STUDIES ON

CYCLOBUTADIENE-METAL COMPLEXES

To my parents Mr. and Mrs. S. EFRATY of Givataim ISRAEL for their love and dedication, and to my uncle and aunt Mr. and Mrs. M. DOBRIN for their devotion.

STUDIES ON CYCLOBUTADIENE-METAL COMPLEXES

By

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SCOPE AND CONTENTS:

Reaction of tetraphenylcyclobutadienepalladium halides, $[(Ph_4C_4)PdX_2]_2$, with $[(C_5H_5)M(CO)_3]_2$ (M=Mo or W) gave complexes of the type $(Ph_4C_4)(C_5H_5)M(CO)X$ (M=Mo, X=Cl, Br or M=W, X=Br). Conversely, reaction of $[(R_4C_4)PdBr_2]_2$ (R= C_6H_5, p-$CH_3C_6H_4$) with $[(C_5H_5)Fe(CO)_2]_2$ or $(C_5H_5)Fe(CO)_2Br$ led not to the expected transfer of the cyclobutadiene ring group onto iron, but to complexes of the type $[(R_4C_4)M(C_5H_5)]^+ FeBr_4^-$ (M=Pd or Ni). These were converted into the diamagnetic bromides. $[(R_4C_4)M(C_5H_5)]^+ Br^-$ which, on treatment with sodium methoxide, gave the cyclobutenyl complexes $(R_4C_4OMe)M(C_5H_5)$ of palladium and nickel.

The complexes $(R_4C_4)Co(CO)_2X$ (R=C_6H_5, p-$CH_3C_6H_4$, X=halogen) have been prepared by ligand-transfer reactions from $[(R_4C_4)PdX_2]_2$. The reactions of $(R_4C_4)Co(CO)_2X$ show considerable similarity to those of $(C_5H_5)Fe(CO)_2X$, and evidence for a very strong metal-ring bond in the cobalt complex is presented. Reaction of $(R_4C_4)Co(CO)_2Br$ with C_6F_5Li gave the very stable $(R_4C_4Co(CO)_2C_6F_5$. With aromatic hydrocarbons in the presence of $AlCl_3$, (R_4C_4)-$Co(CO)_2Br$ gave the stable $[(R_4C_4)Co(\pi\text{-Arene})]^+$; cycloheptatriene also reacted with $(R_4C_4)Co(CO)_2Br$ in the absence of a catalyst to give $[(R_4C_4)Co(C_7H_8)]^+$. Nucleophilic attack occurred readily at the C_7H_8 ring in $[(R_4C_4)Co(C_7H_8)]^+$ and less readily at the benzene ring in $[(R_4C_4)Co$

$(C_6H_6)]^+$ to give (R_4C_4)Co(cycloheptadienyl) and the (R_4C_4)Co(cyclohexadienyl)complexes, respectively.

The order of susceptibility of π-complexed ligands in metal d^8 complexes towards nucleophilic attack, cycloheptatriene $>$ benzene $>$ (R_4C_4) $>$ cyclopentadienyl, is proposed. A novel method for effecting hydride abstraction is reported. Aniline in $[(Ph_4C_4)Co(\pi\text{-Aniline})]^+$ is less basic than aniline itself by approximately 1.5 pK units.

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INTRODUCTION

INTRODUCTION

The INTRODUCTION of this thesis is divided into two major sections. The first is a brief general survey of organometallic chemistry, and includes a discussion of the bonding, structures, preparations and reactions of σ- and π-bonded complexes. The second section deals with the chemistry of cyclobutadiene metal complexes, and includes a comparison to the chemistry of other π-bonded complexes.

I Compounds with Metal-Carbon σ-Bonds

A. Metal-carbon σ-bonds with little or no π-back bonding.

Main Group Elements:

The main group metals are known to form compounds of type R_nM or $R_{n-y}MX_y$, where M is a main group metal, R an organic moiety, and X is halide, hydroxide, alkoxide, etc. The reactivity of these compounds depends on two major factors. These are the nature of the metal, and the nature of the organic moiety.

The nature of the metal is the most important factor in determining the gross behaviour of compounds of the type R_nM. The relative reactivities of these organometallic compounds within a given group or horizontal period of the periodic table have been estimated[1] by their rate of addition to unsaturated compounds (e.g. benzonitrile). A reinterpretation of these results[2a] suggests that the electronegativity of the metal is the main factor determining the relative reactivity of an organometallic compound; that is, the lower the electronegativity, the higher the reactivity. In keeping with this principle, the relative reactivities of alkali metal compounds increase in the order Li $<$ Na $<$ K $<$ Rb $<$ Cs, and those of the alkaline earth elements in the order Be $<$ Mg $<$ Ca $<$ Sr $<$ Ba. Further, the B-subgroup metals such as Cu, Ag, Au, Zn, Cd and Hg form less reactive organometallic derivatives than the A-subgroup metals. Since the electropositive character of the elements decreases from left to right in any given period, the reactivity of organometallic derivatives decreases in the same order.

The electronegativity of the metal modifies the polarity of the metal-carbon bond. Hence, the less electronegative the metal, the greater is the polarity of the bond. This results in enhanced reactivity towards polar reagents. For instance, when alkyls of the alkali or alkaline earth metals are added to water, a very violent reaction occurs. The reaction of methylmagnesium bromide or dimethylzinc is only slightly less violent. Conversely, when the metal-carbon bond is less polar, as in tetramethylsilane or dimethylmercury, the reaction is extremely slow and must be accelerated by an increase in temperature or the use of catalysts.

For a given metal, the reactivity of R_nM is also determined by the nature of the organic moiety, R, and depends on steric and electronic factors[3]. If R_nM is associated and if higher reactivity is connected with lower degrees of association, then a bulky R group, which favours a lower degree of association, will facilitate reaction. Moreover, repulsion between the metal atom and the bulky organic group may weaken the metal-carbon bond and further aid reaction. Conversely, when R is a bulky group, a decreased reactivity of R_nM can be ascribed to protection of the reaction site by the large R groups. The electronic nature of R can also modify the polarity of the metal-carbon bond. Since the metal, M, is usually more electropositive than the organic group, R, a more powerful electron-withdrawing group on the carbon atom attached to the metal, will enhance the polarity of the metal-carbon bond and thus increase its chemical reactivity.

Groups such as phenyl, vinyl or ethynyl will stabilize the metal-carbon bond if overlap between filled π-orbitals on the organic group and empty orbitals on the metal can occur. Trivinylborane, for example, has a low tendency to complex with ammonia and does not react with oxygen.[3]

Thermal-Stability: There is no direct correlation between the thermal-stability of organometallic compounds and their chemical reactivities.[2b] It is observed that in any one group of the Periodic Table, the compounds of the heavier elements are less thermally stable than those of the lighter elements. For example, the alkyls of lead readily decompose at temperatures at which the alkyls of silicon are quite stable. Also, the thermal-stability is higher in the compounds of the more electronegative elements in a given period. The thermal-stabilities of the compounds of a particular element depend largely on the nature of the attached organic groups and in a number of cases, may be greatly enhanced by the substitution of more electronegative groups (such as halogen) for some of the organic groups.

Transition-Metal Elements:

The electronegativities of transition-metals are of about the same magnitude as those of Group II_B elements and, as a result, their compounds are rather chemically similar. By contrast with the main group metals, however, transition-metal-alkyl and -aryl compounds are much less thermally stable; in fact, only very few compounds of the type R_nMt (Mt=transition-metal) such as R_4Ti,[4a] R_3Au[4b] etc., have been made and characterized.

As in the case of main group metals, the thermal-stabilities of the compounds of a particular transition-metal can be greatly enhanced by the substitution of one or more electronegative groups (such as halogen) for one or more organic groups. For example, tetramethyltitanium decomposes at room temperature while dimethyltitanium dichloride and methyltitanium trichloride are considerably more stable.[4a] It appears that the thermal stability of σ-alkyl and -aryl transition-metal compounds increases on descending a group (e.g., for $(Et^{*}_{3}P)_{2}MtR_{2}$, the stability order is Pt < Pd < Ni [4c,6]).

The low thermal-stability of transition-metal-carbon bonds is believed[6,7,8a] to be due to the small energy difference (ΔE) between the highest energy filled molecular orbital and the lowest energy vacant molecular orbital in the complex (Figure 1.)[6,7]. When ΔE is small and of the same order as thermal energies, promotion of an electron from the highest filled to the lowest vacant orbital will occur readily. Two extreme cases may be considered: (i) if the d orbitals are filled, promotion of an electron from the highest energy non-bonding d orbital into a vacant Mt-C antibonding sigma orbital (σ^*) of lowest energy can easily occur if ΔE is small; (ii) if the d orbitals are empty, promotion of an electron from a filled Mt - C σ-orbital to the lowest vacant d orbital can occur.

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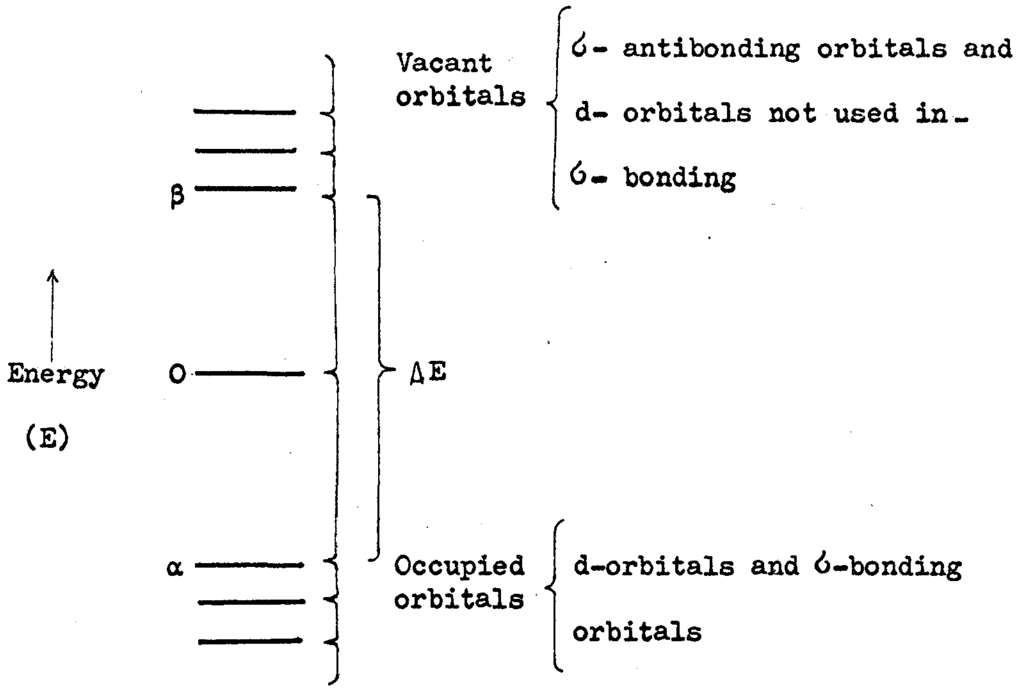
*Et = C_2H_5



α = highest occupied electronic level

β = lowest vacant electronic level

ΔE= must exceed some critical value to confer stability

Figure 1. Suggested condition for stability of organo-transition-metal complexes[6,7].

Either process will weaken the Mt - C σ-bond and give rise to $R\cdot$(or R^-) which will rapidly react further.

On heating, compounds containing Mt - C bonds decompose to give R-R, R-H or an olefin. In all these cases, the products can be thought of as arising from the formation of $R\cdot$ radicals which can couple to yield R-R, or abstract $H\cdot$ to give RH, or lose $H\cdot$ to give an olefin. For example:

$$C_2H_5TiCl_3 \xrightarrow[\text{24 hours}]{\text{room temperature}} C_2H_6 + C_4H_{10} + TiCl_3$$ [4a]

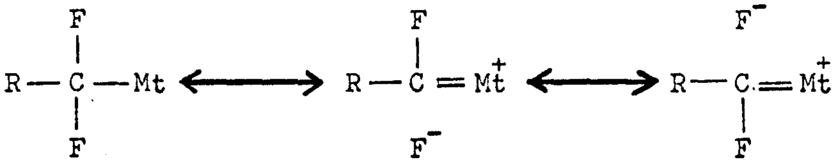
Metal-carbon σ-bonds can be stabilized by the simultaneous presence on the metal of strong field σ-bonded ligands such as CN^-, Ph_3P, CO or π-complexed ligands such as cyclopentadienyl. These ligands all act as π-acceptors. Chatt and Shaw[6,7] suggested that the effect of π-acceptor ligands in these complexes is to increase the energy difference (ΔE) and thus to supress thermal-decomposition.

The stability of the R - Mt bond is dependent to some extent on the electron configuration of the metal. For example, the following configurations enhance stability:

octahedral d^0 $[L_2R_4Ti,\ L_2 = \text{bipyridyl}]$; high spin
octahedral d^3 $[RCr(H_2O)_5^{+2}]$; low spin d^4 $[(C_5H_5)W(CO)_3R]$;
octahedral d^6 [$RM(CO)_5$, M = Mn, Re; $(C_5H_5)Fe(CO)_2R$;
$RCo(CN)_5^{-3}$]; square planar d^8 [L_2MR_2, M = Ni, Pd, Pt
L = trialkyl- or triarylphosphine; $(RAuX_2)_2$] ; and d^{10}
[RCu ; $(Ph_3P)AuR$] . By contrast, however, R_2M and RMX where M = Zn^{II} Cd^{II} and Hg^{II}, i.e., non-transition-metals, are more thermally stable compared to the above d^{10} transition-metal compounds. The higher

thermal-stability of the octahedral high spin d^3 and low spin d^6 metal complexes is believed to be due to the very stable electron configurations t_{2g}^{3} and t_{2g}^{6} corresponding to the half-filled and completely-filled t_{2g} orbitals, respectively. Presumably, ΔE is quite large here.

The most stable σ-bonded transition-metal complexes are those containing perfluoro-alkyl or -aryl groups. This is thought to be due to the importance of such resonance contributions as



$$R-\overset{F}{\underset{F}{C}}-Mt \longleftrightarrow R-\overset{F}{\underset{F^-}{C}}=\overset{+}{Mt} \longleftrightarrow R-\overset{F^-}{\underset{F}{C}}=\overset{+}{Mt}$$

Transition-metal complexes, in which aryl groups are σ-bonded to a metal, are usually more stable than their alkyl analogues. This enhanced stability may be due either to the higher electronegativity of the aryl groups leading to a larger ionic resonance in the Mt - C σ-bond, or to π-bonding between filled metal d orbitals and vacant π-antibonding orbitals (π*) of the aromatic rings.[9]

<u>Synthesis of σ-bonded transition-metal complexes:</u>

There are two major methods for the synthesis of σ-bonded transition-metal complexes. These are the reaction of a halo-derivative of the transition-metal with an organometallic compound, and the reaction of an anionic transition-metal complex with an organic halide e.g.:

$$\text{trans-}(Et_3P)_2PdCl_2 + C_6F_5Li \longrightarrow \underset{(\underline{1})}{\text{trans-}(Et_3P)_2Pd\cdot Cl\cdot C_6F_5} \quad ^{10}$$

$$Na^+\ Mn(CO)_5^- + CH_3I \longrightarrow CH_3Mn(CO)_5 \quad ^{11}$$

Other methods include the insertion of unsaturated organic groups into metal-hydride or metal-alkyl bond, and the addition of alkyl halides to some complexes.

e.g.:

$HCo(CO)_4 + CH_2 = CH_2 \longrightarrow CH_3CH_2Co(CO)_4$ [12]

$CH_3Mn(CO)_5 + CF_2 = CF_2 \longrightarrow CH_3CF_2CF_2Mn(CO)_5$ [13]

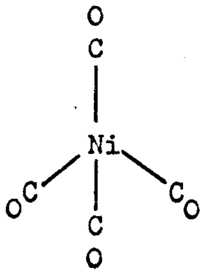
$(\pi\text{-}C_5H_5)Co(CO)_2 + CF_3I \longrightarrow (\pi\text{-}C_5H_5)Co(\sigma\text{-}CF_3)(CO)I$ [14]

B. Metal-carbon σ-bonds stabilized by π-back bonding.

Various neutral molecules such as carbon monoxide, isocyanides, substituted phosphines and nitric oxide form complexes with transition-metals in low oxidation states, e.g.: $Cr(CO)_6$, $(Ph_3P)_4Pt$, $[Mn(CNR)_6]^+$, $(C_5H_5)NiNO$. All of these ligands possess a lone pair of electrons as well as vacant orbitals and are capable of forming multiple bonds to transition-metals. The stoichiometries of many of these complexes can be predicted by the use of the inert-gas formalism. This requires that the number of electrons of the metal, plus the number of lone-pair electrons contributed by the ligands, equal the number of electrons of the next inert-gas. Among the simplest known complexes of this type are the metal carbonyls in which terminal or bridging carbonyl groups are bonded to transition-metal atoms through carbon.

Structural determination have been made on many of these compounds. Some examples are: nickel tetracarbonyl (2), which has a regular tetrahedral[16,17] structure; chromium hexacarbonyl (3),[17,18] with a regular octahedral structure and dicobalt octacarbonyl (4), whose structure is shown below.[19]

The average C-O distance in terminal carbonyl groups is 1.15A compared to 1.13A for carbon monoxide itself.[15] This suggests that the nature of the C-O bond is similar in each. Bridging carbonyl groups, as found for example in (4), have a C-O distance of 1.21A with a bond order of about two and are analogous to a ketonic carbonyl group.



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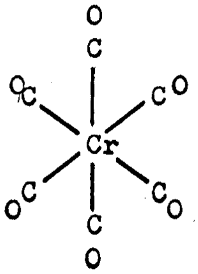

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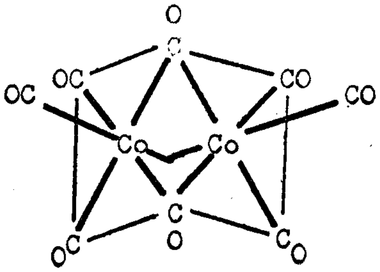

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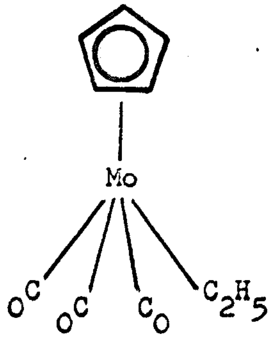


(5)

The transition-metal-carbon bonds, in metal carbonyl, are somewhat shorter than might be estimated for metal-carbon bonds, (although only a few direct comparisons are yet possible). For example, in (σ-ethyl) tricarbonyl (π-cyclopentadienyl) molybdenum (5)[20], the Mo-C(ethyl) bond length is 2.38 ± 0.03A, whereas the Mo-C(carbonyl) bond length is 1.97 ± 0.03A. After correction for the change in hybridisation $\left[r_{c(sp)}\right.$ is almost 0.07A smaller than $\left. r_{c(sp^3)} \right]$, the metal-carbon bond in the carbonyl is still much shorter than in the ethyl. This would imply a bond order greater than unity for the Mo-C(carbonyl).

Carbon monoxide is an exceedingly weak Lewis base and does not form complexes with Lewis acids such as aluminium or boron compounds (the only exception known is the labile $H_3\bar{B} - \overset{+}{C}O$ [21]). Thus donation of the lone-pair electrons on carbon would not be expected to give more than a weak σ-bond with transition-metals. To explain the stability of the metal carbonyls, π-back bonding is invoked to supplement the σ-bond arising from the lone-pair donation.

A simple molecular-orbital description of the bonding in chromium hexacarbonyl (3)[5,22,15] may be taken as an example (Figure 2.).

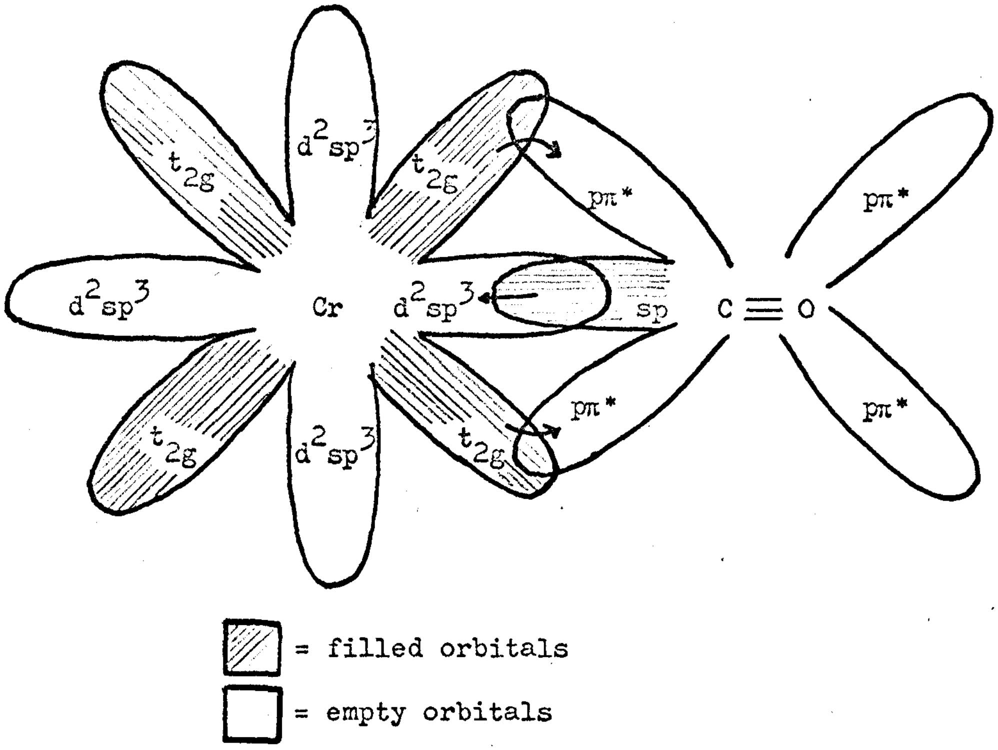


Figure 2. A pictorial representation of the bonding in chromium hexacarbonyl.

The bonding involves a dative overlap of the filled hybrid sp carbon orbital with an empty metal d^2sp^3 hybrid orbital, and a simultaneous dative overlap of a filled t_{2g} (or hybrid dπ) metal orbital with an empty antibonding $p\pi^*$ orbital of the carbon monoxide. This is an example of a synergic mechanism and results in strengthening of the metal-carbon bond, since the drift of metal electrons into the CO $p\pi^*$ orbital tends to make the carbon more negative and hence increase its donor ability.

In valence-bond formalism, the metal carbonyl bond can be represented by

$$\overset{-}{\mathrm{M}}\mathrm{t} - \overset{+}{\mathrm{C}}\equiv \mathrm{O}: \longleftrightarrow \mathrm{Mt} = \mathrm{C} = \ddot{\mathrm{O}}:$$

From either the molecular-orbital or the valence-bond viewpoint, back-bonding lowers the C–O bond order. This should cause the C–O stretching frequency to be lower in metal carbonyls than in free carbon monoxide. Furthermore, an increase in the negative charge on the central metal atom results in greater metal-carbon back bonding and hence a still lower C-O bond order and lower ν CO. On the other hand a greater positive charge on the metal results in less metal-carbon back bonding, increasing both the C-O bond order and νCO. This process can be readily observed by comparing νCO for two isoelectronic and isostructural series of metal carbonyls (Table 1.[22]). [Infra-red absorption bands in the region 1750-1875 cm^{-1} are generally diagnostic of the presence of bridging carbonyl groups, e.g., 1859, 1867 cm^{-1} in $Co_2(CO)_8$[23], provided that no other effects are operating.]

TETRAHEDRAL SERIES		OCTAHEDRAL SERIES	
compound	νCO (cm^{-1})	compound	νCO (cm^{-1})
$Fe(CO)_4^{=}$	1786	$V(CO)_6^{-}$	1859
$Co(CO)_4^{-}$	1886	$Cr(CO)_6$	1981
$Ni(CO)_4$	2057	$Mn(CO)_6^{+}$	2090

Table 1. Carbonyl stretching bands in isoelectronic and isostructural series of metal carbonyls.[22]

A feature of strong field ligands such as carbon monoxide, nitric oxide, tertiary organic phosphines, etc., is their particular effectiveness in stabilizing σ-alkyl, or -aryl derivatives of various transition-metals. Chatt and Shaw[6,7] suggested that these ligands increase the energy difference, ΔE (Figure 1.), by lowering the energy levels of the occupied non-σ-bonding d orbitals through combination with π-type orbitals of low energy in the ligands.

Apart from the ligands mentioned above, π-ligands such as cyclopentadienyl (see section II) are also capable of stabilizing aryl and alkyl transition-metal σ-bonds, presumably in a similar manner. σ-Bonded ligands such as aryl, ethynyl, etc., which possess vacant π* orbitals of appropriate symmetry and energy to combine with filled metal d orbitals, will also be similarly stabilized.

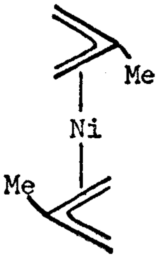
II. π-COMPLEXES

A. Bonding and structure of π-complexes.

Unsaturated organic molecules such as olefins, acetylenes and polyolefins are able to act as ligands to transition-metals in low oxidation states. Complexes of this type which contain up to eight carbon atoms bonded to a transition-metal have been prepared. Some examples are given in Table 2. Various types of π-complexes with different ligands are known. These include "sandwich" complexes such as bis(π-methallyl)nickel (6), ferrocene (7), dibenzenechromium (8); "half-sandwich" complexes such as benzenechromium tricarbonyl (9) and other types such as the cyclopentadienyliron dicarbonyl halides (10) and dicyclopentadienyltitanium dichloride (11).

NUMBER OF π-ELECTRONS UTILIZED	NUMBER OF CARBON ATOMS ENGAGED IN BONDING	TYPE OF COMPLEX	EXAMPLE
2	2	olefin	$C_2H_4PtCl_3{}^-K^+$ Zeise's Salt
2	2	acetylene	$(Ph_3P)_2Pd(C_4F_6)$ bis(triphenylphosphine)(hexafluoro-2-butyne)–palladium (0)
3	3	allyl	$[(C_3H_5)PdCl]_2$ π-allylpalladium chloride dimer
4	4	cyclobutadiene	$(Ph_4C_4)\ Fe(CO)_3$ (π-tetraphenylcyclobutadiene)–iron tricarbonyl.
5	5	cyclopentadienyl	$(\pi\text{-}C_5H_5)_2Fe$ ferrocene
6	6	benzene	$(\pi\text{-}C_6H_6)_2\ Cr$ dibenzenechromium
7	7	cycloheptatrienyl	$(\pi\text{-}C_7H_7)V\text{-}(\pi\text{-}C_5H_5)$ (π-cycloheptatrienyl)–(π-cyclopentadienyl)–vanadium.
8	8	cyclooctatetraene	$(C_8H_8)_3Ti_2$ Tri(cyclooctatetraene)dititanium

Table 2. Examples of some π-complexes.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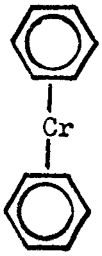
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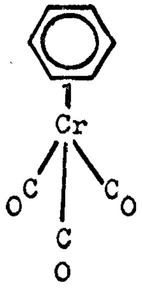
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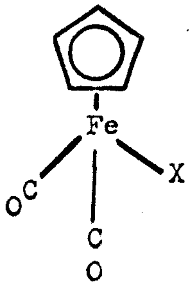
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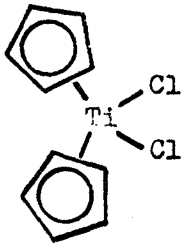

(11)

X-Ray structure determinations on (6)[24,25] (7)[26,27,28,29] (8)[30] and (9)[31] show that the carbon atoms which take part in the bonding to the metal are all approximately equidistant from the metal and usually lie in a plane.

The best known "sandwich" compound is ferrocene (7), which was discovered in 1951 by Pauson[32] and Miller[33] and their co-workers. The "sandwich" structure suggested by Wilkinson, Rosenblum, Whiting and Woodward[34] for this compound was confirmed by X-ray analysis. This analysis reveals that all C-C distances are equivalent (1.40 ± 0.02A) and all the Fe - C distances are 2.04 ± 0.01A. Furthermore, the cyclopentadienyl rings in the solid were shown to have a "staggered" conformation.[28,29] A very similar structure was also found for (8), which has the "eclipsed" conformation.[30] Many "half-sandwich" compounds, such as (9), are also known and X-ray analyses have confirmed the structures of some of them.

The bonding in these so-called "π-complexes" is believed to involve, again, a synergic mechanism. The structure proposed for platinum-olefin complexes by Chatt and Duncanson[35] (Figure 3a) provides a simple illustration. The donor bond (of σ-symmetry), known as a μ-bond, is formed by the overlap of a filled bonding $\pi_z 2p$ molecular orbital of the olefin with a vacant $5d6s6p^2$ hybrid orbital of the platinum atom. The π-type bond is formed by overlap of the vacant antibonding $\pi_z^* 2p$ molecular orbital of the olefin with a filled 5d6p hybrid orbital of the platinum atom. These Pt(II) complexes are square planar and the olefin ligand is perpendicular to the plane containing the platinum atom. The spatial arrangement of atoms in Zeise's Salt $(C_2H_4)PtCl_3^-$ [36,37] as well as in $(C_2H_4)PtCl_2 \cdot NH(CH_3)_2$ [38] (Figure 3b.), has been confirmed by X-ray studies, and similar arrangements have been found for other Pt(II)- and Pd(II)- olefin complexes.[39]

The bonding in the other π-complexes is qualitatively similar to that in these olefin metal complexes, the main differences being in the particular orbitals used on both the metal and the ligand.

