

THE RING-EXPANSION REACTIONS OF
CYCLOBUTENEDIONES AND RELATED MOLECULES
BY TRANSITION METAL COMPLEXES.

A thesis presented for the Degree of
Doctor of Philosophy, in the
Faculty of Science, University of Leicester,
by Edmund Roger Harner.

August 1975

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THESIS
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S T A T E M E N T

The work herein described was carried out by the author in the Department of Chemistry, Leicester University, between November 1972 and August 1975 under the supervision of Dr. R.D.W. Kemmitt. The work has not been, and is not concurrently being submitted for any other degree.

E.R. HAMNER.

August 1975

A C K N O W L E D G E M E N T S

My greatest debt is to my supervisor, Dr. R.D.W. Kemmitt, who, with an endless flow of ideas, encouragement and enthusiasm, has guided me throughout this project.

To Dr. J. Burgess I express thanks for his assistance during the stormy passage through the kinetics section (and am indebted to R.J. Haines for his work on the kinetics of benzocyclobutenedione).

I am particularly grateful to my colleagues, Drs. M.A.R. Smith and N. Singh, who have not only given me their friendship but also the benefit of their extensive knowledge and experience (of which I have imbibed but a little). I would also like to thank the other members of the Inorganic Chemistry Department who have helped to create such a lively atmosphere throughout the last three years.

To my wife, who has toiled though so many hours to produce the typescript, I extend extra-special thanks.

The receipt of an S.R.C. Studentship is acknowledged.

For Barbara and my Mother

SUMMARY

The thesis is divided into four chapters:

- (1) Introduction
- (2) Results and discussion on the reactions of cyclobutenedione derivatives and related molecules with low-valent transition metal complexes.
- (3) A kinetic study of the ring-expansion reactions of some cyclobutenedione derivatives by platinum(0) complexes and
- (4) Experimental.

Chapter 1.

This chapter gives a general survey of the reactions of organic molecules containing small rings with transition metal complexes. The review concentrates on three- and four-membered ring compounds having both electron-donating and electron-withdrawing substituents in their reactions with the later transition metals. Particular accent is placed on the metals iron, rhodium, palladium and platinum.

Chapter 2.

The reactions of cyclobutenedione derivatives and related molecules with transition metal complexes are discussed. Hypotheses are put forward to account for the variation of products found in these reactions when both the nature of the substituent groups in the organic molecule and the transition metal complex are changed.

The spectroscopy results obtained for these complexes are discussed.

Chapter 3.

A kinetic study of the ring-expansion reactions of some cyclobutenedione derivatives by platinum(0) complexes is described. The reactivities of the species $\text{Pt}(\text{PPh}_3)_2$ and $\text{Pt}(\text{AsPh}_3)_2$ are compared, and a theory concerning the solution characteristics of $\text{Pt}(\text{AsPh}_3)_2$ is put forward.

Chapter 4.

All experimental details are given for the reactions studied in chapters 2 and 3. All analysis results, infrared and n.m.r. spectra are detailed.

REFERENCE SYSTEM

References in this thesis are designated a number-letter code of which the first two digits denote the year of publication, the next one or two letters the journal, and the final digits the page number. For journals of which more than one volume appears in one year, the volume number is given in round brackets immediately after the journal letter code. A list of the journals to which the letter codes refer is given in Appendix 1 at the back of the thesis.

Most journals are assigned letter codes bearing an obvious similarity to their titles. Books, a few journals to which references are rarely made, and all other sources are coded MI (miscellaneous) and are listed under the relevant year of publication.

The system is that devised by Professor A.R. Katritzky, with slight modification, and is used with his kind permission.

GENERAL POINTS IN THE THESIS

1) All ^1H n.m.r. spectra are quoted as p.p.m. (δ) downfield from internal tetramethylsilane and positive. ^{19}F n.m.r. spectra are treated individually in the text.

2) A table of abbreviations used in the text is given below:

bipy	=	2,2'-bipyridyl
cod	=	cycloocta-1,5-diene
diphos	=	1,2-diphenylphosphinoethane
π -cp	=	η^5 -cyclopentadienyl
py	=	pyridine
TCCP	=	1,1,2,2-tetracyanocyclopropane
TCNEO	=	tetracyanoethyleneoxide
TCNE	=	tetracyanoethylene
acac	=	acetylacetonate anion
dpm	=	dipivaloylmethanate anion

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Introduction

The reaction of transition metal complexes
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CHAPTER TWO

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iron(0) 125

Cyclic Sulphones with:

platinum(0) 131

palladium(0) 145

iron(0) 147

rhodium(I) 149

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APPENDIX 1

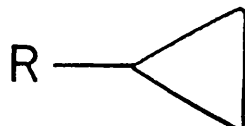
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CHAPTER 1.

INTRODUCTION.

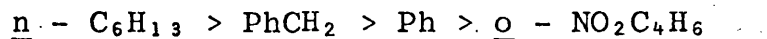
THE REACTION OF TRANSITION METAL COMPLEXES WITH
ORGANIC MOLECULES CONTAINING SMALL RINGS.

It was the postulation that cyclopropane may possess some olefinic character which led Tipper in 1955 to react this molecule with chloroplatinic acid in acetic anhydride (55J2045). The resulting brown amorphous compound was formulated as the dimeric $[\text{PtCl}_2(\text{C}_3\text{H}_6)]_2$ by analogy to Zeise's dimer $[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$. Treatment of the cyclopropane product with potassium cyanide, phosphines or propenylbenzene (61J738, 55J2045, 68TL1937) gave the free cyclopropane quantitatively, pure and unisomerised. The reaction of Zeise's dimer with a range of substituted cyclopropanes (1)



(1)

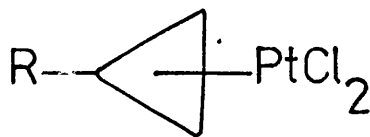
gave a reactivity series for the various substituents R, namely



Compound (1) having $\text{R} = \text{CN}$, COCH_3 and CO_2CH_3 did not react (70JO(24)787, 72J2123).

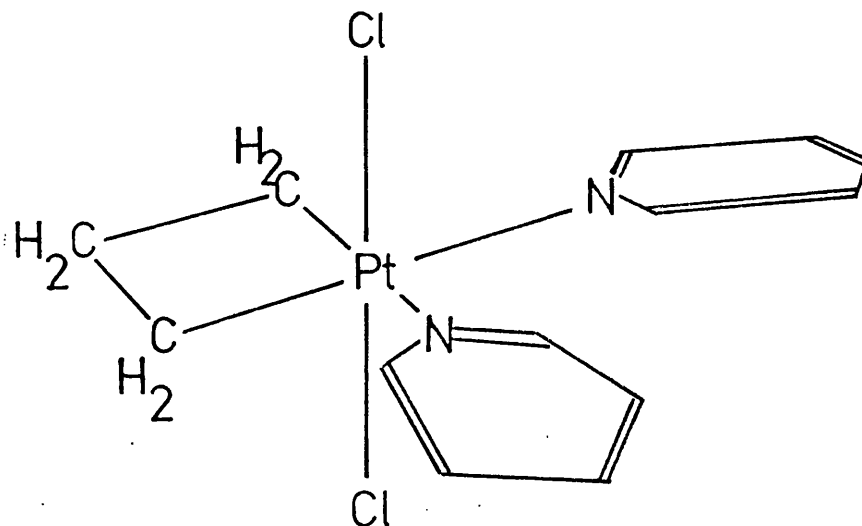
These results led to the conclusion that the complexing ability of the three-membered ring parallels electron density in the ring, leading to the postulated

structure (2) for the cyclopropane complexes.



(2)

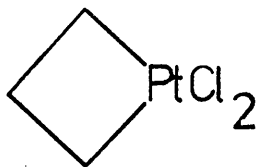
However, the infrared spectra of these complexes suggested a platinacyclobutane ring (61J738), and on treatment of the unsubstituted cyclopropane complex with pyridine, $\text{PtCl}_2(\text{C}_3\text{H}_6)\text{py}_2$ resulted (66CH396), which was shown by x-ray crystal analysis to have the structure (3) (71JO(33)247).



(3)

This led to the conclusion that in the original complex the carbon-carbon bond had been cleaved by the metal

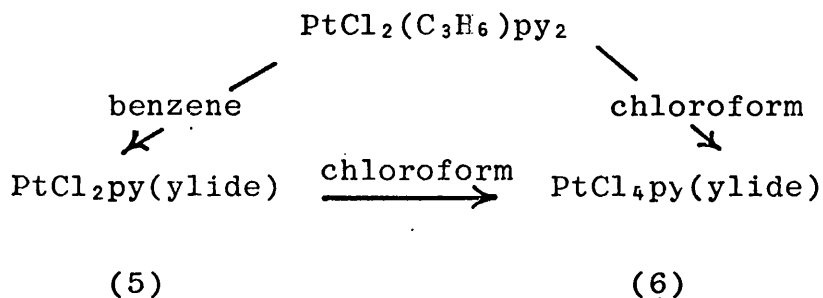
giving the empirical structure (4).



(4)

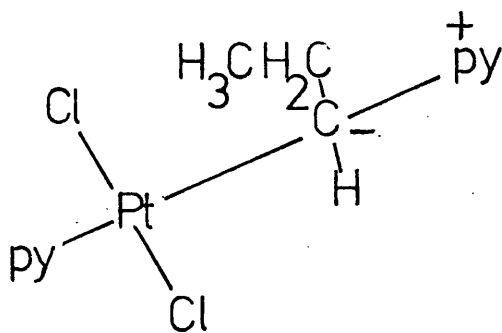
Although other postulates have been made relating the structure to the tetrameric tri-methylplatinum(IV) halides (69J1227) the impossibility of obtaining a satisfactory crystal of the original compound has frustrated all attempts to resolve the controversy by x-ray diffraction methods. The compound is however now generally ascribed the tetrameric structure $[\text{PtCl}_2(\text{C}_3\text{H}_6)]_4$ (68TL1937, 69J1227).

An interesting reaction of the complex $[\text{PtCl}_2(\text{C}_3\text{H}_6)\text{py}_2]$ was discovered in 1971 when this compound was dissolved in various solvents. In benzene solution ylide (5) is formed but in chloroform ylide (6) is produced. (5) may be converted to (6) by chloroform oxidation (Scheme 1).



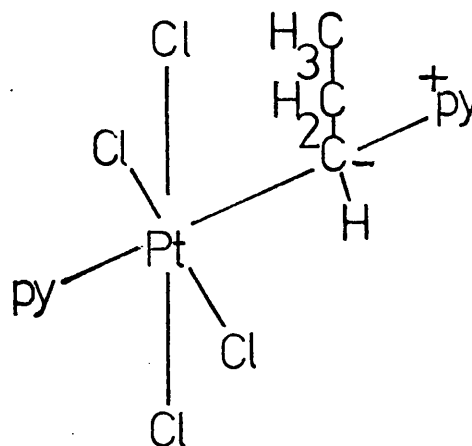
SCHEME 1

The structures were studied by x-ray diffraction methods and are given below (71JO(33)259).



dichloro(pyridiniumpropylide)
-pyridineplatinum(II)

(5)



tetrachloro(pyridinium-
propylide)pyridineplatinum(IV)

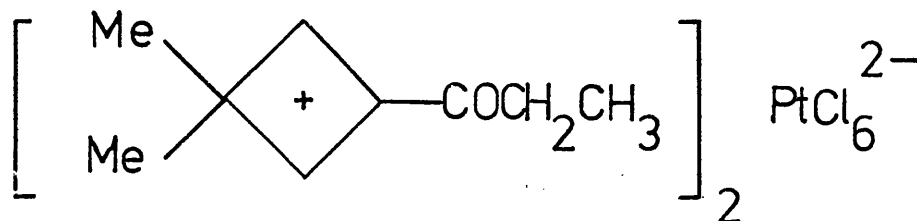
(6)

Treatment of Zeise's acid $\text{H}^+[\text{PtCl}_3(\text{C}_2\text{H}_4)]^-$ in ethanol with cyclopropane gives the propylene complex $[\text{PtCl}_2(\text{CH}_3\text{CH}=\text{CH}_2)]_2$ (70JO(24)787). The isomerisation of cyclopropane has previously only been observed in three cases

- (i) at high temperatures (66MI1)
- (ii) with recoil tritium atoms (62PH2622)
- (iii) catalytically on acid surfaces (59PH1400)

The treatment of chloroplatinic acid in methanol or methylene chloride with 1,1-dimethylcyclopropane leads to an ionic complex given the structure (7). The

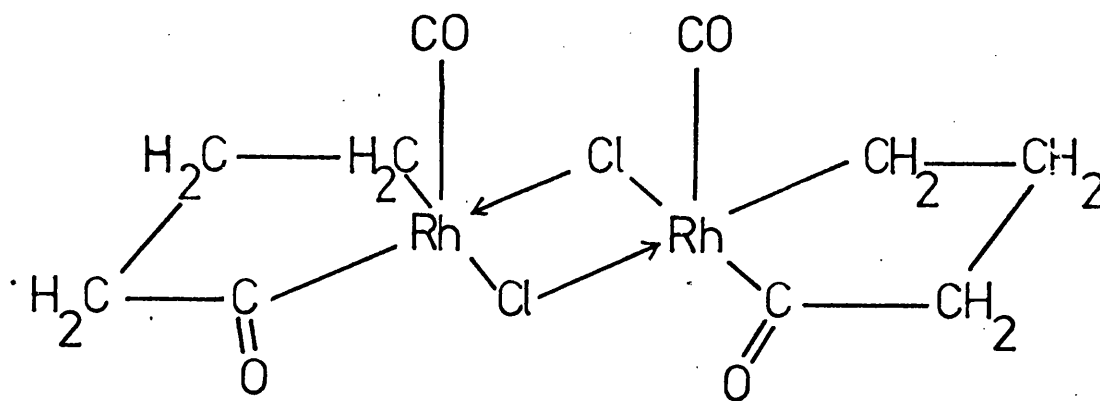
reaction is specific to methylcyclopropanes (71CH128).



(7)

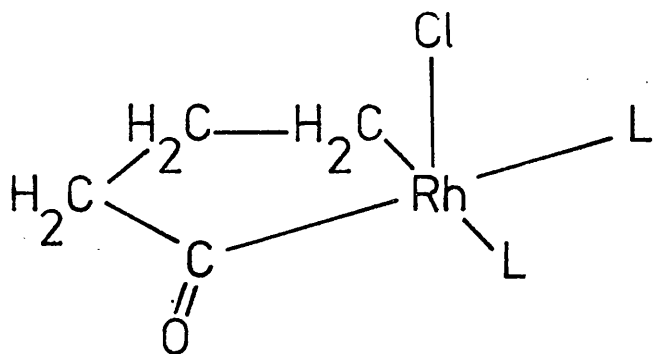
Further studies of the cyclopropane system with platinum complexes may be found in the following references (71TL3313, 73JO(54)C59, 73JO(59)429).

Cyclopropane was subsequently shown by Wilkinson et al to react with the dimeric $[\text{RhCl}(\text{CO})_2]_2$ producing a complex which was formulated as (8) (68J845).



(8)

Compound (5) is cleaved on reaction with PPh_3 or diphos leading to complex (9).



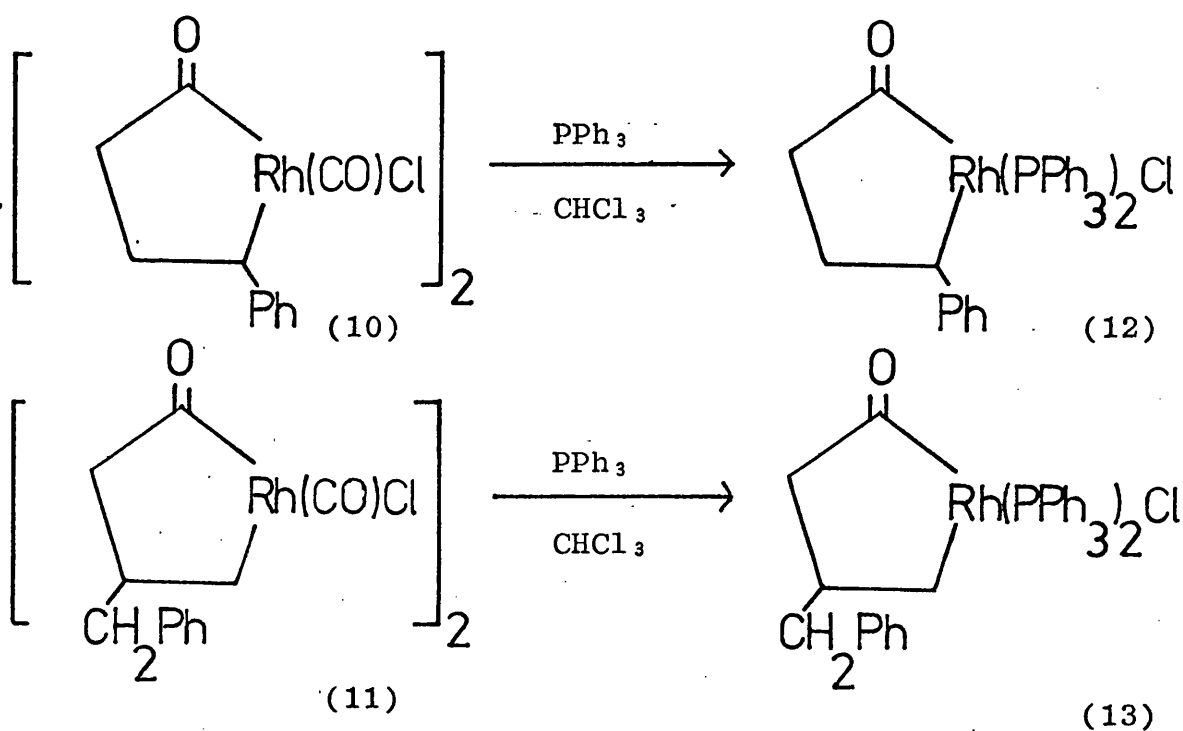
L = PPh_3

L_2 = diphos

(9)

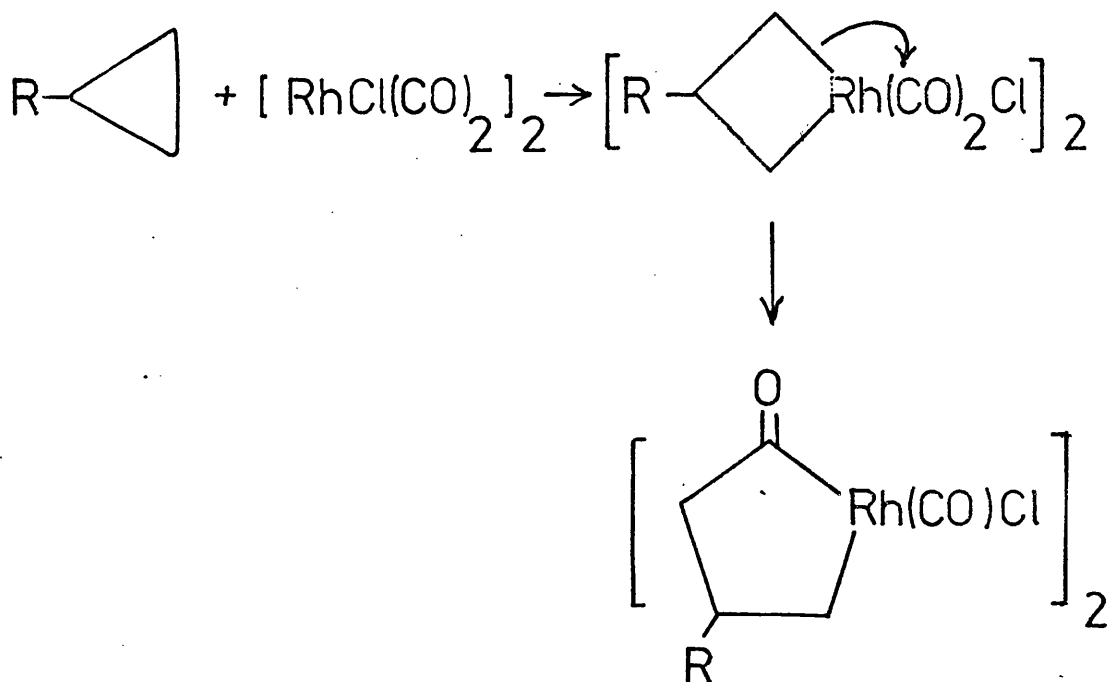
Evidence for the structure of (8) and (9) lies mainly in the interpretation of infrared spectra.

The reaction of the complex $[\text{RhCl}(\text{CO})_2]_2$ with substituted cyclopropanes was reported by McQuillin et al (72J2192). Treatment of phenylcyclopropane and benzylcyclopropane with the rhodium(I) complex gave compounds (10) and (11) respectively. Treatment of these products with PPh_3 in chloroform led to (12) and (13) as shown in Scheme 2.



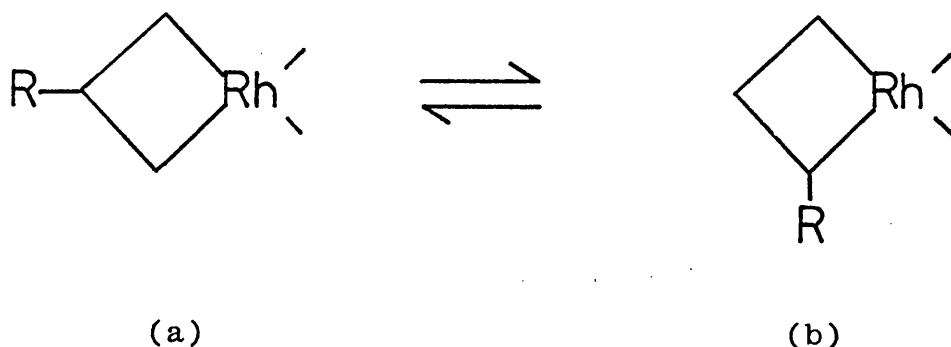
Scheme 2

The mechanism is thought to proceed by rhodium(I) cleavage of a carbon-carbon σ -bond of the cyclopropane followed by rapid carbonyl insertion as shown in Scheme 3.



Scheme 3.

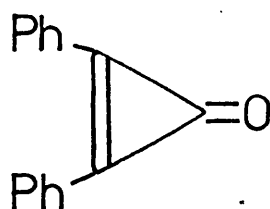
In the case where $\text{R}=\text{Ph}$, attack apparently takes place at the carbon-carbon bond α to the phenyl group, leading to a product in which the R-group is attached to the carbon atom α to the rhodium. In the case of $\text{R}=\text{PhCH}_2$ attack is apparently at the carbon-carbon bond β to the R-group. The actual reason for this is thought to be that an equilibrium exists in the intermediate, as shown in Scheme 4.



Scheme 4.

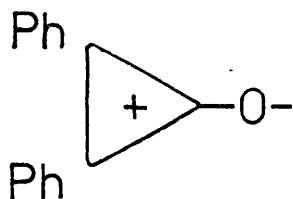
This equilibrium is thought to be thermodynamically controlled, and favours (b) in the case of $R=Ph$ and (a) in the case $R=PhCH_2$.

Interest was now focused on the reactions of the highly strained 1,2-diphenylcycloprop-1-ene-3-one (14) with transition metal ions (67J1004).



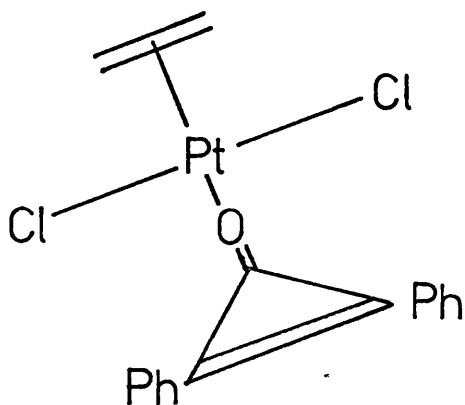
(14)

With zinc(II), cobalt(II), nickel(II), copper(II), ruthenium(II), rhodium(III), palladium(II), platinum(II) and platinum(IV) the complexes formed were thought to be bonded by the oxygen atom, since the charge distribution is more closely represented by (15).



(15)

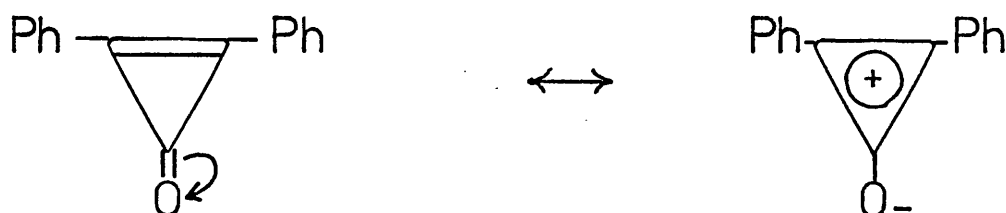
Similar results were found by another group who had reacted Zeise's dimer with (14) (68JO(12)249) to produce a complex formulated as (16).



(16)

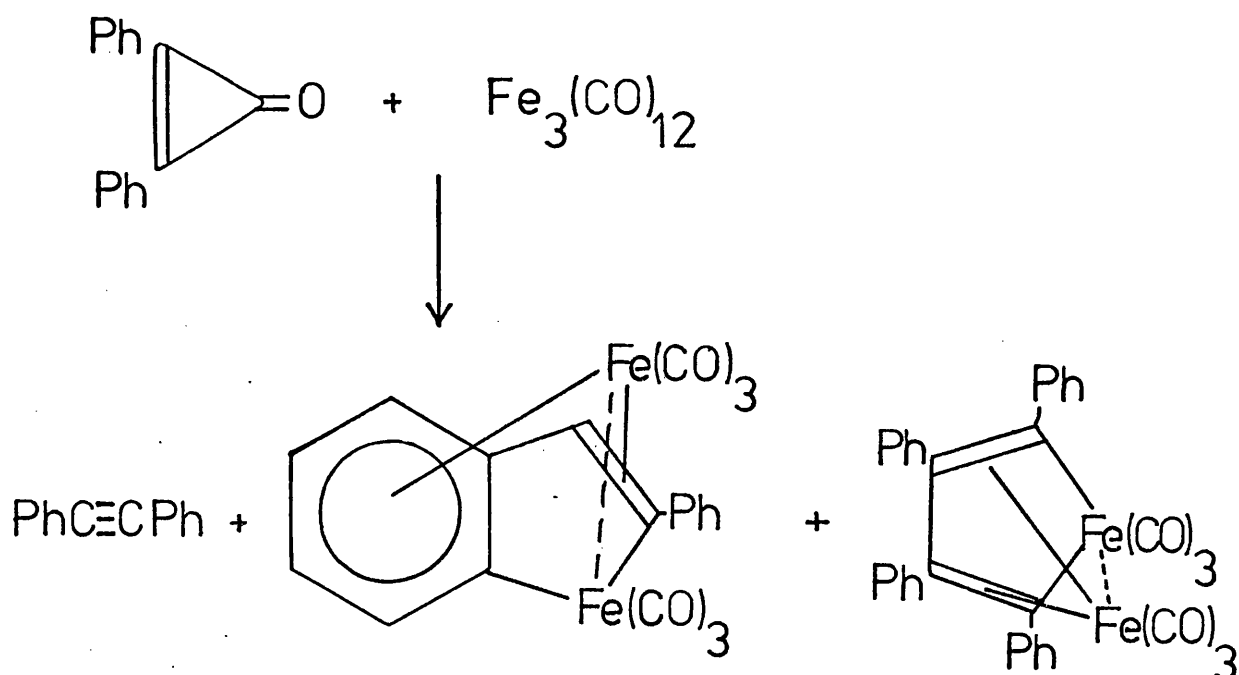
Reaction of diphenylcyclopropenone with $(PtCl_2L)_2$ with $L=cis$ -but-2-ene, carbon monoxide and tri-n-butylphosphine gave similar complexes. The formation of

complexes of the type (16) can be rationalised in terms of the canonical forms of diphenylcyclopropenone given in Scheme 5.



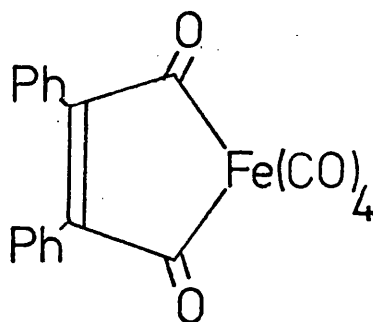
Scheme 5.

On reaction of (14) with $\text{Fe}_3(\text{CO})_{12}$ under reflux in 80-100° b.p. petrol an entirely different reaction took place as shown in Scheme (6), (67J1863).



Scheme 6.

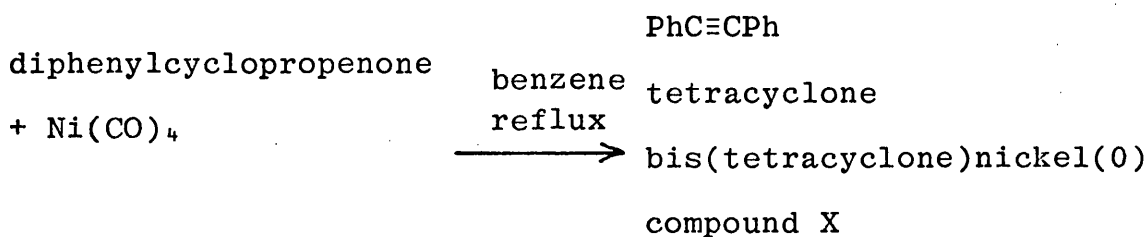
Further investigation of the reaction in benzene with $\text{Fe}_2(\text{CO})_9$ in the absence of light yielded mixed products including (17).



(17)

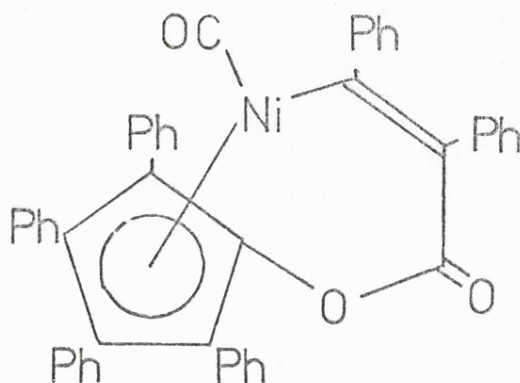
Dicobalt octacarbonyl on the other hand, when treated with diphenylcyclopropenone, di-n-butylcyclopropenone or cycloheptylcyclopropenone in toluene at room temperature gave a red oil, the constitution of which was thought to be $[(\text{cyclopropenone})_6\text{Co}][\text{Co}(\text{CO})_4]_2$ (67J1863). The measured magnetic moments of 5.38BM for these complexes are characteristic of spin-free octahedral cobalt(II) compounds.

When $\text{Ni}(\text{CO})_4$ was treated with diphenylcyclopropenone a mixture of products was isolated including diphenyl acetylene (74JO(69)311), as shown in Scheme 7.



Scheme 7.

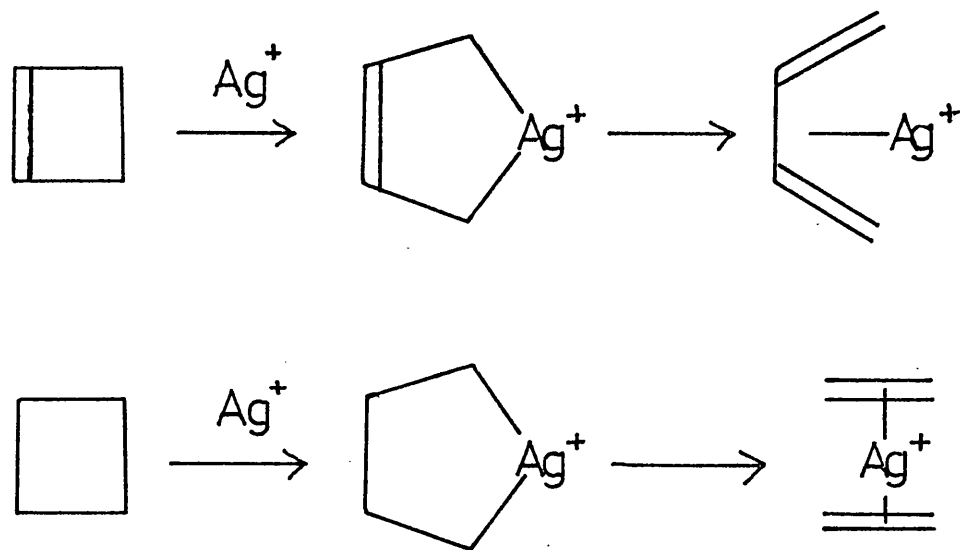
Compound X was a green diamagnetic complex of composition $C_{45}H_{30}NiO_3$ showing $\nu(C\equiv O)$ at 2060 cm^{-1} characteristic of CO as a ligand attached to nickel. The compound was assigned structure (18).



(18)

The reaction of nickel(0) with diphenylcyclopropenone parallels the action with iron(0) in the production of an acetylene but is in direct contrast with the action of cobalt(0) and platinum(II) which have already been discussed.

The isomerisations of some small ring compounds catalysed by transition metal ions also probably proceed via metallocyclic intermediates. The reactions of cyclobutene and cyclobutane with d^{10} silver(I) compounds are thought to proceed through metallocyclic intermediates in which the carbon-carbon σ -bond has cleaved (70JA7499). Scheme 8.

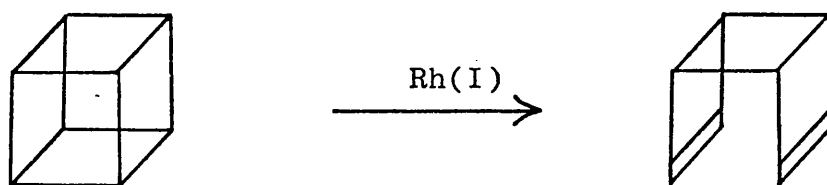


Scheme 8.

In the case of cyclobutene, the expected π -complex is apparently not formed, the carbon-carbon σ -bond being cleaved in preference. Studies with copper(I) gave similar results (65JA2045, 67JA4788). A theoretical application of orbital symmetry rules to such systems gave a clue as to why these isomerisations should occur (67JA2484, 69JA1030, 69TL4813). It was suggested that certain metal systems containing orbital configurations of the prerequisite energies could render otherwise forbidden cycloadditions allowed by providing a template of atomic orbitals through which electron pairs of

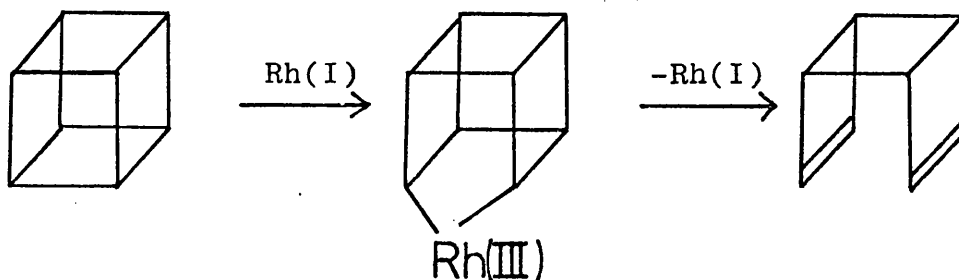
transforming hydrocarbon ligands and metal systems could interchange and flow into the required regions of space.

These ideas received further support when in 1970 Halpern et al reported the thermally forbidden rearrangement of cubane by the catalyst $[\text{RhCl}(\text{nbd})]_2$ (70JA3515), Scheme 9.



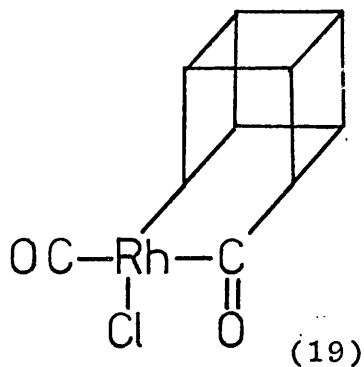
Scheme 9

The rearrangement is thought to proceed by oxidative addition of rhodium(I) into the molecule by a carbon-carbon σ -bond cleavage, which then lifts the Woodward-Hoffmann restraints for (2+2) cycloadditions (Scheme 10).

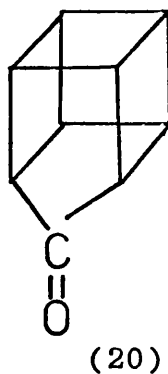


Scheme 10

Evidence for the rhodium(III) intermediate was obtained when the complex used in the rearrangement was $[\text{RhCl}(\text{CO})_2]_2$. The compound (19) was isolated,



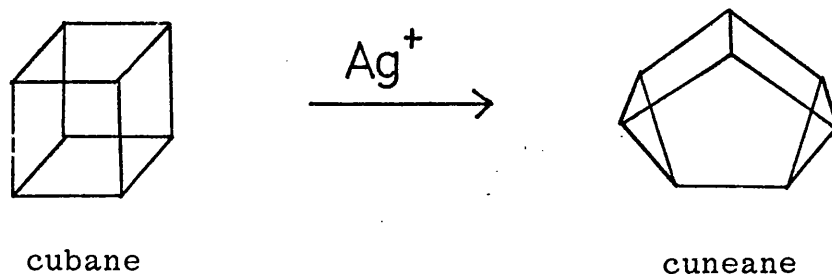
and on treatment with triphenylphosphine in chloroform solution degraded to (20) with evolution of trans- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$.



Thus it was deduced that rhodium(I)-catalysed valence isomerisms probably proceed through a nonconcerted oxidative addition mechanism.

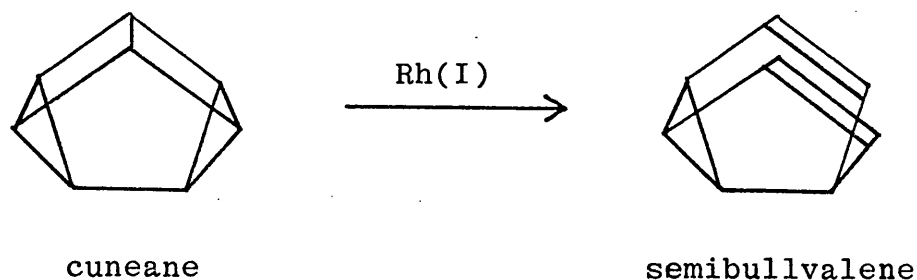
Many similar rearrangements were reported at around this time, including the rearrangement of cubane to cuneane using a d^{10} silver(I) catalyst (70JA6366).

The Ag^+ species obviously acts in a different way from the \underline{d}^8 rhodium(I) as depicted in Scheme 11.



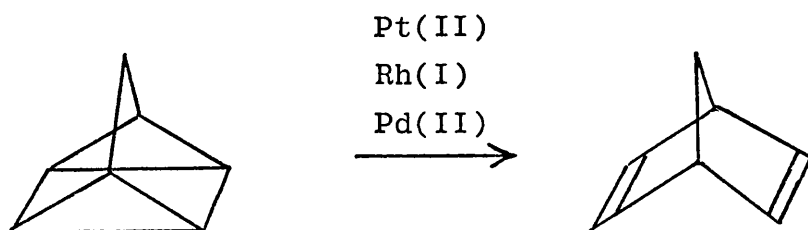
Scheme 11.

It was found that \underline{d}^8 palladium(II) complexes also effected the cubane \rightarrow cuneane rearrangement, and it was thought that the difference in products using rhodium(I) as against silver(I) or palladium(II) resulted not because of the difference of mode of action of \underline{d}^8 over a \underline{d}^{10} species, but occurred due to the ease of oxidative addition of rhodium(I) over that of silver(I) or palladium(II). Treatment of cuneane with the rhodium(I) catalyst $[\text{RhCl}(\text{CO})_2]_2$ resulted in rearrangement to semibullvalene (Scheme 12).



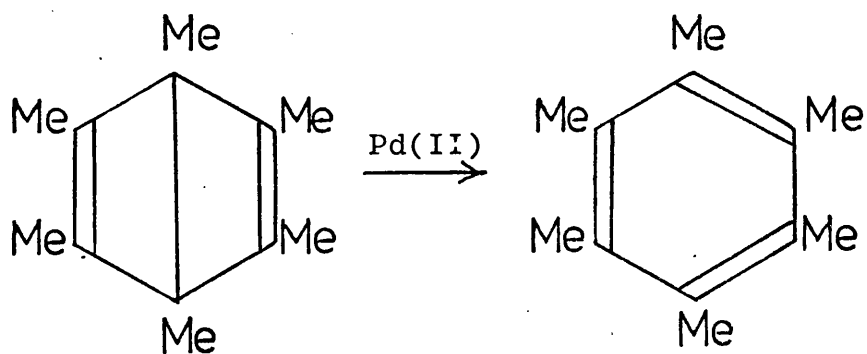
Scheme 12.

Hogeveen et al also reported the rearrangement of quadricyclane to norbornadiene using rhodium(I), palladium(II) or platinum(II) complexes (67JA2486),



Scheme 13

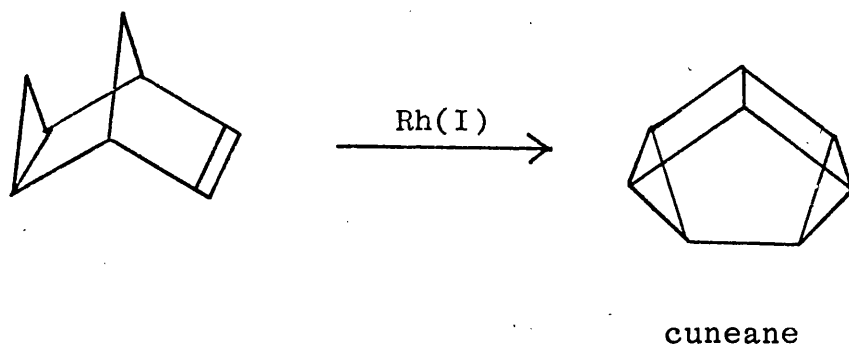
a process thermally forbidden on orbital symmetry grounds. Many other rearrangements have appeared in the literature, some of which are detailed in the following Schemes (14 - 16), with references.



hexamethylDewarbenzene

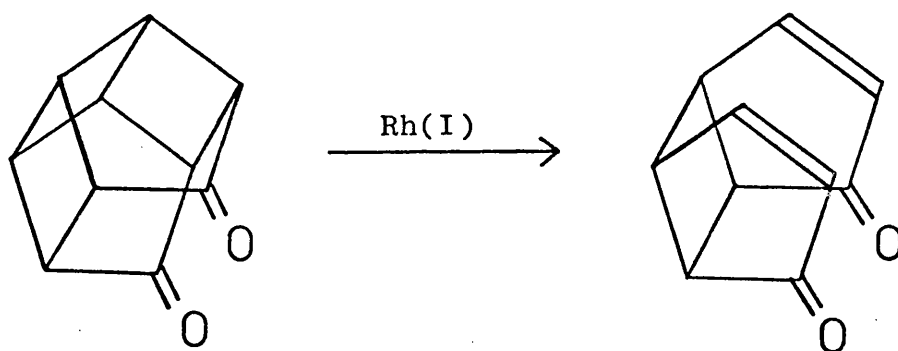
hexamethylbenzene

Scheme 14. (67CH759)



Scheme 15.

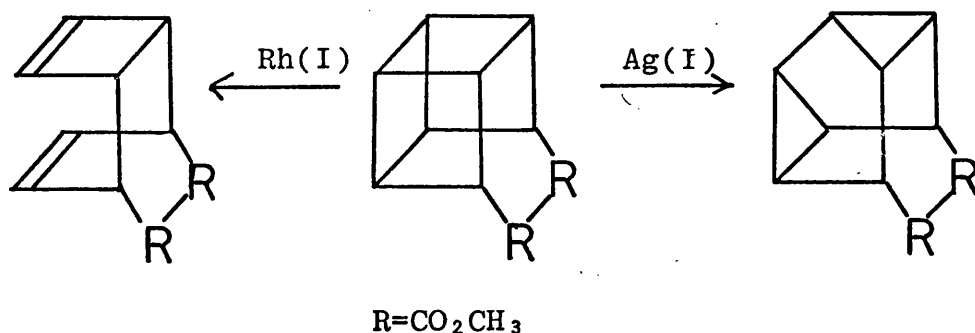
(69TL2509)



Scheme 16.

(70CH1494)

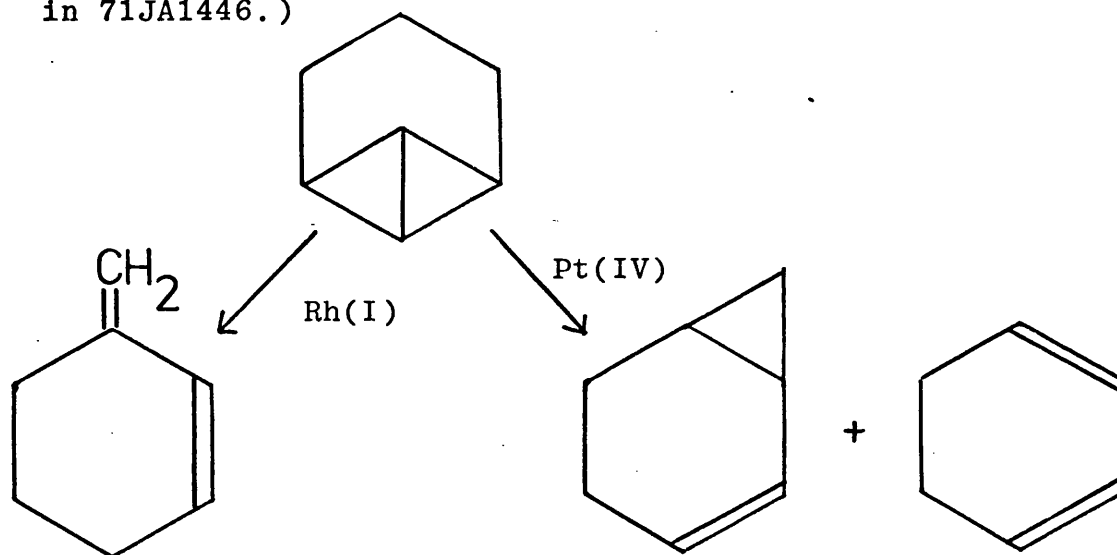
Two other interesting rearrangements were reported contrasting the difference of action of metal catalysts, detailed in Schemes 17 and 18.



Scheme 17.

(71JA7345)

(A similar reaction to the Ag^+ catalysis is reported in 71JA1446.)

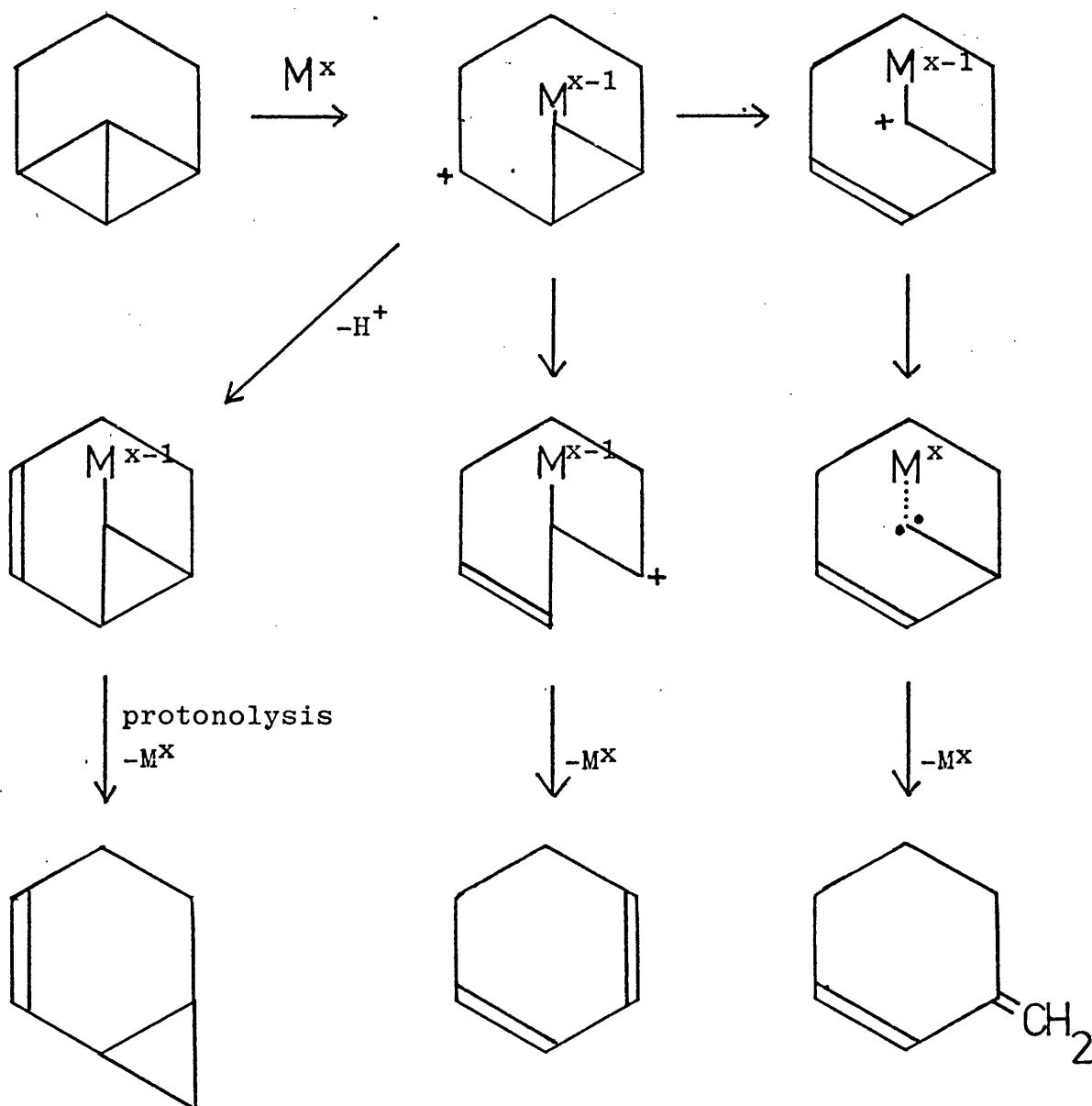


Scheme 18.

(71JA4597,

72JA7748)

In the latter case, the authors have postulated a scheme which explains the variety of products, and this is reproduced in Scheme 19.

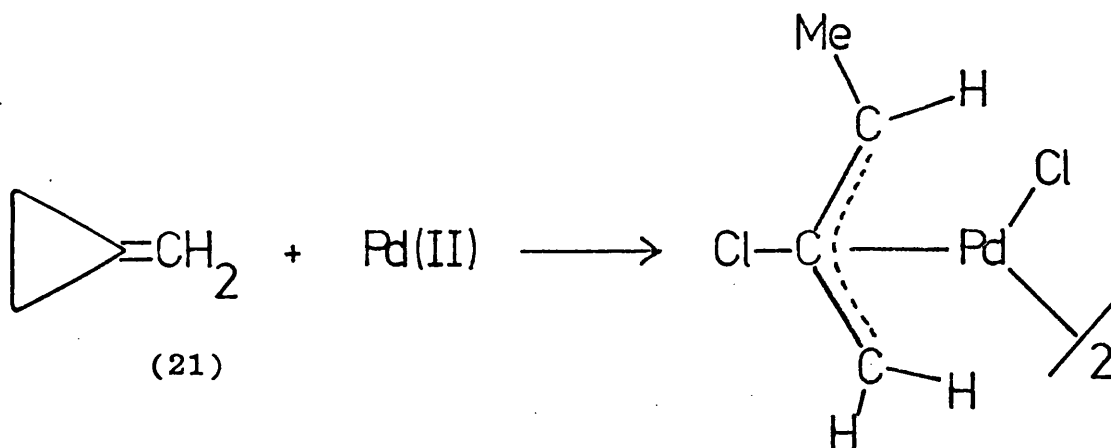


Scheme 19.

Further rearrangements involving transition metal ions may be found in the following references: 72JA7733, 68JA4751, 71JA1042, 71JA1049, 71JA1812, 72JA7741, 71JA1288, 71JA4611, 71JA2335, 72TL3367, 72JA5096, 71JO(26)C65, 70JA7002.

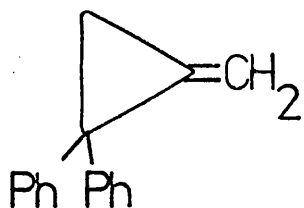
Although many of these reactions are thought to proceed via metal-carbon σ -bonded intermediates, it is not always possible to isolate such complexes. However, with iron, palladium and platinum as the transition metal it is often possible to isolate stable organometallic complexes.

One type of molecule which received some attention contained both a cyclopropane ring and an exocyclic carbon-carbon double bond. Thus Noyori et al reported that reaction of $\text{PdCl}_2(\text{PhCN})_2$ with methylenecyclopropane (21) gave a dimeric complex according to Scheme 20 (69CH525).

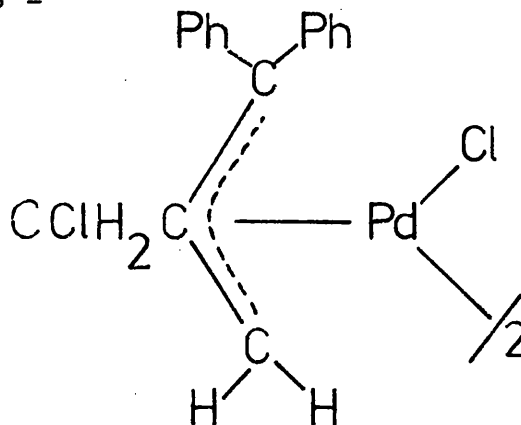


Scheme 20.

The 1,1-diphenyl substituted complex (22) under the same conditions, gave the dimeric π -allyl complex di- μ -chlorobis(2-chloromethyl-1,1-diphenyl π -allyl) dipalladium(II) (23).

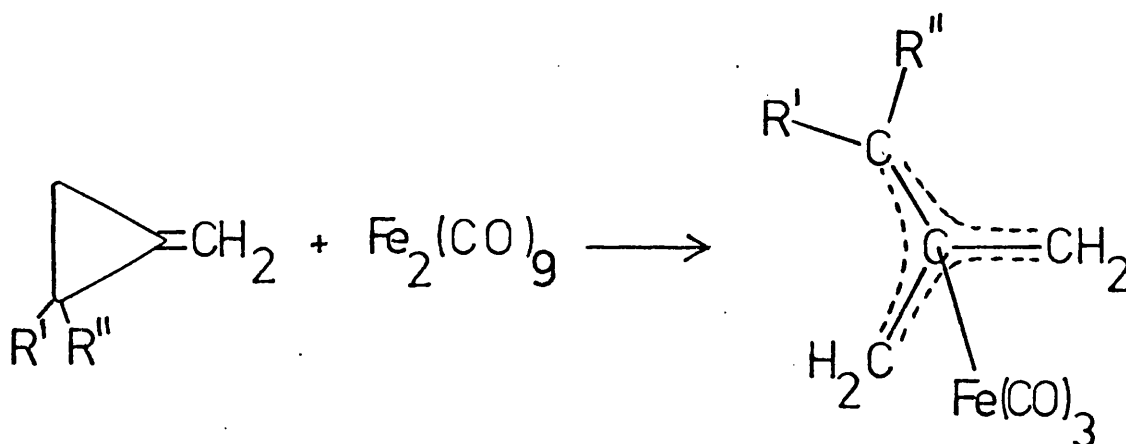


(22)



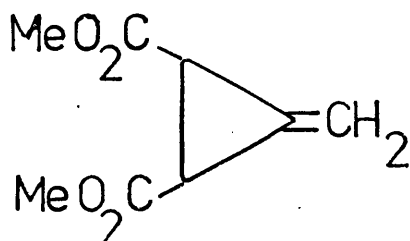
(23)

In contrast it was reported that iron(0) with (22) gave a trimethylene complex in which the iron atom is symmetrically disposed below the 4-carbon trimethylene moiety (69CH89), Scheme 21.



