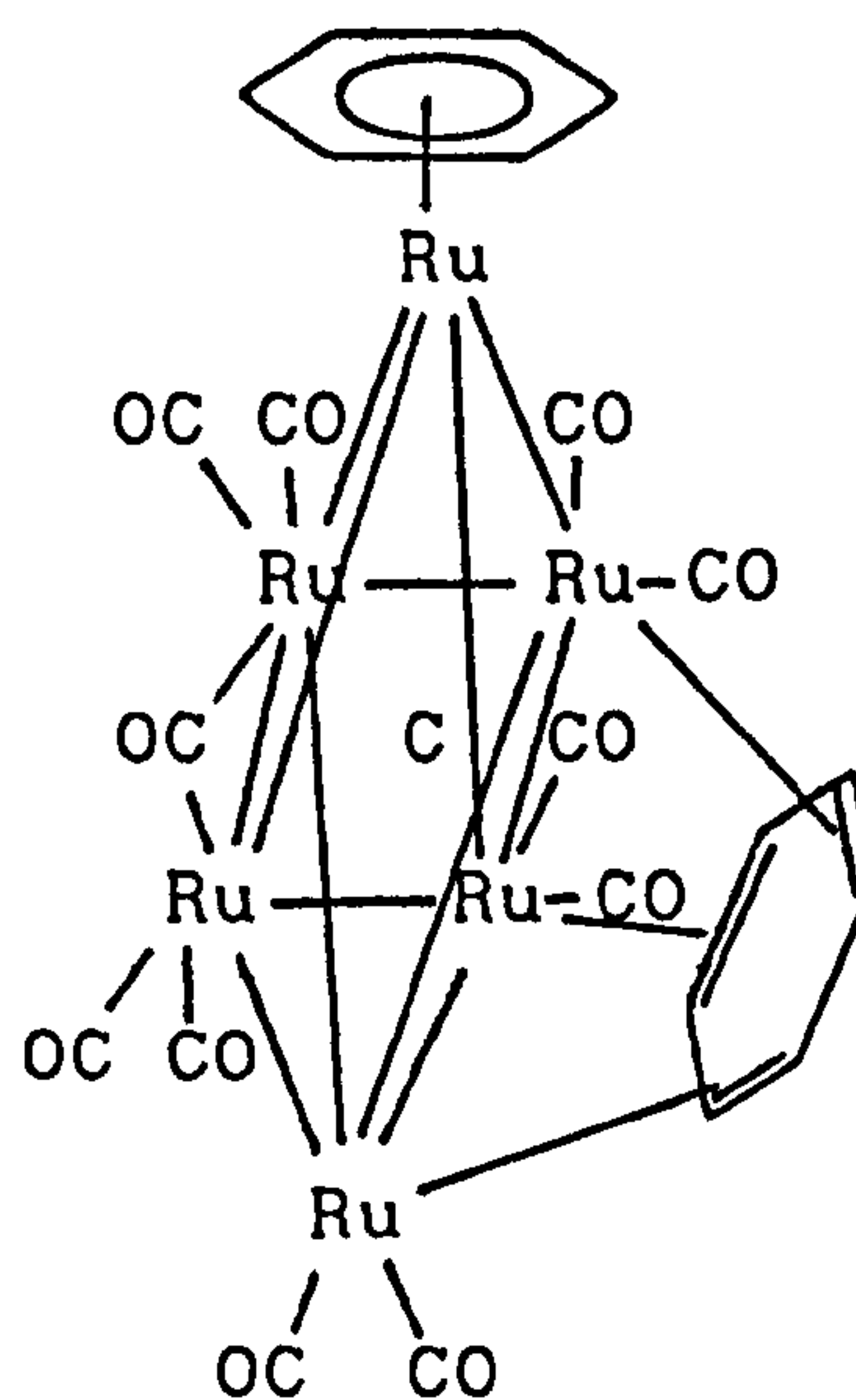
4.1.1 Cluster reactions utilizing simple arene ruthenium derivatives

The aim of the work carried out was to form electron rich arene ruthenium clusters from simple substrates. Before work commenced, no arene ruthenium clusters had been reported, although a few mixed arene ruthenium carbonyl clusters were known.

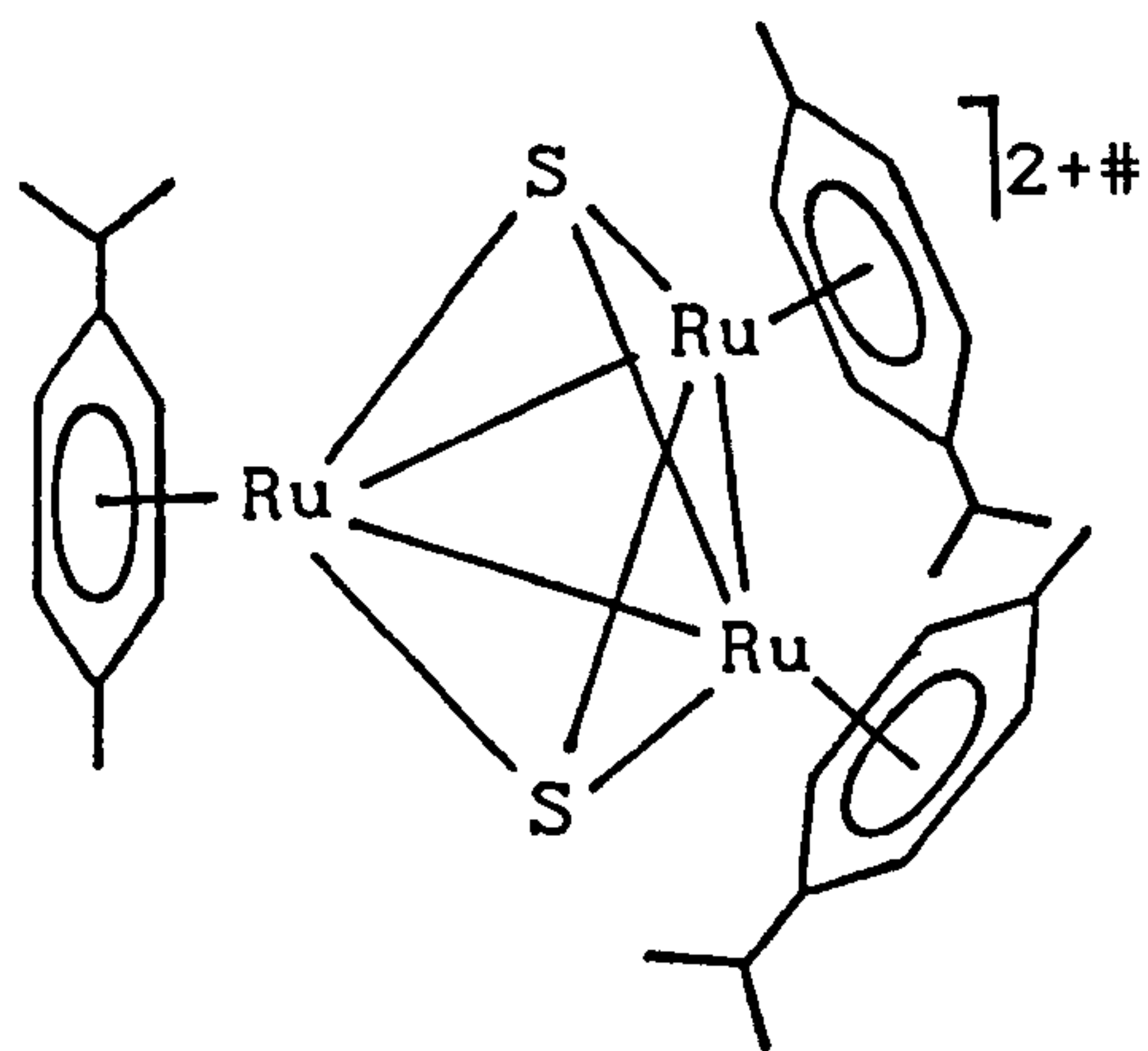


$C_6H_nR_n = C_6H_6$, (ref 128)

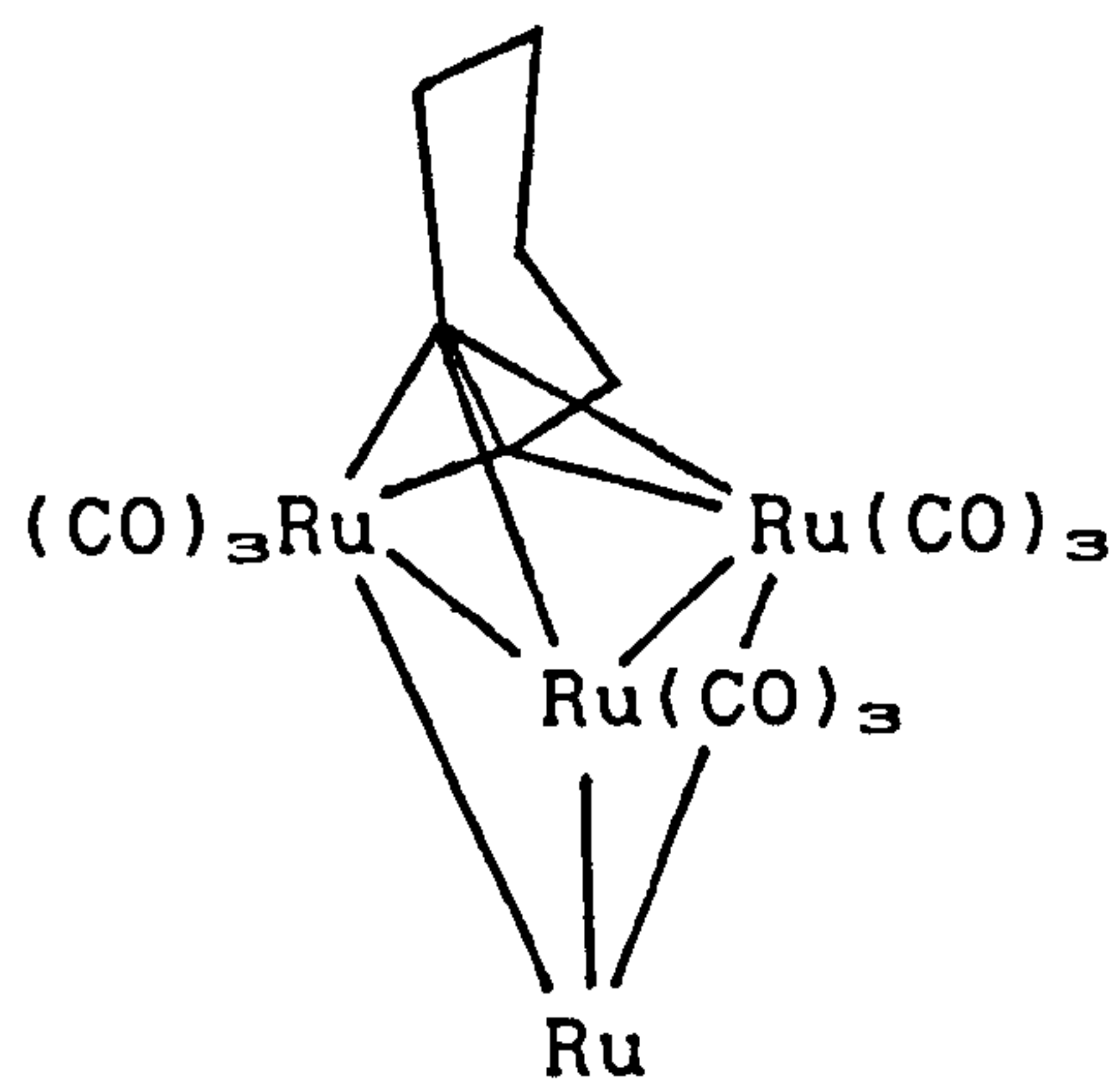
MeC_6H_5 , (ref 129)



(ref 130)



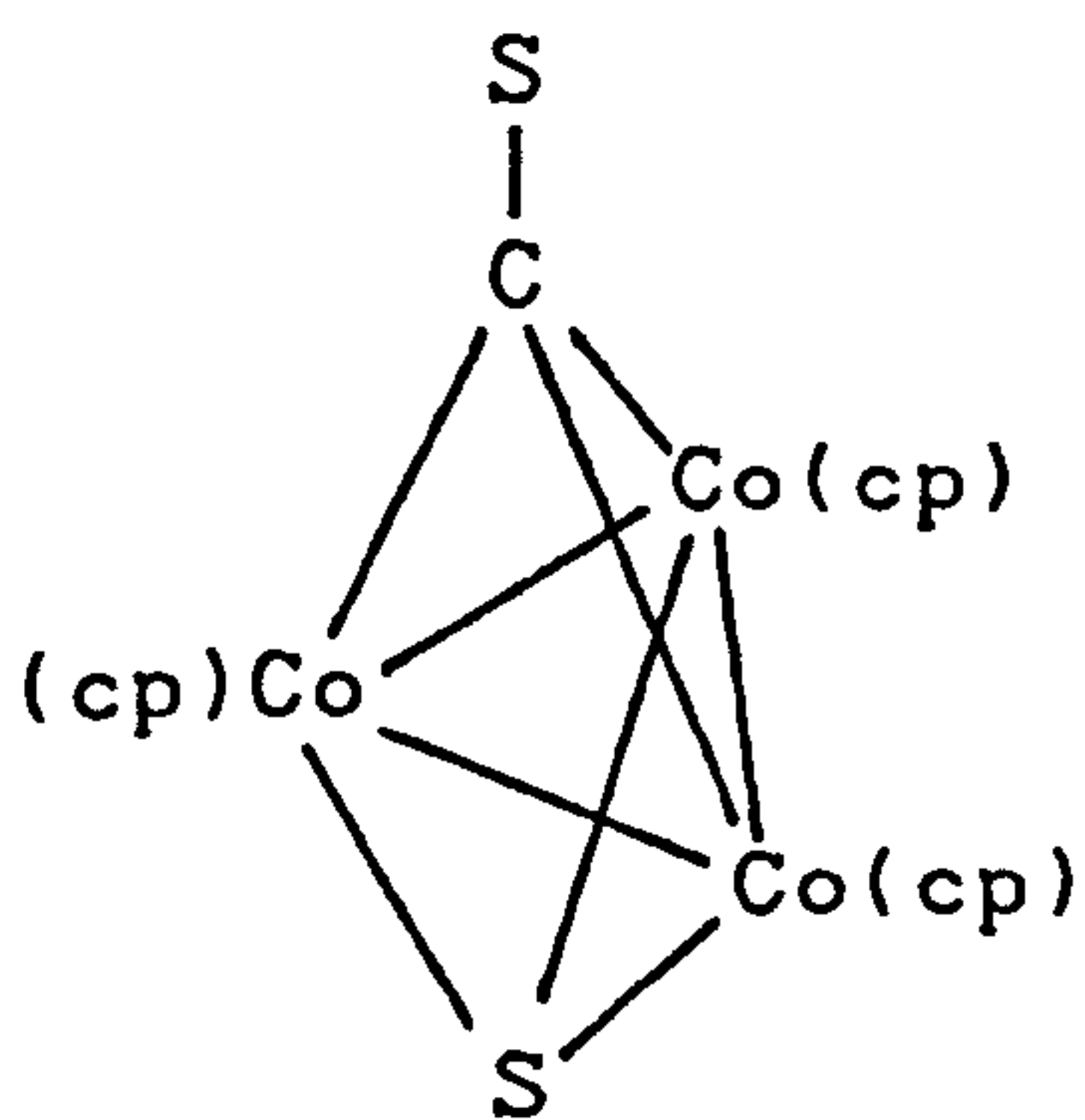
(ref131)



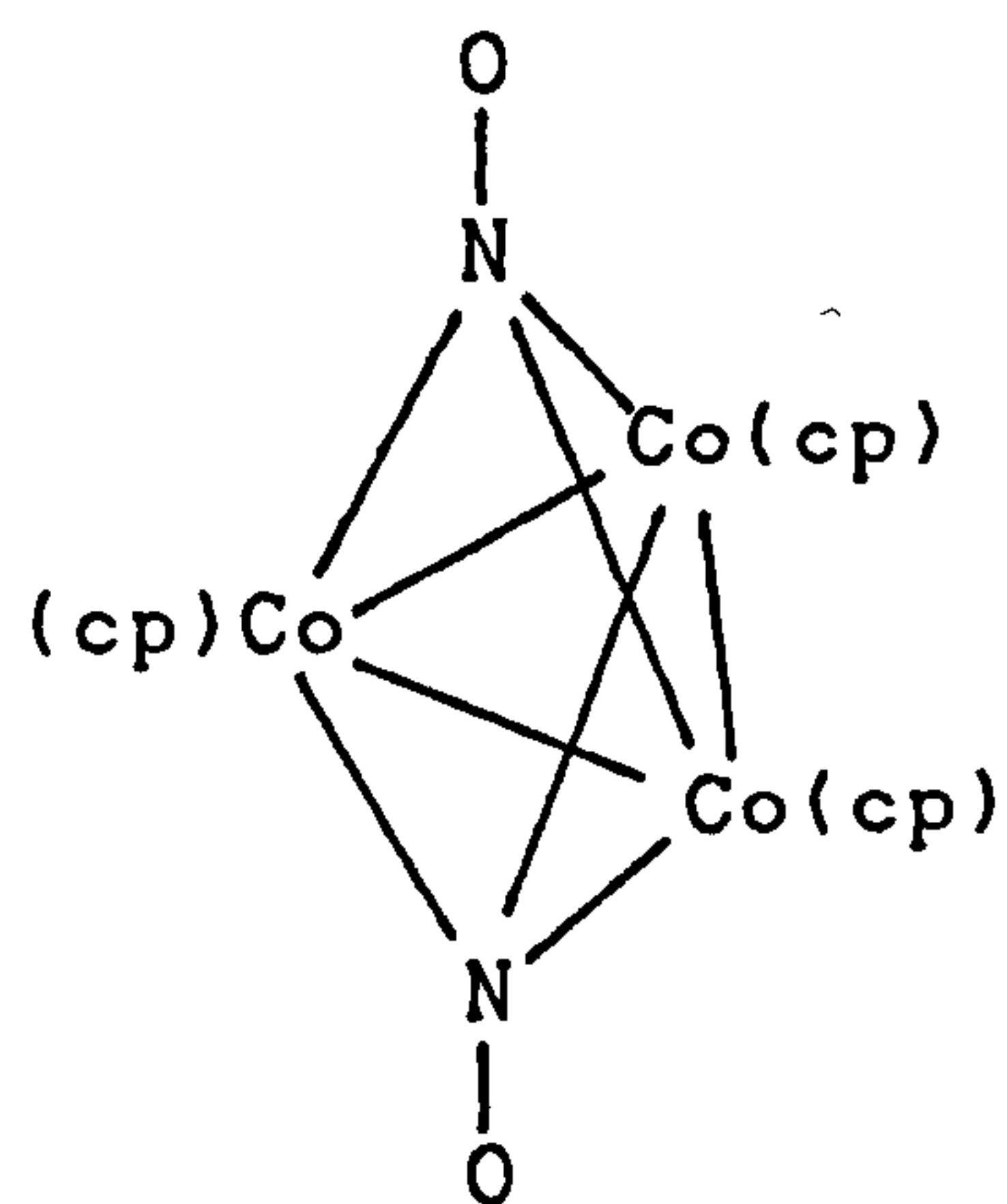
reported whilst working on
ruthenium clusters.

(ref132)

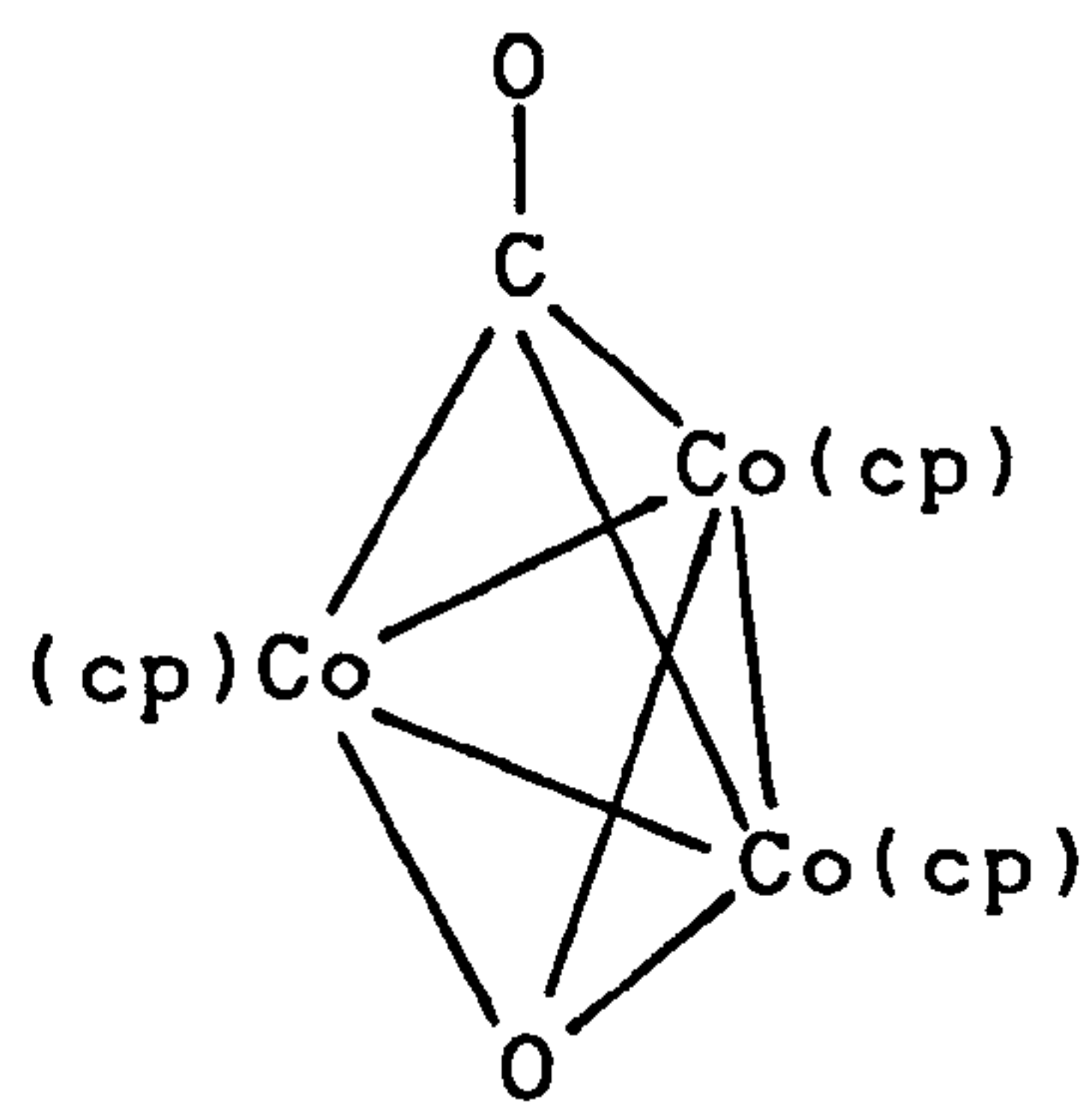
In comparison to these few examples, the Cp_nM_n
clusters are relatively numerous.



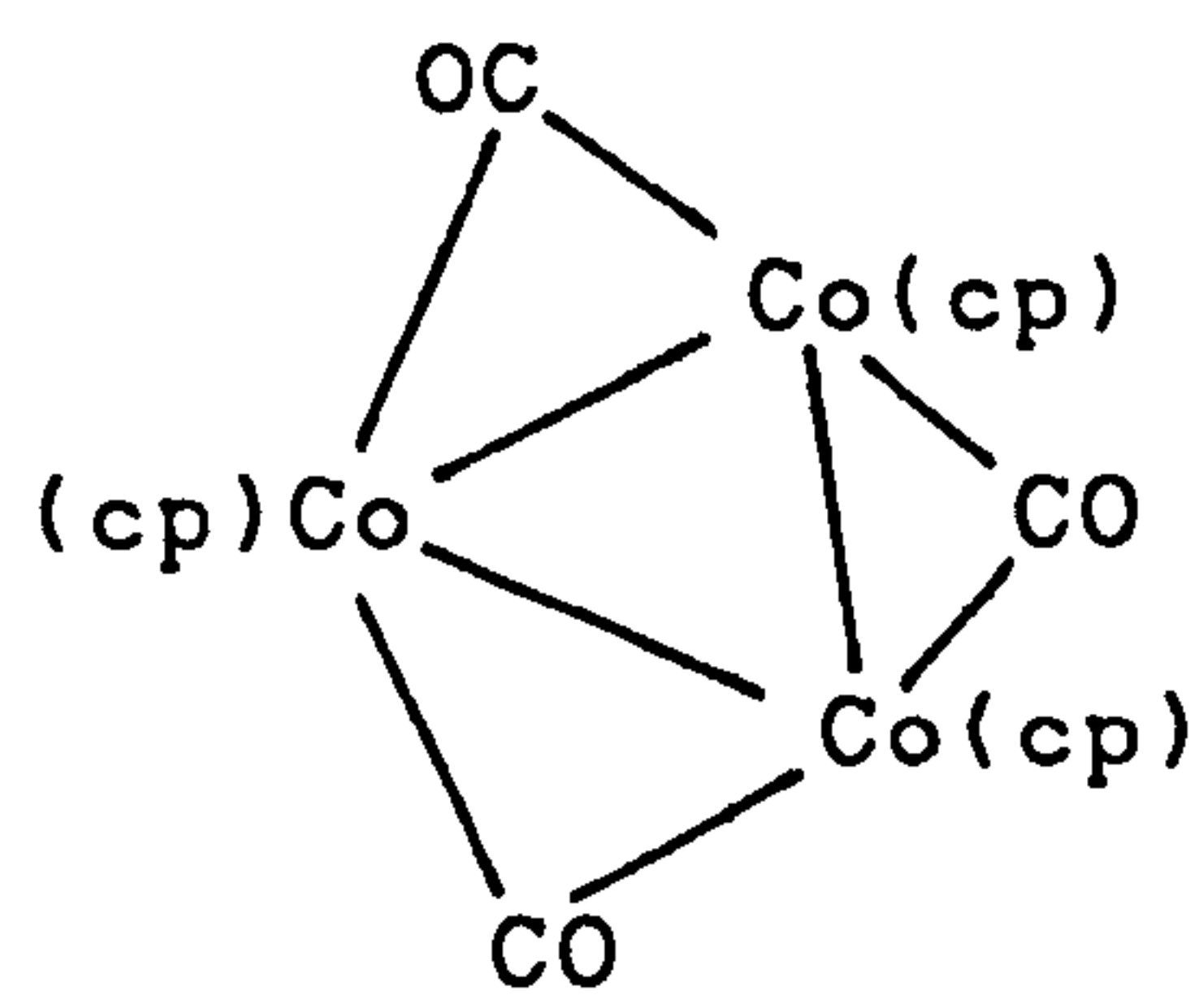
(ref133)



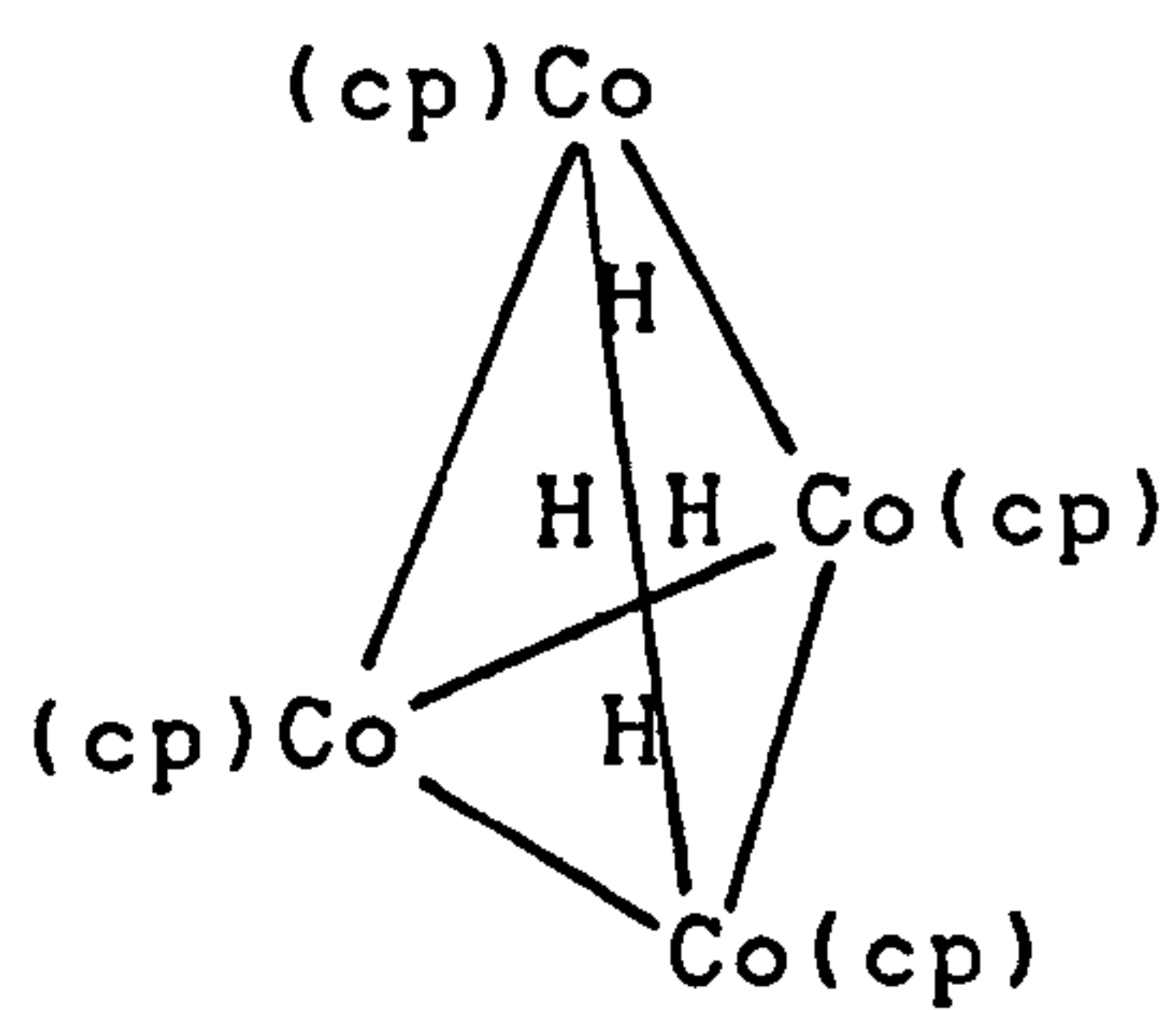
(ref134)



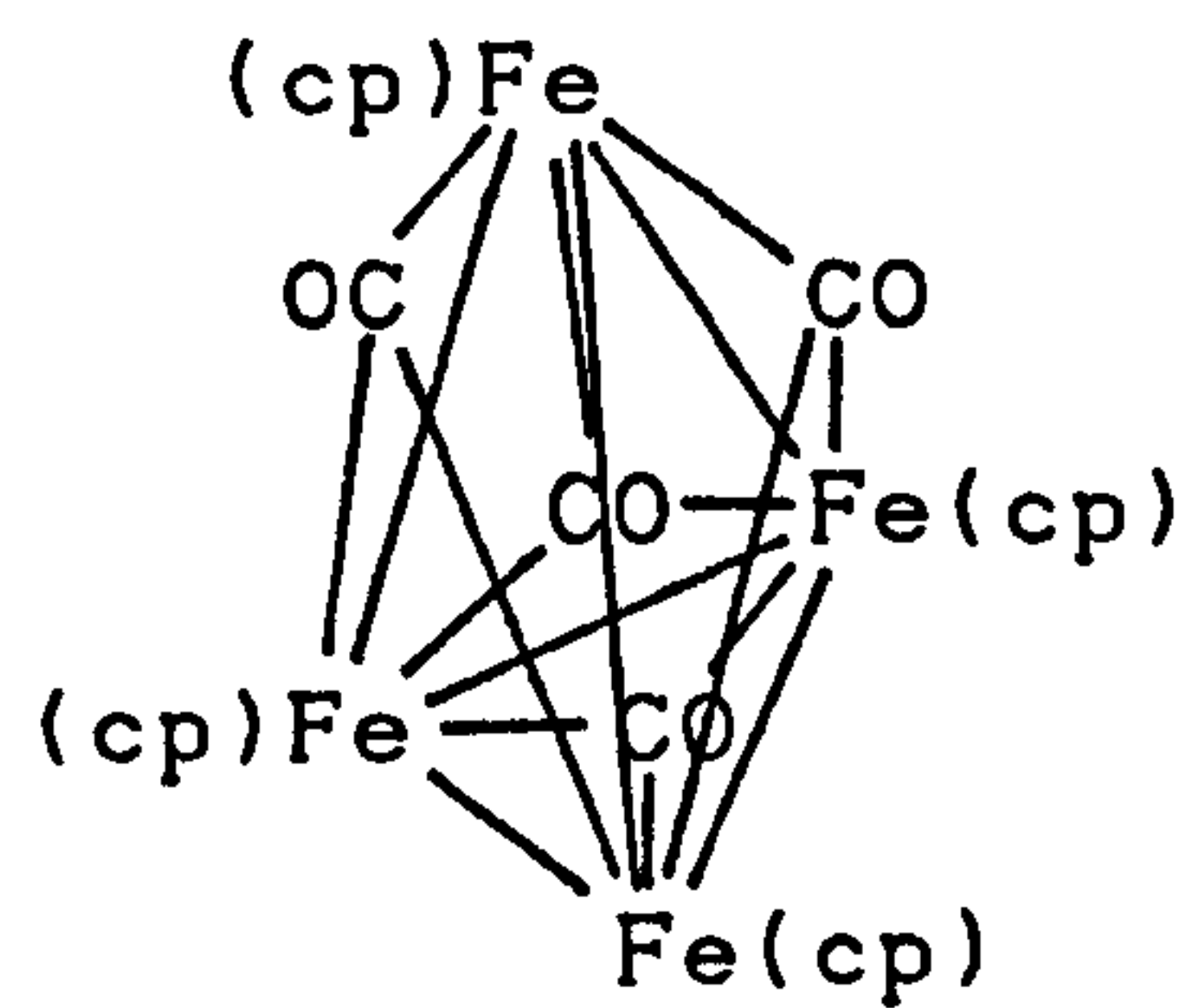
(ref 135)



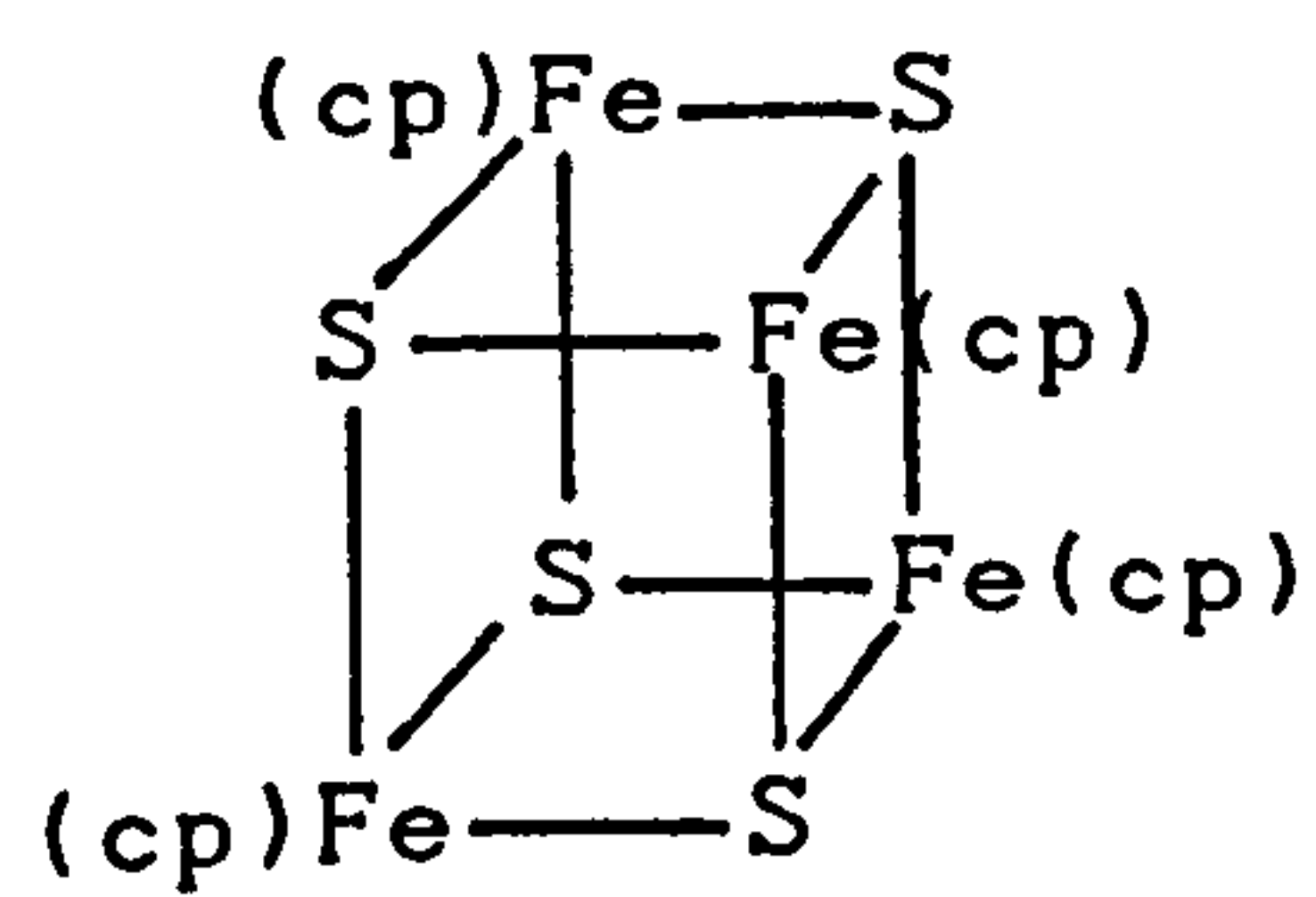
(ref 136)



