

SOME SYNTHETIC AND MECHANISTIC STUDIES
ON ORGANOTRANSITION METALS

By

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ABSTRACT

Mechanistic studies have been carried out on the thermolytic behaviour of bis(pyridine)bis(aryl)platinum(II) complexes $\text{cis-py}_2\text{Pt}(\text{C}_6\text{H}_4\text{R}-4)_2$ ($\text{R} = \text{H}, \text{CMe}_3, \text{CF}_3$). The rearrangements of this system are complex, and mainly comprise two competing reactions, intramolecular reductive elimination of biaryl and hydrogen transfer with formation of arene. The latter involves pyridyne and benzyne - intermediates. The extent of operation of these pathways has been evaluated by systematic deuterium labelling, product distribution analysis and kinetic measurements.

Related thermolytic rearrangements of platinafluorenes $\text{L}_2\text{Pt}(\text{C}_{12}\text{H}_8)$ ($\text{L} = \text{PMe}_3, \text{PEt}_3, \text{PMe}_2\text{Ph}, \text{PPh}_3, \text{P}(\text{tol})_3, \text{dppm}/_2, \text{tert-butpy}$) were also studied. Although closely related to bisarylmatal complexes no C-C reductive elimination took place. Decomposition occurred mainly via hydrogen transfer, most probably from a phosphine ligand, where accessible, or from a biphenylene ligand in an intermolecular reaction forming bridged polynuclear platinum species and diphenyl. Smaller amounts of tetra- and hexaphenyls were detected, reflecting other intermolecular modes of reactivity.

In addition, behaviour of α -functional transition metal complexes have been investigated. 1-acetoxyalkyl derivatives of iron(II) and molybdenum(II) (alkyl = methyl, ethyl) have been synthesised and characterised spectroscopically. It was determined that on interaction with protic acids the M-C bond was not cleaved, but an intermediate metal carbene complex was

formed (via C-O scission) which then reacted with the nucleophile.

As expected, thermolytic decay of the acetoxyethyl compounds occurred via β -hydrogen abstraction. Examination of the methyl analogues, which lack such a ready decomposition path, showed that the C-O bond was thermally more susceptible than the M-C bond.

A related class of compounds, halogenomethylplatinum(II) species, trans- $L_2Pt(CH_2X)Y$ ($L = PPh_3, PEt_3$; $X = Cl, I$; $Y = I$) have also been investigated. Pt-Y scission occurred readily in the presence of Ag^+ . The CH_2-X bond, however, could only be cleaved if the cis-phosphine ligand contained an aryl group cooperating in the cyclisation reaction forming platinaindan. Thermolysis released the CH_2 -moiety and yielded isomeric L_2PtXY compounds. Mechanistic investigations were undertaken to study the fate of the methylene-group. Reactivity with cyclohexene was impaired by competing homologation reactions producing C_2 , C_3 and C_4 hydrocarbons. The extent of either reaction depends on the phosphine ligand and halide, but homologation is always predominant.

To My Mother and Father

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ABBREVIATIONS

bipy	2,2'-bipyridyl
But	butyl
CIDNP	Chemically-Induced Dynamic Nuclear Polarisation
COD	Cycloocta-1,5-diene
cp	Cyclopentadienyl
dmsO	Dimethylsulphoxide
dppb	bis-(1,2-diphenylphosphino)butane
dppm	bis-(1,2-diphenylphosphino)methane
ESR	Electron Spin Resonance
Et	Ethyl
GC/MS	Gas Chromatography/Mass Spectroscopy
HPLC	High Pressure Liquid Chromatography
IR	Infrared
Me	Methyl
NBD	Bicyclo[2.2.1]heptadiene
NMR	Nuclear Magnetic Resonance
PhCF ₃	4-trifluoromethylphenyl
PhCMe ₃	4- <u>tert</u> -butylphenyl
Phpy	2-phenylpyridine
PR ₃	Tertiary phosphine
py	Pyridine
thf	Tetrahydrofuran
tol	Tolyl

CHAPTER ONE

SYNTHESIS AND SPECTROSCOPIC CHARACTERISATION OF (BIS)ARYL (BIS)PYRIDINEPLATINUM(II) ; KINETIC AND MECHANISTIC STUDIES

1.1 Introduction

Thermal rearrangements of square planar bisalkyl or bisaryl platinum(II) complexes R_2PtL_2 (R = aryl, alkyl; L = neutral ligand) have been of continued interest over the past few years.

Much work has focussed on the mechanisms of the thermolysis of the compounds R = alkyl, $L_{1,2}$ = mono- or bidentate P or N donors.¹ For R = aryl only L = monodentate P and L_2 = bidentate P or N ligands have been studied.²⁻⁵ There remained an obvious gap: the monodentate N-donor. We therefore chose to investigate the thermolysis of (bis)aryl(bis)pyridineplatinum(II) complexes: $py_2Pt(C_6H_4X)_2$, $X = H, CMe_3, CF_3$.

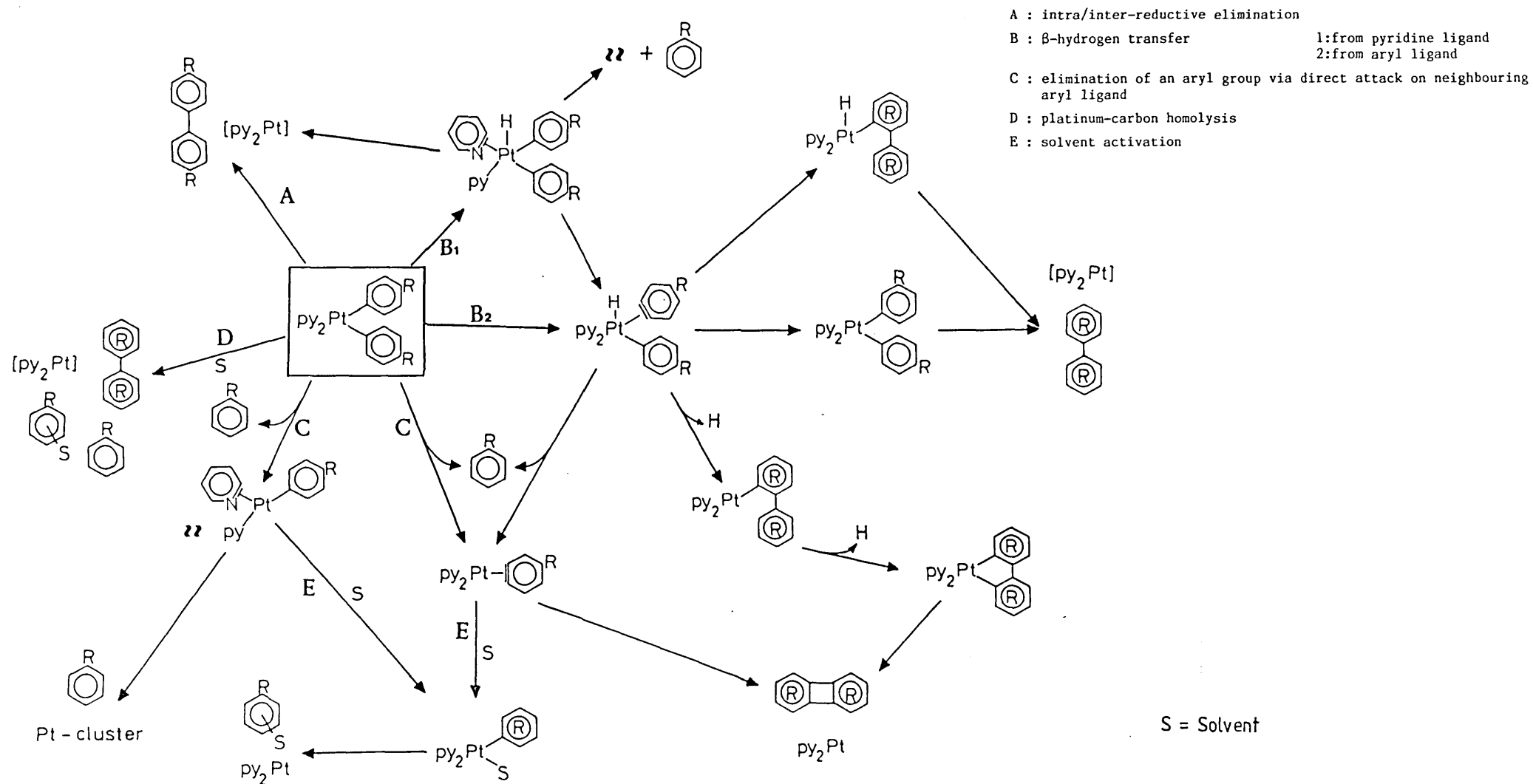
In general, organotransition metals are known to rearrange thermally by a wide variety of mechanisms including :

- (1) hydrogen migrations (β , α , γ and more remote)
- (2) mononuclear and binuclear reductive elimination
- (3) metal-carbon bond homolysis.

Excellent comprehensive reviews of these transformations have already appeared, and will not be duplicated here.⁶⁻¹⁴ Scheme 1 depicts a wide variety of plausible thermolytic pathways for the $py_2Pt(aryl)_2$ system; these will be discussed in the light of established patterns of reactivity, some are more commonly encountered than others.

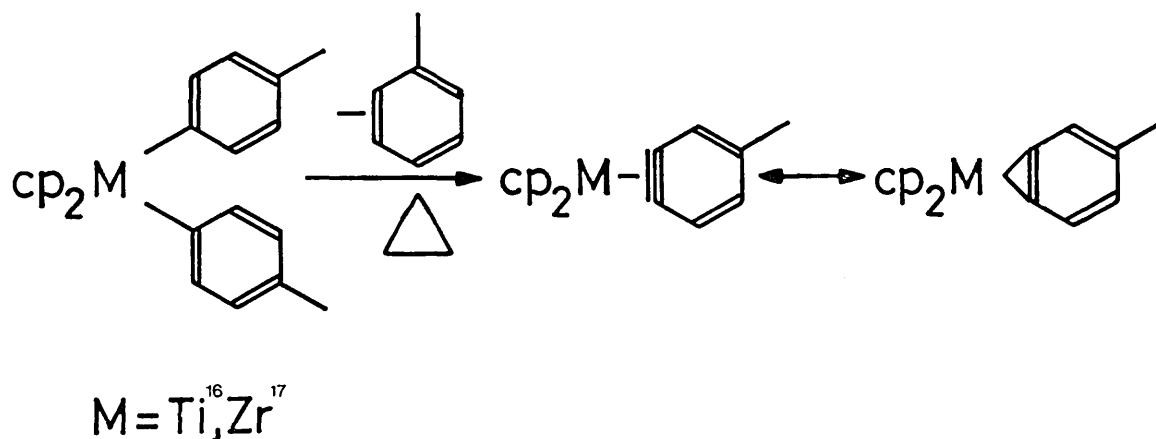
Based on early studies on metal alkyls, organotransition metal compounds were thought to be thermodynamically unstable and that ligands such as CO, cp or phosphines stabilized these compounds due to their π -acidity. It is now established, however, that the lability is rather of kinetic than thermodynamic origin and is determined by the mechanisms

Scheme 1 Thermolysis Pathways for a bis(aryl)bis(pyridine)platinum(II) Compound



available for decomposition.^{6a,10,11,15} Stabilization by π -acid ligands is now attributed to their substitution inertness. The most energetically favourable rearrangement generally involves either a β - or α -hydrogen migration where available. The compound usually requires to be coordinatively unsaturated to allow either to occur. Looking at $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$ there are no hydrogen atoms on the α -carbon and those on the β -carbon are not as readily available as those of alkyl ligands. Formation of benzyne complexes cannot, however, be excluded, since similar species have been occasionally observed (routes $\text{B}_{1,2}$). An example is given in Scheme 2.

Scheme 2 Aryne Formation



Such benzyne (or ortho - phenylene) compounds are reactive intermediates that readily insert CO_2 , ketones or acetylenes. Benzyne formation need not occur only via β -elimination process, but can also happen via direct attack of one of the aryl groups on the other (route C) as Erker has demonstrated for the system cp_2ZrPh_2 .¹⁷ Formation of benzynes is not easily detected. Types and isomerization of products can give an indication of the process. Moreover, it is not only the aryl ligand which can undergo this type of hydrogen transfer. Pyridine has also been observed to participate in similar migration of an ortho-hydrogen (route B₂).

To date, very few such ortho-metallated pyridine complexes are known. Interaction of pyridine with two or three metal centres has been found for Fe¹⁸ and Os.¹⁹ The clusters generated ortho-M-N and M-C σ bonds analogous to the bonding proposed for pyridine chemisorbed on metal surfaces.

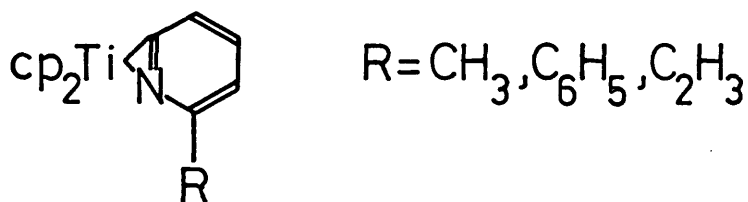
The novel reaction of a 2-substituted pyridine with $\text{cp}_2\text{Ti}(\text{alkyl})$ was reported in 1981 to give the structure shown in Figure 1.²⁰

Interestingly enough pyridine itself or several other substituted pyridines did not react thus. Recently $\text{Lu}(\eta^5\text{-C}_5\text{Me}_5)_2\text{R}$ (R = H, Me) was found to react easily with pyridine to give the first ortho-metallated pyridine compound (Figure 1).²¹

Analogous behaviour was reported in the formation of an uranium compound (Figure 1).²²

Formation of such "pyridyne" species can be monitored via ^1H -NMR or even IR spectroscopy.

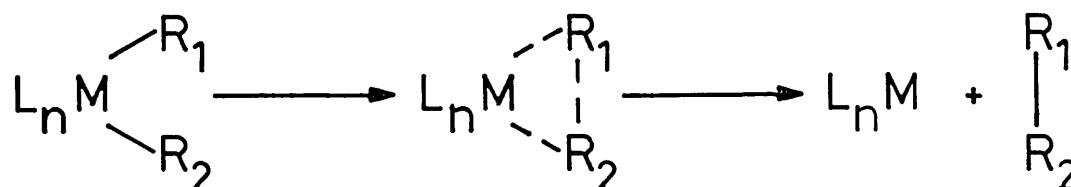
Figure 1 Isolable Pyridyne Complexes of a Variety of Metals



Another well established route of decomposition is reductive C-C elimination (route A, here of biaryl), unfortunately very often masked by other readier reactions such as β -elimination. Reductive elimination has attracted considerable attention for synthetic and industrial use because of its potential for C-C and C-H bond synthesis.

Intramolecular reductive elimination from a transition metal $L_nMR_1R_2$ corresponds to a concerted 1,1-elimination of the groups R_1 , R_2 from the metal centre to give $L_nM + (R_1-R_2)$ (Scheme 3).

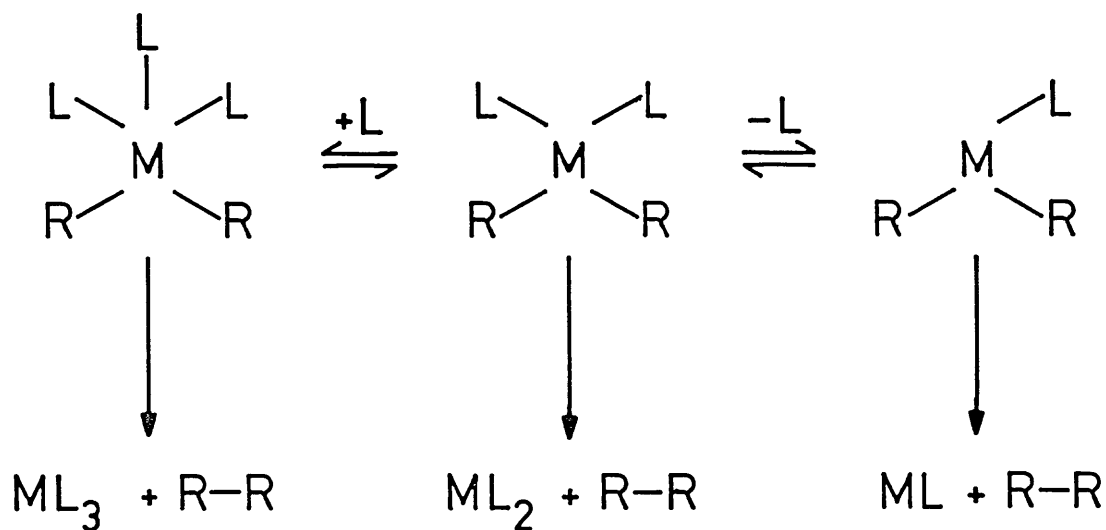
Scheme 3 Concerted Reductive Elimination Mechanism



Both the oxidation number and the coordination number are reduced by two. In theoretical and mechanistic studies the reactivity of the metal-carbon bond has been correlated to the frontier orbitals involved.⁶ The ligands present may also exert a decisive influence. They may either supply electron density and accelerate reductive elimination or inhibit it by withdrawing electron density, or they can cause steric congestion in the transition state.

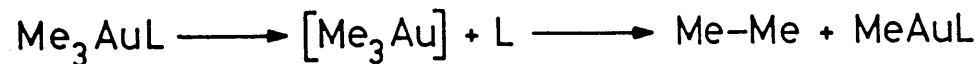
In the case of d^8 -diorganometals (Scheme 4),^{7e} direct elimination of $R_1 - R_2$ from a four-coordinated species is rather rare and occurs only in a few cis-dialkylnickel(II),²³ hydridoalkylplatinum(II)²⁴ and diarylplatinum(II)² complexes, while for Pd(II)²⁵ and Au(III)²⁶ formation of a three-coordinate intermediate was inferred from kinetic evidence (Scheme 5).

Scheme 4 Mechanisms of Reductive Elimination Processes



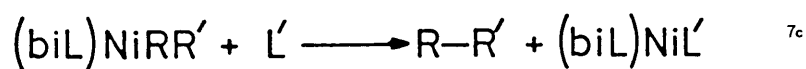
Depending on the intermediate, addition of L will either inhibit or accelerate elimination.

Scheme 5 Dissociative Reductive Elimination Mechanism

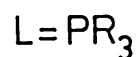
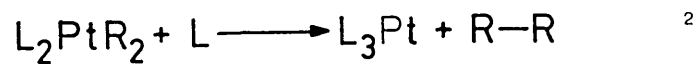
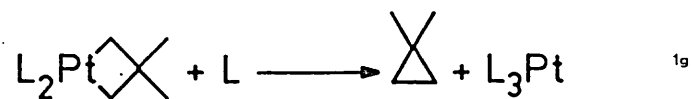


In a polar solvent added phosphine will inhibit the reaction that occurs via preliminary L dissociation. On the other hand, added phosphine can also facilitate reductive elimination (Scheme 6).

Scheme 6 Associative Reductive Elimination Mechanisms



biL = bidentate ligand

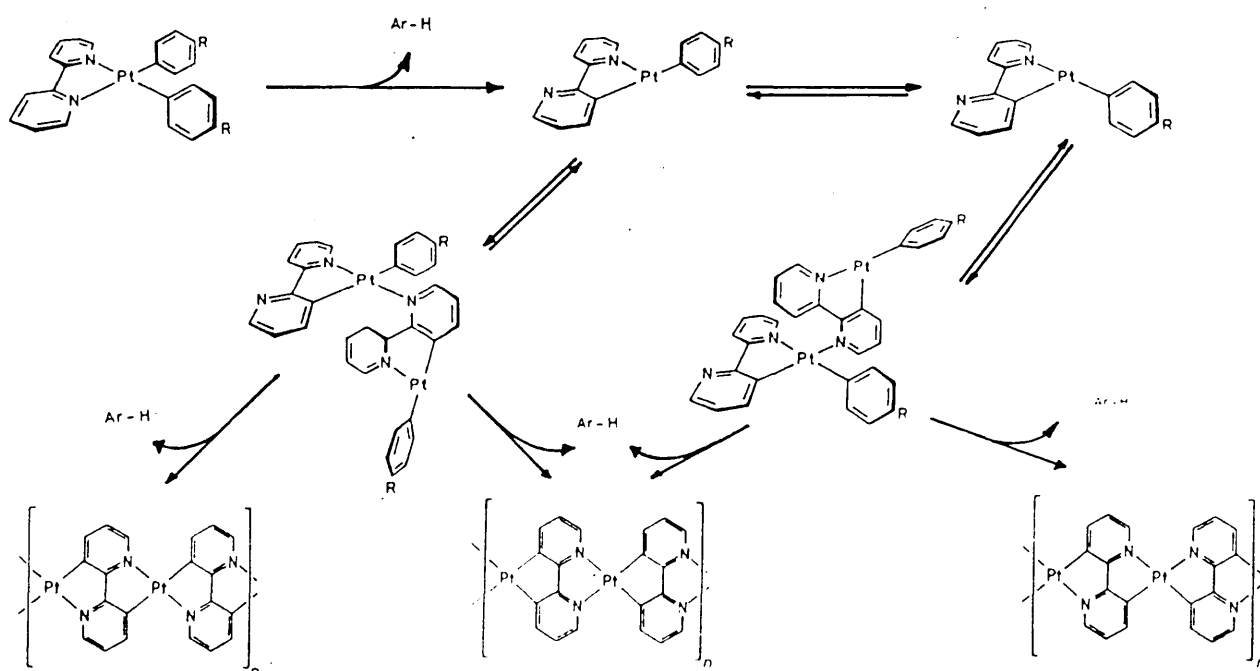


The role of phosphine is still, however, not fully established in this latter case.²

Stereochemistry also plays a vital role in reductive elimination. For concerted elimination cis-orientation of the two eliminating groups is necessary.^{7c} Therefore, trans- L_2MR_2 can reductively eliminate only after prior isomerization. Ertl proposed L-dissociation during the thermolysis of trans- $L_2Pt(aryl)_2$ before the biaryl is eliminated.^{4b}

After reductive elimination, a square planar d^8 -system will form a spherically symmetric d^{10} subshell. The two coordinated species will prefer a linear conformation. Under these circumstances, bidentate phosphine is likely to hinder reaction, not on orbital but on steric grounds unless a large excess of free ligand is present.^{2b} $bipyPt(aryl)_2$ will not reductively eliminate at all, but favours a reaction path via a novel "roll-over" metallation to form a polymeric platinum-species (Scheme 7).⁵

Scheme 7 "Roll-Over" Metlallation Mechanism



Up to now only intramolecular reductive elimination has been discussed. Intermolecular mechanisms have, however, been established. In contrast to the former, metal coordination and formal oxidation state are both reduced by one only. There are only a few examples of C-C and C-H bond formation e.g. (Scheme 8).

Scheme 8 Intermolecular Reductive Elimination Reactions

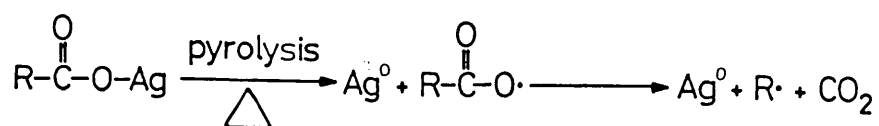
- (1) $2 \text{ cis-H}_2\text{Os}(\text{CO})_4 \rightarrow \text{H}_2\text{Os}_2(\text{CO})_8 + \text{H}_2$ ²⁷
- (2) $\text{HMn}(\text{CO})_5 + \text{MeAu}(\text{PPh}_3) \rightarrow \text{PPh}_3\text{Au-Mn}(\text{CO})_5 + \text{CH}_4$ ²⁸
- (3) $n\text{-Bu}_3\text{PCuH} + n\text{-Bu}_3\text{PCu(alkyl)} \rightarrow 2 \text{ Cu} + 2 n\text{-Bu}_3\text{P} + (\text{H-alkyl})$ ²⁹
- (4) $2 \text{ C}_4\text{H}_9\text{AgPBu}_3 \rightarrow \text{C}_8\text{H}_{18} + 2 \text{ PBu}_3 + 2 \text{ Ag(o)}$ ³⁰

According to Norton's rule binuclear reductive elimination is only possible if (1) one of the metals has a hydride ligand present or available and (2) the other metal has a vacant coordination site.²⁷ This seems applicable only when a dimeric metal species is formed (e.g. 1 + 2). This is, however, no prerequisite for binuclear elimination (e.g. 3 + 4). As shown in the latter, the organic ligands produce the dimer on thermolysis (it is established that no free radicals are involved).

Homolysis was, at one time, considered a common mode of decomposition, especially of metal alkyls, but the results of extensive studies have shown this route to be relatively rare.¹¹ The clearest case of radical reactivity is the thermolysis of Hg(II) and Pb(IV) alkyls (and aryls).

Among the transition metal series, data are available for Mn(II), Ni(II), Pt(IV), Cu(I) and Ag(I). Free radical intermediates have been postulated for some mechanisms, but in only very few examples have radicals been unequivocally observed. The first report of free radical displacement at a square planar Pt(II) species R_2PtL_2 ($R = Me, Et, Me_3SiCH_2, PhCH_2$; $L = Palkyl_3, PMe_2Ph$) was made by Lappert.³¹ An attacking radical displaced an alkyl radical. Puddephatt proposed that radicals were produced under mild conditions in reactions of dialkylplatinum(II) complexes with alkenes in the presence of the spin trap Bu^tNO ;³² this agent has, however, been demonstrated to initiate Pd-C bond homolysis.³³ Fields has reported an interesting study on silver p-tert-butylbenzoate which has a bearing on the outcome of any homolytic pathway in the thermolysis of $py_2Pt(aryl)_2$ (Scheme 9).³⁴

Scheme 9 Homolysis of Silver p-tert-Butylbenzoate

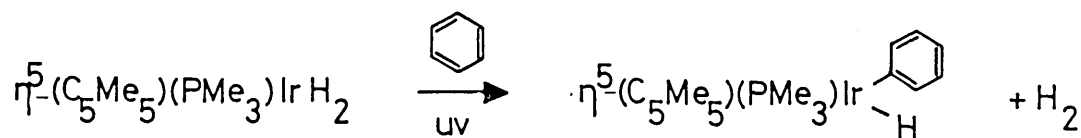


A tert-butyl-phenyl radical is formed. The organic product distribution therefore comprises tert-butylbenzene and coupled products such as di-, ter- and tetraaryl. Noteworthy also is the isomer distribution of the biaryls: 75% 3,3'-, 19% 3,4'- and 3% 4,4'- ditert-butyldiphenyl. The remaining percentages are split among the other isomers. We would therefore expect a similar product distribution for $\text{py}_2\text{Pt}(\text{PhR})_2$ should homolysis take place (route D). In solution we would also expect radical solvent attack.

Observation of radical processes can be difficult. Experiments with radical trapping agents are at times unreliable, since the possibility always exists that the trapping agent reacts with the metal complex and thus initiates homolytic cleavage (vide supra). Detection of possible radical coupling products is not always conclusive because they may arise in other ways. ESR and CIDNP techniques permit observation of carbon based radicals or radical pairs, but only at mild temperatures.

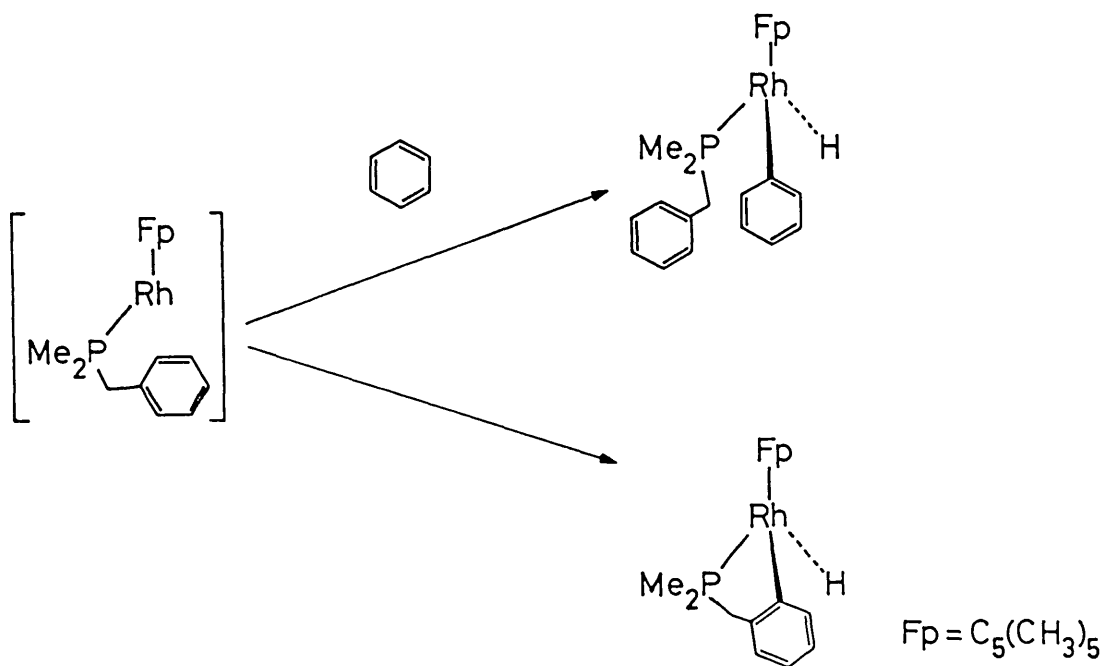
Finally, the possibility of activation of C-H and C-C bonds of solvent molecules is currently topical (route E). In 1983 Bergman et al. were the first to observe activation of C-H bonds in saturated hydrocarbons.³⁵ Irradiation of $\eta^5\text{-(C}_5\text{Me}_5\text{)}(\text{PMe}_3)\text{IrH}_2$ in benzene resulted in loss of H_2 and attack of the solvent (Scheme 10).

Scheme 10 Activation of C-H bonds in $(\text{C}_5\text{Me}_5)(\text{PMe}_3)\text{IrH}_2$



No intramolecularly formed products were found. Recently, Jones et al. have carried out extensive studies on inter- and intramolecular reactivity of aliphatic and aromatic C-H bond activation in the compounds depicted in Scheme 11.³⁶

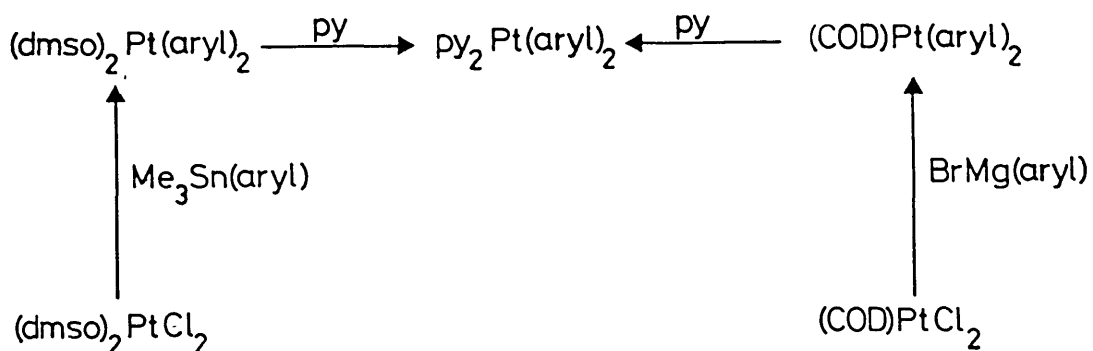
Scheme 11 Kinetic and Thermodynamic Selectivity of C-H bond Activation



The single coordinatively unsaturated metal can form unstrained 5 - member - metallacycles or oxidatively add solvent. It was found that kinetic selectivity can favour the intermolecular route when the neat solvent is the competing reagent even if in thermodynamic terms the unimolecular process should be expected.

The compounds $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$ themselves are easily accessible. cis- $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$ ($\text{R} = \text{H}$, ortho/para- CH_3) have been made previously.^{37,38} There are two different routes for the synthesis, either via a COD³⁸ or a dms³⁹ intermediate as outlined in Scheme 12.

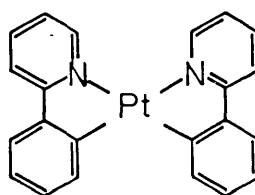
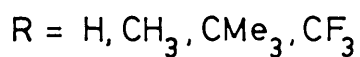
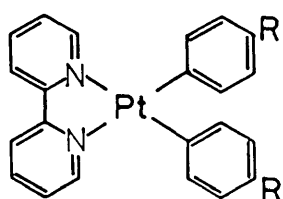
Scheme 12 Syntheses of $\text{py}_2\text{Pt}(\text{aryl})_2$



It is interesting to note the close structural relationship of $\text{py}_2\text{Pt}(\text{aryl})_2$ with two previously reported compounds, Figure 2 and Figure 3.

Figure 2 Structure of $(\text{bipy})\text{Pt}(\text{aryl})_2$

Figure 3 Structure of $\text{Pt}(\text{Phpy})_2$



$(\text{bipy})\text{Pt}(\text{aryl})_2$ has been studied extensively and its reactivity has briefly been mentioned in this Chapter.⁵ $\text{Pt}(\text{Phpy})_2$ is the first example of a homoleptic complex with the anionic ligand Phpy .⁴⁰ Its thermal reactivity has not yet been studied.

1.2 Synthesis and Spectroscopic Characteristics of Bisaryl-Bispyridine Platinum(II) Compounds

1.2.1 Syntheses of $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$

For the synthesis of the compounds $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$ ($\text{R} = -\text{H}, -\text{CMe}_3, -\text{CF}_3$) a modification of the route described by Doyle was employed.³⁸ Dichloro(1,5-cyclooctadiene)^{1d} platinum in ether was utilised as an alternative to its diiodide analogue in benzene and was reacted with an excess of aryl-grignard $\text{BrMgC}_6\text{H}_4\text{R}$ to give $(\text{COD})\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$. Higher yields were achieved by lowering the reaction temperature and prolonging the reaction time instead.