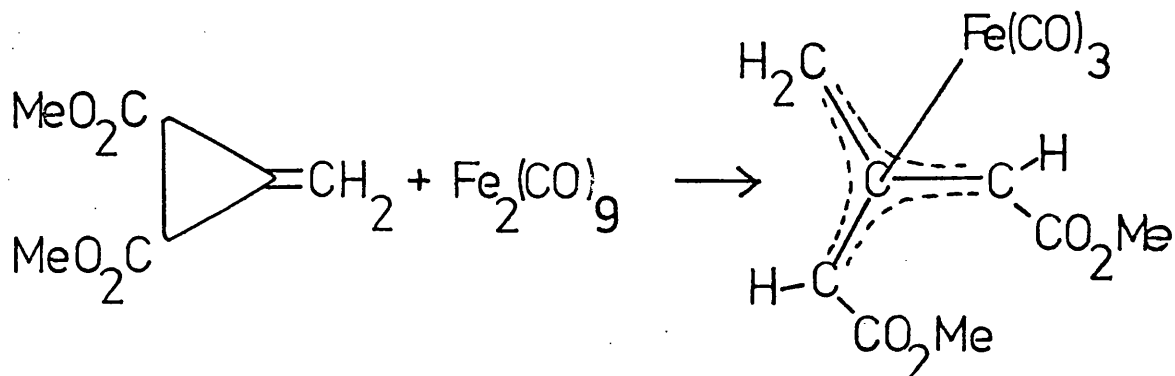
Scheme 21

However, in a study of Feist's methyl ester (24) with iron(0)



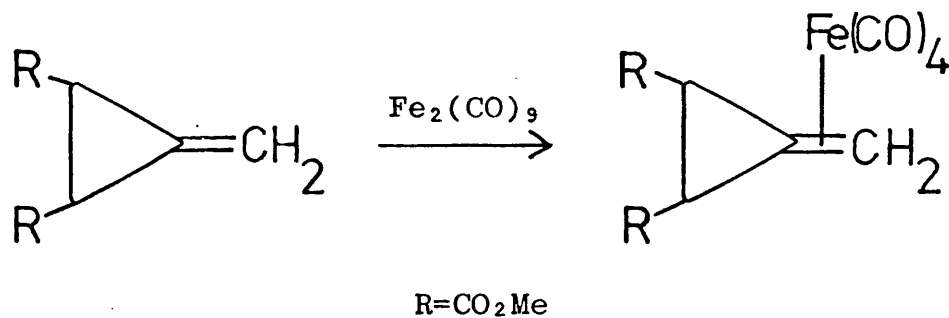
(24)

the initially postulated trimethylene product as shown in Scheme 22 (73JO(57)363)



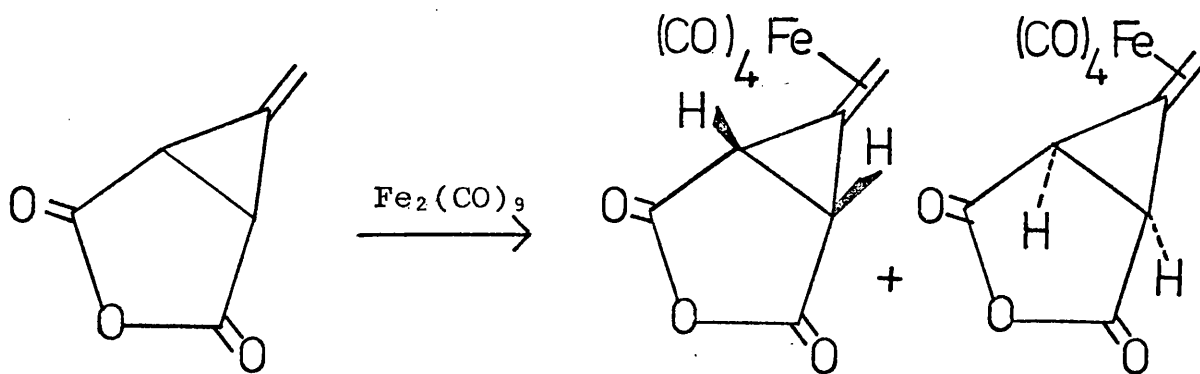
Scheme 22.

was subsequently shown to be a simple π -bonded complex (74JO(67)99) as shown in Scheme 23, which was later confirmed by crystal structure determination (74IC1895).



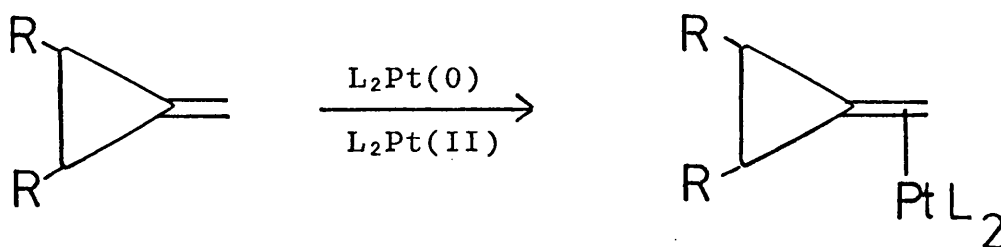
Scheme 23.

Similarly, Feist's anhydride gives stereospecific π -bonded complexes with the iron(0) compound (73JO(57)363) Scheme 24.



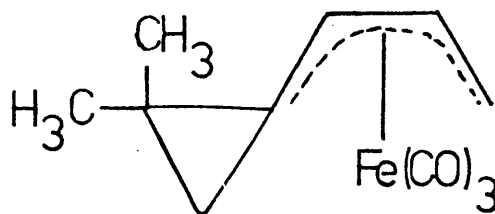
Scheme 24.

π -bonded complexes are also formed by platinum(0) and platinum(II) with Feist's ester as shown in Scheme 25 (74CH686).

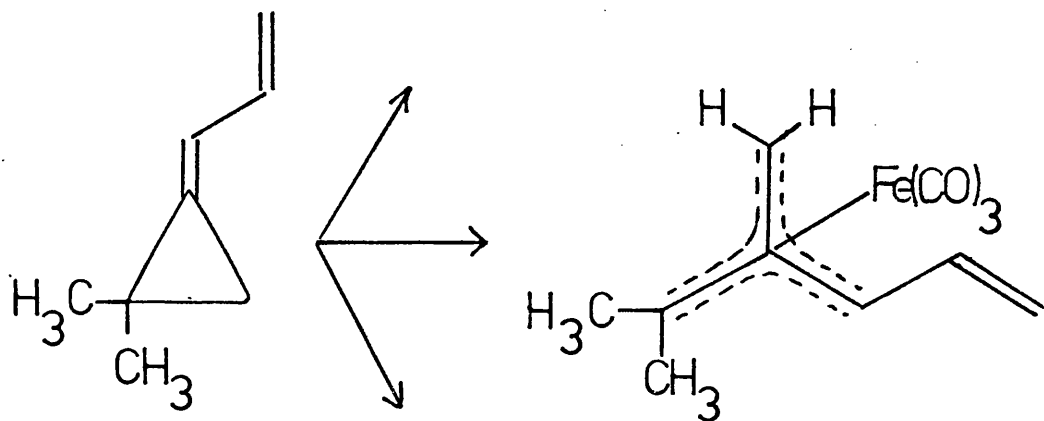


Scheme 25.

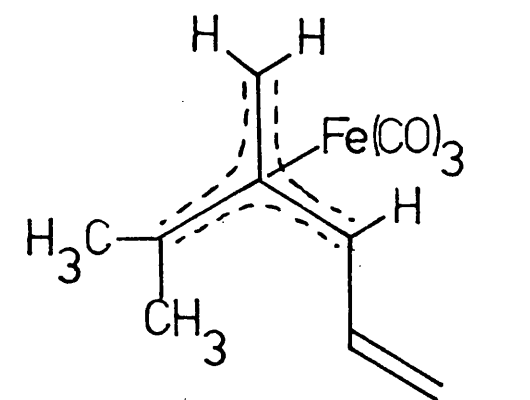
However, trimethylenemethane complexes are formed in the reactions of nonacarbonyldiiron with the dialkene (25), but in addition π -diene complexes are also formed (73JO(61)C55), Scheme 26.



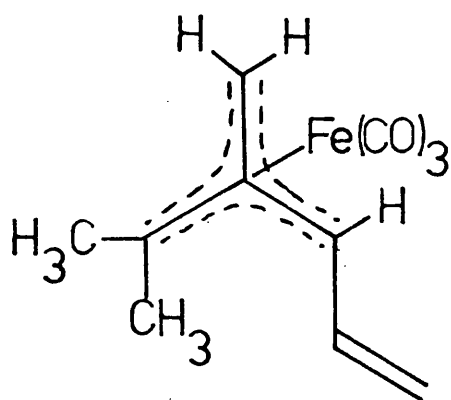
(25a)



(25)



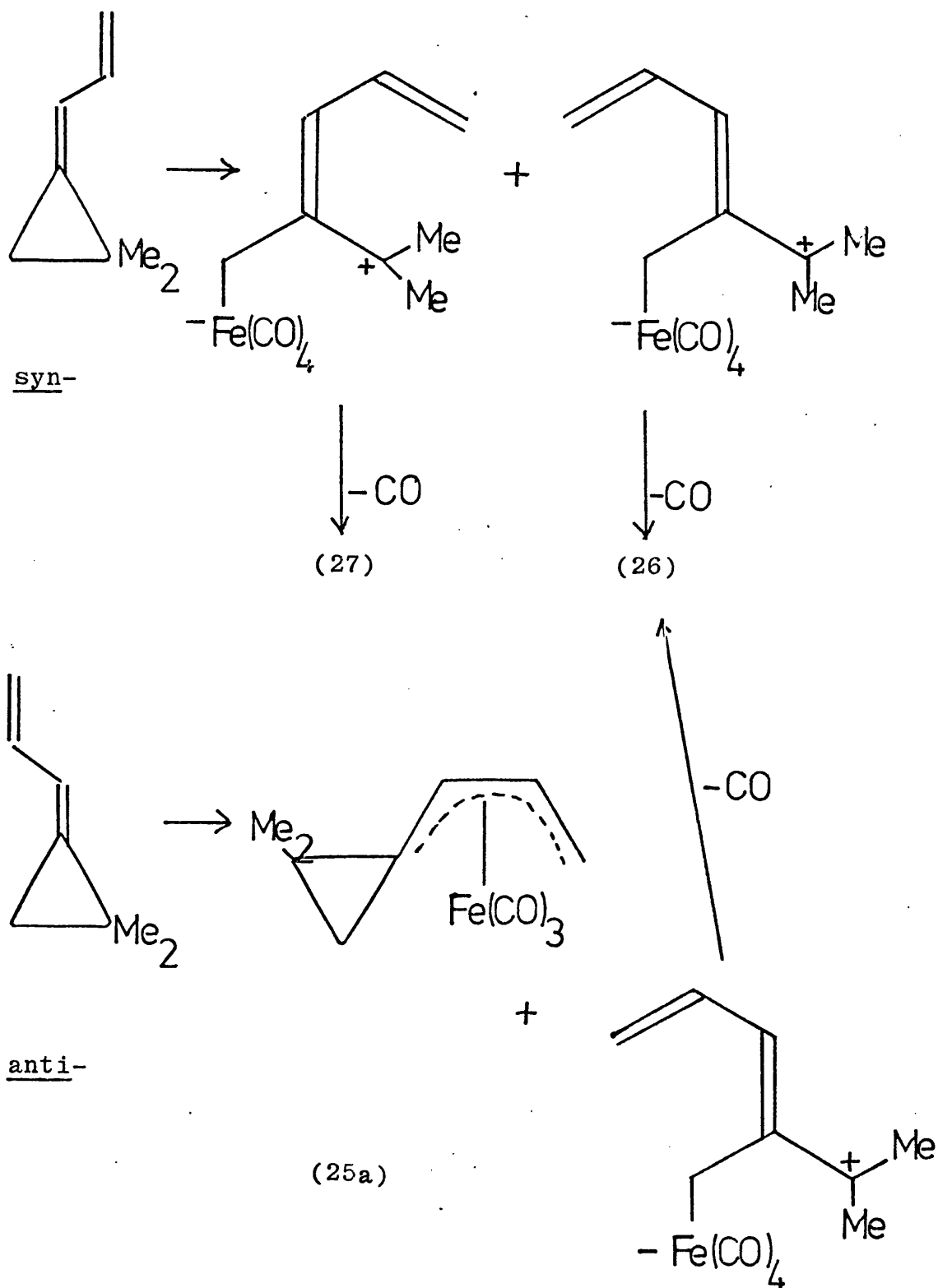
(26)



(27)

Scheme 26.

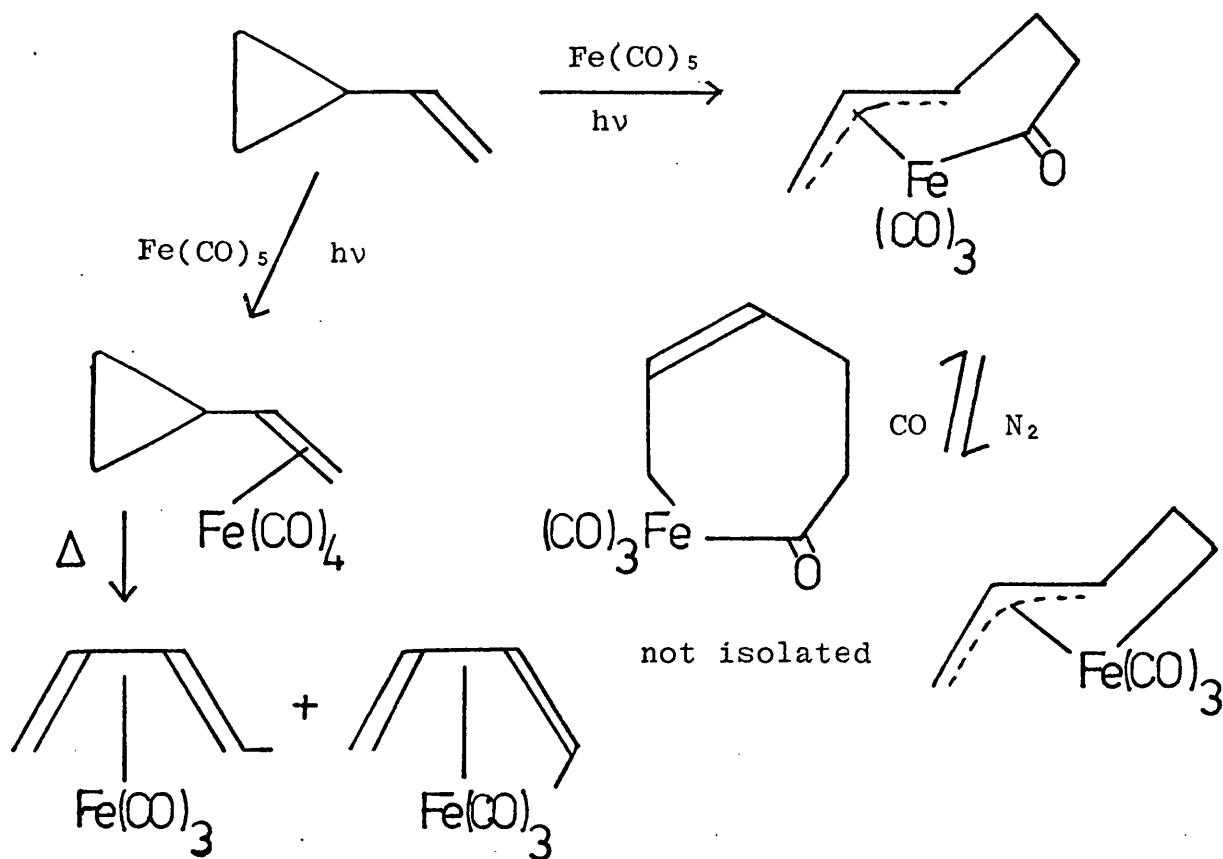
Possible mechanisms explaining the rearrangements involved in producing the variety of products are given in Scheme 27.



Scheme 27.

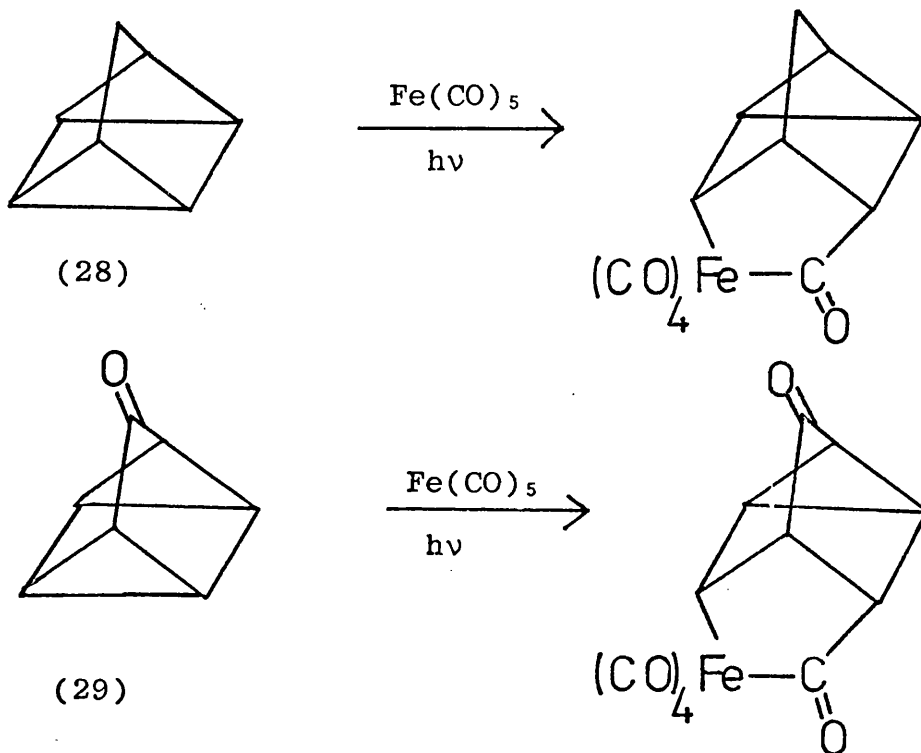
All these reactions involve the cleavage of a carbon-carbon σ -bond in the cyclopropane by the transition metal complex.

The reactions of pentacarbonyliron(0) with cyclopropylethylene under irradiation were reported to give π -complexes, σ - π -allyl complexes, π -diene complexes and carbonyl inserted σ -complexes (74JA2631), Scheme 28.



Scheme 28.

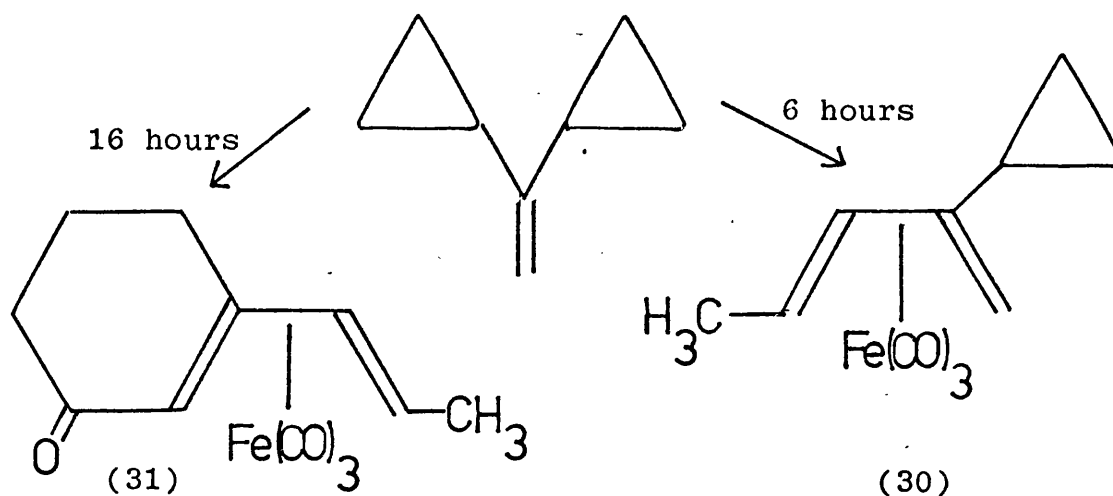
With pentacarbonyliron(0) and ultra-violet irradiation, both quadricyclane (28) and quadricyclone (29) undergo carbonyl insertion giving σ -bonded complexes (74JO(76)C32) by cleavage of a cyclopropane carbon-carbon bond (Scheme 29).



Scheme 29.

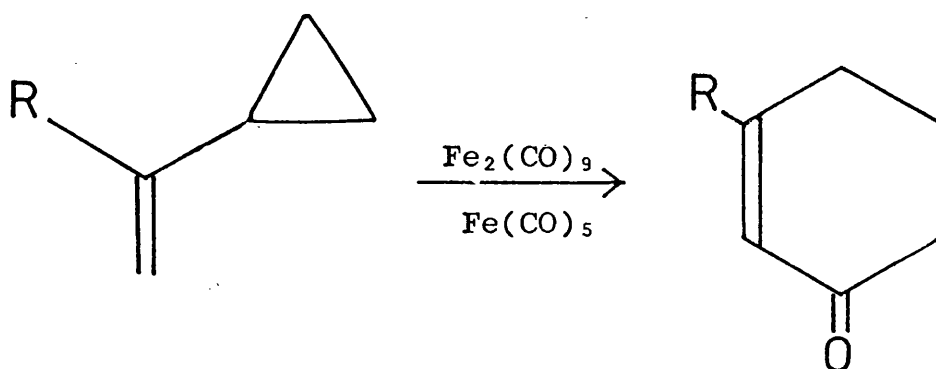
The reaction of 1,1-dicyclopropylethylene with iron(0) complexes also leads to an interesting variety of products (69CH883, 70TL4253). Thus 1,1-dicyclopropylethylene and pentacarbonyliron(0) under irradiation for 6 hours gave the π -bonded complex (30). However, continuation of the reaction for a further 10 hours yielded complex (31) in which a carbonyl group has

inserted and expanded the cyclopropane ring, Scheme 30.



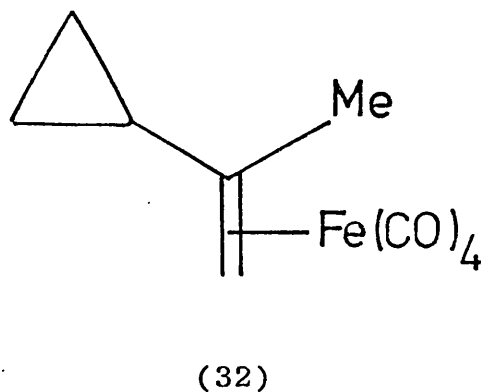
Scheme 30.

This is an example of carbonyl insertion and double ring cleavage by a transition metal complex. The reaction of 1-methyl-1-cyclopropylethene with $\text{Fe}(\text{CO})_5$ or $\text{Fe}_2(\text{CO})_9$ similarly yields a six-membered ring as shown in Scheme 31, also by carbonyl insertion.

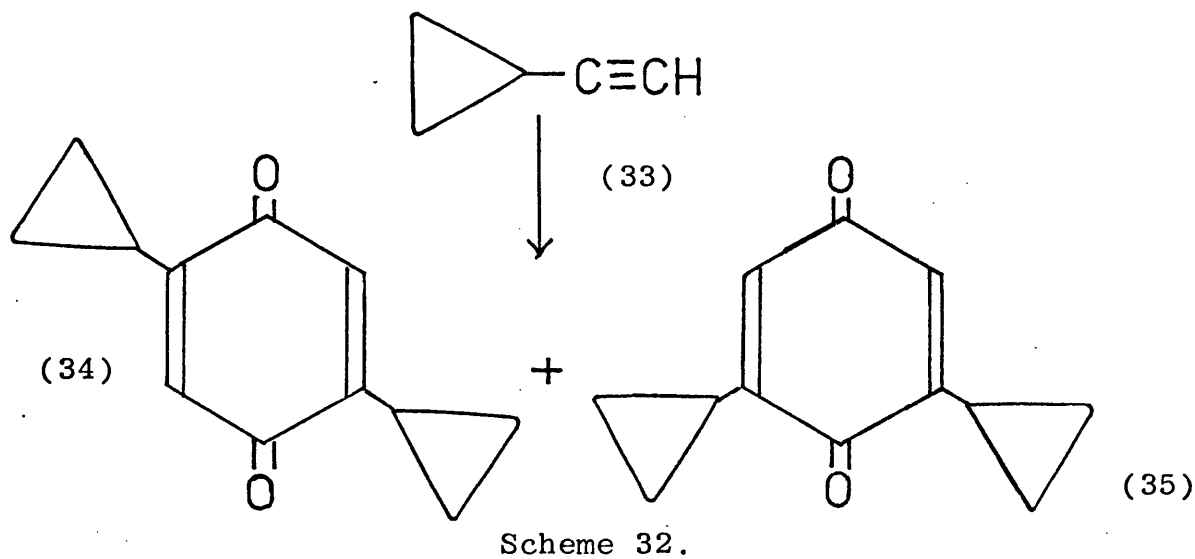


Scheme 31.

The intermediate in Scheme 31 is thought to be (32)

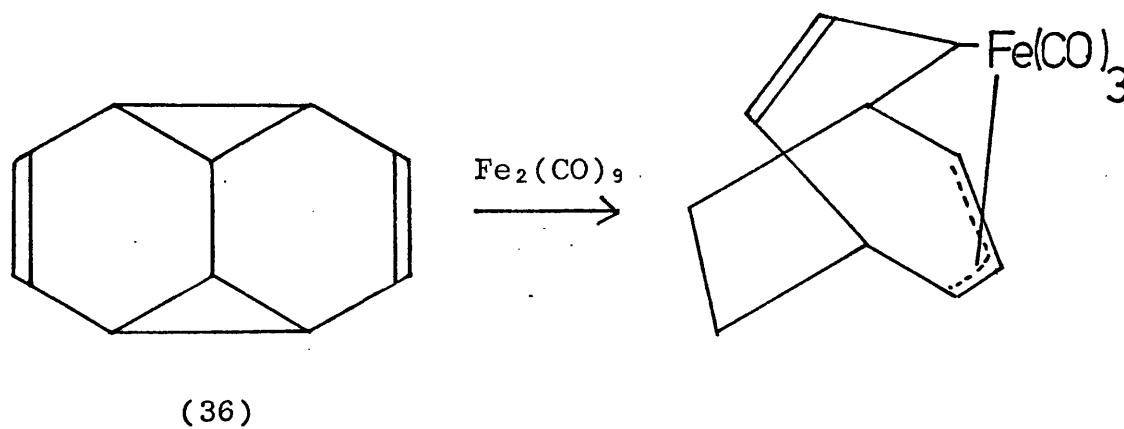


Ben-Shoshan et al extended the study to cyclopropylethyne (33) and found that in the presence of ultraviolet light, $\text{Fe}(\text{CO})_5$ gave the isomers (34) and (35), shown in Scheme 32 (73TL4211), produced by carbonyl

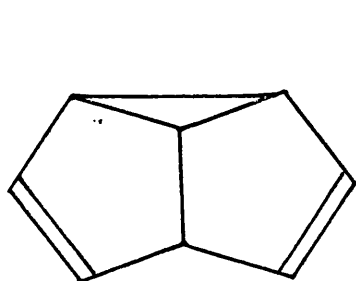


insertion. The mechanisms of these complicated insertions are not fully understood.

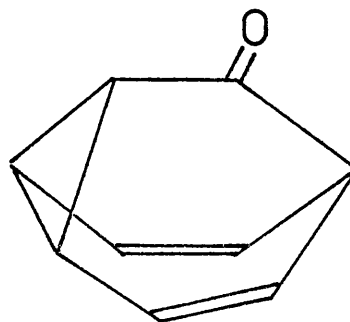
In 1971 Aumann reported that on reaction with $\text{Fe}_2(\text{CO})_9$, bullvalene (36) gave rise to a σ - π -allyl complex formed by cleavage of a carbon-carbon bond in the cyclopropane as shown in Scheme 33 (71AGI188).



There now followed many papers reporting similar σ - π -allyl complexes of iron(0), the most important being with semibullvalene (37) (71JA6709) and barbaralone (38) (72TL2005)..



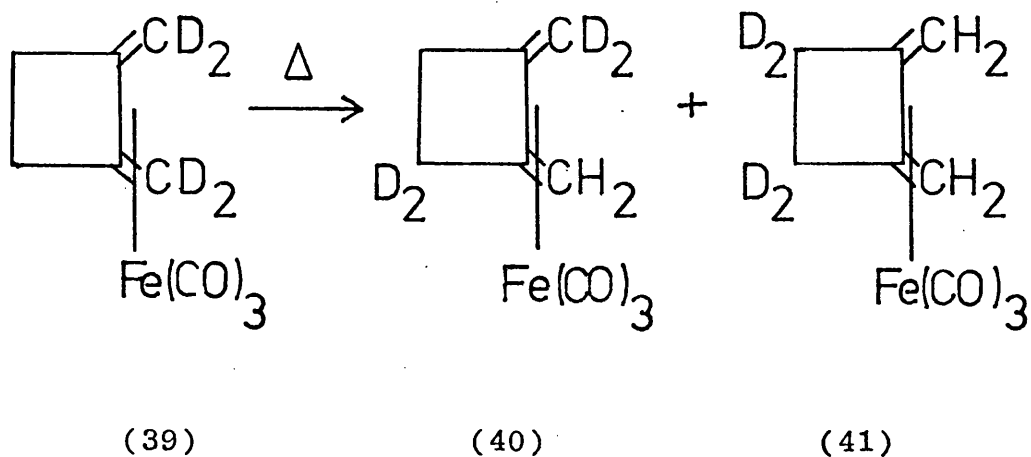
(37)



(38)

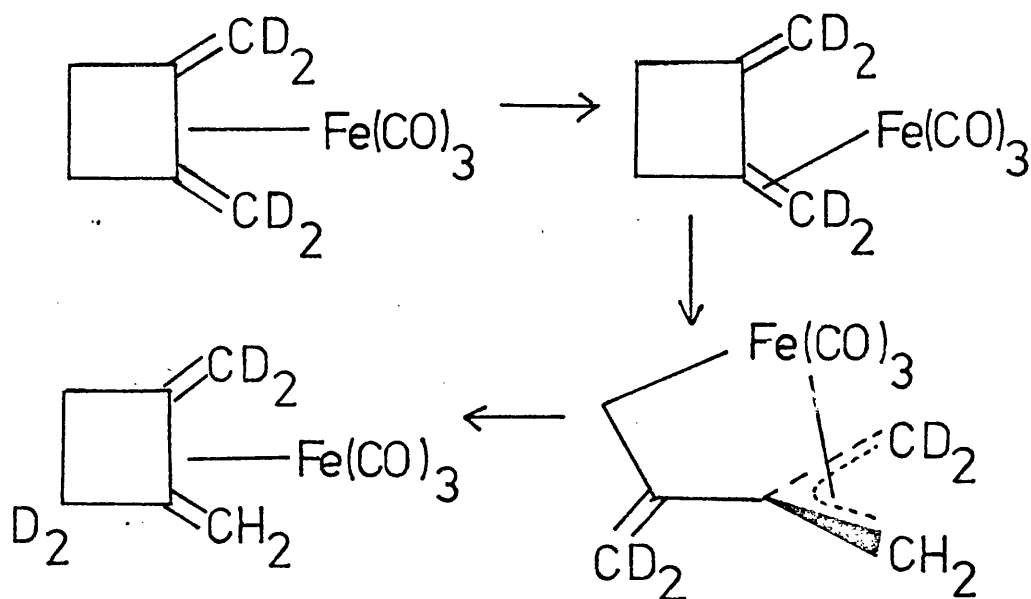
These reactions and those listed below all involve complexing via carbon-carbon bond cleavage, usually the carbon-carbon bond in the cyclopropane part of the molecule, (72CH1156, 73JO(56)315, 74JO(66)C6).

An interesting result of the possibility of σ - π -allyl complexes was reported in 1973, discovered during studies on the complex dimethylenecyclobutane-irontricarbonyl (73TL3959). It was found that on heating the deuteromethylene complex (39) deuterium scrambling occurred giving compounds (40) and (41) as shown in Scheme 34.



Scheme 34.

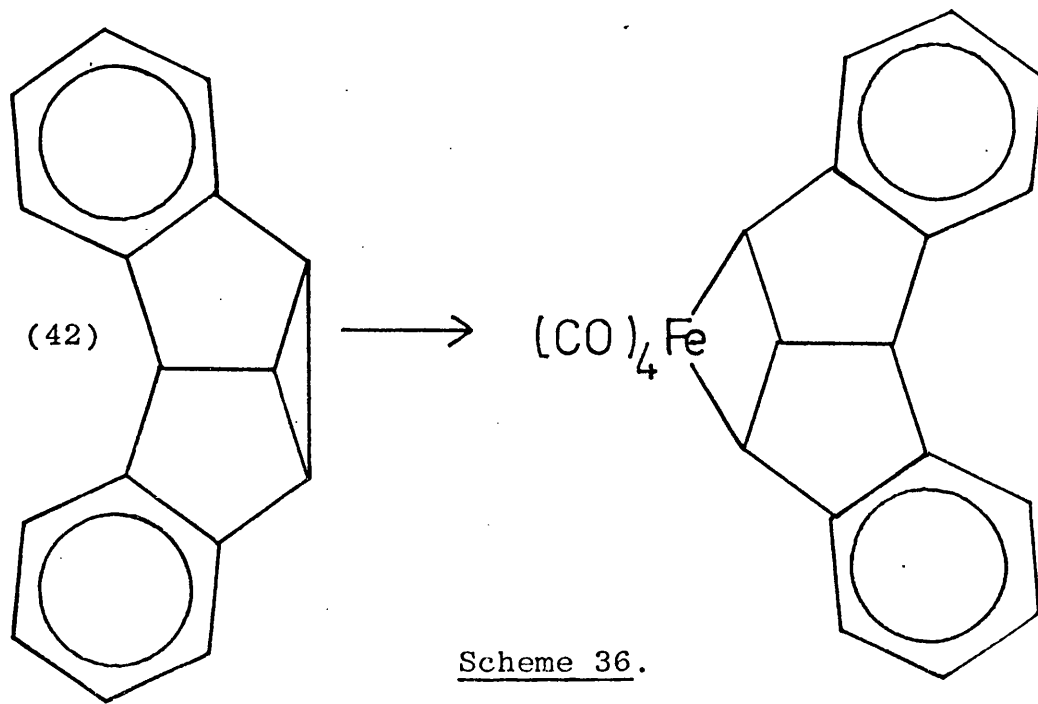
A mechanism was postulated which involved a σ - π -allyl complex which rearranged as in Scheme 35.



Scheme 35.

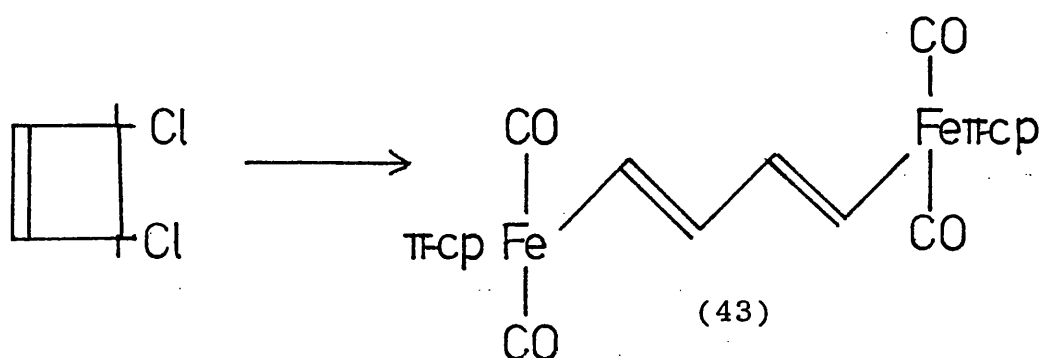
As can be seen in Scheme 35, the iron(0) has cleaved a carbon-carbon σ -bond of the cyclobutane in order to produce the σ - π -allyl intermediate.

In investigations of the reaction of iron(0) compounds with dibenzosemibullvalene (42) a σ - π -allyl complex was not formed, but a σ -bonded $\text{Fe}(\text{CO})_4$ complex was isolated (Scheme 36).



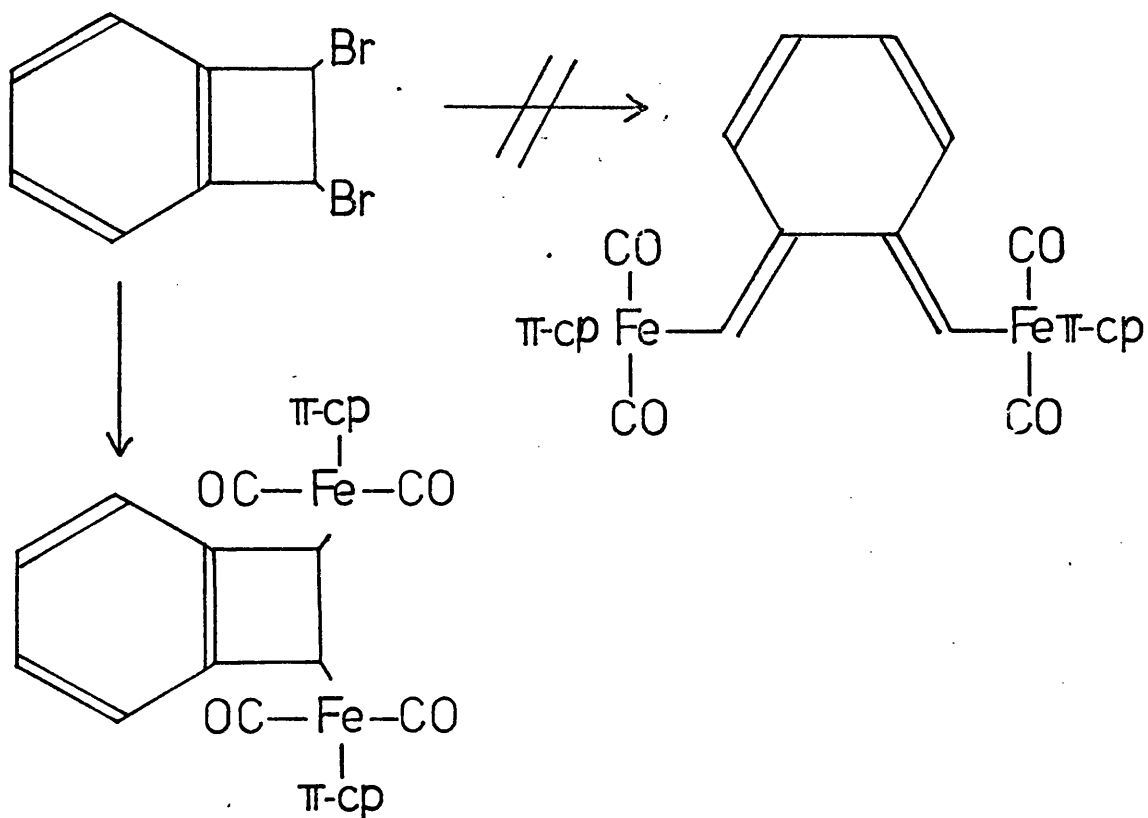
Scheme 36.

A rather novel anomalous reaction was reported in the reactions of iron(0) with cyclobutene derivatives (72JO(38)121). The reaction of 1,2-dichlorocyclobut-3-ene with $[\text{Fe}(\text{CO})_2(\pi\text{-cp})]^- \text{Na}^+$ yielded complex (43) (Scheme 37),



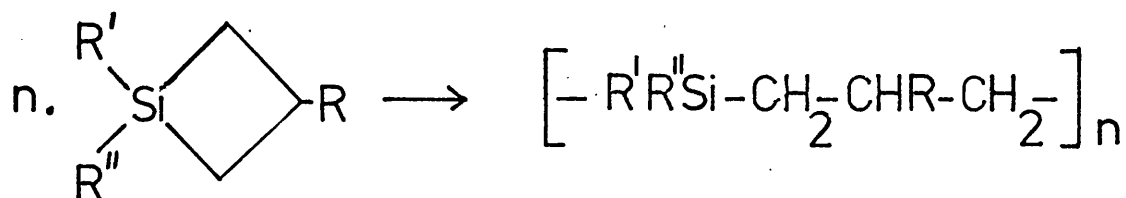
Scheme 37.

but extension of the reaction to the benzocyclobutene-dibromo derivative yielded a substituted product rather than the expected insertion product (Scheme 38).



Scheme 38.

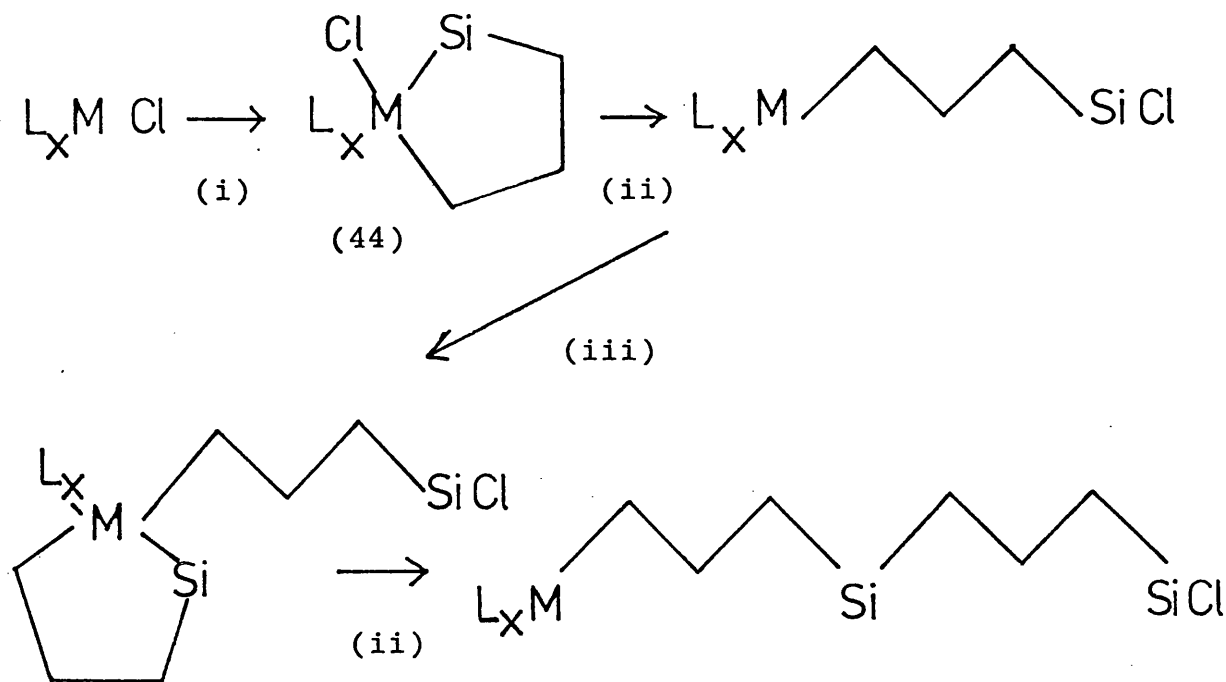
Metallocyclic intermediates have also been postulated in certain polymerisation reactions, an example of which is the important polymerisation of silacyclobutanes to organosilicon polymers having a silicon-carbon backbone (72JO(44)291), Scheme 39.



Scheme 39.

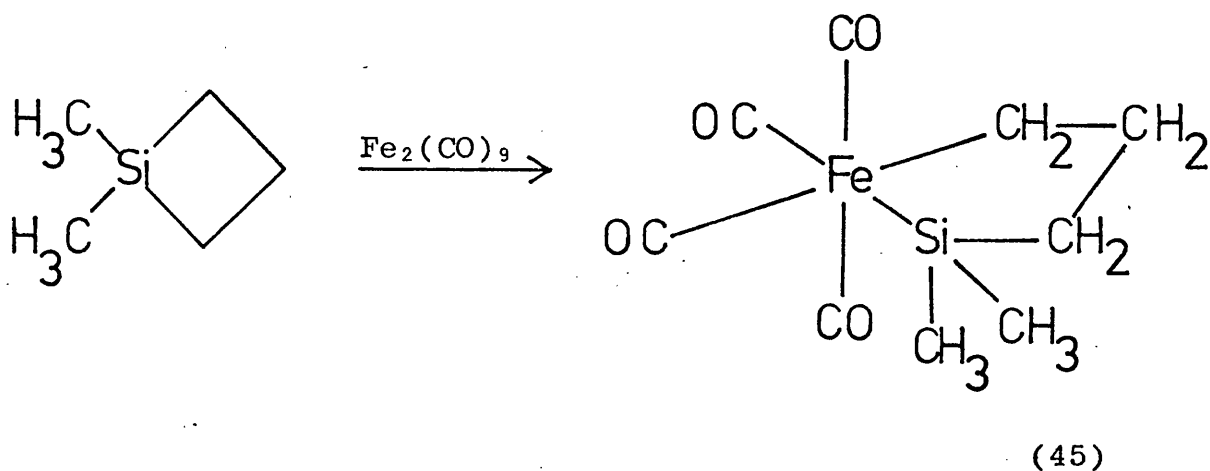
The polymerisation may be effected by the catalysts $[\text{PtCl}_2(\text{C}_2\text{H}_4)]_2$, $\text{RhCl}(\text{PPh}_3)_3$, $[\text{RhCl}(\text{CO})_2]_2$ or cis- $\text{PtCl}_2(\text{PPh}_3)_2$. The mechanism is thought to proceed by the following route (depicted in Scheme 40).

- (i) Oxidative addition of the silicon heterocycle to the transition metal complex (ring-expansion)
- (ii) Formation of linear transition-metal alkyls by halogen transfer (ring-opening)
- (iii) Insertion of further co-ordinated silacyclobutane into the linear metal alkyl (polymer growth)
- (iv) β -hydrogen abstraction (chain termination).



Scheme 40.

The metallocyclic intermediate (44) was not isolated, but a model for the compound was prepared by the analogous reaction with $\text{Fe}_2(\text{CO})_9$ (Scheme 41).



Scheme 41.

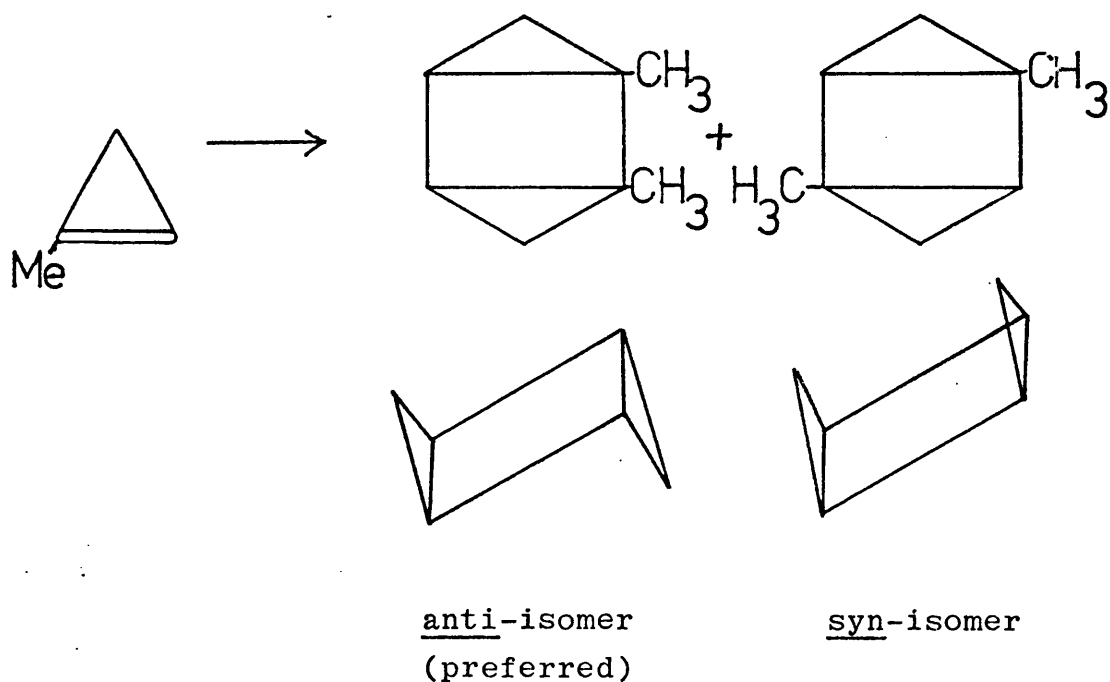
The existence of complex (45) gives credence to the hypothesis of an intermediate such as (44).

In the consideration of the reactions of transition metal complexes with highly strained small ring systems reaction presumably occurs to relieve ring strain in the organic molecule. This can occur by two possible methods:

- (i) By π -co-ordination in unsaturated systems, thereby decreasing carbon-carbon multiple bond order,
- or (ii) By carbon-carbon σ -bond cleavage, yielding a metallocyclic complex in which the strained ring has been expanded.

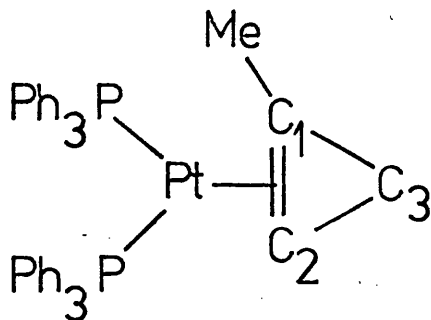
In an attempt to produce a stable π -bonded complex, Weigert et al reacted 1-methylcycloprop-1-ene with PdCl_2 , but only succeeded in obtaining the mixture of

isomers depicted in Scheme 42 (70JA6630).



Scheme 42.

Reaction of 1,3,3-trimethylcycloprop-1-ene with $[\text{PdCl}-(\pi\text{-allyl})]_2$ yielded a similar oligomerisation, but cyclobutene gave no reaction with this palladium(II) complex. Visser et al also found that dimerisation was the result of the reaction of methylcyclopropene with the complexes trans- $\text{Ir}(\text{Cl})(\text{CO})(\text{PPh}_3)_2$, $[\text{RhCl}(\text{CO})_2]_2$, $\text{PdCl}_2(\text{PhCN})_2$ and $\text{PtCl}_2(\text{C}_2\text{H}_4)\text{py}$ (73JO(47)433), but with the platinum(0) complex $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ an olefin-bonded product was formed (46).

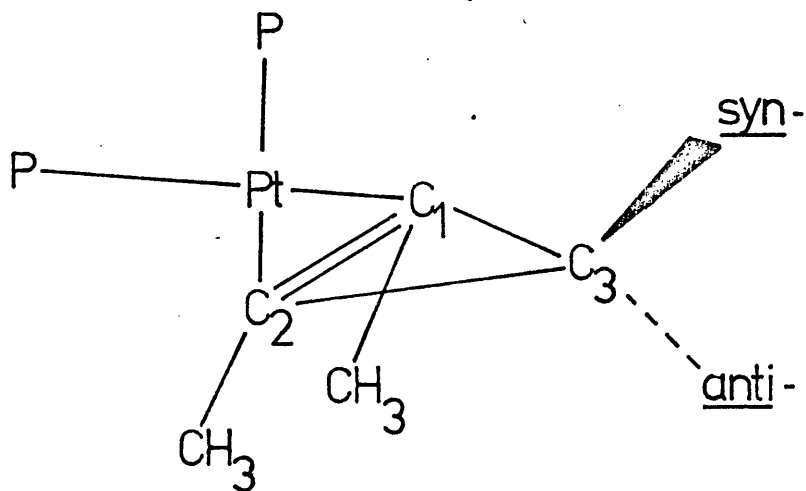


(46)

π -complexes were also formed with the substituted compounds of (46). Carbon disulphide liberated the free cyclopropenes from the complexes, but it was found that in order to liberate apically-substituted cyclopropenes by CS_2 , more heat had to be used (apical position = C_3 in (46)) than with vinyl-substituted complexes. Triphenyl phosphine only liberated the vinyl-substituted cyclopropenes from the complexes. The conclusions drawn were:

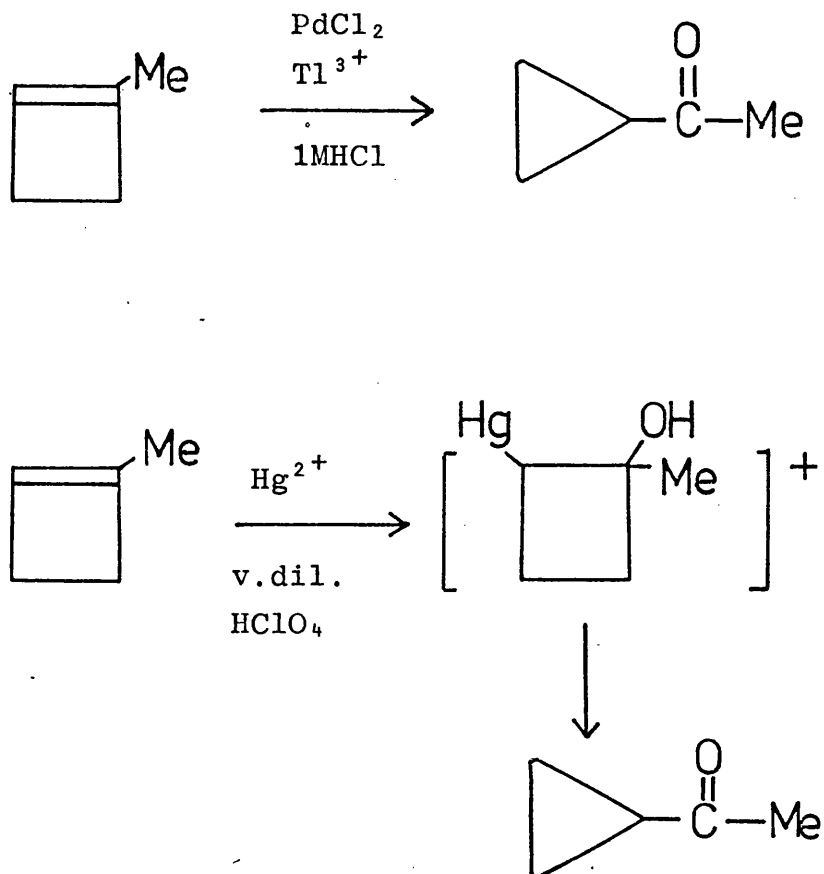
- (i) The strength of the platinum-olefin bond decreases with alkyl substitution
- (ii) Substitution at the vinyl position has a more pronounced effect than substitution at the apical C_3 position.

