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PLATINACYCLOBUTANE CHEMISTRY

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CONTENTS

A. INTRODUCTION

In 1949, Walsh suggested that there is considerable delocalisation of electrons in the cyclopropane ring and similarities in the chemical behaviour of cyclopropane and ethylene could thus be rationalised [1]. Since ethylene had long been known to form complexes with transition metals, Tipper examined the ability of cyclopropane to form such complexes. In 1955 he reported [2] that cyclopropane reacted with hexachloroplatinic (IV) acid, $H_2[PtCl_6]$, in acetic anhydride to give a compound, (I), of empirical formula $PtCl_2(C_3H_6)$,

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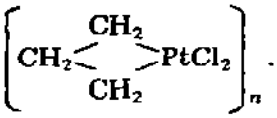
which he considered was probably a dimeric cyclopropane complex of platinum(II) chloride analogous to the famous Zeise's dimer $[\{PtCl_2(C_2H_4)\}_2]$. This conclusion was supported by the observation that reaction of (I) with aqueous potassium cyanide led to the quantitative evolution of cyclopropane, and that the infrared spectrum gave two C—H stretching frequencies similar to those found in free cyclopropane.

Tipper also reported that (I) was insoluble in most common organic solvents and that it formed a bis(pyridine) complex, (II), of formula $[PtCl_2(C_3H_6)(C_5H_5N)_2]$ with pyridine [2]. Chatt noted that these properties did not accord with those of Zeise's dimer which is moderately soluble and which forms the mono(pyridine) complex $[PtCl_2(C_2H_4)(C_5H_5N)]$ with pyridine. He therefore reinvestigated the complexes, and, on the basis of infrared and ^1H NMR spectroscopic data, suggested [3] that the cyclopropane ring had opened to give the platinum(IV) derivative



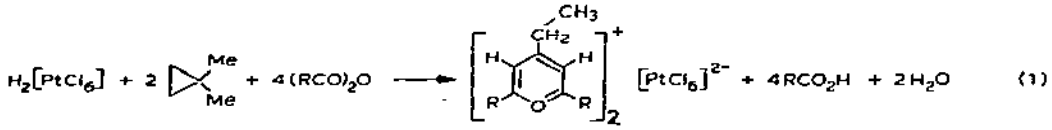
This would be expected to be a chloride-bridged polymer with 6-co-ordinate platinum atoms analogous to the well-known alkylplatinum(IV) halides such as $[(Me_3PtCl)_4]$, and would be expected to form the octahedrally co-ordinated $[PtCl_2(CH_2CH_2CH_2)(C_5H_5N)_2]$ on reaction with pyridine. The formulation of these compounds as platinacyclobutanes was subsequently confirmed by X-ray crystallographic studies by Gillard and co-workers [4]. Interest in the chemistry of these strained-ring compounds has grown steadily since that time, and an added interest has arisen as a result of the implication of metallacyclobutanes in several transition metal catalysed reactions. These will be discussed in a later section of this review.

B. SYNTHESIS OF PLATINACYCLOBUTANES

(i) Platinum(IV) derivatives

(a) Polymeric derivatives typified by $[\{PtCl_2(CH_2CH_2CH_2)\}_n]$

Tipper's original synthesis of $[\{PtCl_2(CH_2CH_2CH_2)\}_n]$ by reaction of cyclopropane with $H_2[PtCl_6]$ in acetic anhydride cannot be used to prepare substituted derivatives. The corresponding complex $[\{PtBr_2(CH_2CH_2CH_2)\}_n]$ can be prepared in this manner [5], but substituted cyclopropanes give rise to pyrylium ion salts rather than platinacyclobutanes (eqn. 1, R = Me).

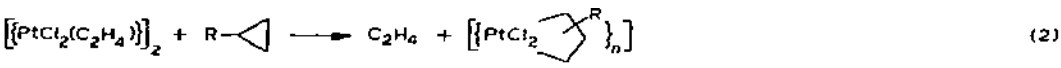


(1)

Similar products are formed from other methyl-substituted cyclopropanes,

and it is clear that the $[PtCl_6]^{2-}$ ion plays no direct part in the reactions but simply acts as a counter-ion [6].

A more general synthetic route, discovered by McQuillin and co-workers [7,8], involves reaction of a cyclopropane derivative with Zeise's dimer $[\{PtCl_2(C_2H_4)\}_2]$ (eqn. 2).



(2)

Owing to the low solubility of the polymeric products, it was not possible to determine directly the position of the substituent R [9]. Many more derivatives have been prepared by this general method and are given in Table 1.

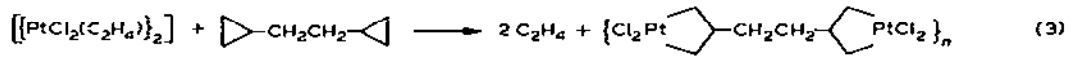
Of particular interest was the observation that electron-releasing groups, R, accelerated the reaction of eqn (2), as determined by allowing two different cyclopropane derivatives to compete in reaction with Zeise's dimer [7,9]. When strongly electron-withdrawing groups were present, e.g. R = CO_2Me, CN or COMe, no reaction occurred and the corresponding platinacyclobutanes could not be prepared [9].

TABLE 1

Tetrameric platinacyclobutanes, $[\{PtCl_2(cyclopropane)\}_4]$ prepared from $[\{PtCl_2(C_2H_4)\}_2]$ and cyclopropanes

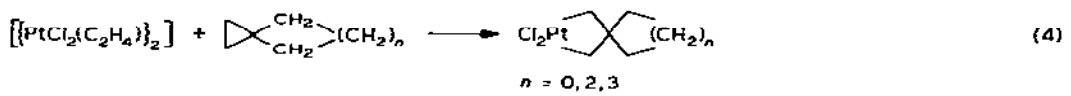
R	Solvent	m.p. (°C) $(RC_3H_5)PtCl_2$	Ref.
H	CH_2Cl_2	148 d	8, 10
Me	thf		11
Et	Et_2O		12
^iPr	Et_2O		12
Bu	thf		11
n-C_6H_{13}	Et_2O	120 d	8, 9
$PhCH_2$	Et_2O	123 d	8, 9
Ph	Et_2O	135 d	8, 9, 13
4-MeC_6H_4	Et_2O	125 d	8, 9, 13
2-MeC_6H_4	Et_2O		13
2-$NO_2C_6H_4$	Et_2O	148 d	8, 9
4-$MeOC_6H_4$	thf		13
4-$EtOC_6H_4$	thf		13
R, R′		$(RR'C_3H_4)PtCl_2$	
1,1-Me_2	Et_2O, thf		11, 12
trans-1,2-Me_2	Et_2O, thf		11, 12
trans-1-Me-2-Bu	Et_2O	119 d	8, 9
trans-1-Me-2-Ph	thf		11
trans-1,2-Ph_2	Et_2O	163 d	8, 9
cis-1,2-Ph_2	Et_2O		14
trans-1,2-(4-$MeC_6H_4)_2$	Et_2O		11
R, R′, R″		$(RR'R''C_3H_3)PtCl_2$	
1,1,2-Me_3	Et_2O		12

1,2-Dicyclopropylethane gave a bis(platinum) derivative according to eq. (3) [9],



(3)

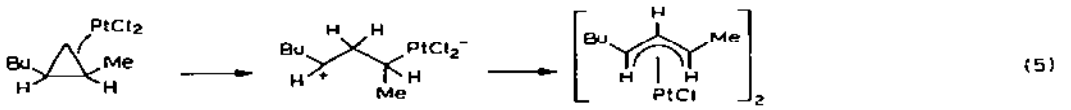
while spiro[2,*n*]alkanes (*n* = 2, 4, 5) reacted according to equation (4) [15].



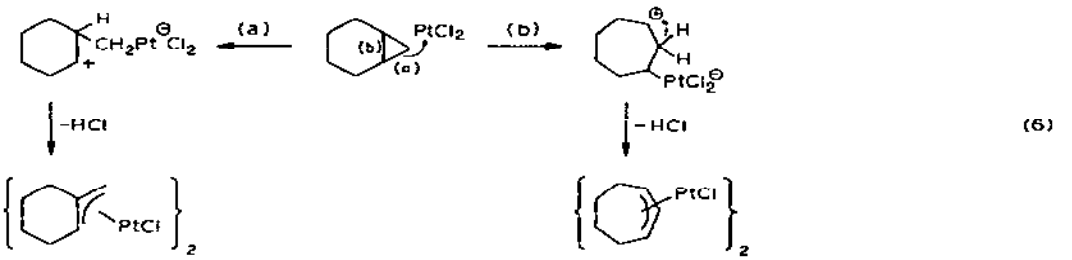
(4)

The most commonly used solvent for these reactions is diethyl ether, but tetrahydrofuran is more convenient in many cases since both product and starting material are soluble whereas neither is easily soluble in diethyl ether. Dichloromethane has also been used as solvent with some success. The reaction temperature must be less than about 50°C since extensive decomposition occurs in solution above this temperature, and solvents should be dry and free of peroxide impurities for best yields.

As noted above, electron-withdrawing groups on the cyclopropane inhibit reaction, and steric effects also appear to be important. Thus, 1,1,2,2-tetramethylcyclopropane failed to react with Zeise's dimer [12] probably due to steric hindrance by the methyl groups. *cis*-1,2-Dialkylcyclopropanes either fail to react with Zeise's dimer [12] or apparently yield π-allylplatinum complexes [9] (eqns. 5,6).

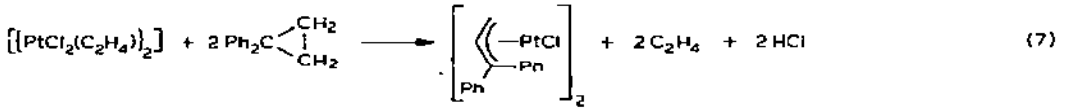


(5)



(6)

π-Allylplatinum complexes may also be formed from arylcyclopropanes in some cases, e.g. from 1,1-diphenylcyclopropane [7] or from *trans*-1,2-bis(2-methoxyphenyl)cyclopropane [11], eq. (7).

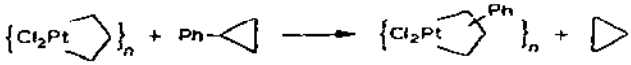


(7)

Despite the above limitations, McQuillin's method is by far the most versa-

tile for synthesis of platinum(IV) metallacyclobutanes.

Since one cyclopropane will displace another from platinacyclobutanes, another synthetic method is obtained as illustrated in eqns. (8) and (9) [16–18].



(8)

(9)

(b) Monomeric derivatives typified by $[\overbrace{PtCl_2(CH_2CH_2CH_2)}(C_5H_5N)_2]$

Complexes of this kind are readily prepared by reaction of the polymeric halogen-bridged platinacyclobutanes described above with nitrogen-donor ligands. The complexes are soluble and so can be readily characterised using NMR spectroscopy. Some examples are given in Tables 2–4.

Complexes with oxygen-donor ligands may be formed in solution but can rarely be isolated. Thus $[\{\overbrace{PtCl_2(CH_2CH_2CH_2)}\}_n]$ appears to be monomeric when dissolved in tetrahydrofuran and is probably present as the solvate $[\overbrace{PtCl_2(CH_2CH_2CH_2)}S_2]$, S = tetrahydrofuran, but evaporation of the solvent gives only the initial polymeric compound [17]. 1,4-Dioxane does give an isolable complex, however, (Table 2) which may be dimeric with bridging dioxane ligands [5]. Dissolution of $[\{\overbrace{PtCl_2(CH_2CH_2CH_2)}\}_n]$ in water gives probably $[\overbrace{PtCl_2(CH_2CH_2CH_2)}(H_2O)_2]$, which behaves as an acid in solution, and in hydrochloric acid it is likely that the complex ion $[\overbrace{PtCl_4(CH_2CH_2CH_2)}]^{2-}$ is formed but then decomposes to $[PtCl_4]^{2-}$ [3].

The co-ordination chemistry of the platinum(IV) metallacyclobutanes is limited to complexes with hard bases of low *trans*-effect, such as oxygen- and nitrogen-donors and chloride or bromide. Reaction with soft ligands leads to

TABLE 2

Monomeric platinacyclobutanes, $[PtX_2(CH_2CH_2CH_2)L_2]$

X	L	m.p. (°C)	Ref.
Cl	C_5H_5N	140–145 d	3
Cl	1/2(bipy)	340–355 d 230–240 d	3 5
Cl	1/2(1,4-dioxane)	110–125 d	5
Cl	NH_3	130 d	19
Cl	1/2(phen)	224 d	20
Br	C_5H_5N	140 d	5
Br	NH_3	105–110 d	19

TABLE 3

Platinacyclobutanes, $[PtCl_2(C_3H_5R)L_2]$

R [a]	L	m.p. (°C)	Ref.
2-Me	C_5H_5N	112	11, 21
2-Me	4-MeC_5H_4N	147 d	21
2-Me	3-MeC_5H_4N	120	21
2-Me	1/2(phen)	302 d	21
2-Et	C_5H_5N	—	12
2-^{i}Pr	C_5H_5N	—	12
2-Bu	C_5H_5N	132 d	21
2-hexyl	C_5H_5N	125	8, 9
2-$PhCH_2$	C_5H_5N	114	8, 9
2-Ph	C_5H_5N	130 d	8, 9
1-Ph	C_5H_5N	130	13
2-Ph	1/2(tmed)	172	13
1-Ph	1/2(tmed)	129	13
2-Ph	1/2(bipy)	235 d	13
1-Ph	1/2(bipy)	229 d	13
1-(4-MeC_6H_4)	C_5H_5N	107	8, 9
2-(2-$NO_2C_6H_4$)	C_5H_5N	220 d	8, 9
2-(2-MeC_6H_4)	C_5H_5N	128 d	13
1-(4-$MeOC_6H_4$)	C_5H_5N	135	13

[a] Prefix 1 or 2 indicates R on carbon α- or β- to platinum respectively. Where mixtures of isomers are present, the dominant isomer is given.

TABLE 4

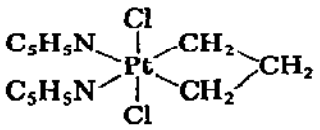
Platinacyclobutanes, $[PtCl_2(C_3H_4RR')L_2]$

R, R′	L	m.p. (°C)	Ref.
2,2-Me_2	C_5H_5N	—	11, 12, 21
2,2-Me_2	1/2(bipy)	125 d	21
2,2-Me_2	1/2(phen)	175 d	21
trans-1,2-Me_2	C_5H_5N	133 d	11, 12, 21
trans-1,2-Me_2	1/2(phen)	252 d	21
trans-1-Me-2-Ph [a]	C_5H_5N	122 d	11, 21
trans-1,2-Ph_2 [b]	C_5H_5N	116	8, 9, 11
trans-1,2-Ph_2 [b]	4-^{t}BuC_5H_4N		11
trans-1,3-(4-$MeC_6H_4)_2$ [c]	C_5H_5N		11
trans-1,3-(4-$MeC_6H_4)_2$ [c]	4-^{t}BuC_5H_4N		11

[a] As mixture with *trans*-1-Ph-2-Me.
[b] As mixture with *trans*-1,3-Ph_2.
[c] As mixture with *trans*-1,2-(4-$MeC_6H_4)_2$.

reductive elimination of cyclopropane and formation of the platinum(II) complex $[PtX_2L_2]$. Ligands which give this type of reaction with $[\{PtCl_2(CH_2CH_2CH_2)\}_n]$ include carbon monoxide [9], alkenes [7,10,22,23] trialkylphosphines, -arsines and -stibines [3,7,22] dialkylsulphides, dimethylsulphoxide [22] and iodide [3] and cyanide ion [2,3]. These ligands will also displace cyclopropane from $[PtCl_2(CH_2CH_2CH_2)(C_5H_5N)_2]$ provided that the ligand is able to compete with pyridine for the co-ordination sites on platinum. Complexes with chelate ligands $[PtCl_2(CH_2CH_2CH_2)(L\frown L)]$, $L\frown L$ = 2,2′-bipyridine or 1,10-phenanthroline, are often stable towards these soft ligands because the chelate ligand is not readily displaced [22].