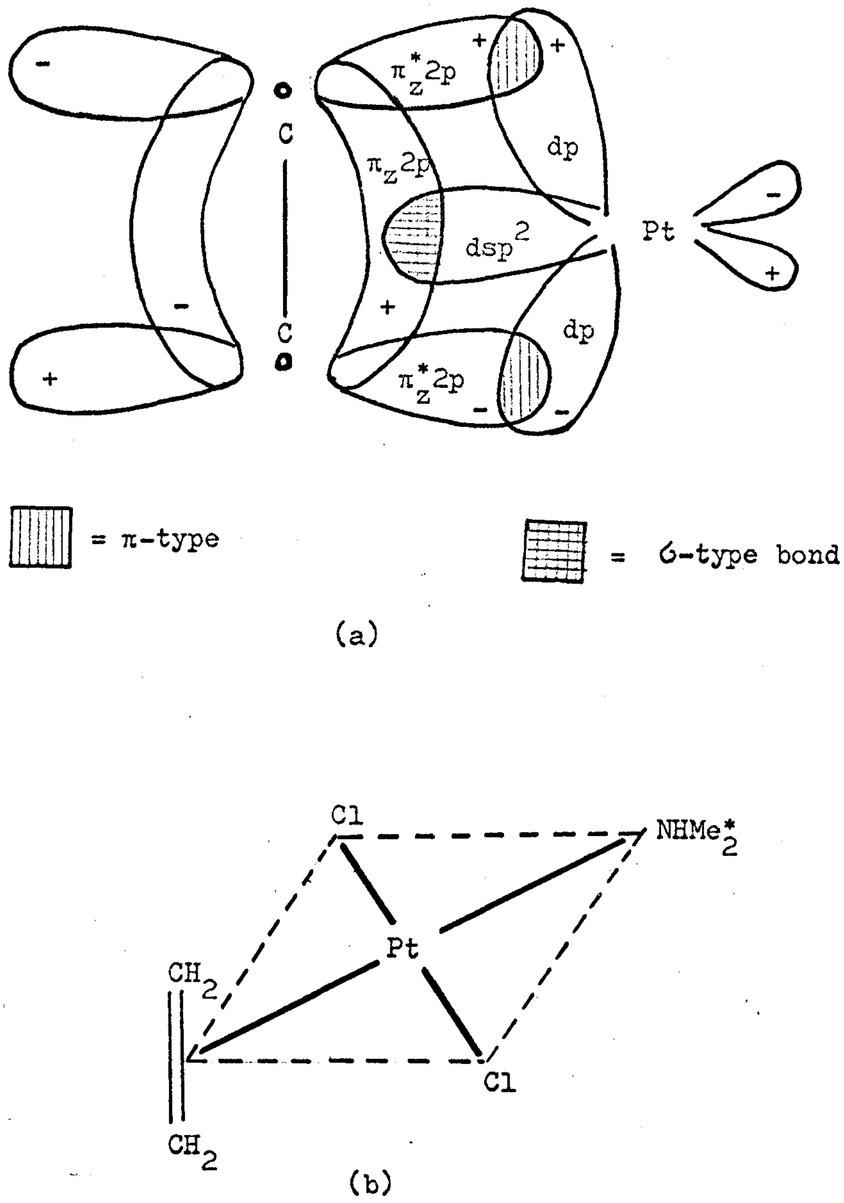


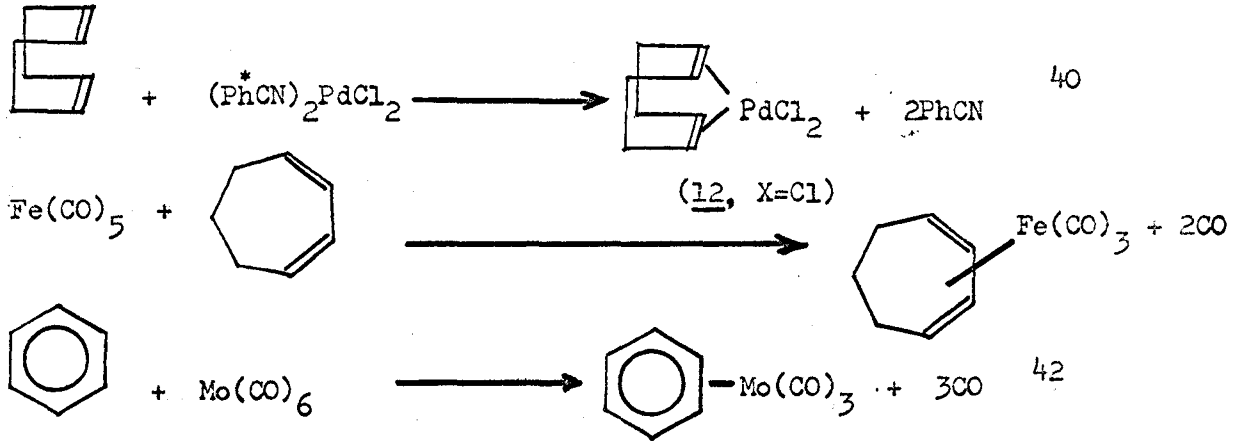
Figure 3. (a) A pictorial representation of the bonding in platinum-olefin complexes.

(b) The spatial arrangement of atoms in $(C_2H_4)PtCl_2 \cdot NHMe_2$

*Me=CH_3

B. Syntheses of π-complexes

Methods for the synthesis of π-complexes may be classified into two broad categories representing the direct and the indirect methods. The direct method: This method consists of a direct reaction between an unsaturated hydrocarbon and an appropriate complex of the metal with displacement of one or more ligands. Obviously, only hydrocarbons which are stable when uncomplexed can be used for this reaction, e.g.:



40

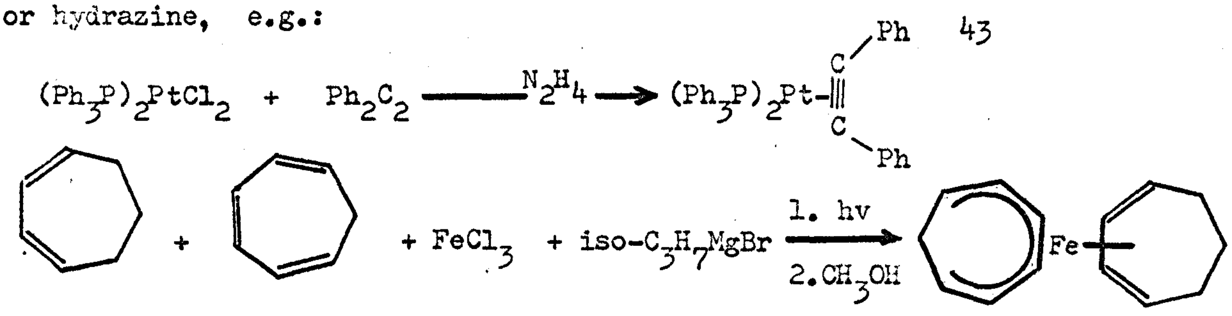
(12, X=Cl)

41

42

(14)

Certain modifications are sometimes necessary. For example, the metal may require reduction to a lower oxidation state before it will complex with the organic ligand. Typical reducing agents are Grignard reagents or hydrazine, e.g.:



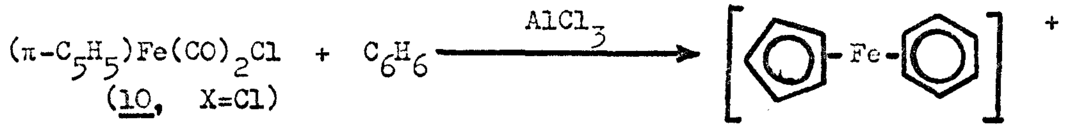
$$(Ph_3P)_2PtCl_2 + Ph_2C_2 \xrightarrow{N_2H_4} (Ph_3P)_2Pt\text{-}\left\|\begin{matrix} C\text{-}Ph \\ | \\ C\text{-}Ph \end{matrix}\right.$$

43

44

*$Ph=C_6H_5$

Some of these reactions are also catalyzed by $AlCl_3$ or by light, e.g.:



(15)

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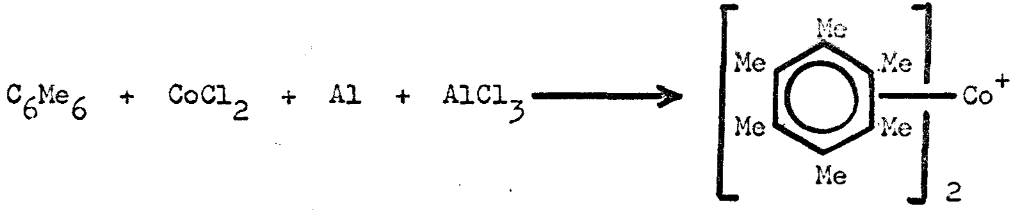

(16)

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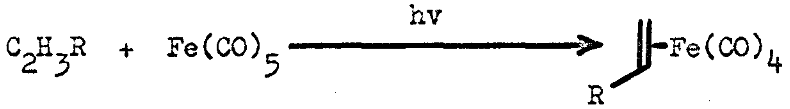

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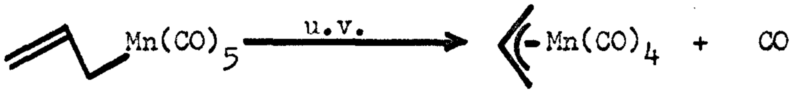
The indirect method: Indirect methods of synthesis are necessary when the free organic ligands are not stable. Some examples of useful indirect methods are:

(i) Conversion of σ-bonded allyls to π-bonded allyls, e.g. ,



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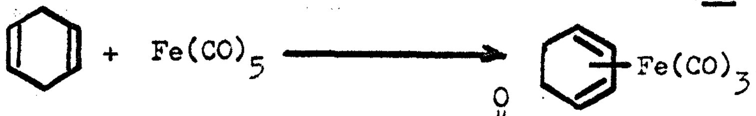
(ii) Reactions in which the organic derivative of the ligand has undergone some alteration. This can take the form of loss or gain of hydrogen, rearrangement of the double bonds, polymerization or loss of halogen, e.g. :

(17)

48



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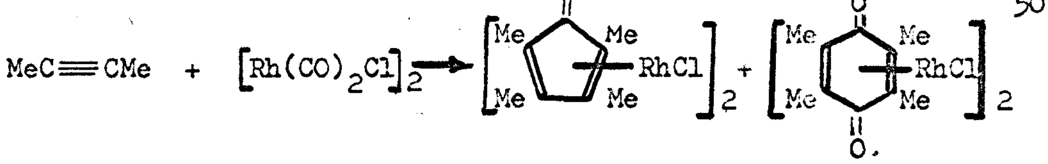
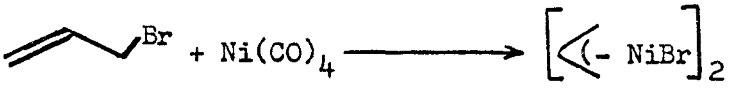


50,51



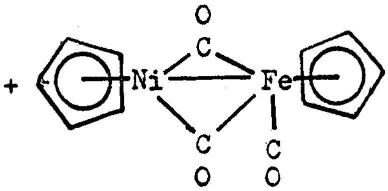
52

(iii) Ligand-exchange and ligand-transfer reactions, e.g.:

$$(\pi\text{-}C_5H_5)_2Ni + Fe(CO)_5 \longrightarrow \left[(\pi\text{-}C_5H_5)Ni(CO)\right]_2$$

$$+ \left[(\pi\text{-}C_5H_5)Fe(CO)_2\right]_2$$

(17)



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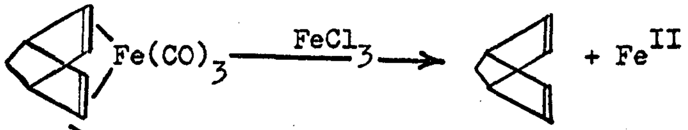
C. Reactions of π-complexes.

Reactions involving π-complexes can be classified into three major categories:

(a) Reactions in which the ligand is displaced unchanged from the complex, or can be recovered in a modified form, e.g.,



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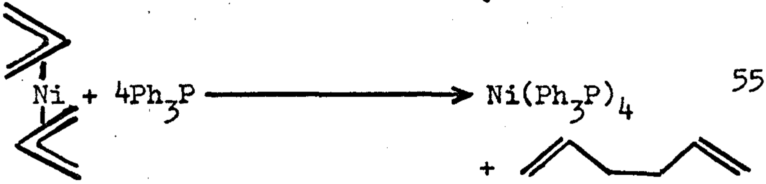
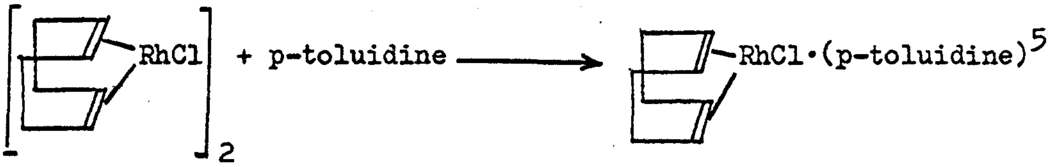


55,56

(b) Reactions in which the π-bonded ligand is unaffected by the reaction. Many reactions of this type are known, e.g.:



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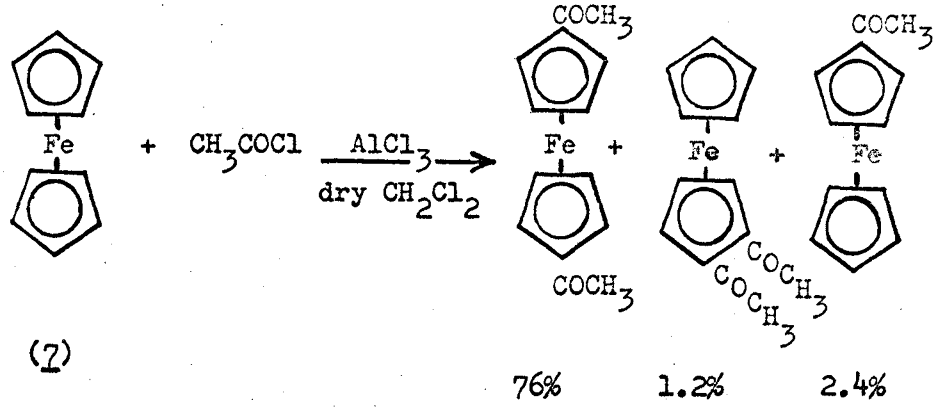
(c) Reactions in which the π-ligand does take part, and the product either retains the character of the starting complex or is transformed into a related π- or σ-metal complex. Reactions of this type can be divided into two types: substitution and addition reactions.

SUBSTITUTION REACTIONS

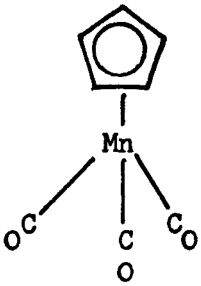
(i) Electrophilic Substitution: The most important substitution reactions yet investigated are the electrophilic substitution reactions. In many cases the π-organometallic complex reacts similarly to an aromatic system. For example, ferrocene (7) will undergo electrophilic substitution reactions even more readily than a highly activated aromatic compound such as anisole. Electrophilic substitution reactions of ferrocene (7) include Friedel-Crafts alkylation and acylation, sulphonation, formylation, mercuration and metalation.[58,59] A typical example is the Friedel-Craft acetylation reaction of ferrocene (7), from which mono-and di-acetylferrocenes are isolated, e.g.:



(7)

[60]

Cyclopentadienylmanganese tricarbonyl (18), ruthenocene, osmocene and benzenechromium tricarbonyl (19) undergo similar electrophilic substitution, although they all are less reactive than ferrocene itself.[58a,59] The reason for the lower reactivity of benzenechromium tricarbonyl (19) towards electrophilic reagents is that the chromium-tricarbonyl group is an electron-withdrawing group which deactivates the benzene ligands towards this reaction. This is also shown by comparing the pKa of benzoic acid (5.68) with that of (π-benzoic acid)-chromium tricarbonyl (20)(4.77[42,61]). The electron-withdrawing power of the tricarbonyl-chromium(0) group is similar to that of the nitro group in the para-position (pKa for p-nitrobenzoic acid 4.48[62a]). Conversely, the pK_b of aniline is increased from 11.70 to 13.31 on π-bonding to chromium-tricarbonyl (21).[42]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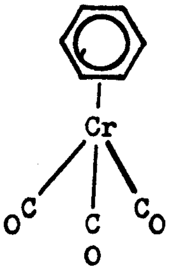
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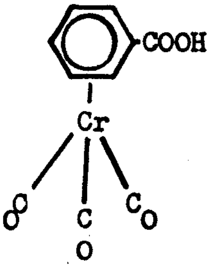
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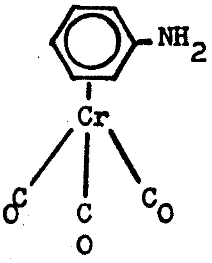
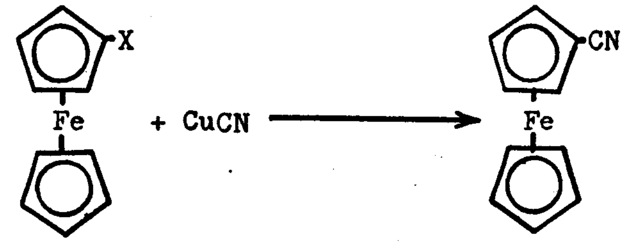
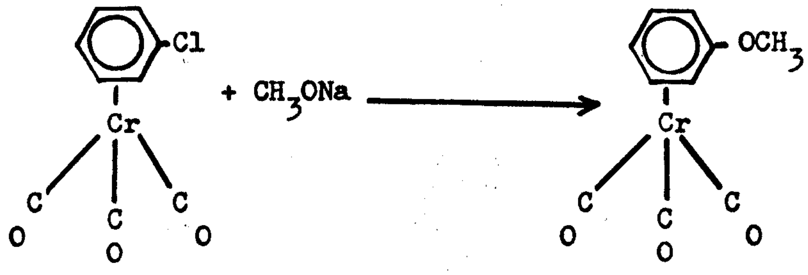

(21)

(ii) Nucleophilic Substitution: Nucleophilic substitution reactions on arenes and cyclopentadienyl ligands, when complexed to a metal, are relatively rare. Ferrocenecarbonitrile (<u>22</u>) can be prepared in good yield by reacting chloro- or bromoferrocene (<u>23</u>) with cuprous cyanide.[63,64]



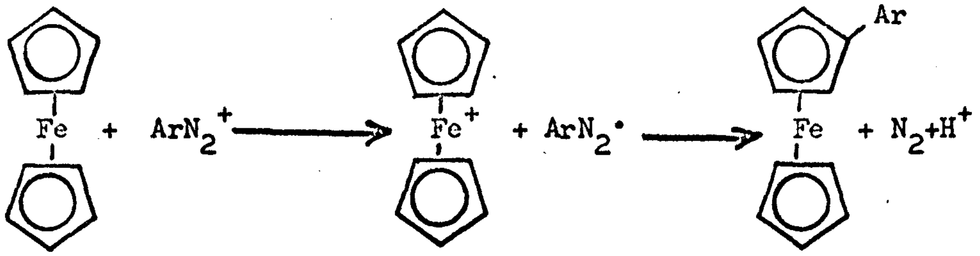
(<u>23</u>, X = Cl, Br) (<u>22</u>)

The facile reaction of (π-chlorobenzene)-chromium tricarbonyl (<u>24</u>) with sodium methoxide to yield (π-anisole)-chromium tricarbonyl (<u>25</u>) demonstrates the enhanced reactivity of π-bonded arenes toward nucleophiles.[61]



(<u>24</u>) (<u>25</u>)

(iii) Free radical substitution: Free radical substitution reactions are also known. For instance, the reaction of ferrocene (<u>7</u>) with aryldiazonium salt constitutes the most convenient and generally applicable procedure for the synthesis of arylferrocenes (<u>26</u>). This reaction almost certainly proceeds via the formation of the ferricenium cation (<u>27</u>) and an aryldiazo radical.[58b]



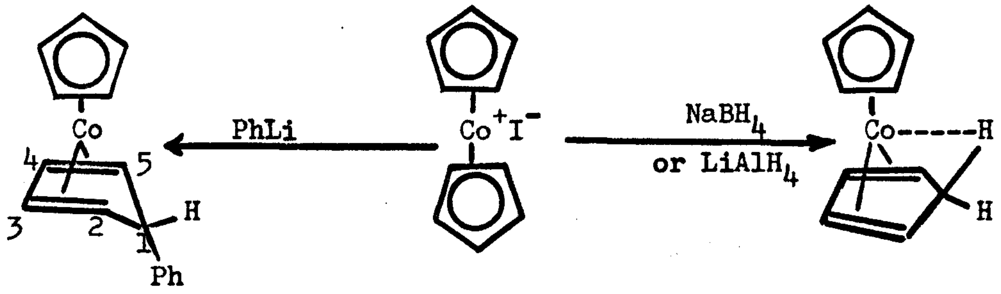
(7) (27) (26)

ADDITION REACTIONS

(i) Nucleophilic Addition: Since unsaturated organic ligands bond to transition-metals by donation of some electron density to the metal, it is to be expected that these complexes will be susceptible to nucleophilic attack. Many such reactions are known, especially when the complex bears a positive charge. A series of compounds in which cyclopentadiene or substituted cyclopentadienes are bonded to cobalt have been prepared using this kind of reaction.

For example, the reaction of cobalticenium iodide (28) with $NaBH_4$ or $LiAlH_4$ gives (π-cyclopentadiene)(π-cyclopentadienyl) cobalt (29)[65]. A characteristic of this type of complex is the anomalously low C-H stretching frequency of 2781 cm^{-1}. The infra-red band itself has been attributed to the endo-hydrogen on the π-cyclopentadiene ring, while its low frequency has been ascribed to some interaction with the metal. In a similar manner, (28) undergoes nucleophilic addition with phenyllithium to give (π-1-phenyl-2,4-cyclopentadiene)(π-cyclopentadienyl) cobalt (30).[66]

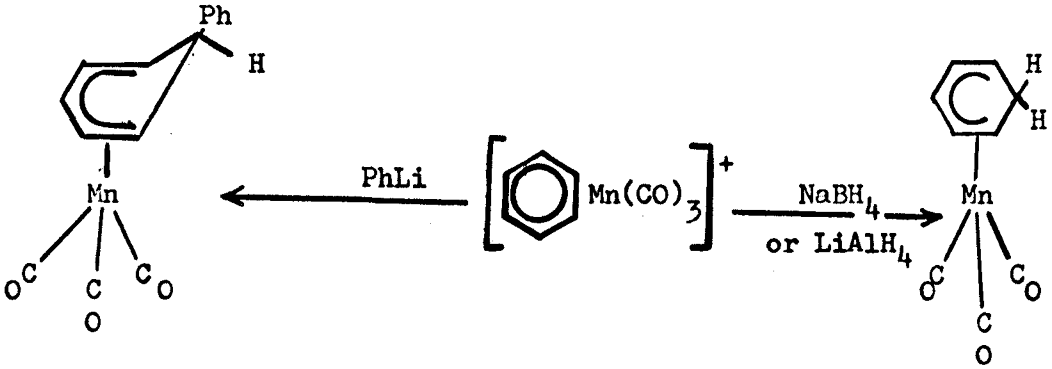
The structure of this compound was confirmed by X-ray analysis,[67] revealing that the phenyl group lies exo-to the cobalt and that the cyclopentadiene is non-planar. One plane described by $C_2C_3C_4C_5$ contains four carbon atoms equivalently bonded to the metal while the other one, containing $C_2C_1C_5$, is tilted away from the metal; the dihedral angle is 36.5°.



(30) (28) (29)

Although the hydrogen atom in (30) is in a formal endo-configuration, it is estimated to be at a distance of 3.05A from the cobalt atom. By contrast to (29), the complex (30) does not show the anomalously low νCH in the infra-red. This is understandable in view of the large Co-----H distance. It has been suggested, therefore, that the CH_2 group in (29) is more nearly coplanar with the diene moiety, or even tilted towards the metal atom. This would put the endo-hydrogen closer to the cobalt and account for the low νCH in (29). However, the opposite view, namely that this low νCH is due to the exo-hydrogen has also been advanced.[153] The benzenemanganese tricarbonyl cation (31) similarly undergoes reaction with $NaBH_4$(or $LiAlH_4$) or phenyllithium to give (π-2.4-

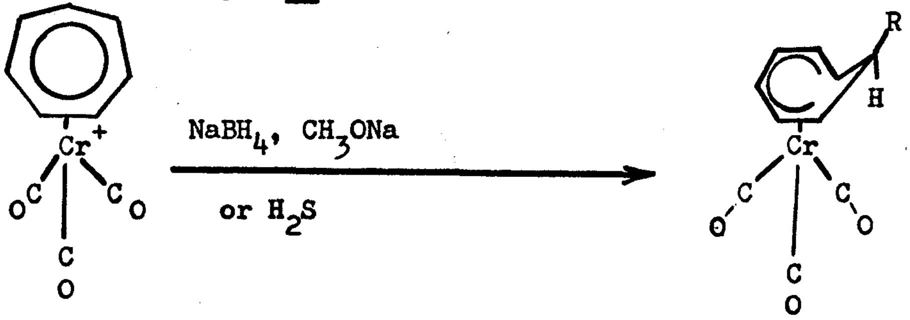
cyclohexadienyl)-manganese tricarbonyl (32)[68] or (π-1-phenyl-2.4-cyclohexadienyl)-manganese tricarbonyl (33)[69], respectively.



(33) (31) (32)

Again, a low νCH 2830 cm^{-1} is found for (32) but not in (33), leading to a similar conclusion about the stereochemistries of the organic ligands. The complexes (29)[65] (32)[68] (33)[69] have all been characterised by H^1 N.M.R. spectra.

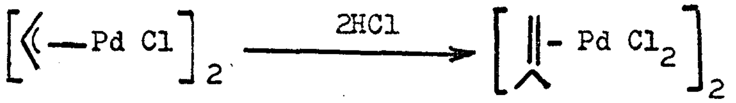
π-Tropylium-metal complexes also undergo nucleophilic addition reactions to form (π-1-monosubstituted-2.4.6-cycloheptatriene)-metal complexes. A typical example is the reaction of (π-tropylium)chromium tricarbonyl cation (34) with $NaBH_4$, CH_3ONa or H_2S, which affords (π-1-monosubstituted-2.4.6-cycloheptatriene)-chromium tricarbonyl (35).[70]



(34) (35, R=H, CH_3O, SH)

The preferred attack of nucleophile on the cation (34) from the side remote from the metal to give the exo-isomer (35) may be largely the result of steric factors. This reaction parallels the corresponding reactions of the cobalticenium cation (28). As in the latter case,[67] the exo-configuration of the product (35) has been established by an X-ray-crystallographic examination of the phenyl derivative (35, R=Ph).[71] This structure closely resembles that of cycloheptatrienemolybdenum tricarbonyl.[72]

(ii) Electrophilic Addition: For reasons discussed above, electrophilic addition reactions are uncommon in these complexes. However, an example may be found in the following reaction:



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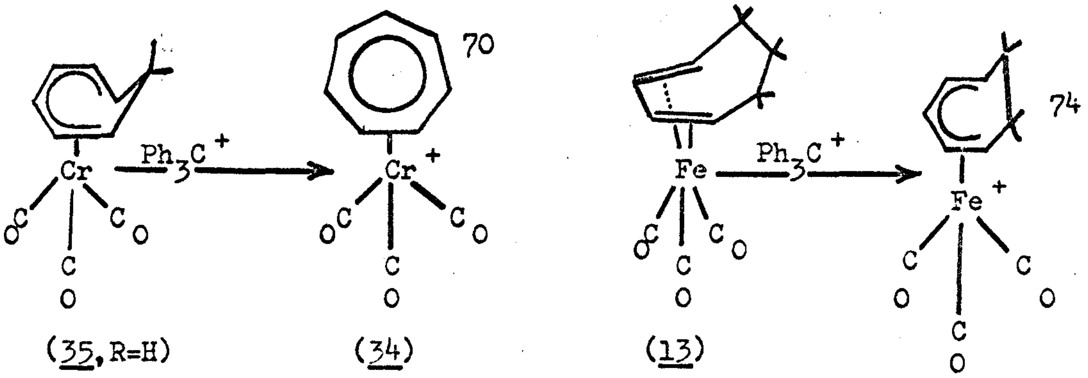
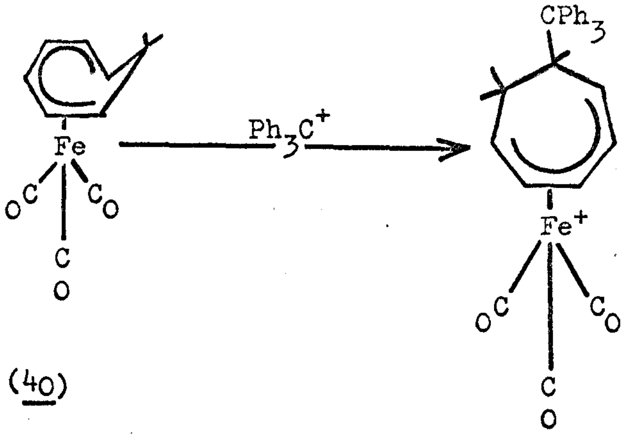
A more common type of reaction involving an electrophile is the hydride abstraction by triphenylmethyl fluoroborate, which occurs, however, at a carbon next to the one π-bonded to the metal. Typical examples are the reactions of (π-1.3-cycloheptadiene)-iron tricarbonyl (13) and cycloheptatrienechromium tricarbonyl (35, R=H) with triphenylmethyl fluoroborate, from which the (π-2.4-cycloheptadienyl)-iron tricarbonyl cation (36) and the (π-tropylium)-chromium tricarbonyl cation (34), respectively, are obtained.



70 74

(35, R=H) (34) (13) (36)

A rare example of true electrophilic addition is found in the reaction between triphenylmethyl cation and (π-2.4-cycloheptatriene)-iron tricarbonyl (37).



(40)

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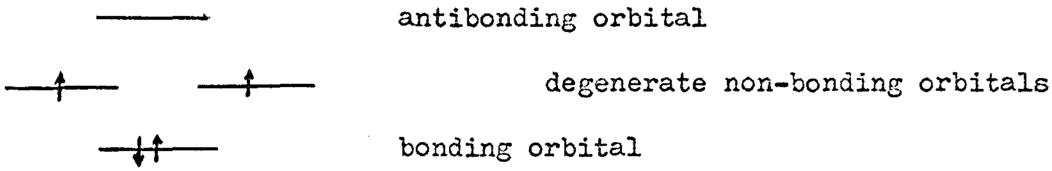
III. Cyclobutadiene-Transition Metal Complexes

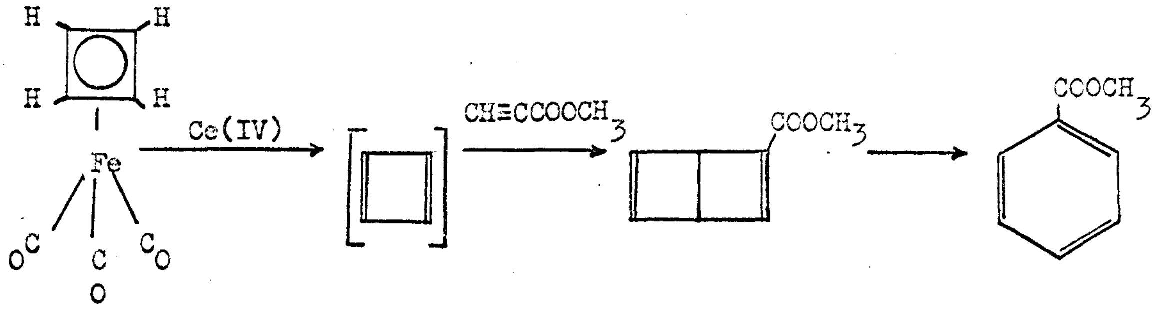
A. Bonding and structure of cyclobutadiene-metal complexes.