A crystal structure of the complex of platinum(0) with 1,2-dimethylcycloprop-1-ene revealed that the methyl groups are bent out of the $\text{C}_1\text{C}_2\text{C}_3$ plane and that the plane of the phosphorus and platinum atoms is 116° to that of the $\text{C}_1\text{C}_2\text{C}_3$ plane (47) (71CH1266).



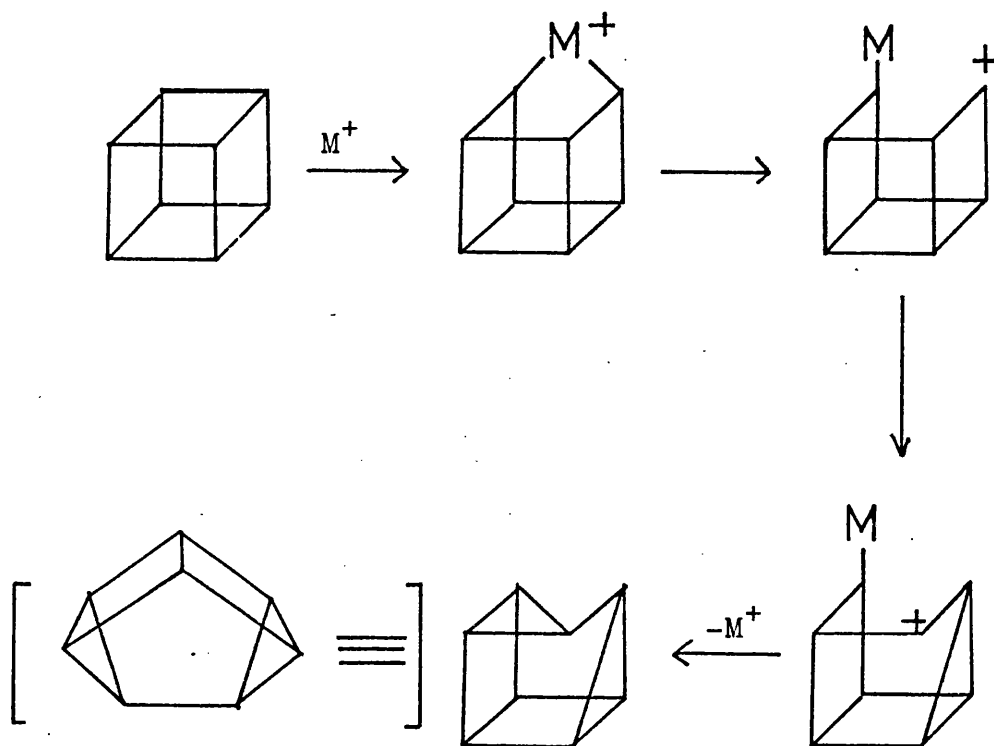
(47)

In studies with methylcyclobutene, Halpern et al discovered an interesting intermediate in the rearrangement with palladium(II) and mercury(II) catalysts (71CH40). With PdCl₂ or a Tl³⁺ catalyst, methylcyclobutene rearranges in 1M HCl to give methylcyclopropyl ketone, but with Hg²⁺ in very dilute HClO₄, an intermediate σ -bonded complex is isolated, which rearranges to the ketone on increasing the acid strength (Scheme 43).



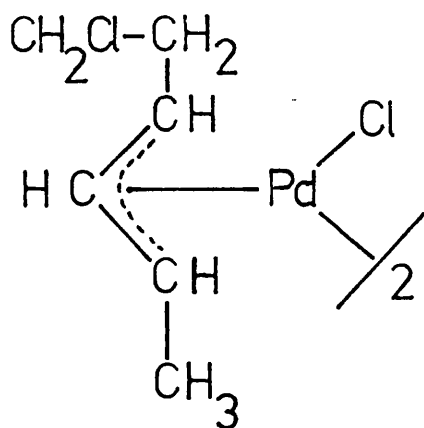
Scheme 43.

This led to a postulate as to the mechanism of rearrangement of cubane to cuneane by Ag^+ which was described earlier. This mechanism is set out in Scheme 44.

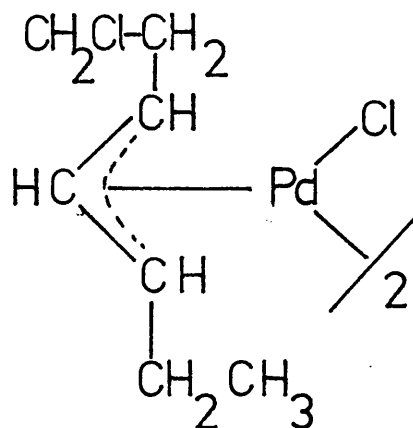


Scheme 44.

Ring-opening of cyclopropane effected by palladium metal on silica was thought not to proceed through a π -allyl mechanism (70JA6658), whereas dicyclopropane and dicyclopropylmethane with $[Pd Cl_2(C_2H_4)]_2$ yielded the π -allyl complexes (48) and (49), respectively.



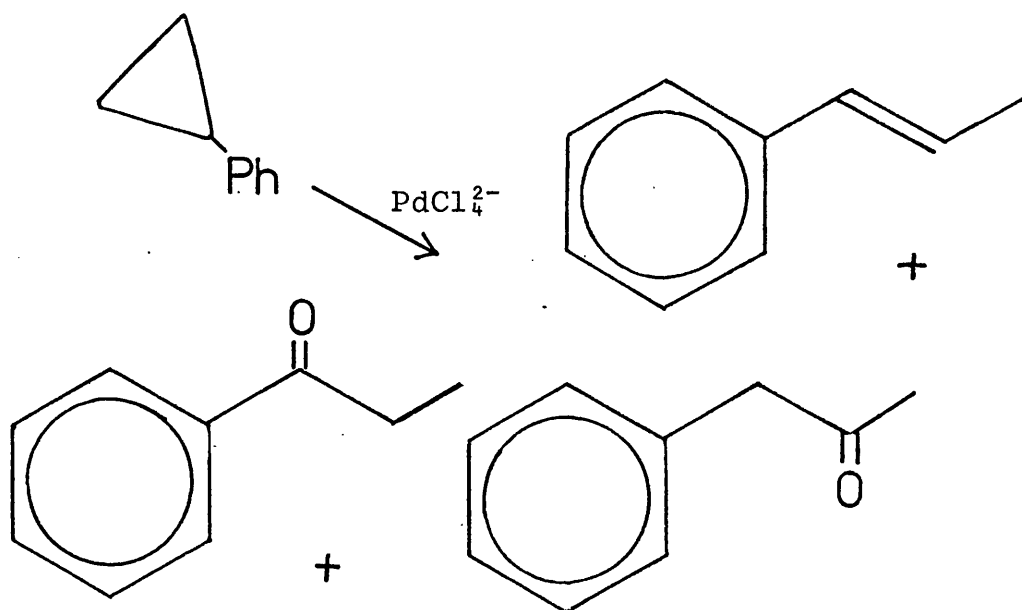
(48)



(49)

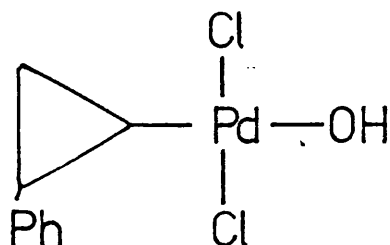
Reaction with the compounds cis- and trans-1,2-dimethylcyclopropane and palladium(II) did not occur.

The reaction of PdCl_4^{2-} with phenylcyclopropane in a 2:1 mixture of glyme and water yielded the mixture of isomers shown in Scheme 45 (71JA471).

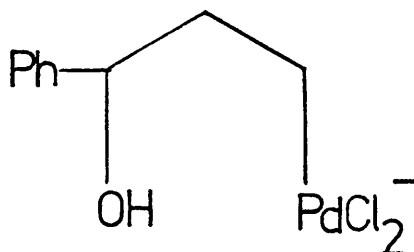


Scheme 45.

In this case intermediates (50) and (51) were suggested with product formation by various hydride shifts.

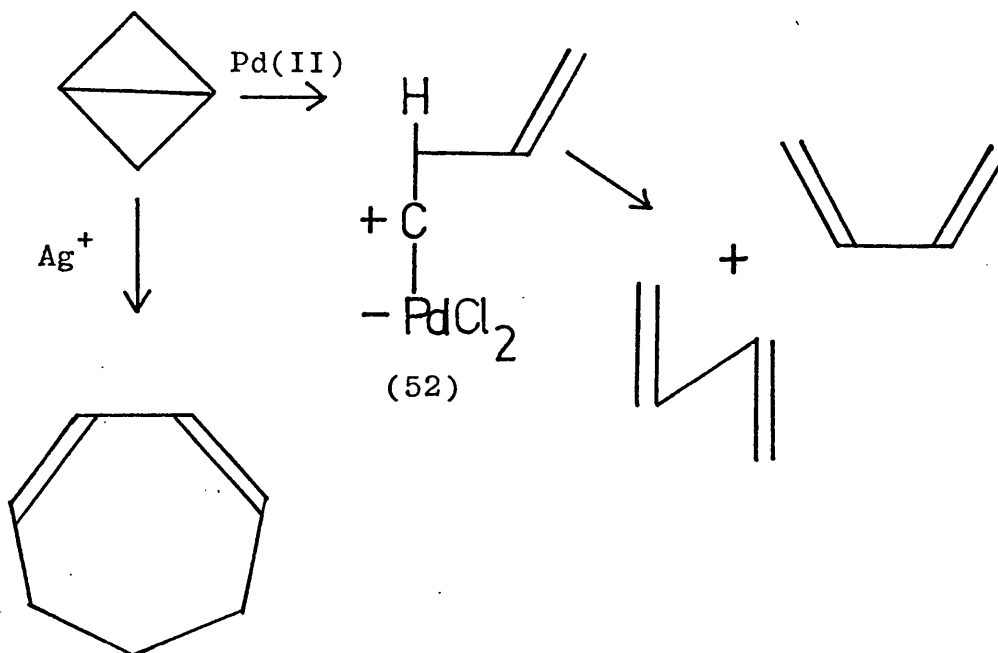


(50)



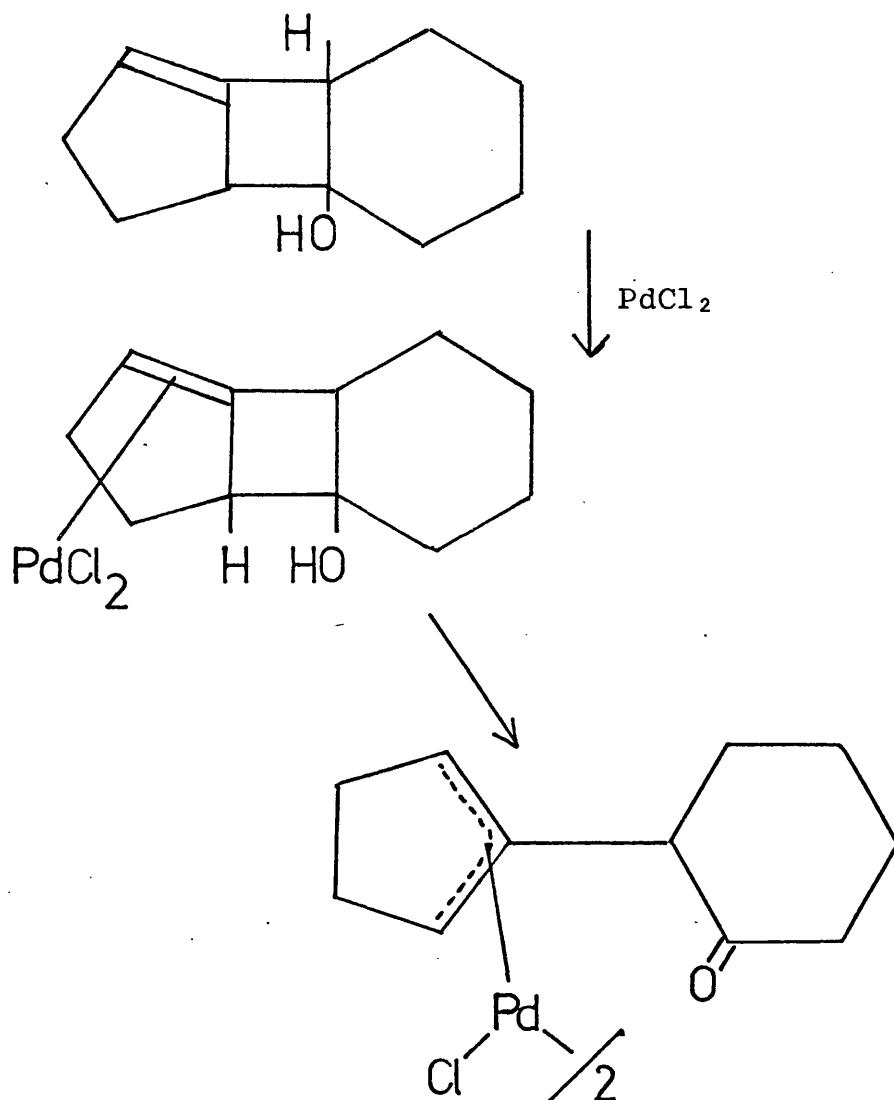
(51)

The reactions of bicyclobutane with L_2PdCl_2 and $AgClO_4$ gave the products shown in Scheme 46, and although the intermediate (52) is postulated for the palladium(II) reaction the different product formed by the silver(I) compound precludes a similar complex in this latter case (71JA4610).



Scheme 46

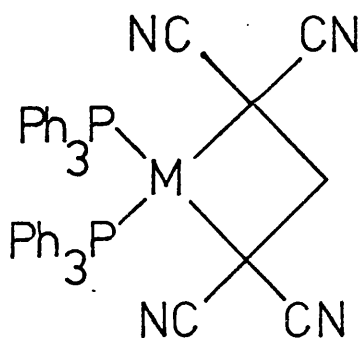
An interesting carbonyl insertion reaction involving palladium was reported by Loubinoux et al (74JO(67)C48) and is shown in Scheme 47.



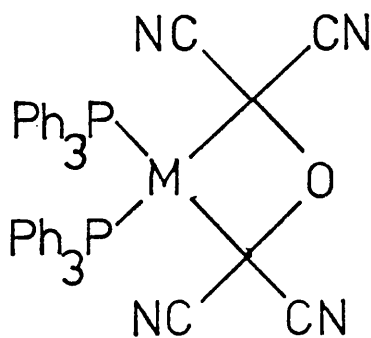
Scheme 47

An example of d^{10} transition metal insertion into carbon-carbon σ -bonds was discussed by Lenarda et al in the reaction of $\text{Pt}(\text{PPh}_3)_4$ and $\text{Pd}(\text{PPh}_3)_4$ with 1,1,2,2-tetracyanocyclopropane (TCCP) and tetracyanoethyleneoxide (TCNEO) (72JO(46)C29).

The complexes formed were thought to be σ -bonded compounds by n.m.r. and infrared analysis, and the structures (53) and (54) respectively were postulated.

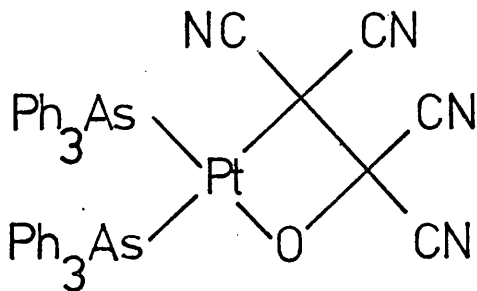


(53)



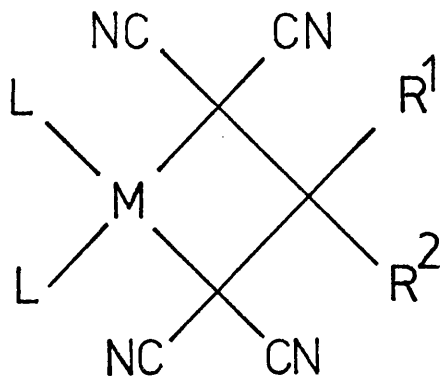
(54)

However, when the arsine derivative of (54) was subjected to an analysis by x-ray diffraction, the structure was found to be that shown in (55), in which the carbon-oxygen bond of the ethyleneoxide has cleaved, and not the carbon-carbon σ -bond as was at first thought (74JA6893).



(55)

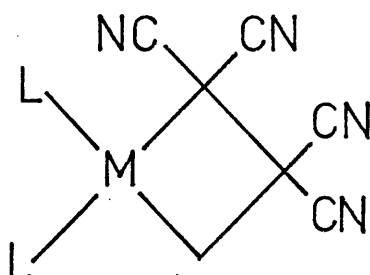
Some attention was now directed towards the TCCP derivative (53), and derivatives (56) were produced (74JO(65)407).



(56)

R ¹	R ²
H	H
CH ₃	CH ₃
CH ₃	C ₂ H ₅
(CH ₂) ₅	(CH ₂) ₅

A rigorous n.m.r. analysis was carried out on these complexes in an attempt to sort out their structures. The arrangement (57), which had been a possibility on the basis of the structure of the TCNEO complex, was rejected on the evidence given below:

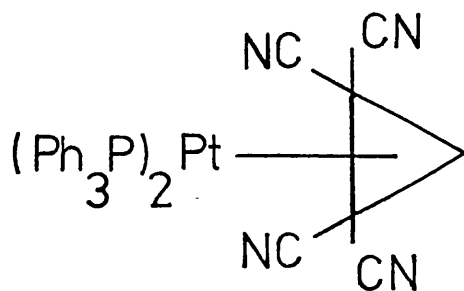


(57)

- (i) The ^{31}P -H coupling constants were very small - far less than calculations based on structure (57) had estimated.
- (ii) The ^{195}Pt -H coupling constant of about 65 Hz was far less than would be expected from a complex of structure (57).
- (iii) Little effect was seen in $J(\text{Pt-H})$ when the arsine derivative was used. This is contrary to expectations for a methylene group attached to platinum. The trans-influence of a phosphorus atom is greater than that of an arsenic atom (68J 3074, 72IC2749). Thus in the phosphine complex, the Pt-CH_2 bond length should be greater than in the arsine derivative, leading to a decrease of the s-character in the bond (per unit). The Pt-H coupling constant, which depends on the s-character in the bond, should, therefore increase on substituting arsenic for phosphorus. The effect was not found to be as appreciable as would be expected in a compound of structure (57).
- (iv) In substituting more basic phosphines for L, the chemical shifts for the substituent R-groups were found not to vary to any extent. Arsine substitution had the same negligible effect.

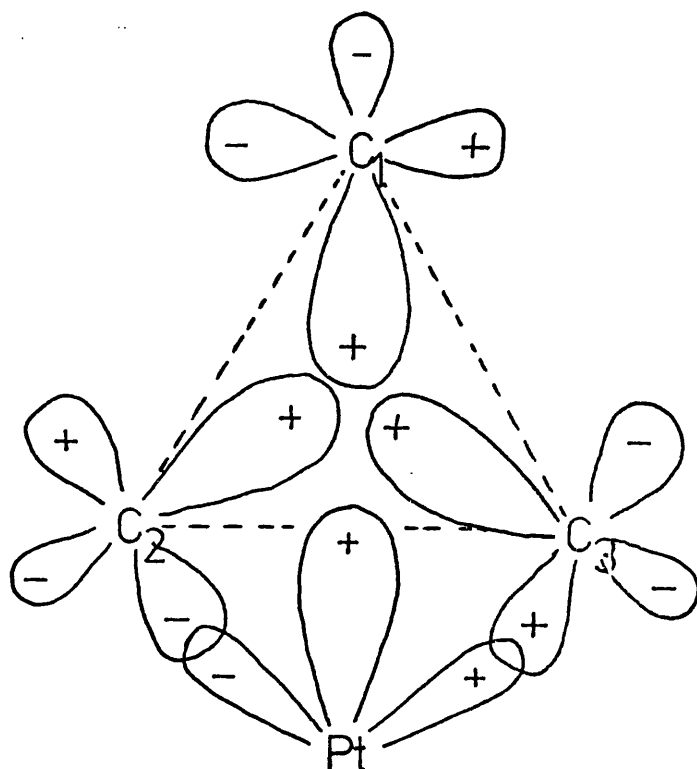
It was thus deduced that the original formulation for the complex (53) was more likely to be correct, but it

was not until the crystal structure was published in 1974 that the problem was unequivocally solved (74JO(70)133). The cleavage of the $(\text{CN})_2\text{C}-\text{C}(\text{CN})_2$ bond by the transition metal was confirmed, but the bonding was discovered to be mid-way between the structure shown in (53) and the π -structure (58). It is interesting that this latter structure is similar to that postulated by Tipper in his original work on cyclopropanes.



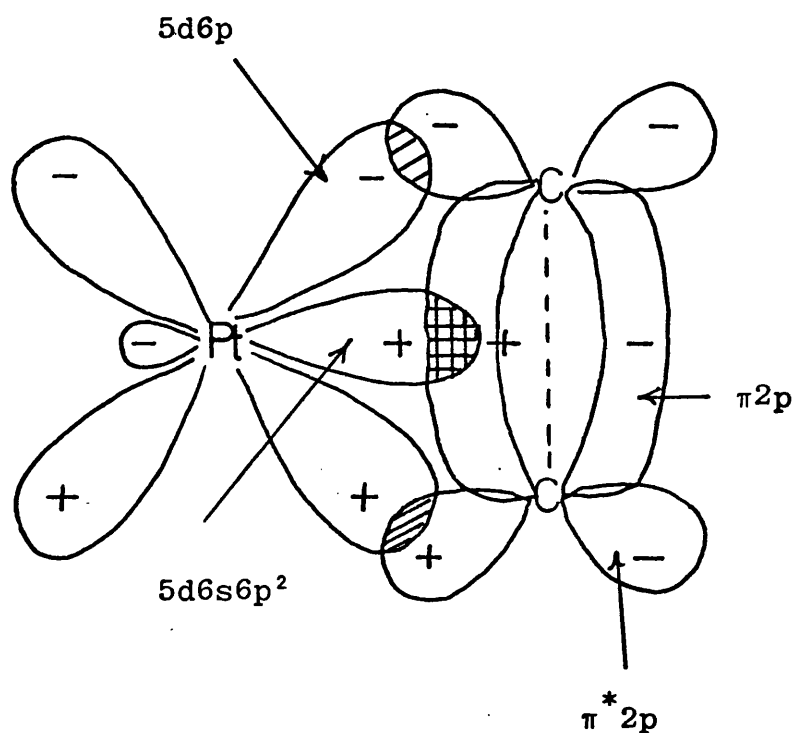
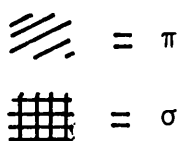
(58)

The proposed interaction of the platinum orbitals with the cyclopropane ring leading to insertion into the carbon-carbon σ -bond is given in (59).



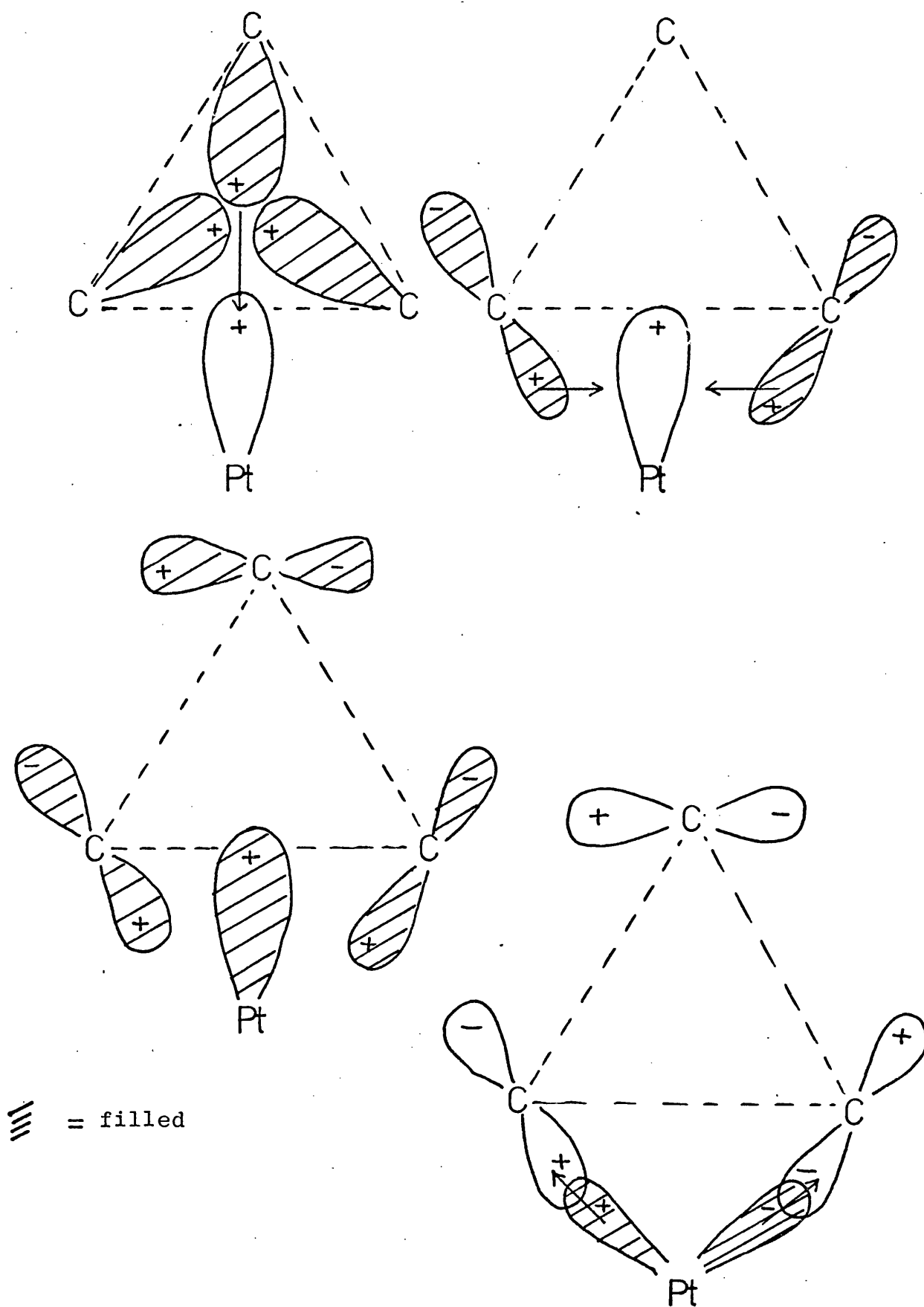
(59)

The bonding in this complex may be compared with the bonding in metal-olefin complexes originally suggested by Dewar for silver(I) (51BFC79) and later developed by Chatt and Duncanson to explain platinum(II) complexes (53J2939), (60).



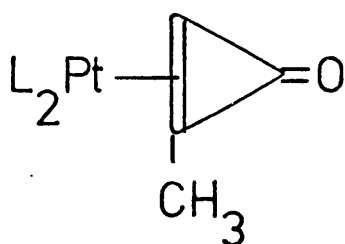
(60)

In this case also, the best explanation of the bonding lies mid-way between σ and π , and similarly in the case of cyclopropane. Puddephatt et al, in n.m.r. studies on the complex $\text{PtCl}_2(\text{C}_3\text{H}_6)\text{py}_2$ also postulate the σ - π bonding in a scheme of orbital interactions (74JO(71)145), Scheme 48.

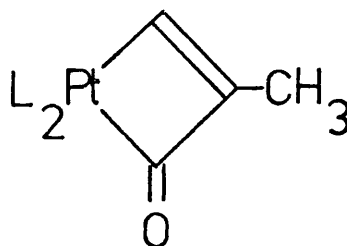


Scheme 48.

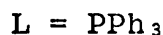
In further attempts to produce stable π -bonded transition metal-small ring complexes, Visser et al studied the reactions of some cyclopropenones with the platinum(0) complex $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$. The reaction of this transition metal complex with 1-methylcycloprop-1-ene-3-one at -65°C resulted in the π -bonded complex (61), which at temperatures higher than -30°C ring-expanded to the platinacyclobutenone complex (62) (72JO(44)C63).



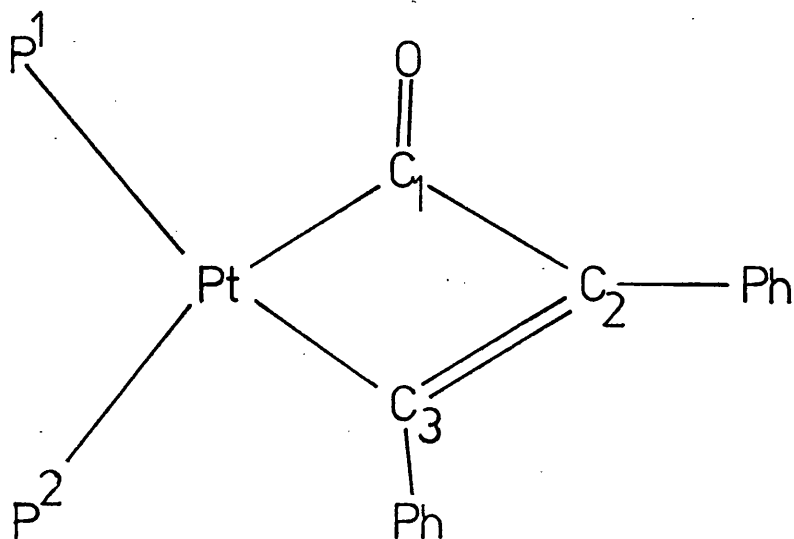
(61)



(62)



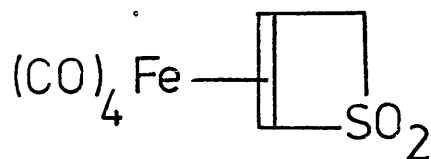
The reaction of 1,2-diphenyl- and 1,2-dimethylcyclopropenone with the platinum(0) complexes resulted in all cases in the ring-expanded metallocyclic complex, characterised by $\nu(\text{C}=\text{O})$ at 1640 cm^{-1} in the i.r. (characteristic of $\text{C}=\text{O}$ α to platinum(II) (68CH1373, 68CD319)). Confirmation of the metallocyclic complex was provided by a crystal structure determination of the diphenyl derivative (72CH672), (63).



(63)

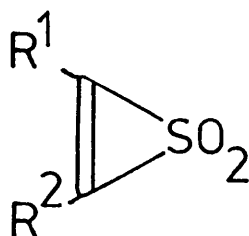
It was found that both the carbon-carbon σ -bond and the carbon-carbon π -bond retain their character; the platinum is in a distorted square planar arrangement and the molecule is almost planar (the PtP_1P_2 plane is bent only 11° away from the $\text{C}_1\text{C}_2\text{C}_3$ plane. Pyrolysis of these complexes did not produce acetylenes as in the case of the iron(0) derivatives previously discussed.

Substituted thiirene-1,1-dioxides also form π -bonded complexes with platinum(0) and palladium(0) (72CH178, 73JO(57)403). Similarly with iron(0) and unsubstituted thiete-1,1-dioxide no ring-opening was observed, the product being the complex (64) (73JOC3963).



(64)

The reaction of $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ and $\text{Pd}(\text{PPh}_3)_4$ with the substituted thiirene-1,1-dioxides (65) yielded complexes on which TCNE had no action.



(65)

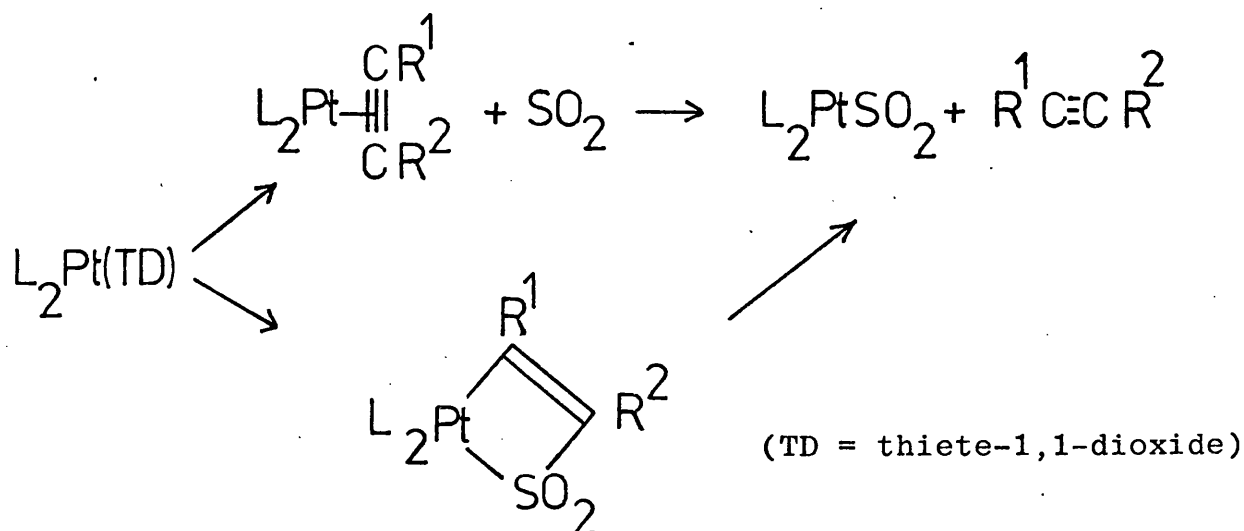
	R^1	R^2
a	H	CH_3
b	CH_3	CH_3
c*	CH_3	Ph
d*	Ph	Ph

* Did not form palladium(0) complexes.

In spite of the fact that TCNE failed to displace these ligands, they were thought to be π -bonded rather than ring-expanded because of the following evidence.

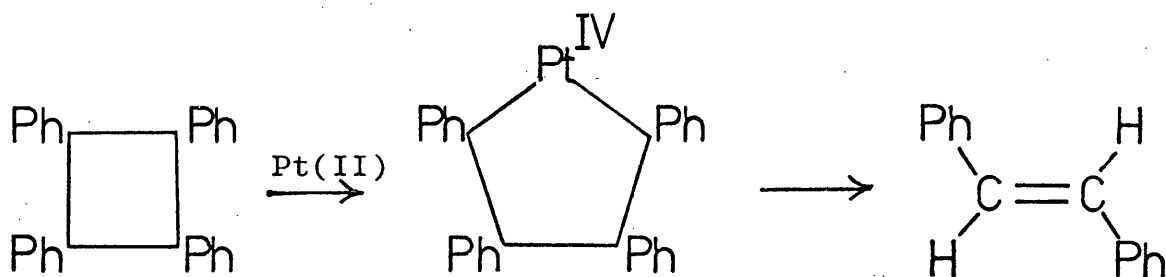
- (i) Infrared spectra of the complexes showed the absence of any $\nu(\text{C}=\text{C})$ bands clearly seen at 1614 cm^{-1} in the free ligand. The SO_2 bands at 1260 cm^{-1} and 1170 cm^{-1} were also shifted.
- (ii) The allylic $\text{CH}_3\text{-H}$ coupling of 1.1 Hz in the n.m.r. of the free ligands disappeared on co-ordination.
- (iii) The Pt-H couplings and ^1H chemical shifts observed in the n.m.r. were similar to those previously seen in olefin-bonded cyclopropenones (71CH1266).
- (iv) In the complex with (65b) ($\text{R}^1=\text{R}^2=\text{CH}_3$) the equivalence of the CH_3 groups in the n.m.r. suggests a symmetrical molecule, only possible in the case of a π -bonded complex.

On pyrolysis these compounds gave acetylenes and SO_2 complexes of platinum(II) (only isolated as SO_4 complexes). The mechanism is thought to proceed in one of two ways (Scheme 49).



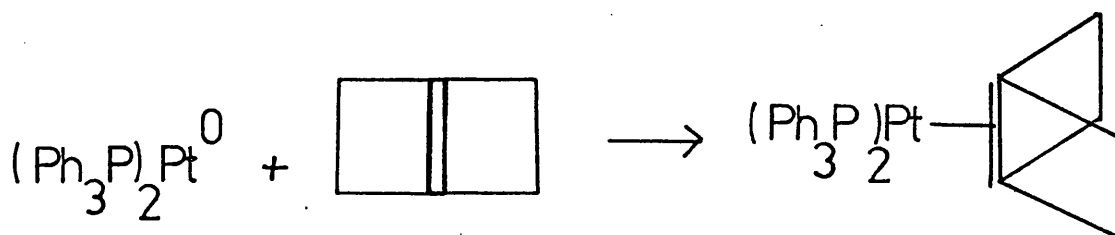
The decomposition of the co-ordinated thiirene-1,1-dioxides parallels the thermal decomposition of thiirane-1,1-dioxides, whose thermal stability is considerably less than free thiirene-1,1-dioxides. The explanation for the ready pyrolysis of the co-ordinated species and the fact that the platinum(0) complexes are more readily pyrolysed than the palladium(0) complexes probably lies in the difference in co-ordinative ability between platinum(0) and palladium(0). This co-ordinative ability in d^{10} transition metals is related to the $(n-1)d^{10} \rightarrow (n-1)d^9 np$ promotion energy (68CD319) which for palladium(0) is 4.23eV and for platinum(0) is 3.28eV. The platinum(0) co-ordinates more strongly than palladium(0), and the bond-order of the olefin bond thus co-ordinated is lower in the case of platinum. Thus in the co-ordinated species, the nature of the ligand closely approaches that of the thiirane-1,1-dioxide (having its carbon-carbon bond-order lowered towards σ -carbon-carbon). Pyrolysis of this complex then follows the same lines as pyrolysis of the free thiirane. The effect of lowering the bond-order is greater in the case of platinum(0), which is reflected by the fact that pyrolysis is more easily carried out in this case than in the case of palladium(0).

In ^1H - ^2H exchange studies, McQuilllin et al found that cyclobutane ring cleavage was effected by platinum(II) giving olefinic products (74CH806), Scheme 50, thought to proceed through a platinacyclopentane derivative.



Scheme 50.

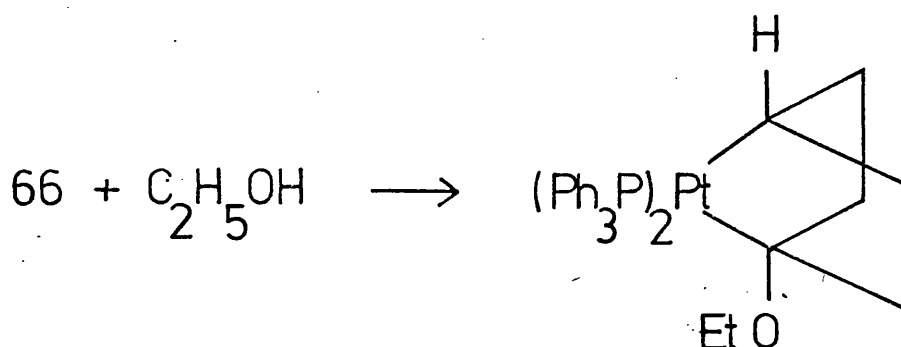
An interesting reaction of platinum(0) and bicyclohexene was recently published by McGinnety et al in which the initial π -complex produced was cleaved in an unusual way by ethanol (74JA6531). The reaction of $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ with bicyclohexene yields the π -complex (66) the structure being confirmed by an x-ray crystal structure determination (Scheme 51).



(66)

Scheme 51.

On treatment of (66) with ethanol, the carbon-carbon bond formerly the carbon-carbon π -bond is completely cleaved with ethanol adding to the two carbon centres as H and OC_2H_5 giving a complex of platinum(II) as shown in Scheme 52. The possibility of ionic intermediates is not discussed.

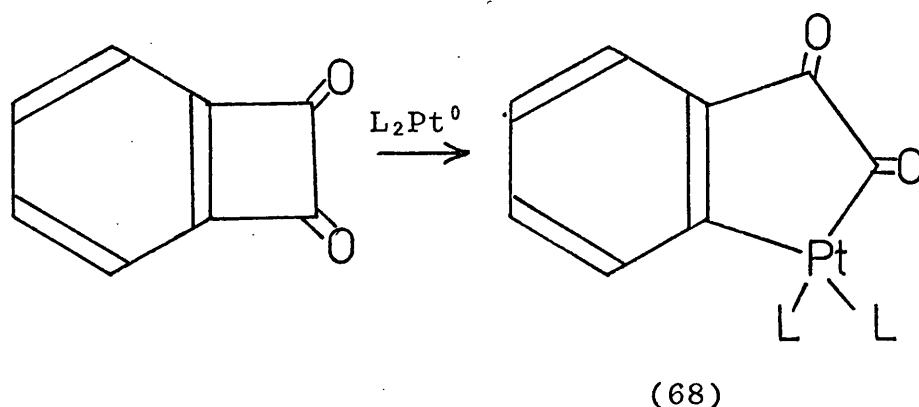


(67)

Scheme 52.

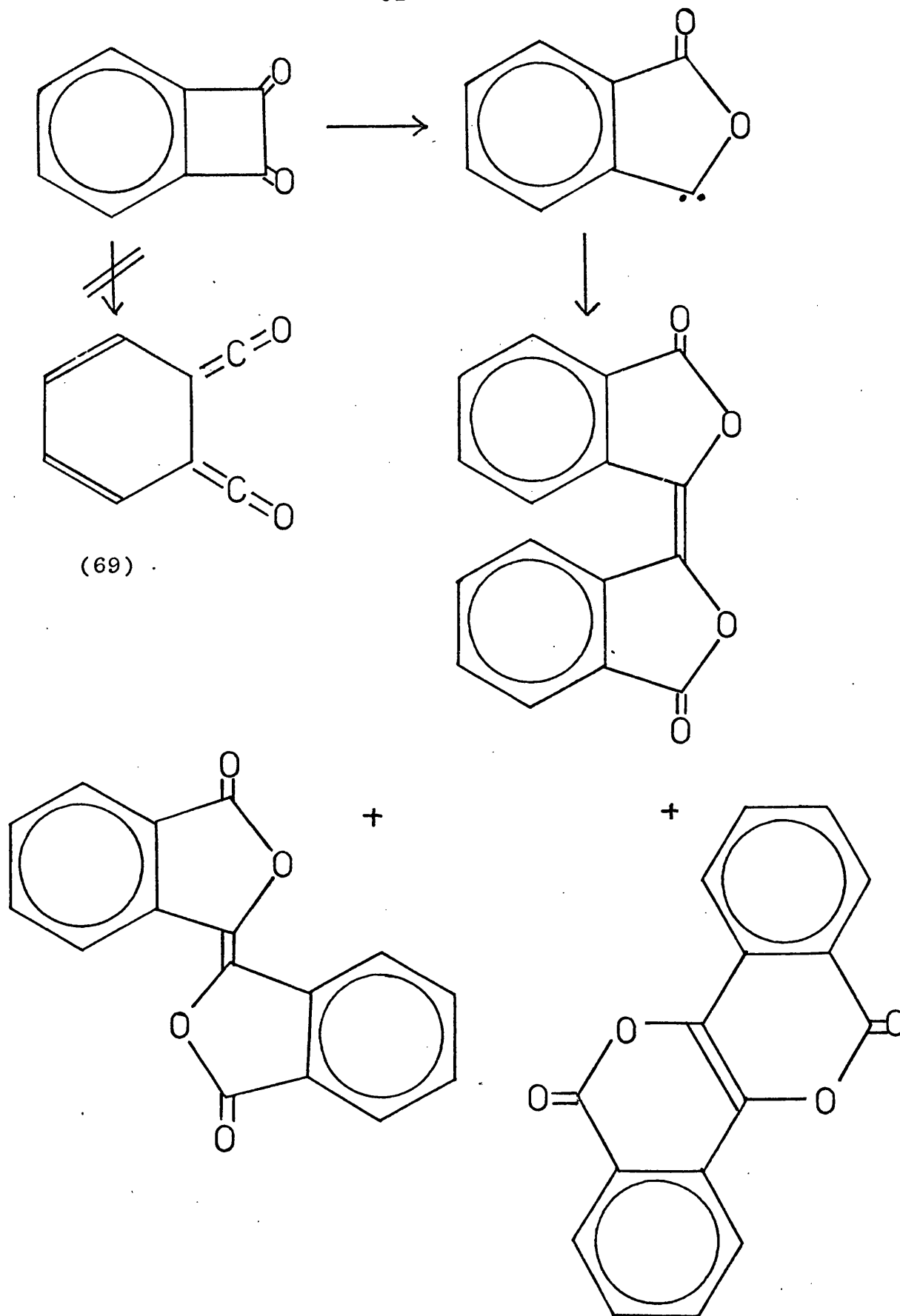
The structure of (67) is confirmed by x-ray diffraction analysis.

Finally, the study of the action of platinum(0) on the strained system of 1,2-benzocyclobutenedione reported by Kemmitt et al (73CH158) led directly to the present work. When $\text{Pt}(\text{PPh}_3)_4$ and benzocyclobutenedione were mixed in benzene a product was formed which had two isomeric forms, one red and the other blue. These isomers were shown to be of the form (68), the colour difference resulting from the difference in the angles of twist of the carbonyl groups about their connecting carbon-carbon bond (Scheme 53).



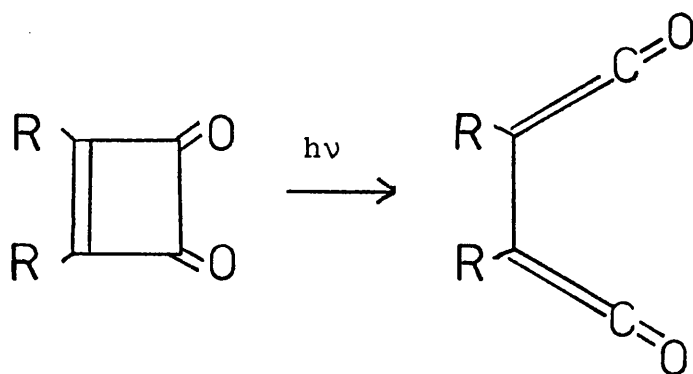
Scheme 53.

The platinum(0) species was shown to have inserted asymmetrically into the molecule, cleaving a carbon-carbon σ -bond of the cyclobutenedione ring α to the phenyl group. However, a symmetrical cleavage reaction of this molecule was reported when the photochemical oligomerisation was studied (71CH1162). In the low-temperature photolysis of benzocyclobutenedione, the expected bis-keten (69) is not formed, as was first suspected, (61JA393, 68CB1457), but a carbene intermediate gives rise to the products observed, as shown in Scheme 54.



Scheme 54.

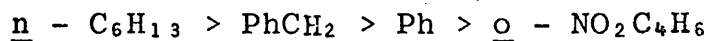
The similar low-temperature photolysis of the cyclobutenedione system does result in symmetrical cleavage leading to the previously postulated bis-keten (Scheme 55).



R = Ph, Me
Scheme 55.

CONCLUSION

One factor which emerges from these studies is that the oxidation state of the transition metal can have a profound effect on the ability of the complex to cause ring-opening of the organic system. Thus in studies on the reactions of various cyclopropane derivatives, $R-\triangle$, with platinum(II) or platinum(IV) complexes, the reactivity series established that



i.e. electron-withdrawing substituents tend to inhibit reaction with the electrophilic platinum(II) and platinum(IV) species. We have not observed any reaction between unsubstituted cyclopropane and the nucleophilic

complex trans-stilbenebis(triphenylphosphine)platinum(0) (75MI1), but reactions with the more electrophilic platinum(II) and platinum(IV) have been reported (q.v.).

The observation that tetracyanoethyleneoxide and 1,1,2,2-tetracyanocyclopropane are ring-expanded by platinum(0) complexes suggests that the presence of electron-withdrawing substituents in an organic ring compound greatly enhances its susceptibility to attack by nucleophilic transition metals. Similar observations have been made with the cyclopropanones (which contain the electron-withdrawing carbonyl group). In this latter case a wide variety of products have been reported depending on the transition metal and the conditions used.

However, little is known about the reactivity of other small ring systems containing electron-withdrawing substituents. In view of the lack of information available on this type of reaction, the work presented in this thesis is concerned with extending the knowledge of this type of system.

CHAPTER 2.

RESULTS AND DISCUSSION ON THE REACTIONS
OF CYCLOBUTENEDIONE DERIVATIVES AND
RELATED MOLECULES WITH LOW-VALENT TRANSITION
METAL COMPLEXES.

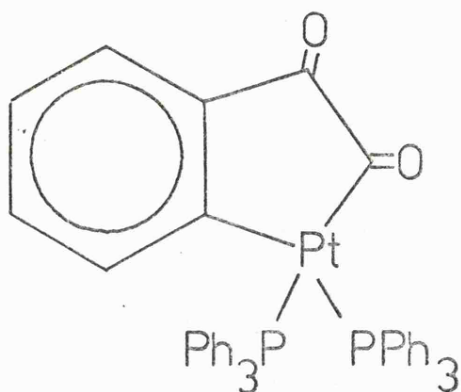
SECTION 1

A STUDY OF THE REACTIONS OF LOW-VALENT
TRANSITION-METAL COMPLEXES WITH DERIVATIVES
OF CYCLOBUT-1-ENE-2,3-DIONE.

(A) Platinum(0)

(i) Trans-stilbenebis(triphenylphosphine)platinum(0)
Pt(PPh₃)₂(trans-stilbene).

Benzocyclobutenedione is known to react with $\text{Pt}(\text{PPh}_3)_4$ to yield a complex (1) which crystallises in two forms, one red and one blue (73CH158).



(1)

A crystal structure determination revealed that the main difference between the two forms was in the angle of twist of the carbonyl groups about their connecting carbon-carbon bond. In this platinacyclopentenedione molecule there are three conflicting effects:

- (i) The divalent platinum atom attempts to occupy a square-planar environment
- (ii) The electronegative oxygen atoms of the carbonyl groups wish to be as far apart as possible.
- (iii) The carbonyl group π -bonds wish to be in an orientation which permits conjugation with the phenyl-ring π -bonds.

These three effects reach a compromise in the two forms of the complex. The crystallographic data are reported in Table 1, and the structures are given in diagrams (2) and (3).

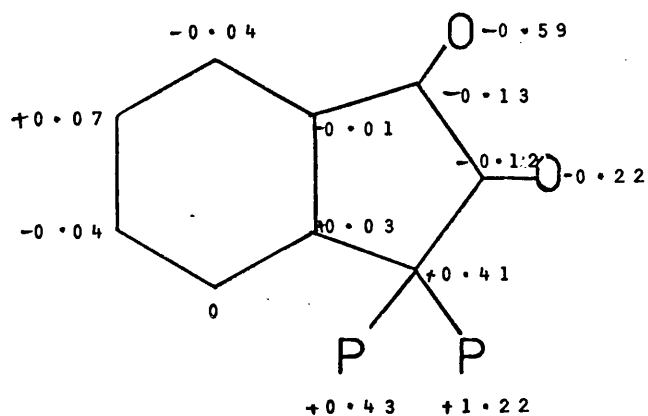
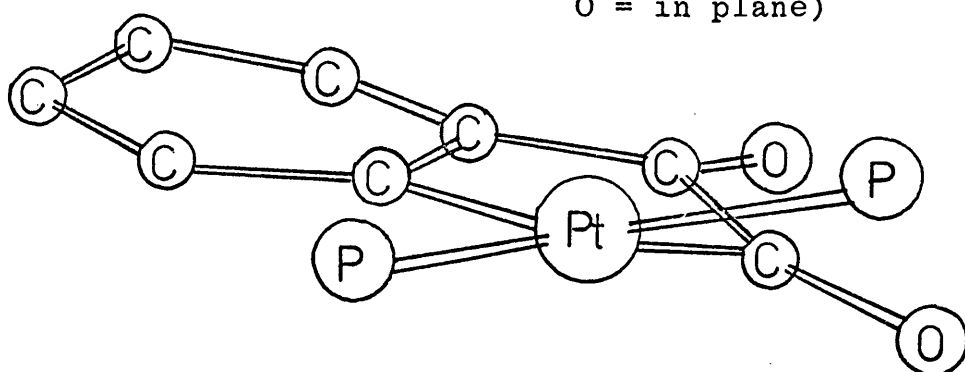
TABLE 1

	BLUE FORM	RED FORM
space group	triclinic $\overline{P1}$	monoclinic $\overline{P2}_1/\overline{C}$
a	9.74 Å	11.79 Å
b	9.797 Å	22.27 Å
c	19.61 Å	15.64 Å
α	99.9°	-
β	96.9°	122.0°
γ	105.6°	-
<u>U</u>	1748 Å ³	3481 Å ³
<u>Z</u>	2	4
R	0.050 for 3999 reflexions	0.057 for 3961 reflexions

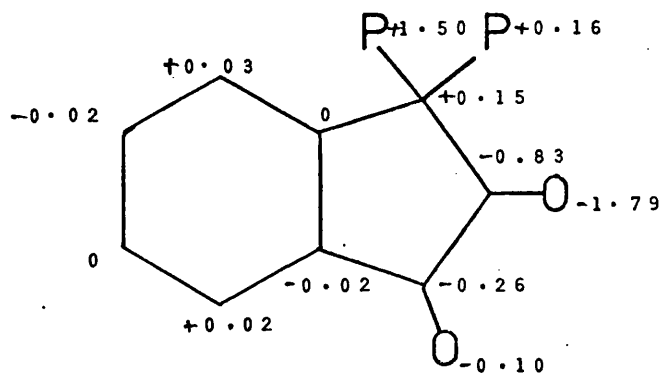
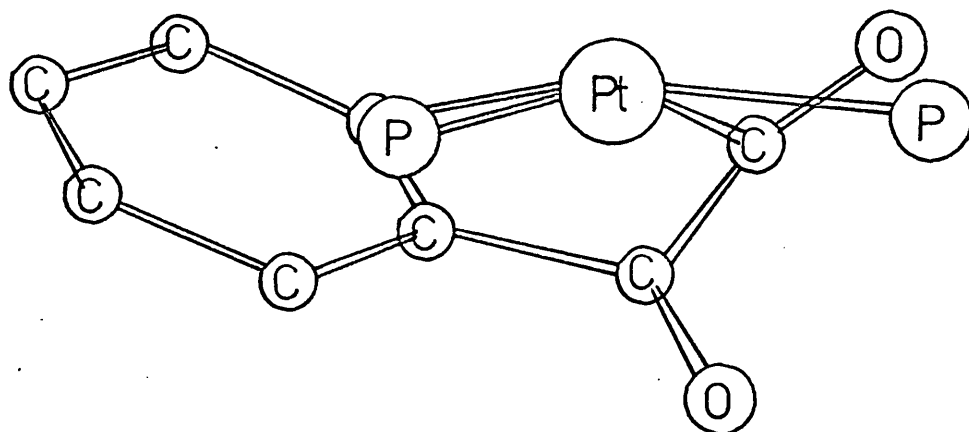
Relative distances - 68 -

out of and into O plane

(+ = out of
- = behind
0 = in plane)



(2) Blue Form

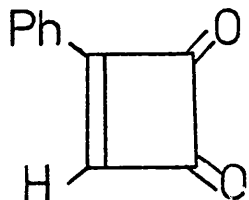


(3) Red Form

The insertion of the platinum(0) species into the carbon-carbon σ -bond of the cyclobutene part of the molecule (1) prompted an investigation of the reactions of other cyclobutenedione derivatives with zero-valent platinum complexes. Although the preliminary reaction with benzocyclobutenedione had been carried out with tetrakis(triphenylphosphine)platinum(0), it was decided to change this starting material for trans-stilbenebis-(triphenylphosphine)platinum(0). Not only is this complex conveniently made, it is stable in air in the dry crystalline state for long periods and the high solubility of trans-stilbene in organic solvents minimises the contamination of possible products by this part of the starting material. Studies on the dissociation of olefin-platinum(0) complexes also suggest that this complex may be an ideal precursor for the reactive moiety $\text{Pt}(\text{PPh}_3)_2$ (68JA4491, 63CC1235, 70IA390).