The complex $[PtCl_2(CH_2CH_2CH_2)(C_5H_5N)_2]$ has been shown to have structure (II), with *trans* chloride and *cis* pyridine ligands [4]



(II)

Although Chatt and co-workers initially proposed the alternative structure with *cis* chloride and *trans* pyridine ligands, all complexes $[PtX_2(CH_2CH_2CH_2)L_2]$ are now thought to have structures analogous to (II), and this has been confirmed by X-ray crystallography for $[PtCl_2(CHPhCHPhCH_2)(C_5H_5N)_2]$ [24].

Further limitations to the co-ordination chemistry of these platinacyclobutanes arise from the observation that bulky nitrogen-donor ligands such as 2-methylpyridine or 2,6-dimethylpyridine and weakly co-ordinating ligands such as methyl cyanide induce decomposition to ylide or alkene complexes of platinum(II), by mechanisms involving initial ligand dissociation followed by α- or β-hydrogen elimination [11,21]. Such decomposition occurs readily even with the ligand pyridine if the platinacyclobutane is heavily substituted, for example in $[PtCl_2(CHMeCMe_2CH_2)(C_5H_5N)_2]$ [25,26].

The oxygen- or nitrogen-donor ligands in complexes (II) are labile and are often easily displaced by other nitrogen-donor ligands. Thus in $[PtCl_2(CH_2CH_2CH_2)(C_5H_5N)_2]$ the co-ordinated pyridine is rapidly displaced by C_5D_5N [25,36], 4-methylpyridine [22], 1,2-diaminoethane [4,5], 2,2′-bipyridine [5] or 1,10-phenanthroline [20]. No kinetic studies of such reactions have been reported, but they would be expected to occur by a dissociative mechanism. The rates are probably high due to the high *trans*-influence of the $(CH_2)_3$ ligand, which leads to weakening of the platinum—pyridine bonds.

(ii) Platinum(II) derivatives

Some metallacyclobutanes of platinum(II) are given in Table 5. They are prepared in the following ways:

(a) Synthesis from platinum(0) complexes

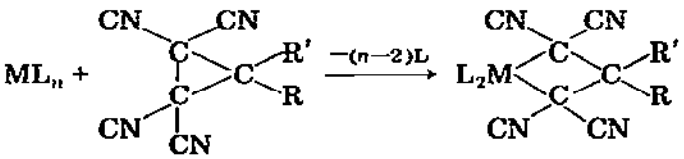
A large number of compounds have been prepared by the reaction of eqn.

TABLE 5

Metallacyclobutanes and metallacyclobutenes of platinum(II)

Complex	m.p. (°C)	Ref.
$[Pt\{C(CN)_2CH_2C(CN)_2\}(PMe_2Ph)_2]$	215—220	27
$[Pt\{C(CN)_2CH_2C(CN)_2\}(PEt_3)_2]$	202—205	27
$[Pt\{C(CN)_2CH_2C(CN)_2\}(PMePh_2)_2]$	243—245	27
$[Pt\{C(CN)_2CH_2C(CN)_2\}(PPh_3)_2]$	220—225	27, 28
$[Pt\{C(CN)_2CH_2C(CN)_2\}(AsPh_3)_2]$	245—246	27
$[Pt\{C(CN)_2CMe_2C(CN)_2\}(PPh_3)_2]$	258—260	27
$[Pt\{C(CN)_2CMe_2C(CN)_2\}(AsPh_3)_2]$	185—187	27
$[Pt\{C(CN)_2CHPhC(CN)_2\}(PPh_3)_2]$	262 d	29
$[Pt\{C(CN)_2CHPhC(CN)CO_2Et\}(PPh_3)_2]$	204 d	29
$[Pt\{C(CN)_2C(CN)_2O\}(PPh_3)_2]$	210—215 d	27, 30
$[Pt\{C(CN)_2C(CN)_2O\}(AsPh_3)_2]$	190—193 d	27, 30
$[Pt\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2]$	212—213 d	31
$[Pt(CPh{=}CPhCO)(PPh_3)_2]$	—	32, 33
$[Pt(CH{=}CMeCO)(PPh_3)_2]$	—	33
$[Pt(CMe{=}CMeCO)(PPh_3)_2]$	—	33
$[Pt\{CPh{=}CPhC{=}C(CN)_2\}(PPh_3)_2]$	—	34
$[Pt(CH_2CMe_2CH_2)(PEt_3)_2]$	—	35

(10) [27—29].



(10)

(R = R′ = H, Me; R = H, R′ = Ph; R = Me, R′ = Et; R, R′ = $(CH_2)_5$; M = Pt, Pd; L = PPh_3, $PMePh_2$, $AsPh_3$; n = 3,4)

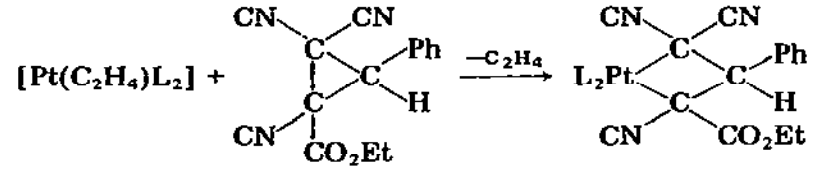
Alternatively the complex $[Pt(C_2H_4)(PPh_3)_2]$ can be used as starting material [27—29]. Further derivatives can be prepared by ligand displacement reactions (eqn. 11, L = PEt_3, $PMePh_2$) [27].

$$[Pt\{C(CN)_2CH_2C(CN)_2\}(AsPh_3)_2] + 2\,L \rightarrow [Pt\{C(CN)_2CH_2C(CN)_2\}L_2] + 2\,AsPh_3 \quad (11)$$

In these reactions platinum(0) acts as a nucleophilic centre and inserts into the C—C bond of the cyclopropane carrying the greatest number of electronegative cyano substituents [27—29].

Similarly 1-carboethoxy-1,2,2-tricyano-*trans*-3-phenylcyclopropane reacts

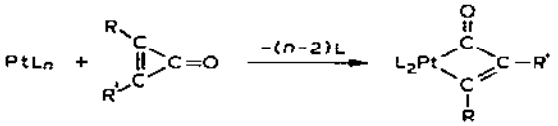
with $[Pt(C_2H_4)(PPh_3)_2]$, with retention of the stereochemistry about the ring (eqn. 12, L = PPh_3) [29].



(12)

These complexes are all thermally stable as indicated by the high decomposition temperatures (Table 5), no doubt partly due to the stabilising effect of the cyano substituents, and few chemical reactions of these compounds are known.

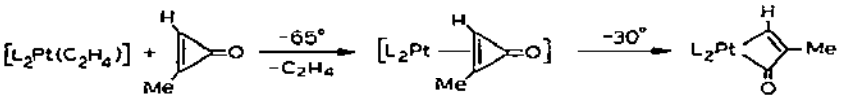
Platinacyclobutenone derivatives can be prepared from cyclopropenones in a similar way (eqn. 13).



(13)

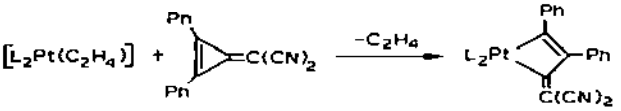
[L = PPh_3, R = H, R' = Me, R = R' = Me, Ph; n = 3,4]

The starting material may be either $[Pt(PPh_3)_4]$ or $[Pt(C_2H_4)(PPh_3)_2]$ [32, 33]. Of particular interest was the detection and isolation of a cyclopropenone complex in one case (eqn. 14, L = PPh_3) [33].



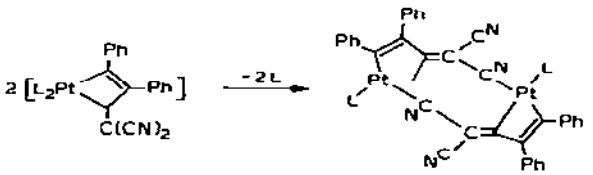
(14)

A similar reaction occurs with 1,2-diphenyl-3-dicyanomethylenecyclopropene (eqn. 15, L = PPh_3) [34].



(15)

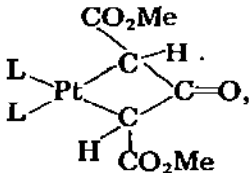
In solution one of the tertiary phosphine ligands could be displaced by a cyano group to give a dimeric complex (eqn. 16, L = PPh_3) [34].



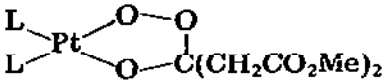
(16)

A remarkable reaction in which a platinacyclobutane derivative is formed

from unstrained reagents has been reported by Kemmitt and co-workers [31]. $[Pt(PPh_3)_4]$ or $[Pt(PhCH{=}CHPh)(PPh_3)_2]$ was heated with the ketone derivative, $MeO_2CCH_2COCH_2CO_2Me$, in the presence of oxygen to give the complex, (III).



(III)

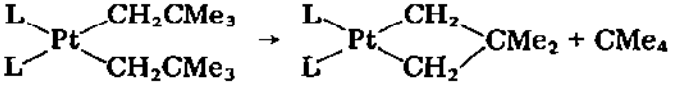


(IV)

Complex (IV) was detected at intermediate stages of reaction and was thought to be a precursor to (III), but the exact mechanism is not yet known.

(b) Synthesis from platinum(II) complexes

A second method of preparing platinacyclobutanes from unstrained reagents was discovered by Foley and Whitesides [35]. It involves thermolysis of *cis*-$[Pt(CH_2CMe_3)_2(PEt_3)_2]$ in cyclohexane at 157°C according to eqn. (17) (L = PEt_3).



(17)

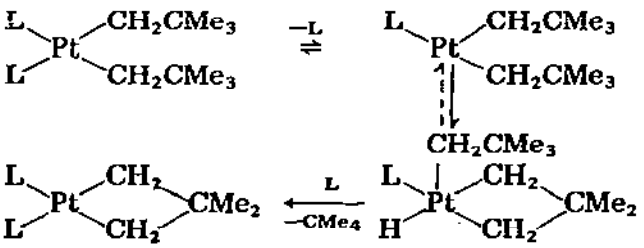
Kinetic studies showed that a triethylphosphine ligand dissociated prior to the rate determining step, and the deuterium-labelling studies of eqns. (18) and (19) showed that the extra hydrogen atom formed in the neopentane arose from the second neopentylplatinum group.

$$[L_2Pt(CH_2CMe_3)_2] \xrightarrow[157^\circ C]{C_6D_{12}} Me_3CCH_2H \quad (97\%\ d_0,\ 3\%\ d_1) \tag{18}$$

$$[L_2Pt(CD_2CMe_3)_2] \xrightarrow[157^\circ C]{C_6D_{12}} Me_3CCD_2H \quad (93\%\ d_2,\ 7\%\ d_3) \tag{19}$$

The mechanism of formation was therefore deduced to be as shown in Scheme 1.

Scheme 1, L = PEt_3



The reaction demonstrates that the C—H bond cleavage occurs by oxidative addition to platinum(II), and may be considered as a γ-elimination reaction [35]. The stability of the presumably strained platinacyclobutane ring, at the high temperature at which it is formed is remarkable.

C. CHARACTERISATION AND STRUCTURES OF PLATINACYCLOBUTANES

(i) Infrared and Raman spectroscopy

Some stretching frequencies for platinacyclobutanes are given in Table 6. For the monomeric derivatives, the Pt—Cl or Pt—Br stretching frequencies are almost constant for different complexes as expected for the structure (II) with mutually *trans* halide ligands. The similarity of the bridging platinum—halide stretching frequencies for the polymeric $[\{PtX_2(CH_2CH_2CH_2)\}_n]$, X = Cl or Br, and for the tetrameric $[(Me_3PtX)_4]$ has led to the suggestion that these compounds have similar tetrameric structures. The detailed structure (IV) has been suggested tentatively [5]. The tetrameric structure is supported by the observation of a peak in the mass spectrum, believed to be the

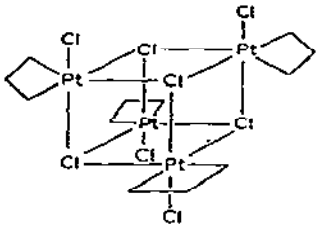
TABLE 6

Vibrational spectra of platinacyclobutanes

Compound	$\nu(PtCH_2CH_2CH_2)$ (cm^{-1})		$\nu(PtX)$ (cm^{-1})		Ref.
	R [a]	IR [a]	R [a]	IR [a]	
$[\{PtCl_2(CH_2CH_2CH_2)\}_n]$		563		330 [b] 230 [c]	3, 5
$[\{PtBr_2(CH_2CH_2CH_2)\}_n]$				252 [b] 206 [d]	5
$[PtCl_2(CH_2CH_2CH_2)(C_5H_5N)_2]$	580 400, 395		325 320	331	37
$[PtCl_2(CH_2CH_2CH_2)(phen)]$	584, 562 430, 422 406		326 323	328	37
$[PtCl_2(CH_2CH_2CH_2)(bipy)]$	596 406, 363		343 331	340	37
$[PtBr_2(CH_2CH_2CH_2)(bipy)]$	582 403, 363		201	215	37

[a] R = Raman, IR = infrared. [b] Terminal PtCl or PtBr stretch. [c] Bridging PtCl stretch, c.f. 220 cm^{-1} for $[(Me_3PtCl)_4]$. [d] Bridging PtBr stretch.

parent ion of $[(PtCl_2C_3H_6)_4]$, at *m/e* 1232 [5].



(IV)

The Raman spectra show peaks due to the $Pt(CH_2)_3$ ring in the regions 562—596 and 363—430 cm^{-1} [37]. In this strained ring system a pure Pt—C stretch cannot be expected, and the frequencies probably have both Pt—C stretching and ring deformation character. The frequencies may be compared with typical methylplatinum stretching frequencies of 540—580 cm^{-1}, and frequencies for the $Pt(CH_2)_4$ ring of 540—590 cm^{-1}, but no conclusions about the degree of strain in the $PtCH_2CH_2CH_2$ ring can be drawn.

(ii) NMR spectroscopy

Some ^1H NMR spectral parameters for platinacyclobutanes are given in Table 7. When tetracyanocyclopropane forms complexes such as $[Pt\{C(CN)_2CH_2C(CN)_2\}(PPh_3)_2]$ the methylene protons shift upfield in the ^1H NMR spectrum, but when cyclopropane and its alkyl substituted derivatives form complexes such as $[PtCl_2(CH_2CH_2CH_2)(C_5H_5N)_2]$ a large downfield shift is observed. It has therefore been suggested that a net platinum to cyclopropane electron drift occurs on interaction of platinum(0) with electronegatively substituted cyclopropanes but that otherwise a net cyclopropane to platinum(II) electron drift is implicated [9,27].