The molecular orbital treatment in the Hückel approximation of cyclobutadiene leads to the conclusion that the molecule, if square plannar, will be a diradical with no resonance stabilization,[74,75,76,77,78a] i.e.:



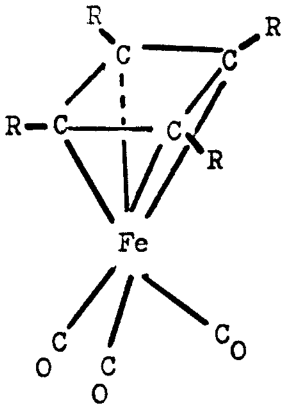
Some chemical evidence favouring a triplet state for the transient tetramethylcyclobutadiene[79] and tetraphenylcyclobutadiene[80] appears to support this view. Recently, however, Pettit *et al*[81] showed that, in Diels-Alder reactions, cyclobutadiene reacts stereospecifically as a diene or a dienophile and usually gives only one isomer. These results suggest that cyclobutadiene is in a rectangular singlet rather than a square planar triplet state. This conclusion is also supported by more recent self-consistent field molecular orbital calculations.[82] Since the various experiments are carried out under different conditions, and with different substituents on the cyclobutadiene, the question of the ground-state of cyclobutadiene and its homologues is still unresolved.

To date, it has not been possible to produce any stable, simple, free cyclobutadiene, although considerable evidence for its existance as an intermediate in some reactions has been accumulated. Recently, Pettit and his co-workers,[83,83,85] following their preparation of cyclobutadieneiron tricarbonyl (38, R=H)[86], have used this complex in attempts to prepare cyclobutadiene. They have found that complex (38, R=H), in presence of cerium (IV) and acetylenic compounds, for instance, yields products which would be expected from Diels-Alder addition of an acetylene to cyclobutadiene. These reactions therefore, are believed to occur via free cyclobutadiene .



In 1956, Longuet-Higgins and Orgel[87] suggested that it should be possible to stabilize cyclobutadiene by bonding to a transition-metal. According to molecular orbital theory, square cyclobutadiene has two unpaired electrons in a doubly degenerate non-bonding orbital, which could be used to form π-bonds to a transition-metal. The situation can be regarded as analogous to that of the cyclopentadienyl radical ($C_5H_5\cdot$), which has one unpaired electron available for π-bond formation to a transition-metal. Longuet-Higgins and Orgel also proposed that both 16- and 18-electron complexes would be formed; the former in complexes derived from a positive ions such as $C_4H_4AuCl_2^+$, and the latter in formally zerovalent complexes such as $C_4H_4Ni(CO)_2$. While the actual compounds predicted by Longuet-Higgins and Orgel have not yet been prepared, the main prediction of this remarkable paper was rapidly fulfilled by the syntheses of tetramethylcyclobutadienenickel chloride dimer (39, R=Me, x=Cl)[88] and tetraphenylcyclobutadieneiron tricarbonyl (38, R=Ph).[89,90]

Accurate X-ray structure determinations have confirmed the structures of (39, R=Me, X=Cl)[91] and (38, R=Ph).[92]



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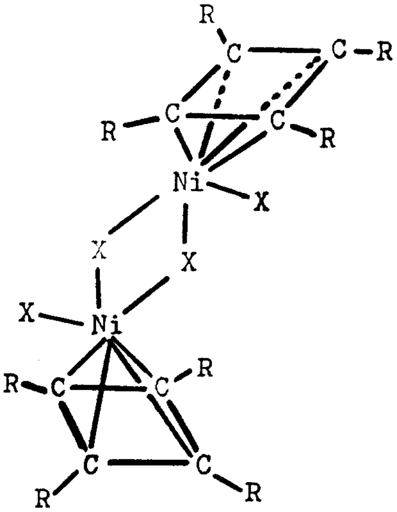


(39)

The two complexes have similar structural features. Both have a square planar cyclobutadiene ring with C–C bond distances of 1.43A and 1.46A and internal bond angles of $90 \pm 1^\circ$ and $90 \pm 2^\circ$, respectively. The metal-cyclobutadiene carbon distances are 2.02A for (39, R=Me, X=Cl) and 2.06A for (38, R=Ph). The phenyl substituents in the iron complex (38, R=Ph) are all twisted in the same direction and are also bent away from the central iron atom. Similarly, the methyl substituents in the nickel complex (39, R=Me, X=Cl) are also bent away from the nickel atom. The crystals of the nickel complex (39, R=Me, X=Cl) used for the structure determination, contained benzene of crystallization. These benzene molecules do not take part in the bonding and are randomly located between the dimer units.

Confirmation that the structure of cyclobutadieneiron tricarbonyl is the same as (38, R=H) comes from the H^1 N.M.R. spectrum, which exhibits only a singlet[86] indicating the presence of four equivalent hydrogen atoms.

Considering that the cyclobutadiene ligand occupies two coordination positions, both complexes (38, R=Ph and 39, R=Me, X=Cl) have formally five-coordinate metal atoms with the ligands similarly arranged about the metal atoms. The Fe-C and cyclobutadiene C-C distances in (38, R=Ph) are very similar to those of ferrocene (7).[29] This resemblance suggests that a similar type of bonding exists in these two kinds of complexes.

The molecular orbital description of the bonding provides a satisfactory explanation for the stability of the cyclobutadiene ring when bonded to transition-metal atoms.[93,8b,78b] The important feature of the bonding in these compounds[78b] is that the metal makes available a pair of electrons in e orbitals which can be paired, in bond formation, with the two electrons occupying the e orbitals of the cyclobutadiene ring. This simultaneously neutralizes the diradical character of the ring and provides extra stabilization as a result of bond formation, which is needed to compensate for the lack of resonance energy in the uncomplexed ring system. In the case of the nickel compound (39, R=Me, X=Cl), a schematic molecular orbital energy level diagram (Figure 4.[78b]) shows the interaction between the d_{xy} and d_{yz} orbitals on the nickel atom and the e molecular orbitals of the cyclobutadiene ring, which results in strong metal-ring π-bonding. The remaining nickel orbitals can either combine to give hybrid orbitals of the right symmetry necessary for nickel-chlorine σ-bond formation, or are available to form, essentially, nonbonding molecular orbitals. This treatment considers two local symmetries by assuming that the nickel atom is surrounded by two parallel planes, formed by the Me_4C_4 ring and the Cl_3 triangle, having colinear four-and three-fold axes passing through the nickel atom. The orbitals of the nickel atom are shown in the centre of

Figure 4, and their symmetries in C_3 and C_4 on the right and left, respectively. All 18 available electrons are paired in the bonding molecular orbitals, thus explaining the observed diamagnetism of this complex.

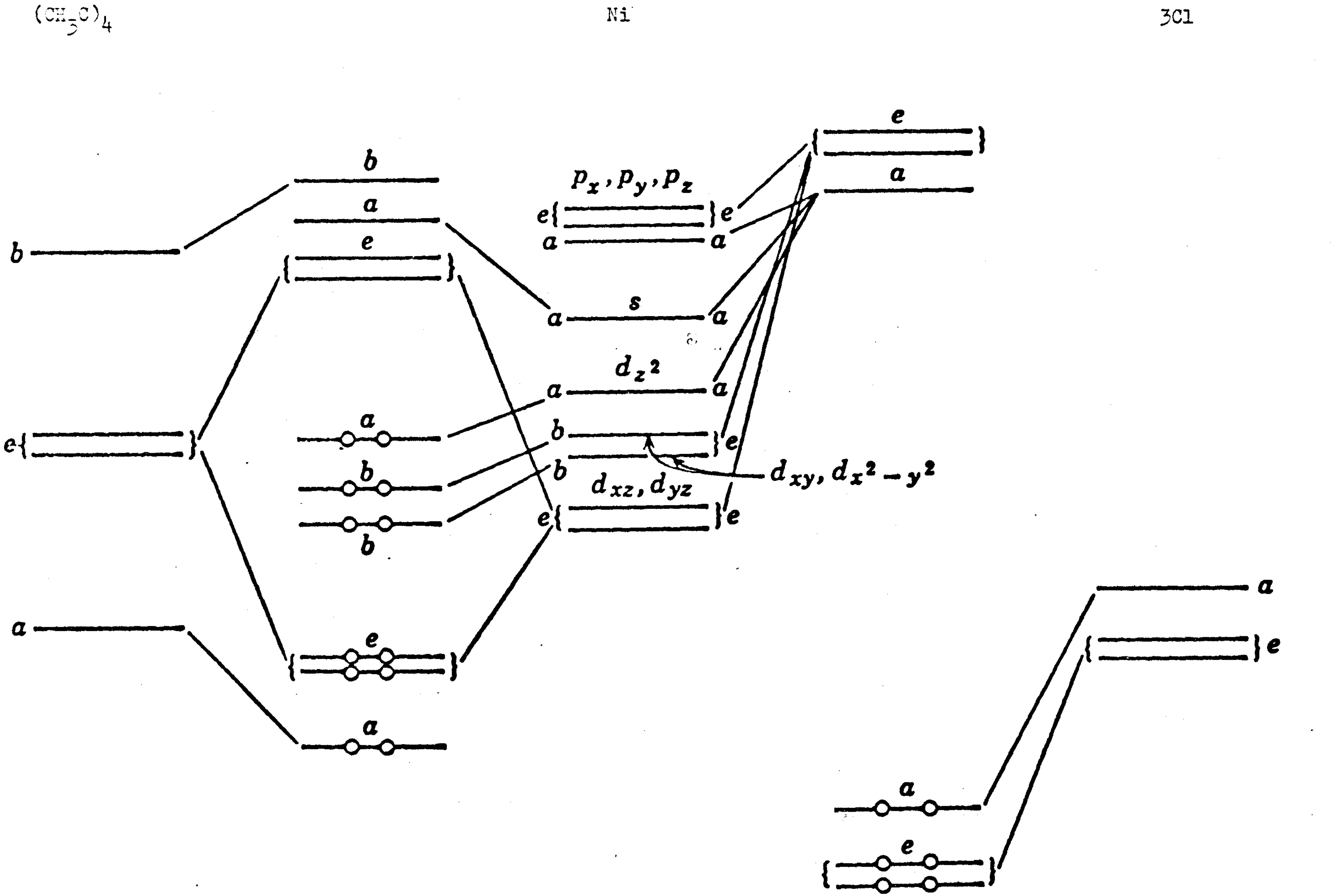
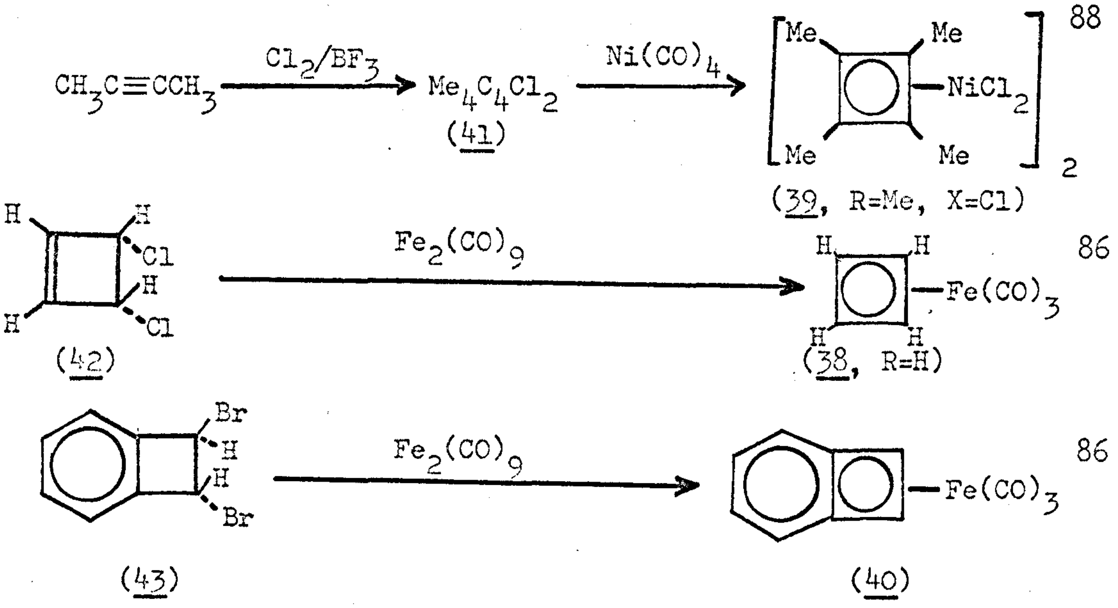


Figure 4. Schematic molecular orbital energy diagram for the bonding in tetramethylcyclobutadiene-nickel chloride dimer[78b]

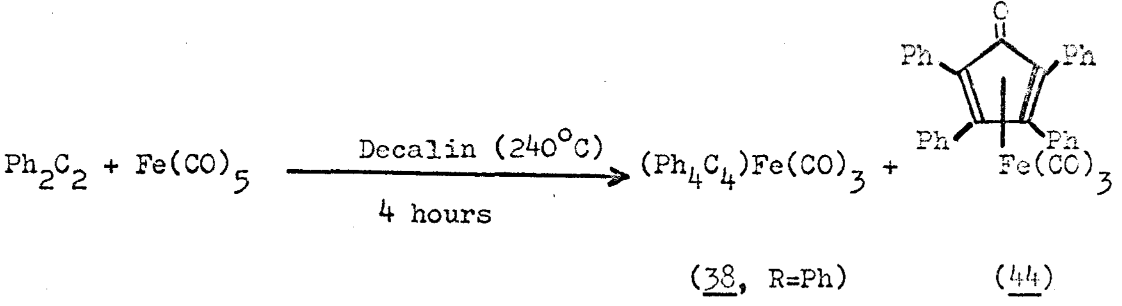
B. Preparation of cyclobutadiene-metal complexes

(a) From 3.4-dihalocyclobutenes: Potentially the most straightforward synthesis of cyclobutadiene-metal complexes is by dehalogenation of 3.4-dihalocyclobutenes by metal carbonyls. This method is limited by the difficulty of preparing most 3.4-dihalocyclobutenes, and by the fact that the dehalogenating agent must be chosen with considerable care since, in some cases, dimers of the cyclobutadiene, rather than cyclobutadiene-metal complexes, are formed. The reaction of 3.4-dichloro-1,2,3,4-tetramethylcyclobutene (41) with $Ni(CO)_4$ gives (39, R=Me, X=Cl). Similarly, cis-3.4-dichlorocyclobutene (42) and trans-dibromobenzocyclobutene (43) react with $Fe_2(CO)_9$ to yield (38, R=H) and (40), respectively.



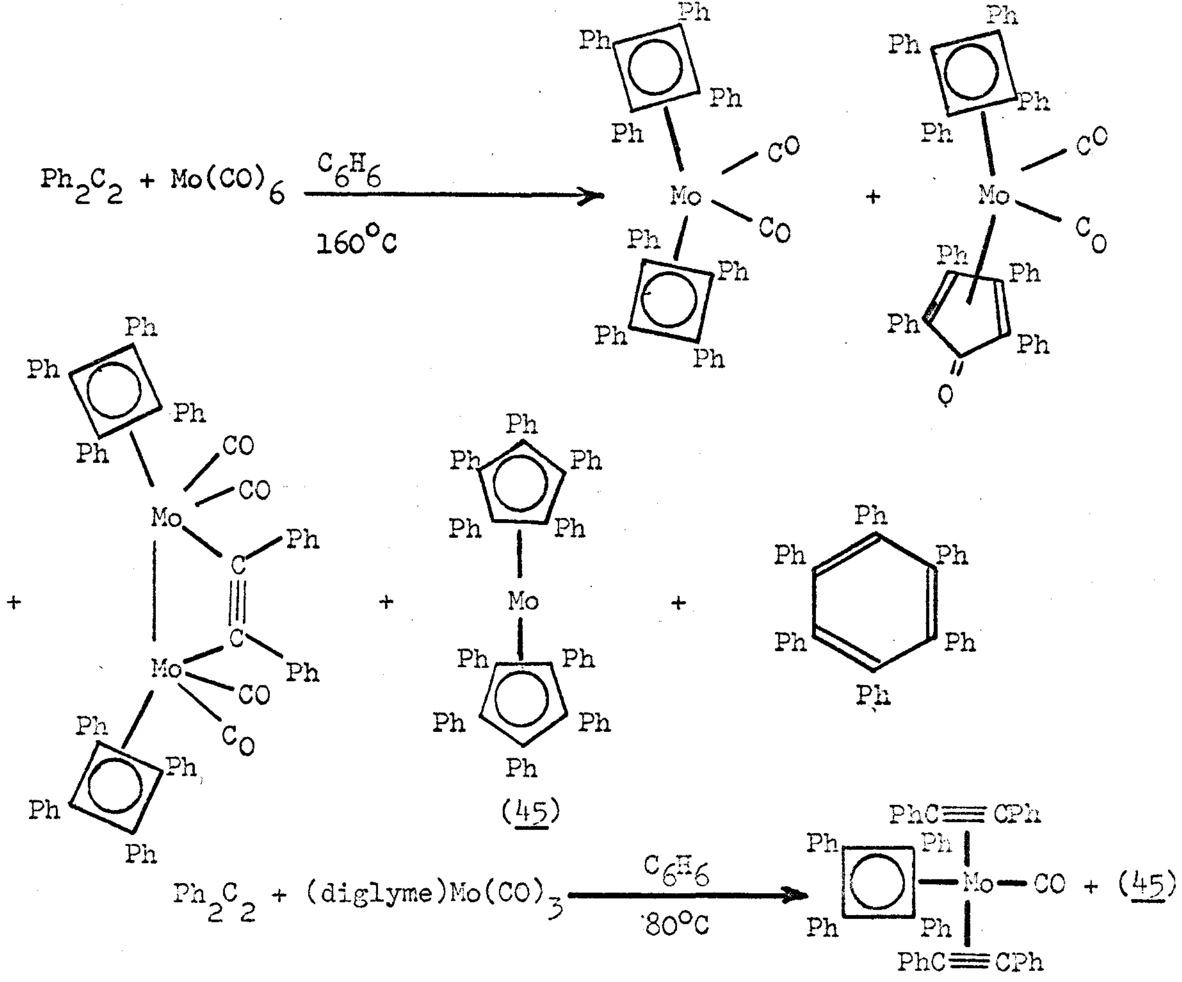
(b) From acetylenes: Acetylenes undergo reactions with metal carbonyls and other transition-metal complexes to yield complex mixtures of products from which some interesting cyclobutadiene complexes can be isolated. These reactions, however, are not useful synthetically due to the large number of products obtained and the difficulty in separating them.

High-temperature reaction of diphenylacetylene with $Fe(CO)_5$ yields small amounts of complex (<u>38</u>, R=Ph) together with the tetracycloneiron complex (<u>44</u>).[90] Trace amounts of the complex (<u>38</u>, R=Ph) also are obtained from the reaction of diphenylacetylene with $Fe_3(CO)_{12}$ at 90°C.[89]



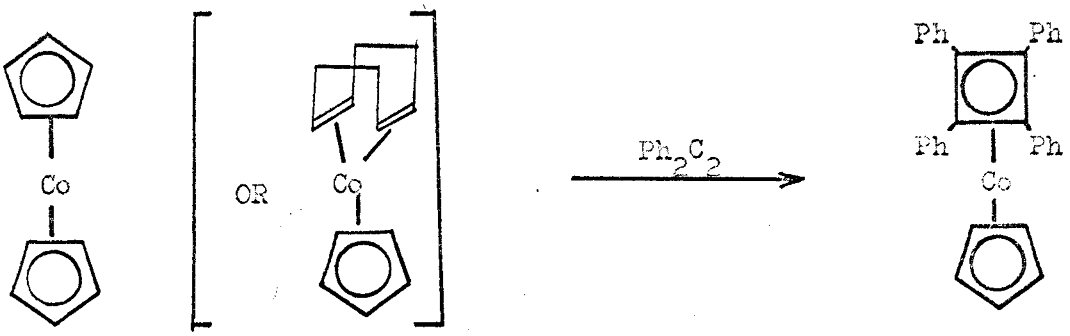
90

Another reaction which appears to yield tetraphenylcyclobutadiene complexes is that of molybdenum hexacarbonyl or diglyme molybdenum tricarbonyl with diphenylacetylene,[94] although these complexes, as yet, have not been fully characterized.



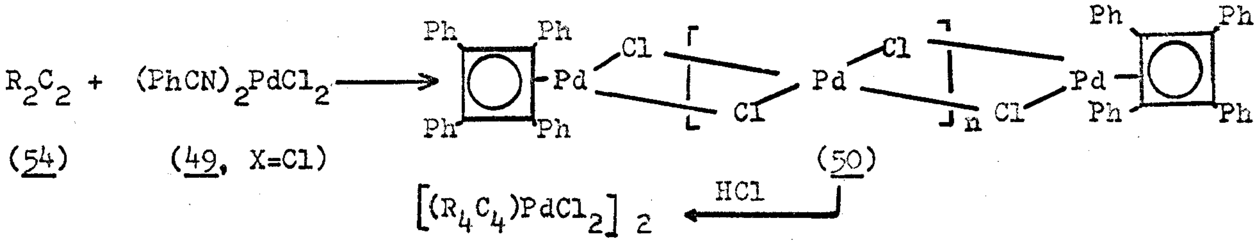
94

Diphenylacetylene also reacts with either cobaltocene (46)[95] or (cyclopentadienyl)(1.5-cyclooctadiene)-cobalt (47)[96,97] to give (π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)-cobalt (48).



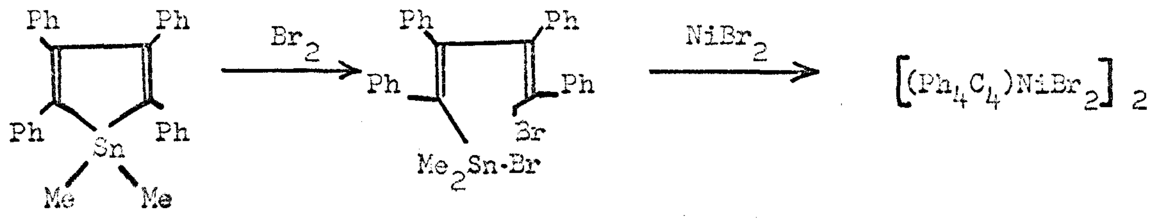
(46) (47) (48, R=Ph)

Bis(benzonitrile)-palladium chloride (49, X=Cl) reacts with acetylenes (54, R=Ph, p-ClC_6H_4, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$)to give cyclobutadiene complexes (50).[98,99,100,101] These complexes can easily be converted into the uncatenated form (51)[99,101] on treatment of their dimethyl formamide solution with hydrochloric acid.



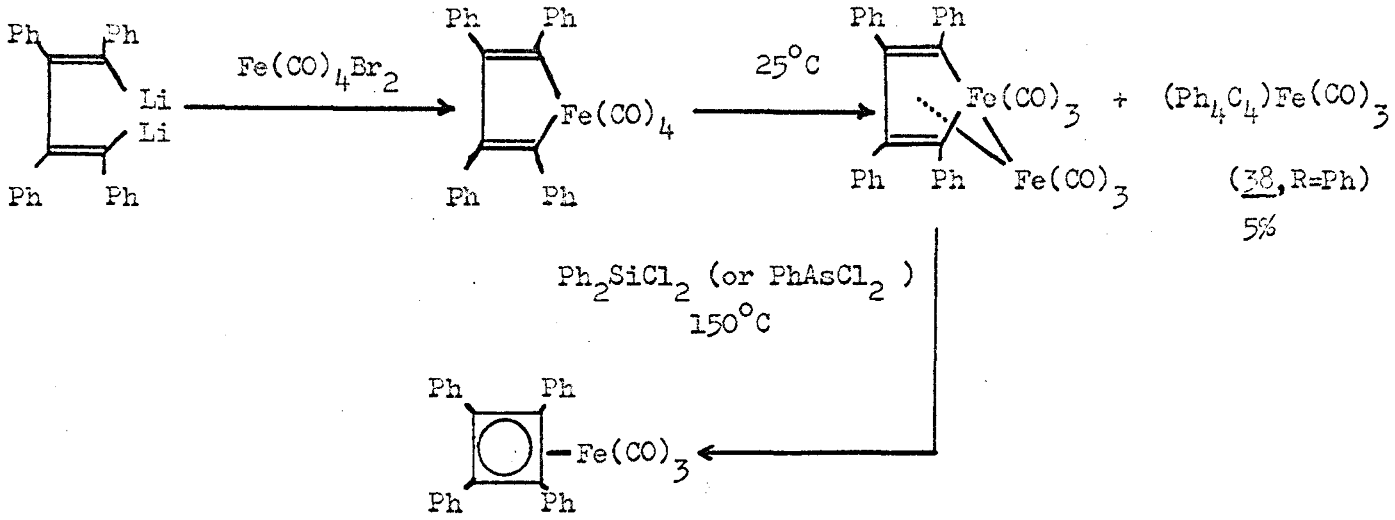
(51, X=Cl)

(c) From 1-Heterocyclopentadienes: A novel method[80] has been used to prepare tetraphenylcyclobutadienenickel bromide (39, R=Ph, X=Br) from 1.1-dimethyl-2.3.4.5-tetraphenylstannole (52), obtained from 1.4-dilithiotetraphenylbutadiene and dimethyltin dichloride. The stannole (52) is cleaved by one mole of bromine to the butadiene (53), which on refluxing with nickel bromide in triglyme gives the cyclobutadienenickel bromide dimer (39, R=Ph, X=Br) in high yield.



(52) (53) (39, R=Ph, X=Br)

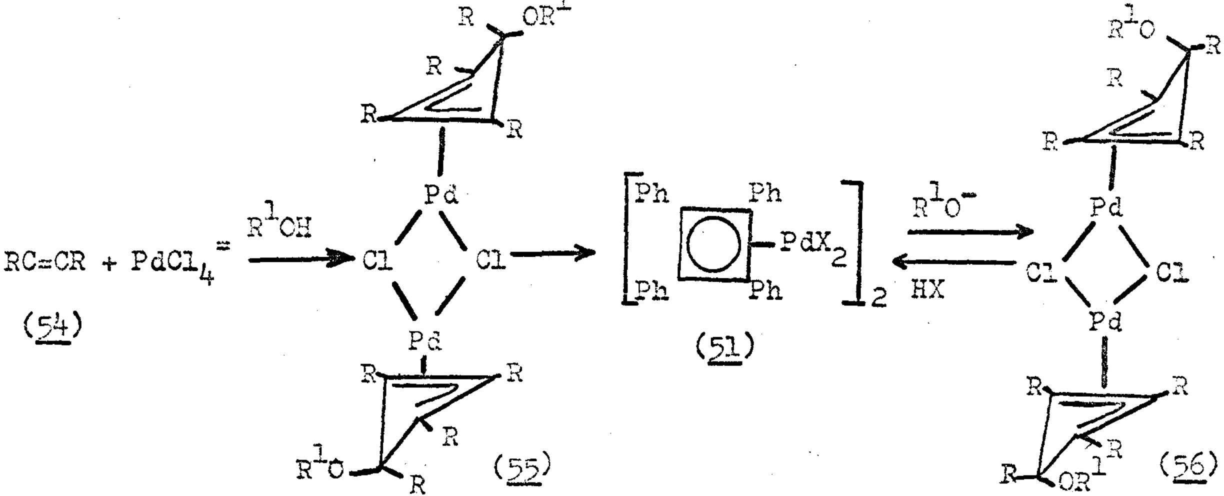
Analogous methods have been used to prepare tetraphenylcyclobutadieneiron tricarbonyl (38, R=Ph)[102]



(38, R=Ph)

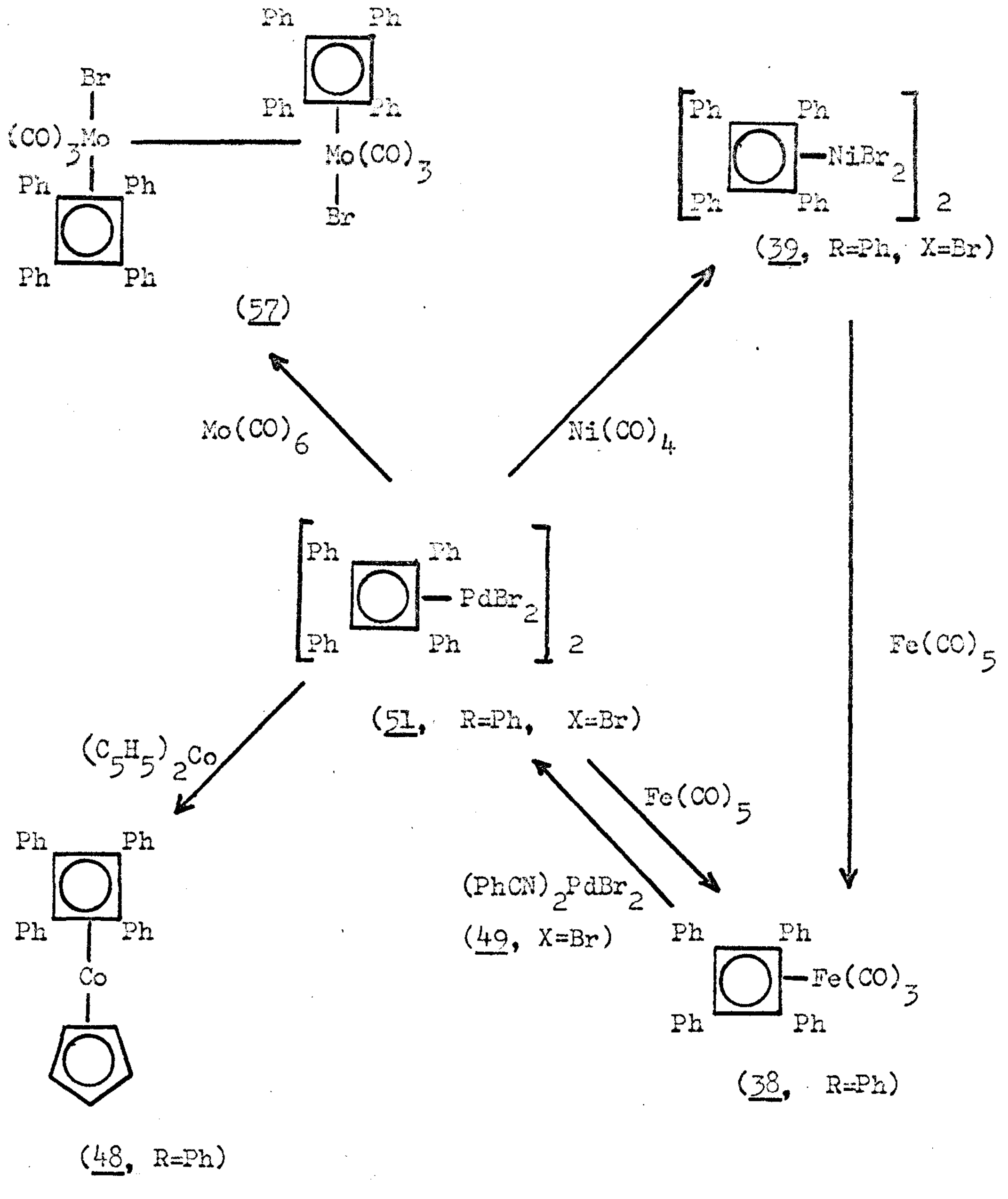
25%

(d) From π-cyclobutenyl complexes: The reaction of diphenylacelylene (54, R=Ph) with palladium chloride or sodium chloropalladite, first studied by Malatesta et al,[103] has yielded a complex[104,98,105] which, subsequently, has been shown by X-ray analysis[106] to be the (π-endo-1-ethoxy -1.2.3.4-tetraphenylcyclobutenyl)palladium chloride dimer (55, R=Ph, R^1=Et). A number of similar complexes (55) with R=Ph, R^1 =Me and R=p-ClC$_6$H$_4$, R^1 =Et, and with different bridging halogens have been prepared.[101,105] These complexes (55) react with hydrogen halides to give the cyclobutadienepalladium halides. For instance, (55, R=Ph, R^1=Et), in dichloromethane solution, on treatment with anhydrous hydrogen bromide yields tetraphenylcyclobutadienepalladium bromide dimer (51, R=Ph, X=Br).[107] The cyclobutadienepalladium complexes (51) react with alcohols, usually in the presence of weak bases, to give cyclobutenylpalladium complexes (56). An X-ray structure determination[106] of (56, R=Ph, R^1=Et)has shown the complex to be isomeric with (55, R=Ph, R^1=Et), with the ethoxy group exo-to the palladium. These reactions are reversed on treatment of (56) with hydrogen halides and constitute another preparation of the cyclobutadienepalladium complexes.