Reaction of $\text{Pt}(\text{PPh}_3)_2$ (trans-stilbene) with benzocyclobutenedione produced a complex identical to that already reported, having $\nu(\text{C}=\text{O})$ at 1690 and 1665 cm^{-1} compared with $\nu(\text{C}=\text{O})$ at 1779 and 1761 cm^{-1} in the pure starting material.

Reaction of the stilbene complex with the derivative 1-phenylcyclobut-1-ene-3,4-dione (4) resulted in the formation of two isomeric complexes depending on the conditions used. In benzene or chloroform solution with warming the red solution produced yielded a crystalline red complex having $\nu(\text{C}=\text{O})$ at 1658 cm^{-1} ,

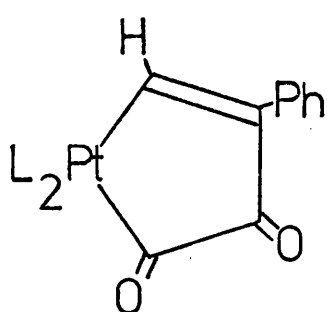


(4)

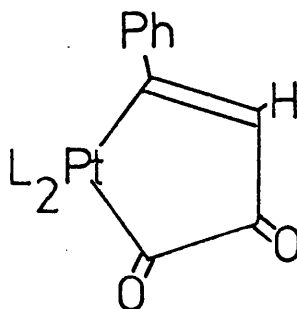
whereas the reaction in diethyl ether resulted in a yellow product having $\nu(\text{C}=\text{O})$ at 1723 cm^{-1} . On warming the yellow compound in benzene or chloroform solution, the red complex was obtained, identical in all particulars to the material obtained directly from the other starting materials. The n.m.r. spectrum of the red compound showed the expected phenyl resonances, together with a doublet of doublets having ^{195}Pt satellites at 9.20δ . This signal is in a similar position to the singlet resonance of the vinylic proton in the starting material (at 9.24δ). However, the n.m.r. of the yellow complex, in addition to the phenyl resonances, contained only a triplet at 4.75δ , also having ^{195}Pt satellites. The upfield shift of the proton resonance in the yellow complex, together with the position of $\nu(\text{C}=\text{O})$ which is closer to the $\nu(\text{C}=\text{O})$ of the starting material of 1776 cm^{-1} than that in the red material, led to the conclusion that the yellow complex was olefin-

bonded, whereas the red isomer was an inserted product.

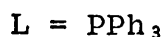
The red material was given the structure (5a) rather than (5b) for the following reasons:



(5a)

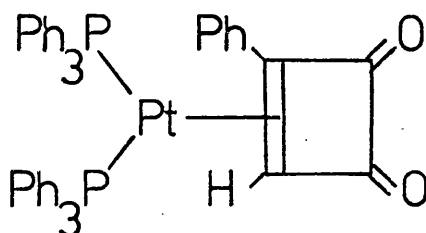


(5b)



- 1) The $\nu(C=O)$ value of 1658 cm^{-1} indicates that the carbonyl environments are markedly different in this material than in the starting material.
- 2) The value of $J(Pt-H)$ of 21.5 Hz is of the order expected for a vinylic proton gem to Pt, whereas if the phenyl group and the proton were interchanged then $J(Pt-H)$ would be expected to be smaller than the observed value.
- 3) The doublet of doublets arises due to cis- and trans-(^3P-H) coupling where cis-($P-H$) $\neq 0$. Coupling of 17.0 Hz (trans-) and 8.5 Hz (cis-) is reasonable for structure (5a), whereas the alternative isomer (5b) would not be expected to give both cis- and trans-($P-H$) coupling, especially of this magnitude.

The yellow isomer was given the structure (6) based on the following evidence



(6)

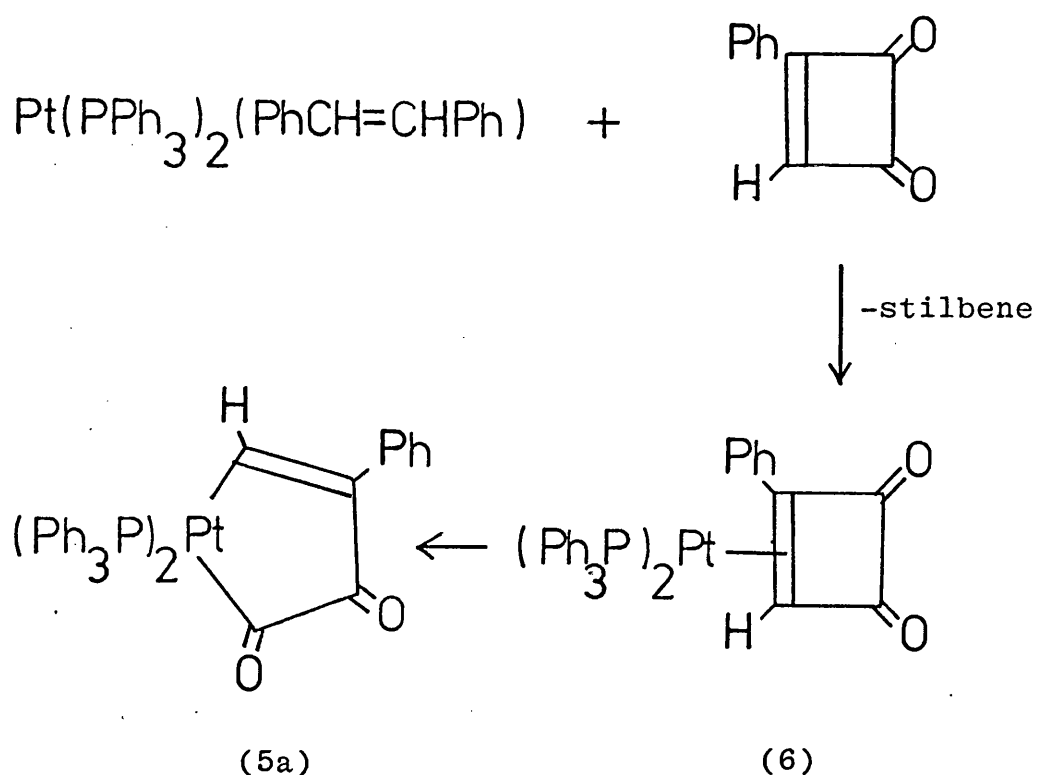
- 1) The shift in $\nu(\text{C}=\text{O})$ from 1776 cm^{-1} in the starting ligand to 1723 cm^{-1} in the complex indicates that the carbonyl environments are similar in these molecules, but in the complex are shifted slightly due to co-ordination.
- 2) On assumption that the platinum(0) is co-ordinated via the carbon-carbon double bond and not the carbon-oxygen π -bond (as seems reasonable from the values of $\nu(\text{C}=\text{O})$), the triplet pattern at 4.75 δ must be due to the unique proton. The upfield shift of this signal is large in comparison to most vinylic upfield shifts in alkenes co-ordinated to platinum(0) (usually $\approx 2.5\text{ p.p.m.}$). The triplet pattern was at first thought to be caused by a fluxional mechanism, rendering the phosphorus-atoms equivalent. However, the production of a proton decoupled ^{31}P n.m.r. spectrum revealed an AB pattern with unsymmetrical ^{195}Pt satellites. The apparent triplet pattern was thus assigned as

an ABX system ($A=B=P$; $X=H$) in which

$$J(AB) \gg |J(AX) - J(BX)|.$$

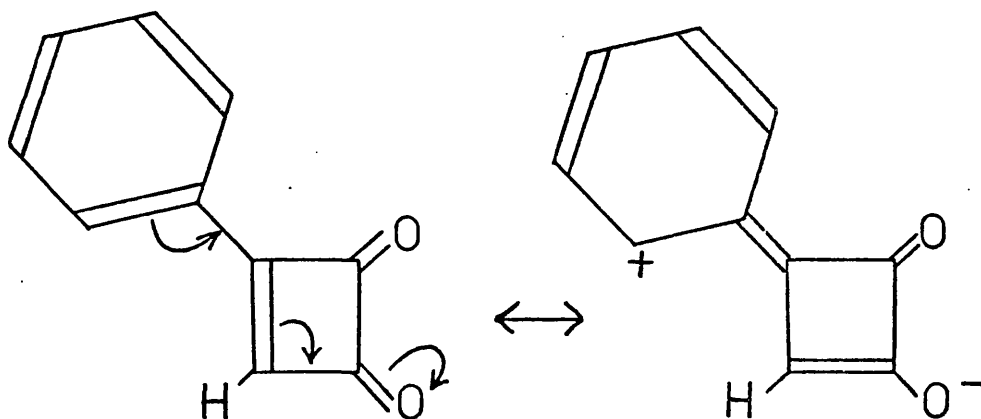
- 3) The values of $J(\text{Pt-H})$ of 48.8 Hz and $J(\text{P-H})$ of 6.7 Hz are indicative of a π -bonded system as shown in (6) as compared with a carbonyl π -bonded system.

The easy conversion of (6) to (5a) would suggest that (6) is an intermediate in the reaction of $\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene})$ and phenylcyclobutenedione, as shown in Scheme 1.



Scheme 1.

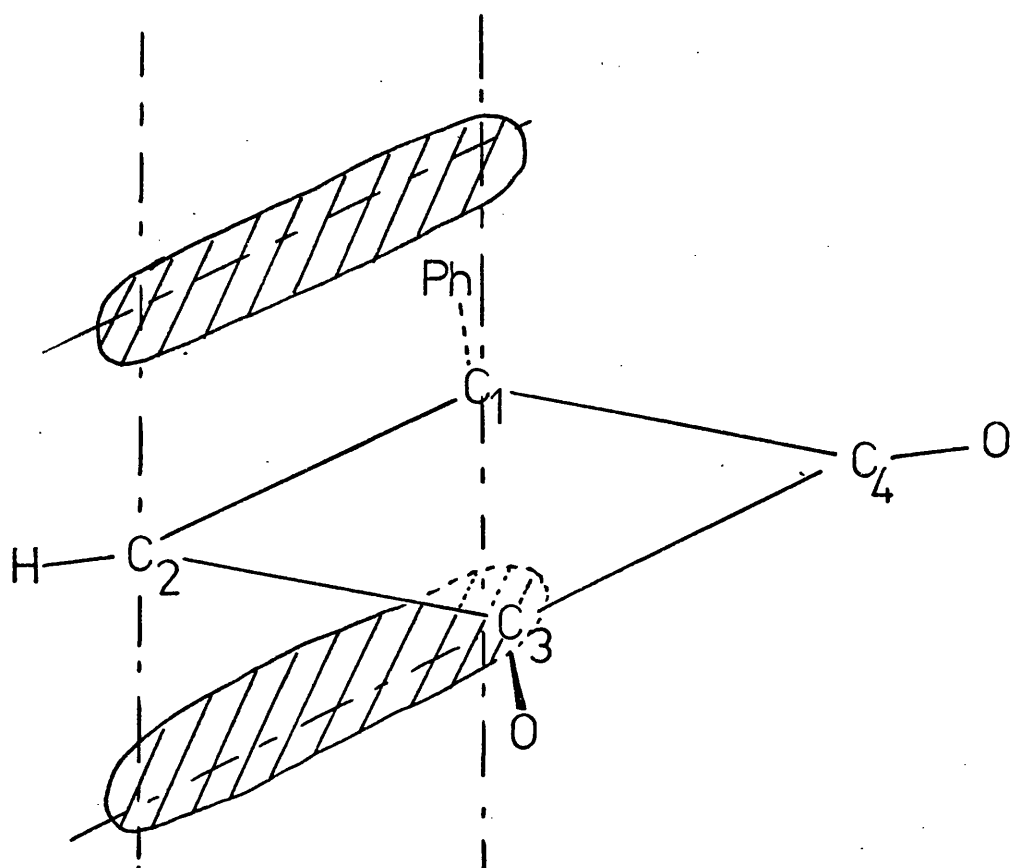
The insertion of the platinum(0) into the bond between the vinylic proton and one carbonyl group creates an interesting situation due to the electronic features of the organic molecule. If the free ligand is considered separately, it can be seen that a conjugated system exists round the ring as shown in Scheme 2, the bond between (H)C-C(CO) being in the system.



Scheme 2.

The conjugated system may not be drawn the other way (i.e. including the carbon-carbon bond (Ph)C-C(CO)). It might be expected then that the insertion reaction would take place at the carbon-carbon σ -bond not 'protected' by the conjugated system, whereas all indications are to the contrary.

It may be that in co-ordinating to the double bond (which is in a plane perpendicular to the plane of the molecule as shown in (7))



(7)

the platinum(0) unit is drawn towards C₃ in (7) due to this conjugation, thus being too far away from the C₁-C₄ bond to effect any insertion at this point. However, if the metal is held in the C₂-C₃ region, this may cause

preferential insertion at this bond. The above argument assumes an intramolecular mechanism for this insertion reaction, but as will be further discussed in Chapter 3, an alternative dissociative mechanism is possible. In this case, the reactive $\text{Pt}(\text{PPh}_3)_2$ species is liberated from the olefin complex and thereafter attacks the organic molecule again exclusively by insertion at the $\text{C}_2\text{-C}_3$ bond. In this case the conjugated system may attract the co-ordinatively unsaturated $\text{Pt}(\text{PPh}_3)_2$ moiety to the $\text{C}_2\text{-C}_3$ side of the molecule. Insertion then follows, oxidising the platinum(0) to d^8 platinum(II).

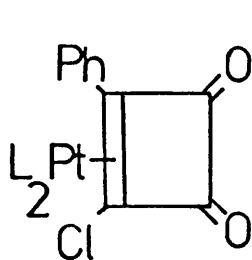
It may be possible, however, that the products in the ring-expansion are thermodynamically controlled and the compound formed by cleavage of the $(\text{Ph})\text{C-C}(\text{CO})$ bond is particularly unfavourable. This argument suggests that the product of the ring-expansion reaction which maintains the conjugated system in the molecule is thermodynamically unfavourable - a situation which is unusual. Finally, the steric hindrance of the phenyl group may contribute to the instability of a complex ring-expanded by insertion at the $(\text{Ph})\text{C-C}(\text{CO})$ bond, whereas no such hindrance exists for the compound formed by cleavage of the $(\text{H})\text{C-C}(\text{CO})$ bond.

Substitution of the proton by the electron-withdrawing group $-\text{Cl}$ in the starting ligand (4) gave rise to two complexes on reaction with $\text{Pt}(\text{PPh}_3)_2$ (trans-stilbene). In benzene or chloroform a red complex having $\nu(\text{C=O})$ at 1656 cm^{-1} and no absorbance in the

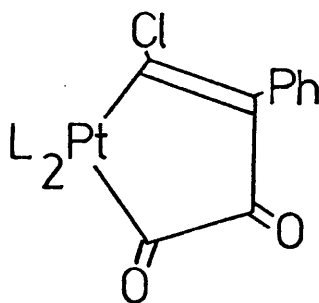
$\nu(\text{Pt-Cl})$ region was isolated. Analysis was consistent with the formulation $\text{Pt}(\text{1-chloro-2-phenylcyclobutene-dione})(\text{PPh}_3)_2$, the absence of a (Pt-Cl) band suggesting that oxidative addition of the carbon-chlorine bond to the platinum(0) had not occurred.

In diethyl ether, however, a yellow crystalline compound was formed, found by analysis to be isomeric with the red material, but having $\nu(\text{C=O})$ at 1732 cm^{-1} and again showing no $\nu(\text{Pt-Cl})$ band.

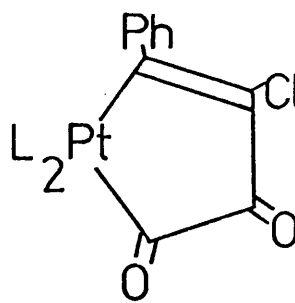
By analogy with the first reaction the structures (8) and (9a) were assigned to the yellow and red complexes respectively. However, the alternative structure (9b)



(8)



(9a)

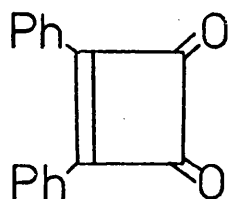


(9b)

cannot be precluded.

At a rough estimate, the rate of conversion of (8)

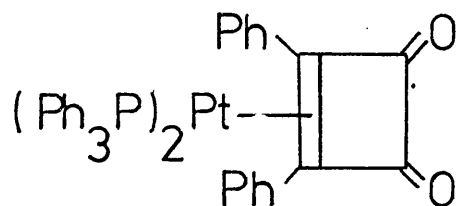
to (9) did not appear to be appreciably faster than the rearrangement of the phenylcyclobutenedione complex. Since the present structural evidence does not differentiate between (9a) and (9b) it is not possible to assess whether or not the presence of an electron-withdrawing substituent adjacent to the conjugated system causes any difference to the mode of attack or the place at which reaction occurs.



(10)

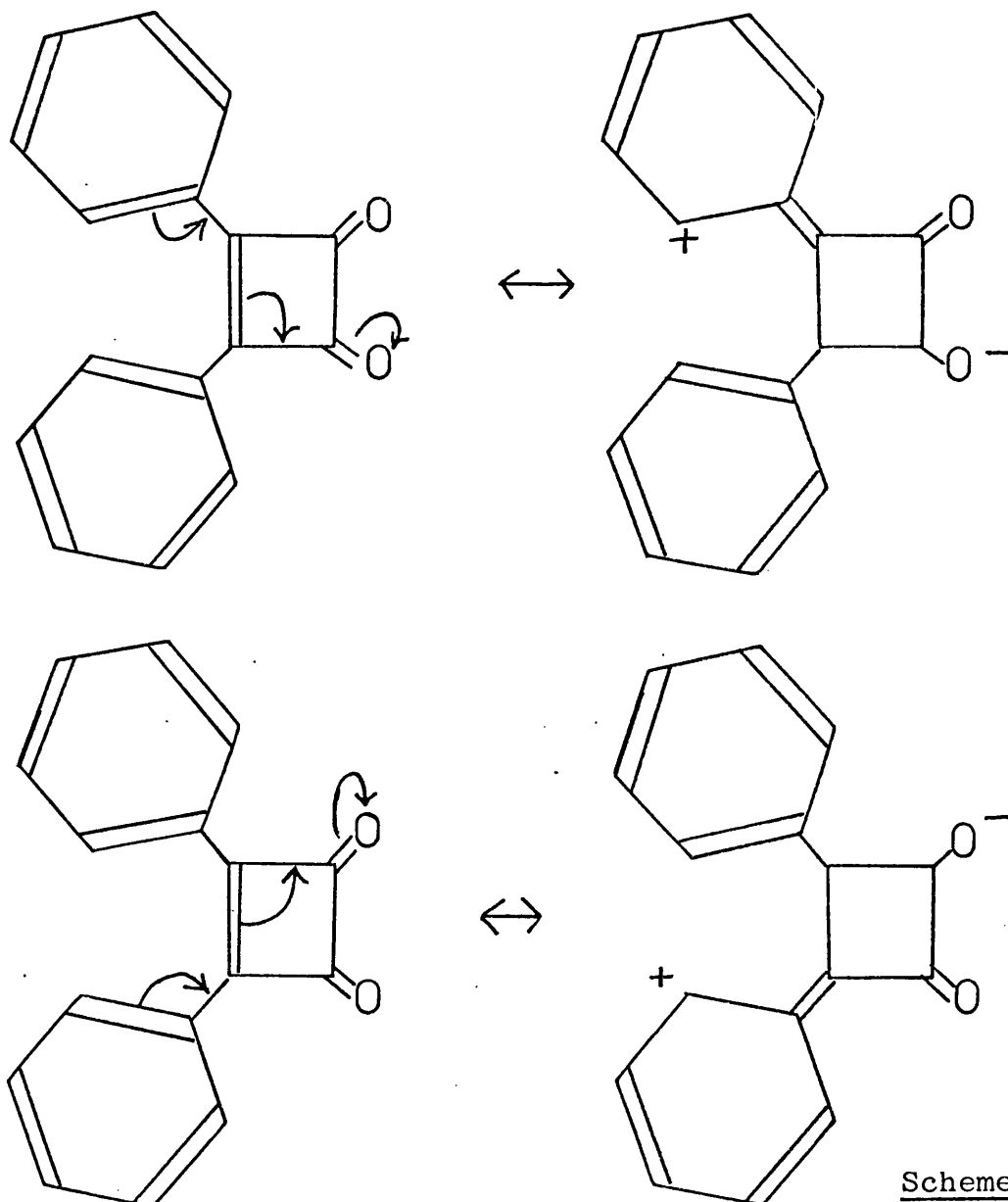
Reaction of (10) with $\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene})$ in diethyl ether gave rise to a yellow complex analysing as $\text{Pt}(\text{dione})(\text{PPh}_3)_2$. The infrared spectrum of this complex gave $\nu(\text{C}=\text{O})$ at 1708 cm^{-1} , indicating a π -bonded complex by analogy to the previous complexes. In this case, however, the yellow crystalline compound did not appear to convert to an inserted product when warmed in benzene. Even after refluxing in this solvent, the yellow complex was recovered still having $\nu(\text{C}=\text{O})$ at 1708 cm^{-1} . It would appear that this molecule only

forms an olefin complex as shown in (11)



(11)

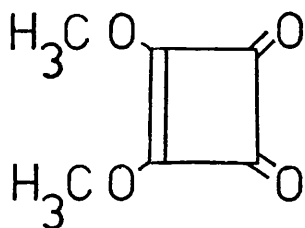
In the diphenyl derivative the conjugation scheme is rather different from that in the previous ligands, Scheme 3,



Scheme 3.

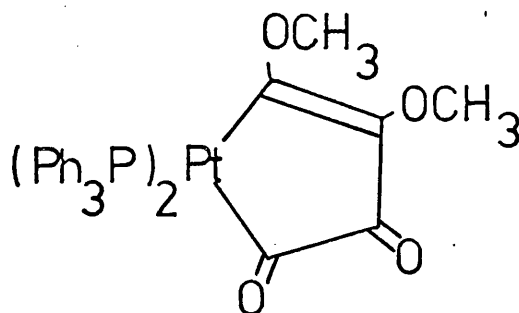
in which it may be seen that the molecule is a totally conjugated system. It might be expected that in the π -bonded platinum(0) complex the metal in its position above the plane of the ring would be symmetrically placed as far as the carbon-carbon bonds (Ph)C-C(C=O) are concerned. An explanation as to why this compound does not rearrange to the platinacyclopentenedione complex may lie in the steric hindrance involved in such a process. The two phenyl groups and the phenyl groups on the phosphorus atoms may be so close together in the ring-inserted product that steric crowding results, thus making the complex unstable.

In direct contrast to the stable olefin complex formed above, reaction of 1,2-dimethoxycyclobutenedione resulted in all cases in a red crystalline material having $\nu(\text{C}=\text{O})$ at 1659 cm^{-1} , indicating a ring-expanded species. In the n.m.r. of the starting material (12)



(12)

only a single resonance was observed at 4.43 δ , whereas in the complex, two singlets were observed at 3.70 and 3.25 δ (apart from the phenyl resonances). In this spectrum, the high-field signal was broadened, whereas the lower-field signal was sharp. The assignment of structure (13) for this complex may give a clue as to the reason for the observed spectrum.

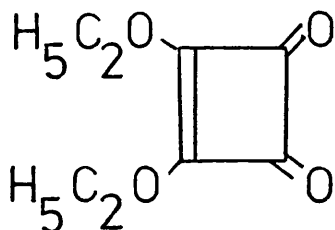


(13)

The observation of two signals for the two methyl groups indicates an unsymmetrical molecule. In this particular case if the complex is ring-expanded and is unsymmetrical only one possibility for the structure exists. In order to show coupling to ^{31}P the effect must travel 5 bonds to the $-\text{CH}_3$ group gem- to platinum and 6 bonds to the group trans- to platinum. $^{195}\text{Pt}-\text{H}$ coupling must travel 4 and 5 bonds respectively. It is not likely that coupling over these distances would be appreciable, but the broadening of the signal at high-field is probably due to this small coupling to

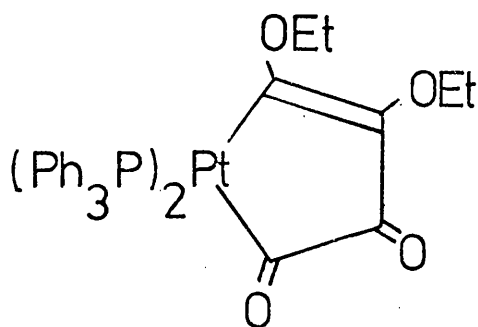
the nearest $-\text{CH}_3$ group (the other being too far away to feel the effect). If instruments of sufficient power and resolution were available, it may have been possible to resolve this coupling, but on the equipment available to the author, no such splitting could be detected. The high-field signal was assigned to the $-\text{CH}_3$ group nearest to platinum.

Thus it would appear that the presence of two methoxy groups in the ligand enhances the ability of the platinum(0) complex to cleave a carbon-carbon σ -bond in this molecule. This effect is also observed in the reaction of the 1,2-diethoxy derivative (14).



(14)

The yellow-orange complex formed on reaction with the platinum(0) stilbene complex shows $\nu(\text{C}=\text{O})$ at 1647 cm^{-1} , again indicative of the ring-expanded complex postulated as (15)

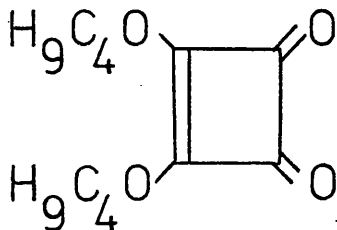


(15)

The n.m.r.spectrum of the starting material (14) shows the expected quartet and triplet of the equivalent ethyl groups, centred at 4.78 δ (quartet) and 1.50 δ (triplet). The product (15) shows 3 patterns other than the phenyl resonances, a multiplet at 3.87 δ and two triplets at 1.18 δ and 0.3 δ . The multiplet on closer inspection proved to be two overlapping quartets. The spectrum appears as would be expected from the formulation (15), the different shifts in the resonances being due to the insertion of the platinum(0) unsymmetrically into the molecule. The signals were all sharp and no broadening was observed in any of the patterns. By analogy to the dimethoxy derivative the high-field signals were assigned to the ethyl group closer to the platinum.

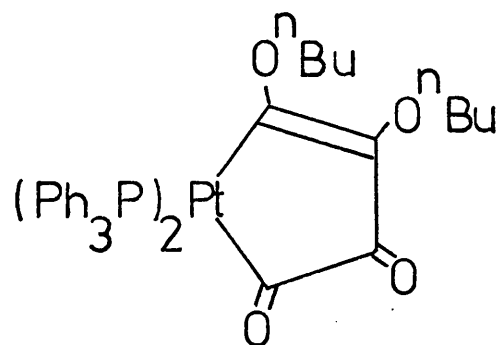
A further example of a complex resulting from an exclusively ring-expanded reaction was observed for

di-n-butoxycyclobutenedione (16).



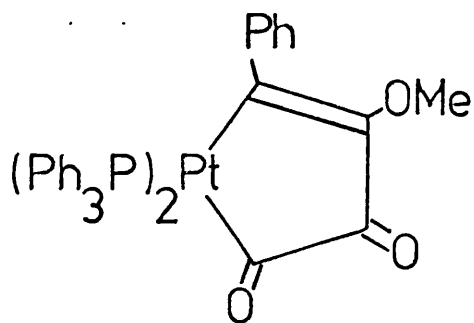
(16)

The canary-yellow complex formed with the platinum-stilbene complex provided a satisfactory analysis for the formulation $\text{Pt}(\text{dione})(\text{PPh}_3)_2$ and showed $\nu(\text{C}=\text{O})$ at 1658 cm^{-1} . In the n.m.r. spectrum, the n-butyl resonances of the complex were split in much the same way as those in the diethoxy and dimethoxy complexes, but the patterns were of great complexity and were not fully assigned. No obvious couplings were noticed in the spectrum and all observed lines were sharp with no evidence of the broadening seen in the $-\text{OCH}_3$ complex. By analogy to the previous alkoxy complexes, the structure of the complex was assigned as (17).

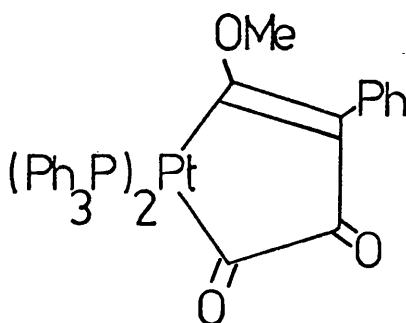


(17)

It was now decided to attempt the reaction using the 1-methoxy-2-phenylcyclobutenedione derivative, and this was prepared. On reaction with the platinum(0) complex an orange-yellow crystalline product was isolated having $\nu(\text{C}=\text{O})$ at 1652 cm^{-1} indicating the ring-inserted species, which could have been (18) or (19).



(18)



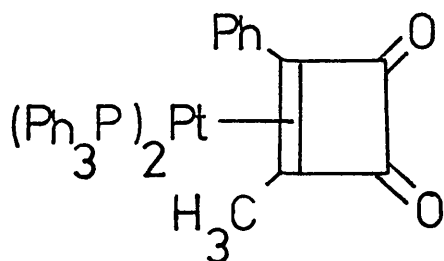
(19)

The n.m.r. spectrum yielded a methyl resonance at 2.75 δ showing the broadness observed in the dimethoxy derivative. The structure (19) was selected as the probable arrangement based on the following reasoning:

- (i) The shift of the methyl resonance from 4.45 δ in the starting material to 2.75 δ is more characteristic of the high-field shift observed in the dimethoxy derivative which was assigned to the methoxy-group closer to platinum. It is likely, therefore, that the single methoxy-group in this present complex is located next to the platinum.
- (ii) The broadening of this line is similar to the broadening previously seen in the dimethoxy-complex, which was tentatively ascribed to the coupling of the ^{31}P and ^{195}Pt atoms.

A different situation arose when the platinum complex $\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene})$ was reacted with the derivative 1-methyl-2-phenylcyclobutenedione. The yellow crystals isolated showed $\nu(\text{C}=\text{O})$ at 1721 cm^{-1} indicating the olefin-bonded derivative. In benzene solution under reflux no conversion to the ring-inserted product was effected. The n.m.r. spectrum showed the methyl resonance as a doublet of doublets with ^{195}Pt satellites centred at 1.48 δ . Based on structure (20) the coupling was assigned to cis-(P-H) and trans-(P-H) with ^{195}Pt satellites.

In this case the observed pattern is a doublet of doublets, in contrast to the special case seen with the phenylcyclobutenedione derivative where the pattern is seen as a triplet due to accidentally equivalent phosphorus atoms.

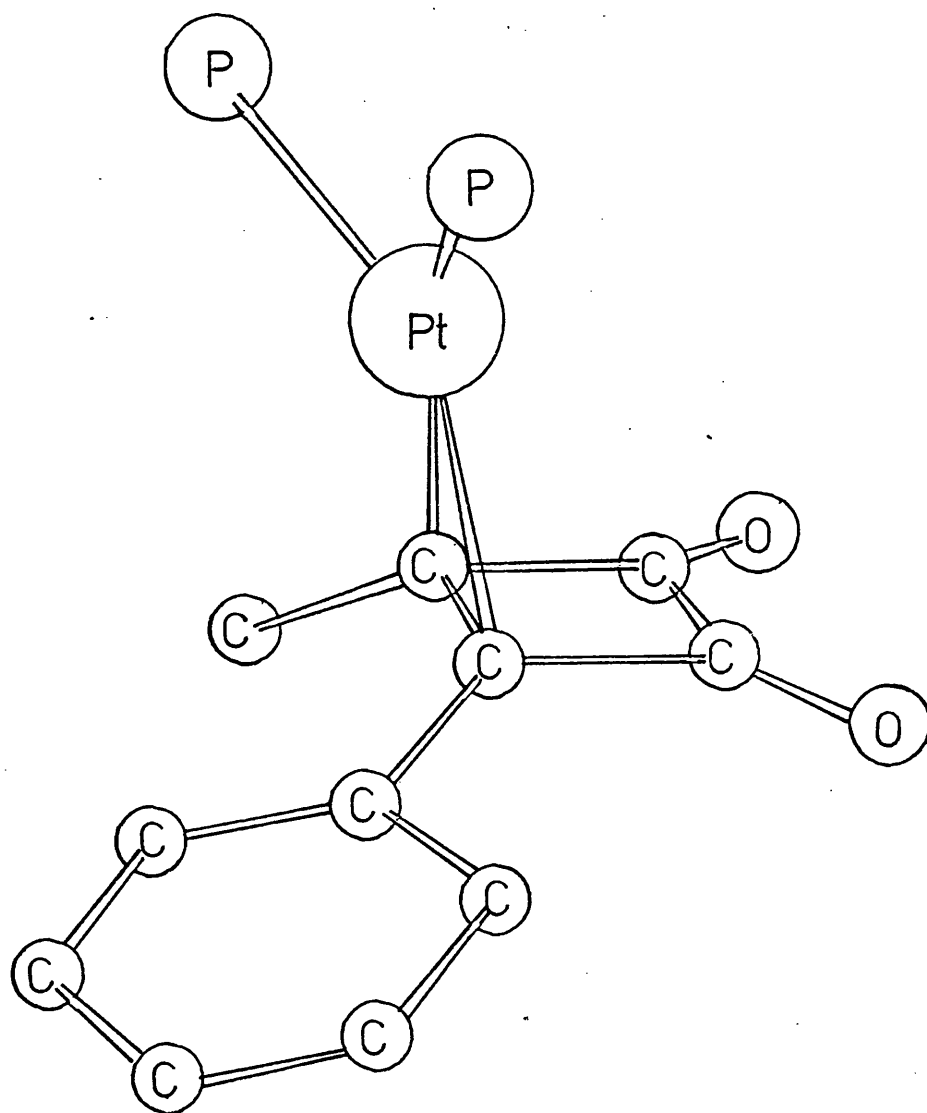


(20)

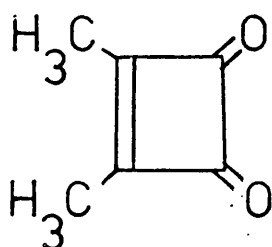
A crystal of complex (20) was subjected to an x-ray diffraction analysis in order to confirm the structure assigned on spectrophotometric evidence and the details are set out below.

The crystals are triclinic space group $\overline{P}1$ having $\underline{a} = 10.967$, $\underline{b} = 12.478$, $\underline{c} = 9.358 \text{ \AA}$, $\alpha = 109.7^\circ$, $\beta = 107.1^\circ$, $\gamma = 103.1^\circ$ and $\underline{Z} = 2$.

The structure was refined by least-squares analysis of counter intensities to $\underline{R} = 0.090$ for 4456 reflexions. The distances from platinum to the olefinic carbon atoms are significantly different (2.04 and 2.13 \AA), the longer being to the phenyl-substituted carbon atom. More surprising, the Pt-P bonds are unequal in length (2.269 and 2.299 \AA). The structure is given in Figure 21.

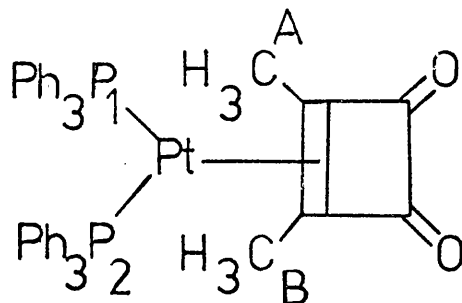


The surprising formation of an exclusively π -bonded complex with the methylphenyl derivative led to the investigation of the reaction between the platinum(0) complex and the dimethyl derivative (22).



(22)

The golden yellow crystals which resulted showed $\nu(\text{C}=\text{O})$ at 1712 cm^{-1} again indicating the π -bonded complex. Refluxing the product in benzene did not effect the required ring-expansion reaction. The n.m.r. spectrum was obtained and showed the methyl resonances as a doublet of doublets with ^{195}Pt satellites. This pattern was interpreted in terms of cis- and trans-(P-H) coupling to the chemically but not magnetically equivalent methyl groups. The cis- and trans-(P-H) coupling must be equal for the two groups, and cis-(P-H) \neq 0 thus rendering the pattern as a doublet of doublets. This position may be clarified by studying the assigned structure (23) and relating the coupling constants accordingly.



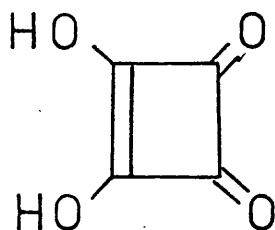
(23)

$$\text{trans-}^4J(\text{P}_1\text{-CH}_3(\text{B}))=\text{trans-}^4J(\text{P}_2\text{-CH}_3(\text{A}))=5.37 \text{ Hz}$$

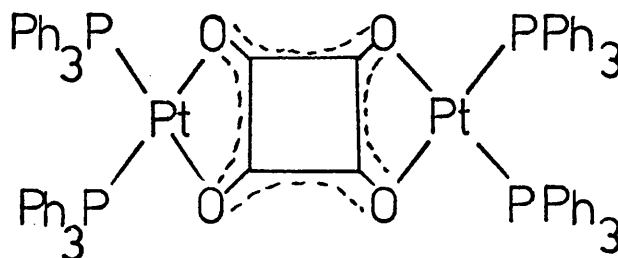
$$\text{cis-}^4J(\text{P}_1\text{-CH}_3(\text{A}))=\text{cis-}^4J(\text{P}_2\text{-CH}_3(\text{B}))=2.16 \text{ Hz}$$

$$^3J(\text{Pt-CH}_3(\text{A}))=^3J(\text{Pt-CH}_3(\text{B}))=16.71 \text{ Hz}$$

The derivatives 1-bromo-2-phenyl and 1,2-dihydroxycyclobutenedione were also prepared and reaction with the platinum(0) complex revealed that this halogen compound was similar to the chloro- derivative earlier discussed. However, the reaction between $\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene})$ and squaric acid (1,2-dihydroxycyclobutenedione (24)) yielded an orange amorphous powder which had no vibrations in the carbonyl region of the spectrum. By analogy to complexes of croconic acid with divalent metal ions, and by analogy to the reaction of squaric acid with other divalent transition metal ions (63JA2589) the dimeric structure (25) was assigned.



(24)



(25)

With the derivatives 1-amino-2-methoxy- and 1,2-diaminocyclobutenedione no satisfactory platinum(0) or platinum(II) complexes could be isolated.

Table 2 gives a summary of the reactions discussed above.

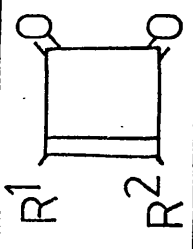
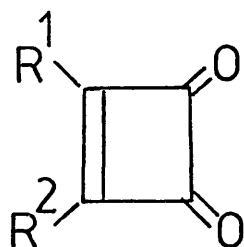
		$\nu(\text{C=O})$ ligand (cm^{-1})	$\delta(\text{H or CH}_3)$ ligand (p.p.m.)	COMPLEX	$\nu(\text{C=O})$ complex (cm^{-1})	$\delta(\text{H or CH}_3)$ complex (p.p.m.)	J(P-H)Hz	J(Pt-H)Hz
R ¹	R ²							
Benzo		1779, 1761	-	inserted	1665	-	-	-
Ph	H	1776	9.24	olefin	1723	4.75	6.7	48.8
Ph	H	1776	9.24	inserted	1658	9.20	17.0(trans-P) 8.5(cis-P)	21.5
Ph	Cl	1812, 1770	-	olefin	1732	-	-	-
Ph	Cl	1812, 1770	-	inserted	1656	-	-	-
Ph	Br	1804, 1766	-	olefin	1728	-	-	-
Ph	OCH ₃	1784	4.45	inserted	1652	2.75	-	-
OCH ₃	OCH ₃	1804, 1744	4.43	inserted	1652	3.25, 3.70	-	-
OC ₂ H ₅	OC ₂ H ₅	1786, 1724	4.78, 1.5	inserted	1647	3.87, 1.18, 0.3	-	-
O ⁿ Bu	O ⁿ Bu	1774, 1724	-	inserted	1658	-	-	-
Ph	Ph	1786, 1776	-	olefin	1708	-	-	-
Ph	CH ₃	1776, 1760	2.60	olefin	1721	1.48	5.6(trans-P) 4.5(cis-P)	11.5
CH ₃	CH ₃	1786, 1764	2.33	olefin	1712	1.64	5.4(trans-P) 2.2(cis-P)	16.71 16.71
OH	OH	1818	-	polymer	-	-	-	-

TABLE 2.

Conclusion.

If we indicate the structure of the organic starting materials by figure (26) then there are some general conclusions which may be made with respect to their reaction with platinum(0) complexes.



(26)

- 1) When the R-group has a positive inductive effect (+I) as in the cases $R^1=Me$, $R^2=Ph$; $R^1=R^2=Me$ then only π -bonded complexes are formed.
- 2) When the R-groups are highly conjugated with the rest of the molecule as when $R^1=R^2=phenyl$ then only π -bonded complexes are formed.
- 3) When the R-groups (or one R-group) has a negative inductive effect (-I) then exclusively ring-expanded complexes are formed (except in the case where $R^1=Ph$, $R^2=halogen$).
- 4) When the inductive effects of the R-groups are zero as in the case of $R^1=Ph$, $R^2=H$, then both

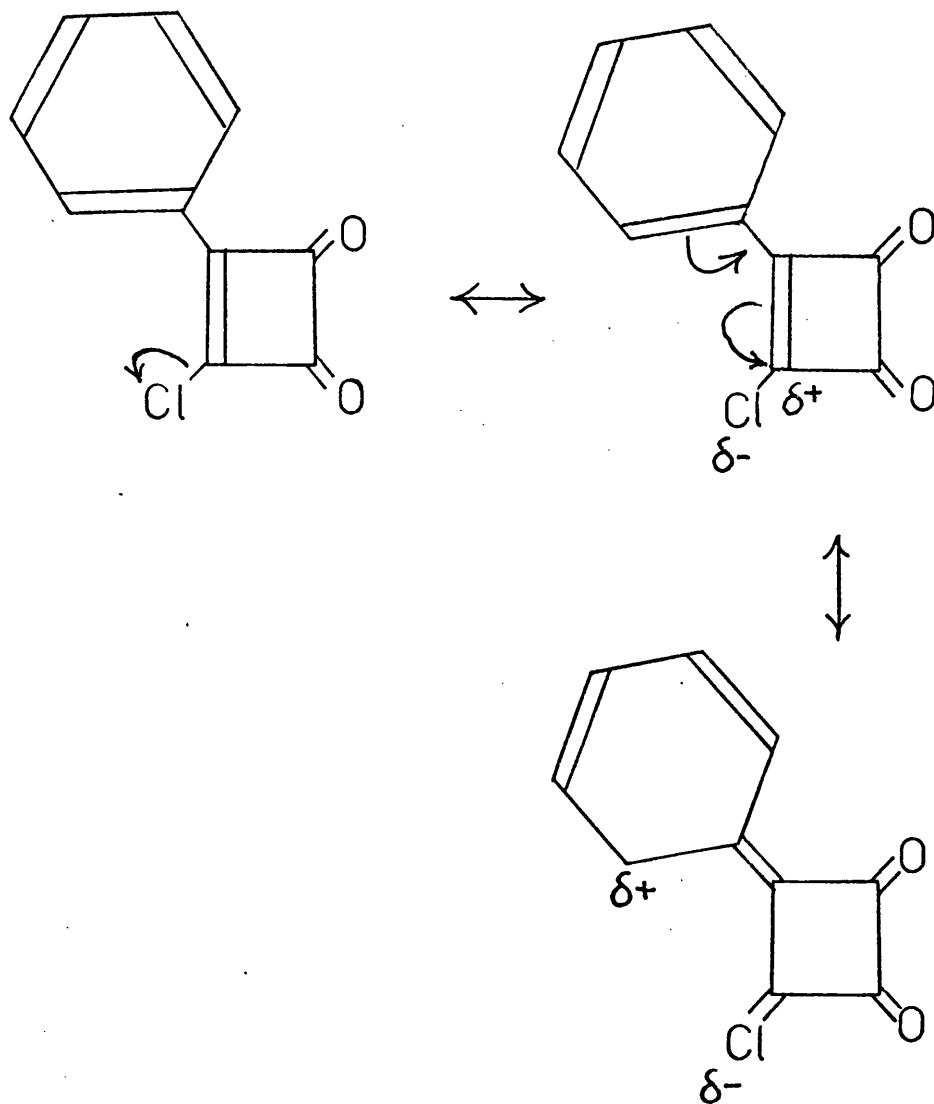
π -bonded and ring-expanded complexes are possible.

The earlier postulate that the conjugation in the molecule may cause the metal to be drawn towards the $(R^2)C-C(CO)$ bond ($R^1=Ph$) is confirmed by the crystal structure of the methyl-phenyl derivative in which the platinum atom clearly sits nearer the carbon-atom not attached to phenyl. A rationalisation may now be made about these complexes.

If the attached groups are capable of increasing the electron density at the alkene bond, then irrespective of the conjugation in the molecule, only the stable olefin-bonded complex is formed. Neglecting the halogen-substituted molecules for the present moment, the attached groups which cause a decrease in electron density at the alkene bond cause exclusively ring-inserted products to be formed. Attached groups which have no inductive effect may produce both olefin and ring-inserted complexes. The two exceptions to this general rule are the diphenyl derivative in which the highly conjugated nature of the molecule may explain why the olefin complex is exclusively formed, and the halogen derivative.

It is more difficult to explain the reason for the anomalous behaviour of the halo derivatives. It may be possible for the small electronegative halogen group to disturb the conjugation scheme to a small extent, thus causing the platinum to lie more over the centre of the alkene bond than it would in the other complexes, (except in the diphenyl complex). This disturbance would not

occur in the larger -I groups such as $-\text{OC}_2\text{H}_5$. Scheme 4 sets out this possibility.



Scheme 4.

The effect may be sufficient to allow the possibility of a stable olefin-bonded complex whereas in all other cases of the -I groups no such possibility exists.

SECTION 1

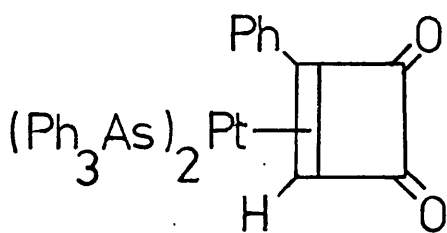
A STUDY OF THE REACTIONS OF LOW-VALENT
TRANSITION-METAL COMPLEXES WITH DERIVATIVES
OF CYCLOBUT-1-ENE-2,3-DIONE.

- (A) Platinum(0)
- (ii) Tetrakis(triphenylarsine)platinum(0)
Pt(AsPh₃)₄

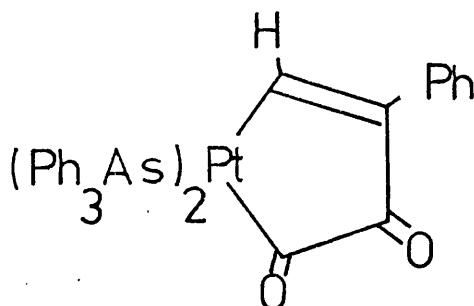
At this stage it was decided to extend the study to include the arsine derivative of platinum(0) in order not only to investigate further the reactions of cyclobutenediones with platinum(0) but also in selected cases to study the chemically phosphorus-decoupled n.m.r. spectra of these complexes.

In all cases below, the platinum complex used as starting material was tetrakis(triphenylarsine)platinum(0).

Reaction of $\text{Pt}(\text{AsPh}_3)_4$ with 1-phenylcyclobut-1-ene-3,4-dione resulted in two complexes depending on the conditions used. In diethyl ether, a yellow complex was isolated having $\nu(\text{C}=\text{O})$ at 1723 cm^{-1} whereas reaction in refluxing benzene gave a red complex whose $\nu(\text{C}=\text{O})$ was at 1657 cm^{-1} . By analogy to their phosphine analogues it was decided to give the yellow and red isomers (which had satisfactory analyses) the structures (27) and (28) respectively.



(27)

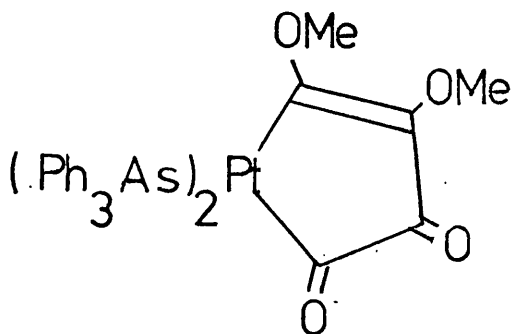


(28)

The ^1H n.m.r. of the π -bonded complex (27) showed a phenyl multiplet and singlet at 5.00 δ having ^{195}Pt satellites. Coupling was assigned as $^2J(\text{Pt-H})=57.5$ Hz. The red ring-expanded complex showed a singlet at 9.40 δ with ^{195}Pt satellites and the expected phenyl resonances. Coupling was assigned as $^3J(\text{Pt-H})=21.5$ Hz.

It is clear that the coupling observed in the phosphine analogues was due to cis- and trans- ^{31}P -H coupling and chemically decoupling the ^{31}P atoms results in simplification of the spectral patterns observed.

Unfortunately, no satisfactory product could be obtained from the reaction between 1-methoxy-2-phenyl-cyclobutenedione, but the dimethoxy derivative gave a red crystalline product having the constitution $\text{Pt}(\text{AsPh}_3)_2(\text{dione})$ by analysis. The carbonyl stretching band lay at 1657 cm^{-1} indicating the ring-expanded complex (29).



(29)

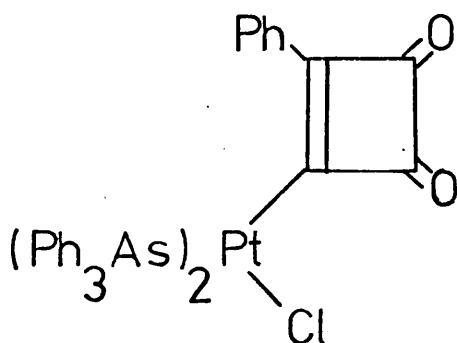
The ^1H n.m.r. spectrum showed the expected phenyl multiplet and two singlets at 3.51 δ and 3.90 δ . As observed in the phosphine analogue, the high-field signal was slightly broadened whereas the singlet at 3.90 δ was sharp. The indication would appear to be that the broadening is due to $^{195}\text{Pt-H}$ coupling rather than $^{31}\text{P-H}$ coupling. The coupling is too small to resolve on standard equipment.

The 1-chloro-2-phenylcyclobutenedione derivative in diethyl ether gave a yellow complex having $\nu(\text{C=O})$ at 1751 cm^{-1} indicative of an olefin-complex, but vibrations were observed at 334, 305, 270 and 260 cm^{-1} . The anomalous behaviour of this organic ligand is carried over into the reactions with the arsine derivative. 1-Methyl-2-phenylcyclobutenedione also yielded a yellow complex with $\text{Pt}(\text{AsPh}_3)_4$ which had $\nu(\text{C=O})$ at 1724 cm^{-1} . The proton n.m.r. consisted of the usual phenyl multiplet and a singlet at 1.60 δ with ill-defined ^{195}Pt satellites. The coupling was, however, measurable, and assigned to $^3\text{J}(\text{Pt-CH}_3)=13.0$ Hz. The complex was analogous to the phosphine derivative.

Conclusion.

The chemical decoupling of the ^{31}P atoms in these complexes indicates that the couplings assigned in part(A) (i) were correct, and that the broadening observed in the high-field signal in the dimethoxy-derivative arises in part from the $^{195}\text{Pt-CH}_3$ coupling, and is not exclusively $^{31}\text{P-CH}_3$ coupling.

The anomalous behaviour of the halo-derivative also occurs in the arsine derivative but with the added complication of numerous bands in the i.r. spectrum in the $\nu(\text{Pt-Cl})$ region. However, no specific platinum-chlorine stretch could be assigned other than the band at 334 cm^{-1} , characteristic normally of $\nu(\text{Pt-Cl})$ in cis- $\text{PtCl}_2(\text{AsPh}_3)_2$. In this case then, the vinyl complex (30) is a possibility.



(30)

No evidence of a Pt-Cl bond was seen in the phosphine analogue, but in this arsine complex this evidence is seen.

The reason for the formation of a vinyl complex may be due in part to the smaller trans-influence in the case of arsenic over that of phosphorus. This would render the platinum-cyclobutene ring distance (in the π -complex) shorter, and thus give the δ -negative chlorine atom closer proximity to the metal than in the phosphine

derivative. This close approach may then provide the means to reaction and the oxidative addition to the platinum(0) may then follow, yielding the vinyl complex (30).

The hypothesis put forward in part (A)(i) explaining the variety of products on the basis of the inductive effects of the groups attached to the organic molecule appears to fit the arsine derivatives in addition to the phosphine complexes. In fact, apart from the chloro-derivative, little difference in the reactions of the arsine and phosphine complexes was observed.

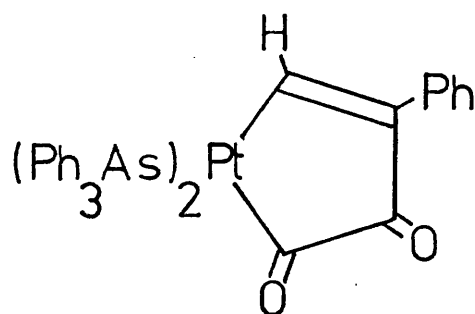
SECTION 1

A STUDY OF THE REACTIONS OF LOW-VALENT
TRANSITION-METAL COMPLEXES WITH DERIVATIVES
OF CYCLOBUT-1-ENE-2,3-DIONE.

(A) Platinum(0)

(iii) Some replacement reactions of the complex
bis(triphenylarsine)(3-phenylcyclopent-3-ene-
1,2-dione)platinum(II)

It is possible to replace the two arsine ligands in compound (31) by other ligands (depending on experimental conditions), thereby giving rise to a series of complexes in which, for example, the effects of more basic phosphines could be studied (71J2472).



(31)

This series of replacement reactions was undertaken primarily to enable a ¹³C n.m.r. analysis to be carried out, and this is at the present time underway, and the results will be published in due course. The preliminary results (other than ¹³C) are discussed below.

It was possible to replace the two arsine groups in complex (31) by the chelating 1,10-phenanthroline in a suspension reaction at room temperature. The carbonyl region of the i.r. spectrum yielded $\nu(\text{C}=\text{O})$ at 1632 and 1654 cm^{-1} compared with the bands at 1677 and 1657 cm^{-1} in the original arsine complex. In a similar

manner, the arsine ligands may be replaced by 1,2-diphenylphosphinoethane (diphos) at room temperature. In this complex $\nu(\text{C}=\text{O})$ was seen at 1642 and 1670 cm^{-1} .