Coupling constants between ^{195}Pt and "cyclopropane" protons are very useful in structure determination, particularly when mixtures of isomers are present [9,13]. For the ring protons, couplings of 52—120 Hz are observed for the coupling $^2J(PtCH)$ but 0—44 Hz for the coupling $^3J(PtCH_2CH)$. Thus ring protons α- or β-to platinum are readily identified, provided that the resonances are not too complex. In complexes of platinum(IV) derived from methyl-substituted cyclopropanes, a methyl group α to platinum gives $^3J(PtCCH_3)$ 20—25 Hz but a methyl group β to platinum gives $^4J(PtCCCH_3)$ 0—7 Hz, and isomers can readily be distinguished using this criterion [11,12].

Carbon-13 NMR spectroscopy has been widely used for identifying mixtures of isomers of platinacyclobutanes, since the spectra are particularly simple. Thus the isomer $[PtCHRCH_2CH_2]$ will give three signals due to ring carbon atoms but $[PtCH_2CHRCH_2]$ will give only two [13]. Some examples are given in Table 8. It has been noted that the coupling constants $^1J(PtC)$ are lower than for alkylplatinum(IV) complexes, and this has been attributed to ring strain which necessitates an angle CPtC considerably less than the normal 90° [19]. On the other hand, the cross-ring coupling $^2J(PtC)$ is large and a

TABLE 7

^{1}H NMR data for platinacyclobutanes [a]

Complex	$\delta(H^{\alpha})$	^2J(PtH)	$\delta(H^{\beta})$	^3J(PtH)	δ(Me)	J(PtH)	Ref.
$[Pt(CH_2CMe_2CH_2)(PEt_3)_2]$	0.73	74	—	—	1.57	—	35
$[Pt\{CH(CO_2Me)COCH(CO_2Me)\}(PPh_3)_2]$	3.88	52	—	—	—	—	31
$[Pt\{C(CN)_2CH_2C(CN)_2\}(PPh_3)_2]$	—	—	4.38	38	—	—	27
$[Pt\{C(CN)_2CH_2C(CN)_2\}(AsPh_3)_2]$	—	—	4.39	44	—	—	27
$[PtCl_2(CH_2CH_2CH_2)(C_5H_5N)_2]$	2.5	83	2.5	—	—	—	3
$[PtCl_2(CH_2CHMeCH_2)(C_5H_5N)_2]$	3.0, 2.7	81, 79	3.1	—	1.3 [c]	5	11
$[PtCl_2(CHMeCH_2CH_2)(C_5H_5N)_2]$	—	—	—	—	0.8 [b]	22	11
$[PtCl_2(CH_2CMe_2CH_2)(C_5H_5N)_2]$	2.6	84	—	—	1.1 [c]	3.5	11, 12
$[PtCl_2(CHMeCHMeCH_2)(C_5H_5N)_2]$	2.3 [d]	79	2.9	—	0.6 [b]	23	11, 12
	3.0 [e]	88			0.9 [c]	7	11, 12
$[PtCl_2(CH_2CHPhCH_2)(C_5H_5N)_2]$	3.0	82	4.1	—	—	—	9
$[PtCl_2(CHPhCH_2CH_2)(C_5H_5N)_2]$	4.9 [f]	101	—	—	—	—	13

[a] H^{α} indicates PtC<u>H</u> protons, H^{β} indicates $PtCH_2C\underline{H}_2CH_2$ protons. [b] Methyl group α- to Pt. [c] Methyl group β- to Pt. [d] $PtC\underline{H}_2$. [e] PtC<u>H</u>Me. [f] PtC<u>H</u>Ph.

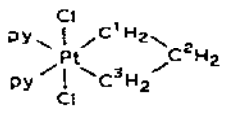
through-space component, implying direct overlap of orbitals on platinum and the β-carbon atom, has been suggested [19]. The direct coupling constant ^1J(CH) for the β-methylene group in $[PtCl_2(CH_2CH_2\overline{CH_2})(C_5H_5N)_2]$ is almost identical with those for other compounds $X(CH_2)_3$, X = O, S, CH_2 etc., consistent with the platinacyclobutane formulation for the complex [19].

The ^{13}C chemical shifts for the ring carbon atoms in the platinum(IV) metallacyclobutanes are in the normal range for alkylplatinum complexes and do not confirm the suggestion [9], based on proton chemical shifts, that there is a significant electron donation from platinum to the ring carbon atoms.

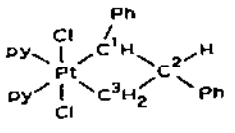
The ^{195}Pt chemical shifts for complexes $[PtX_2(CH_2CH_2\overline{CH_2})(C_5H_5N)_2]$, X = Cl or Br, are about 400 p.p.m. to low field of the values for comparable acyclic analogues, presumably as a result of distortions due to ring strain [19,38].

(iii) X-ray structural studies

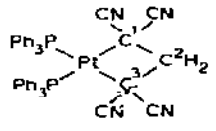
X-ray structure determinations have been reported for the platinacyclobutanes (A)—(F) and for the platinacyclobutanone (G). Some data are summarised in Table 9. Two independent molecules of $[PtCl_2(trans\text{-}CHPhCHPh\overline{CH_2})(C_5H_5N)_2]$, (B) and (C), are present in each unit cell. They differ in the conformation of the β-phenyl group with respect to the PtC_3 ring and data are given for both isomers. The structures are shown in Fig. 1.



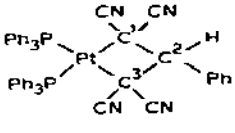
(A), py = C_5H_5N
Ref. 4



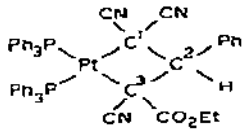
(B) and (C), py = C_5H_5N
Ref. 24



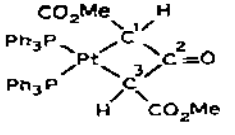
(D), Ref. 28



(E), Ref. 29



(F), Ref. 29



(G), Ref. 31

Fig. 1. Platinacyclobutanes studied by X-ray methods.

TABLE 8

^{13}C NMR data for platinacyclobutanes

Complex	$\delta(C^1)$	$^1J(PtC)$	$\delta(C^2)$	$^2J(PtC^2)$	$\delta(C^3)$	$^1J(PtC^3)$	Ref.
$[PtCl_2(C^1H_2C^2H_2C^3H_2)(C_5H_5N)_2]$	−15.2	335	30.0	105	−15.2	335	19
$[PtBr_2(C^1H_2C^2H_2C^3H_2)(C_5H_5N)_2]$	−17.9	325	30.4	110	−17.9	325	19
$[PtCl_2(C^1H_2C^2HMeC^3H_2)(C_5H_5N)_2]$	1.0	344	42.6	98	1.0	344	11
$[PtCl_2(C^1H_2C^2Me_2C^3H_2)(C_5H_5N)_2]$	3.1	351	42.8	91	3.1	351	21
$[PtCl_2(C^1HMeC^2HMeC^3H_2)(C_5H_5N)_2]$	10.9	336	46.4	98	−2.6	347	21
$[PtCl_2(C^1H_2C^2HPhC^3H_2)(C_5H_5N)_2]$	−4.9	359	48.1	101	−4.9	359	13
$[PtCl_2(C^1HPhC^2H_2C^3H_2)(C_5H_5N)_2]$	5.6	338	35.1	112	−11.3	355	13
$[PtCl_2(C^1HPhC^2HPhC^3H_2)(4\text{-}^tBuC_5H_4N)_2]$	15.1	343	50.6	105	−1.8	377	11
$[PtCl_2(C^1HPhC^2H_2C^3HPh)(4\text{-}^tBuC_5H_4N)_2]$	6.1	340	41.2	130	6.1	340	11
$[Pt\{C^1(CN)_2C^2H_2C^3(CN)_2\}(AsPh_3)_2]$	—	—	54.7	202	—	—	19
$[Pt\{C^1(CN)_2C^2H_2C^3(CN)_2\}(PPh_3)_2]$	—	—	48.1	160	—	—	19
$[Pt\{C^1(CN)_2C^2H_2C^3(CN)_2\}(PMePh_2)_2]$	—	—	47.4	152	—	—	19

TABLE 9

Structural data for platinacyclobutanes

	Molecule						
	A	B	C	D	E	F	G
	Intramolecular distances (Å)						
$Pt—C_1$	2.04	2.06	2.05	2.137	2.137	2.158	2.149
$Pt—C_2$	2.69	2.60	2.62	2.712	2.694	2.687	2.420
$Pt—C_3$	2.19	2.11	2.17	2.139	2.159	2.200	2.128
$C_1—C_2$	1.48	1.59	1.59	1.545	1.557	1.556	—
$C_2—C_3$	1.82	1.48	1.71	1.584	1.548	1.509	—
$C_1—C_3$	2.55	2.39	2.60	2.404	2.394	2.403	—
	Bond angles (deg.)						
$C_1—Pt—C_3$	74	70	76	68.4	67.7	66.9	—
$C_1—C_2—C_3$	101	102	104	100.4	100.9	103.2	—
$Pt—C_1—C_2$	99	90	91	93.5	92.3	91.2	—
	Dihedral angle (deg.)						
$C_3—Pt—C_1$ / $C_1—C_2—C_3$	12	28	22	24.4	28.6	29.7	49.7

The bond distances $C_1—C_2$ and $C_2—C_3$ are longer than in the parent cyclopropanes, the difference being similar to the difference between bond lengths in cyclobutanes and cyclopropanes [29], and the distance $C_1—C_3$ is 2.39—2.60 Å, which is considered too long to be consistent with any significant bonding interaction [4]. These data are therefore in accord with the platinacyclobutane formulation for the compounds.

There is a puckering of the platinacyclobutane ring in all compounds studied, the extent of which can be measured by the dihedral angle between the planes defined by atoms $C_1C_2C_3$ and PtC_1C_3. This angle is about 12° for (A), but 22—30° for (B)—(F) and a remarkable 50° for the platinacyclobutanone (G). The transannular distance $Pt—C_2$ is 2.6—2.7 Å for (A)—(F), but only 2.4 Å for (G) as a result of this puckering. In compound (G) it seems clear that there must be a direct $Pt—C_2$ bonding interaction [31], but the structural data for (A)—(F) do not require such an interaction [29]. The reason for puckering of the ring in (A)—(F) could be due to a $Pt—C_2$ bonding interaction, but similar puckering is also observed in cyclobutane and its derivatives. The barrier to inversion of the ring must be small as in cyclobutanes, since no non-equivalence of axial and equatorial substituents on the ring has been reported.

Finally the angles between exocyclic substituents on a given carbon atom in platinacyclobutanes lie in the range 104—112°, close to values found in

cyclobutane derivatives but considerably smaller than in cyclopropanes, where the angle is typically ~120° [28]. Again this supports the platinacyclobutane formulation.

D. BONDING IN PLATINACYCLOBUTANES

As discussed above, the great majority of the structural and spectroscopic evidence suggests that the platinacyclobutane formulation initially suggested by Chatt is correct. The bonding in the ring would therefore be expected to be similar to that in other compounds $X(CH_2)_3$, where X = O, S or CH_2, and which has been discussed extensively for cyclobutane derivatives [39]. Ibers has pointed out that because the Pt—C bonds are considerably longer than C—C bonds, the strain in the PtC_3 ring should be less than in cyclobutane [29]. For example, in platinacyclobutanes the bond angle $C_1—C_2—C_3$ lies in the range 100—104°, rather than values close to 90° in cyclobutanes [Table 9].

McQuillin noted the ease with which platinum(IV) metallacyclobutanes undergo dissociation of cyclopropane on treatment with π-acceptor ligands such as triphenylphosphine, and felt that this facile formation of a strained ring compound was not consistent with the platinacyclobutane formulation. He proposed a bonding model based on overlap of Walsh orbitals of cyclopropane with suitable orbitals on platinum (Fig. 2) [9].

Thus, donation from the filled Walsh orbitals (i)—(iii) into suitable vacant orbitals on platinum, with backbonding from a filled *d*-orbital on platinum into the antibonding molecular orbital (iv) could occur. This model is analogous to the Dewar—Chatt theory of bonding in metal—alkene complexes, and in principle allows all possible intermediate situations between cyclopropane—platinum and platinacyclobutane formulations for the compounds. Thus, if the backbonding is particularly strong, the platinum will be oxidised and the

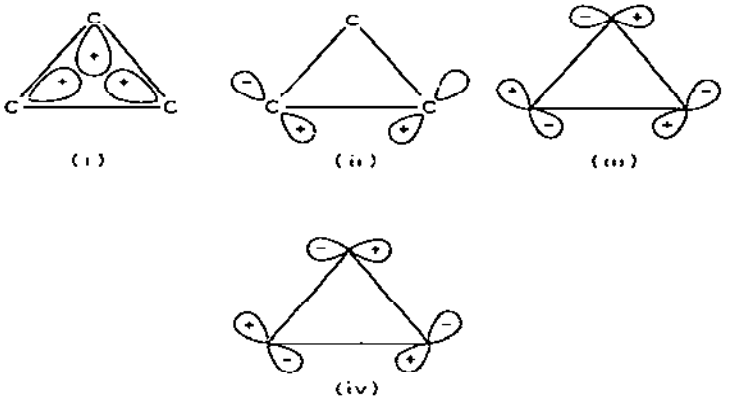


Fig. 2. Walsh orbitals of cyclopropane.

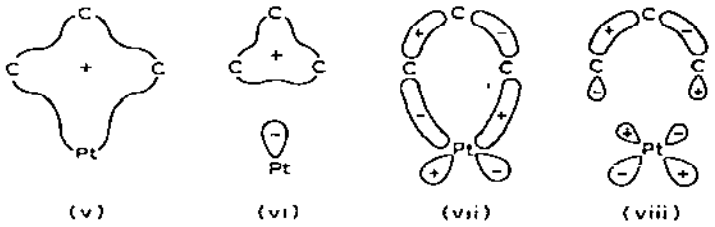
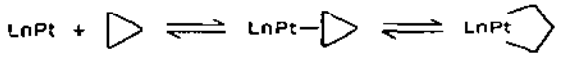


Fig. 3. Proposed filled MO's of PtC_3 ring.

platinacyclobutane formulation will be approached while, if backbonding is weak, the cyclopropane—platinum formulation will be a good approximation.

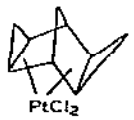
McGinnety used a very similar approach, forming molecular orbitals by linear combination of Walsh orbitals of cyclopropane with suitable σ-acceptor and d-orbitals of platinum. He considered that the eight bonding electrons associated with the PtC_3 ring would be in the four molecular orbitals shown in Fig. 3 [24]. This particular choice of the filled MO's appears unfortunate since it leads to no net platinum—cyclopropane bonding interaction, but the work is valuable in emphasising the probable presence of bent bonds in the strained ring.

Other workers have suggested that these cyclopropane—platinum bonding models are not really useful in describing the ground state structure of platinacyclobutanes, but that they are useful in describing bonding in intermediates or transition states during the "insertion" of platinum into a C—C bond of cyclopropane from a platinacyclobutane (eqn. 20) [19,28]



(20)

Such intermediates have often been termed "edge-complexes". It is, of course, possible that the edge-complex formulation could represent the ground state in certain cases. For example, silver(I) catalyses rearrangements of some cyclopropane derivatives but it is difficult to envisage a silver(III) metallacyclobutane as intermediate in such reactions. One complex of platinum, (H), was formulated as a bis(edge-complex) some years ago before any structural studies of platinacyclobutanes had been completed [40]. It should be reinvestigated, since the proposed formulation must now be regarded as doubtful.