(e) From other cyclobutadiene complexes by ligand-exchange and ligand-transfer reactions: The methods described above suffer from the disadvantage that they are highly specific with regard to the metal and the other reagents used, as well as to the conditions under which the reaction takes place. The discovery of ligand-transfer and ligand-exchange reactions has allowed the preparation of cyclobutadiene complexes of different metals to be realized. The ligand-transfer and ligand-exchange reactions have been thoroughly studied only in the cases of tetraphenylcyclobutadiene and tetrakis(p-substituted)cyclobutadien-palladium halide complexes (51).[100,101,109,110,111] Recently, tetramethylcyclobutadiene has also been successfully transferred from (39, R=Me, X=Cl,I) onto iron and cobalt by the reaction of (39, R=Me, X=Cl, I) with $Fe_3(CO)_{12}$ and $Co_2(CO)_8$, respectively.[112] As yet, no ligand-transfer reactions have been carried out on the unsubstituted cyclobutadiene complexes.

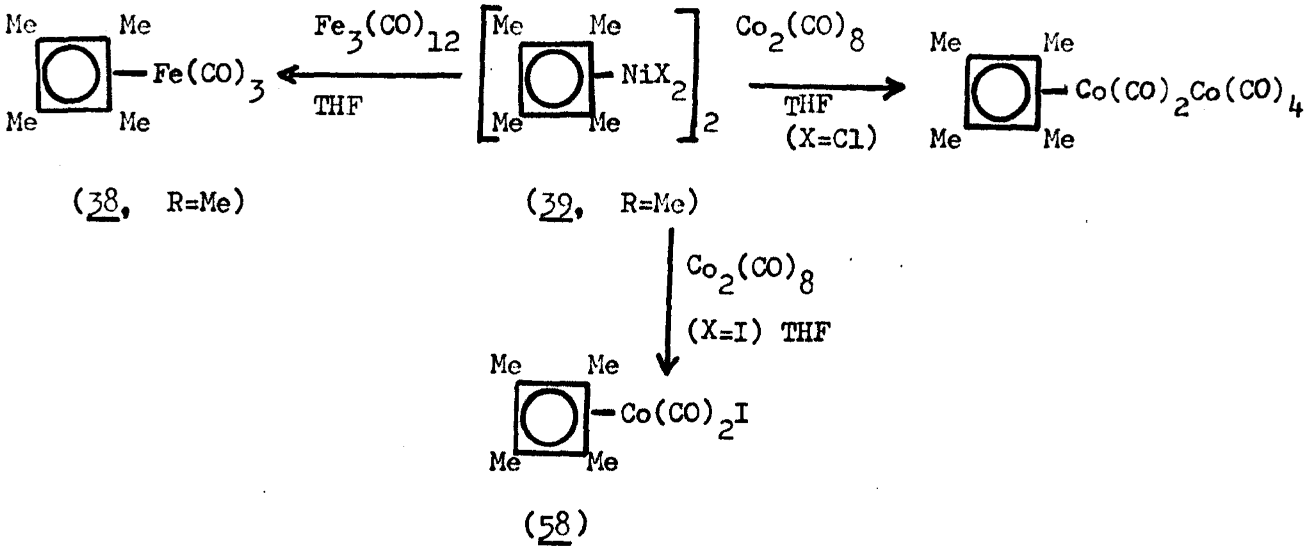
These reactions are usually carried out under heterogenous conditions and no meaningful data on their mechanisms have yet been obtained. It appears, however, that these reactions occur under reducing conditions, and that the metal carbonyls function as dehalogenating agents.[113] Some examples of these reactions are given in Figure 5.



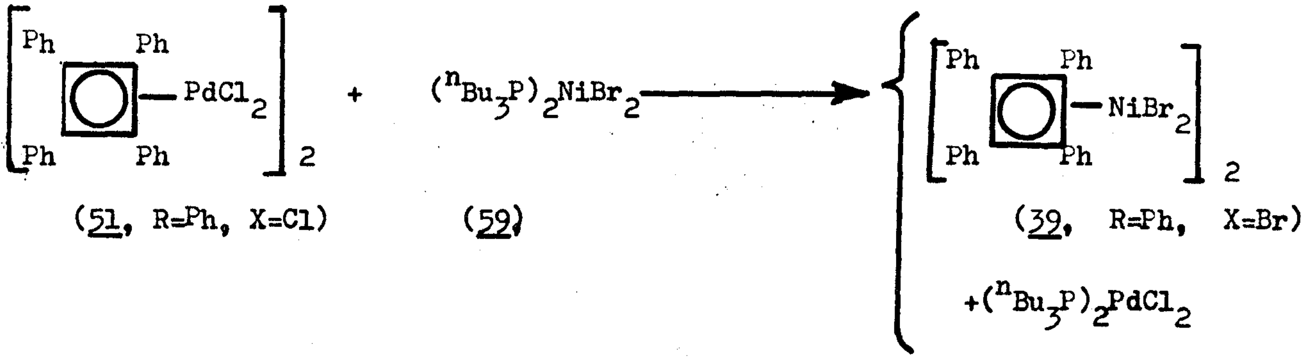
Tetraphenylcyclobutadiene ligand-transfer reacions

Figure 5. Synthesis of cyclobutadiene-metal complexes by ligand-transfer and ligand-exchange reactions

Figure 5. continued



Tetramethylcyclobutadiene ligand-transfer reactions

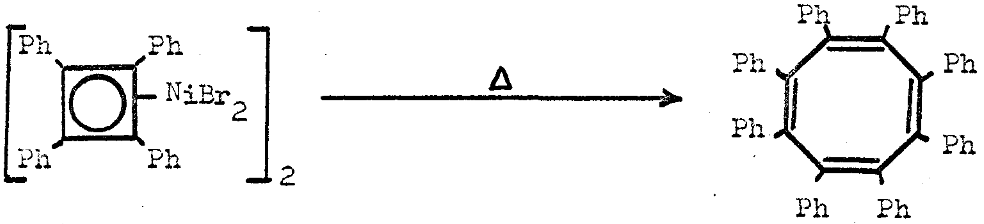


Tetraphenylcyclobutadiene ligand-exchange reaction

C. Reactions of cyclobutadiene-metal complexes.

The reactions of cyclobutadiene-metal complexes can be divided conveniently into three broad categories: (a) reactions such as thermal decomposition, reduction, oxidation, halogenation and with various donor molecules in which the cyclobutadiene ligand is removed from the metal; (b) reactions of electrophilic and nucleophilic reagents at the cyclobutadiene ligand in which the ring remains bonded to the metal; and (c) reactions in which the cyclobutadiene ligand remains untouched.

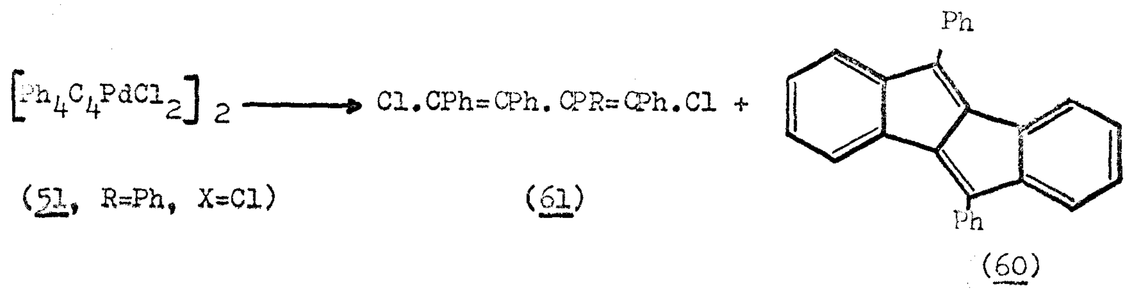
(a) The nature of the organic products obtained by removing the cyclobutadiene ligand from the complex depends on the substituents of the cyclobutadiene ring, the metal, the chosen conditions and the reagents. For example, tetraphenylcyclobutadienenickel bromide dimer (39, R=Ph, X=Br) on pyrolysis yields nickel bromide and hydrocarbon products including octaphenylcyclooctatetraene (60).[80]



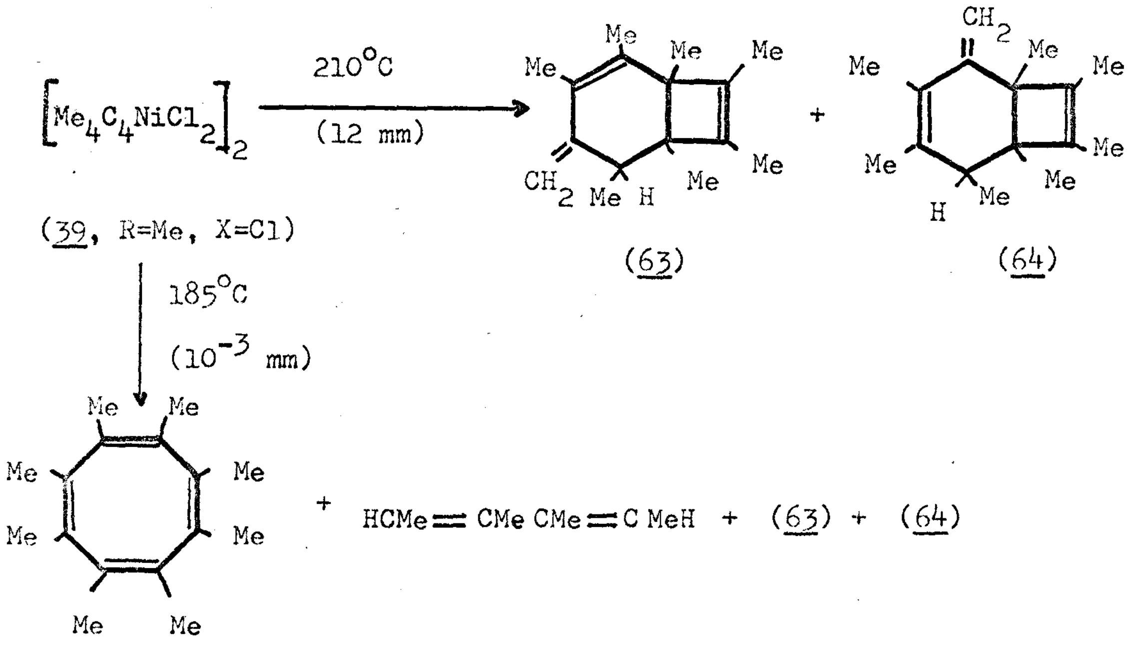
(39, R=Ph, X=Br)

(60)

In contrast, pyrolysis of tetraphenylcyclobutadienepalladium chloride dimer (51, R=Ph, X=Cl) gives palladium metal and 1.4-dichlorotetraphenylbutadiene (61),[104] together with trace amounts of a diphenylindenoindene (62).[98]

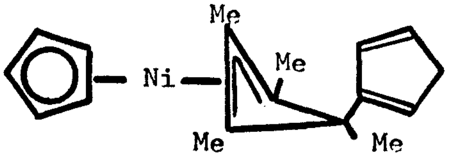


The comparison between the last two reactions illustrates the importance of the metal. Palladium-halogen bonds are weaker than nickel-halogen bonds and, hence, it is reasonable to expect that, on pyrolysis, halogen-containing hydrocarbons would be preferably formed in the case of the palladium complex (51). The effect of the substituents on the cyclobutadiene ring on the nature of the products is illustrated by comparing the products obtained from the thermal decomposition of tetraphenylcyclobutadienenickel bromide dimer (39, R=Ph, X=Br) (shown above) and tetramethylcyclobutadienenickel chloride dimer (39, R=Me, X=Cl).[114] As is seen in the latter example, the products obtained are very sensitive to the reaction conditions.



(b) (i) Reactions with nucleophilic reagents: The first example of a nucleophilic attack on a cyclobutadiene ring was the reaction of the tetramethylcyclobutadienenickel complex (39, R=Me, X=Cl) with excess sodium cyclopentadienide.[115,116] The product of this reaction is (π-cyclopentadienyl)(π-1-exo-cyclopentadiene-1.2.3.4-tetramethylcyclobutenyl) nickel (65), the structure of which has been confirmed by H^1N.M.R.[117] and X-ray analysis.[108] The position of the double bond in the cyclopentadiene ring of (65) is still unknown, and it has been suggested that two isomers may be present.[115]

(39, R=Me, X=Cl) $\xrightarrow{\text{excess } C_5H_5Na}$



(65)

The palladium halide complexes (51, R=Ph) are sufficiently labile to undergo nucleophilic addition reactions with mild nucleophiles such as alcohols. For instance, tetraphenylcyclobutadienepalladium chloride dimer (51, R=Ph, X=Cl) reacts with ethanol to give (56, R=Ph, R^1=Et, X=Cl). An X-ray structure determination shows this compound to have the ethoxy group exo to the metal.[106] This suggests that nucleophilic attack on (51, R=Ph, X=Cl) occurs from the side opposite to the metal.

(ii) Reactions with electrophilic reagents: Pettit *et al*[118] have found recently that cyclobutadieneiron tricarbonyl (38, R=H) undergoes electrophilic substitution reactions under very mild conditions to give a series of monosubstituted cyclobutadieneiron tricarbonyl complexes (66) (Figure 6.). These reactions, which closely parallel the well known substitution reactions of ferrocene (7) and cyclopentadienylmanganese tricarbonyl (18), indicate that the complex (38, R=H) acts as an aromatic system. It has been suggested that these reactions proceed via the π-cyclobutenyliron tricarbonyl cation (67), which might afford a low-energy pathway for the substitution process. Stable cationic complexes of this kind have been previously isolated (e.g., $-Fe(CO)_3^+$).[119]

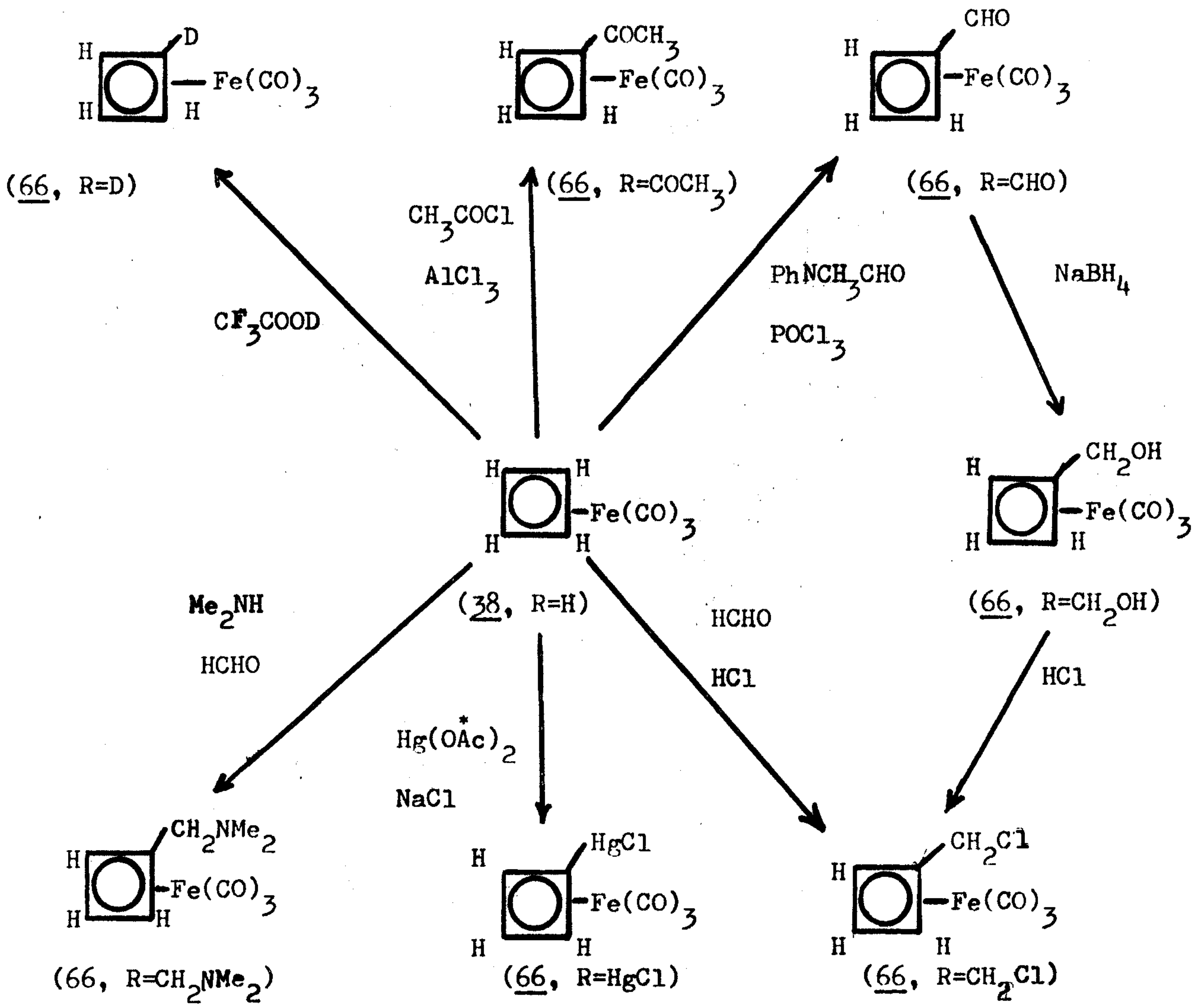
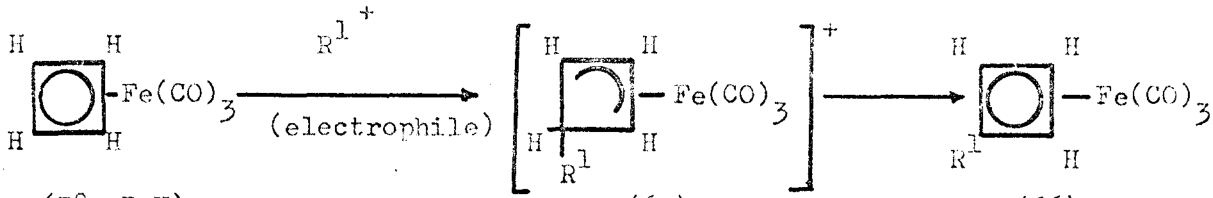


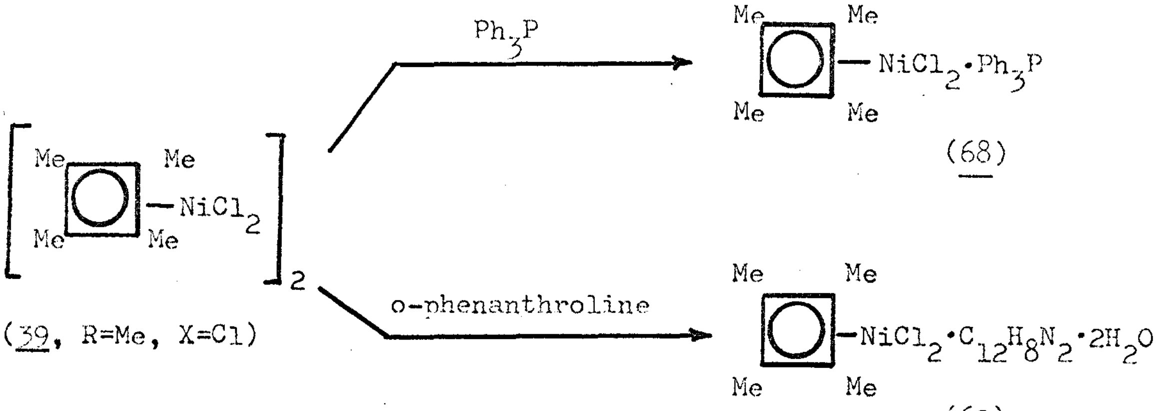
Figure 6. Substitution reactions of cyclobutadieneiron tricarbonyl complex (38, R=H)

* Ac=COCH$_3$



(38, R=H) (67) (66)

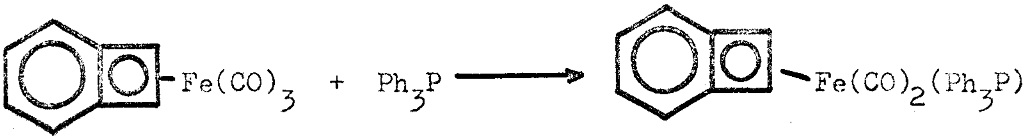
(c) At the time this work was begun, only a few reactions in which the cyclobutadiene ligand remained unchanged were known. For example, donor molecules can coordinate onto the nickel atom in complexes such as (39, R=Me, X=Cl) by breaking the bridging halides. Triphenylphosphine adducts of tetramethylcyclobutadienenickel chloride (68),[114] tetraphenylcyclobutadienenickel bromide,[113b] and an o-phenanthroline complex (69) of the former[120] also have been reported.



(39, R=Me, X=Cl) (68) (69)

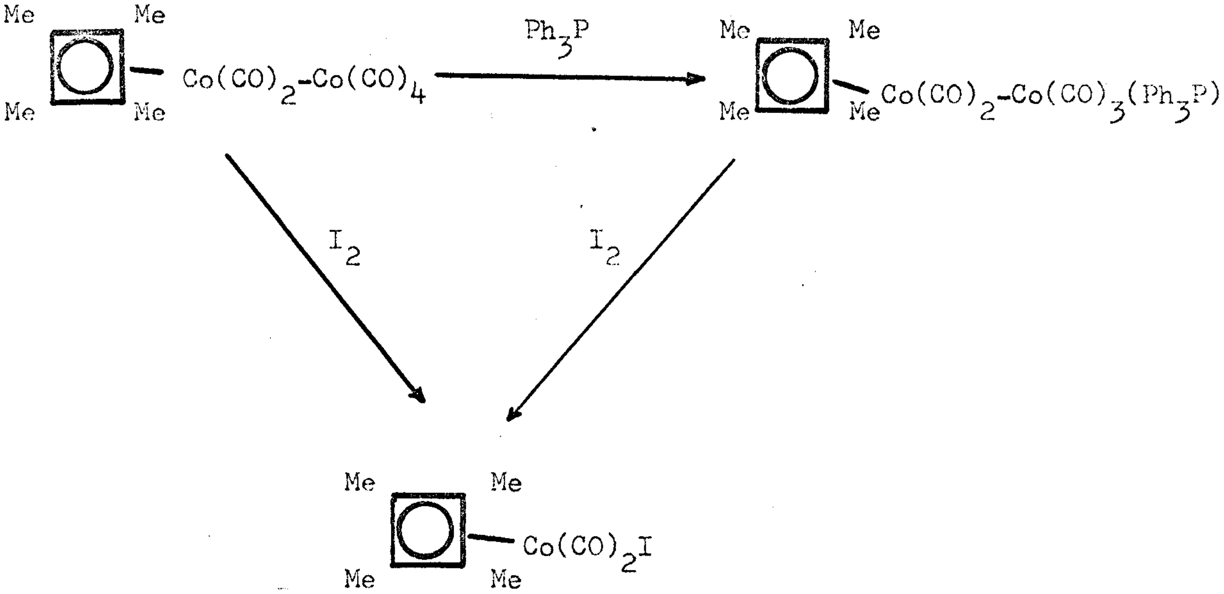
The chlorine atoms of the tetramethylcyclobutadienenickel complex (39, R=Me, X=Cl) can be displaced by other anions on treatment with the appropriate silver salt or in other ways, to give compounds such as (39, R=Me, X=I, Br, N_3, SCN etc.).[121] Tetraphenylcyclobutadienepalladium chloride dimer (51, R=Ph, X=Cl) undergoes analogous reactions.

Recently, it was reported by Pettit et al[86] that benzocyclobutadieneiron tricarbonyl (40) underwent reaction with triphenylphosphine, in which one carbonyl group was displaced by triphenylphosphine, to give benzocyclobutadieneiron (triphenylphosphine) dicarbonyl (70)



(40) (70)

More recently, Bruce and Maitlis[112] found that the tetramethylcyclobutadienecobalt complex $(Me_4C_4)Co_2(CO)_6$ underwent reactions with iodine or triphenylphosphine in which the cyclobutadiene ring remained intact and unchanged.



(58)

RESULTS AND DISCUSSION

RESULTS AND DISCUSSION

The RESULTS AND DISCUSSION is divided into two sections. The first section deals with studies reported in this thesis which extend the ligand-transfer and ligand-exchange reactions developed by Maitlis and Games[100,109,110] for the syntheses of cyclobutadiene- and cyclopentadienyl-metal complexes. The latter reaction originally was discovered by Tilney-Bassett[53].

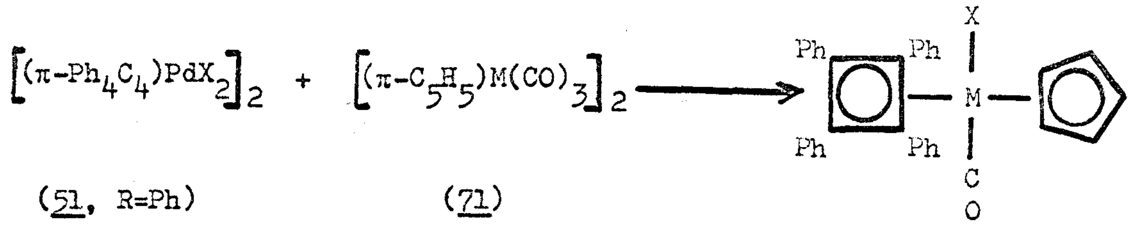
The compounds used as cyclopentadienylating agents were cyclopentadienyliron dicarbonyl bromide (<u>10</u>, X=Br) and cyclopentadienyliron dicarbonyl dimer (<u>17</u>). The tetraphenyl- and tetrakis(p-tolyl)-cyclobutadienepalladium halide complexes (<u>51</u>) were used to prepare the cyclobutadiene complexes. No mechanistic studies as yet have been made on these reactions, thus no attempt will be made to discuss this aspect. Some suggestions in this respect have been made by Maitlis.[113a]

The second section deals with the chemistry of some new cyclobutadiene complexes, including "sandwich" complexes with π-cyclopentadienyl, π-cyclohexadienyl, π-cycloheptadienyl, π-arene and π-cycloheptatriene ligands.

I Cyclobutadiene and Cyclopentadienyl Ligand-Transfer Reactions

A. Tetraphenylcyclobutadiene-molybdenum and -tungsten complexes.

The reaction of tetraphenylcyclobutadienepalladium halides (51, R=Ph) with cyclopentadienylmolybdenum tricarbonyl dimer (71, M=Mo) in either benzene or xylene gave (π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)-molybdenum carbonyl halides (72, M=Mo). The best yield (18%) was obtained from the reaction of (51, R=Ph, X=Cl) with the molybdenum dimer (71, M=Mo) in refluxing xylene for ten minutes, while only a 5% yield of the desired product was formed after 50 hours of reflux in benzene. The bromide analogue (72, M=Mo, X=Br) was formed in 8% yield using refluxing xylene and in only 5% yield in refluxing benzene. Therefore, it appears that higher temperatures and shorter times result in a slightly improved yield.



(51, R=Ph) (71) (72)

Cyclopentadienyltungsten tricarbonyl dimer (71, M=W) was obtained in 60% yield from the direct reaction between dicyclopentadiene and tungsten hexacarbonyl in triglyme. This compound, (71, M=W), underwent an analogous reaction to that described above with (51, R=Ph, X=Cl) in refluxing benzene from which (π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)-tungsten carbonyl chloride (72, M=W, X=Cl), the first characterized cyclobutadiene-tungsten complex, was isolated in very small yield

(0.7%).