The arsines were also replaced by the following ligands:

methyldiphenylphosphine,
2,2'-bipyridyl,
dimethylphenylphosphine,
triphenylphosphite,
diethylphenylphosphine and
triethylphosphine.

All carbonyl stretching bands fell into the range 1632 - 1671 cm^{-1} , indicative of the ring-expanded complexes. The results of the ^{13}C n.m.r. study will be published elsewhere in due course.

SECTION 1

A STUDY OF THE REACTIONS OF LOW-VALENT
TRANSITION-METAL COMPLEXES WITH DERIVATIVES
OF CYCLOBUT-1-ENE-2,3-DIONE.

(B) Palladium(0)

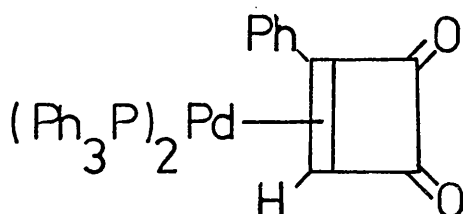
(i) Tetrakis(triphenylphosphine)palladium(0)

Pd(PPh₃)₄

(ii) Tetrakis(triphenylarsine)palladium(0)

Pd(AsPh₃)₄

Treatment of $\text{Pd}(\text{PPh}_3)_4$ in ether with phenylcyclobutenedione led to isolation of a yellow crystalline complex showing $\nu(\text{C}=\text{O})$ at 1776 and 1720 cm^{-1} in the i.r. spectrum. The analysis was consistent with a π -bonded structure assigned as (32).



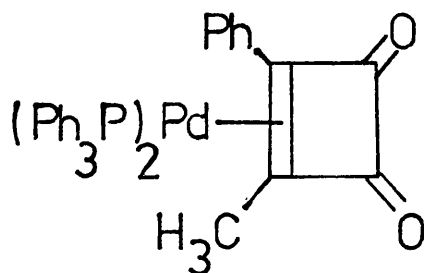
(32)

The ^1H n.m.r. spectrum showed, in addition to the phenyl resonances at 7.10 δ , a doublet at 5.55 δ . This was simply assigned as trans- $^3\text{J}(\text{P}-\text{H})=1.5$ Hz, where cis- $^3\text{J}(\text{P}-\text{H})=0$.

All attempts to convert this compound into the ring-expanded isomer failed due to its unstable nature. Degredation occurred on standing in air for a few minutes and all samples were of necessity stored in vacuo.

Chlorophenylcyclobutenedione did not react with the palladium(0) complex under any of the conditions tried. However, with methylphenylcyclobutenedione, the

palladium(0) complex gave a yellow crystalline product which showed $\nu(\text{C}=\text{O})$ at 1721 cm^{-1} indicative of the olefin-bonded complex. The analysis was consistent with the structure (33).

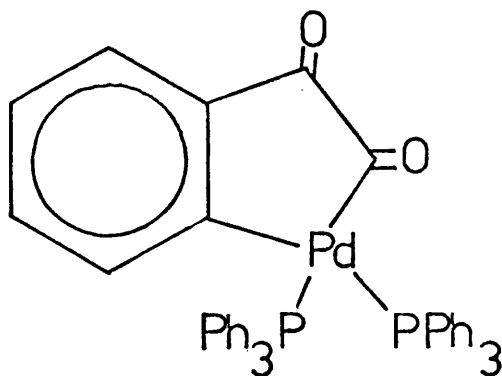


(33)

The ^1H n.m.r. spectrum showed, in addition to the phenyl resonances, a triplet at 1.44δ due to the methyl group. By analogy to the case of the π -bonded phenylcyclobutenedione complex, this coupling was assigned to accidentally equivalent ^3P atoms caused in the ABX system ($\text{A}=\text{B}=\text{P}$, $\text{X}=\text{CH}_3$) by $J(\text{AB}) \gg |J(\text{AX}) - J(\text{BX})|$. The expected doublet of doublets thus becomes a triplet. No ring-expansion in this complex was observed.

With diphenylcyclobutenedione and the palladium(0) compound a yellow complex was isolated from ether showing $\nu(\text{C}=\text{O})$ at 1710 cm^{-1} again characteristic of the olefin-bonded derivative. As all the complexes isolated at this stage were π -bonded complexes and no ring-expansion

had been observed, it was decided to attempt to prepare the benzocyclobutenedione derivative since no olefin-bonding had previously been observed in its reactions with zerovalent platinum complexes. Treatment of $\text{Pd}(\text{PPh}_3)_4$ with benzocyclobutenedione in ether led to isolation of a red crystalline complex having $\nu(\text{C}=\text{O})$ at 1638 cm^{-1} , characteristic of a ring-inserted compound. The analysis was consistent with the structure (34).



(34)

This compound was novel in two ways:

- (a) No palladium(0) ring-inserted complex had previously been made with the cyclobutenedione system.
- (b) In the reported reactions of cyclopropenones no reaction with $\text{Pd}(\text{PPh}_3)_4$ had been observed at all (72JO(44)C63).

An unexpected result was obtained when the palladium(0) complex was treated with the normally reactive dimethoxycyclobutenedione. Under all conditions used, no reaction was observed.

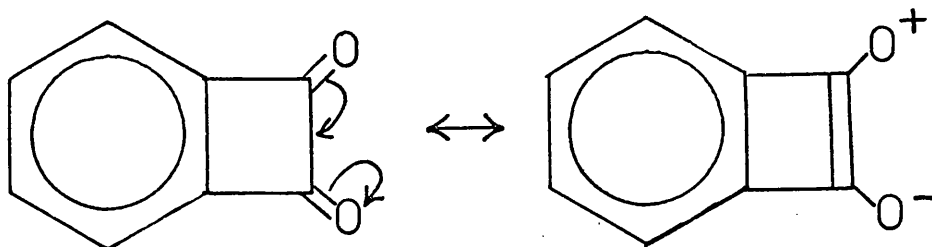
Treatment of the complex $\text{Pd}(\text{AsPh}_3)_4$ with the ligand phenylcyclobutenedione in ether led to the isolation of an orange crystalline compound which was very unstable. The i.r. spectrum showed $\nu(\text{C}=\text{O})$ at 1720 cm^{-1} , characteristic of a π -bonded complex, but the material decomposed in the cell and no i.r. data were obtainable below this region. A rapidly executed ^1H n.m.r. spectrum revealed the expected phenyl resonances and a singlet at 5.88 δ due to the vinylic proton.

The results obtained from the palladium(0) reactions must be viewed in two lights. Firstly the co-ordinative ability of palladium(0) towards olefins is not so high as that of platinum(0). This is because the co-ordinative ability is related in d^{10} transition metals to $(n-1)d^{10} \rightarrow (n-1)d^{10}np$ promotion energy (68CD319), which for platinum(0) is 3.28eV and for palladium(0) is 4.23eV. Secondly, the ease of oxidative addition is not so great in the case of palladium(0) as in platinum(0) or in rhodium(I) complexes (as evidenced in the different modes of catalysis of rhodium(I) and palladium(0) with the cubane system (70JA3515, 70JA6366)). It might be expected on these considerations that palladium(0) would not form the range of stable complexes with the cyclobutenediones as is observed with platinum(0) and that the range would be limited in both π - and σ -bonded compounds. This is exactly the case - the range of π -bonded complexes is limited to the cyclobutenes which in the platinum(0)

chemistry are the most readily formed, i.e. phenylcyclobutenedione, diphenylcyclobutenedione and methylphenylcyclobutenedione. In the two latter cases no ring-expansion was expected due to the electronic factors explained in part (A) (i) and none was found. However, no ring-expansion was observed in the case of phenylcyclobutenedione which readily undergoes ring-expansion in the platinum(0) complex. This observation follows from the known properties of palladium(0) which is less able to undergo facile oxidative addition than the platinum(0). Another factor which might make a small contribution is that in general these palladium(0) complexes appear much less stable to air and heat than their platinum(0) analogues, and the use of more forcing conditions, which might otherwise lead to ring-expansion reactions, tend to cause only degradation of the samples. Oxidative addition to palladium(0) does occur in the benzocyclobutenedione reaction, however, providing an interesting anomaly. Previous studies with cyclopropenones and palladium(0) have produced no reaction, but with this special cyclobutenone the palladium(0) does react. From the evidence available the product would appear to be the ring-expanded complex (34), having unsymmetrically cleaved the carbon-carbon σ -bond of the cyclobutene part of the molecule. In the benzocyclobutenedione molecule the electronic features are rather special, and in explaining the reasons for the ready oxidative addition to palladium(0) these must be considered.

In the benzocyclobutenedione molecule two conjugated systems exist, the aromatic system and the conjugation of

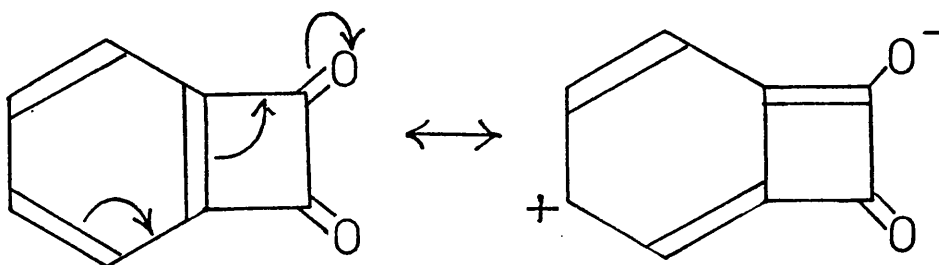
the carbonyl groups, as shown in Scheme 5.



Scheme 5.

There is also a possibility of conjugation according to Scheme 6.

Scheme 6.



However, in the photolysis of benzocyclobutenedione the intermediate is a carbene and not the bis-keten one would expect from symmetrical cleavage of $(\text{CO})\text{C}-\text{C}(\text{CO})$ (71CH1162). This indicates the susceptibility of the carbon-carbon σ -bond $(\text{Ph})\text{C}-\text{C}(\text{CO})$ suggesting that the dual conjugation shown in Scheme 5 is probably the more likely. The carbon-carbon bond joining the phenyl aromatic system and the bis-dione conjugation thus becomes very susceptible to nucleophilic attack (having electrons drawn away in two directions) and the palladium(0) may thus cause cleavage in a process much more energetically favourable than in the other cyclobutenedione cases. The energy barrier is low enough to allow oxidative addition to occur at ambient temperature and no degradation of the palladium(0) complex is observed.

In all other cases, degradation of the alkene complexes occurs before ring-expansion can be effected, or at ambient temperatures no reaction is observed. The arsine analogue of the π -bonded phenylcyclobutenedione was prepared but was very unstable in air, and little information could be obtained by conventional methods. It was decided not to extend the range of these arsine complexes further.

Conclusion.

The range of complexes with palladium(0) is limited as compared with platinum(0) due to the variation of the oxidative addition and co-ordinative properties of these species. In fact, only in the rather special case of benzocyclobutenedione did any oxidative addition occur with palladium(0) although co-ordination leading

to a π -bonded complex did occur in some other reactions. The stability of all the palladium(0) complexes of the cyclobutenediones to atmospheric oxygen and heat was considerably less than the platinum(0) analogues of these molecules.

SECTION 1

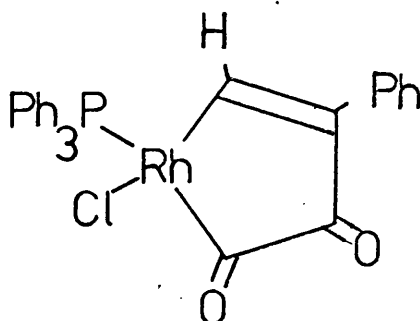
A STUDY OF THE REACTIONS OF LOW-VALENT
TRANSITION-METAL COMPLEXES WITH DERIVATIVES
OF CYCLOBUT-1-ENE-2,3-DIONE.

(C) Rhodium(I)

(i) Chlorotris(triphenylphosphine)rhodium(I)

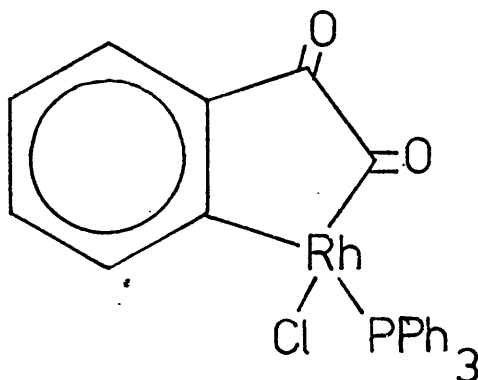
$\text{RhCl}(\text{PPh}_3)_3$

On treatment of $\text{RhCl}(\text{PPh}_3)_3$ with phenylcyclobutenedione in refluxing dichloromethane, a bright orange crystalline complex was isolated having $\nu(\text{C}=\text{O})$ at 1690, 1653 and 1638 cm^{-1} , characteristic of the ring-expanded compounds previously described. ^1H n.m.r. details were not obtained. The analysis was consistent with the structure (35)



(35)

The reaction between the rhodium(I) complex and benzocyclobutenedione resulted in the isolation of a yellow crystalline compound having $\nu(\text{C}=\text{O})$ at 1703 and 1679 cm^{-1} , again characteristic of the ring-expanded platinum analogues previously described. The analysis was consistent with the structure (36)



(36)

With all the other cyclobutenedione derivatives
no reaction was observed under the conditions employed.

SECTION 1

A STUDY OF THE REACTIONS OF LOW-VALENT
TRANSITION-METAL COMPLEXES WITH DERIVATIVES
OF CYCLOBUT-1-ENE-2,3-DIONE.

(C) Rhodium(I)

(ii) Dipivaloylmethanatocycloocta-1,5-dienerhodium(I)
Rh(cod)(dpm)

Under the conditions used, no reaction was observed with any of the cyclobutenedione derivatives used.

SECTION 1

A STUDY OF THE REACTIONS OF LOW-VALENT
TRANSITION-METAL COMPLEXES WITH DERIVATIVES
OF CYCLOBUT-1-ENE-2,3-DIONE.

(C) Rhodium(I)

(iii) Bis(ethylene)acetylacetonatorhodium(I)
 $\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2$

Under the conditions used, no reaction was observed with any of the cyclobutenedione derivatives used.

SECTION 1

A STUDY OF THE REACTIONS OF LOW-VALENT
TRANSITION-METAL COMPLEXES WITH DERIVATIVES
OF CYCLOBUT-1-ENE-2,3-DIONE.

(C) Rhodium(I)

(iv) Conclusions

Bearing in mind the ease of oxidative addition to rhodium(I) as seen in the rearrangement of cubane (70JA3515), it is difficult to explain why the rhodium(I) complexes fail to react with all but two of the cyclobutenedione complexes. Reaction with benzo- and phenylcyclobutenedione proceed as would be expected, leading to the ring-expanded species and not the π -bonded compound (in the case of the phenylcyclobutenedione). However, failure to react with the reactive dimethoxycyclobutenedione and methoxyphenylcyclobutenedione cannot be satisfactorily explained, except by a tentative suggestion that the less nucleophilic nature of the d^8 rhodium(I) over the d^{10} platinum(0) species may be critical in these insertions.

SECTION 1

A STUDY OF THE REACTIONS OF LOW-VALENT
TRANSITION-METAL COMPLEXES WITH DERIVATIVES
OF CYCLOBUT-1-ENE-2,3-DIONE.

(D) Iridium(I)

(i) Trans-chlorocarbonylbis(triphenylphosphine)-
iridium(I)
Trans-IrCl(CO)(PPh₃)₂

This iridium(I) complex did not react with any of the cyclobutenedione derivatives tried.

SECTION 1

A STUDY OF THE REACTIONS OF LOW-VALENT
TRANSITION-METAL COMPLEXES WITH DERIVATIVES
OF CYCLOBUT-1-ENE-2,3-DIONE.

(E) Iron(0)

(i) Nonacarbonyldiiron(0)

Fe₂(CO)₉

In the reaction of $\text{Fe}_2(\text{CO})_9$ with the cyclobutenedione derivatives, only decomposition products resulted.

SECTION 1

A STUDY OF THE REACTIONS OF LOW-VALENT
TRANSITION-METAL COMPLEXES WITH DERIVATIVES
OF CYCLOBUT-1-ENE-2,3-DIONE.

(E) Iron(0)

(ii) Pentacarbonyliron(0)

Fe(CO)₅

In the reaction of $\text{Fe}(\text{CO})_5$ with phenylcyclobutenedione only decomposition products resulted.

SECTION 1

A STUDY OF THE REACTIONS OF LOW-VALENT
TRANSITION-METAL COMPLEXES WITH DERIVATIVES
OF CYCLOBUT-1-ENE-2,3-DIONE.

(D) General conclusion.

It would appear that the reactivity of the cyclobutenediones is confined to attack by nucleophiles, and the nature of the nucleophile is critical. With the extremely nucleophilic \underline{d}^{10} platinum(0) species facile reaction occurs and the ease of oxidative addition in this species further extends its chemistry with cyclobutenediones.

Similarly with the \underline{d}^{10} palladium(0) except here the variation in co-ordinative ability and oxidative addition properties limits the range of products. The unstable nature of these palladium compounds also is a factor in the extent of the chemistry. However, in the case of \underline{d}^8 rhodium(I), although the ease of oxidative addition is high, the species is not nucleophilic enough to effect initial attack on the cyclobutenediones and no reaction occurs. The similar situation occurs in both the \underline{d}^8 iridium(I) and \underline{d}^8 iron(0) cases, the decrease in nucleophilicity being critical to the reaction.

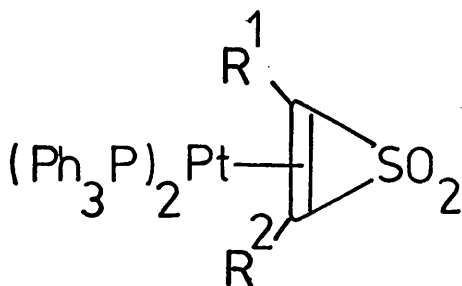
SECTION 2

A STUDY OF THE REACTIONS OF LOW-VALENT
TRANSITION-METAL COMPLEXES WITH CYCLIC SULPHONES.

(A) Platinum(0)

(i) Trans-stilbenebis(triphenylphosphine)platinum(0)
Pt(PPh₃)₂(trans-stilbene)

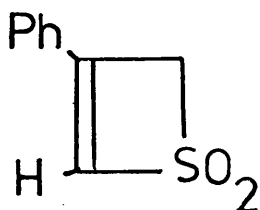
3-phenylthiete-1,1-dioxide is a 4-membered ring analogue of the thiirene-1,1-dioxides. The 3-membered ring compounds (37) form π -complexes with platinum(0)



(37)

and pyrolyse to acetylenes and platinum(II) compounds (72CH178, 73JO(57)403). It was therefore decided to extend the study of sulphone-platinum chemistry to include the 4-membered ring thietes and also to study the reactions of some 5-membered ring sulphones.

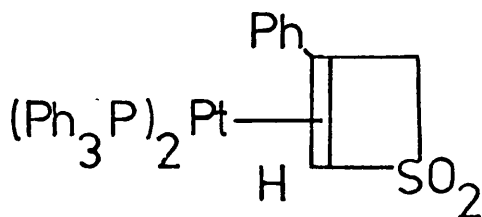
In diethyl ether, 3-phenylthiete-1,1-dioxide (38) reacts with trans-stilbenebis(triphenylphosphine)platinum(0) to yield a white crystalline product.



(38)

The sulphone ligand has characteristic i.r. bands assigned as $\nu_{\text{symm}}(\text{S-O})$ at 1130 cm^{-1} and $\nu_{\text{asymm}}(\text{S-O})$ at 1320 cm^{-1} , and in this platinum(0) complex strong bands are seen at 1130 cm^{-1} and 1276 cm^{-1} which may tentatively be assigned to $\nu_{\text{symm}}(\text{S-O})$ and $\nu_{\text{asymm}}(\text{S-O})$ in the complex. Unlike the thiirene complexes, TCNE replaces the thiete giving the well-known $\text{Pt}(\text{PPh}_3)_2(\text{TCNE})$ complex.

On the basis of this evidence, the thiete complex may be assigned the π -bonded structure (39).

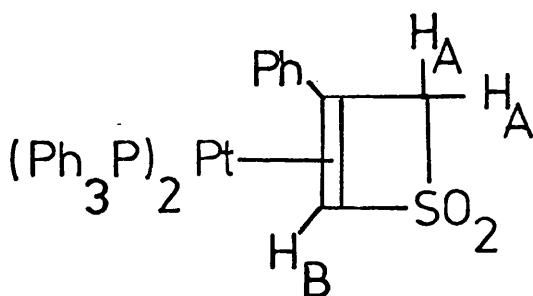


(39)

Further, the upfield shift of ≈ 2.5 p.p.m. of the vinylic proton is indicative of an olefin-bonded complex.

The ^1H n.m.r. of this complex consisted of the usual phenyl multiplet and a multiplet at 4.27 δ . On closer inspection the multiplet was seen to be a doublet with ^{195}Pt satellites and to slightly lower field a doublet of doublets also with ^{195}Pt satellites. Narrow field integration gave the intensities as 2:1 respectively.

The simple doublet pattern for the two methylene protons suggests that they are equivalent, which is very hard to visualise on the basis of the assigned structure (39). However, all other evidence suggests a π -complex, and the equivalence of these protons must be coincidental. cis-(Pt-H) coupling to these protons must be zero, whereas both cis and trans-(P-H) coupling to the methine proton cause the doublet of doublets to appear. Labelling the protons as in (40) below, the couplings are assigned as follows:

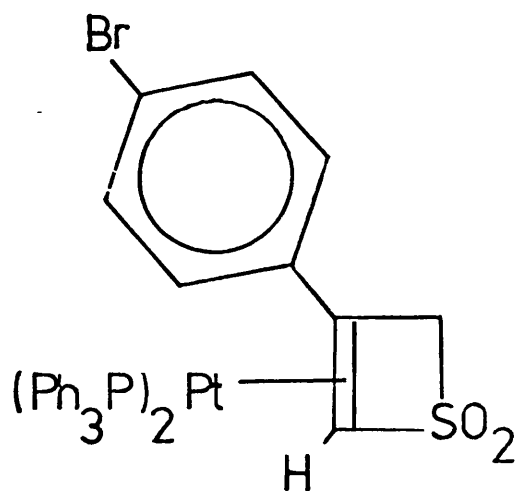


(40)

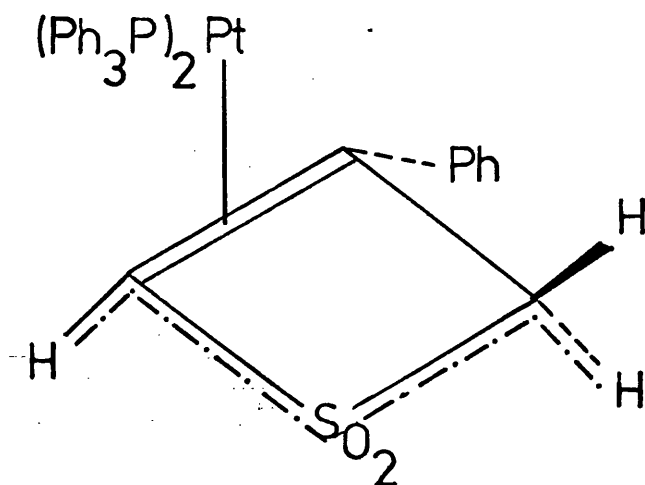
$$\begin{array}{ll}
 \text{trans-}^3\text{J(P-HB)} = 9.8 \text{ Hz} & \text{trans-}^4\text{J(P-HA)} = 9.8 \text{ Hz} \\
 \text{cis-}^3\text{J(P-HB)} = 4.1 \text{ Hz} & \text{cis-}^4\text{J(P-HA)} = 0 \\
 ^2\text{J(Pt-HB)} = 58.2 \text{ Hz} & ^3\text{J(Pt-HA)} = 79.6 \text{ Hz}
 \end{array}$$

Reaction of 3-p-bromophenylthiete-1,1-dioxide with the platinum(0) complex also gave a white crystalline product which by analysis fitted the constitution $\text{Pt(PPh}_3)_2(\text{thiete})$. Again the ligand was replaced on treatment with TCNE, and the i.r. spectrum showed strong

bands at 1130 and 1286 cm^{-1} assigned as $\nu_{\text{symm}}(\text{S-O})$ and $\nu_{\text{asymm}}(\text{S-O})$ respectively. (cf. $\nu_{\text{symm}}(\text{S-O})$ at 1130 cm^{-1} ; $\nu_{\text{asymm}}(\text{S-O})$ at 1312 cm^{-1} in the free ligand) consistent with the proposed structure (41).

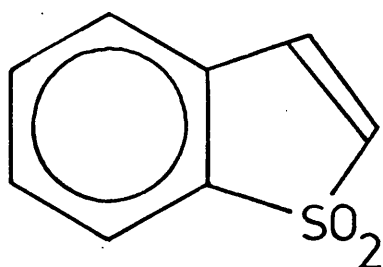


The ^1H n.m.r. of this complex was basically the same as the previous complex, showing a multiplet at 4.27 δ being a doublet and a doublet of doublets, both with ^{195}Pt satellites. However, in this case the doublet was split into two doublets with a coupling of 3.07 Hz (seen as shoulders on the side of the pattern), and the doublet of doublets was similarly split with a coupling of 0.9 Hz (not well-defined but measurable). The further splitting on the doublet is thought to be caused by the cis-(P-H) coupling which was zero in the previous complex, but the coupling to the doublet of doublets is more difficult to explain. It appears that the value of the coupling constant is in the region for long-range proton-proton coupling (usually reckoned to be between 0.5 and 2.0 Hz). A model of this complex shows that if coupling proceeds through the SO_2 part of the molecule a definite W-arrangement is possible thus permitting the conditions required for long-range proton-proton coupling to exist.

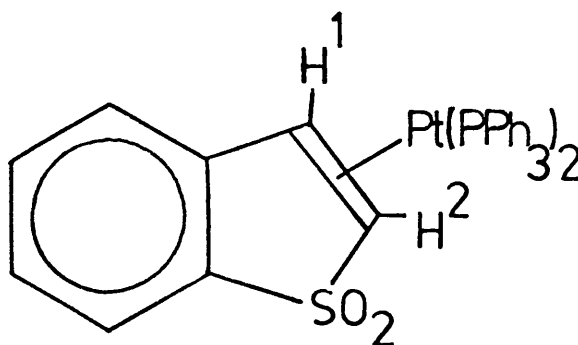


As only one of the methylene protons is in the right orientation, a doublet is observed and not a triplet as might be expected from a methylene group in which the protons are equivalent. The reciprocal coupling to the methylene proton is not seen, probably due to the confusing cis-(P-H) coupling which in itself is not well-defined. A more detailed appraisal of this interesting situation is given in part (ii) of Section 2 (i.e. in the arsine derivative - in which this effect is more clearly observed).

Reaction of 2,3-benzothiophene-1,1-dioxide (43) with the platinum(0)-stilbene complex led to the isolation of a white crystalline compound giving a satisfactory analysis for the proposed structure (44).



(43)

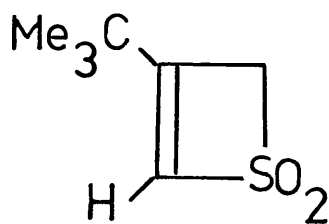


(44)

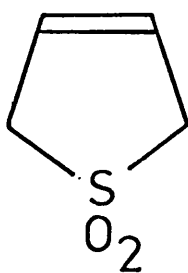
The i.r. spectrum of this compound showed bands at 1130 and 1312 cm^{-1} , tentatively assigned to $\nu_{\text{symm}}(\text{S-O})$ and $\nu_{\text{asymm}}(\text{S-O})$ respectively. However, the ^1H n.m.r. spectrum was highly unsymmetrical with the phenyl

multiplet at 7.14 δ , a broad doublet at 5.58 δ and a doublet at 3.92 δ having what appeared to be ^{195}Pt satellites. On closer inspection of the patterns their highly unsymmetrical nature was clearly seen. The arms of the doublet at 3.92 δ were in the intensity ratio of 1:3, the left-hand (downfield) satellite being a quartet whereas the right-hand (upfield) satellite appeared as a triplet. The broad doublet at 5.58 δ could not be sharpened by mechanical methods. The spectrum was thought to be high-order and attempts to assign the signals were unsuccessful. The structure (44) was given purely by analogy to that found in the thiete-1,1-dioxide and in the thiirene-1,1-dioxide complexes of platinum(0). A ^{13}C n.m.r. analysis of this complex is now underway in the hope that an accurate assignment of structure can be made.

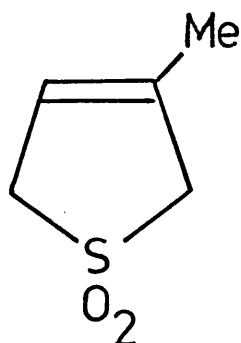
The reaction of $\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene})$ with 3- t butylthiete-1,1-dioxide (45), cyclopent-3-ene-1-sulphone (46) and 3-methylcyclopent-3-ene-1-sulphone (47) led only to recovery of starting materials.



(45)



(46)



(47)

It would appear that the platinum(0) reacts with only a limited number of the cyclic sulphones studied, although steric hindrance in the case of the ^tbutylthiete (45) may account for its lack of action on the platinum(0) complex. With the less sterically hindered molecules facile reaction is observed leading to stable complexes. Reaction of platinum(0) with benzothiophenedioxide (43) occurs readily, but as yet the product is not understood. It is possible of course that as in the benzocyclobutenedione reaction, ring-expansion has occurred, but no discussion of a meaningful nature may be made at this stage, as the constitution of the product is unknown.

SECTION 2

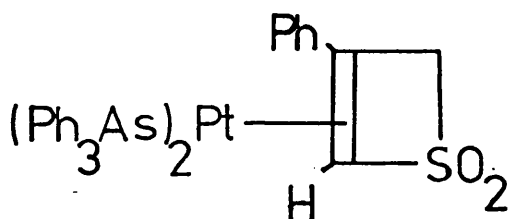
A STUDY OF THE REACTIONS OF LOW-VALENT
TRANSITION-METAL COMPLEXES WITH CYCLIC SULPHONES.

(A) Platinum(0)

(ii) Tetrakis(triphenylarsine)platinum(0)

Pt(AsPh₃)₄

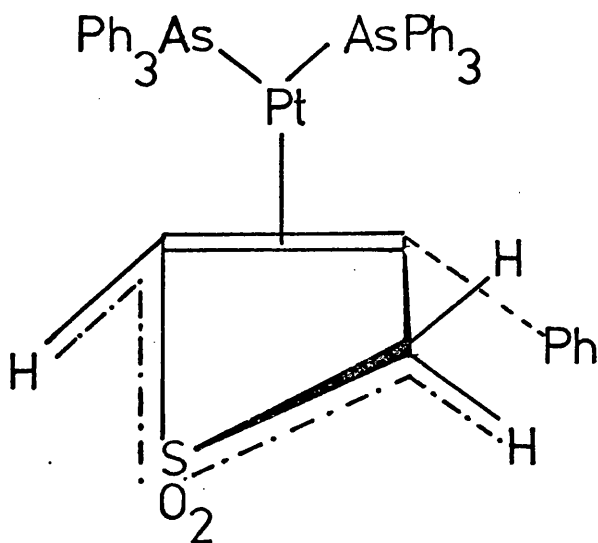
Treatment of tetrakis(triphenylarsine)platinum(0) with 3-phenylthiete-1,1-dioxide in refluxing chloroform leads to the isolation of a cream crystalline complex which was assigned the structure (48) by analogy to the phosphine derivative (39). The analysis was consistent with this assignment. The infrared spectrum showed $\nu_{\text{symm}}(\text{S-O})$ at 1126 cm^{-1} and $\nu_{\text{asymm}}(\text{S-O})$ at 1281 cm^{-1} .



(48)

The ^1H n.m.r. spectrum in deuterochloroform was very interesting. Apart from the phenyl resonances at 7.01δ there was a singlet at 4.72δ having ill-defined ^{195}Pt satellites and a quartet at 4.33δ assigned as an AB pattern resulting from the methylene group. The coincidental equivalence of the methylene protons seen in the phosphine derivative is therefore removed in this arsine analogue. On closer inspection of the spectrum both the singlet and the higher-field arms of the AB quartet appeared split further, this splitting being 2.09 Hz . In order to sort out the reason for this additional coupling, the

^1H n.m.r. spectrum was obtained at a series of temperatures from $+48^\circ\text{C}$ to -72°C , but the splitting persisted throughout the range. The value of 2.09 Hz is in the range for long-range proton-proton coupling (sometimes referred to as W-coupling) and is seen in this case on both the singlet and on the two high-field arms of the AB pattern. In the phosphine analogue the reciprocal splitting on the methylene group is masked by some cis-($^3\text{P-H}$) coupling. In order to be in the appropriate orientation, the coupling must travel through the sulphur atom of the sulphone group. No clear evidence regarding the effects of heteroatoms other than N and O has been established in the field of these long-range couplings, although in cases already studied (75MI2) the presence of oxygen or nitrogen in the W-formation does not appear to affect the couplings greatly. It is quite possible then that the sulphur atom has little or no effect on the coupling scheme as shown in (49).



The value of 2.09 Hz for the coupling is slightly greater than the normal range of long-range proton-proton couplings (usually 0.5 - 2.0 Hz), and it may well be that the sulphur atom actually enhances the effect to a small extent. Initially the ligand molecule is almost planar, but as has been demonstrated in the case of the (1-methyl-2-phenylcyclobut-1-ene-3,4-dione)platinum(0) phosphine complex on complexation, the vinylic groups are bent out of the plane away from the platinum atom. The same situation probably occurs in the present case thus rendering the thiete non-planar and thereby giving rise to the W-formation which results in the interesting couplings observed in the ^1H n.m.r. spectrum.

The preparation of the para-bromophenyl derivative gave identical results in the ^1H n.m.r. spectrum as was expected. The substitution in the phenyl group has no appreciable effect on the stereochemistry of the molecule, and the same W-formation can be drawn giving rise to the same coupling of 2.09 Hz. The effect was apparent in the spectrum down to -72°C when loss of resolution occurred.

Conclusion

In the study of thiete-1,1-dioxides with zerovalent platinum complexes only limited success was achieved; the steric hindrance caused by the bulky tertiary-butyl group in 3-^tbutylthiete-1,1-dioxide probably preventing reaction. However, with 3-phenyl- and 3-p-bromophenyl-thiete-1,1-dioxide both $\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene})$ and

$\text{Pt}(\text{AsPh}_3)_4$ readily react to give stable π -bonded complexes. These have many novel features, including, in the 3-phenylthiete-phosphine compound, not only an accidentally equivalent methylene group, but also evidence of the unusual W-coupling not previously observed in an organometallic complex. The arsine analogues of both these thietes with platinum(0) show clear evidence for this novel long-range proton-proton coupling (in this case not complicated by ^{31}P coupling).

Although the platinum(0) complex with benzothiophene-1,1-dioxide is stable and easily prepared, spectroscopic methods have not been sufficient to elucidate its structure. In a further effort to sort this out, a ^{13}C analysis is at present underway, but no results are available at this time.

Other sulphones available to the author failed to react with the organometallic starting materials.

SECTION 2.

A STUDY OF THE REACTIONS OF LOW-VALENT
TRANSITION-METAL COMPLEXES WITH CYCLIC SULPHONES.

(B) Palladium(0)

(i) Tetrakis(triphenylphosphine)palladium(0)

Pd(PPh₃)₄

Only one reaction of this palladium(0) complex was attempted, that with 3-phenylthiete-1,1-dioxide. Under the conditions used, no reaction took place and starting materials were recovered quantitatively.

Conclusion.

In the reactions of platinum(0) and palladium(0) with thiirene-1,1-dioxides (72CH178, 73JO(57)403) the stability of the palladium(0) complexes is less than that of platinum(0) due to the difference in co-ordinative ability of these species (see introductory chapter for detailed explanation). It may be that this difference is critical in the thiete-1,1-dioxides permitting co-ordination in the case of platinum(0) but forbidding the formation of a palladium(0) analogue.

SECTION 2

A STUDY OF THE REACTIONS OF LOW-VALENT
TRANSITION-METAL COMPLEXES WITH CYCLIC SULPHONES.

(C) Iron(0)

(i) Nonacarbonyldiiron(0)

$\text{Fe}_2(\text{CO})_9$

In the reactions of $\text{Fe}_2(\text{CO})_9$ with 3-phenylthiete-1,1-dioxide and 3-methylpent-3-ene-1-sulphone only decomposition products were isolated. No further reactions were attempted.

SECTION 2.

A STUDY OF THE REACTIONS OF LOW-VALENT
TRANSITION-METAL COMPLEXES WITH CYCLIC SULPHONES.

(D) Rhodium(I)

(i) Chlorotris(triphenylphosphine)rhodium(I)

$\text{RhCl}(\text{PPh}_3)_3$

With 3-phenylthiete-1,1-dioxide, the rhodium(I) complex showed no reaction under the conditions used.

SECTION 2.

A STUDY OF THE REACTIONS OF LOW-VALENT
TRANSITION-METAL COMPLEXES WITH CYCLIC SULPHONES.

(E) General conclusions.

The variation in the co-ordinative abilities between \underline{d}^{10} platinum(0) and \underline{d}^{10} palladium(0), \underline{d}^8 iron(0) and \underline{d}^8 rhodium(I) may well be critical in their reactions with the thiete-1,1-dioxides. The increased ease of oxidative addition in the case of rhodium(I) would appear not to compensate for the lack of co-ordinative ability (as compared with platinum(0)). It is interesting to note, however, that unsubstituted thiete-1,1-dioxide does form an alkene complex with iron(0) (73JOC3963).

SECTION 3.

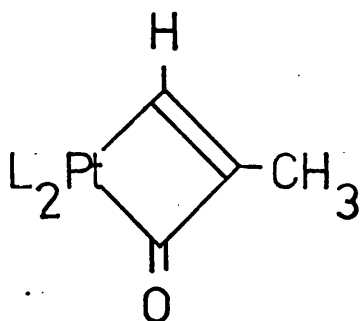
A STUDY OF THE REACTIONS OF LOW-VALENT
TRANSITION-METAL COMPLEXES WITH DERIVATIVES
OF CYCLOPROPENONE.

(A) Platinum(0)

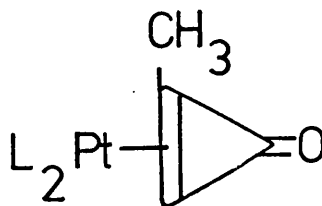
(i) Trans-stilbenebis(triphenylphosphine)platinum(0)

Pt(PPh₃)₂(trans-stilbene)

The reaction between platinum(0) and 1-methylcycloprop-1-ene was reported to produce a ring-expanded complex (50), but at low temperatures the olefin-bonded complex (51) had been detected (72JO(44)C63).

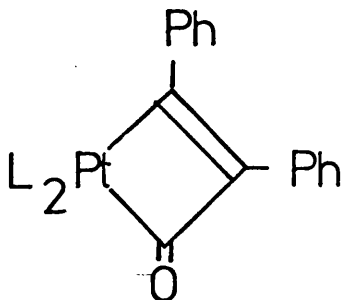


(50)



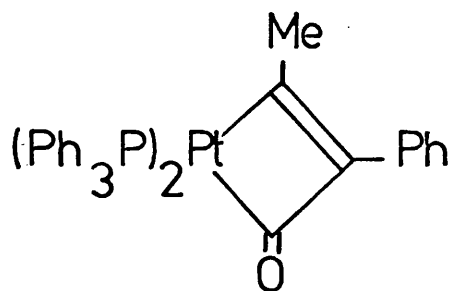
(51)

However, reaction between 1,2-dimethyl- and 1,2-diphenyl-cyclopropenone was reported to give exclusively the ring-expanded complexes. The structure of the diphenyl product was studied by x-ray diffraction and proved to be (52)



(52)

In the present work the reaction between the platinum(0)-stilbene complex and diphenylcyclopropenone in diethyl ether resulted in the isolation of a crystalline complex identical in all respects to that reported in the literature (72CH672, 72JO(44)C63). 1-methyl-2-phenylcycloprop-1-ene-3-one on treatment with the platinum(0) complex in ether also gave a yellow crystalline product not previously reported. The analysis was consistent with the structure (53),

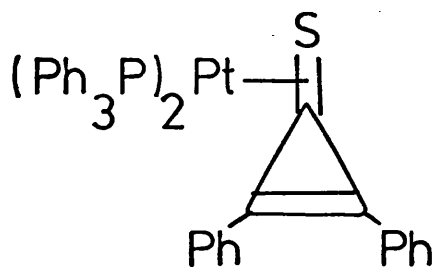


(53)

and the infrared spectrum showed $\nu(\text{C}=\text{O})$ at 1666 cm^{-1} (indicative of $\text{C}=\text{O}$ attached to platinum(II) (68CD319, 68CH1373)). The proton n.m.r. showed the methyl resonance as a doublet at 1.48δ having ^{195}Pt satellites. cis-Phosphorus coupling must be zero in this compound. The couplings were assigned as
trans- $^4\text{J}(\text{P}-\text{H})=7.54\text{ Hz}$ $^3\text{J}(\text{Pt}-\text{H})=51.6\text{ Hz}$

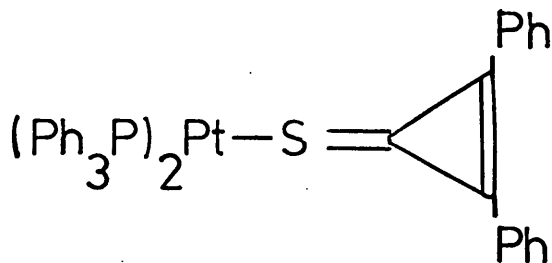
The thione derivative of the diphenylcyclopropenone complex was readily prepared by reaction of $\text{Pt}(\text{PPh}_3)_2$ (trans-stilbene) and diphenylcyclopropenethione.

The yellow crystalline complex thus formed had satisfactory analyses, but showed no bands in the infrared region around 1370 cm^{-1} (indicative of $\text{C}=\text{S}$). Evidence suggests that the product may be bonded through the carbon-sulphur double bond, (54).



(54)

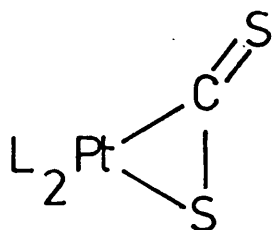
or alternatively bonded via the sulphur atom, (55)



(55)

This latter possibility parallels the reactions of diphenylcyclopropenone with other transition metals (67J1004, 68JO(12)249), in which the metal is bonded via the oxygen atom rather than by the carbon-carbon π -bond.

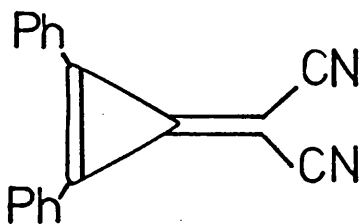
In studies with carbon disulphide and zerovalent platinum, complex (56) had been reported (67J865).



(56)

The absence of any C=S stretching bands in the i.r. (which might appear shifted in the sulphur-co-ordinated compound) strongly suggests that the complex is bonded as in (54) rather than sulphur-bonded as in (55).

A crystalline complex was obtained on reaction of Pt(PPh₃)₂(trans-stilbene) with 1,1-dicyano-2,2-diphenylcyclopropenylethylene (57)



(57)

but no consistent analysis could be obtained. Infrared bands in the carbon-carbon π -bond region were observed, but could not be assigned.

SECTION 3.

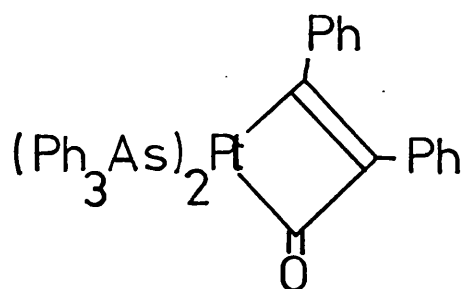
A STUDY OF THE REACTIONS OF LOW-VALENT
TRANSITION-METAL COMPLEXES WITH DERIVATIVES
OF CYCLOPROPENONE.

(A) Platinum(0)

(ii) Tetrakis(triphenylarsine)platinum(0)

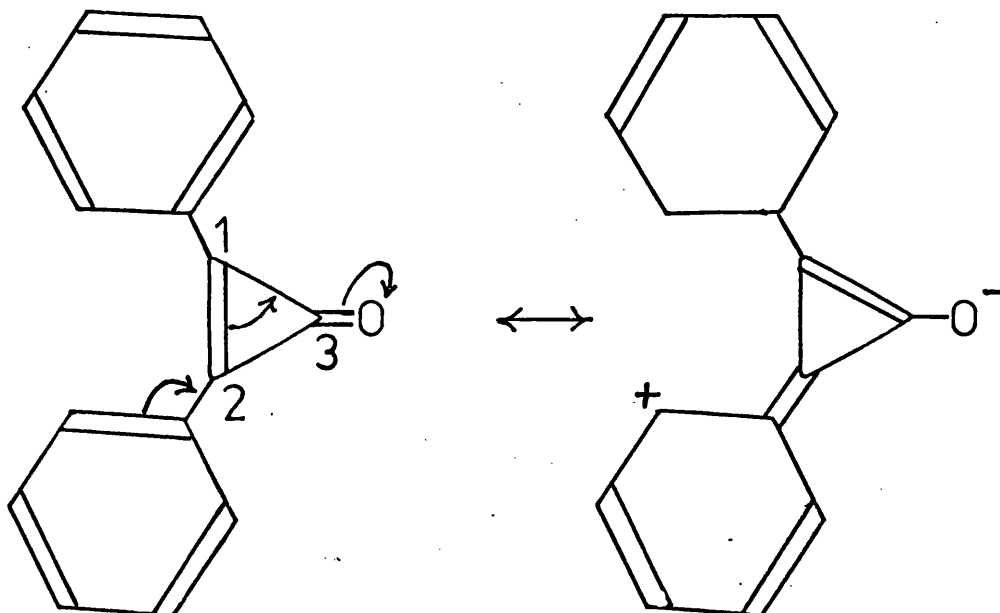
Pt(AsPh₃)₄

Treatment of this platinum(0) complex with diphenylcyclopropenone in chloroform resulted in the isolation of yellow crystals showing $\nu(\text{C}=\text{O})$ at 1655 cm^{-1} . The analysis was consistent with the arsine analogue (58).



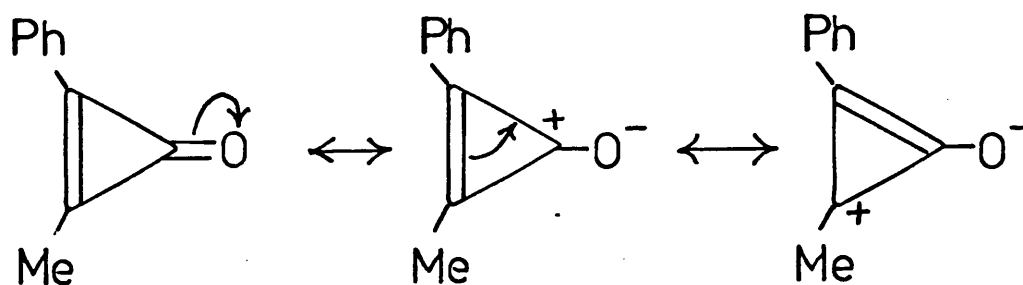
(58)

In the diphenylcyclopropenone molecule, as in benzocyclobutenedione, there are two effects which draw the electrons away from the carbon-carbon bond undergoing attack, Scheme 7.



Scheme 7.

The conjugation of the phenyl groups and the π -bond in the molecule is similar to the situation in diphenylcyclobutenedione (q.v.), but here the electronegativity of the single oxygen atom tends to draw charge away in the opposite direction, thus rendering the carbon-carbon bonds C_1-C_3 and C_2-C_3 (in Scheme 7) particularly susceptible to nucleophilic attack. The platinum(0) attacks at this point and forms the ring-inserted product. The formation of the ring-expanded complex in methylphenylcyclopropenone is in marked contrast to the exclusively π -bonded compound formed with platinum(0) and methylphenylcyclobutenedione. The explanation of this difference may lie in the fact that in the three-membered ring conjugation may occur in a different way, Scheme 8.



Scheme 8.

The positive charge now lying on the carbon atom attached to the methyl group is partly stabilised by the positive inductive effect of this group. However, the carbon-carbon bond (CH_3)C-C(O) is now particularly susceptible to attack by nucleophiles and it is here that insertion takes place, leading to the ring-expanded species. In the four-membered molecule, a similar state of affairs is not possible, because the alkene bond is already in a conjugated system and is not free to contribute to the type of intermediate shown in Scheme 8. Preparation of the arsine analogue is consistent with the above argument.

Conclusion.

Although the phenyl-substituted cyclopropenones may be considered as 3-membered-ring analogues of the cyclobutenediones, their electronic features are in contrast and the products with the nucleophilic platinum(0) species are exclusively ring-inserted.

The olefin-bonded complexes are much more stable in the cyclobutenediones than in the cyclopropenones as evidenced by the inability to isolate a dimethyl-cyclopropenone π -bonded complex, whereas the dimethyl-cyclobutenedione forms exclusively an olefin-bonded complex.

An identical situation exists with the 1,2-diphenyl derivatives - only a ring-expanded complex could be isolated with the cyclopropenone whereas a

stable olefin complex was formed with the cyclobutenedione. However, at low temperatures an olefin-bonded complex was formed with platinum(0) and 1-methylcyclopropenone but on warming above -30°C ring-expansion occurred. A comparison of the spectroscopic data for the various cyclopropenone and cyclobutenedione complexes is given in Table 3.

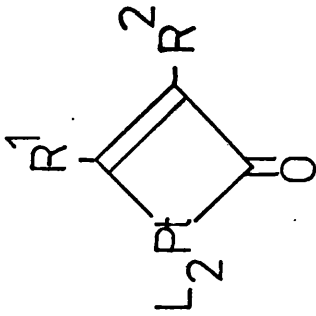
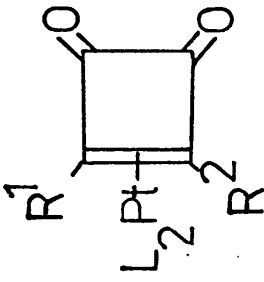
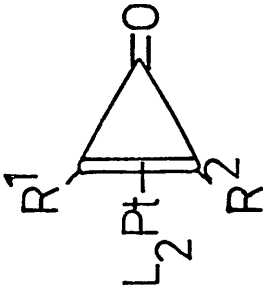
	R ¹	R ²	ν(C=O)	CH ₃			H		
				δ p.p.m.	J(P-H)Hz	J(Pt-H)Hz	δ p.p.m.	J(P-H)Hz	J(Pt-H)Hz
	CH ₃	CH ₃	1640vs	1.55 1.18	0 6	13 47.5			
	Ph	Ph	1655vs						
	H	CH ₃	1640	1.57	0	13			
	CH ₃	CH ₃	1712	1.64	2.2(cis-P) 5.4(trans-P)	16.71 16.71			
	Ph	Ph	1708						
	H	CH ₃	1750	1.43	6.5	25.5	3.71	7.5	53.5

TABLE 3.

SECTION 3.

A STUDY OF THE REACTIONS OF LOW-VALENT
TRANSITION-METAL COMPLEXES WITH DERIVATIVES
OF CYCLOPROPENONE.

(B) Rhodium(I)

(i) Chlorotris(triphenylphosphine)rhodium(I)

$\text{RhCl}(\text{PPh}_3)_3$

This rhodium(I) complex did not react with diphenylcyclopropenone at ambient temperature. Under more forcing conditions only decomposition products were formed.

Conclusion.

The failure to react may be due to the less nucleophilic nature of the d^8 rhodium(I) which may be the critical feature rather than the ease of oxidative addition usually shown by this species. The failure parallels the negative results obtained in studies of the reactions of rhodium(I) compounds with cyclobutenedione derivatives.

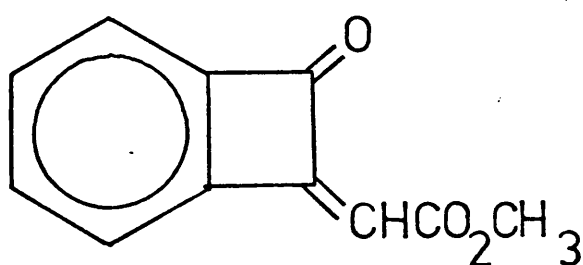
SECTION 4

A STUDY OF THE REACTIONS OF ZERO-VALENT
PLATINUM COMPLEXES WITH CYCLOBUTENE
DERIVATIVES CONTAINING EXOCYCLIC CARBON-
CARBON DOUBLE BONDS.

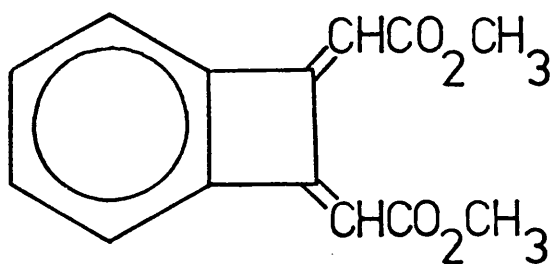
(A) Platinum(0)

(i) Trans-stilbenebis(triphenylphosphine)platinum(0)
Pt(PPh₃)₂(trans-stilbene)

Treatment of the platinum(0) stilbene complex with both 1-methylenemethylcarboxy-2,3-benzocyclobutene-4-one (59) and 1,2-dimethylenemethylcarboxy-3,4-benzocyclobutene (60) in ether led to the isolation of yellow products.



(59)



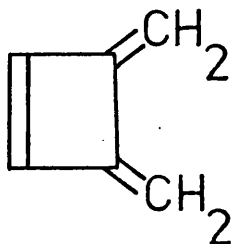
(60)

However, the extreme difficulty in separating these two starting materials (which are both formed in the same preparative reaction) resulted in a mixture of products which have proved impossible to separate up to the present.

Repeated recrystallisations of the platinum complex of (59) led to yellow crystals which showed $\nu(\text{C}=\text{O})$ at 1748 cm^{-1} , characteristic of the carbonyl group in the π -bonded cyclobutenedione complexes in section 1(A), but attempts to sort out the structure by proton n.m.r. proved fruitless due to persistent contamination by the dimethylene compound. All attempts at crystallising the platinum-dimethylene complex resulted in failure, only

a yellow oily solid being obtained. Infrared data showed bands at 1686 and 1707 cm^{-1} .

Dimethylenecyclobutene (61) produced a white



(61)

crystalline complex with the platinum(0)-stilbene compound which showed infrared bands at 1700 and 1480 cm^{-1} . Sadly the complex decomposed in all n.m.r. solvents in which it dissolved, and no ^1H n.m.r. was available.

Conclusion.

These interesting derivatives of cyclobutene readily react with platinum(0) complexes but due to the difficulty of preparation or separation of the products no useful conclusions could be drawn as to the structure of the products.

