TETRASUBSTITUTED-CYCLOBUTADIENEPALLADIUM HALIDES

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By

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SCOPE AND CONTENTS: Diphenylacetylenes, RC_2R, ($R=C_6H_5$, $p\text{-}ClC_6H_4$, $p\text{-}CH_3C_6H_4$, $p\text{-}CH_3OC_6H_4$) reacted with palladium (II) complexes to give $[R_4C_4OEtPdCl]_2$, or $[R_4C_4(PdCl_2)_n]_2$ and R_6C_6. Hydrogen halides converted $[R_4C_4OEtPdCl]_2$ to $[R_4C_4PdX_2]_2$.

Particularly significant were the reactions in which a cyclobutadiene (R_4C_4) was transferred from palladium or nickel onto other metals. A very interesting reaction was the unprecedented ligand exchange.

$$[R_4C_4PdX_2]_2 + 2(R'_3P)_2NiX_2 \longrightarrow [R_4C_4NiX_2]_2 + 2(R'_3P)_2PdX_2$$

R'OH reacted with $[R_4C_4PdX_2]_2$ (except $R=p\text{-}CH_3OC_6H_4$) to give exo$[R_4C_4OR'PdX]_2$ and acids reversed this reaction. Some complexes $[R_4C_4PdC_5H_5]^+$ were also made by ligand transfer of the cyclopentadienyl ligand onto palladium.

^1H N.M.R. studies of compounds derived from p,p'-disubstituted diphenylacetylenes showed that the phenyl

region of the spectrum could be used to determine if the compound possessed the symmetry of a cyclobutadiene compound.

ACKNOWLEDGEMENTS

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The author is indebted to Dr. D. M. Clugston and Mr. K. Moseley for the mass spectrometric molecular weight determinations.

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NOTATION

The following system of numbering the compounds has been adopted throughout the thesis. When a compound was derived from diphenylacetylene and a substituted diphenylacetylene, a letter follows the numerical designation of the compound. The letter a after the number indicates that the compound was derived from diphenylacetylene, b indicates that the compound was derived from p,p'-dichlorodiphenylacetylene, c from p,p'-ditolylacetylene and d from p,p'-dianisylacetylene, e.g.

(4a)	tetraphenylcyclobutadieneiron tricarbonyl
(4b)	tetrakis(p-chlorophenyl)cyclobutadieneiron tricarbonyl
(4c)	tetrakis(p-tolyl)cyclobutadieneiron tricarbonyl
(4d)	tetrakis(p-anisyl)cyclobutadieneiron tricarbonyl

INTRODUCTION

INTRODUCTION

The INTRODUCTION of this thesis is divided into four sections: *A*, organometallic compounds with little or no dπ-pπ back bonding; *B*, organometallic compounds with dπ-pπ back bonding; *C*, the reactions of acetylenes with transition metal compounds in which organometallic compounds are formed; and *D*, cyclobutadiene-transition metal compounds.

Organometallic compounds are defined as those compounds which contain a metal to carbon bond.[1a]

A. Organometallic compounds with little or no dπ-pπ back bonding.

The metallic elements of the main group of the periodic table are known to form compounds of the type R_nM and $R_{n-x}MX_x$, where M is a metal, R an organic moiety, and X an anion.

For the class of compounds R_nM the nature of the metal is the most important factor in determining the chemical properties of the compound. When M is a highly electropositive metal and R is an alkyl or aryl group, the bonding in the compound is essentially ionic and the compound is best formulated as R^-M^+, e.g. $CH_3^-K^+$. These compounds are highly reactive to any reagent containing a polar bond. For instance, alkyls of the alkali metals react violently with water, e.g.[1b]

$$CH_3^-K^+ + H_2O \longrightarrow CH_4 + KOH$$

As the electropositive nature of the main group elements increases on going down a group, the reactivity of these compounds increases in the series Li<Na<K<Rb<Cs. Going from left to right in a short period of the periodic table, the electropositive nature of the metal decreases. Consequently all other factors being equal, the reactivity of these compounds to polar reagents decreases in the

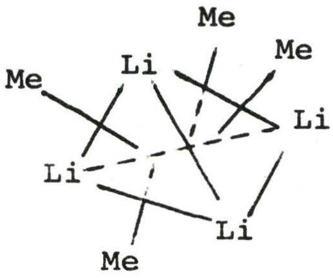
order IA>IIA>IIIA.

In cases where the difference in electronegativity of the metal and the organic moiety is less a more covalent bond is formed and the metal-carbon bond is less susceptible to cleavage by polar reagents. For example, the alkyl and aryl derivatives of tin are unaffected by water at room temperature.[1c]

The nature of the organic moiety is important in comparing the reactivities of organic compounds of one specific metal. The greater the ability of the organic moiety to support a negative charge the less reactive, or more stable, the compound is likely to be to attack by polar reagents.[2]

In general, compounds containing highly electronegative ligands, e.g. halides, sulphate, are more stable to attack by polar reagents than a compound of the same metal containing only alkyl or aryl ligands. For example, the organoberyllium halides are stable to carbon dioxide whereas dialkylberyllium compounds react readily.[1d]

Many of the organometallic compounds of the main group metals are polymeric. Polymeric structures are frequently found when the central metal atom of the monomer would be electron deficient. For example, methyllithium (1) is tetrameric and has the structure:[3]



(1)

This structure permits each lithium atom to have a share in eight electrons and thus achieve the electronic configuration of the next inert gas.

The organometallic compounds of the main group metals are synthesized by substitution, e.g.

$$2LiEt + CdBr_2 \longrightarrow CdEt_2 + 2LiBr^{4},$$

or

$$C_6H_6 + Hg(OAc)_2 \longrightarrow C_6H_5HgOAc + HOAc^{5},$$

or by addition reactions

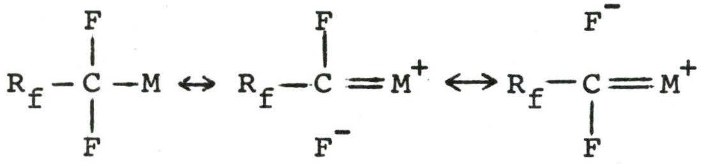
$$Ph_2C = CPh_2 + 2Na \longrightarrow 2Na^+ + \left[Ph_2C = CPh_2\right]^{=} \quad {}^{6}$$

The transition metals are not sufficiently electropositive to permit the formation of ionic compounds of the type $R_n^{-1}\ M^{+n}$, so the bonding is covalent. Transition metal alkyls and aryls tend to be thermally unstable. For example, tetramethyltitanium, a comparatively stable transition metal alkyl, decomposes at room temperature,[7] whereas tetramethyltin is stable to about 400°.[8] A theory to explain the low thermal stability of σ-bonded transition metal alkyls has been proposed by Chatt.[9,10] The energy difference, ΔE, between the highest energy filled orbital in the metal-carbon bond and the lowest energy unfilled orbital is thought to be about equal to the thermal energy at room temperature. If the thermal energy is sufficient to promote an electron from the metal-carbon bond to an unfilled orbital the metal-carbon bond will be weakened and the organic moiety, usually as a radical, ceases to be bonded to the central metal atom. The products observed in the thermal decomposition of transition metal alkyls or aryls are those expected to arise from free radicals. For example,

$$\mathrm{EtTiCl_3} \xrightarrow{20°} \mathrm{C_2H_6} + \mathrm{C_4H_{10}} + \mathrm{Ti(III)}$$ [11]

Some electronic configurations of the metal atom give relatively stable compounds, e.g. d^0 [L_2R_4Ti], octahedral; d^3 [$RCr(H_2O)_5^{++}$], octahedral; d^6 [$RMn(CO)_5$], low spin; d^8 [L_2MR_2], square planar; and d^{10} [$RCu]_n$. The stability is probably associated with the large values of ΔE for these electronic configurations.

Compounds which contain perfluoro-alkyl and aryl groups are more thermally stable than their hydrocarbon analogues. The metal-perfluoro-organic group bond can be thought of as strengthened by contributions from resonance forms such as;



$$R_f-\underset{F}{\overset{F}{C}}-M \leftrightarrow R_f-\underset{F^-}{\overset{F}{C}}=M^+ \leftrightarrow R_f-\underset{F}{\overset{F^-}{C}}=M^+$$

Ligands which cause large crystal field splittings (e.g. cyanide ion, carbonyl, and nitric oxide) stabilise compounds containing metal-alkyl or -aryl bonds. This is thought to be due to those ligands increasing ΔE, in agreement with Chatt's proposal.[9,10]

Compounds containing transition metals σ-bonded to an alkyl or aryl group are generally prepared by reactions such as the following:

$Na^+Mn(CO)_5^- + CH_3I \longrightarrow CH_3Mn(CO)_5 + NaI$[12]

$CrCl_3 \cdot 3THF^* + 3PhMgBr \longrightarrow Ph_3Cr \cdot 3THF + 3MgX_2$[13]

*THF = tetrahydrofuran

B. Organometallic compounds with $d\pi$-$p\pi$ back bonding.

I. Structure and bonding.

Various neutral molecules (e.g. carbon monoxide, alkenes, alkynes and substituted phosphines) form stable compounds with transition metals in low oxidation states, e.g. $Ni(CO)_4$, $(C_2H_4)PtCl_2 \cdot NH(CH_3)_2$, $PhC_2PhCo_2(CO)_6$, and $(Ph_3P)_4Pt$. These ligands all have two properties in common. They possess electrons which are available for donation, and they possess vacant orbitals of the correct symmetry and energy to overlap with filled d orbitals of the central transition metal atom.

The stoichiometry of some of these compounds can be determined by using the effective atomic number formalism. This requires that the central metal atom has eighteen electrons associated with it, which gives the metal atom the effective electronic configuration of the next highest inert gas, e.g. $Ni(CO)_4$

$$Ni^{o}[Ar]d^{10} \quad + \quad 4 \times 2 \longrightarrow Ni[Kr]$$

Carbon monoxide is a very poor Lewis base and the existence of only σ-bonding between it and the metal could not explain the stability of the metal carbonyls.

A detailed picture of the bonding in chromium hexacarbonyl is shown in Figure 1.[14,15]

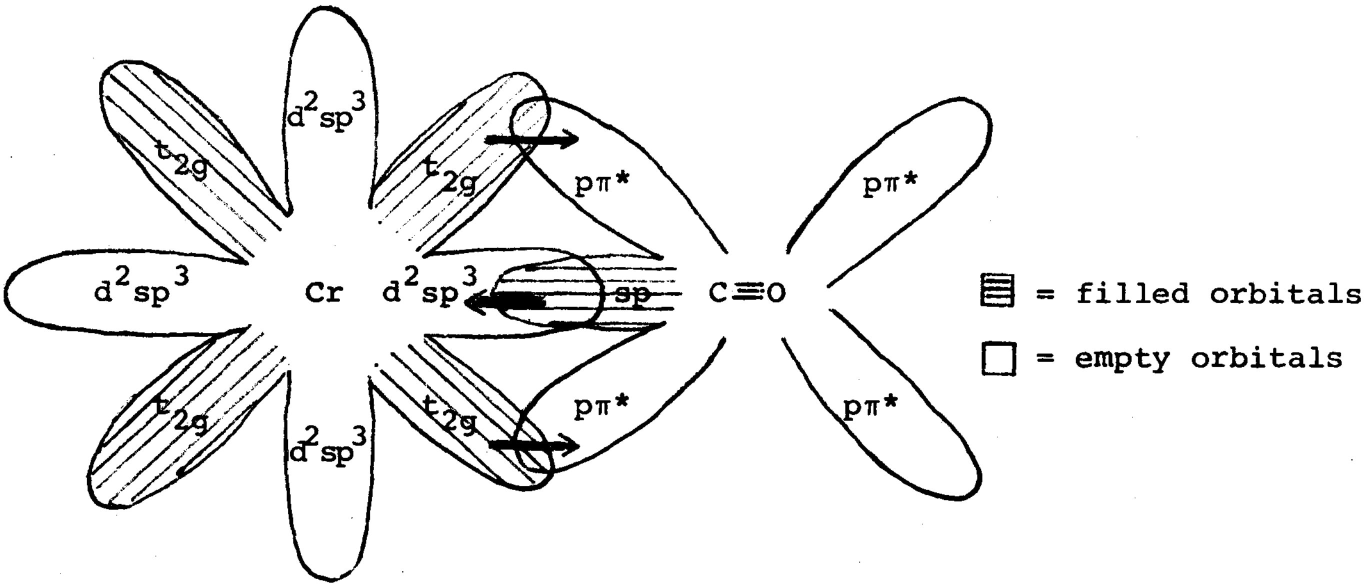


Figure 1. Schematic representation of the bonding in chromium hexacarbonyl.

The bonding involves electron donation from the filled sp hybrid orbital of carbon to the vacant d^2sp^3 hybrid orbital of the chromium atom. At the same time the electron density of the chromium atom is lowered by overlap of the filled t_{2g} orbitals with one of the vacant $2p\pi^*$ orbitals of the carbon monoxide. The drift of electrons into the $2p\pi^*$ orbital of carbon monoxide tends to make it a better donor while the lowering of electron density on the chromium tends to make it a better acceptor. These two mutually reinforcing processes are described as synergic bonding.

The bonding between low valent transition metals and unsaturated organic molecules or ions has been described in similar terms. As an example, a detailed picture of the bonding between ethylene and platinum in Zeise's salt is shown in Figure 2.[7,16]

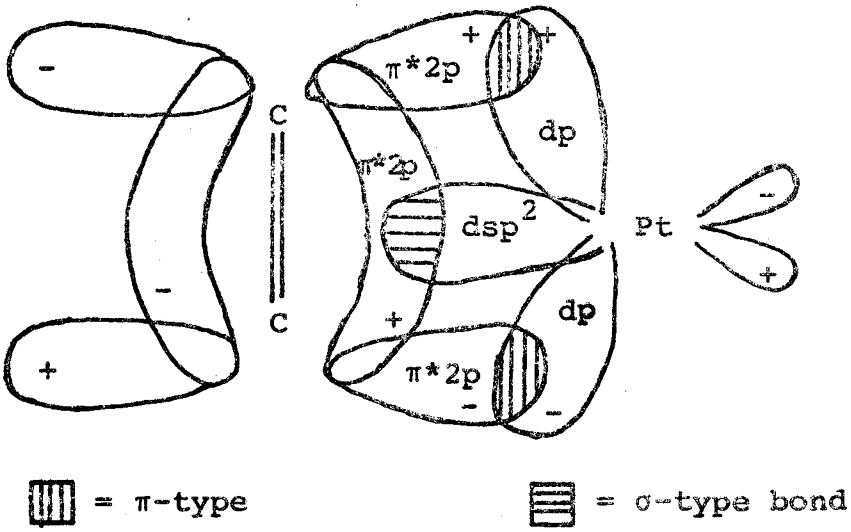


Figure 2. Schematic representation of the bonding between platinum and ethylene in Zeise's salt.

The bonding involves the formation of a σ-bond by overlap of the vacant $5d6s6p^2$ hybrid orbital of platinum and the filled $2p\pi$ orbital of ethylene, and the formation of a π-bond by overlap of the filled 5d6p hybrid orbital of platinum with the vacant $2p\pi^*$ orbital of ethylene.

There is a large variety of compounds in which more than one carbon atom from the same ligand is bonded to the central metal atom. The binding in these compounds is similar to that in chromium hexacarbonyl and Zeise's salt except that different orbitals are used to obtain an effective overlap. A pictorial representation such as those given above is not always possible for these systems, which are better described in terms of a molecular orbital diagram. An example of this is the bonding in cyclobutadiene-metal complexes which is described in section D.

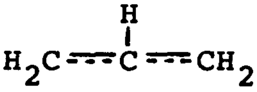
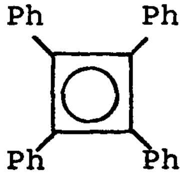
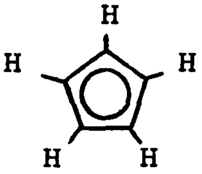
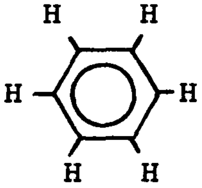
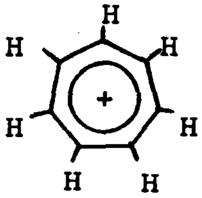
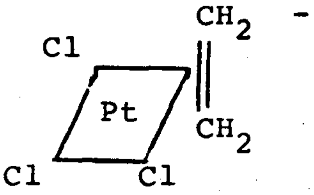
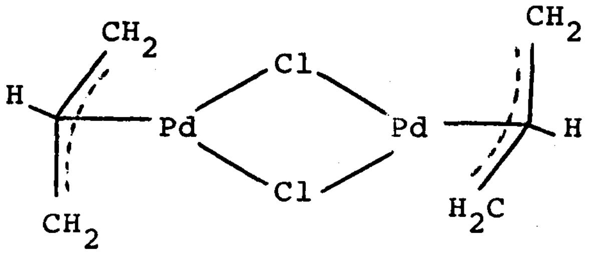
Ligand	Number of carbons π-bonded to metal	Compound
$H_2C{=}CH_2$	2	$C_2H_4PtCl_3^- \; K^+$ Zeise's salt
 $H_2C \cdots C(H) \cdots CH_2$	3	$[(C_3H_5PdCl]_2$ π-allylpalladium chloride dimer
	4	$(Ph_4C_4)Fe(CO)_3$ tetraphenylcyclobutadieneiron tricarbonyl
	5	$(C_5H_5)_2Fe$ ferrocene
	6	$(C_6H_6)_2Cr$ dibenzenechromium
	7	$(C_7H_7)(C_5H_5)V$ (π-cycloheptatrienyl)-(π-cyclopentadienyl)-vanadium

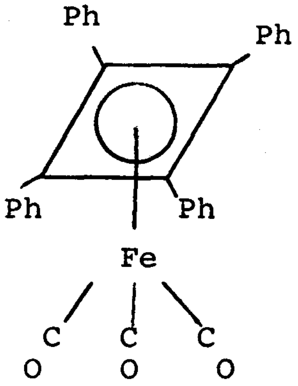
Table 1. Examples of some π-complexes.



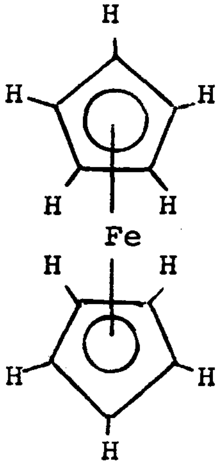
(2)



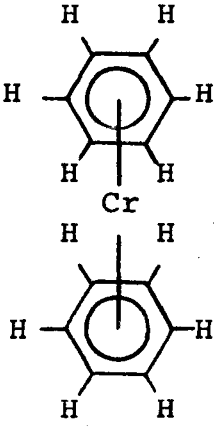
(3)



(4a)



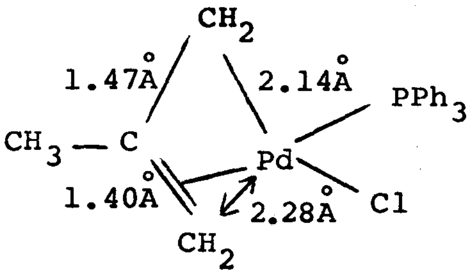
(5)



(6)

X-ray structure determinations on (2)[17], (3)[18], (4a)[19], (5)[20,21,22] and (6)[23] show that the carbon atoms in the organic ligand are all approximately equidistant from the metal atom, and that the distances between adjacent ring carbon atoms in a given ligand are all nearly equal. The bonding depends on the symmetry of the molecule.

An example of an asymmetrically bonded ligand is shown below.

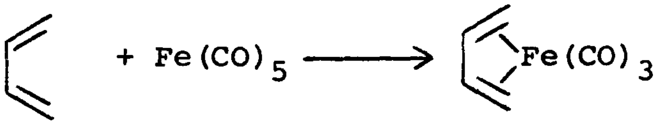


[24]

(7)

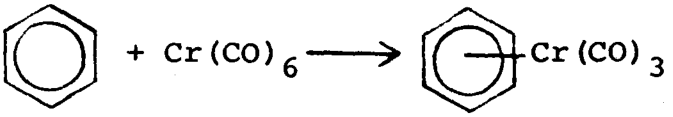
II. Synthesis of π-bonded organometallics.

There are two major methods of synthesizing π-bonded organometallic compounds. The direct method involves a substitution reaction between an uncomplexed ligand and a transition metal compound to yield a complex in which the ligand is bonded to the metal, but is not otherwise grossly changed, e.g.



[25]

(8)



[26]

(9)

Sometimes the transition metal must be reduced before it will react with the organic ligand, e.g.

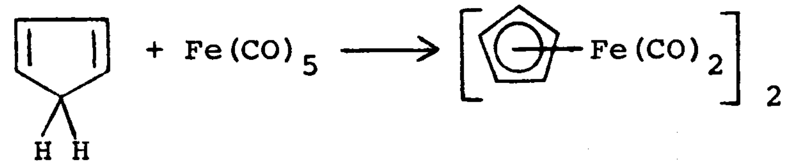
$$(Ph_3P)_2PtCl_2 + PhC_2Ph \xrightarrow{N_2H_4} (Ph_3P)_2Pt(PhC_2Ph)$$ 27

(10)

$$CrCl_3 + C_6H_6 \xrightarrow{Al/AlCl_3} (C_6H_6)_2Cr^+$$ 28

(11)

The other method is indirect and the final ligand is synthesised in the presence of the transition metal. This method must be used when the final ligand is not stable in the free form, e.g.



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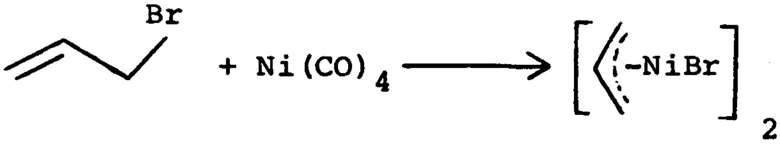
(12)



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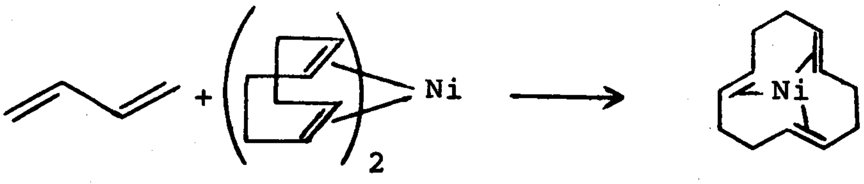
(13)



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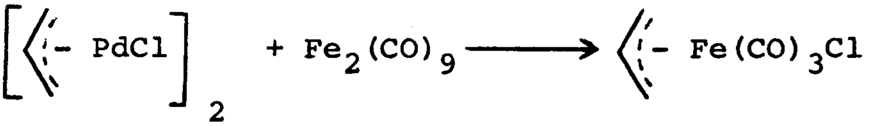
(14)



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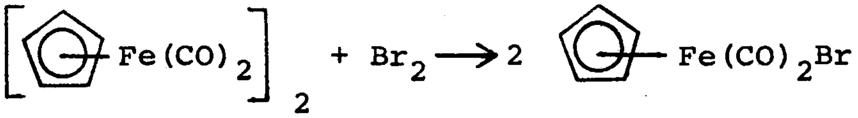
(3) (15)

III. Reactions of π-complexes.

Reactions of π-complexes may be divided into four main types.

(1) Reactions in which the reaction site is not the organic ligand, e.g.



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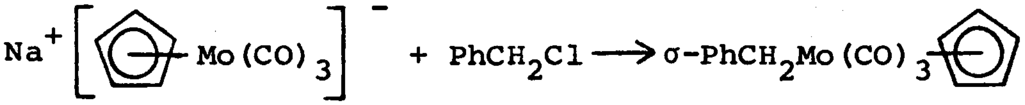
(12) (16)



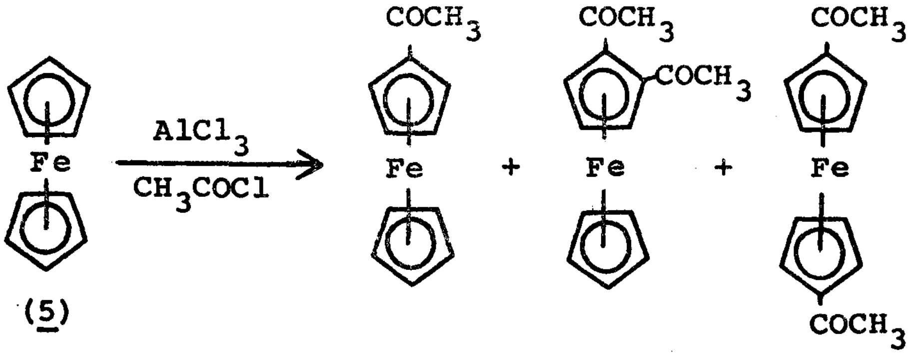
33

(17)

(2) Reactions in which the π-complexed ligand takes part but which give a product in which the altered organic moiety is still bonded to the metal, e.g.

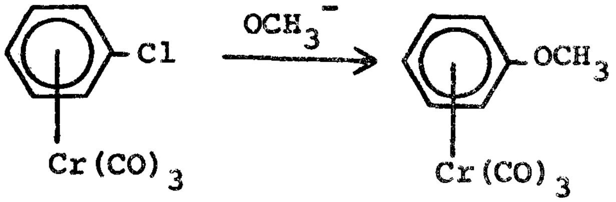
(a) Electrophilic substitution: Electrophilic substitution reactions are important reactions in which the ligand is altered, but remains bonded to the metal. Many π-bonded organometallic compounds undergo electrophilic substitution in the same manner as benzene. For example, ferrocene (5) undergoes Friedel-Crafts acetylation;

34



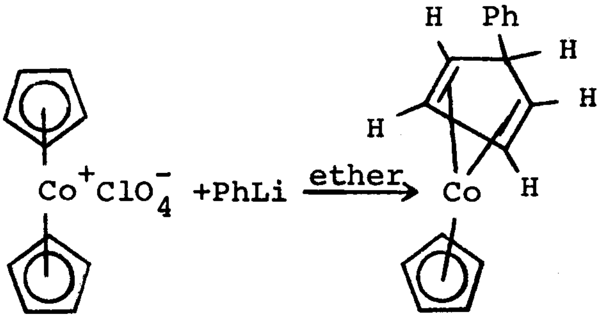
(5)

(b) Nucleophilic substitution: Nucleophilic substitution in organic benzenoid compounds occurs when the aromatic ring is suitably deactivated, e.g. by m-NO_2. It is found that a π-bonded $Cr(CO)_3$ group has a similar effect to that of m-NO_2 and will activate chlorobenzene to nucleophilic substitution by alkoxide under mild conditions.