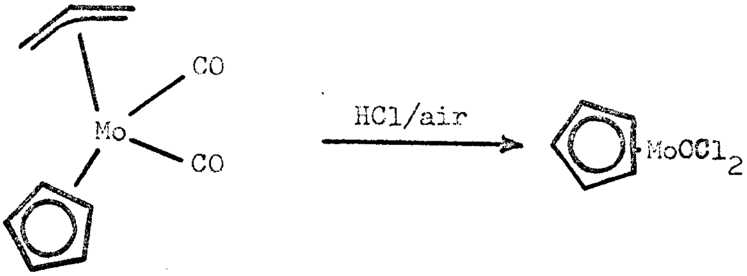
The molybdenum and tungsten complexes (72), which were monomeric, orange-red crystalline solides, had almost identical infra-red spectra (Appendix-I) with one terminal carbonyl stretching band (Table 3.).

compound	ν_{co} cm^{-1}	medium
(72, M=Mo, X=Br)	1998	KBr disc
(72, M=Mo, X=Cl)	1961	KBr disc
(72, M=Mo, X=Cl)	1973	CCl_4 solution
(72, M=W, X=Cl)	1958	KBr disc

Table 3. Carbonyl stretching bands in the molybdenum and tungsten complexes (72).

The H^1 N.M.R. spectrum of the diamagnetic molybdenum carbonyl chloride (72, M=Mo, X=Cl) showed a fairly broad peak at 2.68τ due to the phenyl protons, and a sharp singlet at 4.55τ due to the cyclopentadienyl protons with relative intensities 20:5. This confirmed the proposed structure.

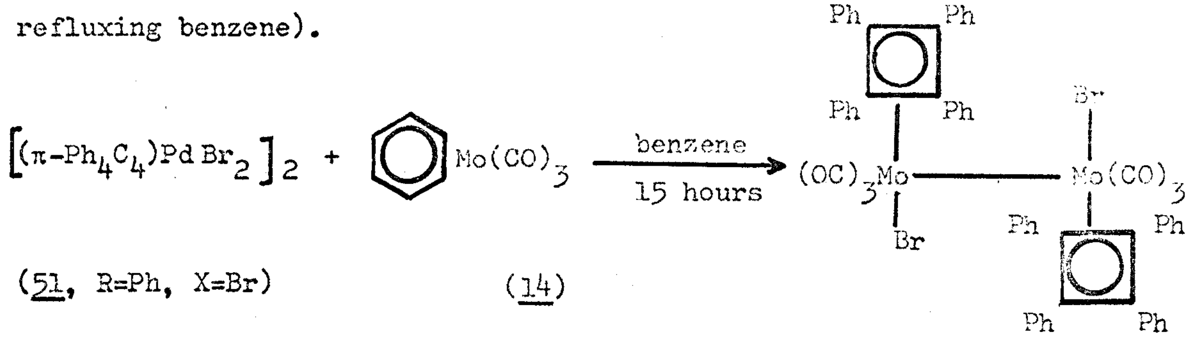
In contrast to the reaction of (π-allyl)(π-cyclopentadienyl)-molybdenum dicarbonyl (73) with hydrogen chloride in the presence of air in which (π-cyclopentadienyl)-molybdenum oxide dichloride (74) was formed,[123] the complex (72, M=Mo, X=Cl) was stable to such treatment.



(73) (74)

This may be due to a much stronger cyclobutadiene-molybdenum bond compared to π-allyl-molybdenum one, although steric hindrance may also be important.

Another tetraphenylcyclobutadienemolybdenum complex was prepared by the reaction of (51, R=Ph, X=Br) with benzenemolybdenum tricarbonyl (14) in refluxing benzene for 15 hours. The product of this reaction was the (π-tetraphenylcyclobutadiene)-molybdenum tricarbonyl bromide dimer (57), previously prepared by Maitlis and Games,[109,110] by reaction between (51, R=Ph, X=Br) and molybdenum hexacarbonyl (67 hours in refluxing benzene).

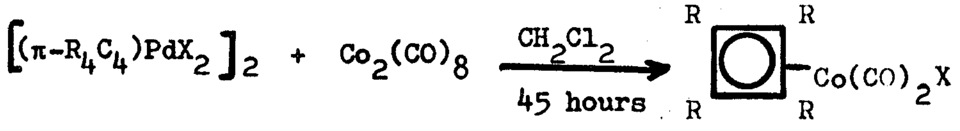


(51, R=Ph, X=Br) (14) (57)

This complex (57) was obtained in 14% yield here as compared with a 7% yield reported by Maitlis and Games.

B. Cyclobutadiene-cobalt complexes.

The previously described transfer of the tetraphenylcyclobutadiene group from palladium onto molybdenum and tungsten gave optimum yields when carried out under heterogenous conditions [the palladium complex, (51, R=Ph), being only slightly soluble in noncoordinating solvents] , by heating the reactants in an inert solvent, usually an aromatic hydrocarbon. Attempts to transfer the tetraphenylcyclobutadiene ring onto cobalt by the reactions of (51, R=Ph, X=Cl, Br, I) with dicobalt octacarbonyl under these conditions were unsuccessful; but it was found that the desired reactions occurred readily under homogenous conditions, on stirring the reactants together in dichloromethane for 45 hours at 25°C. The products obtained from these reactions were the (π-tetraphenylcyclobutadiene)-cobalt dicarbonyl halides (75, R=Ph, X=Cl, Br, I), which were red-brown crystalline solids and fairly stable in air. In solution, these complexes (75) were air-sensitive.



(51)

(75)

Suprisingly, these complexes of Co(I) [d^8 ion] were found to be strongly paramagnetic, with gram magnetic susceptibilities of $X^{296^\circ K} = + 2.14 \times 10^{-6}$ and $X^{284^\circ K} = + 3.23 \times 10^{-6}$ for (75, R=Ph, X=Br) and (75, R=Ph, X=Cl), respectively. This is in contrast to most other cobalt(I) complexes which obey the effective atomic number formalism and are diamagnetic [e.g., $(C_5H_5)Co(C_5H_6)$,[125] $(C_5H_5)Co(Ph_4C_4)$[97,95] and $(C_5H_5)Co(CO)_2$[124]].

After careful purification, however, the paramagnetism of (75, R=Ph, X=Br) was appreciably reduced and the measured gram magnetic susceptibility was only $X^{296^oK} = -0.15 \times 10^{-6}$. These results almost certainly indicate the presence of small amounts of analytically* undetectable highly paramagnetic impurities rather than paramagnetic complexes. Another cobalt(I) complex, the bis(hexamethylbenzene)-cobalt(I) cation (16) has recently been found by Fischer and Lindner[46] to exhibit paramagnetism corresponding to the presence of two unpaired electrons. In this compound, however, the effective atomic number of the cobalt is two greater than that of Krypton.

The cobalt complex (75, R=Ph X=Br) was found to be monomeric in chloroform solution, and the H^1 N.M.R. spectrum, taken on a highly purified sample, showed a fairly broad (26 c/s) unresolved multiplet centred at 2.60τ due to the phenyl protons. The {π-tetrakis(p-tolyl)cyclobutadiene}-cobalt dicarbonyl bromide (75, R=To**, X=Br) was prepared similarly. Its H^1 N.M.R. spectrum showed an AB quartet centred at 2.68τ, due to the aromatic protons, in addition to a resonance at 7.67τ due to the methyl protons. As will be shown below, this kind of spectrum implies that all the p-tolyl groups present in the molecule are equivalent.

The infra-red spectra of these compounds (Appendix-I) were very similar and showed two terminal carbonyl stretching bands in approximately the same positions (Table 4.).

* by elemental analysis

** To=p-$CH_3C_6H_4$

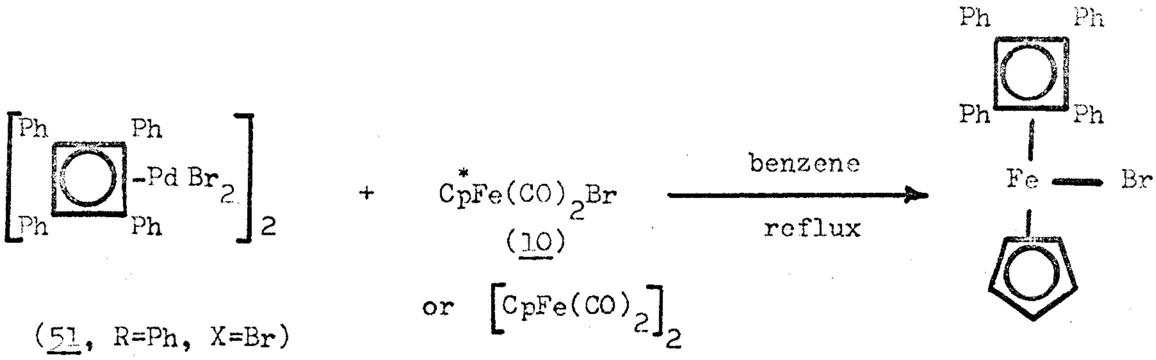
compound	ν_{co} cm^{-1}	medium
(75, R=Ph, X=Cl)	2062 2028	KBr disc
(75, R=Ph, X=Br)	2062 2028	KBr disc
(75, R=Ph, X=Br)	2060 2020	Benzene Solution
(75, R=Ph, X=I)	2062 2028	KBr disc
(75, R=Ph, X=I)	2055 2020	Benzene Solution
(75, R=To, X=Br)	2058 2022	KBr disc
(75, R=To, X=Br)	2055 2020	Benzene Solution

Table 4. Carbonyl stretching bands in the cyclobutadienecobalt dicarbonyl halides (75).

Further evidence for the structures of these complexes comes from their reactions discussed below. These bear a close resemblance to the reactions of cyclopentadienyliron dicarbonyl halides (10).

C. Cyclopentadienylation reactions

It was anticipated that on reaction of tetraphenylcyclobutadienepalladium bromide dimer (51, R=Ph, X=Br) with cyclopentadienyliron dicarbonyl bromide (10, X=Br) or with cyclopentadienyliron dicarbonyl dimer (17), transfer of cyclobutadiene from the palladium onto iron would occur to give (π-cyclopentadienyl)-(π-tetraphenylcyclobutadiene)-iron bromide (76), by analogy to the reaction of (51, R=Ph, X=Br) with the cyclopentadienyl-molybdenum or -tungsten tricarbonyl dimers (71, M=Mo,W).



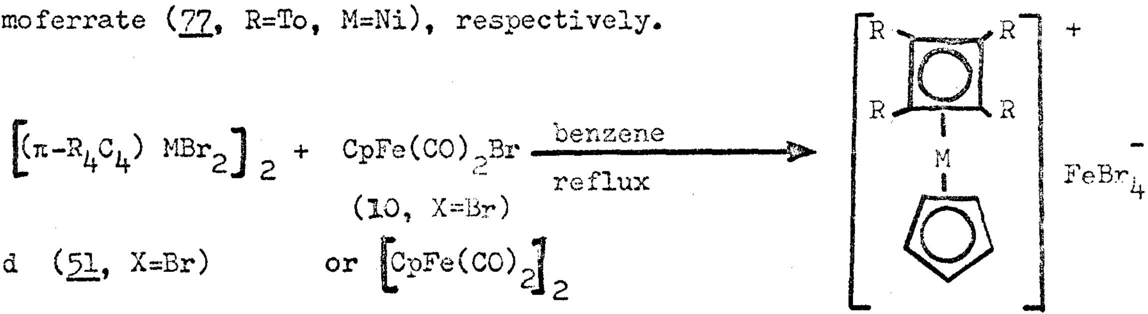
(51, R=Ph, X=Br) (10) (17) (76)

In fact, the reaction of (51, R=Ph, X=Br) with either (10, X=Br) or (17) in refluxing benzene gave [(π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)-palladium] tetrabromoferrate, (77, R=Ph, M=Pd), in high yield. The bromide (10, X=Br) gave a better yield than the dimer (17). A small amount of ferrocene (7) and iron metal were the only other products which were isolated from this reaction.

---

*Cp=C_5H_5

Tetraphenylcyclobutadienenickel bromide dimer (39, R=Ph, X=Br) underwent an analogous reaction to give [(π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)nickel] tetrabromoferrate (77, R=Ph, M=Ni). The tetrakis(p-tolyl)-cyclobutadienepalladium bromide dimer (51, R=To, X=Br) and tetrakis(p-tolyl)-cyclobutadienenickel bromide dimer (39, R=To, X=Br) underwent the same reactions to give [(π-cyclopentadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} palladium] tetrabromoferrate (77, R=To, M=Pd) and [(π-cyclopentadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} nickel] tetrabromoferrate (77, R=To, M=Ni), respectively.



M=Pd (51, X=Br)

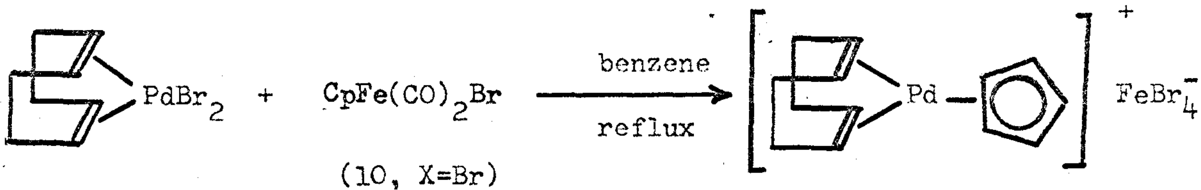
M=Ni (39, X=Br)

(10, X=Br)

(17)

(77)

(π-1.5-Cyclooctadiene)palladium bromide (12, X=Br) also reacted with either (10, X=Br) or (17) in refluxing benzene to give [(π-1.5-cyclooctadiene)-(π-cyclopentadienyl)-palladium] tetrabromoferrate (78), again in high yield.



(12, X=Br)

(10, X=Br)

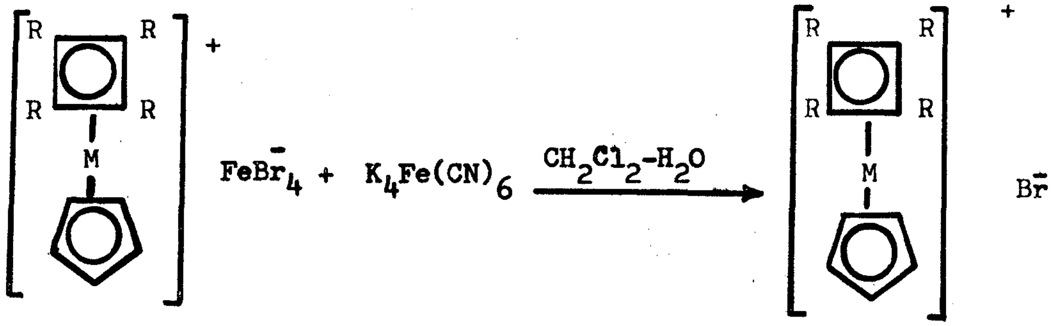
or $[CpFe(CO)_2]_2$

(17)

(78)

The tetrabromoferrates (77), and (78) were dark paramagnetic crystalline solids, (stable in air); magnetic susceptibility measurements on (77, R=Ph, M=Pd), (77, R=Ph, M=Ni) and (78) gave μ_{eff} 6.1, 5.4 and 5.9 B.M., respectively. This is close to that expected for tetrahedral Fe(III) (5.9 B.M.).

The tetrabromoferrates (77) were readily converted into the corresponding bromides (79) by reaction with potassium ferrocyanide in water-dichloromethane.



(77) (79)

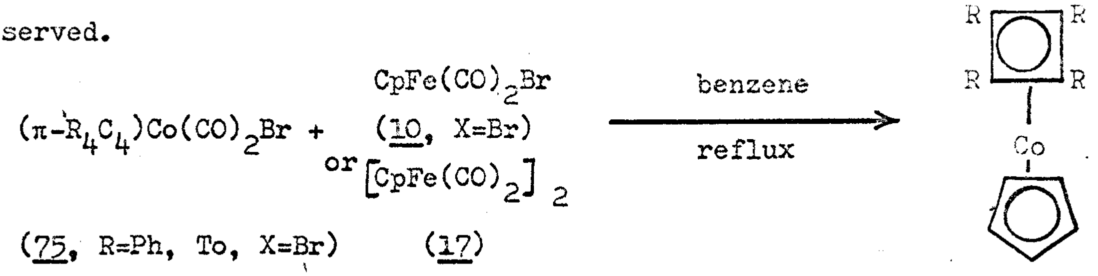
The H^1 N.M.R. spectra of (79, R=Ph, M=Pd) and (79, R=Ph, M=Ni) showed two sharp resonances attributed to the phenyl and cyclopentadienyl protons with the expected intensity ratio. Similarly, the H^1N.M.R. spectra of (79, R=To, M=Pd) and (79, R=To, M=Ni) showed a sharp AB quartet due to the aromatic protons, in addition to the cyclopentadienyl and methyl protons resonances, with the expected intensity ratio (Table 5.).

Compound					To		
number	M	R	C_5H_5(τ)	Ph(τ)	aromatic(AB)(τ)	CH_3(τ)	Intensity Ratio
(79)	Pd	Ph	3.66	2.39			1:4
(79)	Pd	To	3.95		2.55 2.68 2.78 2.91	7.65	5:16:12
(79)	Ni	Ph	4.22	2.39			1:4
(79)	Ni	To	4.38		2.50 2.63 2.75 2.89	7.64	5:16:12

Table 5. The H^1N.M.R. spectra of (π-cyclopentadienyl)(π-cyclobutadiene)-palladium and -nickel bromides (79, M=Pd, Ni).

Further confirmation of the structures of (79,R=Ph) was obtained from elemental analyses and infra-red spectra (Appendix -I). The infra-red spectra were identical to each other showing that the same organic ligands were present. Only very small differences existed between the infra-red spectra of (79, R=Ph) and (79, R=To).

This novel cyclopentadienylation reaction was also extended to organocobalt complexes. The reaction of (π-tetraphenylcyclobutadiene)-cobalt dicarbonyl bromide (75, R=Ph, X=Br) with either cyclopentadienyliron dicarbonyl bromide (10, X=Br) or cyclopentadienyliron dicarbonyl dimer (17) in refluxing benzene gave the known (π-cyclopentadienyl)(π-tetraphenyl-cyclobutadiene)-cobalt (48, R=Ph)[95,96,97] in high yield. Here, however, the dimer (17) gave a better yield than the bromide (10, X=Br). The H^1N.M.R. and infra-red spectra of this compound were identical to those of an authentic sample;[109] the identity was confirmed also by a mixed melting-point determination. The cobalt complex (48, R=To), obtained in an analogous reaction, was characterized by elemental analysis infra-red spectrum and H^1N.M.R. spectrum. The H^1N.M.R. spectrum of this compound (48, R=To) (Appendix-II) showed the typical AB quartet of the aromatic protons observed whenever four equivalent p-tolyl group are present. Singlets at 5.50τ and 7.87τ due to cyclopentadienyl and methyl protons were also observed.



(75, R=Ph, To, X=Br) (17)

(48)

The reactions involving transfer of the cyclopentadienyl ligand described above were performed on complexes already possessing a π-bonded ligand. The only case in which a cyclopentadienyl ligand was successfully transferred to a compound not already possessing a π-bonded ligand was in the reaction of titanium tetrachloride with (17) in refluxing xylene

$$[(\pi\text{-}C_5H_5)Fe(CO)_2]_2 + TiCl_4 \xrightarrow[\text{reflux}]{\text{xylene}} (\pi\text{-}C_5H_5)TiCl_3$$

(17) (80)

$$2(\underline{80}) + H_2O \longrightarrow [(\pi\text{-}C_5H_5)TiCl_2]_2O + 2HCl$$

(81)

$$n(\underline{81}) + nH_2O \longrightarrow 2[(\pi\text{-}C_5H_5)TiClO]_n + nH_2O$$

(82)

The first product of this reaction was probably π-cyclopentadienyltitanium trichloride (80), however, due to the ease with which this was hydrolysed via (81),[126] the product actually isolated was the cyclopentadienyltitanium oxychloride polymer (82). This complex (82) was obtained in 5% yield and was characterized by elemental analysis, melting-point, and infra-red spectrum.

II The Chemistry of Cyclobutadiene-Metal Complexes.

A. Cyclobutadiene-cobalt complexes.

The chemistry of (π-tetraphenylcyclobutadiene)cobalt dicarbonyl halides (75, R=Ph) reported in this thesis, showed many similarities to that of the cyclopentadienyliron dicarbonyl halides, (10), although some interesting differences have been observed. For example, the reaction of (75, R=Ph, X=Cl, Br) with triphenylphosphine in benzene at 25°C led to the replacement of one carbonyl group by one triphenylphosphine (Ph_3P) to give (π-tetraphenylcyclobutadiene)(triphenylphosphine)-cobalt carbonyl halides (83, X=Cl, Br). The iron complex (10, X=Cl) reacted less readily with Ph_3P; furthermore, on heating the reactants together in tetrahydrofuran (THF) the halide was replaced by Ph_3P to give [(π-cyclopentadienyl)(triphenylphosphine)iron dicarbonyl] chloride (84, X=Cl).[127] Irradiation (ultra-violet) of (10, X=I) and Ph_3P, however, led to the formation of (π-cyclopentadienyl)(triphenylphosphine) iron carbonyl iodide (85, X=I).[128] On refluxing (10, X=Cl, I) and Ph_3P in benzene, both products (84, X=Cl, I) and (85, X=Cl, I) were isolated.[154] The latter complexes were isoelectronic with those of (83, X=Cl, Br).

$$(\pi\text{-}Ph_4C_4)Co(CO)_2X + Ph_3P \xrightarrow[25^{\circ}C]{\text{benzene}} (\pi\text{-}Ph_4C_4)Co(CO)(Ph_3P)\,X$$

(75, R=Ph, X=Cl, Br) (83, X=Cl, Br)

$$(\pi\text{-}C_5H_5)Fe(CO)_2Cl + Ph_3P \xrightarrow[\text{reflux}]{\text{THF}} \left[(\pi\text{-}C_5H_5)Fe(CO)_2(Ph_3P)\right]^+ Cl^-$$

(10, X=Cl) (84, X=Cl)

$$(\pi\text{-}C_5H_5)Fe(CO)_2I + Ph_3P \xrightarrow[20^\circ C]{THF/h\nu} (\pi\text{-}C_5H_5)Fe(CO)(Ph_3P)I$$

(10, X=I) (85, X=I)

$$(\pi\text{-}C_5H_5)Fe(CO)_2X + Ph_3P \xrightarrow[reflux]{benzene} (84,\ X=Cl,\ I) + (85,\ X=Cl,\ I)$$

(10, X=Cl, I)

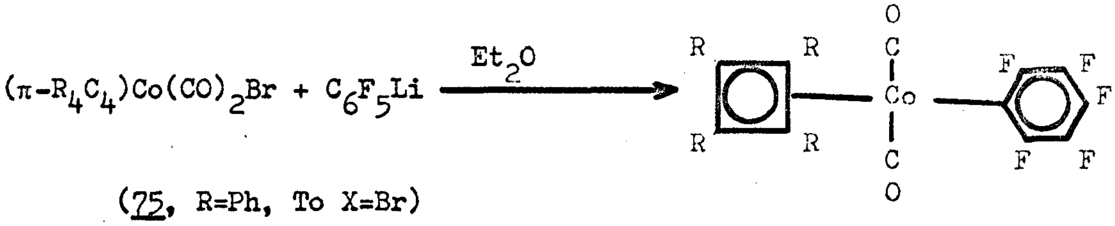
The cobalt complexes (83, X=Cl, Br) appeared to be reasonably air-stable in the solid, but were rapidly air-oxidized in solution. As obtained, the complexes (83, X=Cl, Br) appeared to be paramagnetic. After careful purification, however, the paramagnetism was reduced considerably, and it was possible to observe a solution H^1N.M.R. spectrum. This spectrum agreed with the proposed structure. As for the parent compound (75, R=Ph), it was assumed that this was also a diamagnetic complex of Co(I), since it obeyed the effective atomic number formalism.

In addition to the bands expected from the organic ligands, the infra-red spectra of (85, X=Cl, Br)(Appendix -I) showed a strong carbonyl band at 2000 cm^{-1}. This can be compared to the bands at 1960 and 1965 cm^{-1} found for (85, X=Cl) and (85, X=Br) respectively;[154] the decrease in ν_{co}, by comparison with (75), implies a higher Co-CO bond order in (83) than in (75). This is to be expected since it is known that Ph_3P is a poorer π-acceptor than CO, and, hence, replacement of one CO by Ph_3P must increase the back-donation from the metal onto the remaining carbonyl group.

By analogy to the reaction of cyclopentadienyliron dicarbonyl halide (10) with pentafluorophenyllithium, which gave (σ-pentafluorophenyl)-dicarbonyl-(π-cyclopentadienyl)iron (86);[129,130] the halogen in (75, R=Ph, X=Br) was replaced by reaction with pentafluorophenyllithium.

The latter reaction gave the very stable, yellow, crystalline, diamagnetic (σ-pentafluorophenyl)dicarbonyl(π-tetraphenylcyclobutadiene)cobalt (87, R=Ph)

(10, X=Br) (86)



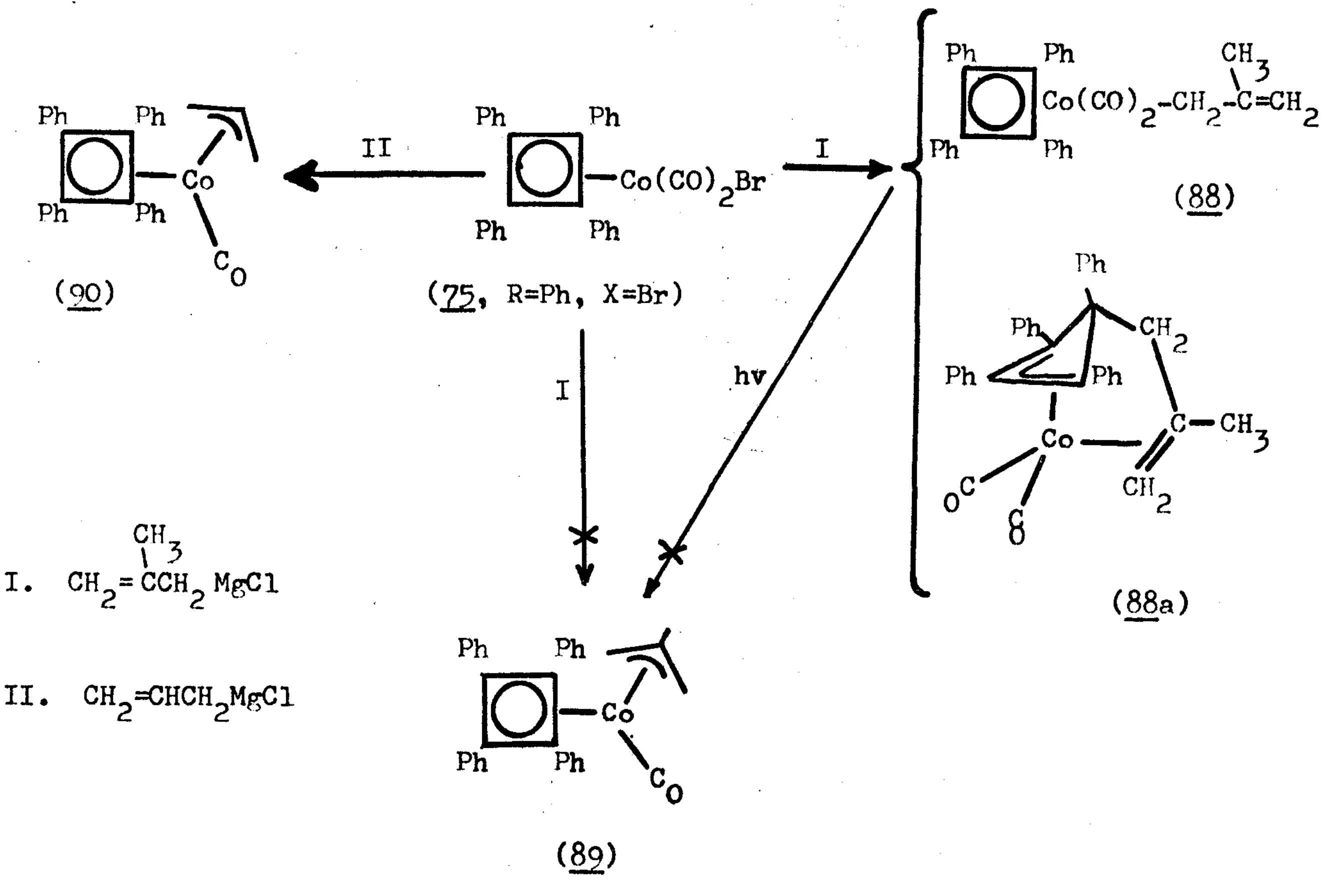
(75, R=Ph, To X=Br)

(87)

The structure of (87, R=Ph) was verified by elemental analysis, a molecular weight determination, infra-red spectrum and H^1 and F^{19} N.M.R. spectra. The latter showed the characteristically large low-field shift of the ortho-fluorines in the pentafluorophenyl group when bonded to a transition-metal. Similar large low-field shifts also were observed for the other σ-bonded pentafluorophenyl-metal complexes such as trans-bis(triethylphosphine) chloro(σ-pentafluorophenyl)palladium (1).[10] Additional confirmation that attack of the pentafluorophenyl group had indeed occurred on the metal, and not on the cyclobutadiene ring, was obtained from the H^1 N.M.R. spectrum of the p-tolyl analogue(87, R=To) (Appendix-II). This showed the AB quartet due to the aromatic protons, characteristic of molecules with all four p-tolyl group equivalent, and implied the presence of a cyclobutadiene ring. The infra-red spectra of (87) showed two strong terminal carbonyl bands at 2008 cm^{-1} and 2050 cm^{-1} for (87, R=Ph) (Appendix-I), and at 2010 cm^{-1} and 2050 cm^{-1} for (87, R=To). This can be compared to the strong bands at 2003 cm^{-1} and 2054 cm^{-1} found for (86).[130] As for the iron complexes (10) and (86), there appeared to be very little difference in ν_{co} between (87) and the halide complexes (75).