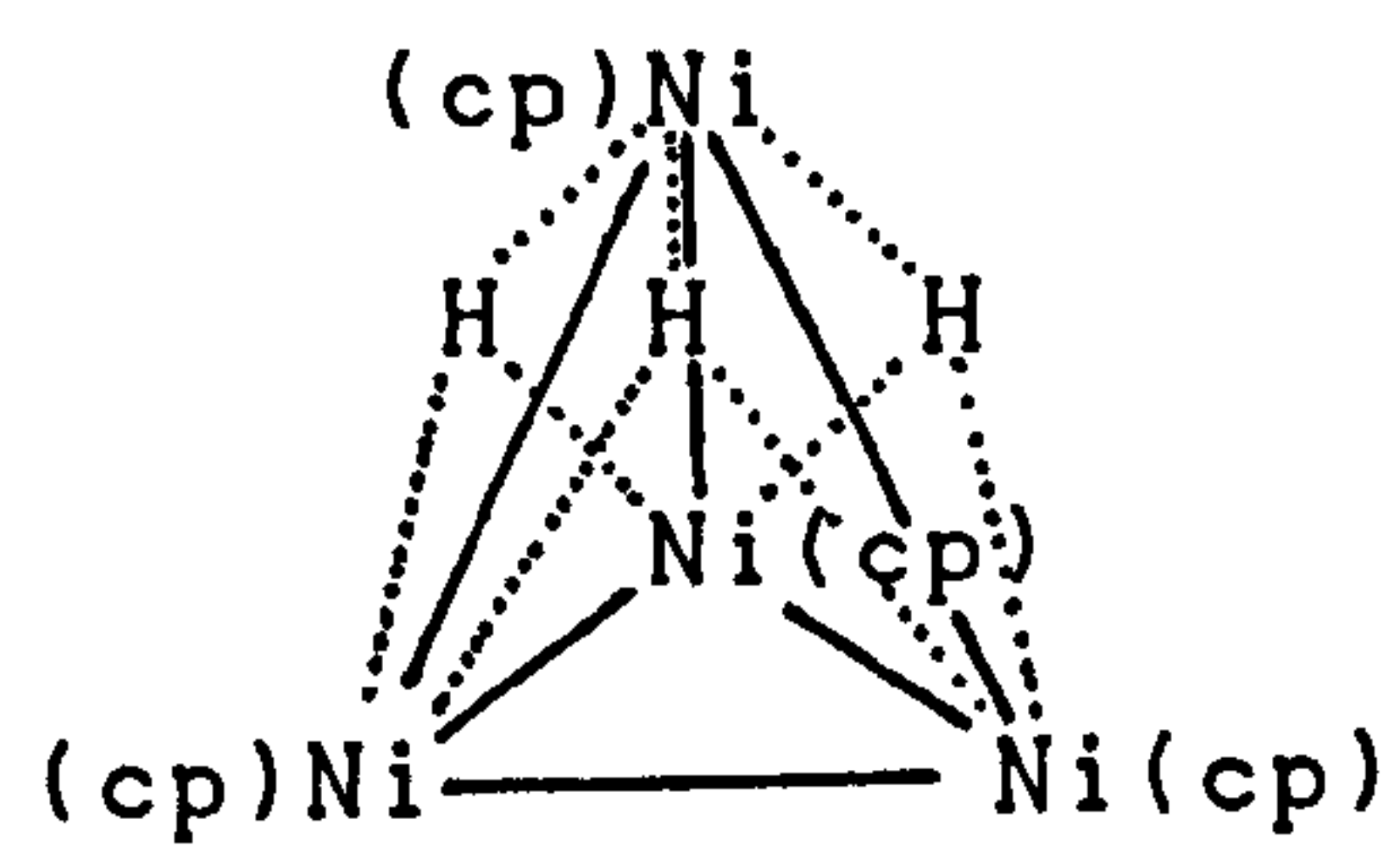
(ref 137)



(ref 136)



(ref 138, 139)



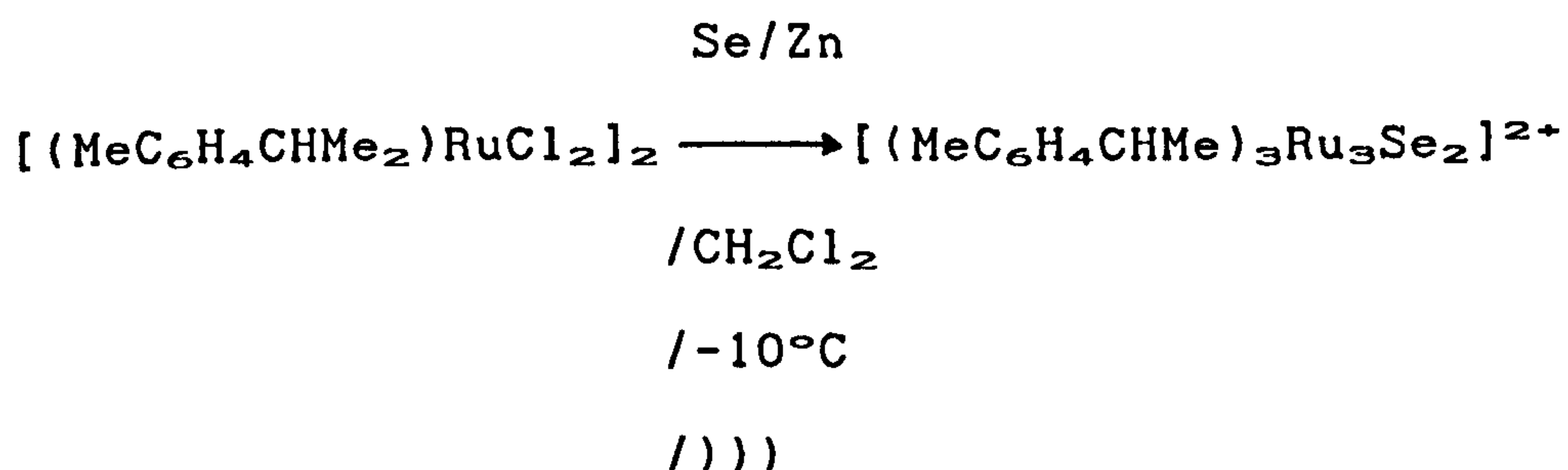
(ref 140)

4.12 Ultrasound as a synthetic tool for cluster reactions

Ultrasound was investigated as an alternative route to enter the arene ruthenium cluster field. The conditions which successfully afforded the arene ruthenium bis(ethylene) complexes were used, (see chapter 2), substituting the ethylene with alternative ligands.

4.1.3 Arene ruthenium selenium cluster chemistry

Selenium was examined as a cluster reagent. The reduction potential of zinc is -0.76V^{96} , selenium could be utilised, as the reduction of Se to Se^{2-} is -0.78V and primarily would be present in solution in the neutral state, whereas sulphur would readily reduce to S^{2-} (-0.508V).



Sonication of the cymene ruthenium chlorodimer in the presence of selenium and zinc, afforded a dark purple/black solution. On taking the solution

to dryness and abstracting the residue into H₂O, the [PF₆]⁻ salt of the dicationic trimer could be obtained.

¹H nmr spectroscopy of the pure complex showed the cymene ligands to be equivalent. Mass spectrometry also confirmed the presence of the molecular ion, (865amu) and a fragmentation pattern for the molecular ion with the loss of one cymene ligand (735amu).

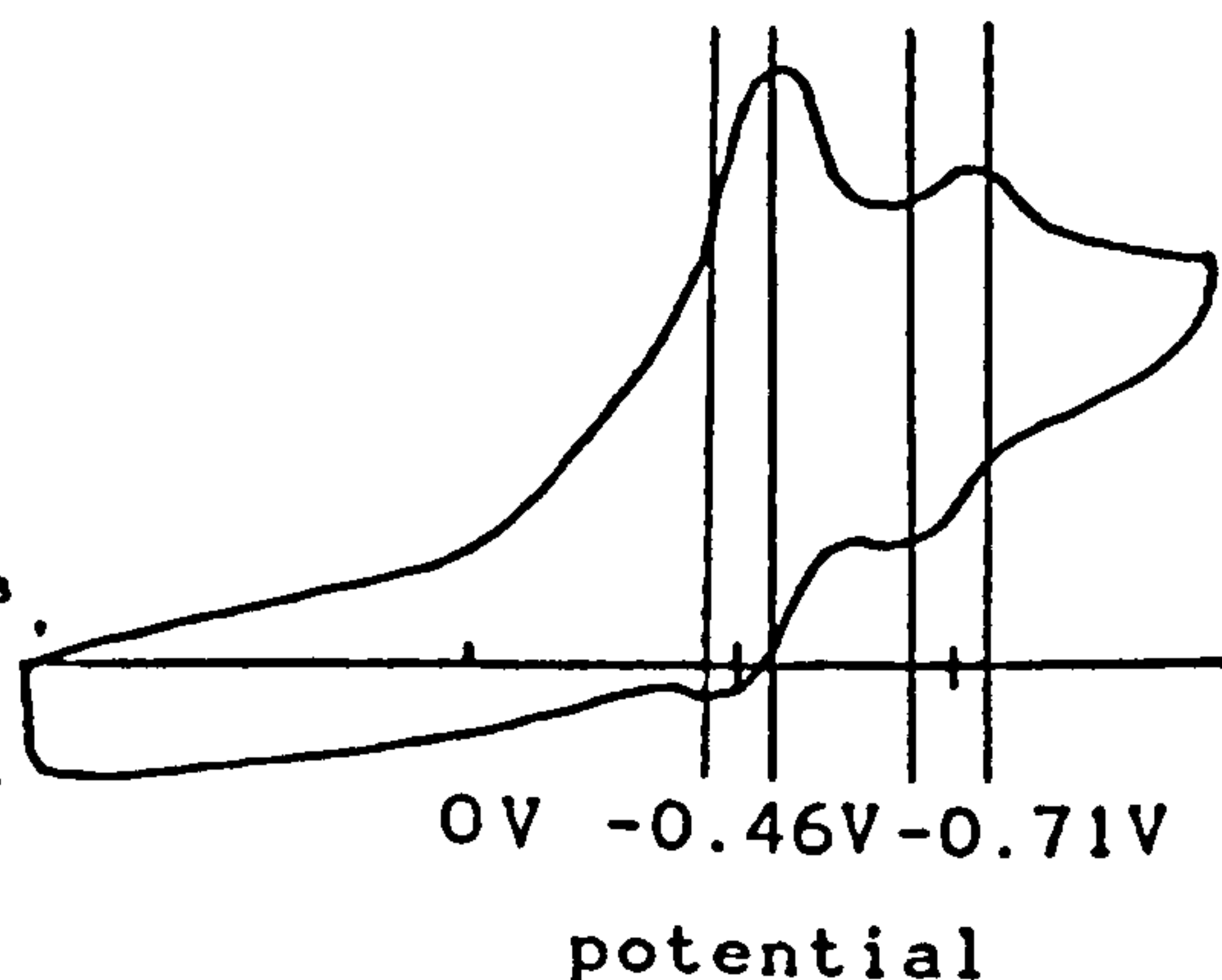
The ¹H nmr spectra of the initial reaction mixture showed the presence of other arene proton absorptions; possibly assignable to the neutral cluster. Attempts to isolate the complex giving rise to these signals were unsuccessful. Integrals indicated that the reaction mixture was composed of a 50:50 mixture of the dicationic trimer and the presumed neutral species. This reflected in the yield of 24% for the [PF₆]⁻ salt of the selenium cluster.

Cyclic voltammetry was used to establish that [(MeC₆H₄CHMe)₃Ru₃Se₂](PF₆)₂ undergoes two very closely spaced one electron reductions, centred at -0.46 and -0.71v, comparable to the recently reported sulphur analogue (-0.567 and -0.704v).¹³¹ Both reductions appear reversible.

The redox potentials in the related cobalt cluster, Cp₃Co₃S₂ for two one electron processes are well separated, 0.46V.¹⁴¹

Fig 4.1

Cyclic voltammogram of
 $[(\text{MeC}_6\text{H}_4\text{CHMe})_3\text{Ru}_3\text{Se}_2]^{2+}$
 in CH_3CN , conc 0.0006mol.cm^{-3} ,
 electrolyte NEt_4BF_4 , internal
 reference to ferrocene.



The report of the related complexes
 $[(\text{MeC}_6\text{H}_4\text{CHMe})_3\text{Ru}_3\text{S}_2]^{2+}$ and $[(\text{MeC}_6\text{H}_4\text{CHMe})_3\text{Ru}_3\text{S}_2]^{1+}$
 (see section 4.1.5) also included X-ray
 crystallographic studies that were used to
 rationalise the electrochemical behaviour of the
 sulphur analogue. The conclusions may be applicable
 to the selenium cluster.

The basis of the unusual behaviour was made
 clear by the crystallographic results; two electron
 reduction of the dicationic cluster cleaves one
 Ru-Ru bond. (See Fig.4.2). It follows that a one
 electron reduction would lead to partial
 metal-metal bond cleavage.

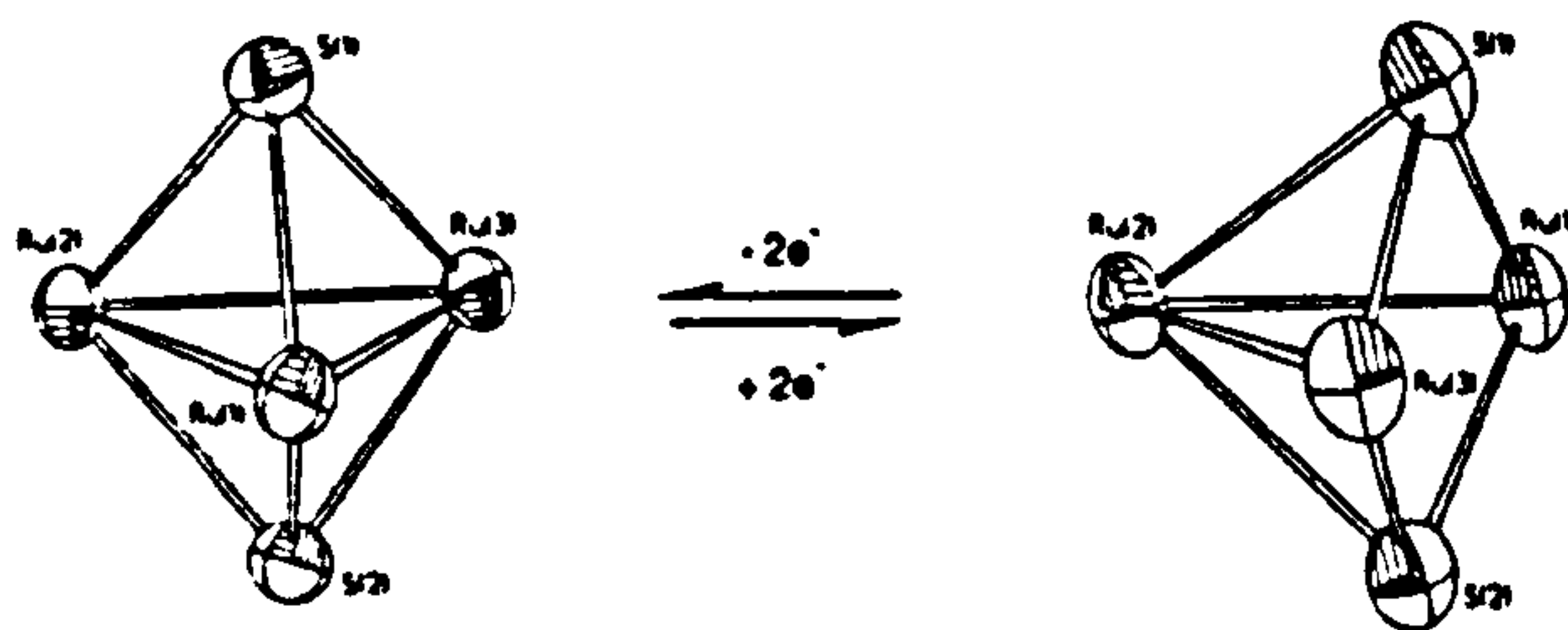


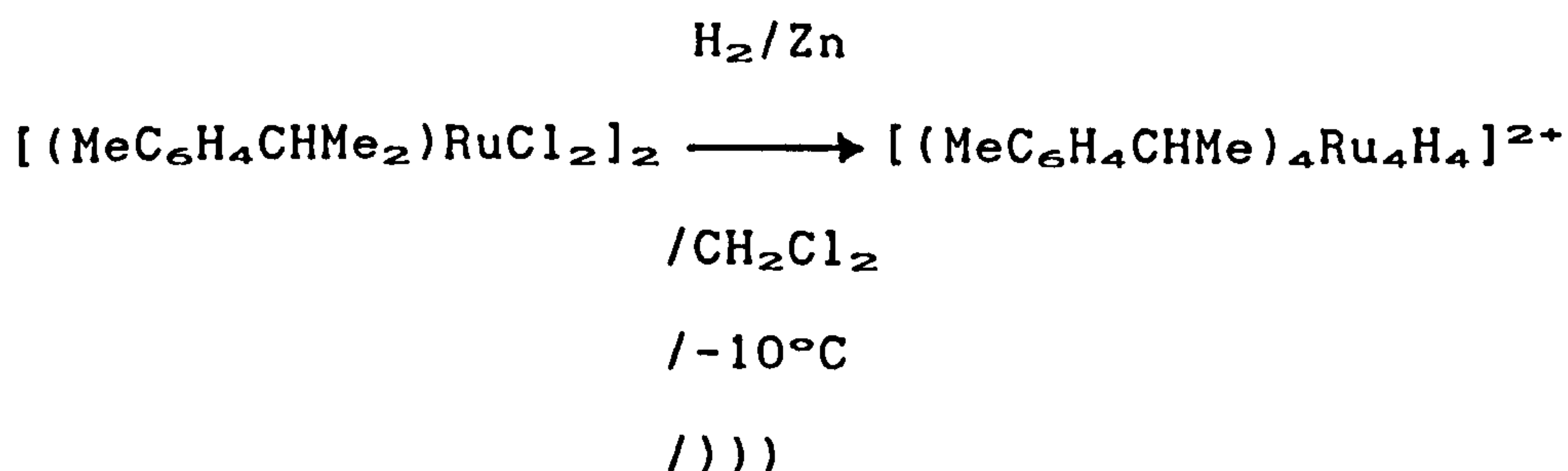
Fig.4.2 The Ru_3S_2 cores of the cationic and neutral
 sulphido clusters.

Thus the close spacing of the two, one electron reductions is readily explained.

4.1.4 Arene ruthenium hydride cluster chemistry

As reported in chapter 1 (1.2.1.5), arene ruthenium hydride complexes have been synthesised from a range of arene ruthenium containing substrates. A large number have been obtained, by the reaction of the arene ruthenium chlorodimer with hydrogen in the presence of NEt_3 ⁴⁴, or in 2-propanol with Na_2CO_3 .⁴⁴

The ultrasonic reduction, which was used successfully to afford the arene ruthenium bis(ethylene) complexes, appeared to be an ideal route into hydride chemistry. The ultrasonic reaction of the arene ruthenium chlorodimer (arene= $\text{MeC}_6\text{H}_4\text{CHMe}_2$), with hydrogen in the presence of a reducing agent, Zn, was investigated.

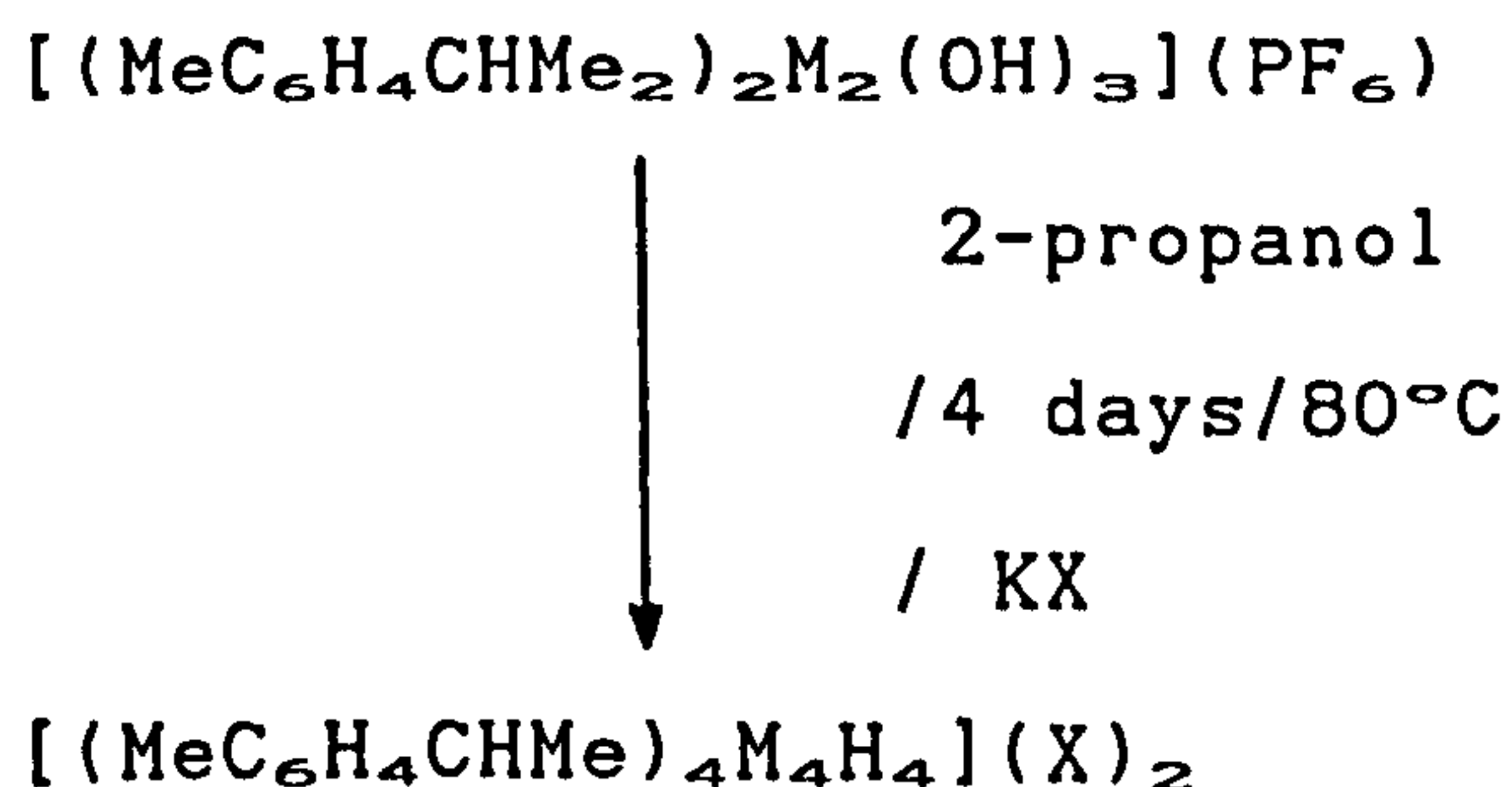


After sonication in a reaction vessel which was capable of maintaining the hydrogen pressure at 1

to 2 atmospheres, a deep intense purple solution was afforded. On taking the solution to dryness and abstracting the residue into water, the tetranuclear tetra hydride dicationic cluster could be afforded as a $[\text{PF}_6]^-$ or $[\text{BF}_4]^-$ salt.

^1H nmr spectra of the pure isolated cluster, contained absorptions which could be assigned to cymene ligands which were equivalent and the ratio of arene to hydride was 1:1. Comparison to the briefly reported electron-deficient clusters $[(\text{arene})_4\text{M}_4\text{H}_4]^{2+}$ ($\text{M}=\text{Ru}, \text{Os}$),¹⁴² confirmed that the ultrasonic reaction afforded the tetranuclear tetra hydride dicationic cluster as the most robust product.

^1H nmr spectroscopy of the initial reaction mixture indicated the presence of a number of hydride species. This implies the ultrasound conditions are mild in comparison to the known route for the above cluster.¹⁴²



$\text{M} = \text{Ru}, \text{X} = \text{PF}_6; \text{Os}, \text{X} = \text{BF}_4.$

These intermediate hydride species are likely to be related to those reported in chapter 1 (section 1.2.1.5).

The dimer $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Ru}_2\text{Cl}_2(\mu\text{-Cl})(\mu\text{-H})]$ was positively identified as one. Also, it was believed that a number of the hydride species not isolated were related to the above cluster. Different recrystallisation conditions could affect the ratio of the hydride signals and a near pure sample of the tetra nuclear tetra hydride cluster, on slow recrystallisation, could generate more of the previous minor product. The mild conditions utilised to form the above cluster generate hydride containing species of lower nuclearity. This was reflected in the yield of the desired product. The tetranuclear tetrahydride dicationic cluster was isolated as either the $[\text{PF}_6]^-$ or $[\text{BF}_4]^-$ salt in 5 to 10% yield.

This cluster is a member of an interesting class of compounds with respect to the stereochemistry of the hydride ligands. The hydrides could be edge bridged or face capped.

The literature reports different conclusions for different M_4H_4 systems, as can be seen from table 4.1

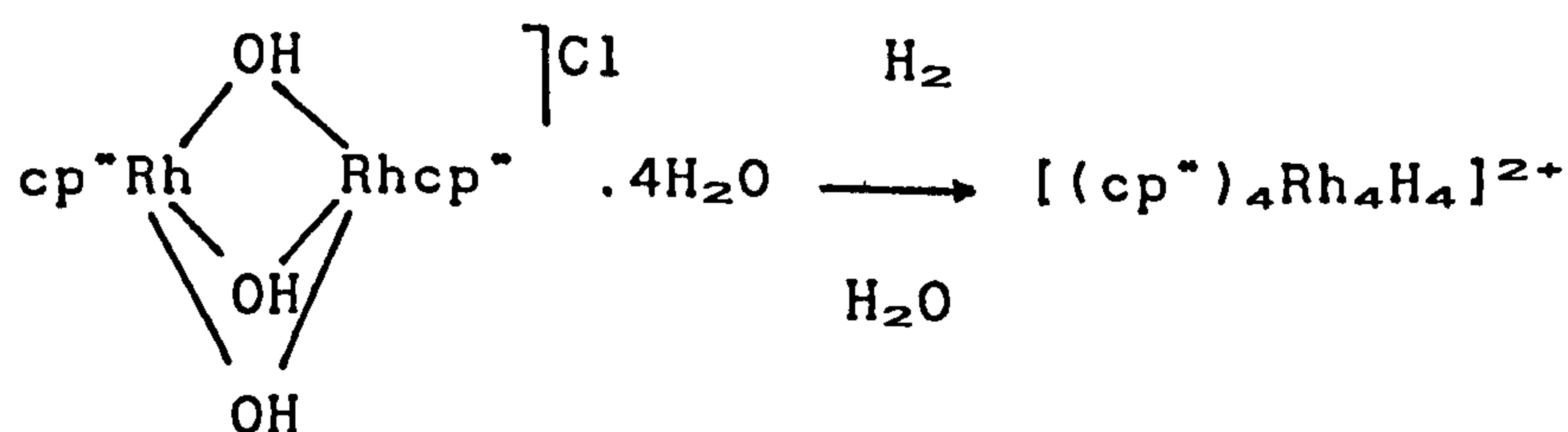
The assignment of the stereochemistry demonstrates the drawback of X-ray crystallography. The position of light atoms such as hydrogen can

not always be positively assigned. Alternative methods have to be pursued, the most reliable being neutron diffraction. However, the disadvantage of this latter technique is the requirement of considerably larger crystals of the complex in question.

Table 4.1. Type of hydride bonding in a range of tetranuclear clusters.

Complex	Type of hydride bonding	Ref.
$(cp)_4Co_4H_4$	face	137
$(cp^*)_4Rh_4H_4^{2+}$	face	143
$Re_4(CO)_{12}H_4$	face	144
$Ru_4(CO)_{12}H_4$	edge	145
$Os_4(CO)_{12}H_4$	edge	146
$Ru_4(CO)_{11}P(OMe)_3H_4$	edge	144
$Ru_4(CO)_{10}(PPh_3)_2H_4$	edge	145
$Ru_4(CO)_{10}(diphos)H_4$	edge	147

Maitlis et al reported the synthesis of the tetrarhodium tetrahydride dicationic cluster $[(cp^*)_4Rh_4H_4]^{2+}$.¹⁴⁸



The $[\text{BF}_4]^-$ salt was characterised by X-ray crystallography. The dication contained four rhodium atoms each bearing a cp^* ligand, arranged in a distorted tetrahedral manner (D_{2d} sym) with two short (2.655\AA) and four long (2.829\AA) Rh-Rh bonds. The presence of four hydrides was shown by nmr spectroscopy. Earlier work¹⁴⁹ suggested that in polynuclear hydride clusters the hydrides bridged the longer M-M bonds; Thus they proposed that the four hydrides bridged the four long Rh-Rh bonds.

However, a later low temperature neutron diffraction study established that the four hydrides in fact bridged the four faces of the distorted tetrahedron ($\mu_3\text{-H}$) at a distance of 0.957\AA above the plane formed by three rhodium atoms.¹⁴³

Confirmation was obtained by a detailed analysis of the ^1H and ^{13}C nmr spectra. Comparison of the actual nmr data with that expected for a theoretical model showed very good agreement. (The model was based on four hydrides bridged over the four faces, the $^1J_{\text{Rh-Rh}}$ coupling determined from the ^{13}C nmr and that there were three equal one bond Rh-H couplings and one two bond Rh-H coupling).

This also suggests that the hydrides take no part in a fluxional process.

The distortion of the tetrahedral structure is

believed to be electronic and not steric.

Calculation of Van der Waals interactions have showed that the distortion is unlikely to be steric in origin.¹⁴³ A theoretical analysis¹⁵⁰ of bonding in tetranuclear hydride clusters suggested that the rhodium cluster should be paramagnetic with two unpaired electrons. The analysis was based on the assumption that the highest occupied molecular orbital has three nearly degenerate energy levels. (See Fig.4.3) However, a Jahn-Teller type distortion involving a pair of electrons, splits the highest occupied molecular orbital, affording the complex as diamagnetic with distortion away from Td symmetry.

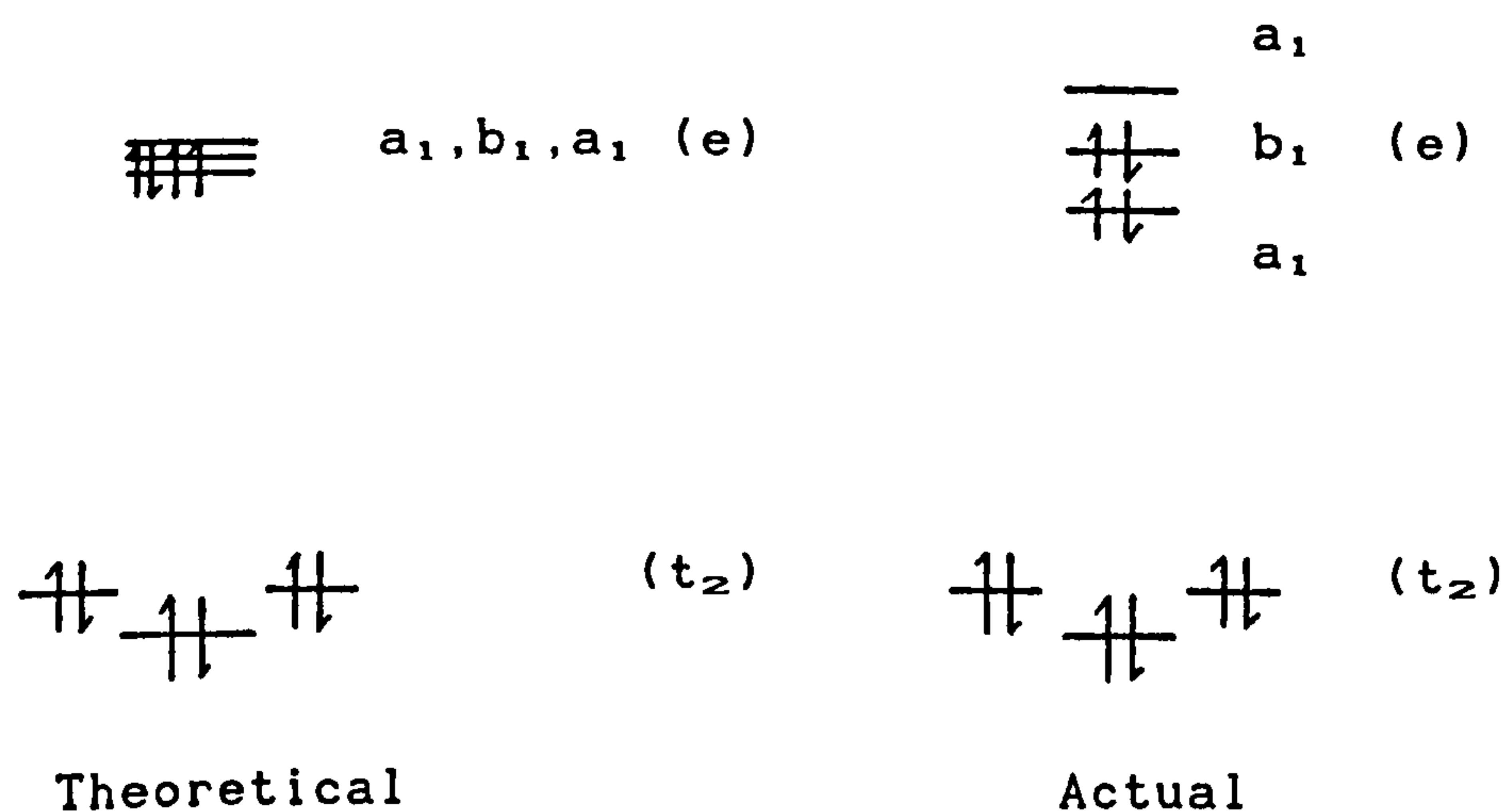
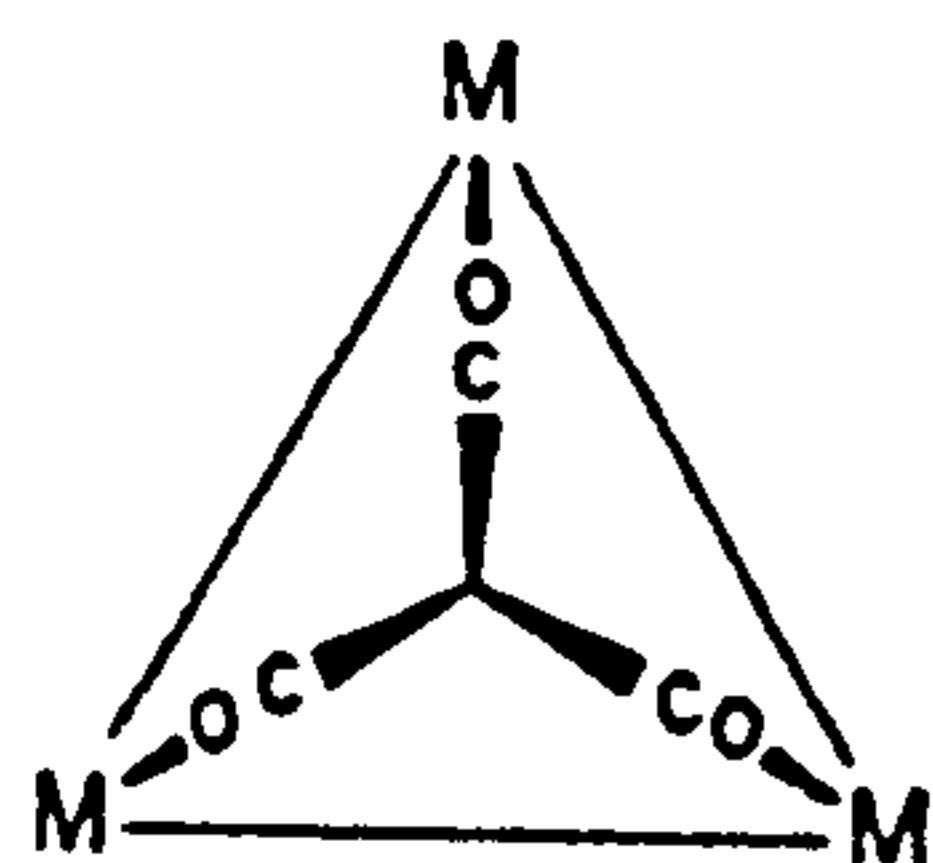


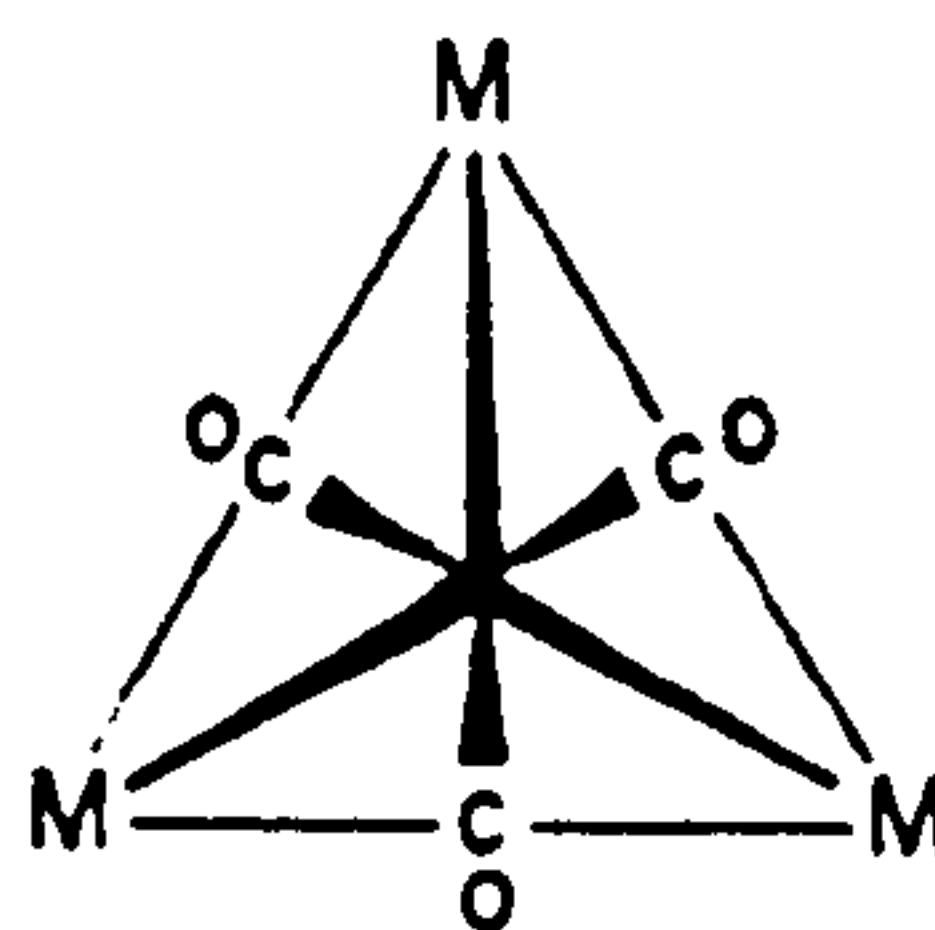
Fig 4.3. Hoffmann's frontier orbitals for M_4cp_4 cluster (M = Rh)

The carbonyl clusters $\text{Re}_4(\text{CO})_{12}\text{H}_4$, $\text{Ru}_4(\text{CO})_{12}\text{H}_4$ and $\text{Os}_4(\text{CO})_{12}\text{H}_4$ have also been structurally characterised. The rhenium system has tetrahedral symmetry and essentially equivalent Re-Re bond lengths. "Fourier averaging" techniques were introduced to locate the hydride atoms on the faces of the tetrahedron.¹⁴⁴

The arrangement of the carbonyl groups for these clusters gives an insight into the location of the hydride ligands. $\text{Re}_4(\text{CO})_{12}\text{H}_4$ has four face-bridging hydrides and eclipsed carbonyl groups (A) whereas the ruthenium¹⁴⁵ and osmium¹⁴⁶ carbonyl clusters show staggered carbonyls (B) and are believed to have four edge bridging hydrides.