(18)

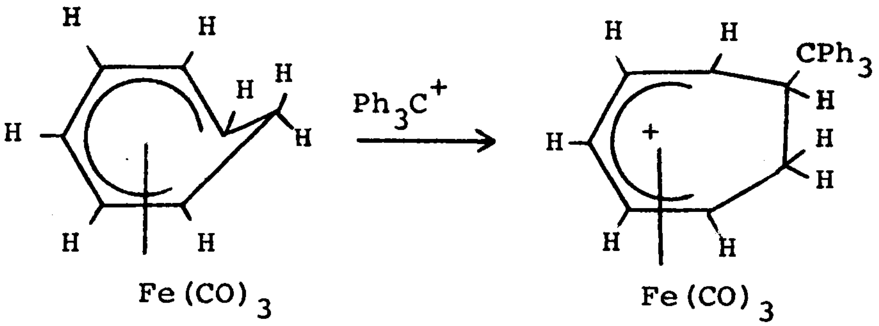
(c) Nucleophilic addition: As part of the bonding in π-bonded organometallic compounds can be considered to consist of electron donation from the organic ligand to the transition metal it is not surprising that many of these compounds are susceptible to nucleophilic addition. This is particularly true if the compound has a positive charge, e.g.



(19)

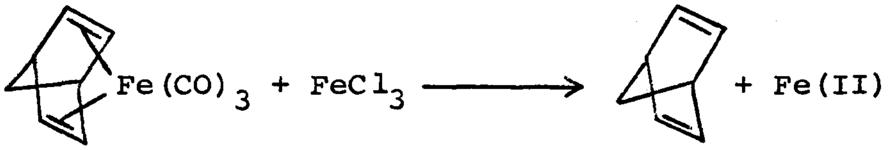
X-ray analysis has shown that the phenyl group is exo to the cobalt atom.[36]

(d) Electrophilic addition: This is quite rare for the reason mentioned above, but one reaction which illustrates electrophilic addition is shown below.[37]



(20)

(3) Reactions in which the π-complexed ligand is displaced from the metal atom and recovered in essentially the same form as it was bonded to the metal, e.g.



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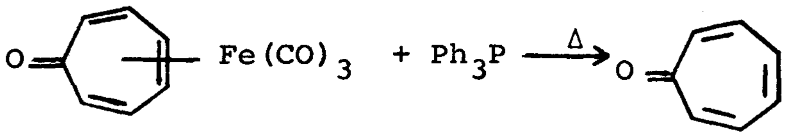

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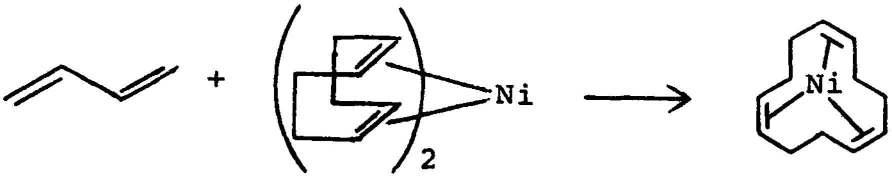
(4) Reactions in which the ligand is liberated but is recovered in a modified form. These reactions are important in understanding the catalytic reactions of metal π-complexes. In these reactions an organic reactant ligand is converted catalytically into a product under conditions where the reaction would not proceed in the absence of the metal catalyst, e.g.



(14)

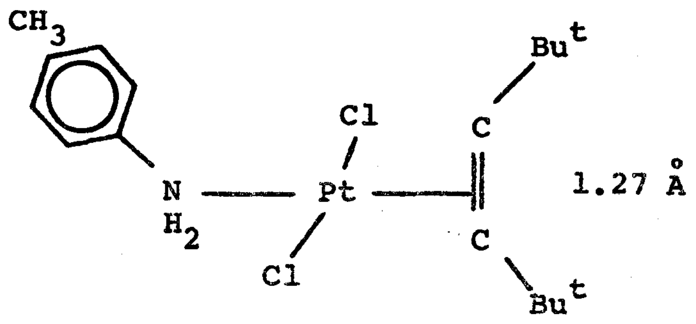
C. The reactions of acetylenes with transition metal compounds in which organometallic compounds are formed.

Reppe and co-workers[40] discovered that aqueous alkaline solutions of $Fe(CO)_5$, (i.e. $HFe(CO)_4^-$) gave hydroquinone, cyclopentadienone and indanone when reacted with acetylene under certain conditions. In addition to pure organic products some organoiron complexes were isolated. This led to the proposal that organoiron complexes were intermediates in the polymerisation of acetylenes. This opened up the field for the search for other transition metal complexes.

Currently a great deal of work is being done using a variety of acetylenes and a wide range of transition metal compounds.

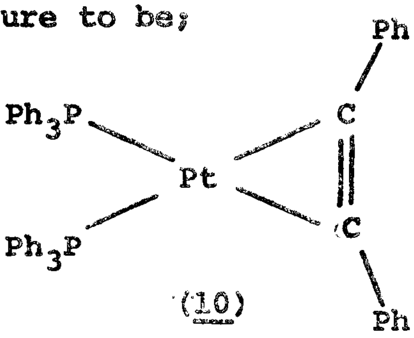
I. Mono-nuclear metal-acetylene complexes

Hel'man[41] prepared the first stable acetylene transition metal complex, *trans*-$[PtCl_2(py)(ac)]$, (py = pyridine and ac = $HOCMe_2C \equiv CMe_2COH$). Chatt *et al.*[42,43] were able to isolate analogous compounds with different acetylenes, but only when the acetylene contained at least one bulky alkyl group, e.g. $C(CH_3)_3$. From a consideration of the infrared spectra of these complexes, which showed a lowering of the $C \equiv C$ stretching frequency of 150-200 cm^{-1}, they concluded that there was only a weak bond formed between the platinum and the acetylene, and proposed a structure similar to Zeise's salt (2), with the acetylene perpendicular to the coordination plane. An X-ray structural determination of $[PtCl_2(p\text{-toluidine})(Bu^tC_2Bu^t)]$ (21) by Davies *et al.*[44] confirmed these predictions and showed the structure to be;



(21)

Chatt et al.[45] also prepared a different series of compounds, $(Ph_3P)_2Pt(ac)$, in which the C≡C stretching frequency of the coordinated ligand is lowered 400-500 cm^{-1} from the free acetylene. The large difference in the lowering of the C≡C stretching frequency between these compounds and the compounds mentioned above led Chatt to propose that in this case there was a strong interaction between the acetylene and the platinum atom. The bonding was envisaged as two σ-bonds between the platinum and the two acetylenic carbon atoms. This would result in a planar complex with the carbon atoms rehybridized to sp^2 carbon atoms. These predictions were shown to be accurate by the X-ray structural determination of $(Ph_3P)_2Pt(PhC_2Ph)$ (10) by Grim et al.[46] which showed the structure to be;



(10)

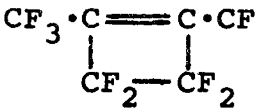
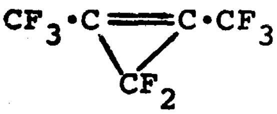
The two phosphorus, platinum and one of the carbon atoms are coplanar. The C≡C bond is inclined by 14° to this plane. The C≡C bond distance of 1.32 Å is typical of an olefinic double bond.

Wilke and Herrmann[47] have described $(Ph_3P)_2Ni(RC_2R)$ (R=Ph or Me) and Wilkinson et al.[48] have described $(Ph_3P)_2Pt(CF_3C_2CF_3)$. Maitlis and co-workers[49] have extended the number of complexes of the type L_2MRC_2R' to include the following:

$L = Ph_3P$, M = Ni, Pd, Pt, $R = R' = CF_3$;
$L = Ph_3P$, M = Ni, Pt, R = R' = Ph and R = Ph, R' = Me;
$L = Ph_3P$, M = Pd, Pt, R = R' = COOMe;
$L = n - Bu_3P$, Me_2PhP, M = Pd, Pt, $R = R' = CF_3$. From the large decrease in the C≡C stretching frequency and the nuclear magnetic resonance spectra (^1H and ^{19}F), these complexes appear to be planar in solution.

Other mono-nuclear acetylene complexes have been reported for vanadium,[50] chromium,[51] molybdenum,[52] tungsten,[52,53,54] manganese,[48,55,56,57] rhenium,[53] cobalt,[58] rhodium,[59,60] iridium,[60,61] nickel,[62] and platinum.[63,64,65,66]

There have been no X-ray crystal structures done on any of these compounds, although the decrease in C≡C stretching frequency has been used as a criterion to distinguish between a monodentate π-bonded acetylene and a bidentate σ-bonded acetylene. On this basis Wilkinson et al.[57,59] have suggested that the acetylene in

$(\pi\text{-}C_5H_5)Mn(CO)_2(CF_3C_2CF_3)$ (<u>22</u>) was π-bonded to Mn(I), whereas the acetylene in $(Ph_3P)_2RhCl(CF_3C_2CF_3)$ (<u>23</u>) was bonded by two σ-bonds to give a metallacyclopropene ring. Parshall and Jones[61] noted that the C $\equiv$ C stretching frequency in $(Ph_3P)_2Ir(CO)(CF_3C_2CF_3)$ (<u>24</u>) at 1773 cm^{-1} was between that for  (<u>25</u>) (at 1715 cm^{-1}) and  (<u>26</u>) (at 1820 cm^{-1}), which would be expected if the iridium in (<u>24</u>) were part of a metallacyclopropene ring.

Whether the two different types of bonding in (<u>10</u>) and (<u>21</u>) represent two discrete energy minima or just the two extremes of a gradual range of bonding types is not fully known yet. Maitlis <u>et</u> <u>al.</u>[49] have recently advanced a theory which allows the type of bonding in the complex to be predicted. They have suggested that there is a continuum of bonding types and that the type of bonding in a given complex depends on the relative energies of the acetylene π and π^* orbitals and the bonding s, p and d orbitals of the metal atom.

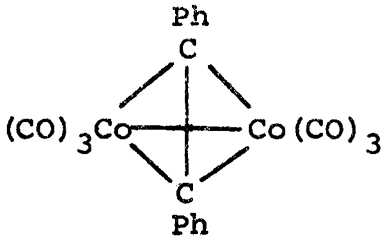
If the metal orbitals lie between the π and π^* orbitals of the acetylene, then both pairs of molecular orbitals formed from metal and π and metal and π^* orbitals will have considerable metal and acetylene character. This will remove electron density from the acetylene π

orbitals to the area between the acetylene and the metal and will allow considerable back bonding to the acetylene π^* orbitals. This will result in a reduction of the C≡C bond order. This type of bonding would be favoured by electron withdrawing substituents on the acetylene and electron donating groups on the metal. Platinum (O) has its bonding orbitals between the π and π^* orbitals of acetylene and would be expected to form a complex of this type, which is in agreement with the experimental observations.[48, 49,66] On the other hand, if the metal orbitals are below both the π and π^* orbitals of the acetylene, then the bonding molecular orbital will have mostly metal character and the antibonding orbital will have more acetylene character. The effective result of this is that some of the electron density originally on the acetylene will be transferred toward the metal to form a weak dative bond. Complexes of this type are expected to be formed between metals in higher oxidation states carrying electro-negative ligands and acetylenes bearing electron donating groups. These predictions agree with the experimental work on complexes of the type $PtCl_2L(RC_2R)$.[41,42,43]

II. Polynuclear acetylene complexes

Acetylenes have two sets of mutually perpendicular π and π^* orbitals. For this reason acetylenes can act as bridging groups in polynuclear acetylene complexes.

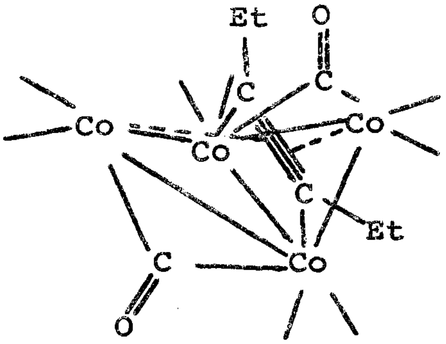
Several workers[67,68,69] have reported that a variety of acetylenes, (ac), react with dicobalt octacarbonyl to give diamagnetic complexes of the type $Co_2(CO)_6(ac)$ (27). An X-ray structural determination of (27) (ac = PhC_2Ph) by Sly[70] showed the structure to be:



(27)

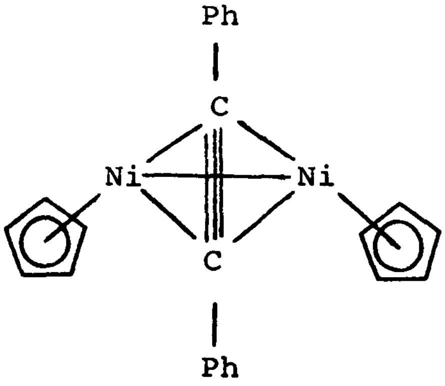
Here the acetylenic carbon atoms and the cobalt atoms are close to the apices of a tetrahedron. The C≡C bond length has been increased to a value of 1.46 Å, which is closer to that for a $Csp^3 - Csp^3$ single bond (1.54 Å).

A reaction involving cobalt skeletal rearrangement as well as substitution is shown by the formation of $Co_4(CO)_{10}(ac)$ (28) from 3-hexyne and tetracobalt dodecacarbonyl.[71] The structure of (28) is shown below.[72]



(28)

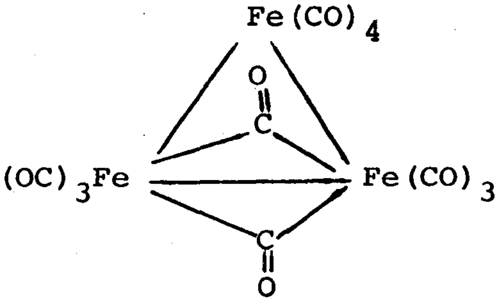
Several workers[73,74,75,76] have prepared compounds of the type $\left[(\pi\text{-}C_5H_5)Ni\right]_2(ac)$ (29) from an acetylene and nickelocene or $(\pi\text{-}C_5H_5)_2Ni_2(CO)_2$. An X-ray structural determination of the structure of (29) (ac = PhC_2Ph) by Mills *et al.*[77] showed the structure to be:



(29)

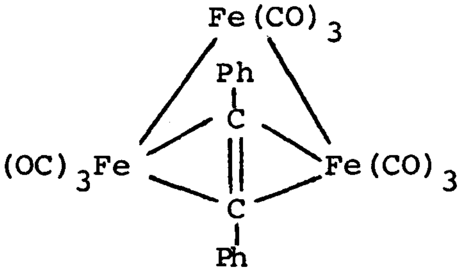
Some reactions of acetylenes with transition metal compounds (notably carbonyls or their derivatives) do not lead cleanly to one major acetylene containing product. In some cases a wide variety of products is obtained in which the acetylene has been polymerised with or without incorporation of carbon monoxide or metal carbonyl fragments. As an example, some reactions of acetylenes with iron carbonyls are discussed here. One of the most studied and understood series of reactions is that between diphenylacetylene and iron carbonyls. In this series of reactions a pathway to the isolated products was proposed on the basis of a multicentred reaction site.

The structure of triiron dodecacarbonyl (30) has been determined by Dahl *et al.*[78] who showed it to be;



(<u>30</u>)

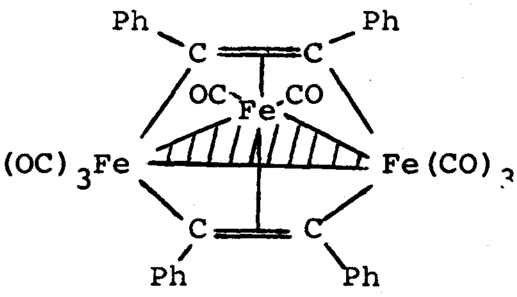
The first compound of this series, $(PhC_2Ph)Fe_3(CO)_9$ (<u>31</u>), has been shown[79] to have the structure;



(<u>31</u>)

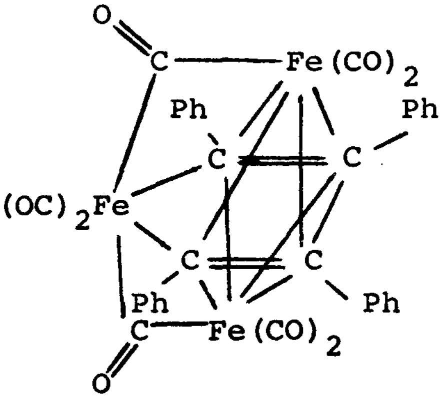
The formation of this complex may be thought of as the replacement of the two bridging and one terminal carbonyl by diphenylacetylene.

There are two isomers of formula $(PhC_2Ph)_2Fe_3(CO)_8$ (<u>32</u>) (<u>33</u>) which can be prepared by reaction of (<u>31</u>) with additional diphenylacetylene. The less stable isomer has been shown to have the following structure;[80]



(32)

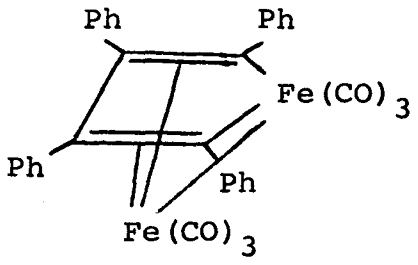
This compound can be thought of as triiron dodecacarbonyl (30) doubly substituted by diphenylacetylene. The distance from one acetylenic carbon atom to the nearest acetylenic carbon atom of the other molecule of diphenylacetylene is 3.10 Å, which shows that the molecules of diphenylacetylene are not bonded together in (32). This complex can be converted to a more stable isomer (33) by heating under reflux in benzene.



(33)

The X-ray crystallographic structure of (33)[80] shows that the two diphenylacetylene units are linked by one C-C bond, and that an iron atom has been incorporated to form a ferracyclopentadiene ring.

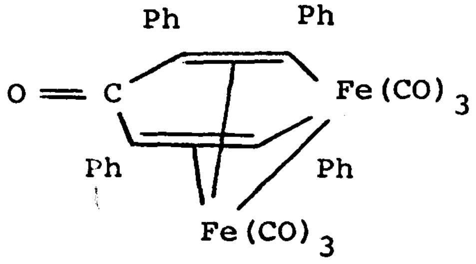
There are three known binuclear iron carbonyl complexes with diphenylacetylene. The complex (33) on heating to 150° is converted to $(PhC_2Ph)_2Fe_2(CO)_6$ (34) which on the basis of chemical reactions has been assigned the structure;[81,82]



(34)

Structurally, (34) may be thought of as arising from (33) by loss of an $Fe(CO)_2$ unit and a small rearrangement of the remaining carbonyl groups.

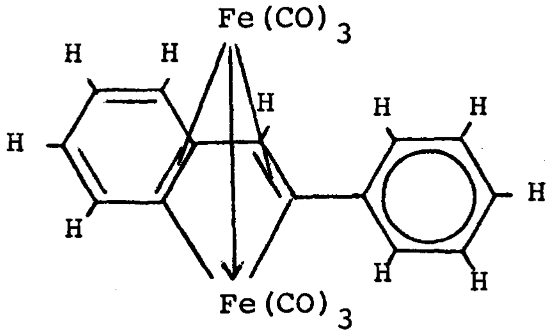
A complex $(PhC_2Ph)_2Fe_2(CO)_7$ (35) is formed in low yield in the reaction of diphenylacetylene with triiron dodecacarbonyl (30). The structure suggested for (35) is based on chemical evidence.[83,84,85]



(35)

It seems likely that carbon monoxide insertion competes to some extent with ferracyclopentadiene formation in the isomerisation of (32) to (33). If this is so, then the formation of (35) is easily explained.

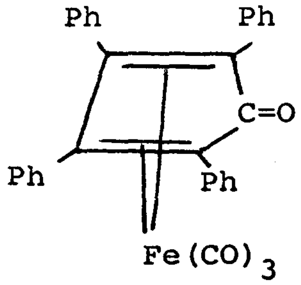
An X-ray crystallographic structural determination[86] of $(PhC_2Ph)Fe_2(CO)_6$ (36)[85,87] showed the following structure;



(36)

This complex may also arise from (31).

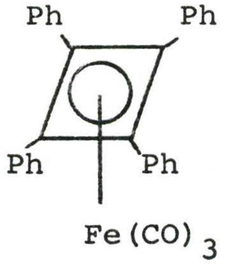
There are two known mononuclear complexes. $(PhC_2Ph)_2Fe(CO)_4$ (37) is thought to have the structure;



(37)

This is based on the direct synthesis from tetraphenylcyclopentadienone and iron carbonyl.[83,84] This complex (37) can be produced from either $(PhC_2Ph)_2Fe_2(CO)_6$ (34) or $(PhC_2Ph)_2Fe(CO)_7$ (35) by the action of heat or light. These reactions illustrate the lower stability of Fe-C σ bonds compared to Fe-C π bonds.

The complex $(PhC_2Ph)_2Fe(CO)_3$ (4a)[85,87] has been shown by X-ray crystallographic analysis to be tetraphenylcyclobutadieneiron tricarbonyl.[19]



(4a)

Whether (4a) is produced by decomposition of more complex iron carbonyl-diphenylacetylene compounds or by substitution of diphenylacetylene on iron pentacarbonyl is not certain as the preparation of $Fe_3(CO)_{12}$ in situ involves $Fe(CO)_5$.

D. Cyclobutadiene-transition metal compounds

I. Structure and bonding.

All attempts to prepare free stable cyclobutadiene have failed. Molecular orbital calculations have suggested that this failure is due, not to ring strain, but to the molecule having a triplet ground state.[88,89,90,91] By combination of the four p_z atomic orbitals of the carbon atoms, four molecular orbitals are formed. ψ_1 is low energy and bonding, ψ_2 and ψ_3 are degenerate and non-bonding, and ψ_4 is relatively high energy and anti-bonding. According to Hund's rules of maximum multiplicity, the ground state would be expected to be a triplet state.

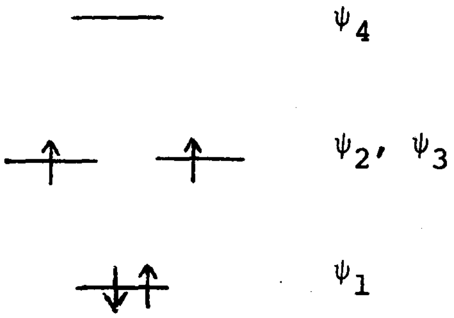


Figure 3. Schematic representation of the molecular orbitals in cyclobutadiene.

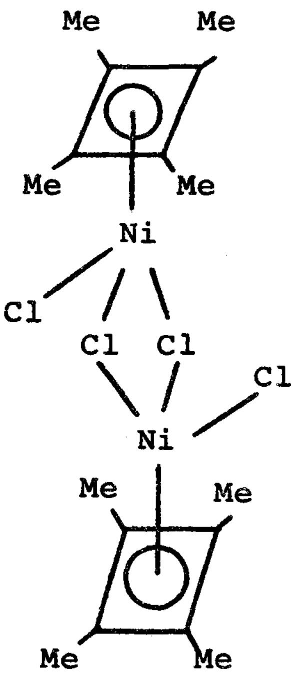
Some chemical evidence for the triplet ground state of tetramethylcyclobutadiene[92] and tetraphenylcyclobutadiene[93] has been reported. However, a more precise self-consistent field calculation of the ground state of cyclobutadiene[94] has suggested that the ground state is a rectangular singlet. Pettit[95] has shown that cyclobutadiene reacts sterospecifically in Diels-Alder reactions, giving only one isomer, and supporting a singlet ground state.

As all the arguments about the ground state are based on different derivatives of cyclobutadiene and different reactions, the precise nature of the ground state of cyclobutadiene is still uncertain.

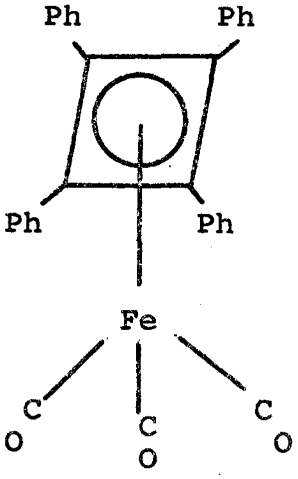
In 1956 Longuet-Higgins and Orgel[96] suggested that the two unpaired π electrons in cyclobutadiene, according to molecular orbital theory, could be used in bonding to a transition metal in a manner analogous to that in cyclopentadienylmetal compounds. As cyclobutadiene had two, whereas cyclopentadienyl had one electron which could be used in bonding to the metal, they predicted that cyclobutadiene to metal bonds would be stronger than cyclopentadienyl to metal bonds. They suggested that $(\pi\text{-}C_4H_4)Ni(CO)_2$ might exist and that cyclobutadiene complexes might be formed in the reaction of acetylenes with palladium (II) complexes.

Some of these predictions were confirmed by the preparation of tetramethylcyclobutadienenickel chloride dimer (38)[97,98] and tetraphenylcyclobutadieneiron tricarbonyl (4a).[85,87]

X-ray structure determinations have been carried out on these two compounds (38)[99] and (4a).[19] The crystals of the nickel complex (38) contain disordered molecules of benzene of crystallisation which lower the accuracy of the determination, but the carbon-carbon ring bonds are all approximately equal (1.43 Å), as are the nickel to ring carbon distances (2.04 Å). The internal angles of the cyclobutadiene ring are all 91±2° and the methyl groups are slightly bent away from the nickel atom. The molecule is dimeric with each nickel bonded to two bridging and one terminal chlorine and the nickel chloride moiety has approximately C_{3v} symmetry.



(38)



(4a)

The X-ray crystallographic structure of (4a) shows a square planar cyclobutadiene ring with carbon-carbon distances of 1.46 Å, and all ring carbon to iron distances equal to 2.06 Å. Here the phenyl rings are also bent back from the iron and twisted in the same sense.

Confirmatory evidence for the square planar configuration of π-bonded cyclobutadiene has been found by Yannoni[100] in his investigation of the ^1H N.M.R. spectrum of cyclobutadieneiron tricarbonyl (39).

The bonding between the cyclobutadiene ring and the metal has been described.[101,102,103] The important feature is that the metal makes available two electrons in e orbitals which can overlap with the two electrons in e orbitals of the cyclobutadiene ring. This neutralises the diradical nature of the square planar C_4H_4 ligand with its triplet ground state, and stabilises it by bond formation. In Fig. 4 a schematic representation of the bonding in tetramethylcyclobutadienenickel chloride shows the strong interaction of the d_{xz} and d_{yz} orbitals of nickel with the e orbitals of the ligand.[103] The remaining nickel orbitals can be used to bond the three chlorine atoms and to form nonbonding orbitals.

This treatment can, with suitable modifications where necessary, explain the bonding in many of the presently known cyclobutadiene-metal complexes.

II. Preparations of cyclobutadiene-metal complexes.

(a) From 3,4 dihalocyclobutenes: In theory the dehalogenation of 3,4 dihalocyclobutenes with metal carbonyls is the most direct synthesis of cyclobutadiene compounds. However, this method is limited by the general unavailability of 3,4 dihalocyclobutenes, and by the fact that the metal carbonyl must be chosen carefully to prevent formation of cyclobutadiene dimers rather than cyclobutadiene complexes.