(H)

Another bonding problem which is not yet clearly understood is the reason for puckering of the platinacyclobutane ring. It is possible that, as in cyclo-

butanes, the barrier to ring inversion is very low. The degree of puckering could then be determined by a need to minimise steric interactions (torsional strain) or to maximise packing forces in crystalline solids. However, this explanation would not be consistent with the very large puckering observed in the platinacyclobutanone complex (G), where a transannular PtC bonding interaction must be invoked [31]. There have been no detailed molecular orbital calculations performed on platinacyclobutanes, and such studies are clearly necessary in order to resolve these problems.

Thermochemical studies on the decomposition of platinacyclobutanes have been carried out in order to determine the ring strain [41]. Platinum(IV) derivatives were found to decompose quantitatively on heating solid samples to 140—200°C according to eqns. (21) and (22) [X = Cl or Br, L = nitrogen-donor ligand, e.g. pyridine, 2,2′-bipyridine].

$$\overbrace{PtX_2(CH_2CH_2CH_2)} \rightarrow PtX_2 + x\ CH_3CH{=}CH_2 + (1-x)\ \overbrace{CH_2CH_2CH_2} \qquad (21)$$

$$[\overbrace{PtX_2(CH_2CH_2CH_2)}L_2] \rightarrow [PtX_2L_2] + x\ CH_3CH{=}CH_2 + (1-x)\ \overbrace{CH_2CH_2CH_2} \qquad (22)$$

The mole fraction of propene formed, x, varied from 0.17 to 0.88 depending on the nature of the ligands X and L and the temperature of decomposition. Enthalpies of reaction were determined using differential scanning calorimetry and are given in Table 10.

The following thermochemical cycle can be formulated for the reactions

$$[PtX_2(C_3H_6)L_2]\ (s) \rightarrow [PtX_2L_2]\ (s) + {}^{\bullet}CH_2CH_2CH_2{}^{\bullet}\ (g) \qquad \Delta H_1$$

$$x\ {}^{\bullet}CH_2CH_2CH_2{}^{\bullet}\ (g) \rightarrow x\ CH_3CH{=}CH_2\ (g) \qquad x\Delta H_2 = -258.5x\ \text{kJ mol}^{-1}$$

$$(1-x)\ {}^{\bullet}CH_2CH_2CH_2{}^{\bullet}\ (g) \rightarrow (1-x)\ \overbrace{CH_2CH_2CH_2}\ (g)$$

$$(1-x)\Delta H_3 = -225.9(1-x)\ \text{kJ mol}^{-1}$$

Thus $\Delta H_{exp} = \Delta H_1 - 258.5x - 225.9(1-x)$ kJ mol^{-1}.

Since ΔH_{exp} and x were determined experimentally, ΔH_1 could be calculated. The approximation must be made that $\Delta H_1 = 2E(\text{Pt—C}) - S$, where E(Pt—C) is the Pt—C bond energy and S is the ring strain. If S is ignored then the energy of the strained Pt—C bonds can be calculated and these fall in the region 113—124 kJ mol^{-1} (Table 10). This treatment assumes that all the ring strain is in the Pt—C bonds. Alternatively, it can be assumed that E(Pt—C) is the same as in unstrained alkylplatinum complexes and the ring strain, S, can then be calculated. The best value for E(Pt—C) may be 144 kJ mol^{-1}, found by a similar differential scanning calorimetry study for $[PtIMe_3(PMe_2Ph_2)]$ [42]. The resulting values of the ring strain, S, are in the range 41—54 kJ mol^{-1} (Table 10). The errors involved in these determinations are difficult to estimate, but a strain energy in the region of 50 kJ mol^{-1} seems reasonable. This may be compared with the conventional ring strain energies in cyclopropane and cyclobutane of 115 and 111 kJ mol^{-1} respectively [43]. Thus, as expected, the ring strain appears to be considerably lower than in cyclo-

TABLE 10

Thermochemical results obtained by DSC for the decomposition of platinacyclobutanes

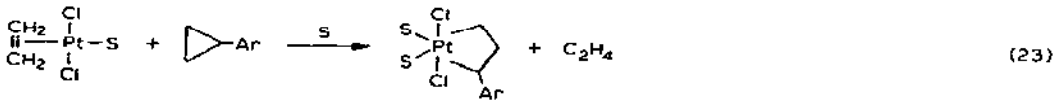
Complex	T_i [a] (°C)	T_f [a] (°C)	ΔH_{exp} [b] (kJ mol^{-1})	E(PtC) [c] (kJ mol^{-1})	S [d] (kJ mol^{-1})
$[\{PtCl_2(C_3H_6)\}_n]$	148	169	−10.4 ± 0.2	119.5	49
$[\{PtBr_2(C_3H_6)\}_n]$	134	165	−3.5 ± 0.2	121.5	45
$[PtCl_2(C_3H_6)(C_5H_5N)_2]$	147	165	−17.5 ± 0.3	117.0	54
$[PtBr_2(C_3H_6)(C_5H_5N)_2]$	142	167	−17.0 ± 0.1	117.4	53
$[PtCl_2(C_3H_6)(bipy)]$	—	—	0.0	121.4	45
$[PtBr_2(C_3H_6)(bipy)]$	—	—	0.0	123.7	41

[a] T_i and T_f are temperatures at which decomposition began and ended.
[b] Enthalpy change for reaction (21) or (22).
[c] Calculated assuming all strain in Pt—C bonds or S = 0.
[d] Calculated assuming E(PtC) = 144 kJ mol^{-1}.

butane, due to the presence of long Pt—C bonds which allows relief of angle strain in the ring and to the fact that the natural bond angles in octahedral platinum(IV) complexes are only 90° rather than the tetrahedral angle of ~109° expected for carbon.

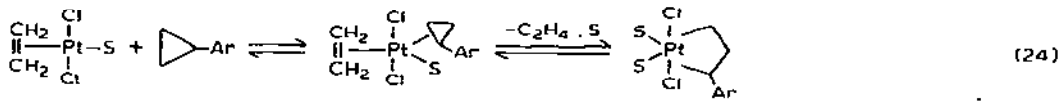
E. MECHANISM OF FORMATION OF PLATINACYCLOBUTANES

Kinetic studies on platinacyclobutane formation were carried out on the reaction of Zeise's dimer with arylcyclopropanes in tetrahydrofuran. The reactions were shown to occur according to eqn. (23) (S = tetrahydrofuran) [17].



(23)

The reactions followed second order kinetics, being first order in both platinum complex and cyclopropane, and the following general mechanism was proposed [17] (eqn. 24).



(24)

The mechanism involves initial co-ordination of the cyclopropane to give an "edge-complex" followed by ring-opening to give the platinacyclobutane with loss of alkene. It is not known which step is rate-determining.

Competition experiments showed that the reaction of Zeise's dimer with cyclopropanes, RC_3H_5, the reactivity sequence was R = n-C_6H_{13} > $PhCH_2$ > Ph > 2-$NO_2C_6H_4$ [9] and kinetic studies showed the reactivity sequence R =

4-$EtOC_6H_4$ >> 4-MeC_6H_4 > C_6H_5 [17]. Thus electron-releasing substituents on the cyclopropane enhance reactivity, and it seems that the donor ability of the cyclopropane is important in determining the reaction rates. Thus the ability of the cyclopropane to donate electron density to platinum, probably in forming the edge-complex intermediates, is important.

The formation of platinacyclobutanes occurs with retention of stereochemistry about the cyclopropane ring. Thus, for example, *trans*-1,2-diphenylcyclopropane reacts with Zeise's dimer to give the corresponding platinacyclobutane in which the phenyl groups remain mutually *trans* and pure *trans*-1,2-diphenylcyclopropane is recovered on treatment of the platinacyclobutane with triphenylphosphine [7,9,13,14]. Similar experiments have been carried out with *cis*-1,2-diphenylcyclopropane [9,14] (this fails to give a pure platinacyclobutane), *trans*-1,2-di(4-tolyl)cyclopropane [11], *trans*-1-methyl-2-phenylcyclopropane [11,21], *trans*-1,2-dimethylcyclopropane, with *cis*- and *trans*-1-phenyl-2-deuteriocyclopropane [14,43], and with isomers of 1-hexyl-2,3-dideuteriocyclopropane [43b] and in each case the stereochemistry about the ring is retained. Thus, intermediates such as $Cl_2Pt\overset{\ominus}{C}H_2CHR\overset{\oplus}{C}HR'$, in which free rotation about the C—C bonds would lead to loss of stereochemistry about the ring, are ruled out. However, the rate of platinacyclobutane formation increases with solvent polarity, so that some polarity in the intermediates or transition state is indicated [17].

The substituent effects on the rate of reaction of $[Pt_2Cl_4(C_2H_4)_2]$ with arylcyclopropanes 4-$XC_6H_4C_3H_5$ are also inconsistent with a highly polar intermediate. Thus the relative rates k_2(X = OMe)/k_2(X = H) are ca. 8 for reaction of 4-$XC_6H_4C_3H_5$ with $[Pt_2Cl_4(C_2H_4)_2]$, ca. 4 for reaction with $[\{PtCl_2(CH_2CH_2CH_2)\}_n]$ and ca. 350 for reaction with mercury(II) acetate. In the last case a polar intermediate $[AcOHgCH_2CH_2CHAr^+]$ is implicated, and the much lower substituent effects for reaction with platinum(II) strongly indicate a much less polar intermediate.

Another important effect in mechanistic considerations is the position of insertion of platinum on reaction with substituted cyclopropanes. McQuillin carried out the first investigations [7—9], characterising the platinum(IV) metallacyclobutanes as the pyridine adducts which were purified by chromatography and crystallisation; e.g. eqn. (25).

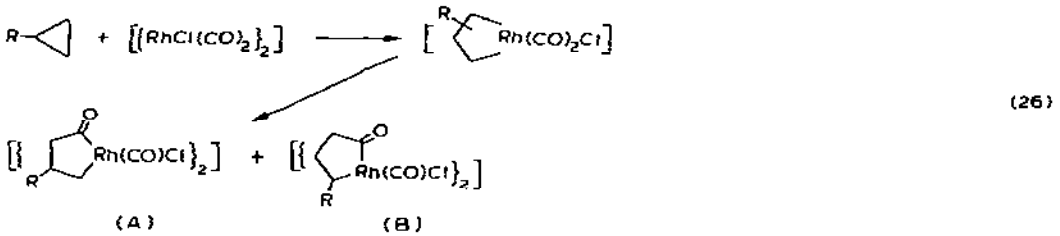
$$[\{PtCl_2(C_2H_4)\}_2] + PhC_3H_5 \rightarrow [PtCl_2(C_3H_5Ph)] \xrightarrow{C_5H_5N} [\overline{PtCl_2(CH_2CHPhCH_2)}(C_5H_5N)_2] \quad (25)$$

McQuillin therefore deduced that insertion into the least substituted bond occurred. However, it was subsequently shown that the initial product was largely the isomer $[\overline{PtCl_2(CHPhCH_2CH_2)}(C_5H_5N)_2]$, but that this subsequently isomerised to the more stable isomer isolated by McQuillin [44]. Thus insertion of platinum actually occurs into the most substituted bond, adjacent to the phenyl group.

A similar effect is observed on reaction with *trans*-1,2-diarylcyclopropanes. Thus *trans*-1,2-di(4-tolyl)cyclopropane gave first $[PtCl_2(CHArCH_2CHAr)(C_5H_5N)_2]$ but this subsequently isomerised to give largely $[PtCl_2(CHArCHArCH_2)(C_5H_5N)_2]$, Ar = 4-tolyl. Again it seems that the initial insertion occurred at the most substituted bond of the cyclopropane [11]. With *trans*-1,2-diphenylcyclopropane the product first isolated was a mixture of the two isomers, and further isomerisation of the 1,3- to the 1,2-diphenylpropane-1,3-diylplatinum isomer then occurred. In cases like this it is impossible to determine the relative rates for insertion into the most substituted or least substituted C—C bond of the cyclopropane, since it is obviously possible that skeletal isomerisation occurred prior to isolation of the products.

With methylcyclopropane some 1-methyl isomer $[PtCl_2(CHMeCH_2CH_2)(C_5H_5N)_2]$ was formed along with the more stable 2-methyl isomer $[PtCl_2(CHMeCH_2)(C_5H_5N)_2]$ [11] but with all other alkylcyclopropanes (RC_3H_5 with R = Et, ^{i}Pr, Bu, n-C_6H_{13}, $PhCH_2$) only the isomer $[PtCl_2(CH_2(CH_2CHRCH_2)(C_5H_5N)_2]$ could be detected [7—9,11,12]. 1,1-Dialkylcyclopropanes gave only the isomer $[PtCl_2(CH_2CRR'CH_2)(C_5H_5N)_2]$ (R, R' = Me, Me; $(CH_2)_n$, n = 2, 4, 5) [12,15], while *trans*-1,2-dialkylcyclopropanes gave only $[PtCl_2(CHRCHR'CH_2)(C_5H_5N)_2]$ (R, R' = Me, Me; Me, Bu; Me, Ph) [7—9,11,12]. Thus it has been assumed that insertion of platinum into the least substituted bond of the cyclopropane occurs [9,12]. However, recent evidence indicates that skeletal isomerisation reactions may occur rapidly in these cases [11] and hence an equilibrium mixture of isomeric products will be obtained. Thus it is not possible to determine the initial point of insertion of platinum into the cyclopropane ring.

Some support for the suggestion that insertion occurs at the least substituted bond is found in reactions of cyclopropanes with $[(RhCl(CO)_2)_2]$ (eqn. 26)

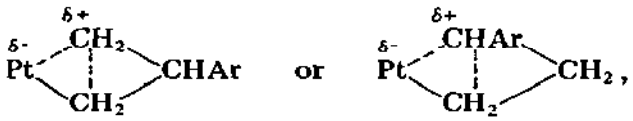


(26)

When R = Ph, isomer (B) was obtained, indicating that the initial rhodacyclobutane had the partial structure $RhCHPhCH_2CH_2$ but, when R = $PhCH_2$, isomer (A) was obtained, presumably from the rhodacyclobutane $RhCH_2CH(CH_2Ph)CH_2$. This would be consistent with insertion of rhodium into the most substituted bond of phenylcyclopropane but the least substituted bond of benzylcyclopropane [16]. However, even in this case it is possible that initial insertion into the most substituted bond occurred but that rapid isomerisation to the more stable 2-benzylpropane-1,3-propane diylrhodium

isomer occurred before the carbonyl insertion reaction took place. Until this situation is clarified, it seems wise to draw no mechanistic conclusions from the nature of isomeric products formed from alkylcyclopropanes.

If steric effects determined the position of insertion, then insertion of platinum into the least substituted bond of the cyclopropane would be expected. Insertion into the most substituted bond of phenylcyclopropane can be explained if initial co-ordination to platinum occurs through the aryl group, since the ring would then be held in such a position that insertion of platinum into the adjacent C—C bond would occur [17]. In this regard it is interesting that phenylcyclopropane reacts with chromium atoms to give $[Cr(\eta^6\text{-}C_6H_5\text{-}\lhd)_2]$, with co-ordination of phenyl groups only [45]. Alternatively, if a polar transition state were formed,



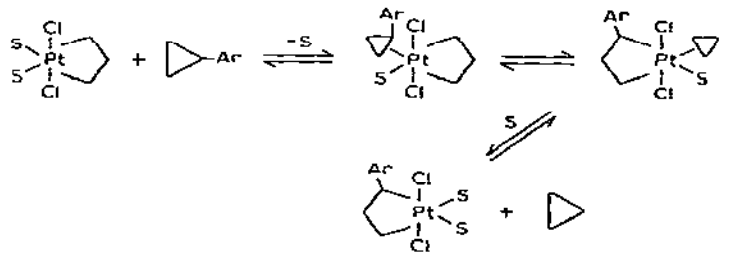
the ability of the aryl group to stabilise the positively charged carbon atom could determine the preferred isomer formed [17]. It is difficult to rationalise the preferred insertion of platinum into the most substituted bond of 1,2-diarylcyclopropanes by either of the above theories.