In a next step the COD-platinum compound was suspended in neat pyridine and left to react with the solvent for several hours at 50°C to give cis- $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$. Recrystallization yielded colourless ($\text{R} = \text{H}, \text{CMe}_3$) or yellowish ($\text{R} = \text{CF}_3$) crystals. They are air-, moisture- and light-stable at room temperature over a long period of time. Their identities were established by ^1H , ^{13}C , where applicable ^{19}F , and ^{195}Pt -NMR, as well as IR and elemental analysis. The compounds are fairly soluble in acetone, chloroform and methylene chloride, but only moderately in benzene, toluene and xylene. Isomeric purity was established by ^{195}Pt -NMR and IR (see 1.2.2.3 and 1.2.2.4). Assignment of cis-configuration was in accordance with the literature, and is not unexpected due to the stronger trans-influence of the aryl ligand.⁴⁰

A different procedure described by Pidcock via a dmsO precursor $(\text{dmsO})_2\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$ was less reliable and lower in yield.³⁹

Compounds for the deuterium labelling studies were prepared the same way. Pyridine-d⁵ was commercially available. The deuterated aryl group tert-butylphenyl-d⁴, however, had to be synthesized by alkylation of benzene-d⁶ to form tert-butyl-benzene-d⁵. Subsequent bromination mainly produced the Grignard precursor p-bromo-tert-butyl-benzene-d⁴.

Genuine samples of biaryls as spectroscopic and chromatographic reference compounds were readily obtained by coupling reactions. Either an arylhalide was coupled with a Grignard reagent in the presence of a catalytic amount of Cl₂Pd(dppb)⁴¹ or organomagnesium halides were reacted in the presence of CoCl₂⁴². The latter procedure formed symmetrical and/or asymmetrical biaryls dependent upon the Grignard reactant mixture.

1.2.2 Spectroscopic Characteristics of COD- and dmsO-Precursors and py₂Pt(C₆H₄R)₂

1.2.2.1 ¹H and ¹⁹F-NMR

The following numbering system was employed (Figure 4), based on IUPAC conventions previously adopted in the literature.

Figure 4 Numbering System for py₂Pt(C₆H₄R)₂

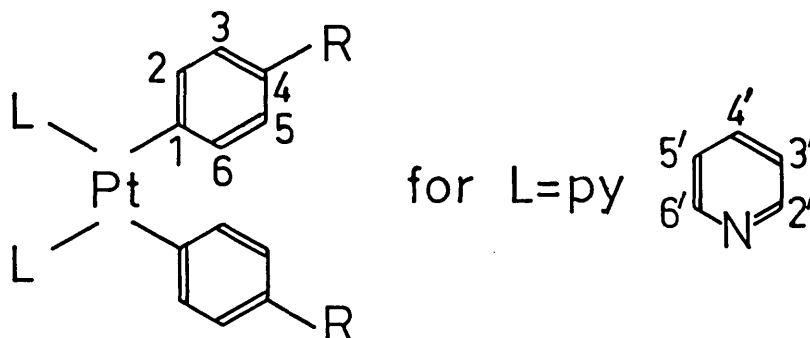


Table 1 ^1H -NMR Characteristics of $(\text{COD})\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$

Compound	Aryl ^a			COD ^a	
R	$\delta(^1\text{H}_2)$	$\delta(^1\text{H}_3)$	$\delta(^1\text{H}_4)/(^1\text{H}_\text{R})$	$\delta(\text{CH})$	$\delta(\text{CH}_2)$
H	7.27 $^3\text{J}(\text{H}_2\text{H}_3) = 7.9 \text{ Hz}$ $^4\text{J}(\text{H}_2\text{H}_4) = 1.2 \text{ Hz}$ $^3\text{J}(\text{Pt-H}_2) = 70 \text{ Hz}$	7.02 $^3\text{J}(\text{H}_2\text{H}_3) = 7.2 \text{ Hz}$	6.84	5.12 $\text{J}(\text{Pt-H}) = 39 \text{ Hz}$	2.52 $\text{J}(\text{Pt-H}) = 16 \text{ Hz}$
CMe ₃	b	b	1.18	5.11 $\text{J}(\text{Pt-H}) = 38 \text{ Hz}$	2.50 $\text{J}(\text{Pt-H}) = 15 \text{ Hz}$
CF ₃	7.36 $^3\text{J}(\text{Pt-H}_2) = 74 \text{ Hz}$ $^3\text{J}(\text{H}_2\text{H}_3) = 8 \text{ Hz}$	7.20 $^4\text{J}(\text{HF}) = 3 \text{ Hz}$ $^3\text{J}(\text{H}_3\text{H}_2) = 8 \text{ Hz}$	91.7 ^c	5.06 $\text{J}(\text{Pt-H}) = 39 \text{ Hz}$	2.53 $\text{J}(\text{Pt-H}) = 16 \text{ Hz}$

Table 2 ^1H -NMR Characteristics of $(\text{dmso})_2\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$

Compound	Aryl ^a			dmso ^a
R	$\delta(^1\text{H}_2)$	$\delta(^1\text{H}_3)$	$\delta^1\text{H}_4 / \delta^1\text{H}_\text{R}$	$\delta(\text{CH}_3)$
H	7.68 $^3\text{J}(\text{H}_2\text{H}_3) = 7 \text{ Hz}$ $^4\text{J}(\text{H}_2\text{H}_4) = 1.8 \text{ Hz}$	multiplet ^b 7.05 - 6.8	7.29 $^3\text{J}(\text{H}_3\text{H}_4) = 8 \text{ Hz}$	2.81 $\text{J}(\text{Pt-H}) = 15 \text{ Hz}$
CF ₃	7.43 $^3\text{J}(\text{H}_2\text{H}_3) = 8 \text{ Hz}$	7.13 $^3\text{J}(\text{H}_3\text{H}_2) = 8 \text{ Hz}$	87.44 ^c	2.85 $\text{J}(\text{Pt-H}) = 16 \text{ Hz}$

a in ppm relative to internal Me₄Si in CDCl₃ ; b obscured ; c ^{19}F -NMR in ppm relative to CFCl₃

Nuclei coupled to ^{195}Pt (spin $\frac{1}{2}$, 34% abundance) display a 1:4:1 series of resonances. Coupling constants are measured between the two outer peaks.

Listed in Table 1 and 2 are the ^1H and ^{19}F -NMR parameters of the precursors $(\text{COD})\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$ ($\text{R} = \text{H}^*$, CMe_3 , CF_3) and $(\text{dmsO})_2\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$ ($\text{R} = \text{H}^{**}$, CF_3).

For the former, the most prominent features are the two COD-signals and their spin-spin interaction with ^{195}Pt producing the 1:4:1 "triplet" : $\delta ^1\text{H}$ (olefinic) = 5.06 - 5.12 ppm, $J(\text{Pt} - \text{H}) = 38\text{--}39$ Hz and $\delta ^1\text{H}$ (aliphatic) = 2.50 - 2.53 ppm, $J(\text{Pt} - \text{H}) = 15 - 16$ Hz. $J(\text{Pt} - \text{H})$ coupling constants of the aryl group were $^3J(\text{Pt} - \text{H}_2) = 70 - 74$ Hz. These results are in close agreement with Clark's observations for closely related compounds.⁴³

For the dmsO-compounds the methyl group of the S-donor ligand shows a characteristic signal at δ 2.81 - 2.85 ppm $J(\text{Pt} - \text{H}) = 15 - 16$ Hz. No coupling $^3J(\text{Pt} - \text{H})$ was detected for the aryl ligands.

The ^1H -NMR characteristics of $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$ are listed in Table 3 and show some distinctive features. Easily recognisable are the signals related to the coordinated pyridine. Compared to the free ligand all protons are at lower field, but remain in the same sequence with increasing downfield shift $\text{H}_{\text{meta}} < \text{H}_{\text{para}} < \text{H}_{\text{ortho}}$. The last displays a characteristic doublet of doublets with ^{195}Pt "satellites". Coupling $^3J(\text{Pt} - \text{H})$ ranges between 16 - 20 Hz, comparable to analogous $(\text{bipy})\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$ compounds.⁵ Coupling

* Although reported previously, no NMR-data available³⁸

** Also measured by Pidcock³⁹

Table 3 ^1H -NMR Characteristics of $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$

Compound	δ /ppm pyridine ^a				δ / ppm aryl ^a			
R	$^1\text{H}_2$	$^1\text{H}_3$	$^1\text{H}_4$		$^1\text{H}_2$	$^1\text{H}_3$	($^1\text{H}_4/^1\text{H}_\text{R}$)	
H^b	8.474	7.207	7.750	$^3\text{J}(\text{Pt}-\text{H}_\text{o}) = 16 \text{ Hz}$ $^3\text{J}(\text{H}_\text{o}-\text{H}_\text{m}) = 4.8 \text{ Hz}$ $^3\text{J}(\text{H}_\text{m}-\text{H}_\text{p}) = 7.6 \text{ Hz}$ $^4\text{J}(\text{H}_\text{o}-\text{H}_\text{p}) = 1.7 \text{ Hz}$	7.020	6.797	6.881 ^d	$^3\text{J}(\text{Pt}-\text{H})^e$ $^3\text{J}(\text{H}_\text{o}-\text{H}_\text{m}) = 6.7 \text{ Hz}$ $^3\text{J}(\text{H}_\text{m}-\text{H}_\text{p})^e$ $^4\text{J}(\text{H}_\text{o}-\text{H}_\text{p}) = 2.8 \text{ Hz}$
CMe_3^c	8.220	6.167	6.621	$^3\text{J}(\text{Pt}-\text{H}_\text{o}) = 20 \text{ Hz}$ $^3\text{J}(\text{H}_\text{o}-\text{H}_\text{m}) = 6.3 \text{ Hz}$ $^3\text{J}(\text{H}_\text{m}-\text{H}_\text{p}) = 9.2\text{Hz}$ $^4\text{J}(\text{H}_\text{o}-\text{H}_\text{p}) = 1.4 \text{ Hz}$	7.419	7.015	1.269	$^3\text{J}(\text{Pt}-\text{H}) = 64.7 \text{ Hz}$ $^3\text{J}(\text{H}_\text{o}-\text{H}_\text{m}) = 8.3 \text{ Hz}$
CF_3^b	8.447	7.262	7.784	$^3\text{J}(\text{Pt}-\text{H}) = 19 \text{ Hz}$ $^3\text{J}(\text{H}_\text{o}-\text{H}_\text{m}) = 4.8 \text{ Hz}$ $^3\text{J}(\text{H}_\text{m}-\text{H}_\text{p}) = 7.0 \text{ Hz}$ $^4\text{J}(\text{H}_\text{o}-\text{H}_\text{p}) = 1.6 \text{ Hz}$	7.183	7.033	91.67 ^f	$^3\text{J}(\text{H}_\text{o}-\text{H}_\text{m}) = 8.0 \text{ Hz}$ $^3\text{J}(\text{HPt})^e$

a in ppm relative to internal Me_4Si ; b in CDCl_3 ; c in *o*-xylene- d^{10} ; d multiplet ; e obscured ; f ^{19}F -NMR in ppm relative to CFC_3

constants of the protons on the pyridine ring are in general identical with the free ligand, although variations may occur due to solvent effects. The aryl group also displays a deshielded ortho-proton. Spin-interaction with platinum is obscured by other overlapping signals.

1.2.2.2 ^{13}C - NMR

^{13}C { ^1H } characteristics are listed in Table 4. The numbering system is that defined in Section 1.2.2.1. The insolubility of $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{CF}_3)_2$ precludes spectroscopic measurement in solution. The spectra are complicated due to the number and variety of aromatic carbons in the compounds $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$. Assignments are based on comparisons with the spectra of free pyridine and on the intensity of the peaks. Because the spectra were recorded with hydrogen decoupling irradiation, carbons with attached hydrogen(s) experience a nuclear Overhauser enhancement. The quaternary carbons, by corollary, appear at lower intensity compared to tertiary ones and are therefore often not detectable.

$^1\text{J}(\text{Pt} - \text{C})$ coupling constants were not measurable due to the low solubility of the compounds.

1.2.2.3 ^{195}Pt - NMR

In Table 5, the ^{195}Pt -NMR characteristics are listed.

Coupling with ^{14}N (spin = 1, 99.63% abundance) was not detected because of the rapid quadrupolar relaxation of the ^{14}N nucleus, nor was

Table 4 ^{13}C -NMR Characteristics of $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$

R	$\delta(^{13}\text{C}) \text{ ppm} : \text{pyridine}$			$\delta(^{13}\text{C}) \text{ ppm} : \text{aryl}$				
	C2' C6'	C3' C5'	C4'	C1	C2 C6	C3 C5	C4	R
H ^a	151.9	123.7	137.0	153.5	135.7	127.2	128.7	
CMe_3^a	151.7	122.9	136.4	b	138.2	125.0	b	$\underline{\text{CMe}}_3$ 41.5 $\underline{\text{CMe}}_3$ 31.6
free ^c pyridine	150.6	124.5	136.4					

a in CDCl_3 relative to internal Me_4Si ; b not detected ; c reference 44

Table 5 ^{195}Pt -NMR Characteristics of $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$ ^a

R	$\delta(^{195}\text{Pt})\text{ppm}$ ^b
H	- 2229
CMe_3	- 1328
CF_3	c

a rel. K_2PtCl_4 in H_2O (external reference)

b in CDCl_3

c too insoluble

interaction with ^{15}N (spin = 3/2, 0.37% abundance), due to the low isotopic abundance.

Such coupling is rarely observed and then only under special circumstances.⁴⁵

In addition, the isomeric purity was established, since only one signal was obtained.

1.2.2.4 Infrared Spectroscopy of $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$

I.R. characteristics are displayed in Table 6.

Platinum-carbon stretching frequencies are found in the region of $600 - 500 \text{ cm}^{-1}$.⁴⁶ It has been reported that for cis-isomers the absorption associated with this stretching occurs in two bands while trans-isomers show only a single absorption.³⁸

Pt-C, Pt-N or combination bonds are difficult to differentiate because

Table 6 IR Characteristics of $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$ ^a

R	Infrared Absorption (cm^{-1})
H	3045m, 3030m, 2990v, 2970v, 1640vw, 1590vs, 1565vs, 1475m, 1460s, 1440vs, 1420s, 1390m, 1350m, 1340w, 1250w, 1236m, 1211s, 1203m, 1180w, 1150w, 1080m, 1070s, 1065vs, 1046m, 1025vs, 1014s, 950w, 900w, 880w, 768s, 749vs, 740vs, 701vs, 662m, 641m, 506m ^b 464w, 400vw
CMe ₃	3060m, 3000w, 2955s, 2900m, 2860m, 1600s, 1582m, 1571w, 1480s, 1448s, 1390sh, 1378m, 1359m, 1351m, 1268m, 1240w, 1210w, 1210m, 1155w, 1125s, 1107m, 1070m, 1061m, 1045m, 1014m, 945w, 920vw, 820vs, 761vs, 728w, 698vs, 640m, 580m ^b , 570m ^b , 460vw
CF ₃	2980m, 2920m, 1625w, 1590w, 1560w, 1495w, 1392w, 1325m, 1261m, 1195s, 1180m, 1165w, 1125w, 1072w, 1052w, 930w, 760vs, 715sh, 575vs ^b , 550vs ^b , 465vs, 440vs

a KBr-disc

b Pt-C stretch

w - weak, m - medium, s - strong, vs - very strong, sh - shoulder

they are similar in energy. For the unsubstituted py_2PtPh_2 , the symmetry will approximate D_{4h} closely. Only one band at low energy, 506 cm^{-1} , is observed in agreement with the $\nu_6(E_u)$ infrared active stretching frequency.⁴⁷ For substituted $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$ ($\text{R} = \text{CMe}_3$ and CF_3) symmetry is closer to C_{2v} and two absorption bands of equal intensity are displayed at 580, 570 and 575, 550 cm^{-1} respectively.

It has been pointed out, however, that such Pt-C assignments may be ambiguous, especially for derivatives containing aryl-groups and coordinated pyridines because of the occurrence of other ligand vibrations in the same region.⁴⁶

1.3 Thermal Behaviour of $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{CMe}_3)_2$

1.3.1 Product Analysis and Reaction Mechanism

$\text{py}_2\text{Pt}(\text{PhCMe}_3)_2^*$ was the most suitable complex for detailed study because of its greater solubility (max. solubility ca. $4 \cdot 10^{-3}\text{M}$ at room temperature) and its distinctive NMR-characteristics for the CMe_3 -moiety.

Decomposition of $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$ in toluene at 90°C gives a wide variety of organic products, as shown in Scheme 13.

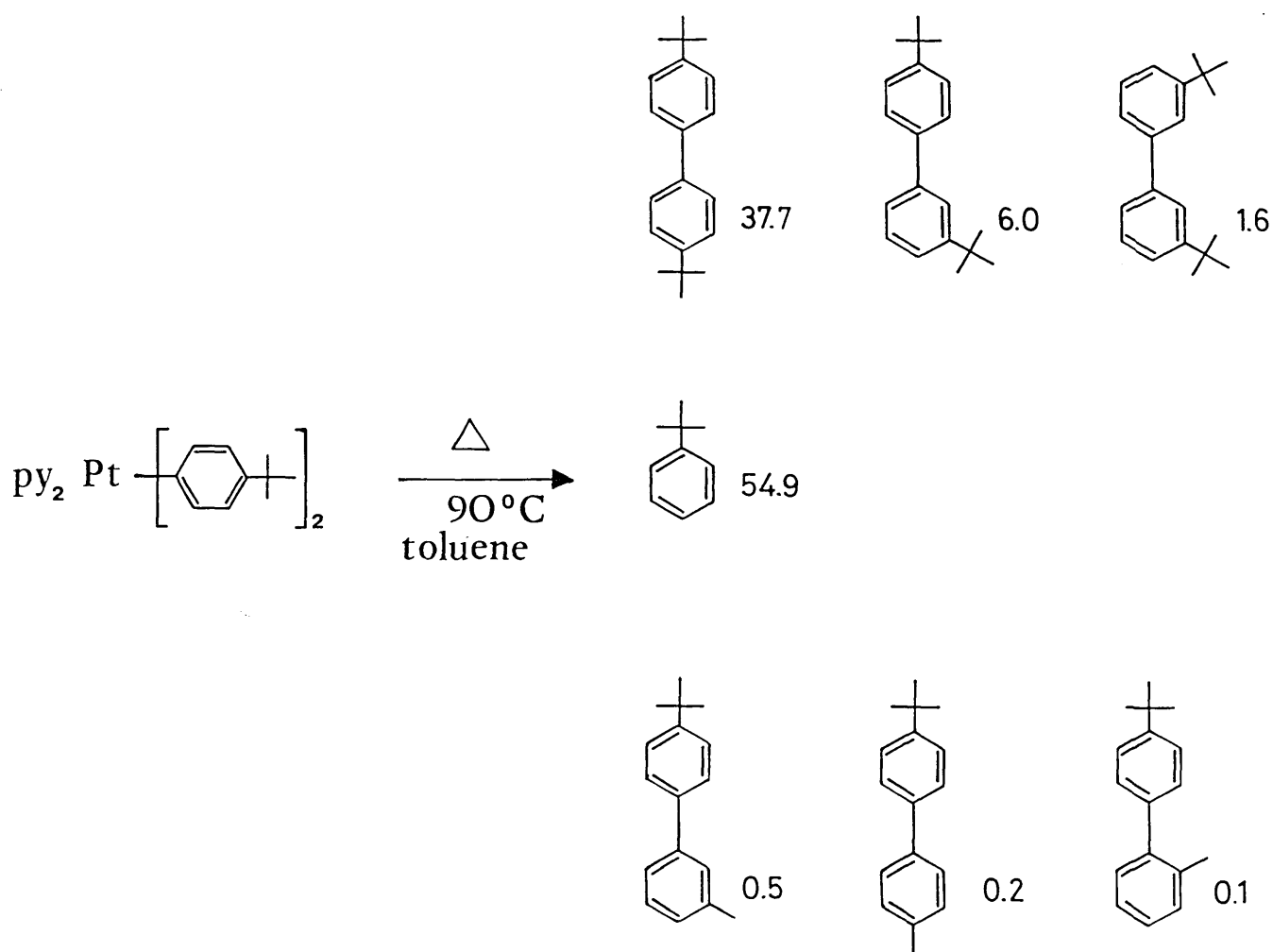
It should be noted that the product yields in this and subsequent schemes/tables are quoted in mol%, which is defined as:

$$\text{mol\%} = \frac{\text{mol product}}{(\text{mol Pt-C bonds})} \cdot 100\%$$

Mol(Pt-C bond) was chosen to avoid values over 100%, since two aryl groups per platinum can be liberated. At this temperature, the main product is tert-butylbenzene. In addition, there are three of the isomeric forms of bis-tert-butyldiphenyl. Obviously the ortho-position is sterically unfavourable for the tert-butyl group. Three isomeric solvent-derived products are also detected in low amounts. The thermolysis is accompanied by a progressive change in solution colour from colourless to yellow. Prolonged heating gives rise to an additional product 4-benzyl-tert-butylbenzene (> 10 half lives). Variation of concentration ($1\text{--}3 \cdot 10^{-3}\text{M}$)

* Hereafter, for simplicity, cis- $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{CMe}_3\text{-}4)_2$ will be represented as $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$

Scheme 13 Organic Product Distribution of $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$ Thermolysis at 90°C



or solvent had no influence on the product distribution, except for the solvent-derived products. In benzene 4-tert-butyldiphenyl was observed. In ortho or para- xylene and mesitylene, solvent adduct concentrations were too insignificant to be identified.

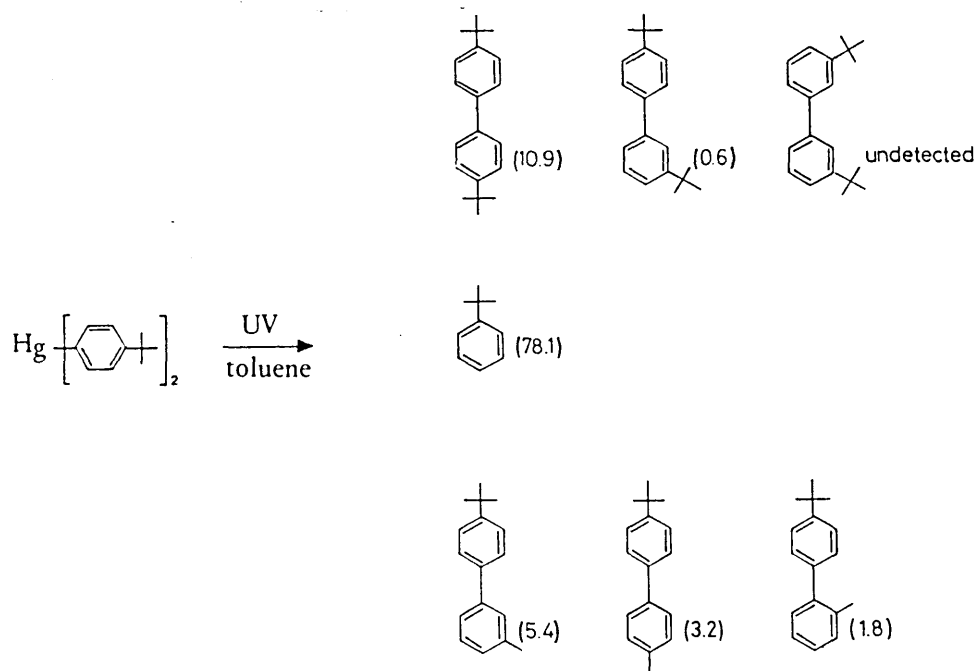
Metal-Carbon Homolysis

Complex product distributions often arise from free radical processes. As a preliminary experiment, duroquinone was added to the thermolysis solution. There was no effect on the product distribution. This experiment, however, only indicates the absence of a radical chain reaction but not necessarily of homolytic platinum-carbon cleavage.

Mercury compounds HgR_2 ($\text{R} = \text{alkyl/aryl}$) are known to decompose homolytically on irradiation.⁴⁸ To generate a product distribution authentically derived from aryl radicals, a toluene solution of $\text{Hg}(\text{PhCMe}_3)_2$ - at the same concentration as for thermolyses of $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$ - was photolysed at 0°C and the solution analysed (Scheme 14). It was established that $\text{Hg}(\text{PhCMe}_3)_2$ did not undergo thermolytic reactions at these temperatures.

Although the same types of compounds are formed, a comparison of the product distribution of thermal decomposition of $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$ with that of the photolysis of $\text{Hg}(\text{PhCMe}_3)_2$ displays several important disparities.

Scheme 14 Organic Product Distribution of $\text{Hg}(\text{PhCMe}_3)_2$ Photolysis



mol% are given in brackets

There is a significant increase in PhCMe_3 and solvent-adduct formation for the photolytic reaction. Consequently, only 11.5 mol% of aryl-moieties couple to yield biaryls. A clear difference in molar distribution is found for the isomeric biaryls as well as for the three isomeric solvent-derived products. The ratios of the latter (listed in brackets in Table 7) show a certain similarity, however. Since solvent adducts give rise to less than 1 mol% of the organoplatinum thermolysis products, a major homolytical pathway can be excluded, even should this similarity be caused by radicals.

Table 7 Comparison of Product Distribution of Photolysed $\text{Hg}(\text{PhCMe}_3)_2$ and Thermolysed $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$ in toluene

Compound	PhCMe_3	$\text{Me}_3\text{CPhPhCMe}_3$				MePhPhCMe_3			
		Total	Isomer 4,4'	3,4'	3,3'	Total	Isomer 3',4'	4',4'	2',4'
$\text{Hg}(\text{PhCMe}_3)_2$	78.1	11.5	10.9 (94.8) ^b	0.6 (5.2) ^b	a	10.4	5.4 (51.7) ^b	3.2 (30.7) ^b	1.8 (17.6) ^b
$\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$	54.9	45.4	37.7 (83.0) ^b	6.0 (13.2) ^b	1.6 (3.8) ^b	0.8	0.5 (52.4) ^b	0.2 (26.8) ^b	0.1 (20.7) ^b

a not detected ; b % of isomer of total amount of biaryl

An often encountered problem in reactions of organometallic compounds are secondary reactions heterogeneously catalysed by metal or metal bearing residues produced from the originally homogeneous system. Although no platinum metal is visible in the thermolysis solution, it is certainly possible that colloidal Pt(o) might be responsible for solvent products in a secondary reaction.

Generation of tert-butylphenyl radicals from silver p-tert-butylbenzoate has been studied previously (as noted in the Introduction).³⁴ Again, product distributions different from those discussed above were obtained under the different conditions (gas phase, 300°C). In this case, there was evidence of extensive isomerization from the 4-tert-butyl to the 3-tert-butyl phenyl radical.

To be sure of an authentic generation of tert-butylphenyl radicals, $\text{Hg}(\text{PhCMe}_3)_2$ was heated at 90°C for several days. No decomposition products were detected.

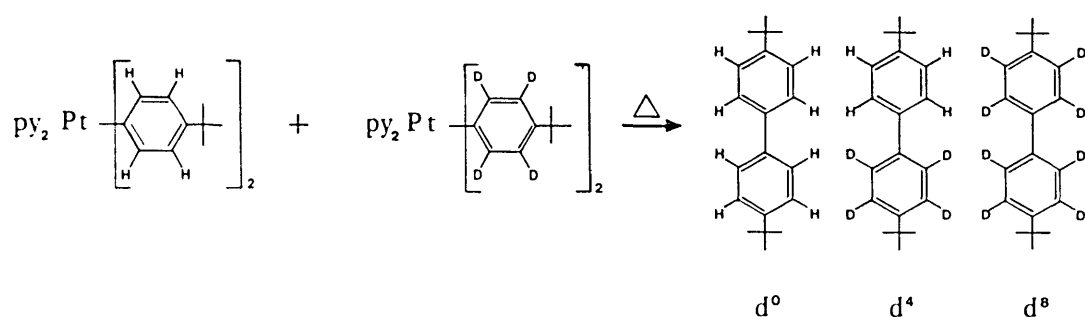
It is noteworthy that Razuvaev did not observe bibenzyl or diphenylmethane in the corresponding photolysis of the related compound HgPh_2 in toluene, although both compounds are possible radical reaction products.⁴⁹

Biaryl Formation

Having excluded the possibility of radical formation of biaryl, the most plausible mechanism remains concerted carbon-carbon reductive elimination. In order to establish the molecularity of the elimination

equimolar amounts of $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{CMe}_3)_2$ and $\text{py}_2\text{Pt}(\text{C}_6\text{D}_4\text{CMe}_3)_2$ were thermolysed in the same reaction solution. There are three possible biaryl products d^0 , d^4 and d^8 - bis-(tert-butyl)diphenyl (Scheme 15).

Scheme 15 "Cross-Over" Experiment



Only the d^0 - and d^8 - species are expected from a purely intra-molecular reaction. At the other extreme, for a random intermolecular process a statistical distribution of all ^htree in which the "mixed" d^4 -species is the major product, would be predicted. As emerged, the relative extent of biaryl production by the two complexes is different (as discussed in the next section) but, most significantly, analysis of the reaction mixture showed that biaryl formation itself is predominantly intramolecular (98.1%). Only 1.9% of d^4 -species was detected (detailed product distribution is listed in Table 8).

Thermolysis of an equimolar amount of $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$ and py_2PtPh_2 provided inconclusive results because the rates of decomposition of the two differ substantially due to the effects of the 4-substituents $\text{R} = \text{CMe}_3$ and $\text{R} = \text{H}$. The two also have disparate solubilities. Due to the limited solubility of py_2PtPh_2 only low reaction concentrations could be used, and reliable measurements were therefore impossible.

tert-Butylbenzene Formation

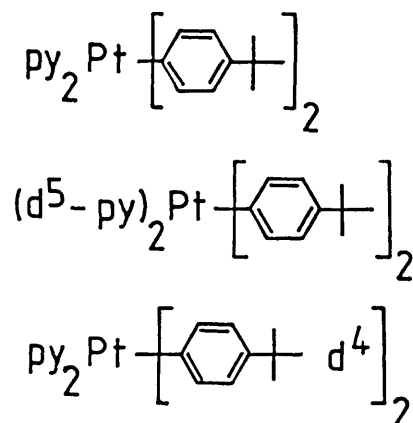
During the thermolysis of $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$, in addition to bis-(tert-butyl)diphenyl, a significant amount of tert-butylbenzene is formed (see Scheme 13). Formation of the latter requires hydrogen abstraction from some site in either the solvent or the compound itself.

To locate the source of transferred hydrogen, deuterium labelling studies were undertaken.

It has to be pointed out that results thus obtained can be ambiguous. If deuterium is transferred in a labelled system, one can conclude that hydrogen is transferred in the unlabelled system. If deuterium is not transferred, one cannot reliably infer that hydrogen would not be transferred, because deuterium substitution may suppress abstraction through its kinetic isotope effect.

To offset these difficulties as much as possible, the molecule was systematically and selectively deuterated in its various sites. The complexes depicted in Figure 5 were prepared and characterised.