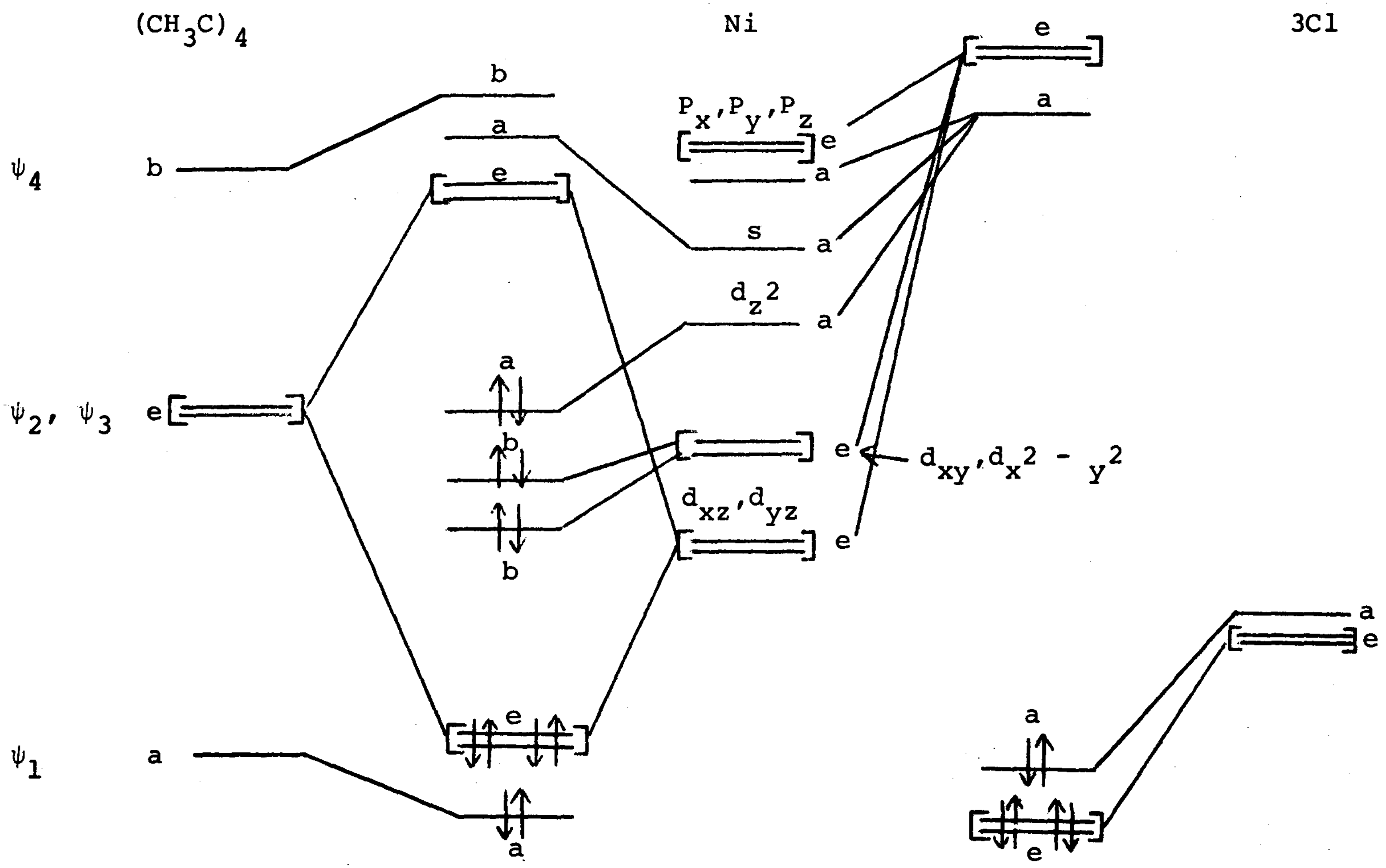
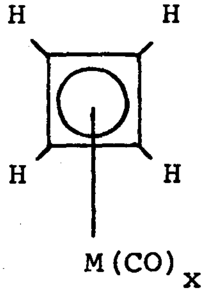
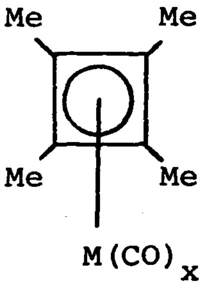


Figure 4. Schematic molecular orbital energy diagram for the bonding in tetramethylcyclobutadienenickel chloride dimer (<u>48</u>).

Pettit[104,105] has reacted 3,4 dichlorocyclobutene and dichloro-3,4-tetramethylcyclobutene with $Fe_2(CO)_9$, $Na_2Fe(CO)_4$ and $Ru_3(CO)_{12}$, $W(CO)_6$, $Mo(CO)_6$ and $Cr(CO)_6$ in the presence of sodium in tetrahydrofuran to give the following complexes:



(39)

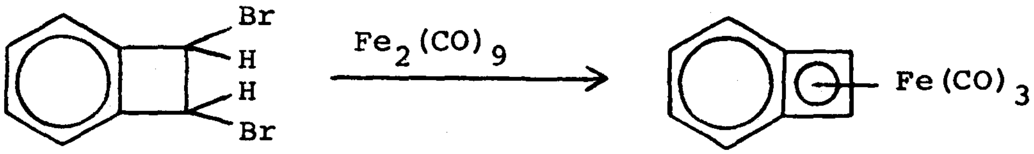


(40)

	M	x
(a)	Fe	3
(b)	Ru	3
(c)	Mo	4
(d)	W	4

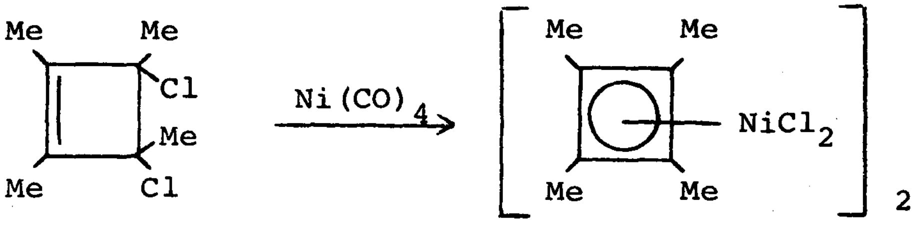
	M	x
(a)	Fe	3
(b)	Cr	3
(c)	Mo	4
(d)	W	4

Pettit[104] has also reported the reaction between trans-dibromobenzocyclobutene (41) and $Fe_2(CO)_9$ to yield (42)



(41) (42)

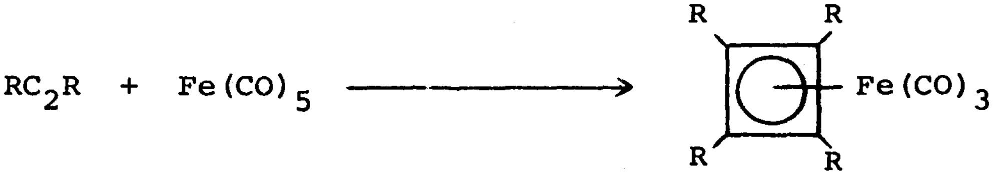
The first synthesis of a cyclobutadiene complex was that by Criegee and Schroeder[97,98] who reacted $Ni(CO)_4$ and 3,4 dichlorotetramethylcyclobutene (43) to give (38).



(43) (38)

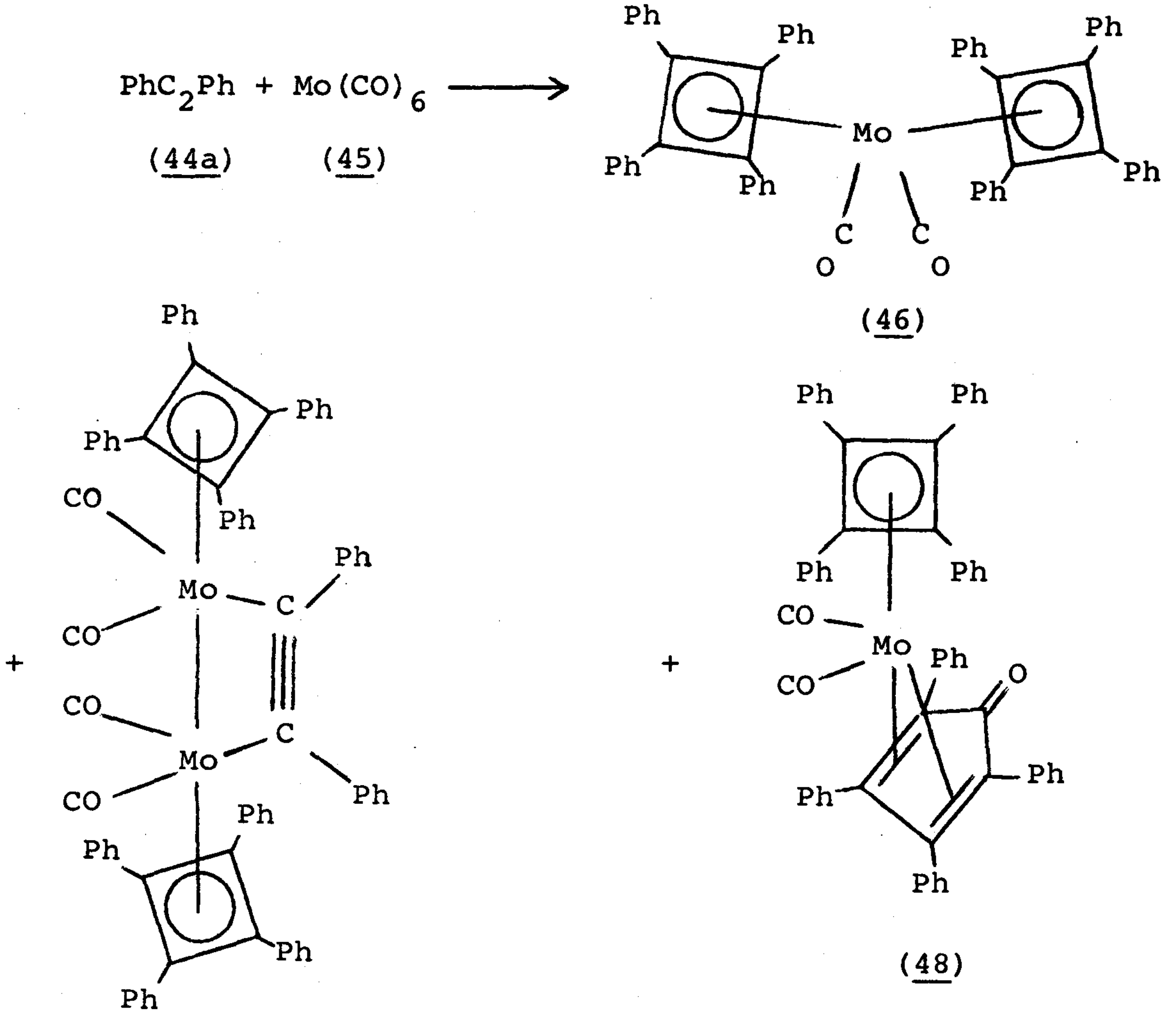
(b) From acetylenes: As discussed above acetylenes react readily with transition metal complexes to yield a wide variety of products. Some of these products are cyclobutadiene complexes. The reactions are not generally used synthetically due to the variety of products obtained and the difficulty in separating them.

Both diphenylacetylene (44a)[85,87,106,107] and p,p' dichlorodiphenylacetylene (44b)[106] react with iron carbonyls to yield a few percent of a cyclobutadieneiron tricarbonyl compound.



(44a,b) (4a,b)

Molybdenum hexacarbonyl and diglyme molybdenum tricarbonyl react with (44a) to give several complexes which are believed to contain tetraphenylcyclobutadiene rings.[107,108,109]

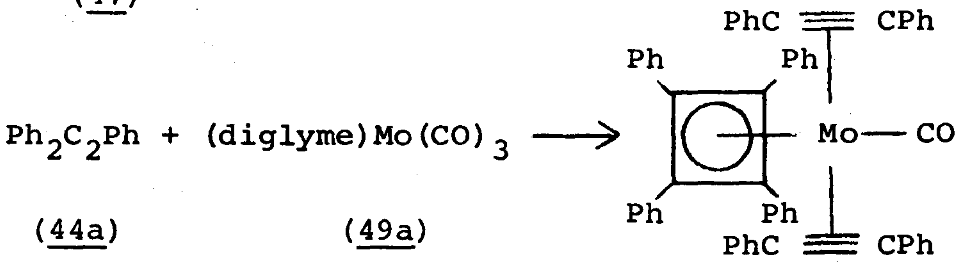


(44a) (45)

(46)

(47)

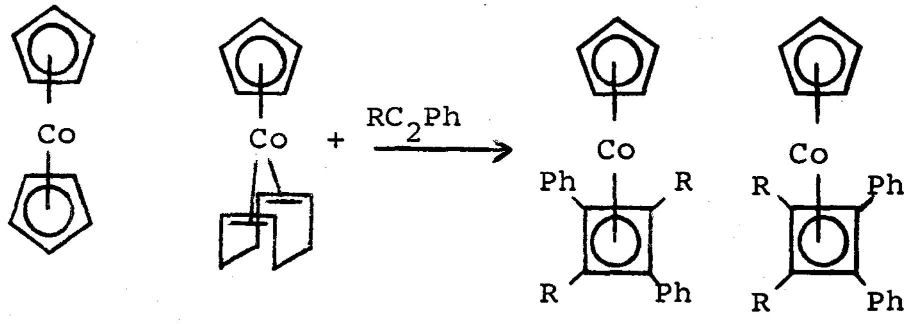
(48)



(44a) (49a)

(50)

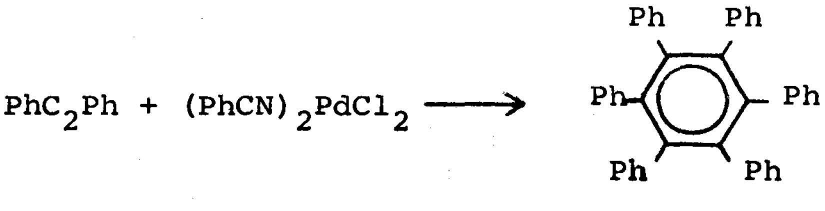
A large variety of phenylacetylenes react with cobaltocene[110] or (cyclopentadienyl)-(1,5 cyclooctadiene)cobalt[111,112,113] to give (π-cyclopentadienyl)(π-cyclobutadiene)cobalt compounds (51).



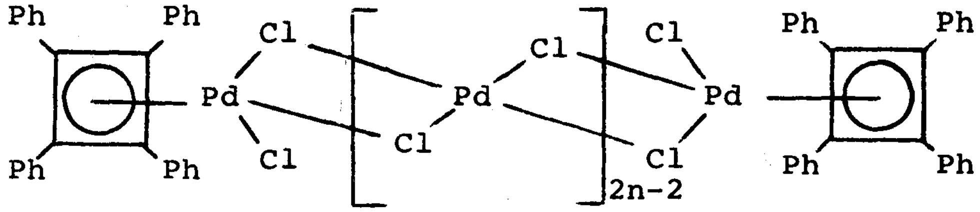
(51)

(R = Ph, $Si(CH_3)_3$, $SnPh_3$, CH_3, $COCH_3$, CHO, CF_3, H)

Bis(benzonitrile)palladium chloride has been reported to react with diphenylacetylene in benzene to give a mixture of hexaphenylbenzene (52a) and tetraphenylcyclobutadienepalladium chloride dimer (53a)[114,115]



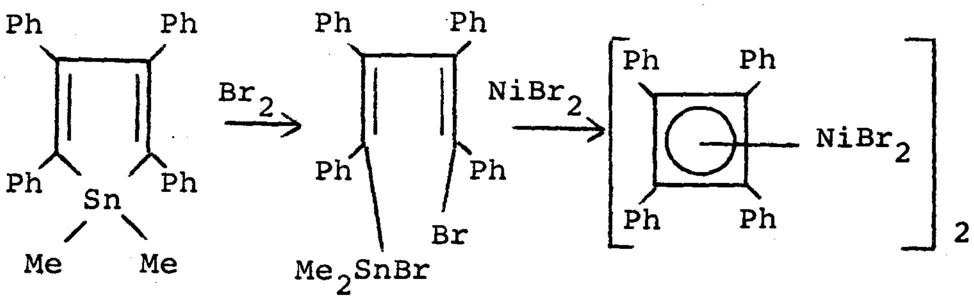
(52a)



(53a)

The catenated form of (53a) may be converted to the uncatenated form by treatment with N,N-dimethylformamide and concentrated hydrochloric acid.

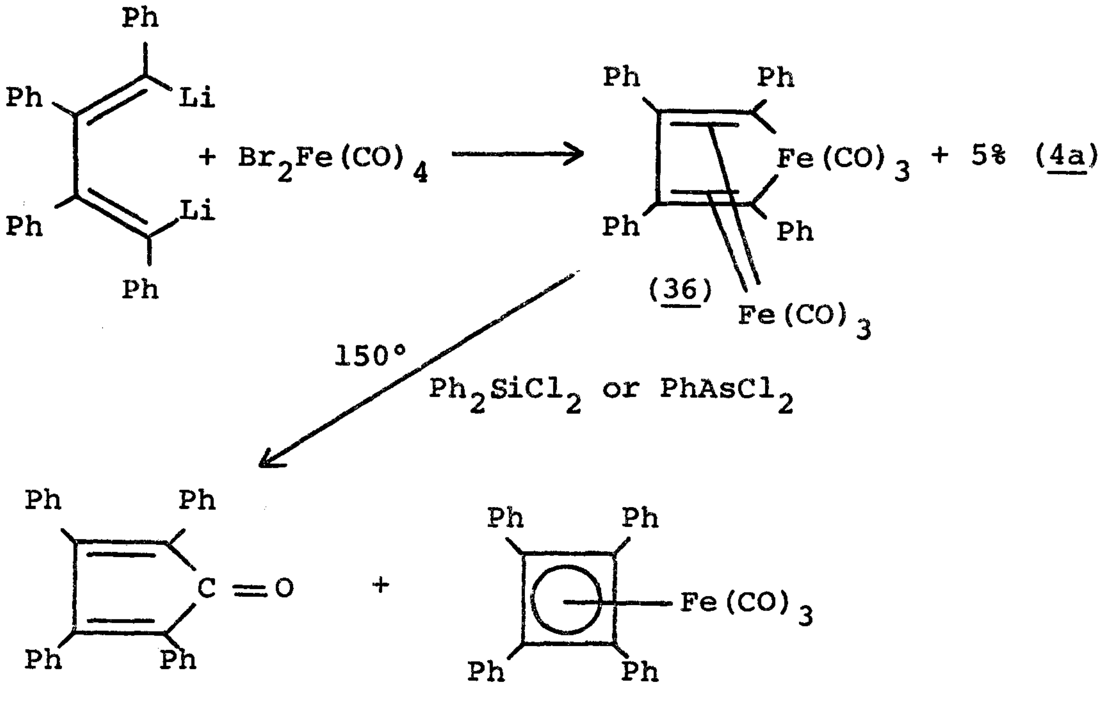
(c) From 1-heterocyclopentadienes: Freedman[116] has prepared tetraphenylcyclobutadienenickel bromide dimer (54a) from 1,1-dimethyl-2,3,4,5-tetraphenylstannole (62).



(62)

(54a)

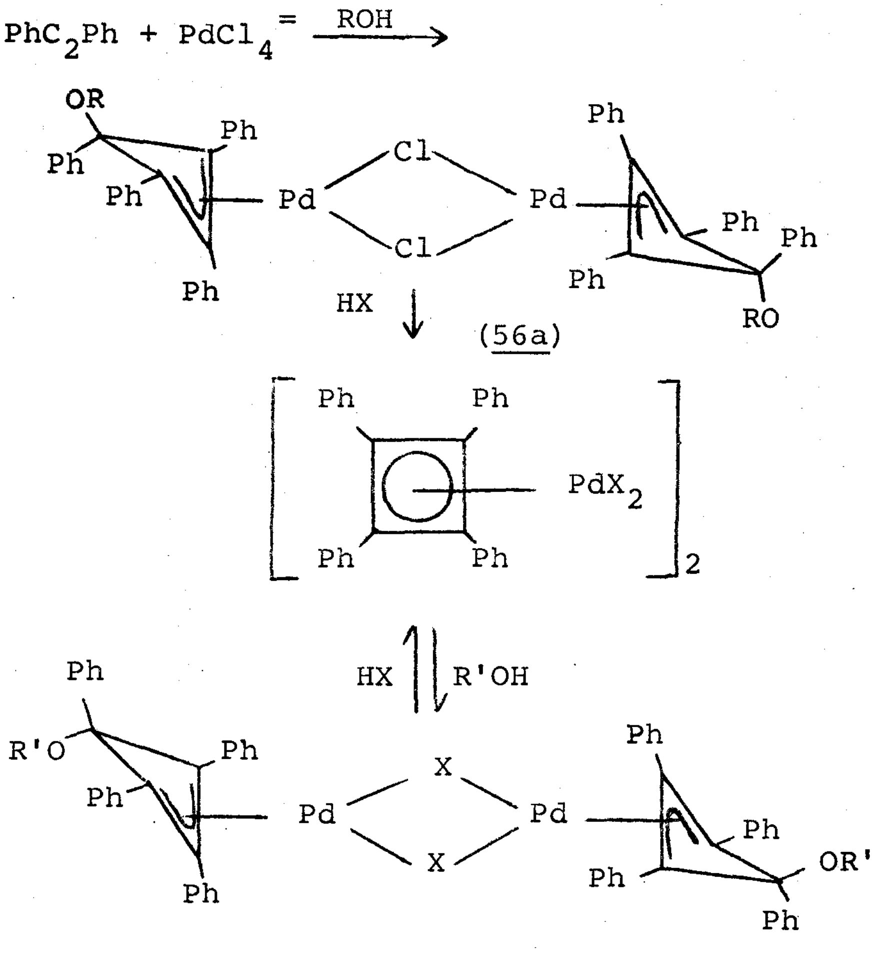
Hubel[117,118] has prepared tetraphenylcyclobutadieneiron tricarbonyl (4a) by the following sequence of reactions:



(37) (4a)

(d) From cyclobutenyl compounds: Malatesta[119] prepared a complex from diphenylacetylene and palladium chloride or sodium tetrachloropalladate in ethanol which subsequent chemical studies[115,120,121] and an X-ray structural determination[122] have shown to be di-μ-chloro-di[π-(endo-4-ethoxy-1,2,3,4 tetraphenylcyclobutenyl)palladium] (56a). This compound reacted with hydrogen halides to yield tetraphenylcyclobutadienepalladium halide complexes. The tetraphenylcyclobutadienepalladium halide complexes also reacted with alcohols to give (57a), an isomer of (56a), and which Dahl[122] has shown to be di-μ-chloro-di[π-(exo-4-ethoxy-1,2,3,4 tetraphenylcyclobutenyl)palladium]

(57a). This reaction was reversed by treatment of (57a) with hydrogen halides.



(57a)

(e) From other cyclobutadiene complexes by ligand transfer reactions: The methods described above have the disadvantage that they are extremely specific with regard to the metal and other reagents used.

Maitlis and co-workers[123,124,125,126,127,128] have reacted tetraphenyl and tetramethylcyclobutadiene compounds with a variety of transition metal complexes to yield other cyclobutadiene complexes. These reactions were generally carried out heterogeneously, so no meaningful kinetic data have yet been obtained. Some examples of these reactions are given in Fig. 5. Sears and Stone[129] have carried out one additional ligand exchange reaction in which triruthenium dodecacarbonyl and tetraphenylcyclobutadienepalladium bromide dimer (59a) were reacted to yield tetraphenylcyclobutadieneruthenium tricarbonyl (60a).

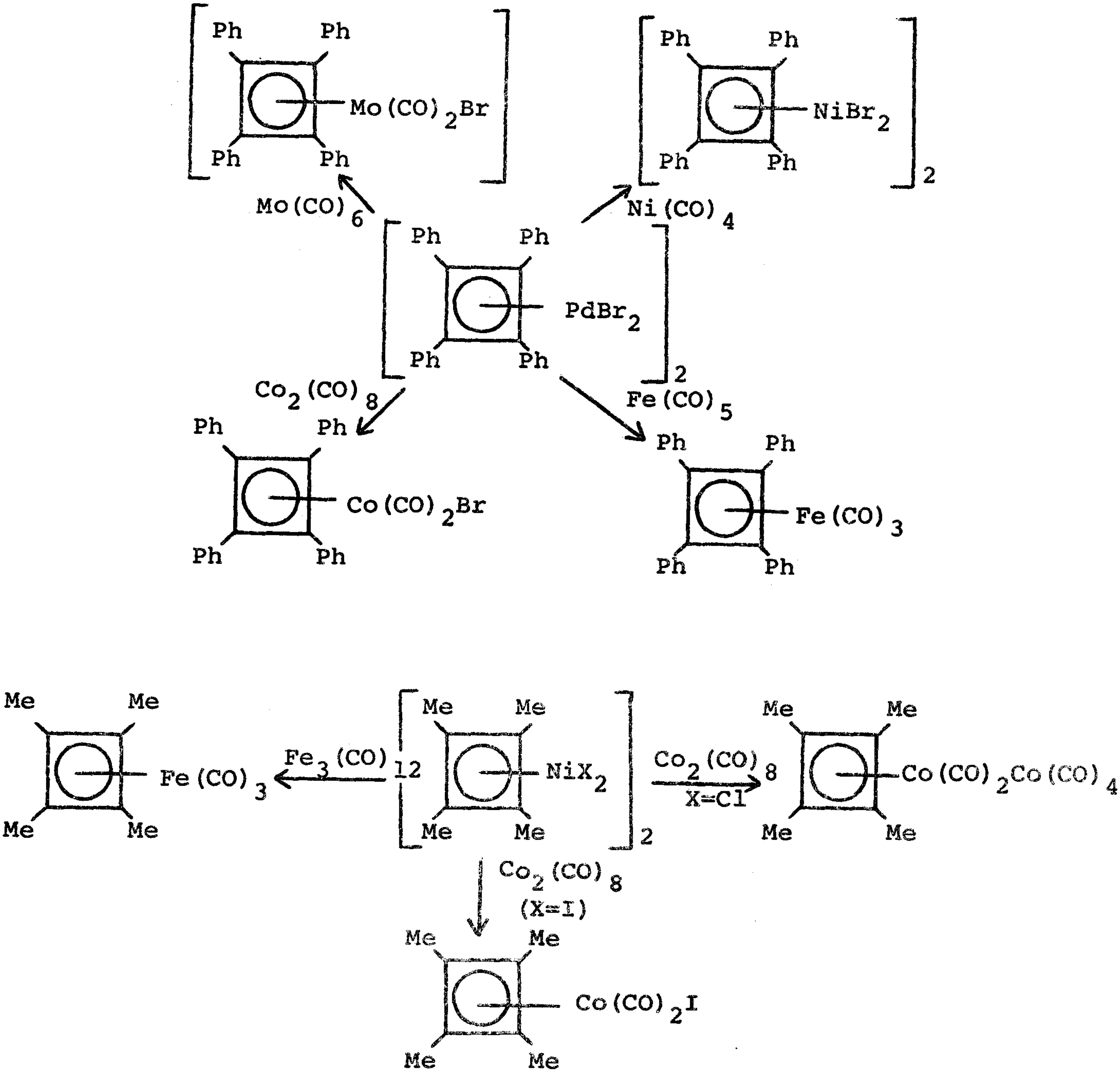


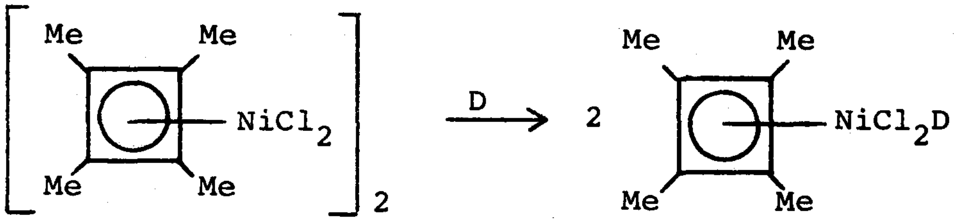
Figure 5. Examples of some ligand-transfer reactions.