Attempts to obtain crystals suitable for x-ray studies were not successful.

SECTION 5

A STUDY OF THE REACTIONS OF ZEROVALENT PLATINUM COMPLEXES WITH SOME MISCELLANEOUS CYCLOBUTENES AND RELATED MOLECULES.

In all cases the platinum(0) starting complex was trans-stilbenebis(triphenylphosphine)platinum(0), $\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene})$.

(i) Cyclobutanone

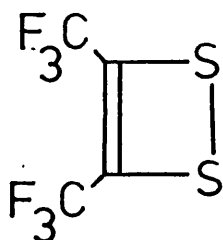
This molecule did not react with the platinum(0) complex under the conditions used.

SECTION 5.

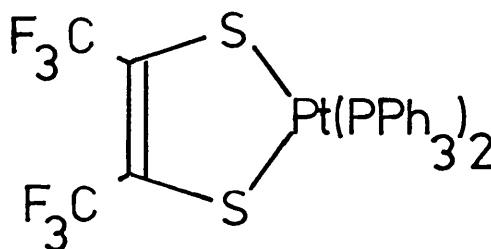
A STUDY OF THE REACTIONS OF ZEROVALENT
PLATINUM COMPLEXES WITH SOME MISCELLANEOUS
CYCLOBUTENES AND RELATED MOLECULES.

(ii) Bis(perfluoromethyl)-1,2-dithietene.

Treatment of the platinum complex with this ligand (62) in ether led to the isolation of yellow crystals identical in all respects to those reported in the literature (64IC814). The postulated structure is shown in (63)



(62)



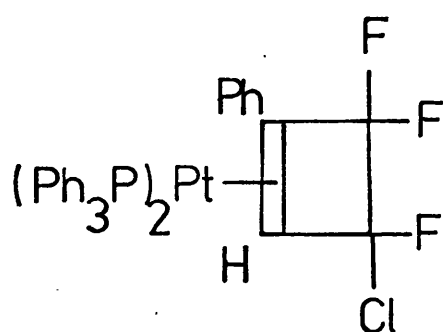
(63)

SECTION 5.

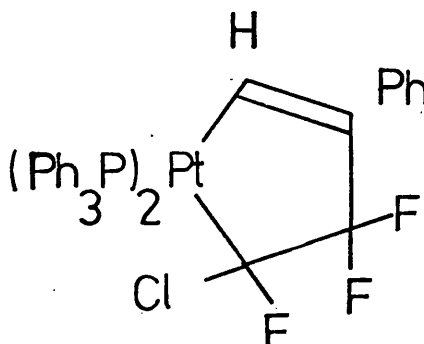
A STUDY OF THE REACTIONS OF ZEROVALENT
PLATINUM COMPLEXES WITH SOME MISCELLANEOUS
CYCLOBUTENES AND RELATED MOLECULES.

(iii) 1-chloro-1,2,2-trifluoro-3-phenylcyclobut-3-ene.

This compound readily gave a crystalline complex with the platinum(0) starting material. The analysis was consistent with the structures (64) or (65).



(64)



(65)

No vinylic proton was observed in the ^1H n.m.r. possibly due to the signal being shifted into the phenyl region (more likely in the case of (65) than (64)). The ^{19}F n.m.r. is very difficult to interpret. In the starting material an extremely complex spectrum is seen, which is much simplified in the complex. These spectra are shown in Figures (66) and (67). It is clear that these are higher order spectra and so far attempts to interpret them have failed.

^{19}F spectrum of
(64)/(65).

- 176 -

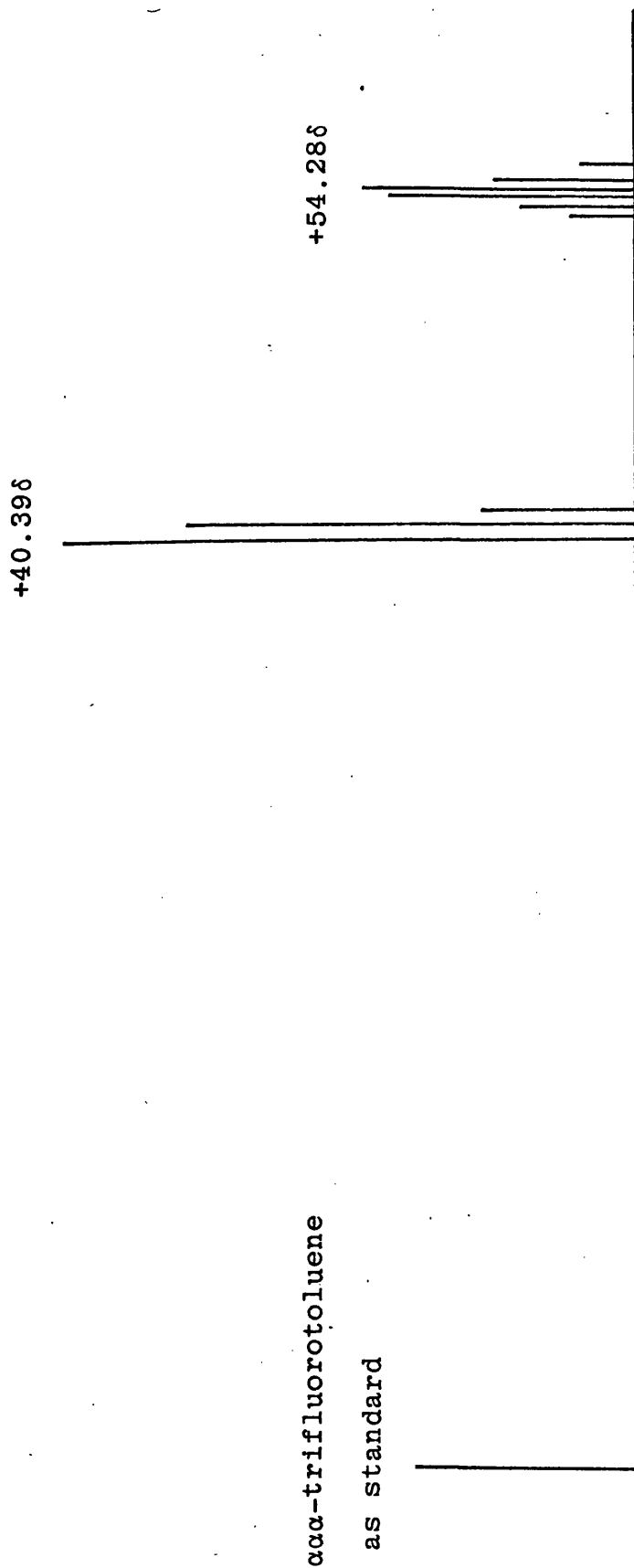


Figure (66)

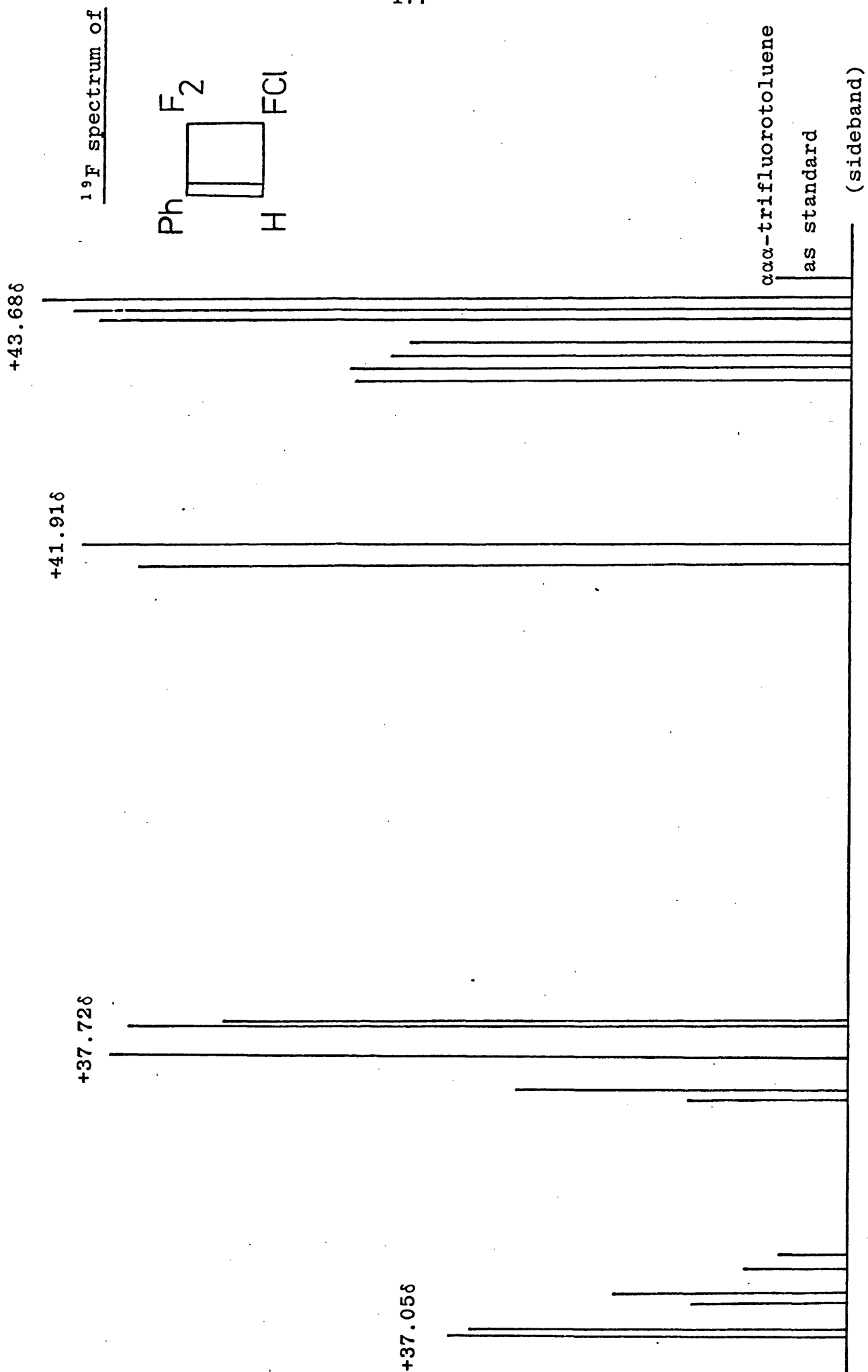


Figure (67)

SECTION 5.

A STUDY OF THE REACTIONS OF ZEROVALENT
PLATINUM COMPLEXES WITH SOME MISCELLANEOUS
CYCLOBUTENES AND RELATED MOLECULES.

(iv) Hexa-1,5-diyne.

This compound readily forms a stable crystalline complex with platinum(0) whose analysis is consistent with a 1:1 reaction (the insolubility of this product makes recrystallisation impossible and explains the inaccuracy of the analysis results). The infrared spectrum is identical in all respects to that of the complex formed between platinum(0) and dimethylenecyclobutene (q.v.), and the same difficulties arose as in that case with respect to ^1H n.m.r. It is likely that the two complexes are identical, but definite evidence is lacking at the present time.

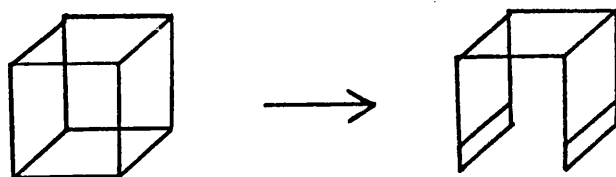
CHAPTER 3.

A KINETIC STUDY OF THE RING-EXPANSION REACTIONS
OF SOME CYCLOBUTENEDIONE DERIVATIVES BY
PLATINUM(0) COMPLEXES.

THE KINETICS OF THE RING-EXPANSION OF CYCLOBUTENEDIONES
WITH PLATINUM(0) COMPLEXES.

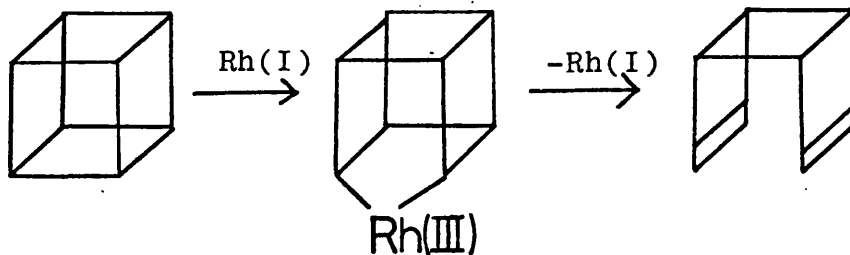
1. Introduction.

In recent times, a great deal of interest has centred on the chemistry of transition metal cleavage of carbon-carbon σ -bonds. This interest was initiated by Tipper's work on the action of platinum(0) on cyclopropane (55J2045) and more recently received added stimulus after the discovery that transition metals could catalyse normally forbidden isomerisations such as those of cubane (70JA3515). The thermally forbidden isomerisation shown in Scheme 1



Scheme 1

may be easily effected by the presence of a catalyst such as rhodium(I), Scheme 2.

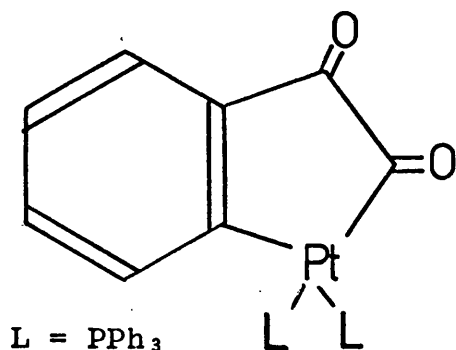


Scheme 2

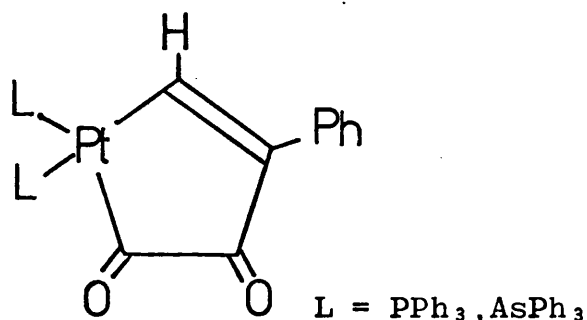
The isomerisation is thought to proceed via a rhodium(III) intermediate wherein the rhodium(I) species has cleaved a carbon-carbon σ -bond.

Postulation as to the nature of the intermediates involved in such reactions and those in other rearrangements such as in cyclobutenes wherein a metallocyclic derivative is thought to be important (70JA7499) has led the organometallic chemist into the investigation in depth of these intermediates.

The isolation and characterisation of "intermediates" in which a transition metal has cleaved a carbon-carbon σ -bond has been most fruitful in the chemistry of Iron, and much work has been carried out in this field (73JO(56) 315, 73JO(57)363, 73JO(61)C55). However, it is also known that platinum(0) may cleave carbon-carbon σ -bonds to form similar intermediates (72JO(46)C29, 72JO(44)C63) and the present work was initiated when Kemmitt et al discovered that platinum(0) complexes inserted into a carbon-carbon σ -bond in benzocyclobutenedione to form a stable platina-cyclopentenedione derivative (1) (73CH158) and that a similar platinacyclopentenedione complex formed with platinum(0) and 1-phenylcyclobut-1-ene-3,4-dione (2) (74CH841).

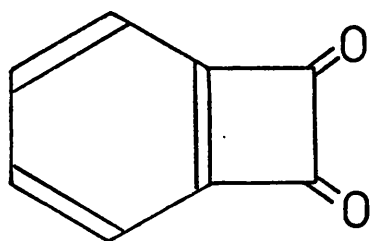


(1)

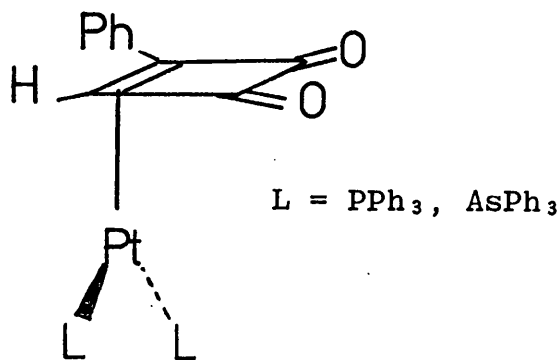


(2)

In the reaction of platinum(0) with benzocyclobutenedione (3) the possibility of an intermediate olefin-bonded complex was thought unlikely, whereas an olefin-bonded complex of phenylcyclobutenedione had been isolated as an air-stable crystalline solid, and was fully characterised (4).



(3)



(4)

It was decided that a kinetic study of the ring-expansion reactions of these various cyclobutenedione systems would lead to a deeper understanding of the mechanisms involved in the carbon-carbon bond cleavages concerned. The study was finally extended to reactions of the type $4 \rightarrow 2$ where $L = \text{AsPh}_3$ in order not only to further investigate the carbon-carbon bond cleavage, but to gain insight into the relative reactivities of the $\text{Pt}(\text{PPh}_3)_2$ and $\text{Pt}(\text{AsPh}_3)_2$ species, little work on which has previously been undertaken.

Note: In the text abbreviated names of compounds are sometimes used where no confusion may arise, e.g.

1-phenylcyclobut-1-ene-3,4-dione as phenylcyclobutenedione;

1,2-dimethoxycyclobut-1-ene-3,4-dione as dimethoxycyclobutenedione.

2. The reaction of benzocyclobutenedione with platinum(0) complexes (75MI3)

Benzocyclobutenedione (3) reacts quantitatively with tetrakis(triphenylphosphine)platinum(0), $\text{Pt}(\text{PPh}_3)_4$; with trans-stilbenebis(triphenylphosphine)platinum(0), $\text{Pt}(\text{PhCH=CHPh})(\text{PPh}_3)_2$; and with tolanbis(triphenylphosphine)-platinum(0), $\text{Pt}(\text{PhC}\equiv\text{CPh})(\text{PPh}_3)_2$ to give the platinacyclopentene derivative (1; $\text{L} = \text{PPh}_3$). In benzene solution at room temperature the reaction between compound (3) and both $\text{Pt}(\text{PPh}_3)_2$ (trans-stilbene) and $\text{Pt}(\text{PPh}_3)_4$ is fairly rapid. (Reaction with the stilbene complex is complete in a matter of seconds, and the half-life of the reaction with the tetrakisphosphine complex is only about 50 seconds.) The half-life of the reaction between the tolan complex and (3) however is greater than 1000 seconds and lends itself to a convenient kinetic study by conventional monitoring methods.

It was found that in mixtures containing an excess of dione the kinetic pattern followed was that of a reaction first-order in the platinum(0) complex, and the observed first-order rate constants are given in Table 1.

From these results a value of the activation energy E_a was calculated using an Arrhenius least-squares computer programme, and was found to be $28.73 \text{ kcal mol}^{-1}$. From this value the other activation parameters ΔH^\ddagger and ΔS^\ddagger were calculated using the equations (61MI1):

$$\Delta H^\ddagger = E_a - RT$$

$$\Delta G^\ddagger = \frac{k_1}{h} = \frac{kT}{h} e^{\frac{-\Delta G^\ddagger}{RT}}$$

$$\Delta G^\ddagger = H^\ddagger - T\Delta S^\ddagger$$

$$\Delta H^\ddagger = 118 \pm 4^* \quad \text{kJ mol}^{-1}$$

$$\Delta S^\ddagger = 85 \pm 13^* \quad \text{JK}^{-1}\text{mol}^{-1}$$

TABLE 1

Observed first-order rate constants $10^4 k_{\text{obs}}/\text{s}^{-1}$ for the reaction of benzocyclobutenedione with $\text{Pt}(\text{PPh}_3)_2(\text{tolan})$ in benzene solution. Initial $[\text{Pt}(\text{PPh}_3)_2(\text{tolan})] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$.

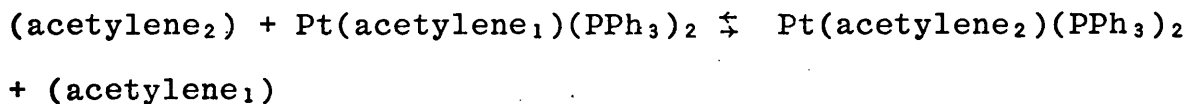
Temp/K	$10^2 [\text{dione}]/\text{mol dm}^{-3}$					
	1.0	2.0	3.0	4.0	5.0	6.0
291.2	1.6	1.4	1.5	1.3		1.5
299.6	4.6	4.6	4.8	4.8	4.8	4.6
307.2		15.2	15.9	14.6	15.0	15.5
316.0	75.0		77.0	76.0		75.0

It is clear from these figures that the order of the reaction with respect to dione is zero. This indicates that the loss of tolan from the complex $\text{Pt}(\text{PPh}_3)_2(\text{tolan})$

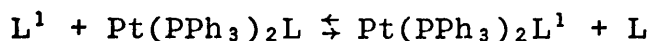
* This uncertainty represents the 90% confidence limits (calculated from tables) (71MI1).

is the rate-determining step. This conclusion appears to be consistent with the faster reactions observed when (3) reacts with $\text{Pt}(\text{PPh}_3)_4$ or $\text{Pt}(\text{PPh}_3)_2(\text{trans-stilbene})$ as it has been reported that loss of (PPh_3) or stilbene from these complexes does proceed faster than loss of tolan (73CH631). The positive value of the activation entropy confirms the dissociative loss of tolan in the rate-determining step.

From the above results, the observed kinetic pattern implies that following the rate-determining loss of tolan from $\text{Pt}(\text{PPh}_3)_2(\text{tolan})$, insertion of the species $\text{Pt}(\text{PPh}_3)_2$ into the carbon-carbon bond of the cyclobutene ring is relatively rapid. This mechanistic hypothesis seems reasonable in view of the known reactivity and properties of the monomeric $\text{Pt}(\text{PPh}_3)_2$ moiety which is thought to be the reactive species when $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ is placed in benzene solution (68JA4491). The reaction of this unit with such as $\text{PhC}\equiv\text{CPh}$ is immeasurably fast, indicating the extreme reactivity of the $\text{Pt}(\text{PPh}_3)_2$ moiety. The transient reactive $\text{Pt}(\text{PPh}_3)_2$ has also been postulated as an intermediate in the exchange reaction:



(63CC1235). It has also been reported that $[\text{Pt}(\text{PPh}_3)_2]_x$ has been isolated, and that this polymer acts as a monomer in solution, as evidenced by exchange reactions of the type:



(70IA390).

The foregoing study on benzocyclobutenedione sheds some light on the reactivity of the platinum(0) complexes, but does not provide any indication as to the mechanism of insertion into the carbon-carbon bond of the cyclobutenedione.

3. Reaction of 1-phenylcyclobut-1-ene-3,4-dione with platinum(0) complexes.

Depending on the experimental conditions, phenylcyclobutenedione reacts with platinum(0) complexes to give either an alkene-bonded complex (4) or a platinacyclopentene complex (2). The olefin-bonded species can be isolated and has been fully characterised. A solution of this alkene complex in chloroform or benzene is readily converted into the ring-expanded platinacyclopentene complex, and it may be postulated that the alkene complex is an intermediate in the reaction of platinum(0) with the cyclobutenedione to form the ring-expanded complex.

It was first necessary to see if the rate-determining step involved in the reaction of $Pt(PPh_3)_2(tolan)$ with phenylcyclobutenedione to give the platinacyclopentenenedione species was identical to that involved in the benzocyclobutenedione case. If this is the case, then a study of the first-order rate constants of the two reactions should yield similar results (under identical conditions). The results are given in Table 2, overleaf.

TABLE 2

First-order rate constants ($10^4 k_{\text{obs}}/\text{s}^{-1}$) for the reaction of $\text{Pt}(\text{PPh}_3)_2(\text{tolan})$ with benzocyclobutenedione and various excesses of phenylcyclobutenedione in chloroform solution at 298K.

benzocyclobutenedione	phenylcyclobutenedione		
	2 x excess	4 x excess	8 x excess
4.5	3.2	3.4	2.9

The similarity in the rate constants for the two reactions strongly suggests that they have a common rate-determining step, namely loss of tolan from the platinum(0) complex.

In order to investigate the mechanism of the actual insertion into the carbon-carbon bond, a kinetic study of the rearrangement of the alkene complex (4) to the ring-expanded complex (2) was undertaken. This rearrangement is a clear example of a redox isomerisation, few good examples of which have previously been observed.

The kinetics were examined in a range of solvents in order to determine the activation parameters, and thereby to suggest possible mechanisms for the oxidative insertion of platinum(0) into the carbon-carbon σ -bond of the cyclobutenediones. The reactions followed first-order kinetics accurately over at least three half-lives under all the conditions used in the investigation. The observed first-order rate constants for the reaction of the alkene complex (4) with $\text{L} = \text{PPh}_3$ are reported in Table 3 and

TABLE 3

Observed first-order rate constants (k) for the redox isomerisation of Pt(phenylcyclobutene-dione)(PPh₃)₂. Initial [complex] = 10⁻² mol dm⁻³.

CHLOROFORM*		BENZENE†		TOLUENE		BENZYL ALCOHOL	
T/K	10 ⁵ k/s ⁻¹	T/K	10 ⁵ k/s ⁻¹	T/K	10 ⁵ k/s ⁻¹	T/K	10 ⁵ k/s ⁻¹
298.5	4.2	299.6	1.1	308.2	11.2	308.2	8.4
298.8	2.6	303.5	2.1				
299.6	4.4	307.8	5.0				
300.6	3.5	308.4	5.4				
303.4	6.5	312.3	14.0				
303.4	6.5	314.4	14.6				
308.4	11.5	317.2	23.2				
308.4	11.8						
312.3	21.5						
312.3	20.4						
313.7	20.2						
314.4	22.1						
317.2	37.4						
317.2	41.3						
317.3	37.9						
318.4	35.6						

* Plotted on Graph 1.

† Plotted on Graph 2.

the activation parameters are reported in Table 4.

TABLE 4

Activation parameters* for the redox isomerisation of Pt(phenylcyclobutenedione)(PPh₃)₂ in chloroform and benzene. Uncertainties cited are those for the 90% confidence limits.

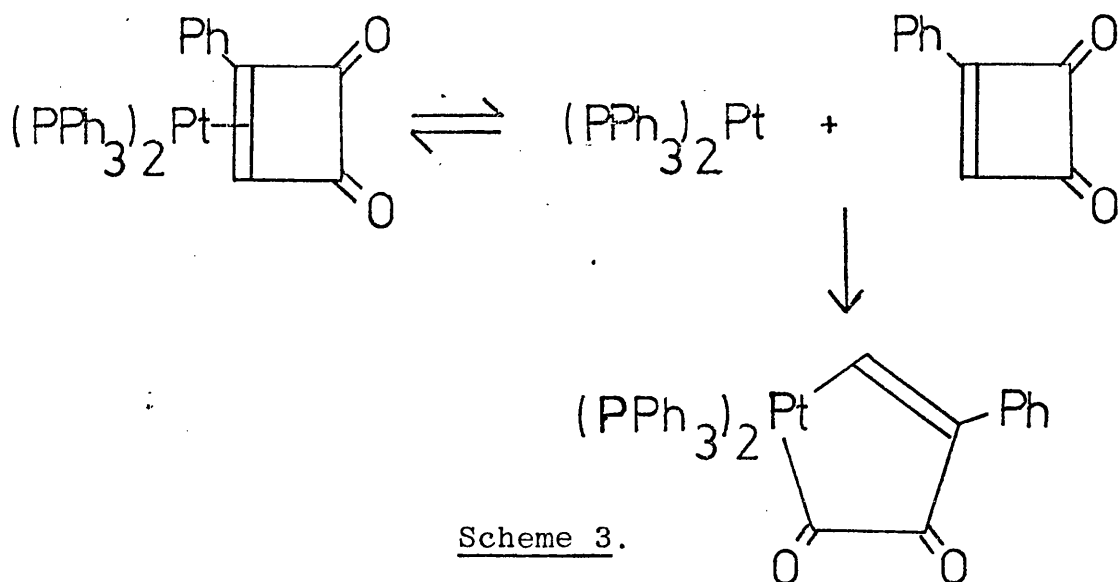
	$\Delta H^\ddagger / \text{kJ mol}^{-1}$	$\Delta S^\ddagger / \text{JK}^{-1} \text{mol}^{-1}$
chloroform	98 ± 4	-3 ± 13
benzene	138 ± 7	$+122 \pm 25$

* Calculated as previously described on Page 184.

If the mechanism were intramolecular, then one would expect an activation entropy (ΔS^\ddagger) to be close to zero. This would appear to be the case in the solvent chloroform in which ΔS^\ddagger is zero within experimental uncertainty. However, in benzene solution ΔS^\ddagger is markedly positive, suggesting a dissociative mechanism. We may now make an hypothesis about the mechanism in the various solvents. In chloroform, the Pt(PPh₃)₂ species is not lost from the alkene complex, but simply moves within the molecule, rearranging to give the ring-expanded species.

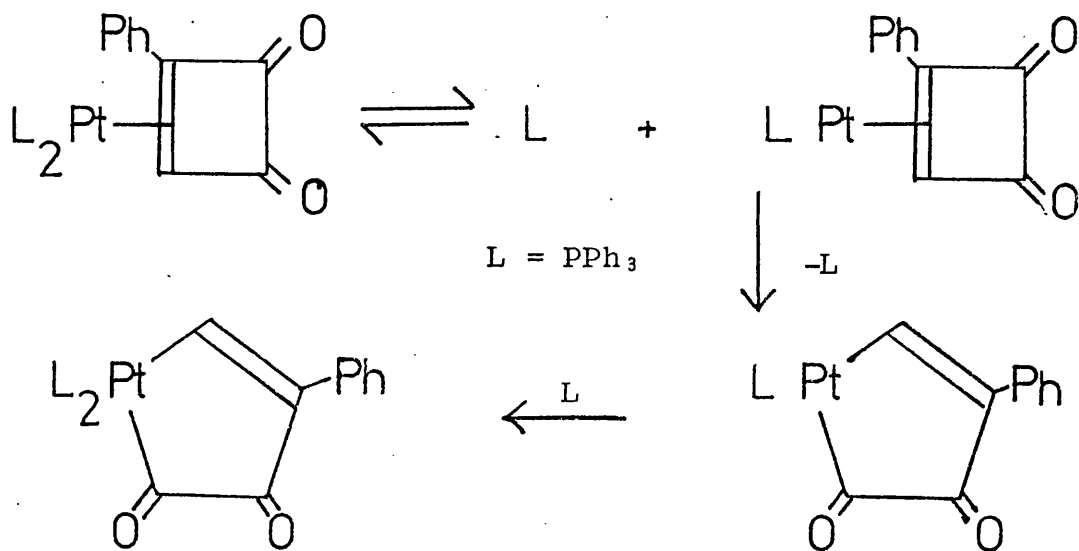
For the apparently dissociative mechanism in benzene solution there are two possibilities:

- (a) rate-determining loss of Pt(PPh₃)₂ from the alkene complex, followed by rapid insertion of the species into a carbon-carbon σ -bond of the cyclobutenedione ring (Scheme 3)

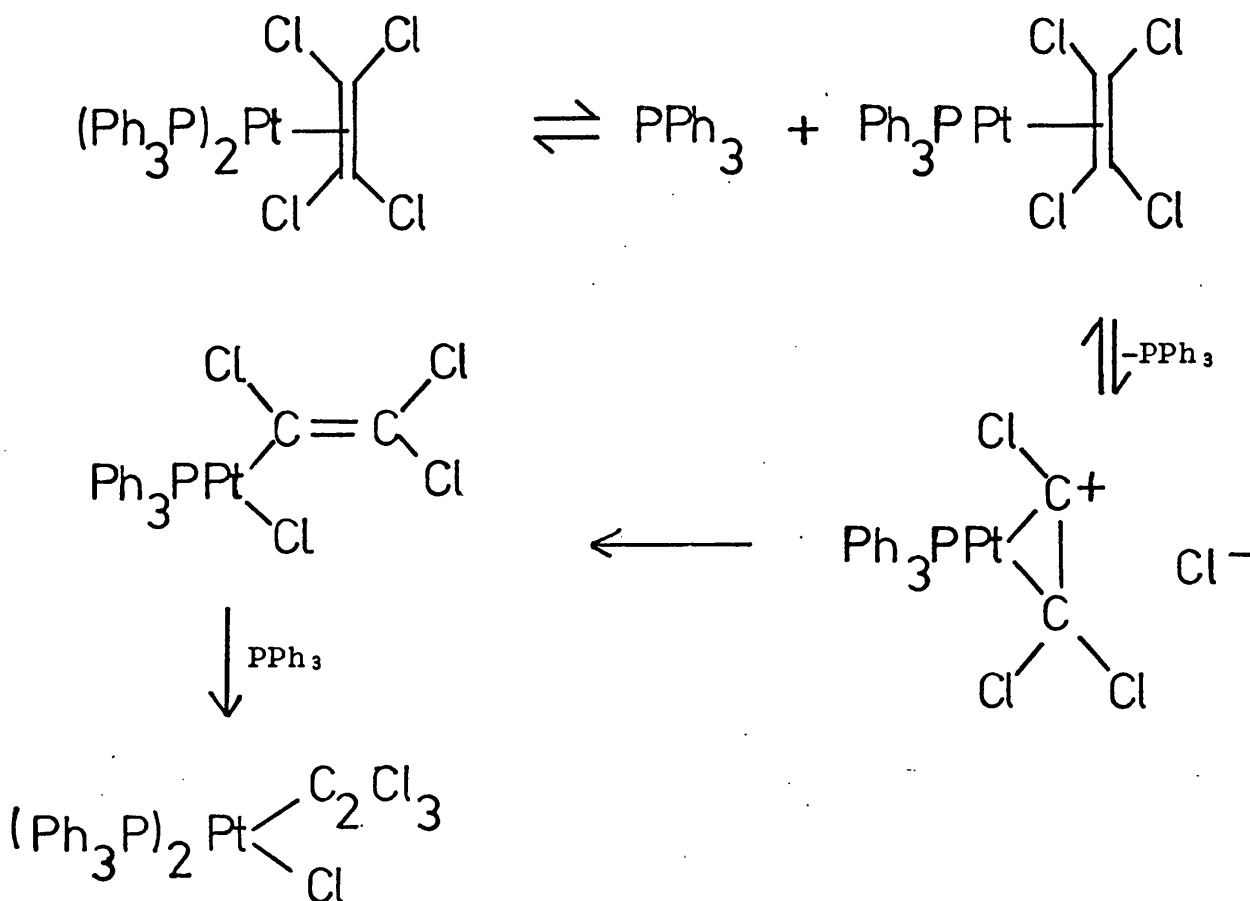


Such dissociation of $\text{Pt}(\text{PPh}_3)_2$ from a platinum(0) alkene complex has often been suggested, and in one case the dissociation constant of the complex $\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$ had been determined as $3.0 \times 10^{-3} \text{ M}$ (68JA4491). Recently, however, an interpretation of spectrophotometric evidence has suggested very little dissociation for this complex (72JA2669). Precedent for the insertion of platinum(0) into a carbon-carbon σ -bond has also been reported in the reaction of $\text{Pt}(\text{PPh}_3)_4$ with 1,1,2,2-tetracyanocyclopropane (74JO(70)133, 74JO(65)407),

- (b) loss of one PPh_3 unit, rapid rearrangement of the remainder of the complex followed by recombination of the PPh_3 to the ring-expanded system (Scheme 4)



This mechanism has a precedent in the reported isomerisation of the alkene complex $\text{Pt}(\text{C}_2\text{Cl}_4)(\text{PPh}_3)_2$ to the vinyl complex $\text{Pt}(\text{Cl})(\text{ClC}=\text{CCl}_2)(\text{PPh}_3)_2$ in benzene (68JO(15)217). In this case, the isomerisation is thought to proceed as in Scheme 5.



Scheme 5.

Bearing in mind the controversy surrounding the postulate of the monomeric $\text{Pt}(\text{Ph}_3\text{P})_2$ moiety, the author, in balance, prefers the mechanism in Scheme 3 over that in Scheme 4.

The suggestion of a difference in mechanism in different solvents also has a precedent in the isomerisation of $\text{Pt}(\text{CCl}_2=\text{CCl}_2)(\text{PPh}_3)_2$ to the vinyl derivative $\text{Pt}(\text{Cl})(\text{CCl}=\text{CCl}_2)(\text{PPh}_3)_2$ wherein the mechanism is thought

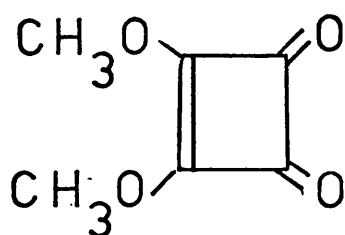
to be different in benzene than in other solvents, proceeding as in Scheme 5. In solvents other than benzene, an intramolecular mechanism is envisaged, with no loss of PPh_3 . In this case, the difference in mechanism is attributed to the specially favourable solvation of triphenylphosphine by benzene, encouraging reversible loss of triphenylphosphine from the $\text{Pt}(\text{CCl}_2=\text{CCl}_2)(\text{PPh}_3)_2$. Attack by chloride in the vacant site then becomes possible before recombination of the PPh_3 species. It may be possible, however, that the solvation effect of benzene in the case of $\text{Pt}(\text{C}_2\text{Cl}_4)(\text{PPh}_3)_2$ may promote the loss of $\text{Pt}(\text{PPh}_3)_2$ rather than the simple PPh_3 unit, and make the mechanism similar to the present case, with the slight difference that the reactive $\text{Pt}(\text{PPh}_3)_2$ unit thereafter cleaves a carbon-chlorine bond rather than a carbon-carbon σ -bond. This particular hypothesis seems a little unlikely when one considers the strength of the platinum-olefin bonding in this compound, and also that no values of the dissociation of the Cl^- from the molecule $\text{Cl}_2\text{C}=\text{CCl}_2$ in solution have ever been reported (75MI4).

In either case it may be suggested that the favourable solvation by benzene of the PPh_3 portions of the complex results in ease of dissociation and thereby rearrangement by a dissociative mechanism. In chloroform solution, however, no such favourable solvation occurs, and the mechanism is intramolecular wherein the $\text{Pt}(\text{PPh}_3)_2$ species never leaves the complex, but simply inserts into the carbon-carbon bond in a concerted fashion. The chemical

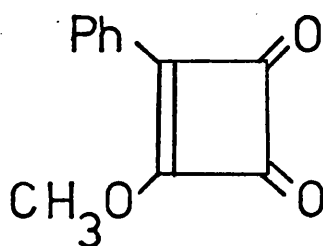
and electronic factors which may influence this insertion have been discussed in a previous chapter.

4. Reaction of platinum(0) complexes with other cyclobutenediones.

The reaction of 1,2-dimethoxycyclobut-1-ene-3,4-dione (5) and 1-methoxy-2-phenylcyclobut-1-ene-3,4-dione (6)



(5)



(6)

with $\text{Pt}(\text{PPh}_3)_2(\text{tolan})$ both yield the platinacyclopentene derivative (2), and it has proved impossible to isolate, or even detect, an alkene intermediate in these reactions. The kinetic pattern was again found to be first-order, and the rate constants at 298K in chloroform solution are given in Table 5 (which also contains the first-order rate constants for the benzo- and phenyl-cyclobutenedione reactions for comparison).

TABLE 5

First-order rate constants ($10^4 k_{\text{obs}}/\text{s}^{-1}$) for the reactions of $\text{Pt}(\text{PPh}_3)_2(\text{tolan})$ with various cyclobutenediones. All constants are for chloroform solutions at 298K.

cyclobut-1-ene-3,4-dione			
1,2-benzo	1-phenyl	1-methoxy-2-phenyl	1,2-dimethoxy
4.5	3.2*	5.1*	3.3*

* Quoted for a 2 x excess of dione over platinum (0) complex.

The similarity of these rate constants is consistent with the rate-determining dissociation of the tolan in each case.

5. Extension of the study to include the rearrangement of $\text{Pt}(\text{AsPh}_3)_2(\text{phenylcyclobutenedione})$.

It was known that the arsine analogue of (4) also undergoes oxidative rearrangement to the arsine analogue of (2), and it was decided to extend the study to this system in order to see if there was evidence for a similar difference in mechanism dependent on solvent, and also to investigate the relative reactivities of $\text{Pt}(\text{PPh}_3)_2$ and $\text{Pt}(\text{AsPh}_3)_2$, little work on which has previously been reported.

The kinetics of the rearrangement of $\text{Pt}(\text{AsPh}_3)_2(\text{phenylcyclobutenedione})$ in chloroform and benzene was again first-order over several half-lives, and the first-order rate constants are reported in Table 6. Activation parameters (calculated as previously described) are reported in Table 7.

Sadly, the reproducibility of the rate constants for the rearrangement of this bis-arsine complex is much less satisfactory than for the bis-phosphine complex. The uncertainties in the calculated activation parameters are too great for a rigorous mechanistic conclusion to be drawn. However, the large negative entropy values indicate that a different mechanism may be operating, and that it may be similar in both solvents.

TABLE 6

Observed first-order rate constants (k) for the redox isomerisation of $\text{Pt}(\text{AsPh}_3)_2(\text{phenylcyclobutenedione})$.

Initial [complex] = $10^{-2} \text{ mol dm}^{-3}$.

chloroform*		benzene†	
T/K	$10^5 \underline{k}/\text{s}^{-1}$	T/K	$10^5 \underline{k}/\text{s}^{-1}$
292.8	1.5	292.8	3.3
298.0	3.6	298.0	2.0
298.4	2.6	298.4	1.9
298.5	2.0	298.5	0.8
299.0	3.9	299.0	2.5
300.2	9.2	300.2	7.0
301.9	4.4	301.9	6.8
302.4	8.5	302.4	6.3
303.0	7.6	303.0	4.8
303.0	8.2	303.0	4.7
303.5	6.7	303.5	5.2
306.0	4.8	306.0	8.2
307.9	10.2	307.9	6.9
308.0	8.4	308.5	5.9
308.5	9.7	308.5	5.1
308.5	7.9	313.0	6.4
313.0	10.8	316.4	12.8
313.2	11.6	318.1	9.9
316.4	24.2		
318.1	15.3		

* Plotted on Graph 3.

† Plotted on Graph 4.

TABLE 7

Activation parameters* for the isomerisation of Pt(AsPh₃)₂(phenylcyclobutenedione) in chloroform and benzene. Uncertainties cited are for the 90% confidence limits.

	$\Delta H^\ddagger / \text{kJ mol}^{-1}$	$\Delta S^\ddagger / \text{JK}^{-1} \text{mol}^{-1}$
chloroform	67 ± 9	-104 ± 31
benzene	53 ± 15	-154 ± 50

* Calculated as previously described on Page 184.

The indications of a highly associated mechanism given by the activation entropy values, together with the poor reproducibility of the rate constants, may lead us to conclude that the explanation is due to some inherent factor in the Pt(AsPh₃)₂ moiety which does not occur in the Pt(PPh₃)₂ species. It may also be seen that the variations in rate constants seem to be greatest at the lower temperatures used in the study. This state of affairs has been found previously in work carried out with platinum-arsine complexes (74MI1). It may be possible that Pt(AsPh₃)₂(cyclobutenedione) is completely dissociated in solution, and that the Pt(AsPh₃)₂ units polymerise in solution to various degrees depending on the conditions of light and storage temperature (which, in experiments so far carried out, were variable). At lower temperatures of reaction, the range of polymers may be at a maximum, accounting for the maximum lack of reproducibility. The polymers may not be so strongly bound together as to

prohibit further reaction with the dione, which then occurs at different rates depending on the various polymer units present in solution. The proposal that $\text{Pt}(\text{AsPh}_3)_2(\text{cyclobutenedione})$ is totally dissociated was tested by plotting a graph of concentration of complex against the optical density of the solution (monitored at 427 nm)(Graph 5). The plot gave a straight line, indicating the possibility of total dissociation. If the hypothesis of total dissociation is correct, and that the degree of polymerisation is a function of temperature and light (which may vary), then both the negative ΔS^\ddagger and lack of reproducibility are accounted for.

The lack of any corroborative evidence for the above hypothesis in the literature, or of any information as to the solution characteristics of $\text{Pt}(\text{AsPh}_3)_2$ would appear to be a serious omission in the chemistry of platinum(0), and the indications are that this chemistry could prove both novel and exciting. Further work on this topic is now in progress.

6. Experimental.

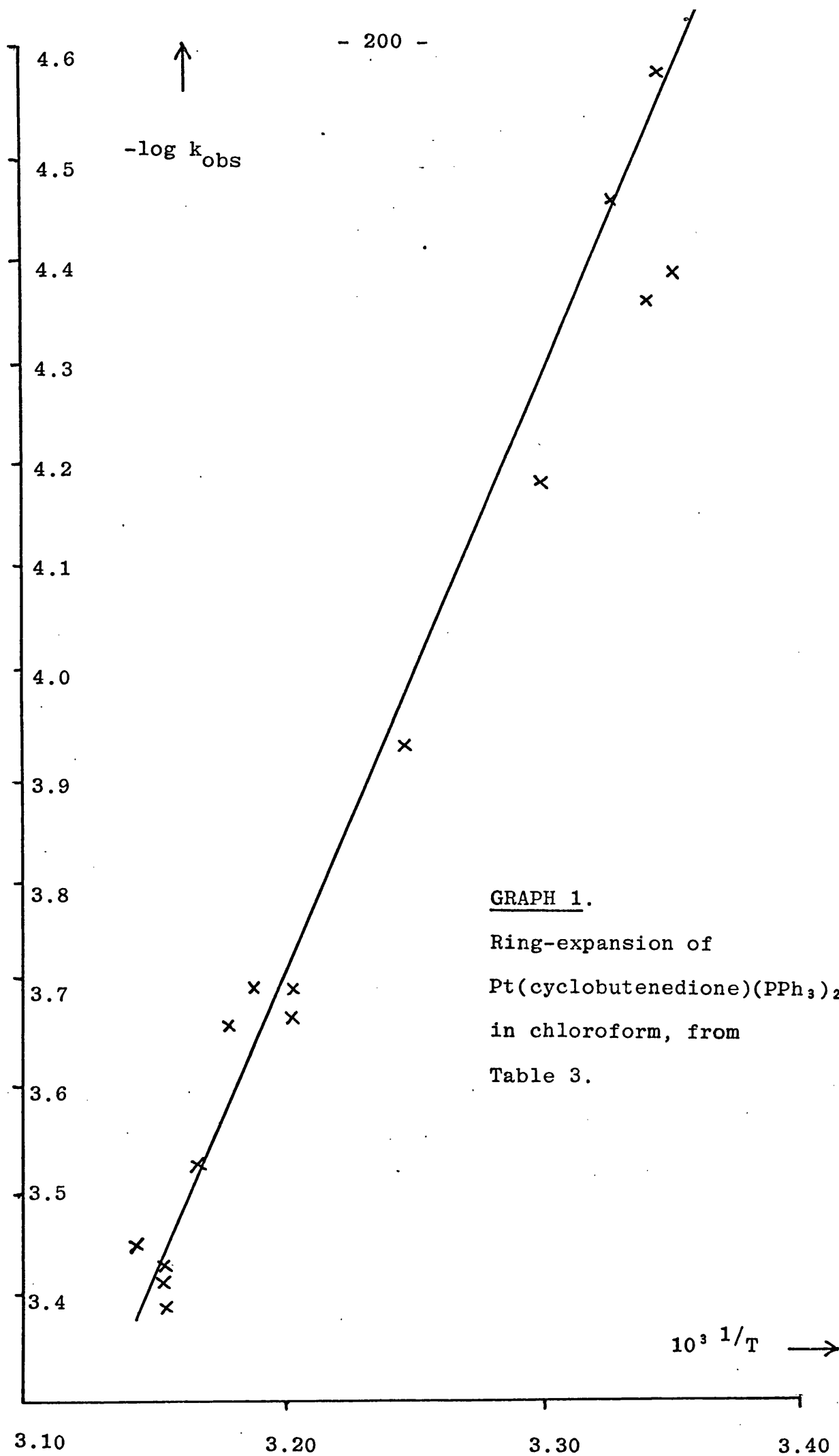
(a) Chemicals.

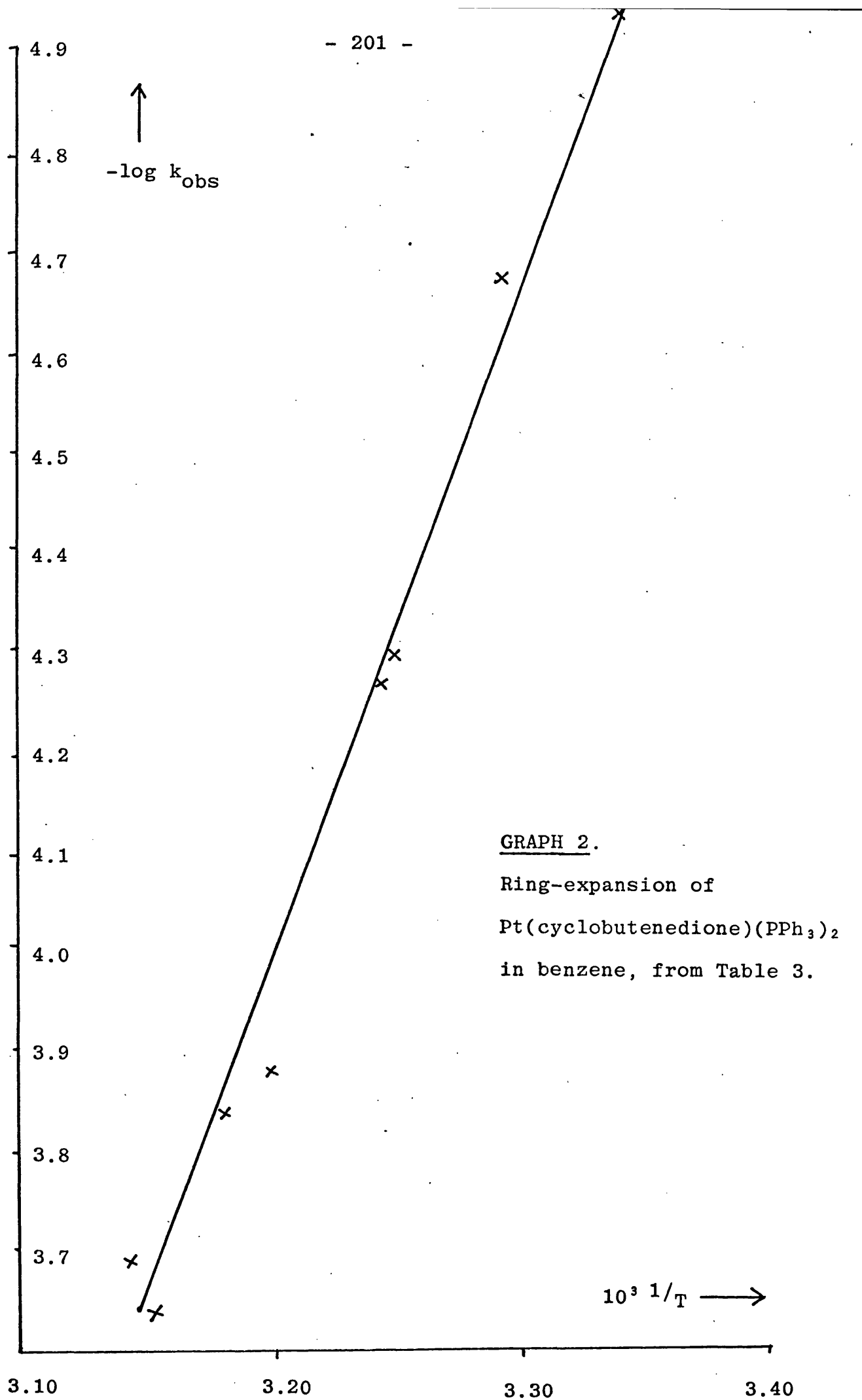
All chemicals were prepared as described elsewhere in this thesis.

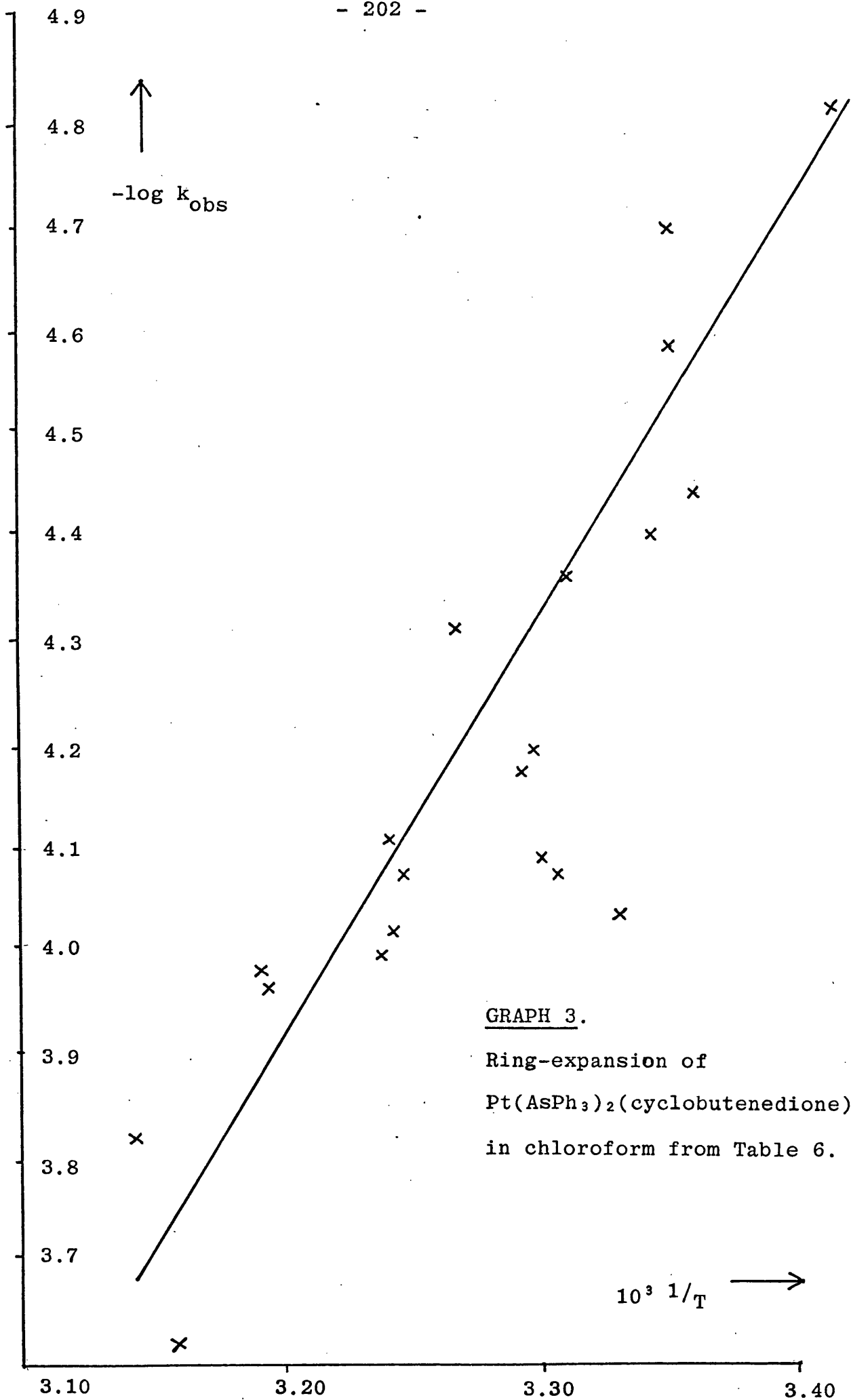
(b) Kinetics.