Figure 5 Compounds Employed for Deuterium Labelling Studies



In addition, all these compounds were decomposed both in d^0 and d^8 -toluene at 90°C . Organic product distributions are displayed in Table 8.*

Deuteration of the solvent had no effect on the product distribution except possibly on the solvent derived products. Their low concentrations, however, make reliable distinction difficult. There is, though, some deuterium incorporation in the biaryl (6.0 Mol%) and tert-butylbenzene (5.9 Mol%). There is a striking contrast in behaviour between the non-deuterated and deuterated organoplatinum compounds. tert-butylbenzene formation for the latter is greatly reduced if not totally suppressed. Initial comparison of the thermolyses of undeuterated complex with $(\text{py-d}^5)_2\text{Pt}(\text{PhCMe}_3)_2$ (d^{10}) only, indicated significant deuterium transfer from the pyridine ligand. Apparently conflicting results were obtained

* The individual results are genuine, since the cross-over experiment gives the same values as the two reactions independently

Table 8 Mol-% of Product Distribution of Deuterium Labelling Studies (Thermolysis Temperature 90°)

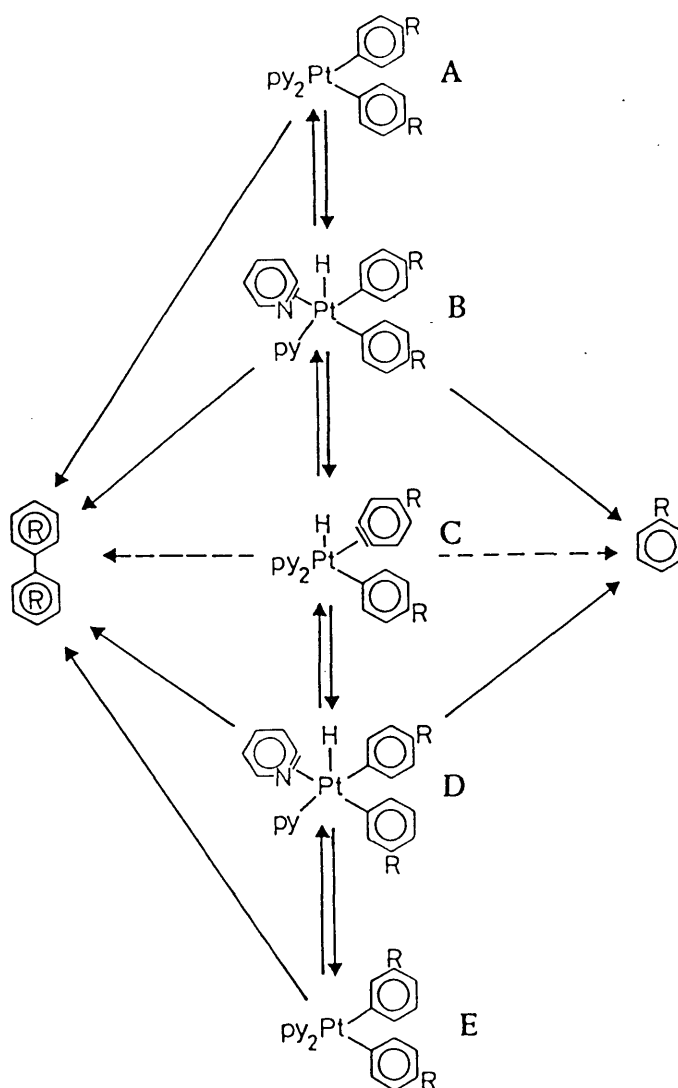
	Toluene	PhCMe ₃						CMe ₃ PhPhCMe ₃										Solvent Adducts
		Total	d ⁰	d ¹	d ³	d ⁴	d ⁵	Total	4,4'	3,4'	3,3'	d ⁰	d ¹	d ²	d ⁴	d ⁷	d ⁸	
py ₂ Pt(PhCMe ₃) ₂	d ⁰	54.9	54.9	—	—	—	—	45.4	37.7	6.0	1.6	45.4	—	—	—	—	—	0.8
	a	53.9	48.0	5.9	—	—	—	45.5	38.3	5.6	1.6	39.5	4.4	1.6	—	—	—	1.1
(py-d ⁵) ₂ Pt(PhCMe ₃) ₂	d ⁰	2.4	2.4	—	—	—	—	96.8	96.8	—	—	96.8	—	—	—	—	—	0.8
	d ⁸	1.2	1.1	0.1	—	—	—	98.8	98.8	—	—	88.9	9.9	—	—	—	—	0
py ₂ Pt(PhCMe ₃ -d ⁴) ₂	d ⁰	3.5	—	—	0.4	2.2	0.9	96.1	90.2	5.8	0.1	—	—	—	—	—	96.1	0.4
	d ⁸	3.2	—	—	0.5	1.8	0.9	96.7	90.2	5.9	0.6	—	—	—	—	30.1	66.6	0.1
py ₂ Pt(PhCMe ₃) ₂ + py ₂ Pt(PhCMe ₃ -d ⁴) ₂	d ⁰	40.6	29.1	1.9	3.3	5.0	1.3	59.2	52.6	5.9	0.8	12.9	1.4	—	1.1	12.5	31.3	0.2

a in p-xylene-d¹⁰

on thermolysis of $\text{py}_2\text{Pt}(\text{C}_6\text{D}_4\text{CMe}_3)_2$ (d^8) where hydrogen abstraction from pyridine is possible, only very small amounts of tert-butylbenzene were detected. Deuteration also has a significant influence on isomerization; for the d^{10} -complex no, and for the d^8 -complex, reduced isomerization is observed.

Biaryl and arene formation seem to be two competing reactions, the fine balance between the two being disturbed by deuteration. Based on these observations, the mechanistic scheme depicted in Scheme 16 is proposed.

Scheme 16 Proposed Thermolysis Mechanism



The reaction pathway must proceed via several intermediates, which selective deuteration makes less accessible because of the isotope effect.

In an initial step $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$ A isomerizes to a pyridyne species B. Deuterated pyridine will make this step more difficult and straightforward reductive elimination will be preferential, as is seen from the product distribution in Table 8. No arene or isomerization is observed.

The non-deuterated species B has three reaction alternatives. It can isomerize by direct attack on the aryl group to a benzyne species C or it can reductively eliminate either biaryl or arene.

For the deuterated aryl species (d^8) isomerization A to B will not be hindered; B to C, however, is influenced by a primary isotope effect and a raised activation barrier will render this reaction less favourable. Reduced isomerization is observed for the d^8 -species.

The benzyne compound C can either rearrange to B or D. Reductive elimination of biaryl and arene is less probable, since biaryl elimination would have to proceed over two steps and for arene elimination only one group is available, as opposed to two.

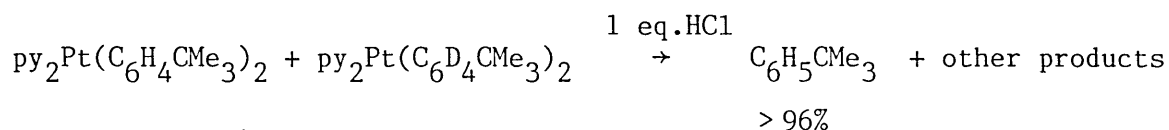
This does not explain, however, why the pyridyne complex - d^8 should, apparently, release so little arene. The reason for this must also stem from an isotope effect.

Deuterium has already been established as exerting an effect on the platinum-carbon bond cleavage.²⁴ Comparison of the rates of decomposition of $[\text{Pt H}(\text{CH}_3)(\text{PPh}_3)_2]$ and $[\text{PtD}(\text{CH}_3)(\text{PPh}_3)_2]$ revealed an appreciable normal

primary isotope effect of $k_H/k_D = 3.3 \pm 0.3$. Furthermore, as observed by Puddephatt for the reductive elimination of ethane from L_2PtIme_3 ($L = PMe_2Ph$) a secondary kinetic deuterium isotope effect $K(L_2PtI(CH_3)_3)/K(L_2PtI(CD_3)_3) = 1.10 \pm 0.05$ is found.⁵⁰

The pyridyne species $B-d$ ⁸ seems to experience a sufficiently large kinetic isotope effect to prefer to rearrange to A or even E which may reductively eliminate biaryl than to eliminate biaryl or arene itself, since only 3.5 mol% of arene is detected. The other possibility is that there is a larger isotope effect on the arene elimination process than that for biaryl.

In an effort to evaluate the extent of such an effect, we investigated the protolytic platinum-carbon cleavage, allowing free competition between labelled and unlabelled systems, as shown in the following equation:



Mechanistic investigations on platinum complexes studying the kinetics of electrophilic cleavage of the platinum-carbon bond protolysis established that the scission depends on the nature of the cleaved group and the trans activating ability of the ligand trans to the carbon group.⁵¹

In principle, electrophilic cleavage can take place by (a) direct attack on the M-C bond, (b) attack on the aromatic ring in the case of metal-aryl derivatives and (c) a prior oxidative addition to the metal followed by reductive elimination. With a weak trans ligand (such as Cl), oxidative addition to the metal will be favoured, whereas with a strong trans ligand (such as I, alkyl, aryl or PR_3), direct proton transfer in a three center transition state will predominate as is seen in the

protolysis of cis-(PPh₃)₂Pt(C₆H₄Y)₂.^{51a}

It is interesting to note that a three coordinated intermediate produces a very large kinetic isotope effect $k_H/k_D = 6$ for the platinum-carbon cleavage with DCl.

In the case of cis-py₂Pt(PhCMe₃)₂ protolysis, fully fledged prior oxidative addition to the platinum can be expected due to the weak trans-effect of the pyridine ligand.

Elimination from the labile 6-coordinated platinum-intermediate, in which the metal ion can be assigned the formal oxidation state IV, is proposedly the rate-controlling step.^{51c}

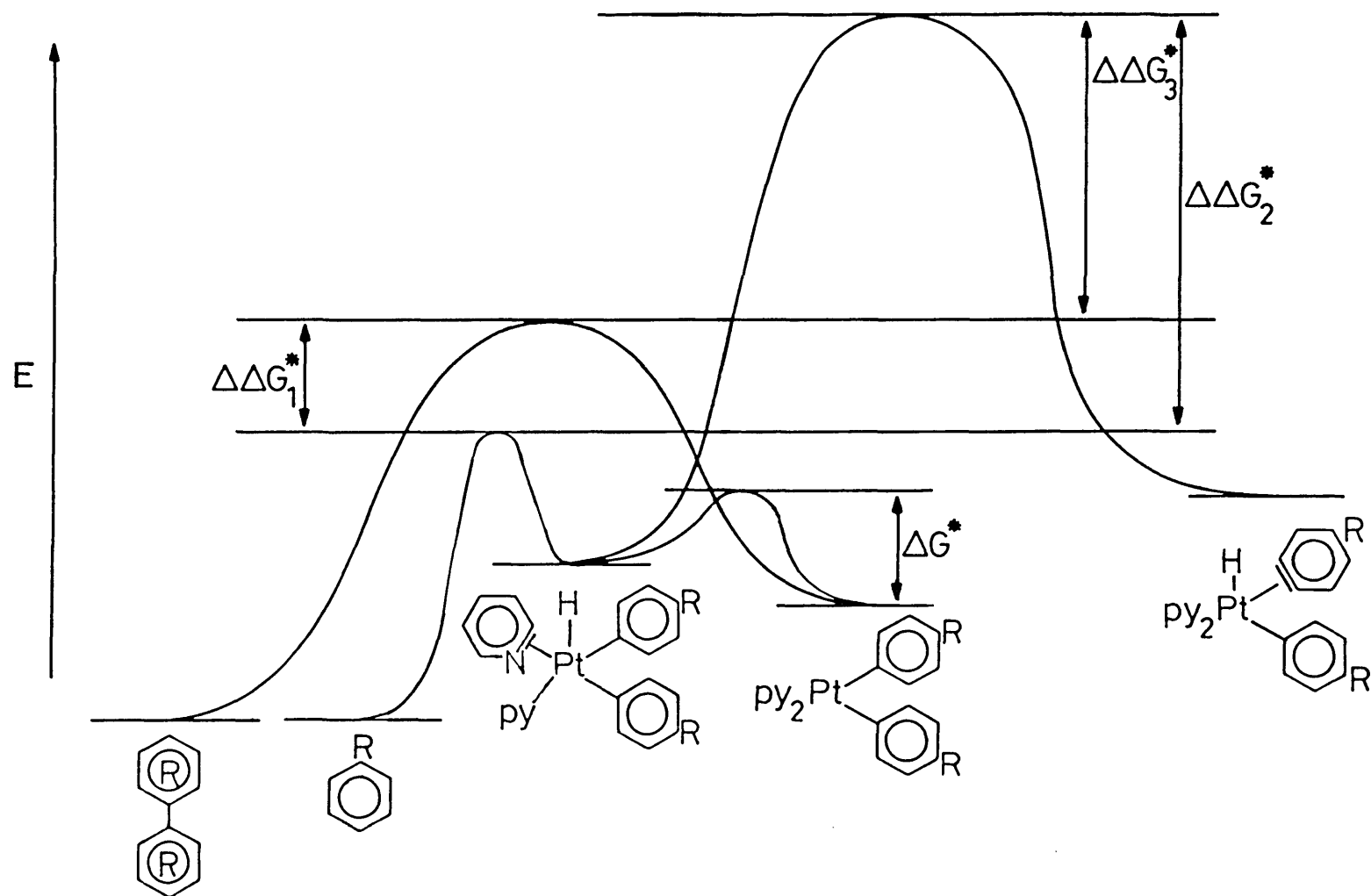
Addition of one equivalent of HCl to a 1:1 mixture of d⁰/d⁸-py₂Pt(PhCMe₃)₂ produced tert-butylbenzene-d⁰ to over 96%. The strong preference must originate from a kinetic isotope effect, most plausibly on the reductive elimination of tert-butylbenzene, and illustrates that for the pyridyne species B-d⁸ reductive elimination of tert-butylbenzene-d⁴ is affected by a large isotope effect.

In general, py₂Pt(C₆D₄CMe₃)₂ experiences isotope effects on isomerization and reductive elimination of biaryl and arene. Since hardly any tert-butylbenzene is formed and isomerization is low, biaryl elimination presumably occurs mainly from A or B. Unfortunately, differentiation is impossible.

It is clear, however, that there is a larger isotope effect on the reductive elimination of arene than of biaryl.

An energy profile of the thermolytic processes of py₂Pt(PhCMe₃)₂ is depicted in Figure 6. No absolute values are available. Only

Figure 6 Energy-Profile of the Thermolysis Process of $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$



approximate estimates of $\Delta\Delta G^\ddagger$ values could be made based on the product distributions at 90°C.

Reductive elimination of biaryl can either occur via direct reductive elimination or via pyridyne intermediate. It is, however, unlikely that both reaction pathways have identical activation barriers, more likely one is favoured. It is assumed that in this case direct reductive elimination occurs.

A relatively small $\Delta\Delta G_1^\ddagger$ was obtained: $\Delta\Delta G_1^\ddagger = 0.6$ kJ/mol. This is not very surprising considering the virtually equimolar amounts of biaryl and arene formed. In contrast, $\Delta\Delta G_2^\ddagger = 3.3$ kJ/mol and $\Delta\Delta G_3^\ddagger = 2.7$ kJ/mol are larger for the transition from the pyridyne to the benzyne species. Overall, isomerization is only a minor reaction.

Kinetic comparison at 65°C showed a significant rate-reduction for the d^8 -species, while the d^{10} -compound did not decompose but required higher temperatures (>75°C).

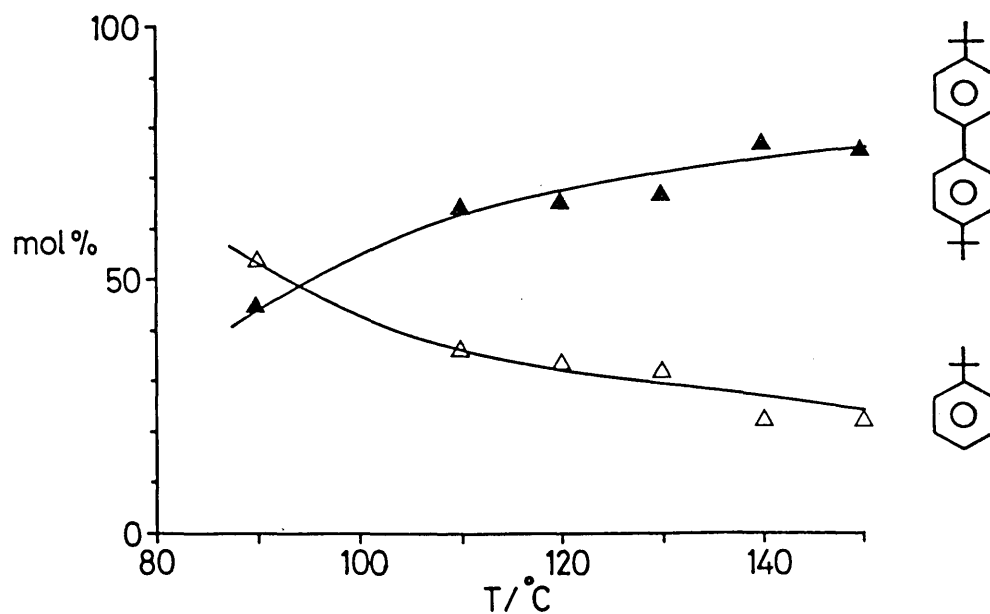
	$py_2Pt(PhCMe_3)_2$	$py_2Pt(PhCMe_3-d^4)_2$	$(py-d^5)_2Pt(PhCMe_3)_2$
65°C:k	$4.8 \cdot 10^{-2}$	$2.7 \cdot 10^{-2}$	no decomposition
$t_{1/2}$	14.44 h	25.7 h	

An isotope effect is expected. Similar magnitudes of k_{d^8} and $k_{d^{10}}$ would have indicated that reductive elimination occurs from the parent

compound (A). The overall larger isotope effect on the d^{10} -species, which is either due to a primary isotope effect on the pyridyne complex formation or on the reductive elimination of tert-butylbenzene- d^1 from (B), is more likely to originate from the latter, since there is such a distinctive difference between the two rate-constants k_d^{10} and k_d^8 ; as has been discussed previously, large kinetic isotope effects were measured for the reductive elimination which governs reactions of $L_2Pt(C_6H_4Y)_2$ with DC1.

Temperature variations have a significant influence, not only on reaction rates but also on the product distribution. As shown in Figure 7, the higher the temperature the more biaryl is formed. The isomer distribution is not visibly affected, nor is the level of solvent products (0.3 - 1.5%).

Figure 7 Temperature Dependence of Arene and Biaryl Formation



At 90° tert-butylbenzene formation accounts for 55 mol% and drops with increasing temperature to nearly 20 mol% at 150°C. In a mass-spectrometer at 200°C biaryl is exclusively detected.

In the overall equation $\Delta G^\ddagger = \Delta H^\ddagger - T \Delta S^\ddagger$ for the thermolysis of $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$ the enthalpy of activation will not change significantly over the temperature range observed. The two processes producing arene and biaryl must, however, have different activation entropies, one more negative than the other. The more negative activation entropy (presumably of the biaryl formation) will have a bigger influence on the final product distribution.

Direct comparison of the two processes is impossible, because the different systems have too many internal variables, such as relative substituent effects on the C-C and C-H elimination. In Scheme 16 and Figure 6 isomerization is shown to occur prior to elimination.

This could be experimentally verified. A solution of $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$ was decomposed to 50%. The residual unreacted complex was reacted with bromine to cleave the Pt-C bonds and form bromo-tert-butylbenzene. If isomerization had occurred prior to Pt-C cleavage, different isomers would be identified (Table 9).

Table 9 Results of Bromine Addition

$\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$	bromo- <u>tert</u> -butylbenzene		
	para	meta	ortho
decomposed to 50%	81	19	0
unreacted	> 98	-	-

The result confirms isomerization of the parent compound. It was independently established that bromine reacted with $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$ to give only 4-bromo-tert-butylbenzene*.

An isotope effect for isomerization of ca. 3 is observed (degree of isomerization of $d_0:d_8 = 2.81$). This is in the range expected for a primary isotope effect.

Thermolysis in the Absence of Solvent

Thermal decomposition of $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$ in the absence of solvent resulted in the formation of mainly tert-butylbenzene, some bis-tert-butyldiphenyl and an air-sensitive, greenish residue. Mol% distribution is shown in Table 10 below.

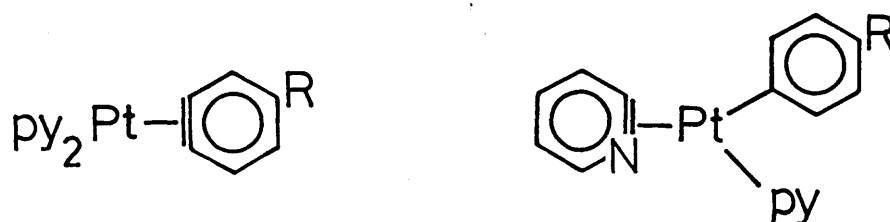
Table 10 Product Distribution of $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$ Thermolysis in the Absence of Solvent

	PhCMe_3	$\text{Me}_3\text{CPhPhCMe}_3$			
		Total	Isomer		
			4,4'	3,4'	3,3'
$\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$	89.7	10.3	9.4 (91.1)	0.7 (7.0)	0.2 (1.9)

() % isomer of total amount of biaryl

* Bromine reacts with the solvent toluene

The high relative level of eliminated arene is surprising. Since there is no solvent the only hydrogen source can be the compound itself, via an intra- or intermolecular route. The latter will lead to cluster-formation, the former will give rise to either of the two types of compounds shown below:



Characterisation via IR* showed an interesting vibration at 1580 cm^{-1} . Bennet et al. have tentatively assigned the " $\nu(\text{C}\equiv\text{C})$ " vibration of benzyne in the compound $\text{Ni}(\text{C}_6\text{H}_4)(\text{Cy}_2\text{PCH}_2\text{CH}_2\text{PCy}_2)$ to a sharp, strong band at 1583 cm^{-1} ⁵². Although they could not rule out the possibility of other aromatic ring C-C stretching vibrations contributing to the 1583 cm^{-1} absorption, it was considered very likely to be a modified " $\nu(\text{C}\equiv\text{C})$ " of an alkyne (For Pt(o) and Ni(o) these species are found at around 1700 cm^{-1}).

The strong absorption at 1580 cm^{-1} of the decomposition product of $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{CMe}_3)_2$ is a possible indication for formation of a benzyne or a pyridyne product.

* Infrared Absorptions(KBr disc)

3045w, 2950m, 2920m, 2860w, 1600w, 1580s, 1535s, 1500w, 1485w, 1445s, 1410m, 1255m, 1150w, 1115w, 810m, 750s, 690m cm^{-1}

The similar atomic masses of carbon and nitrogen will have little influence on the absorption frequency.

Elemental analysis gives rise to the following approximate ratio py:Pt:aryl = 2:1:1. Air-sensitivity impairs precise analysis.

Low solubility, on the other hand, rather suggests cluster formation with bridging pyridines¹⁹ or aryls.⁵³ Both types of structure have been observed previously.

The nature of the residue precluded further steps to identify this compound.

The predominant reaction is arene elimination. Based on previously discussed reactivities a likely reaction pathway is that via pyridyne complex formation. Lability of the latter will give rise to secondary reactions such as cluster formation in this highly concentrated environment. Parallel reductive elimination yields biaryl.

Influence of Mercury on Thermolysis

Unwanted heterogeneous reactions catalysed by bulk or finely divided metal produced by decomposition are often encountered in reactions of organotransition metal complexes. Some methods have been used to detect heterogeneous components in complex mechanisms. Whitesides, in his studies of reaction mechanisms of platinum(II) compounds, suppressed heterogeneous reactions by selective poisoning with metallic mercury.⁵⁴ The latter forms an amalgam with the platinum reaching the final composition

of PtHg_4 . It is pointed out that this technique has limitations because other reaction pathways, such as insertion of mercury into the Pt-C bonds and transmetallation, are possible.

Addition of mercury to a thermolysis solution of $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$ in toluene resulted in a massive reduction of solvent adduct, tert-butylbenzene formation and isomerization, as shown in Table 11.

Table 11 Influence of Hg on Product Distribution $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$ at 90°C (in toluene)

Compound	$\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$	$\text{py}_2\text{Pt}(\text{PhCMe}_3)_2+\text{Hg}$
bis(<u>tert</u> -butyl)diphenyl	45.4 (37.7/6.0/1.6) ^a	79.8 (72.8/6.1/0.9) ^a
<u>tert</u> -butylbenzene	54.9	19.8
solvent adduct	0.8	0.4

a isomers (4,4'/3,4'/3,3'-bis(tert-butyl)diphenyl)

In the absence of the previously discussed deuterium studies the reduction of arene might reasonably have been assigned to some involvement of, for example, colloidal platinum. Since that has been excluded - especially by the "cross-over" reaction - a different active role for mercury must operate. More difficult to explain, however, is the alteration of pathway in favour of biaryl evolution, since insertion of mercury into

the Pt-C bond or transmetallation (compare with photolysis of $\text{Hg}(\text{PhCMe}_3)_2$) are more likely to encourage hydrogen transfer and arene formation.

It is therefore possible that the mercury interacts with the pyridyne species, obstructing the elimination of arene.

Formation of solvent derived products was thought to occur via a secondary reaction pathway catalysed by colloidal platinum. Since no other mechanistic explanation has emerged and the presence of mercury does reduce the formation of solvent adducts, it is possible that in this case suppression of an unwanted heterogeneous side reaction occurs.

1.3.2 Kinetic Studies

The thermal rearrangements of $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$ were observed by monitoring the disappearance of the parent complex and the appearance of tert-butylbenzene and bis-tert-butyldiphenyl. Thermolysis is first order for at least one half life. Empirical first-order rate constants are listed in Table 12 and presented in Figure 8.

The parameters **conform** to the Arrhenius equation (Figure 9)

$$\ln k = \ln A - (E_a/RT) *$$

The overall activation energy is $E_a = + 131.2 \pm 15.7^1 \text{ kJmol}^{-1}$ ** and the frequency factor A corresponds to $8.98 \cdot 10^{18}$.

* $R = 8.314 \text{ J/K.mol}$

** The error was estimated graphically

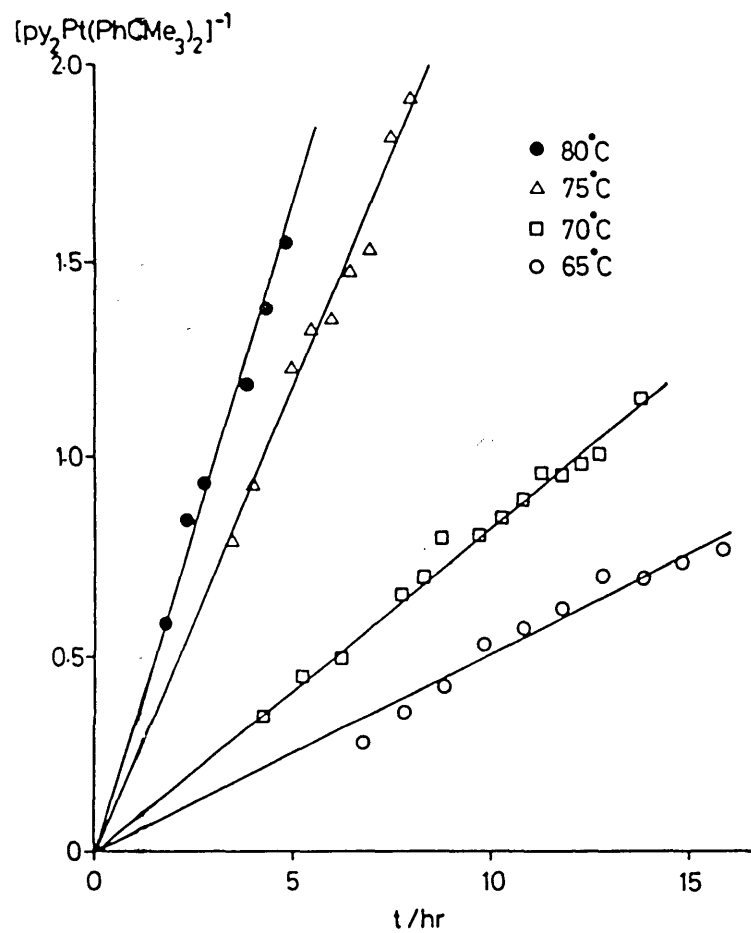


Figure 8 First Order Plot for Thermal Decomposition of $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$

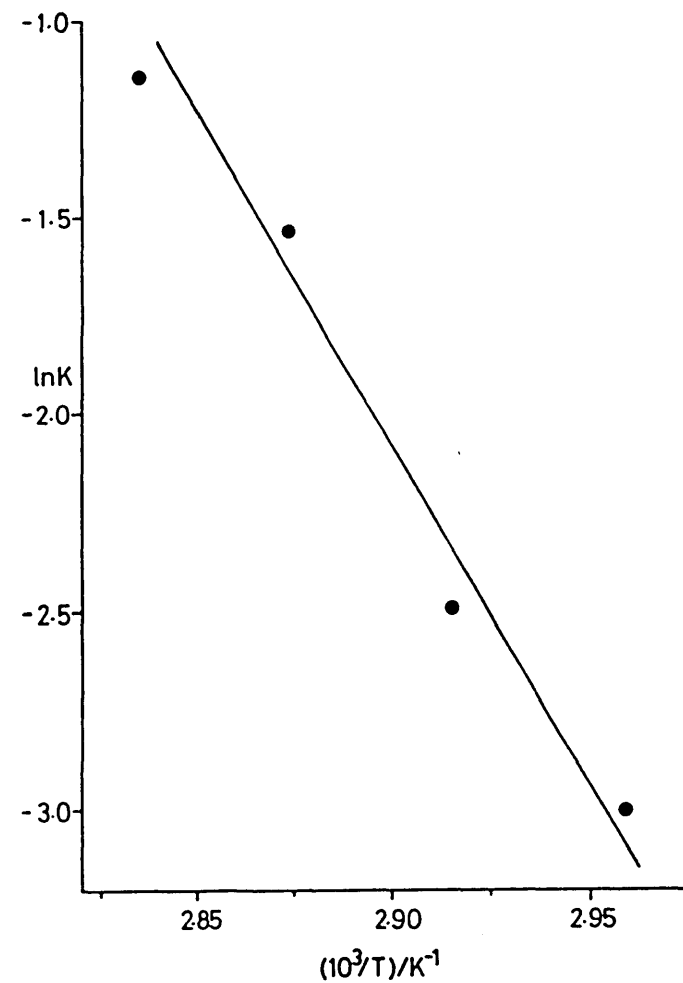


Figure 9 Arrhenius Plot of the First-Order Rate constant k for decomposition of $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$

Table 12 Kinetic Parameters for the Decomposition of $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$

T/°C	10^{-2}K/s^{-1}	$t_{1/2}/\text{h}$	Correlation Coefficient r
65	4.8	14.44	0.997
70	8.2	8.45	0.991
75	21.7	3.19	0.997
80	31.6	2.19	0.992

Gradients of plot and error were determined by least square computation

The overall activation entropy is derived from

$$\Delta S^\ddagger = 19.155 (\log A - 13.23)$$

and found to be $\Delta S^\ddagger = + 109.3 \pm 13.7 \text{ JK}^{-1}\text{mol}^{-1}$.

Activation enthalpy $\Delta H^\ddagger$ and free energy of activation $\Delta G^\ddagger$ were computed from the following relationships:

$$\Delta H^\ddagger = E_a - R \cdot T \quad \text{kJmol}^{-1}$$

$$\Delta G^\ddagger = \Delta H^\ddagger - T \cdot \Delta S^\ddagger \quad \text{kJmol}^{-1}$$

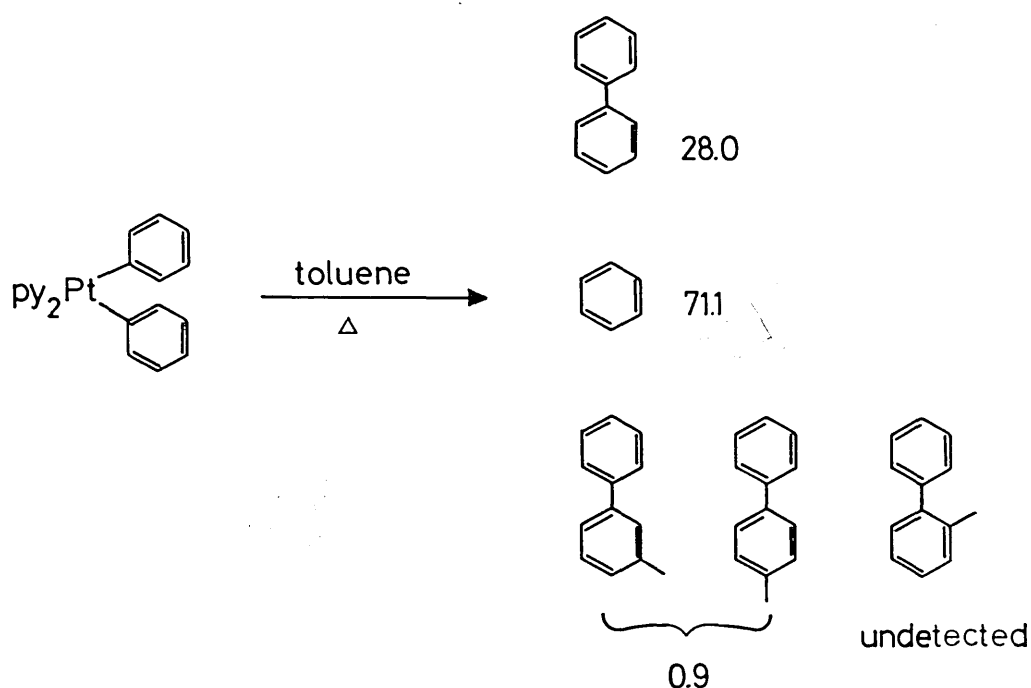
At 90°C, $\Delta H^\ddagger = 128.2 \text{ kJmol}^{-1}$ and $\Delta G^\ddagger = 88.5 \text{ kJmol}^{-1}$. Addition of free pyridine had no influence on the rate constant or product distribution. Pyridine dissociation or association do therefore not occur prior to or during the rate-determining step. This also instigates against isomerization $\text{cis} \rightleftharpoons \text{trans}$ $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$ as a control on preferred pathway during thermolysis, since addition of free pyridine would be expected to have an effect on the rate and/or product distribution.²

As mentioned in the Introduction, direct elimination from a four-coordinate species is rather rare and has only been observed for a few cis-dialkylnickel(II)²³ and hydridoalkylplatinum(II)²⁴ complexes. Also, this unusual behaviour is in contrast to other systems which feature a C-H activation step. Kinetic comparisons with such species are discussed in Section 1.5.2.

1.4 Thermal Behaviour of py_2PtPh_2

Decomposition of py_2PtPh_2 in toluene yielded a similar product distribution to $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$, as shown in Scheme 17.

Scheme 17 Organic Product Distribution of py_2PtPh_2 Thermolysis at 94°C



At 94°C the major product is benzene. Some diphenyl is also eliminated and minor amounts of isomeric solvent products. The extent of isomerization cannot be estimated since the isomers could not be differentiated at such low levels.

Due to the general similarity of the product distribution to that discussed in Section 1.3.1, it is assumed that again the same two competing

reactions afford diphenyl on the one hand and benzene on the other.

At a comparable reaction temperature, there is more benzene formed than tert-butylbenzene. $R = \text{CMe}_3$ is an electron donating group and will favour reductive elimination compared to $R = \text{H}$. The substituent effect clearly acts more powerfully on the C-C reductive elimination than on C-H coupling. This may of course be due to the cooperative effect of two such substituents during formation of biaryl. More comprehensive kinetic investigations of py_2PtPh_2 thermolysis were not pursued due to the inconveniently low solubility of the complex.