III. Reactions of cyclobutadiene complexes.

The reactions of cyclobutadiene complexes can be divided into three general categories: (a) Reactions in which the cyclobutadiene ring is untouched; (b) Reactions of the cyclobutadiene ring with electrophilic or nucleophilic reagents in which the ring remains bonded to the metal; and (c) Reactions in which the cyclobutadiene ring is displaced from the metal.

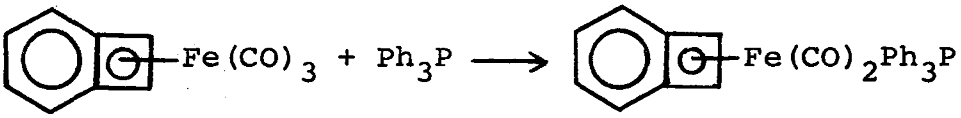
(a) The chlorine atoms of tetramethylcyclobutadiene-nickel chloride dimer (38) and tetraphenylcyclobutadienepalladium chloride (53a) can be exchanged for other anions by several methods. Typical conditions are (1) alkali halides in acetone[121], (2) hydrogen halides in dichloromethane[130], and (3) treatment with silver salts.[131]

Some donor molecules are capable of cleaving the bridging halogen atoms in cyclobutadienepalladium and nickel halides, but only in a few cases has it been possible to isolate the monomeric adduct. Triphenylphosphine adducts of tetramethylcyclobutadienenickel chloride (38)[132] and tetraphenylcyclobutadienenickel bromide (54a)[133] and an o-phenanthroline complex of (38) have been reported.[134]



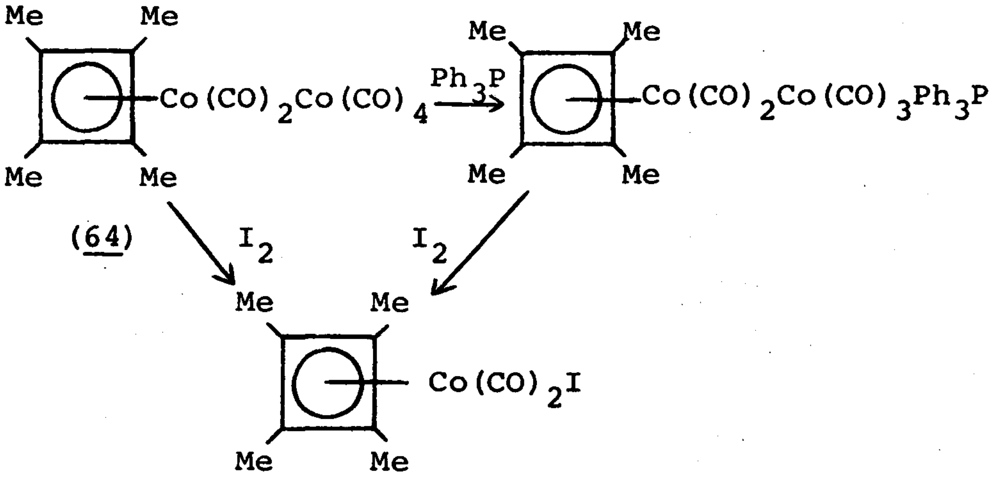
(38) (61) D=Ph_3P, o-phenanthroline

Recently, Pettit has shown that triphenylphosphine replaced one carbonyl group in benzocyclobutadieneiron tricarbonyl (42).[104]



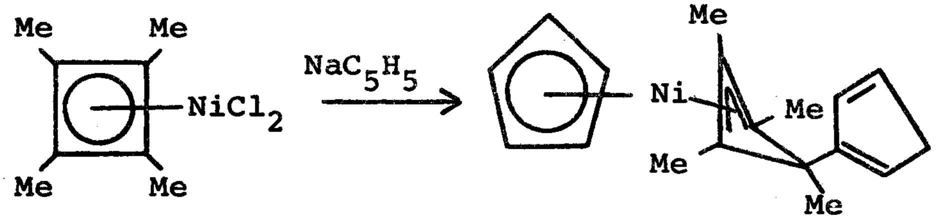
(42) (63)

Maitlis and Bruce[127] have found that tetramethylcyclobutadienedicobalt hexacarbonyl (64) reacted with iodine or triphenylphosphine.



(64)

(b) Cyclobutadiene rings bonded to nickel (II) or palladium (II) have been shown to undergo reaction with several nucleophiles. Tetramethylcyclobutadienenickel chloride (38) reacted with sodium cyclopentadienide to give (π-cyclopentadienyl)(π-1-exo - cyclopentadiene-1,2,3,4-tetramethylcyclobutenyl) nickel (65).[97,98,135] The structure of this compound was proved by an X-ray analysis, although the position of the double bond in the cyclopentadiene ring is uncertain.[136]

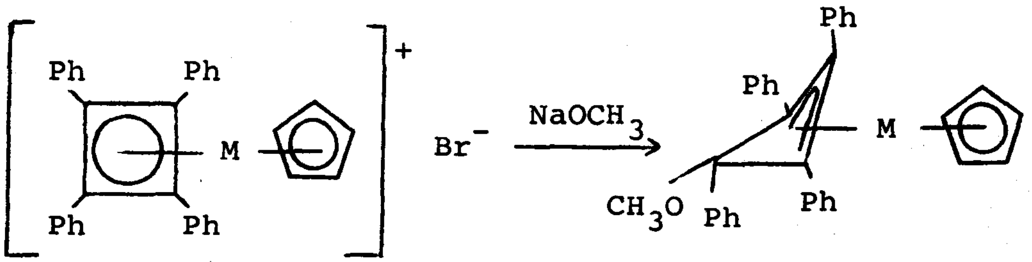


(38)

(65)

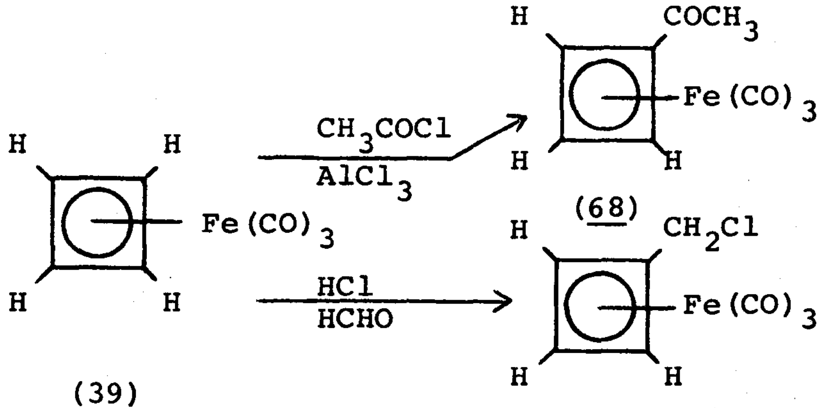
Tetraphenylcyclobutadienepalladium chloride (53a) has been shown to react with ethanol to form di-μ-chloro-di[π-exo-4-ethoxy-1,2,3,4-tetraphenylcyclobutenyl)]palladium] (57a).[121,122]

Maitlis *et al.*[137] have reported the formation of (66, M = Pd,Ni) from (67, M = Pd,Ni) by reaction with sodium methoxide. The ^{1}H N.M.R. spectra showed that the methoxy group was not on the cyclopentadiene ring. The methoxy group has been shown to be exo to the metal here.



(67, M = Pd,Ni) (66, M = Pd,Ni)

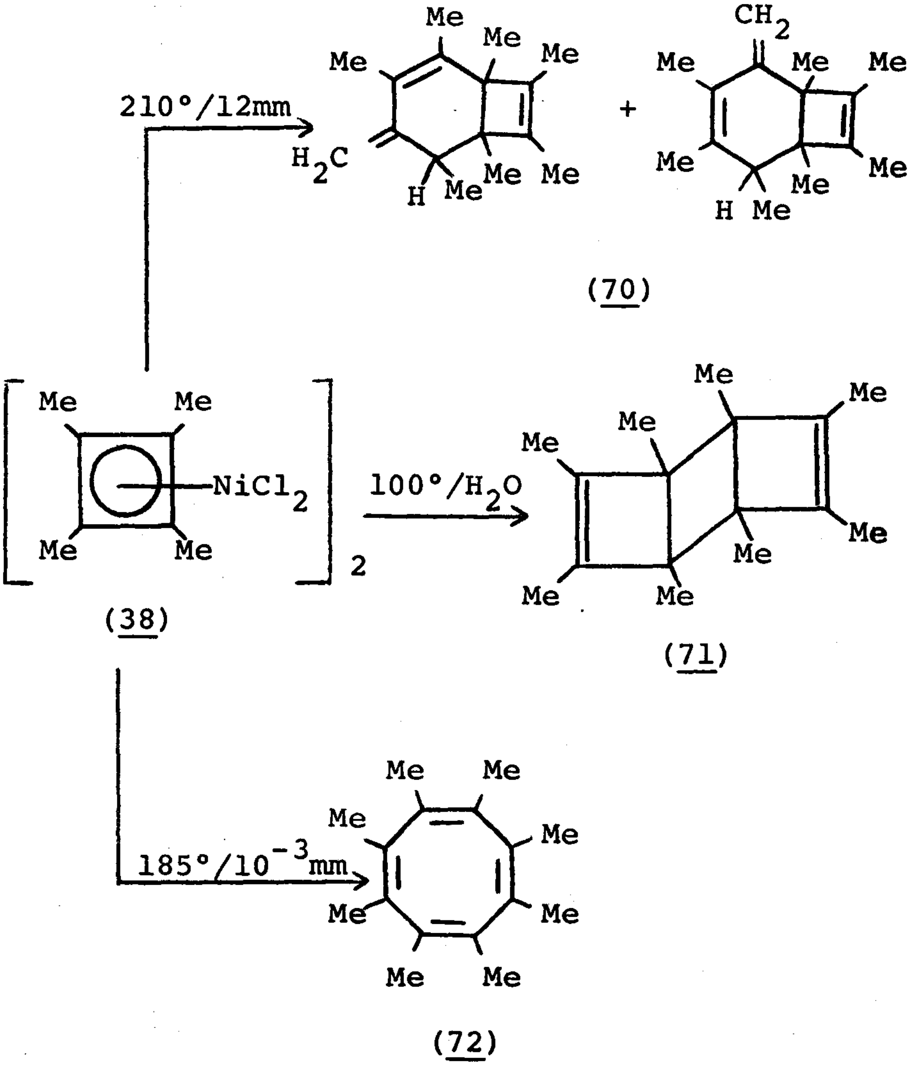
Cyclobutadieneiron tricarbonyl (39) has been shown to undergo electrophilic substitution by several reagents,[138] e.g.



(39) (68) (69)

The generality of electrophilic substitution on cyclobutadiene metal complexes is not known, and Pettit *et al*. have reported that cyclobutadienemolybdenum tricarbonyl triphenylphosphine did not react with acetyl chloride and aluminum chloride under conditions where (<u>39</u>) gave a 95% yield of (<u>68</u>).[105]

(c) The nature of the products obtained by removing the cyclobutadiene from the complex depends on the substituents on the ring, the metal, the reagents and the conditions of reaction. For example, tetramethylcyclobutadienenickel chloride (<u>38</u>) reacted as shown below.[97,98,132,134]



(<u>70</u>)

(<u>38</u>)

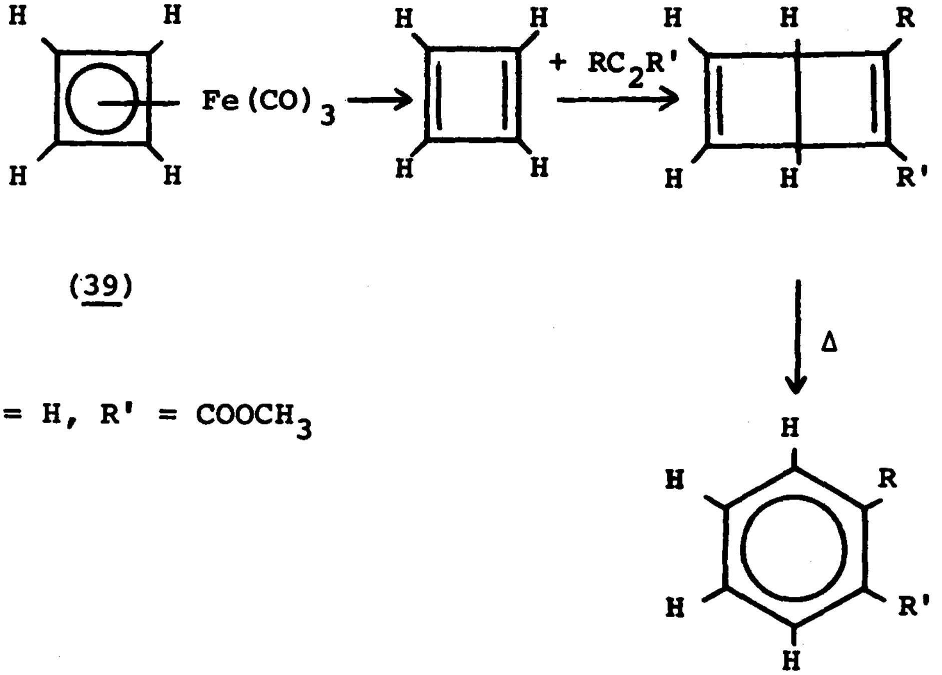
(<u>71</u>)

(<u>72</u>)

Tetraphenylcyclobutadienenickel bromide (54a) on pyrolysis yielded nickel bromide and octaphenylcyclooctatetraene (73a, R = Ph).[116,133] In contrast, tetraphenylcyclobutadienepalladium chloride (53a), on pyrolysis, gave palladium metal, two isomers of 1,4-dichlorotetraphenylbutadiene and a trace of diphenylindenoindene.[115,120] If oxygen was present, tetraphenylfuran was formed.[114,116]

The reaction of (53a) with tri-n-butylphosphine or other tertiary phosphines gave octaphenylcyclooctatetraene (73a, R = Ph).[139] This compound (73a, R = Ph) was originally thought to be octaphenylcubane,[140,141] but an X-ray crystallographic analysis disproved this.[142]

The oxidation of cyclobutadieneiron tricarbonyl (39) by ceric nitrate has been investigated by Pettit et al.[95] It was found that in the presence of acetylenes, bicyclohexadienes were formed, which on heating isomerised to the corresponding benzene.



(39)

R = H, R' = $COOCH_3$

This result was interpreted to mean that cyclobutadiene free from its metal complex was produced in these reactions and that it has a finite, though short, lifetime.

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

The RESULTS AND DISCUSSION is divided into three sections. The first section deals with the reactions of diphenylacetylenes, RC_2R, with palladium (II) complexes in several solvents.

The second section covers the ligand-transfer and ligand-exchange reactions. Reactions in which the tetraphenylcyclobutadiene ligand was modified but remained bonded to the central metal atom, and reactions in which the tetraphenylcyclobutadiene ring was removed from the central metal atom with subsequent modification are also discussed in this section.

The third section deals with an investigation of the ^1H N.M.R. spectra of the compounds discussed in the foregoing sections.

A. Reactions of Diphenylacetylenes with Palladium (II) Complexes.

I. Reactions in non-hydroxylic solvents.

In non-hydroxylic solvents diphenylacetylenes, RC_2R, (44a,b,c,d) reacted with bis(benzonitrile)palladium chloride to give two types of product. One was a hexaphenylbenzene, R_6C_6, (52a,b,c,d) formed by the trimerisation of the acetylene. The other product was the tetraphenylcyclobutadienepalladium chloride dimer, $[R_4C_4(PdCl_2)_n]_2$ (53a,b,c,d) n=2,2.5,3.

The results of a series of these reactions are shown in Table 2.

It was found that increased dilution of the reactants (runs 1 and 2, and 7 and 8) favoured a higher yield of the cyclobutadienepalladium chloride complex (53a,b) and a lower yield of the benzene compound (52a,b). A higher mole ratio of palladium to acetylene in the reactants favoured a higher yield of the cyclobutadienepalladium chloride complex (53a,b) (runs 1 and 2, and 7 and 8). Blomquist and Maitlis[120] have reported that when bis(benzonitrile)palladium chloride in benzene was added to a solution of diphenylacetylene (44a) in benzene a 90% yield of hexaphenylbenzene (52a) was obtained. In all the reactions reported here a solution of the acetylene was added to a solution of bis(benzonitrile)palladium chloride. This gave lower yields of the hexaphenylbenzenes and higher yields of the complexes.

In these cases reaction occurred in a medium of high bis(benzonitrile)palladium chloride concentration and low acetylene concentration, and this reduced the tendency of the acetylene to trimerise. In runs 2 and 7 where the ratio of acetylene (44a,b) to palladium complex was

	Acetylene mmole	Solvent ml	$(PhCN)_2PdCl_2$ mmole	Solvent ml	Trimer Yield %	$[R_4C_4(PdCl_2)_n]_2$ Yield %
1.	(44a) 5.61	benzene 340	5.78	benzene 340	60	34 (a)
2.	(44a) 2.8	benzene 50	1.4	benzene 50	(c)	19 (b)
3.	(44a) 2.8	benzene 50	2.8	benzene/diglyme 50/3	54	29 (a)
4.	(44a) 2.8	diglyme 50	2.8	diglyme 50	55	19 (a)
5.	(44a) 2.8	ether 300	2.8	ether 100	no reaction (d)	
6.	(44a) 2.8	ether 100	2.8	ether 100	12	11 (a)
7.	(44b) 24.2	benzene 550	10.1	benzene 275	45	18 (e)
8.	(44b) 13.0	benzene 800	13.0	benzene 800	32	43 (a)
9.	(44c) 8.4	benzene 300	9.2	benzene 300	39	44 (a)
10.	(44d) 8.4	benzene 800	8.4	benzene 800	26	58 (a)

Table 2. Reactions of diphenylacetylenes with bis(benzonitrile)palladium chloride in non-hydroxylic solvents.

Footnote to Table 2. (a) n=3. (b) n=2.5. (c) Not estimated. (d) Reaction carried out at -40°C. (e) n=2.

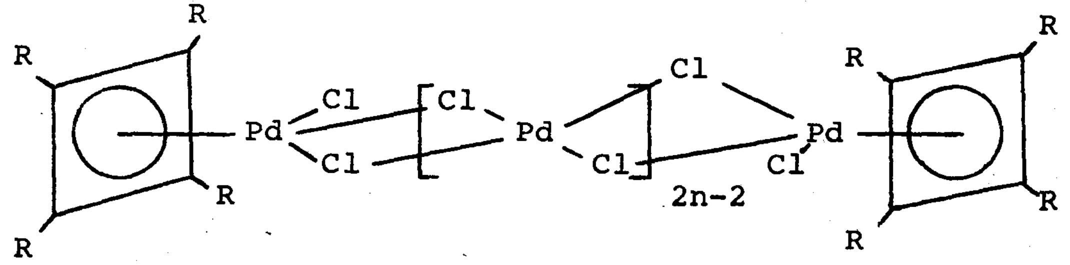
approximately 2:1, compared to equimolar amounts in all other reactions, the value of n, the number of units of palladium chloride in the complex (53a,b) fell to 2.5 and 2 respectively.

The use of a weakly coordinating solvent did not change the nature of the products. The effect of using diglyme as the solvent was to lower the yield of (53a) by 10%, and to leave the yield of (52a) approximately constant. When the reaction was carried out in diethyl ether the yield of hexaphenylbenzene (52a) fell to 12%, and the yield of tetraphenylcyclobutadienepalladium chloride (53a) fell to 11%. It has been reported[130] that the dipyridyl and tri-n-butylphosphine complexes of palladium chloride, which are less labile, did not react with diphenylacetylene (44a) in benzene under these conditions. Presumably, diethyl ether and to a lesser extent diglyme, tied up the palladium chloride more effectively than the very labile benzonitrile, but not as effectively as to prevent reaction altogether.

No reaction occurred when the reaction was carried out at -40°C in diethyl ether.

No conclusions could be drawn from the variation of the yields reported for different acetylenes under similar reaction conditions. The yields reported in Table 2 for the substituted diphenylacetylenes were the highest of several runs made on each acetylene, and the yield was found to vary, depending on the exact rate of addition of the acetylene to the bis(benzonitrile)palladium chloride solution.

The tetraphenylcyclobutadienepalladium chloride complexes (53a,b,c,d), n>1, and (53a), n=1, were too insoluble for molecular weight determinations or for ^{1}H N.M.R. spectra.

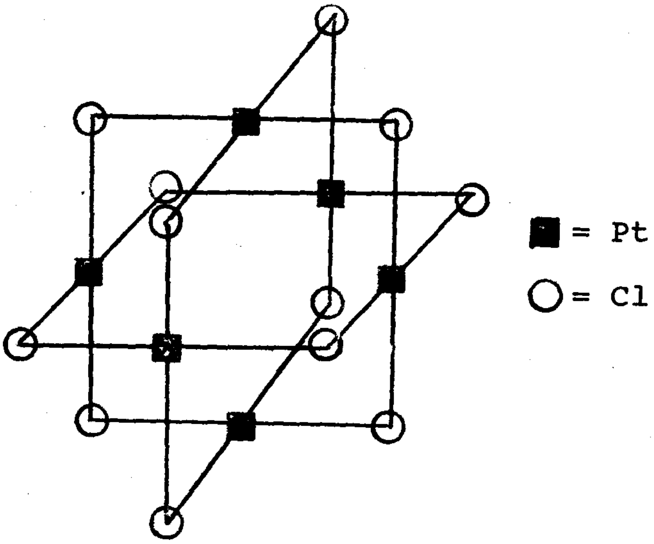


(53a,b,c,d)

The structure for (53a), n=1, was verified by the chemical evidence of Blomquist and Maitlis[120] and the X-ray structural determination of the similar compound $[(CH_3C)_4NiCl_2]_2$ (38).[99]

The structures of the tetraphenylcyclobutadienepalladium chloride compounds (53b,c,d), n=1, were presumed similar. These compounds were sufficiently soluble for osmometric molecular weight determinations and the dimeric structure was confirmed.

The structures of (53a,b,c,d), n>1, were originally thought to be as shown above.[114,123,143] These were based on the original X-ray structure determination of α-palladium chloride which showed it to have a square planar catenated structure.[144] Subsequent work has shown that this structure was associated with a metastable high temperature crystal modification of palladium chloride. The X-ray crystal structure of platinum chloride is shown below. Schafer *et al.* have shown that β-palladium chloride, the crystal modification stable at room temperature was isostructural by powder pattern techniques.[145]



Donati and Conti[146] have found that (π-allyl)-palladium chloride (3) added palladium chloride to give $(\pi\text{-allyl})_2Pd_3Cl_4$ (74). The infrared spectrum of (74) showed absorptions attributed to a terminal Pd-Cl stretching frequency. An unspecified palladium structure with metal-metal bonds was proposed.

Despite the above evidence of palladium forming cluster compounds, the catenated structures of (53a,b,c,d) are still thought to be correct for the following reasons: (a) The palladium atoms in the cluster structure have eight d electrons and eight electrons arising from sharing with the chlorine atoms for a total of sixteen electrons. A coordination compound between this palladium chloride cluster and an electron donor would more likely be formed with a two electron donor, rather than cyclobutadiene which is a four electron donor in all its other known compounds. (b) The infrared spectra of all compounds (53) of different n prepared from the same acetylene were identical in the region of common absorption by organic groups (2-16 μ). (c) The cluster skeleton of palladium chloride would have to be extensively altered to include the tetraphenylcyclobutadienepalladium chloride compounds (53a) n=2.5 and (53b) n=2 in the series. (53b) n=2 was not a mixture of (53b) n=3 and (53b) n=1, as the latter was benzene soluble and would have appeared in the benzene washings of the compound (53b) n=2 had it been present.

The members of the series of hexaphenylbenzenes (52a,b,c,d) were all white, crystalline, monomeric, high melting solids.

A possible mechanism for the formation of these products will be discussed at the end of the next section.

II. Reactions in hydroxylic solvents.

When acetylenes (44a,b,c) were reacted with palladium (II) complexes in ethanolic solvents the acetylenes (44a,b,c) were dimerised and an ethoxide ion

	Acetylene	Palladium Compound	Product	Yield (%)
1.	(44a)	Na_2PdCl_4	(56a)	90
2.	(44b)	$(PhCN)_2PdCl_2$	(56b)	66
3.	(44c)	$(PhCN)_2PdCl_2$	(56c)	65

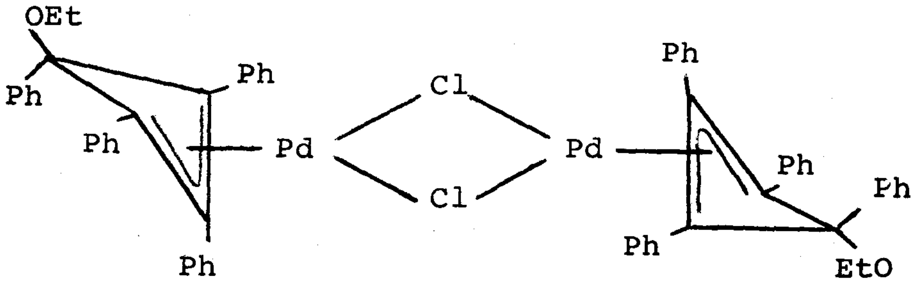
Table 3. Reactions of diphenylacetylenes with palladium (II) complexes in ethanolic solvents.

incorporated to yield di-μ-chloro-[π-(endo-4-ethoxy-1,2,3,4 tetraphenylcyclobutenyl)palladium] compounds (56a,b,c). The results of these reactions are shown in Table 3.