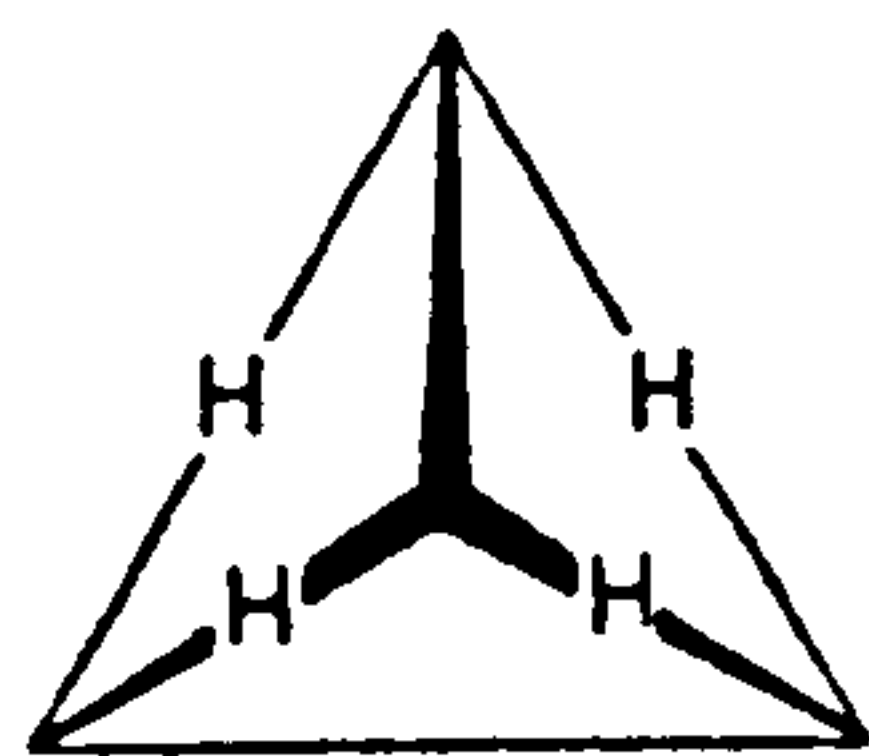
(A)



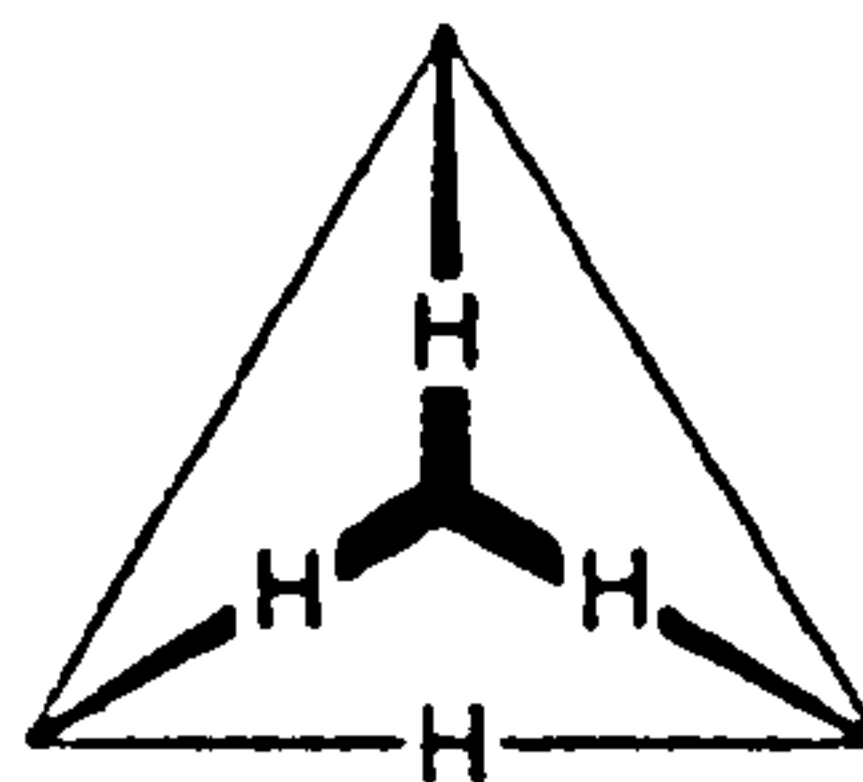
(B)

In addition crystallographic studies on the derivatives $\text{Ru}_4(\text{CO})_{11}\text{P}(\text{OMe})_3\text{H}_4$ ¹⁴⁴, $\text{Ru}_4(\text{CO})_{10}(\text{PPh}_3)_2\text{H}_4$ ¹⁴⁵ and $\text{Ru}_4(\text{CO})_{10}(\text{diphos})\text{H}_4$ ¹⁴⁷ all show staggered carbonyls and four edge bridging hydrides, although the disposition of the edges bearing hydrides differs: $\text{Ru}_4(\text{CO})_{12}\text{H}_4$, $\text{Ru}_4(\text{CO})_{11}\text{P}(\text{OMe})_3\text{H}_4$ and $\text{Ru}_4(\text{CO})_{10}(\text{PPh}_3)_2\text{H}_4$ have

configuration (C) while $\text{Ru}_4(\text{CO})_{10}(\text{diphos})\text{H}_4$ has configuration D.¹⁴⁵



(C)



(D)

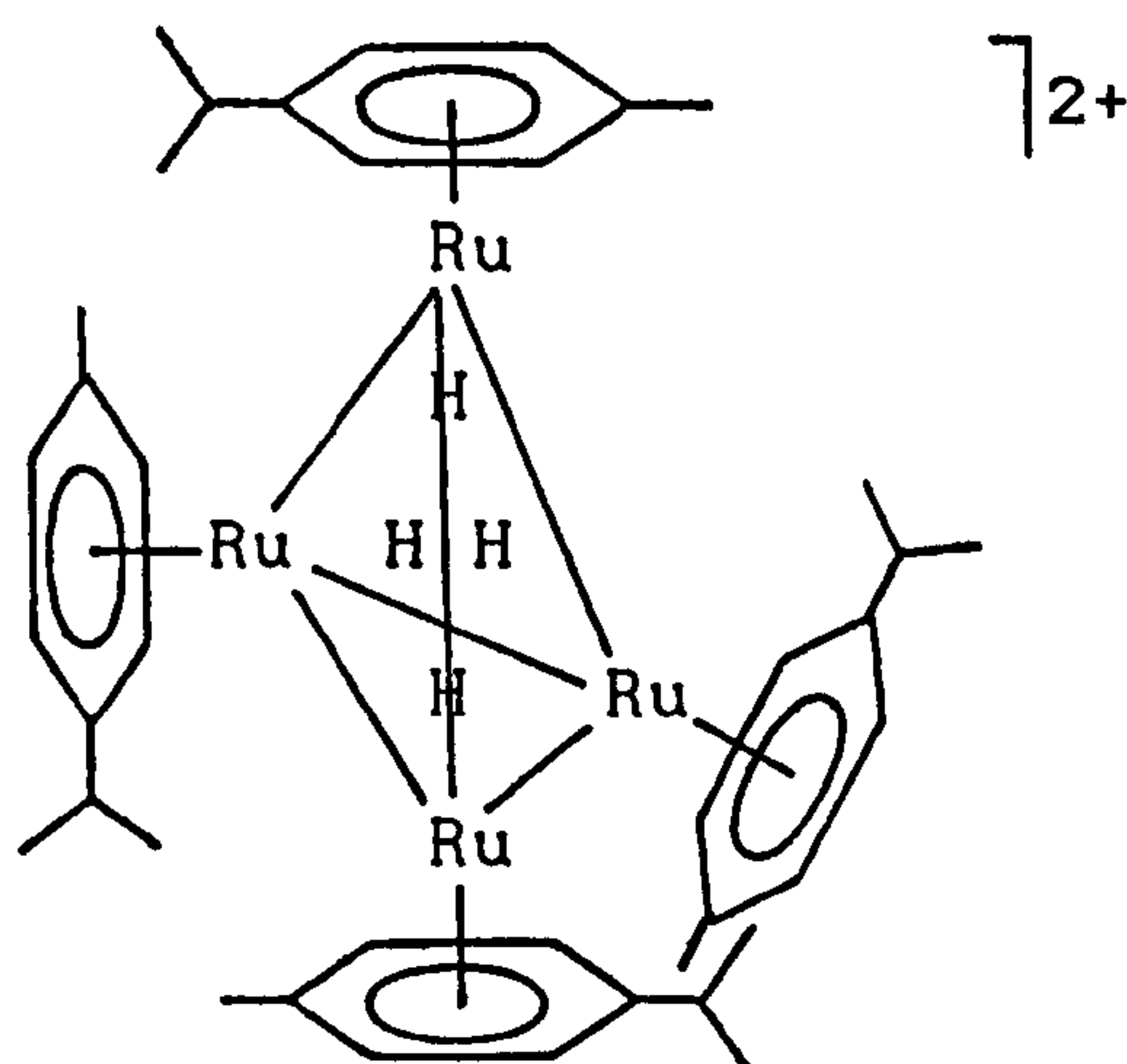
^1H nmr spectroscopic analysis of the $\text{Ru}_4(\text{CO})_{12-x}[\text{P}(\text{OMe})_3]_x\text{H}_4$ ($x = 1, 2, 3, 4$) complexes show a single chemical shift for the hydride ligands. Also each hydride appears to be equivalently spin coupled to all the phosphorus nuclei in any particular complex. The observed equivalence of the environments of the hydrides could come about from their rapid exchange of positions along the edges. This hydride mobility might well involve face bridging in the transition state.¹⁵¹

The fluxionality of the hydrides has also been confirmed for the $\text{Os}_4(\text{CO})_{12}\text{H}_4$ complex. ^{187}Os nmr determined that at ambient temperatures all hydrides are coupled to four osmium atoms, thus the molecule must be fluxional.¹⁴²

In contrast the rhodium complex appears essentially rigid at ambient temperatures; the model which confirmed the hydrides being face

capping was based on three equal one bond Rh-H couplings and one two bond Rh-H coupling.¹⁴³

The stereochemistry of the $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_4\text{Ru}_4\text{H}_4]^{2+}$ complex, has not been fully determined. Early crystallographic studies indicate the presence of a distorted tetrahedron, but location of the hydrides is not expected. At present the hydride bonding mode can only be postulated. The cluster is isoelectronic with the rhodium tetranuclear cluster and it can be assumed that they will be more chemically similar than the carbonyl species. On this basis, the hydride bonding mode is proposed as $\sqrt{3}$ -H face capping.



From the preliminary investigations of this system, the synthesis of the above hydride cluster from $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2$, applying ultrasound in the presence of a reducing agent and hydrogen, has been shown to be successful. Further work is being carried out to investigate whether the reaction is

general for a series of arenes, and whether the neutral cluster can be isolated from the reduction of the dicationic species.

Electrochemical behaviour

Transition metal cluster compounds are being actively researched for their properties as models for industrial and biological systems. The suitability of clusters hinges on the ability of the clusters to add or lose electrons - a property that is readily investigated by cyclic voltammetry.

The electrochemistry of the $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_4\text{Ru}_4\text{H}_4]^{2+}$ cluster was examined. The complex was expected to exhibit two one electron reductions to afford the neutral cluster. This was confirmed by cyclic voltammetry. (See fig. 4.4)



Both reductions are fully reversible. It appears that the neutral cluster would be stable in solution and isolable on the chemical reduction of the dication species.

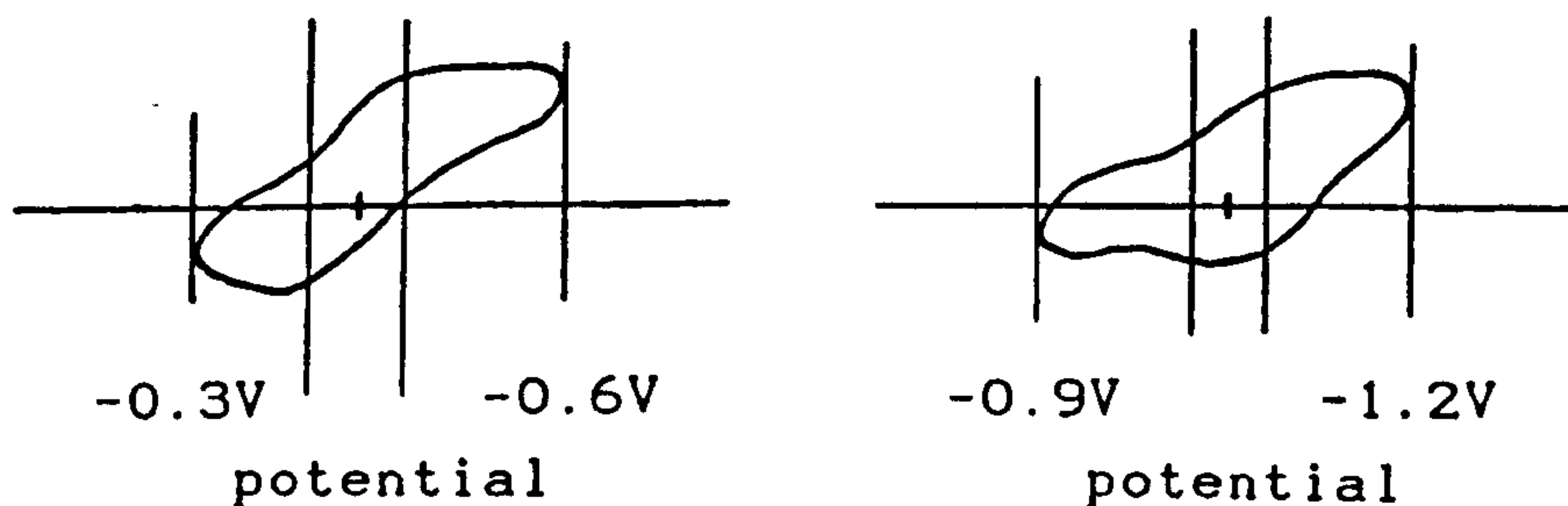


Fig 4.4 Cyclic voltammogram of $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_4\text{Ru}_4\text{H}_4]^{2+}$ in CH_3CN , conc 0.0005mol.cm^{-3} , electrolyte NEt_4BF_4 , internal reference to ferrocene.

A third process was monitored on an oxidation sweep of the dicationic cluster.

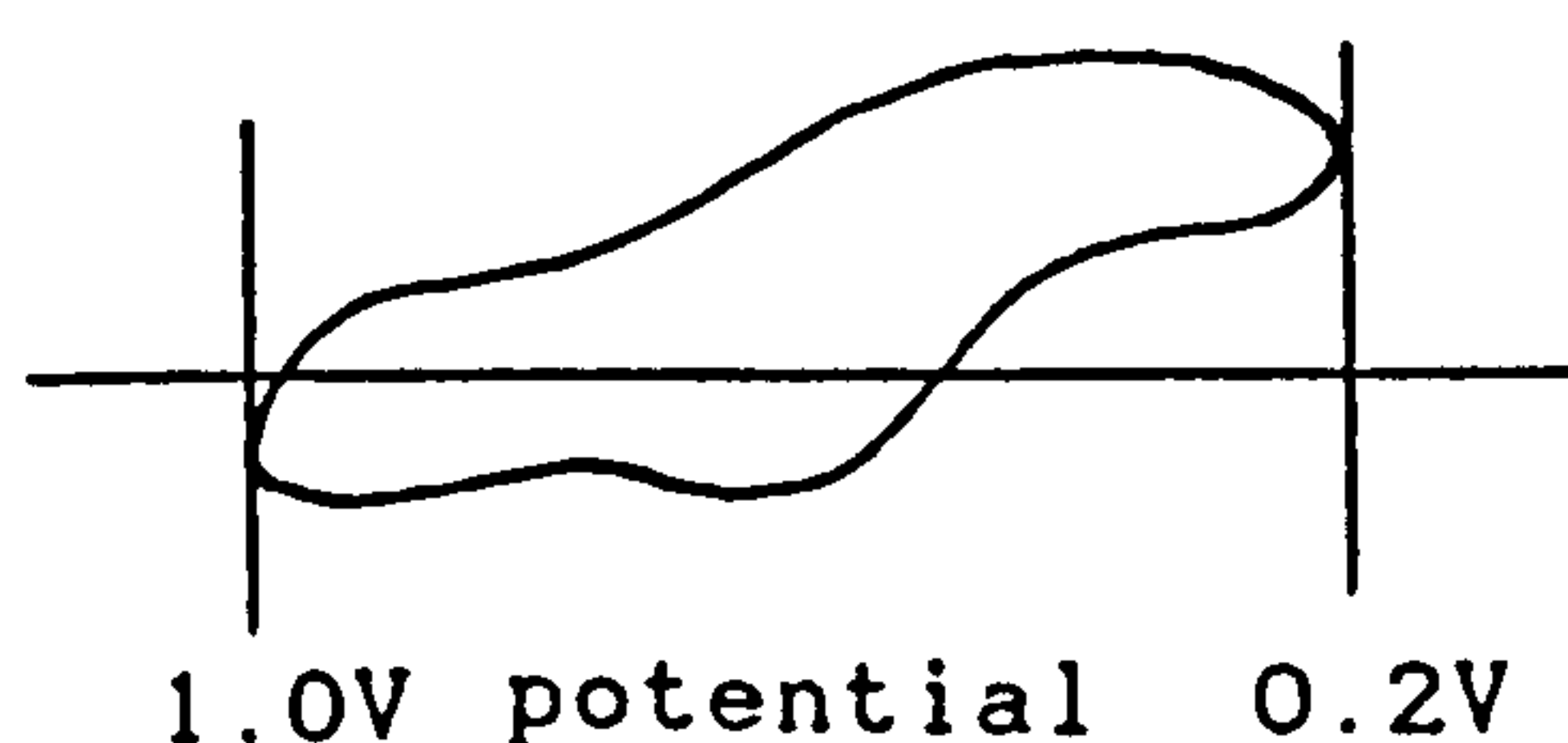


Fig 4.5 Cyclic voltammogram of $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_4\text{Ru}_4\text{H}_4]^{2+}$ in CH_3CN , conc 0.0005mol.cm^{-3} , electrolyte NEt_4BF_4 , internal reference to ferrocene.

This process is believed to be the loss of an electron and the generation of the tricationic cluster.



Initially the oxidation appeared to be reversible, but decomposition of the product occurs, rendering the process irreversible.

The electrochemistry of the dicationic cluster, $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_4\text{Ru}_4\text{H}_4]^{2+}$, implies that this system could act as a readily accessible electron sink for one or two electrons, the electrons in question being readily removed when desired. The integrity of the cluster appears to be lost when the dicationic cluster is oxidised.

Catalytic activity

Lately polynuclear clusters have been investigated with respect to catalytic activity. The principle is that several adjacent metal atoms will act in a similar manner to the surface of a bulk metal, and at the same time retain the advantages of homogenous catalysts, in the areas of selectivity and the mild operating conditions.

In an investigation of the water-gas shift reaction, (applied to vary the ratio of CO and H₂ in synthesis gas to those needed for synthesis of such products as ammonia, methanol or substituted natural gas),



it was determined that the catalytic system was initiated by $\text{Ru}_4(\text{CO})_{13}\text{H}_2$, $\text{Ru}_4(\text{CO})_{12}\text{H}_4$ or $\text{Ru}_3(\text{CO})_{12}$, giving solutions which were spectroscopically indistinguishable after an initial "maturing" period of 24 hours.¹⁵²

$[\text{Ru}_4(\text{CO})_{12}\text{H}_3]^-$ and $[\text{Ru}_3(\text{CO})_{11}\text{H}]^-$ have been observed in the ^1H nmr spectra of active catalytic solutions. It was determined that the tetranuclear species was present only when hydrogen was allowed to accumulate in the catalytic system, whereas the trimer was favoured when the carbon monoxide partial pressure was increased.

Earlier studies¹⁵³ of the water gas shift reaction showed that when $\text{Ru}_3(\text{CO})_{12}$ was added to an alkaline alcoholic solution, over a 30 day period, a total of 150 moles of H_2 was evolved per mole of catalyst at 1 atmosphere of CO at 100°C . Catalytic activity increased rapidly at higher temperatures.

The tetranuclear ruthenium tetrahydride dicationic cluster would not be expected to show catalytic activity for the water-gas shift reaction, as it has no carbonyl ligands.

A common reaction catalytically investigated, is the hydrogenation of alkenes. The complex $[\text{Ru}_4(\text{CO})_{12}\text{H}_4]$ has been shown to react with ethylene at 72°C to form two moles of ethane per mole of cluster. In the presence of excess hydrogen, this cluster complex acts as a catalyst for the

hydrogenation of ethylene in heptane solution.¹⁵⁴

From the above studies, an intermediate was proposed for the catalytic cycle, $[\text{Ru}_4(\text{CO})_{11}\text{Et}(\text{H})_3]$, involving an ethyl linkage to the ruthenium cluster. From the protonation studies of the arene ruthenium bis(ethylene) complexes with trifluoroacetic acid, (chapter 2), the ethylene ligands were substituted by the acid counteranion, some of which was converted to ethane. An intermediate product was detected which, as in the above system, involved an ethyl linkage to a ruthenium metal, $[(\text{arene})\text{Ru}(\text{C}_2\text{H}_4)(\text{O}_2\text{CF}_3)\text{Et}]$ (arene = C_6H_6 , $\text{MeC}_6\text{H}_4\text{CHMe}_2$).

To date, no evidence has yet been reported of the use of the $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_4\text{Ru}_4\text{H}_4]^{2+}$ or $[(\text{cp}^*)_4\text{Rh}_4\text{H}_4]^{2+}$ clusters as catalysts. It would appear that both species have the potential for catalytic activity in hydrogenation reactions, although careful reaction studies need to be carried out to determine if they in fact do.

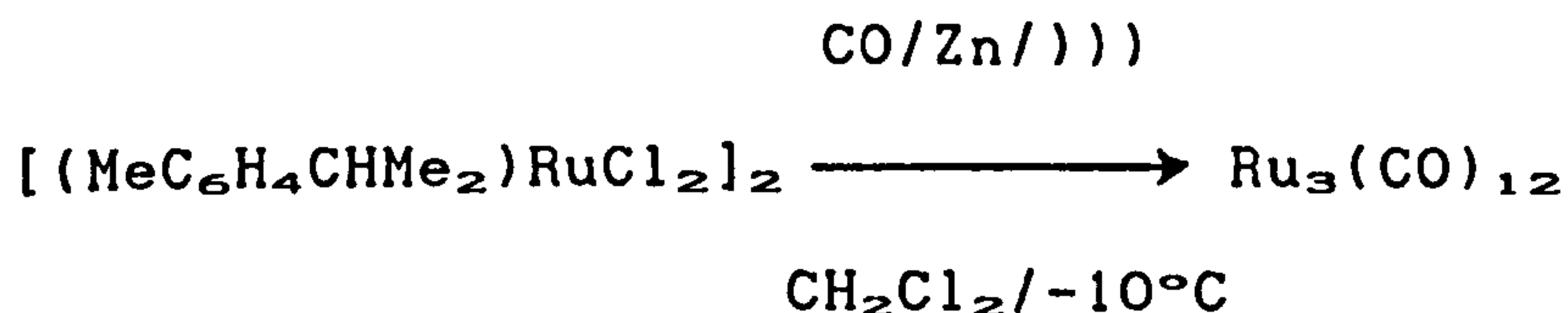
Mechanism

For the preparation of the selenium and the hydrogen clusters above, no evidence has been obtained which could be applied towards a postulated mechanistic route for either trinuclear or tetranuclear species. It can be assumed that the

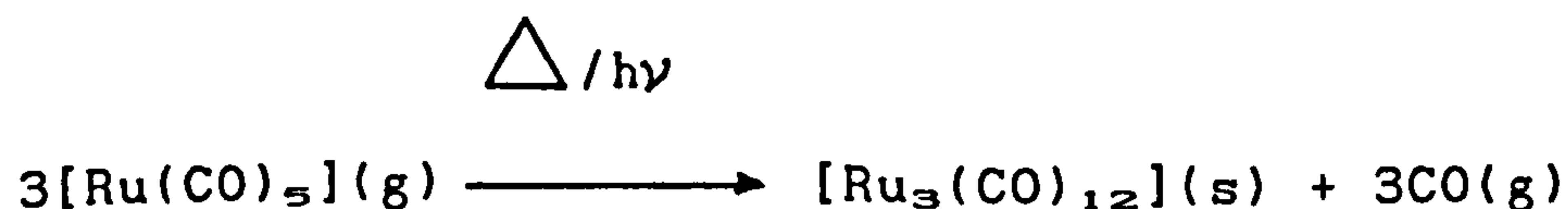
arene ruthenium moiety complex structure, postulated for the reactions that have been carried out in chapter 2 and 3, is generated initially in the formation of these cluster complexes.

4.1.5 Ruthenium carbonyl cluster chemistry

The known carbonyl cluster, ruthenium dodecacarbonyl, was the only isolable ruthenium complex isolated when using carbon monoxide as a clusterification ligand.



$[\text{Ru}_3(\text{CO})_{12}]$ was originally observed in 1910 by Mond et al^{155, 156, 157, 158}, from the reaction between ruthenium black and carbon monoxide at 300°C and approximately 400 atmospheres. Later Manchot and Manchot¹⁵⁹ in 1936, revealed that $\text{Ru}_3(\text{CO})_{12}$ was formed by the thermal or photochemical decomposition of $[\text{Ru}(\text{CO})_5]$:¹⁶⁰



Since then a large number of high pressure

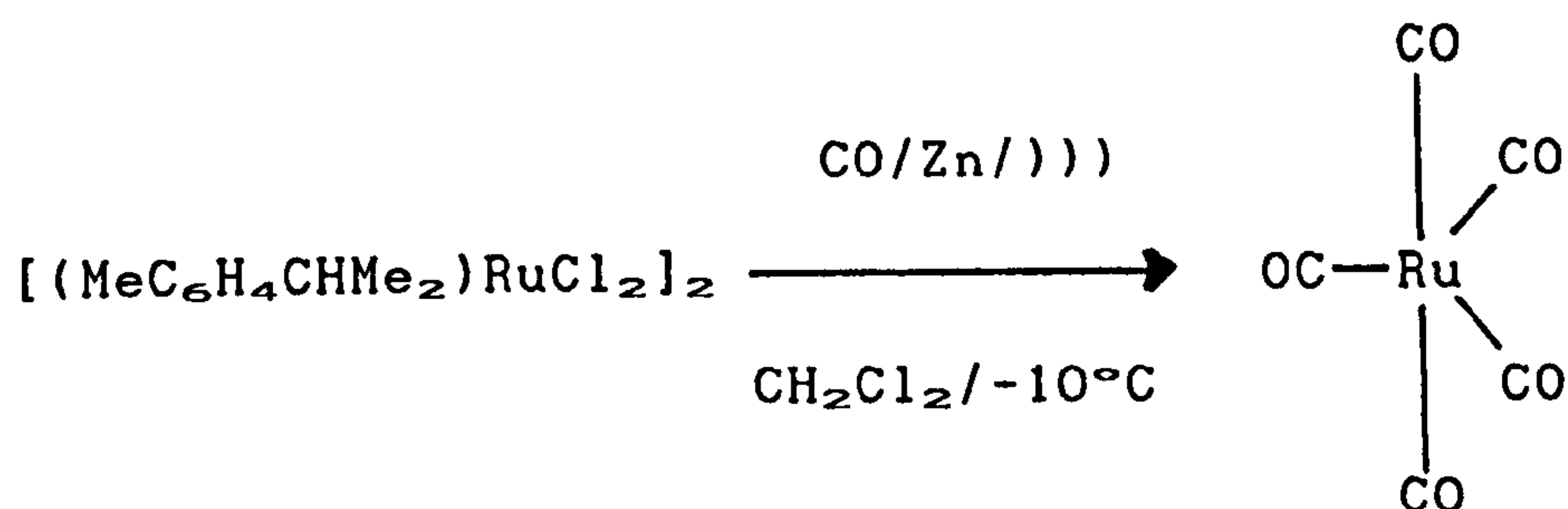
preparative routes have been developed, largely involving reductive carbonylation of ruthenium(III) and ruthenium(II) complexes. A number of these reductions are carried out in the presence of a halogen acceptor (ie Zn).¹⁶¹



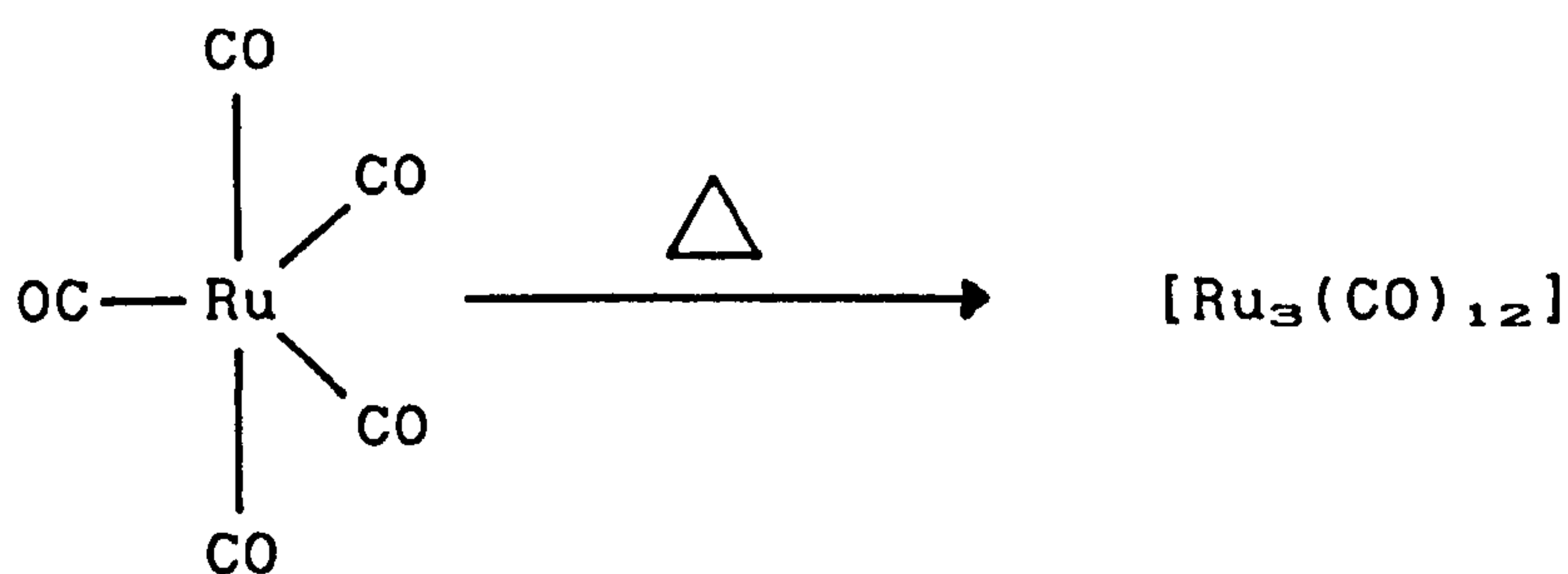
More recently the major synthetic advances in the preparation of $[\text{Ru}_3(\text{CO})_{12}]$ have been concerned with its synthesis at atmospheric pressure. eg Dawes and Holmes¹⁶² treated a 2-ethoxyethanol solution of RuX_3 ($\text{X} = \text{Cl}, \text{Br}$ or I), at reflux, with carbon monoxide. The resulting solution was cooled, treated with ethanol and granulated zinc, then heated to reflux under a flow of carbon monoxide to give $[\text{Ru}_3(\text{CO})_{12}]$ in almost quantitative yields.

Following the ultrasound synthesis of $[\text{Ru}_3(\text{CO})_{12}]$ by infrared spectroscopy afforded an understanding of the route for the conversion of the cymene ruthenium chlorodimer to the ruthenium dodecacarbonyl cluster.

The reaction was initially carried out at -10°C and the carbonyl stretches monitored were comparable to ruthenium pentacarbonyl. (See table 4.2).



On standing and allowing the reaction mixture to come up to room temperature, thermal decomposition of ruthenium pentacarbonyl occurred to afford $[\text{Ru}_3(\text{CO})_{12}]$.



This was confirmed by the carbonyl stretches observed. (See table 4.2).

Table 4.2 Infrared data of carbonyl complexes

Complex	$\nu(\text{CO})$ actual / cm^{-1}	$\nu(\text{CO})$ expected / cm^{-1}
$[\text{Ru}(\text{CO})_5]$	2033, 1995	2035, 1999
ref dichloromethane		
$[\text{Ru}_3(\text{CO})_{12}]$	2059, 2029,	2057, 2030
ref cyclohexane	(2020-2000)sh	2010

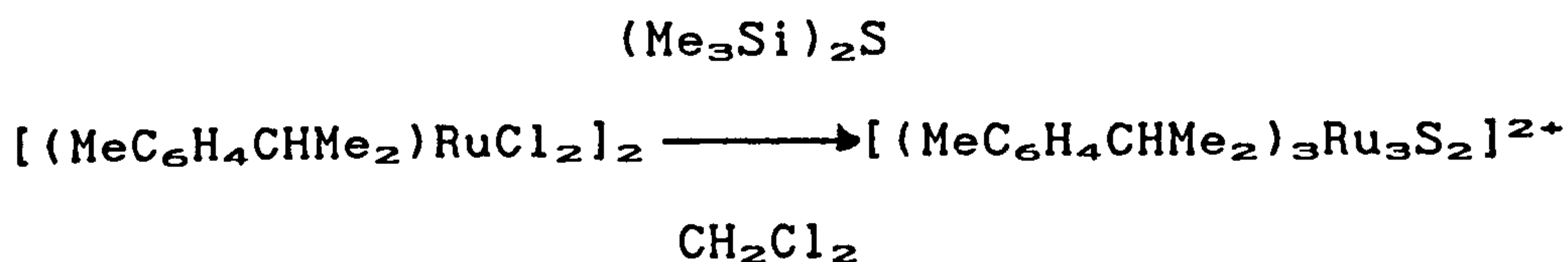
The work up process - relying on uncontrolled thermal decomposition of $[\text{Ru}(\text{CO})_5]$ and recrystallisation from a solvent system of dichloromethane / hexane - affords $[\text{Ru}_3(\text{CO})_{12}]$ in low yield, <10%. An investigation of reaction vessels and work up techniques utilised may however improve the yield and afford this route as a viable alternative method to generate $[\text{Ru}_3(\text{CO})_{12}]$.

4.1.6 Arene ruthenium sulphido cluster chemistry

When investigating the incorporation of nitrogen containing ligands into the arene ruthenium coordination sphere, see chapter 5, Me_3SiN_3 was determined as a useful source of the N_3 ligand. Thus the related sulphur compound, $(\text{Me}_3\text{Si})_2\text{S}$, was investigated to see whether it could be used successfully to react with $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2$, to form sulphido clusters.

The bis(trimethylsilyl)sulphur ligand was prepared from a literature preparation¹⁸⁴, where sulphur was added to a solution of superhydride (lithium triethylborohydride), stirred and then reacted with chlorotrimethylsilane.

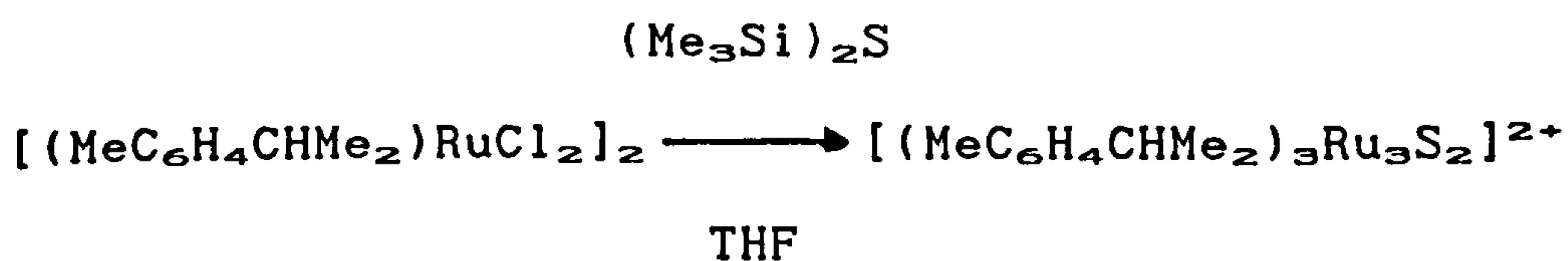
Ultrasound was found to hinder reactions, so simple stirring of the two reactants in dichloromethane was carried out.



Prolonged stirring (12 hours) with a large excess of ligand, afforded a dark solution. On taking the reaction mixture to dryness, abstracting the residue with H_2O , the $[\text{PF}_6]^-$ salt of the dicationic sulphido cluster could be obtained. ^1H nmr spectra showed the presence of one type of cymene ligand.