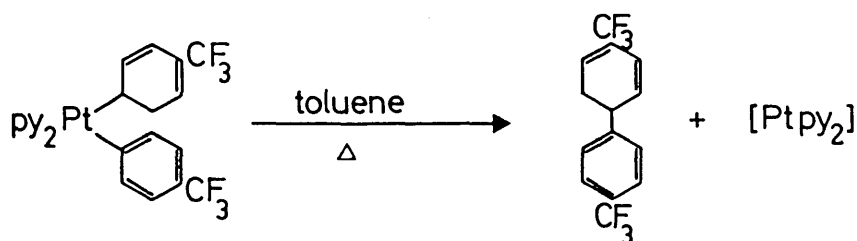
1.5 Thermal Behaviour of $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{CF}_3)_2$

1.5.1 Product Analysis and Reaction Mechanism

In contrast to the thermal decomposition of $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$ ($\text{R} = \text{H}$, CMe_3) where a complex array of products is obtained, thermolysis of $\text{py}_2\text{Pt}(\text{PhCF}_3)_2$ * gives mainly 4,4'-bis-(trifluoromethyl)diphenyl. A minor amount of trifluoromethylbenzene (5.6 mol%) is formed. There is no temperature dependence on the product distribution between 80 – 110°C. No isomeric biaryls or solvent derived products are observed.

The absence of radical thermolysis products, such as solvent adducts, trifluoromethylbenzene in significant quantities and the stereospecificity of biaryl formation implies intramolecular reductive elimination as the main thermolytic pathway (Scheme 18).

Scheme 18 $\text{py}_2\text{Pt}(\text{PhCF}_3)_2$ Thermolysis



* Hereafter, for simplicity cis- $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{CF}_3-4)_2$ will be represented as $\text{py}_2\text{Pt}(\text{PhCF}_3)_2$

In contrast to the previously discussed mechanisms the different CF_3 - substituent must either further the ability for reductive elimination or make pyridyne/benzyne formation unfavourable. The former seems the less likely since it has been established that electron donating substituents (in para position) facilitate reductive elimination;¹⁴ the electron withdrawing CF_3 substituent should have the opposite influence. More probably the electron withdrawing substituent renders pyridyne or benzyne formation far less favourable, and thermolysis will therefore proceed only via reductive elimination, at a slower rate than pure reductive elimination from $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$.

1.5.2 Kinetics of $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{CF}_3)_2$ and Comparison with the Kinetics of $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{CMe}_3)_2$ and Other Compounds

The thermal decay of $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{CF}_3)_2$ was observed to be first order by monitoring the disappearance of the precursor and appearance of the biaryl via ^{19}F -NMR spectroscopy. The first order plots for thermolysis of $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{CF}_3)_2$ are shown in Figure 10. Empirical first-order rate constants are listed in Table 13.

Figure 11 displays the Arrhenius plot derived from the first order rate constants k . The same equation as in Section 1.3.2 was employed to calculate the following parameters:

Activation Energy	E_a	$= 59.2 \pm 1.7$	kJ/mol
Frequency Factor	A	$= 8.5 \cdot 10^7$	
Entropy	$\Delta S^\ddagger$	$= -102.1 \pm 3.1$	$\text{J/mol}\cdot\text{K}$

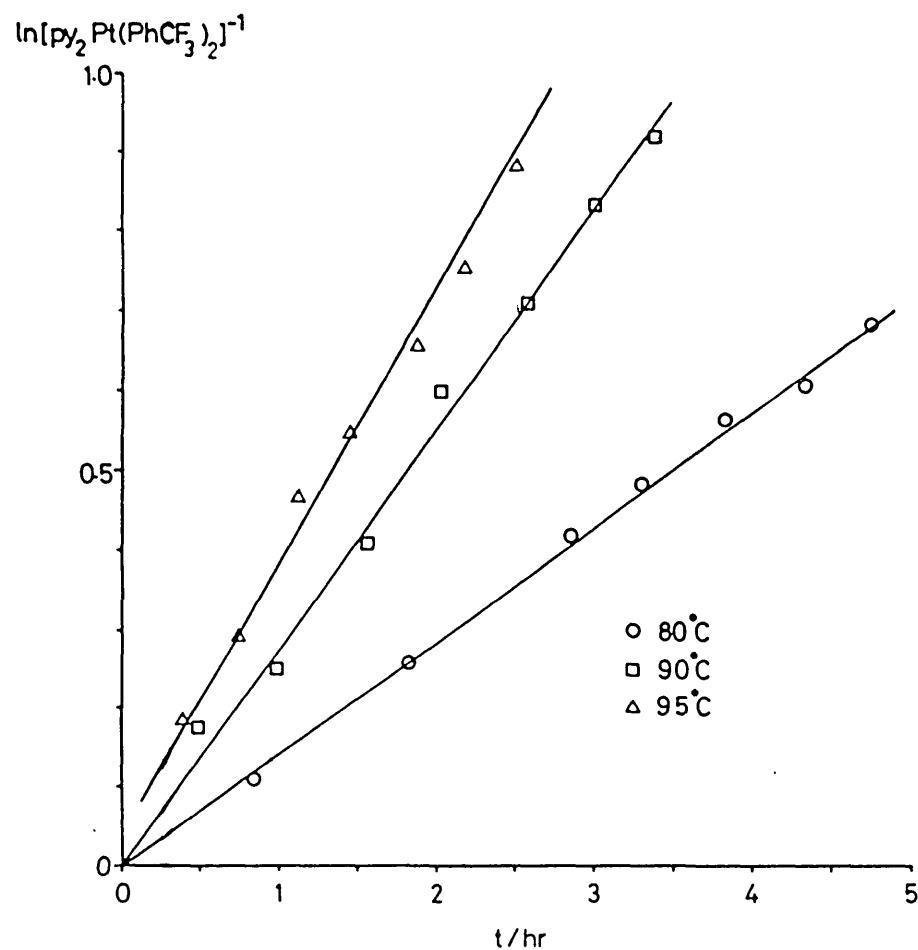


Figure 10 First Order Plot for Thermal Decomposition of $\text{py}_2\text{Pt}(\text{PhCF}_3)_2$

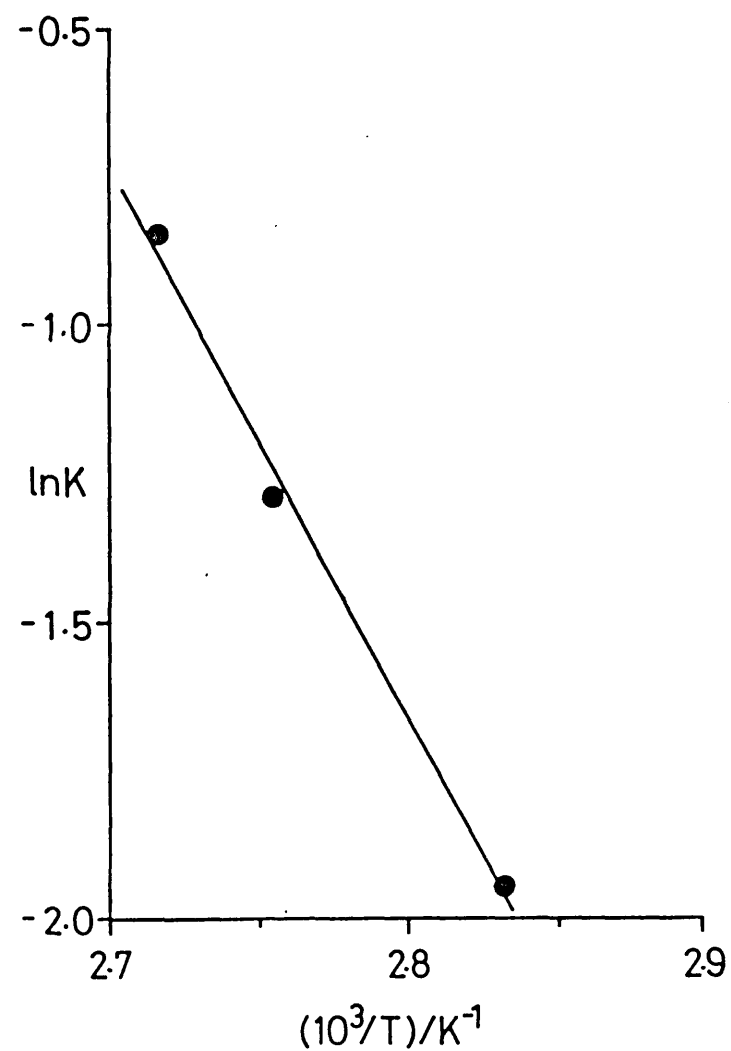


Figure 11 Arrhenius Plot of the First-Order Rate constant k for decomposition of $\text{py}_2\text{Pt}(\text{PhCF}_3)_2$

Table 13 Kinetic Parameters for the Decomposition of $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{CF}_3)_2$

T/°C	10^{-1}k/s^{-1}	$t_{1/2}/\text{h}$	Correlation Coefficient r^*
80	1.45	4.79	0.998
90	2.75	2.52	0.997
95	3.21	2.15	0.997

* Gradients of plot and error were determined by least square computation

Listed in Table 14 are the values of activation energy E_a , frequency factor A, entropy of activation $\Delta S^\ddagger$ and enthalpy of activation $\Delta H^\ddagger$ for the compounds $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$, $\text{py}_2\text{Pt}(\text{PhCF}_3)_2$, $(\text{PPh}_3)_2\text{Pt}(\text{PhMe})_2$,^{2b} bipy-Pt(PhCMe_3)₂⁵ and bipyPt($\text{CH}_2\text{CMe}_2\text{Ph}$)₂.^{1j}

A striking similarity is found between $\text{py}_2\text{Pt}(\text{PhCF}_3)_2$ and $(\text{PPh}_3)_2\text{Pt}(\text{PhMe})_2$. Frequency factors and activation energies are comparable: in particular the negative values for $\Delta S^\ddagger$ - considered to indicate loss of conformational freedom in the transition state - are nearly identical.

Both compounds have been established to decompose via an unimolecular reductive elimination process. However, it is interesting to note that in spite of the different 4-substituents their energies are so similar. It seems therefore as if the pyridine and triphenylphosphine ligand exert opposing effects on the reductive elimination, more or less counterbalancing the electronically opposed effects of the 4-substituents.

Table 14 Comparison of Kinetic Data for Some Thermal Rearrangements

	$\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$	$\text{py}_2\text{Pt}(\text{PhCF}_3)_2$	$(\text{PPh}_3)_2\text{Pt}(\text{PhMe})_2$	$\text{bipyPt}(\text{PhCMe}_3)_2$	$\text{bipyPt}(\text{CH}_2\text{CMe}_2\text{Ph})_2$
E_a (kJ/mol)	131.2	59.2	76.3	149.6	129.3
A	$9.0 \cdot 10^{18}$	$8.5 \cdot 10^7$	$1.1 \cdot 10^8$	$9.7 \cdot 10^{14}$	$2.8 \cdot 10^{15}$
LogA	18.95	7.9	8.0	14.99	15.44
$\Delta S^\ddagger$ (J/K·mol)	+ 109.3	- 102.1	- 99.0	+ 33.7	+ 42.9
$\Delta H^\ddagger_{90^\circ}$ (kJ/mol)	128.2	56.18	74.0	146.6	126.8

In the case of $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$, where arene formation and reductive elimination occur simultaneously, a large positive $\Delta S^\ddagger$ value and a significantly different E_a are observed. For the latter compound, these parameters are the complex sum of two competing elimination reactions and isomerization and quantitative comparisons consequently are impossible.

Parameters for the roll-over metallation mechanism of the structurally related compound $\text{bipyPt}(\text{PhCMe}_3)_2$ and cyclometallation of $\text{bipyPt}(\text{CH}_2\text{CMe}_2\text{Ph})_2$ have been included in Table 14 and show no similarity to any of the previously discussed compounds. The positive entropy of activation was thought there to indicate a disordered intermediate associated with the rate limiting Pt-N scission step, a prerequisite already excluded here on independent grounds.

1.6 A Novel Pt(o) Species

So far all aspects of the organic product distribution of the $\text{py}_2\text{Pt}(\text{PhR})_2$ thermolysis have been discussed. The fate and nature of the platinum and pyridine ligands remained unmentioned.

While monitoring thermolysis by ^1H -NMR, evidence was found for a novel $[\text{Pt}(\text{o})\text{py}_n]$ species. In the case of $\text{py}_2\text{Pt}(\text{PhCMe}_3)_2$, the signal assigned to the ortho-hydrogen in the pyridine bound to platinum progressively gave way to a broad signal shifted downfield by 0.14 ppm (in toluene- d^8). For $\text{py}_2\text{Pt}(\text{PhCF}_3)_2$, a more clearly resolved signal pattern, a doublet of doublets, was observed at the same chemical shift (δ 8.54 ppm, $\Delta\delta$ = 0.05 ppm downfield) with ^{195}Pt -*"satellites"* $^3\text{J}(\text{Pt-H})$ = 99 Hz, as shown in Figure 12.

Two significantly smaller doublet of doublets are also visible at lower field (Table 15). Overall, however, only some 40 mol% of the original pyridine remains detectable in solution. The bulk of pyridine is precipitated as a component of a brown residue. Based on the micro-analysis of the latter* and the amount of pyridine left in solution, it can be deduced that the novel platinum species has stoichiometry $[\text{Pt}(\text{o})\text{py}_4]$.

The remarkably large $^3\text{J}(\text{Pt-H})$ is unprecedented and is thought to originate from a higher s-contribution. Broadening of the satellites has been observed before and is ascribed to field gradient anisotropy.⁴⁵

* Found C : 27.11; H : 2.21; N : 5.49%)

Figure 12 ^1H -NMR Signal Pattern of the ortho-Hydrogens of the Coordinated Pyridine Species $[\text{Pt}(\text{o})\text{py}_4]$

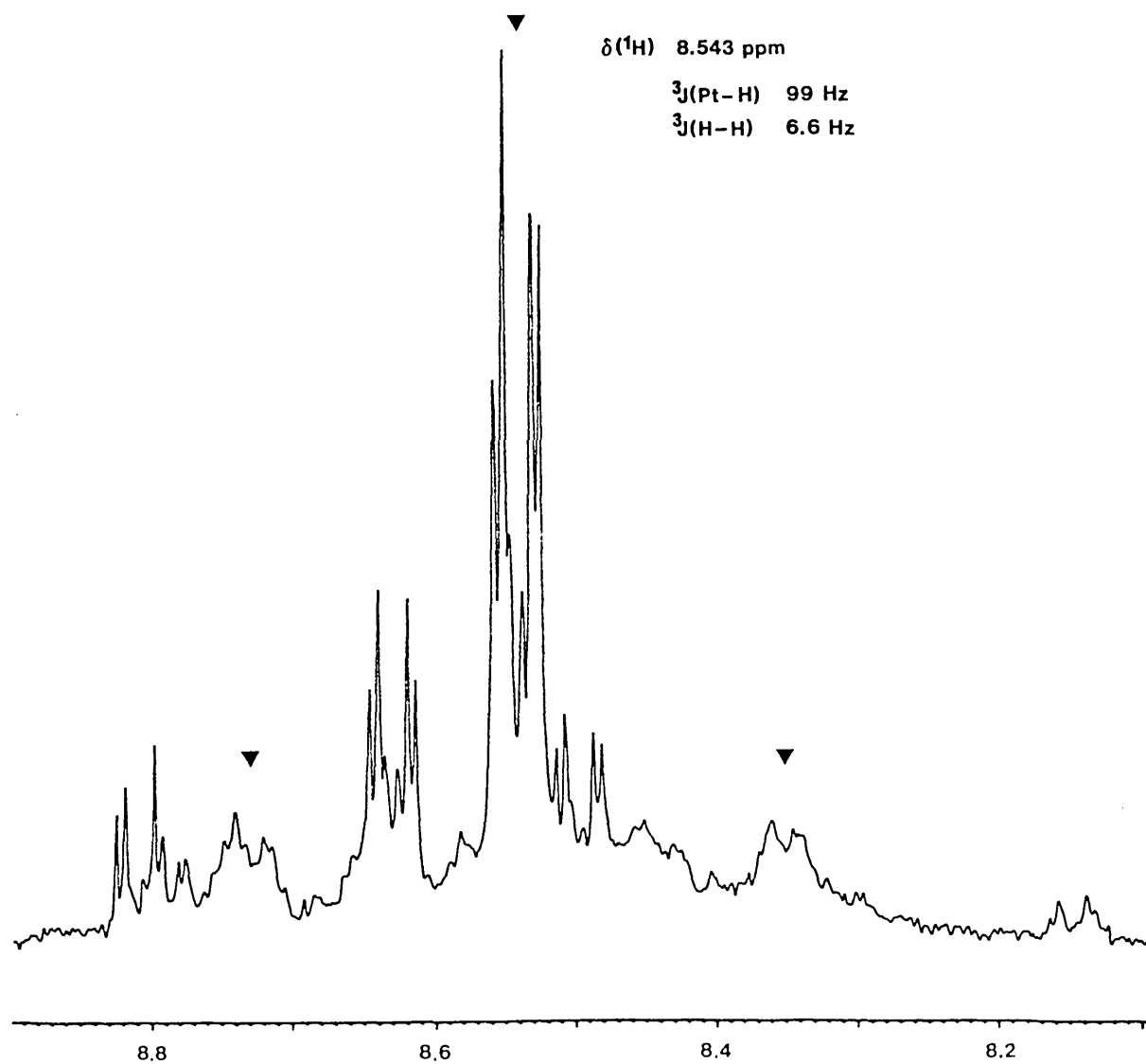


Table 15 Mol% and ^1H -NMR Parameters of $\text{py}_2\text{Pt}(\text{PhCF}_3)_2$ Thermolysis Products

	$\delta[\text{ortho-H}(\text{pyridine})]\text{ppm}^{\text{a}}$	$^3\text{J}(\text{Pt-H})\text{Hz}^{\text{b}}$	$^3\text{J}(\text{HH})\text{Hz}$	Mol%
py Species in Solution	8.543	99	6.6	27.5
	8.630	c	6.6	8.5
	8.881	c	6.6	3.9
Undecomposed $\text{py}_2\text{Pt}(\text{PhCF}_3)_2$	8.489	19	4.8	

a in toluene- d^8 ; b error of measurement $\pm 0.4\text{Hz}$; c not detected

Theoretically reductive elimination from $\text{py}_2\text{Pt}(\text{aryl})_2$ should yield biaryl and $[\text{Pt}(\text{o})\text{py}_2]$. The latter has never been observed previously. For the thermolysis of $(\text{PPh}_3)_2\text{Pt}(\text{tol})_2$ it has been found that the $[\text{Pt}(\text{o})(\text{PPh}_3)_2]$ fragment is not effectively stabilized by solvation in toluene and undergoes secondary rearrangements via oxidative insertion of the low valent metal into the P-C and C-H bond with subsequent reductive elimination.²

A similar route of secondary decomposition is observed for the $[\text{Pt}(\text{o})\text{py}_2]$ fragment: $[\text{Pt}(\text{o})\text{py}_4]$ and a platinum-pyridine polymeric structure of approximate ratio $\text{Pt:py} = 2:3$ is formed. Although pyridine

has a weaker interaction with platinum (lower π -acidity) than phosphine, the absence of an easy decomposition route will make stabilisation of this fragment possible.

— [Pt(o)py₄] is more likely to be detected for thermolysis of py₂Pt(PhCF₃)₂, since this compound fragments exclusively via reductive elimination unlike py₂Pt(PhCMe₃)₂. This may also explain the better resolution of the ¹H-NMR signals.

Several experiments were undertaken to establish the presence of a [Pt(o)py₄] species.

It was clearly established by HPLC that there is no free pyridine in solution. Evaporation of the solvent resulted in a brown residue that could only partly be redissolved and showed different NMR-characteristics. IR spectroscopy* and elemental analysis indicated a platinum-pyridine polymeric structure.

Endeavours to trap [Pt(o)py₄] in solution with a chelating or bulky ligand were unsuccessful. On addition of an excess of dppe or PPh₃ to a solution of decomposed py₂Pt(PhCMe₃)₂, a brown/black solid precipitated over a period of 10 minutes. Addition of PPh₃ to a decomposed solution of py₂Pt(PhCF₃)₂ immediately formed a whitish powder. ³¹P-NMR showed a weak resonance at δ 24.24 ppm in addition to free phosphine. Poor signal to noise ratio obscured any Pt-P coupling. Addition of bromine to a decomposed solution of py₂Pt(PhCMe₃)₂, however, yielded a bright orange py₂PtBr₄, which could have arisen via oxidative addition to [Pt(o)py₄].

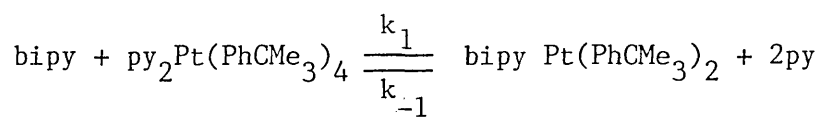
* Infrared Absorption (KBr-disc)

3040m, 2995s, 2895m, 2860m, 1595s, 1575w, 1475s, 1445vs, 1375w, 1355m, 1260m, 1200w, 1150w, 1115m, 1060m, 1040w, 1010m, 810s, 755s, 690vs, 630w, 560m, 550w cm⁻¹.

1.7 Ligand Substitution Reactions of $(py)_2Pt(aryl)_2$

At room temperature addition of PPh_3 , dppe or bipy to $py_2Pt(PhCMe_3)_2$ resulted in immediate ligand exchange to form the corresponding bisaryl.

Attempts to measure the equilibrium constant of



via UV or ^1H -NMR were unsuccessful since $K = \left[\frac{k_1}{k_{-1}} \right]$ is so large. The reaction is favoured by an entropy effect.

Treatment of py_2PtPh_2 in toluene with CO at $60^\circ C$ gave the readily identified compound $(CO)_2PtPh_2^*$.⁵⁵

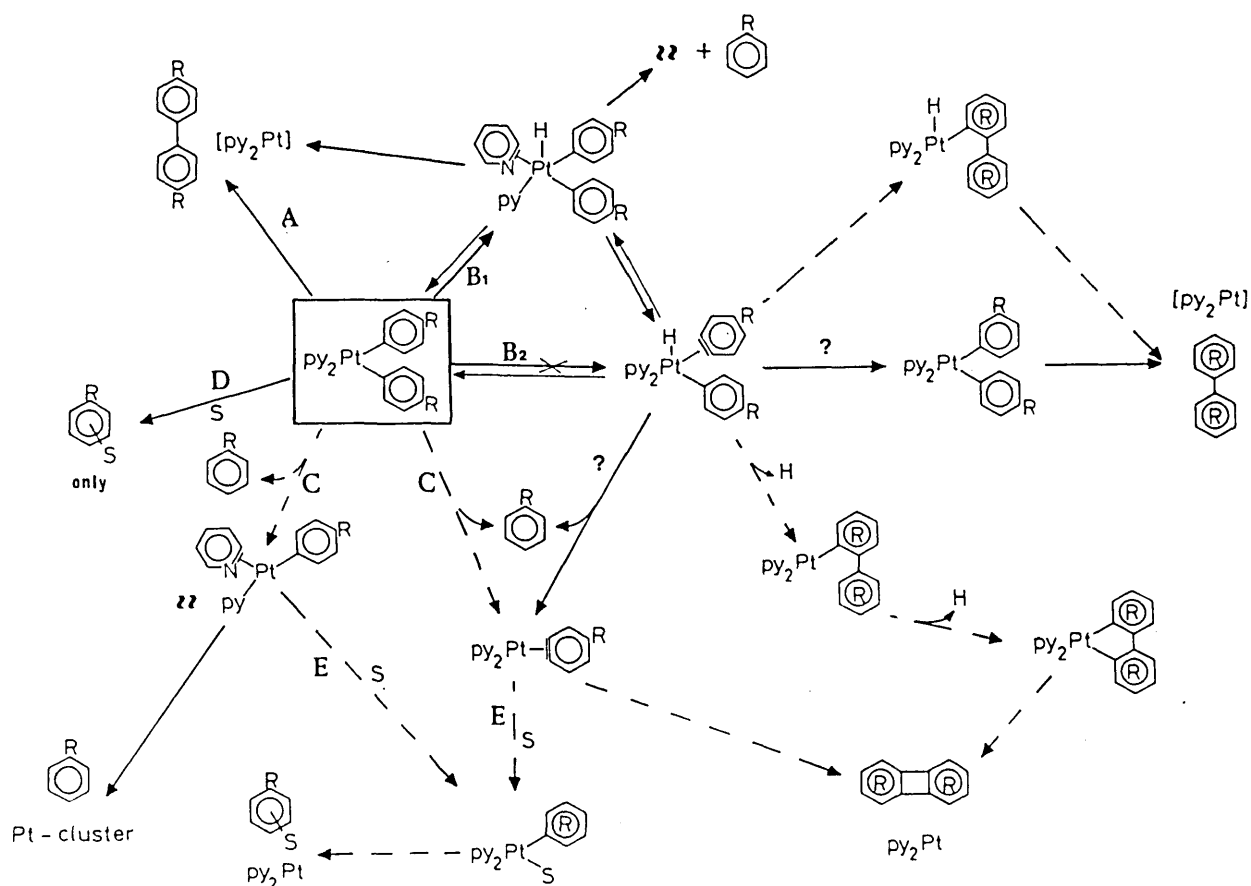
No carbonyl insertion into the platinum-carbon bond occurred. It has been reported before that in compounds L_2PtPh_2 no insertion but substitution of ligands takes place.⁵⁶ For $L = PPh_3$, $PMePh_2$ the reaction only proceeded as far as cis- $PtPh_2(CO)L$, for $L = COD$ complete conversion to $(CO)_2PtPh_2$ was observed.

* IR (KBr-disc): $\nu(CO)$: 2120, 2040 cm^{-1}

1.8 Concluding Remarks

In the Introduction to this chapter, a scheme with a variety of thermal rearrangements was outlined. Based on the foregoing observations of the thermolysis of $\text{py}_2\text{Pt}(\text{PhR})_2$ the same scheme is now displayed again (Scheme 19). The rearrangements actually taking place are emphasized.

Scheme 19 Thermolysis Pathways of $\text{py}_2\text{Pt}(\text{aryl})_2$



For $\text{py}_2\text{Pt}(\text{PhCF}_3)_2$ the only decomposition mechanism is concerted reductive elimination (A). For $\text{py}_2\text{Pt}(\text{PhR})_2$ ($\text{R} = \text{CMe}_3, \text{H}$) the two reaction pathways are reductive elimination (A) and hydrogen-migration (B), plus consequential reactions. Solvent derived products are most likely formed by a secondary homolytic M-C bond cleavage reaction (D). Solvent activation (E) cannot be fully excluded. Concerted reductive elimination from the parent compound was shown to be intramolecular.

Hydrogen-migration mainly occurs from the parent compound to yield a pyridyne species which can reductively eliminate arene or biaryl or isomerize to a benzyne intermediate. The latter is less likely to reductively eliminate.

Reductive elimination of biaryl yields the novel $[\text{Pt}(0)\text{py}_4]$ species, not isolable, but detectable by ^1H -NMR.

The different mechanisms are dependent on the substituents. In the $\text{py}_2\text{Pt}(\text{PhR})_2$ electron-withdrawing substituents (in para position) facilitate reductive elimination, be it C-C or C-H coupling and formation of pyridyne/benzyne-intermediates.

The electron withdrawing substituent CF_3 makes formation of the latter less favourable and, although the substituent effect is less beneficial for reductive elimination, it is the only thermolysis mechanism.

1.9 Experimental

General (applicable for all experimental sections)

NMR - measurements were performed on Bruker WM 250 (^1H 250.13 MHz; ^{13}C 62.9 MHz; ^{31}P 101.3 MHz; FT Model), JEOL FX 90 Q (^1H 89.55 MHz; ^{13}C 22.13 MHz; ^{19}F 84.27 MHz; ^{31}P 36.21 MHz; ^{195}Pt 19.21 MHz; FT Model) and Perkin-Elmer R32 (^1H 90 MHz CW Mode) instruments. IR data were obtained on a Perkin-Elmer 683 spectrophotometer and UV-data on a Perkin-Elmer 55.

HPLC analyses were carried out using an automated Spectro-Physics SP 8100 system equipped with SP 8440 UV/visible detector and a SP 4200 computing integrator (25 cm column of ODS bonded on 5 μ silica). Mass spectra were recorded on a VG 7070 E instrument. Gas chromatography/mass spectrometry (GC/MS) were obtained on a VG 7070 E instrument (Imperial College), Finnigan MAT 1020B GC/MS system (Hammersmith Hospital).

For gas-chromatography, a Perkin-Elmer, Sigma 1B Analyser and gas chromatographic system was employed (4 m column, 20% SE 30 on Chromasorb D, mesh 80/100).

Elemental analyses were by Imperial College Microanalytic laboratories, unless otherwise stated.

Melting points were determined in capillaries.

All chemical manipulations were carried out in dry degassed solvents under an atmosphere of argon.

Diethylether, petroleum ether (40-60° fraction) and thf were distilled under nitrogen from sodium benzophenone anion.

Benzene, toluene, toluene-d⁸ and pyridine were distilled from sodium under argon, as were p-xylene and mesitylene.

p-xylene-d¹⁰ and pyridine-d⁵ were used as in ampoules and stored over molecular sieves.

Irradiations were performed by using the output of a 400 W medium-pressure mercury arc lamp in a water-cooled quartz jacket (model RB 400, Applied Photophysics Ltd.).

All chemical manipulations were carried out under an atmosphere of purified argon.

When referred to as "standard recovery", the following manipulations are meant:

The organic layer is extracted into ether, dried over MgSO₄, decolourized with activated charcoal and evacuated to dryness.

Preparation of $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{CMe}_3)_2$

(modified from Reference 38)

An excess of Grignard $\text{BrMgC}_6\text{H}_4\text{CH}_3$ (6 ml of 0.69 M solution) is slowly added to a suspension of CODPtCl_2 (560 mg, 1.5 mmol) in ether (15 ml) at -78°C . The reaction temperature is maintained at -20°C for 12 h and allowed to reach room temperature before hydrolysis. The reaction solution is quenched with cold aqueous ammonium chloride and recovered by "standard method" (vide supra). The colourless crystals of $\text{CODPt}(\text{C}_6\text{H}_4\text{CMe}_3)_2$ are obtained in good yield (71-86%) and further purification is not required.

$\text{CODPt}(\text{C}_6\text{H}_4\text{CMe}_3)_2$ (680 mg, 1.2 mmol) is dissolved in pyridine (10 ml) and heated for 4-5 h at 50°C . The solvent is removed under vacuum at room temperature. Recrystallization from methanol/methylenedichloride gives colourless crystals (overall yield 66-82%).

$\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$ ($\text{R} = \text{H}, \text{CF}_3$) and compounds for deuterium labelling studies were prepared similarly. Analytical data are collected in Table 16.

R	mp [$^\circ\text{C}$]	Elemental Analysis					
		C		H		N	
		Calc.	Found	Calc.	Found	Calc.	Found
H	157°C dec	52.05	51.84	3.97	3.84	5.52	5.45
CMe_3	175°C dec	58.15	58.19	5.81	5.93	4.50	4.50
CF_3	207°C dec	44.73	44.86	2.80	2.74	4.35	4.19

Table 16 Analytical Data for $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{R})_2$

Preparation of the Grignard Precursor p-bromo-tert-butylbenzene-d⁴⁵⁷

To a mixture of tert-butylbenzene-d⁵* (2.24 g, 16 mmol), bromine (2.56 g, 0.82 ml, 16 mmol), conc. sulphuric acid (14 ml) and distilled water (2 ml) was added silver sulphate (4.98 g, 16 mmol). Under light exclusion the solution was stirred for 16 h and subsequently poured carefully into dilute sodium metabisulphite solution. Because of the exothermic reaction the flask was cooled in ice. BrC₆D₄CMe₃ was recovered by standard method (vide supra) (yield 82%). The resulting yellow oil was distilled under vacuum (56–58°C at 6 Torr) to give a colourless liquid.

Preparation of Organic Reference Compounds (Coupling Products)

Method A⁴²: Applied for following compounds

4,4'-bis-tert-butyldiphenyl, 3,4'-bis-tert-butyldiphenyl,
3,3'-bis-tert-butyldiphenyl, 4-tert-butyl-2'-methyl-diphenyl,
4-tert-butyldiphenyl

On a 1.2 mmolar scale a solution of arylmagnesium halide or an equimolar mixture of two different Grignards was cooled to -78°C by means of an acetone/dry ice bath. To the well stirred solution was added slowly an equimolar amount of anhydrous CoCl₂ by flushing from a dropping funnel with ether. The solution was stirred for one hour, left to warm up to 0°C and hydrolysed by filtration into an ice-ammonium chloride mixture. Standard recovery (vide supra).

* prepared by Friedels-Craft alkylation of benzene-d⁶ with tert-butyl chloride in the presence of anhydrous FeCl₃

Method B⁴¹: Applied for the following compounds :

4-tert-butyl-4'-methyl-diphenyl, 4-tert-butyl-3'-methyl-diphenyl
4-benzyl-tert-butylbenzene

On a 1.2 mmolar scale tert-butylphenyl Grignard is added slowly to an equimolar amount of arylhalide or benzyhalide in the presence of a catalytic amount (2 mg) of (dppb)PtCl₂. The solution was refluxed for 5-7 days and hydrolysed with an ice-ammonium chloride mixture. Standard recovery (vide supra).

Preparation of Grignard Precursor m-bromo-tert-butylbenzene⁵⁸

para-amino-meta-bromo-tert-butylbenzene*(1 g, 4.3 mmol) was dissolved in a mixture of water, ethanol and sulphuric acid (20 ml/3 ml/ 4 ml) and cooled to -5°C in a salt-ice bath. To the solution was added dropwise NaNO₂ (0.6 g, 8.6 mmol) maintaining a temperature below 0°C. Then over a period of 10 minutes H₃PO₄ (13 ml) was added. The mixture was left to warm up slowly to room temperature and stirred for another 14 h. An orange oil separated from the whitish solution. Standard recovery (vide supra) (Yield 81%).

The Grignard in ether was obtained in low, but usable yield. Refluxing in thf could possibly improve reactivity.