Attempts to produce di-μ-chloro-di[π-(endo-4-ethoxy-1,2,3,4 tetrakis{p-chlorophenyl}cyclobutenyl)-palladium] (56b) by using sodium tetrachloropalladite as a source of palladium all failed. A precipitate was obtained in these reactions which may have contained some (56b), but had a variable colour and palladium analysis, and decomposed when purification was attempted.

The reaction of p,p'-dimethoxytolan (44d) with bis(benzonitrile)palladium chloride did not give the expected product (56d), but gave a 59% yield of tetrakis-(p-anisyl)cyclobutadienepalladium chloride (53d) n=2.5. The reaction between (44d) and sodium tetrachloropalladite was also unsuccessful and after a short reaction time metallic palladium was deposited. The failure to prepare di-μ-chloro-di[π-(endo-4-ethoxy-1,2,3,4 tetrakis{p-anisyl}-cyclobutenyl)palladium] (56d) was the only qualitative difference in this series of reactions. This was thought to be due to the powerfully electron donating p-methoxy groups preventing nucleophilic attack by ethanol on the reaction intermediate. In general, the effects of the mildly electron donating p-methyl and mildly electron withdrawing p-chloro groups on this and other reactions were limited to variations in the yields.

The structure of one of this series of compounds (56a) has been determined by X-ray crystallography by Dahl and Oberhansli.[122]



(56a)

The structures of (56b,c) were thought to be analogous, based on their analyses, dimeric molecular weights, chemical properties and ^{1}H N.M.R. spectra.

No kinetic studies were done on any of the reactions discussed so far in the RESULTS AND DISCUSSION as they were all carried out under heterogeneous conditions. The nature of the products suggested a mechanistic pathway similar to that found in the Wacker synthesis of aldehydes and ketones from alkenes in the presence of a palladium catalyst.[147] The essence of the mechanism in the Wacker synthesis was the replacement of two labile chloride ions from tetrachloropalladite anion by a molecule of ethylene and one of water. This was followed by loss of a proton and electronic rearrangement, through a species containing a carbon-palladium σ-bond, to the products. Examination of the ratio of isomeric benzene products from the cyclotrimerisation of unsymmetrical acetylenes has afforded some inconclusive evidence that the reaction intermediate may have the symmetry of cyclobutadiene.[148,149] The existence of a five membered metallocycle as a reaction intermediate has been shown in the reaction of diphenylacetylene (44a) with triiron dodecacarbonyl, discussed in the INTRODUCTION, and in the cyclotrimerisation of dimethylacetylenedicarboxylate by the nitrogen complex of bis(triphenylphosphine)iridium (I) chloride.[150] Heck[151] has reacted phenylpalladium chloride with a large variety of olefinic substrates to produce substituted olefins and has suggested the reaction proceeded by 1,2 addition of the phenylpalladium chloride across the double bond, followed by elimination of H-Pd-Cl and subsequent conversion to hydrochloric acid and metallic palladium.

It seems likely that the reaction of diphenylacetylenes (44a,b,c,d) with palladium (II) complexes proceeds by reaction of an acetylene molecule with a Pd-X moiety (X=Cl or OEt) to form a π complex which rearranges to give 1,2 addition compound. Insertion of a second molecule of acetylene may give an intermediate as shown in Figure 6.

The intermediate shown in brackets may then react further in two ways. One of which would be a third 1,2 addition of another acetylene molecule and expulsion of palladium chloride to give the hexaphenylbenzenes (52a,b,c,d). When ethanol was present no (52a,b,c,d) were

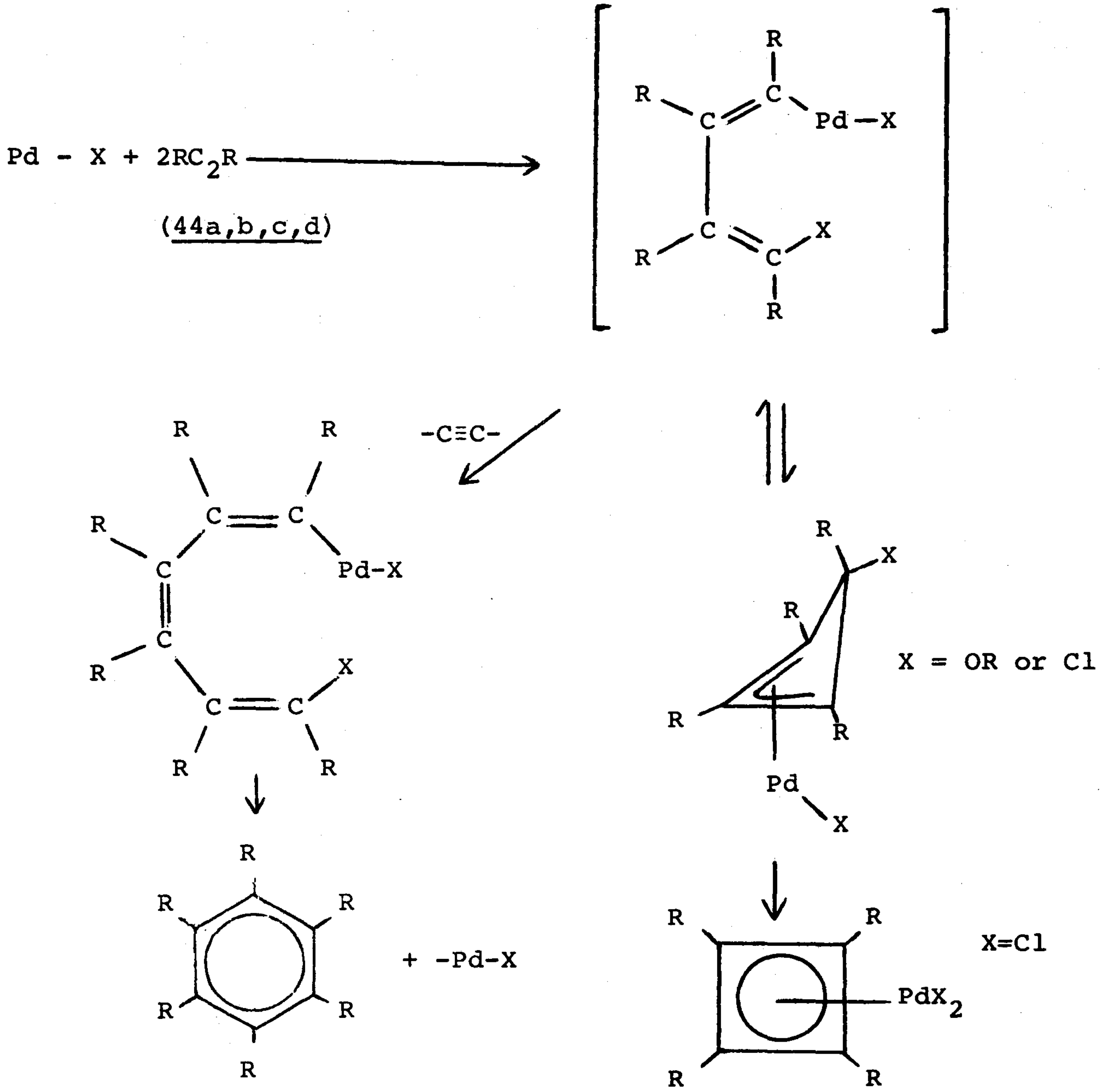


Figure 6. Possible mechanism for the reaction of diphenylacetylenes with palladium (II) complexes.

formed, which showed that the formation of a cyclobutenyl complex was energetically preferable. The cyclobutenyl compounds (56a,b,c) were stable when X=OR, a relatively poor leaving group. When X=Cl, a better leaving group, the chloro group migrated to the palladium atom to give the tetraphenylcyclobutadienepalladium chlorides (53a,b,c,d). When p,p'-dianisylacetylene (44d) was reacted with palladium (II) complexes in ethanol the electron donating p-methoxy groups caused expulsion of the ethoxy group from the cyclobutenyl compound to afford tetrakis(p-anisyl)cyclobutadienepalladium chloride (53d).

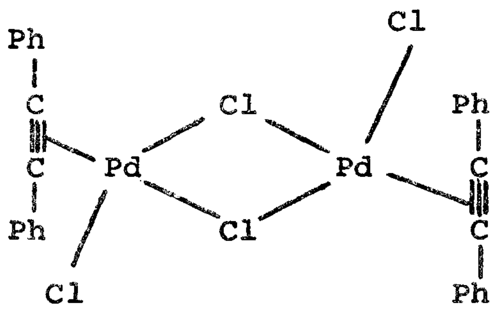
All attempts to produce di-μ-bromo-di[π-(endo-4-ethoxy-1,2,3,4 tetraphenylcyclobutenyl)nickel] (75a) failed. No reaction occurred between diphenylacetylene (44a) and nickel bromide in ethanol, due (at least in part) to the inertness of nickel bromide. When bis(1,2 dimethoxyethane)nickel bromide (76) was dissolved in an ethanol solution of (44a) the complex (76) dissociated completely and no reaction occurred.

In the reactions discussed so far the diphenylacetylene (44a,b,c,d) was always dimerised or trimerised. The reactions carried out in diethyl ether and diglyme in the hope of obtaining a complex containing only one molecule of acetylene led to the usual products. When bis(triethylammonium)tetrachloropalladite was reacted with (44a) in water a brown complex (77a) was obtained in

87% yield, for which analysis showed the empirical formula $[C_{14}H_{10}\cdot PdCl_{1.7}(OH)_{0.3}\cdot H_2O]_n$. The compound (77a) decomposed in solution so neither recrystallisation nor a molecular weight determination were possible. The ^{1}H N.M.R. spectrum of a rapidly decomposing solution of (77a) showed only phenyl protons. The infrared spectra of (77a), hexaphenylbenzene (52a), tetraphenylcyclobutadienepalladium chloride (53a), di-μ-chloro-di[π-(endo-4-ethoxy-1,2,3,4 tetraphenylcyclobutenyl)palladium] (56a), and diphenylacetylene (44a) are shown in Appendix 1. Comparison of these spectra showed that the spectrum of (77a) closely resembled that of diphenylacetylene (44a). No absorption was assignable to a modified C≡C stretching frequency which suggested that the acetylene was not greatly distorted from its geometry in the free state.

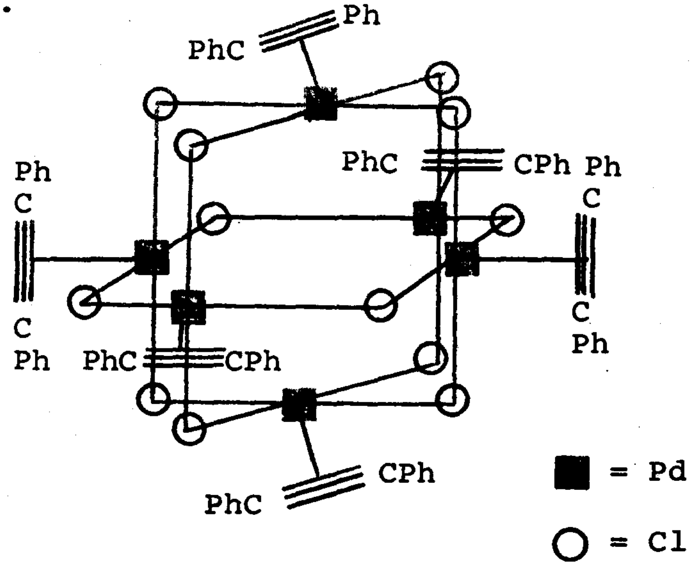
Treatment of (77a) with tri-n-butylphosphine afforded diphenylacetylene (44a), bis(tri-n-butylphosphine)-palladium chloride and a trace of hexaphenylbenzene (52a). No octaphenylcyclooctatetraene (73a) was formed as would be expected if (77a) were tetraphenylcyclobutadienepalladium chloride (53a).[139] Treatment of (77a) with sodium borohydride gave diphenylacetylene (44a), metallic palladium and a trace of hexaphenylbenzene (52a). Vallarino *et al.*[121] and Huttel and Neugebauer[114] have reported that tetraphenyl-1-butene was produced when (53a) was reduced with sodium borohydride. When (77a) was dissolved in N,N-dimethylformamide or methylene chloride and rapidly filtered, none of the insoluble hexaphenylbenzene (52a) was isolated. When the complex (77a) was treated with pyridine a 52% yield of bis(pyridine)palladium chloride was isolated. Thin layer chromatography of the mother liquor showed the presence of diphenylacetylene (44a) and bis(pyridine)palladium chloride.

The results of the experiments described above showed that the organic moiety of the complex $[C_{14}H_{10}\cdot PdCl_{1.7}(OH)_{0.3}\cdot H_2O]_n$ (77a) was diphenylacetylene (44a). As no molecular weight determination was possible, the structure of (77a) was uncertain. The most likely structure was thought to be as shown below with the carbon-carbon triple bonds perpendicular to the plane of the palladium and chlorine atoms. This would be similar to the known structures of compounds of the type $PtCl_2(RC_2R)L$.[42,43,44,45]



(77a)

The interesting possibility of the structure of (77a) being based on hexameric palladium chloride[145] cannot be ruled out. In both of these possible structures of (77a) some substitution of chloride by hydroxide groups must have occurred.



(77a)

III. Methods for removing the catenated palladium chloride from tetraphenylcyclobutadienepalladium chloride complexes (53a,b,c,d) n>1.

For use in subsequent syntheses it was necessary to remove the extra catenated palladium chloride from the tetraphenylcyclobutadienepalladium chloride complexes (53) n>1. As the uncatenated complexes (53), n=1, except (53a), were soluble in organic solvents, subsequent reactions could be carried out homogeneously.

In one method[143] the very insoluble catenated complex (53a,b,c,d), n>1, in methylene chloride was treated with gaseous hydrogen chloride or bromide. The results of a series of these reactions are shown in Table 4.

The hydrogen halide attacked the catenated palladium chloride to give the methylene chloride soluble compound, H_2PdX_4. This compound appeared to coat the insoluble starting material and impede further reaction, which resulted in low yields of the uncatenated compounds.

During this work a more efficient method of removing the catenated palladium chloride was published.[114] The catenated compound (53a), n=3, was dissolved in N,N-dimethylformamide, and the filtered solution was poured into concentrated hydrochloric acid. The uncatenated compound (53a), n=1, was insoluble in this solvent and was removed by filtration. This method was extended to complexes derived from other acetylenes. The results are shown in Table 5.

Mechanical losses were the probable cause of the less than quantitative yield in these conversions. N,N-dimethylformamide formed a strong complex with palladium chloride, which was soluble in both N,N-dimethylformamide and in the N,N-dimethylformamide-hydrochloric acid mixtures. The N,N-dimethylformamide may have formed a labile donor complex with the tetraphenylcyclobutadienepalladium chloride monomer similar to other monomeric adducts (61).[132,133,134]

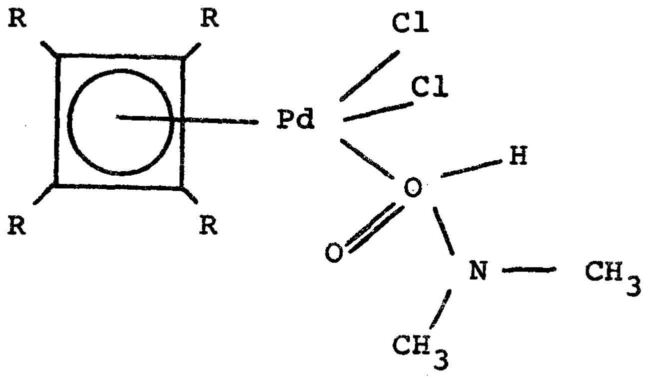
	Starting Compound	Product	Conversion
1.	(<u>53a</u>) n=3	(<u>53a</u>) n=1	36%
2.	(<u>53a</u>) n=3	(<u>59a</u>)[(a)] n=1	39%
3.	(<u>53b</u>) n=3	(<u>59b</u>)[(a)] n=1	23%
4.	(<u>53c</u>) n=3	(<u>59c</u>)[(a)] n=1	40%
5.	(<u>53d</u>) n=3	(<u>59d</u>)[(a)] n=1	36%

Table 4. Efficiency of hydrogen halides for removing catenated palladium chloride.

Footnote to Table 4. (a) HBr was used and the corresponding tetraphenylcyclobutadienepalladium bromide (<u>59</u>) was formed.

	Starting Compound	Product	Conversion
1.	(53a) n=3	(53a) n=1	86%
2.	(53b) n=3	(53b) n=1	89%
3.	(53c) n=3	(53c) n=1	91%
4.	(53d) n=3	(53d) n=1	84%

Table 5. Efficiency of N,N-dimethylformamide for removing catenated palladium chloride.



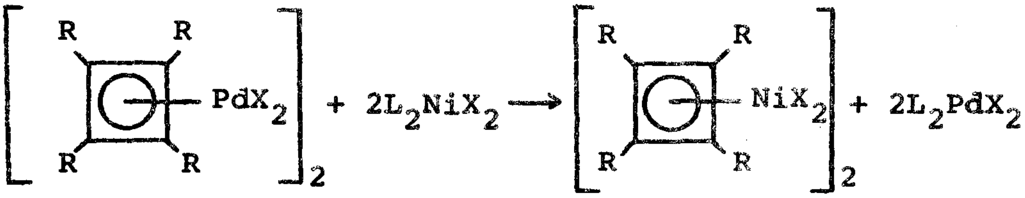
(79a,b,c,d)

When the donor complex (79a,b,c,d) was poured into concentrated hydrochloric acid, it decomposed, and two tetraphenylcyclobutadienepalladium chloride moieties dimerised.

B. Reactions in which a cyclobutadiene ring is transfered from one transition metal to another.

I. Ligand exchange reactions.

Tetraphenylcyclobutadienepalladium halides (53a,b,c,d) and (59a,b,c,d) could be converted to the corresponding nickel chloride compounds (80a,b,c,d) and bromide compounds (54a,b,c,d) by reaction with bis(tert-phosphine)nickel halides in refluxing chlorobenzene.

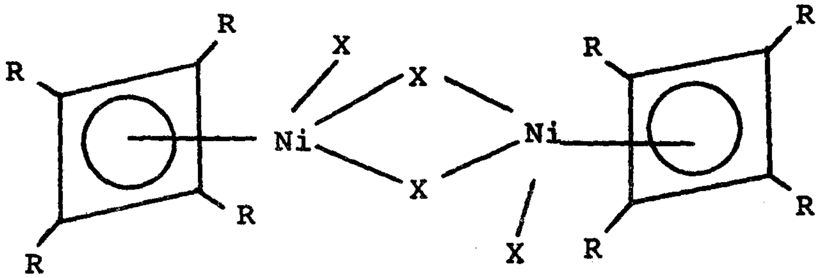


(53a) (X=Cl) (80a)

(59a,b,c,d) (X=Br) (59a,b,c,d)

The results of a series of these reactions are shown in Table 6.

The nickel complexes (54a) and (80a) were too insoluble for molecular weight determinations, but (54b,c,d) were shown to be dimeric in chloroform. The structures of these nickel complexes, (80a), (54a,b,c,d), based on their palladium analogues (53a,b,c,d) and (59a,b,c,d), and the crystal structure of tetramethylcyclobutadienenickel chloride (38)[99] are shown below.



(54a,b,c,d)   (80a,b,c,d)

The discrepancy in the yields of tetraphenylcyclobutadienenickel bromide (54a) and 1,2-bis(diphenylphosphino-)-ethane palladium bromide in reaction 1 arose from the fact that the solubilities of the two compounds were very similar. Separation was effected by column chromatography on silica gel, on which (54a) clings very tenaciously. In reaction 2 the bis(tri-n-butylphosphine)-palladium bromide formed was very soluble and the nickel complex was purified by washing it free of the bis(tri-n-butyl-

		Products			
	Reactant	$[R_4C_4(NiX_2)]_2$			L_2PdX_2
	$[R_4C_4(PdX_2)]_2$	Yield %	Mol. wt. calc.	obs.	Yield %
1.	(59a) (X=Br)	33	1150	(a)	82 (b)
2.	(59a)	90	1150	(a)	46
3.	(53a) (X=Cl)	82	932	(a)	(c)
4.	(59b)	72	1425	1390	(c)
5.	(59c)	73	1262	1210	(c)
6.	(59d)	77	1390	1340	(c)

Table 6. Ligand exchange reactions.

Footnote to Table 6. (a) Too insoluble for mol. wt. determination.

(b) $L = 1/2\ Ph_2PCH_2CH_2PPh_2$.

(c) Not estimated.

phosphine)palladium bromide on a sintered glass funnel with petroleum ether. This resulted in a much higher yield, although both reactions 1 and 2 went to about the same extent. There appeared to be no correlation between the electron donating or withdrawing p-substituents on the phenyl rings and the ease or extent of reaction.

The reaction did not take place in refluxing benzene. The high temperature necessary to cause reaction was probably required to dissociate the nickel-phosphine complex.[153]

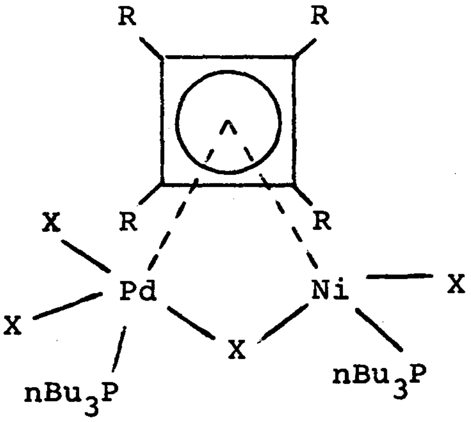
$$(\text{n-Bu}_3\text{P})_2\text{NiX}_2 \overset{\Delta}{\rightleftharpoons} (\text{n-Bu}_3\text{P})\text{NiX}_2 + \text{n-Bu}_3\text{P}$$

The first step in this ligand exchange reaction was probably attack of the free phosphine at the palladium atom. Once the phosphine was bonded to the palladium, the cyclobutadiene-palladium bond was weakened, since no tetraphenylcyclobutadienepalladium halide phosphine complex, similar to tetraphenylcyclobutadienenickel bromide triphenylphosphine[133] could be isolated. The next step may proceed in two ways. One possibility is that complete scission of the cyclobutadienepalladium bond and attack of a free tetraphenylcyclobutadiene on the coordinately unsaturated nickel halide mono phosphine complex occurs.

$$\text{R}_4\text{C}_4\text{PdX}_2\cdot\text{n-Bu}_3\text{P} \longrightarrow \text{R}_4\text{C}_4 + (\text{n-Bu}_3\text{P})\text{PdX}_2$$

$$\text{R}_4\text{C}_4 + (\text{n-Bu}_3\text{P})\text{NiX}_2 \longrightarrow \text{R}_4\text{C}_4\text{NiX}_2 + \text{n-Bu}_3\text{P}$$

The second possible pathway assumes that the tetraphenylcyclobutadiene does not ever become completely detached from the metal atoms. A possible intermediate is shown below in which both metals are bonded to the ring (either from the same side as shown, or from opposite sides).



When tetraphenylcyclobutadienepalladium bromide (<u>59a</u>) was reacted with tri-n-butylphosphine in the presence of a 10 molar excess of diphenylacetylene (<u>44a</u>), according to the equation:

$$[Ph_4C_4(PdBr_2)]_2 + 4n\text{-}Bu_3P + 20C_{14}H_{10}$$

(<u>59a</u>) (<u>44a</u>)

$$\longrightarrow Ph_8C_8 + 2(n\text{-}Bu_3P)_2PdBr_2 + 20C_{14}H_{10}$$

absolutely no hexaphenylbenzene (<u>52a</u>) was formed. This differed from the reaction of Pettit *et al.*[95] in which cyclobutadieneiron tricarbonyl (<u>39</u>) was oxidized in the presence of methylacetylenecarboxylate to yield methylbenzoate. The formation of free cyclobutadiene was proposed to explain the products of this reaction. The fact that no hexaphenylbenzene (52a) was formed in the former reaction implied that at no time in the reaction was any free tetraphenylcyclobutadiene formed. For this reason it appears that the second reaction pathway is a better description of the mechanism.

When the ligand exchange reaction was tried with the labile nickel complex, bis(1,2-dimethoxyethane)-nickel bromide (76), tetraphenylcyclobutadienepalladium bromide (59a) was recovered in 96% yield from the reaction. The nickel complex (76) dissociated completely into nickel bromide and 1,2-dimethoxyethane in chlorobenzene.

When a ligand exchange reaction was attempted between (π-cyclopentadienyl)tetraphenylcyclobutadiene-palladium bromide (81a) and bis(tri-n-butylphosphine)nickel bromide, the starting material (81a) was recovered in 90% yield. This was thought to be due to the absence of bridging bromide atoms in (81a)[137,153] which provided the site for attack by the phosphine when tetraphenylcyclobutadienepalladium bromide (59a) was used as a starting material.

Three other first row transition metal halide phosphine complexes were used in attempted metathetical reactions with tetraphenylcyclobutadienepalladium halides (53a) (59b). None of these reactions led to the transfer of the cyclobutadiene moiety onto the other transition metal.

No ligand exchange occurred between tetrakis(p-chlorophenyl)cyclobutadienepalladium bromide (59b) and bis(tri-n-butylphosphine)ferrous bromide and 68% of (59b) was recovered. This may be due to the inertness of bis(tri-n-butylphosphine)ferrous bromide.

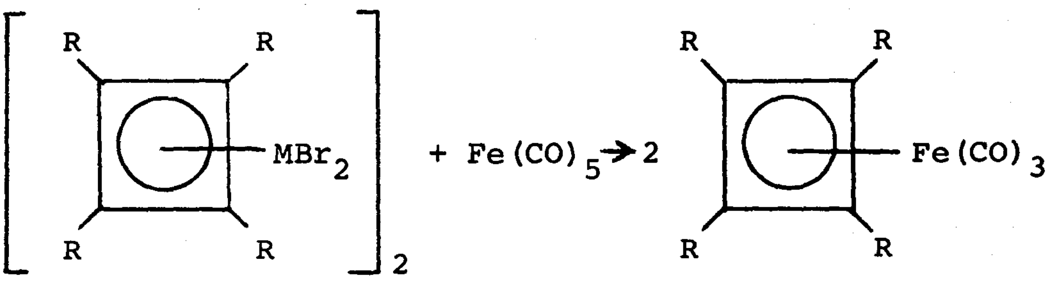
When (59b) was reacted with bis(tri-n-butylphosphine)cobalt bromide a 63% yield of octakis(p-chlorophenyl)cyclooctatetraene (73b) was recovered. No compound containing a tetrakis(p-chlorophenyl)cyclobutadienecobalt moiety was obtained. Bis(tri-n-butylphosphine)cobalt bromide was quite labile (even when pure it still smelled of tri-n-butylphosphine) and if any reaction occurred here, analogous to the nickel case, any tetrakis(p-chlorophenyl)-cyclobutadienecobalt bromide formed rapidly reacted further to give (73b) and cobalt bromide. A second factor against the formation of tetrakis(p-chlorophenyl)cyclobutadiene-cobalt (II) bromide is that cobalt (II) has a d^7 electronic configuration, and such a complex would be expected to be paramagnetic and therefore not obey the effective atomic number formalism.