Before further work was carried out upon this system, J.R. Lockemeyer et al reported their extensive findings in their investigation of arene metal sulphido clusters.¹³¹

The solvent system they utilised was warm tetrahydrofuran, which afforded the dicationic cluster.



Comparison of the ^1H nmr spectra of the complex afforded from each route, shows the product to be the same in each case.

J.R. Lockemeyer et al investigated the electrochemical behaviour of the sulphido

dicationic cluster, determining that the cluster undergoes two one electron reductions to form the neutral cluster, by the reduction of the dication with cp_2Co .

The group also obtained crystal structure determinations for both the dicationic and neutral sulphido clusters. Comparison of the respective Ru_3S_2 cores explains the ^1H nmr behaviour of the cymene ligands in each complex.

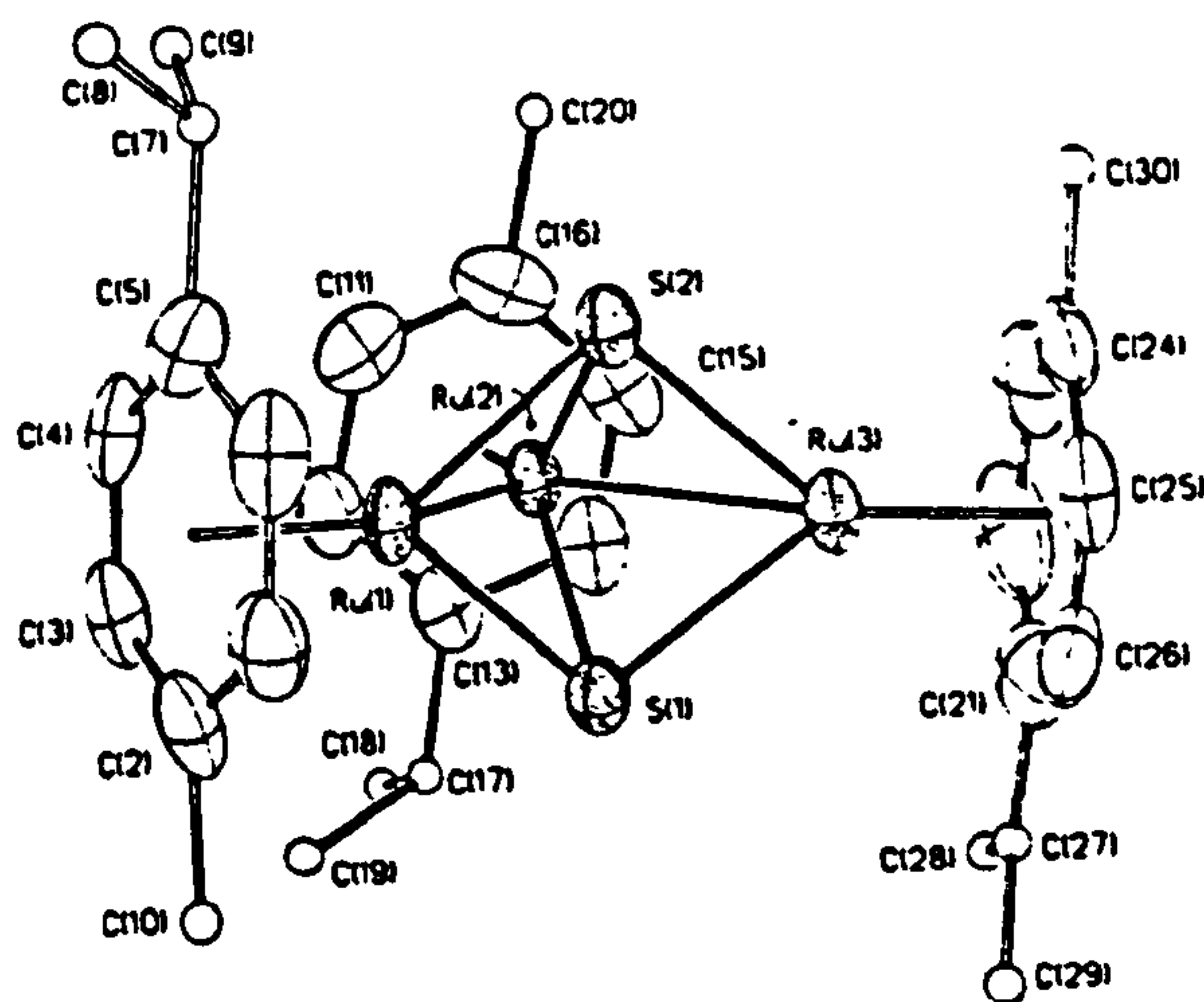
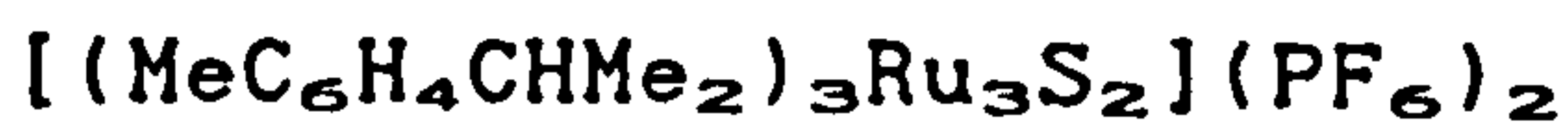
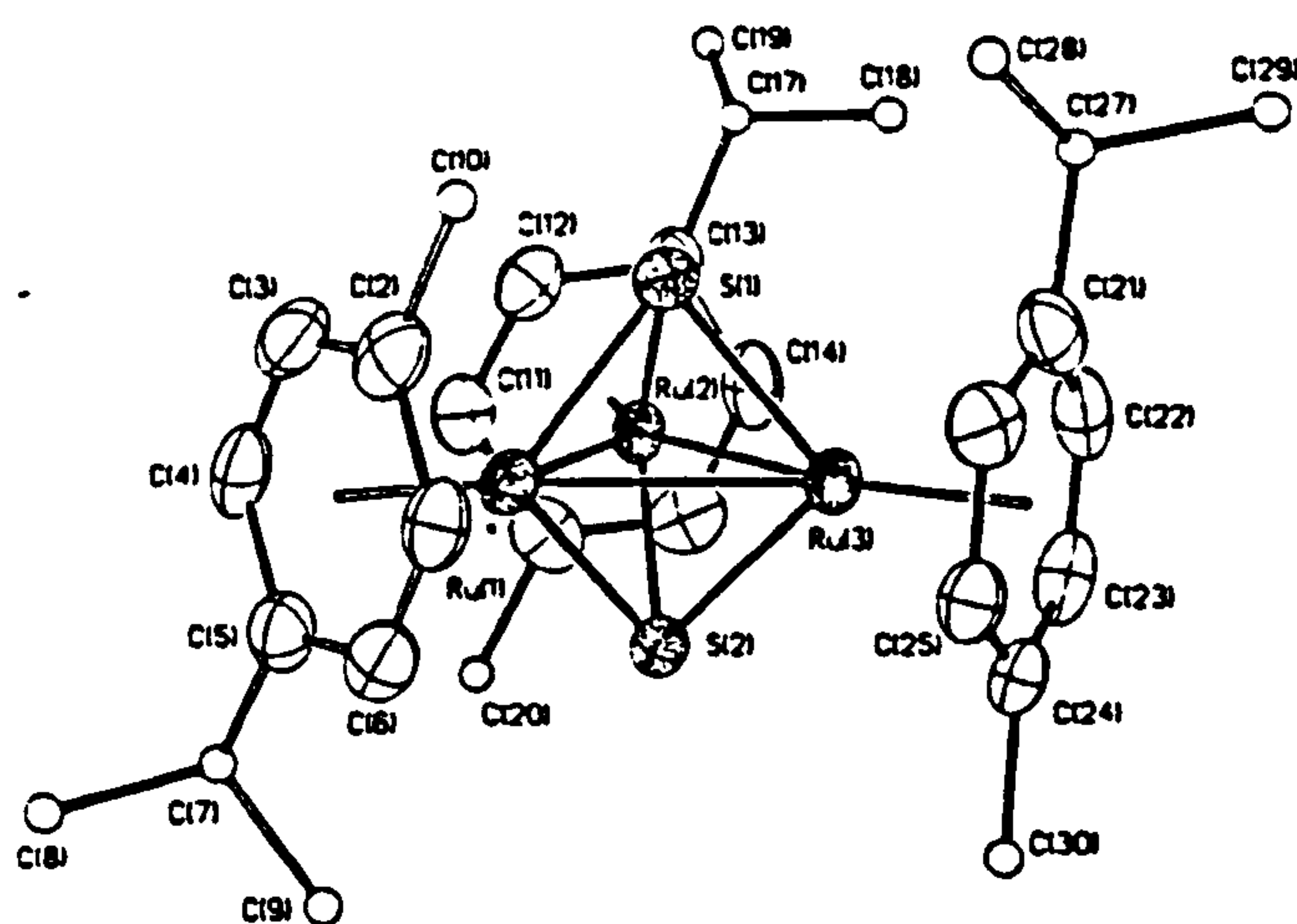


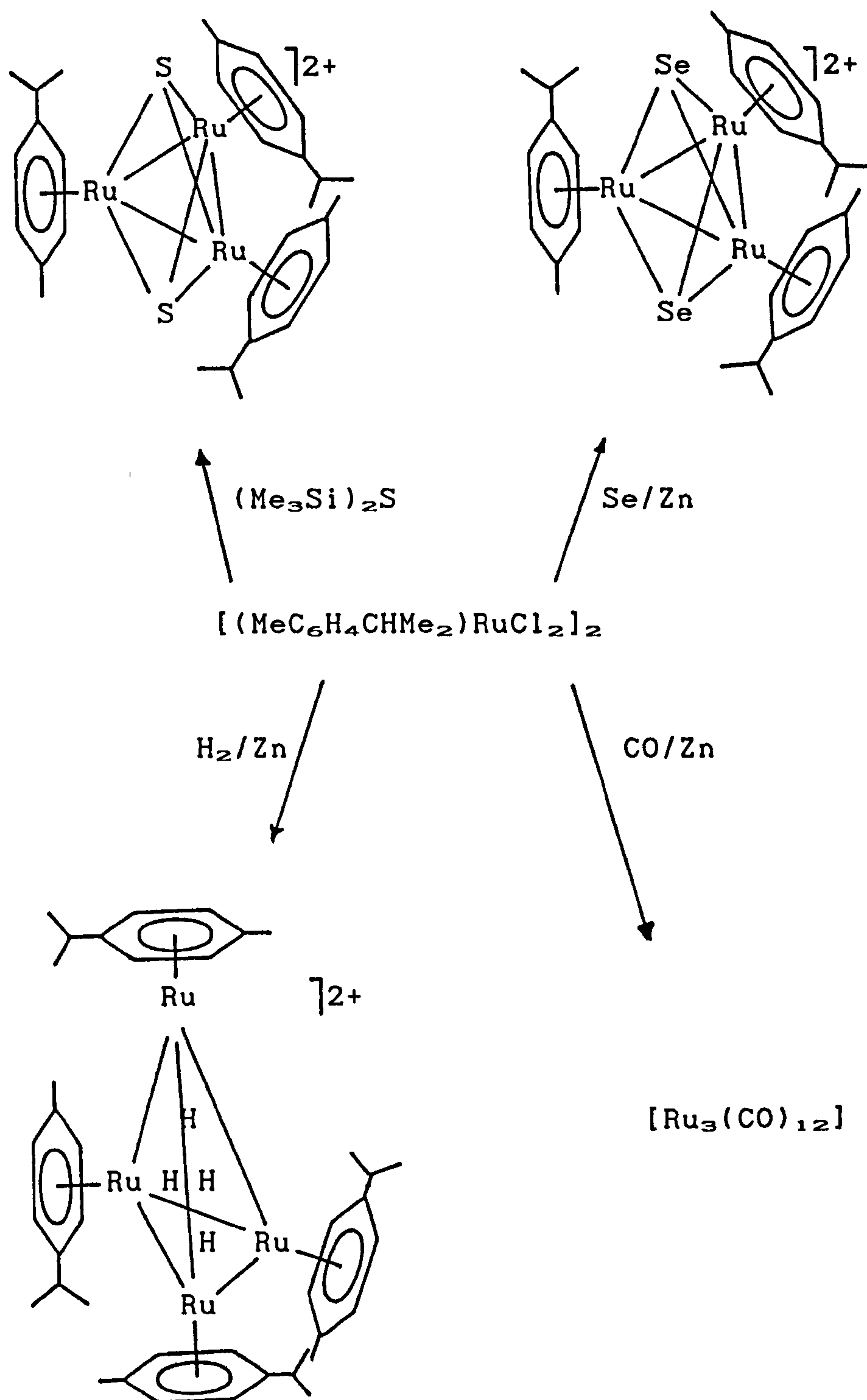
Fig.4.6 Comparison of the Ru_3S_2 cores.

The neutral cluster, unlike the dicationic species, has ^1H nmr signals assignable to three cymene environments. The dication is comprised of a regular trigonal bipyramidal Ru_3S_2 core (see Fig. 4.6), whereas the neutral species consists of a square pyramidal Ru_3S_2 core.

Thus the variation in the symmetry of the cores of the clusters explains why the dicationic cluster has one cymene ligand environment, whereas the neutral cluster has three.

As no extensive investigation was carried out on this system, the yield was not optimised. This was reflected in the value of 22% compared to the literature reported 77%. Although the solvent system used was different, temperature was more likely to be the crucial factor.

4.2 Reaction scheme of clusters synthesised in
chapter 4



4.3 Experimental

$[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_3\text{Ru}_3\text{Se}_2](\text{PF}_6)_2$

To a solution of $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2$ (300mg; 0.48mmol) in CH_2Cl_2 (40ml) at -10°C , was added Se (500mg; 6.3mmol) and Zn (500mg; 7.6mmol), (see appendix for reaction vessel Fig. 5). Ultrasound was applied (4hrs). The reaction mixture was filtered away from the excess Se and Zn and the filtrate taken to dryness. The residue was abstracted into H_2O (15ml) and an oily solid precipitated out on the addition of excess NH_4PF_6 in H_2O (3ml). The oily solid was dissolved in acetone (10ml), filtered and dried over MgSO_4 . The solution was filtered away from the MgSO_4 and a solid was precipitated on addition of ether, determined to be $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_3\text{Ru}_3\text{Se}_2](\text{PF}_6)_2$ (Yield 89mg; 24%, Anal. Found: C 31.55, H 3.95%), (formula $\text{Ru}_3\text{C}_{30}\text{H}_{42}\text{Se}_2\text{P}_2\text{F}_6$ calc. C 31.23, H 3.67%).

Characterisation. ^1H nmr spectroscopy (CD_3COCD_3) shows cymene ligands in one environment, $\delta = 6.27$, (m, 4H, C_6H_4), 2.73, (spt, 1H, CHMe_2), 2.49, (s, 3H, MeC_6H_4), 1.43ppm, (d, 6H, CHMe_2). FAB mass spectrometry confirmed the presence of a molecular ion $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_3\text{Ru}_3\text{Se}_2]^+$ (865amu) and a fragmentation pattern related to a species with the loss of one cymene ligand, $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Ru}_3\text{Se}_2]^+$

(735amu).



The reaction vessel (see appendix Fig. 5) containing $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2$ (300mg;0.48mmol), CH_2Cl_2 (40ml) and Zn (500mg;7.6mmol) was flushed with hydrogen and a head pressure (1 to 2 atmospheres) set. The reaction was kept at -10°C and ultrasound applied (5hrs). The reaction mixture was filtered away from the excess Zn and the filtrate taken to dryness. The residue was abstracted into H_2O (15ml) and a flocculant purple solid precipitated on addition of excess NH_4BF_4 in H_2O (3ml). The solid was filtered, dissolved in acetone (10ml) and dried over MgSO_4 . The solution was filtered away from the MgSO_4 and a purple solid precipitated on addition of isopropyl ether. Slow recrystallisation from an acetone / isopropylether mixture afforded crystals. (Yield 21mg;8%).

Characterisation. Comparison of the ^1H nmr data (CD_3COCD_3) to that of a genuine sample was carried out. $\delta = 6.5$, (m,4H, C_6H_4), -18.6ppm , (s,1H,Ru-H).¹⁴²



The reaction vessel (see appendix Fig. 5) containing $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2$ (300mg;0.48mmol),

CH_2Cl_2 (40ml) and Zn (500mg;7.6mmol) was flushed with carbon monoxide and a head pressure (0.5atmospheres) set. The reaction vessel was cooled to -10°C and ultrasound applied (4hrs). The reaction mixture was filtered away from the excess Zn and the filtrate allowed to come up to room temperature. The filtrate was taken to dryness and recrystallised from dichloromethane and hexane to afford $[\text{Ru}_3(\text{CO})_{12}]$. (Yield 22mg;11%).

Characterisation. Comparison of the infrared data of the product and that of a genuine sample was carried out. $\nu(\text{CO})$ 2059,2029,2020-2000(sh) cm^{-1} . (reference cyclohexane)¹⁶³

$[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_3\text{Ru}_3\text{S}_2](\text{PF}_6)_2$

$[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2$ (200mg;0.32mmol) in CH_2Cl_2 (10ml) was stirred while $(\text{Me}_3\text{Si})_2\text{S}$ (300mg;1.6mmol) was added dropwise. The reaction was stirred further (16hrs) and then taken to dryness. The residue was abstracted into H_2O (15ml) and on addition of excess NH_4PF_6 in H_2O (3ml) a dark brown solid was precipitated from solution, determined to be $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_3\text{Ru}_3\text{S}_2](\text{PF}_6)_2$. (Yield 49mg;22%)

Characterisation. Comparison of the ^1H nmr data (CD_3COCD_3) with that of a genuine sample was carried out. $\delta = 6.0$, (m,4H, C_6H_4), 2.40, (s,3H,

MeC₆H₄), 1.32ppm, (d, C₆H₄CHMe₂). ¹³C

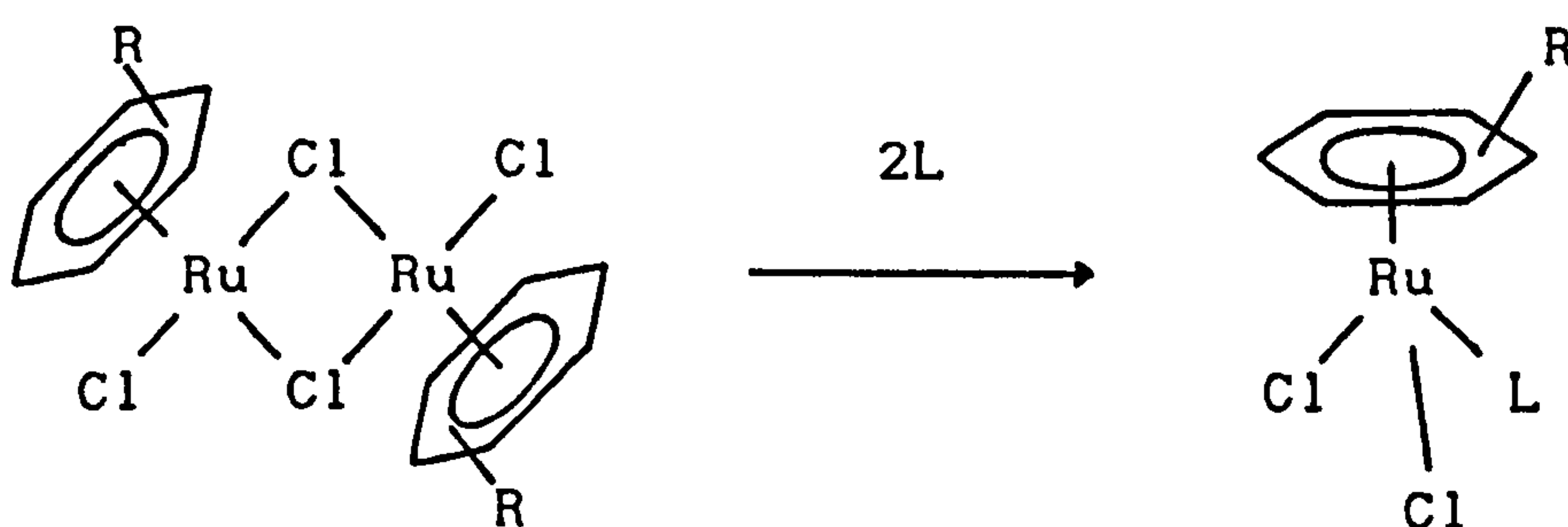
CHAPTER FIVE

Chapter 5

5.1 Arene ruthenium complexes containing nitrogen ligands

The initial aim of the work was to incorporate nitrogen based ligands into the arene ruthenium coordination sphere and investigate whether cluster like complexes could be afforded.

The simple bridge cleavage reaction,

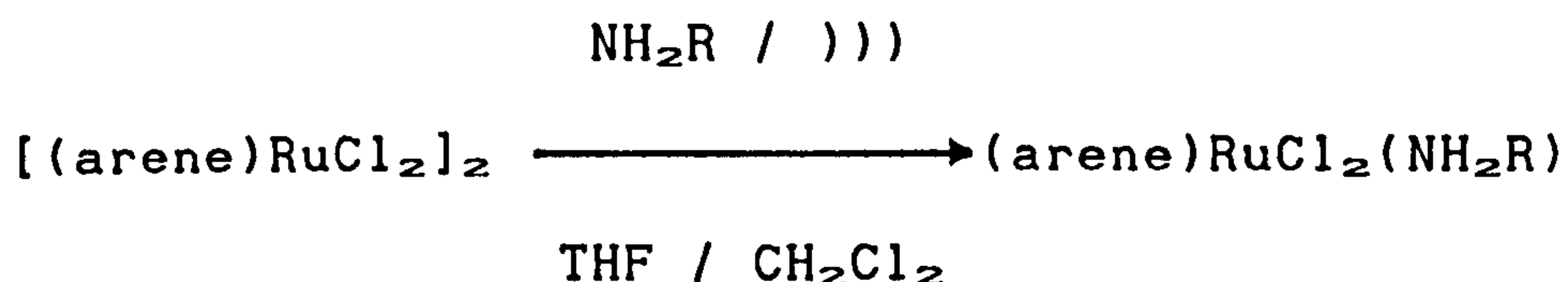


appeared to be the ideal route to incorporate a nitrogen ligand.

To overcome the problem of the $[(C_6H_6)RuCl_2]_2$ dimer's insolubility, ultrasound was used to promote a more efficient reaction.

5.1.1 Preparation of neutral arene ruthenium primary amine complexes.

A series of primary amines, aliphatic and aromatic, were the first nitrogen containing ligands investigated.



arene = C₆H₆, R = Et, CMe₃, C₆H₄Me.

arene = MeC₆H₄CHMe₂, R = CMe₃

Application of ultrasound to a reaction mixture of [(arene)RuCl₂]₂ (arene = C₆H₆, MeC₆H₄CHMe₂), in the presence of an aromatic or aliphatic primary amine, afforded the mononuclear half sandwich complexes shown above. The reactions were rapid and quantitative.

¹H nmr spectra were utilised to confirm that the ratio of the arene to ligand incorporated in the above complexes was 1:1. Use of this technique also determined that the tertiarybutylamine complex crystallised out of solution with a tertiarybutylamine solvate, the two types of NH₂CMe₃ ligands being distinguishable by their chemical shift values.

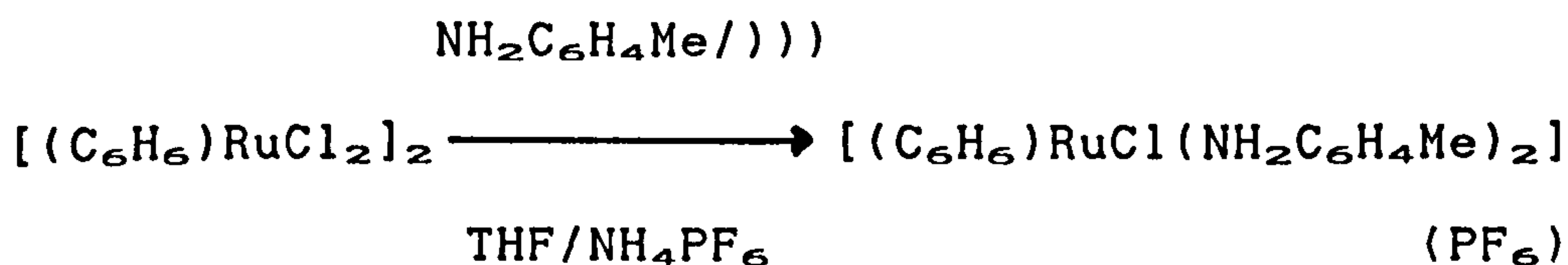
FAB mass spectrometry was utilised to confirm the masses of the expected molecular ions. (The presence of the RuCl₂ units was confirmed by the isotope patterns of the complexes).

Infrared spectroscopy was an ideal method to characterise the above complexes. Infrared absorptions that were assignable to the terminal

Ru-Cl stretch (280 to 270cm^{-1}) and the symmetrical and unsymmetrical N-H stretches (3400 to 3200cm^{-1}) of the primary amine ligand, implied successful synthesis of the half sandwich complexes.

5.1.2 Preparation of cationic primary amine complexes

From the reaction of the aromatic primary amine, p-toluidine, with $[(\text{C}_6\text{H}_6)\text{RuCl}_2]_2$, was afforded a second product. This was determined to be the cationic disubstituted amine complex. Addition of NH_4PF_6 to the reaction mixture, drove the reaction towards the disubstituted product.



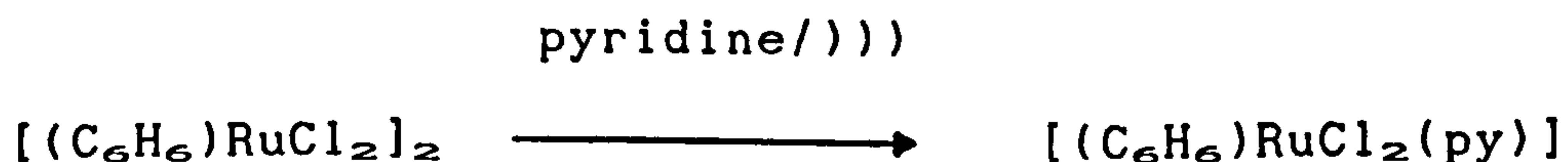
^1H nmr spectroscopy confirmed, by integration of the signals assignable to the arene and primary amine ligands, that the complex was disubstituted. However, there appears to be no simple explanation as to why the signal assigned to the neutral arene species is at a lower field position than that of the cationic complex.

Stephenson et al²⁵, investigated the related neutral and cationic phosphine half sandwich

complexes, where $L = \text{PPh}_3$, PMePh_2 and PMe_2Ph . A trend was observed for the ^1H nmr chemical shift positions of the respective arene ligands of the complexes, a shift of 0.12 to 0.52ppm to low field for cationic species.

5.1.3 Investigation of alternative amine type ligands

The reaction was also investigated for secondary and tertiary amines. No reaction occurred, even with extended reaction times. However, pyridine underwent the bridge cleavage reaction to afford the monosubstituted mononuclear complex, $[(\text{C}_6\text{H}_6)\text{RuCl}_2(\text{py})]$. The complex was characterised with reference to spectroscopic evidence of a genuine sample.²⁵



5.1.4 Mechanism

A combination of hard and soft acid/base theory and steric effects, can be used to rationalise the different substitution reactions of $[(\text{C}_6\text{H}_6)\text{RuCl}_2]_2$. The ruthenium centre in the dimer is ruthenium(II) bound to the soft arene ligand and consequently is soft itself.

Thus reaction with soft nucleophiles such as PPh_3 is rapid.^{1,29} Non sterically demanding borderline ligands such as pyridine would be expected, and do, undergo the bridge cleavage reaction.

However, in the case of relatively hard ligands, such as amines, steric factors become increasingly important; Hence the lack of reaction of secondary and tertiary amines, whereas primary amines undergo the reaction quantitatively.

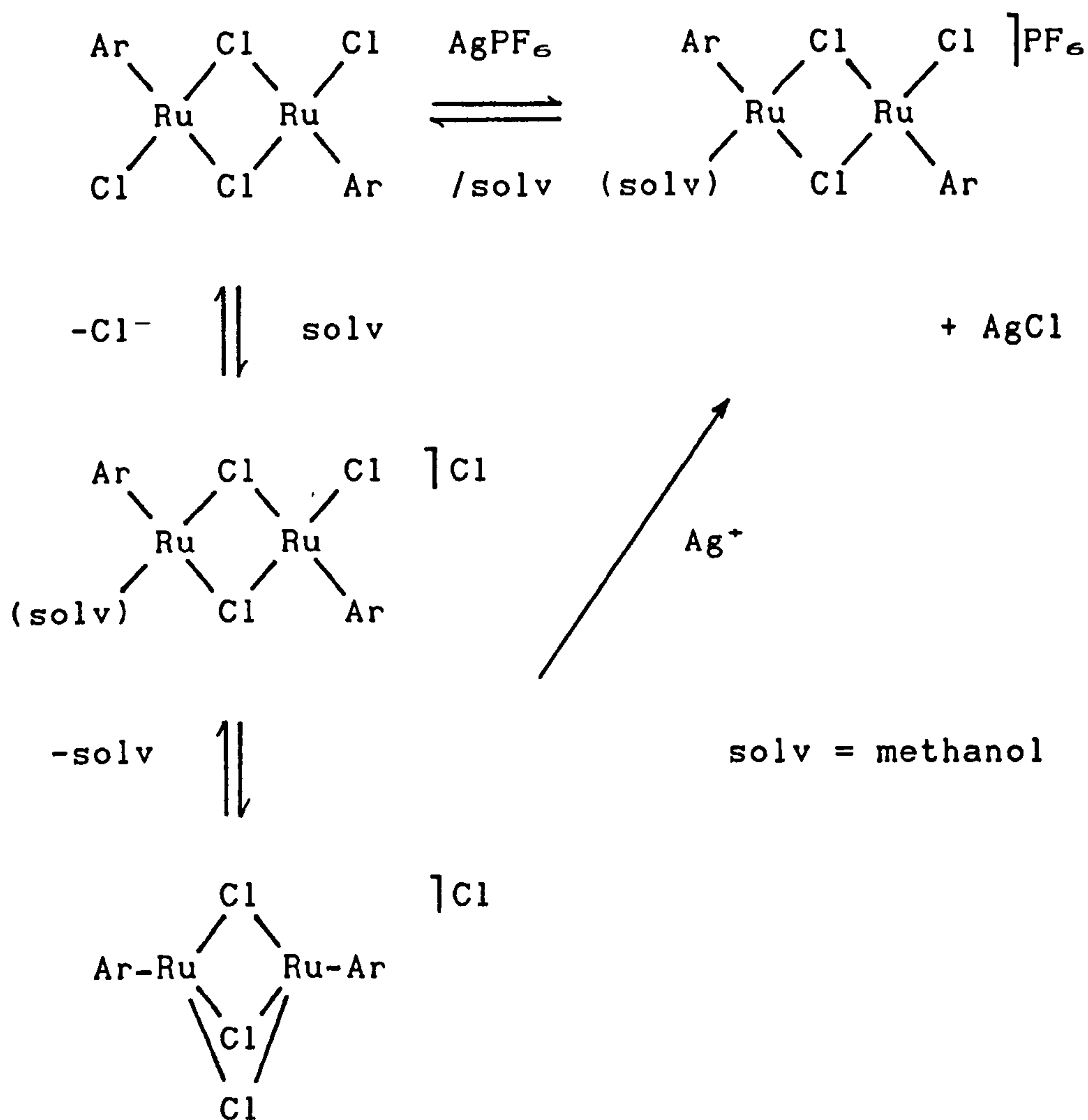
An explanation for the formation of the disubstituted amine complex $[(\text{C}_6\text{H}_6)\text{RuCl}(\text{NH}_2\text{C}_6\text{H}_4\text{Me})_2]^+$, is that the aromatic amine is softer compared to the aliphatic analogues.

Stephenson, when investigating the reactivity of the arene ruthenium chloro dimers with methanol as the solvent system, postulated the formation of a triply chloro bridged species in the dimer's reactions. (See Scheme 5.1)

However, the investigations of the reaction of the arene ruthenium chloro dimers with primary amines, was carried out with less polar and non coordinating solvents.

It is postulated that the mechanism is more likely to involve chloro bridge cleavage of the neutral dimer. As synthesis of new complexes was the primary aim of the project, investigation of

the kinetics of the reactions was not carried out. However, determining the factors which affect the

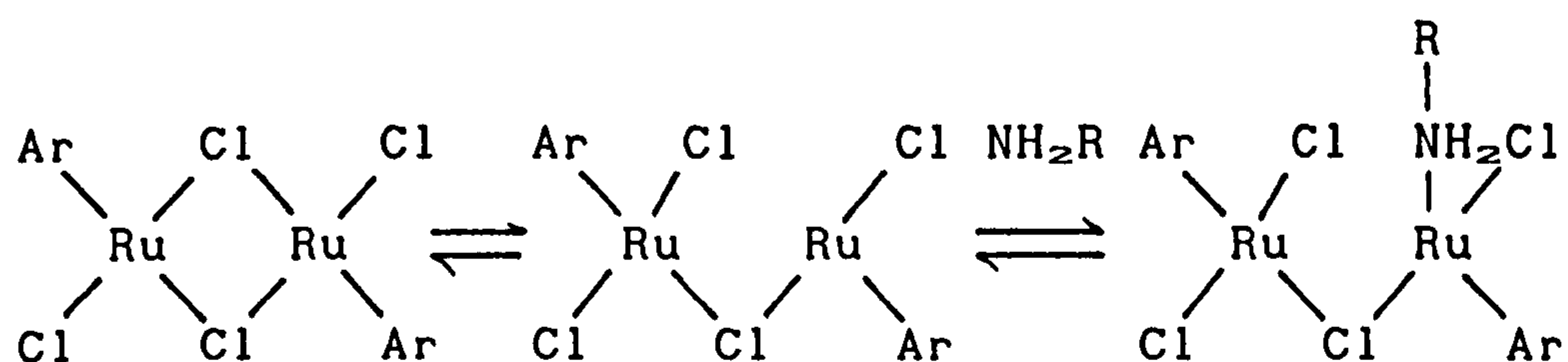


Scheme 5.1 Stephenson's postulated triply chloro bridged species formed in the dimer's reactions.

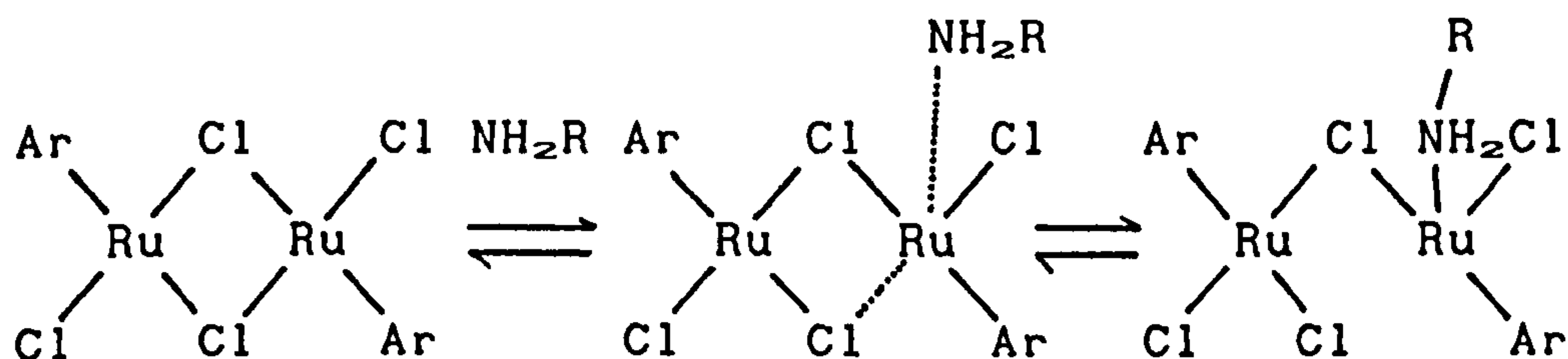
rate of reaction would have provided information on the bridge cleavage mechanism. Thus it is not possible to determine whether the individual steps (scheme 5.2) occur, via one of the three basic

mechanistic routes that are generally recognised:-

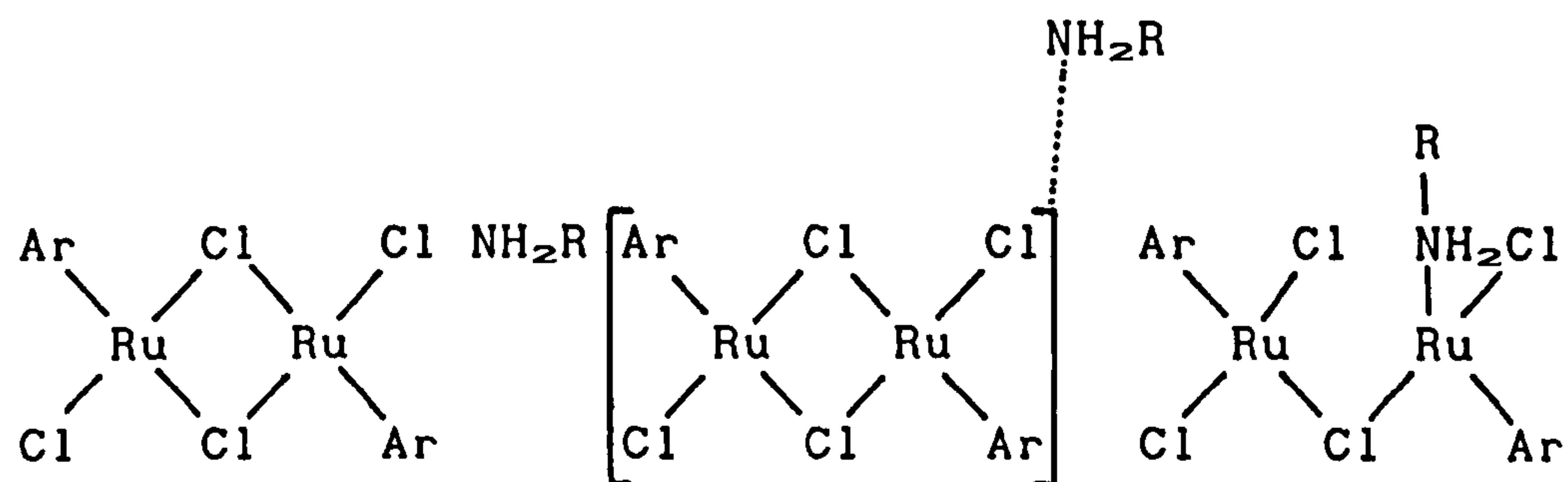
D(*dissociative*), where a reaction shows no dependence on the species reacting with the metal complex and has an intermediate containing a reduced coordination number.