* Obtained from Maybridge Chemical Co. and used as supplied.

Preparation of $\text{Hg}(\text{C}_6\text{H}_4\text{CMe}_3)_2$ (Modified from Reference 59)

A solution of HgCl_2 (570 mg, 2.1 mmol) in thf (20 ml) was slowly added to an excess of tert-butylphenyl grignard. The solution was refluxed for 24 hours. The reaction mixture was hydrolysed with dilute HCl in ice. Standard recovery (vide supra) Yield (78%).

^1H -NMR data in ppm rel. to TMS (acetone- d_6): 1.34 s (Me), 7.47 d (4H, H_2 aromatic), 7.56 d (4H, H_3 aromatic), $^3\text{J}(\text{H}_2\text{H}_3) = 8.7$ Hz.

Thermolysis Reactions

A toluene solution (0.4 ml) of known concentration (1.2×10^{-3} M) of the compound was filled into cleaned and dried tubes (internal diameter 5 mm, external diameter 8 mm, length approximately 150 mm) and freeze/thaw degassed in three cycles. The tubes were sealed under vacuum. The reaction tubes were kept at a constant and specified temperature by immersion into a thermostatically controlled ($\pm 0.2^\circ\text{C}$) silicone oil bath (Haake W13/D8) for a timed period.

To reaction mixtures studied for the effect of mercury on the reaction mixture a drop of mercury (approximately 35 mg, 0.2 mmol) was added. Qualitative and quantitative product analyses were conducted by GC and HPLC.

GC - Analysis

For $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{CMe}_3)_2$: temperature was held at 130°C for 5 minutes, increased at $35^\circ\text{C}/\text{min.}$ to 190°C , maintained for 10 minutes and finally increased once more at the same rate to 220°C . Length of run: 80 minutes, flow rate: 1 ml/min. (4 m column, 20% SE 30 on chromasorb D, mesh 80/100). Retention indices are listed in Table 17.

Table 17 GC - Retention Indices

Compound	Retention Index	Response Factor
<u>tert</u> -butylbenzene	0.31	1.03
bitolyl (standard)	1	1
4- <u>tert</u> -butyl-3'-methyldiphenyl	1.56	
4- <u>tert</u> -butyl-4'-methyldiphenyl	1.36	
bis- <u>tert</u> -butyldiphenyl-3,3'	1.97	1
bis- <u>tert</u> -butyldiphenyl-3,4'	2.37	1
bis- <u>tert</u> -butyldiphenyl-4,4'	2.77	1
4- <u>tert</u> -butyldiphenyl	1.26	
4-benzyl- <u>tert</u> -butylbenzene	1.28	

Calculations were made in mol % of platinum-carbon bonds :

$$\text{mol \%} = \frac{\text{mol product}}{\text{mol (platinum-carbon bond)}_0} \times 100 \%$$

Mass balances were 100% ($\pm 5\%$) versus an internal standard bitolyl.

For $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{CF}_3)_2$ and py_2PtPh_2 : temperature was held at 100°C for 8 minutes increased at $40^\circ\text{C}/\text{min.}$ to 210°C and maintained to the end of the run. Length of run ca. 30 min. Retention indices are shown in Table 18.

Table 18 GC - Retention Indices

Compound	Retention Index
benzene	0.16
trifluoromethylbenzene	0.20
toluene	0.29
diphenyl	0.67
bis-trifluoromethyldiphenyl	0.67
4-methyl-diphenyl	0.81
bitolyl	1

HPLC - Analysis

Only qualitative analyses were carried out. Reaction products were eluted with a mixture of methanol and water (85/15%) and the U.V. absorption monitored at 254 nm. Flow rate: 1 ml/min., oven temperature: 45°C. (25 cm column of ODS bonded on 5 μ silica). Retention indices are listed in Table 19. tert-Butylbenzene is obscured by toluene.

Table 19 HPLC - Retention Indices

Compound	Retention Index
bitolyl	1
4- <u>tert</u> -butyl-1'-methyldiphenyl	1.39
4- <u>tert</u> -butyl-3'-methyldiphenyl	1.61
4- <u>tert</u> -butyl-4'-methyldiphenyl	1.67
3,3'-bis- <u>tert</u> -butyldiphenyl	2.47
3,4'-bis- <u>tert</u> -butyldiphenyl	2.62
4,4'-bis- <u>tert</u> -butyldiphenyl	2.75
4- <u>tert</u> -butyldiphenyl	1.26
4-benzyl - <u>tert</u> -butylbenzene	1.28

Deuterium labelling studies were conducted in the same way. Product distribution was analysed by GC and deuterium incorporation was obtained by GC/MS.

NMR - Kinetics

Thick walled NMR-tubes (Wilmad 503 PS, cleaned and dried previous to use) were filled with 0.4 ml of solution of known concentration, freeze/thaw degassed for three cycles and sealed under vacuum.

For $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{CMe}_3)_2$ in p-xylene- d^{10} kinetics were run on Bruker WM 250. The tert-butyl group provided a convenient peak (9 protons) for analysis of kinetic rearrangements. Kinetics of $\text{py}_2\text{Pt}(\text{C}_6\text{H}_4\text{CF}_3)_2$ (in d^8 -toluene) were monitored via ^{19}F -NMR on the JEOL 90 FXQ (frequency 2000 Hz, offset 36.688 MHz).

Photolysis of $\text{Hg}(\text{C}_6\text{H}_4\text{CMe}_3)_2$

A 1 mmolar solution of $\text{Hg}(\text{C}_6\text{H}_4\text{CMe}_3)_2$ in toluene was irradiated under anaerobic conditions for 4 h at 0°C using a medium pressure Hg lamp. The reaction mixture was analysed by GC and HPLC.

Reaction For Replacement of Pyridine with CO

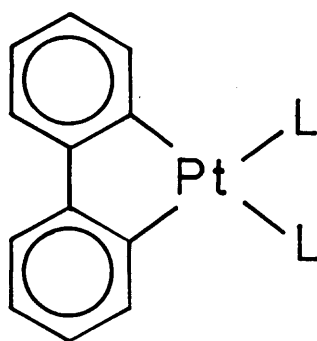
py_2PtPh_2 (30 mg, 0.05 mmol) was dissolved in toluene (20 ml) and heated at 60°C in a sealed reactor under an atmosphere of CO (100 atm.). The mixture was stirred overnight. The solution was recovered, the solvent removed and the greenish residue characterised by IR.

CHAPTER TWO

SYNTHESIS, SPECTROSCOPIC CHARACTERISATION AND
MECHANISTIC STUDIES OF PLATINAFLUORENES

2.1 Introduction to Platinafluorenes

For further studies on thermal rearrangement, especially reductive elimination we extended our interest to a skeleton closely related to $L_2Pt(aryl)_2$, namely the platinafluorene system (Figure 13).

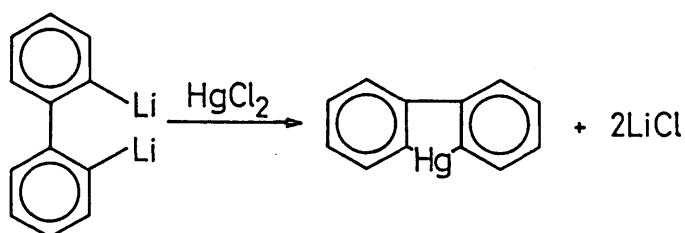


These complexes are interesting because of their contrasts:

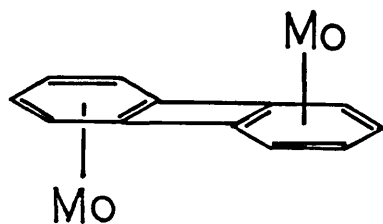
- (1) rigidity of biaryl ligand
- (2) total planarity
- (3) steric accessibility of the metal due to stereo-chemical feature(2).

Only few metallafluorenes are known. Wittig in 1954 reported a novel synthesis of a "mercury-biphenylene".⁶⁰ He reacted a lithium reagent with the mercury(II)dichloride as shown in Scheme 20.

Scheme 20 Synthesis of "Mercury-biphenylene"

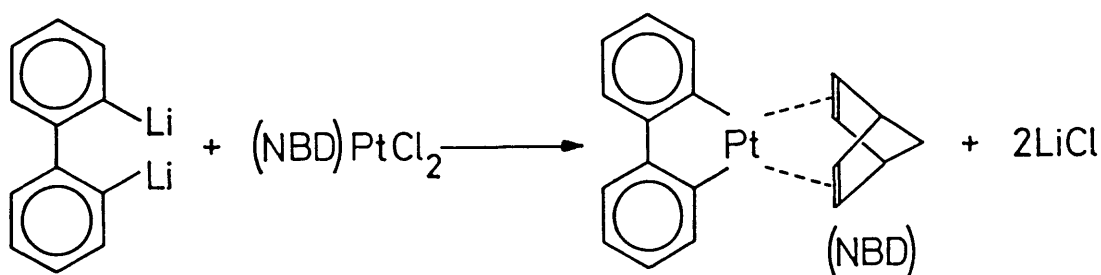


It was later established, however, via ebullioscopic molecular weight determination, that this species was a tetrameric ring, allowing the mercury its preferred near linear configuration.⁶¹ Attempts to form Pt, Ni, Fe or Mo-fluorene systems by Chatt *et al.* were equally unsuccessful. Instead of heterocyclic compounds they obtained η^6 -coordination of the six-membered ring to yield⁶²:



The first transition-metallafluorene was reported in 1967 with Titanium.⁶³ Subsequently, a few similar structures of V,⁶⁴ Zr, Co, Rh, Ir and Pt⁶⁵ were described. The latter was the first platinafluorene species obtained, but was only detected in low yields (10%) (Scheme 21).

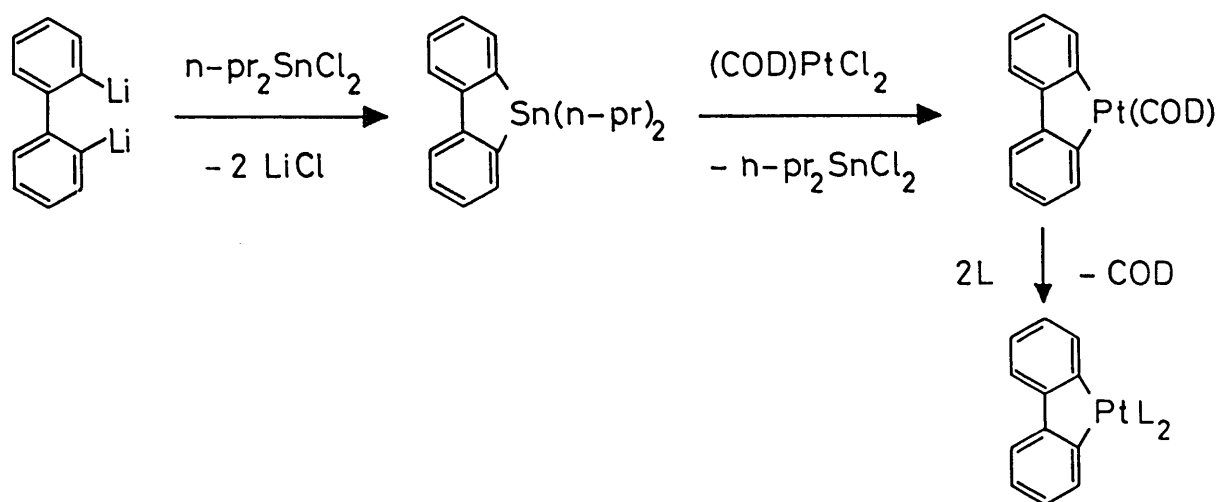
Scheme 21 Formation of the First Platinafluorene (NBD)Pt(C₁₂H₈)



An alternative and better route to form platinafluorenes was developed by Usón.⁶⁶ He increased his yield to 80% by using a tin precursor to react with the transition metals Pt and Au (Scheme 22).

Nothing has been reported on reactivities of these compounds except for a very recent paper on analogous nickel compounds.⁶⁷ No thermal rearrangements have been studied.

Scheme 22 Synthesis of Platinafluorenes



2.2 Synthesis and Spectroscopic Characteristics of Platinafluorenes

2.2.1 Synthesis

The compounds $(C_{12}H_8)PtL_2$ ($L = PMe_3, PEt_3, PMePh_2, PPh_3, P(tolyl)_3, \text{tert-butpy}; L_2 = dppm$) were prepared in a similar way to that described by Usón.⁶⁶ The tin reagent $(C_{12}H_8)Sn(n\text{-but})_2$ is reacted with $(COD)PtCl_2$ in refluxing ether to give $(C_{12}H_8)Pt(COD)$. Ligand substitution of COD for phosphine-containing ligands occurred at ambient temperature over several hours. For nitrogen ligands heating was required. The phosphine complexes are yellow crystalline solids, $(\text{tert-butpy})_2Pt(C_{12}H_8)$ is a whitish powder.

Their identity was established by ^1H , ^{31}P , ^{13}C -NMR, IR spectroscopy and elemental analysis.

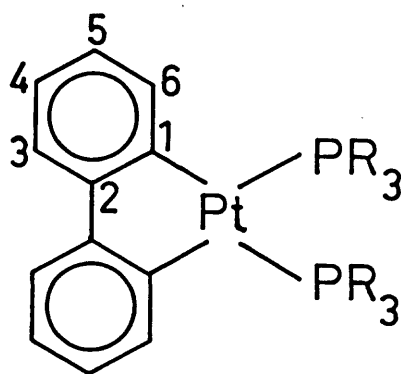
dmsO-ligands are often more easily replaced than COD. Attempts to synthesize $(dmsO)_2Pt(C_{12}H_8)$ failed however, due to thermal instability. Although the compound might have been initially formed, removal of the solvent required heating and the product decomposed before isolation was possible.

Substitution of COD with 1,10-phenantroline, 4,9-diphenyl-1,10-phenantroline and 4,4'-bis~~tert~~butyl-2,2'-bipyridyl were unsuccessful, even when the ligand was added in large excesses and reaction mixtures were heated to 60°C.

2.2.2 Spectroscopic Characteristics

2.2.2.1 ^1H -NMR

Since no NMR-characteristics have been reported previously for platinafluorenes, ^1H -NMR parameters are listed in Table 20. The following numbering system was employed.



Certain chemical shift trends have been established. The data is incomplete because signals of the fluorene-moiety are often obscured by those of the other ligands.

A generally recurring shift pattern was found in which $\delta\text{H}_3, \delta\text{H}_6 > \delta\text{H}_4 > \delta\text{H}_5$ (increasing downfieldshift). H_6 and H_3 are both similarly strongly deshielded and could only be differentiated by the coupling $^3\text{J}(\text{Pt}-\text{H})$ for H_6 .

Depending on the ligand H_3 resonates further downfield than H_6 , as observed for $\text{L} = \text{PMe}_3$ and dppm , while for $\text{L} = \text{PEt}_3$ and $\text{L}_2 = \text{COD}$ the sequence is reversed $\text{H}_6 > \text{H}_3$.

Coupling $^3\text{J}(\text{HH}) = 6.8 - 7.5$ and $^4\text{J}(\text{HH}) = 1.2 - 1.6$ Hz coincide well with data obtained for $(\text{C}_{12}\text{H}_8)\text{Ticp}_2$ ($^3\text{J}(\text{HH}) = 7.5$; $^4\text{J}(\text{HH}) = 1.9$ Hz).⁶⁸

Table 20 ^1H -NMR Characteristics of $(\text{C}_{12}\text{H}_8)\text{ML}_2$

M	L_2	$\delta(\text{ppm})^a$				J (Hz)						Other ^1H Parameters of Ligand	
		H_3	H_4	H_5	H_6	$\text{H}_3\text{-H}_4$	$\text{H}_4\text{-H}_5$	$\text{H}_5\text{-H}_6$	$\text{H}_3\text{-H}_5$	$\text{H}_4\text{-H}_6$	M-H ₆	$\delta(\text{ppm})$	J (Hz)
Sn	n-but ₂	7.985	7.426	7.302	7.658	7.7	7.1	6.8	-	-	28.9	C(1') 1.643 C(2')+(3') 1.371 C(4') 0.901	$^3\text{J}(\text{HH}) = 7.0$ $^2\text{J}(\text{SnH}) = 54$ Multiplet $^3\text{J}(\text{HH}) = 7.2$
Pt	COD	7.130	7.042	6.936	7.343	7.2	7.4	7.2	1.3	1.3	17	H(olefinic) 5.58 H(aliphatic) 2.53	J(Pt-H) = 39.4 J(Pt-H) = 14.3
Pt	(PMe ₃) ₂	8.151	7.493	7.135	7.952	7.5	6.8	7.5			40	Me 1.115	$^3\text{J}(\text{Pt-H}) = 19$ $^2\text{J}(\text{P-H}) = 4.1$
Pt	(PEt ₃) ₂	7.395	6.989	6.867	7.489	7.4	7.2	7.3	1.6	1.4	48	CH ₂ 1.127 CH ₃ 1.980	$^3\text{J}(\text{HH}) = 7.4$
Pt	(PPh ₃) ₂	b	6.848	6.279	b	b	7.5	b	b	b	b	H(2') 7.460 H(3') 7.077 H(4') 7.202	$^3\text{J}(\text{HH}) = 7.2$ $^3\text{J}(\text{HH}) = 7.5$ $^3\text{J}(\text{HH}) = 7.5$
Pt	(PMePh ₂) ₂	b	6.909	6.519	b	b	7.2	7.2	c	1.2	d	Me 1.841 Ph ₂ 7.15-7.58	$^3\text{J}(\text{Pt-H}) = 21$ $^2\text{J}(\text{P-H}) = 7$ Multiplet
Pt	(Ptolyl ₃) ₂	b	b	6.279	b	b	b	b	b	b	b	H(2') 7.400 H(3') 6.844 Me 2.258	$^3\text{J}(\text{HH}) = 8 \text{ Hz}$
Pt	dppm	7.811	6.940	6.654	7.781	7.1	7.3	7.1	1.5	1.3	53	CH ₂ 4.383 H(aromatic) 7.31-7.45	$^2\text{J}(\text{P-H}) = 9.4$ multiplet

a relative to internal Me₄Si in CDCl₃ ; b obscured by other signals ; c signal too broad ; d not visible

Values of the coupling $J(\text{Pt-H})$ are not available for all compounds, but range between 40 – 53 Hz for the phosphine compounds.

(~~tert~~-butpy)₂Pt(C₁₂H₈) was too insoluble to be analysed by NMR techniques.

2.2.2.2 ¹³C-NMR

¹³C-NMR parameters are listed in Table 21 for (C₁₂H₈)Pt(PR₃)₂ (R = Et, Ph). The same numbering system is employed as that mentioned in Section 2.2.2.1.

¹³C-NMR parameters were difficult to measure because of low solubility and obscuring of the fluorene resonances by aryl substituents on phosphine ligands.

For the carbon shifts following sequence was found (in decreasing downfield shift); $\delta(\text{C}_1) > \delta(\text{C}_6) > \delta(\text{C}_3) > \delta(\text{C}_4) > \delta(\text{C}_5)$. The tertiary carbons were more easily observed than the quaternary ones because of the Overhauser enhancement arising from hydrogen decoupling (see also Section 1.2.2.2). Assignments are therefore based on the intensity of the peaks and $J(\text{Pt-C})$ coupling. Values of $^3J(\text{Pt-C})$ and $^2J(\text{Pt-C})$ are very similar. $^3J(\text{Pt-C})$ in related platinum(II) alkyls and metallacyclic complexes have been found to be consistently higher than $^2J(\text{Pt-C})$. This effect is probably due to anomalously low values of the two-bond coupling, but theories governing coupling constants in these systems are not well developed.^{1,69}

Unfortunately, $^1J(\text{Pt-C}_1)$ was not observed, because of poor signal to noise ratio, nor was the C₂-resonance.

Table 21 ^{13}C -NMR Characteristics of $(\text{C}_{12}\text{H}_8)\text{Pt}(\text{PR}_3)_2$ in CDCl_3 ^a

R	$\delta(\text{C}_1)$	$\delta(\text{C}_2)$	$\delta(\text{C}_3)$	$\delta(\text{C}_4)$	$\delta(\text{C}_5)$	$\delta(\text{C}_6)$	$\delta(\text{R})$
Et	c	a	126.3 $^4\text{J}(\text{P}-\text{C}) = 6\text{Hz}$ $^3\text{J}(\text{Pt}-\text{C}) = 5\text{Hz}$	124.2	120.2	137.9 $^3\text{J}(\text{P}-\text{C}) = 6\text{Hz}$ $^2\text{J}(\text{Pt}-\text{C}) = 58\text{Hz}$	CH ₂ 19.5 $^1\text{J}(\text{P}-\text{C})=15\text{Hz}$ CH ₃ 9.4 $^2\text{J}(\text{P}-\text{C})=10\text{Hz}$
Ph	157.5	b	124.5	123.9	119.5	130.2	C' ₁ 133.5 $^1\text{J}(\text{P}-\text{C})=45\text{Hz}$ C' ₂ 128.6 C' ₃ /C' ₄ 127.4

a in ppm relative to internal Me_4Si

b obscured by other signals

c too weak to be recorded

2.2.2.3 ³¹P-NMR

In Table 22 are listed the ³¹P-NMR parameters of (C₁₂H₈)Pt(PR₃)₂.

Table 22 ³¹P-NMR Parameters of (C₁₂H₈)Pt(PR₃)₂ in CDCl₃

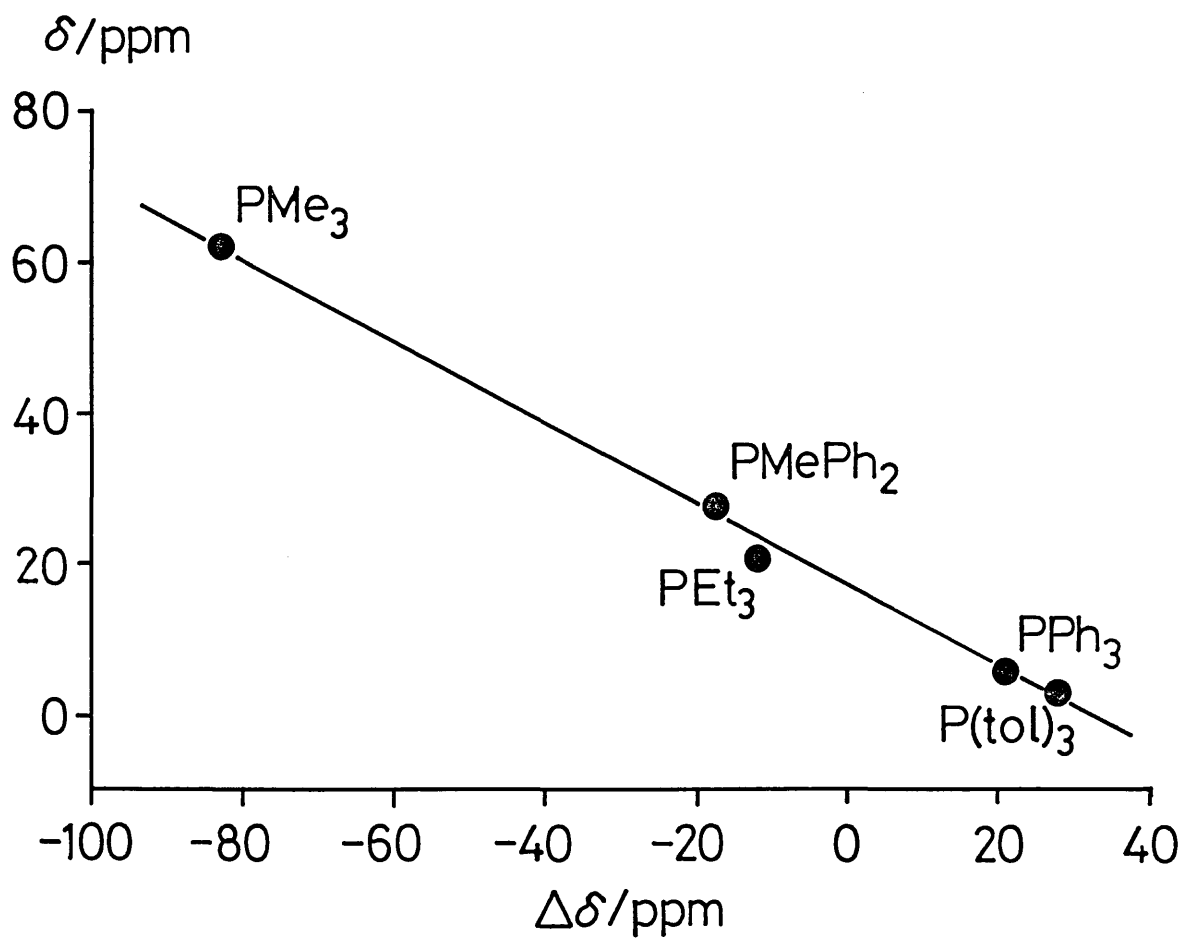
L	δ _{ppm} ^a	¹ J(¹⁹⁵ Pt- ³¹ P)Hz	Cone Angle °	¹ J(Pt-P) for PtPh ₂ L ₂
dppm/ ₂	-28.81	1564	107	1392 ^{2b}
PMe ₃	-20.62	1928	118	
PEt ₃	8.75	1923	132	1704 ⁷⁰
PMePh ₂	10.58	1954	136	1762 ^{2b}
PPh ₃	27.44	2018	145	1748 ^{2b}
Ptolyl ₃	24.75	2034	145	

a relative to external 60% H₃PO₄

For free phosphine the cone angle χ (CPC) (also listed in Table 22) is the major parameter affecting the ³¹P-chemical shift. As the group on the phosphorous increases in size, the cone angle and the shift move downfield. Empiricism has shown for coordinated trivalent phosphorous a linear relationship between the coordination chemical shift, $\Delta\delta = (\delta(\text{complex}) - \delta(\text{free phosphine}))$ and the resonance position of the free phosphine.⁷¹

A linear relationship is found for the present series (C₁₂H₈)Pt(PR₃)₂ and is shown in Figure 14.

Figure 14 Plot of the Coordination Chemical Shift, $\Delta\delta$ against the ^{31}P -NMR Chemical Shift of the Free Ligand, δ



Additionally listed in Table 22 are some coupling constants $^1J(^{195}\text{Pt}-^{31}\text{P})$ of the structurally closely related diphenyl platinum phosphine complexes. Comparison with the fluorene compounds shows a consistently larger coupling for the latter. This is probably an indication of angular distortion at the platinum. Constraint of the five-membered ring hinders efficient interaction of the donor-orbital of the ligating carbon with the platinum orbitals shared with the trans phosphine ligand. This effective reduction of the trans-influence of the fluorene moiety is reflected in the larger coupling. Conformation would require crystallographic proof which currently is not available. The values of coupling constants $^1J(\text{Pt}-\text{C}_1)$ would also allow useful comparison, but these are not apparent due to the low solubilities of the platinafluorenes and consequently poor signal to noise ratio.

2.2.2.4 Infrared Spectroscopy

I.R. characteristics are listed in Table 23.

Common features for all phosphine platinafluorenes are two absorption bands of equal intensity between $450 - 425 \text{ cm}^{-1}$, possibly assignable to $\nu(\text{Pt}-\text{P})$. For metal complexes in normal oxidation states the range for $\nu(\text{Pt}-\text{P})$ has been ascribed to the range $460 - 320 \text{ cm}^{-1}$.⁷² For (tert-butpy)₂-Pt(C₁₂H₈) the two absorptions are missing. It has to be pointed out, however, that Nakamoto disputes this range of $\nu(\text{MP})$ and places these vibrations at lower frequencies.⁴⁷

For most of the compounds the two typical Pt-C carbon stretches for cis square planar platinum(II) compounds are observed between 580 - 510 cm^{-1} .

Table 23 IR Characteristics for $(C_{12}H_8)PtL_2$

L_2	Infrared Absorption (cm^{-1})
COD ^a	3020m, 2940m, 2915m, 2865m, 2820m, 1550w, 1525w, 1470m, 1452m, 1425s, 1380m, 1335m, 1305m, 1255m, 1242m, 1225w, 1180w, 1160w, 1115m, 1100m, 1050m, 1030m, 1018m, 965m, 930w, 875m, 865m, 860m, 820w, 800w, 770m, 750vs, 735s, 660w, 615m, 460w, 420m
$(PMe_3)_2^b$	3150m, 2950m, 2895w, 1555w, 1470m, 1380m, 1290w, 1245s, 1210m, 1090m, 650s, 620m
$(PEt_3)_2^a$	3040w, 2970m, 2930m, 2870w, 1580vw, 1555vw, 1455s, 1420s, 1375m, 1250m, 1040s, 770m, 740s, 630m, 440m, 420sh
$(PMePh_2)_2^a$	3060m, 2930m, 1580w, 1575w, 1480m, 1440s, 1390w, 1310w, 1220w, 1190m, 1105s, 1030m, 1020w, 990w, 900s, 890s, 740s, 700s, 625w, 520s, 460m, 440m
$(PPh_3)_2^a$	3040m, 2930w, 1585w, 1570w, 1485m, 1435s, 1385w, 1315w, 1265w, 1245w, 1185m, 1160m, 1090s, 1055w, 1030m, 1015w, 850w, 805w, 740s, 700s, 620m, 550s, 535s, 510sh, 475w, 450w, 430w
$(Ptoly1_3)_2^a$	3010m, 2940m, 2910m, 2850m, 1595m, 1555w, 1536w, 1493m, 1465w, 1445m, 1424m, 1392m, 1373w, 1335vw, 1309w, 1255w, 1185m, 1110m, 1090s, 1049w, 1031m, 1015m, 964w, 800s, 847s, 830s, 805m, 640m, 625s, 609m, 522vs, 512vs, 502sh, 450w, 430w
dppm ^a	3050m, 2900w, 1585w, 1570w, 1485m, 1465w, 1440s, 1390w, 1355w, 1310w, 1275w, 1245w, 1215w, 1185w, 1155w, 1105s, 1030w, 1000m, 740s, 730s, 700m, 695s, 670m, 620m, 550m, 520m, 485m, 460w, 445w, 425w

Table 23 (Continued)

L ₂	Infrared Absorption (cm ⁻¹)
(tert-but-py) ₂ ^a	3080w, 3040w, 2960m, 2930w, 2905w, 2865w, 1610s, 1596m, 1575w, 1542m, 1494m, 1471m, 1460m, 1448m, 1416vs, 1393m, 1384w, 1361m, 1272m, 1241m, 1223m, 1198w, 1150w, 1125w, 1110m, 1065s, 1055m, 1035m, 1024m, 996w, 924w, 835vs, 820m, 740vs, 615w, 576s, 548w, 502m, 412m

a KBr-disc

b in CDCl₃ (solution cells)

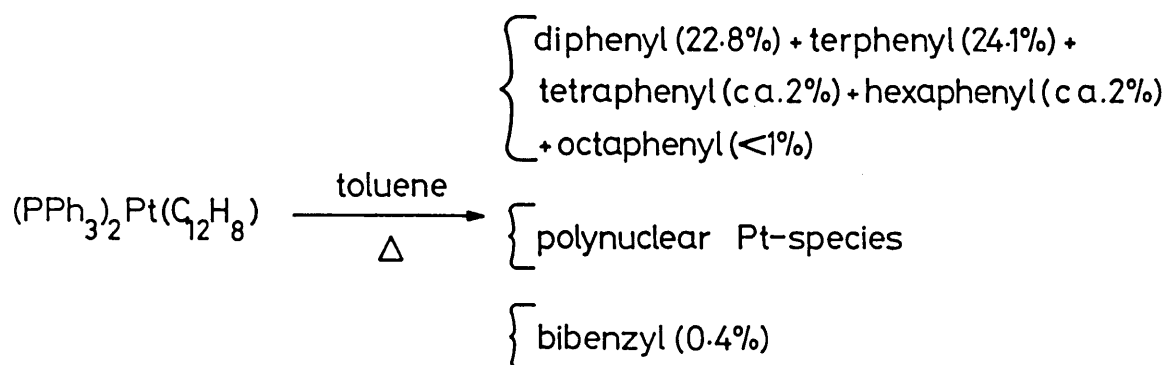
vs - very strong, s-strong, m-medium, w-weak, sh-shoulder

2.3 Thermal Behaviour of Platinafluorenes

2.3.1 Thermolysis of $(PPh_3)_2Pt(C_{12}H_8)$

Thermal decomposition of $(PPh_3)_2Pt(C_{12}H_8)$ was carried out in toluene at high temperature (100°C). The resulting product distribution is depicted in Scheme 23.

Scheme 23 Product Distribution of $(PPh_3)_2Pt(C_{12}H_8)$ Thermolysis



Mol% are given in parentheses*

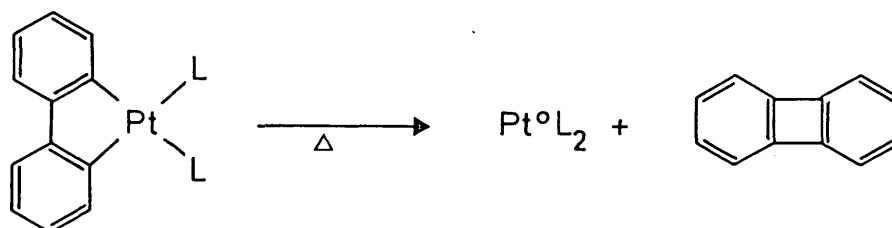
* mol% is defined here as: $\text{mol\%} = (\text{mol of product/mol of platinum}) \times 100\%$

The thermolysed reaction solution changed from light yellow to orange. A few yellowish crystals precipitated out of solution on cooling. Analysis showed these to be a mixture of tetraphenyl and hexaphenyl. Gas chromatography revealed that the main organic decomposition products in solution were diphenyl and terphenyl. Bibenzyl formation occurred only over prolonged thermolysis time.