Ring-opening of cyclopropanes by electrophilic reagents is a general reaction, though only platinum is known to give simple insertion into a C—C bond, and species analogous to the edge-complex intermediate have often been proposed and supported by molecular orbital calculations (e.g. for protonated cyclopropane) [46]. Complex pre-equilibria, for example between edge- and corner-protonated cyclopropanes, often make mechanistic conclusions based on ratios of isomeric products invalid. For example, mercury(II) acetate opens the most substituted C—C bond of *cis*-1,2-diphenylcyclopropane but the least substituted C—C bond of *trans*-1,2-diphenylcyclopropane [47].

The proposed rearrangement of edge-complex to platinacyclobutane in eqn. (24) could occur by dissociation of ethylene from platinum, thus allowing platinum to act as a stronger π-donor to the co-ordinated cyclopropane and hence lead to ring-opening in a concerted non-polar process but it is also possible that a polar intermediate is formed as discussed above.

The cyclopropane for cyclopropane substitution reactions of eqns. (8) and (9) probably proceed by similar mechanisms, since the kinetics are also second order and the substituent effects on reactivity are similar to those discussed above. The mechanism shown in eq. (27) has been suggested [17] (S = solvent, tetrahydrofuran).

No kinetic studies of the formation of platinum(II) metallacyclobutanes from cyclopropanes and platinum(0) complexes (eqns. 10—12) have been reported. However, since electronegative substituents on the cyclopropane are necessary and since platinum inserts into the bond carrying most electro-



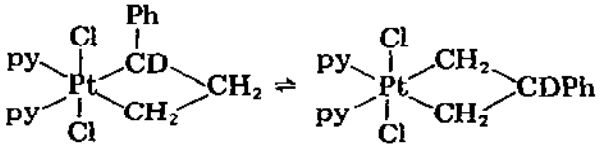
(27)

negative substituents, it is clear that platinum(0) acts as a nucleophile whereas platinum(II) acts as an electrophile. Otherwise, a similar mechanism involving intermediate edge-complexes is likely [27,29].

F. ISOMERISATION OF PLATINACYCLOBUTANES

Reaction of phenylcyclopropane with Zeise's dimer and then with pyridine gives complex (J), but this then rearranges to an equilibrium mixture of (J) and (K) in relative proportions 1 : 2.3 (Scheme 2) [44]. This process is a new addition to the list of molecular rearrangements in organometallic chemistry, and several research groups have studied the reaction mechanism.

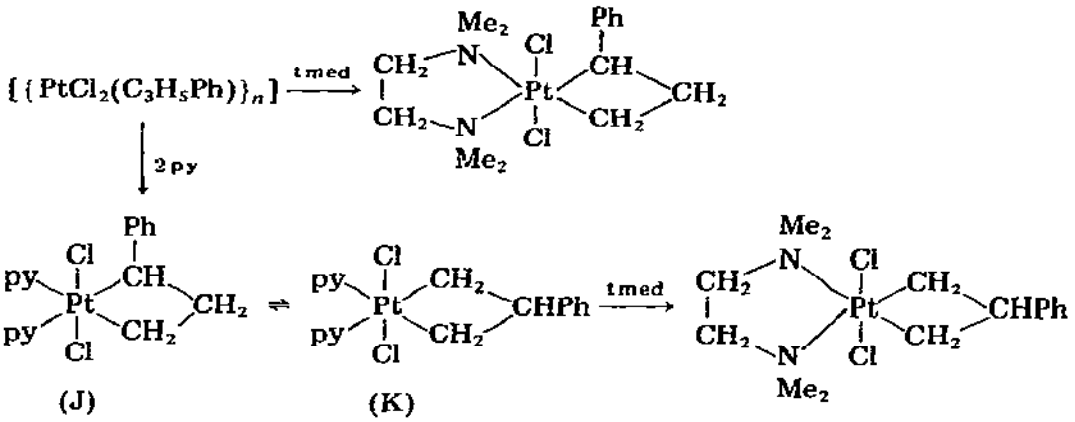
The complexes derived from 1-phenyl-1-deuteriocyclopropane rearranged according to eqn. (28), showing that a skeletal rearrangement rather than phenyl migration was involved [13].



(28)

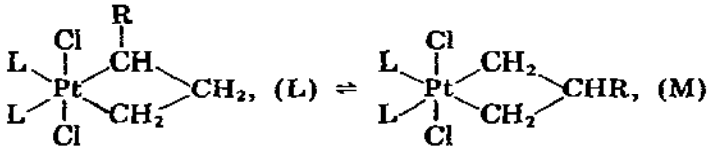
When isomerisation (J) ⇌ (K), Scheme 2, was carried out in the presence of labelled phenylcyclopropane or 4-tolylcyclopropane none or very little of this added cyclopropane was incorporated in the product [14,36,43]. In addition, phenylcyclopropane was shown not to react with *cis* or *trans*-$[PtCl_2(C_5H_5N)_2]$ [13,36]. These experiments show that reaction occurs intramolecularly, without dissociation of phenylcyclopropane from platinum or

Scheme 2



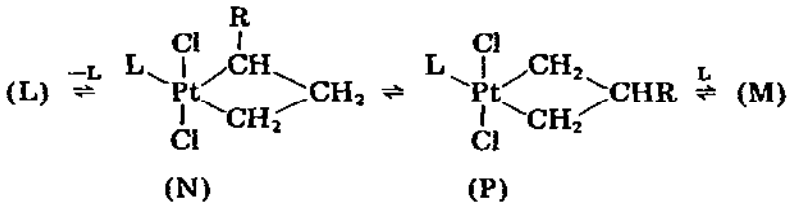
addition of a second molecule of arylcyclopropane to platinum at any stage.

The rate of isomerisation (J) ⇌ (K) is greatly reduced in the presence of free pyridine, and does not occur at all readily when chelate nitrogen donor ligands are present [13,44]. Thus isomeric complexes with *N,N,N'*,*N'*-tetramethylethylenediamine or 2,2'-bipyridyl ligands could be prepared (Scheme 2) and shown not to interconvert under mild conditions. For the analogous complexes derived from 4-tolylcyclopropane the isomerisation of eqn. (29) (L = pyridine, R = 4-tolyl) was shown to follow first order kinetics, and the rate constant was strongly dependent on the pyridine concentration.



(29)

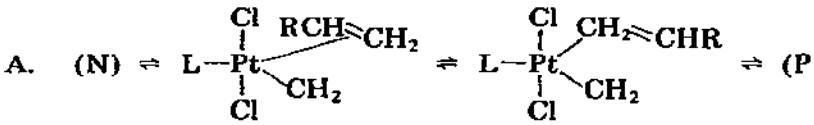
At 50°C in $CDCl_3$ solution the relationship $k_{obs} = 1/(4200 + 7 \times 10^5 [C_5H_5N])$ was obtained. Since pyridine did not interact with either starting material or product, it is clear that reversible dissociation of pyridine from platinum giving a 5 co-ordinate 16-electron complex must occur prior to the skeletal rearrangement [13,44]. Independent studies have shown that pyridine ligands are easily displaced by C_5D_5N [35,36] or by bidentate ligands [4,5,13,20] presumably by a dissociative mechanism, whereas chloride ligands apparently do not dissociate readily from platinum [36]. The lability of the pyridine ligands is clearly a result of the high *trans*-influence of the organic ligand, which is *trans* to pyridine. The isomerisation must therefore occur according to eqn. (30), and the problem is to understand how the reaction (N) ⇌ (P) occurs [44].



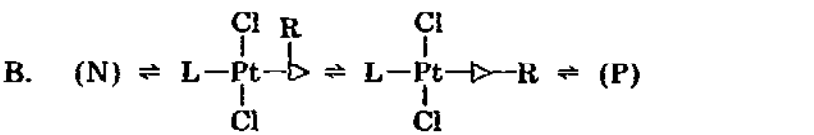
(30)

(N) (P)

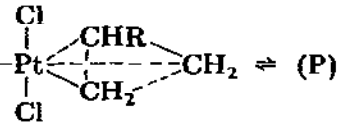
Three mechanisms of isomerisation of (N) ⇌ (P) have been seriously considered, and are shown in eqns. (31)—(33).



(31)



(32)

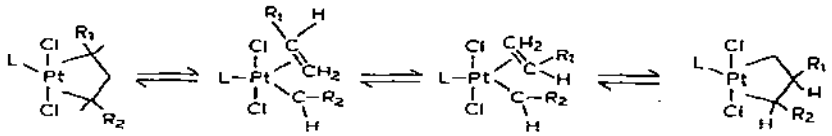
C. (N) ⇌  ⇌ (P) (33)

Mechanism (A) involves formation of an intermediate alkene—carbene complex of platinum(II) in which the alkene can rotate and then form the isomerised platinacyclobutane. It strongly resembles a key step in the olefin metathesis reaction catalysed by transition metal complexes [48] and so has obvious attractions. The intermediates are 18-electron complexes and could not be formed without prior dissociation of a ligand L [44].

Mechanism (B) involves reductive elimination promoted by ligand dissociation to give an edge-complex, which then undergoes edge to edge migration followed by ring opening to give the isomerised platinacyclobutane [14,36,43]. Such reductive elimination is known to be favored by ligand dissociation which reduces electron density on platinum and allows the edge-complex to be formed with the favored square planar stereochemistry [42].

Mechanism (C) involves a concerted process in which C—C and Pt—C bond cleavage and formation occur in a concerted way. The intermediate resembles the intermediate in Mechanism (A) except that complete C—C bond cleavage never occurs and also resembles the sideways-bond cyclopropane in Mechanism (B) which must presumably be formed during the edge to edge isomerisation [14,44].

According to Mechanism (A), thermal decomposition of platinacyclobutanes might be expected to yield ethylene and $RCH{=}CH_2$ (eqn. 31), but such products are seldom observed in significant yield [20,41,44] *. Also if alkene for alkene exchange could occur in the intermediates, then incorporation of added alkenes into the platinacyclobutanes would be expected but has not been observed [14,43,49]. More convincing evidence against Mechanism (A) was obtained by studies of platinacyclobutanes derived from *cis*- or *trans*-1,2-disubstituted cyclopropanes. According to mechanism (A) *cis—trans* isomerisation of ring substituents would be expected as shown in eqn. (34).

 (34)

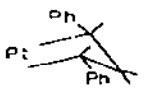
Since the alkene and carbene are expected to rotate independently *cis—trans* isomerisation follows naturally. However, it has now been conclusively demonstrated that such isomerisation does not occur, and that skeletal isomerisation occurs with complete retention of stereochemistry about the ring.

* Such products may be obtained thermally or photochemically under certain conditions, as discussed in Section G of this review. If mechanism A is correct then decomposition of (N) or (P) to give RC_3H_5 must be preferred to decomposition of the carbene—alkene intermediates to give $RCH{=}CH_2$. Clearly, kinetic schemes can be written to accommodate this.

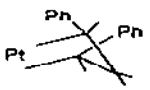
The most convincing experiments were carried out using platinacyclobutanes derived from *cis*- or *trans*-1-phenyl-2-deuteriocyclopropane, since there is then no thermodynamic preference for either *cis*- or *trans*-isomers and hence the retention of stereochemistry must be due to kinetic control [14,43]. Similar experiments have been carried out with complexes derived from *cis*- and *trans*-1,2-diarylcyclopropanes with similar results [11,13,14].

Mechanism (A) can only be correct if the alkene and carbene in the intermediate rotate in unison and there is no obvious reason why this should be the case, unless complete C—C bond cleavage does not occur. This case is equivalent to the Mechanism (C) as explained above. No means of distinguishing between mechanisms (B) and (C) have yet been devised, and both are consistent with available data [13,14,36,43,44].

Since these skeletal rearrangements are quite general with platinacyclobutane complexes, it is possible to study factors influencing the relative stabilities of isomeric complexes. For the equilibrium (L) ⇌ (M) of eqn. (29), with R = Me, the equilibrium constant was found to increase with the bulk of the ligands L being 2.4 (L = CD_3CN), 4.0 (L = tetrahydrofuran) and 5.7 (L = C_5H_5N) [11]. Also when R = Et, ^iPr, Bu or n-C_6H_{13} none of isomer (L) could be detected when L = pyridine [9,11,12]. Thus it seems that increased steric effects favor isomer (M) in which the alkyl group, R, is remote from platinum. When R = aryl, *ortho* substituents destabilise (L) with respect to (M) and this is again a steric effect [13]. When R is 4-XC_6H_4, electron releasing groups X favor isomer (M) and this must be an electronic effect [13]. Overall it seems that electron-withdrawing substituents favor isomer (L) and electron-releasing substituents favor (M), and that steric effects favor (M) [11,13]. The relative stabilities of isomers derived from 1,1- and *trans*-1,2-disubstituted cyclopropanes can be understood in terms of these principles [13]. In complexes derived from *cis*- or *trans*-1,2-diphenylcyclopropane, molecular models indicate the relative stabilities *trans*-1,2 > *trans*-1,3 > *cis*-1,3 >> *cis*-1,2-diphenylpropane-1,3-diylplatinum species [13]. Using space-filling molecular models it is not possible to make the last isomer due to severe steric hindrance between the two phenyl groups and between phenyl groups and other ligands on platinum. Considering only the platinacyclobutane ring, it might be expected that the *cis*-1,3 isomer, (Q), might be most stable, since the substituents could occupy pseudo-equatorial positions on a puckered metallacyclobutane ring as shown below [50].



(Q)



(R)

However, extra steric hindrance between the phenyl groups and the other ligands on platinum appear to make this isomer less favorable than the *trans*-1,3-isomer, (R), in which the axial—axial Ph—H steric interaction would be less if the ring adopted a less-puckered structure.

No isomerisation reactions of platinum(II) metallacyclobutanes have been reported.

G. REACTIONS OF PLATINACYCLOBUTANES

Most reactions of platinacyclobutanes involve cleavage of the strained PtC_3 ring, and reactions are broadly classified according to the nature of products formed.

(i) Hydrogenolysis to give alkanes

Tetrameric platinacyclobutanes of the type $[\{PtCl_2(C_3H_5R)\}_4]$ when dissolved in alcohol react rapidly with hydrogen to give the products shown in Table 11 [7]. It is not known if the alkanes formed result from mixtures of isomeric platinacyclobutanes or if isomerisation occurs during hydrogenolysis. In some cases, parent cyclopropanes are formed along with hydrogenated products and this is also the case if the complexes are reduced with lithium aluminum hydride. Molecular hydrogen is usually activated by oxidative addition, but this is clearly not possible in this case and the mechanism of reaction is not known.

Table 11 also gives the products formed in the platinum-catalysed hydrogenation of the parent cyclopropanes in ethanol [51]. In many cases there are strong similarities in product distribution.