A(*associative*), where a reaction depends on the nature and the coordination of the species reacting and has an intermediate containing an increased coordination number.



I(*interchange*), where a reaction involves the concerted exchange of ligands between the inner and outer coordination spheres of the metal and has an intermediate containing no altered coordination number.

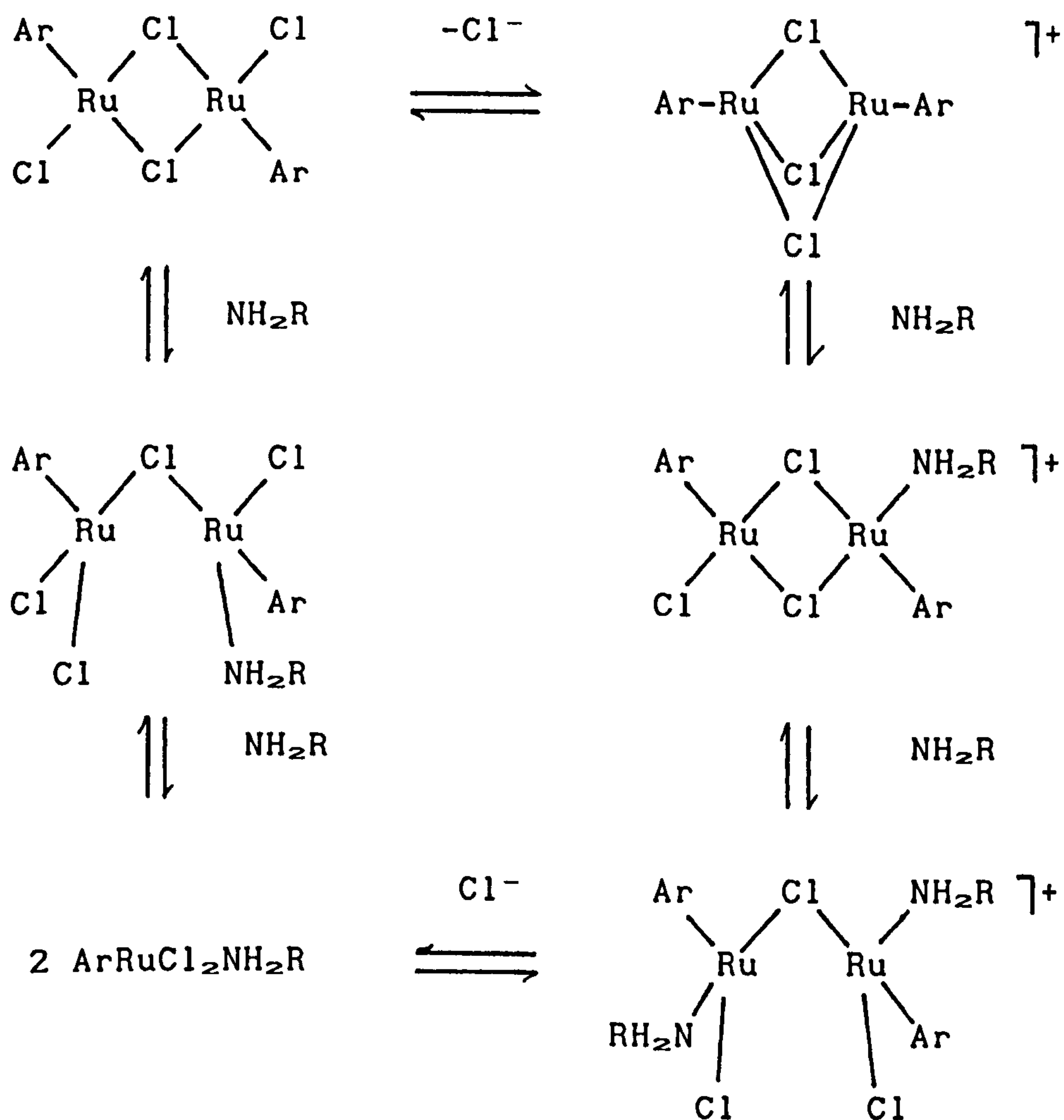


Interchange reactions may have a variety of transition states, ranging between the transition state displaying substantial bonding of the metal to both the entering and leaving groups, in which there is some dependence of rate on the entry group - I_a , and that of one in which only very weak bonding to the entry and leaving groups occurs and there is only a very slight dependence of the rate on the entry group - I_d .

Scheme 5.2 shows two different routes to the neutral mononuclear complexes formed, one from the neutral dimer, the other from the triply chloro bridged dimer. It is believed that the route from the neutral dimer will be more applicable due to the solvent system used. As mentioned above, it is not possible to determine whether the individual steps occur via the D, A, I_a , or I_d mechanistic routes. As shown in scheme 5.2, the final step utilising Stephenson's postulated triply bridged intermediate, involves a chloride ion. The reaction conditions used involved a large excess of the ligand in solution, which would compete with the

chloride ion, affording a mixture of reaction products. However, the reaction generally affords the monosubstituted mononuclear species in 80 to 90% yield - providing support that the intermediates are neutral species.

The three basic mechanistic routes, D, A and I, when applied to chloro bridge cleavage, still cater for the p-toluidine disubstituted product. After the initial ligand attack, a second amine attacks at the same ruthenium ruthenium centre.

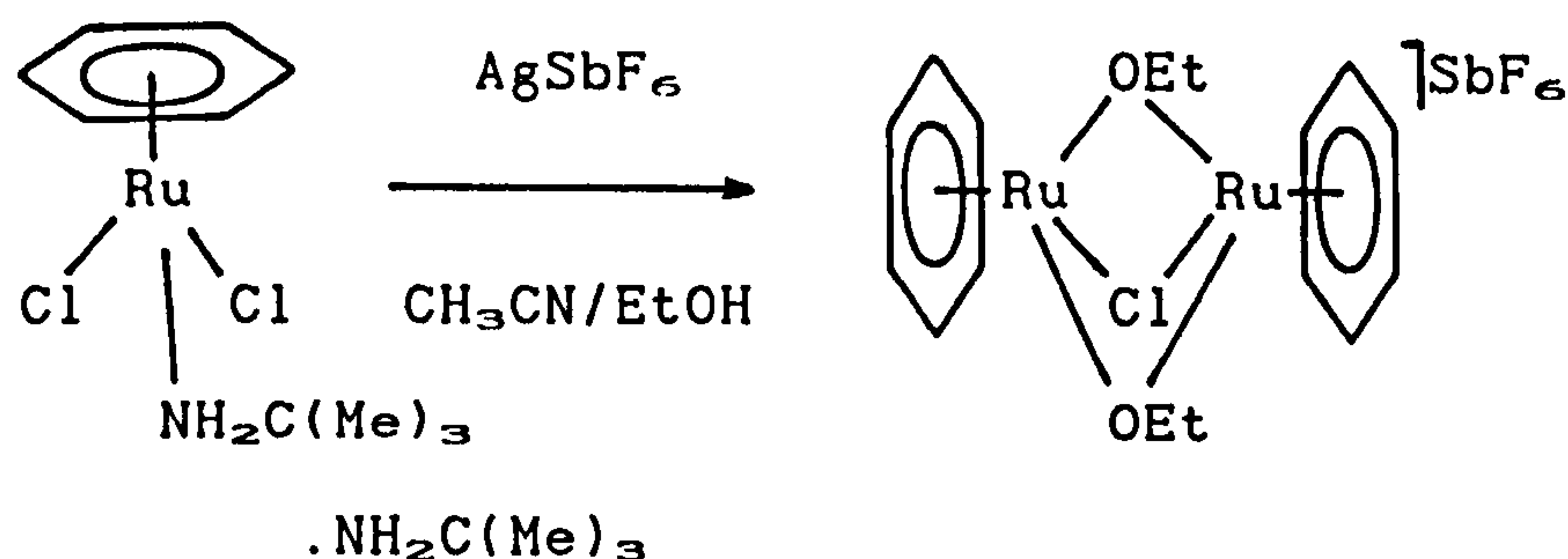


Scheme 5.2 Postulated mechanism for the formation of $\text{ArRuCl}_2\text{NH}_2\text{R}$

5.1.5 Chemistry of primary amine complexes

The reactivity of the mononuclear species was investigated with respect to reduction, reaction with base and cation formation via chloride abstraction.

5.1.5.1 Cation formation



After stirring $[(\text{C}_6\text{H}_5)\text{RuCl}_2\text{NH}_2\text{C}(\text{Me})_3] \cdot \text{NH}_2\text{C}(\text{Me})_3$ with AgSbF_6 in acetonitrile, the precipitated AgCl was removed and ethanol added to the reaction mixture to afford an orange crystalline solid.

The structure of the product, the ethoxide chloride bridging dimer, was determined by infrared, FAB mass spectrometry and microanalysis. ^1H nmr spectra could not be obtained due to the product's insolubility in chloroform and instability in acetone.

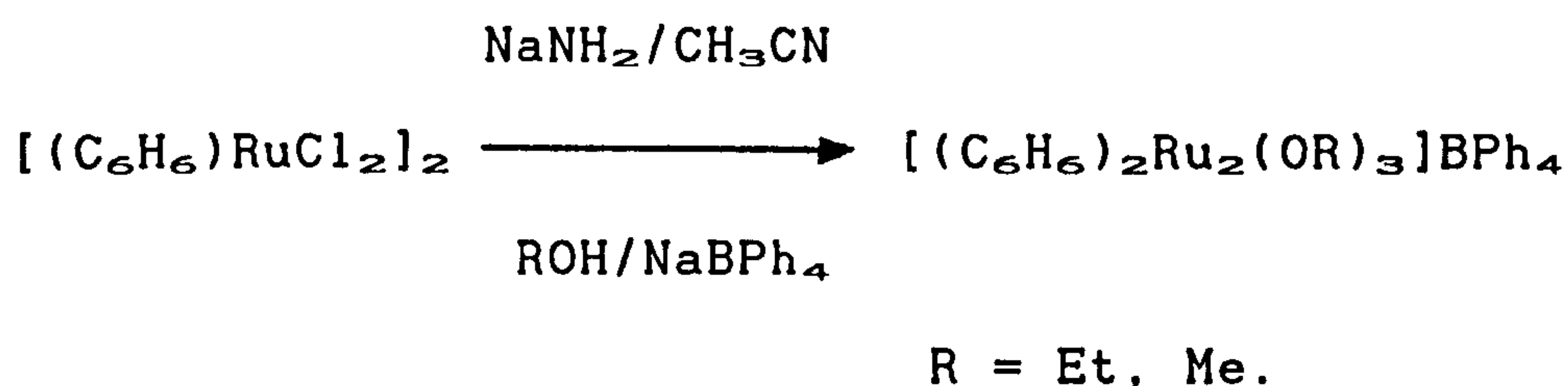
Infrared spectroscopy indicated absorptions due to an ethoxide $\nu(\text{C}-\text{O})$ stretch (1044cm^{-1}), the bridging mode of the ruthenium chloride stretch

(258cm⁻¹) and the presence of the counteranion, [SbF₆]⁻ (660, 356, 287cm⁻¹).

Microanalysis of the dimer confirmed the presence of one chloride atom and the purity of the complex. (See experimental).

The FAB mass spectrum showed the presence of a peak assignable to the molecular ion [(C₆H₆)₂Ru₂(OEt)₂Cl]⁺, and fragmentation patterns related to species with loss of one or two ethoxide ligands.

Referring to Stephenson's work on alkoxide bridged dimers⁸⁰,



it was discovered that the reaction conditions were such as to favour alkoxide bridging. On stirring [(C₆H₆)RuCl₂]₂ with acetonitrile and NaNH₂, a dark oil was afforded. On treatment with ROH/NaBPh₄ (R = Et, Me), the triply bridged complexes [(C₆H₆)₂Ru₂(OR)₃]BPh₄ were obtained.

It should be noted that Stephenson reported no such mixed alkoxide-halide triply bridged dimers.

This simple reaction, cation formation, involves the isolation of a species with no

coordinated amine. This implies that the Ru-N bonds of the amine complexes may be relatively weak.

The weakness of the Ru-N bond has been previously exploited, with the $[(\text{arene})\text{Ru}(\text{CH}_3\text{CN})_3]^{2+}$ complex, as a source of the $[(\text{arene})\text{Ru}]^{2+}$ fragment.²

5.1.5.2 Deprotonation and reduction

The simple mononuclear half sandwich complexes were also investigated with respect to deprotonation and reduction.

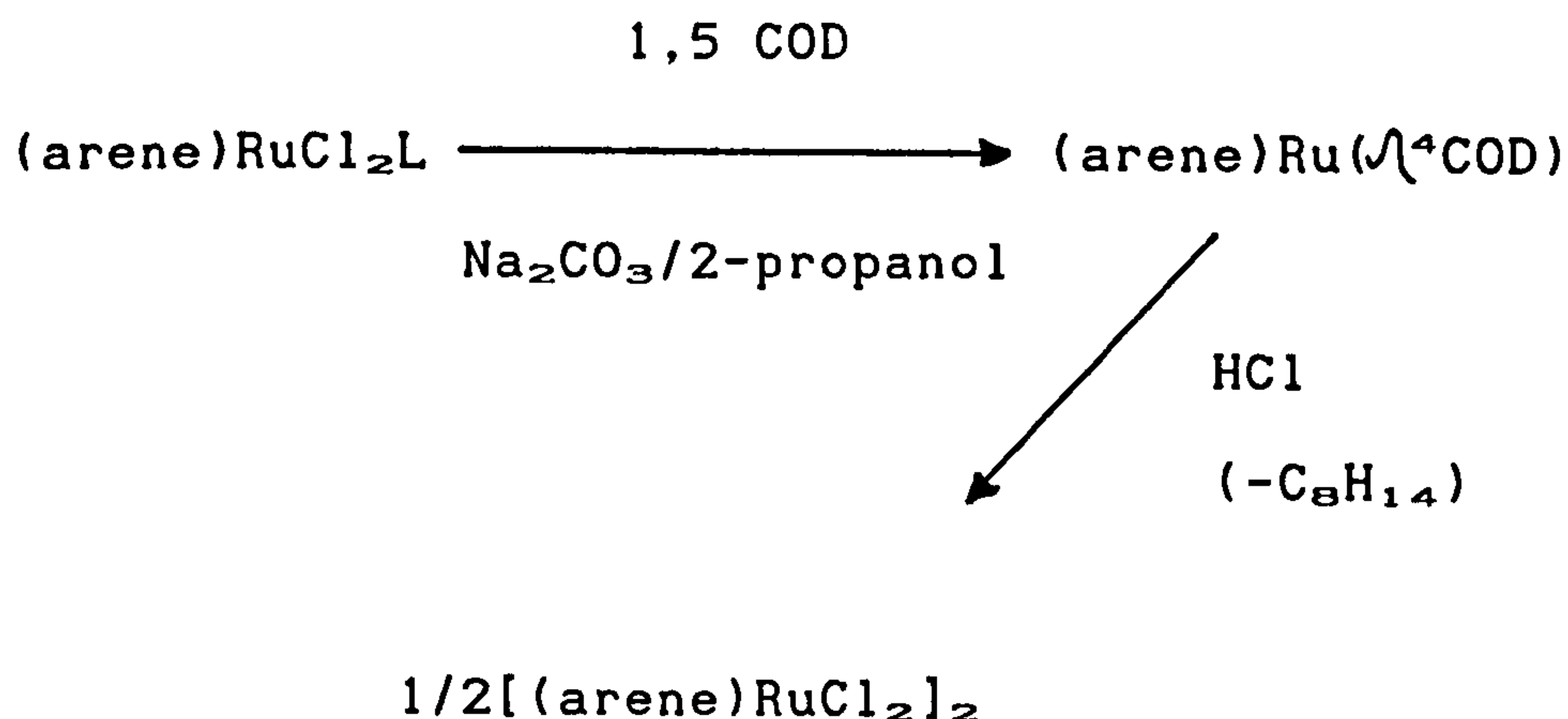
The aim of reacting the primary amine complexes with 1,8 diazabicyclo[5.4.0]undec-7-ene (DBU) was to form an imine by removal of HCl from the coordination sphere, which could then undergo simple dimerisation reactions.

Simple reduction reactions with Na-naphthalene were also investigated, to try and afford Ru(0) species.

In the case of both reactions, no isolable arene ruthenium complex could be obtained.

Bennett et al⁵⁵ have very recently reported the synthesis of a series of primary amine complexes, $(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5)$, $(\text{C}_6\text{H}_6)\text{RuCl}_2(\text{NH}_2\text{CH}_2\text{CH}_2\text{C}_6\text{H}_5)$, $(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2(\text{C}_2\text{H}_5\text{CH}(\text{NH}_2)\text{CH}_3)$ and $(\text{C}_6\text{H}_6)\text{RuCl}_2(\text{C}_2\text{H}_5\text{CH}(\text{NH}_2)\text{CH}_3)$.

The chemistry reported about these complexes, is associated with the reconversion of the half sandwich complexes to their dimeric precursors. This takes place in two steps, the formation of the ruthenium(0) complex (arene)Ru(η^4 COD), and subsequent treatment of this species with HCl.



(arene = C₆H₆, MeC₆H₄CHMe₂; L = PPh₃, PPhMe₂, NH₂CH₂CH₂C₆H₅ and C₂H₅CH(NH₂)CH₃)

After completion of this work, further investigation of this simple system was carried out by S. Harrison.¹⁸⁵ The complex (MeC₆H₄CHMe₂)RuCl₂NH₂C₆H₄Me was successfully synthesised and an X-ray crystal structure obtained. The complex is diagrammatically represented in figure 5.1. The Ru-N bond length was determined to be 2.118(2)Å. With reference to the known ruthenium nitrogen complex, [(C₆H₆)RuCl(NH₃)₂]⁺, there appears to be no

variation in the Ru-N bond length, $[2.129(10)\text{\AA}]^{B4}$, that could help explain the lability of the amine ligand on reaction of the complex.

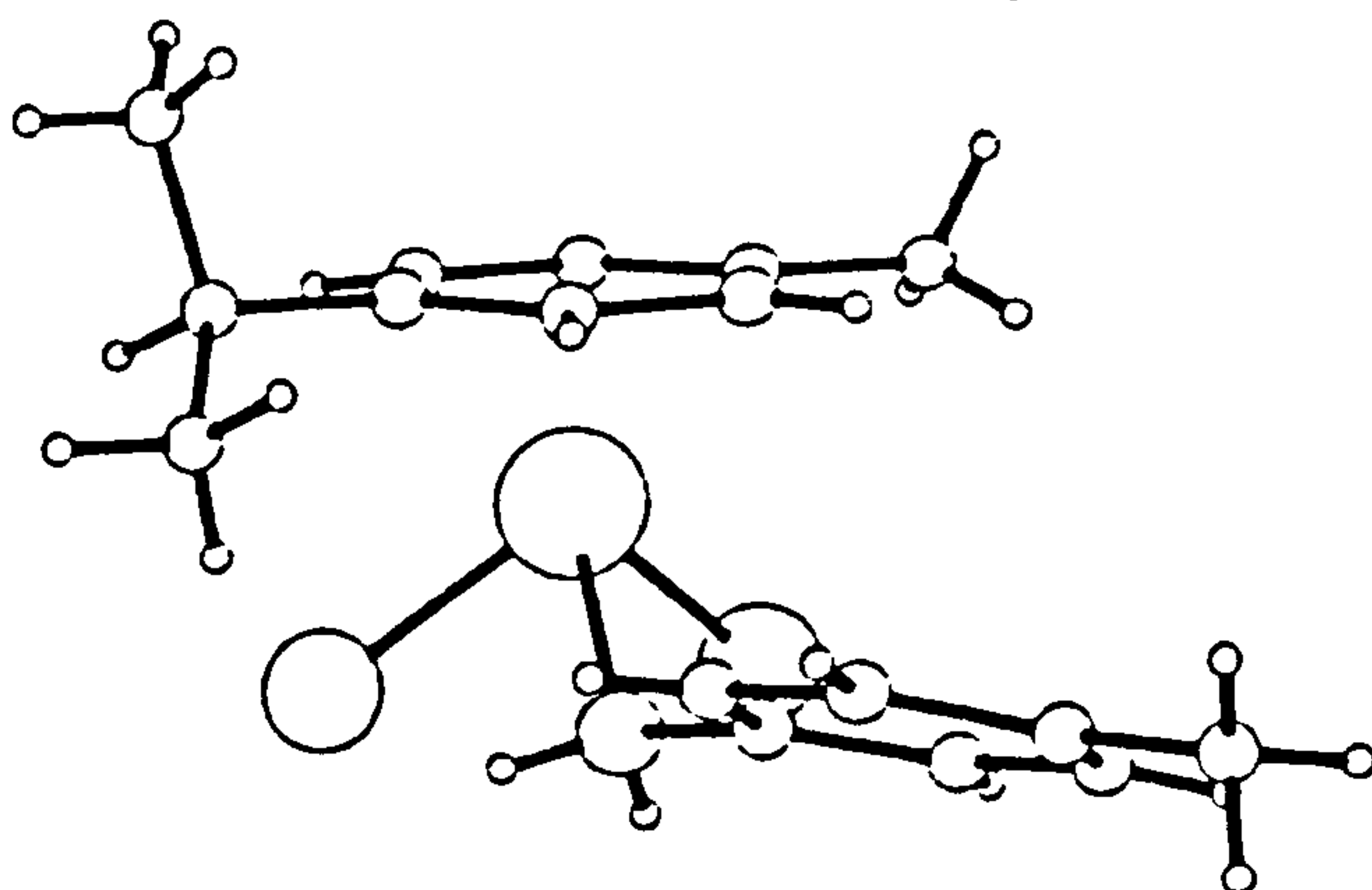


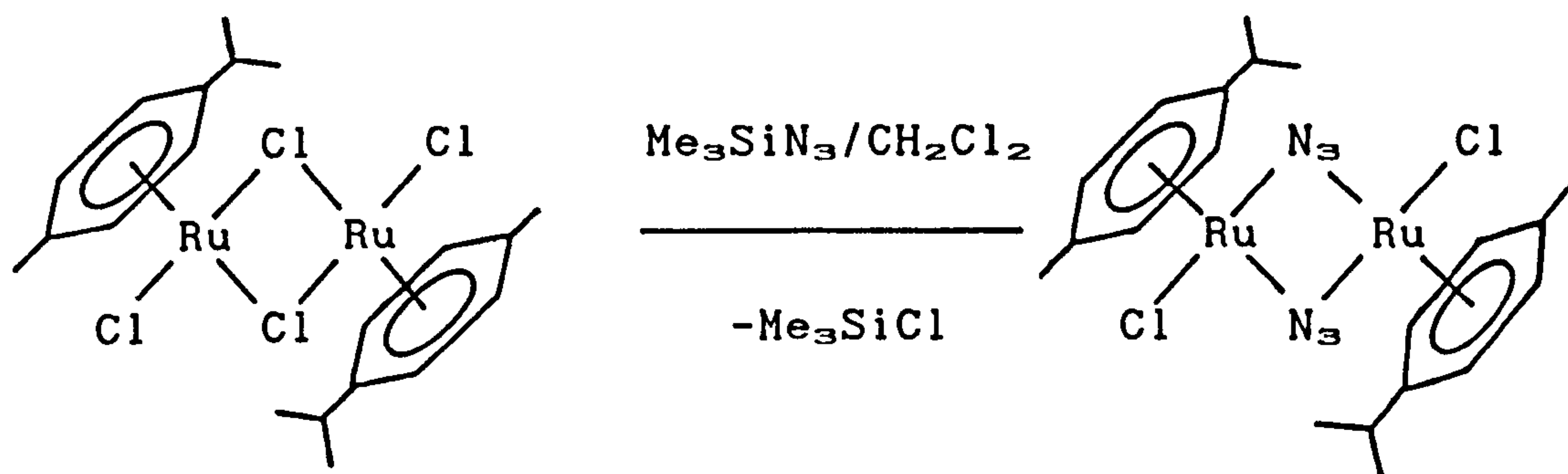
Fig. 5.1 Diagrammatically representation of $(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2\text{NH}_2\text{C}_6\text{H}_4\text{Me}$

5.1.6 Conclusions

As shown above, incorporating nitrogen based ligands into arene ruthenium complexes has been successful, with the introduction of a range of primary amines and pyridine. However, the reactions investigated to date showed that it was not possible to carry out any ligand based chemistry on these new substrates.

It was decided to investigate a different type of nitrogen based ligand. Azidotrimethylsilane was chosen for being an anionic nonsterically demanding ligand and for having the potential to eliminate trimethylsilylchloride, thus removing chloride from the coordination sphere.

5.2.1 Preparation of arene ruthenium azido complexes



Ultrasound was not required for this reaction.

Simple stirring of $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2$ with a large excess of Me_3SiN_3 (14:1), rapidly and quantitatively afforded the product, obtained as an orange crystalline solid on addition of hexane.

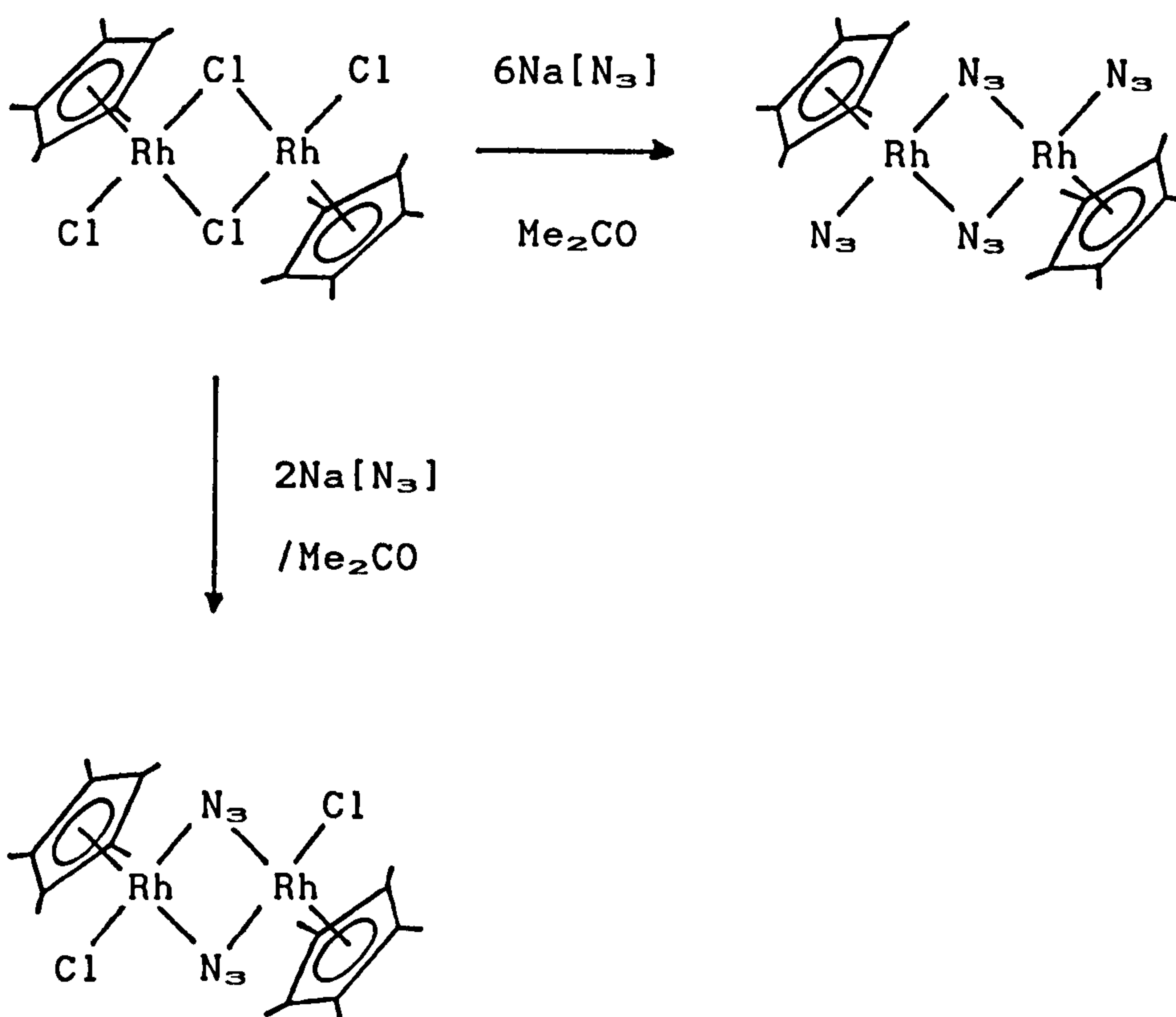
^1H nmr spectroscopy indicated the presence of new signals assignable to a complex with one type of freely rotating cymene ligand. These signals were shifted slightly to higher field with respect to the parent chloro dimer.

Infrared spectroscopy indicated absorptions relating to an azide, $\nu_{\text{as}}(\text{N}_3)$ stretch (2057cm^{-1}) and a terminal ruthenium chloride stretch, $\nu(\text{Ru-Cl})$ (281cm^{-1}).

An X-ray crystal structure determination was carried out to confirm the dimeric nature of the product. (See section 5.2.2).

Relatively little chemistry has been carried out upon coordinated azide transition metal complexes. However, the $[(\text{C}_5\text{Me}_5)\text{Rh}(\text{N}_3)_2]_2$ and $[(\text{C}_5\text{Me}_5)\text{Rh}(\text{N}_3)\text{Cl}]_2$ systems have been prepared and

investigated.¹⁶⁴ The complexes were obtained by reacting the isoelectronic $[\text{cp}^*\text{RhCl}_2]_2$ dimer with $\text{Na}[\text{N}_3]$ in acetone. The favoured product was the tetrakis azido species; the analogue of the ruthenium complex could only be afforded if stoichiometric quantities of $\text{Na}[\text{N}_3]$ were used.



Of these two complexes, the tetrakis azido complex undergoes a more diverse range of reactions. These include bridge cleavage, carbonylation (to afford $[(\text{cp}^*)_2\text{Rh}_2(\text{NCO})_4]$ and $[(\text{cp}^*)_2\text{Rh}_2(\text{NCO})_2(\mu\text{-NCO})(\mu\text{-N}_3)]$) and reaction with CS_2 to yield $[(\text{cp}^*)_2\text{Rh}_2(\text{SCN})_4]$.

However, the reaction conditions utilised for the synthesis of the cymene ruthenium azide dimer,

whether varied in terms of ligand concentration or reaction time, did not afford the tetrakis azido substituted analogue of the rhodium system. This is probably a reflection of the respective nucleophilicity of the azide ligands used in both preparations. The ionic azide is a stronger nucleophile than Me_3SiN_3 and thus when $\text{Na}[\text{N}_3]$ is utilised, the $[(\text{cp}^*)_2\text{Rh}_2(\text{N}_3)_4]$ dimers can be afforded.

5.2.2 Structure of $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)]_2$

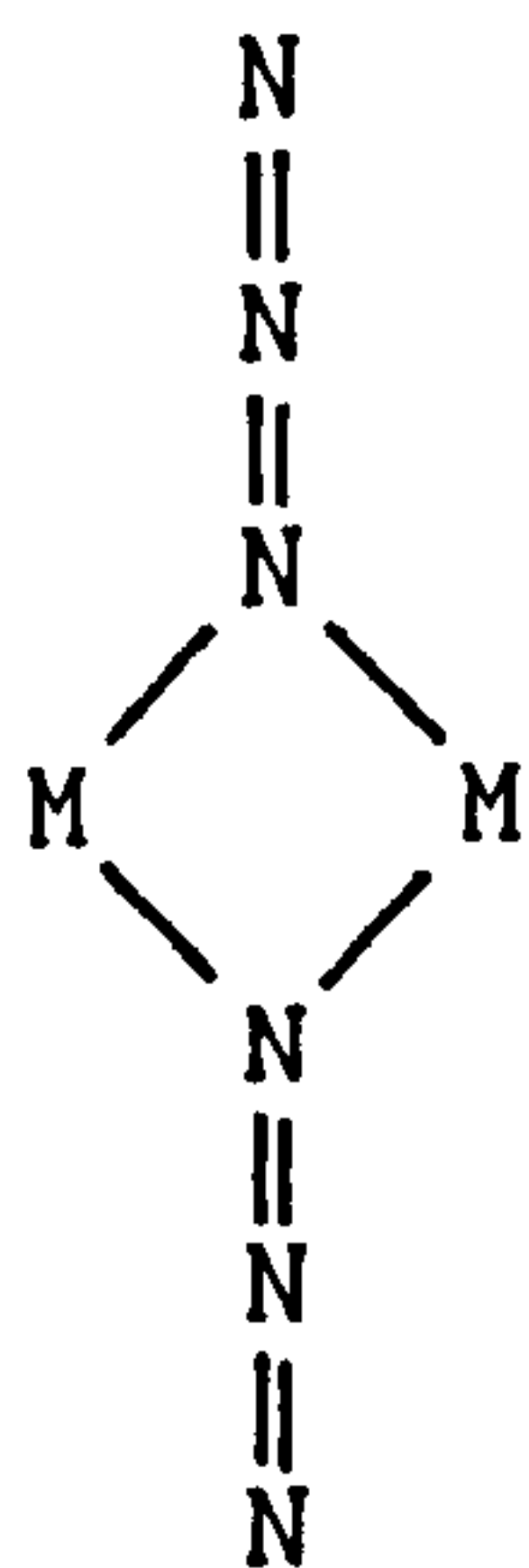
Azide complexes of transition metals are conveniently divided into three groups;

a) complexes containing an azide group bound to one metal atom.

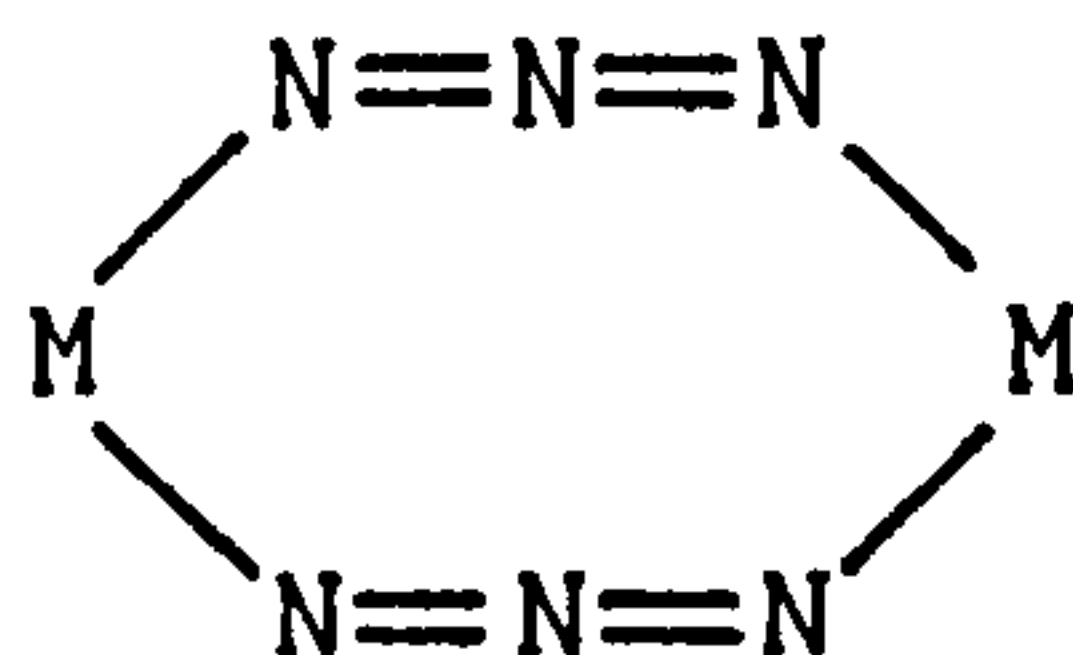
b) complexes containing an azide group bridging two metal atoms through the same nitrogen. (see below)

c) complexes containing an azide group bridging two metal atoms through the two end nitrogens. (see below)

The factors influencing the mode of bridging are not fully understood. Structures of group b), with a four membered ring, may have to overcome a non-bonding repulsion which increases due to



b)



c)

crowding of the coordination sphere, as there is a relatively short metal-metal distance. Thus when steric crowding is an important factor, group c), with the eight membered ring, may be favourable.

Coordination of azides to transition metals can be easily detected by an intense infrared absorption band which occurs above 2000cm^{-1} .¹⁶⁵ A single $\nu_{\text{as}}(\text{N}_3)$ stretching mode is observed in the infrared at 2057cm^{-1} , as is expected for molecules in the C_1 point group in which only the A_1 mode is infrared active. The $\nu_{\text{s}}(\text{N}_3)$ stretching mode would be expected at about 1300cm^{-1} ; although it is often observed as a weak band, it is not seen in the present example.

However, when characterising new azide systems, one should avoid making comparisons between complexes which are of different geometry or which contain different metal atoms in different

oxidation states. Generally, determination whether the azide ligand is terminal or bridging, cannot be established solely from infrared data. It should also be noted that the vibrational mode of bridging azides, b) or c) as depicted above, cannot be assigned from the number of infrared active vibrations since both structures have similar symmetry.¹⁶⁵

Thus an X-ray crystal structure determination of the cymene ruthenium chloro azido complex was necessary to clarify the nature of the azide ligand bonding.