On the basis of the product distribution, metal-carbon homolysis could be excluded immediately as a major reaction route. Wittig, in attempts to form Fe(II), Co(II) and Ni(II) - fluorenes with dilithium reagent $\text{Li}_2\text{C}_{12}\text{H}_8$, found the transition metals to catalyse the radical formation of diphenyl and polymers thereof.⁶¹ The products obtained were mainly diphenyl, some ortho-tetraphenyl, ortho-hexaphenyl and ortho-octaphenyl and the cyclic products tetraphenylene, hexaphenylene and octaphenylene. The distribution varied depending on the metals involved. Wittig pointed out that no biphenylene was ever detected. The thermolysed solutions of $(\text{PPh}_3)_2\text{Pt}(\text{C}_{12}\text{H}_8)$ contained no cyclic polyphenylenes nor were any significant levels of solvent derived products detected. A major homolytical decomposition pathway was thus excluded on these grounds.

Bibenzyl formation is most likely to be induced in a secondary reaction, perhaps by colloidal Pt(0) or other low valent metal species produced by the thermolysis, a type of side reaction discussed in Section 1.3.1.

There was no incidence of biphenylene, the expected product of the reductive elimination pathways shown below:



There is no orbital constraint on concerted reductive elimination from PtL_2 in this case, but presumably the steric strain inherent in cyclobutadiene formation contributes to an unfavourably high activation barrier.⁶⁶ It is interesting to note in this context that very recently the reverse reaction has been reported for the first time.⁶⁷ Oxidative insertion of nickel(0) complexes into the strained carbon-carbon bond of biphenylene has resulted in the product $\text{L}_n\text{Ni}(\text{C}_{12}\text{H}_8)$, (L = phosphine, COD).

Deuterium labelling provided additional evidence that the incidence of solvent activation is low.

Thermolysis of $(\text{PPh}_3)_2\text{Pt}(\text{C}_{12}\text{H}_8)$ in toluene- d^8 showed less than 10% deuterium incorporation in the diphenyl. In terphenyl, incorporation was less than 1%. Of course it has to be considered (as mentioned in Section 1.3.1) that a deuterium isotope effect might be operational and

that therefore significantly more hydrogen might be transferred from an undeuterated solvent. The very low levels of other solvent derived products, however, mitigate against this explanation.

The observed terphenyl originates from the coupling of an initially phosphorous-bound phenyl ring with the diphenyl ligand. This was established by analysis of the thermolysis products of $(P(tol)_3)_2Pt(C_{12}H_8)$ (Table 24).

Table 24 Product Distribution of $(P(tol)_3)_2Pt(C_{12}H_8)$

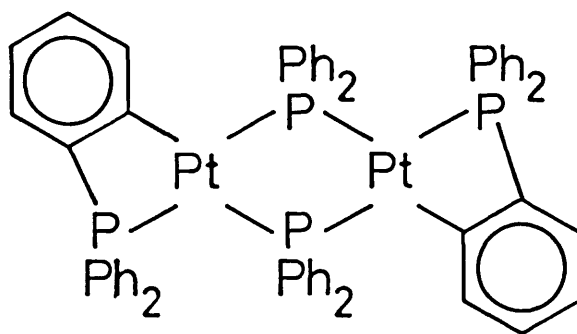
Thermolysis Product	Mol%
diphenyl	16.7
Me-terphenyl	9.3
terphenyl	0.6
TOTAL	26.6

Only traces of terphenyl were found. Clearly, the additional phenyl group comes from the phosphine ligand and not by intermolecular transfer from another fragmenting platinafluorene.

The liberation of terphenyl, in common with that of the other organic products of this thermolytic rearrangement - diphenyl, tetraphenyl and hexaphenyl -, requires hydrogen transfer from some source within the system. As has been established (vide supra) the solvent is not a major

provider and the only remaining source for hydrogen is the compound itself.

Hydrogen transfer might occur from a phosphine substituent via cyclometallation of the phosphine ligand or from a second platinafluorene molecule with formation of a bridged species. The latter has found recent precedent in the structurally closely related (μ -biaryl)[PtPh(tert-butpy)]₂⁵ and the low mass balance of evolved hydrocarbons in these reactions is quite consistent with such a rearrangement. Triarylphosphines are known to undergo intramolecular-aromatic substitution to form ortho-metallated species.⁷³ Thermolysis of (PPh₃)₂Pt(tol)₂ yielded the reactive species Pt⁰(PPh₃)₂ which in a secondary reaction rearranged via oxidative insertion of the low valent metal into the C-H bond.² A further example is the irradiation of L₂Pt(C₂O₄)⁷⁴. The primary product Pt⁰L₂ underwent a secondary photochemical or thermal reaction yielding:



In the I.R. for the latter a strong, sharp absorption band at 725 cm⁻¹ was attributed to the C-H out-of-plane deformation mode of the ortho-disubstituted phenyl group. A further band at 1115 cm⁻¹ was assigned to the ortho-metallated arylphosphine for the former.²

In Scheme 24 the various hydrogen transfer pathways are outlined. It is thought likely that an initial hydrogen-transfer yields the 1-diphenylplatinum species A. Possible evidence for A is the lack of cyclic tetraphenyls. A can abstract a further hydrogen to give diphenyl and a bridging binuclear platinum-species B or an ortho-metallated species as suggested for C.

Binuclear reductive elimination of two complexes A yields polymeric diphenyls and platinum clusters. And finally A can abstract a phenyl group of the phosphine ligand resulting in terphenyl and a possible platinum species D, as has been discussed previously.

Evidence in support of these contentions must await selective deuteration studies using, for example, $\text{PPh}_3\text{-d}^{15}$ or $\text{P}(\text{Ph-2,6-d}_2)_3$.⁷⁵

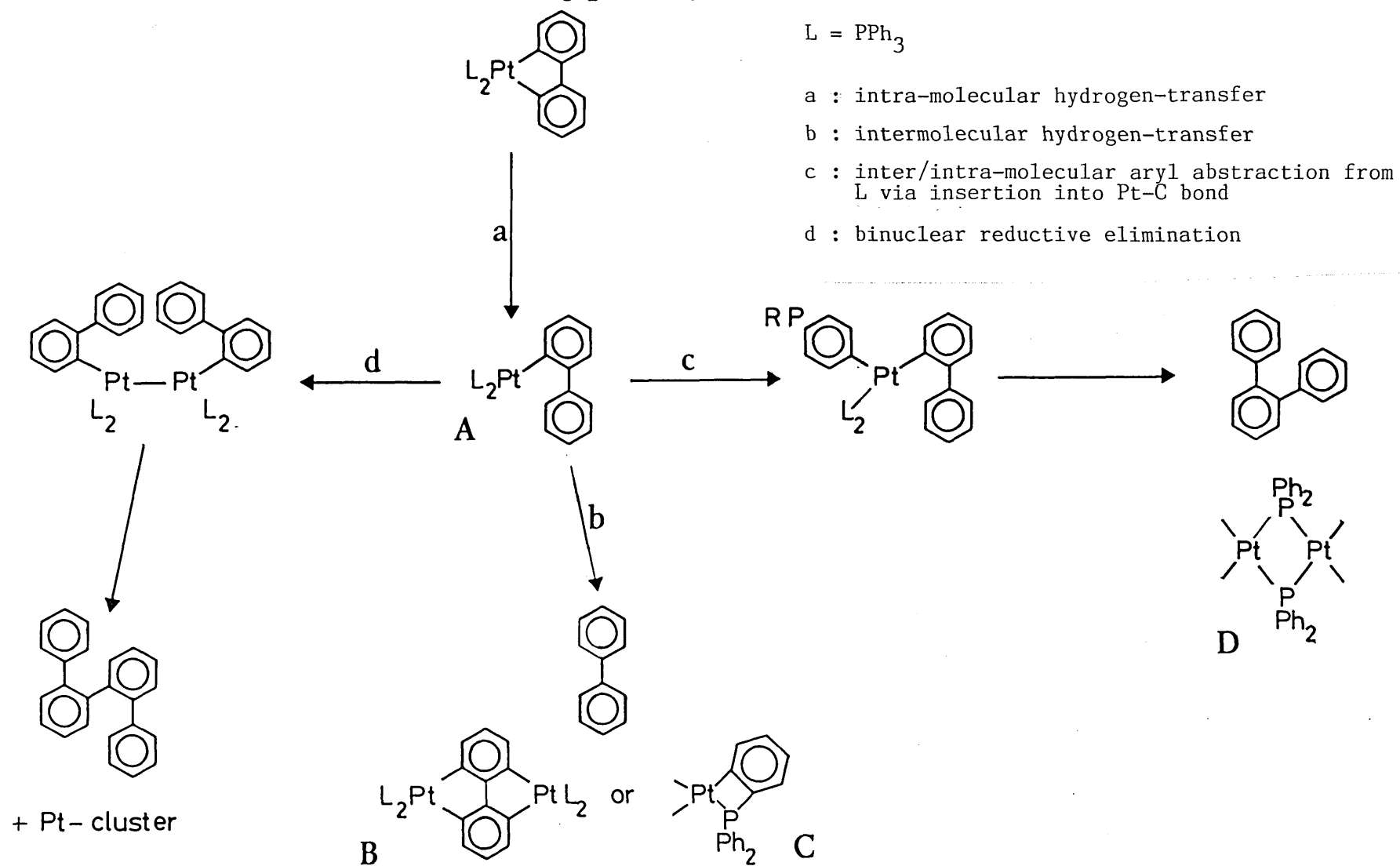
The residual platinum containing species was analysed by ^{31}P -NMR, IR* and microanalysis, which suggested a mixture of compounds.

The IR spectrum shows the platinum compound to contain the ligand PPh_3^{**} . A strong absorption at 545 cm^{-1} is characteristic of a Pt-C bond. There are strong absorptions at 740, 720 and 690 cm^{-1} . Aromatic C-H deformation frequencies in complexes containing σ -bonded ortho-disubstituted aryl are observed between $750 - 730\text{ cm}^{-1}$ for various transition metals.⁷⁶ Further evidence for ortho-metallated triarylphosphine is given by the absorption at 1118 cm^{-1} (vide supra).⁷⁴

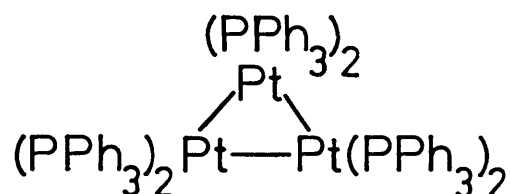
* 3050m, 2960m, 2915m, 2860m, 1480w, 1440s, 1380w, 1260m, 1118s, 1095s, 1020m, 995m, 800m, 740s, 720s, 690s, 620w, 545s, 505m cm^{-1} (KBr-disc)

** Characteristic vibrations of PPh_3 : 3060m, 1440s, 996w cm^{-1}

Scheme 24 Thermolysis Mechanism of $(\text{PPh}_3)_2\text{Pt}(\text{C}_{12}\text{H}_8)$



On the grounds of the IR-data the formation of platinum clusters containing Pt-Pt-bonds, such as depicted below, could be excluded.⁷⁷



The ^{31}P -NMR displays a singlet at $\delta 28.21$ ppm (toluene- d^8). No coupling with ^{195}Pt is evident. Thermolysis in the presence of free PPh_3 gave rise to the same resonance in the ^{31}P -NMR spectrum plus an additional minor peak at 26.07 ppm ($^1J(\text{Pt-P}) = 3190$ Hz).

The singlet suggests that the thermolysis product either does not contain any platinum (this is in contradiction to the microanalysis results obtained) or is a fluxional species in solution (rapid dissociation of PPh_3).

Limited solubility, however, excluded low temperature NMR.

2.3.2 Thermolyses of Other Platinafluorenes

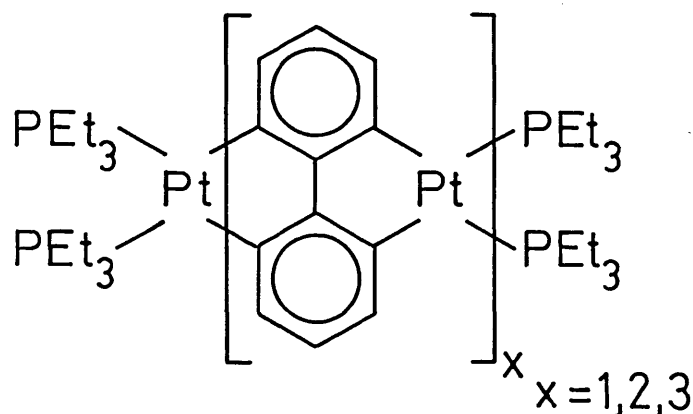
Only preliminary investigations have been carried out on the metallafluorene systems $L_2Pt(C_{12}H_8)$ ($L = PEt_3, PMe_3, PMe_2Ph, t\text{-butpy}$; $L_2 = dppm$).

Thermolysis of $(PEt_3)_2Pt(C_{12}H_8)$ was monitored by ^{31}P -NMR. Only one new phosphorous containing product was observed, $\delta 11.13$ ppm ($^1J(Pt-P) = 2824$ Hz). GC-analysis of the reaction solution showed only 17.6 mol% of diphenyl liberated. Minimal amounts of tetraphenyl and hexaphenyl were detected. No biphenylene was found.

Involvement of the ligand PEt_3 is less likely than for PPh_3 , although hydrogen transfer has been observed from PEt_3 . No ethyl-diphenyl was detected corresponding to the terphenyl formation discussed in Section 2.3.1.

Based on these results, microanalysis and comparison with the reaction pathways of $(PPh_3)_2Pt(C_{12}H_8)$ formation of a bridged species, as shown in Figure 15 is thought likely.

Figure 15 Polynuclear Thermolysis Product



Thermolysis of $L_2Pt(C_{12}H_8)$ $L = PMe_3, PMe_2Ph$ and $L_2 = dppm$ resulted in liberation of diphenyl and polymers thereof. No biphenylene was ever detected. No decomposition was found for (tert-butpy) $_2Pt(C_{12}H_8)$ over 14 days at 100°C.

These investigations are far from complete and require further exploration.

2.4 Concluding Remarks

Thermolysis of platinafluorenes does not afford the reductive elimination product biphenylene, nor does platinum-carbon homolysis occur. The main product is diphenyl. Smaller amounts of tetra- and hexaphenyl, and phosphine ligand permitting, terphenyl are detected.

One motive to study the thermolysis of platinafluorenes is the possibility of solvent activation. Evidence is that in the event solvent activation forms only a small proportion of products inspite of the fact that intermolecular reactivity between platinum complexes is clearly implicated. This feature deserves further investigation.

Thermal rearrangement takes place mainly via H-transfer, most probably from a phosphine ligand where accessible, or from a biphenylene ligand in an intermolecular reaction. Since not all biphenylene units are liberated, it is assumed that bridged polynuclear platinum species are formed.

The investigations of the platinafluorenes are far from being complete and further work is required. More detailed analysis of the platinum-containing species and possibly kinetic studies would produce more mechanistic evidence and give a better understanding of the complex thermal rearrangements.

2.5 Experimental

Preparation of 2,2'-Dibromodiphenyl⁷⁸

To a stirred and cooled (-78°C) solution of ortho-dibromobenzene (12 gr, 0.05 mol) in anhydrous THF (125 ml) was added an ethereal solution of n-butyllithium (19 ml of 1.5 M solution). During the slow addition, the temperature was never allowed to rise above 5°C . The reaction mixture was hydrolysed with 5% HCl (25 ml) at 0°C .

Standard recovery (vide supra). The residue was treated with ethanol (10 ml) to give 2,2'-dibromodiphenyl (mp $80-81^{\circ}\text{C}$).

Preparation of 2,2'-Dilithiodiphenyl⁷⁹

To a lithium sand (1.1 gr, 0.05 M) in anhydrous ether (15 ml) was added a small quantity of 2,2'-dibromodiphenyl to start the reaction. The remaining 2,2'-dibromodiphenyl (1.4 gr, 4.7 mM) was added slowly over a period of 30 minutes to avoid the solution boiling. The mixture was stirred for 5 h and left to settle overnight. Titration with 0.1 N HCL showed a 0.12 M solution (yield 70%).

Preparation of (n-but)₂Sn(C₁₂H₈)⁷⁹

To a solution of Di-n-butyltindichloride (0.47 gr, 1.6 mM) in anhydrous ether was added cautiously a dilithiodiphenyl solution (13 ml, 0.12 M) over 30 minutes. The suspension was stirred for two hours at

room temperature and subsequently hydrolysed with water-saturated ether. The solution was dried with Na_2SO_4 and the solvent evaporated off. The obtained oil could not be crystallized (yield 78%).

Preparation of $(\text{COD})\text{Pt}(\text{C}_{12}\text{H}_8)$ (modified from Reference 66)

$(n\text{-but})_2\text{Sn}(\text{C}_{12}\text{H}_8)$ (157 mg, 0.4 mM) was added to a solution of $\text{Cl}_2\text{Pt}(\text{COD})^{\text{td}}$ (112 mg, 0.3 mM) in chloroform (10 ml) and refluxed for 24 h. The resulting solution was evaporated to dryness and the residue washed with petrolether (yield 81%).

Preparation of $(\text{PPh}_3)_2\text{Pt}(\text{C}_{12}\text{H}_8)$

To replace the COD-ligand a stoichiometric amount of PPh_3 (120 mg, 0.45 mM) was added to a solution of $(\text{COD})\text{Pt}(\text{C}_{12}\text{H}_8)$ (100 mg, 0.2 mM) in CH_2Cl_2 and stirred for 2 days. The solvent was evaporated to dryness and the residue recrystallized with ether/methanol.

Analogue procedures were employed for $\text{L} = \text{PMe}_3$, PPh_3 , PMePh_2 , $\text{P}(\text{tolyl})_3$, tert-butpy, and $\text{L}_2 = \text{dppm}$. Reaction times and temperatures and analytical data are collected in Table 25.

Table 25 Analytical Data of Platinafluorenes

L	Reaction Temperature	Reaction Time/ Days	mp/ °C	Yield/ %
PMe ₃ ^b	R.T.*	5	203 - 205	55
PEt ₃	R.T.	2	141 - 143	95
PPh ₃	R.T.	1	210 - 212	75
PMePh ₂ ^b	R.T.	4	158 - 160	64
P(tolyl) ₃	R.T.	5	a	32
tert-butpy ^c	50°C	7	297 dec.	20
dppm/ ₂ ^b	R.T.	4	250 dec.	81

a not measured

b kindly prepared by T.J. Higgs, B.Sc. Dissertation, IC, 1984

c recrystallized in refluxing acetone

* R.T. : Room Temperature

The GC-reference compound biphenylene was prepared according to Reference 80.

Thermolysis

A toluene solution (0.4 ml) of known concentration (2.10^{-3} M) of the compound was filled into tubes (as described in Section 1.9). The solution was freeze/thaw degassed in three cycles. The tubes were sealed under vacuum. The tubes were kept at 100°C for 24 - 48 h in a thermostatically controlled silicone oil bath.

The reaction products were analysed by GC and GC/MS.

GC-Analysis

For the detection of diphenyl and biphenylene temperature was held constant at 190°C for 30 minutes.

Length of run: 30 min, flow rate: 1 ml/min, (4 m column, 20% SE 30 on Chromasorb D, mesh 80/100).

Retention indices are listed in Table 26.

Table 26 Retention Indices for Biphenylene Detection

Compound	Retention Index
diphenyl	0.59
biphenylene	0.67
bitolyl	1
bibenzyl	0.84

For the detection of terphenyl temperature was held constant at 210°C for 60 minutes (Table 27).

Table 27 Retention Indices for Terphenyl Detection

Compound	Retention Index
bitolyl	1
terphenyl	2.33
Me-terphenyl	3.06

CHAPTER THREE

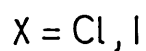
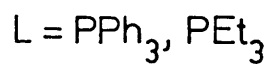
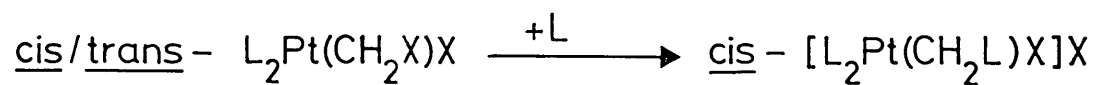
SYNTHESIS AND SPECTROSCOPIC CHARACTERISATION OF
trans-IODOMETHYL-IODOBIS(TRIETHYLPHOSPHINE)PLATINUM(II) ;
REACTIVITIES AND THERMAL BEHAVIOUR OF
HALOMETHYL-BIS-(PHOSPHINE)PLATINUM(II) COMPLEXES

3.1 Introduction

In parallel with the investigations described in Chapters 1 and 2 we expanded our mechanistic studies to α -substituted alkyl derivatives of platinum. Considerable current interest in the chemistry of these α -functional compounds has evolved because of their importance as key intermediates in a variety of metal-mediated organic transformations. Notably, among these derivatives are 1-hydroxyalkyls, which feature as intermediates in the palladium catalysed oxidative hydrolysis of alkenes (Wacker Prozess)⁸¹ and in the Fischer Tropsch and related reductions of carbon monoxide catalysed by a variety of metals.⁸² Several hydroxy-methyl metal complexes have been successfully isolated in investigations aimed at modelling the latter process.⁸³⁻⁸⁶ Halogenomethyl complexes appear attractive as electronegatively substituted metal alkyls and as key intermediates for a variety of other alkyl complexes via nucleophilic substitution.⁸⁷ Halogenomethylmetal compounds are, as a rule, labile. Their instability has been used as carbene-propagators in for example Simmons-Smith⁸⁸ and Seyferth⁸⁹ reactions. To date, there is a limited range of examples of d^8 complexes.

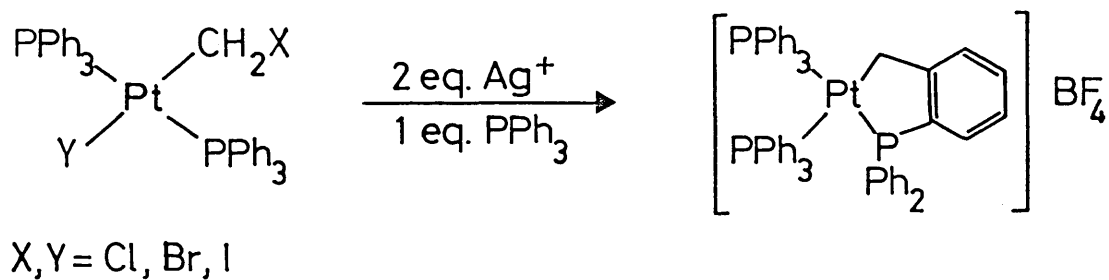
Oxidative addition of CH_2XY ($X = Cl, Br, I$; $Y = Cl, Br, I$) to $Rh(I)$, $Ir(I)$, $Pt(II)$ and $Sn(II)$ have been previously described.^{90,91} Little is known about the reactivity of these halogenomethyl platinum(II) complexes. Well established is ylide formation, as shown in Scheme 25.⁹²

Scheme 25 Formation of a Cationic Ylide Complex of Platinum(II)



In contrast addition of AgBF_4 and ligand to $\text{L}_2\text{Pt}(\text{CH}_2\text{X})\text{Y}$ ($\text{L} = \text{Ph}_3$; $\text{X}, \text{Y} = \text{Cl}, \text{Br}, \text{I}$) formed a platinacycle under mild conditions (Scheme 26).⁹¹

Scheme 26 Formation of Platinaindan



The reaction is independent of X and Y and the cycle is formed in the amount proportional to the silverfluoroborate added. It is thought that the Pt-halide bond is broken first and the mechanism includes two processes, (1) halogen abstraction from the parent compound and (2) electrophilic displacement of hydrogen from an aromatic ring.

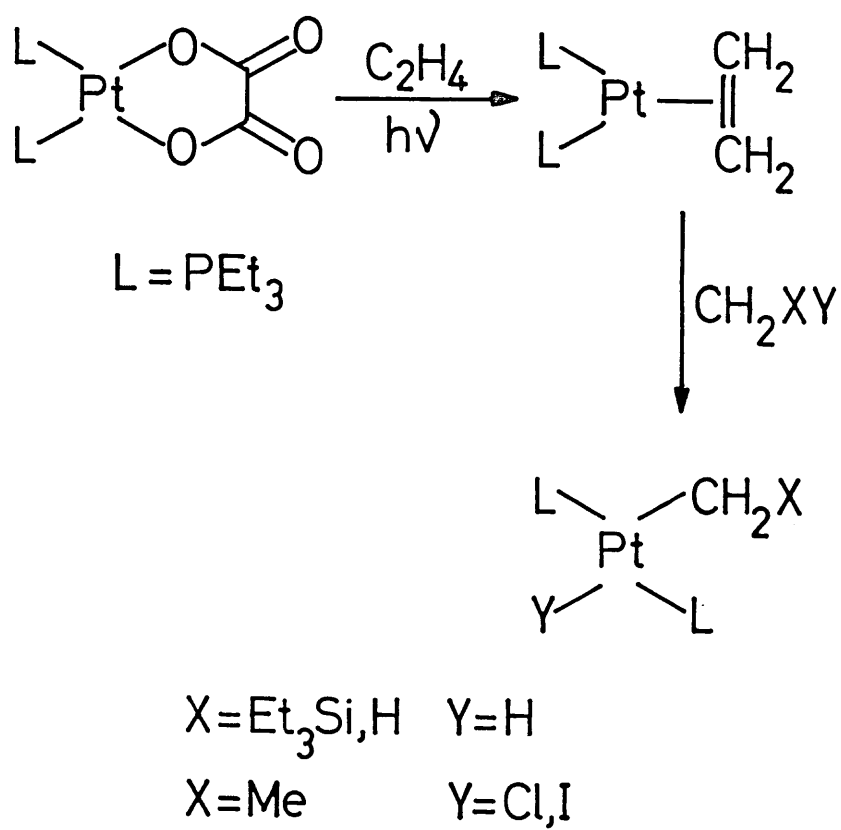
The silver ion is commonly used as an electrophilic promoter of these and similar reactions.⁹³ Recently it was found that thallium(I) salts have distinct advantages over silver (I) because they are weaker oxidizing agents and form fewer complexes.⁸⁷ Thermal reactivity of these compounds has not been examined in spite of the fact that such species are commonly assumed to be carbene precursors.

Only indirect observations have been made. The thermolysis $(\text{PBut}_3)_2\text{Pt} \sqrt{\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2}$ in CH_2Cl_2 was thought to lead to formation of trans- $(\text{PBut}_3)_2\text{Pt}(\text{CH}_2\text{Cl})\text{Cl}$ (55% of Pt species) plus three minor products.^{1c} The subsequent decomposition yielded $(\text{PBut}_3)_2\text{PtCl}_2$. Scherer stated that $(\text{PPh}_3)_2\text{Pt}(\text{CH}_2\text{Cl})\text{Cl}$ in refluxing CH_2Cl_2 did not decompose.⁹⁴ Only after photolysis was cis- $\text{PtCl}_2(\text{PPh}_3)_2$ formed. In both cases no explanation for the missing methylene fragment was given.

Based on earlier studies of the photochemical behaviour of $\text{L}_2\text{M}(\text{C}_2\text{O}_4)$ ($\text{M} = \text{Pt}, \text{Pd}$ and $\text{L} = \text{PPh}_3, \text{AsPh}_3$) Trogler⁹⁵ described an elegant synthetic route to obtain halogenomethylplatinum(II) derivatives as shown in Scheme 27.

Initial photolysis in the presence of ethylene forms a neutral $\text{Pt}(\text{o})$ species. Oxidative addition of a dihalogenomethane affords an isolable halogenomethyl complex.

Scheme 27 Synthesis of α -Functional Methyl(phosphine)platinum(II) Compounds



3.2 Synthesis and Spectroscopic Characteristics of trans-Iodomethyl-Iodobis(triethylphosphine)platinum(II)

3.2.1 Synthesis

Conversion of bis(triethylphosphine)dichloride platinum(II) to the oxolate and subsequent photolysis in the presence of ethylene yielded the reactive platinum(0) species $[(\text{PEt}_3)_2\text{Pt}(\text{C}_2\text{H}_4)]$ which readily added CH_2I_2 oxidatively at room temperature to give the thermodynamically favoured trans-(PEt_3)₂Pt(CH_2I)I. The same preference was observed for trans-(PPh_3)₂-Pt(CH_2I)I.⁹⁰

The identity of trans-(PEt_3)₂Pt(CH_2I)I was established by its elemental analysis, NMR-characteristics, IR and mass spectrometry.

Addition of CH_2Cl_2 , CCl_2Ph_2 and $\text{Me}_3\text{SiCHCl}_2$ to the ethylene precursor did not yield the expected oxidative addition product. Products were mainly cis and trans-(PEt_3)₂PtCl₂ (see Table 31), unreacted (PEt_3)₂Pt(C_2H_4) and few other minor products.

These results confirm difficulties reported more recently by Trogler.⁹⁶ He found that irradiation of (PEt_3)₂Pt(C_2O_4) in CH_2Cl_2 formed at least five platinum containing species, out of which cis-(PEt_3)₂PtCl₂ and trans-(PEt_3)₂PtH(Cl) were identified. No oxidative addition product (PEt_3)₂Pt-(CH_2Cl)Cl was found however.

3.2.2 Spectroscopic Characteristics

Listed in Table 28 are the NMR-characteristics of trans-(PEt₃)₂Pt(CH₂I)I.

Although trans-(PEt₃)₂Pt(CH₂I)I has been independently reported recently, there are no spectroscopic data available.^{94, 92} Spectroscopic comparisons have been made for a series of the closely related halogenomethylplatinum(II) compounds (PPh₃)₂Pt(CH₂X)Y (X,Y = Cl, Br, I) studying the influence of the halogens on shifts and coupling.⁹⁷ It is therefore interesting to compare the effect of different phosphine ligands on L₂Pt(CH₂X)Y.

In the ¹H-NMR the methylene hydrogens appear at 1.95 ppm as a triplet with platinum satellites caused by coupling with two phosphorus nuclei as well as with platinum. Compared to the analogue trans-(PPh₃)₂Pt(CH₂I)I (δ(CH₂) = 2.30 ppm), the methylene group experiences less deshielding, probably because the better π-donor PEt₃ enriches the d-orbital population around Pt, which is to some extent responsible for shielding the α-hydrogens. The same influence is observed in the ³¹P-NMR for the coupling constants J(Pt-PEt₃) < J(Pt-PPh₃), ΔJ_{ca.} 800 Hz. In the ¹³C-NMR the methylene signal is observed as a "triplet" at 15.54 ppm due to ²J(P-C) coupling with ¹⁹⁵Pt satellites.

The ¹³C-NMR data of trans-(PPh₃)₂Pt(CH₂I)I (δ(CH₂) = 1.6 ppm, ¹J(Pt-C) = 859 Hz) does not appear consistent with our work and the parameters of trans-(PPh₃)₂Pt(CH₂Cl)Cl, and is therefore not comparable.

Table 28 NMR-Characteristics of $(\text{PEt}_3)_2\text{Pt}(\text{CH}_2\text{I})\text{I}$

	δ ppm	
$^1\text{H}^{\text{a}}$	$\delta(\text{CH}_2)$	1.948 $^2\text{J}(\text{Pt-H}) = 59 \text{ Hz}, \quad ^3\text{J}(\text{P-H}) = 12 \text{ Hz}$
	$\delta(\text{P}-\underline{\text{CH}}_2-\text{CH}_3)$	2.216
	$\delta(\text{P}-\text{CH}_2-\underline{\text{CH}}_3)$	1.028
$^{13}\text{C}^{\text{a}}$	$\delta(\text{CH}_2)$	15.54 $^1\text{J}(\text{Pt-C}) = 126 \text{ Hz}, \quad ^2\text{J}(\text{P-C}) = 17 \text{ Hz}$
	$\delta(\text{P}\underline{\text{CH}}_2\text{CH}_3)$	18.10 $^1\text{J}(\text{P-C}) = 18 \text{ Hz}, \quad ^2\text{J}(\text{Pt-C}) = 28 \text{ Hz}$
	$\delta(\text{PCH}_2\underline{\text{CH}}_3)$	8.46 $^2\text{J}(\text{P-C}) = 19 \text{ Hz}$
$^{31}\text{P}^{\text{b}}$	- 0.23	$^1\text{J}(\text{Pt-P}) = 2268 \text{ Hz}$

a in ppm relative to internal Me_4Si in CDCl_3

b in ppm relative to external 60% H_3PO_4 in CDCl_3

Listed in Table 29 are listed the observed infrared frequencies.

Table 29 IR Characteristics of $(\text{PEt}_3)_2\text{Pt}(\text{CH}_2\text{I})\text{I}$

Infrared Absorption (cm^{-1}) ^a	2960s, 2915m, 2860m, 1560w, 1450m, 1420m, 1410m, 1375m, 1255m, 1240m, 1030s, 1015m, 1010m, 980w, 872w, 766vs, 725s, 712m, 681w, 635m, 422m, 395w
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a KBr-disc

Listed in Table 30 are mass spectroscopic data for $(\text{PEt}_3)_2\text{Pt}(\text{CH}_2\text{I})\text{I}$. Mass spectroscopy is interesting in the fact that in the fragmentation pattern the molecular ion $(\text{PEt}_3)_2\text{Pt}(\text{CH}_2\text{I})\text{I}^+$ is not observed, the largest fragment detected is $(\text{PEt}_3)_2\text{PtI}_2^+$. Stepwise loss of iodide and then of PEt_3 occurs readily.

Table 30 Mass Spectroscopic Data for $(\text{PEt}_3)_2\text{Pt}(\text{CH}_2\text{I})\text{I}$

m/e	Rel. Int. %	Fragment
685	43.4	$(\text{PEt}_3)_2\text{PtI}_2^+$
558	100	$(\text{PEt}_3)_2\text{PtI}^+$
429	44.8	$(\text{PEt}_3)_2\text{Pt}^+$
313	13.1	$(\text{PEt}_3)\text{Pt}^+$
194	17.9	Pt^+

Listed in Table 31 are the ^{31}P -NMR characteristics of reference compounds mentioned in Sections 3.2.1 and 3.4.