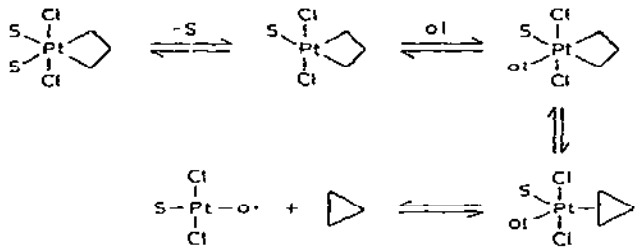
TABLE 11

Products of hydrogenolysis of platinacyclobutanes and cyclopropanes

Compound	Catalyst	Products (%)		
$PtCl_2(C_3H_5Ph)$		Ph–∧	Ph–≺	$C_6H_{11}Pr$
C_3H_5Ph	Pt	56 90	14 3	30 7
$PtCl_2(C_3H_5CH_2Ph)$		$PhCH_2$–◁	Ph–⌐	Ph–≺
		20	26	51
			$C_6H_{11}CH_2Pr$	$C_6H_{11}CH_2CHMe_2$
$PhCH_2C_3H_5$	Pt		3 25	0 75
$PtCl_2(C_3H_5\text{-}nC_6H_{13})$		C_5H_{13}–◁	C_6H_{13}–∧	C_6H_{13}–≺
$n\text{-}C_6H_{13}C_3H_5$	Pd	40	15 5	45 95
$PtCl_2(trans\text{-}1,2\text{-}Ph_2C_3H_4)$		$C_6H_{11}(CH_2)_3C_6H_{11}$		$C_6H_{11}CH(CH_3)CH_2C_6H_{11}$
$trans\text{-}1,2\text{-}Ph_2C_3H_4$	Pt	36 42		64 58
$PtCl_2(cis\text{-}1,2\text{-}Ph_2C_3H_4)$		$C_6H_{11}(CH_2)_3C_6H_{11}$		$C_6H_{11}CH(CH_3)CH_2C_6H_{11}$
$cis\text{-}1,2\text{-}Ph_2C_3H_4$	Pt	9.5 35		90.5 65

(ii) Reductive elimination of cyclopropanes

Cyclopropanes are formed in many reactions of platinacyclobutanes, often along with other products. Treatment of $[\{PtCl_2(CH_2CH_2CH_2)\}_4]$ with arylcyclopropanes [17], alkenes [7,10,22,23], carbon monoxide [9], sulphur, phosphorus, arsenic or antimony donors [2,4,7,22], cyanide or iodide gives cyclopropane in almost quantitative yield. Analogous reactions are found with complexes derived from substituted cyclopropanes. Kinetic studies have been carried out on the displacement of cyclopropane by alkenes [23] and by other cyclopropanes [17]. The displacement by alkenes was deduced to occur by the mechanism of eqn. (35) (S = tetrahydrofuran, ol = olefin).



(35)

From studies of the kinetics of this reaction in both directions [17,23], it was deduced that the equilibrium constant for the reaction of eqn. (36) should be 5.4 (S = tetrahydrofuran at unit activity, ol = olefin).

$$[PtCl_2(C_3H_5Ph)S_2] + ol \rightleftharpoons [PtCl_2(ol)S] + PhC_3H_5 \qquad (36)$$

Similar elimination of cyclopropane by soft ligands occurs with the monomeric complexes $[PtX_2(CH_2CH_2CH_2)L_2]$ (X = halide, L = nitrogen donor), provided that the incoming ligand can compete effectively with the ligand L for a co-ordination site at platinum. For example, with $[PtCl_2(CH_2CH_2CH_2)(C_5H_5N)_2]$, the rate of cyclopropane displacement according to eqn. (37), follows the order $L = PPh_3 > AsPh_3 > SbPh_3$, while alkenes and cyclopropanes fail to react. The order clearly follows the complexing ability of these ligands for platinum [22].

$$[PtCl_2(CH_2CH_2CH_2)(C_5H_5N)_2] + 2\ L \rightarrow cis\text{-}[PtCl_2L_2] + \triangleright + 2\ C_5H_5N \qquad (37)$$

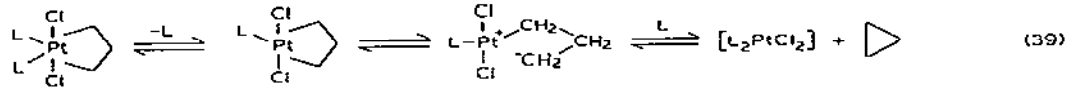
Complexes $[PtCl_2(CH_2CH_2CH_2)(L\frown L)]$, where $L\frown L$ is 2,2′-bipyridine or ethylenediamine, are only slowly decomposed, even by reaction with PPh_3, because the chelate ligands do not easily dissociate and hence the phosphine cannot co-ordinate to the platinum centre [22].

In contrast, platinum(II) metallacyclobutanes are evidently stable with soft ligands though on oxidation cyclopropane is easily lost, probably via a short-

lived platinum(IV) intermediate (eqn. 38) [35].

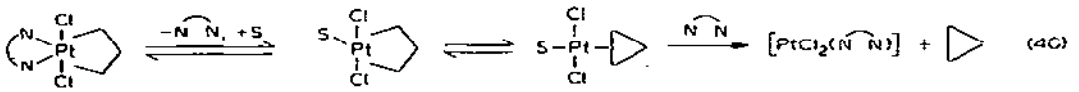
$$[\overline{Pt(CH_2CMe_2CH_2)}(PEt_3)_2] + I_2 \rightarrow [PtI_2(PEt_3)_2] + Me_2C\begin{matrix}CH_2\\ |\\ CH_2\end{matrix} \quad (38)$$

Heating platinum(IV) metallacyclobutanes leads to elimination of cyclopropane, usually along with other products. On the basis of kinetic studies, Gillard and co-workers proposed that cyclopropane (along with an ylide complex of platinum, vide infra) was formed from $[PtCl_2(CH_2CH_2CH_2)(C_5H_5N)_2]$ by the mechanism of eqn. (39), (L = C_5H_5N) [35].



(39)

Thermal decomposition of $[\overline{PtCl_2(CH_2CH_2CH_2)}(bipy)]$ in hot chlorobenzene occurs to give $[PtCl_2(bipy)]$, cyclopropane (~80%) and propene (~20%). A kinetic study showed that complete dissociation of 2,2'-bipyridine occurred prior to elimination of cyclopropane and the following mechanism was proposed [20] (eqn. 40, N⌒N = bipy).



(40)

Reductive elimination via the edge complex rather than a dipolar intermediate was preferred.

Photolysis of these compounds also gives some cyclopropane along with other products. The evidence suggests that the chelate ligand does not dissociate in this case, and it seems that ionisation of chloride may occur followed by a radical process [52,53]. The ratio of cyclopropane to propene, ethylene and other products was strongly dependent on the solvent and on the nature of additives to the solution, being highest in polar solvents (CH_3CN, DMSO) in the presence of soft ligands (I^- or $SbPh_3$) [53].

The reductive elimination of cyclopropane generally occurs with retention of stereochemistry about the ring as shown by the data in Table 12. This observation is consistent with reductive elimination by a concerted mechanism involving an edge-complex intermediate, but not with a mechanism involving ionic or radical intermediates since rotation about C—C bonds could then occur. However, under some conditions *cis—trans* isomerisation can occur to some extent. Thus reaction of $[\overline{PtCl_2(trans\text{-}CHPhCHPhCH_2)}(C_5H_5N)_2]$ in chloroform solution with aqueous KCN gave 86% *trans*- and 14% *cis*-1,2-diphenylcyclopropane, while the analogous platinacyclobutane from *cis*-1,2-diphenylcyclopropane gave 9% *trans*- and 91% *cis*-1,2-diphenylcyclopropane under these conditions. Under these conditions it is possible that an ionic intermediate, $Pt^-CH_2CHPh^+CHPh$, is formed to some extent thus allowing *cis—trans* isomerisation. Similar effects were observed in the

TABLE 12

Stereochemistry of cyclopropane formation from platinacyclobutanes

Complex	Reagent	Cyclopropane	Ref.
$[\{PtCl_2(trans\text{-}1,2\text{-}Ph_2C_3H_4)\}_n]$	CN^-	*trans*-$1,2\text{-}Ph_2C_3H_4$	7, 9, 54
$[\{PtCl_2(cis\text{-}1,2\text{-}Ph_2C_3H_4)\}_n]$	CN^-	*cis*-$1,2\text{-}Ph_2C_3H_4$	7, 9
$[PtCl_2(trans\text{-}CHPhCHPhCH_2)(C_5H_5N)_2]$	CN^-	86% *trans* and 14% *cis*-$1,2\text{-}Ph_2C_3H_4$	54
$[PtCl_2(trans\text{-}CHPhCHPhCH_2)(C_5H_5N)_2]$	PPh_3	*trans*-$1,2\text{-}Ph_2C_3H_4$	14, 54
$[PtCl_2(cis\text{-}1,2\text{-}Ph_2C_3H_4)(C_5H_5N)_2]$	CN^-	9% *trans* and 91% *cis*-$1,2\text{-}Ph_2C_3H_4$	54
$[PtCl_2(cis\text{-}1,2\text{-}Ph_2C_3H_4)(C_5H_5N)_2]$	PPh_3	*cis*-$1,2\text{-}Ph_2C_3H_4$	14, 54
$[PtCl_2(trans\text{-}1,2\text{-}Me_2C_3H_4)(C_5H_5N)_2]$	PPh_3	*trans*-$1,2\text{-}Me_2C_3H_4$	11, 55
$[PtCl_2(cis\text{-}1\text{-}Ph\text{-}2\text{-}DC_3H_4)(C_5H_5N)_2]$	PPh_3	*cis*-$1\text{-}Ph\text{-}2\text{-}DC_3H_4$	43
$[PtCl_2(cis\text{-}2\text{-}Ph\text{-}1\text{-}DC_3H_4)(C_5H_5N)_2]$	PPh_3	*cis*-$1\text{-}Ph\text{-}2\text{-}DC_3H_4$	43
$[PtCl_2(trans\text{-}1\text{-}Ph\text{-}2\text{-}DC_3H_4)(C_5H_5N)_2]$	PPh_3	*trans*-$1\text{-}Ph\text{-}2\text{-}DC_3H_4$	14
$[PtCl_2(trans\text{-}2\text{-}Ph\text{-}1\text{-}DC_3H_4)(C_5H_5N)_2]$	PPh_3	*trans*-$1\text{-}Ph\text{-}2\text{-}DC_3H_4$	14
$[\{PtCl_2(trans\text{-}1,2\text{-}Me_2C_3H_4)\}_n]$	(+)-DIOP	RR-*trans*-$1,2\text{-}Me_2C_3H_4$ [a]	55
$[\{PtCl_2(trans\text{-}1,2\text{-}Me_2C_3H_4)\}_n]$	(−)-DIOP	SS-*trans*-$1,2\text{-}Me_2C_3H_4$ [b]	55
$[\{PtCl_2(trans\text{-}1,2\text{-}Me_2C_3H_4)\}_n]$	(−)-β-pinene	SS-*trans*-$1,2\text{-}Me_2C_3H_4$ [c]	55

Enantiomeric excess: [a] 35%, [b] 31%, [c] 5%.

platinacyclobutane from *trans*-1,2-di(4-tolyl)-cyclopropane [54]. Since the stereochemistry of the platinacyclobutane is sometimes deduced from that of the cyclopropane formed in such reactions, it is clear that cyanide should not be used to regenerate the cyclopropane.

Of particular interest is the observation that $[\{PtCl_2(\overline{trans\text{-}CHMeCHMeCH_2}\})_n]$ on treatment with 0.5 mole equivalent of a chiral phosphine or olefin gives chiral *trans*-1,2-dimethylcyclopropane in fair optical yield, giving a useful method for kinetic resolution of *trans*-1,2-dimethylcyclopropane [55]. The other optical isomer is obtained by reaction of the residual $[\{PtCl_2(trans\text{-}CHMeCHMeCH_2)\}_n]$ with triphenylphosphine.

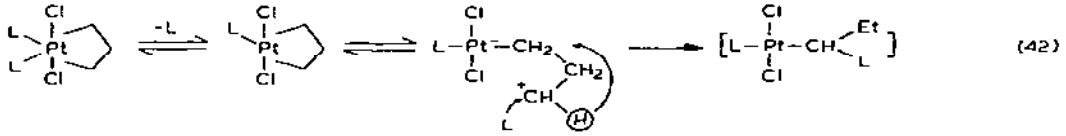
(iii) Reactions giving ylide complexes

Chatt showed that heating a benzene solution of $[PtCl_2(\overline{CH_2CH_2CH_2})(C_5H_5N)_2]$ led to formation of a yellow isomer [3], and this was subsequently shown by Mason and co-workers to be an ylide complex (eqn. 41, L = pyridine) [4,56].

$$[PtCl_2(CH_2CH_2CH_2)L_2] \rightleftharpoons \left[\begin{array}{c} Cl \\ | \\ L-Pt^- \\ | \\ Cl \end{array} \!\!-CH\!\!\begin{array}{l} \diagup\, L^+ \\ \diagdown\, Et \end{array}\right] \qquad (41)$$

If the reaction was carried out in chloroform, the platinum(IV) ylide derivative $[PtCl_4(py)(CHEtpy)]$ was formed by oxidation by the solvent.

A study of the kinetics of the rearrangement to the ylide complex showed that reaction was retarded by added pyridine and a dipolar intermediate was suggested (eqn. 42, L = pyridine) [35].



(42)

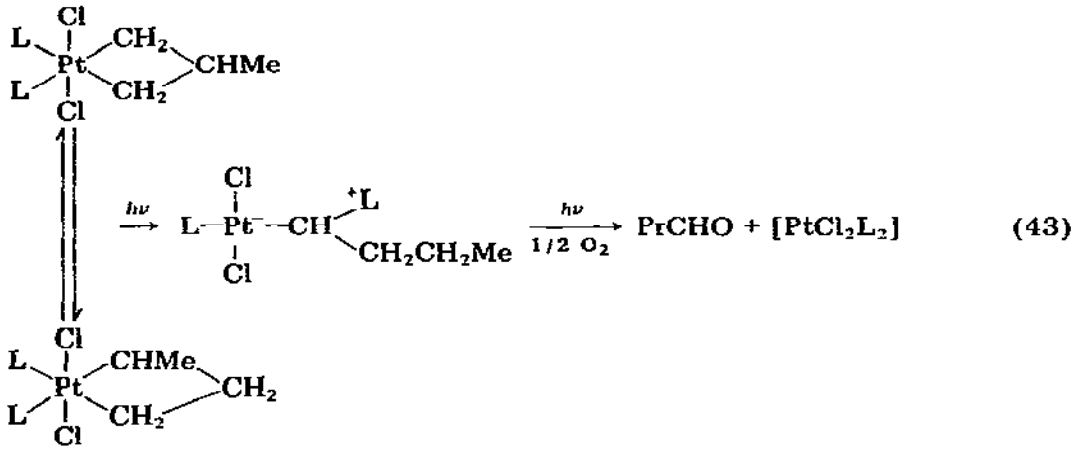
TABLE 13

Ylide complexes from platinacyclobutanes

Complex	Ligand, L	Ylide	Ref.
$\{PtCl_2(CH_2CHMeCH_2)\}_n$ [a]	2-Mepy	$[PtCl_2L\{CH(L)CH_2CH_2Me\}]$	21
$\{PtCl_2(CH_2CHBuCH_2)\}_n$	2-Mepy	$[PtCl_2L\{CH(L)CH_2CH_2Bu\}]$	21
$\{PtCl_2(CH_2CHPhCH_2)\}_n$	2-Mepy	$[PtCl_2L\{CH(L)CH_2CH_2Ph\}]$	21, 57
$\{PtCl_2(CH_2CH(4\text{-}tol)CH_2)\}_n$ [a]	2-Mepy	$[PtCl_2L\{CH(L)CH_2CH_2(4\text{-}tol)\}]$	21
$\{PtCl_2(CH_2CMe_2CH_2)\}_n$	2-Mepy	$[PtCl_2L\{CH(L)CH_2CHMe_2\}]$	21, 57

[a] Present as mixture with α-alkyl or α-aryl isomer.