An attempt was made to synthesize carbonyl(π-methallyl)(π-tetraphenylcyclobutadiene)cobalt (89) by the reaction of methallylmagnesium chloride with (π-tetraphenylcyclobutadiene)cobalt dicarbonyl bromide (75, R=Ph, X=Br). The only product formed in this reaction was (σ-methallyl)(π-tetraphenylcyclobutadiene)dicarbonyl cobalt (88). The yellow-orange crystalline (σ-methallyl)cobalt complex (88) was characterized by elemental analysis, molecular weight determination, and infra-red spectrum; the latter showing two strong terminal carbonyl bands at 1976 cm^{-1} and 2028 cm^{-1} (Appendix-I). The complex (88) was extremely air-stable and all attempts to convert it into the (π-methallyl)cobalt complex (89) by refluxing in benzene or by ultra-violet irradiation failed. On the basis of the above data an alternative structure (88a) could be also considered. This structure (88a) would explain the inability to convert the σ-complex (88), either thermally or photochemically, to the π-complex (89). There are, however, two arguments against such a formulation: (i) it has been previously shown that nucleophilic attack on a cyclobutadiene-cobalt dicarbonyl halide (75) occurs at the metal (c.f. reaction with C_6F_5Li above), and (ii) when the attack does occur on the cyclobutadiene ring, the attacking group occupies the position exo—to the metal (see INTRODUCTION). At present, therefore, and in the absence of H^1N.M.R. data, due to the presence of an analytically* undetectable paramagnetic impurity, the structure of this complex is in doubt; since all other σ-allyl complexes are very readily transformed into π-allyl complexes (see INTRODUCTION).

Preparation of the analogous σ- or π-allyl complex also was attempted by the reaction of (75, R=Ph, X=Br) with allylmagnesium chloride. It was not possible to obtain a completely pure product, but examination of the infra-red spectrum of the crude product (Appendix-I) showed the presence of one ν_{co} at 1988 cm^{-1}, in contrast to that of the methallyl complex (88). This suggested that the product of the above reaction was (π-allyl)(π-tetraphenylcyclobutadiene)carbonyl cobalt (90). This conclusion was also supported by elemental analysis, and molecular weight determination.



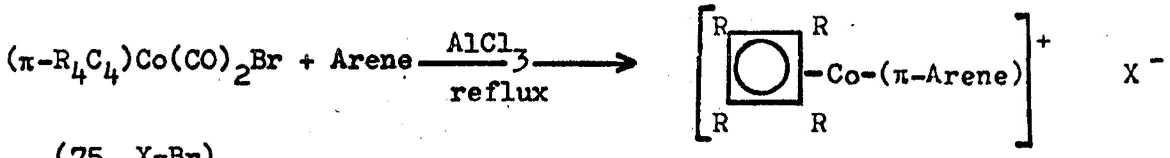
I. $CH_2=C(CH_3)CH_2MgCl$

II. $CH_2=CHCH_2MgCl$

---

* by elemental analysis

By analogy to the reaction of cyclopentadienyliron dicarbonyl halide (10) with benzene and aluminium chloride, which gave (π-benzene)(π-cyclopentadienyl)iron cation (15).[45,69] (see INTRODUCTION), (π-tetraphenylcyclobutadiene)cobalt dicarbonyl bromide (75, R=Ph, X=Br) readily underwent an aluminium chloride-catalyzed reaction with aromatic hydrocarbons. In this reaction two carbonyls and the bromide were replaced to give the cationic (π-arene)(π-tetraphenylcyclobutadiene)cobalt complexes (91). These cationic complexes (91), when treated with saturated aqueous KBr or NH_4PF_6, gave (91, R=Ph, X=Br) and (91, R=Ph, X=PF_6) respectively. These complexes were characterized by elemental analyses, and the infra-red spectra (Appendix-I). The H^1 N.M.R. spectra of (91, X=Br) all were in agreement with the postulated structures (Table 6.). The H^1 N.M.R. spectrum of the p-tolyl complex (91, R=To, Arene=benzene, X=Br) (Appendix-II) showed conclusively that the cyclobutadiene ring was still intact in these complexes.



(75, X=Br)

(91)

The presence of the (π-Arene)-cobalt system in these complexes was verified by the H^1 N.M.R. spectra of (91, R=Ph, Arene=benzene, X=Br) (91, R=Ph, Arene=p-xylene X=Br) and (91, R=Ph, Arene=mesitylene, X=Br). Each of these complexes showed a sharp singlet at 3.35τ, 3.48τ and 3.76τ, respectively, due to the aromatic protons on the π-bonded arenes. These values can be compared to the resonances at 2.63τ, 2.95τ and 3.22τ,

Compound				Ph(τ)	To		Arene	
number	R	X	arene		aromatic(τ)	CH_3(τ)	aromatic(τ)	others(τ)
(91)	To	Br	benzene		2.57 2.70 2.78 2.91	7.66	3.51	
(91)	Ph	Br	benzene	2.50			3.35	
(91)	Ph	Br	toluene	2.50			3.25[a] 3.50[a]	8.13(CH_3)
(91)	Ph	Br	p-xylene	2.52			3.48	8.18(CH_3)
(91)	Ph	Br	mesitylene	2.51			3.76	7.97(CH_3)
(91)	Ph	Br	n-butyl-benzene	2.59			3.36[a] 3.64[a]	8.05[a] 8.80[a] 9.28[a](^{n}Bu*)
(91)	Ph	Br	biphenyl	2.83[a]				

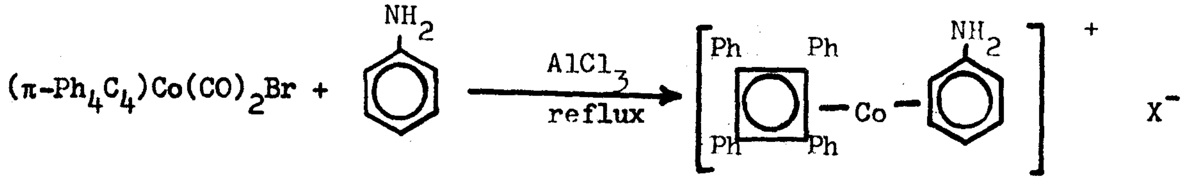
a unresolved multiplet

Table 6. The H^1 N.M.R. spectra of [(π-Arene)(π-cyclobutadiene)-cobalt] bromides (91).

*^{n}Bu = $CH_3CH_2CH_2CH_2$

observed for the same uncomplexed arenes, respectively. These typical upfield shifts of the π-bonded arenes protons may be attributed in part to the increase in the shielding on the aromatic protons, due to the decrease in the π-electron ring current resulting from the π-bond formation to the metal.[62b]

A very unusual compound, the (π-aniline)(π-tetraphenylcyclobutadiene)cobalt cation (92), was also obtained when the Friedel-Crafts reaction of (75, R=Ph, X=Br) with aniline was carried out in the presence of excess aluminium chloride. The aniline complex (92) was characterized as the bromide and hexafluorophosphate salts (92, X=Br, PF_6). The infrared spectrum (Nujol) of (92, X=PF_6) (Appendix-I) showed the presence of a free NH_2 group with νNH at 3390, 3497 cm^{-1}. A potentiometric titration of the aniline complex (92, X=Br) in 50% aqueous methanol with 0.1 N sodium hydroxide gave a pK_b value of 11.00 ± 0.10. Aniline under the same conditions had a measured pK_b of 9.50 ± 0.10, showing that the basicity of aniline was appreciably reduced in the complex.

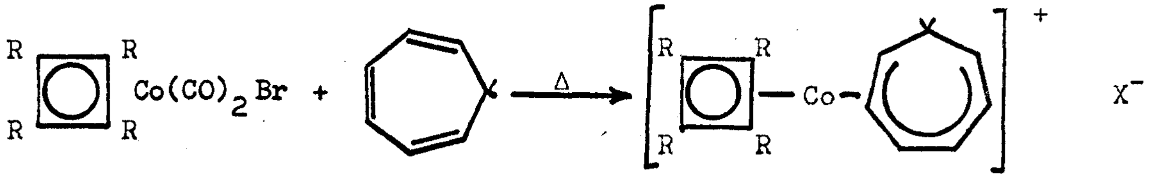


(75, R=Ph, X=Br)

(92)

The only other reported π-bonded aniline complex was the (π-aniline)-chromium tricarbonyl (21).[42,61,131] Potentiometric titration of (21) and aniline, under the same conditions, showed that the complex (21) was less basic than the free aniline by about 1.6 pK units.[42] A similar difference of 1.5 pK between (92, X=Br) and a free aniline molecule suggests that the (π-Ph_4C_4)-cobalt group has approximately the same electron - withdrawing effect as the $Cr(CO)_3$ group. Since the complex (92) bears a positive charge and might be expected to have a much greater tendency to lower the basicity of the aniline, this is somewhat suprising. One possible reason why this is not observed is that the positive charge is delocalized over the whole molecule and, hence, its net effect on the NH_2 will be small.

The cobalt complexes (75, R=Ph, X=Br) and (75, R=To, X=Br) reacted with cycloheptatriene on heating, in the absence of a catalyst, to give the cycloheptatriene complexes (93).



(75, X=Br)

(93)

The green complexes (93), as obtained, were not pure and could not be purified without decomposition. From the elemental analyses, the anions of these green complexes appeared to contain bromide (X=Br), together with varying amounts of $CoBr_2$ [1.1 moles for (93, R=Ph) and 1.5 moles for (93, R=To)] . The presence of this extra cobalt associated with the anion was verified by treatment of (93, R=Ph, X=Br•1.1 $CoBr_2$) with aqueous potassium thiocyanate, by which the complex (93, X=½ $Co(NCS)_4$, R=Ph) was obtained. This complex showed the presence of a single strong band due to a terminal NCS group at 2066 cm^{-1}; Sabatini and Bertini[132] quote a value of 2065 cm^{-1} for νNCS in $(Et_4N)_2Co(NCS)_4$. Treatment of the crude complexes (93, R=Ph, To) with aqueous KI or NH_4PF_6 gave the pure complexes (93, R=Ph, X=I,PF_6; 93, R=To, X=PF_6). Unfortunately, these complexes were too insoluble to permit the measurement of the H^1 N.M.R. spectra. Elemental analyses, infra-red spectra (Appendix-I), and chemical properties, however, were in agreement with the proposed structures, which were assigned, by analogy, with those of the π-arene complexes (91).

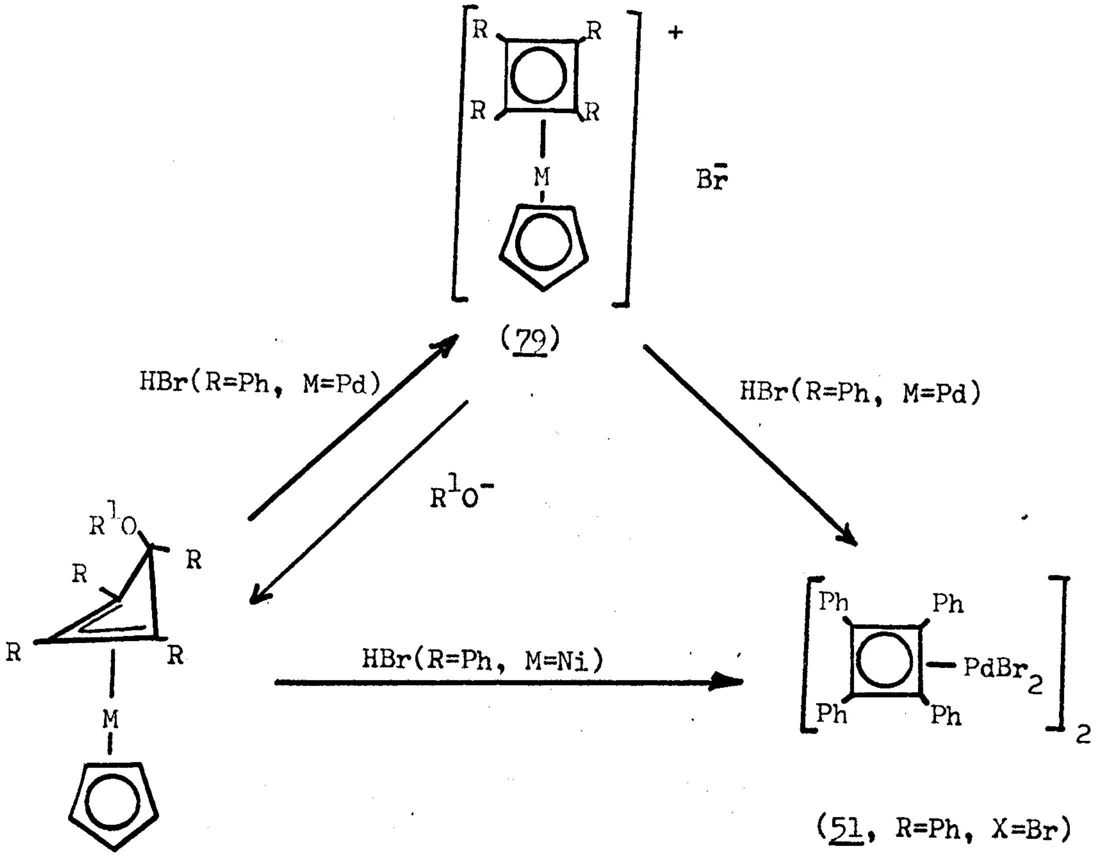
The complexes (91) and (93) were yellow, crystalline solids, insoluble in non-polar solvents and moderately soluble in polar solvents such as methanol-water mixtures. They were air-stable and, in most cases, thermally stable to over 150°C. Their melting and decomposition points depended on the anion present; the hexafluorophosphates having particularly high melting and decomposition temperatures.

B. Reactions of cyclobutadiene-metal complexes with nucleophiles

The addition of alkoxide to the cyclobutadiene ring in (79) was similar to the reaction already described by Chatt *et al*, in which dienepalladium (II)[40] and platinum (II)[133] halides underwent nucleophilic attack by alkoxide at an olefinic carbon. The [(π-cyclopentadienyl)-(π-tetraphenylcyclobutadiene)-metal] bromides (79, R=Ph, M=Pd, Ni) reacted with alkoxide to give the non-ionic (π-cyclopentadienyl)(π-exo-1-alkoxy-1.2.3.4-tetraphenylcyclobutenyl)-metal complexes (94, R=Ph, M=Ni, Pd). The structures of these complexes were assigned on the bases of elemental analyses, molecular weight determinations, infra-red spectra (Appendix I) and H^1 N.M.R. spectra (Table 7). The latter showed the presence of phenyl and methoxy groups (with the expected intensity ratios) and a sharp singlet, due to the cyclopentadienyl protons, confirming that addition to the cyclopentadienyl ring had not occurred. Additional confirmation that attack of the methoxide group had indeed occurred on the cyclobutadiene, not the cyclopentadiene ring, was obtained from the H^1 N.M.R. spectra of the p-tolyl analogues (94, R=To, R^1= Me, M=Pd, Ni) (Appendix-II). These spectra did not exhibit the sharp AB quartet in the aromatic proton region, which has been shown to be characteristic of four equivalent p-tolyl group. The p-tolyl groups are, therefore, no longer equivalent, as would be expected for a structure such as (94). Moreover, it has been shown by Games[134] that (π-exo-1-ethoxy-1.2.3.4-tetraphenylcyclobutenyl)-palladium chloride dimer (56, R=Ph, R^1=Et, X=Cl) could be converted into (94, R=Ph, R^1=Et, M=Pd) on treatment with sodium cyclopentadenide. This also established the stereochemistry of the complexes (94).

Compound			R^1 =			To		Intensity Ratio
number	M	R	$CH_3(\tau)$	$C_5H_5(\tau)$	Ph(τ)	aromatic(τ)	$CH_3(\tau)$	
(94)	Pd	Ph	6.58	4.55	2.26 2.63			3:5:20
(94)	Pd	To	6.71	4.65		2.40 2.52 2.60 2.96 3.08	7.76	3:5:16:12
(94)	Ni	Ph	6.70	5.10	2.40 2.80			3:5:20
(94)	Ni	To	6.82	5.20		2.52 2.61 2.68 2.99 3.09 3.11	7.75	3:5:16:12

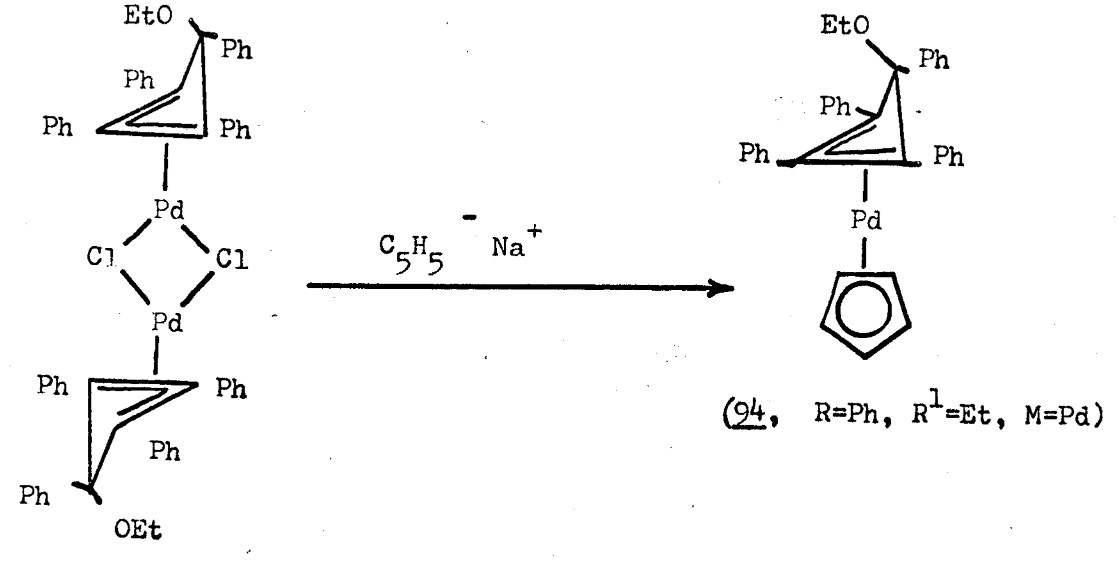
Table 7. The H^1 N.M.R. spectra of (π-cyclopentadienyl)(π-cyclobutenyl) -palladium and -nickel complexes (<u>94</u>, M=Pd, Ni).



($\underline{79}$)

($\underline{51}$, R=Ph, X=Br)

($\underline{94}$)

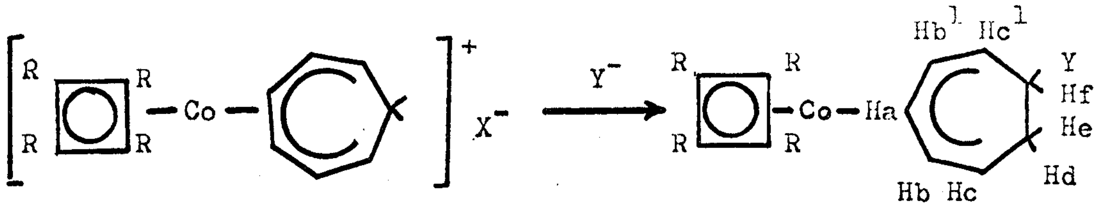


($\underline{94}$, R=Ph, R^1=Et, M=Pd)

($\underline{56}$, R=Ph, R^1=Et, X=Cl)

A similar reaction to the above was investigated by Criegee and Ludwig.[115,116] These workers treated tetramethylcyclobutadienenickel chloride dimer (39, R=CH_3 X=Cl) with sodium cyclopentadenide to give (π-cyclopentadienyl)-(π-1-exo-cyclopentadiene-1.2.3.4-tetramethylcyclobutenyl)nickel (65) (see INTRODUCTION). Here again, the attack of the nucleophile ($C_5H_5^-$) occurred at the cyclobutadiene ring exo-to the metal.[108]

The cationic (π-cycloheptatriene)(π-tetraphenylcyclobutadiene)-cobalt complexes (93, R=Ph) readily underwent nucleophilic attack by water (in the presence of triethylamine), methoxide, or borohydride to give the non-ionic(π-2-substituted-3.5-cycloheptadienyl)-(π-tetraphenylcyclobutadiene)cobalt complexes (95, R=Ph, Y=OH, OCH_3 and H).



(93) (95)

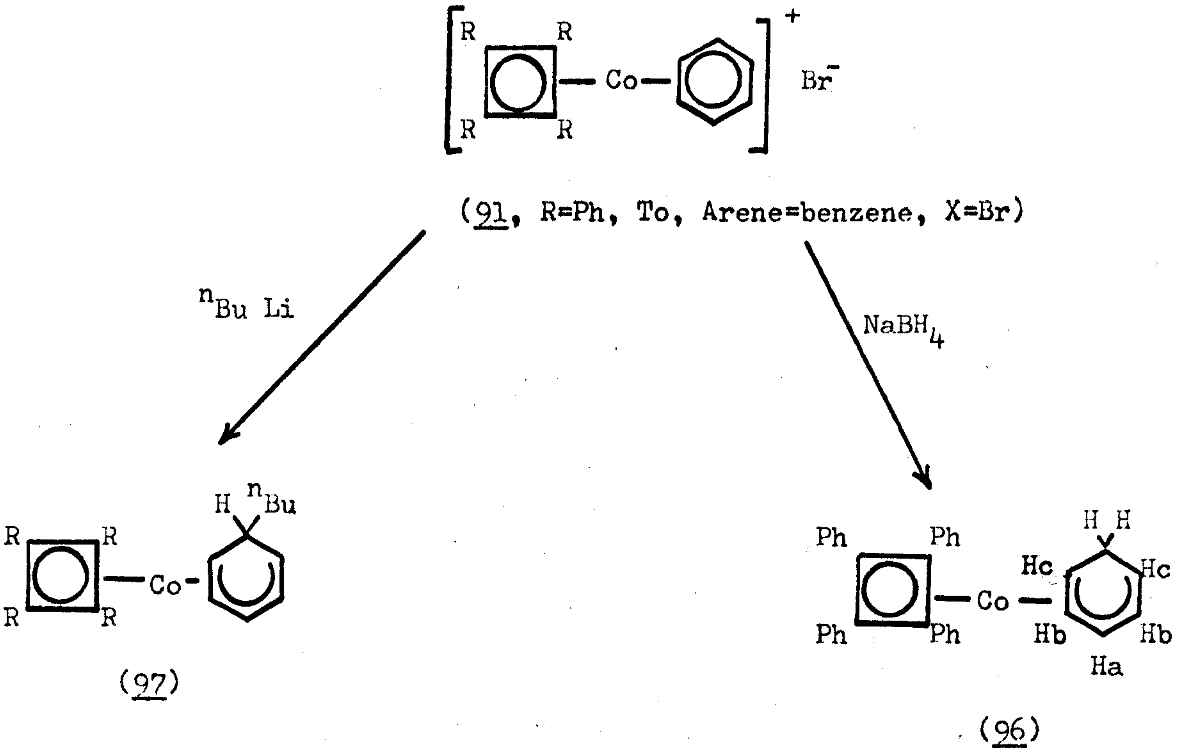
The H^1 N.M.R. spectrum of the p-tolyl complex (95, R=To, Y=OMe)(Appendix-II) showed an AB quartet in the aromatic proton region. This implies attack by the methoxide on the cycloheptatriene ring, and it was presumed to have occurred at one end of the triene giving (π-2-methoxy-3.5-cycloheptadienyl)-{π-tetrakis(p-tolyl)cyclobutadiene} cobalt (95, R=To, Y=OMe), with five of the seven carbon atoms coordinated to the cobalt. The H^1 N.M.R. spectrum of the cycloheptadienyl protons was extremely complex and not easily resolvable. For (95, R=Ph, Y=H), the pairs of protons Hb and H^1b, Hc and

H^1c, Hd and Hf, He and Y were equivalent and five multiplets centred at 4.2(Ha), 5.2(Hb), 6.0(Hc), 7.5($>CH_2$) and 8.5τ($>CH_2$) were observed. That at 4.2τ was just resolvable into a triplet, as expected for Ha. Due to the even lower symmetry of the cycloheptadienyl ring in (95, R=Ph, Y=Ome), the spectrum observed was more complex than that of (95, R=Ph, Y=H) since now Hb and H^1b, Hc and H^1c etc. were different; multiplets were found at 4.35(triplet, Ha), 5.20, 5.60, 6.30, 6.95, 7.90 and 8.80τ. These observations were in general agreement with the results reported for other π-2.4-cycloheptadienyl complexes.[41,135,136] Apart from the H^1 N.M.R. spectra, complexes (95) were also characterized by elemental analyses, molecular weight determinations and infra-red spectra (Appendix-I).

By contrast with the cycloheptatriene complexes (93), the π-benzene complexes (91) were inert to nucleophilic attack and could be recovered, even after reaction with potassium methoxide or methylmagnesium bromide. However, reaction of (91, R=Ph, Arene=benzene, X=Br) with sodium borohydride in aqueous methanol gave a 20% yield of (π-2.4-cyclohexadienyl)(π-tetraphenylcyclobutadiene)cobalt (96). This complex was characterized by elemental analysis, molecular weight measurement and spectra. The H^1 N.M.R. spectrum was particularly significant as it did not show the sharp singlet due to the π-complexed benzene, but instead showed five multiplets at 4.09(Ha), 5.40(Hb), 6.14(Hc), 7.68($>CH_2$), and 8.52τ($>CH_2$). These were assigned to the π-cyclohexadienyl protons. Due to the low solubility of the complex, these multiplets could not be resolved. However, the general form of the spectrum was similar to that reported for (π-2.4-cyclohexdienyl)manganese tricarbonyl (32) by Winkhaus and Wilkinson.[137,68]

The reaction of (<u>91</u>, R =Ph, To, Arene=benzene, X=Br) with n-butyllithium in hexane gave (π-1-butyl-2.4-cyclohexadienyl) complexes (<u>97</u>, R=Ph, To). The H^1 N.M.R. spectrum of the p-tolyl analogue (<u>97</u>, R=To) (Appendix-II) showed an AB quartet in the aromatic proton region and did not show the singlet due to the π-complexed benzene. This confirmed the conclusion that nucleophilic attack on (<u>91</u>, R=Ph, To, Arene=benzene, X=Br) occurred on the benzene rather than on the cyclobutadiene ring. Complexes (<u>97</u>, R=Ph, To) were also characterized by elemental analyses, molecular weight measurements and infra-red spectra (Appendix-I). The infra-red spectrum of (<u>96</u>) also showed the relatively intense and anomalously low C-H stretching frequency at 2762 cm^{-1}; this was absent in the (π-1-butyl-2.4-cyclohexadienyl) complexes (<u>97</u>, R=Ph, To). This is in agreement with the work of Wilkinson <u>et al</u>, who also reported a low νCH for cyclohexadienyl-manganese tricarbonyl (<u>32</u>)[68] and the absence of this band for the (π-1-phenyl-2.4-cyclohexadienyl)-manganese tricarbonyl (<u>33</u>).[69]

The results of X-ray structure determinations on the products obtained from nucleophilic attack on various π-complexed ring systems showed that the attacking group was exo-to the metal.[67,108,106,71,140,141,142] By analogy, the same was presumed to have occurred in the substituted cyclohexadienyl and cycloheptadienyl complexes described above. This argument, however, need not necessarily hold for the complexes (<u>96</u>) and (95, R=Ph, Y=H), since the reaction of (<u>91</u>, R=Ph) and (<u>93</u>, R=Ph) with borohydride may proceed via a cobalt-hydride, which then rearranges to give the products with the entering H now endo-to the metal. Wilkinson <u>et al</u>,[45,138,69,139] have given evidence for this type of process in other cases.



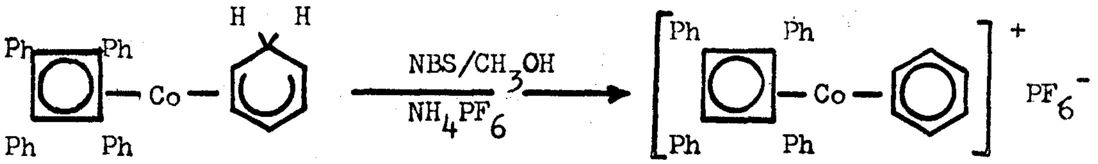
(91, R=Ph, To, Arene=benzene, X=Br)

(97)

(96)

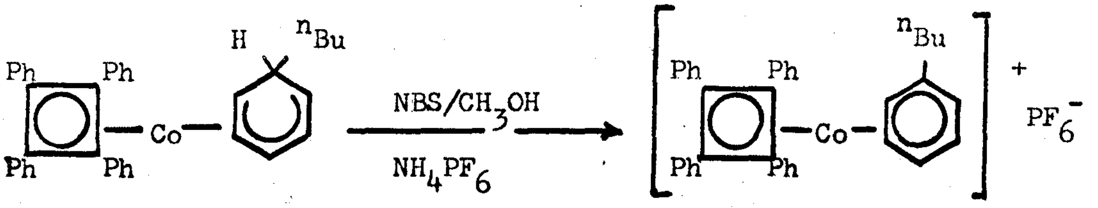
C Hydride abstraction reactions

A number of reagents have been used to effect hydride abstraction reactions including Ph_3C^+,[41,135] air in the presence of acid and H_2O_2 in acid solution.[65,143] Attempts to effect the reaction using the latter reagent on the cyclohexadienyl complexes (96) and (97, R=Ph) were not successful. The reaction of (96) and (97, R=Ph) with N-bromosuccinimide (NBS) in methanol, however, gave the cations (91), which were precipitated as the hexafluorophosphates (91, R=Ph, Arene=benzene, $X=PF_6$) and (91, R=Ph, Arene=butylbenzene, $X=PF_6$) in 82% and 63%, respectively. Both of these complexes were identified by comparison with authentic samples prepared directly from (75, R=Ph, X=Br) and benzene or n-butylbenzene.