Table 31 ^{31}P -NMR Characteristics of bis(phosphine)platinum dihalides

Compound	$\delta^{31}\text{P}$ ppm ^a	$^1\text{J}(^{31}\text{P}-^{195}\text{Pt})$ Hz	$^2\text{J}(\text{PP})$ Hz
$(\text{PEt}_3)_2\text{PtCl}_2$ - <u>trans</u>	11.62	2408 ⁹⁸	13
- <u>cis</u>	8.57	3518	
$(\text{PEt}_3)_2\text{PtI}_2$ - <u>trans</u>	11.36	2399	
$(\text{PPh}_3)_2\text{PtI}_2$ ^b - <u>trans</u>	11.18	2494	
$(\text{PPh}_3)_2\text{PtCl}_2$ ^c - <u>cis</u>	13.50	3673	
$(\text{PPh}_3)_2\text{PtClI}$ - <u>trans</u>	17.41	2551	
- <u>cis</u>	12.18	3555	
	10.20	3686	

a in CDCl_3

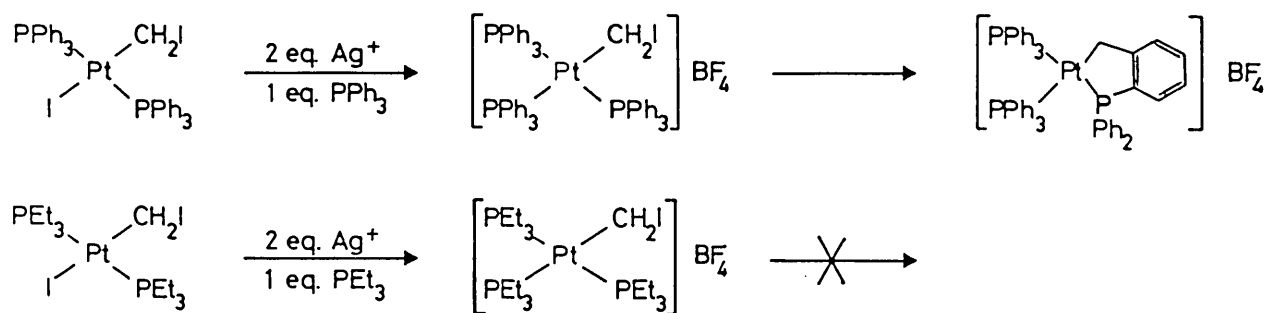
b made from $\text{CODPtI}_2 + \text{PPh}_3$

c made from $\text{CODPtCl}_2 + \text{PPh}_3$

3.3 Reactivity of trans-(PEt₃)₂Pt(CH₂I)I and Related Compounds

In contrast to the reactivities observed by Yang and Young⁹¹ for the compounds (PPh₃)₂Pt(CH₂X)Y (X,Y = Cl, Br, I)*, the methylene-iodide bond in (PEt₃)₂Pt(CH₂I)I could not be cleaved readily by addition of the silver salt AgBF₄ with or without the presence of excess phosphine. Only platinum-iodide bond scission occurred (Scheme 28) to yield [(PEt₃)₃Pt(CH₂I)]BF₄ (NMR-data in Table 32).

Scheme 28 Electrophilic Reactivity of trans-L₂Pt(CH₂I)I



The Pt-I cleavage was very fast and did not visibly depend on the Ag⁺-concentration for >1 equivalent.

* The nature of the halogen had no influence on the reactivity

It is interesting to compare the reactivity for the two different phosphine compounds trans-L₂Pt(CH₂I)I. For L = PPh₃ the initial platinum-iodide cleavage is followed by H-abstraction from the aromatic ring and subsequent cyclisation. For L = PEt₃ the reaction stops after the platinum-iodide scission. There was no CH₂-I cleavage even in the presence of a large excess of silver salt, nor the less likely hydrogen abstraction from the ethyl group.¹⁹ Hydrogen transfer from PEt₃ has only been observed for cyclometallation reactions where there is an attack of platinum on carbon, not electrophilic attack of carbon on carbon. Addition of PMe₂Ph to trans-(PEt₃)₂Pt(CH₂I)I in the presence of excess Ag⁺ yielded mainly trans-[(PEt₃)₂(PMe₂Ph)Pt(CH₂I)]BF₄ and the metallacycle (30%) displayed in Figure 16. NMR parameters are listed in Table 32.

Figure 16 Cationic Platinaindan Complex

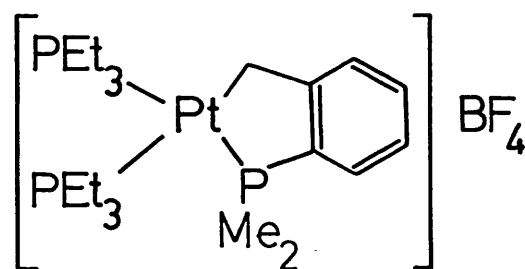
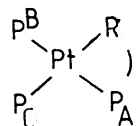


Table 32 ^{31}P -NMR Characteristics of Platinum-Iodide Scission Products

Compound	$\delta(^{31}\text{P})$ ppm c,e			$^1\text{J}(\text{Pt}-\text{P}_X)$ Hz	$^2\text{J}(\text{P}_X\text{P}_Y)$ Hz
	P_A	P_B	P_C		
$[(\text{PEt}_3)_3\text{Pt}(\text{CH}_2\text{I})]\text{BF}_4^a$	22.71	14.74	22.71	$\text{P}_{A,C}$ 2263 P_B 3466	P_AP_B 20
<u>trans</u> $[(\text{PEt}_3)_2(\text{PMe}_2\text{Ph})\text{Pt}(\text{CH}_2\text{I})]\text{BF}_4^b$	21.88	-10.86	21.88	$\text{P}_{A,C}$ 2226 P_B 3497	P_AP_B 22
$[(\text{PEt}_3)_2\text{Pt}\overline{\text{CH}_2(\text{PMe}_2\text{Ph})}]\text{BF}_4^b$	18.58	11.59	6.18	P_A 2548 P_B 2228 P_C d	P_BP_C 22 P_AP_C 22 P_AP_B 392

a in benzene- d^6 ; b in acetone- d^6 ; c relative to external 60% H_3PO_4 ; d obscured

e numbering system:



The presence of a phenyl group makes possible electrophilic hydrogen displacement from an aromatic ring. This behaviour confirms suggestions made that platinum-iodide cleavage occurs first. Only subsequent isomerization to cis-[(PEt₃)₂(PMe₂Ph)Pt(CH₂I)]BF₄ renders cyclisation possible. It also shows that the ligand PEt₃ is inert to attack of carbon on carbon.

Addition of the Lewis acid AlCl₃ had no effect, while addition of AgBF₄ only yielded a mixture of many unidentifiable products. Addition of PEt₃ to a toluene solution of trans-(PEt₃)₂Pt(CH₂I)I showed a slight peak broadening of the free phosphine in the ³¹P-NMR, characteristic of associative exchange.⁹⁶ There was no ylide-formation.

The route via preliminary platinum-halide cleavage was employed for the synthesis of halogenomethylhydrideplatinum(II) compounds. Addition of NaBH₄ to trans-(PPh₃)₂Pt(CH₂Cl)I yielded the unstable hydride trans-(PPh₃)₂Pt(CH₂Cl)H*.

Synthesis of the analogous compound trans-(PEt₃)₂PtH(CH₂I) was more difficult, the reaction being less clean. The hydride** proved to be very short lived and rearranged to trans-(PEt₃)₂Pt(CH₃)I probably by initial reductive elimination and then by oxidatively adding CH₃I.

* ¹H-NMR (toluene-d⁸) : δ - 5.76 ppm ¹J(Pt-H) = 600 Hz,
²J(P-H) = 17 Hz. ³¹P-NMR : δ 28.6 ppm, ¹J(Pt-P) = 3089 Hz

** ³¹P-NMR (toluene-d⁸) : δ 10.82 ppm J = 2791 Hz

From the reaction mixture yellow crystals were isolated and were identified as trans-(PEt₃)₂Pt(CH₃)I*. It is unlikely that the methyl compound is formed directly. It has been established that only the Pt-I is cleaved by Ag⁺ and therefore addition of NaBH₄ will proceed via hydride formation first.

In the case of trans-hydridophenylplatinum(II) compounds trans-L₂Pt(H)Ph (L = phosphine) attention has been drawn previously to the dependence on the tertiary phosphine of the stability to heat and light.⁹⁹ The marked difference between PPh₃ and PEt₃ was emphasized, in particular the greater lability of the latter.

* ³¹P-NMR (toluene-d⁸) : δ 7.40 ppm J = 2745 Hz
¹H-NMR : δ 1.18 s (3H, Me), 1.83 (12H, CH₂; ³J(HH) = 7.8 Hz,
³J(HP) = 3.7 Hz)
 1.07 ppm (18H, CH₃, ³J(HH) = 7.8 Hz)

3.4 Thermolysis of $\text{trans}-(\text{PEt}_3)_2\text{Pt}(\text{CH}_2\text{I})\text{I}$ and Related Compounds

3.4.1 Product Distribution

The thermal behaviour of $\text{L}_2\text{Pt}(\text{CH}_2\text{X})\text{Y}$ has not previously been studied in detail. As mentioned in the introduction, thermolysis of cis/trans- $(\text{PPh}_3)_2\text{Pt}(\text{CH}_2\text{Cl})\text{Cl}$ has been observed to result in the loss of the CH_2 -moiety and formation of trans- $(\text{PPh}_3)_2\text{PtCl}_2$, but no mechanism was suggested. Thermolysis of trans- $\text{L}_2\text{Pt}(\text{CH}_2\text{X})\text{Y}$ ($\text{L} = \text{PEt}_3$, $\text{X} = \text{Y} = \text{I}$; $\text{L} = \text{PPh}_3$, $\text{X} = \text{Cl}, \text{I}$, $\text{Y} = \text{I}$) in benzene resulted also in loss of the methylene group and formation of corresponding L_2PtXY -species.

Listed in Table 33 are the platinum-containing thermolysis products in mol% based on the ^{31}P -NMR analysis of residual solution. (Addition of cyclohexene had no influence on the platinum species except in the last case). Mol% are defined as follows :

$$\text{mol\%} = \frac{\text{mol product}}{\text{mol Pt}} \times 100\%$$

$\text{L}_2\text{Pt}(\text{CH}_2\text{X})\text{Y}$			Thermolysis Products Mol%			
L	X	Y	<u>trans</u> - L_2PtI_2	<u>cis</u> - L_2PtCl_2	<u>cis</u> - L_2PtClI	Minor and Unidentified Products
PEt_3	I	I	100	-	-	-
			(100)	-	-	-
PPh_3	I	I	70	-	-	30 [3]
			(68)	-	-	32 [3]
	Cl	I	43	-	-	57 [2]
			(20)	(31)	(24)	(13) [4]

() Values in the presence of cyclohexene

[] Number of types of products

Table 33 Product Distribution of $\text{L}_2\text{Pt}(\text{CH}_2\text{X})\text{Y}$ Thermolysis

Whatever mechanisms form the platinum-containing species, these compounds are subject to subsequent isomerization and the initially obtained product distribution may be quite different. It has been found that the trans/cis isomer ratio is favoured by bulkier ligands such as PPh_3 (more than PEt_3) and for iodide more than chloride.

Benzene was used as solvent and may have facilitated isomerization since the presence of unsaturated compounds is known to promote this type of reaction.

trans- L_2PtI_2 ($\text{L} = \text{PPh}_3, \text{PEt}_3$) were proved to be the thermodynamically favoured isomers*. However, in the case of the thermolysis of $(\text{PPh}_3)_2\text{Pt}(\text{CH}_2\text{Cl})\text{I}$ a product distribution close to the thermodynamically most favourable was only obtained in the presence of cyclohexene, as shown in Table 34.

The organic product distribution was analysed by GC (Table 35). Cyclohexene was selectively added to reaction solutions in an endeavour to trap any liberated methylene-moiety. Gases, such as methane, ethane, ethylene, propene and various butenes** and the cyclohexene addition products, norcarane and two isomers thereof, methylene-cyclohexane and 1-methylcyclohexene, were detected. The identities of the latter were

* To a solution of $(\text{COD})\text{PtI}_2$ in benzene two equivalents of L were added, heated for several hours and the product analysed by ^{31}P -NMR. Only trans- $(\text{PPh}_3)_2\text{PtI}_2$ was detected.

** Due to unavailability of reference compounds, only the trans-2-butene could be identified. The presence of n-butane was excluded.

Table 34 Product Distribution of Isomeric $(PPh_3)_2PtXY$

Product Distribution	$(PPh_3)_2PtXY$ in mol%					
	I/I		Cl/Cl		Cl/I	
	<u>trans</u>	<u>cis</u>	<u>trans</u>	<u>cis</u>	<u>trans</u>	<u>cis</u>
Thermodynamic	32	–	6	36	13	13
Thermolytic	1 43	–	–	–	–	–
	a 2 20	–	–	31	7	24

a in the presence of cyclohexene

Unidentified Products (^{31}P -NMR) :	1	$\delta 27.48$	$J = 3309 \text{ Hz};$	57%
	2	$\delta 21.07$	$J = 2889 \text{ Hz};$	8%
		$\delta 10.26$	$J = \text{obscured};$	7%
		$\delta 27.54$	$J = 3309 \text{ Hz};$	3%

confirmed by their mass spectroscopic fragmentation patterns (Table 36). Small amounts of the reductive elimination products, dihalomethanes, were also found.

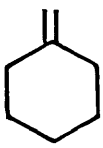
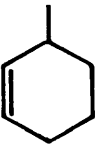
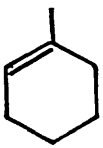
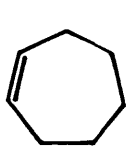
Mass balances for the organic products are relatively low. According to ^{13}C and ^{31}P -NMR no parent compound is left. It seems likely that the majority of products are gases. The measurement-inaccuracy is attributed to a significant loss of the low boiling gases before injection into the GC.

Table 35 Organic Product Distribution in mol%^a of trans-L₂Pt(CH₂X)Y-thermolysis in Benzene

Product	(PEt ₃) ₂ Pt(CH ₂ I)I		(PPh ₃) ₂ Pt(CH ₂ Cl)I		(PPh ₃) ₂ Pt(CH ₂ I)I		
	-	+ cyclohexene	-	+ cyclohexene	-	+ cyclohexene	d
methane	0.9	0.8	0.43	0.13	0.45	2.18	1.1
ethane/ethylene ^c	12.8	5.4	0.38	0.56	0.68	0.96	2.4
propene	3.3	1.5	0.01	0.07	0.19	0.21	0.9
butenes	3.3	4.1	0.62	0.65	0.45	0.26	0.2
<u>trans</u> -2-butene	2.0	0.5	-	0.03	-	-	0.3
norcarane	-	0.8	-	26.94	-	11.89	-
methylene- cyclohexane	-	-	-	12.17	-	8.46	-
1-methyl- cyclohexene	-	b	-	3.0	-	2.32	-
CH ₂ I ₂	0.6	-	-	0.03	1.06	1.39	11.28
CH ₂ Cl/I	-	-	-	traces	-	-	-
TOTAL	22.9	13.1	1.44	43.58	2.83	27.67	16.18

a mol% = $\frac{\text{mol product}}{\text{mol Pt-C bonds}} \times 100\%$; b obscured ; c both compounds observed, but not fully separable ; d in d⁶-benzene

Table 36 Mass Spectroscopic Data of Norcarane and Isomers

m/e	Rel. Int. %					Fragment
						
96	20.9	42.5	74.5	43.4	44.4	$C_7H_{12}^+$
81	76.9	100	100	100	72.5	$C_6H_9^+$
68	100	77.6	80.8	43.8	100	$C_5H_8^+$
55	79.1	43.3	69.2	37.8	79.6	$C_4H_7^+$
39	72.4	28.4	41.9	23.4	53.5	$C_3H_3^+$
27	51.5	14.2	38.1	15.2	36.9	$C_2H_3^+$

Overall the main products are C₂- and C₄-hydrocarbons. The ratios, however, vary according to the nature of the phosphine ligands and the halides. The presence or absence of cyclohexene had little influence on the gas-distribution. Norcarane is the main addition product of cyclohexene and the CH₂-fragment. Minor amounts of methylenecyclohexane and even smaller quantities of 1-methylcyclohexene were detected. No other isomers, such as cycloheptene or 3-methylcyclohexene were formed.

3.4.2 Thermolytic-Mechanism

So far only the product distribution has been investigated without relation to any type of mechanism. As mentioned previously, the platinum species obtained does not yield much information because isomerization will obscure the primary product(s). Scherer explained the thermolysis of cis/trans-(PPh₃)₂Pt(CH₂Cl)Cl as a radical reaction based on the observation that refluxing the compound in CH₂Cl₂ did not lead to decomposition, but that additional photolysis yielded cis-(PPh₃)₂PtCl₂.⁹⁴

There has been considerable controversy on the question of the ground state of the free methylene.¹⁰¹ It has been postulated as a radical (triplet) and as a nonradical (singlet). It is therefore impossible to draw any theoretical conclusions regarding the free entity. Only an experimental product distribution can give an indication as to whether the rearrangement involves a homolytic mechanism.

Our investigations were all carried out under light exclusion to avoid any adventitious photolysis. Initially detected toluene (possible solvent adduct) proved to be a solvent impurity. To verify that no solvent

attack takes place $(\text{PPh}_3)_2\text{Pt}(\text{CH}_2\text{Cl})\text{I}$ was thermolysed in benzene- d^6 . No toluene- d^6 was found. Of course, an isotope effect would be expected; it is unlikely that radical formation of solvent adducts should be totally suppressed.

Comparison of experimental results of CH_2 generated by photolysis and pyrolysis of CH_2N_2 with those of thermolysis of $(\text{PPh}_3)_2\text{Pt}(\text{CH}_2\text{X})\text{Y}$ in the presence of cyclohexene display an interesting contrast (Table 37).¹⁰¹

Table 37 Product Distribution of Methylene with Cyclohexene Under Various Reaction Conditions

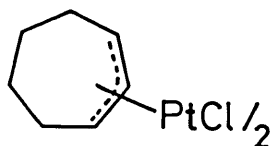
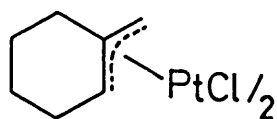
Methylene Source	Reaction Condition	Products %				
		Norcarane	Me-cyclohexene			Methylene cyclohexane
			3-	4-	1-	
CH_2N_2 photolysis	- 75°C	40	25	25	10	-
CH_2N_2 pyrolysis	265°C	32		54	14	-
$(\text{PPh}_3)_2\text{Pt}(\text{CH}_2\text{Cl})\text{I}$	140°C	64	-	-	7	29
$(\text{PPh}_3)_2\text{Pt}(\text{CH}_2\text{I})\text{I}$	140°C	52	-	-	11	37

Free methylene reacts preferentially to yield 3- and 4-methylcyclohexene, products that are not even detected in the thermolysis of $(\text{PPh}_3)_2\text{Pt}(\text{CH}_2\text{X})\text{Y}$.

The latter, however, produces mainly norcarane and significant amounts of methylenecyclohexane which is not present at all for the former reaction. Amounts of 1-methylcyclohexene are comparable. This disparity is strong evidence that "free" methylene is not released by thermolysis of $L_2Pt(CH_2X)Y$.

Based on this result and the absence of solvent adducts a major homolytic reaction pathway is excluded.

Powell et al. studied the oxidative addition reaction of norcarane to the Zeise-salt $\eta^2-(C_2H_4)PtCl_2$.¹⁰² Quenching the product yielded methylenecyclohexane, 1-methylcyclohexene and cycloheptene in a ratio 2:2:1. Comparison with our product distribution obtained in the presence of cyclohexene (Table 37) excluded the formation of the two intermediates suggested by Powell:



There are traces of the reductive elimination products CH_2XY ($X = Cl, I$; $Y = I$). Trans configuration makes this type of reaction less favourable since isomerization to cis has to occur first. No 1,2-dihaloethane is found as a result of binuclear reductive elimination.

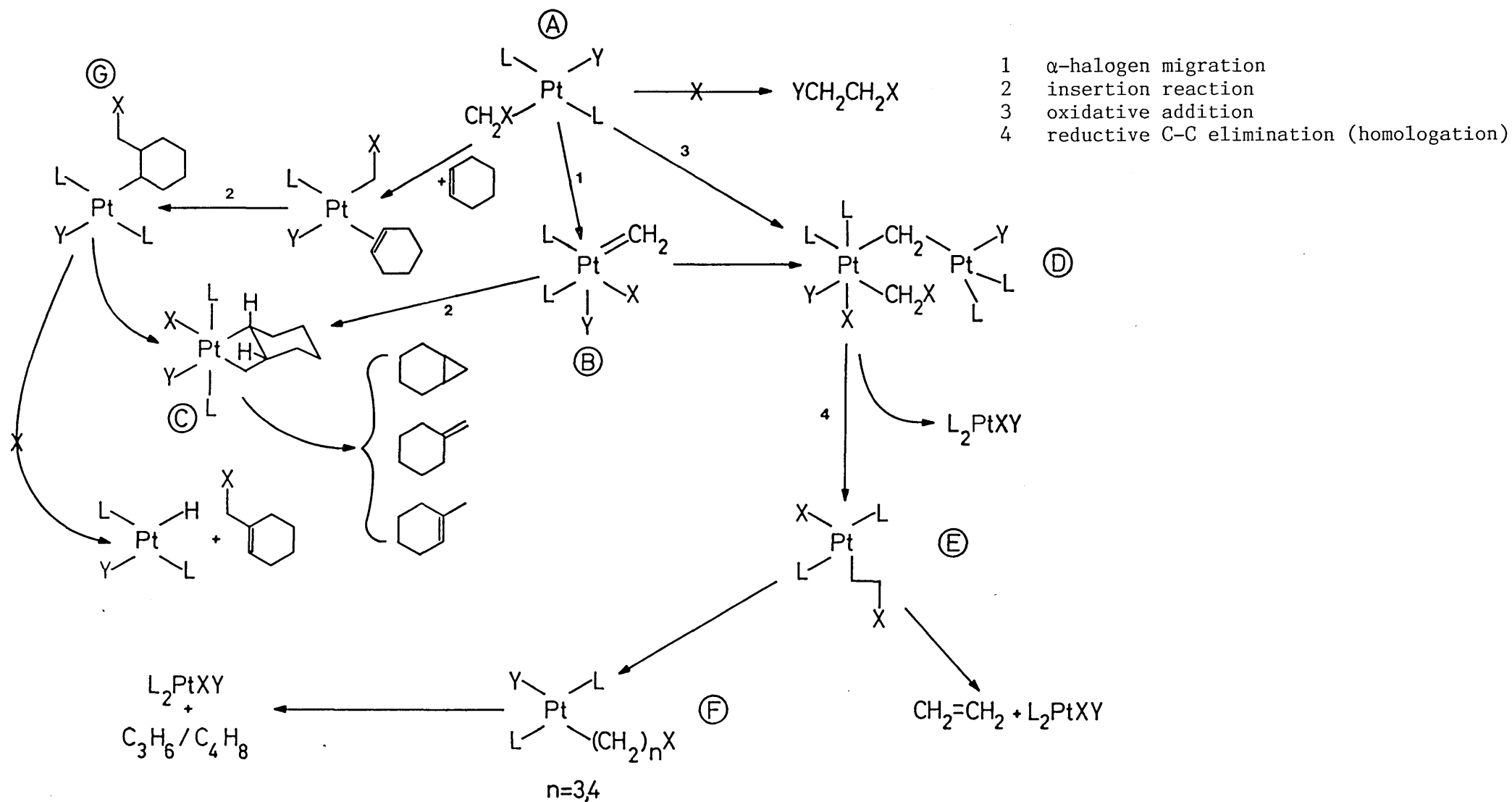
Based on all these observations, a possible reaction pathway for the thermolysis is outlined in Scheme 29.

The compound $L_2Pt(CH_2X)Y$ A rearranges via α -halogen migration to the five coordinate methylene species B. This very reactive species reacts with cyclohexene to yield C. Alternatively, C might be formed by migratory "insertion" into a platinum-carbon bond. Depending on the ensuing elimination sequence, norcarane, methylenecyclohexene and 1-methylcyclohexene and a dihalide platinum species are formed. Intermediate C explains the different isomer distribution of C_7H_{12} observed in Table 35. The methylene unit is not released. β -Elimination from C will yield methylenecyclohexane and 1-methylcyclohexene, and reductive elimination, norcarane.

In the absence of cyclohexene the intermediate species B might be expected to form a binuclear species D. Alternatively, oxidative addition of A to a second molecule of A might yield the same compound D. Reductive carbon-carbon elimination results in the 2-haloethyl compound E and elimination of L_2PtXY . E can either lose ethylene via β -halogen migration yielding L_2PtXY , or can form a further binuclear species and eliminate propene or butene and L_2PtXY .

Insertion of cyclohexene into the $Pt-CH_2$ bond to give G cannot be excluded, but is unlikely. G can either rearrange to C or eliminate 1'-halo-1-methylcyclohexene and yield the hydride $L_2Pt(H)I$. The latter two products were not detected.

Scheme 29 Thermolysis Mechanisms of trans-L₂Pt(CH₂X)Y



Similarly, the absence of $L_2Pt(H)I$ excludes the possibility of reductive elimination of halo-propene or halo-butene from F. This is in contrast to the presence of 5-chloro-1-pentene and the corresponding hydridoplatinum species in the thermolysis of $L_2Pt(\overline{CH_2})_3CH_2$ ($L = PBut_3$) in CH_2Cl_2 where significant amounts of $L_2Pt(CH_2Cl)Cl$ were also formed.^{1c} No detectable binuclear reductive elimination of 1,2-dihaloethane occurs.

The nature of the phosphine ligands and halides determines the equilibrium of the cyclohexene addition product C and the binuclear species D. In the case of $L = PEt_3$, $X = Y = I$ the latter appears to be favoured. Only traces of norcarane are found. For $L = PPh_3$ there is a significant mol% of norcarane and isomers (Table 35). The binuclear species D is more susceptible to steric congestion than B. Therefore a larger ligand is likely to favour C more.

Oxidative addition of methylhalides CH_3X to derivatives of Vaska's iridium complex $L_2Ir(CO)Y$ is faster for $X = I$ than for $X = Cl$.¹⁴ Similarly, oxidative addition of $L_2Pt(CH_2I)I$ to yield the binuclear species D will occur more readily than for the Cl-analogue. Therefore, a larger proportion of the available methylene groups is observed to yield cyclohexene adducts.

Formation of methane and ethane is thought to occur via hydrogen transfer to the methylene group from various sources, for example solvent, ligands. No deuterium studies have been undertaken to clarify this point.

3.5 Concluding Remarks

The phosphine ligand has a significant influence on the reactivity of the compounds trans- $L_2Pt(CH_2X)Y$. For $L = PPh_3$ addition of two equivalents of Ag^+ and one equivalent of L resulted in formation of the platinaindan. For $L = PEt_3$ the cyclisation is rendered impossible and only platinum-halide cleavage occurs. However, if $L = PMe_2Ph$ is added some metallacycle is detected. This result confirms initial platinum-halide bond scission and only subsequent isomerization will make platinaindan formation possible. It is interesting to note that once PMe_2Ph is in a position cis to $-CH_2X$ immediate cyclisation takes place. The primary platinum-halide cleavage with Ag^+ enables easy access to hydride formation $L_2Pt(CH_2X)H$ by adding $NaBH_4$. The hydrides once formed are very short lived.

$L_2Pt(CH_2X)Y$ ($L = PPh_3, PEt_3$; $X = Cl, I$; $Y = I$) are not ready alkylidene transfer reagents. The ability to react the CH_2 -moiety selectively with cyclohexene is impaired by competing homologation reactions producing C_2 -, C_3 - and C_4 -hydrocarbons. The extent of either reaction depends on the phosphine ligand and halide, but homologation is always predominant.

Best results for cyclohexene addition products were obtained for trans-(PPh_3) $_2Pt(CH_2Cl)I$. Larger yields might possibly be achieved with a larger phosphine ligand.

3.6 Experimental

Preparation of trans-Iodomethyl-iodobis(triethylphosphine)platinum(II)

An ethylene saturated solution of $(\text{PEt}_3)_2\text{Pt}(\text{oxolate})^*$ (300 mg, 0.75 mmol) in a 1:1 mixture of acetonitrile/benzene (100 ml) was irradiated for 4 h at room temperature to give the intermediate $[(\text{PEt}_3)_2\text{Pt}(\eta^2\text{-C}_2\text{H}_4)]$.

An equimolar amount of diiodomethane** (21 mg, 0.75 mmol) was added and stirred for 22 h at room temperature. The solvent was removed by evaporation, leaving a yellow oil that readily crystallized in a mixture of ether/methanol to give fine yellow needles. (Yield 20-50%), mp: 116°C. Found: C, 23.41; H, 4.64. Calc. for $\text{C}_{13}\text{H}_{32}\text{P}_2\text{Pt}$: C, 22.32; H, 4.58%.

The reference compound norcarane was synthesised by a well established route.⁸⁸

trans-(PPh_3)₂Pt(CH_2Cl)I and trans-(PPh_3)₂Pt(CH_2I)I were synthesised by Professor Zhen-Yun Yang and Dr G.B. Young.

Reactivities

All reactivity experiments were conducted on a NMR scale under light exclusion.

Halogen-Abstraction Reactions :

To a toluene-d⁸ solution of $(\text{PEt}_3)_2\text{Pt}(\text{CH}_2\text{I})\text{I}$ and one equivalent of

* Prepared according to Reference 95 (and references therein)

** It is important to use purified CH_2I_2

phosphine was added two equivalents of AgBF_4 in methanol- d^4 . The reaction was monitored by ^{31}P -NMR.

Reactions with NaBH_4 :

To a solution of $\text{L}_2\text{Pt}(\text{CH}_2\text{X})\text{Y}$ ($\text{L} = \text{PEt}_3, \text{PPh}_3$; $\text{X} = \text{Cl}, \text{I}$; $\text{Y} = \text{I}$) in toluene- d^8 a solution of NaBH_4 in methanol- d^4 was added at -30°C . The reaction was monitored by ^1H -NMR and ^{31}P -NMR at -30°C .

Thermolysis

Benzene solutions (0.4 ml) of known concentrations, n -hexane as standard and for methylene trapping reactions cyclohexene, were cannulated into tubes (as described in Section 1.9) and freeze/thaw degassed in three cycles. The tubes were sealed under vacuum and heated at 140°C for 4 days in a thermostatically controlled silicone oil bath.

The reactions mixtures were analysed via GC, GC/MS and ^{31}P -NMR.

GC-Analysis

Oven temperature was held at 100°C throughout the run. Length of run: 30 min, flow rate: 1 ml/min. (4 m column, 20% SE 30 on chromasorb D, mesh 80/100).

Retention indices are listed in Table 38.

Table 38 Retention Indices of Thermolysis Products of trans-L₂Pt(CH₂X)Y

Compound	Retention Index
methane	0.260
ethane/ethylene ^a	0.282
propylene	0.336
propane	0.334
<u>n</u> -butane	0.443
<u>trans</u> -2-butene	0.450
methylene-cyclohexane	2.28
3-methylcyclohexene	2.28
1-methylcyclohexene	2.51
cycloheptene	2.99
norcarane	3.22
dichloromethane	0.53
chloriodomethane	1.54
diiodomethane	4.73
<u>n</u> -hexane	1

a Could not be resolved under these conditions

CHAPTER FOUR

SYNTHESIS, SPECTROSCOPIC CHARACTERISATION AND SOME REACTIONS OF 1-ACETOXYALKYL DERIVATIVES OF IRON(II) AND MOLYBDENUM(II)

4.1 Introduction

So far we had only looked at square planar platinum compounds and their reactivities. In Chapter 3 attention had been focussed on α -functional platinum complexes $L_2Pt(CH_2X)Y$. In search of other easily substituted α -functional alkyl metals, we extended our studies to two different metals: iron and molybdenum.¹⁰³ As mentioned in Chapter 3, there have been several studies on α -functional alkyl metals such as platinum and other transition metals (for references, see Chapter 3).