Ylide complexes can also be formed from ring-substituted platinacyclobutanes and photochemical as well as thermal activation is possible; further photolysis of the ylide complexes gives aldehydes (eqn. 43, L = pyridine) [21,57].

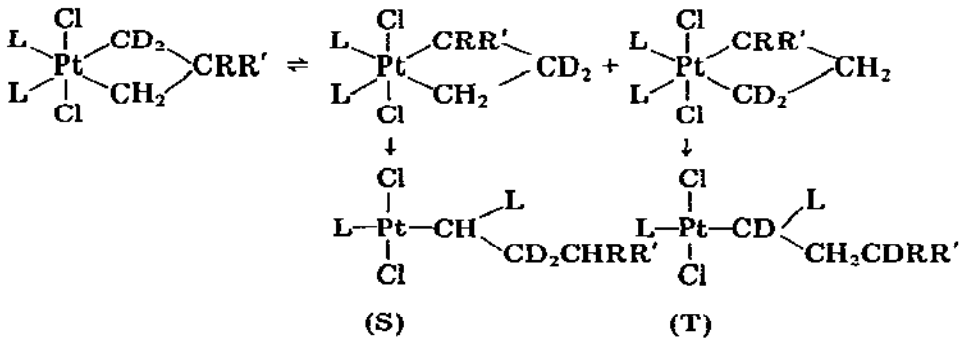


(43)

Of particular interest, is the observation that the equilibrium mixture of isomeric platinacyclobutanes gave only one isomer of the ylide complex, that expected to be formed from the minor α-methyl isomer. Ylide complexes are often formed at room temperature if the bulkier ligand 2-methylpyridine is used, and again the ylides are formed as single isomers (Table 13).

The ylide $[PtCl_2L\{CH(L)CH_2CHMe_2\}]$, L = 2-methylpyridine, is presumably formed from the platinacyclobutane $[PtCl_2(CH_2CH_2CMe_2)L_2]$, although this isomer was so much less stable than $[PtCl_2(CH_2CMe_2CH_2)L_2]$ that it could not be detected in solution. It was therefore suggested that skeletal isomerisation was fast compared to the rate of ylide formation and that the least stable isomer decomposed preferentially [57].

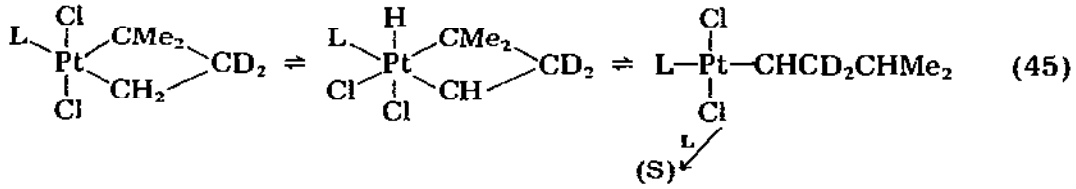
In two cases, labelling experiments proved that reaction to give ylide complexes involved a 1,3-H shift (eqn. 44; R, R′ = Ph, H or Me, Me; L = 2-methylpyridine) [21,57].



(44)

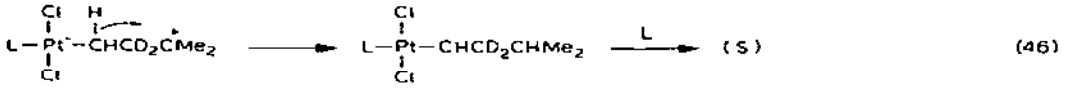
(S) (T)

When R = R′ = Me, the ratio of (S) (formed by H-migration): (T) (formed by D-migration) was ca. 1.6 and, if skeletal isomerisation is fast compared to ylide formation, this represents a deuterium isotope effect. The reaction was assumed to occur by an α-elimination (e.g. eqn. 45) [57].



(45)

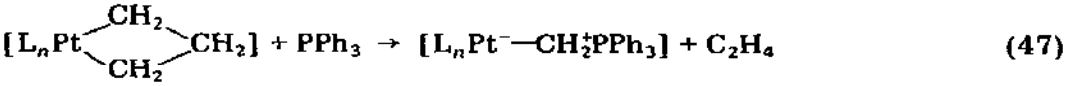
An alternative would involve formation of the most stable dipolar intermediate (eqn. 46), followed by a 1,3-hydride shift.



(46)

However, 1,2-hydride shifts are more common in carbonium ions so this mechanism is considered less likely. The H-shift mechanism proposed by Gillard cannot readily explain the products from ring substituted platinacyclobutanes [35].

In some cases, thermal or photochemical reaction of platinacyclobutanes in the presence of triphenylphosphine leads to formation of ethylene (vide infra) and parallel formation of phosphine ylide complexes has been tentatively suggested, though direct evidence is lacking (eqn. 47) [58].



(47)

(iv) Reactions giving alkene complexes

Cushman and Brown reported the first example of this reaction (eqn. 48, L = pyridine) [25].

(48)

They suggested two possible mechanisms illustrated in eqn. (49)

(49)

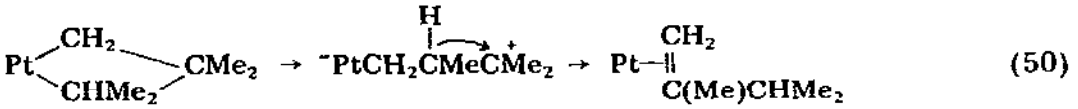
TABLE 14

Alkene complexes from platinacyclobutanes

Platinacyclobutane	Ligand, L	Product	Ref.
$[PtCl_2(CH_2CHMeCH_2)]$	CD_3CN	$[PtCl_2(L)(CH_2{=}CHCH_2Me)]$	11
$[PtCl_2(CH_2CHMeCH_2)]$	2,6-$Me_2C_5H_3N$	$[PtCl_2(L)(CH_2{=}CHCH_2Me)]$	21
$[PtCl_2(CH_2CMe_2CH_2)]$	2,6-$Me_2C_5H_3N$	$[PtCl_2(L)(CH_2{=}CHCHMe_2)]$	21, 57
$[PtCl_2(CH_2CMe_2CH_2)]$	CD_3CN	$[PtCl_2(L)(CH_2{=}CHCHMe_2)]$	21
$[PtCl_2(CHMeCHMeCH_2)]$	2-MeC_5H_4N	$[PtCl_2(L)(CH_2{=}CMeEt)]$	21
$[PtCl_2(CHMeCHMeCH_2)]$	CD_3CN	$[PtCl_2(L)(CH_2{=}CMeEt)]$	21
$[PtCl_2(CHMeCMe_2CH_2)]$	C_5H_5N	$[PtCl_2(L)(CH_2{=}CMe\text{-}^iPr)]$	12, 25, 59

Johnson and Cheng later proved that Mechanism (ii) involving isomerisation of the platinacyclobutane followed by a 1,2-hydride shift was correct by elegant selective deuterium labelling experiments. The H-shift is believed to occur by β-elimination followed by reductive elimination, and β-elimination of ring hydrogen rather than a hydrogen from an α-methyl group was preferred. However, some of the latter process did occur [59].

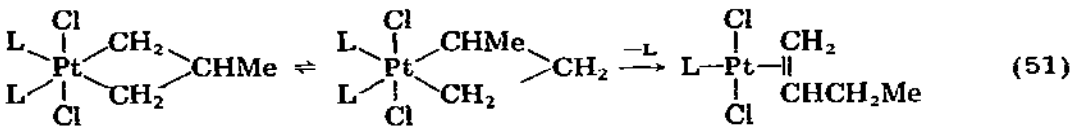
A dipolar mechanism, proceeding through the most stable carbonium ion possible, is not inconsistent with the mechanistic evidence but seems less likely (eqn. 50).



(50)

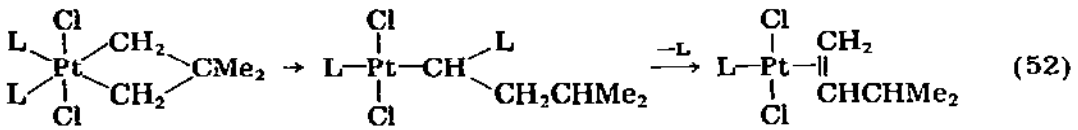
Formation of alkene complexes of platinum is also favored from platinacyclobutanes with weakly co-ordinating or bulky nitrogen-donor ligands (Table 14).

In one case, the preliminary isomerisation of the platinacyclobutane complex could be demonstrated directly (eqn. 51, L = CD_3CN) [11].



(51)

The formation of alkene complex from reaction of $[\{PtCl_2(CH_2CMe_2CH_2)\}_n]$ and 2,6-dimethylpyridine was shown by low temperature NMR studies to be preceded by formation of an ylide complex, itself formed by the α-elimination mechanism (eqn. 52, L = 2,6-dimethylpyridine).



(52)

The formation of alkene complex from ylide complex involves loss of the ylide ligand, L, followed by a 1,2-H shift [57]. In this case the ylide complex is probably destabilised by steric hindrance. A similar mechanism is probable when L = CD_3CN, since this weak donor would be unable to give a stable ylide.

It is clear that rather small structural differences can cause a change in the mode of decomposition of platinacyclobutanes from the β-elimination to the α-elimination mechanism, but the reasons for the mechanistic change are not understood. Further labelling studies are needed to determine the modes of decomposition of other platinacyclobutanes.

(v) Reactions giving η^3-allyl complexes

η^3Allylplatinum(II) complexes may be obtained by heating platinacyclobutanes (eqn. 53) [7,9].

$$[\{\overbrace{PtCl_2(CHPhCH_2CH_2)}\}_n] \xrightarrow[CCl_4]{heat} [(\langle\!-PtCl)_2] + HCl \qquad (53)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\quad Ph$$

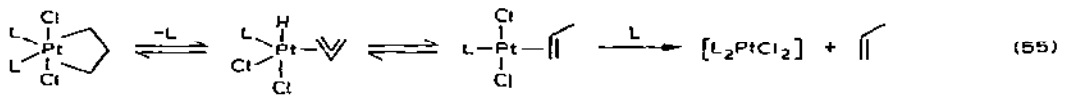
In other cases, the platinacyclobutane may not be detected but is presumed to be formed as an intermediate (eqn. 54) [7,9]

$$Ph_2C\begin{matrix}CH_2\\|\\CH_2\end{matrix} + \{PtCl_2(C_2H_4)\}_2 \rightarrow (\langle\!-PtCl)_2 + C_2H_4 + HCl \qquad (54)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad Ph$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad Ph$$

Bulky substituents appear to promote decomposition of platinacyclobutanes in this way. Thus, cyclopropanes *trans*-1,2-$R_2C_3H_4$ with Zeise's dimer gave platinacyclobutanes when R = Me or Ph, but η^3-allyl complexes when R = 2-$MeOC_6H_4$ or 2,5-$(MeO)_2C_6H_3$ [11].

Only when the platinacyclobutane contained aryl substituents on the ring have η^3-allyl complexes been isolated, though they are thought to be formed in some other systems [9].

η^3-Allyl complexes have been proposed as intermediates in the formation of alkene complexes from platinacyclobutanes (eqn. 55) [20,41].



(55)

Clearly whether η^3-allyl or η^2-alkene complexes are formed depends on whether the presumed intermediate η^3-allylplatinum(IV) species undergoes reductive elimination of HCl or of propene.

(vi) Reactions giving alkenes

Decomposition of platinacyclobutanes to give alkenes is very common. It is generally believed that alkene complexes of platinum(II) are first formed,

either directly or via ylide complexes as discussed in section G, (iv), and that the alkene is then displaced from platinum. Both thermal and photochemical decomposition of complexes $[PtX_2(CH_2CH_2CH_2)L_2]$ give propene along with cyclopropane and other products, the product distribution depending on the nature of X and L, the solvent, temperature and nature of additives to the solutions [3,4,20,41,52,53,58]. Generally, propene formation must be preceded by ligand dissociation to create a vacant co-ordination site needed for the α- or β-elimination process but, in the photochemical decomposition, there is some evidence that a direct 1,2-hydride shift occurs without ligand dissociation [53].

Of particular interest are reactions of platinacyclobutanes to give ethylene by a reaction involving C—C bond cleavage. Ethylene can be the major product in both thermal and photochemical decomposition of the complexes $[PtX_2(CH_2CH_2CH_2)(phen)]$ in polar solvents such as CH_3CN or DMSO and in the presence of tertiary phosphines. For example, the very slow thermal reaction at room temperature when X = Br in CH_3CN or DMSO in the presence of PPh_3 gives 90% ethylene and methane, propene and cyclopropane. When the reaction is carried out in CD_2Cl_2 as solvent, some $CH_2{=}CD_2$ is formed. It is clear that the transformation $PtCH_2CH_2CH_2 \rightarrow PtCH_2 + C_2H_4$ must occur at some stage, and the role of the added phosphine may be to trap the carbene as the stable ylide complex, $LnPtCH_2PPh_3$ [53,58].

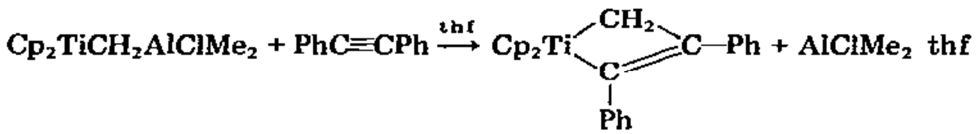
(vii) Other reactions of platinacyclobutanes

The platinacyclobutane $[Pt(CH_2CMe_2CH_2)(PEt_3)_2]$ reacts with DCl to give largely $Me_2C(CH_2D)_2$ and $[PtCl_2(PEt_3)_2]$, but platinum(IV) metallacyclobutanes react only slowly with acid [35]. Photolysis of $[PtCl_2(CH_2CH_2CH_2)(phen)]$ in the presence of toluene or PhSH gives some propane, and in the presence of CBr_4 it gives some 1,3-dibromopropane. These products are suggested to arise by abstraction of H or Br by the radical species $[Cl_2(phen)PtCH_2CH_2CH_2^{\bullet}]$ [53].

H. OTHER TRANSITION METALLACYCLOBUTANES

Rather few metallacyclobutanes have been characterised for transition metals other than platinum, and a brief review is presented here. No attempt at comprehensive literature coverage has been made.

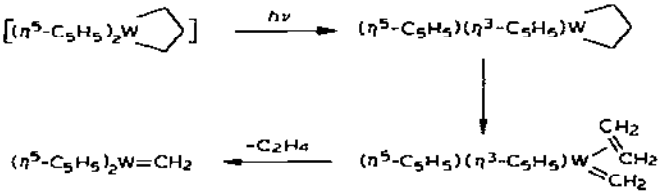
The interesting titanium complex $(\eta^5\text{-}C_5H_5)_2TiCH_2AlClMe_2$ acts as a methylene complex. It catalyses olefin metathesis, though the presumed titanacyclobutane intermediates have not been directly characterised, and reacts with diphenylacetylene to give an isolable titanacyclobutene (eqn. 56) [60].