Similarly, when tetraphenylcyclobutadienepalladium chloride (53a) was reacted with tri-n-butylphosphine-cuprous chloride an 85% yield of octaphenylcyclooctatetraene (73a) was obtained. Here also the copper-phosphine complex was labile.

II. Ligand transfer reactions.

In the ligand transfer reactions several interconversions of the inorganic moiety of the cyclobutadiene complex between MX_2 and $M(CO)_3$ are discussed.

Tetraphenylcyclobutadieneiron tricarbonyl (4a) could be prepared from tetraphenylcyclobutadienepalladium (59a) or nickel bromides (54a) in good yield by refluxing in benzene with iron pentacarbonyl.



(59a,b,c,d) (54a) (4a,b,c,d)

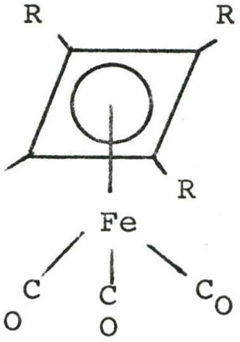
The results of a series of these reactions are shown in Table 7.

These compounds (4a,b,c,d) were characterized by chemical analyses, molecular weights, infrared and ^1H N.M.R. spectra. The complex (4a) prepared in this manner had an identical infrared spectrum and melting point to that reported by Hubel et al.[85,87] An X-ray crystallographic structure determination[19] of (4a) verified that the compound was tetraphenylcyclobutadieneiron tricarbonyl. The complex (4b) prepared by ligand transfer

	Reactant		Product $(R_4C_4)Fe(CO)_3$	
			Mol. wt.	
	$[(R_4C_4)MBr_2]_2$	Yield %	Calcd.	Found
1.	(54a) M=Ni	90	496	496
2.	(59a) M=Pd	78	496	496
3.	(59b)	56	634	634
4.	(59c)	52	552	552
5.	(59d)	17	616	616

Table 7. Formation of tetraphenylcyclobutadieneiron tricarbonyls.

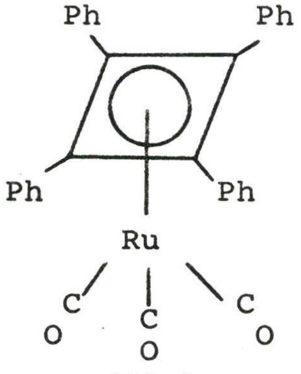
had an infrared spectrum which was identical to that of an authentic sample of tetrakis(p-chlorophenyl)cyclobutadieneiron tricarbonyl prepared by Hubel *et al.*[106] The complexes (4c,d) were assigned similar structures.



(4a,b,c,d)

A similar reaction between tetraphenylcyclobutadienepalladium bromide (59a) and triruthenium dodecacarbonyl was carried out in chlorobenzene under reflux to yield 42% of tetraphenylcyclobutadieneruthenium tricarbonyl (60a). Chlorobenzene (b. pt. 138° C) was used in this reaction as ruthenium-ruthenium bonds must be cleaved and as the reaction did not proceed in refluxing benzene. The infrared spectrum of (60a) was very similar to that of the iron analogue (4a) and identical to that reported by Sears and Stone[129] for tetraphenylcyclobutadieneruthenium tricarbonyl (60a) which they prepared independently; (υ CO at 4.87, 5.07 and 5.13 μ). The melting point (216-219°C) agreed with that for their sample of (60a) (217-219°C). Mass spectrometric analysis showed peaks at m/e of 542, $(Ph_4C_4)Ru(CO)_3^+$;

514, $(Ph_4C_4)Ru(CO)_2^+$; 486, $(Ph_4C_4)RuCO^+$; 458, $(Ph_4C_4)Ru^+$ and $Ph_4C_4^+$. These values are based on ^{102}Ru, the most abundant isotope. Chemical analysis agreed well with the proposed formula of the product (60a). On the basis of this evidence (60a) was assigned a structure analogous to (4a).



(60a)

The mechanism of the formation of (4a,b,c,d) and (60a) is unknown, but probably proceeds through a complex of the tetraphenylcyclobutadienepalladium bromide and the metal carbonyl, in which the metal carbonyl acts as a debrominating agent.

Reaction of tetraphenylcyclobutadieneiron tricarbonyl (4a) with bis(benzonitrile)palladium chloride in benzene under reflux for 12 hours afforded a 91% yield of crude tetraphenylcyclobutadienepalladium chloride (53a), n=3. This was identified by its infrared spectrum and palladium analysis. Purification of the product (53a), n=3, by treatment with gaseous hydrogen bromide gave a 62% overall yield of tetraphenylcyclobutadienepalladium bromide (59a). This was the only case in which a tetraphenylcyclobutadiene ring was transferred onto a palladium atom.

Figure 7 summarises all the successful ligand exchange and transfer reactions.

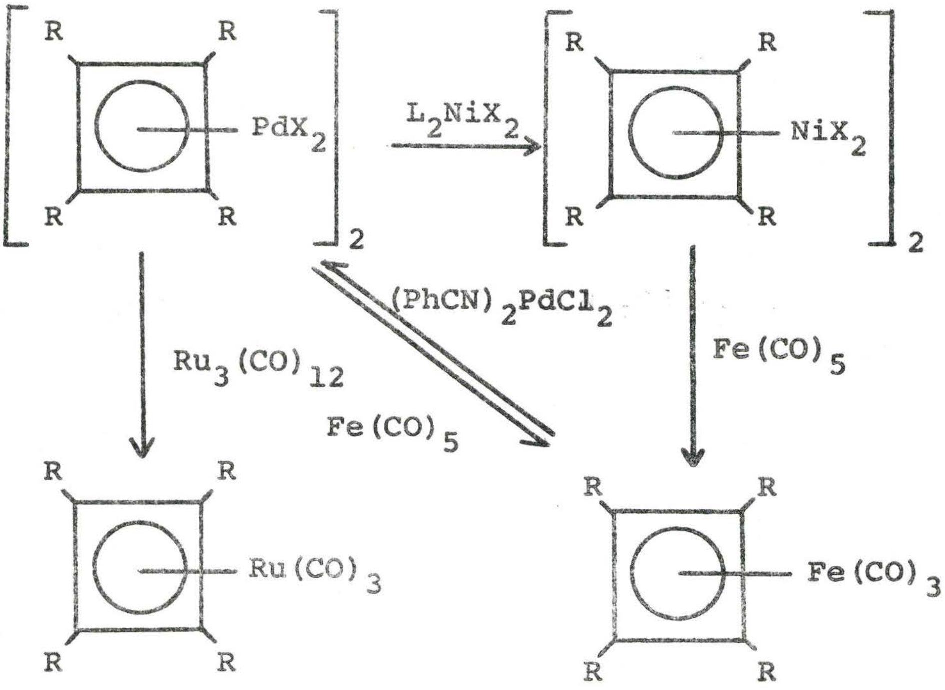


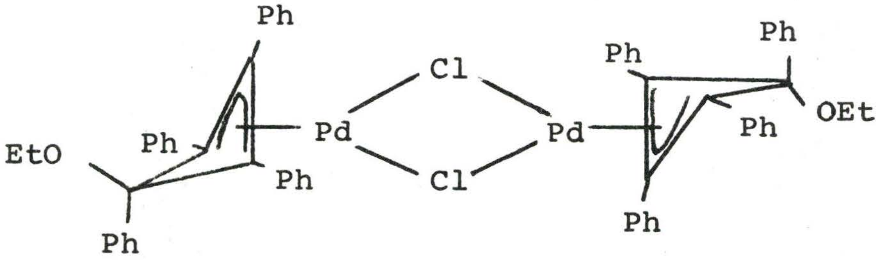
Figure 7. Successful ligand exchange and transfer reactions.

In all cases the central metal atom of the reactant and product had a d^8 electronic configuration. The cyclobutadiene ring contributed four electrons and the halide or carbonyl groups six electrons and thus the central metal atom had the electronic configuration of the next highest inert gas and obeyed the inert gas formalism.

III. Reactions in which the cyclobutadiene ring was modified but remained bonded to the central metal atom.

Tetraphenylcyclobutadienepalladium chlorides (53a,b,c) and bromide (59a) reacted with ethanol and methanol to form di-μ-halo-di[π-(exo-4-alkoxy-1,2,3,4 tetraphenylcyclobutenyl)palladium] compounds (57b,c), (83a), (84a), (85a). The results of a series of these reactions are shown in Table 8.

These compounds were characterized by elemental analysis, infrared and ^{1}H N.M.R. spectra and molecular weight determinations. An X-ray crystallographic structure determination has been done on di-μ-chloro-di(π-(exo-4-ethoxy-1,2,3,4 tetraphenylcyclobutenyl)palladium] (57a).[122] The structure of (57a) is shown below.



(57a)

The structures of (57b,c), (83a), (84a) and (85a) were assumed to be similar.

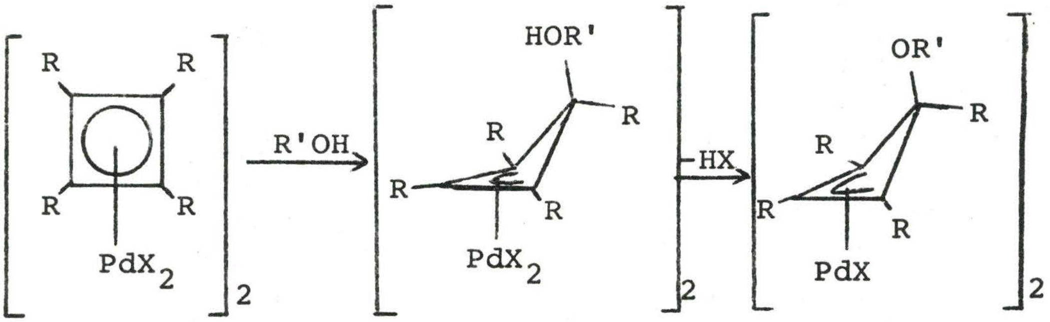
	Reactants			Product $[R_4C_4OR'PdX]_2$		
				Mol. wt.		
	$[R_4C_4PdX_2]_2$	R'OH	Yield %	Calcd.	Found	
1.	R=Ph, X=Br	R'=Et	95			(83a)
2.	R=Ph, X=Cl	R'=Me	95			(84a)
3.	R=Ph, X=Br	R'=Me	93			(85a)
4.	(53b) X=Cl	R'=Et	53	1362	1350	(57b)
5.	(53c) X=Cl	R'=Et	59	1199	1150	(57c)

Table 8. Formation of di-μ-halo-di[π-(exo-4-alkoxy-1,2,3,4 tetraphenylcyclobutenyl)palladium] compounds.

In the formation of these cyclobutenyl compounds one important difference was found. The complexes di-μ-chloro-di[π-(exo-4-ethoxy-1,2,3,4 tetrakis{p-anisyl}-cyclobutenyl)palladium] (57d) and its bromo analogue (83d) could not be prepared. When tetrakis(p-anisyl)cyclobutadienepalladium chloride (53d) was stirred in ethanol for two days it was recovered unchanged quantitatively. Longer reaction times led to decomposition of (53d) and the formation of metallic palladium. When (53d) was treated with the stronger nucleophile, ethoxide, palladium metal appeared almost immediately. In one further attempt to carry out nucleophilic attack of the cyclobutadiene ring tetrakis(p-anisyl)cyclobutadienepalladium bromide (59d) was stirred with a 10% solution of ethanethiol in ethanol at room temperature. A yield of 50% of polymeric palladium ethylmercaptide was obtained, which was identified by its infrared and ^{1}H N.M.R. spectra.

When tetraphenylcyclobutadienenickel bromide (54a) was stirred in ethanol for one day no reaction occurred and (54a) was recovered quantitatively. Treatment of (54a) with sodium ethoxide in ethanol afforded a brown complex (86a) whose infrared spectrum was identical to that of di-μ-bromo-di[π-(exo-4-ethoxy-1,2,3,4 tetraphenylcyclobutenyl)palladium] (83a). All attempts to purify (86a) led to decomposition of the complex which was visibly contaminated with sodium bromide. As a result of this, no analysis was done on this compound (86a), but the infrared spectrum suggested it was di-μ-bromo-di[π-(exo-4-ethoxy-1,2,3,4 tetraphenylcyclobutenyl)nickel] (86a). The instability of this compound (86a) was in agreement with the much lower stability of nickel π-allyls compared to palladium π-allyls.[154]

The mechanism proposed for these reactions is nucleophilic attack by ethanol on one of the cyclobutadiene ring carbon atoms followed by elimination of a hydrogen and a halide ion. This is similar to the mechanism found by Chatt et al.[155] for the reaction between alcohols and 1,5 dicyclopentadienepalladium chloride.



This mechanism would explain why tetrakis(p-anisyl)cyclobutadienepalladium chloride (53d) with its four powerfully electron donating p-methoxy groups, $\sigma_{p\text{-}CH_3O} = -0.27$,[156] does not react with ethanol. Tetraphenylcyclobutadienepalladium chloride (53a) $\sigma_H = 0.00$, (53b) $\sigma_{p\text{-}Cl} = 0.23$, and (53c) $\sigma_{p\text{-}CH_3} = -0.17$ undergo the reaction quite readily.[120,156] Electron donating substituents deactivate aromatic compounds to nucleophilic substitution as has been shown by Bunnett and Zahler who reported that a methoxy group substituent retarded or completely prevented nucleophilic substitution of a chloro group by hydroxyl in several substituted benzene compounds.[157]

These cyclobutenyl compounds (57a,b,c) and their endo isomers (56a,b) reacted with hydrogen halides in methylene chloride to yield the corresponding cyclobutadienepalladium halide complex. The results of a series of these reactions are shown in Table 9.

The structure of these compounds was discussed in section I of the RESULTS AND DISCUSSION of this thesis.

No reaction occurred when the cyclobutenyl compounds (56b) (endo) and (57b) (exo) were treated with gaseous hydrogen chloride, whereas both reacted with hydrogen bromide to yield the cyclobutadiene compound (59b) in good yield. The cyclobutenyl compounds in which the phenyl rings were unsubstituted (56a), (57a) reacted readily with hydrogen chloride to give the cyclobutadiene compound $[Ph_4C_4PdCl_2]_2$, (53a). These results can be explained by proposing electrophilic protonation of the ether oxygen and nucleophilic addition of halide at the palladium atom, followed by elimination of ethanol. When the cyclobutenyl compound is deactivated by electron withdrawing p-chloro groups, it is necessary to use the stronger nucleophile, bromide, to give the cyclobutadiene compound. This electrophilic mechanism is in agreement

	Reactants $[R_4C_4OEtPdCl]_2$	HX	Product $[R_4C_4PdX_2]_2$ Yield %	
1.	(56a) (endo)	X=Cl	76	(53a)
2.	(56a)	X=Br	82	(59a)
3.	(56b)	X=Br	82	(59b)
4.	(56c)	X=Br	61	(59c)
5.	(57a) (exo)	X=Cl	100	(53a)
6.	(57b) (exo)	X=Br	62	(59b)

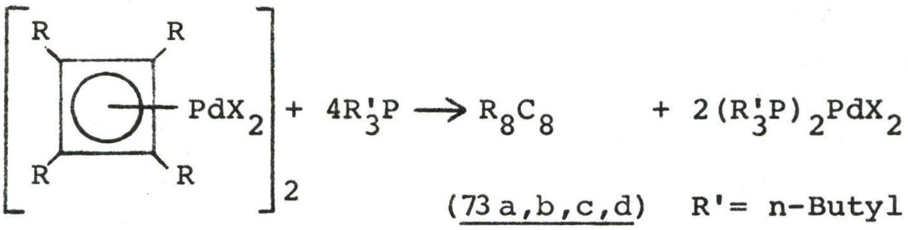
Table 9. Conversion of cyclobutenyl to cyclobutadiene compounds.

with the work of Chatt et al. on palladium complexes of diolefins.[155]

These reactions in which di-μ-chloro-di[π-(endo-4-ethoxy-1,2,3,4 tetraphenylcyclobutenyl)palladium] compounds (56a,b,c), formed by the reaction of the corresponding tolan with bis(benzonitrile)palladium chloride in ethanol, were treated with a gaseous hydrogen halide afforded the corresponding tetraphenylcyclobutadienepalladium halide in the best overall yield and in the shortest time.

IV. Reactions in which the cyclobutadiene ring was removed from the central metal atom.

Tetraphenylcyclobutadienepalladium halides reacted with tertiary phosphines in refluxing benzene under nitrogen to give the organic dimer of the tetraphenylcyclobutadiene moiety.[139,158]



$$+ 4R'_3P \longrightarrow R_8C_8 \quad + 2(R'_3P)_2PdX_2$$

(73a,b,c,d) R'= n-Butyl

The results of a series of these reactions are shown in Table 10.

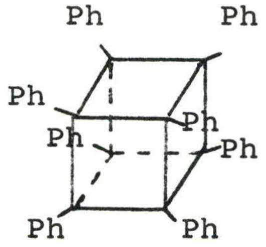
These compounds were characterised by chemical analyses, infrared spectra and molecular weights.

The dimer of tetraphenylcyclobutadiene (73a) was

	Reactant $[R_4C_4(PdX_2)]_2$		Product R_8C_8 Yield %	Mol. wt. Calcd.	Mol. wt. Found
1.	(53a), X=Cl, n=1	(73a)	70	713	712
2.	(59a), X=Br, n=1	(73a)	95		
3.	(53b), X=Cl, n=2	(73b)	73	989	982
4.	(53b), X=Cl, n=3	(73b)	54		
5.	(53c), X=Cl, n=3	(73c)	40	825	825
6.	(53d), X=Cl, n=3	(73d)	94	953	953
7.	(53d), X=Cl, n=1.5	(73d)	90		

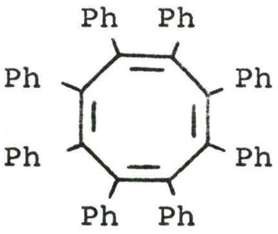
Table 10. Formation of cyclooctatetraenes.

originally thought to have the octaphenylcubane structure.[140,141]



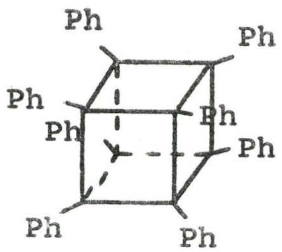
(73a)

However, when the X-ray crystallographic analysis of the structure was completed[142] the compound (73a) was shown to be octaphenylcyclooctatetraene.

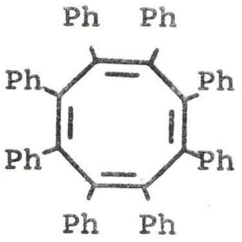


(73a)

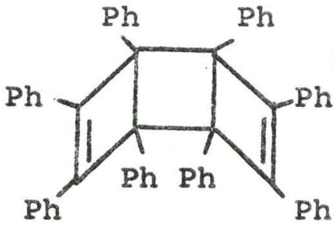
Neither the infrared spectrum nor the melting point of (73a) changed on vacuum sublimation or on melting. This demonstrated that the octaphenylcyclooctatetraene structure of (73a) was the most thermally stable of at least five possible isomers of the dimer of tetraphenylcyclobutadiene.



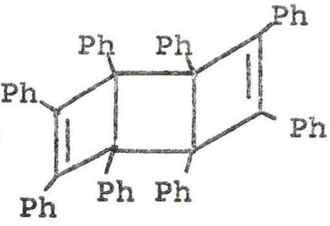
(73a)



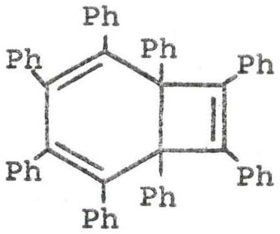
(73a)



(73a)



(73a)



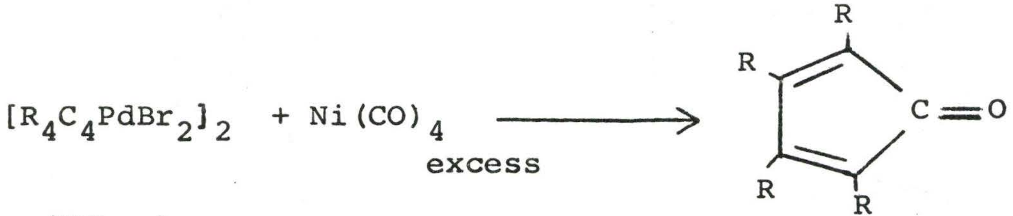
(73a)

The dimer of tetrakis(p-chlorophenyl)cyclobutadiene (73b) was similarly shown to be the most thermally stable isomer. The Raman spectrum of (73b) showed a strong absorption at 1642 cm^{-1} which was assigned to a carbon-carbon double bond. On these observations (73b) was assigned the octakis(p-chlorophenyl)cyclooctatetraene structure.

The dimers of tetrakis(p-tolyl)cyclobutadiene (73c) and tetrakis(p-anisyl)cyclobutadiene (73d) were assigned similar structures.

There has been considerable discussion whether a free cyclobutadiene ring occurred at any time in the course of these reactions.[93,115,139,143,158] Generally the evidence was against the formation of free cyclobutadiene during the reaction, although the subject was not settled. As discussed in section II of the RESULTS AND DISCUSSION of this thesis, the reaction between tetraphenylcyclobutadienepalladium chloride (53a) and tri-n-butylphosphine in the presence of a ten molar excess of diphenylacetylene (44a) gave no hexaphenylbenzene (52a), but afforded a 92% yield of octaphenylcyclooctatetraene (73a). This indicated that at no time during the course of these reactions was any free tetraphenylcyclobutadiene formed.

Two tetrakis(p-substituted phenyl)cyclobutadienepalladium bromides (59b,c) were reacted with nickel tetracarbonyl to yield the corresponding tetraphenylcyclopentadienones (78b,c)



$$[R_4C_4PdBr_2]_2 + Ni(CO)_4 \xrightarrow[\text{excess}]{}$$

(59b,c)

(78b,c)

In these reactions the nickel tetracarbonyl was added to a refluxing solution of the cyclobutadienepalladium bromide (59b,c). No tetraphenylcyclobutadienenickel bromide (54b,c) was produced in the reaction. This differed from the ligand transfer reactions of Maitlis and

Games[124] in which tetraphenylcyclobutadienepalladium bromide (59a) in benzene was stirred with nickel tetracarbonyl at room temperature and then gradually heated to reflux to yield 47% of tetraphenylcyclobutadienenickel bromide (54a) and only 17% of tetraphenylcyclopentadienone (78a).

The mechanism of these reactions was not studied, but an intermediate complex between the tetraphenylcyclobutadienepalladium bromide (59a,b,c) and nickel tetracarbonyl must have been formed in which the nickel tetracarbonyl acted as a dehalogenating agent. When carbon monoxide was passed through a solution of tetrakis(p-chlorophenyl)cyclobutadienepalladium bromide (59b) in methylene chloride no reaction occurred and (59b) was recovered in near quantitative yield. This supported the proposal that a complex intermediate containing the cyclobutadiene compound and nickel tetracarbonyl was formed, and that the reaction did not proceed by simple carbon monoxide insertion, arising from nickel tetracarbonyl decomposition. Presumably at refluxing benzene temperature the intermediate broke down too fast to allow ligand transfer to the nickel atom, but allowed the relatively simple process of carbonyl insertion in the cyclobutadiene ring. At lower temperatures the intermediate was more stable and ligand transfer competed successfully with carbonyl insertion.

C. ^{1}H N.M.R. studies of some tetrakis(p-substituted phenyl)cyclobutadiene compounds and their derivatives.

I. Cyclopentadienyl compounds.

After the method of Maitlis *et al.*[137,153] tetraphenylcyclobutadienepalladium bromides (59a,b,c,d) were reacted with cyclopentadienyliron dicarbonyl bromide according to the reaction shown below.

$$[R_4C_4PdBr_2]_2 + 4C_5H_5Fe(CO)_2Br \longrightarrow 2R_4C_4PdC_5H_5FeBr_4$$

(59a,b,c,d) (82a,b,c,d)

These red paramagnetic (π-cyclopentadienyl)tetraphenylcyclobutadienepalladium tetrabromoferrates (82a,b,c,d) were converted to the corresponding diamagnetic bromides (81a,b,c,d) by reaction with potassium hexacyanatoferrite (II).

$$R_4C_4PdC_5H_5FeBr_4 + K_4Fe(CN)_6 \longrightarrow R_4C_4PdC_5H_5Br$$

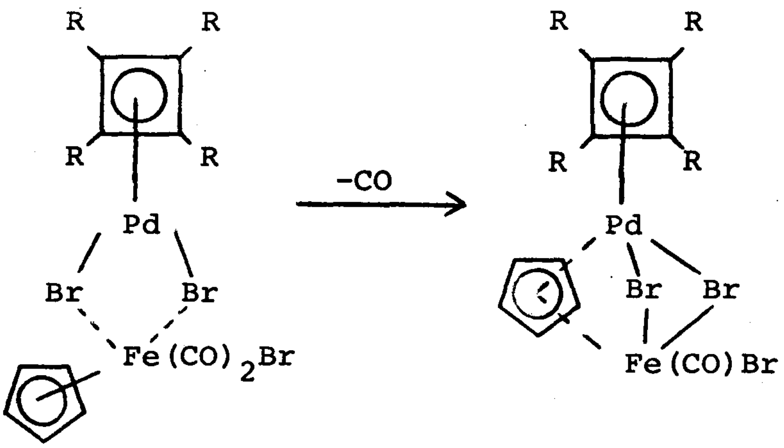
(82a,b,c,d) (81a,b,c,d)

The yields for these reactions are shown in Table 11.

The cyclopentadienyliron dicarbonyl bromide acted as a debrominating agent, and the reaction may have proceeded through intermediates such as are shown below.

		Product	
	Reactant $[R_4C_4PdBr_2]_2$	$R_4C_4PdC_5H_5FeBr_4$ Yield %	$R_4C_4PdC_5H_5Br$ Yield %
1.	(59a)	85	83
2.	(59b)	82	72
3.	(59c)	95	91
4.	(59d)	98	84

Table 11. Cyclopentadienylation reactions.



No reaction occurred when tetraphenylcyclobutadienepalladium bromide (<u>59a</u>) was reacted with neat dicyclopentadiene at 120-130°C in an attempt to produce (π-cyclopentadienyl)tetraphenylcyclobutadienepalladium bromide (<u>81a</u>) in a one step synthesis. Presumably the dicyclopentadiene could not act as a debrominating agent.

The ^1H N.M.R. spectra of these compounds were run in deuterochloroform with tetramethylsilane as an internal standard in an attempt to correlate the electronic properties of the p-substituents with the position of the cyclopentadienyl resonance. The ^1H N.M.R. spectra and the Hammet σ values for the p-substituent are tabulated in Table 12.