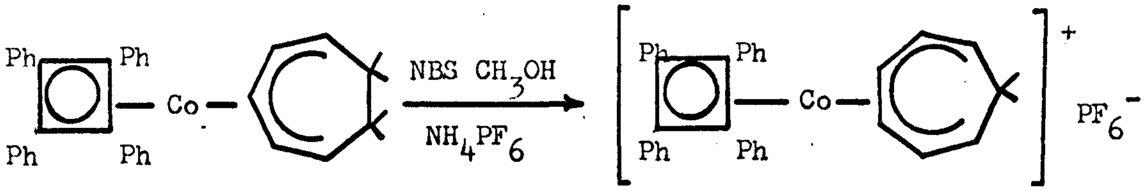
(96)

(91, R=Ph, Arene=benzene, $X=PF_6$)



(97, R=Ph) (91, R=Ph, Arene=butylbenzene, $X=PF_6$)

The hydride abstraction by N-bromosuccinimide in methanol was also used to reconvert the cycloheptadienyl complex (95, R=Ph, Y=H) to the cycloheptatriene complex (93, R=Ph), isolated as the hexafluorophosphate in 18% yield. This was identical to a sample prepared directly from the reaction of cycloheptatriene complex (93, R=Ph, X=Br•1.1 $CoBr_2$) with ammonium hexafluorophosphate.



(95, R=Ph, X=H) (93, R=Ph, X=PF_6)

As was evident from the much poorer yield of the cycloheptatriene complex (93, R=Ph, X=PF_6) compared to that of (91, R=Ph, Arene=benzene, X=PF_6) and (91, R=Ph, Arene=n-butylbenzene, X=PF_6) complexes, the use of N-bromosuccinimide in methanol is likely to be of synthetic use only when the product is sufficiently stable.

III Conclusions

The ligand-transfer reactions between cyclopentadienyl-metal complexes [such as (10, X=Br), (17) and (71, M=Mo, W)] and cyclobutadiene-metal complexes [such as (51, R=Ph, To, X=Br), (39, R=Ph, To, X=Br) and (75, R=Ph, To, X=Br)] were studied. It was found that these reactions can follow one of two paths: (i) the cyclobutadiene group can be transferred from palladium onto other metals such as molybdenum or tungsten; or (ii) the cyclopentadienyl group can be transferred from iron onto palladium, nickel, cobalt, and titanium. The particular path taken by a system will depend on the relative strengths of the metal-ring bonds, amongst other factors, and it may be possible to use this as a qualitative measure of the strengths of these bonds. The results described in this thesis suggest that the (π-C_5H_5)-Fe bond, as found in (17) and (10, X=Br), appears to be weaker (i.e., the cyclopentadienyl ligand is more susceptible to transfer onto other metals) compared with that of (π-C_5H_5)-M in (71, M=Mo,W).

The (π-tetraphenylcyclobutadiene)cobalt dicarbonyl iodide (75, R=Ph, X=I) showed two strong terminal carbonyl stretching bands at 2020 cm^{-1} and 2055 cm^{-1}, slightly higher than those in cyclopentadienyliron dicarbonyl iodide (10, X=I) at 2000 cm^{-1} and 2044 cm^{-1}.[144] A direct comparison is not strictly valid since the metals, their oxidation states and the d electron configurations of the metals are different. However, since the iron in (10, X=I) is formally in the +2(d^6) state, whereas the cobalt in (75, R=Ph, X=I) is formally in the +1(d^8) state, a greater degree of back-bonding from the metal to the carbonyl would be expected for the cobalt complex than for the iron. This implies a stronger Co-CO bond and, hence, a lower ν_{CO} in (75, R=Ph, X=I) than in (10, X=I). Since the opposite is found, this means that the cobalt is bonded very strongly elsewhere, namely, to the cyclobutadiene ring. This conclusion is in agreement with the prediction of Longuet-Higgins and Orgel[87] that a metal-cyclobutadiene bond is likely to be stronger than a metal-cyclopentadienyl bond.

Information regarding the relative cyclopentadienyl- and cyclobutadiene-metal bond strengths was also obtained from the reactions of the [(π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)palladium] bromide (83, R=Ph, M=Pd) and (π-cyclopentadienyl)(π-exo-1-methoxy-1.2.3.4-tetraphenylcyclobutenyl)palladium (95, R=Ph, R^1=CH_3, M=Pd) with hydrogen bromide. Each of these reactions gave tetraphenylcyclobutadienepalladium bromide dimer (54, R=Ph, X=Br). In contrast, the analogous nickel complex (95, R=Ph, R^1=CH_3, M=Ni) gave only (83, R=Ph, M=Ni) under the same conditions. These results suggest that the cyclopentadienyl-nickel bond may be stronger than the cyclopentadienyl-palladium bond. This might explain why only few cyclopentadienyl-palladium complexes are known compared to the many cyclopentadienyl-nickel complexes. Furthermore, the palladium-cyclopentadienyl, and not the palladium-cyclobutadiene bond, was broken. This provides a dramatic illustration of the stability of some cyclobutadiene complexes, and also supports the suggestion of Longuet-Higgins[87] and Orgel that, since the cyclobutadiene-metal π-bond involves two electrons while the cyclopentadiene-metal π-bond involves only one, the former should be stronger.

The ease with which nucleophilic attack on the cycloheptatriene complexes $[(\pi\text{-}R_4C_4)Co(\pi\text{-}C_7H_8)]^+$, (93) occurred was not suprising since addition to one end of the conjugated triene, which was presumed to have happened in this reaction, is a favourable process. Similarly, the inertness of the benzene complexes $\left[(\pi\text{-}R_4C_4)Co(\pi\text{-}C_6H_6)\right]^+$, (91, Arene= benzene, X=Br) to nucleophiles was not unexpected; however, the direction of attack, namely the attack on the π-benzene rather than on the π-tetraphenylcyclobutadiene was unexpected, particularly in view of the ease with which the isoelectronic Ni(II) and Pd(II) complexes $\left[(\pi\text{-}R_4C_4)M(\pi\text{-}C_5H_5)\right]^+Br^-$ (79, M=Ni, Pd) were attacked by alkoxide ion on the cyclobutadiene ring. This suggests that the order of reactivity of π-complexed organic ligands (on d^8 metal ions) towards nucleophiles is:

cycloheptatriene > benzene > tetraphenylcyclobutadiene > cyclopentadienyl,

the last ligand being the most stable. Confirmation of this order is provided by the observation (i) of Wilkinson et al,[45,138] that the (π-benzene)(π-cyclopentadienyl)iron cation (15) undergoes attack on the benzene to give the (π-cyclohexadienyl)(π-cyclopentadienyl)iron and (ii) of Fischer and Kohl[145] that borohydride attack on $\left[(C_5H_5)W(C_6H_6)(CO)\right]^+ PF_6^-$ occurs on the π-complexed benzene ring as well as on the metal. Green et al[146,147] have also shown that cations such as $\left[(C_5H_5)Fe(CO)_2(C_2H_4)\right]^+$ and $\left[(C_5H_5)Mo(CO)_3(C_2H_4)\right]^+$ are attacked at the π-ethylene, giving the σ-ethyl compounds, which indicates again that the cyclopentadienyl ligand is by far the least reactive.

The basicity of the π-bonded aniline in (92, X=Br) is found to be 1.5 pK units higher than that of the free aniline. This difference can be explained by a decrease in the electron density on the aromatic ring of π-bonded aniline.

EXPERIMENTAL

EXPERIMENTAL

Melting-points: These were obtained using a Thomas Hoover capillary melting-point apparatus and are uncorrected. Melting-points of all organometallic compounds were measured in sealed capillaries evacuated to about 1.0 mm pressure. Melting-points above 250°C were determined on an electrically heated air bath apparatus.

Molecular weight measurements: These were made on a vapour pressure osmometer (Mechroleb Inc., Model 301 A) in chloroform.

Infra-red spectra: These were recorded as potassium bromide discs (unless otherwise stated) on a Beckman I.R. 5 or Beckman I.R. 10 spectrometer.

Nuclear magnetic resonance spectra: High-resolution F^{19} spectra were obtained at 56.445 MC/S and H^1 spectra at 60.000 MC/S on a Varian Associates D.P. 60, N.M.R. spectrometer. H^1 N.M.R. spectra were also obtained on a Varian A 60 spectrometer. N.M.R. spectra were taken in deuterochloroform, unless otherwise stated.

Magnetic measurements: These were made at temperatures as specified by Dr. B. J. Marshall of the Texas Technological College.

Solvents: Light petroleum used was the fraction collected over the range 30 - 60°C. Ligroin used was the fraction collected over the range 65 - 110°C. Ether*, tetrahydrofuran (both freshly distilled), benzene and n-hexane were dried over sodium metal. Methylene chloride, chloroform and cyclohexane were dried over anhydrous sodium sulphate. All other solvents used such as methanol, ethanol, n-octane, toluene, p-xylene,

* Ether = Et_2O

mesitylene, etc., were analytical grade reagents.

Chromatography: Chromatographic columns were made up of silica-gel (28-200 Mesh), Florisil (60-100 Mesh) or alumina (80-200 Mesh). All column materials were supplied by the Fisher Scientific Company.

Procedure: All reactions described here were carried out under a nitrogen atmosphere.

Reagents:

1. Tetraphenylcyclobutadienepalladium halide dimers were prepared by the method of Maitlis and Games.[107]
2. Cyclopentadienylmolybdenum tricarbonyl dimer was prepared from molybdenum hexacarbonyl and dicyclopentadiene by the method of Hayter.[148]
3. Benzenemolybdenum tricarbonyl was prepared by the method of Strohmeier.[149]
4. pp'-Ditolylacetylene was prepared by the method of Coleman, Holst and Maxwell.[150]
5. Bis(tri-n-butylphosphine)nickel bromide was prepared by the method of Jensen.[151]
6. Cyclopentadienyliron dicarbonyl dimer was prepared by the method developed by King and Stone.[48]
7. Cyclopentadienyliron dicarbonyl bromide was prepared by the method of Hallam and Pauson.[152]
8. 1.5-Cyclooctadienepalladium bromide was prepared by the method of Chatt, Vallarino and Venanzi.[40]

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

Page	Compound or Reaction
95	(π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)molybdenum carbonyl chloride (72, M=Mo, X=Cl).
96	(π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)molybdenum carbonyl bromide (72, M=Mo, X=Br).
97	(π-tetraphenylcyclobutadiene)molybdenum tricarbonyl bromide dimer (57).
97	cyclopentadienyltungsten tricarbonyl dimer (71, M=W).
98	(π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)tungsten carbonyl bromide (72, M=W, X=Br)
98	tetrakis(p-tolyl)cyclobutadienepalladium bromide dimer (51, R=To, X=Br).
99	tetrakis(p-tolyl)cyclobutadienenickel bromide dimer (39, R=To, X=Br).
100	[(π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)palladium] tetrabromoferrate (77, R=Ph, M=Pd).
101	[(π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)nickel] tetrabromoferrate (77, R=Ph, M=Ni).
102	[(π-cyclopentadienyl){π-tetrakis(p-tolyl)cyclobutadiene}palladium] tetrabromoferrate (77, R=To, M=Pd).

Page	Compound or Reaction
102	[(π-cyclopentadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} nickel] tetrabromoferrate (77, R=To, M=Ni).
103	[(π-1.5-cyclooctadiene)(π-cyclopentadienyl)palladium] tetrabromoferrate (78).
104	[(π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)palladium] bromide (79, R=Ph, M=Pd).
105	[(π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)nickel] bromide (79, R=Ph, M=Ni).
105	[(π-cyclopentadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} palladium] bromide (79, R=To, M=Pd)
107	[(π-cyclopentadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} nickel] bromide (79, R=To, M=Ni).
107	(π-cyclopentadienyl){π-(4-exo-methoxy-1.2.3.4-tetraphenylcyclobutenyl.)} palladium (94, R=Ph, R^1=CH$_3$, M=Pd).
108	(π-cyclopentadienyl) {π-(4-exo-methoxy-1.2.3.4-tetraphenylcyclobutenyl)} nickel (94, R=Ph, R^1=CH$_3$, M=Ni).
109	(π-cyclopentadienyl){π-(4-exo-methoxy-1.2.3.4-tetrakis(p-tolyl) cyclobutenyl)} palladium (94, R=To, R^1=CH$_3$, M=Pd).
109	(π-cyclopentadienyl){π-(4-exo-methoxy-1.2.3.4-tetrakis(p-tolyl) cyclobutenyl)} nickel (94, R=To, R^1=CH$_3$, M=Ni).
110	Reaction of (94, R=Ph, R^1=CH$_3$, M=Pd) with HBr.
111	(π-tetraphenylcyclobutadiene)cobalt dicarbonyl bromide (75, R=Ph, X=Br).

Page	Compound or Reaction
112	(π-tetraphenylcyclobutadiene)cobalt dicarbonyl chloride (75, R=Ph,X=Cl).
112	(π-tetraphenylcyclobutadiene)cobalt dicarbonyl iodide (75, R=Ph, X=I).
113	{π-tetrakis(p-tolyl)cyclobutadiene} cobalt dicarbonyl bromide (75, R=To, X=Br)
113	(π-tetraphenylcyclobutadiene)(triphenylphosphine)cobalt carbonyl bromide (83, X=Br).
114	(π-tetraphenylcyclobutadiene)(triphenylphosphine)cobalt carbonyl chloride (83, X=Cl).
115	(π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)cobalt (48, R=Ph).
115	(π-cyclopentadienyl {π-tetrakis(p-tolyl)cyclobutadiene}cobalt (48,R=To).
116	(σ-pentafluorophenyl)dicarbonyl(π-tetraphenylcyclobutadiene)cobalt (87, R=Ph).
117	(σ-pentafluorophenyl)dicarbonyl {π-tetrakis(p-tolyl)cyclobutadiene} cobalt (87, R=To)
118	[(π-benzene)(π-tetraphenylcyclobutadiene)cobalt] bromide (91, R=Ph, Arene=benzene, X=Br).
119	[(π-benzene)(π-tetraphenylcyclobutadiene)cobalt] hexafluorophosphate (91, R=Ph, Arene=benzene, X=PF_6).
119	[(π-benzene) {π-tetrakis(p-tolyl)cyclobutadiene}cobalt] bromide (91, R=To, Arene=benzene, X=Br).
120	[(π-toluene)(π-tetraphenylcyclobutadiene)cobalt] bromide (91, R=Ph, Arene=toluene, X=Br).

Page	Compound or Reaction
121	[(π-p-xylene)(π-tetraphenylcyclobutadiene)cobalt] bromide (91, R=Ph, Arene=p-xylene, X=Br).
121	[(π-mesitylene)(π-tetraphenylcyclobutadiene)cobalt] bromide (91, R=Ph, Arene=mesitylene, X=Br).
122	[(π-biphenyl)(π-tetraphenylcyclobutadiene)cobalt] bromide (91, R=Ph, Arene=biphenyl, X=Br).
123	[(π-n-butylbenzene)(π-tetraphenylcyclobutadiene)cobalt] bromide (91, R=Ph, Arene=n-butylbenzene, X=Br).
123	[(π-n-butylbenzene)(π-tetraphenylcyclobutadiene)cobalt] hexafluorophosphate (91, R=Ph, Arene=n-butylbenzene, $X=PF_6$).
124	(π-2.4-cyclohexadienyl)(π-tetraphenylcyclobutadiene)cobalt (96).
124	Conversion of the (96) into the (91, R=Ph, Arene=benzene, $X=PF_6$).
125	(π-1-n-butyl-2.4-cyclohexadienyl)(π-tetraphenylcyclobutadiene)-cobalt (97, R=Ph).
126	(π-1-n-butyl-2.4-cyclohexadienyl){π-tetrakis(p-tolyl)cyclobutadiene}cobalt (97, R=To).
127	Conversion of the (97, R=Ph) into the (91, R=Ph, Arene = n-butylbenzene, $X=PF_6$).
127	[(π-aniline)(π-tetraphenylcyclobutadiene)cobalt] bromide (92, X=Br).
128	[(π-aniline)(π-tetraphenylcyclobutadiene)cobalt] hexafluorophosphate (92, $X=PF_6$).
128	potentiometric pKa measurements on (92, X=Br) in (50%) aqueous methanol.

Page	Compound or Reaction
130	[(π-cycloheptatriene)(π-tetraphenylcyclobutadiene)cobalt] bromide•1.1 cobaltous bromide (93, R=Ph, X=Br•1.1 $CoBr_2$)
130	[(π-cycloheptatriene)(π-tetraphenylcyclobutadiene)cobalt] iodide (93, R=Ph, X=I).
131	[(π-cycloheptatriene)(π-tetraphenylcyclobutadiene)cobalt] hexafluorophosphate (93, R=Ph, X=PF_6).
132	[(π-cycloheptatriene)(π-tetraphenylcyclobutadiene)cobalt] tetrathiocyanatocobaltat (93, R=Ph, X=$\frac{1}{2}Co(NCS)_4$).
132	[(π-cycloheptatriene) {π-tetrakis(p-tolyl)cyclobutadiene} cobalt] bromide•1.5 cobaltous bromide (93, R=To, X=Br•1.5 $CoBr_2$)
133	[(π-cycloheptatriene) {π-tetrakis(p-tolyl)cyclobutadiene} cobalt] hexafluorophosphate (93, R=To, X=PF_6).
133	(π-3.5-cycloheptadienyl)(π-tetraphenylcyclobutadiene)cobalt (95, R=Ph, Y=H).
134	Conversion of the (95, R=Ph, Y=H) into the (93, R=Ph, X=PF_6).
135	(π-2-hydroxy-3.5-cycloheptadienyl)(π-tetraphenylcyclobutadiene) cobalt (95, R=Ph, Y=OH).
135	(π-2-methoxy-3.5-cycloheptadienyl)(π-tetraphenylcyclobutadiene) cobalt (95, R=Ph, Y=OCH_3).
136	(π-2-methoxy-3.5-cycloheptadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} cobalt (95, R=To, Y=OCH_3).
137	Attempted synthesis of (π-allyl)(π-tetraphenylcyclobutadiene) carbonyl cobalt (90).

Page	Compound or Reaction
137	Attempted synthesis of (σ-methallyl)(π-tetraphenylcyclobutadiene) dicarbonyl cobalt (88).

(π-Cyclopentadienyl)(π-tetraphenylcyclobutadiene)molybdenum carbonyl chloride.

(72, M=Mo, X=Cl)

Method A: A suspension of 1.0 g(0.98 mmole) of tetraphenylcyclobutadienepalladium chloride dimer and 0.75 g(1.5 mmoles) of cyclopentadienylmolybdenum tricarbonyl dimer were refluxed in 50 ml xylene with vigorous stirring for ten minutes. The reaction mixture was then filtered and the filtrate chromatographed on Florisil. A small amount of the initial molybdenum dimer complex was eluted in benzene-xylene and was completely removed with dichloromethane and benzene. Finally, a red band was eluted in ether, yielding a red solution. The solvent was removed on a rotary evaporator at 25°C, and ligroin was added to give red-brown crystals of (π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)molybdenum carbonyl chloride, m.p.261-266°C(decomp.). Yield, 0.20 g, 18% based on the starting palladium complex.

Analysis. Found: C,70.16; H,4.52; Cl,6.34; Mo,16.43 O,3.12; mol. wt. 619. Calculated for $C_{34}H_{25}ClMoO$: C,70.28; H,4.34; Cl,6.10; Mo,16.51 O,2.75; mol. wt. 581.

The compound, in CCl_4 solution, had νco 1973 cm^{-1} (Appendix-I) and the H^1 N.M.R. showed two resonances at 2.68τ and 4.55τ, with an intensity ratio of 20:5 due to the phenyl and cyclopentadienyl protons, respectively.

Method B: A suspension of 2.7 g (2.5 mmoles) of tetraphenylcyclobutadienepalladium chloride dimer and 1.5 g (3.0 mmoles) of cyclopentadienylmolybdenum tricarbonyl dimer were refluxed in 200 ml benzene for 50 hours (with stirring). The hot reaction mixture was filtered, the filtrate evaporated to 40 ml and then chromatographed on alumina. The desired molybdenum product (72, M=Mo, X=Cl) was eluted in ether. Yield, 0.16 g, 6.0% based on the strating palladium complex. The melting-point and infra-red spectrum (Appendix-I) were identical to those of the compound obtained by Method A.

(π-Cyclopentadienyl)(π-tetraphenylcyclobutadiene)molybdenum carbonyl bromide

(72, M=Mo, X=Br)

Method A: A suspension of 1.0 g(0.83 mmole) of tetraphenylcyclobutadienepalladium bromide dimer and 1.0 g(2.0 mmoles) of cyclopentadienylmolybdenum tricarbonyl dimer was refluxed in 40 ml xylene for 35 minutes. The red-brown crystalline product (π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)-molybdenum carbonyl bromide, m.p.248-250°C(decomp.), was separated from the reaction mixture, as previously described for the chloride complex (72, M=Mo, X=Cl) under Method A. Yield, 0.080 g, 8.0% based on the starting palladium complex.

Analysis. Found: C,65.06; H,4.20; mol.wt. 620. Calculated for $C_{34}H_{25}BrMoO$: C,65.29: H,4.03; mol.wt. 625. The infra-red spectrum (Appendix-I) was identical to that for the chloride (72, M=Mo, X=Cl) and showed ν_{co} at 1998 cm^{-1} (KBr disc)

Method B: A suspension of 2.0 g (1.6 mmoles) of tetraphenylcyclobutadienepalladium bromide dimer and 1.0 g (2.0 mmoles) of cyclopentadienylmolybdenum tricarbonyl dimer were refluxed in 150 ml benzene for 45 hours. The red-brown product (72, M=Mo, X=Br), identical to that mentioned above, was separated from the reaction mixture as previously described for the chloride (72, M=Mo, X=Cl) under Method B. Yield, 0.090 g, 5.0% based on the starting palladium complex. The melting-point and infra-red spectrum (Appendix-I) were identical to those of the compound obtained by Method A.

(π-Tetraphenylcyclobutadiene)molybdenum tricarbonyl bromide dimer (57)

A suspension of 0.49 g (0.40 mmole) tetraphenylcyclobutadiene-palladium bromide dimer and of 0.54 g (2.1 mmoles) of benzenemolybdenum tricarbonyl was refluxed and stirred in 30 ml benzene for 15 hours. The hot reaction mixture was filtered and the filtrate was then chromatographed on alumina. The product, (π-tetraphenylcyclobutadiene)molybdenum tricarbonyl bromide dimer, m.p. 278-280°C (Lit.280°C[110]), was eluted from the column with light petroleum-benzene (1:1 V/V) as a red solution, and was crystallized from benzene-cyclohexane mixture. Yield, 0.070 g, 14% based on the starting palladium complex. The infra-red spectrum (Appendix-I) was identical to that of the authentic sample.

Cyclopentadienyltungsten tricarbonyl dimer (71, M=W)

A solution of 11.0 g (31.2 mmoles) of tungsten hexacarbonyl in 40 ml dicyclopentadiene and 60 ml triglyme, was stirred and refluxed for 3 hours. On cooling cyclopentadienyltungsten tricarbonyl dimer, m.p. 240-245°C(Lit. 240-242°C) crystallized from the reaction mixture, yield, 6.0 g, 60% based on tungsten hexacarbonyl. The infra-red spectrum was identical with that reported in the literature. To overcome the sublimation of tungsten hexacarbonyl out of the reaction vessel, the condenser was fitted with a glass rod connected to a mechanical stirrer from above. This caused the sublimed material, which tended to block the lower part of the condenser, to fall back into the reaction mixture.

(π-Cyclopentadienyl)(π-tetraphenylcyclobutadiene)tungsten carbonyl bromide (72, M=W, X=Br)

A suspension of 2.0 g (1.6 mmoles) of tetraphenylcyclobutadienepalladium bromide dimer and 1.0 g (1.5 mmoles) of cyclopentadienyltungsten tricarbonyl dimer was refluxed and stirred in 200 ml benzene for 43 hours. The orange-yellow crystalline product (π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)tungsten carbonyl bromide, m.p. 227-228°C(decomp.), was separated from the reaction mixture as previously mentioned for the molybdenum chloride complex, (72, M=Mo, X=Cl), under Method B. Yield, 0.015 g, 0.70% based on the starting palladium.

Analysis. Found: C,57.35; H,3.80; mol. wt. 700. Calculated for $C_{34}H_{25}BrOW$: C,57.20; H,3.54; mol.wt. 713.

The infra-red spectrum (Appendix-I) was similar to those of the molybdenum complexes (72, M=Mo, X=Cl, Br) above with νCO at 1958 cm^{-1} (KBr disc).

Tetrakis(p-tolyl)cyclobutadienepalladium bromide dimer (51, R=To, X=Br)

A solution of 8.00 g (136 mmoles) of sodium chloride and 6.00 g (33.8 mmoles) of palladium chloride in 30 ml of hot water was cooled to 25°C, and then filtered into a solution of 20.0 g (96.0 mmoles) of pp'-ditolylacetylene in 500 of ethanol (95%). The reaction mixture was stirred at 25°C for two hours, then filtered to give yellow-brown crystals, 18.0 g (15.0 mmoles) of crude di-μ-chloro-di{π-(endo-4-ethoxy-1.2.3.4-tetrakis(p-tolyl)cyclobutenyl)palladium} (55, R=To, R^1=Et). Yield, 89.0% based on palladium chloride. Anhydrous hydrogen bromide was passed for 40 minutes into a solution of the above palladium complex (55, R=To, R^1=Et) in 250 ml of dichloromethane and then the crude product, tetrakis(p-tolyl)cyclobutadienepalladium bromide dimer was precipitated with light petroleum. The crude product was purified by digestion with boiling cyclohexane and a pure sample, m.p.332-336°C(decomp), was obtained by recrystallization from dichloromethane and light petroleum. Solvent of crystallization was removed by washing with hot benzene and vacuum drying at 80°C. Yield, 20.0 g, 98.0% based on the starting palladium complex.

Analysis. Found: C,56.74; H,3.98; mol.wt. 1280. Calculated for $C_{32}H_{28}PdBr_2$: C,56.60; H,4.16; mol.wt. 1358. The H^1 N.M.R. spectrum showed a sharp A B quartet centred at 2.60τ (2.27τ; 2.40τ; 2.80τ; 2.93τ; J=8.0 c/s) and a singlet at 7.72τ due to the aromatic and methyl protons of the p-tolyl groups, with an expected intensity ratio of 16:12, respectively.

Tetrakis(p-tolyl)cyclobutadienenickel bromide dimer (39, R=To, X=Br)

A suspension of 1.2 g (0.90 mmole) of tetrakis(p-tolyl)cyclobutadienepalladium bromide dimer and 1.1 g (1.8 mmoles) of bis(tri-n-butylphosphine)nickel bromide was refluxed in 100 ml of chlorobenzene for 90 minutes. The hot solution was filtered, the filtrate evaporated to dryness on a rotary evaporator, and the crude product was crystallized from dichloromethane and light petroleum. The pure, green crystals, of tetrakis(p-tolyl)cyclobutadienenickel bromide dimer, m.p. 328-330°C (decomp.) were obtained by recrystallization from hot benzene, and vacuum drying at 80°C. Yield, 0.60 g, 53%.

Analysis. Found: C, 60.89; H,4.43; mol. wt. 1210. Calculated for $C_{32}H_{28}NiBr_2$: C, 60.90; H,4.47; mol. wt. 1262. The infra-red spectrum was identical to that of the palladium complex (51, R=To, X=Br).

The H^1 N.M.R. spectrum exhibited a sharp A B quartet centred at 2.49τ (2.06τ; 2.19τ; 2.79τ; 2.92τ; J=8.0 c/s) and a single resonance at 7.80τ due to the aromatic and methyl protons of the p-tolyl groups with an expected intensity ratio of 16:12, respectively.

[(π-Cyclopentadienyl)(π-tetraphenylcyclobutadiene)palladium] tetrabromoferrate (77, R=Ph, M=Pd)

A suspension of 2.0 g (1.6 mmoles) of tetraphenylcyclobutadiene-palladium bromide dimer and 2.0 g (7.8 mmoles) of cyclopentadienyliron dicarbonyl bromide was refluxed in 100 ml benzene for 3 hours. The hot reaction mixture was filtered, the insoluble product was washed carefully with hot benzene and then digested with several portions of dichloromethane, until the solvent had no longer any appreciable colour. The washings were combined, reduced in volume to 50 ml on a rotary evaporator, and light petroleum was then added dropwise with continual shaking to give air-stable red-purple crystals of [(π-cyclopentadienyl)(π-tetraphenylcyclobutadiene) palladium] tetrabromoferrate, m.p. above 400°C. Yield, 2.4 g, 85% based on the palladium complex.

Analysis. Found: C,44.90; 41.70; H,2.90; 2.90; Fe, 6.50; Br,34.80; 35.0. Calculated for $C_{33}H_{25}PdFeBr_4$: C,43.90; H,2.80; Fe,6.20; Br,35.40. Apart from the main product (77, R=Ph, M=Pd), the other two products were ferrocene which was obtained, in 40% yield*, after chromatography on alumina of the mother liquor, and iron metal which was left as an insoluble residue after the extraction of the tetrabromoferrate complex with dichloromethane.

* Based on that required for the reactions:

$$\left[(Ph_4C_4)PdBr_2\right]_2 + 4(C_5H_5)Fe(CO)_2Br \longrightarrow 2\left[(Ph_4C_4)Pd(C_5H_5)\right]^+FeBr_4^- + (C_5H_5)_2Fe + 8CO + Fe$$

The use of cyclopentadienyliron dicarbonyl dimer instead of cyclopentadienyliron dicarbonyl bromide, under the same conditions, in this reaction gave only a 42% of the tetrabromoferrate complex (77, R=Ph, M=Pd).
A magnetic susceptibility measurement gave $X^{300^\circ K}$ g (corr.)=1.71×10^{-5}. This corresponds to a magnetic moment(μ_{eff}) of 6.1 B.M. due to the high spin, tetrahedral, tetrabromoferrate anion. The infra-red spectrum (Appendix-I) was similar to the spectra of the other (π-cyclopentadienyl)-(π-tetraphenylcyclobutadiene)metal complexes.

[(π-Cyclopentadienyl)(π-tetraphenylcyclobutadiene)nickel] tetrabromoferrate (77, R=Ph, M=Ni)

A suspension of 1.0 g (0.87 mmole) of tetraphenylcyclobutadienenickel bromide dimer[153] and 1.0 g (3.9 mmoles) of cyclopentadienyliron dicarbonyl bromide was refluxed in 50 ml benzene for 2.5 hours. The purple [(π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)nickel] tetrabromoferrate, m.p. above 400°C, was isolated by the same procedure used for the palladium tetrabromoferrate complex (77, R=Ph, M=Pd).
Yield, 1.1 g, 77% based on the starting nickel complex.