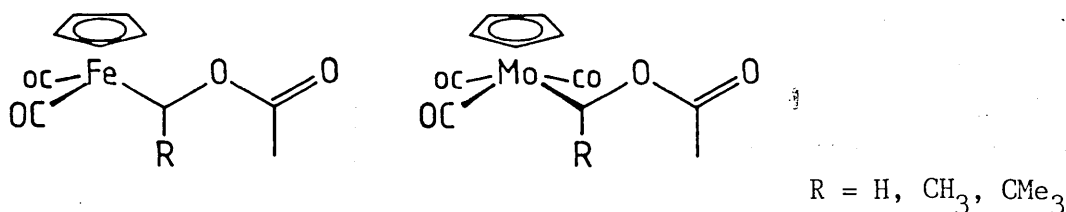
As alkyl group we chose an acetoxyalkyl ligand. It seemed attractive as precursor to an assortment of α -functional alkylmetals including hydroxy-alkyls, as well as offering a relatively unexplored class of α -functional organometals. It also seemed possible that such species might have intermediate rôles in metal catalysed homologation reactions such as the formation of ethylidene diacetate from methyl-acetate and synthesis gas.¹⁰⁴

Only two acetoxyalkylmetal derivatives have been reported so far. Green⁸³ in 1967 reported an indirect synthesis of $cp(CO)_2Fe(CH_2OCOCH_3)$ which has found synthetic application lately.¹⁰⁵ And during our investigations Lin prepared an analogous ruthenium complex.⁸⁵

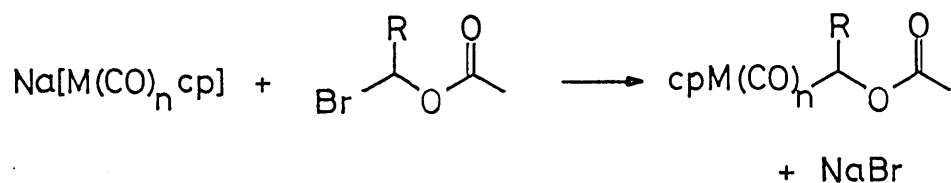
4.2 Synthesis and Spectroscopic Characteristics

4.2.1 Synthesis of $\text{cpM}(\text{CO})_n(\text{CHROCOCH}_3)$

For our investigations we chose the following series of compounds:



It is important to note that for $\text{R} = \text{H}$ and CMe_3 , there are no $\beta\text{-H}$ and greater kinetic stability should be expected. We developed a general and direct synthesis route of 1-acetoxyalkyl derivatives by reaction of the sodium salt of the metal with the 1-bromoalkylacetate



Reaction of bromomethylacetate with sodium cyclopentadienylcarbonylmetallates yielded acetoxymethyl metal species via a nucleophilic displacement of the bromide. The iron complex is a red oil at room temperature, at -20°C orange crystals are formed. The analogous molybdenum compound affords dark yellow to olive coloured crystals. Both compounds are moderately air-sensitive, but are thermally stable indefinitely at -20°C under inert atmospheres. Corresponding reaction with 1-bromoethylacetate is slower and produced $\text{cpM}(\text{CO})_n(\text{CHROCOMe})$ in lower yields.

Increased steric bulk and higher thermal lability due to β -hydrogen atoms are possible reasons for poorer yield. Both compounds form dark oils and decompose even below 0°C over several days. This made purification difficult, excluded elemental analysis and severely limited the range of reactivity studies. Both derivatives are extremely air-sensitive. 1-Bromo-tert-butylacetate failed to react, presumably because of steric hindrance.

All compounds were characterised by ^1H -, ^{13}C - NMR, I.R.- measurements and by mass spectrometry. Elemental analysis was only possible for acetoxymethylmetal derivatives.

4.2.2 Spectroscopic Characteristics of $\text{cpM}(\text{CO})_n(\text{CHROCOCH}_3)$

4.2.2.1 NMR-Data

All compounds display at least three characteristic resonances in their ^1H -NMR spectra. One, a singlet, at higher field derives from the hydrogens from the acetoxyl group. The position of the signal varies little and is not influenced by the metal centre or by different substituents on the α -carbon of the acetoxyl-alkyl ligand. The chemical shift of the η^5 -cyclopentadienyl moiety, a singlet, is affected by the metal but not the various substituents. Cp bound to Mo resonates 0.4–0.6 ppm lower field than the corresponding iron derivatives (Table 39).

The α -hydrogen(s) of the acetoxylalkyl group are similarly influenced by the different nature of the two metals. The presence of a α -methyl substituent has a deshielding effect and induces a downfield shift for the α -H signal relative to the acetoxymethyl homologues. The methyl group gives rise to a 1:3:3:1 quartet for the α -H-signal. The β -hydrogens themselves appear as the expected doublet, the shift again influenced by the metal.

These trends in chemical shifts for hydrogens close to the metal centre, as the metal is varied, must derive in part from the inductive effects of the $\text{M}(\text{C}_5\text{H}_5)(\text{CO})_n$ fragment and also from contributions to shielding by the nonbonding metal d-electrons. Although the $\text{Mo}(\text{CO})_3$ and $\text{Fe}(\text{CO})_2$ moieties are isolobal, without detailed calculations it is not clear to what extent the differing spatial extensions of 3d and 4d orbitals will be offset by the disparities in metal-ligand bond lengths. The simple view

Table 39 NMR Characteristics for Acetoxyalkylmetals

Complex	$\delta^1\text{H}^{\text{a}}$				$\delta^{13}\text{C}^{\text{a}}$					
	CHR	CH_3	C_5H_5	CH_3'	CHR	CH_3	C_5H_5	CH_3'	$\text{C} \equiv \text{O}$	$\text{C} = \text{O}$
$\text{CpFe(CO)}_2\text{CH}_2\text{OAc}^{\text{b}}$	4.88	1.76	4.01	–	53.72	21.2	85.34	–	216.05	170.44
$\text{CpFe(CO)}_2\text{CMeHOAc}^{\text{b}}$	5.31q ^c	1.74	4.24	1.29d ^c	68.08d	21.37	85.57	31.76	216.48	169.05
$\text{CpMo(CO)}_3\text{CH}_2\text{OAc}^{\text{b}}$	5.40	1.73	4.59	–	50.97	20.93	92.61	–	239.40 ^d 226.90 ^e	170.58
$\text{CpMo(CO)}_3\text{CMeHOAc}^{\text{b}}$	7.06q ^f	1.69	4.68	1.83d ^f	64.34	21.28	92.90	30.23	240.03 ^d 227.05 ^e	169.35

a in ppm relative to Me_4Si ; b in benzene- d_6 ; c $^3\text{J}(\text{H-H}) = 6 \text{ Hz}$; d trans to CHROAc ;

e cis to CHROAc ; f $^3\text{J}(\text{H-H}) = 7 \text{ Hz}$; g in acetone- d_6 ; h not measured.

is that the Mo(II) centre is a d^4 -species with three powerfully π -acidic carbonyl groups and is likely to be relatively deshielding - either by induction or by more contracted d-orbitals - than the corresponding d^6 Fe(II) system with only two carbonyl ligands.

The ^{13}C chemical shifts are less sensitive to the nature of the metal centre. In fact, the shifts for the carbon σ -bonded to Mo(II) are very slightly shielded relative to the iron congener. For the 1-acetoxyethyl complexes the expected downfield shift is found (Table 39).

The resonances of the CO ligands are not influenced by the alkyl ligand, but occur at significantly lower field for the Mo compounds.

Similar downfield shifts have been reported for related compounds and were interpreted as an indication of increasing retrodonative M-L π -bonding, consistent with the ^1H -NMR shift trends.¹⁰⁶

4.2.2.2 IR-Data

Of major diagnostic value are the ligand vibrations $\nu(\text{C} \equiv \text{O})$ and $\nu(\text{C} = \text{O})$. The absorption patterns of the two acetoxymethyl compounds are very similar. Very strong bands occur at 2010 and 1950 cm^{-1} for acetoxymethyl iron species, the corresponding $\nu(\text{C} \equiv \text{O})$ of the Mo congener appear at 2010 cm^{-1} and 1945 cm^{-1} . The ester carbonyl absorptions were found at 1730 and 1725 cm^{-1} respectively. These similarities are all the more remarkable since the coordination geometries and the apparent extent of M-C π -bonding differ.

Table 40 IR Characteristics for Acetoxyalkylmetals and Derivatives

Complex	Infrared Absorption (cm ⁻¹)										
CpFe(CO) ₂ CH ₂ OAc ^a	3950w 1370s	3110w 1270s	2980sh 1137s	2930m 1110vs	2860vs 1031s	2010vs 944s	1950vs 843m	1780s 833m	1730s 750vs	1435m	1420m
CpFe(CO) ₂ CMeHOAc ^a	3940w 1430w 1020sh	3110w 1415m 1000m	2980w 1367m 975m	2940m 1345w 945w	2850br 1325w 925m	1990vs 1240w 850m	1925vs 1180m 830m	1905sh 1100m 750w	1890s 1080m 645m	1765s 1060m 600s	1445w 1035s
CpMo(CO) ₃ CH ₂ OAc ^b	3940w 935m	3120w 855w	2010vs 830m	1945vs 820m	1725s 810m	1250s 705w	1165m 630w	1095s	1045m	995m	950m
CpMo(CO) ₃ CMeHOAc ^a	3940w 1425m	3120w 1370m	2950w 1240s	2920w 1190m	2870w 1100m	2020vs 1075m	1995s 1010m	1940vs 930m	1885w	1850vs 815s	1720s 775m

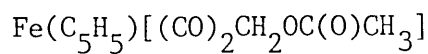
a thin film, KBr Plates; b Nujol mull, KBr Plates

The spectra for the acetoxyethyl are not matching and are more complex in the $\nu(\text{C} \equiv \text{O})$ region. Three bands are observed for the iron complex, while the molybdenum shows five (Table 40).

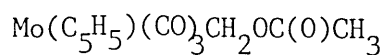
4.2.2.3 Mass Spectrometry

Only the acetoxymethyl complexes displayed sufficient thermal stability to allow characterisation by mass spectrometry. The salient features of their very similar fragmentation patterns appear in Table 41. Both species give rise to very weak molecular ions. Stepwise loss of carbonyl ligands occurs readily for both metals and some or all of these fragmentations give rise to metastable peaks. Scission of both of the C-O bonds in the ligand, generating $[(\text{C}_5\text{H}_5)\text{MCH}_2\text{O}]^+$ and $[(\text{C}_5\text{H}_5)\text{MCH}_2]^+$ is observed in each case; the former is more apparent for Mo, the latter for Fe. Both systems produce strong ion currents for $[\text{M}(\text{C}_5\text{H}_5)]^+$.

Table 41 Mass Spectroscopic Data for Acetoxymethylmetal Complexes



m/e	Rel.Int. (%)	Fragment
250	2	$\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2(\text{CH}_2\text{OAc})^+$
222	18	$\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})(\text{CH}_2\text{OAc})^+$
194	92	$\text{Fe}(\text{C}_5\text{H}_5)(\text{CH}_2\text{OAc})^+$
151	23	$\text{Fe}(\text{C}_5\text{H}_5)\text{CH}_2\text{O}^+$
133	85	$\text{Fe}(\text{C}_5\text{H}_5)\text{CH}_2^+$
121	100	$\text{Fe}(\text{C}_5\text{H}_5)^+$
56	49	Fe^+



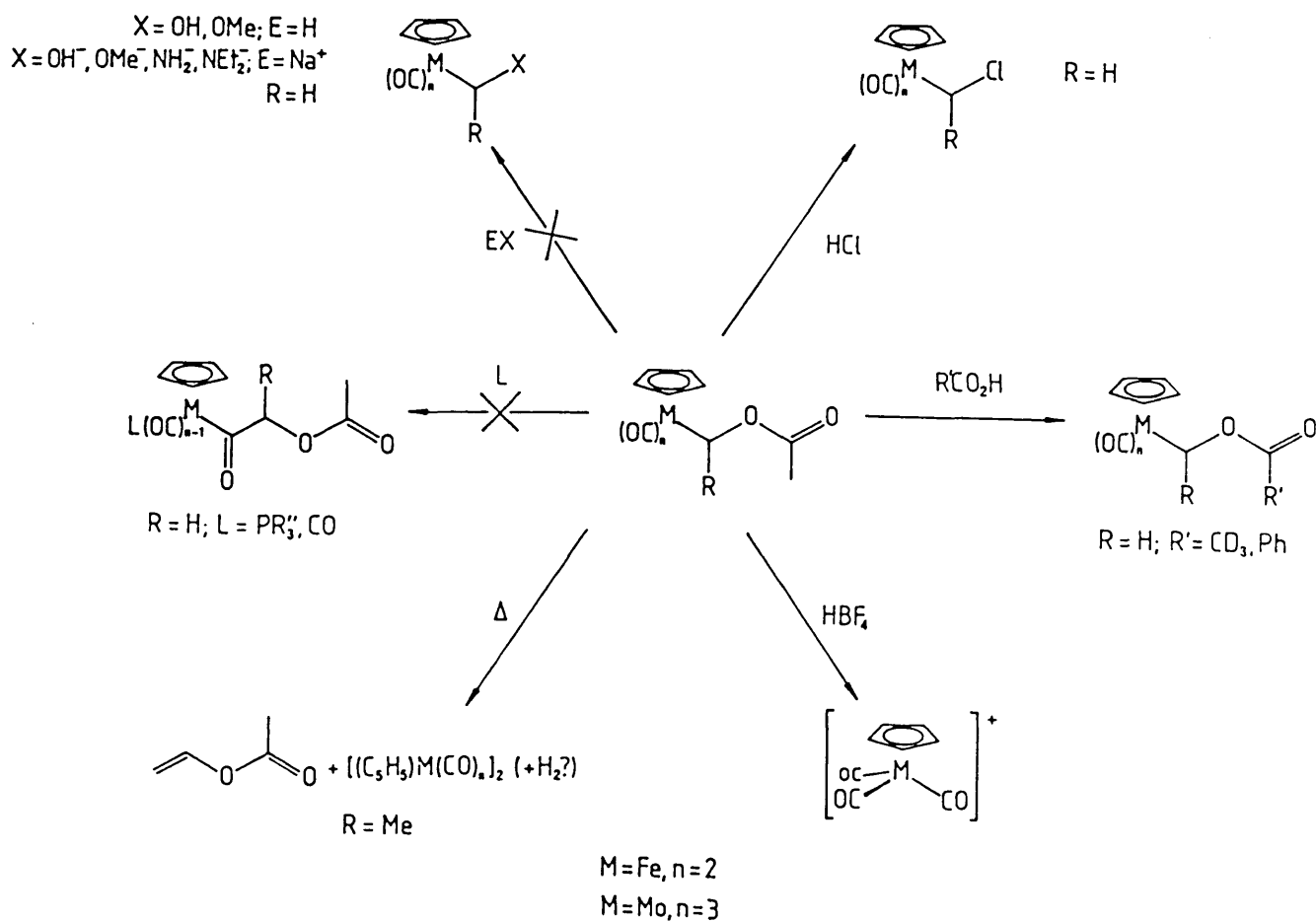
m/e	Rel.Int. (%)	Fragment
318	1	$\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3(\text{CH}_2\text{OAc})^+$
290	9	$\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_2(\text{CH}_2\text{OAc})^+$
262	18	$\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})(\text{CH}_2\text{OAc})^+$
234	60	$\text{Mo}(\text{C}_5\text{H}_5)(\text{CH}_2\text{OAc})^+$
191	100	$\text{Mo}(\text{C}_5\text{H}_5)\text{CH}_2\text{O}^+$
175	25	$\text{Mo}(\text{C}_5\text{H}_5)\text{CH}_2^+$
161	68	$\text{Mo}(\text{C}_5\text{H}_5)^+$
96	20	Mo^+

4.3 Reactivity of $\text{cpM}(\text{CO})_n(\text{CH}_2\text{OCOMe})$

There are two interesting sites of attack in the compounds $\text{cpM}(\text{CO})_n\text{CH}_2\text{OCOMe}$ - (a) $\text{M}-\text{CH}_2$ bond and (b) the CH_2-O bond. There have been extensive studies on electrophilic cleavage of the iron-carbon bond in the closely related system $\text{cpFe}(\text{CO})\text{L}(\text{R})$ (e.g. $\text{R} = \text{Me}, \text{Et}$; $\text{L} = \text{PPh}_3$) with mercury(II) salts and halogens.¹⁰⁷

In contrast we detected interesting reactivity patterns of the CH_2-O bond as is shown in Scheme 30.

Scheme 30 Reactivities of $\text{cpM}(\text{CO})_n(\text{CH}_2\text{OCOMe})$



The two acetoxymethyl compounds reacted smoothly with dry HCl to yield, under mild conditions, the chloromethyl derivatives*. Similar reactivity has been observed for $\text{cpFe(CO)}_2\text{CH}_2\text{OMe}$.⁸³ Similar carboxalate metathesis with carboxylic acid resulted from addition of a twofold excess of benzoic acid to the acetoxymethyl compounds.

The reaction was somewhat faster for the molybdenum analogue, however a maximum conversion of 80% was only possible over several days at room temperature**. Acetate exchange with acetic acid- d^4 was not observed under the same conditions. In neat acetic acid- d^4 , heated at 60°C a slow exchange up to 90% was observed. A catalytic amount of HBF_4 accelerated the exchange to completion within 24 hours. On a NMR-scale there was some indication that addition of excess p-toluene-sulphonic acid yielded the tosylate ester. Attempts to isolate these on a larger scale led only to decomposition. When the acetoxymethyl compounds were reacted with HBF_4 alone acetic acid and $[\text{Mcp(CO)}_n]\text{BF}_4^{108,109}$ were the only isolable, identifiable products.

* $\delta^1\text{H}$ -NMR rel. to TMS in d^6 -acetone: $\text{cpFe(CO)}_2\text{CH}_2\text{Cl}$ 5.02 ppm (5H, cp), 4.20ppm (2H, CH_2); $\text{cpMo(CO)}_3\text{CH}_2\text{Cl}$ 4.56ppm (5H, cp), 4.00ppm (2H, CH_2)

IR Characteristics (Nujol mull, KBr plates), $\nu(\text{cm}^{-1})$

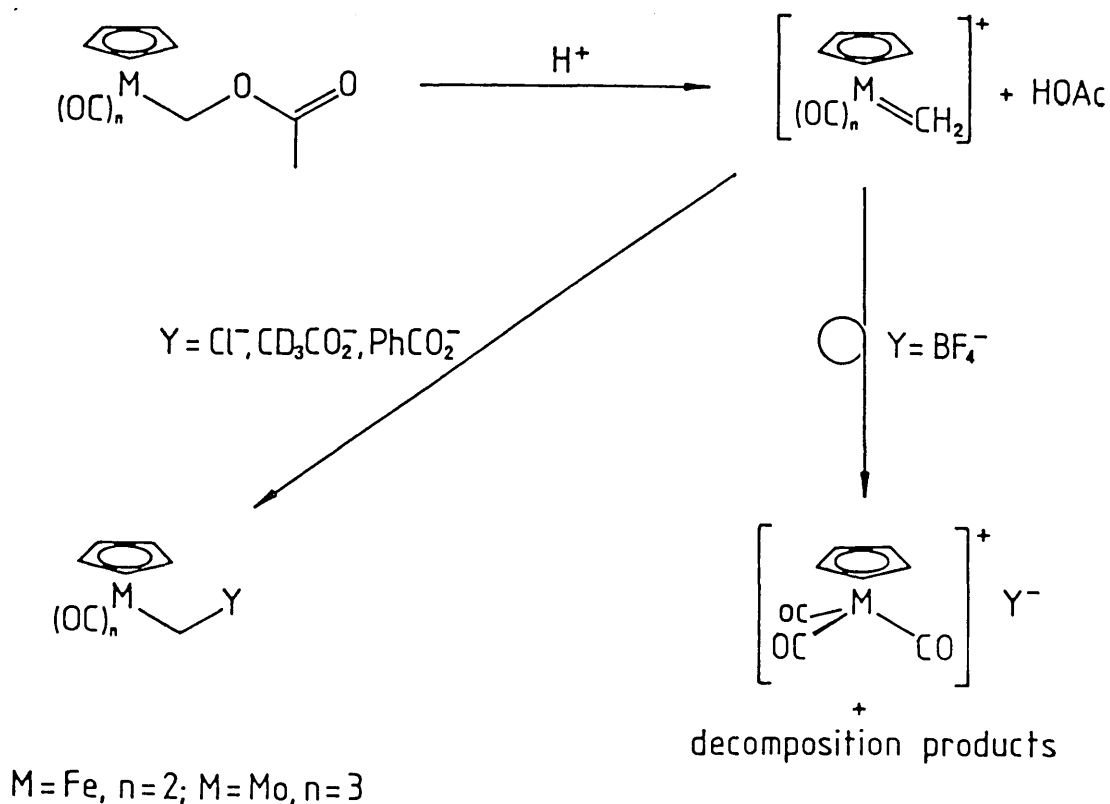
$\text{CpFe(CO)}_2\text{CH}_2\text{Cl}^b$	3960w	3120w	2060s	2025vs	1955vs	1945sh	1465m	1435m	1420m	1350vs	1340w
	1150m	1100m	1060vs	1040m	1000m	840s	835m	750m			
$\text{CpMo(CO)}_3\text{CH}_2\text{Cl}^b$	2040vs	1965vs	1950vs	1840vs	820m	722m					

** ^1H NMR data (benzene- d_6) for: $\text{Fe(C}_5\text{H}_5\text{)(CO)}_2\text{CH}_2\text{OC(O)Ph}$: 8.15 dd (2H, aromatic), 7.31-7.03 m (3H, aromatic), 5.48s (2H, CH_2), 4.21 (5H, C_5H_5); $\text{Mo(C}_5\text{H}_5\text{)(CO)}_3\text{CH}_2\text{OC(O)Ph}$: 8.105 dd (2H, aromatic), 7.16-6.88 m (3H, aromatic), 5.39s (2H, CH_2), 4.62s (5H, C_5H_5); free acetic acid appears at 1.57 ppm.

Organic esters do not generally undergo such transcarboxylation reactions easily. If the carbonium ion of the migrating alkyl moiety forms particularly readily, however, such exchange reactions have occasionally been observed.

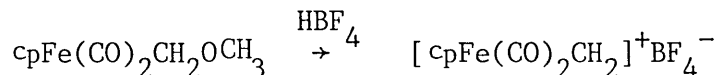
As has been seen before, the C-O bond is more susceptible to protolytic cleavage than the M-C bond. It is proposed that a carbene metal cation of the type $[\text{Mcp}(\text{CO})_n\text{CH}_2]^+$ is formed transiently. Thus, all the protolytic reactions proceed via electrophilic attack on the ester oxygen, causing C-O scission to yield acetic acid. In a next step the carbene metal species reacts with a nucleophile (as shown in Scheme 31).

Scheme 31 Electrophilic Attack Via Carbene Intermediate



Carbene intermediates were not detected either directly or by their reaction in the presence of cyclohexene.

Several years ago, Jolly and Pettit reported the apparent generation of the cationic iron carbene complex:¹¹⁰



It was shown that the methylene group reacted with olefins to give cyclopropanes. So far though attempts to observe $[\text{CpFe(CO)}_2=\text{CH}_2]^+$ have never been successful, and has been said to be best regarded as transient intermediates.¹¹¹ Brookhart has established that even at low temperature, immediate disproportionation occurs with formation of equimolar amounts of $[\text{cpFe(CO)}_2(\text{C}_2\text{H}_4)]^+$ and $[\text{cpFe(CO)}_2]^+$.¹¹² Different and more stable carbene precursors have been suggested, e.g. $[\text{cpFe(CO)}_2\text{CH}_2\text{S}(\text{CH}_3)_2]\text{BF}_4$.¹¹³ The latter is considered a convenient cyclopropanation reagent. Very recently it has been discovered that $\text{cpM(CO)}_n(\text{CH}_2\text{Cl})$ ($\text{M} = \text{Fe}$, $n = 2$; Mo , $n = 3$) generated conveniently methyldiene salts which readily react further.¹¹¹

In contrast to organic esters no hydrolysis of the acetoxymethyl derivatives to give the hydroxymethyl derivatives was achieved. The transesterification to give the known methoxy methylmetals with methanol with or without a catalytic amount of HBF_4 did not succeed.

Treatment of the methylacetate compounds with an equimolar amount of KOH , even in the presence of 18-crown-ether did not yield a hydroxymethyl species. Reactions with NaOMe , NaNH_2 , and NaNEt_2 proved equally unsuccessful. Insertion of CO into the metal-carbon bond

was not observed either by addition of PPh_3 or PMe_3 to induce CO migration or under 120 atm of CO.

This inertness is not surprising. The methyl complex $\text{cpFe(CO)}_2\text{Me}$ forms its acetyl derivative only at high CO pressure and temperatures (325 atm, approaching 97°C).¹¹⁴ Recently, three procedures to facilitate CO insertion have been reported for the above mentioned compound.¹¹⁵ They are (a) incorporation of different ancilliary ligands, (b) choice of appropriate solvent (polar solvents seem to enhance insertion rate) and (c) addition of an acid catalyst.

Despite these findings for the methyl derivatives, it was also noted that the same was not applicable for substituted methyls.

4.4 Thermolysis of $\text{cpM(CO)}_n(\text{CHROCOMe})$

At room temperature under dark and anaerobic conditions, the acetoxyethyl complexes decompose to give vinylacetate and the dimer $[\text{M(CO)}_n\text{cp}]_2$ in 1:2 ratio via β -hydrogen elimination. Presumably, hydrido-metal complexes are formed. A subsequent binuclear elimination of dihydrogen gives rise to the dimeric products (gas evolution was not monitored). Thermolytic rearrangement of the methylacetate compounds demanded much higher temperatures and led to a complex variety of organic products. Methylacetate was not found, but small amounts of acetic acid were traced, further indication that the C-O bond is thermally more liable than the M-C bond.

4.5 Experimental

Reaction products were separated on a 25 cm column of ODS bonded on 5 μ silica, eluting with methanol and monitoring at 215 nm. Elemental analyses were by Pascher, Bonn.

Preparation of Bromomethylacetate¹¹⁶

Paraformaldehyde (12 g, 0.4 mol) was mixed with acetyl bromide (30 cm³, 0.4 mol) under dry nitrogen. A catalytic amount of ZnCl₂ (0.2 g, 1.5 mmol) was added. When the considerably exothermic reaction had subsided, the reaction was stirred for a further 3 hr at 90–95°C. Pure bromomethylacetate was recovered from the reaction mixture by distillation (b.p. 132–138°C, 760 Torr). ¹H-NMR (chloroform-d): 5.76 (s, 2H), 2.11 (s, 3H).

Preparation of 1-Bromoethylacetate

This was achieved by a modification of the method in Reference 116; no zinc catalyst was employed. A 25% excess of acetaldehyde (36 cm³, 35.2 g, 0.8 mol) was slowly added to stirred acetyl bromide (38 cm³, 73.8 g, 0.6 mol) at 40°C and with exclusion of light. The mixture was stirred for a further 2 hr at 40°C, and the product was purified by distillation at reduced pressure (30°C at 6 Torr). ¹H-NMR (chloroform-d): 6.67 (q, 1H), 2.1 (s, 3H), 2.00 (d, 3H).

Preparation of Acetoxymethyl-Cyclopentadienyldicarbonyl Iron (II)

To a stirred 0.4% sodium amalgam [prepared from 23 cm³ mercury and

0.96 g (43 mg-atom) sodium] was added a solution of $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2]_2$ (6.4 g, 20 mmol) in thf (80 cm³). The mixture was stirred for 24 hr. The yellow ethereal solution of $\text{Na}[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2]$ was filtered off and to it was slowly added at ambient temperature, bromomethylacetate (5.4 cm³, 8.82 g, 57.8 mmol). These reagents were stirred for a further 24 hr. The solvent was removed at reduced pressure and the residue extracted with petroleum ether. The supernatant was filtered off and the solvent once more evaporated leaving a red oil, which, from its ¹H-NMR spectrum, was predominantly the desired product. Purification was achieved by liquid chromatography at 0°C on grade A activated alumina.

Two yellow by-products were eluted first, using petroleum ether and $\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2[\text{CH}_2\text{OC}(\text{O})\text{Me}]$ was eluted as a third fraction using 1:1 petroleum ether/diethyl ether. The compound is an orange-red oil at ambient temperature but is crystalline at -20°C. (Yield 7.6 g, 76% prior to chromatography). Found; C, 47.91; H, 4.03; Calc. for $\text{C}_{10}\text{H}_{10}\text{O}_4\text{Fe}$: C, 48.04; H, 4.04%.

Preparation of 1-Acetoxyethylcyclopentadienyldicarbonyliron(II)

A solution of $\text{Na}[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2]$ (40 mmol) in thf (100 cm³) prepared as above was very slowly added to a vigorously stirred sample of 1-bromoethylacetate (6 cm³, 40 mmol) at -78°C. The mixture was stirred for 4 hours at this temperature, and then allowed to reach ambient. The solvent was evaporated at reduced pressure leaving an oily residue. This was extracted with petroleum, filtered and concentrated under vacuum to a

dark red gum. Purification by chromatography at 0°C on alumina as described above afforded a dark red oil. The thermal lability of this compound at ambient temperatures precluded elemental analysis.

Preparation of Acetoxymethylcyclopentadienyldicarbonylmolybdenum(II)

To $\text{Na}[\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3]$, in thf (70 cm³), prepared from $[\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3]_2$ (2.0 g, 4 mmol) and a 0.2% sodium amalgam (8 cm³) was slowly added bromomethylacetate (1.2 cm³, 8 mmol). The mixture was stirred for 24 hr before the solvent was evaporated at reduced pressure. The brown residue was extracted with 40–60° petroleum ether (40 cm³) the supernatant filtered off and evaporated to dryness, leaving a dun oil, which crystallised on cooling. Recrystallisation from 1:1 ether/petroleum ether yielded dark yellow crystals of $\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3[\text{CH}_2\text{OC}(\text{O})\text{Me}]$ (yield 2.3 g, 91.2%). Found: C, 41.42; H, 3.20. Calc. for $\text{C}_{10}\text{H}_{10}\text{O}_5\text{Mo}$: C, 41.53; H, 3.17%.

Preparation of 1-Acetoxyethylcyclopentadienyldicarbonylmolybdenum(II)

$\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3[\text{CHMeOC}(\text{O})\text{Me}]$ was prepared by the same procedure as $\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3\text{CH}_2\text{OC}(\text{O})\text{Me}$ except that the petroleum extract was purified by chromatography at 0°C on grade A activated alumina. The first (unidentified) product was eluted with 40–60° petroleum ether; the second, and desired, product with 1:1 ether/petroleum ether. This was recovered as red/brown oil (yield 0.4 g, 16%). The high thermal lability even at ambient temperature precluded elemental analysis.

Reaction of $\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2[\text{CH}_2\text{OC}(\text{O})\text{Me}]$ with Hydrogen Chloride

Dry, gaseous HCl was passed into a solution of $\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2-[\text{CH}_2\text{OC}(\text{O})\text{Me}]$ (0.20 g, 0.8 mmol) in 40–60° petroleum ether (40 cm³) for 15 min. The solvent was evaporated at reduced pressure, yielding an orange oil. Orange crystals of $\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2\text{CH}_2\text{Cl}$, identified by its NMR and IR characteristics,⁸³ were obtained from 40–60° petroleum (yield 0.15 g, 83%).

Reaction of $\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3[\text{CH}_2\text{OC}(\text{O})\text{Me}]$ with Hydrogen Chloride

Dry, gaseous HCl was bubbled into a solution of $\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3-[\text{CH}_2\text{OC}(\text{O})\text{Me}]$ (0.13 g, 0.4 mmol) in 40–60° petroleum ether (30 cm³) for 20 min. The supernatant was filtered from a small amount of fine brown precipitate. The solvent was evaporated to give $\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3\text{CH}_2\text{Cl}$, pure by NMR (yield 0.11 g, 93%).

Reaction $\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3[\text{CH}_2\text{OC}(\text{O})\text{Me}]$ with HBF_4

To a stirred solution of $\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3[\text{CH}_2\text{OC}(\text{O})\text{Me}]$ (0.085 g, 0.3 mmol) in diethyl ether (40 cm³) at ambient temperature was dropwise added an ethereal solution of HBF_4 (1 cm³ of 0.4 M solution, 0.4 mmol). The mixture was stirred for 30 min. and the solvent reduced in volume and cooled. Red crystals of $[\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3]\text{BF}_4$ were identified from their published characteristics (yield 0.076 g, 76%).¹⁰⁸ A violet precipitate, identified as $[\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3]_2$ may also be produced on longer stirring. Acetic acid was the major organic byproduct of the reaction, characterised by HPLC analysis of the reaction mixture and by its ¹H-NMR spectrum.

Reaction of $\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2[\text{CH}_2\text{OC}(\text{O})\text{Me}]$ with HBF_4

To a stirred solution of $\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2[\text{CH}_2\text{OC}(\text{O})\text{Me}]$ (0.100 g, 0.4 mmol) in diethyl ether (10 cm^3) was slowly added, at ambient temperature, a solution of HBF_4 in the same solvent (3 cm^3 of 0.28 M, 0.84 mmol). A red oil separated immediately. The supernatant was removed by cannula, and the red oil concentrated in vacuo. The characteristics of the resulting crystalline material agreed closely with those reported for $[\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_3]\text{BF}_4$.¹⁰⁹ Acetic acid was identified by HPLC and ^1H -NMR as the predominant organic by-product.

Carboxylate Exchange on $\text{Fe}(\text{C}_5\text{H}_5)(\text{CO})_2[\text{CH}_2\text{OC}(\text{O})\text{Me}]$ and $\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3[\text{CH}_2\text{OC}(\text{O})\text{Me}]$

These reactions were monitored by ^1H -NMR in an appropriate solvent (benzene- d_6) to which the carboxylic acid was added, or in acetic acid- d_4 . The appearance of the characteristic signal for the methyl substituent of $\text{CH}_3\text{CO}_2\text{H}$ (2.08 ppm in acetic acid- d_4) was used to monitor the rate and extent of exchange. In addition, the spectroscopic characteristics of the organometallic product were verified.

Carbonyl Insertion Studies

Two approaches were used. (i) The acetoxymethylmetal (ca. 3 mmol) was dissolved in acetone (10 cm^3) and maintained at 23°C in a sealed reactor under an atmosphere of CO (120 atm). The mixture was stirred overnight. There was no reduction in gas pressure. The solution was recovered, the solvent removed and the residual material characterised by NMR and IR spectra.

(ii) The metalloester (ca. 1 mmol) was dissolved in acetone or nonane and a 5-fold excess of tertiary phosphine introduced. The mixture was heated to 50 or 90°C overnight. The solvent was evaporated and the residual material was spectroscopically analysed.

Thermal Decomposition

Toluene solutions of known concentrations of the 1-acetoxymethyl complexes were decomposed under dark and anaerobic condition at 55°C. The complex array of organic products was analysed by HPLC, acetic acid was the only identifiable product. 1-acetoxyethyl complexes were cleanly decomposed at room temperature under dark and anaerobic conditions. Vinylacetate was identified by HPLC.

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