The crystal was triclinic, of space group $P\bar{1}$. This implies that the complex has the crystallographic imposed symmetry of a point of inversion, midway between the metal atoms. (Fig.5.2) The consequence of this, was that only half of the structure needed

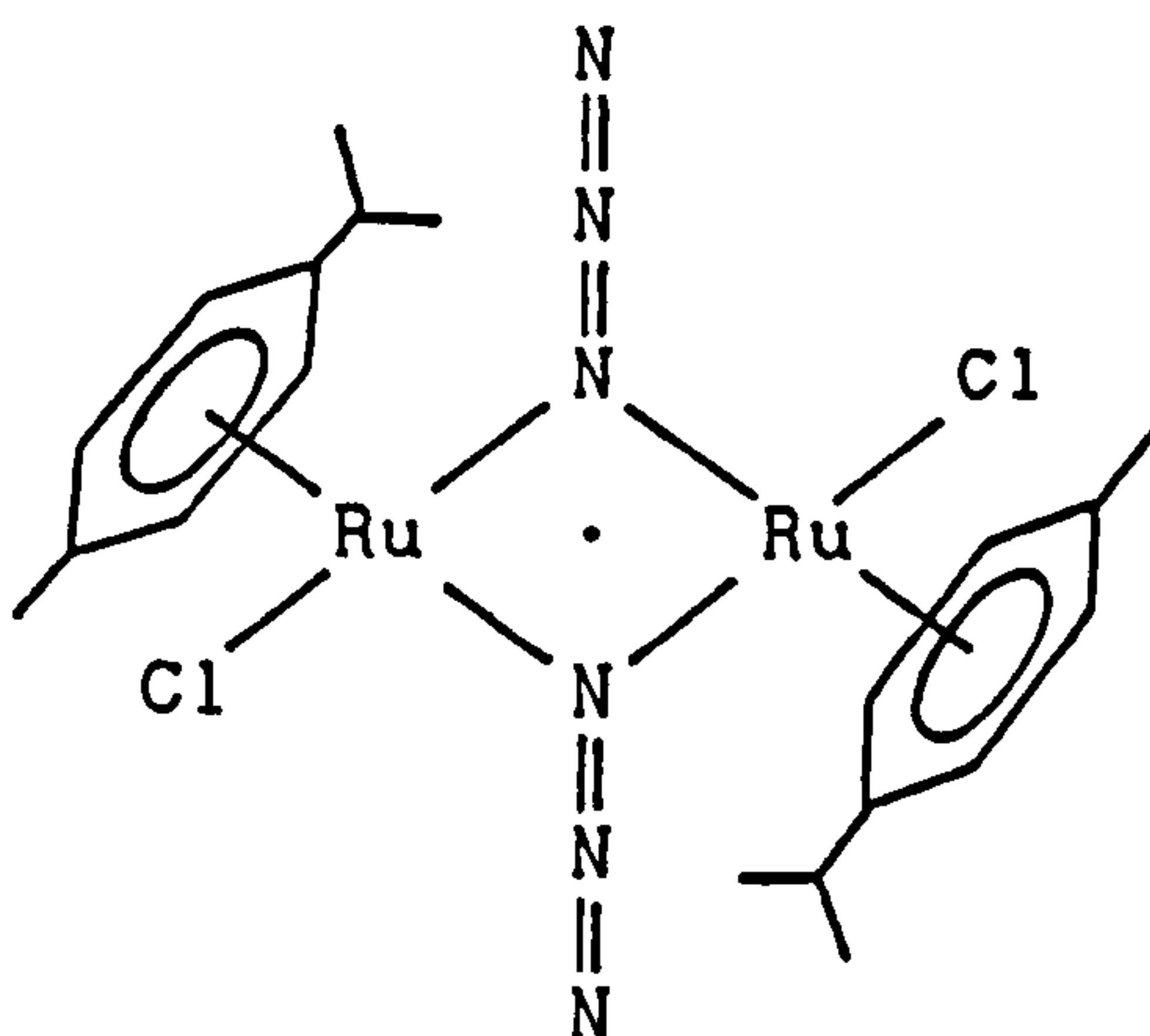


Fig 5.2 Diagram of $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)]_2$ showing point of inversion.

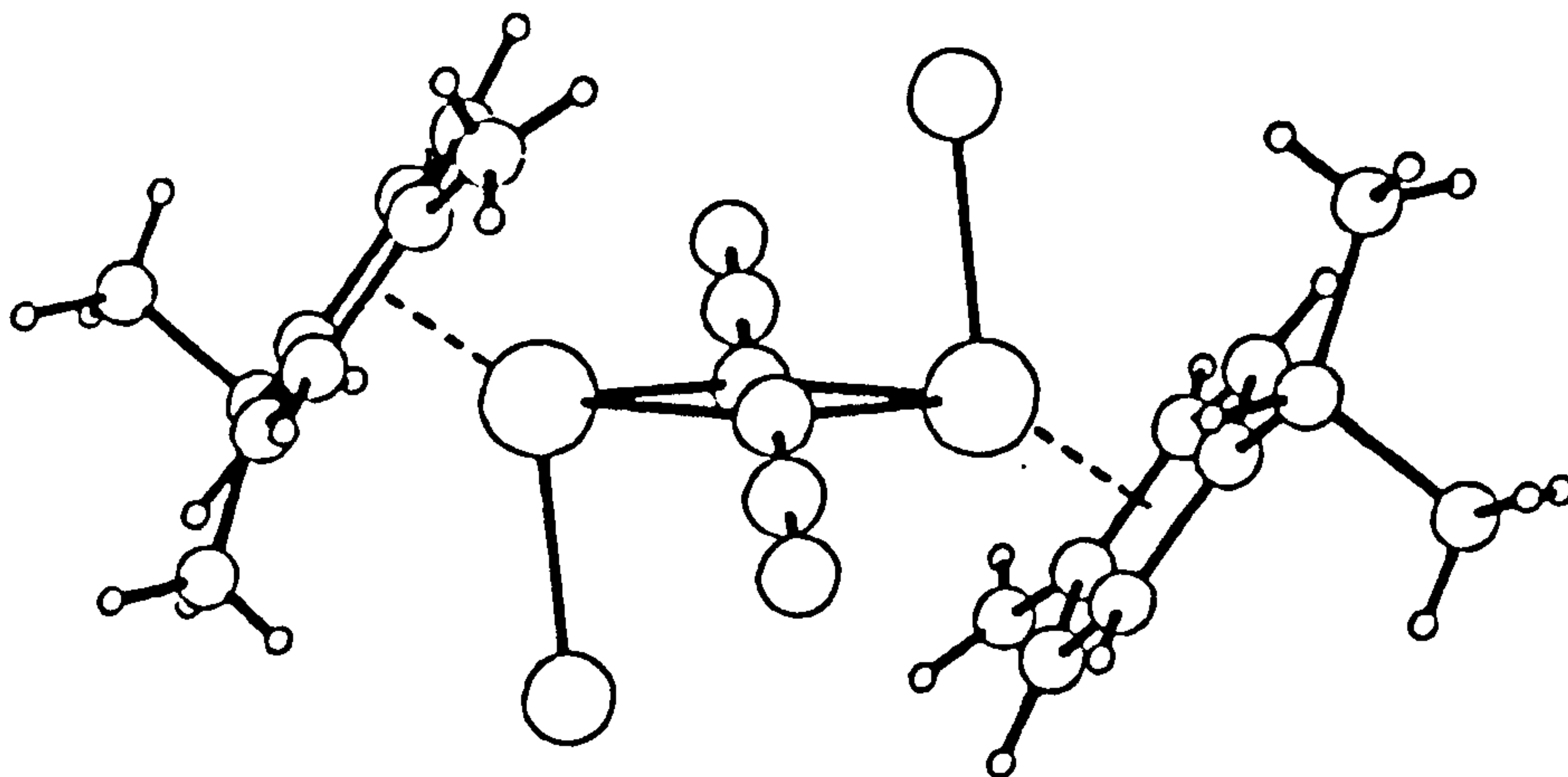


Fig 5.3 Diagrammatic representation of $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)]_2$.

to be solved, as the other half is merely a reflection of the first. Thus table 5.3 contains just half of the bond lengths and angles of the dimer.

As shown in figure 5.3, the complex was determined to be dimeric, with the two azide ligands bridging the two metals. The bonding mode of the azide bridge was type b), bridging the two metal atoms through the same nitrogen.

The cymene ring is essentially planar and the distance from the ring to the metal is $1.657(1)\text{\AA}$, a distance very similar to that found in $[(\text{C}_6\text{Me}_6)\text{RuCl}_2]_2$.⁸⁵

A trend may be proposed on comparison of neutral half sandwich complexes and arene dimers. The distance between the arene carbon atoms and the metal are slightly shorter for the dimer complexes. (See table 5.2)

Table 5.2 Ruthenium arene carbon bond lengths

Complex	Ru-C / Å
$[(\text{HMB})\text{RuCl}_2]_2$	2.179(2) - 2.209(2)
$[(\text{CYM})\text{RuCl}(\text{N}_3)]_2$	2.152(3) - 2.195(3)
$(\text{BZ})\text{RuCl}_2\text{PMe}_2\text{Ph}$	2.190(10) - 2.270(10)
$(\text{CYM})\text{RuCl}_2\text{PMe}_2\text{Ph}$	2.220(10) - 2.250(10)

This may be explained in terms of electron donation to the metal from the arene. The half sandwich complexes contain a nucleophilic ligand, which has donated electron density to the metal. This limits the electron donation the metal may accept from the arene and thus increases the metal-arene bond length, with respect to that observed in the dimer species. However, steric factors involving the nucleophilic ligand may contribute to this apparent trend.

The Ru-Cl distance of 2.395(1)Å is very close to that determined for the hexamethylbenzene complex.

The surprising feature of the structure, is that the ligating nitrogens are pyramidally coordinated, not planar, with the angles about the nitrogen summing to 351.6° . The ruthenium atoms and ligating nitrogens lie in a plane, whilst N(2) and N(3) lie $0.514(2)$ and $0.992(3)\text{\AA}$ respectively out of the plane.

An examination of non-bonding interactions and a space filling model of the molecule failed to reveal any steric interactions that might cause the bending.

A related rhodium complex also contains a bridging azide ligand and has the same overall geometry, but in this case the angles about the ligating nitrogen do not differ significantly from those required for planarity.¹⁶⁴ (See figure 5.4)

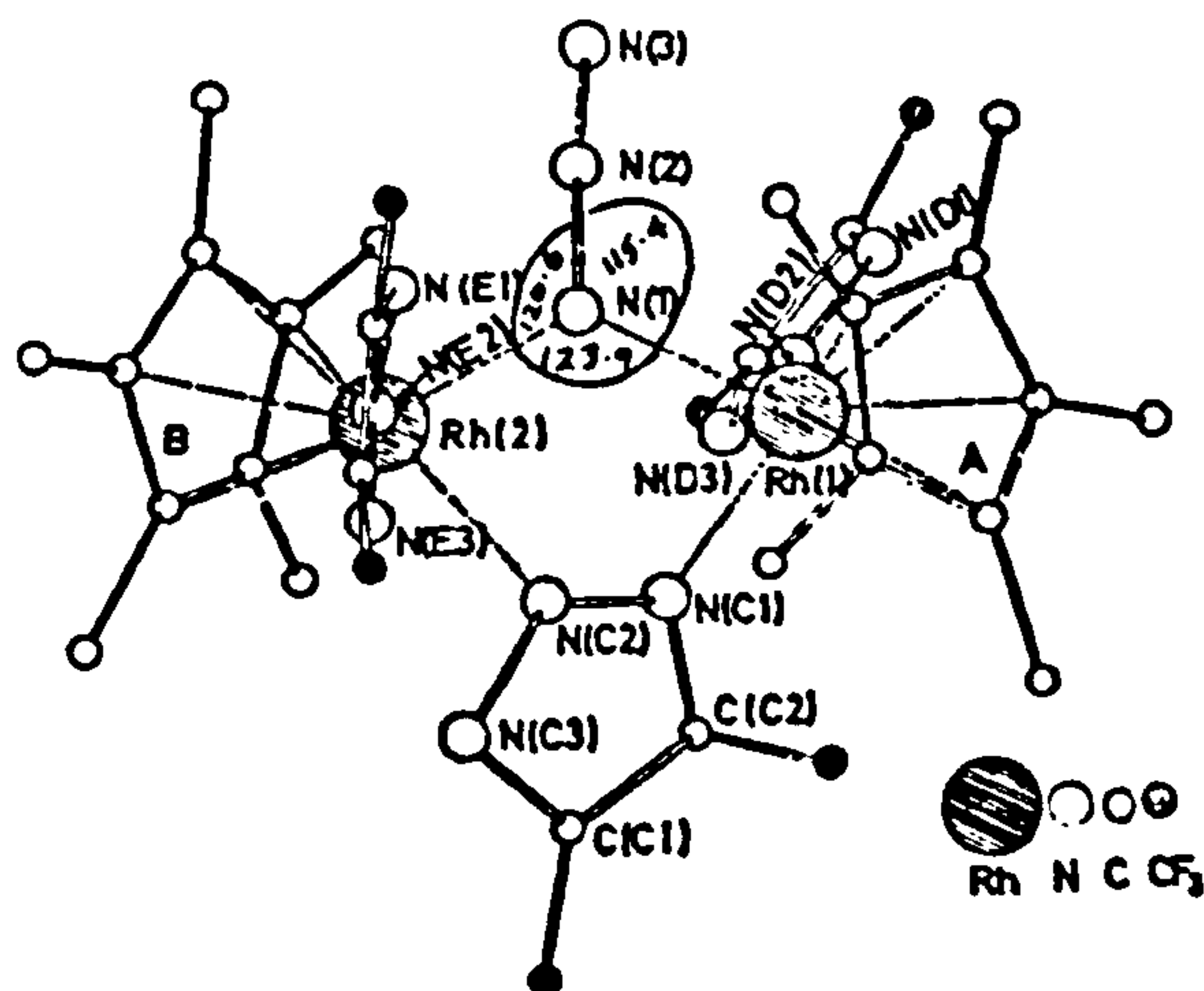


Fig 5.4 Diagrammatical representation of $[(C_5Me_5)_2Rh_2\{N_3C_2(CF_3)_2\}_3(N_3)]$

Table 5.3 Bond lengths (Å) and angles (°) for
 $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)]_2$. with estimated standard
deviations in parentheses.

Ru1	Ru1'	3.448(1)	C1	C2	1.419(5)
Ru1	C11	2.395(1)	C1	C6	1.408(5)
Ru1	N1	2.165(3)	C2	C3	1.409(5)
Ru1	N1'	2.176(3)	C3	C4	1.412(5)
Ru1	C1	2.182(3)	C3	C8	1.518(6)
Ru1	C2	2.161(3)	C4	C5	1.409(5)
Ru1	C3	2.195(3)	C5	C6	1.409(5)
Ru1	C4	2.152(3)	C6	C7	1.495(5)
Ru1	C5	2.176(3)	C8	C9	1.534(7)
Ru1	C6	2.187(3)	C8	C10	1.513(7)
N1	N2	1.141(5)	N2	N3	1.148(5)

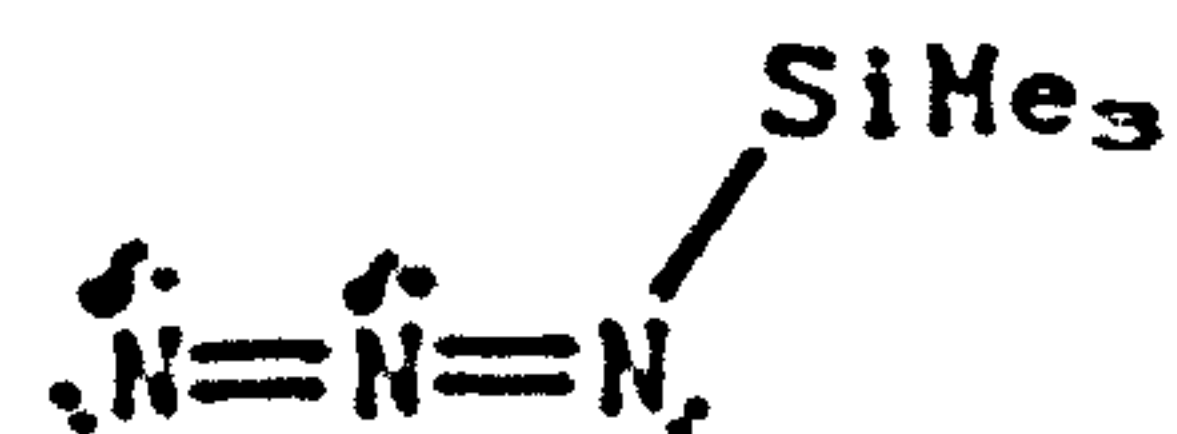
C11	Ru1	N1	85.6(1)
C11	Ru1	N1'	85.4(1)
C11	Ru1	C1	104.2(1)
C11	Ru1	C4	137.3(1)
N1	Ru1	N1'	74.8(1)
N1	Ru1	C1	170.0(1)
N1	Ru1	C4	91.4(1)
N1'	Ru1	C1	107.4(1)
N1'	Ru1	C4	134.7(1)
Ru1	N1	Ru1'	105.2(1)
Ru1	N1	N2	122.4(1)
Ru1'	N1	N2	124.1(1)
N1	N2	N3	177.7(1)

Table 5.3 continued

C2	C1	C6	120.2(2)
C1	C2	C3	121.7(1)
C2	C3	C4	116.8(2)
C2	C3	C8	123.4(2)
C4	C3	C8	119.7(2)
C3	C4	C5	122.4(2)
C4	C5	C6	120.0(2)
C1	C6	C5	118.8(2)
C1	C6	C7	119.9(2)
C5	C6	C7	121.2(2)
C3	C8	C9	109.0(2)
C3	C8	C10	114.0(2)
C9	C8	C10	110.8(2)

5.2.3 Mechanism

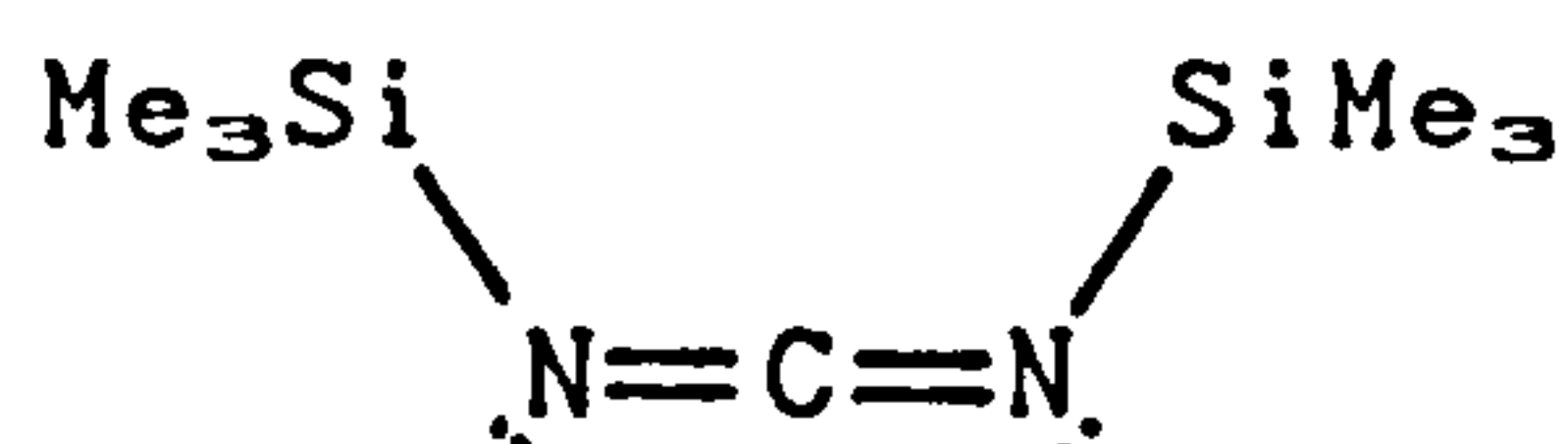
The reagent azidotrimethylsilane, when undergoing nucleophilic attack, has two nucleophilic nitrogens:



It would appear that the terminal nitrogen is more nucleophilic and most likely to form the metal

azide bond.

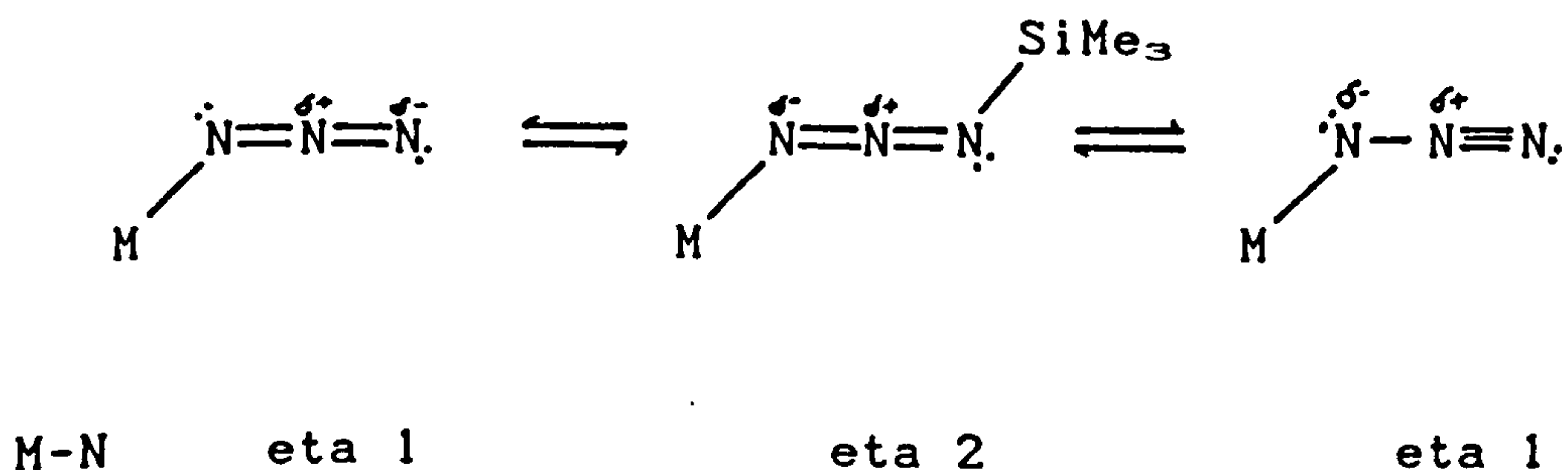
After completion of this work, an investigation of the bis(trimethylsilyl) carbodiimide ligand,



was carried out.¹⁶⁶ On stirring or heating with $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2$, no reaction occurred.

The nucleophilic nitrogens of this ligand have a similar environment to that of the nitrogen in the azidotrimethylsilane, which is linked to the trimethylsilyl leaving group. This non reactivity implies that the terminal nitrogen was most likely to coordinate to the ruthenium metal centre.

It is postulated that the azidotrimethylsilane coordinates to the ruthenium centre before elimination of Me_3SiCl , effecting the azide metal bond to be pseudohalide, with subsequent bridging via the lone pair on the said nitrogen.



At present there is no information to indicate

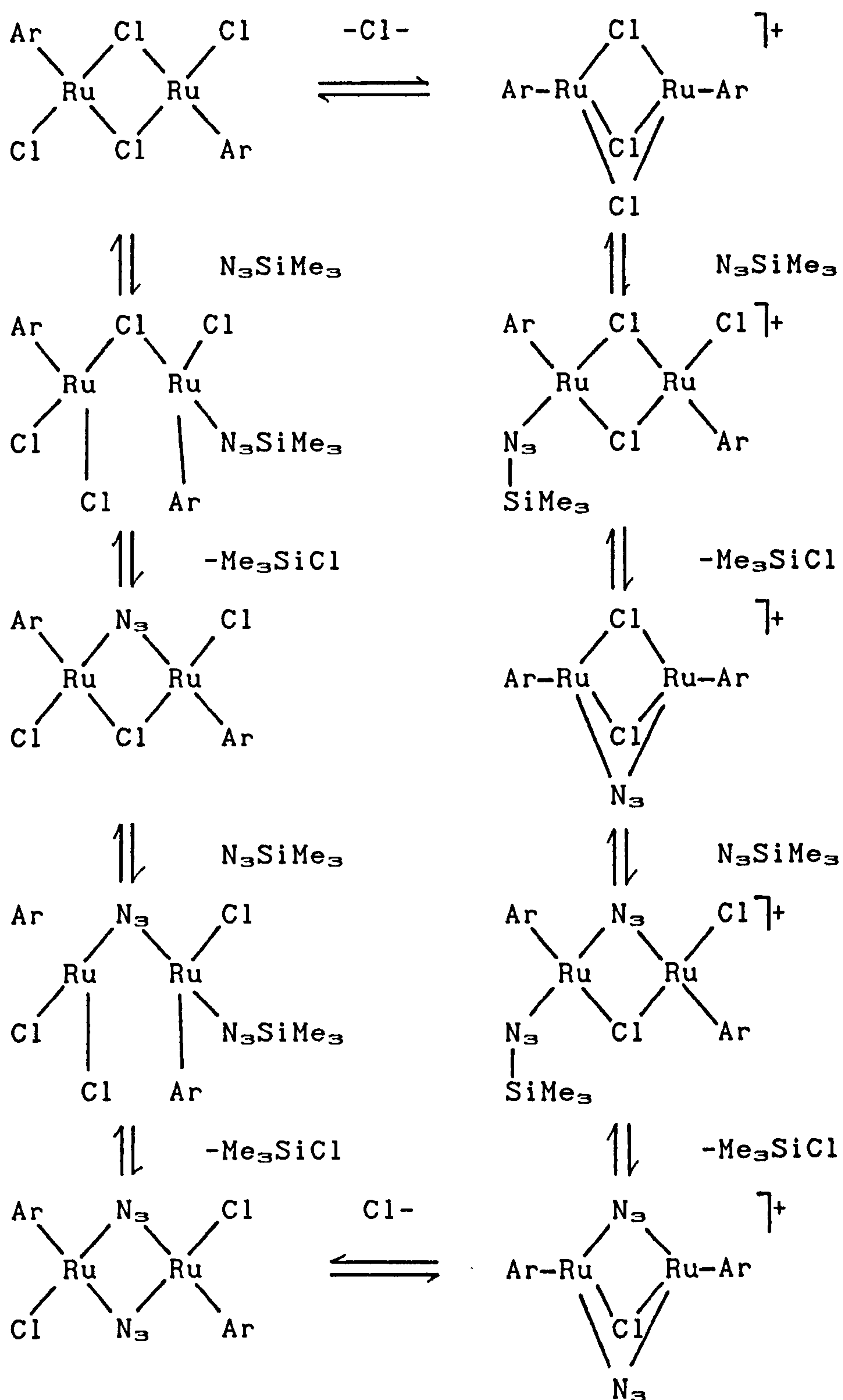
whether this elimination process occurs inter or intra molecularly.

The mechanism proposed for the bridge cleavage reaction by primary amines, depicted in scheme 5.2, can be applied to the formation of the azide dimer. Dimerisation of two (arene) $\text{RuCl}_2\text{N}_3\text{SiMe}_3$ complexes with the elimination of two moles of Me_3SiCl , could afford the azide dimer.

However, it seems more likely that after initial attack by Me_3SiN_3 at a ruthenium centre, the elimination of Me_3SiCl generates a vacant coordination site at the other metal centre, enabling the formation of a bridging azide bond and keeping the two metal system intact.

This is depicted in scheme 5.3, where the azide dimer is obtained by two possible routes. As in scheme 5.2, the routes are derived from the neutral dimer and the triply bridged dimer.

It is not possible to determine whether the individual steps involving nucleophilic attack occur associatively, dissociatively or via an interchange method. The solvent system should favour the neutral dimer route, but there is evidence that this system readily forms triply bridged species.



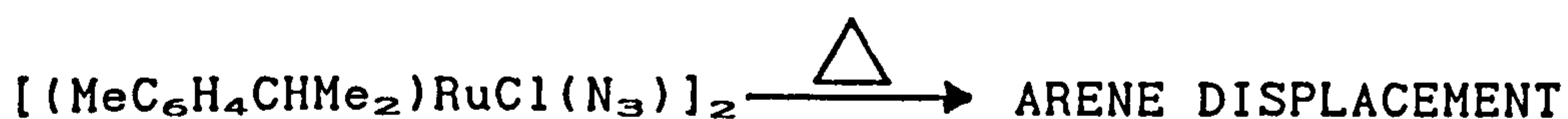
Scheme 5.3 Postulated mechanism for the formation of $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)]_2$.

5.2.4 Investigation of the chemistry of the azide dimer

The $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)]_2$ dimer was investigated to compare its reactivity with that of the chloro dimer starting material. The complex was examined to see how close to the isoelectronic parent dimer it behaved and if ligand chemistry of the azide ligand could take place.

5.2.4.1 Thermolysis

Thermolysis was investigated as a method to cleave the RuN-N_2 bond. The $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)]_2$ dimer was refluxed in toluene for 4 hours. The solution, which turned from orange to black, was monitored throughout the reaction by ^1H nmr and infrared spectroscopy. Loss of arene was readily proved by the presence of free cymene ligand in ^1H nmr spectra.

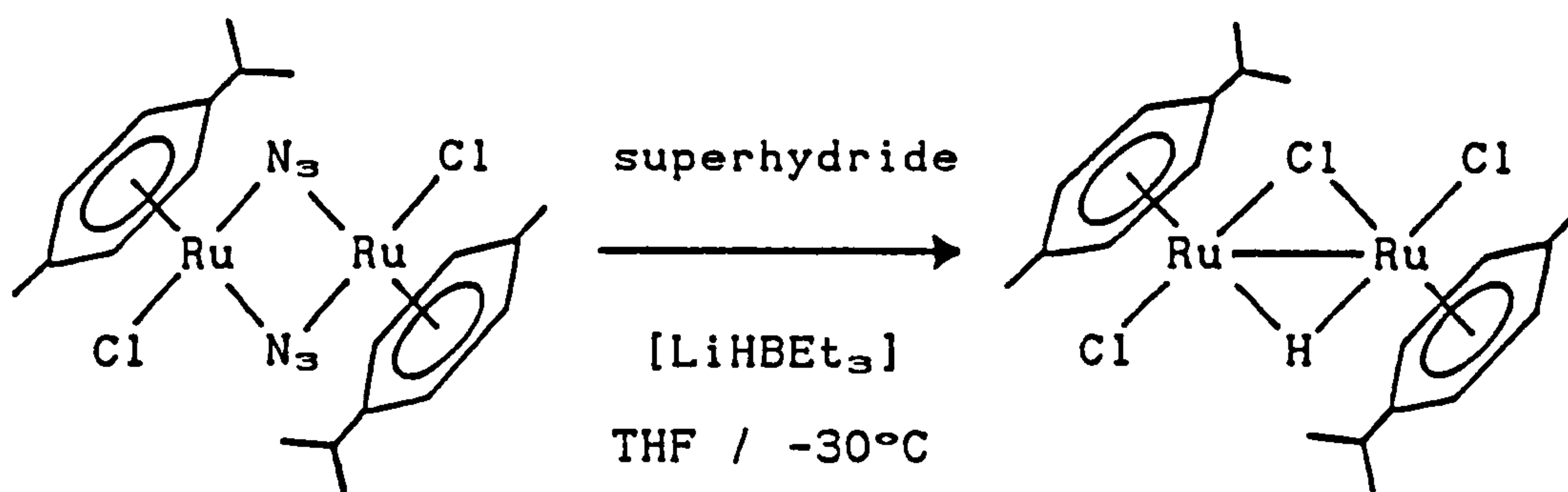


No arene containing product was obtained by thermolysis of the azide dimer. However, heavy metal azides were produced as black microcrystalline powders, which once detonated on handling.

Simple photolysis was also investigated, with the aim of cleaving the RuN-N₂ bond. Only decomposition of the dimer appeared to occur.

5.2.4.2 Hydride reaction

The azide dimer was reacted with different sources of hydride to give a number of hydride containing products. The reactions were followed by ¹H nmr spectroscopy. One product was isolated and characterised.



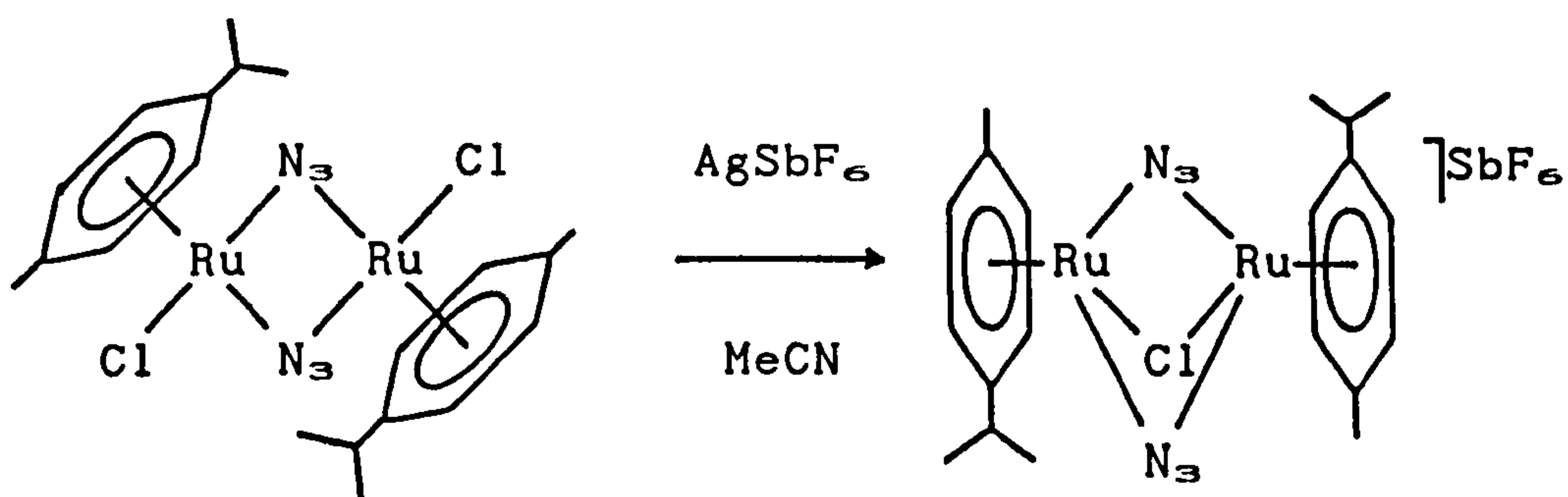
Superhydride was added dropwise to a solution of [(MeC₆H₄CHMe₂)RuCl(N₃)]₂ in tetrahydrofuran, at -30°C. A range of products containing hydride ¹H nmr signals were obtained as a complex mixture. Although a minor product, from a number of purification steps, one complex was fully characterised. This product was confirmed to be the monohydride chloride species, by comparison of the ¹H nmr spectra with that of the known complex.⁴⁴ (See experimental).

Formation of the above hydride dimer.

illustrates that the azide ligand can be removed from the coordination sphere. However, the reaction is not straight forward and hence does not provide an entry into ligand-based chemistry of the azide group.

5.2.4.3. Cation formation

The analogous reaction of the formation of the triply chloro bridged dimer, from the parent chloro dimer was investigated.



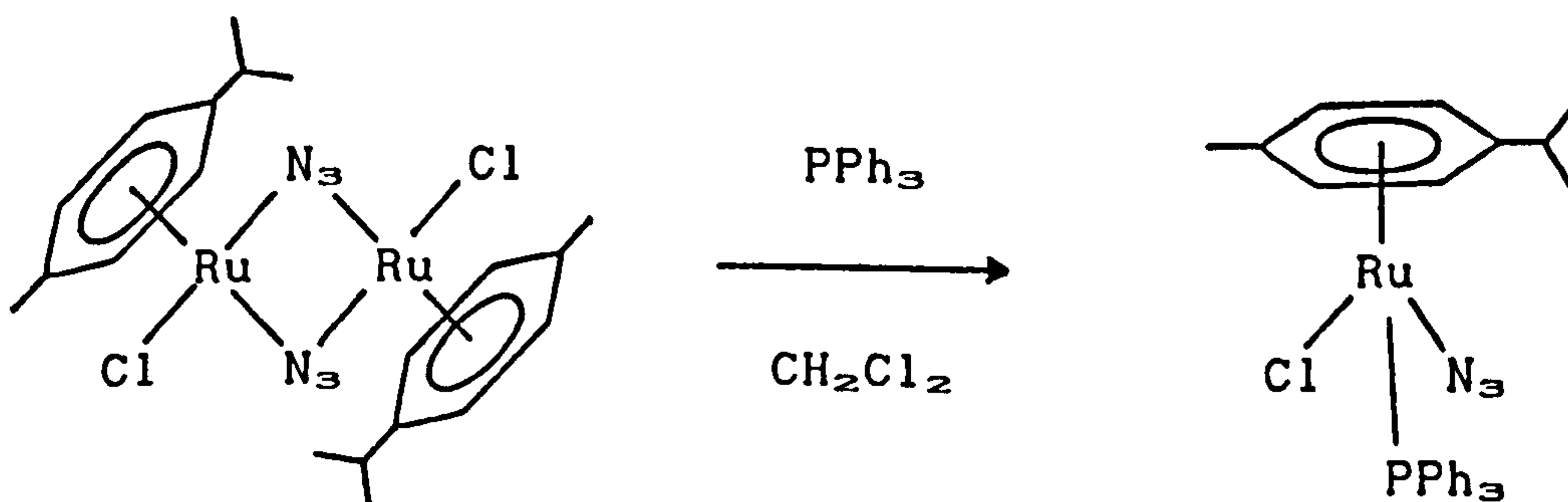
Stirring $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)]_2$ in acetonitrile, in the presence of AgSbF_6 , affords the triply bridged dimer $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Ru}_2\text{Cl}(\text{N}_3)_2]\text{SbF}_6$. The reaction was readily reversible. The neutral dimer was formed when the cation dimer was allowed to stand overnight in a chlorinated solvent. Although a simple reaction, this illustrates that the azide dimer can undergo reaction and retain the dimeric form.