Linear relationships between N.M.R. absorptions and Hammet sigma values have been obtained in some simpler systems, e.g. Gutowsky *et al.*[160] have obtained a linear relationship between the position of the ^{19}F resonance of p-substituted fluorobenzenes and the Hammet σ values of the substituents. However, it was apparent

	Compound	^{1}H N.M.R. Spectra	Hammet σ values		
	$R_4C_4PdC_5H_5Br$	C_5H_5 (p.p.m.)	σ_p (a)	σ_m (b) $=I$ (c)	R (d) $=\sigma_p - I$
1.	(81a) (H)	6.34	0.00	0.00	0.00
2.	(81b) (Cl)	6.20	+0.23	+0.37	-0.14
3.	(81c) (CH_3)	6.05	-0.17	-0.07	-0.10
4.	(81d) (CH_3O)	6.02	-0.27	+0.12	-0.39

Table 12. ^{1}H N.M.R. spectra of cyclopentadienyl compounds.

Footnote to Table 12. (a) Hammet's sigma value for the given p-substituent.

(b) Hammet's sigma value for the given m-substituent.

(c) Taft's[159] inductive contribution (based on $\sigma_p = I + R$).

(d) Taft's resonance contribution.

from Table 11 that there was no linear relationship between the position of the ^{1}H N.M.R. resonance of the cyclopentadienyl group and any of the Hammet sigma values. The differences in the positions of the cyclopentadienyl resonance may have been due to different degrees of interaction between the deuterochloroform solvent molecules and the p-substituents of the phenyl rings.

II. ^{1}H N.M.R. studies of compounds derived from p,p'-disubstituted diphenylacetylenes.

The ^{1}H N.M.R. spectra of several compounds are shown in Tables 13, 14 and 15, depending on the starting p,p'-disubstituted diphenylacetylene.

The ^{1}H N.M.R. spectra of compounds derived from p,p'-disubstituted diphenylacetylenes were found to be more amenable to analysis than the spectra of compounds derived from diphenylacetylene (44a). The spectra of the latter usually gave a complex multiplet or an unexplained singlet in the phenyl region from which no information concerning the equivalence or non-equivalence of the phenyl rings could be deduced.[137] The ^{1}H N.M.R. spectra of tetrakis(p-chlorophenyl)cyclobutadienepalladium bromide (59b) and di-μ-chloro-di[π-(endo-4-ethoxy-1,2,3,4 tetrakis{p-tolyl}cyclobutenyl)palladium] (56c) are shown in Appendix 2. These spectra were typical of those recorded in Tables 12, 13, 14 and 15.

		^{1}H N.M.R. Spectra		
Compound	Phenyl p.p.m.	J_{AB} p.p.m.	$\Delta_B-\Delta_A$ p.p.m.	Other p.p.m.
1. $[R_4C_4PdBr_2]_2$	7.7 (AB)	0.15	0.39	
2. $[R_4C_4NiBr_2]_2$	7.6 (AB)	0.12	0.49	
3. $R_4C_4Pd(C_5H_5)Br$	7.3 (AB)	0.14	0.25	C_5H_5 6.20
4. $[R_4C_4OEtPdCl]_2$ (exo)	7.3 (M)			$-CH_2-$3.5, $-CH_3$ 1.1
5. $[R_4C_4OEtPdCl]_2$ (endo)	7.4 (M)			$-CH_2-$3.7, $-CH_3$ 1.3
6. R_4C_5O	7.1 (M)			

Table 13. ^{1}H N.M.R. spectra of compounds derived from p,p'-dichlorodiphenylacetylene.

		^{1}H N.M.R. Spectra			
Compound	CH_3 p.p.m.	Phenyl p.p.m.	J_{AB} p.p.m.	$\Delta_B-\Delta_A$ p.p.m.	Other p.p.m.
1. $[R_4C_4PdBr_2]_2$	2.28	7.4 (AB)	0.15	0.51	
2. $[R_4C_4NiBr_2]_2$	2.22	7.5 (AB)	0.13	0.72	
3. $R_4C_4Pd(C_5H_5)Br$	2.35	7.5 (AB)	0.14	0.18	C_5H_5, 6.05
4. $R_4C_4Ni(C_5H_5)Br$	2.36	7.5 (AB)	0.14	0.22	C_5H_5, 5.62
5. $R_4C_4Fe(CO)_3$	2.27	7.1 (AB)	0.13	0.22	
6. $[R_4C_4OEtPdCl]_2^{(a)}$	2.10,2.25,2.45	6.8 (M)			$-CH_2-$3.32, $-CH_3$ 0.91
7. $[R_4C_4OEtPdCl]_2^{(b)}$	2.10,2.35	7.5 (M)			$-CH_2-$3.55, $-CH_3$ 1.03
8. R_4C_5O	2.22	7.5 (M)			

Table 14. ^{1}H N.M.R. spectra of compounds derived from p,p'-ditolylacetylene.

			^{1}H N.M.R. Spectra		
	OCH_3	Phenyl	J_{AB}	Δ_B-Δ_A	Other
Compound	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
1. $[R_4C_4PdBr_2]_2$	3.81	7.3 (AB)	0.15	0.75	
2. $[R_4C_4NiBr_2]_2$	3.89	7.4 (AB)	0.14	0.89	
3. $R_4C_4PdC_5H_5Br$	3.92	7.2 (AB)	0.15	0.55	C_5H_5, 6.02

Table 15. ^{1}H N.M.R. spectra of compounds derived from p,p'-dianisylacetylene

Those compounds for which chemical evidence or X-ray structural determinations showed a cyclobutadiene structure, viz. $[R_4C_4PdCl_2]_2$ (53b,c,d), $[R_4C_4PdBr_2]_2$ (59b,c,d), $[R_4C_4NiBr_2]_2$ (54b,c,d), $R_4C_4Fe(CO)_3$ (4b,c,d) and $R_4C_4PdC_5H_5Br$ (81b,c,d), all showed an AB quartet in the phenyl region of their ^1H N.M.R. spectra. Every pair of protons on one side of a phenyl ring gave an AB quartet. The pair of protons on the other side of the same phenyl ring gave rise to a degenerate quartet. If the four phenyl rings of the compound were magnetically equivalent, then the four AB quartets which arose from separate phenyl rings would be degenerate and the ^1H N.M.R. spectrum in the phenyl region would show one AB quartet. An example of this was the spectrum of tetrakis-(p-chlorophenyl)cyclobutadienepalladium bromide (59b) which is shown in Appendix 2. The intensity and separation of these four peaks depended on the ratio of the coupling constant, J_{AB}, and the difference in chemical shifts of the two protons, $\Delta_B - \Delta_A$. The AB quartet would have been complicated if cross-ring coupling between protons on opposite sides of the phenyl rings had occurred. Batdorf with a resolution of $1{:}10^7$ did not observe any cross-ring coupling in p-disubstituted benzenes.[161] Rapid rotation of the whole organic moiety of the molecule would make the phenyl rings equivalent as far as ^1H N.M.R. spectra were concerned, but any rotation was probably quite slow due to the high moment of inertia of the organic ligand to rotation.

The ^1H N.M.R. spectra of all those compounds which chemical evidence or X-ray structural determination showed did not contain cyclobutadiene rings were more complicated in the phenyl region, viz. $[R_4C_4OC_2H_5PdCl]_2$ (56b,c) (endo isomer), (57b,c) (exo isomer) and R_4C_5O (78b,c). The spectrum of di-μ-chloro-di[π-(endo-4-ethoxy-1,2,3,4 tetrakis{p-tolyl}cyclobutenyl)palladium] (56c) is shown in Appendix 2. In this case the ^1H N.M.R. spectrum in the phenyl region consisted of two AB quartets, two A'B' quartets and four A"B" quartets overlapped but not superimposed on each other.

In those compounds derived from p,p'-ditolylacetylene it was thought that the resonance of the p-methyl group would be sufficiently sensitive to electronic environment to be used as a test for the equivalence of the phenyl rings. This was possible for only one of the compounds, di-μ-chloro-di[π-(endo-4-ethoxy-1,2,3,4 tetrakis{p-tolyl}cyclobutenyl)palladium] (56c) which showed three methyl resonances with relative intensities of 1:1:2 (Appendix 2). This confirmed the structure of (56c) as similar to that of its analogue di-μ-chloro-di[π-(endo-4-ethoxy-1,2,3,4-tetraphenylcyclobutenyl)palladium] (56a) which was determined by X-ray crystallography.[122] However, the exo isomer of (56c) showed only two methyl resonances (of equal intensity) when three were expected. A second example of this accidental degeneracy was found in the ^{1}H N.M.R. spectrum of tetrakis(p-tolyl)cyclopentadienone (78c) which showed only one methyl resonance where two were expected. Thus the ^{1}H N.M.R. spectrum in the phenyl region must be used as a diagnostic test to determine whether the compound has sufficiently high symmetry to be a cyclobutadiene derivative. This method worked well on the majority of compounds discussed in the RESULTS AND DISCUSSION of this thesis, but there were limitations. The compound must have been prepared from a p,p'-disubstituted diphenylacetylene, it must be soluble which eliminated compounds of the type $[R_4C_4(PdCl_2)_3]_2$ and it must be diamagnetic which eliminated compounds of the type $R_4C_4PdC_5H_5FeBr_4$.

EXPERIMENTAL

EXPERIMENTAL

Melting-points: These were obtained using a Thomas Hoover melting-point apparatus. When the melting-point was above 250°C an electrically heated air bath apparatus was used. The melting-points of all organometallic compounds were determined in evacuated capillaries and are uncorrected.

Molecular weights: These were determined on a Mechrolab osmometer (Model 301A) in chloroform. The molecular weights of compounds having sufficient volatility were determined on a Hitachi Perkin-Elmer mass spectrometer (Model RMU-6A).

Infrared spectra: These were recorded as potassium bromide windows from 2 to 16 μ on a Beckmann spectrometer (Model IR5).

Nuclear magnetic resonance spectra: High resolution ^1H spectra were obtained in deuterochloroform on a Varian A 60 spectrometer. Tetramethylsilane was used as an internal standard.

Raman spectra: These were run on solid samples (length 3 cm.) with a Toronto mercury arc and a Hilger spectrometer.

Palladium analyses: These were carried out by ignition of 100 mg samples and reduction of the palladium residue with methanol vapour.

Column chromatography: Chromatographic columns were made up of alumina (80-200 mesh) supplied by Fisher Scientific Co.

Thin layer chromatography: The plates were made up from an aqueous slurry of Silica Gel G, supplied by Canlab, and dried at 90°C for one hour.

Solvents: The light petroleum ether used was that fraction with a boiling range 30-60°C. All other solvents were reagent grade and dried by standard procedures.

Reagents: Diphenylacetylene, (tolan), was obtained from Orgmet. p,p'-Dichlorotolan was prepared by a modification of the method of Jonas[162] by Maitlis *et al.*[143] P,p'-Dimethyltolan and p,p'-dimethoxytolan were prepared by the method of Coleman *et al.*[163] Tetraphenylcyclobutadienepalladium chloride (53a) and bromide (59a) were prepared in 10 g. quantities by the method of Maitlis and Games.[130] Bis(tri-n-butylphosphine)nickel bromide was prepared by the method of Jensen.[164]

The compounds and reactions described in the EXPERIMENTAL, are the following:

Page	Compound or Reaction
108	Reactions of diphenylacetylenes with bis(benzonitrile)palladium chloride in non-hydroxylic solvents.
109	Conversion of $[R_4C_4(PdCl_2)_3]_2$ to $[R_4C_4PdX_2]_2$ by HX in CH_2Cl_2.
109	Conversion of $[R_4C_4(PdCl_2)_3]_2$ to $[R_4C_4PdCl_2]_2$ by treatment with N,N-dimethylformamide and concentrated HCl.
114	Reaction of diphenylacetylenes with palladium (II) complexes in ethanolic solvents.
116	Reaction of diphenylacetylene with bis(tri-ethylammonium) tetrachloropalladite in water.
118	Preparation of $[R_4C_4NiBr_2]_2$ from $[R_4C_4PdBr_2]_2$.
119	Preparation of $R_4C_4Fe(CO)_3$ from $[R_4C_4MBr_2]_2$.
121	Preparation of $Ph_4C_4Ru(CO)_3$ from $[Ph_4C_4PdBr_2]_2$.
123	Preparation of $[Ph_4C_4PdBr_2]_2$ from $Ph_4C_4Fe(CO)_3$.
123	Attempted ligand transfer reactions.
125	Preparation of $[R_4C_4OR'PdX]_2$ from $[R_4C_4PdX_2]_2$.
127	Preparation of R_8C_8.
129	Preparation of R_4C_5O.
131	Cyclopentadienylation reactions.
131	Conversion of $[R_4C_4OEtPdCl]_2$ to $[R_4C_4PdX_2]_2$.

Reaction of diphenylacetylenes (44a,b,c,d) with bis(benzonitrile)palladium chloride in non-hydroxylic solvents.

$$RC_2R + (PhCN)_2PdCl_2 \longrightarrow R_6C_6 + [R_4C_4(PdCl_2)_n]_2$$

(44a)	(52a)	(53a) n=2.5,3
(44b)	(52b)	(53b) n=2,3
(44c)	(52c)	(53c) n=3
(44d)	(52d)	(53d) n=3

Diphenylacetylene (R=Ph)

A solution of 1.00 g (5.61 mmole) of diphenylacetylene (44a) in 340 ml of benzene was added dropwise with stirring over a period of two or three hours to a solution of 2.21 g (5.78 mmole) of bis(benzonitrile) palladium chloride in 340 ml of benzene. The solid was filtered off and boiled with two 100 ml portions of benzene. As hexaphenylbenzene (52a) was soluble in hot benzene, whereas the complex (53a) n=3 was totally insoluble, this was a convenient method for separating the products. This left 0.84 g (0.47 mmole) of brick red tetraphenylcyclobutadienepalladium chloride (53a) n=3; yield 34%, based on the diphenylacetylene (44a) used. Anal. Calcd. for $C_{56}H_{40}Cl_{12}Pd_6$: Pd 35.9%. Found: Pd 35.6%.

The combined benzene fractions were run through a column of alumina to remove the unreacted bis(benzonitrile)-

palladium chloride. Reduction of this volume of benzene to about 50 ml gave 0.60 g (1.1 mmole) of white crystalline hexaphenylbenzene (52a); yield 60%; m.p. 438-440°; Lit. 439-441°.[165]

The results of a series of similar reactions are shown in Table 16.

Conversion of $[R_4C_4(PdCl_2)_3]_2$ (53a,b,c,d) to $[R_4C_4PdX_2]_2$ by HX in CH_2Cl_2.

$$[R_4C_4(PdCl_2)_3]_2 + HX \longrightarrow [R_4C_4PdX_2]_2$$

$$\text{(53a,b,c,d) } n=3 \qquad\qquad \text{(53a) } n=1, \text{ (59b,c,d)}$$

While this work was being carried out a better method for removing the catenated palladium chloride from $[R_4C_4(PdCl_2)_3]_2$ (53a,b,c,d) was published by Huttel and Neugebauer.[114] This method consisted of dissolving the compound $[R_4C_4(PdCl_2)_3]_2$ (53a,b,c,d) in N,N-dimethylformamide; on pouring the solution into concentrated hydrochloric acid, the complex $[R_4C_4PdCl_2]_2$ (53a,b,c,d) precipitated. The results of a series of similar reactions are shown in Table 18.

	Acetylene RC_2R(a)	Yield of Trimer (%)	Analysis of Trimer						$[R_4C_4(PdCl_2)_n]_2$			
			C	H	Mol. wt. (found)	C	H	Mol. wt. (calc.)	% Yield	n	% Pd found	% Pd calc.
1.	(44a)	60							34	3	35.6	35.9
2.	(44a)	(b)							19	2.5	33.2	33.2
3.	(44a)	54							29	3	35.7	35.9
4.	(44a)	55							19	3	35.6	35.9
5.	(44a)		No reaction(c)(d)									
6.	(44a)	12(e)							11	3	35.4	35.9
7.	(44b)	45	68.16	3.36	740(f)(g)	68.03	3.26	741	18	2	25.2	25.1
8.	(44b)	32							43	3	31.0	31.1
9.	(44c)	39	93.05	7.01	619(h)	93.19	6.81	619	44	3	33.6	33.7
10.	(44d)	26	80.86	6.16	714(i)	80.67	5.93	714	58	3	31.8	31.6

Table 16. The reactions of diphenylacetylenes (44a,b,c,d) with bis(benzonitrile)palladium chloride to give the cyclobutadienepalladium chlorides (53a,b,c,d) $[R_4C_4(PdCl_2)_n]_2$ and the benzenes (52a,b,c,d) R_6C_6. (See footnote on following page.)

Footnote to Table 16: All reactions were carried out at 25° except as in (c). (a) mole ratio, concentration and solvent are shown in Table 2. (b) yield of Ph_6C_6 not estimated. (c) reaction temperature -40°. (d) 48% recovery of bis(benzonitrile)palladium chloride. (e) unreacted diphenylacetylene and bis(benzonitrile)palladium chloride detected by thin layer chromatography. (f) all molecular weights of benzenes, R_6C_6 (52b,c,d) determined mass spectroscopically. (g) m.p. 433°; Lit. 404-405°.[166] (h) sublimed in a sealed tube 320-340°. (i) m.p. 408-409°.

				$[R_4C_4PdX_2]_2$ Analysis							
				Found				Calculated			
	$[R_4C_4(PdCl_2)_3]_2$	HX	Yield %	Pd	C	H	Mol. wt.	Pd	C	H	Mol. wt.
1.	(<u>53a</u>)	HCl	36	19.9 (a)			(b)	19.9			
2.	(<u>53b</u>)	HBr	23	14.0	43.89	2.05	1520	14.0	44.22	2.12	1521
3.	(<u>53c</u>)	HBr	40	15.6	56.74	3.98	1280	15.7	56.60	4.16	1358
4.	(<u>53d</u>)	HBr	36	15.7	44.65	3.42	1410	15.7	51.74	3.80	1485

Table 17. Conversion of $[R_4C_4(PdCl_2)_3]_2$ to $[R_4C_4PdX_2]_2$ by treatment with HX.

Footnote to Table 17. (a) First prepared by Blomquist and Maitlis.[120]

(b) too insoluble for a molecular weight determination.

			$[R_4C_4PdCl_2]_2$ Analysis							
			Found				Calculated			
	$[R_4C_4(PdCl_2)_3]_2$	Yield %	Pd	C	H	Mol. wt.	Pd	C	H	Mol. wt.
1.	(53a)	86	19.9 (a)			(b)	19.9			
2.	(53b)	89	15.8	51.15	2.77	1320	15.8	50.08	2.40	1344
3.	(53c)	91	17.9	65.15	4.78	1180	17.7	65.05	4.76	1110
4.	(53d)	84	16.3	58.72	4.37	1310	16.1	58.78	4.31	1260

Table 18. Conversion of $[R_4C_4(PdCl_2)_3]_2$ to $[R_4C_4PdCl_2]_2$ by treatment with N,N-dimethylformamide and concentrated HCl.

Footnote to Table 18. (a) First prepared by Blomquist and Maitlis.[120]

(b) Too insoluble for a molecular weight determination.

Di-μ-chloro-di[π-(endo-4-ethoxy-1,2,3,4 tetrakis{p-substituted phenyl}cyclobutenyl)palladium], $[R_4C_4OEtPdCl]_2$ (56b,c).

The reaction of diphenylacetylene (44a) with sodium tetrachloropalladite in aqueous ethanol to yield di-μ-chloro-di[π-(endo-4-ethoxy-1,2,3,4 tetraphenylcyclobutenyl)palladium] (56a) in 90% yield has already been described by Maitlis and Games.[130]

A solution of 0.78 g (2.0 mmole) of bis(benzonitrile)palladium chloride in 50 ml of methylene chloride was added to a suspension of 1.00 g (4.0 mmole) of p,p'-dichlorodiphenylacetylene (44b) in 100 ml of ethanol. After stirring for 30 min. a clear solution resulted which slowly deposited a copious yellow precipitate. This was filtered off after a further hour of stirring at room temperature. Di-μ-chloro-di[π-(endo-4-ethoxy-1,2,3,4 tetrakis{p-chlorophenyl}cyclobutenyl)palladium] (56b) was recrystallized from methylene chloride-ethanol; yield 0.90 g (0.66 mmole), 66%. Anal. Calcd. for $C_{60}H_{42}Cl_{10}O_2Pd_2$: C, 52.85; H, 3.11; Cl, 25.99; Pd, 15.7; mol. wt., 1362. Found: C, 52.99; H, 3.38; Cl, 26.06; Pd, 15.5%; mol. wt., 1380. This compound (56b) gradually darkened above 280° and melted at 310°. All attempts to prepare (56b) using sodium tetrachloropalladite, as described for diphenylacetylene (44a)[130] led to a product whose colour and composition varied considerably. No experimental procedure was found for purifying this crude product.

A solution of 0.78 g (2.0 mmole) of bis(benzonitrile)palladium chloride in 50 ml of methylene chloride was reacted with a suspension of 0.84 g (4.1 mmole) of p,p-ditolylacetylene (44c) in 100 ml of ethanol as described above. After two hours the yellow precipitate was filtered off and recrystallized to yield 0.79 g (0.66 mmole) of di-μ-chloro-di[π-(endo-4-ethoxy-1,2,3,4-tetrakis{p-tolyl}cyclobutenyl)palladium] (56c); yield 65%. Anal. Calcd. for $C_{68}H_{66}Cl_2O_2Pd_2$: C, 68.11; H, 5.55; Pd, 17.8%; mol. wt., 1199. Found: C, 67.92; H, 5.43; Pd, 17.5%; mol. wt., 1160.

A solution of 0.81 g (2.1 mmole) of bis(benzonitrile)palladium chloride in 50 ml of methylene chloride was reacted with 1.00 g (4.20 mmole) of p,p'-dianisylacetylene (44d) in 100 ml of ethanol as described above. After two hours, 0.85 g (0.57 mmole) of the brick red cyclobutadiene complex, $[(p\text{-}CH_3OC_6H_4C)_4(PdCl_2)_{1.5}]_2$ (53d) was filtered off; yield 54%. This was identified by its infrared spectrum and its conversion to octakis(p-anisyl)-cyclooctatetraene (73d). Anal. Calcd. for $C_{64}H_{56}Cl_6O_8Pd_3$: Pd, 21.5%. Found: Pd, 21.6%.

Sodium chloride 0.24 g (4.0 mmole) and palladium chloride 0.36 g (2.0 mmole) were dissolved in 30 ml of water and poured into a solution of 0.96 g (4.0 mmole) of p,p'-dianisylacetylene (44d) in 100 ml of ethanol at room temperature. No stable compound was formed and within 30 min. a mirror of metallic palladium was deposited.

Reaction of diphenylacetylene (44a) with bis(triethylammonium)tetrachloropalladate in water.

A standard solution of bis(triethylammonium)tetrachloropalladate was made by adding 28.0 ml of a 0.100 N hydrochloric acid solution (2.80 mmole) slowly from a burette to a well cooled mixture of 2.83 g (2.80 mmole) of triethylamine in 50 ml of water. This solution was stirred with 2.48 g (1.40 mmole) of palladium chloride for 12 hours. At this time all the palladium chloride was dissolved and the solution was made up to exactly 100 ml.

Finely ground diphenylacetylene (44a) 0.63 g (0.35 mmole) was added to 25.0 ml (0.35 mmole) of the solution of bis(triethylammonium)tetrachloropalladate, and the mixture vigorously stirred for 24 hours. A copious pale brown precipitate was filtered off and washed with water until the washings were free of chloride ion. This product was dried and washed free of unreacted diphenylacetylene (44a) with petroleum ether, to leave a residue of 1.08 g of a brown complex. Anal. Calcd. for $C_{14}H_{10}PdCl_{1.7}(OH)_{0.3}\cdot H_2O$: C, 45.69; H, 3.37; Cl, 16.38; Pd, 28.91. Found: C, 45.76; H, 4.00; Cl, 16.41; Pd, 29.40. This compound (77a) could not be recrystallized as it rapidly decomposed in all solvents in which it was soluble. For this reason a molecular weight determination was not possible. The ^{1}H N.M.R. spectrum of (77a) showed the presence of phenyl protons only. The infrared spectrum is shown in Appendix 1.

In an attempt to determine the nature of this compound (77a) 0.42 g was suspended in 50 ml of dry methanol and 0.090 g (2.4 mmole) of sodium borohydride was added. An instant precipitate of palladium appeared. After 15 min. this precipitate was filtered off and washed with a few ml of methanol. The palladium residue was then washed with 20 ml of hot benzene, which on cooling deposited 0.07 g (0.01 mmole) of hexaphenylbenzene (52a), identified by its infrared spectrum. The methanolic filtrate was taken to dryness, but the pale yellow residue could not be crystallized. Comparative thin layer chromatography showed that this residue was predominantly diphenylacetylene (44a).

Diphenylacetylene (44a) (0.50 g, 2.8 mmole) after reaction with sodium borohydride (0.22 g, 5.8 mmole) in methanol afforded 0.42 g (2.4 mmole) of unreacted diphenylacetylene (44a); recovery, 84%.

In an additional experiment 0.40 g of this compound (77a) was dissolved in methylene chloride and filtered as rapidly as possible. The residue was washed with methylene chloride and extracted with hot benzene. No hexaphenylbenzene (52a) was isolated from the benzene fraction, which suggested that only a negligible amount of (52a) was present in the complex (77a).

When 0.50 g of (77a) was treated with 0.56 g (1.0 mmole) of tri-n-butylphosphine in refluxing benzene, no octaphenylcyclooctatetraene (73a) was formed. A trace of hexaphenylbenzene (52a) was isolated and thin layer chromatography showed the products to be largely diphenylacetylene (44a) and bis(tri-n-butylphosphine)palladium chloride.

When 0.50 g of (77a) was stirred in 50 ml of pyridine for two hours, 0.30 g (0.90 mmole) of bis(pyridine)-palladium chloride was isolated; yield 62%. Thin layer chromatography of the mother liquor of bis(pyridine)palladium chloride showed only bis(pyridine)palladium chloride and diphenylacetylene (44a).

Ligand transfer reactions.

Preparation of $[R_4C_4NiBr_2]_2$ from $(R_4C_4PdBr_2]_2$.

$$\underset{(59a,b,c,d)}{[R_4C_4PdBr_2]_2} + 2(n\text{-}Bu_3P)NiBr_2 \rightarrow \underset{(54a,b,c,d)}{[R_4C_4NiBr_2]_2} + 2(n\text{-}Bu_3P)PdBr_2$$

A suspension of 1.00 g (0.80 mmole) of tetraphenylcyclobutadienepalladium bromide (59a) in 200 ml of chlorobenzene was refluxed for 5 min. under nitrogen to remove oxygen from the system. Bis(tri-n-butylphosphine)nickel bromide (1.00g, 1.60 mmole)[164] was added and the reaction mixture refluxed for two hours. The colour of the solution changed from red to green quite rapidly. The solution was filtered hot and the volume of the filtrate was reduced to about 50 ml on the rotary evaporator. This solution and any insoluble material in the filter paper were chromatographed on a silica column.