The kinetic runs were carried out in 1 cm silica cells in the thermostatted cell compartment of a Unicam SP800A recording spectrophotometer; optical densities were monitored at 523 nm for the benzocyclobutenedione reactions, and at 490 nm for all the others. Rate constants

and thence activation parameters were computed using the PDP11 computer by use of a standard least-mean-squares programme. Values for ΔH^\ddagger , ΔG^\ddagger and ΔS^\ddagger were calculated as previously cited in the text.

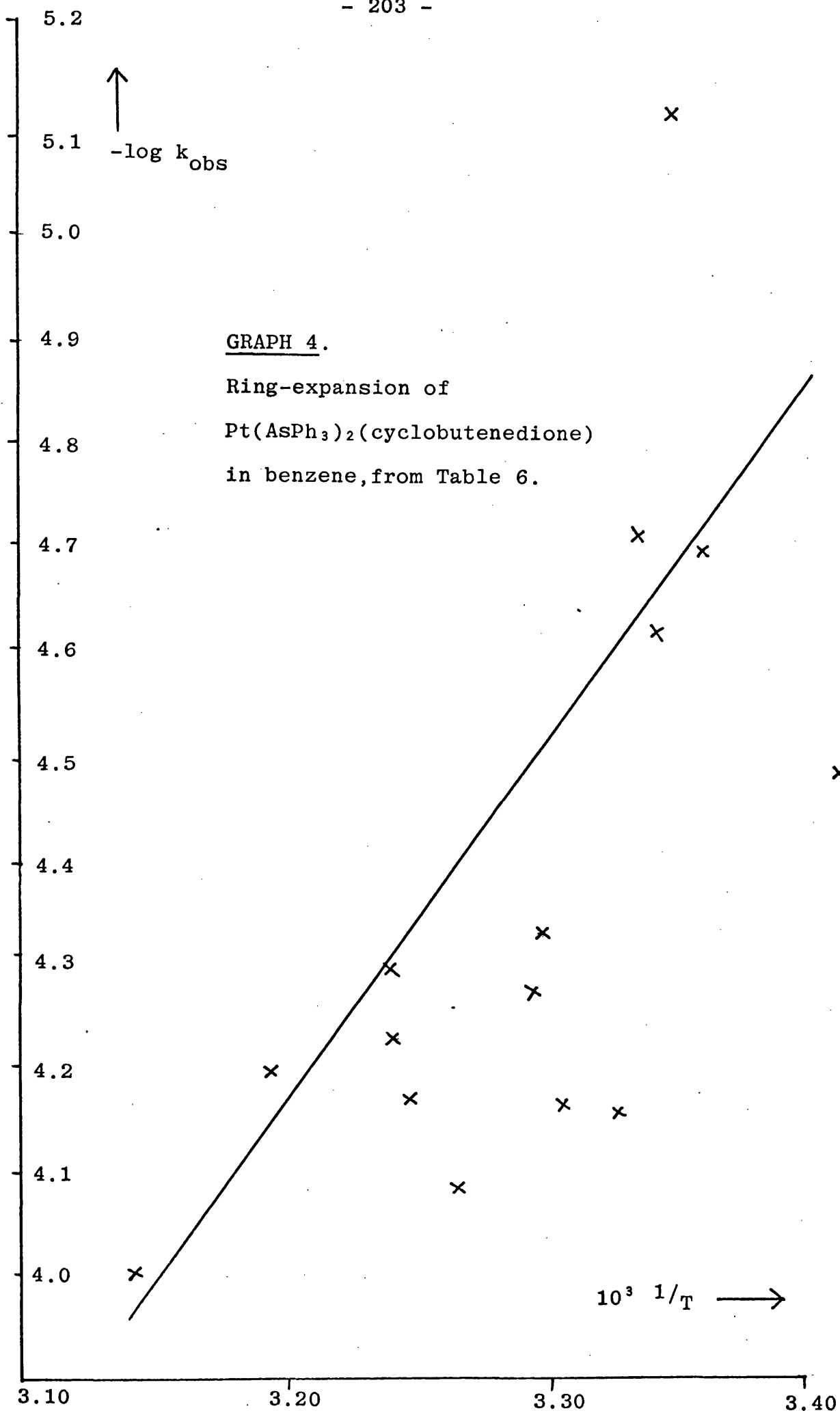


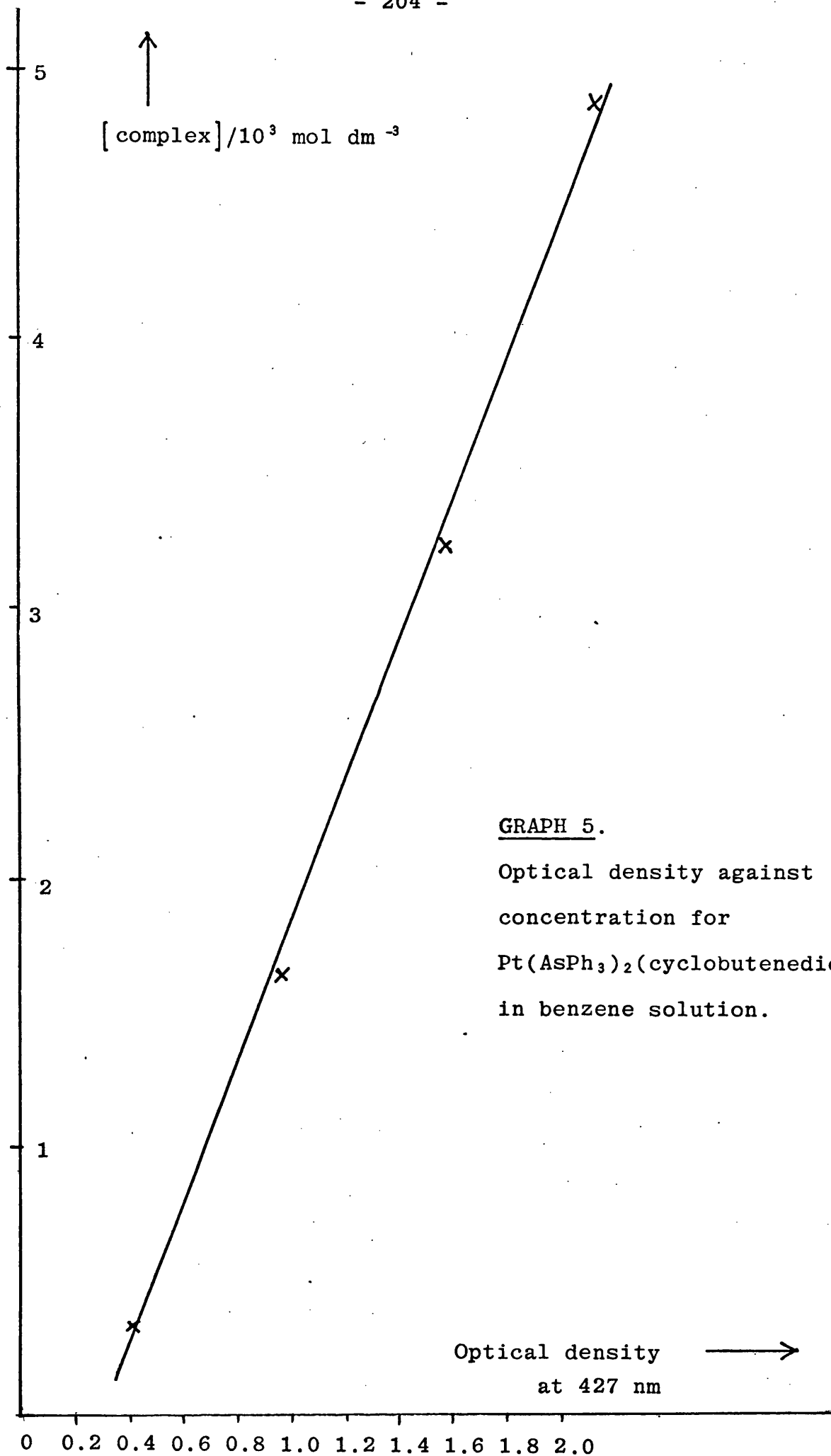




GRAPH 3.

Ring-expansion of
 $\text{Pt}(\text{AsPh}_3)_2(\text{cyclobutenedione})$
in chloroform from Table 6.





GRAPH 5.

Optical density against
concentration for
 $\text{Pt}(\text{AsPh}_3)_2(\text{cyclobutenedione})$
in benzene solution.

CHAPTER 4.

EXPERIMENTAL.

SECTION 1

THE REACTIONS OF LOW-VALENT TRANSITION
METAL COMPLEXES WITH DERIVATIVES OF
CYCLOBUT-1-ENE-2,3-DIONE.

(A) Platinum(0)

(i) Trans-stilbenebis(triphenylphosphine)platinum(0)
Pt(PPh₃)₂(trans-stilbene)

(1) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1-phenylcyclobut-1-ene-3,4-dione (diethyl ether
solvent)

0.45g (0.5 mmol) of $\text{Pt}(\text{PPh}_3)_2$ (trans-stilbene) and 0.14g (0.88 mmol) ligand were stirred as a suspension in dry degassed diethyl ether at room temperature under an atmosphere of dry nitrogen for 15 minutes. The resulting yellow compound was filtered, washed with ether and dried in vacuo.

Yield 0.33g (75.7%)

M.p. 140-141°C

Analysis For $\text{C}_{46}\text{H}_{36}\text{O}_2\text{P}_2\text{Pt}$

	%C	%H	M.W.
CALC	62.94	4.14	877.8
FOUND	62.84	4.54	874.0

Infrared spectrum (cm^{-1})

1723vs, 1595w, 1590w, 1582w, 1498m, 1480sh, 1436vs,
 1310w, 1184w, 1160w, 1096vs, 1078s, 1030m, 1000m, 990w,
 856w, 770msh, 752vs, 700vs, 660m, 546vs, 530vs, 512vs.

^1H n.m.r. spectrum

Observed in CDCl_3 solution: a multiplet centred at 7.07 δ and a triplet at 4.57 δ with ^{195}Pt satellites.

Relative intensities 35:1. $J(\text{Pt}-\text{H})=48.8$ Hz;

$J(\text{P}-\text{H})=6.7$ Hz. The apparent triplet spectrum arises

due to an ABX system ($\text{A}=\text{B}=\text{P}$; $\text{X}=\text{H}$), in which $J(\text{AB}) \gg |J(\text{AX}) -$

$J(\text{BX})|$. Observed $J=\frac{1}{2}|J(\text{AX})+J(\text{BX})|$. This is confirmed

by the ^{31}P spectrum (proton decoupled).

^{31}P n.m.r. spectrum (external $\text{P}(\text{OMe})_3$ as standard)

Observed in CH_2Cl_2 solution: An AB quartet system

$\delta_{\text{A}} = +114.7$ p.p.m.; $\delta_{\text{B}} = +112.4$ p.p.m.; $J(\text{P}_{\text{A}}\text{P}_{\text{B}}) = 34$ Hz

$J(\text{PtP}_{\text{A}}) = 4194$ Hz; $J(\text{PtP}_{\text{B}}) = 4072$ Hz.

(2) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1-phenylcyclobut-1-ene-3,4-dione (chloroform
solvent)

0.45 g (0.5 mmol) $\text{Pt}(\text{PPh}_3)_2$ (trans-stilbene) and 0.14g (0.88 mmol) ligand were dissolved in 20 cm³ of dry degassed chloroform and stirred at 30°C in an atmosphere of dry nitrogen for 24 hours. The resulting red solution was reduced in bulk and dry diethyl ether added to the cloud point. The red product which crystallised was filtered off and dried in vacuo.

Yield 0.38g (87.2%)

M.p. 203.0-203.2°C

Analysis For $\text{C}_{46}\text{H}_{36}\text{O}_2\text{P}_2\text{Pt}$

	%C	%H	M.W.
CALC	62.94	4.14	877.8
FOUND	63.17	4.37	941.0

Infrared spectrum (cm⁻¹)

1679vs, 1667sh, 1658vs, 1586w, 1572w, 1530m, 1480s, 1438vs, 1328w, 1308w, 1210w, 1184w, 1163w, 1098vs, 1074w, 1030m, 1002m, 930m, 916m, 896w, 850m, 786m, 752s, 700vs, 626w, 606w, 538vs, 530vs, 516vs, 502vs.

¹H n.m.r. spectrum

Observed in CDCl_3 solution: a multiplet centred at 7.27δ and a doublet of doublets at 9.20δ with ¹⁹⁵Pt satellites. Relative intensities 35:1. ³J(P-H) = 17.0 Hz (trans-P); ³J(P-H) = 8.5 Hz (cis-P); ²J(Pt-H) = 21.5 Hz.

(3) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1-methyl-2-phenylcyclobut-1-ene-3,4-dione.

0.45g (0.5 mmol) Pt(PPh₃)₂(trans-stilbene) and
0.09g (0.53 mmol) ligand were stirred together in dry
degassed diethyl ether at room temperature under an
atmosphere of dry nitrogen for 15 minutes. The resulting
fine yellow crystals were filtered and dried in vacuo.

Yield 0.41g (91.9%)

M.p. 148-149°C

Analysis For C₄₇H₃₈O₂P₂Pt

	%C	%H	M.W.
CALC	63.36	4.30	892.0
FOUND	63.01	4.51	890.0

Infrared spectrum (cm⁻¹)

1736vs, 1721vs, 1692vs, 1596w, 1590w, 1574w, 1496w,
1480vs, 1432vs, 1330w, 1310m, 1182m, 1160m, 1120m, 1096vs,
1072m, 1028s, 1000m, 970m, 856w, 768s, 750vs, 700vs,
624w, 578w, 540vs, 520vs, 510sh.

¹H n.m.r. spectrum

Observed in CDCl₃ solution: a multiplet centred at
6.91δ and a doublet of doublets at 1.48δ with ¹⁹⁵Pt
satellites. Relative intensities 35:3. ³J(Pt-CH₃)=
11.5 Hz; ⁴J(P-CH₃)=5.6 Hz (trans-P); ⁴J(P-CH₃)=4.5 Hz
(cis-P).

(4) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1-chloro-2-phenylcyclobut-1-ene-3,4-dione.

0.45g (0.5 mmol) Pt(PPh₃)₂(trans-stilbene) and 0.10 g (0.52 mmol) of ligand were stirred in diethyl ether as previously described. The yellow crystals resulting were filtered and dried in vacuo.

Yield 0.405g (88.8%)

M.p. 165.0°C (decomp)

Analysis For C₄₆H₃₅O₂P₂PtCl

	%C	%H	%Cl	M.W.
CALC	60.56	3.87	3.89	912.0
FOUND	59.60	3.89	3.75	894.0

Infrared spectrum (cm⁻¹)

1758msh, 1732vs, 1712bvs, 1643m, 1587w, 1576w, 1500w, 1482m, 1438vs, 1310w, 1180w, 1152bw, 1096s, 1030w, 1000m, 980w, 872w, 850w, 804w, 770sh, 763sh, 750vs, 712sh, 704vs, 672w, 624w, 594w, 542vs, 524vs, 513vs, 506vs, 506s, 496sh.

(5) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1-methoxy-2-phenylcyclobut-1-ene-3,4-dione.

0.45g (0.5 mmol) Pt(PPh₃)₂(trans-stilbene) and 0.10g (0.53 mmol) ligand were stirred in dry diethyl ether as before. The reaction was allowed to proceed for 45 minutes, when the orange-yellow crystals were filtered and dried in vacuo.

Yield 0.38g (83.7%)

M.p. 168-169°C

Analysis For C₄₇H₃₈O₃P₂Pt

	%C	%H	M.W.
CALC	62.19	4.22	908.0
FOUND	61.71	4.22	894.0

Infrared spectrum (cm⁻¹)

1682sh, 1658sh, 1650vs, 1600s, 1586m, 1576w, 1515vs, 1433vs, 1380s, 1365s, 1316sh, 1304s, 1273m, 1210vs, 1192m, 1168w, 1182m, 1130vs, 1102vs, 1096vs, 1072w, 1030m, 1000m, 970vs, 952vs, 920s, 882s, 820w, 810w, 768sh, 755sh, 745vs, 700b vs, 645s, 628m, 616m, 540vs, 528vs, 513vs, 505vs, 470m.

¹H n.m.r. spectrum

Observed in CDCl₃ solution: a multiplet centred at 7.17δ and a broad singlet at 2.75δ. No coupling could be seen in this complex probably due to the distance between proton and ¹⁹⁵Pt or ³¹P. However, the broadening of the singlet suggests that some coupling is occurring, but is difficult to resolve.

(6) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1,2-diphenylcyclobut-1-ene-3,4-dione

0.45 g (0.5 mmol) $\text{Pt}(\text{PPh}_3)_2$ (trans-stilbene) and 0.12g (0.51 mmol) ligand were stirred in dry diethyl ether as previously described. The resulting yellow crystals were filtered and dried in vacuo.

Yield 0.44g (93.3%)

M.p. 161-164°C (decomp)

Analysis For $\text{C}_{52}\text{H}_{46}\text{O}_2\text{P}_2\text{Pt}$

	%C	%H	M.W.
CALC	65.47	4.23	954.0
FOUND	64.96	4.48	924.0

Infrared spectrum (cm^{-1})

1744sh, 1708vs, 1678sh, 1600m, 1587m, 1576s, 1500s,
1480vs, 1448s, 1436vs, 1310m, 1261w, 1182m, 1160m, 1096vs,
1080s, 1030m, 1000s, 958w, 832w, 790m, 772m, 744vs, 730vs,
722vs, 680bvs, 636s, 606s, 576s, 521vs, 505vs, 498vs,
480vs.

(7) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1,2-dimethoxycyclobut-1-ene-3,4-dione.

0.45g (0.5 mmol) Pt(PPh₃)₂(trans-stilbene) and
0.08g (0.56 mmol) ligand were stirred in diethyl ether
under the same conditions as previously described.
A red crystalline complex was formed after only 15
seconds. This was filtered and dried in vacuo.

Yield 0.41g (95.1%)

M.p. 173-174°C

Analysis For C₄₂H₃₆O₄P₂Pt

	%C	%H	M.W.
CALC	58.54	4.16	862.0
FOUND	58.03	4.07	872.0

Infrared spectrum (cm⁻¹)

1660sh, 1652vs, 1590w, 1572w, 1510vs, 1484vs, 1441vs,
1313m, 1204s, 1188s, 1096vs, 1080vs, 1032w, 996w,
938s, 890w, 832m, 752s, 744s, 736s, 730s, 698vs, 688vs,
528vs, 514vs, 500sh.

¹H n.m.r. spectrum

Observed in CDCl₃ solution: a multiplet at 7.31δ and
two broad singlets at 3.70 and 3.25δ. Intensities
30:3:3. The higher-field singlet was broadened more than
the signal at 3.70δ. The broadening is probably due to
coupling effects from ³¹P and ¹⁹⁵Pt but not resolvable
due to the distances involved. The high-field signal
is probably due to the protons of the methoxy-group
next to the platinum, the ¹⁹⁵Pt 'coupling' broadening
this signal more than the more distant methoxy group
signal. (See text for full details.)

(8) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1,2-diethoxycyclobut-1-ene-3,4-dione.

0.45g (0.5 mmol) Pt(PPh₃)₂(trans-stilbene) and 0.09g (0.53 mmol) ligand were stirred in diethyl ether as in (7). Immediately the solids dissolved and after 10 minutes, orange crystals had precipitated out. These were collected and dried in vacuo.

Yield 0.35g (77.8%)

M.p. 142-144°C

Analysis For C₄₄H₄₀O₄P₂Pt

	%C	%H	%P
CALC	59.42	4.53	6.97
FOUND	59.58	4.54	6.73

Infrared spectrum (cm⁻¹)

1647b vs, 1591w, 1575w, 1480b vs, 1435vs, 1307s, 1191vs, 1163s, 1145sh, 1110m, 1096vs, 1060vs, 970vs, 883w, 875m, 850w, 835m, 760vs, 750vs, 707b vs, 638m, 590w, 540vs, 530vs, 512vs, 504vs, 462w.

¹H n.m.r. spectrum

Observed in CDCl₃ solution: a multiplet at 7.12δ, a multiplet at 3.87δ and two triplets at 1.18 and 0.3δ. Relative intensities 30:4:3:3. Under higher resolution the multiplet at 3.87δ was seen to be two quartets overlapping. No ³¹P or ¹⁹⁵Pt coupling was observed in this compound and all signals were sharp and did not appear broadened.

(9) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1,2-dimethylcyclobut-1-ene-3,4-dione.

0.45g (0.5 mmol) Pt(PPh₃)₂(trans-stilbene) and 0.055g (0.5 mmol) ligand were stirred in diethyl ether as for the previous reactions. This reaction was allowed to proceed for 24 hours. The golden crystals which formed were filtered and dried in vacuo.

Yield 0.32g (77.10%)

M.p. 153-157°C

Analysis For C₄₂H₃₆O₂P₂Pt

	%C	%H	%P
CALC	55.82	4.01	6.85
FOUND	55.51	4.32	6.89

Infrared spectrum (cm⁻¹)

1724sh, 1712vs, 1584w, 1568w, 1492m, 1480m, 1431s, 1238w, 1110sh, 1094vs, 1030sh, 989m, 976m, 968m, 764s, 746s, 696vs, 545m, 526vs, 513vs, 500s, 488w, 444w, 424w.

¹H n.m.r. spectrum

Observed in benzene solution: a multiplet centred at 7.10δ and a multiplet at 1.64δ. Relative intensities 30:6. At wider sweep, the multiplet at 1.64δ was seen to be a doublet of doublets with ¹⁹⁵Pt satellites.

This pattern was indicative of an olefin complex in which the two trans-(P-CH₃) are equal and the two cis-(P-CH₃) are equal and non-zero. The inequivalent -CH₃ groups were labelled A and B, the two phosphorus atoms labelled 1 and 2, and the couplings assigned as follows:

trans- ⁴J(P₁-CH₃(B)) = trans ⁴J(P₂-CH₃(A)) = 5.37 Hz

cis- ⁴J(P₁-CH₃(A)) = cis- ⁴J(P₂-CH₃(B)) = 2.16 Hz

³J(Pt-CH₃(A)) = ³J(Pt-CH₃(B)) = 16.71 Hz

(10) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1,2-di-n-butoxycyclobut-1-ene-3,4-dione.

0.45g (0.5 mmol) Pt(PPh₃)₂(trans-stilbene) and
0.13 g (0.58 mmol) ligand reacted in diethyl ether as
before. After 20 minutes a canary yellow crystalline
product was isolated and dried in vacuo.

Yield 0.23g (50.9%)

M.p. 147-148°C

Analysis For C₄₈H₄₈O₄P₂Pt

	%C	%H	%P
CALC	60.95	5.11	6.54
FOUND	60.88	5.02	6.42

Infrared spectrum (cm⁻¹)

1662sh, 1658b vs, 1586w, 1564m, 1492vs, 1436vs, 1386m,
1364m, 1280m, 1264w sh, 1176s, 1160sh, 1096vs, 1088s,
1030w, 9803, 960w, 880w, 847w, 748s, 710sh, 696vs,
636w, 624w, 588w, 535vs, 526vs, 516vs, 500vs, 460w,
440w, 424w.

¹H n.m.r. spectrum

Observed in CDCl₃ solution: a triplet centred at 3.97δ,
a triplet centred at 3.78δ and a complex multiplet between
1.86δ and 0.53δ. The phenyl ring-protons constituted
another multiplet centred at 7.24δ. The relative
intensities were 3:14:30. The signals were assigned
as follows:

Two triplets to the -OCH₂ protons (4H) and the complex
multiplet to the other portion of the C₄H₉O chains.

No(³¹P-H) or (¹⁹⁵P-H) coupling was observed.

11) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1-bromo-2-phenylcyclobut-1-ene-3,4-dione.

0.45g (0.5 mmol) Pt(PPh₃)₂(trans-stilbene) and
0.12g (0.51 mmol) ligand reacted in ether as before.
After two hours the yellow crystals were collected
by filtration and dried in vacuo.

Yield 0.20g (42.0%)

M.p. 138-141°C (decomp)

Analysis For C₄₆H₃₅O₂P₂PtBr

	%C	%H
CALC	57.73	3.69
FOUND	57.36	3.87

Infrared spectrum (cm⁻¹)

1750sh, 1728bvs, 1600w, 1590w, 1586w, 1500w, 1452vs,
1438vs, 1366vs, 1312w, 1185w, 1160w, 1096vs, 1078sh,
1022m, 1000m, 990sh, 881m, 849m, 828w, 804w, 760sh,
748vs, 704bvs, 670w, 660sh, 623w, 588w, 556m, 540sh,
520vs, 496sh, 458m, 428w.

(12) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1,2-dihydroxycyclobut-1-ene-3,4-dione.

0.30g (0.33 mmol) $\text{Pt}(\text{PPh}_3)_2$ (trans-stilbene) and 0.05g (0.44 mmol) ligand reacted in diethyl ether as before. After 30 minutes an orange precipitate was filtered and dried in vacuo.

Yield 0.19g (46.7%)

M.p. 139°C

Analysis For $\text{C}_{76}\text{H}_{60}\text{O}_4\text{Pt}_2\text{P}_4$

	%C	%H	M.W.
CALC	58.84	3.90	1551
FOUND	51.44	3.43	

Infrared spectrum (cm^{-1})

1664m, 1656m, 1544bs, 1496vs, 1480s, 1362s, 1186w,
1160w, 1096vs, 1000w, 880w, 854w, 756s, 750s, 710vs,
698vs, 636m, 624w, 559vs, 535vs, 526vs, 505s, 464w,
452w.

(13) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1-amino-2-methoxycyclobut-1-ene-3,4-dione.

0.45g (0.5 mmol) $\text{Pt}(\text{PPh}_3)_2$ (trans-stilbene) and 0.07g (0.55 mmol) ligand stirred in diethyl ether as previously described. The product was a brown-orange powder and was filtered off after about 30 minutes. The product was dissolved in dry chloroform and diethyl ether added to the cloud point. The flask and contents were stored at 0°C to facilitate crystallisation, but only a dark brown amorphous powder was obtained, which by inspection and preliminary i.r. analysis was not further characterised. Repetition of the reaction using chloroform, benzene and diethyl ether as solvents produced only a similar unsatisfactory product, which was not characterised.

(14) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ benzocyclobutenedione.

0.45g (0.5 mmol) $\text{Pt}(\text{PPh}_3)_2$ (trans-stilbene) and 0.08g (0.51 mmol) ligand reacted in diethyl ether as previously described. After 30 minutes, a red crystalline product was isolated and was dried under vacuum.

Yield 0.33g (77.5%)

M.p. 192°C (decomp)

Infrared spectrum (cm^{-1})

1690vs, 1665vs, 1652sh, 1610sh, 1580vs, 1550m, 1480vs, 1446sh, 1432vs, 1400w, 1368w, 1320w, 1300w, 1268m, 1266w, 1218vw, 1184w, 1160w, 1098vs, 1092sh, 1072w, 1056vw, 1044w, 1038vw, 1000w, 964w, 920vw, 896sh, 886m, 876s, 856w, 775w, 764sh, 756vs, 748vs, 700bvs, 586m, 538vs, 528vs, 512vs, 504vs, 490s.

(15) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1,2-diaminocyclobut-1-ene-3,4-dione.

0.45g(0.5 mmol) $\text{Pt}(\text{PPh}_3)_2$ (trans-stilbene) and 0.06g (0.53 mmol) ligand were stirred together in diethyl ether as before. An orange-buff coloured precipitate began to be apparent through the yellow starting materials. This precipitate was isolated and dried under vacuum. The product proved to be of an unsatisfactory nature on preliminary i.r. evidence, and all efforts to convert it into an identifiable compound subsequently failed.

The reaction was repeated in dry benzene at room temperature with a similar result. The reaction was abandoned.

(16) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1-chloro-2-phenylcyclobut-1-ene-3,4-dione.

0.45g (0.5 mmol) Pt(PPh₃)₂(trans-stilbene) and 0.10g (0.52 mmol) ligand were stirred together in dry degassed chloroform under an atmosphere of dry nitrogen for 24 hours at room temperature. The resulting red solution was reduced in bulk and petroleum ether (b.p. 40-60) was added to the cloud point. The red crystals were carefully recrystallised from chloroform/diethyl ether.

Yield 0.29g (63.0%)

M.p. 189-191°C

Analysis For C₄₆H₃₅O₂P₂PtCl

	%C	%H	%Cl	M.W.
CALC	60.56	3.87	3.89	912
FOUND	59.66	3.90	4.04	-

Infrared spectrum (cm⁻¹)

1656bvs, 1600w, 1588w, 1576w, 1523s, 1480s, 1440vs, 1434sh, 1312w, 1286w, 1272w, 1184w, 1162w, 1098vs, 1088sh, 1030w, 1000w, 958w, 912w, 880s, 775w, 760sh, 752s, 746sh, 708sh, 698vs, 622w, 584vw, 554w, 540vs, 527vs, 514vs, 498vs, 456w, 432w, No peaks below 400 cm⁻¹ were observed.

SECTION 1

THE REACTIONS OF LOW-VALENT TRANSITION
METAL COMPLEXES WITH DERIVATIVES OF
CYCLOBUT-1-ENE-2,3-DIONE.

(A) Platinum(0)

(ii) Tetrakis(triphenylarsine)platinum(0)
Pt(AsPh₃)₄

(1) Tetrakis(triphenylarsine)platinum(0)
+ 1-phenylcyclobut-1-ene-3,4-dione.

0.62g (0.44 mmol) $\text{Pt}(\text{AsPh}_3)_4$ and 0.07g (0.45 mmol) ligand were stirred in degassed dry diethyl ether at room temperature under an atmosphere of dry nitrogen. After 5 minutes the suspension had become canary yellow. The reaction was allowed to proceed for a further ten minutes when the crystalline product was filtered, washed with ether and dried in a vacuum desiccator.

Yield 0.25g (58.8%)

M.p. 116-120°C

Analysis For $\text{C}_{46}\text{H}_{36}\text{As}_2\text{O}_2\text{Pt}$

	%C	%H	M.W.
CALC	57.21	3.76	966
FOUND	56.71	3.82	-

Infrared spectrum (cm^{-1})

1723bvs, 1685sh, 1656sh, 1598w, 1583m, 1505w, 1489s, 1443vs, 1343vw, 1312m, 1279w, 1185m, 1160m, 1120m, 1083vs, 1048m, 1030s, 1008vs, 990m, 914bw, 853bw, 796w, 743vs, 698vs, 680m, 651m.

^1H n.m.r. spectrum

Observed in CDCl_3 solution: a multiplet centred at 7.07 δ and a singlet at 5.00 δ with ^{195}Pt satellites. Relative intensities 35:1. Coupling was assigned as $^2\text{J}(\text{Pt-H}) = 57.5 \text{ Hz}$.

(2) Tetrakis(triphenylarsine)platinum(0)
+ 1-phenylcyclobut-1-ene-3,4-dione.

0.62g (0.44 mmol) Pt(AsPh₃)₄ and 0.07g (0.45 mmol) ligand were stirred together in dry degassed chloroform at room temperature under an atmosphere of dry nitrogen. The solids dissolved giving a yellow solution. The reaction was allowed to proceed for 24 hours, when the solution had changed to a golden orange colour. This solution was reduced to small bulk under reduced pressure and then diethyl ether was added to the cloud point. Crystallisation was allowed to proceed for five days at 0°C. Finally, the fine orange crystals were collected by filtration and dried in vacuo.

Yield 0.20g (47.1%)
M.p. 192-193°C (decomp)
Analysis For C₄₆H₃₆As₂O₂Pt

	%C	%H	M.W.
CALC	57.21	3.76	966
FOUND	56.73	3.87	-

Infrared spectrum (cm⁻¹)

1677vs, 1657vs, 1600w, 1583m, 1533s, 1490vs, 1445vs, 1328m, 1310s, 1291w, 1210w, 1185m, 1160w, 1118w, 1082s, 1030s, 1004s, 978m, 933s, 919s, 893m, 851s, 795s, 742vs, 698vs, 673vs.

¹H n.m.r. spectrum

Observed in CDCl₃ solution: a multiplet centred at 7.05δ and a triplet centred at 9.40δ. Relative intensities 42:1. The 1:4:1 triplet was assigned to ¹⁹⁵Pt-H with ³J(Pt-H) = 21.5 Hz.

(3) Tetrakis(triphenylarsine)platinum(0)
+ 1-chloro-2-phenylcyclobut-1-ene-3,4-dione.

0.6g (0.42 mmol) $\text{Pt}(\text{AsPh}_3)_4$ and 0.08g (0.44 mmol) ligand stirred together in diethyl ether as before. The suspension lightened, and the mixture was left stirring for 24 hours. After this time, the product was filtered. The impure product (by inspection) was dissolved in chloroform and filtered. The solution was then reduced in bulk to about 3 cm³ and dry diethyl ether added to the cloud point. The product was stored at 0°C, leading to the formation of fine yellow crystals which were filtered and dried in vacuo.

Yield 0.12g (28.7%)

M.p. 280-283°C (decomp)

Analysis For $\text{C}_{46}\text{H}_{35}\text{As}_2\text{ClO}_2\text{Pt}$

	%C	%H	M.W.
CALC	55.24	3.53	1000
FOUND	54.65	3.57	-

Infrared spectrum (cm⁻¹)

1751vs, 1730vs, 1718vs, 1601m, 1580m, 1530vs, 1492vs, 1448vs, 1389s, 1348w, 1328w, 1313s, 1260vs, 1180s, 1160m, 1142w, 1090sh, 1088vs, 1034s, 1012vs, 978w, 940bw, 928w, 874s, 834s, 788s, 758vs, 748vs, 740sh, 700vs, 680w, 672m, 472vs, 464sh, 452sh, 392w, 372m, 346vs, 334vs, 305s, 270m, 260s.

(4) Tetrakis(triphenylarsine)platinum(0)
+ 1,2-dimethoxycyclobut-1-ene-3,4-dione.

0.67g (0.47 mmol) $\text{Pt}(\text{AsPh}_3)_4$ and 0.07g (0.5 mmol) ligand were dissolved in dry degassed chloroform (20 cm³). The solution was stirred at room temperature under an atmosphere of dry nitrogen for 2 hours. The resulting red solution was filtered, reduced in bulk and dry diethyl ether was added to the cloud point. Crystallisation was allowed to proceed at 0°C. The resulting red crystals were filtered off and dried in vacuo.

Yield 0.20g (44.7%)

M.p. 181-183°C

Analysis For $\text{C}_{42}\text{H}_{36}\text{As}_2\text{O}_4\text{Pt}$

	%C	%H	M.W.
CALC	53.10	3.82	950
FOUND	53.09	4.03	-

Infrared spectrum (cm⁻¹)

1657vs, 1581m, 1517vs, 1489vs, 1461vs, 1447vs, 1425vs, 1386vs, 1317vs, 1275w, 1204vs, 1189sh, 1157s, 1984vs, 1029s, 1007s, 991s, 951s, 911m, 849s, 757sh, 747vs, 739vs, 698vs, 677w.

¹H n.m.r. spectrum

Observed in CDCl_3 solution: a multiplet centred at 7.10 δ and two singlets at 3.51 δ and 3.90 δ . Relative intensities 30:3:3. No ^{195}Pt satellites were observed, but the higher-field singlet was broadened slightly as in the phosphine analogue (q.v.), indicating that ^{195}Pt 'coupling' may be the main factor involved in the signal broadening in these complexes.

(5) Tetrakis(triphenylarsine)platinum(0)
+ 1-methoxy-2-phenylcyclobut-1-ene-3,4-dione.

0.64g (0.45 mmol) $\text{Pt}(\text{AsPh}_3)_4$ and 0.09g (0.5 mmol) ligand were stirred together in dry degassed diethyl ether in the same way as previously described. The reaction was allowed to proceed for 24 hours, when the suspension had deepened to a dark orange colour. The product was isolated by filtration. Infrared analysis indicated a complicated mixture of products, but attempts to isolate and crystallise a satisfactory product failed, leading only to dark decomposition products which were not characterised.

Repetition of the reaction in chloroform led only to a mixture of decomposition products (which were not characterised).

(6) Tetrakis(triphenylarsine)platinum(0)
+ 1-methyl-2-phenylcyclobut-1-ene-3,4-dione.

0.70g (0.5 mmol) $\text{Pt}(\text{AsPh}_3)_4$ and 0.09g (0.5 mmol) ligand were stirred together in diethyl ether as before. After 24 hours the crude product (by inspection) was filtered off. The yellow solid was dissolved in chloroform and filtered. An equal volume of petroleum ether (b.p. 40-60) was added and the solution refiltered. The filtrate was reduced in bulk, and diethyl ether added to the cloud point. Crystallisation at 0°C afforded yellow crystals, which were collected by filtration and dried in vacuo.

Yield 0.24g (53.5%)

M.p. 129-130 $^\circ\text{C}$ (decomp)

Analysis For $\text{C}_{47}\text{H}_{38}\text{As}_2\text{O}_2\text{Pt}$

	%C	%H	M.W.
CALC	57.62	3.91	980
FOUND	57.05	4.04	-

Infrared spectrum (cm^{-1})

1724vs, 1696m, 1600sh, 1578m, 1500w, 1482vs, 1434vs, 1366sh, 1306m, 1272w, 1188w, 1154w, 1108sh, 1080sh, 1072s, 1026s, 1000m, 976bw, 848w, 810w, 760sh, 752sh, 742vs, 698vs, 672w, 612w, 580w, 484s, 476s.

^1H n.m.r. spectrum

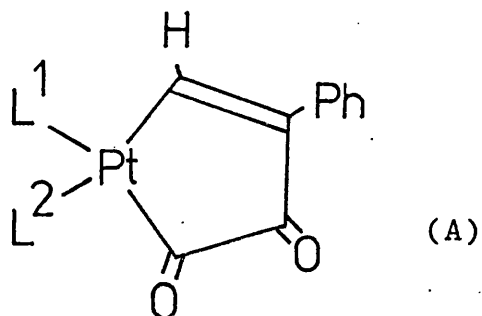
Observed in CDCl_3 solution: a multiplet at 7.04δ and a singlet at 1.60δ with ill-defined ^{195}Pt satellites. However, the coupling was measurable and assigned as $^3\text{J}(\text{Pt}-\text{CH}_3) = 13.0 \text{ Hz}$.

SECTION 1

THE REACTIONS OF LOW-VALENT TRANSITION
METAL COMPLEXES WITH DERIVATIVES OF
CYCLOBUT-1-ENE-2,3-DIONE.

- (A) Platinum(0)
- (iii) Some replacement reactions of the bis-arsine
complex with phenylcyclobutenedione.

Complexes of the type:



(1) $L^1, L^2=1,10$ -phenanthroline (o-phen)

0.20g (0.2 mmol) of complex (A), $L^1=L^2=AsPh_3$, in a suspension in dry degassed diethyl ether was treated dropwise with an ethereal solution of o-phen.

Instantly, a maroon precipitate replaced the red suspension, and this was removed by filtration after 10 minutes, and was dried in vacuo.

Yield 0.10g (87.0%)

M.p. $>300^{\circ}C$ (decomp)

Analysis For $C_{22}H_{14}N_2O_2Pt$

	%C	%H	%N	M.W.
CALC	49.53	2.65	5.25	533
FOUND	49.89	2.80	5.26	-

Infrared spectrum (cm^{-1})

$\nu(C=O)$ at 1632 and 1654 cm^{-1} , observed o-phen bands and Ph bands, but no $AsPh_3$ bands.

(2) $L^1, L^2=1,2$ -diphenylphosphinoethane (diphos)

0.20g (0.2 mmol) complex (A), $L^1=L^2=AsPh_3$ and 0.09g (0.21 mmol) diphos were mixed together in dry degassed diethyl ether at room temperature. The suspension was stirred for 30 minutes before the dark red crystals were filtered and dried in vacuo.

Yield 0.14g (90%)

M.p. 258-261°C - partially melts at 210°C (decomp)

Analysis For $C_{36}H_{30}O_2P_2Pt$

	%C	%H	M.W.
CALC	57.52	4.02	752
FOUND	57.51	3.74	-

Infrared spectrum (cm^{-1})

$\nu(C=O)$ 1642(vs), 1670(s).

(3) $L^1, L^2 = \text{cycloocta-1,5-diene (cod)}$

0.20g (0.2 mmol) of arsine complex (A), $L^1 = L^2 = \text{AsPh}_3$ was treated with 0.03g cod in dry degassed ether as above. The mixture was stirred overnight under an atmosphere of dry nitrogen. The red crystals were filtered and dried in vacuo. These proved to be pure unreacted starting material (A; $L^1 = L^2 = \text{AsPh}_3$).

(4) $L^1=L^2$ =methyldiphenylphosphine (PMePh_2)

0.30g (0.31 mmol) arsine complex (A),

$L^1=L^2=\text{AsPh}_3$, was stirred in diethyl ether under an atmosphere of dry nitrogen. 0.13g (0.64 mmol) methyldiphenylphosphine (PMePh_2) was syringed into the suspension. The colour changed slightly straight away, and after 5 minutes the red crystals were filtered and dried in vacuo.

Yield 0.22g (94%)

M.p. 201-203°C (decomp)

Analysis For $\text{C}_{36}\text{H}_{32}\text{O}_2\text{P}_2\text{Pt}$

	%C	%H	M.W.
CALC	57.37	4.28	754
FOUND	57.01	3.83	-

Infrared spectrum (cm^{-1})

$\nu(\text{C}=\text{O})$ 1641(vs), 1670(s).

(5) $L^1, L^2=2,2'$ -bipyridyl (bipy)

0.20g (0.2 mmol) arsine complex (A),
 $L^1=L^2=AsPh_3$, was stirred in an ether suspension with
0.03g (0.21 mmol) bipy as previously described. A
greenish flocculent material immediately precipitated
which was filtered and dried in the vacuum desiccator.

Yield 0.1g (98.2%)

M.p. 243.245°C (decomp)

Analysis For $C_{20}H_{14}N_2O_2Pt$

	%C	%H	%N	M.W.
CALC	47.15	2.77	5.50	509
FOUND	46.63	2.68	5.32	-

Infrared spectrum (cm^{-1})

$\nu(C=O)$ 1663(vs), 1641(s), 1633(s).

(6) $L^1=L^2$ =dimethylphenylphosphine (PMe_2Ph)

0.30g (0.3 mmol) of arsine complex (A), $L^1=L^2=\text{AsPh}_3$, was stirred as an ethereal suspension under dry nitrogen as before. 0.09g (0.63 mmol) dimethylphenylphosphine (PMe_2Ph) was syringed into the suspension. The precipitate gradually became more granular, and after 15 minutes was filtered off and dried in vacuo.

Yield 0.13g (66.5%)

M.p. 108-111°C (decomp)

Analysis For $\text{C}_{26}\text{H}_{28}\text{O}_2\text{P}_2\text{Pt}$

	%C	%H	M.W.
CALC	49.60	4.48	630
FOUND	49.46	4.35	-

Infrared spectrum (cm^{-1})

$\nu(\text{C}=\text{O})$ 1633(vs), 1640(sh), 1674(sh), 1671(s).

$\nu(\text{Pt}-\text{C})$ 545.5(w) (calibrated on CO_2)

(7) $L^1=L^2$ =triphenylphosphite ($P(OPh)_3$)

0.20g (0.2 mmol) arsine complex (A),

$L^1=L^2=AsPh_3$ was treated with an ethereal solution of triphenylphosphite ($P(OPh)_3$) 0.13g (0.42 mmol) as previously described. All the reactants went into solution. After 30 minutes petroleum ether (b.p. 40-60) was added, and the orange product crystallised out. The microcrystalline product was filtered and dried under vacuum.

Yield 0.18g (92.3%)

M.p. 148-150°C

Analysis For $C_{46}H_{36}O_8P_2Pt$

	%C	%H	M.W.
CALC	56.73	3.73	974
FOUND	56.74	3.63	-

Infrared spectrum (cm^{-1})

$\nu(C=O)$ 1685(s), 1656(vs).

(8) $L^1=L^2$ =diethylphenylphosphine (PEt_2Ph)

0.30g (0.3 mmol) arsine complex (A),
 $L^1=L^2=\text{AsPh}_3$, and 0.11g (0.6 mmol) diethylphenylphosphine,
(PEt_2Ph), were mixed together in dry degassed petroleum
ether (b.p. 40-60)/diethyl ether (60:40). On stirring
an oily salmon-pink solid separated which became
crystalline on prolonged scratching with a glass rod.
This was separated by filtration, and dried under vacuum.

Yield 0.16g (75.0%)

M.p. 120-121°C

Analysis For $\text{C}_{30}\text{H}_{36}\text{O}_2\text{P}_2\text{Pt}$

	%C	%H	M.W.
CALC	52.63	5.30	685
FOUND	52.08	5.09	-

Infrared spectrum (cm^{-1})

$\nu(\text{C}=\text{O})$ 1666(s), 1639(vs).

$\nu(\text{Pt}-\text{C})$ 542.0(w) (calibrated on CO_2)

(9) $L^1=L^2$ =triethylphosphine (PEt_3)

0.30g (0.3 mmol) arsine complex (A), $L^1=L^2=\text{AsPh}_3$ was treated with 0.105 cm³ (\sim 0.6 mmol) of triethylphosphine (PEt_3) under dry nitrogen using petroleum ether (b.p. 40-60)/diethyl ether (90:10) as a solvent. The suspension was stirred vigorously for 15 minutes. The salmon pink product was washed with 40-60 petrol after filtration and dried under vacuum.

Yield . . . 0.15g (84%)

M.p. . . . 88-89°C

Analysis . . . For $\text{C}_{22}\text{H}_{36}\text{O}_2\text{P}_2\text{Pt}$

	%C	%H	M.W.
CALC	44.79	6.15	590
FOUND	44.82	6.01	-

Infrared spectrum (cm⁻¹)

$\nu(\text{C}=\text{O})$ 1668(s), 1640(vs)

$\nu(\text{Pt}-\text{C})$ 541(w) ('calibrated on CO_2)

SECTION 1

THE REACTIONS OF LOW-VALENT TRANSITION
METAL COMPLEXES WITH DERIVATIVES OF
CYCLOBUT-1-ENE-2,3-DIONE.

(B) Palladium(0)

(i) Tetrakis(triphenylphosphine)palladium(0)
Pd(PPh₃)₄

(1) Tetrakis(triphenylphosphine)palladium(0)
+ 1-phenylcyclobut-1-ene-3,4-dione.

0.5g (0.44 mmol) Pd(PPh₃)₄ and 0.07g (0.45 mmol) ligand were stirred together in dry degassed diethyl ether at room temperature under an atmosphere of dry nitrogen. All the solids dissolved after 2 minutes and at the end of 10 minutes a yellow crystalline product had precipitated. This was filtered, washed with dry ether and dried in vacuo.

Yield 0.21g (62%)

M.p. 101-103°C (decomp)

Analysis For C₄₆H₃₆O₂P₂Pd

	%C	%H	M.W.
CALC	70.03	4.60	789
FOUND	69.26	4.83	-

Infrared spectrum (cm⁻¹)

1776bvs, 1720bvs, 1700sh, 1596m, 1550s, 1484s, 1436vs, 1308m, 1246m, 1184w, 1158w, 1144w, 1120w, 1094vs, 1076w, 1056w, 1028w, 1000w, 904m, 856w, 818m, 790sh, 776m, 752s, 698vs, 676m, 664w, 622vw, 566w, 532vs, 521vs, 510vs, 424bvw.

¹H n.m.r. spectrum

Observed in CDCl₃ solution: a multiplet centred at 7.10δ and a doublet at 5.55δ. Relative intensities 35:1. The coupling was assigned as

trans- ³J(P-H) = 1.5 Hz

cis- ³J(P-H) = 0 Hz

(2) Tetrakis(triphenylphosphine)palladium(0)
+ 1-methyl-2-phenylcyclobut-1-ene-3,4-dione.

0.6g (0.5 mmol) Pd(PPh₃)₄ and 0.09g (0.52 mmol) ligand were stirred together in ether under an atmosphere of dry nitrogen as before. The solids immediately dissolved and after about 20 minutes a yellow crystalline product began to form. After one hour the product was filtered and washed with ether. The product was dried under vacuum.

Yield 0.30g (75%)

M.p. 95-97°C

Analysis For C₄₇H₃₈O₂P₂Pd

	%C	%H	M.W.
CALC	70.30	4.77	803
FOUND	72.11	5.08	-

Infrared spectrum (cm⁻¹)

1721vs, 1692s, 1586s, 1485s, 1424vs, 1328w, 1312m, 1286w, 1244vw, 1182m, 1154m, 1124m, 1096sh, 1086vs, 1074m, 1030vs, 1006vs, 986m, 926w, 856bm, 771sh, 746vs, 716m, 704vs, 698vs.

¹H n.m.r. spectrum

Observed in CDCl₃ solution: a multiplet centred at 7.03δ and a triplet at 1.44δ. Relative intensities 35:3. The coupling was assigned as follows

$$^4J(\text{P}-\text{CH}_3) = 6.30 \text{ Hz}$$

The observed triplet pattern is thought to arise from a similar case as that already seen in bis(triphenylphosphine)-(phenylcyclobutenedione)platinum(0), where in the ABX system (A=B=P X=CH₃ protons) $J(\text{AB}) \gg |J(\text{AX}) - J(\text{BX})|$, the expected doublet of doublets → a triplet as observed.

(3) Tetrakis(triphenylphosphine)palladium(0)
+ benzocyclobutenedione.

0.48g (0.42 mmol) $\text{Pd}(\text{PPh}_3)_4$ and 0.06g (0.45 mmol) ligand were stirred in dry degassed ether under dry nitrogen as before. The suspension became red after only one minute, but the mixture was left stirring for a further 24 hours. The red crystalline product was filtered off, washed and dried under vacuum.

Yield 0.29g (91.5%)

M.p. 92-95°C (decomp)

Analysis For $\text{C}_{12}\text{H}_8\text{O}_2\text{P}_2\text{Pd}$

	%C	%H	M.W.
CALC	69.25	4.47	768
FOUND	70.46	4.78	-

Infrared spectrum (cm^{-1})

1638vs, 1583s, 1485vs, 1442vs, 1313w, 1280w, 1185vs, 1163w, 1145s, 1122m, 1098vs, 1085sh, 1075sh, 1030m, 1105s, 978w, 915w, 898vs, 885vs, 851m, 788m, 783m, 747vs, 726m, 698vs, 660s.

(4) Tetrakis(triphenylphosphine)palladium(0)
+ 1,2-diphenylcyclobut-1-ene-3,4-dione.

0.46g (0.4 mmol) $\text{Pd}(\text{PPh}_3)_4$ and 0.1g (0.43 mmol) ligand were stirred together in dry ether as has been previously described. The reaction was allowed to proceed for 2 hours although no apparent changes took place in the starting materials. The yellow solid was filtered off, washed and dried in a vacuum desiccator.

Yield 0.33g (95.4%)

M.p. Decomposes over 60°C

Analysis. For $\text{C}_{32}\text{H}_{40}\text{O}_2\text{P}_2\text{Pd}$

	%C	%H	M.W.
CALC	72.18	4.66	865
FOUND	71.68	4.83	-

Infrared spectrum (cm^{-1})

1751m, 1710vs, 1693m, 1586s, 1580m, 1506m, 1485vs, 1458m, 1443vs, 1343m, 1313m, 1273bw, 1282m, 1260m, 1098vs, 1083vs, 1030vs, 1003s, 980m, 925w, 888w, 883w, 859m, 803s, 793s, 764vs, 746vs, 723m, 698vs.

(5) Tetrakis(triphenylphosphine)palladium(0)
+ 1-chloro-2-phenylcyclobut-1-ene-3,4-dione.

0.4g (0.34 mmol) $\text{Pd(PPh}_3)_4$ and 0.07g (0.36 mmol) ligand were stirred together in ether as above. No apparent change was observed, and after 3 hours the yellow solid was filtered off. Infrared analysis confirmed that no reaction had taken place, the i.r. spectrum being identical to that of a mixture of the starting materials. The reaction was repeated in dry degassed benzene, but only resulted in a black residue which was not characterised.

(6) Tetrakis(triphenylphosphine)palladium(0)
+ 1,2-dimethoxycyclobut-1-ene-3,4-dione.

0.47g (0.42 mmol) $\text{Pd}(\text{PPh}_3)_4$ and 0.06g (0.44 mmol)

ligand were stirred in diethyl ether as before. No obvious change was observed. After 3 hours the yellow amorphous powder was filtered, washed and air dried. Infrared analysis indicated exclusively starting materials. Repetition of the reaction in benzene afforded pure starting materials exclusively, the infrared spectrum being that of a mixture of the starting materials.

SECTION 1

THE REACTIONS OF LOW-VALENT TRANSITION
METAL COMPLEXES WITH DERIVATIVES OF
CYCLOBUT-1-ENE-2,3-DIONE.

(B) Palladium(0)

(ii) Tetrakis(triphenylarsine)palladium(0)

$\text{Pd}(\text{AsPh}_3)_4$

(1) Tetrakis(triphenylarsine)palladium(0)
+ 1-phenylcyclobut-1-ene-3,4-dione.

0.57g (0.43 mmol) $\text{Pd}(\text{AsPh}_3)_4$ and 0.07g (0.45 mmol) ligand were stirred together in dry degassed ether under nitrogen as before. The suspension was stirred for 72 hours when the mixture was filtered. The deep orange precipitate was dissolved in ethanol and slowly evaporated in vacuo until crystallisation began. The mixture was stored at 0°C under nitrogen. The orange crystals were collected by filtration and dried in vacuo.

Yield 0.20g (45.5%)

M.p. 121-124 $^\circ\text{C}$ (decomp)

Analysis For $\text{C}_{46}\text{H}_{36}\text{As}_2\text{O}_2\text{Pd}$

	%C	%H	M.W.
CALC	63.00	4.14	877
FOUND	62.70	4.10	-

Infrared spectrum (cm^{-1})

$\nu(\text{C}=\text{O})$ at 1720 cm^{-1} (compound rapidly decomposes in air in a Nujol mull, and no satisfactory spectrum was obtained below the carbonyl region of the i.r. spectrum).

^1H n.m.r. spectrum

Observed in degassed CDCl_3 solution: apart from the usual phenyl signals, only a sharp singlet at 5.88 δ .
Relative intensities 35:1.

SECTION 1

THE REACTIONS OF LOW-VALENT TRANSITION
METAL COMPLEXES WITH DERIVATIVES OF
CYCLOBUT-1-ENE-2,3-DIONE.

(C) Rhodium(I)

(i) Chlorotris(triphenylphosphine)rhodium(I)
 $\text{RhCl}(\text{PPh}_3)_3$

(1) Chlorotris(triphenylphosphine)rhodium(I)
+ 1-phenylcyclobut-1-ene-3,4-dione.