^1H nmr spectra indicated that the cymene

ligands were not rotating freely on the nmr time scale, and thus the arene proton region was complex. The $\nu_{as}(\text{N}_3)$ stretch, (2062cm^{-1}), shifts to higher wavenumber relative to the neutral dimer and infrared spectroscopy also confirms the cationic nature of the product, by the assignment of absorptions relating to the counteranion $[\text{SbF}_6]^-$. (See experimental)

5.2.4.4. Simple cleavage reactions

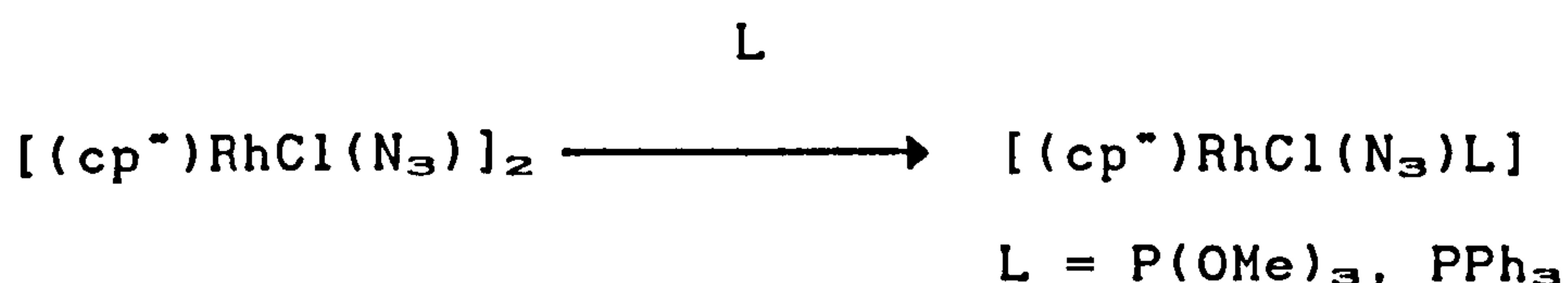
The classic bridge cleavage reaction was investigated for the azide dimer. It was determined that the azide dimer was more robust with respect to bridge cleavage than the chloro dimer. Application of the identical reaction conditions that were used to form the tertiarybutylamine half sandwich complexes, $(\text{arene})\text{RuCl}_2\text{L}$, afforded a mixture that always contained some starting material. However, a soft nucleophile such as PPh_3 reacted readily and quantitatively to form the expected monosubstituted mononuclear half sandwich complex:



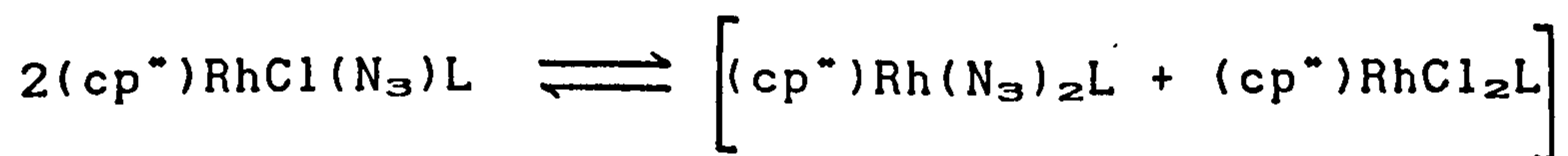
Infrared spectroscopy indicated the presence of one $\nu_{as}(N_3)$ stretch (2039cm^{-1}). With reference to the $\nu_{as}(N_3)$ stretch of the starting material, it can be assumed to be terminal in nature.

The ^1H nmr spectra of the complex showed three sets of signals assignable to cymene ligands.

The rhodium system on reaction with P(OMe)_3 or PPh_3 , also gave three sets of product signals, indicated by ^{31}P and ^1H nmr spectroscopy.¹⁶⁴



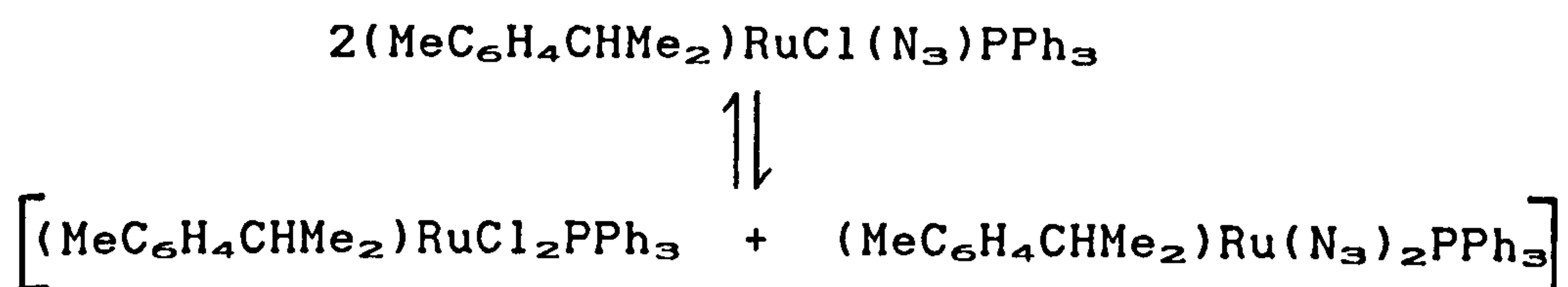
Maitlis et al ascribed the three product signals to have been derived from the disproportionation in solution of the initial half sandwich complex,



This appeared to be the case for the ruthenium system. Varying the recrystallisation procedure, altered the ratio of the signals. Of the three products expected to be present if disproportionation had occurred, the $(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2\text{PPh}_3$ complex would be readily identifiable by comparison of ^1H nmr spectra of the

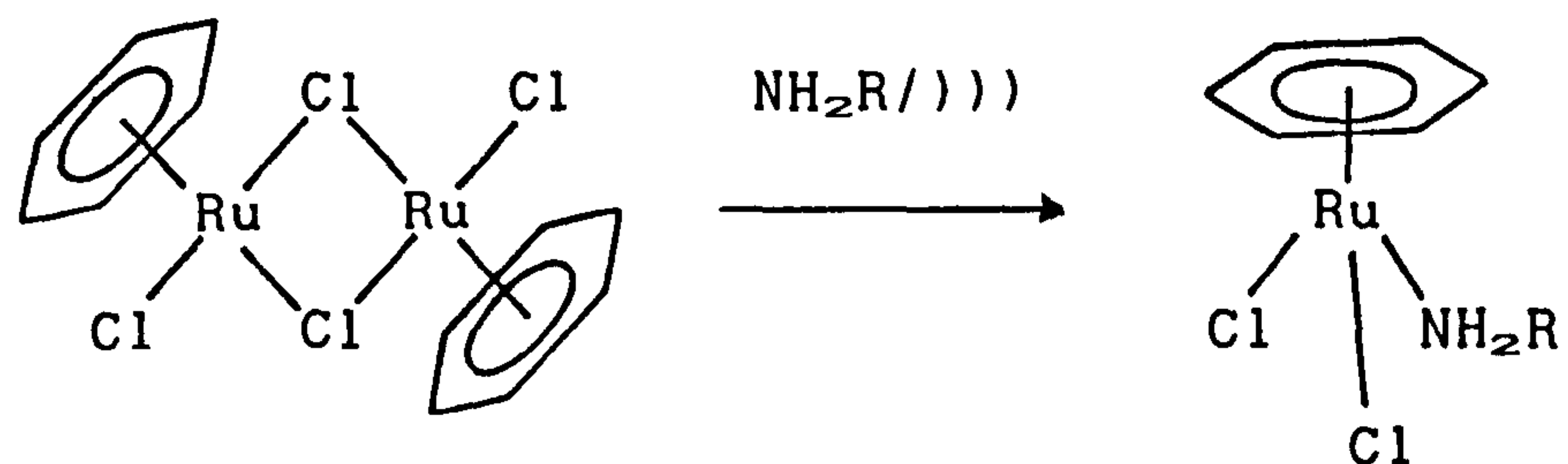
mixture of products, and a pure sample of $(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2\text{PPh}_3$. Good overlap of one set of arene ligand signals was observed.

Characterisation of $(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2\text{PPh}_3$ as a component of the mixture, implied, as for the isoelectronic rhodium system, that the initial half sandwich complex afforded from the bridge cleavage reaction disproportionates in solution.

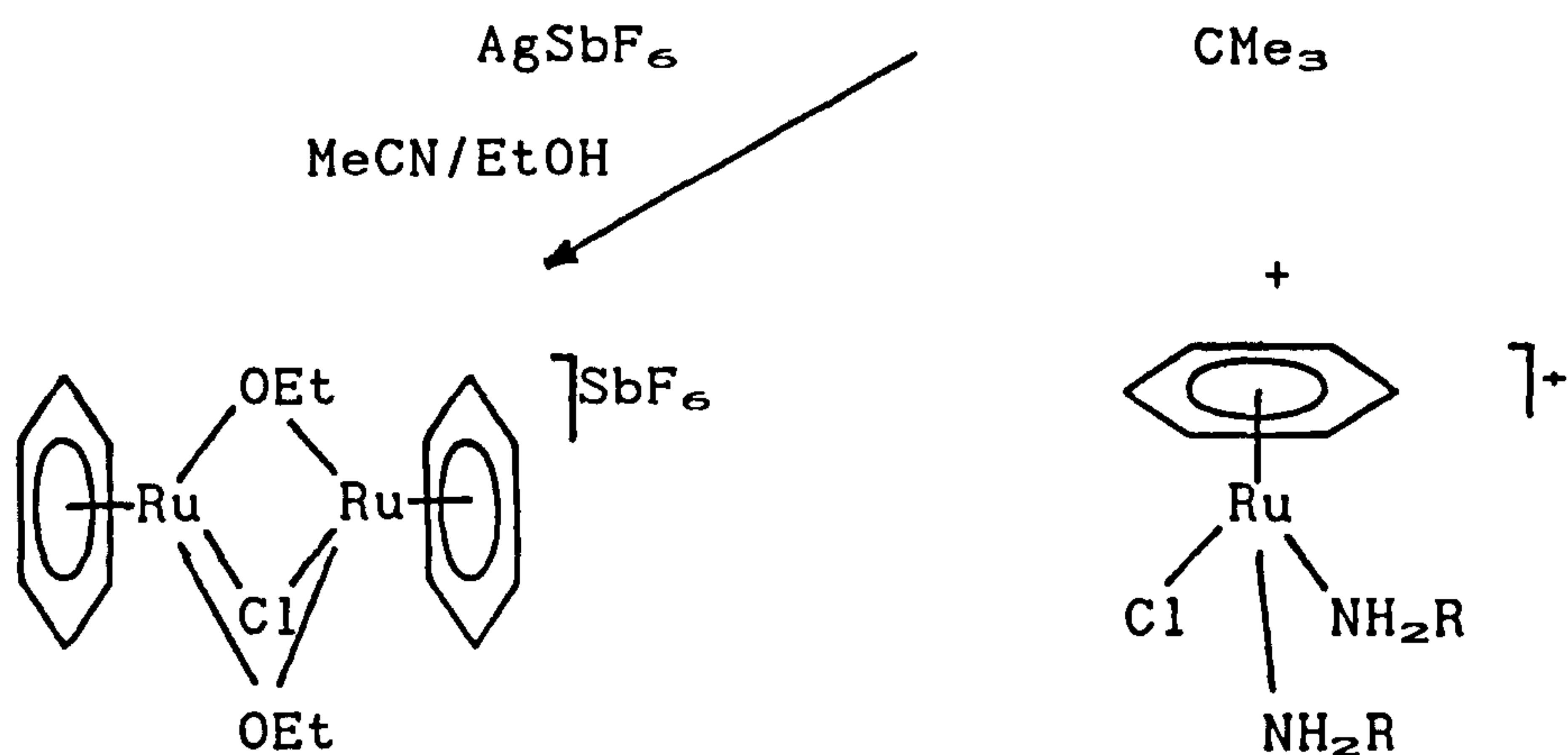


5.3. Reaction schemes of complexes found in chapter 5

5.3.1 Reaction scheme of amine complexes

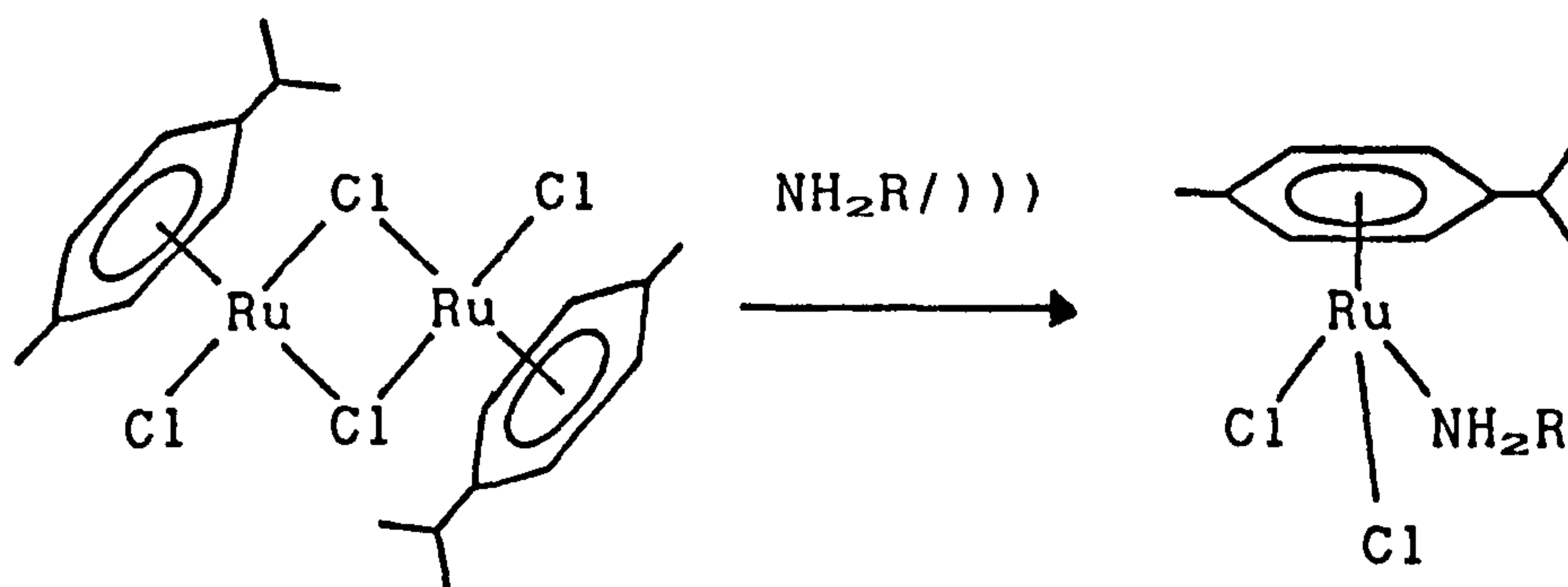


$\text{R} = \text{Et}, \text{C}_6\text{H}_4\text{Me},$
 CMe_3



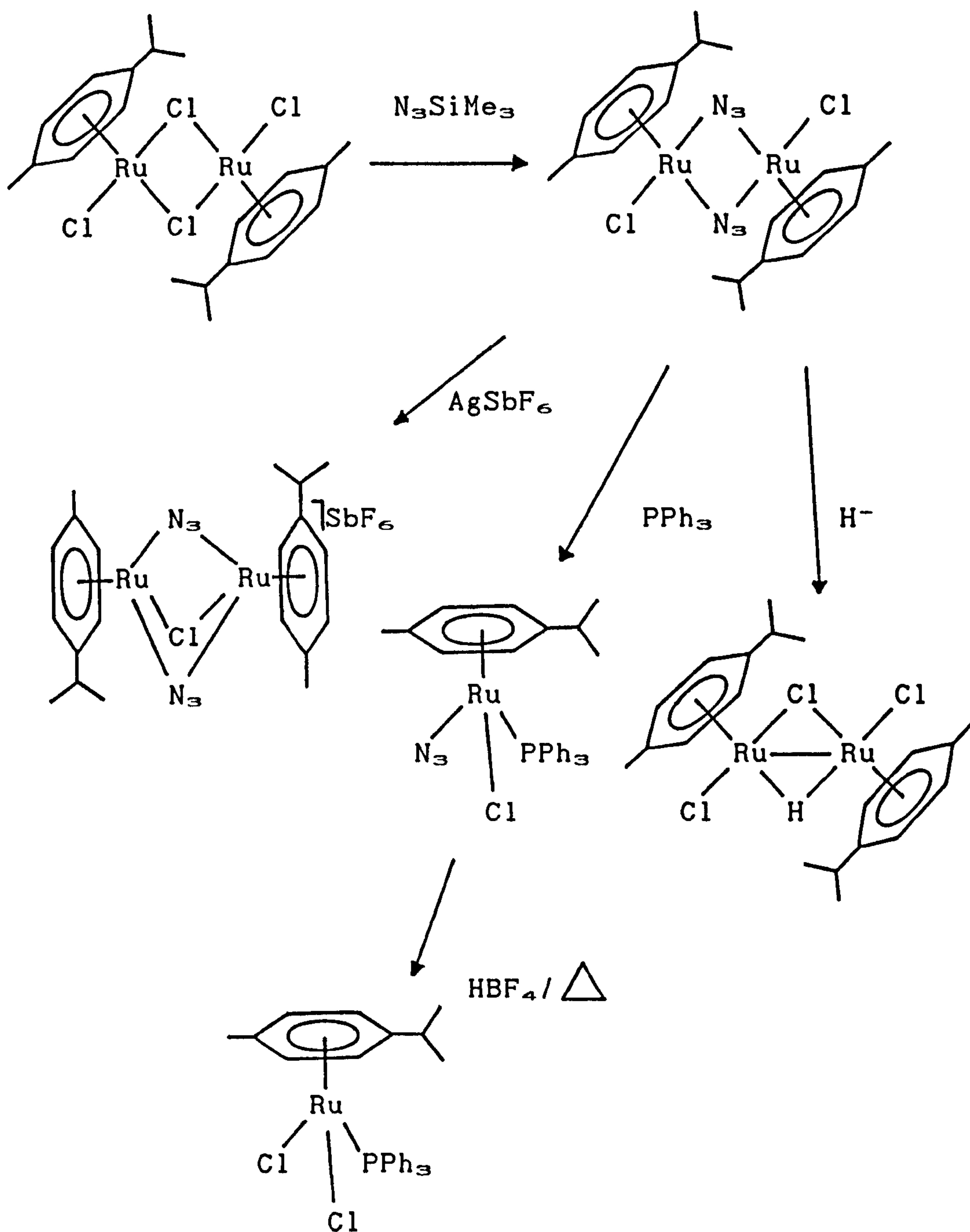
$\text{R} = \text{CMe}_3$

$\text{R} = \text{C}_6\text{H}_4\text{Me}$



$\text{R} = \text{CMe}_3$

5.3.2. Reaction scheme of azide related complexes



5.4 Experimental

$[(C_6H_6)RuCl_2(NH_2C_6H_4Me)]$

To a suspension of $[(C_6H_6)RuCl_2]_2$ (150mg; 0.3mmol) in thf (10ml), a solution of $NH_2C_6H_4Me$ (230mg; 2.2mmol) in thf (5ml) was added and subjected to ultrasound (90mins). After cooling, the yellow precipitate was collected and recrystallised from a $CH_2Cl_2/EtOH$ mixture to give $[(C_6H_6)RuCl_2(NH_2C_6H_4Me)]$ (162mg, 76%, Anal. Found: C 43.87, H 4.35%), (formula $RuC_{13}H_{15}Cl_2N$ calc: C 43.71, H 4.23%).

Characterisation. 1H nmr spectroscopy (table 5.4.1) showed coordinated benzene and monosubstituted amine. Infrared (table 5.4.3) showed the presence of a terminal ruthenium chloride stretch.

$[(C_6H_6)RuCl_2(NH_2Et)]$

To a suspension of $[(C_6H_6)RuCl_2]_2$ (50mg; 0.1mmol) in CH_2Cl_2 (10ml) at $0^\circ C$, was added NH_2Et (31.5mg; 0.05ml; 0.7mmol) dropwise. After subjection to ultrasound (90mins), a yellow brown solid was precipitated out of the solution with excess hexane, to give $[(C_6H_6)RuCl_2(NH_2Et)]$ (23mg, 40%, Anal. Found: C 31.91, 4.27%), (formula

$\text{RuC}_8\text{H}_{13}\text{Cl}_2\text{N}$ calc: C 32.55, H 4.44%).

Characterisation. ^1H nmr spectroscopy (table 5.4.1) showed coordinated benzene and monosubstituted amine. $^{13}\text{C}\{-^1\text{H}\}$ nmr clarifies the presence of the amine (table 5.4.6). Infrared (table 5.4.3) showed the presence of a terminal ruthenium chloride stretch.



To a suspension of $[(\text{C}_6\text{H}_6)\text{RuCl}_2]_2$ (1.23g; 2.46mmol) in thf (5ml), was added $\text{NH}_2\text{C}(\text{Me})_3$ (1.26g; 1.83ml; 17.2mmol). After subjection to ultrasound (90mins) a mustard yellow brown solid was filtered off, to give

$[(\text{C}_6\text{H}_6)\text{RuCl}_2\{\text{NH}_2\text{C}(\text{Me})_3\}]\cdot\text{NH}_2\text{C}(\text{Me})_3$ (1.67g, 87%,

Anal. Found: C 42.31, H 7.68%), (formula

$\text{RuC}_{14}\text{H}_{28}\text{Cl}_2\text{N}_2$ calc: C 42.42, H 7.12%)

Characterisation. ^1H nmr spectroscopy (table 5.4.1) showed coordinated benzene, monosubstituted amine and an amine solvate. Infrared (table 5.4.3) showed the presence of a terminal ruthenium chloride stretch.



To a suspension of $[(\text{C}_6\text{H}_6)\text{RuCl}_2]_2$ (50mg; 0.1mmol) in thf (5ml), was added a solution

of $\text{NH}_2\text{C}_6\text{H}_4\text{Me}$ (107mg;1.0mmol) and NH_4PF_6 (49mg;0.3mmol) in thf (15ml). This was subjected to ultrasound (90mins), and a light green precipitate was collected after addition of hexane (excess).

Characterisation. ^1H nmr spectroscopy (table 5.4.1) showed coordinated benzene, disubstituted amine. FAB mass spectrometry (table 5.4.5) showed an isotope pattern related to a Ru-Cl system.

$[(\text{C}_6\text{H}_6)\text{RuCl}_2(\text{py})]$

$[(\text{C}_6\text{H}_6)\text{RuCl}_2]_2$ (800mg,1.6mmol) was added to $\text{C}_5\text{H}_5\text{N}$ (40ml) and subjected to ultrasound (90mins). A mustard yellow solid was precipitated from solution with hexane (excess), to give $[(\text{C}_6\text{H}_6)\text{RuCl}_2(\text{py})]$ (954mg, 92%, Anal. Found: C 40.54, H 3.70%), (formula $\text{RuC}_{11}\text{H}_{11}\text{Cl}_2\text{N}$ calc: C 40.14, H 3.37%).

Characterisation. Infrared (table 5.4.3) showed the presence of a terminal ruthenium chloride stretch and the ^1H nmr spectra (table 5.4.1) was compared to a genuine sample.²⁵

$[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2\{\text{NH}_2\text{C}(\text{Me})_3\}]$

$[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2$ (102mg;0.17mmol) was added to $\text{NH}_2\text{C}(\text{Me})_3$ (83mg;0.12ml;1.15mmol) in thf (5ml). After subjection to ultrasound (90mins) a

yellow solid was afforded on reduction of the volume with hexane present, to give $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2\{\text{NH}_2\text{C}(\text{Me})_3\}]$ (104mg, 80%, Anal. Found: C 44.17, H 6.78%), (formula Ru $\text{C}_{14}\text{H}_{25}\text{Cl}_2\text{N}$ calc. C 44.33, H 6.64%).

Characterisation. ^1H nmr spectroscopy (table 5.4.1) showed coordinated cymene and monosubstituted amine. Infrared (table 5.4.3) showed the presence of a terminal ruthenium chloride stretch.

$[(\text{C}_6\text{H}_6)_2\text{RuCl}(\text{OEt})_2]\text{SbF}_6$

To a solution of $[(\text{C}_6\text{H}_6)\text{RuCl}_2\{\text{NH}_2\text{C}(\text{Me})_3\}]\cdot\text{NH}_2\text{C}(\text{Me})_3$ (300mg; 0.76mmol) in MeCN (20ml) was added a solution of AgSbF_6 (286mg; 0.84mmol) in MeCN (5ml) with stirring (30mins). The precipitated AgCl was filtered off and an orange solid was precipitated out of solution with the gradual addition of EtOH, to give $[(\text{C}_6\text{H}_6)_2\text{RuCl}(\text{OEt})_2]\text{SbF}_6$ (96mg, 35%, Anal. Found: C 26.47, H 3.06%), (formula $\text{Ru}_2\text{C}_{16}\text{H}_{22}\text{ClF}_6\text{O}_2\text{Sb}$ calc: C 26.70, H 3.08%).

Characterisation. Infrared (table 5.4.3) showed the presence of alkoxide ligands, a bridging ruthenium chloride stretch and the counteranion $[\text{SbF}_6]^-$. FAB mass spectrometry (table 5.4.5) showed the presence of the expected molecular ion.

$[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)]_2$

$[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2$ (200mg; 0.33mmol) was dissolved in CH_2Cl_2 (5ml). N_3SiMe_3 (530mg; 0.61ml; 4.6mmol) was added dropwise and the mixture stirred (30mins). A reddish orange crystalline powder was precipitated on the addition of hexane and the reduction of the volume under reduced pressure. Recrystallisation was carried out from CH_2Cl_2 / EtOH to give $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)]_2$ (186mg, 90%, Anal. Found: C 37.93, H 4.50%), (formula $\text{Ru}_2\text{C}_{20}\text{H}_{28}\text{Cl}_2\text{N}_6$ calc: C 38.40, H 4.48%).

Characterisation. An X-ray crystal structure determination was carried out (see section 5.2.2) to obtain full clarity. ^1H nmr spectroscopy (table 5.4.2) showed the coordinated cymene, ^{13}C - $\{^1\text{H}$ nmr} nmr spectra showed the various carbons of the arene (table 5.4.6). Infrared (table 5.4.4) showed the bridging antisymmetric azide stretch and a broad ruthenium chloride stretch.

$[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Ru}_2\text{Cl}(\text{N}_3)_2]\text{SbF}_6$

$[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)]_2$ (250mg; 0.4mmol) was dissolved in MeCN (10ml) and AgSbF_6 (151mg; 0.44mmol) in MeCN (5ml) was added. The solution was stirred and then filtered to remove AgCl precipitate. The product was crystallised by

addition of ethanol to give

$[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Ru}_2\text{Cl}(\text{N}_3)_2]\text{SbF}_6$ (208mg, 63%, Anal. Found: C 28.95, H 3.47%), (formula $\text{Ru}_2\text{C}_{20}\text{H}_{28}\text{ClF}_6\text{N}_6\text{Sb}$ calc: C 29.09, H 3.39).

Characterisation. ^1H nmr spectroscopy (table 5.4.2) indicated that the cymene ligand was not rotating freely. Infrared (table 5.4.4) showed the bridging antisymmetric azide stretch and the presence of the counteranion $[\text{SbF}_6]^-$.

$[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)\text{PPh}_3]$

PPh_3 (450mg; 1.7mmol) in CH_2Cl_2 (15ml) was added dropwise to a stirred solution of $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)]_2$ (150mg; 0.24mmol) in CH_2Cl_2 (15ml). A red solid was collected after treatment of the reaction mixture with hexane and the volume reduced under reduced pressure, giving $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)\text{PPh}_3]$ (234mg, 85%, Anal. Found: C 58.82, H 5.12), (formula $\text{RuC}_{28}\text{H}_{29}\text{ClN}_3\text{P}$ calc: C 58.48, H 5.08%).

Characterisation. ^1H nmr spectroscopy (table 5.4.2) indicated that there was a number of arene environments (see section 5.2.4.4). Infrared (table 5.4.4) showed the terminal antisymmetric azide stretch and a broad terminal ruthenium chloride stretch.

$[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Ru}_2\text{Cl}_3\text{H}]$

$[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)]_2$ (41mg; 0.07mmol) in thf (10ml) at -30°C , had superhydride (0.25ml; of 0.5ml in 2.5ml thf) added dropwise. The reaction mixture was stirred and gradually brought to room temperature and then stirred further (12hrs.). The filtrate was collected and treated with hexane. The resulting precipitate was recrystallised (twice) with a mixture of CH_2Cl_2 / hexane and the subsequent filtrate taken to dryness. The deep red filtrate contained $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Ru}_2\text{Cl}_3\text{H}]$. (Yield poor).

Characterisation. ^1H nmr spectroscopy data (table 5.4.2) was compared to that of a genuine sample.⁴⁴

Crystal data

$\text{Ru}_2\text{C}_{20}\text{H}_{28}\text{Cl}_2\text{N}_6$. $M = 625.52 \text{ g mol}^{-1}$, triclinic, $a = 7.586(2)\text{\AA}$, $b = 8.376(2)\text{\AA}$, $c = 9.689(2)\text{\AA}$, $\alpha = 101.40(1)^\circ$, $\beta = 87.00(1)^\circ$, $\gamma = 102.54(2)^\circ$, $U = 589.07(3)\text{\AA}^3$, space group $P\bar{1}$ (No.2), $Z = 1$, $D_c = 1.76\text{g cm}^{-3}$, $F(000) = 312$, graphite-monochromated Mo- $\text{K}\alpha$ radiation, $\lambda = 0.71069\text{\AA}$, $\mu(\text{Mo-}\text{K}\alpha) = 14.97\text{cm}^{-1}$, crystal dimensions $0.5 \times 0.25 \times 0.5\text{mm}$.

Structure determination

Cell dimensions and their standard deviations were obtained by least squares refinement of diffractometer setting angles for 12 centred reflections close to 13° in 2θ . Intensities of 3442 independent reflections ($1^\circ < \theta < 25^\circ$) were measured on a Hilger and Watts Y290 diffractometer in an ω - 2θ scan mode.

The structure analysis used 3203 reflections with $I \geq 3\sigma(I)$ after correction for Lorentz and polarisation factors. No correction was made for absorption.

Solution by Patterson and difference syntheses was followed by full-matrix least-squares refinement with anisotropic thermal parameters for all atoms except H using the CRYSTALS suite of programs. All the H atoms were located in difference maps and included, but not refined. The refinement for 192 parameters converged to $R = 0.039$ and $R_w = 0.046$, employing a weighting scheme based on Chebyshev polynomials. A final difference map contained no significant features. Complex neutral-atom approximation and coefficients given in reference 186.

Table 5.4.1 ¹H nmr data of amine complexes/ppm #

Complex	Arene	Ligand
(C ₆ H ₆)RuCl ₂ (NH ₂ Et) (1)	5.63(s)	Me 1.23(t), CH ₂ 3.2(q)
(C ₆ H ₆)RuCl ₂ NH ₂ CMe ₃ (2) .NH ₂ CMe ₃	5.72(s)	CMe ₃ (coord) 1.34(s) CMe ₃ (solv) 1.11(s)
(C ₆ H ₆)RuCl ₂ NH ₂ C ₆ H ₄ Me (3)	5.33(s)	C ₆ H ₄ 7.32-7.14(m) Me 2.33(s)
[(C ₆ H ₆)Ru(NH ₂ C ₆ H ₄ Me) ₂ (4) Cl]PF ₆	5.01(s)	C ₆ H ₄ 7.34-7.06(m)
(C ₆ H ₆)RuCl ₂ (py) (5)	5.31(s)	(py) 9.12-7.34(m)
(MeC ₆ H ₄ CHMe ₂)RuCl ₂ (6)	5.50-5.43 (m), C ₆ H ₄ 3.05(spt) <u>CHMe₂</u> 2.26(s) C ₆ H ₄ <u>Me</u> 1.29-1.26 (d), <u>CHMe</u>	CMe ₃ 1.33(s)

solvent CDCl₃.

s, singlet; m, multiplet; t, triplet; q, quartet;

d, doublet; spt, septet.

chem. shift values quoted in terms of δ .

Table 5.4.2 ^1H nmr data of azide complexes /ppm #

Complex	Arene	
$[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)]_2$ (8)	C_6H_4	5.33-5.22(m)
	$\underline{\text{CH}(\text{Me})}_2$	2.92(spt)
	$\text{C}_6\text{H}_4\underline{\text{Me}}$	2.24(s)
	$\text{CH}(\underline{\text{Me}})_2$	1.28, 1.25(d)
$[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Ru}_2\text{Cl}(\text{N}_3)_2]$ (9)	C_6H_4	5.57-5.36(m)
	SbF_6	
	$\underline{\text{CH}(\text{Me})}_2$	2.75(spt)
	$\text{C}_6\text{H}_4\underline{\text{Me}}$	2.23(s)
$[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)\text{PPh}_3]$ (10)	C_6H_4	5.50-4.80(m)
	$\underline{\text{CH}(\text{Me})}_2$	2.82(spt)
	$\text{C}_6\text{H}_4\underline{\text{Me}}$	1.86-1.81(3xs)
	$\text{CH}(\underline{\text{Me}})_2$	1.29-1.08(3xd)
$[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Ru}_2\text{Cl}_3\text{H}]$ (11)	C_6H_4	5.64-4.83(m)
	$\underline{\text{CH}(\text{Me})}_2$	3.02(spt)
	$\text{C}_6\text{H}_4\underline{\text{Me}}$	2.29(s)
	$\text{CH}(\underline{\text{Me}})_2$	1.46, 1.44(d)

solvent CDCl_3 .

chem. shift values quoted in terms of δ .

Table 5.4.3 Infrared data of amine complexes/cm⁻¹ #

Complex	$\nu(\text{CH})$	$\nu(\text{NH})$	$\delta(\text{NH})$	$\text{fp}(\text{CH})^*$	$\nu(\text{Ru-Cl})/\text{other}$
(1)	3077 3035	3277 3206	1571	839.0	273
(2)	3084	3273 3215	1609	840.2	275
(3)	3061	3223 3255	1610	833.6	276
(4)	3028	3326 3369		824.2	
(5)	3058			831.0	274
(6)	3058	3266 3209	1566	872.0 804.0	273
(7)	3090			852.4	258 $\nu(\text{CO})$ 1044 $\nu(\text{SbF}_6)$
(7) = $[(\text{C}_6\text{H}_6)_2\text{Ru}_2\text{Cl}(\text{OEt})_2]\text{SbF}_6$					660, 356, 287

(numbers assigned from table 5.4.1)

* flapping mode of arene protons

run as nujol mulls

Table 5.4.4 Infrared data of azide complexes/cm⁻¹ #

Complex	$\nu(\text{CH})$	$\nu_{\text{as}}(\text{N}_3)$	$\nu_{\text{p}}(\text{CH})^*$	$\nu(\text{Ru-Cl})/\text{other}$
(8)	3053	2057	883,862 834,804	281
(9)	3082	2062	885,834 806	$\nu(\text{SbF}_6)$ 658,372,288
(10)	3056 3021	2039	899,855 834	$\nu(\text{PPh}_3)$ 1481

(numbers assigned from table 5.4.2)

* flapping mode of arene hydrogens

run as nujol mulls

Table 5.4.5 FAB mass spectrometry data of complexes
in chapter 5 /amu.

Complex	system	MW	fragmentation
(1)	RuCl ₂	295	260 (-Cl)
(2)	RuCl ₂	324	288 (-Cl) 252 (-NH ₂ CMe ₃)
(4)	RuCl	429	322 (-NH ₂ C ₆ H ₄ Me) 286 (322-Cl) 244 (322-C ₆ H ₆)
(7)		485	440 (-EtO) 395 (-2EtO)
(10)	RuCl		533 (575-N ₃) 496 (533-Cl) 361 (496-CYM)

(complex numbers assigned as above)

Table 5.4.6 ^{13}C - $\{^1\text{H}\}$ nmr data of complexes in
chapter 5 /ppm #

Complex	Arene		Ligand	
(1)	C_6H_6	83.46	Me	18.68
			CH_2	45.43
(3)	C_6H_6	83.17	Me	20.87
			C_6H_4	130.14, 119.99
			$\underline{\text{C}}\text{Me}$	135.40
			$\underline{\text{C}}\text{NH}_2$	143.17
(8)	C_6H_4	81.67, 80.07		
	$\underline{\text{C}}\text{Me}$	97.27		
	$\underline{\text{C}}\text{CH}$	100.29		
	CH	30.39		
	Me	22.30, 18.03		

solvent CDCl_3 .

(complex numbers assigned as above)

CHAPTER SIX

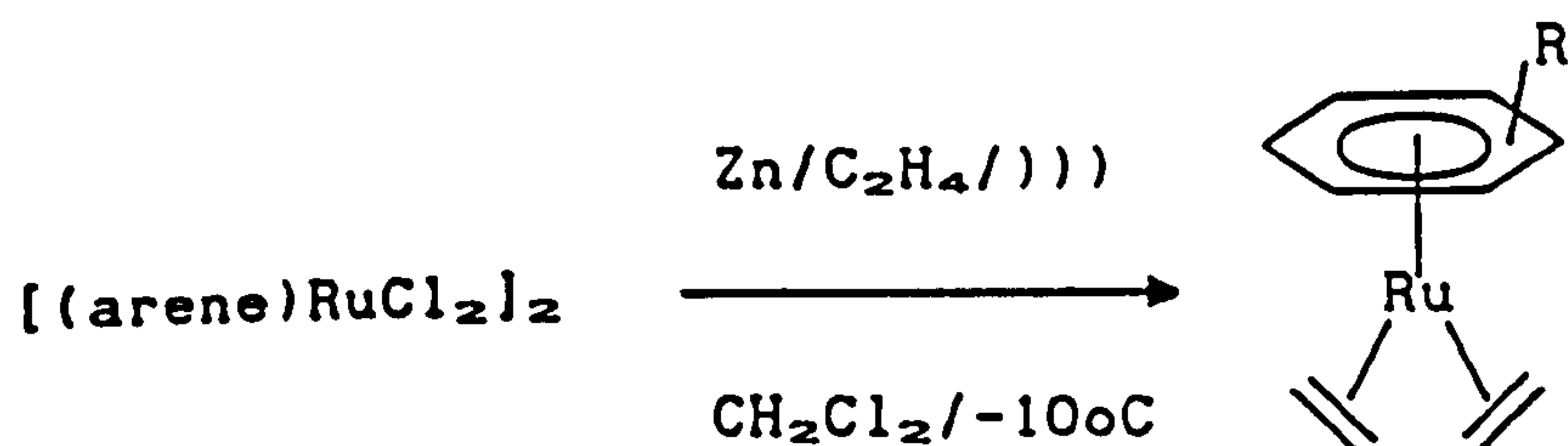
Chapter 6

6.1 Conclusions and future work

The aim of this project was the synthesis of arene ruthenium clusters from simple arene ruthenium substrates.

In the search for the target complexes a range of novel systems and compounds were synthesised and investigated.

In chapter two, the new arene ruthenium bis(ethylene) complexes (arene = cymene, benzene), described were made by an ultrasonic zinc reduction method.