Methylene chloride eluted the yellow very soluble bis(tri-n-butylphosphine)palladium bromide. 1:1 methylene chloride-tetrahydrofuran was used to elute the tetraphenylcyclobutadienenickel bromide (54a) (0.83 g, 0.72 mmole); yield 90%. Decomposition point 317°. The very soluble bis(tri-n-butylphosphine)palladium bromide was isolated in 46% yield from the methylene chloride fraction. Details of related reactions are shown in Table 19.

Preparation of $R_4C_4Fe(CO)_3$ from $[R_4C_4MBr_2]_2$.

$$[R_4C_4MBr_2]_2 + Fe(CO)_5 \longrightarrow R_4C_4Fe(CO)_3$$

(59a,b,c,d) (M=Pd) (4a,b,c,d)

(54a) (M=Ni)

To a suspension of 1.00 g (0.80 mmole) of tetraphenylcyclobutadienepalladium bromide (59a) in 100 ml of benzene, 5 ml of freshly filtered iron pentacarbonyl was added. The reaction mixture was refluxed under nitrogen for 2 hours and then filtered hot. The filtrate was taken to dryness on a rotary evaporator. This residue was dissolved in benzene and chromatographed on an alumina column. The very soluble (4a) eluted first in benzene-petroleum-ether (1:9 V/V). This fraction was taken to dryness and recrystallized from ethanol to yield 0.62 g (1.24 mmole),

	Reactants(b)		Analysis of product $[(R_4C_4)NiBr_2]_2$(a)					
			Found			Calculated		
	$[(R_4C_4)PdBr_2]$	Yield %	C	H	Mol. wt.	C	H	Mol. wt.
1.	(59a)	90	58.27	3.40	(c)	58.49	3.51	
2.	(53a)(d)	82	69.02	4.32	(c)	69.18	4.16	
3.	(59b)	72	47.03	2.34	1390	47.24	2.26	1425
4.	(59c)	73	60.89	4.43	1210	60.90	4.47	1262
5.	(59d)	77	54.87	4.50	1340	54.97	4.26	1390

Table 19. Formation of $[R_4C_4NiBr_2]_2$.

Footnote to Table 19. (a) The infrared spectra of these nickel complex were identical to those of their palladium analogues. (b) The other reactant was $(n\text{-}Bu_3P)_2NiBr_2$ in all cases except 2. (c) Too insoluble for molecular weight determinations. (d) in this case $[Ph_4C_4PdCl_2]_2$ (53a) and $(n\text{-}Bu_3P)_2NiCl_2$[164] were reacted.

78%, of tetraphenylcyclobutadieneiron tricarbonyl (4a). M.p. 232°, Lit. 234°.[85,87]

Details of related reactions are shown in Table 20.

Tetraphenylcyclobutadieneruthenium tricarbonyl (60a).

Tetraphenylcyclobutadienepalladium bromide (59a) (0.41 g, 0.33 mmole) and triruthenium dodecacarbonyl[167] (0.42 g, 0.66 mmole) were refluxed together in 50 ml of chlorobenzene under nitrogen for 12 hours. The reaction mixture was filtered hot, and the yellow filtrate taken to dryness on a rotary evaporator. The solid was extracted with methylene chloride, and the product was precipitated by pouring into petroleum ether. Filtration afforded 0.15 g (0.28 mmole) of yellow tetraphenylcyclobutadieneruthenium tricarbonyl (60a); yield 42%. M.p. 218-219°. Anal. Calcd. for $C_{31}H_{20}O_3Ru$: C, 68.75; H, 3.75; mol. wt., 542. Found: C, 68.77; H, 3.88; mol. wt., 542 (mass spectrometrically). The infrared spectrum of (60a) showed υ_{CO} at 4.87, 5.07 and 5.13 μ[129] and was similar to that of tetraphenylcyclobutadieneiron tricarbonyl (4a). Mass spectrometric analysis showed peaks at m/e 542 for M^+,$[Ph_4C_4Ru(CO)_3]$, $M\text{-}CO^+$, $M\text{-}2CO^+$, $M\text{-}3CO^+$, and $Ph_4C_4^+$ only (based on ^{102}Ru). Thin layer chromatography showed the compound (60a) to be pure.

				Analysis of product $(R_4C_4)Fe(CO)_3$					
	Reactant			Found			Calculated		
	$[(R_4C_4)PdBr_2]_2$	Yield %	M.p.	C	H	Mol. wt.	C	H	Mol. wt.
1.	(59a)	78(a)	232°						
2.	(53a) (M=Ni)	90(a)	230°						
3.	(59b)	56(b)	242°	58.72	2.88	634(c)	58.71	2.58	634
4.	(59c)	52	229-230°	76.23	5.06	552(c)	76.10	5.11	552
5.	(59d)	17	98-99°	68.04	4.59	616(c)	68.19	4.58	616

Table 20. Formation of $R_4C_4Fe(CO)_3$.

Footnote to Table 20. (a) The infrared spectrum agreed with that of an authentic sample.[85,87]

(b) The infrared spectrum agreed with that of an authentic sample.[117]

(c) Molecular weights determined mass spectroscopically.

Tetraphenylcyclobutadienepalladium bromide (59a) by ligand exchange.

Tetraphenylcyclobutadieneiron tricarbonyl (4a) (0.45 g, 0.91 mmole) and 1.80 g (4.70 mmole) of bis-(benzonitrile)palladium chloride were refluxed together in 100 ml of benzene under nitrogen for 12 hours. The reaction mixture was filtered hot and the residue air dried. This residue was washed with about 500 ml of 20% hydrochloric acid to remove iron salts, and air dried. This left 1.45 g (0.83 mmole) of $[R_4C_4(PdCl_2)_3]_2$ (53a). Anal. Calcd. for $C_{56}H_{40}Cl_{12}Pd_6$: Pd, 35.9%. Found: Pd, 36.2%. The infrared spectrum of this crude material was identical to that of pure $[Ph_4C_4PdCl_2]_2$ (53a). To remove the catenated palladium chloride, the complex (53a), n=3, was treated with gaseous hydrogen bromide as previously described to yield 0.35 g (0.28 mmole) of tetraphenylcyclobutadienepalladium bromide (59a), n=1; yield 62%, based on the tetraphenylcyclobutadieneiron tricarbonyl (4a).

Attempted ligand transfer reactions.

A number of unsuccessful ligand transfer reactions were attempted under the same conditions for the reaction between $[R_4C_4PdBr_2]_2$ (59a,b,c,d) and $(n\text{-}Bu_3P)_2NiBr_2$. Tetrakis(p-chlorophenyl)cyclobutadienepalladium bromide (59b) was used sometimes since characterization of the products was easier. The results of these reactions are shown in Table 21.

	Reactants	Products (yield %)
1.	$[(p\text{-}ClC_6H_4C)_4PdBr_2]_2$(a); $2(n\text{-}Bu_3P)_2CoBr_2$[168]	$(p\text{-}ClC_6H_4C)_8$(b) (63%); $CoBr_2$(c)(e); $(n\text{-}Bu_3P)_2PdBr_2$(d)(e)
2.	$[Ph_4C_4PdCl_2]_2$(g); $4\ n\text{-}Bu_3PCuCl$[169](f)	Ph_8C_8(c) (90%); $(n\text{-}Bu_3P)_2PdCl_2$(b) (54%)
3.	$[(p\text{-}ClC_6H_4C)_4PdBr_2]_2$(a); $2(n\text{-}Bu_3P)_2FeBr_2$[179](f)	$[(p\text{-}ClC_6H_4C)_4PdBr_2]_2$(b) (68%)
4.	$[Ph_4C_4PdBr_2]_2$(a); $(CH_3OCH_2CH_2OCH_3)_2NiBr_2$[171]	$[Ph_4C_4PdBr_2]_2$(c) (96%)
5.	$Ph_4C_4PdC_5H_5Br$(a); $(n\text{-}Bu_3P)_2NiBr_2$	$Ph_4C_4PdC_5H_5Br$(b) (68%)

Table 21. Attempted ligand transfer reactions.

Footnote to Table 21. (a) Refluxed in chlorobenzene. (b) Isolated from the filtrate. (c) Initial residue. (d) Detected by thin layer chromatography on the filtrate. (e) Yield not estimated. (f) Prepared in situ before addition of $[R_4C_4PdBr_2]_2$. (g) Refluxed in benzene.

Di-μ-halo-di[π-(exo-4-alkoxy-1,2,3,4-tetrakis{p-substituted phenyl}cyclobutenyl)palladium].

$$[R_4C_4PdX_2]_2 + 2R'OH \longrightarrow [R_4C_4OR'PdX]_2$$

(53a,b,c) X=Cl (57a,b,c) R=Et; (84a) R=Me

(59a) X=Br (83a) R=Et; (85a) R=Me

Tetraphenylcyclobutadienepalladium bromide (59a) (0.50 g, 0.40 mmole) was stirred in 100 ml of absolute ethanol at room temperature for 24 hours. The product (83a) was filtered off and dried under vacuum to yield 0.45 g (0.38 mmole); yield 90%. Thin layer chromatography showed the compound to be pure. Anal. Calcd. for $C_{60}H_{50}Br_2O_2Pd_2$: Pd, 18.1%. Found: Pd, 17.9%. The infrared spectrum of (83a) (X=Br) was identical to that of (57a) (X=Cl) prepared by Blomquist and Maitlis.[120] Details of related reactions are shown in Table 22.

In addition to the successful experiments described in Table 22, attempts were made under similar conditions to prepare the analogues $[(p\text{-}CH_3OC_6H_4C)_4OEtPdCl]_2$ (57d) and $[Ph_4C_4OEtNiBr]_2$ (86a). No reaction occurred when either $[p\text{-}CH_3OC_6H_4C)_4PdCl_2]_2$ (53d) or $[Ph_4C_4NiBr_2]_2$ (54a) were stirred in ethanol for periods of up to 48 hours. (53d) was treated with sodium ethoxide in ethanol, but the complex decomposed to metallic palladium. When (54a) was treated with sodium ethoxide a brown solid was

						Product $[R_4C_4OR'PdX]_2$					
						Analysis					
	Reactants				Found				Calculated		
	$[(R_4C_4)PdX_2]_2$	R'OH	Yield %	C	H	Pd	Mol. wt.	C	H	Pd	Mol. wt.
1.	(59a) (X=Br)	R'=OEt	95[(a)] [(b)]			17.9				18.1	
2.	(53a) (X=Cl)	R'=OMe	95[(a)] [(b)]			20.1				20.0	
3.	(59a)	R'=OMe	93[(a)] [(b)]			18.3				18.6	
4.	(53b)	R'=OEt	53[(c)]	53.16	3.15	15.4	1350	52.82	3.11	15.6	1362
5.	(53c)	R'=OEt	59[(c)]	66.23	5.33	17.6	1150	68.11	5.33	17.8	1199

Table 22. Di-μ-halo-di[π-(exo-4-alkoxy-1,2,3,4-tetrakis{p-substituted phenyl}cyclobutenyl)-palladium].

Footnote to Table 22. (a) Too insoluble for molecular weight determinations. (b) Homogeneous by thin layer chromatography. (c) Recrystallized from methylene chloride-petroleum ether.

immediately formed. This brown complex was shown to be impure (86a) contaminated with sodium bromide and sodium ethoxide. All attempts to purify (86a) led to decomposition. Reaction of tetrakis(p-anisyl)cyclobutadienepalladium bromide (59d) with the stronger nucleophile, ethanthiol, in ethanol afforded a 50% yield of polymeric palladium ethylmercaptide.

Octaphenylcyclooctatetraenes (73a,b,c,d).

$$[R_4C_4PdX_2]_2 + 4n\text{-}Bu_3P \rightarrow R_8C_8 + 2(n\text{-}Bu_3P)_2PdX_2$$

(53b,c,d) (X=Cl) (73a,b,c,d)
(59a) (X=Br)

Tetraphenylcyclobutadienepalladium bromide (59a) (1.50 g, 1.20 mmole) was suspended in 150 ml of benzene under nitrogen and refluxed for a few minutes to remove oxygen from the system. Tri-n-butylphosphine (1.07 g, 5.28 mmole) was added to the hot benzene suspension. The reaction mixture turned dark green almost immediately and then pale yellow. Refluxing was continued for one hour and then the reaction mixture was cooled to room temperature and filtered. This afforded 0.81 g (1.1 mmole) of the very insoluble octaphenylcyclooctatetraene (73a); yield 95%. M.p. 424-426°; Lit. 426-428°.[140]

Details of similar reactions are shown in Table 23.

				Product R_8C_8 Analysis					
	Reactant			Found			Calculated		
	$[R_4C_4(PdX_2)_n]_2$	Yield %	M.p.	C	H	Mol. wt.	C	H	Mol. wt.
1.	(59a) (X=Br)	95(a)	424-426°			712(b)			713
2.	(53b) n=2 (X=Cl)	73(c)	373-375°	68.07	3.29	982(b)	68.03	3.26	989
3.	(53b) n=3	54(c)							
4.	(53c) n=3	40(c)	359-361°	93.33	7.00	825(b)	93.19	6.81	825
5.	(53d) n=3	94(c)	329-331°	80.50	6.00	953(b)	80.68	5.92	953

Table 23. Formation of octaphenylcyclooctatetraenes.

Footnote to Table 23. (a) The infrared spectrum of this compound (73a) was identical to that of an authentic sample. (b) Determined mass spectrometrically. (c) These products were soluble in benzene and were isolated by stripping the filtrate and extracting the soluble bis(tri-n-butylphosphine)palladium chloride with petroleum ether.

The Raman spectrum of octakis(p-chlorophenyl)cyclooctatetraene (73b) in the solid state showed absorptions at 621, 641, 854, 869, 1000, 1036, 1196, 1292, 1341, 1447, 1498, 1542, 1597 and 1642 cm^{-1}.

In a manner similar to that described above tetraphenylcyclobutadienepalladium bromide (59a) (0.30 g, 0.24 mmole) and diphenylacetylene (44a) (0.86 g, 4.8 mmole) in 100 ml of benzene were reacted with 0.20 g (0.98 mmole) of tri-n-butylphosphine. Filtration of the hot solution gave 0.11 g of octaphenylcyclooctatetraene (73a). The filtrate was taken to dryness and the solid residue extracted with ethanol to yield an additional 0.05 g of (73a). Total yield 0.16 g (0.22 mmole); 92%, identified by infrared spectrum and melting point. Comparative thin layer chromatography of both the benzene and ethanol filtrates showed the presence of only diphenylacetylene (44a) and bis(tri-n-butylphosphine)palladium bromide. No trace of hexaphenylbenzene (52a) was observed in the reaction.

Tetraphenylcyclopentadienones R_4C_5O.

$$\underset{(59b,c)}{[R_4C_4PdBr_2]_2} + Ni(CO)_4 \longrightarrow \underset{(78b,c)}{R_4C_5O}$$

Tetrakis(p-chlorophenyl)cyclobutadienepalladium bromide (59b) (0.75 g, 0.46 mmole) was refluxed in benzene under nitrogen to remove oxygen from the system. Nickel tetracarbonyl (4.0 ml) was added to the solution and an immediate darkening of the red solution occurred. After 2 hours of refluxing, the solution was filtered hot and the filtrate taken to near dryness and then chromatographed on alumina. Filtration afforded 0.24 g (0.46 mmole) of red tetrakis(p-chlorophenyl)cyclopentadienone (78b); yield 50%. Anal. Calcd. for $C_{29}H_{146}Cl_4O$: C, 66.70; H, 3.08; mol. wt., 522. Found: C, 66.90; H, 3.24; mol. wt., 522 (mass spectrometrically). No tetrakis(p-chlorophenyl)cyclobutadienenickel bromide (54b) was observed in this reaction.

Similarly, tetrakis(p-tolyl)cyclobutadienepalladium bromide (59c) (0.50 g, 0.37 mmole) was reacted with 4 ml of nickel tetracarbonyl to yield 0.19 g (0.43 mmole) of tetrakis(p-tolyl)cyclopentadienone (78c); yield 58%. Anal. Calcd. for $C_{33}H_{28}O$: C, 89.95; H, 6.41; mol. wt., 441. Found: C, 89.80; H, 6.64; mol. wt., 441 (mass spectrometrically). M.p. 240-241°.

When carbon monoxide was bubbled into a solution of tetrakis(p-chlorophenyl)cyclobutadienepalladium bromide (59b) in methylene chloride at room temperature for 20 min., no reaction occurred and (59b) was recovered in 91% yield.

Cyclopentadienylation reactions.

$$[R_4C_4PdBr_2]_2 + 4C_5H_5Fe(CO)_2Br \longrightarrow R_4C_4PdC_5H_5FeBr_4$$

(59a,b,c,d) (82a,b,c,d)

$$R_4C_4PdC_5H_5FeBr_4 + K_4Fe(CN)_6 \longrightarrow R_4C_4PdC_5H_5Br$$

(82a,b,c,d) (81a,b,c,d)

These compounds (81a,b,c,d) were prepared by the method of Maitlis *et al.*[137] $[R_4C_4PdBr_2]_2$ (59a,b,c,d) was reacted with (π-cyclopentadienyl)iron dicarbonyl bromide in benzene under reflux to yield the paramagnetic complexes $R_4C_4PdC_5H_5FeBr_4$ (82a,b,c,d). These were treated with potassium hexacyanoferrate (II) to yield the diamagnetic compounds $R_4C_4PdC_5H_5Br$ (81a,b,c,d). The results of these reactions are shown in Table 24.

Conversion of $[R_4C_4OEtPdCl]_2$ to $[R_4C_4PdX_2]_2$ by treatment with HX.

$$[R_4C_4OEtPdCl]_2 + HX_{excess} \longrightarrow [R_4C_4PdX_2]_2$$

(59a,b,c) (endo) (53a) (X=Cl)

(57a,b) (59a,b,c) (X=Br)

			Products		
			$R_4C_4PdC_5H_5Br$		
		$R_4C_4PdC_5H_5FeBr_4$		Analysis	
	$[R_4C_4PdBr_2]_2$	Yield %	Yield %(a)	% Pd Found	% Pd Calcd.
1.	(59a)	85	83(b)	17.8	17.5
2.	(59b)	82	72(c)	14.5	14.3
3.	(59c)	95	91(c)(d)	16.0	16.1
4.	(59d)	98	84(c)	14.6	14.7

Table 24. Cyclopentadienylation reactions.

Footnote to Table 24. (a) Based on $[R_4C_4PdBr_2]_2$. (b) Infrared spectrum identical to that of a pure sample.[137] (c) Homogeneous by thin layer chromatography. (d) ^1H N.M.R. spectrum shown in Appendix 2.

	Reactants		Product
	$[R_4C_4OEtPdCl]_2$	HX	$[R_4C_4PdX_2]_2$ (b) Yield %
1.	(56a) (endo)	X=Cl	76[120,143]
2.	(56a)	X=Br	82
3.	(57a) (exo)	X=Cl	ca 100
4.	(56b)	X=Br (a)	82
5.	(57b)	X=Br (a)	62
6.	(56c)	X=Br (a)	61

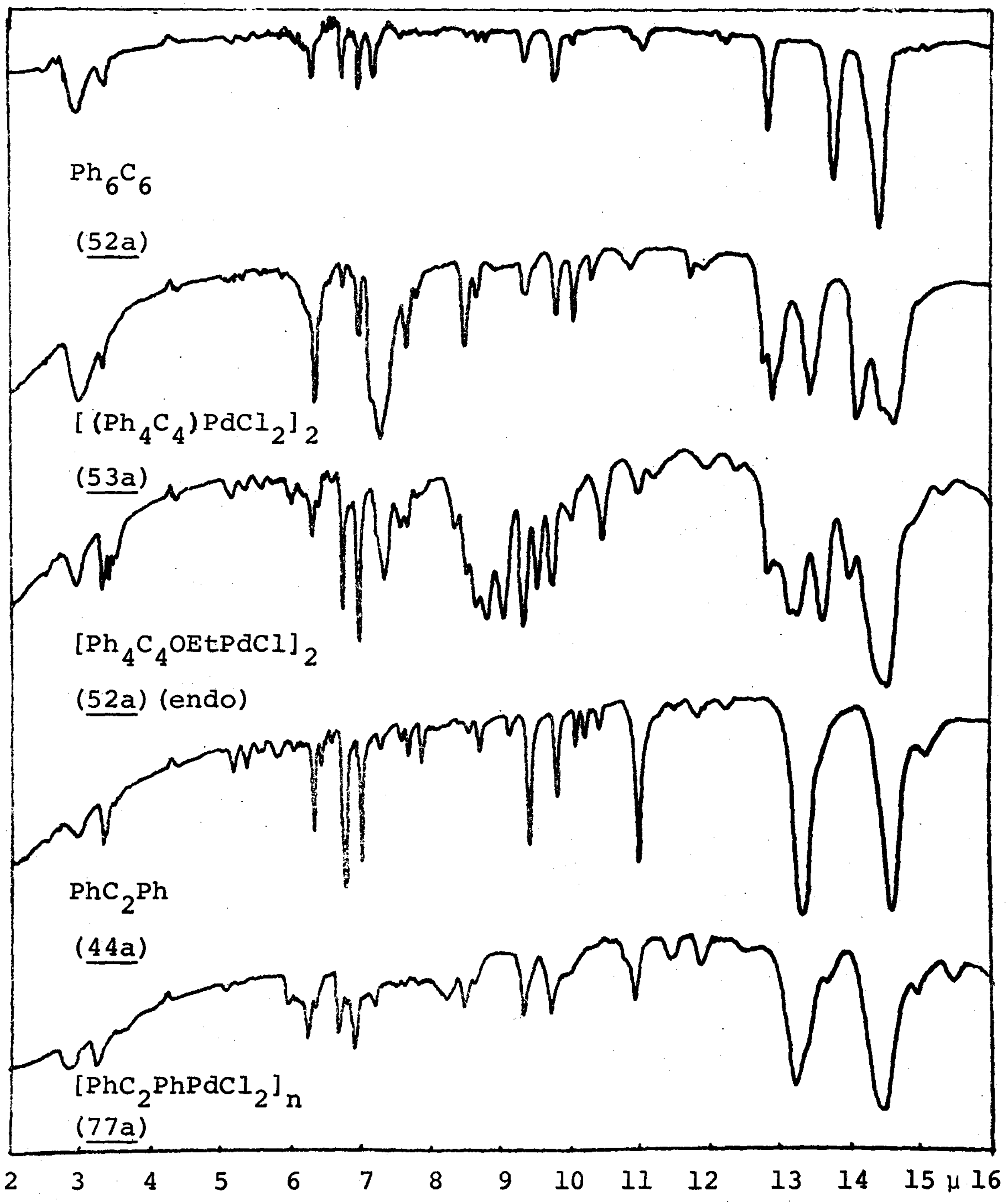
Table 25. Conversion of $[R_4C_4OEtPdCl]_2$ to $[R_4C_4PdX_2]_2$.

Footnote to Table 25. (a) Did not react with gaseous HCl.

(b) Product identified by comparison of infrared spectrum with that of an authentic sample.

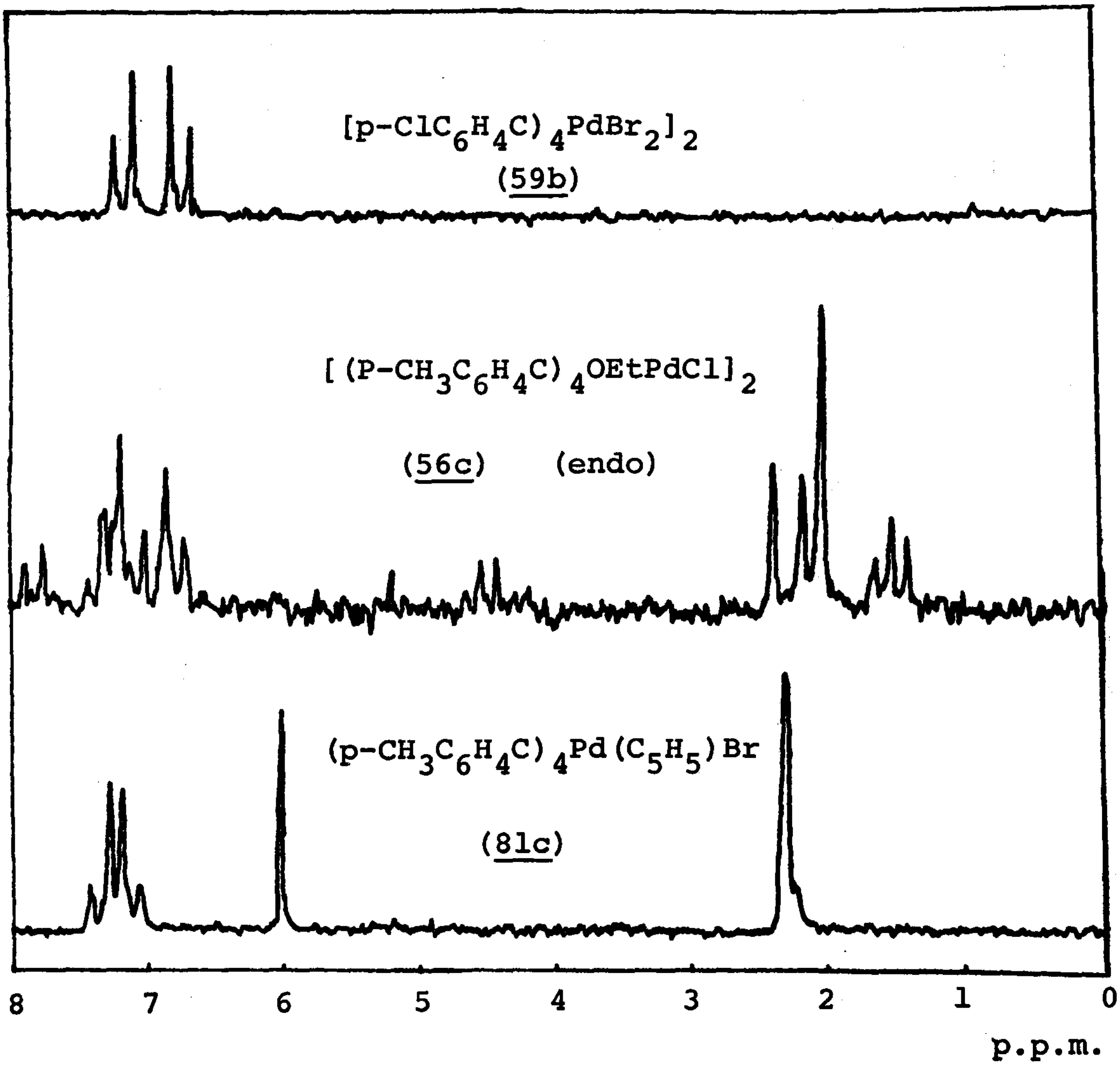
APPENDICES

APPENDIX 1



INFRARED SPECTRA

APPENDIX 2



^{1}H N.M.R. SPECTRA

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