(56)

Several metallacyclobutane derivatives of molybdenum(IV) and tungsten(IV) have been prepared according to eqn. (57) [M = Mo, W; R = H (X = $NaBH_4$), D (X = $NaBD_4$), $CH_2{=}CHCH_2$ (X = $ClMgCH_2CH{=}CH_2$)].

(57)

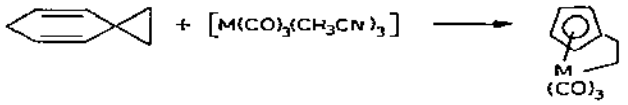
These compounds are formed by nucleophilic attack on the β-carbon of the η^3-allyl group [61]. Similar derivatives with methyl substituents on the ring were prepared in a similar way. Thermal decomposition of $[(\eta^5\text{-}C_5H_5)_2WCH_2CH_2CH_2]$ gave a mixture of cyclopropane and propene but photolysis gave mostly ethylene and some methane. The mechanism of eqn. (58) was suggested to account for these products [62].



(58)

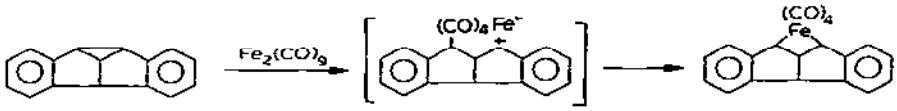
The chemistry clearly resembles that of the platinum(IV) metallacyclobutanes discussed earlier.

The cyclopropyl ring is opened to give a derivative which appears to have some metallacyclobutane character in the following reaction (eqn. 59, M = Mo or W) [63].



(59)

A very stable ferracyclobutane has been prepared as shown in eqn. (60) from dibenzosemibullvalene [64].



(60)

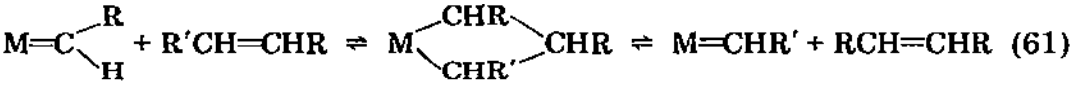
The dipolar intermediate was proposed rather than a concerted insertion into the cyclopropane ring. Similar intermediates were proposed for reactions of other cyclopropyl derivatives with $[Fe_2(CO)_9]$, but did not lead to stable metallacyclobutanes. The ferracyclobutane undergoes reversible carbon monoxide insertion into one of the Fe—C bonds, and similar chemistry of dibenzosemibullvalene with rhodium(I) complexes has been studied [81].

I. METALLACYCLOBUTANES AS REACTION INTERMEDIATES

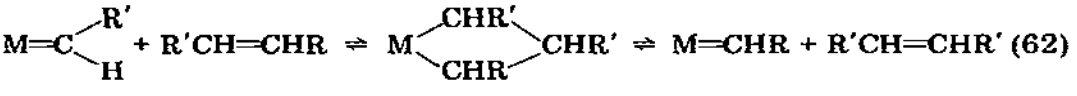
Metallacyclobutanes are now commonly proposed as reaction intermediates in both stoichiometric reactions and transition metal catalysed reactions. It is not possible to give a comprehensive coverage here, but a brief review of selected topics is given below.

(i) Alkene metathesis

Most authors now accept the Herisson—Chauvin mechanism of alkene metathesis illustrated in eqns. (61) and (62) [65].



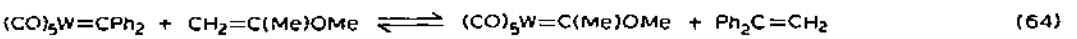
(61)



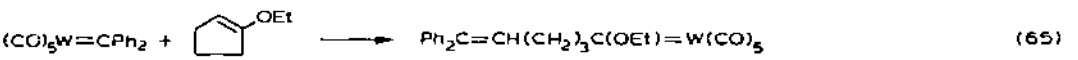
(62)

The evidence has been summarised in several excellent reviews and will not be repeated here [48]. Some recently discovered reactions which are relevant are given below. Exchange of alkylidene units between metal—carbene complexes and alkenes has been demonstrated (eqns. 63—65) [60,66,67].

(63)

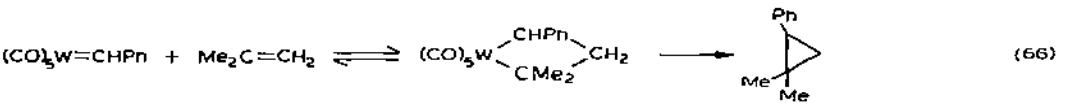


(64)



(65)

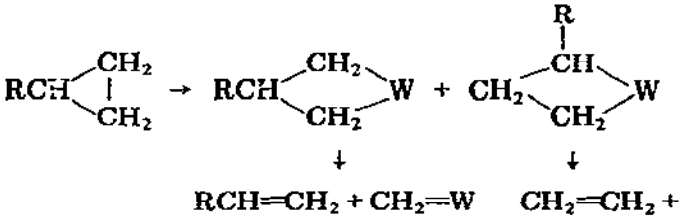
Cyclopropanes have been formed from metal—carbene complexes and alkenes (eqn. 66).



(66)

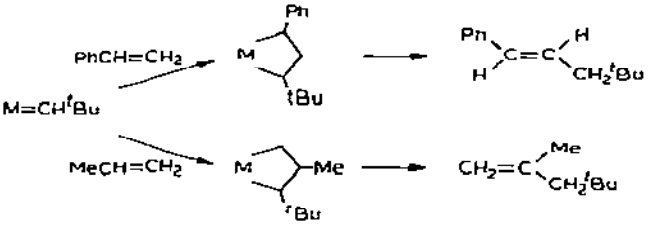
In this case, the tungstacyclobutane intermediate is now considered doubtful and a dipolar intermediate is preferred [68]. The stereochemistry of alkene metathesis has often been rationalised in terms of specific steric interactions in metallacyclobutanes [48,68,69], and puckered platinacyclobutanes, which can isomerise to give the more stable isomer, have been used as models to assess these steric effects.

The elimination of methylene units from cyclopropanes can be achieved by olefin metathesis catalysts such as $PhWCl_3$—$AlCl_3$, and metallocyclobutane intermediates are proposed (eqn. 67) [70].



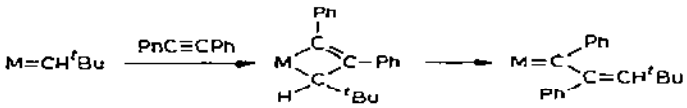
$$RCH{=}CH_2 + CH_2{=}W \qquad CH_2{=}CH_2 + RCH{=}W \tag{67}$$

The decomposition of metallacyclobutanes to metal—alkene complexes (Section G(iv)) has been proposed as a termination step in the alkene metathesis chain reaction [48]. Tantalacyclobutanes have been suggested as intermediates in reactions of tantalum—carbene complexes with alkenes (eqn. 68, M = $(\eta^5\text{-}C_5H_5)Cl_2Ta$) [71].



(68)

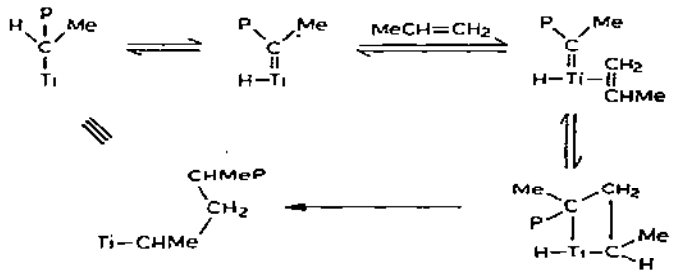
In this case higher alkenes are formed, but with diphenylacetylene a new carbene complex is obtained (eqn. 69) [72].



(69)

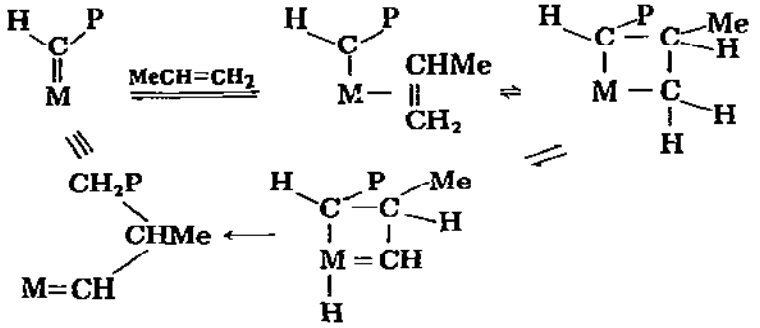
(ii) Olefin dimerisation and polymerisation

The intriguing suggestion has been made that Ziegler—Natta polymerisation of alkenes may occur by a mechanism involving metallacyclobutanes (eqn. 70, P = polymer) [73].



(70)

Very similar schemes can be written for alkene dimerisation and oligomerisation catalysed by metal complexes [73]. Based on the known chemistry of platinacyclobutanes, a modified scheme has been proposed (eqn. 71) [57].



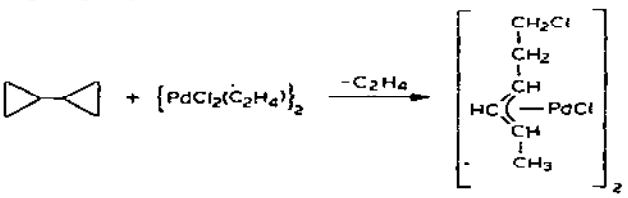
(71)

These schemes are highly speculative, but the intermediacy of metallacyclobutanes is perhaps indicated by the similarity of catalysts for Ziegler Natta polymerisation and for alkene metathesis [73].

(iii) Reactions of cyclopropanes

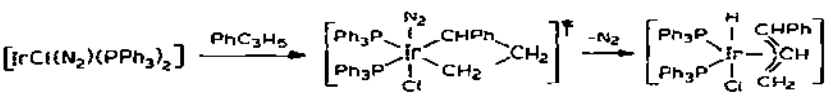
Skeletal rearrangements of strained ring carbocyclic compounds are often catalysed by transition metal complexes. An excellent review of this subject has been published [74], and the material will not be repeated here. When C_3 rings are present, the rearrangements can often be interpreted in terms of insertion of the metal into the C_3 ring to give a metallacyclobutane, followed by decomposition of the metallacyclobutane by one of the modes discussed earlier, though it must be said that this interpretation has not always been adopted by workers in this field.

η^3-Allyl complexes are formed by reaction of cyclopropanes with several palladium(II) complexes, and intermediate palladacyclobutanes or cyclopropane edge complexes have sometimes been suggested as intermediates [75] e.g. eqn. (71).



(71)

In one case a hydrido(η^3-allyl)metal complex is formed from phenylcyclopropane (eqn. 72) [76].



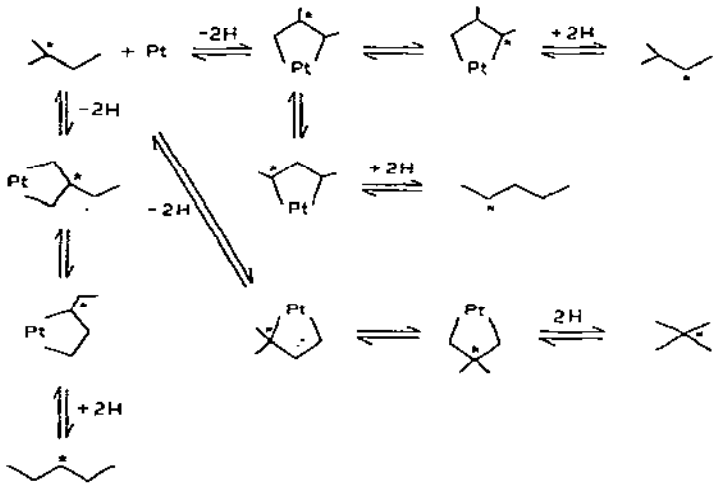
(72)

This is a rare example where the β-elimination step occurs and the hydrido species produced does not undergo further reaction to give alkene or other products [76].

Cyclopropanes are adsorbed and hydrogenated on platinum and other noble metal surfaces, and the nature of the adsorbed species has been discussed [77–79]. The product distribution from Pt catalysed hydrogenation of substituted cyclopropanes resembles that from hydrogenolysis of platinacyclobutanes and similar intermediates may be invoked [51]. However, recent NMR studies on cyclopropane adsorbed on platinum suggest that the cyclopropane ring is intact but with longer C—C bonds than in free cyclopropane. A sideways-bound cyclopropane was therefore suggested rather than a platinacycloalkane [74].

(iv) Skeletal isomerisation and cracking of hydrocarbons

A key reaction in the petrochemicals industry is the reforming of hydrocarbons over platinum metal catalysts. Species resembling platinacyclobutanes have been proposed to account for some of the products formed. For example, the "bond shift" mechanism for isomerisation of hydrocarbons could occur by the mechanism of eqn. (73) (C* = ^{13}C labelled carbon) [80].



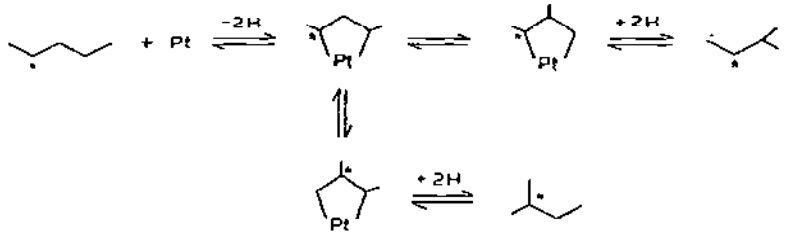
(73)

This scheme takes into account the known skeletal isomerisation of platinacyclobutanes, which indicates that only a single platinum centre may be needed *. The initially proposed scheme involved several platinum atoms acting co-operatively, and this may of course be the case at a platinum surface. Also,

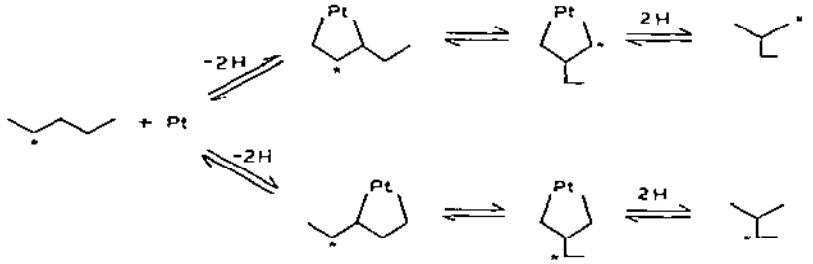
* Note added in proof. A very similar mechanism has been independently proposed by Parshall et al. [82].

it should be pointed out that the original workers believe the n-pentane to be formed by a different mechanism from the iso- and neo-pentanes [80].

Similarly isomerisation of n-pentane to iso-pentane can be explained (eqns. 74 and 75).



(74)



(75)

The product distribution can be explained if the reactions of eqns. (74) and (75) occur at relative rates of ca. 3 : 1, that is if there is a preference for the initial platinacyclobutane to be formed by attack of platinum at a secondary over a primary carbon atom.

Since C—C bond cleavage can occur in platinacyclobutanes, the cracking to lower hydrocarbons can also occur by a mechanism analogous to that proposed for alkene metathesis and using the above platinacyclobutane species.

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Erratum

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Scheme III on p. 72 was used with permission from O. Farver, M. Goldberg and I. Pecht, *Eur. J. Biochem.*, 104 (1980) 71—77.