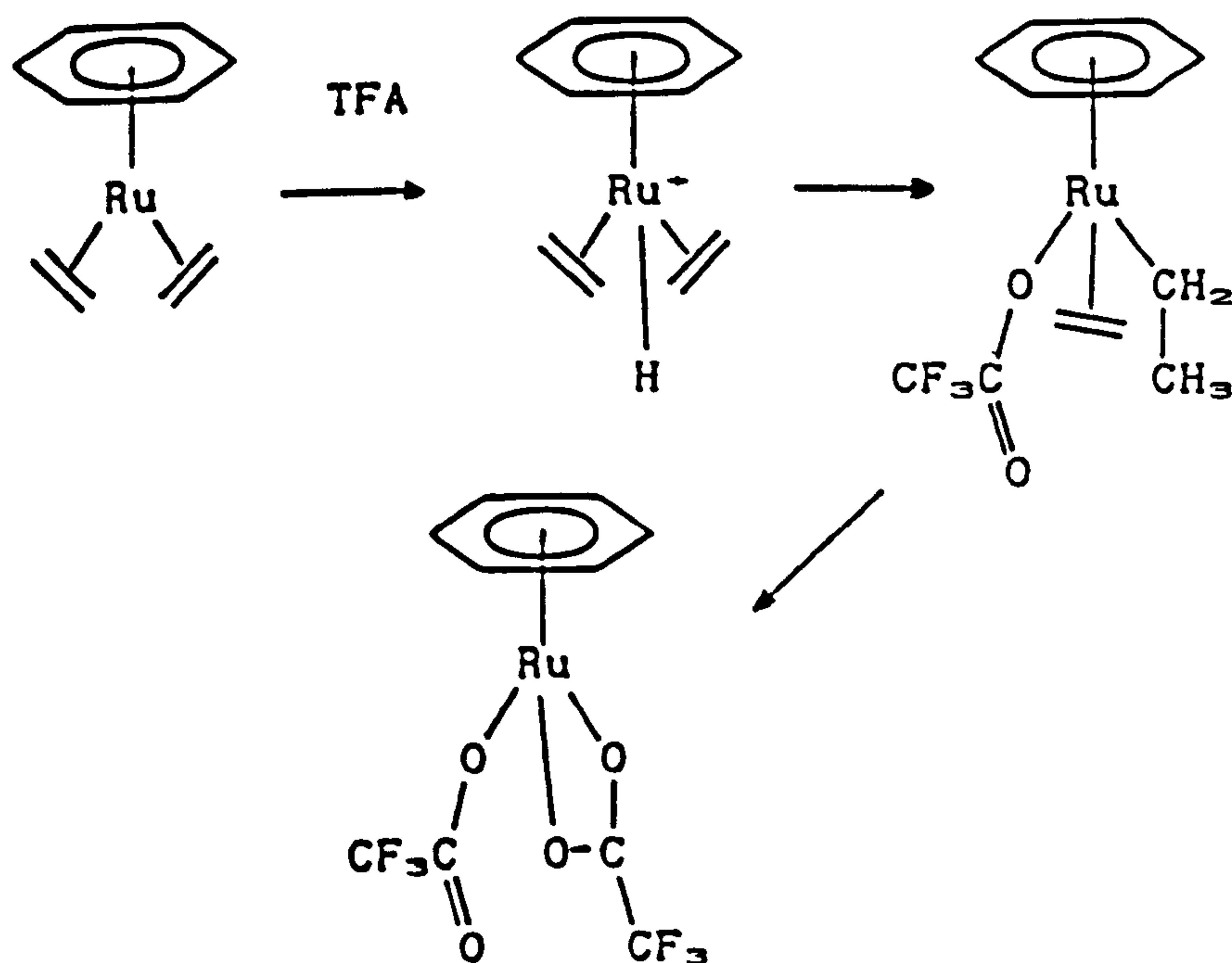
arene = $\text{MeC}_6\text{H}_4\text{CHMe}_2$, C_6H_6

The complex $(\text{C}_6\text{H}_6)\text{Ru}(\text{H})(\text{C}_2\text{H}_4)_2^+$, was shown to be a classic C-M-H alkyl hydride system and does not have an agostic structure, $\text{M}^{\delta+}\text{H}-\text{C}$. Hence it can be concluded that with respect to electron density donated to the metal centre, $(\text{C}_6\text{H}_6)\text{Ru}(\text{H})(\text{C}_2\text{H}_4)_2^+$ is analogous to the $(\text{cp}^+)\text{RhPMe}_3(\text{H})(\text{C}_2\text{H}_4)^+$ complex and

'not $(\text{cp}^*)\text{Rh}(\text{H})(\text{C}_2\text{H}_4)_2^+$.

Variable temperature nmr experiments demonstrated two dynamic processes. At low temperatures spinning of the ethylene ligands could be slowed. At higher temperatures a fluxional process involving exchange of the hydride ligand and the hydrogens on the ethylenes was observed. This was confirmed by a deuteration study which showed that exchange between the hydride and the hydrogens of the ethylene ligand did occur.

Following the protonation of $(\text{C}_6\text{H}_6)\text{Ru}(\text{C}_2\text{H}_4)_2$ with trifluoroacetic acid, by ^1H nmr spectroscopy, a sequence of products can be assigned for the thermodynamically favoured pathway to the bis(trifluoroacetate) complex.



A comparison of the protonation studies of alternative (arene)Ru(0) olefin complexes would be useful. They could be used to confirm or dispute the arguments put forward about the relative π -back bonding properties playing a major role in the chemistry of these metal bases.

No nucleophilic substitution was observed to occur for these neutral bis(ethylene) complexes, thus ligand substitution was not possible. It was determined that arene loss occurred preferentially to ethylene substitution on thermolysis in the presence of nucleophiles. However, photochemical studies could show these complexes to be useful substrates and they could be examined in matrix media and their behaviour compared to that of the Group 9 triad analogues.

The complexes (arene)Ru(C₂H₄)₂ (arene = C₆H₆, MeC₆H₄CHMe₂), although providing some information on the hydrogenation of alkenes, could not be utilised as substrates for cluster formation. Complexes with more labile ligands needed to be synthesised.

The tetrahydrofuran complex, [(cymene)Ru(THF)₂]⁺, discussed in chapter three, was shown to be a useful arene ruthenium and ruthenium metal moiety for a number of reactions. However, the tetrahydrofuran complex could not be fully characterised as the complex lost its

integrity on removal of solvent. The new complex $(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuBr}(\text{C}_3\text{H}_5)$ was generated when the tetrahydrofuran complex was reacted with allylbromide. It was determined that in solution the stereochemistry of the allyl ligand was endo with respect to the arene.

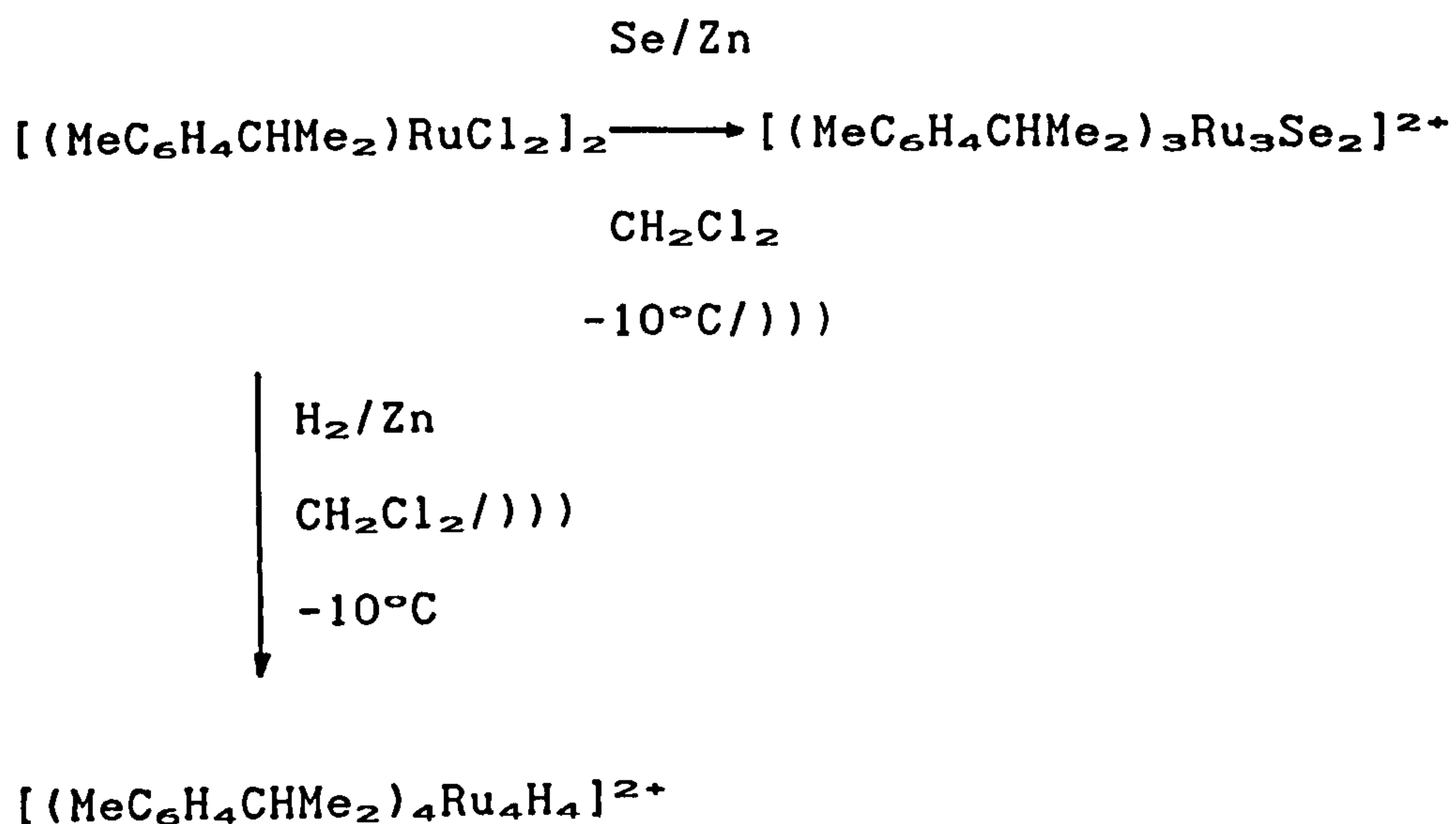
Also the orthometallated complexes $\text{Ru}(\text{H})[(\text{C}_6\text{H}_4\text{O})\text{P}(\text{OPh})_2][\text{P}(\text{OPh})_3]_3$ and $\text{Ru}[(\text{C}_6\text{H}_4\text{O})\text{P}(\text{OPh})_2]_2[\text{P}(\text{OPh})_3]_2$ were formed on reaction of the tetrahydrofuran complex with triphenylphosphite at 0°C and 27°C respectively.

To date no suitable reactions have been discovered to use this complex as a substrate for cluster synthesis. Before further investigations of the synthetic usefulness of the tetrahydrofuran complex is carried out, more needs to be understood about its makeup.

However, the complex does appear to have the potential of being a useful source of arene ruthenium or ruthenium atoms in cluster chemistry. Future investigations could determine the complex's similarity to the cpCo moiety as a cluster reagent. A likely application of this complex appears to be in mixed metal cluster synthesis.

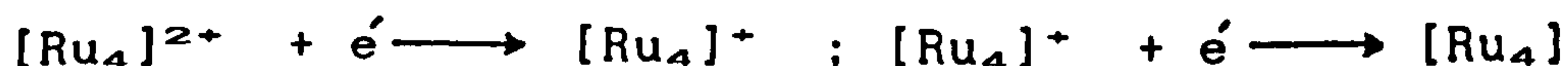
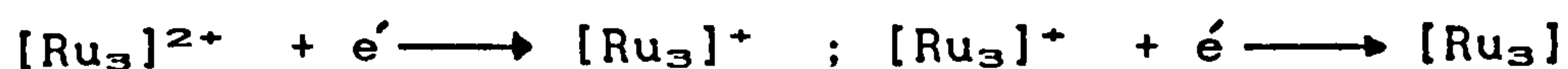
Within chapter four, is described the successful synthesis of arene ruthenium clusters from the simple substrate $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2$.

The ultrasonic zinc reduction was applied to afford the new trinuclear 48 electron ruthenium selenium tricapped cluster, $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_3\text{Ru}_3\text{Se}_2]^{2+}$, and the tetranuclear 58 electron ruthenium hydride cluster, $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_4\text{Ru}_4\text{H}_4]^{2+}$. (See scheme 6.1).



Scheme 6.1. Ultrasonic zinc reduction of cluster complexes from $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2$.

The electrochemistry of both the complexes was investigated using cyclic voltammetry. The two cluster complexes both underwent fully reversible two one electron reductions.



The neutral species appear to be stable and should be readily isolable.

Future work could include the isolation of the neutral clusters, the selenium clusters could then be compared directly to the sulphido analogues.¹³¹ Also as the hydride cluster has previously been prepared via an alternative route,¹⁴² investigation as to whether this route is general for a number of arene species would be profitable. Subsequent investigations by S. Harrison¹⁸⁷ have demonstrated that the benzene and mesitylene analogues can be prepared via the ultrasonic zinc reduction route.

The reaction conditions when investigated with carbon monoxide present, did not generate an arene cluster. However, the formation of $\text{Ru}_3(\text{CO})_{12}$ from the thermolysis of the initially produced $\text{Ru}(\text{CO})_5$, has the potential to be a clean alternative to the normally used auto clave route to this useful substrate. Further work with the aim to optimise the yield, would need to be carried out before this reaction would be synthetically useful.

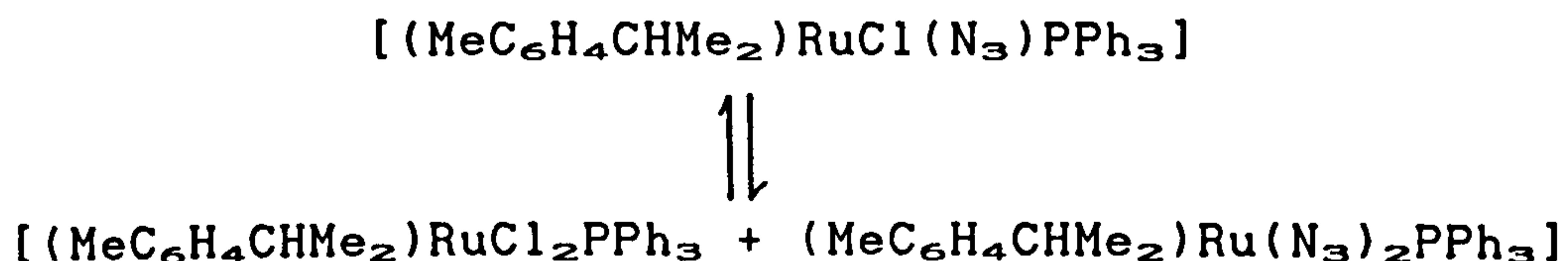
Alternative substituents that might aid clusterification reactions such as NO and isocyanides have been briefly investigated with no success. Despite this, the ultrasonic reduction has the potential to be a useful general route to a range of new clusters, and possibly mixed metal clusters.

An alternative approach to cluster synthesis attempting to utilise nitrogen based groups was explored (cf. Se), and the findings reported in chapter five.

The simple half sandwich arene ruthenium dichloro amine complexes were prepared in good yield for a range of arene and primary amine ligands.

However, chemical manipulations of the coordinated ligand afforded complexes with no ruthenium nitrogen bonds within the coordination sphere. Thus, the amine complexes appeared to be synthetically unsuitable for the search for clusters.

Trimethylsilylazide was reacted with $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}_2]_2$ to generate a nitrogen bridging dimer, $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)]_2$. The chemistry of this complex was investigated, but the nuclearity could not be increased to three or four. The complex undergoes chloride loss in the presence of AgSbF_6 to generate the triply bridged cationic dimer $[(\text{MeC}_6\text{H}_4\text{CHMe}_2)_2\text{Ru}_2\text{Cl}_3(\text{N}_3)_2]\text{SbF}_6$. Also the azide dimer undergoes bridge cleavage in the presence of triphenylphosphine, to form the half sandwich complex $(\text{MeC}_6\text{H}_4\text{CHMe}_2)\text{RuCl}(\text{N}_3)\text{PPh}_3$. However, from our studies a disproportionation reaction was observed to occur;



so further investigation of this reaction needs to be carried out to determine whether the individual components of this equilibrium can be isolated.

In conclusion this project has led to the successful development of a new synthetic route to arene ruthenium clusters, utilising an ultrasonically activated zinc reduction. The project has also uncovered new areas of arene ruthenium chemistry, with the generation of the arene ruthenium bis(ethylene) complexes and a highly reactive tetrahydrofuran complex. The chemistry of arene ruthenium complexes containing nitrogen-based ligands has been extended.

APPENDIX

Appendix

Ultrasound in synthesis

The last few years have seen a great surge of interest in the application of ultrasound to chemistry¹⁶⁷ including that of organo transition metal complexes.

Mechanisms of the chemical effects of ultrasound

The chemical effects of ultrasound derive from several different physical mechanisms, depending on the nature of the system. Fundamentally, sonochemistry is centred about cavitation - the formation of gas bubbles (or cavities) of a liquid and the subsequent effect upon them by the expansion and compression waves generated by passing sound through the liquid.

Acoustic cavitation can be considered to involve at least three discrete stages: nucleation, bubble growth and, under proper conditions, implosive collapse. The dynamics of cavity growth and collapse are strikingly dependent on local environment, neatly separated into two systems;

- 1) Cavitation in a homogeneous liquid
- 2) Cavitation near a liquid-solid interface

Nucleation of cavitation

Cavitation is initiated at a nucleation site where the tensile strength of a liquid is dramatically lowered. (Tensile strength of a liquid is determined by the attractive intermolecular forces which maintain its liquid state). An obvious site would be small gas bubbles present in the liquid. The nucleation mechanism generally accepted at this time involves gas entrapped in small-angle crevices of particulate contaminants, as shown schematically in figure 1.^{168,169}



Figure 1. Nucleation of acoustic cavitation

As the crevice-stabilised nucleus is subjected to large, negative acoustic pressures, the bubble volume grows, releasing small bubbles into solution or undergoing violent collapse itself. In liquids undergoing cavitation, after the initial cycle of cavitation, the implosive collapse of bubbles generates microcavities which in turn can act as

nucleation sites for the next cycle.¹⁷⁰

Cavitation in a homogeneous liquid

Flynn¹⁷¹ proposed the generally accepted division of cavitation phenomenon in homogeneous liquids into (1) transient cavitation, in which a short lived bubble undergoes large changes in size in a few acoustic cycles and may terminate in a violent collapse, and (2) stable cavitation, in which a bubble oscillates many times with limited change about its radius. Both stable and transient cavitation may occur simultaneously in a solution, and a bubble undergoing stable cavitation may change to transient cavitation if the radius becomes suitable for efficient collapse.

It is transient cavitation which gives rise to sonochemistry - an idealised representation of bubble growth and collapse is shown in figure 2.

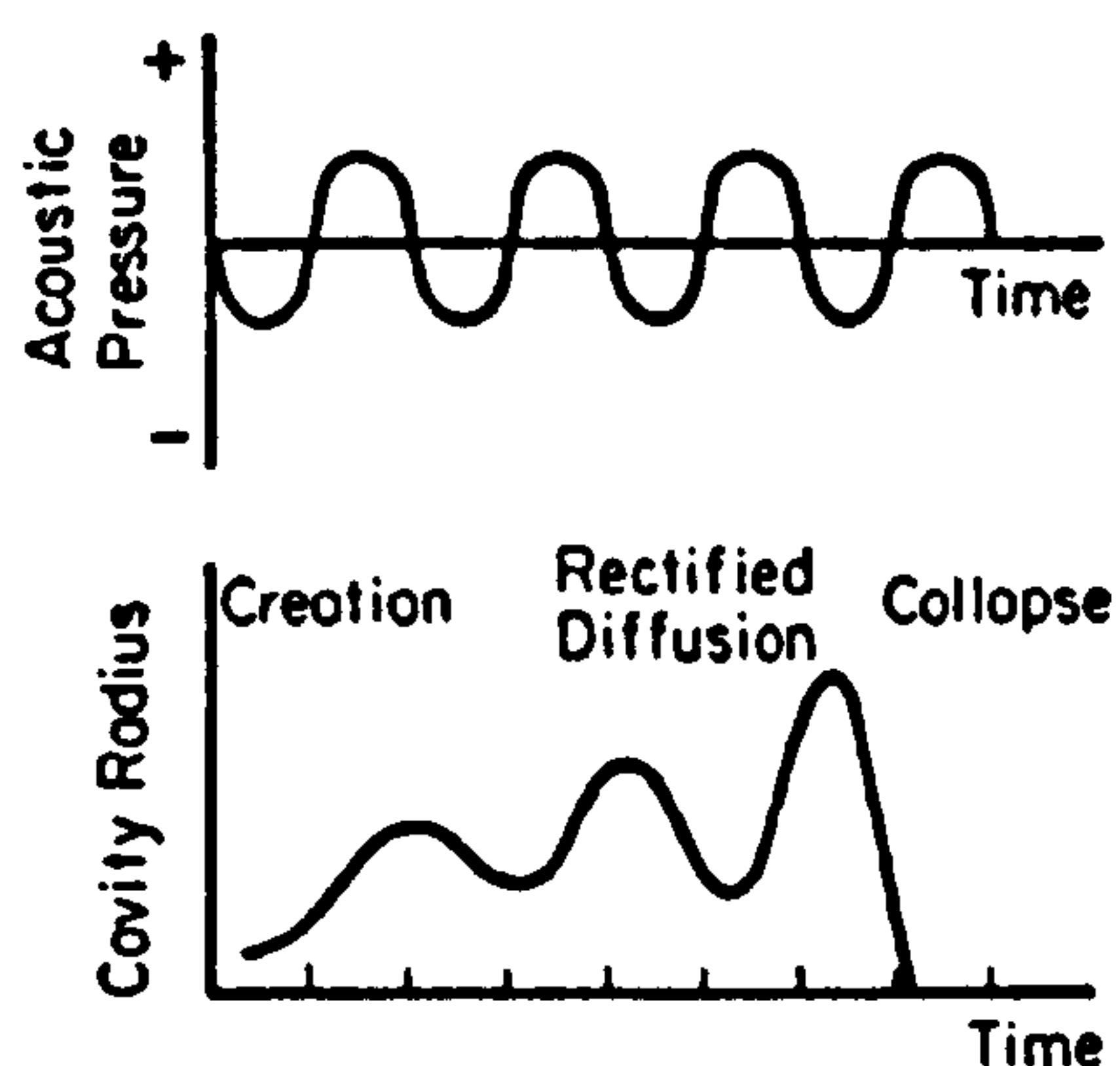


Fig.2 Idealised representation of bubble growth and collapse during transient cavitation

Historically, there have been two separate proposals for the mechanism responsible for sonochemical reactions in homogeneous media;

(A) "hot-spot" pyrolysis^{172.173}

(B) electrical discharge^{174.175}

The implosive collapse of a bubble will produce adiabatic heating of its contents, estimates of ca.5000K and ca.1000 atmospheres with effective residence times of <100nsecs. have been proposed, giving support to (A). Recently, due to the proposals of electrical discharge during cavitation not being well understood on the molecular level and inconsistent with observed sonochemical reactivities, (B) is less in favour.

Cavitation at surfaces

When a liquid-solid interface is subjected to ultrasound, transient cavitation still occurs. However, no longer does spherical implosion of the cavity occur, but an asymmetric collapse occurs generating a jet of liquid directed at the surface, as seen in the high speed microphotographs taken by Ellis^{176.177} and Lauterborn¹⁷⁸ (see figure 3). The jet velocities measured by Lauterborn are greater than 100m/second.

The origin of this jet formation is essentially a shaped-charged effect: the rate of collapse is

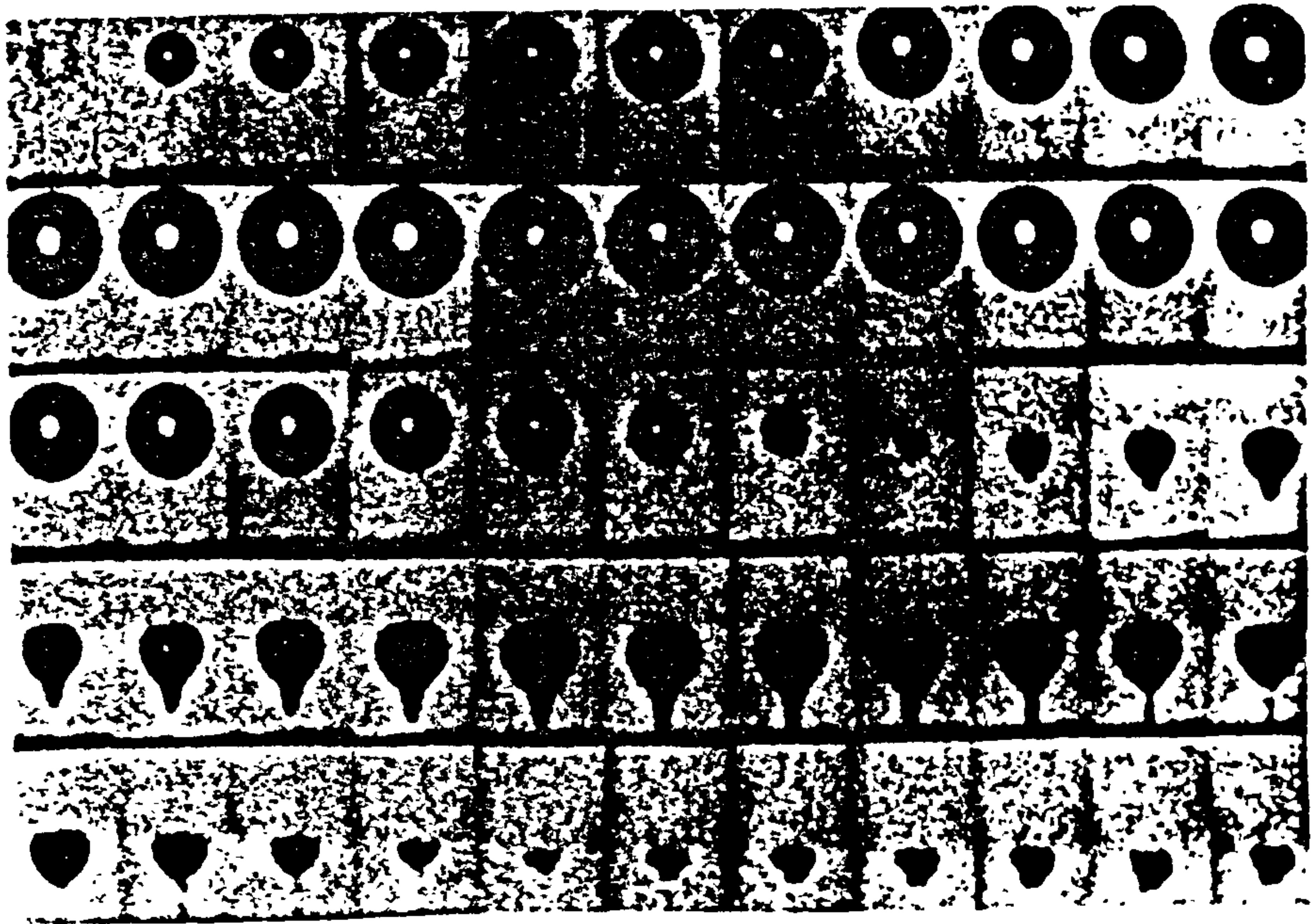


Fig.3. Cavitation near a surface. Sequence is from left to right, top to bottom;

proportional to the local radius of curvature. As collapse of a bubble near a surface begins, it does so with a slight elliptical asymmetry, which is self-reinforcing and generates the observed jet.

The impact of this jet can generate a localised erosion responsible for surface pitting and ultrasonic cleaning. A second contribution to erosion created by cavitation is the impact of shock waves generated by cavitation collapse (magnitude can be as high as 10^4 atmospheres). The relative magnitudes of these two effects depends heavily on the system under investigation.

Enhanced chemical reactivity of solid surfaces

are associated with these processes and recently an investigation of the sonochemistry of zinc powder has been reported.¹⁷⁹

Scanning electron micrographs were taken of irradiated Zn samples (Fig.4). Dramatic changes in particle morphology and aggregation are observed. The Zinc particles initially are extremely smooth and spherical, but upon sonication the surface is noticeably roughened. At the same time, particle

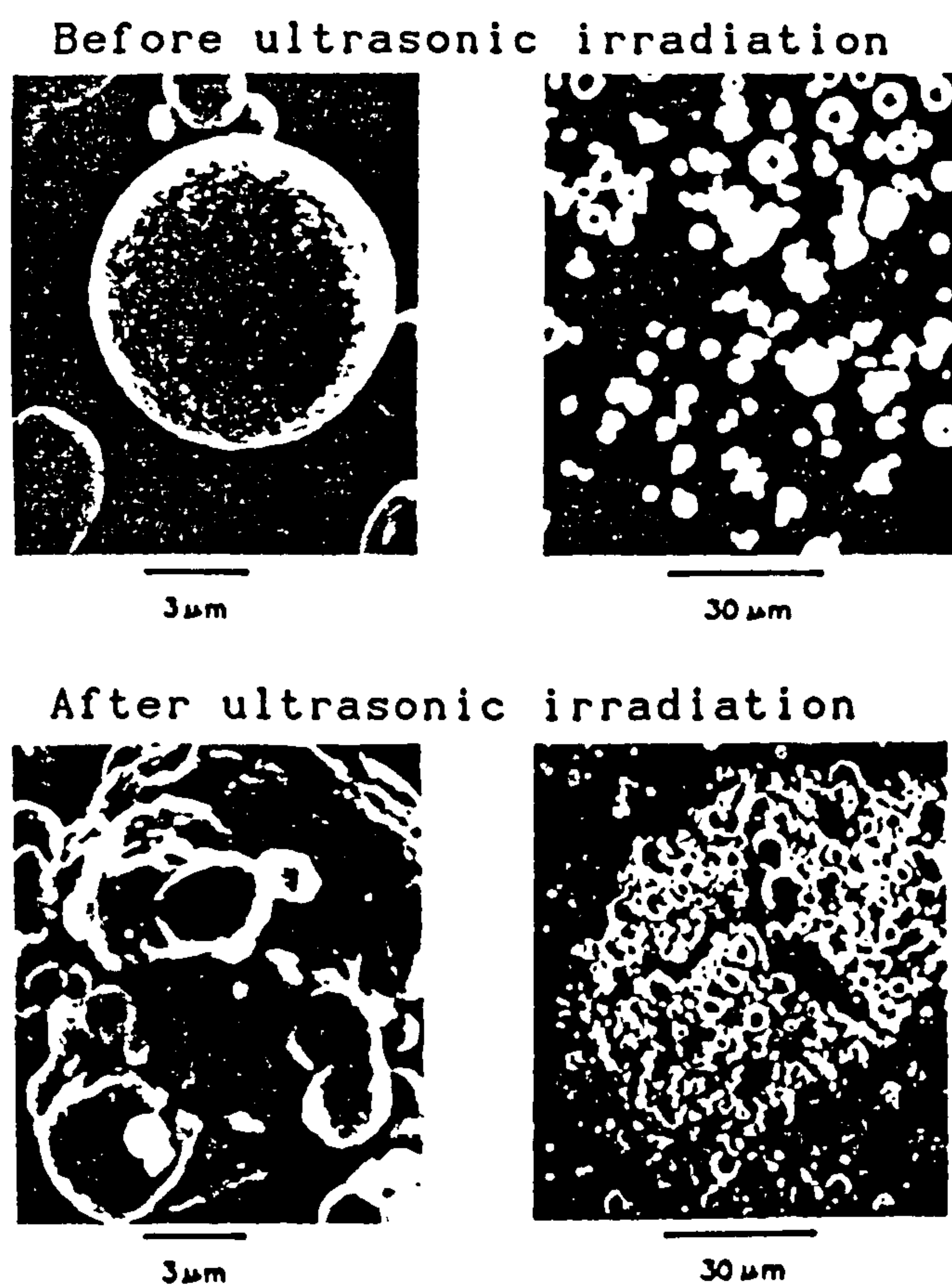


Fig. 4. Scanning electron micrographs of zinc powder (5 μ m mean diameter) before and after ultrasonic irradiation, obtained on a Hitachi S-800 SEM.

agglomeration occurs, forming ca. 50 μ m aggregates within 30 minutes of irradiation.

Associated with these changes in surface morphology are changes in surface composition. Elemental depth profiles using sputtered neutral mass spectrometry (SNMS) were obtained on zinc powders before and after irradiation. The appreciable oxide coating initially present on the zinc powder is significantly reduced after ultrasound irradiation.

Suslick and Doktycz believed that the observed changes in particle morphology, aggregation and surface composition are due to high velocity interparticle collisions. Ultrasonic irradiation of liquid-solid slurries creates shockwaves and turbulent flow which produces such collisions.

If particles collide head-on, they can do so with enough energy to cause localised melting at the point of contact. This results in particle agglomeration and the exposure of highly reactive zinc metal. If particles collide at a glancing angle, increased surface roughness and cracking of the oxide layer can result.

The sonochemical activation of zinc powder comes from the loss of oxide passivation.

Reactor designs

A variety of devices have been used for ultrasonic irradiation of solutions. There are three general designs in use presently.

1) The ultrasonic cleaning bath.¹⁸⁰

2) The "cup-horn" sonicator. (originally designed for cell disruption).¹⁸¹

3) The direct immersion ultrasonic horn.¹⁸²

In the synthetic arene ruthenium chemistry covered in this thesis, types 1) and 3) were used. The chemistry in Chapter 5 involved with ultrasound was carried out in an ultrasonic cleaning bath, the most accessible source of laboratory ultrasound. Although used successfully, there are several potential drawbacks to its use. There is no control of the acoustic intensity, and reproducible positioning of the reaction flask in the bath is critical, since standing waves in the bath will create nodal spots where cavitation will not occur. Similarly, the height of the bath liquid and of the solution within the reaction vessel are extremely important.¹⁸⁰ Temperature control can rise >25K during the course of a long irradiation, influencing the intensity of the cavity collapse and the rate of background thermal reactivity.

The most intense source of ultrasound generally used in the chemical laboratory is the direct

immersion ultrasonic horn, which has been adapted for inert atmosphere work, as shown in figure 5, or for moderate pressures (<10 atmospheres). This set up was used for experiments carried out in Chapters 2, 3 and 4.

The acoustic intensities are easily and reproducibly variable. The cooling bath keeps the reaction at a constant temperature, compensating for the heat produced from the high power levels used.

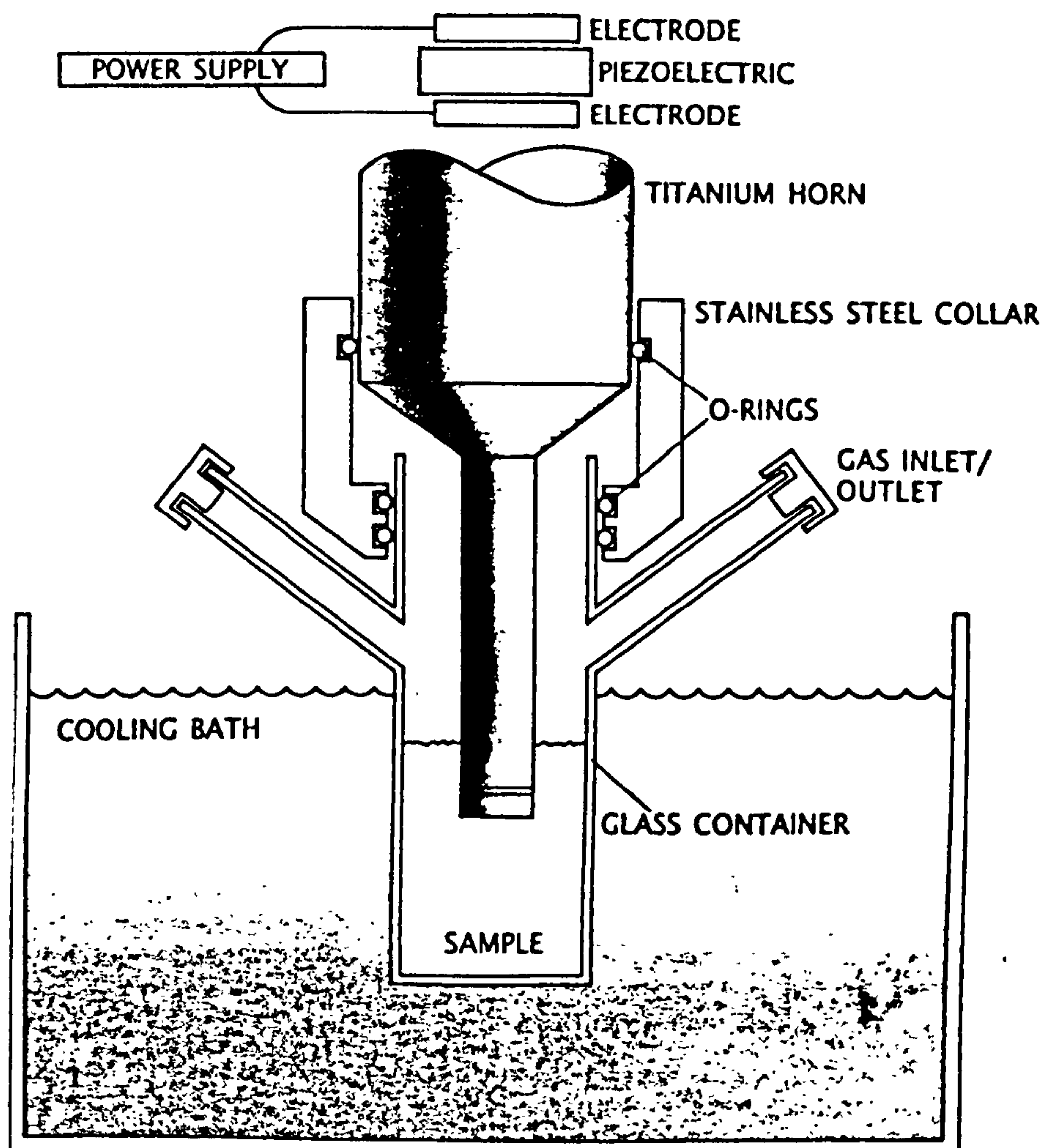


Fig.5. Ultrasonic immersion horn.

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