0.31g (0.3 mmol) $\text{RhCl}(\text{PPh}_3)_3$ and 0.06g (0.3 mmol) ligand were stirred together in dry degassed dichloromethane under an atmosphere of dry nitrogen. The solution was stirred at room temperature for 1 hour, and then gently refluxed for 24 hours. The orange solution was stripped to small bulk under reduced pressure and 40-60 b.p. petroleum ether added to the cloud point. Crystallisation was allowed to proceed at 0°C , affording a bright orange microcrystalline product. This was filtered and dried under vacuum.

Yield 0.10g (53.8%)

M.p. 217°C (decomp)

Analysis For $\text{C}_{28}\text{H}_{21}\text{RhClPO}_2$

	%C	%H	%Cl
CALC	60.17	3.79	6.35
FOUND	60.94	3.96	8.67

Infrared spectrum (cm^{-1})

1690s, 1678m, 1653vs, 1638vs, 1588w, 1574w, 1485s, 1446sh, 1442vs, 1436vs, 1334w, 1312w, 1296w, 1266w, 1224w, 1190m, 1163w, 1096vs, 1067vs, 1152m, 1036w, 1010w, 976w, 828vw, 884s, 796m, 783s, 753s, 746vs, 726w, 696vs, 630w, 624s, 584s, 546msh, 528vs, 520vs, 508s, 502s.

^1H n.m.r. spectrum

All attempts to obtain a satisfactory spectrum failed.

(2) Chlorotris(triphenylphosphine)rhodium(I)
+ benzocyclobutenedione.

0.45g (0.49 mmol) $\text{RhCl}(\text{PPh}_3)_3$ and 0.22g (1.4 mmol) ligand were stirred together in dry degassed benzene at about 60°C under an atmosphere of dry nitrogen. The orange solution began to develop a crystalline precipitate, and after a total of 4 hours the bright yellow crystals were filtered off and washed with 40-60 b.p. petroleum ether. The product was air dried for 15 minutes.

Yield 0.23g (86.5%)

M.p. 241°C (decomp)

Analysis $\text{C}_{26}\text{H}_{19}\text{O}_2\text{PClRh}$

	%C	%H	M.W.
CALC	58.82	3.54	535
FOUND	60.06	5.74	476

Infrared spectrum (cm^{-1})

1735m, 1703s, 1679s, 1568w, 1548w, 1450sh, 1432vs, 1364m, 1267w, 1184w, 1168w, 1152w, 1096vs, 1040s, 856m, 792w, 754sh, 744m, 710sh, 696s, 688m, 528m, 520s, 506s.

(3) Chlorotris(triphenylphosphine)rhodium(I)
+ 1-methoxy-2-phenylcyclobut-1-ene-3,4-dione.

0.6g (0.65 mmol) $\text{RhCl}(\text{PPh}_3)_3$ and 0.15g (0.8 mmol) ligand were stirred in refluxing dry benzene under an atmosphere of dry nitrogen for 1 hour. Only the tan-coloured dimer of $[\text{RhCl}(\text{PPh}_3)_2]_2$ was recovered from the reaction (identified by inspection).

Repetition of the reaction in acetonitrile (in which the dimeric species is not formed), produced no reaction at all, and pure starting materials were recovered (i.r. spectra were identical to those of the starting materials).

(4) Chlorotris(triphenylphosphine)rhodium(I)
+ 1,2-dimethoxycyclobut-1-ene-3,4-dione.

0.20g (0.22 mmol) $\text{RhCl}(\text{PPh}_3)_3$ and 0.10g (0.7 mmol) ligand were stirred together in dry degassed dichloromethane under an atmosphere of dry nitrogen at room temperature. After 1 hour the bulk was reduced, and dry diethyl ether added to the cloud point. Crystallisation gave only starting materials and a dark brown residue (which was not characterised).

- (5) Chlorotris(triphenylphosphine)rhodium(I)
+ 1-chloro-2-phenylcyclobut-1-ene-3,4-dione.

0.46g (0.5 mmol) $\text{RhCl}(\text{PPh}_3)_3$ and 0.08g (0.42 mmol) ligand were dissolved in dry degassed benzene and warmed under an atmosphere of dry nitrogen at 40°C for 1 hour. During this time, a yellow solid had begun to precipitate, and this was filtered off from the solution. Preliminary infrared analysis showed the solid to be of an unsatisfactory nature and it was discarded. The filtrate was reduced in bulk, and dry diethyl ether added to the cloud point. Crystallisation at 0°C gave no satisfactory product. Attempts at working the solution up by other means yielded only decomposition products. The reaction was abandoned.

(6) Chlorotris(triphenylphosphine)rhodium(I)
+ 1,2-diphenylcyclobut-1-ene-3,4-dione.

0.26g (0.28 mmol) $\text{RhCl(PPh}_3)_3$ and 0.05g (0.21 mmol) ligand were dissolved in dry degassed benzene and warmed at 40°C under an atmosphere of dry nitrogen for 1 hour. No change was observed in the state of the reactants. The solution was then refluxed for 24 hours, but no apparent change had taken place. The solution was reduced in bulk, and ethanol was added to the cloud point. Crystallisation was allowed to take place at 0°C . From the tan-coloured precipitate thus formed, it was deduced that no reaction had taken place.

Inspection of the product and an infrared spectrum indicated only the dimeric product $[\text{RhCl(PPh}_3)_2]_2$.

(7) Chlorotris(triphenylphosphine)rhodium(I)
+ 1,2-dihydroxycyclobut-1-ene-3,4-dione.

0.925g (1.0 mmol) $\text{RhCl}(\text{PPh}_3)_3$ and 0.228g (2.0 mmol) ligand were stirred in refluxing dry degassed benzene under an atmosphere of dry nitrogen for 12 hours. On cooling, a tan-coloured powder was isolated from the mixture, which proved, by inspection, to be the dimeric compound $[\text{RhCl}(\text{PPh}_3)_2]_2$.

Repetition of the reaction in acetonitrile indicated that no reaction had taken place, as only the unreacted starting materials were recovered.

(8) Chlorotris(triphenylphosphine)rhodium(I)
+ 1-methyl-2-phenylcyclobut-1-ene-3,4-dione.

0.11g (0.12 mmol) $\text{RhCl}(\text{PPh}_3)_3$ and 0.02g (0.13 mmol) ligand were dissolved in 15 cm³ dry degassed dichloromethane under dry nitrogen as before. The solution was stirred at room temperature for 15 minutes. No visible reaction was observed. The solution was warmed for a further 15 minutes. The solution was then reduced in bulk under reduced pressure, and diethyl ether was added to the cloud point. The product was filtered. This proved to be a mixture of unreacted starting materials, the infrared spectrum being simply a mixture of the spectra of the two starting materials.

SECTION 1

THE REACTIONS OF LOW-VALENT TRANSITION
METAL COMPLEXES WITH DERIVATIVES OF
CYCLOBUT-1-ENE-2,3-DIONE.

(C) Rhodium(I)

(ii) Dipivaloylmethanatocycloocta-1,5-dienerhodium(I)

Rh(cod)(dpm)

- (1) Dipivaloylmethanatotocycloocta-1,5-dienerrhodium(I)
+ 1-phenylcyclobut-1-ene-3,4-dione.

0.39g (1.0 mmol) Rh(cod)(dpm) and 0.2g (1.3 mmol) ligand were mixed together and refluxed in dry degassed benzene under an atmosphere of dry nitrogen for 12 hours. The solution became murky and brown and only a mixture of decomposition products could be isolated from the reaction mixture. (These were not characterised.)

(2) Dipivaloylmethanocycloocta-1,5-dienerrhodium(I)
+ benzocyclobutenedione..

0.4g (1 mmol) Rh(cod)(dpm) and 0.2g (1.3 mmol) ligand stirred in dry degassed benzene at room temperature for 1 hour under an atmosphere of dry nitrogen. No apparent reaction was seen. The solution was refluxed for a further 4 hours, and was then reduced in bulk and treated with diethyl ether to the cloud point. The light brown residual product formed indicated on preliminary i.r. evidence simply a mixture of starting materials. No reaction had taken place.

SECTION 1

THE REACTIONS OF LOW-VALENT TRANSITION
METAL COMPLEXES WITH DERIVATIVES OF
CYCLOBUT-1-ENE-2,3-DIONE.

(C) Rhodium(I)

(iii) Bis(ethylene)acetylacetonatorhodium(I)

Rh(acac)(C₂H₄)₂

- (1) Bis(ethylene)acetylacetonatorhodium(I)
+ 1-phenylcyclobut-1-ene-3,4-dione.

0.26g (1 mmol) Rh(acac)(C₂H₄)₂ and 0.16g (1 mmol) ligand were stirred together in dry degassed diethyl ether under an atmosphere of dry nitrogen. The solution began to darken, and after 15 minutes had become a murky brown. The mixture was left stirring for a further 2 hours when the solution was filtered. The brown residue showed no carbonyl or ligand bands in the i.r., and a t.l.c. of the filtrate gave a single brown spot which did not move up the plate. The reaction was abandoned.

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THE REACTIONS OF LOW-VALENT TRANSITION
METAL COMPLEXES WITH DERIVATIVES OF
CYCLOBUT-1-ENE-2,3-DIONE.

(D) Iridium(I)

(i) Trans-chlorocarbonylbis(triphenylphosphine)-
iridium(I)
trans-IrCl(CO)(PPh₃)₂

- (1) Trans-chlorocarbonylbis(triphenylphosphine)Iridium(I)
+ 1-phenylcyclobut-1-ene-3,4-dione.

0.82g (1.0 mmol) trans-IrCl(CO)(PPh₃)₂ and 0.16g (1.0 mmol) ligand were mixed together in dry degassed benzene under an atmosphere of dry nitrogen. The reaction was carried out at 30°C for 72 hours. The resulting red solution was reduced in bulk and treated with dry diethyl ether to the cloud point. Crystallisation at 0°C afforded orange-yellow crystals which proved to be unreacted Vaska's complex. The filtrate gave, on work-up, only a dark brown oil, which was not characterised.

Repetition of the reaction in refluxing dichloromethane for 3 days gave only starting materials and dark brown decomposition products. The reaction was abandoned.

- (2) Trans-chlorocarbonylbis(triphenylphosphine)Iridium(I)
+ 1-chloro-2-phenylcyclobut-1-ene-3,4-dione.

0.82g (1.0 mmol) trans-IrCl(CO)(PPh₃)₂ and 0.23g (1.0 mmol) ligand were reacted as above in benzene. The reaction was allowed to proceed for 1 hour, when the solution was filtered and the orange filtrate reduced in bulk. Orange-yellow crystals were precipitated by addition of an equal volume of ethanol which were then collected and air dried. Infrared analysis showed that the crystals were Vaska's complex, and thus no reaction had occurred. The mother liquor afforded only decomposition products, and was discarded.

(3) Trans-chlorocarbonylbis(triphenylphosphine)Iridium(I)
+ 1,2-dimethoxycyclobut-1-ene-3,4-dione.

0.82g (1.0 mmol) trans-IrCl(CO)(PPh₃)₂ and 0.14g (1.0 mmol) ligand were stirred together in benzene as before. The mixture was refluxed for 12 hours. The resulting orange solution was worked up as in (1) above, and again the orange-yellow crystals proved to be unreacted Vaska's complex (i.r. evidence).

SECTION 1

THE REACTIONS OF LOW-VALENT TRANSITION
METAL COMPLEXES WITH DERIVATIVES OF
CYCLOBUT-1-ENE-2,3-DIONE.

(E) Iron(0)

(i) Nonacarbonyldiiron(0)

$\text{Fe}_2(\text{CO})_9$

(1) Nonacarbonyldiiron(0) + 1-phenylcyclobut-1-ene-3,4-dione.

0.364g (1 mmol) $\text{Fe}_2(\text{CO})_9$ and 0.146g (1 mmol) ligand were stirred together in dry degassed dichloromethane under an atmosphere of dry nitrogen. The suspension darkened after about 5 minutes to dark brown. After a further 30 minutes, the solution was filtered, and the dark brown filtrate was reduced in bulk. This was placed onto a 30 cm fluorosil chromatography column and eluted with dichloromethane. A yellow first fraction was reduced in bulk and was treated with petroleum ether (b.p. 40-60) to the cloud point. The yellow crystals obtained proved to be the organic starting material (its infrared spectrum was identical to that of an authentic sample). No further product could be obtained from the column.

Repetition of the reaction using benzene as solvent yielded the same results.

The reaction was finally attempted in ether suspension, but in this case only a black residue could be isolated from the reaction (which was not characterised). The reaction was abandoned.

(2) Nonacarbonyldiiron(0) + 1,2-dimethoxycyclobut-
1-ene-3,4-dione.

0.30g (0.82 mmol) $\text{Fe}_2(\text{CO})_9$ and 0.3g (2.1 mmol) ligand were stirred together in dry degassed dichloromethane at room temperature, under an atmosphere of dry nitrogen. After 1 hour the solution/suspension had taken on a green tint. The brown solids were filtered off leaving a yellow-green filtrate. This was reduced in bulk and petroleum ether (b.p. 40-60) was added to the cloud point. The resulting white solid was collected and dried under vacuum. Infrared analysis showed this to be the organic starting material (it was identical to the spectrum of an authentic sample).

SECTION 1

THE REACTIONS OF LOW-VALENT TRANSITION
METAL COMPLEXES WITH DERIVATIVES OF
CYCLOBUT-1-ENE-2,3-DIONE.

(E) Iron(0)

(ii) Pentacarbonyliron(0)

Fe(CO)₅

(1) Pentacarbonyliron(0) + 1-phenylcyclobut-1-ene-3,4-dione.

0.2g (1.0 mmol) $\text{Fe}(\text{CO})_5$ and 0.34g (2.1 mmol) ligand were mixed in dry degassed benzene under an atmosphere of dry nitrogen. The mixture was stirred at room temperature for 1 hour and then refluxed for 24 hours. The solution was reduced in bulk and diethyl ether added to the cloud point. Crystallisation was allowed to proceed at 0°C for 4 weeks. The dark brown amorphous powder obtained was judged by inspection to be decomposition product and was discarded.

SECTION 2

THE REACTIONS OF LOW-VALENT TRANSITION
METAL COMPLEXES WITH CYCLIC SULPHONES.

(A) Platinum(0)

(i) Trans-stilbenebis(triphenylphosphine)platinum(0)

Pt(PPh₃)₂(trans-stilbene)

(1) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 3-phenylthiete-1,1-dioxide.

0.45g (0.5 mmol) $\text{Pt}(\text{PPh}_3)_2$ (trans-stilbene) and 0.09g (0.50 mmol) ligand were stirred together in dry degassed diethyl ether at room temperature under an atmosphere of dry nitrogen. The solids dissolved, and after about 2 minutes a white crystalline product began to form. After a further 10 minutes the crystals were filtered off, washed with ether and dried in a vacuum desiccator.

Yield 0.34g (75.6%)

M.p. 172-173°C (decomp)

Analysis For $\text{C}_{45}\text{H}_{38}\text{P}_2\text{SO}_2\text{Pt}$

	%C	%H	M.W.
CALC	60.06	4.26	900
FOUND	60.23	4.32	883

Infrared spectrum (cm^{-1})

1596w, 1588w, 1576w, 1495m, 1483s, 1476sh, 1444w, 1434vs, 1330w, 1312w, 1276vs, 1196vs, 1168w, 1130vs, 1110vs, 1096vs, 1087sh, 1056w, 1030w, 1000w, 972m, 930w, 912w, 897w, 796m, 768m, 760m, 752vs, 710sh, 640w, 624w, 604w, 568w, 540vs, 516vs, 516vs, 503vs, 498s, 480m.

^1H n.m.r. spectrum

Observed in benzene solution: a multiplet at 7.02 δ and a multiplet at 4.27 δ . Relative intensities 35:3. At higher resolution, the multiplet at 4.27 δ was seen to be a doublet with ^{195}Pt satellites, and at slightly lower field, a doublet of doublets also with ^{195}Pt satellites. Relative intensities were 2:1. The presence of a doublet

for the methylene protons suggests that these are equivalent (and are denoted H_A). As the structure is a doublet, then $\text{cis-}J(P-H_A) = 0$ Hz. The methine proton is denoted H_B , and the couplings are assigned on the basis of an olefin-type complex (see text).

$$\text{trans- } {}^3J(P-H_B) = 9.8 \text{ Hz}$$

$$\text{cis- } {}^3J(P-H_B) = 4.1 \text{ Hz}$$

$$\text{trans- } {}^4J(P-H_A) = 9.8 \text{ Hz}$$

$$\text{cis- } {}^4J(P-H_A) = 0 \text{ Hz}$$

$${}^2J(\text{Pt}-H_B) = 58.2 \text{ Hz}$$

$${}^3J(\text{Pt}-H_A) = 79.6 \text{ Hz}$$

(2) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 3-p-bromophenylthiete-1,1-dioxide.

0.45g (0.5 mmol) $\text{Pt}(\text{PPh}_3)_2$ (trans-stilbene) and 0.15g (0.54 mmol) ligand reacted as in (1) above. The reaction was allowed to proceed for 30 minutes before the white crystals were collected and dried in vacuo.

Yield 0.35g (78.0%)

M.p. 189-191°C (decomp)

Analysis For $\text{C}_{45}\text{H}_{37}\text{SO}_2\text{P}_2\text{BrPt}$

	%C	%H	%Br
CALC	55.22	3.81	8.17
FOUND	55.02	3.96	7.62

Infrared spectrum (cm^{-1})

1588m, 1574w, 1488vs, 1484sh, 1440sh, 1436vs, 1420w, 1398m, 1368w, 1332s, 1312w, 1286vs, 1196vs, 1180w, 1160w, 1130vs, 1124sh, 1110vs, 1102vs, 1096vs, 1068w, 1048w, 1038w, 1008w, 1002w, 969w, 932w, 906w, 848w, 840w, 828s, 788m, 766w, 758sh, 746vs, 708sh, 698vs, 660m, 626w, 601w, 562w, 540vs, 528vs, 513vs, 506sh, 496m, 460s.

^1H n.m.r. spectrum

Observed in CDCl_3 solution: patterns similar to the unsubstituted thiete dioxide, namely a multiplet at 7.02 δ and a multiplet at 4.27 δ (relative intensities approximately 34:3). At increased resolution, the low-field multiplet was seen to be a doublet with ^{195}Pt satellites and at slightly lower field a doublet of doublets also with ^{195}Pt satellites. These intensities

were in the ratio 2:1. In this case, however, further splitting was observed on both the patterns, but was unsymmetrical. Couplings were assigned on the basis of a π -complex (H_A = methylene protons, H_B = methine proton).

$$\text{trans- } {}^4J(P-H_A) = 9.51 \text{ Hz}$$

$$\text{cis- } {}^4J(P-H_A) = 0 \text{ Hz}$$

$${}^3J(Pt-H_A) = 82.3 \text{ Hz}$$

$$\text{trans- } {}^3J(P-H_B) = 8.53 \text{ Hz}$$

$$\text{cis- } {}^3J(P-H_B) = 4.12 \text{ Hz}$$

$${}^2J(Pt-H_B) = 54.8 \text{ Hz}$$

Additional couplings (see text for explanation)

$$J(\text{doublet of doublets}) = 0.9 \text{ Hz}$$

$$J(\text{doublet}) = 3.07 \text{ Hz}$$

(3) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 2,3-benzothiophene-1,1-dioxide.

0.45g (0.5 mmol) Pt(PPh₃)₂(trans-stilbene) and 0.08g (0.49 mmol) ligand were stirred together in dry diethyl ether under an atmosphere of dry nitrogen at room temperature. After 10 minutes the white crystalline solid formed was filtered off, washed with dry ether and dried in vacuo.

Yield 0.39g (84.9%)

M.p. 205-207°C (decomp)

Analysis For C₄₄H₃₆SO₂PtP₂

	%C	%H	%S	M.W.
CALC	59.65	4.10	3.61	886
FOUND	59.59	4.50	3.52	-

Infrared spectrum (cm⁻¹)

1596w, 1574w, 1482vs, 1436vs, 1414vw, 1312vs, 1296sh, 1268w, 1256w, 1185w, 1160vs, 1136m, 1130m, 1121s, 1096vs, 1072w, 1030w, 1000w, 976w, 929w, 887w, 858w, 832w, 760vs, 750vs, 710vs, 682m, 624w, 588w, 556s, 532vs, 516vs, 508vs.

¹H n.m.r. spectrum

Observed in CDCl₃ solution: a multiplet at 7.14δ, a broad doublet at 5.58δ and a doublet at 3.92δ with ¹⁹⁵Pt satellites (relative intensities 34:1:1). All patterns were highly unsymmetrical, characteristic of higher order spectra. Rigid assignments were not made and the spectrum is discussed in the text.

- (4) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 3-^tbutylthiete-1,1-dioxide.

0.45g (0.5 mmol) Pt(PPh₃)₂(trans-stilbene) and 0.08g (0.5 mmol) ligand were stirred together in dry diethyl ether under an atmosphere of dry nitrogen. No apparent reaction was observed, and on isolating the yellow solid from the solution an infrared spectrum indicated that the material was the stilbene complex. A white compound obtained by evaporation of the ethereal solution to dryness had an infrared spectrum identical to that of pure 3-^tbutylthiete-1,1-dioxide.

Reaction of these materials in chlorinated solvents (in which both dissolved) resulted only in the production of a white solid found to be cis-PtCl₂(PPh₃)₂ (m.p. 310°C, infrared spectrum identical to an authentic sample).

- (5) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ cyclopent-3-ene-1-sulphone.

0.45g (0.5 mmol) $\text{Pt}(\text{PPh}_3)_2$ (trans-stilbene) and 0.074g (0.62 mmol) ligand were stirred together in dry diethyl ether under an atmosphere of dry nitrogen. After 15 minutes the light yellow suspension was filtered and the yellow precipitate dried in vacuo. An infrared spectrum of the compound was identical to that of pure stilbene complex.

The reaction was carried out in chlorinated solvents (in which both materials dissolved), but the white compound isolated from the solution proved to be cis- $\text{PtCl}_2(\text{PPh}_3)_2$ (m.p. 305°C , infrared spectrum identical to that of an authentic sample).

- (6) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 3-methylcyclopent-3-ene-1-sulphone.

0.45g (0.5 mmol) $\text{Pt}(\text{PPh}_3)_2$ (trans-stilbene) and 0.066g (0.5 mmol) ligand were stirred together in dry diethyl ether under an atmosphere of dry nitrogen. No apparent reaction was observed, and the yellow precipitate isolated from the suspension had an infrared spectrum identical to that of $\text{Pt}(\text{PPh}_3)_2$ (trans-stilbene)

Repetition of the reaction using chlorinated solvents resulted in the production of cis- $\text{PtCl}_2(\text{PPh}_3)_2$ (m.p. 305°C , infrared spectrum identical to that of an authentic sample).

SECTION 2

THE REACTIONS OF LOW-VALENT TRANSITION
METAL COMPLEXES WITH CYCLIC SULPHONES.

(A) Platinum(0)

(ii) Tetrakis(triphenylarsine)platinum(0)

Pt(AsPh₃)₄

(1) Tetrakis(triphenylarsine)platinum(0)
+ 3-phenylthiete-1,1-dioxide.

0.66g (0.47 mmol) $\text{Pt}(\text{AsPh}_3)_4$ and 0.09g (0.49 mmol) ligand were stirred under reflux in dry chloroform under an atmosphere of dry nitrogen. The reaction was allowed to proceed for 5 hours, after which time the solution was filtered, reduced in bulk under partial vacuum and treated with diethyl ether to the cloud point. Crystallisation over 2 days gave cream-coloured crystals, which were isolated and dried in a vacuum desiccator.

Yield 0.25g (53.9%)

M.p. 185-186°C (decomp)

Analysis For $\text{C}_{45}\text{H}_{38}\text{O}_2\text{SAs}_2\text{Pt}$

	%C	%H	M.W.
CALC	54.72	3.88	988
FOUND	54.73	3.88	-

Infrared spectrum (cm^{-1})

1600m, 1593m, 1503sh, 1585sh, 1444vs, 1421w, 1385vs, 1335m, 1308w, 1281vs, 1235w, 1197vs, 1108s, 1158w, 1154w, 1126vs, 1109s, 1098s, 1084vs, 1062m, 1030s, 1005s, 995sh, 971s, 927w, 922w, 901w, 857w, 842w, 840w, 799s, 767vs, 759vs, 744vs, 698vs, 675m.

^1H n.m.r. spectrum

Observed in CDCl_3 solution: a multiplet at 7.01 δ and a singlet at 4.72 δ with ill-defined ^{195}Pt satellites. An AB quartet was also observed at 4.33 δ . However, the singlet and the two high-field arms of the quartet appeared split further (with no effect on the low-field arms of the quartet). This condition is discussed further in the text.

The couplings were assigned as follows:

$$^2J(\text{Pt-olefin H}) = 71.0 \text{ Hz}$$

$$J(\text{AB}) = 11.5 \text{ Hz}$$

Secondary coupling = 2.09 Hz (see text).

(2) Tetrakis(triphenylarsine)platinum(0)
+ 3-p-bromophenylthiote-1,1-dioxide.

0.67g (0.48 mmol) $\text{Pt}(\text{AsPh}_3)_4$ and 0.13g (0.5 mmol) ligand were stirred together in dry degassed chloroform at room temperature under an atmosphere of dry nitrogen. The solution lightened during the course of 24 hours, when it was filtered and the filtrate reduced to small bulk under partial vacuum. Dry diethyl ether was added to the cloud point, and the solution left to crystallise at 0°C , affording pale yellow crystals which were isolated and dried in vacuo.

Yield 0.28g (39.2%)

M.p. 184-187 $^\circ\text{C}$ (decomp)

Analysis For $\text{C}_{45}\text{H}_{37}\text{As}_2\text{BrO}_2\text{PtS}$

	%C	%H	M.W.
CALC	50.67	3.50	1067
FOUND	50.97	3.61	1040

Infrared spectrum (cm^{-1})

1697s, 1492vs, 1447vs, 1426sh, 1405sh, 1387s, 1341m, 1307s, 1289vs, 1201vs, 1157m, 1135vs, 1115vs, 1084bvs, 1057s, 1030s, 1015sh, 1007s, 975s, 947w, 927w, 915w, 857sh, 831vs, 799sh, 792s, 747bvs, 704vs, 677m, 653s.

^1H n.m.r. spectrum

Observed in CDCl_3 solution: a similar spectrum to that with the unsubstituted complex, which is discussed in the text. Coupling was assigned as follows:

$$^2\text{J}(\text{Pt-olefin H}) = 66.5 \text{ Hz}$$

$$\text{J}(\text{AB}) = 11.3 \text{ Hz}$$

Secondary coupling = 2.09 Hz (see text).

The results of a variable temperature run are also discussed in the text.

(3) Tetrakis(triphenylarsine)platinum(0)
+ 3-^tbutylthiete-1,1-dioxide.

0.48g (0.32 mmol) $\text{Pt}(\text{AsPh}_3)_4$ and 0.05g (0.32 mmol) ligand were stirred in dry degassed chloroform in the usual way. After 2 hours the solution was filtered and the filtrate worked up as in (2). Only pure starting materials were obtained (i.r. spectra were identical to those of authentic samples).

The reaction was repeated, this time using refluxing chloroform for a period of 12 hours. Work-up of the resulting yellow solution yielded no product of a satisfactory nature, the yellow solution only containing decomposition products mixed with unreacted starting materials, as revealed by a preliminary i.r. analysis.

SECTION 2

THE REACTIONS OF LOW-VALENT TRANSITION
METAL COMPLEXES WITH CYCLIC SULPHONES.

(B) Palladium(0)

(i) Tetrakis(triphenylphosphine)palladium(0)

Pd(PPh₃)₄

- (1) Tetrakis(triphenylphosphine)palladium(0)
+ 3-phenylthiete-1,1-dioxide.

0.34g (0.3 mmol) $\text{Pd(PPh}_3)_4$ and 0.05g (0.3 mmol) ligand were stirred in dry degassed benzene at room temperature under an atmosphere of dry nitrogen. The solution was then refluxed for 24 hours. The cooled solution was reduced in bulk on the rotary evaporator and diethyl ether added to the cloud point. The resulting fine yellow powder was subjected to an infrared analysis and proved to be simply a mixture of starting materials.

SECTION 2

THE REACTIONS OF LOW-VALENT TRANSITION
METAL COMPLEXES WITH CYCLIC SULPHONES.

(C) Iron(0).

(i) Nonacarbonyldiiron(0)

$\text{Fe}_2(\text{CO})_9$

(1) Nonacarbonyldiiron(0) + 3-phenylthiete-1,1-dioxide.

0.9g (2.5 mmol) $\text{Fe}_2(\text{CO})_9$ and 0.9g (5.0 mmol) ligand were mixed in dry degassed diethyl ether under an atmosphere of dry nitrogen. The solution was refluxed for 2 hours during which time the suspension had become a murky brown colour. The solids were filtered off leaving a dark green filtrate. On standing white crystals began to form, and these were collected and air-dried. The green filtrate was concentrated to small bulk under reduced pressure, and left to crystallise at 0°C for 2 days. The brown-green amorphous powder resulting was filtered and dried in vacuo. Infrared analysis showed the white crystals to be pure organic starting material, and that the brown powder contained no carbonyl groups. The powder was discarded.

(2) Nonacarbonyldiiron(0) + 3-methylpent-3-ene-1-sulphone.

0.18g (0.5 mmol) $\text{Fe}_2(\text{CO})_9$ and 0.066g (0.5 mmol) ligand were stirred in refluxing dry degassed diethyl ether under an atmosphere of dry nitrogen. The reaction was allowed to proceed for 2 hours during which time the suspension had become green. The solution was filtered, and the green filtrate was concentrated under reduced pressure. White crystals formed from this solution, and were removed by filtration. The mother liquor was treated with petroleum ether (b.p. 40-60) to the cloud point and left to crystallise at 0°C . The brown precipitate formed was collected and air-dried.

Infrared analysis showed the white crystals to be pure organic starting material, whereas the brown compound was a product of unsatisfactory nature, by inspection, and no further characterisation was attempted.

SECTION 2

THE REACTIONS OF LOW-VALENT TRANSITION
METAL COMPLEXES WITH CYCLIC SULPHONES.

(D) Rhodium(I)

(i) Chlorotris(triphenylphosphine)rhodium(I)

$\text{RhCl}(\text{PPh}_3)_3$

(1) Chlorotris(triphenylphosphine)rhodium(I)
+ 3-phenylthiete-1,1-dioxide.

0.46g (0.5 mmol) $\text{RhCl}(\text{PPh}_3)_3$ and 0.09g (0.5 mmol) ligand were stirred together in dry degassed dichloromethane under an atmosphere of dry nitrogen. The reaction was allowed to proceed for 1 hour at room temperature and the solution was then refluxed for 12 hours. The solution was reduced in bulk and 40-60 b.p. petroleum ether added to the cloud point. The tan-coloured powder resulting was seen, by inspection, to be the dimeric $[\text{RhCl}(\text{PPh}_3)_2]_2$.

Repetition of the reaction in acetonitrile resulted in recovery of pure starting materials whose i.r. spectra were identical to those of authentic samples.

SECTION 3

THE REACTIONS OF LOW-VALENT TRANSITION
METAL COMPLEXES WITH CYCLOPROPENONE DERIVATIVES.

(A) Platinum(0)

(i) Trans-stilbenebis(triphenylphosphine)platinum(0)
Pt(PPh₃)₂(trans-stilbene)

- (1) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1,2-diphenylcycloprop-1-ene-3-one.

0.45g (0.5 mmol) Pt(PPh₃)₂(trans-stilbene) and
.0.10g (0.49 mmol) ligand were stirred in dry degassed
diethyl ether at room temperature under an atmosphere
of dry nitrogen. After 1 minute, all solids had
dissolved, and at the end of 30 minutes a canary yellow
crystalline product had precipitated. These crystals
were filtered, washed with dry ether and dried in vacuo.

Yield 0.35g (75.8%)

M.p. 160°C (Lit. 158-160°C)

Infrared spectrum (cm⁻¹)

1654vs, 1648sh, 1632sh, 1568w, 1524w, 1492sh, 1478vs,
1436vs, 1366w, 1180w, 1150vw, 1096vs, 1084m, 1064m,
1024w, 890s, 804m, 782s, 774s, 760sh, 750vs, 730m,
708sh, 698vs, 676sh, 578s, 538vs, 528vs, 520vs, 496sh.

Comparison of the above spectrum and m.p. with that
given in the literature (72JO(44)C63) indicated that
this complex was identical to that reported.

(2) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1-methyl-2-phenylcycloprop-1-ene-3-one.

0.45g (0.5 mmol) Pt(PPh₃)₂(trans-stilbene) and 0.072g (0.5 mmol) ligand were reacted in dry degassed diethyl ether as has been previously described. After 30 minutes, the yellow crystalline product was filtered, washed with ether and dried in vacuo.

Yield 0.32g (74.1%)

M.p. 155-157°C

Analysis For C₄₆H₃₈OP₂Pt

	%C	%H	%P	M.W.
CALC	63.96	4.43	7.18	864
FOUND	63.96	4.43	7.17	-

Infrared spectrum (cm⁻¹)

1666vs, 1590w, 1576w, 1536bw, 1486s, 1440vs, 1435vs, 1368sh, 1314w, 1255w, 1175w, 1156w, 1124w, 1096vs, 1074w, 1056w, 1030w, 924vw, 852bvw, 786m, 764s, 744s, 708vs, 698vs, 695vs, 625w.

¹H n.m.r. spectrum

Observed in CDCl₃ solution: a multiplet centred at 7.15δ and a doublet centred at 1.48δ having ¹⁹⁵Pt satellites. Relative intensities 35:3. Couplings are as follows:

trans- ⁴J(P-H) = 7.54 Hz

cis- ⁴J(P-H) = 0 Hz

³J(Pt-H) = 51.6 Hz

(3) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1,2-diphenylcycloprop-1-ene-3-thione.

0.45g (0.5 mmol) $\text{Pt}(\text{PPh}_3)_2$ (trans-stilbene) and 0.11g (0.5 mmol) ligand were stirred together in dry diethyl ether as before described. The suspension darkened, and after 15 minutes the yellow-brown solid was filtered off, washed with dry ether and dried in vacuo.

Yield 0.32g (67.9%)

M.p. 128-129°C

Analysis For $\text{C}_{51}\text{H}_{40}\text{SP}_2\text{Pt}$

	%C	%H	%P
CALC	65.04	4.28	6.58
FOUND	63.96	4.73	6.08

Infrared spectrum (cm^{-1})

1795bm, 1678bm, 1691vs, 1686vs, 1570s, 1493vs, 1478vs, 1444m, 1434vs, 1388w, 1330w, 1308w, 1225s, 1182s, 1152s, 1112s, 1090vs, 1068vs, 1024m, 974w, 918m, 880vw, 844m, 744bvs, 969bvs, 628w, 424w, 592s, 580m, 542vs, 520bvs, 500vs, 488vs, 464w, 452m, 424m.

(4) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1,1-dicyano-2,2-diphenylcyclopropenylethylene.

0.38g (0.3 mmol) Pt(PPh₃)₂(trans-stilbene) and 0.08g (0.3 mmol) ligand were stirred together in dry diethyl ether as previously described. The suspension darkened in colour slightly, and was left stirring for 24 hours. The yellow precipitate was then filtered, washed and dried in a vacuum desiccator.

Yield 0.24g (50.0%)

M.p. 147-149°C

Analysis For C₅₃H₄₀N₂PtP₂

	%C	%H	%N
CALC	66.18	4.19	2.91
FOUND	62.33	4.16	3.19

Infrared spectrum (cm⁻¹)

2245s, 2218vs, 1660m, 1600m, 1590w, 1576w, 1552vs, 1532m, 1482vs, 1438vs, 1364s, 1328m, 1188m, 1160w, 1120w, 1096vs, 1072w, 1030m, 1000m, 912w, 882m, 852bw, 792w, 783w, 752vs, 704bvs, 672w, 628w, 616w, 610w, 603w, 590m, 582w, 552m, 540s, 528vs, 524s, 512s, 468w, 426w.

SECTION 3

THE REACTIONS OF LOW-VALENT TRANSITION
METAL COMPLEXES WITH CYCLOPROPENONE DERIVATIVES.

(A) Platinum(0)

(ii) Tetrakis(triphenylarsine)platinum(0)

Pt(AsPh₃)₄

(1) Tetrakis(triphenylarsine)platinum(0)
+ 1,2-diphenylcyclopropenone.

0.80g (0.57 mmol) $\text{Pt}(\text{AsPh}_3)_4$ and 0.12g (0.58 mmol) ligand were mixed and stirred together in dry degassed chloroform at room temperature under an atmosphere of dry nitrogen. The solution immediately lightened in colour, and after 3 hours the pale yellow solution was filtered, washed with chloroform and reduced in bulk to about 5 cm³. Dry diethyl ether was added to the cloud point, and the solution left to crystallise at 0°C, affording pale yellow crystals, which were filtered off and dried in vacuo.

Yield 0.15g (19.95%)
M.p. 140-143°C (decomp)
Analysis For $\text{C}_{51}\text{H}_{40}\text{As}_2\text{OPt}$

	%C	%H	M.W.
CALC	60.42	3.98	1014
FOUND	60.79	4.03	-

Infrared spectrum (cm⁻¹)

1712s, 1660sh, 1655vs, 1620w, 1602w, 1585w, 1487vs, 1446vs, 1386s, 1311s, 1277w, 1227w, 1187m, 1157m, 1136w, 1099sh, 1085vs, 1069s, 1029s, 1007s, 987s, 925s, 899s, 857w, 815s, 785s, 769s, 752vs, 741vs, 727vs, 701vs, 698vs, 684sh, 677sh.

SECTION 3

THE REACTIONS OF LOW-VALENT TRANSITION
METAL COMPLEXES WITH CYCLOPROPENONE DERIVATIVES.

(B) Rhodium(I)

(i) Chlorotris(triphenylphosphine)rhodium(I)
 $\text{RhCl}(\text{PPh}_3)_3$

(1) Chlorotris(triphenylphosphine)rhodium(I)
+ 1,2-diphenylcycloprop-1-ene-3-one.

0.46g (0.5 mmol) $\text{RhCl}(\text{PPh}_3)_3$ and 0.1g (0.43 mmol) ligand were stirred together in dry degassed benzene under an atmosphere of dry nitrogen. The reaction was allowed to proceed at room temperature for 1 hour and the solution was then refluxed for 48 hours. The solution was filtered, and then reduced in bulk under partial vacuum. Dry diethyl ether was added to the cloud point, and the solution allowed to stand at 0°C for 2 days. Only a dark brown amorphous powder was obtained, which was judged, by inspection, to be a decomposition compound and was discarded. Attempts at obtaining any satisfactory products from this reaction failed, yielding either unreacted starting materials or decomposition products (which were not characterised).

SECTION 4

THE REACTIONS OF LOW-VALENT TRANSITION
METAL COMPLEXES WITH CYCLOBUTENE DERIVATIVES
CONTAINING EXOCYCLIC CARBON-CARBON BONDS.

- (A) Platinum(0)
- (i) Trans-stilbenebis(triphenylphosphine)platinum(0)
Pt(PPh₃)₂(trans-stilbene)

(1) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1-methylenemethylcarboxy-2,3-benzocyclobutene-4-one.

0.45g (0.5 mmol) Pt(PPh₃)₂(trans-stilbene) and 0.09g (0.48 mmol) ligand were stirred together in dry degassed diethyl ether at room temperature under an atmosphere of dry nitrogen. The solids slowly dissolved and the mixture was stirred for 2 hours. After this time a canary-yellow crystalline product had precipitated, and this was filtered, washed with ether and dried in a vacuum desiccator.

Yield . 0.14g (30.5%)

M.p. 144-147^oC

Analysis For C₄₇H₃₈P₂O₃Pt

	%C	%H	M.W.
CALC	62.18	4.21	908
FOUND	60.55	4.64	-

Infrared spectrum (cm⁻¹)

1748vs, 1670vs, 1596sh, 1576vs, 1496sh, 1479s, 1436vs, 1413s, 1362vs, 1344sh, 1308sh, 1254vs, 1196m, 1160bvs, 1120vs, 1096vs, 1020m, 976s, 908m, 880m, 852w, 824s, 808s, 760sh, 750vs, 745sh, 728m, 696vs, 664w, 544vs, 504bvs, 452w, 430m.

¹H n.m.r. spectrum

No satisfactory spectrum was obtained for this product due to contamination by the di-exocyclicmethylene ligand, (q.v.).

(2) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1,2-dimethylenemethylcarboxy-3,4-benzocyclobutene.

0.45g (0.5 mmol) Pt(PPh₃)₂(trans-stilbene) and 0.15g (0.62 mmol) ligand were stirred together in degassed ether at room temperature under an atmosphere of dry nitrogen for 48 hours. The solution was filtered and the filtrate reduced to dryness under vacuum. The resulting yellow oil was dissolved in dry chloroform and chromatographed using a 30 cm column packed with silica gel using chloroform as elutant. The last fraction was taken and reduced to small bulk on the rotary evaporator. Oily yellow crystals were formed, and these were isolated and dried in vacuo. However, no satisfactory dry crystals could be obtained.

Yield 0.12g (24.9%)

M.p. -

Analysis For C₅₀H₄₂O₄P₂Pt

No satisfactory analysis could be obtained due to the impure nature of the product.

Infrared spectrum (cm⁻¹)

1707s, 1686vs, 1620w, 1586w, 1578w, 1496sh, 1480s, 1440sh, 1432vs, 1396vs, 1364vs, 1302w, 1296w, 1262m, 1184m, 1154sh, 1140vs, 1124s, 1096vs, 1028w, 1018w, 976m, 882m, 850w, 786m, 748s, 736s, 700vs, 668w, 624vw, 552w, 542s, 524vs, 514sh, 502s, 460m.

¹H n.m.r. spectrum

Observed in CDCl₃ solution: a multiplet centred at 7.06δ and four singlets at 5.01, 3.58, 2.94 and 0.07δ in the relative intensities 34:1:1:3:3. Trace amounts of starting ligand were observed as singlets at 5.70 and 3.69δ. It was suspected that contamination by the mono-ketone was causing confusion in this spectrum.

(3) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1,2-dimethylenecyclobut-3-ene.

0.45g (0.5 mmol) $\text{Pt}(\text{PPh}_3)_2$ (trans-stilbene) and 0.041g (0.53 mmol) ligand were stirred in dry ether as previously described. The reactants dissolved, and after 10 minutes a white crystalline precipitate was seen to form. The reaction was allowed to proceed for 3 hours, whereupon the white product was isolated and dried in vacuo.

Yield 0.21g (52.6%)

M.p. 152-156°C

Analysis For $\text{C}_{42}\text{H}_{36}\text{P}_2\text{Pt}$

Insufficient complex remained to send a sample for analysis.

Infrared spectrum (cm^{-1})

1700bs, 1588m, 1572w, 1480vs, 1433vs, 1364vs, 1300m, 1178m, 1158m, 1116sh, 1096vs, 1067w, 1128w, 970w, 880w, 868m, 852m, 760sh, 746vs, 696vs, 626w, 574w, 547s, 532sh, 514vs, 500vs, 456m, 440w, 420m.

^1H n.m.r. spectrum

This was not obtained due to the complex being either totally insoluble in all suitable solvents, or rapidly decomposing in solution (in deuteriochloroform, no apparent solution was formed, but on standing the complex discoloured leading to a brown residue which was characterised as cis- $\text{PtCl}_2(\text{PPh}_3)_2$, m.p. 308°C, i.r. identical to that of an authentic sample).

SECTION 5

THE REACTIONS OF ZERO-VALENT PLATINUM
COMPLEXES WITH SOME MISCELLANEOUS
CYCLOBUTENES AND RELATED MOLECULES.

In all cases the platinum(0) starting
complex was trans-stilbenebis(triphenylphosphine)-
platinum(0), Pt(PPh₃)₂(trans-stilbene)

- (1) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ cyclobutanone.

0.45g (0.5 mmol) $\text{Pt}(\text{PPh}_3)_2$ (trans-stilbene) and 0.035g (0.5 mmol) ligand were stirred together in dry degassed diethyl ether at room temperature under an atmosphere of dry nitrogen. The suspension became lighter, but only pure starting materials were isolated from the reaction (i.r. evidence).

Solution reaction between these materials similarly only produced pure starting materials, the infrared spectra being identical to those of the starting materials.

(2) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ bis(perfluoromethyl)-1,2-dithietene.

0.45g (0.5 mmol) Pt(PPh₃)₂(trans-stilbene) and 0.11g (0.5 mmol) ligand were stirred together in dry degassed diethyl ether at room temperature under an atmosphere of dry nitrogen. No apparent reaction was observed, and after 24 hours the yellow crystals were filtered off, washed with ether and dried under vacuum.

Yield 0.42g (88.8%)

M.p. >300°C

Analysis For C₄₀H₃₀P₂S₂F₆Pt

	%C	%H	M.W.
CALC	50.79	3.20	946
FOUND	50.84	3.44	-

Infrared spectrum (cm⁻¹)

1594w, 1570w, 1544vs, 1480vs, 1434vs, 1364s, 1312m, 1280sh, 1250bvs, 1218m, 1190sh, 1140bvs, 1122bvs, 1096vs, 1070sh, 1030w, 1000w, 978vw, 912vs, 882m, 848m, 760sh, 746vs, 722vs, 700bvs, 624w, 540vs, 530vs, 518vs, 506vs, 496vs, 468m, 451w, 430m, 378w.

¹⁹F n.m.r. spectrum

The complex was totally insoluble in all solvents, and the n.m.r. spectrum was, unfortunately, impossible to obtain.

(3) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ 1-chloro-1,2,2-trifluoro-3-phenylcyclobut-3-ene.

0.45g (0.5 mmol) Pt(PPh₃)₂(trans-stilbene) and 0.1g (0.5 mmol) ligand were stirred together in dry degassed diethyl ether under an atmosphere of dry nitrogen at room temperature. All solids dissolved after 1 minute, and the colourless solution was allowed to stir for 24 hours, after which time a fine crystalline precipitate had formed. The product was filtered, washed with ether and dried in vacuo.

Yield 0.09g (19.1%)

M.p. 195-195.5°C

Analysis For C₄₆H₃₆P₂F₃ClPt

	%C	%H	M.W.
CALC	58.88	3.87	-
FOUND	58.75	3.86	

Infrared spectrum (cm⁻¹)

1697s, 1600w, 1590w, 1568w, 1483m, 1436vs, 1364vs, 1352vs, 1344sh, 1330sh, 1318sh, 1276vw, 1194w, 1186m, 1168w, 1160w, 1122s, 1096vs, 1064m, 1020w, 1014s, 976s, 882m, 848vw, 826m, 776m, 760s, 752s, 744s, 698vs, 662vw, 624w, 600w, 540vs, 530vs, 518vs, 508s, 310w.

¹H n.m.r. spectrum

Observed in CDCl₃ solution: a multiplet at 6.99δ.

No other signals were observed even with a concentrated sample at high amplitude. It is possible that the single proton resonance has been displaced downfield into the phenyl-ring-proton region and is thus masked.

¹⁹F n.m.r. spectrum

Observed in CHCl₃ solution: two patterns - an asymmetrical 3-line pattern at 40.39 p.p.m. upfield from external ααα-trifluorotoluene, and a multiplet at 54.28 p.p.m. upfield from the standard. This spectrum is discussed in the text.

(4) Trans-stilbenebis(triphenylphosphine)platinum(0)
+ hexa-1,5-diyne.

0.45g (0.5 mmol) Pt(PPh₃)₂(trans-stilbene) and 0.04g (0.51 mmol) ligand were stirred together in dry degassed diethyl ether at room temperature under an atmosphere of dry nitrogen. After 1 minute all the solids had dissolved, and the reaction was allowed to proceed for 8 hours. During this time a creamy-white crystalline precipitate developed. These crystals were filtered, washed with dry ether and dried in vacuo.

Yield . 0.35g (87.7%)

M.p. 147-148°C

Analysis For C₄₂H₃₆P₂Pt

	%C	%H	M.W.
CALC	63.22	4.55	798
FOUND	57.16	4.96	-

Infrared spectrum (cm⁻¹)

1722s, 1588w, 1572w, 1478vs, 1432vs, 1364vs, 1308w, 1180m, 1148w, 1102s, 1096vs, 1066w, 1030m, 910w, 964w, 882m, 858m, 846m, 758s, 754s, 746vs, 969bvs, 614w, 575w, 548s, 528sh, 516bvs, 500sh, 456w, 438w, 424m, 378w.

¹H n.m.r. spectrum

This complex was either totally insoluble or rapidly decomposed in all suitable n.m.r. solvents. It was, therefore, impossible to obtain a spectrum.

SECTION 6

PREPARATION OF STARTING MATERIALS

(i) ORGANIC.

The following materials were prepared by the literature methods (quoted after the compound).

1-phenylcyclobut-1-ene-3,4-dione	(60JA1793)
1-methyl-2-phenylcyclobut-1-ene-3,4-dione	(71S542)
1-chloro-2-phenylcyclobut-1-ene-3,4-dione	}
1-methoxy-2-phenylcyclobut-1-ene-3,4-dione	
1,2-diphenylcyclobut-1-ene-3,4-dione	
1-bromo-2-phenylcyclobut-1-ene-3,4-dione	
1,2-dimethoxycyclobut-1-ene-3,4-dione	}
1,2-diethoxycyclobut-1-ene-3,4-dione	
1,2-diaminocyclobut-1-ene-3,4-dione	
1-amino-2-methoxycyclobut-1-ene-3,4-dione	
1,2-dimethylcyclobut-1-ene-3,4-dione	(70LA101)
1,2-di-n-butoxycyclobut-1-ene-3,4-dione	(65LA55)
1,2-benzocyclobut-1-ene-3,4-dione	(57JA3606, 63JA2076)
1,2-diphenylcycloprop-1-ene-3-one	(65JA1320)
1,2-diphenylcycloprop-1-ene-3-thione	(64BJ1897)
1-methylenemethylcarboxy-2,3-benzocyclobutene- 4-one	}
1,2-dimethylenemethylcarboxy-3,4- benzocyclobutene	
1,2-dimethylenecyclobut-3-ene	(67JA342)
1-chloro-1,2,2-trifluoro-3-phenylcyclobut- 3-ene	(60JA1793)

The following materials were donated by members of Leicester University Chemistry Department (acknowledgements quoted after compound).

bis(perfluoromethyl)-1,2-dithietene	(S.A. Bone)
3-phenylthiete-1,1-dioxide	}
3- <u>p</u> -bromophenylthiete-1,1-dioxide	
3- <u>t</u> -butylthiete-1,1-dioxide	
2,3-benzothiophene-1,1-dioxide	
cyclopent-3-ene-1-sulphone	
3-methylcyclopent-3-ene-1-sulphone	}
1-methyl-2-phenylcycloprop-1-ene-3-one	
	(Dr. N. Singh)

(ii) ORGANOMETALLIC AND INORGANIC

<u>trans</u> -stilbenebis(triphenylphosphine)platinum(0)	(62J3269)
tetrakis(triphenylphosphine)platinum(0)	(68IG105)
tolanbis(triphenylphosphine)platinum(0)	(64CC1063)
tetrakis(triphenylarsine)platinum(0)	(58J2323)
tetrakis(triphenylphosphine)palladium(0)	(72IG121)
tetrakis(triphenylarsine)palladium(0)	(69J1793)
chlorotris(triphenylphosphine)rhodium(I)	(67IG68)
<u>trans</u> -chlorocarbonylbis(triphenylphosphine)- iridium(I)	(68IG101)
bis(ethylene)acetylacetonatorrhodium(I)	(62IC722 67JA4621)
dipivaloylmethanatocycloocta-1,5- dienerhodium(I)	(72J2549)
Nonacarbonyldiiron(0)	(66IG178)

MISCELLANEOUS INFORMATION

(i) Melting Points

All melting points were measured on a Riechert hot-stage apparatus and are uncorrected.

(ii) Infrared spectra

All spectra were recorded as mulls (Nujol or hexachlorobutadiene) between Caesium-iodide plates or as potassium bromide discs. Spectra were recorded on a Perkin-Elmer 225 Spectrophotometer and spectra were calibrated against a 0.5 mm polystyrene film.

(iii) ^1H and ^{19}F n.m.r. spectra

Preliminary ^1H spectra were recorded on a Varian Associates T60 Spectrometer; all other spectra were recorded on a JEOL JNMPS 100 spectrometer (at 94MHz for ^{19}F and 100MHz for ^1H).

(iv) Analyses

Analyses were carried out by the following:

Beller Mikroanalytisches Laboratorium

F. Pascher Mikroanalytisches Laboratorium

C.H.N. Analysis Ltd.

The Microanalytical Department, University of
Heidelberg.

(v) Solvents

Solvents were dried by standing over sieves and were degassed by freeze-pumping (using dry nitrogen as flood-gas) under high vacuum.

(vi) Commercial Re-agents

High-grade commercial reagents were used at all times, and no further purification was deemed necessary. Reagents were used as received.

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APPENDIX 1

Letter Codes for Journal Titles.

<u>Code</u>	<u>Full Title</u>
AGI	Angewandte Chemie (International Edition)
BF	Bulletin de la Société chimique de France
BJ	Bulletin of the Chemical Society of Japan
CB	Chemische Berichte
CC	Canadian Journal of Chemistry
CD	Coordination Chemistry Reviews
CH	Chemical Communications
IA	Inorganica Chimica Acta
IC	Inorganic Chemistry
IG	Inorganic Syntheses
J	Journal of the Chemical Society
JA	Journal of the American Chemical Society
JO	Journal of Organometallic Chemistry
JOC	Journal of Organic Chemistry
LA	Justus Liebig's Annalen der Chemie
MI	Miscellaneous
PH	Journal of Physical Chemistry
S	Synthesis
TL	Tetrahedron Letters

SUMMARY

The thesis is divided into four chapters:

- (1) Introduction
- (2) Results and discussion on the reactions of cyclobutenedione derivatives and related molecules with low-valent transition metal complexes.
- (3) A kinetic study of the ring-expansion reactions of some cyclobutenedione derivatives by platinum(0) complexes and
- (4) Experimental.

Chapter 1.

This chapter gives a general survey of the reactions of organic molecules containing small rings with transition metal complexes. The review concentrates on three- and four-membered ring compounds having both electron-donating and electron-withdrawing substituents in their reactions with the later transition metals. Particular accent is placed on the metals iron, rhodium, palladium and platinum.

Chapter 2.

The reactions of cyclobutenedione derivatives and related molecules with transition metal complexes are discussed. Hypotheses are put forward to account for the variation of products found in these reactions when both the nature of the substituent groups in the organic molecule and the transition metal complex are changed.

The spectroscopy results obtained for these complexes are discussed.

Chapter 3.

A kinetic study of the ring-expansion reactions of some cyclobutenedione derivatives by platinum(0) complexes is described. The reactivities of the species $\text{Pt}(\text{PPh}_3)_2$ and $\text{Pt}(\text{AsPh}_3)_2$ are compared, and a theory concerning the solution characteristics of $\text{Pt}(\text{AsPh}_3)_2$ is put forward.

Chapter 4.

All experimental details are given for the reactions studied in chapters 2 and 3. All analysis results, infrared and n.m.r. spectra are detailed.