Analysis. Found: C,48.70; 48.70; H,3.40; 3.40; Br, 35.50.
Calculated for $C_{33}H_{25}NiFeBr_4$: C,46.30; H,2.90; Br, 37.40.
The infra-red spectra was identical to that of the palladium tetrabromoferrate complex (77, R=Ph, M=Pd). A magnetic susceptibility measurement gave $X^{300^\circ K}$ g (corr.) = 1.42×10^{-5}. This corresponds to a magnetic moment (μeff) of 5.4 B.M. due to the high spin, tetrahedral, tetrabromoferrate anion.

[(π-Cyclopentadienyl){π-tetrakis(p-tolyl)cyclobutadiene} palladium] tetrabromoferrate (77, R=To, M=Pd)

A suspension of 1.2 g (0.92 mmole) of tetrakis(p-tolyl)cyclobutadienepalladium bromide dimer and 1.2 g(4.9 mmoles) of cyclopentadienyliron dicarbonyl bromide were refluxed in 90 ml benzene for 3 hours. The purple, [(π-cyclopentadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} palladium] tetrabromoferrate, m.p. above 300°C, was isolated by the same procedure used for the palladium tetrabromoferrate complex (77, R=Ph, M=Pd). The complex was dried at 80°C (under vacuum) for 24 hours. Yield, 0.98 g, 55% based on the starting palladium complex.

Analysis. Found: C,46.53; H,3.66. Calculated for $C_{37}H_{33}PdFeBr_4$: C,46.30; H3.47.

The infra-red spectrum was similar to the spectra of the other (π-cyclopentadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} metal complexes (Appendix-I).

[(π-Cyclopentadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} nickel] tetrabromoferrate (77, R=To, M=Ni)

A suspension of 0.45 g (0.36 mmole) of tetrakis(p-tolyl)cyclobutadienenickel bromide dimer and 0.45 g (1.7 mmoles) of cyclopentadienyliron dicarbonyl bromide was refluxed in 60 ml benzene for 3 hours. The purple [(π-cyclopentadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} nickel] tetrabromoferrate, m.p. above 300°, was isolated by the same procedure used for the palladium tetrabromoferrate complex (77, R=Ph, M=Pd). The complex was dried at 80°C(under vacuum) for 24 hours. Yield, 0.37 g, 57% based on the starting nickel complex.

Analysis. Found: C,48.58; H,3.60. Calculated for $C_{37}H_{33}NiFeBr_4$: C,48.80; H,3.67.

The infra-red spectrum was identical to that of the palladium-tetrabromoferrate complex (77, R=To, M=Pd).

[(π-1.5-Cyclooctadiene)(π-cyclopentadienyl)palladium] tetrabromoferrate (78)

A suspension of 1.0 g (2.6 mmoles) of 1.5-cyclooctadienepalladium bromide and 1.5 g (5.9 mmoles) of cyclopentadienyliron dicarbonyl bromide was refluxed in 50 ml benzene for 2.5 hours. The purple-red [(π-1.5-cyclooctadiene)(π-cyclopentadienyl)palladium] tetrabromoferrate, m.p. above 300°C, was isolated by the same procedure used for the palladium tetrabromoferrate complex (77, R=Ph, M=Pd). The complexed was dried at 25°C (under vacuum) for 24 hours. Yield, 1.0 g, 61% based on the starting palladium complex.

Analysis. Found: C,23.99; H,2.53; Br,48.86. Calculated for $C_{13}H_{17}PdFeBr_4$: C,24.05; H,2.64; Br,49.24.

The infra-red spectrum (Appendix-I) was typical of the organic ligands presence in the complex. A magnetic susceptibility measurement gave $X^{300°K}_{g}$ (corr.)=2.12×10^{-5}. This corresponds to a magnetic moment (μ_{eff}) of 5.8 B.M., due to the high spin, tetrahedral, tetrabromoferrate anion. The use of cyclopentadienyliron dicarbonyl dimer instead of cyclopentadienyliron dicarbonyl bromide under the same conditions in this reaction gave only an 8.0% yield of the tetrabromoferrate complex (78). Although this complex was air-stable at 25°C and thermally stable to above 300°C, it was chemically reactive and all attempts to convert it into the diamagnetic bromide,

$[(C_8H_{12})Pd(C_5H_5)]^+Br^-$ or to react it with nucleophiles such as sodium methoxide failed, due to decomposition of the complex.

[(π-Cyclopentadienyl)(π-tetraphenylcyclobutadiene)palladium] bromide (79, R=Ph, M=Pd)

A solution of 0.95 g (2.2 mmoles) of potassium ferrocyanide trihydrate in 25 ml of water was added to a solution of 1.9 g (2.1 mmoles) of [(π-cyclopentadienyl)(tetraphenylcyclobutadiene)palladium] tetrabromoferrate in 100 ml dichloromethane. The reaction mixture was stirred vigorously for two hours at 25°C. The dichloromethane layer was separated from the blue aqueous solution, washed several times with water, dried over anhydrous Na_2SO_4, filtered and concentrated to 50 ml on a rotary evaporator. The air stable, diamagnetic, orange crystalline [(π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)palladium] bromide, m.p. 193°C (decomp.), was precipitated by slow addition of light petroleum to the dichloromethane solution. Yield, 1.2 g, 94% based on the starting palladium complex.

Analysis. Found: C,65.19; H,4.18; Pd,17.82; Br,13.46.

Calculated for $C_{33}H_{25}PdBr$: C,65.20; H,4.14; Pd,17.50; Br,13.15.

The infra-red spectrum was similar to the spectrum of the other (π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)metal complexes (Appendix-I). The H^1 N.M.R. spectrum showed a sharp peak at 2.39τ due to the phenyl protons, and a sharp resonance at 3.66τ due to the cyclopentadienyl protons. The intensity ratio was the expected 20:5.

[(π-Cyclopentadienyl)(π-tetraphenylcyclobutadiene)nickel] bromide (79, R=Ph, M=Ni)

A solution of 0.80 g (0.94 mmole) of [(π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)nickel] tetrabromoferrate in 100 ml of dichloromethane was added to a solution of 0.50 g (1.1 mmoles) of potassium ferrocyanide trihydrate in 40 ml of water. The yellow-orange crystalline, diamagnetic [(π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)nickel] bromide, m.p. 193°C (decomp.), was isolated by the same procedure used for the palladium bromide complex (79, R=Ph, M=Pd). Yield, 0.52 g, 92% based on the starting nickel complex.

Analysis. Found: C,70.75; H,4.50; Ni,10.48; Br,14.26.
Calculated for $C_{33}H_{25}NiBr$: C,70.07; H,4.62; Ni,10.56; Br, 14.72.
The infra-red spectrum (Appendix-I) was identical to that of the palladium bromide complex (79, R=Ph, M=Pd). The H^1 N.M.R. spectrum showed a sharp peak at 2.39τ due to the phenyl protons, and a sharp resonance at 4.22τ due to the cyclopentadienyl protons. The intensity ratio was the expected 20:5.

[(π-Cyclopentadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} palladium] bromide (79, R=To, M=Pd)

A solution of 0.70 g (0.73 mmole) of [(π-cyclopentadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} palladium] tetrabromoferrate in 100 ml of dichloromethane was added to a solution of 0.36 g (0.84 mmole) of potassium ferrocyanide trihydrate in 25 ml of water. The yellow crystalline, diamagnetic, [(π-cyclopentadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} palladium] bromide dihydrate*, m.p. 188-190°C (decomp.), was isolated by the same procedure used for the palladium bromide complex (79, R=Ph, M=Pd). Yield, 0.44 g, 87% based on the starting palladium complex.

Analysis. Found: C,63.74; 63.60; 63.56; H,5.13; 4.99; 5.04.
Calculated for $C_{37}H_{33}PdBr\cdot 2H_2O$: C,63.80; H,5.34.
The dihydrated complex was crystallized from dichloromethane-benzene then was vacuum dried at 80°C for 24 hours to give the anhydrous, yellow, [(π-cyclopentadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} palladium] bromide.

Analysis. Found: C,66.89; H,5.22.
Calculated for $C_{37}H_{33}PdBr$: C,67.00; H,5.03. The infra-red spectrum of the anhydrous complex was identical to the spectra of the other (π-cyclopentadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} metal complexes. The H^1 N.M.R. spectrum showed a sharp AB quartet centred at 2.72τ (2.55τ; 2.68τ; 2.77τ; 2.90τ; J=8.1 c/s), and resonances at 7.63τ and 3.95τ due to the aromatic and methyl protons of the p-tolyl groups and the cyclopentadienyl protons with an expected intensity ratio of 16:12:5, respectively.

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* This tendency of hydrate formation has also been shown to be the case for other tetrakis(p-tolyl)cyclobutadiene metal complexes (see below).

[(π-Cyclopentadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} nickel] bromide (79, R=To, M=Ni)

A solution of 0.30 g (0.33 mmole) of [(π-cyclopentadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} nickel] tetrabromoferrate in 100 ml of dichloromethane was added to a solution of 0.16 g (0.36 mmole) of potassium ferrocyanide trihydrate in 20 ml of water. The yellow crystalline, diamagnetic, [(π-cyclopentadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} nickel] bromide dihydrate, m.p. 164-168°C (decomp.), was isolated by the same procedure used for the palladium bromide complex (79, R=Ph, M=Pd). Yield, 0.18 g, 87% based on the starting nickel complex.

Analysis. Found: C,68.02; H,5.30.
Calculated for $C_{37}H_{33}NiBr \cdot 2H_2O$: C,68.50; H,5.74. The dihydrate complex was recrystallized from dichloromethane-benzene, then was vacuum dried at 80°C for 24 hours to give the anhydrous, yellow, [(π-cyclopentadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} nickel] bromide.

Analysis. Found: C,72.23; H,5.51.
Calculated for $C_{37}H_{33}NiBr$: C,72.10; H,5.40. The infra-red spectrum of the anhydrous complex was identical to that of the palladium bromide complex (79, R=To, M=Pd). The H^1 N.M.R. spectrum showed a sharp AB quartet centred at 2.68τ (2.48τ; 2.62τ; 2.74τ; 2.88τ; J=8.5 c/s), and resonances at 7.64τ and 4.38τ due to the aromatic and methyl protons of the p-tolyl groups and the cyclopentadienyl protons, with an expected intensity ratio of 16:12:5, respectively.

(π-Cyclopentadienyl) {π-(4-exo-methoxy-1.2.3.4-tetraphenylcyclobutenyl)} palladium (94, R=Ph, R^1=CH_3, M=Pd)

A methanol solution (1.3 ml) of sodium methoxide (1.1 mmoles) was added to a solution of 0.50 g (0.82 mmole) of [(π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)palladium] bromide in 30 ml of methanol. A dark-orange precipitate was formed immediately, which was filtered off and recrystallized from benzene-methanol to give (π-cyclopentadienyl) {π-(4-exo-methoxy-1.2.3.4-tetraphenylcyclobutenyl)}palladium, m.p. 152-154°C (decomp.). Yield, 0.28 g, 61% based on the starting palladium complex.

Analysis. Found: C,72.91; H,5.03; Pd,19.21; mol.wt. 544.
Calculated for $C_{34}H_{28}PdO$: C,72.40; H,5.15; Pd,19.45; mol. wt. 567.
The H^1 N.M.R. spectrum showed two strong, rather broad, peaks at 2.26τ and 2.63τ due to the phenyl protons, and sharp singlets at 4.55τ and 6.58τ due to the cyclopentadienyl and methoxy protons, respectively. The intensity ratio was the expected 20:5:3.

(π-Cyclopentadienyl) {π-(4-exo-methoxy-1.2.3.4-tetraphenylcyclobutenyl)} nickel (94, R=Ph, R^1=CH_3, M=Ni)

A methanol solution (1.0 ml) of sodium methoxide (0.87 mmole) was added to a solution of 0.14 g (0.25 mmole) of [(π-cyclopentadienyl) (π-tetraphenylcyclobutadiene)nickel] bromide in 18 ml of methanol. A dark-red precipitate, was formed immediately, which was filtered off, washed with methanol and vacuum dried, at 25°C, to give (π-cyclopentadienyl) {π-(exo-methoxy-1.2.3.4-tetraphenylcyclobutenyl)}nickel, m.p. 195-198°C (decomp.). Yield 0.10 g, 78% based on the starting nickel complex.
Analysis. Found: C,79.67; H,5.70; Ni,11.30; mol. wt. 520.
Calculated for $C_{34}H_{28}NiO$: C,79.85; H,5.52; Ni,11.48; mol. wt. 511.

The infra-red spectrum (Appendix-I) was identical to that of the palladium complex (94, R=Ph, R^1=CH_3, M=Pd). The H^1 N.M.R. spectrum showed two strong, rather broad, peaks at 2.40τ and 2.80τ due to the phenyl protons, and sharp singlets at 5.10τ, and 6.70τ due to the cyclopentadienyl and methoxy protons, respectively. The intensity ratio was the expected 20:5:3.

(π-Cyclopentadienyl) {π-(4-exo-methoxy-1.2.3.4-tetrakis(p-tolyl)cyclobutenyl)} palladium. (94, R=To, R^1=CH_3 M=Pd)

A methanol solution (0.60 ml) of sodium methoxide (0.42 mmole) was added to a solution of 0.20 g (0.30 mmole) of [(π-cyclopentadienyl)-{π-tetrakis(p-tolyl)cyclobutadiene} palladium] bromide in 25 ml of methanol. A dark red precipitate, was formed immediately, which was filtered off, washed with methanol and vacuum dried, at 25°C, to give (π-cyclopentadienyl) {π-(4-exo-methoxy-1.2.3.4-tetrakis(p-tolyl)cyclobutenyl)} palladium, m.p. 195-198°C (decomp.). Yield, 0.14 g, 76% based on the starting palladium complex.

Analysis. Found: C,74.15; H,5.76; mol. wt. 614. Calculated for $C_{38}H_{36}PdO$: C,74.25; H,5.88; mol. wt. 615. The H^1 N.M.R. spectrum showed diffuse peaks at 2.40τ; 2.52τ; 2.60τ; 2.96τ and 3.08τ due to the aromatic protons, and sharp singlets at 4.65τ; 6.71τ and 7.76τ assigned to the cyclopentadienyl, methoxy and methyl protons, respectively. The intensity ratio was 16:5:3:12 as expected.

(π-Cyclopentadienyl) {π-(4-exo-methoxy-1.2.3.4-tetrakis(p-tolyl)cyclobutenyl)} nickel (94, R=To, R^1=CH_3, M=Ni)

A methanol solution (1.0 ml) of sodium methoxide (0.51 mmole) was added to a solution of 0.12 g (0.20 mmole) of [(π-cyclopentadienyl){π-tetrakis(p-tolyl)cyclobutadiene} nickel] bromide in 15 ml of methanol. A dark-red precipitate, was formed immediately which was filtered off, washed with methanol and vacuum dried, at 25°C, to give (π-cyclopentadienyl){π-(4-exo-methoxy-1.2.3.4-tetrakis(p-tolyl)cyclobutenyl)} nickel, m.p. 202-205°C (decomp.). Yield, 0.066 g, 59% based on the starting nickel complex.

Analysis. Found: C,80.51; H,6.26; mol. wt. 566. Calculated for $C_{38}H_{36}NiO$: C,80.50; H,6.38; mol. wt. 567. The infra-red spectrum was identical to that of the palladium complex (94, R=To, R^1=CH_3 M=Pd). The H^1 N.M.R. spectrum showed diffuse peaks at 2.52τ; 2.61τ; 2.68τ; 2.99τ; 3.09τ and 3.11τ due to the aromatic protons, and sharp singlets at 5.20τ; 6.82τ and 7.75τ assigned to the cyclopentadienyl, methoxy and methyl protons, respectively. The intensity ratio was 16:5:3:12 as expected.

Reaction of (π-cyclopentadienyl){π-(4-exo-methoxy-1.2.3.4-tetraphenylcyclobutenyl)} nickel with Hydrogen Bromide

A solution of 0.050 g (0.098 mmole) of (π-cyclopentadienyl){π-(4-exo-methoxy-1.2.3.4-tetraphenylcyclobutenyl)} nickel in 7.0 ml of dichloromethane was treated with dry hydrogen bromide for 10 minutes, at 25°C. The solution turned pale-orange, the solvent was then evaporated and the solid residue crystallized from dichloromethane-ligroin to give 0.053 g (98%) of [(π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)nickel] bromide, identified by melting-point [193°C(decomp.)] and infra-red spectrum.

(π-Tetraphenylcyclobutadiene)cobalt dicarbonyl bromide (75, R=Ph, X=Br)

A solution of 7.1 g (5.7 mmoles) of tetraphenylcyclobutadienepalladium bromide dimer in 750 ml of dichloromethane was degassed by refluxing for 30 minutes, then was cooled to 25°C and 50 ml toluene solution of dicobalt octacarbonyl (43 mmoles) were added. The reaction mixture was stirred at 25°C for 45 hours, then filtered, and the volume was reduced to 30 ml on a rotary evaporator. On the addition of 500 ml of light petroleum a red-brown crystalline (π-tetraphenylcyclobutadiene)-cobalt dicarbonyl bromide, m.p. 255-262°C (decomp.), was obtained. Yield, 3.7 g, 59% based on the starting palladium complex.

Analysis. Found: C,65.60; H,3.63; Co,10.81; Br,14.78; O,6.08; mol. wt. 538. Calculated for $C_{30}H_{20}CoO_2Br$: C,65.40; H,3.66; Co,10.71; Br, 14.48; O,5.82; mol. wt. 551. The compound in benzene had two strong terminal νCO bands at 2060 and 2020 cm^{-1}; the rest of the infra-red spectrum (2-16μ; KBr disc) was similar to the spectra of the other tetraphenylcyclobutadiene metal complexes. The compound was found to exhibit unexpected temperature-dependent paramagnetism due to the presence of some analytically-undetected paramagnetic impurities. Magnetic susceptibility measurements[154] gave unreproducible results for samples purified by different methods: $X^{296^\circ K}_g = +0.64 \times 10^{-6}$; $+2.14 \times 10^{-6}$; $X^{78^\circ K}_g = +3.66 \times 10^{-6}$; $+7.42 \times 10^{-6}$; $X^{4.2^\circ K}_g = +32.00 \times 10^{-6}$; $+66.00 \times 10^{-6}$.

However, after very careful recrystallizations from dichloromethane and methanol, the compound was shown to be diamagnetic at 23°C, although at lower temperatures it became somewhat paramagnetic: $X^{296^\circ K}_g = -0.15 \times 10^{-6}$; $X^{78^\circ K}_g = +0.25 \times 10^{-6}$; $X^{4.2^\circ K}_g = +4.8 \times 10^{-6}$. The H^1 N.M.R. spectrum showed a fairly broad, single resonance at 2.60τ due to the phenyl protons.

(π-Tetraphenylcyclobutadiene)cobalt dicarbonyl chloride (75, R=Ph, X=Cl)

A solution of 4.4 g (4.2 mmoles) of tetraphenylcyclobutadienepalladium chloride dimer in 500 ml of dichloromethane was degassed by refluxing for 30 minutes, then was cooled to 25°C and 2.1 g (6.4 mmoles) of dicobalt octacarbonyl were added. The orange-red crystalline, (π-tetraphenylcyclobutadiene)cobalt dicarbonyl chloride, m.p. 200°C (decomp.), was isolated by the same procedure used for the cobalt bromide complex (75, R=Ph, X=Br). Yield, 2.7 g, 65% based on the starting palladium complex. Analysis. Found: C,71.26; H,4.10. Calculated for $C_{30}H_{20}CoO_2Cl$: C,71.00; H,3.98. The compound exhibited two strong terminal ν_{co} bands at 2062 and 2028 cm^{-1}; the rest of the infra-red spectrum (Appendix-I) was identical to that of (75, R=Ph, X=Br).

(π-Tetraphenylcyclobutadiene)cobalt dicarbonyl iodide (75, R=Ph, X=I)

A solution of 4.0 g (2.8 mmoles) of tetraphenylcyclobutadienepalladium iodide dimer in 500 ml of dichloromethane was degassed by refluxing for 30 minutes, then was cooled to 25°C, and 2.5 g (7.3 mmoles) of dicobalt octacarbonyl were added. The dark-red, crystalline, (π-tetraphenylcyclobutadiene)cobalt dicarbonyl iodide, m.p. 268-271°C (decomp.), was isolated by the same procedure used for the cobalt bromide complex (75, R=Ph, X=Br). Yield, 0.60 g, 17% based on the starting palladium complex. Analysis. Found: C,60.38; H,3.41. Calculated for $C_{30}H_{20}CoO_2I$: C,60.20; H,3.37. The compound, in benzene solution, had two strong terminal ν_{co} bands at 2055 and 2020 cm^{-1}; the rest of the infra-red spectrum

(2-16μ; KBr disc) was identical to that of (75, R=Ph, X=Br)

{π-Tetrakis(p-tolyl)cyclobutadiene}cobalt dicarbonyl bromide (75, R=To, X=Br)

A solution of 3.0 g (2.2 mmoles) of tetrakis(p-tolyl)cyclobutadiene-palladium bromide dimer in 400 ml of dichloromethane was degassed by refluxing for 30 minutes, then was cooled to 25°C and 1.7 g (5.0 mmoles) of dicobalt octacarbonyl were added. The orange-red, crystalline {π-tetrakis (p-tolyl)cyclobutadiene} cobalt dicarbonyl bromide, m.p. 258-260°C (decomp.), was isolated by the same procedure used for the cobalt bromide complex (75, R=Ph, X=Br). Yield, 0.95 g, 35% based on the starting palladium complex.

Analysis. Found: C,67.05; H,4.47. Calculated for $C_{34}H_{28}CoO_2Br$: C,67.20; H,4.49. The compound, in benzene solution, had two strong terminal ν_{co} at 2055 and 2020 cm^{-1}, the rest of the spectrum (2-16μ; KBr disc) was similar to that of (75, R=Ph, X=Br). The H^1 N.M.R. spectrum showed an A B quartet centred at 2.68τ (2.42τ; 2.57τ; 2.80τ; 2.94τ; J=8.0 c/s) and a singlet at 7.67τ assigned to the aromatic and methyl protons. The intensity ratio was 16:12 as expected.

(π-Tetraphenylcyclobutadiene)(triphenylphosphine)cobalt carbonyl bromide (83, X=Br)

A solution of 0.60 g (1.1 mmoles) of (π-tetraphenylcyclobutadiene) cobalt dicarbonyl bromide and 0.40 g (1.5 mmoles) of triphenylphosphine were stirred together in 50 ml benzene for 7 hours at 25°C. The reaction mixture was then filtered, and the filtrate reduced in volume to 20 ml on a rotary evaporator. The dark-brown, crystalline, (π-tetraphenylcyclobutadiene)(triphenylphosphine)cobalt carbonyl bromide, m.p. 225-230°C (decomp.), was isolated on slow addition of light petroleum to the mother-liquor. Yield, 0.62 g, 72% based on the starting cobalt complex.

Analysis. Found: C,72.45; H,4.76; Br,9.76. Calculated for $C_{47}H_{35}CoOPBr$: C,72.10; H,4.47; Br,10.10.

The infra-red spectrum showed a strong carbonyl band at 2000 cm^{-1}, and the H^1 N.M.R. spectrum exhibited two closely spaced resonances at 2.72τ and 2.76τ due to the phenyl protons. The compound exhibited temperature dependent paramagnetism, which was attributed to the presence of some analytically-undetectable impurities. However, after very careful purification the paramagnetism was appreciably reduced; $\chi^{292^\circ K}{}_g = +0.6 \times 10^{-6}$; $\chi^{78^\circ K}{}_g = +3.0 \times 10^{-6}$. This compound was unstable in solution, and all attempts to obtain meaningful osmometric molecular weight failed.

(π-Tetraphenylcyclobutadiene)(triphenylphosphine)cobalt carbonyl chloride (83, X=Cl)

A solution of 0.43 g (0.85 mmole) of (π-tetraphenylcyclobutadiene) cobalt dicarbonyl chloride and 0.30 g (1.1 mmoles) of triphenylphosphine were stirred together in 50 ml benzene for 7 hours at 25°C, then the reaction mixture was filtered and the filtrate reduced in volume to 10 ml on a rotary evaporator. The dark-brown, crystalline, (π-tetraphenylcyclobutadiene)(triphenylphosphine)cobalt carbonyl chloride, m.p. 213-215°C (decomp.), was isolated on slow addition of light petroleum to the mother-liquor. Yield, 0.54g, 86% based on the starting cobalt complex.

Analysis. Found: C,76.15; H,4.75. Calculated for $C_{47}H_{35}CoOPCl$: C,76.25; H,4.76. The infra-red spectrum (Appendix-I) showed a strong terminal carbonyl band at 2000 cm^{-1}; the rest was identical to that of the bromide (83, R=Ph, X=Br).

(π-Cyclopentadienyl)(π-tetraphenylcyclobutadiene)cobalt (48, R=Ph)

A solution of 0.75 g (1.4 mmoles) of (π-tetraphenylcyclobutadiene) cobalt dicarbonyl bromide and 0.35 g (1.4 mmoles) of cyclopentadienyliron dicarbonyl bromide in 100 ml benzene was refluxed for 2.5 hours. The hot reaction mixture was filtered, the filtrate reduced in volume to 20 ml and then chromatographed on Florisil. A yellow band which was eluted with light petroleum-benzene (1:1 V/V), gave, after evaporation, a yellow crystalline product. This product was recrystallized from light petroleum-benzene to give pure (π-cyclopentadienyl)(π-tetraphenylcyclobutadiene)cobalt, m.p. 248-252°C, mixed m.p. with an authentic sample 252-255°C. The infra-red spectra were identical. Yield, 0.53 g, 78%.

The same product (48, R=Ph) was also obtained under the same conditions from the reaction of 0.25 g (0.45 mmole) of (π-tetraphenylcyclobutadiene)cobalt dicarbonyl bromide with 0.25 g (0.98 mmole) of cyclopentadienyliron dicarbonyl dimer in 50 ml benzene. Yield, 0.16 g, 73% based on the starting cobalt complex.

(π-Cyclopentadienyl){π-tetrakis(p-tolyl)cyclobutadiene}cobalt (48, R=To)

A solution of 0.22 g (0.36 mmole) of {π-tetrakis(p-tolyl)cyclobutadiene}cobalt dicarbonyl bromide and 0.12 g (0.47 mmole) of cyclopentadienyliron dicarbonyl bromide in 50 ml benzene, was refluxed for 2.5 hours.

The yellow, crystalline, (π-cyclopentadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} cobalt, m.p.304-306°C, was isolated by the same procedure used for the tetraphenylcyclobutadiene-cobalt complex (48, R=Ph). Yield, 0.14 g, 71% based on the starting cobalt complex.

Analysis. Found: C,82.73; H,6.29. Calculated for $C_{37}H_{33}Co$: C,82.90; H6.20. The infra-red spectrum was similar to the spectra of the other (π-cyclopentadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} metal complexes. The H^1 N.M.R. spectrum showed a sharp A B quartet centred at 2.91τ(2.65τ; 2.79τ; 3.04τ; 3.16τ; J=8.0 c/s) due to the aromatic protons, and resonances at 5.50τ and 7.87τ assigned to the cyclopentadienyl and methyl protons, respectively. The intensity ratio was 16:15:12 as expected.

(σ-Pentafluorophenyl)dicarbonyl(π-tetraphenylcyclobutadiene)cobalt

(87, R=Ph)

(π-Tetraphenylcyclobutadiene)cobalt dicarbonyl bromide (0.45g; 0.82 mmole) was added to a solution of pentafluorophenyllithium [prepared at -78°C from 0.40 g (1.6 mmoles) of bromopentafluorobenzene and 0.88 ml of a hexane solution of n-butyllithium (16%; 1.5 mmoles) in 50 ml ether] at 0°C. The suspension was allowed to warm up to 25°C, and then was left to stir for 12 hours. The yellow precipitate of the product, formed slowly, was filtered off, washed with ether and crystallized from dichloromethan-methanol to give, pure, (σ-pentafluorophenyl)dicarbonyl (π-tetraphenylcyclobutadiene)cobalt, m.p. 164°C (decomp.). Yield, 0.27 g, 53% based on the starting cobalt complex.

Analysis. Found: C, 67.99; H, 3.22; F, 14.80; mol. wt. 625 ($CHCl_3$). Calculated for $C_{36}H_{20}CoO_2F_5$: C, 67.73; H, 3.16; F, 14.88; mol. wt. 638. The compound, in $CHCl_3$ solution, had νco 2010; 2050 cm^{-1} due to the terminal carbonyls present; the rest of the infra-red spectrum (2-16μ; KBr disc) (Appendix-I) was typical of the organic ligands present in the complex. The H^1 N.M.R. spectrum exhibited a sharp singlet at 2.70τ due to the phenyl protons, and indicated the complex to be diamagnetic. The F^{19} N.M.R. spectrum, relative to $CFCl_3$ as internal standard, in dichloromethane solution, showed three multiplets centred at 108.5 p.p.m., 163.4 p.p.m. and 164.7 p.p.m. assigned to the ortho (o), para (P) and meta (m) fluorine nuclei, respectively (Jo,m=24.6 c/s; Jm,p=19.2 c/s)

(σ - Pentafluorophenyl)dicarbonyl {π-tetrakis(p-tolyl)cyclobutadiene} cobalt (87, R=To)

{π-Tetrakis(p-tolyl)cyclobutadiene} cobalt dicarbonyl bromide (0.36 g; 0.59 mmole) was added to a solution of pentafluorophenyllithium [prepared at -78°C from 0.50 g (2.0 mmoles) of bromopentafluorobenzene and 1.0 ml of a hexane solution of n-butyllithium (16%; 1.7 mmoles) in 40 ml ether] at 0°C. The yellow, crystalline, (σ-pentafluorophenyl)dicarbonyl {π-tetrakis(p-tolyl)cyclobutadiene}cobalt, m.p. 172-173°C (decomp.), was isolated by the same procedure used for the analogous complex (87, R=Ph). Yield, 0.33 g, 79% based on the starting cobalt complex.

Analysis. Found: C, 68.96; H, 3.94; F, 13.87; mol. wt. 687 ($CHCl_3$). Calculated for $C_{40}H_{28}CoO_2F_5$: C, 69.20; H, 4.07; F, 13.67; mol. wt. 695. The compound, in $CHCl_3$ solution, had νco 2010; 2050 cm^{-1} due to the two terminal carbonyls present, the rest of the infra-red spectrum (2-16μ; KBr disc) was very similar to that of the analogous complex (87, R=Ph). The H^1 N.M.R. spectrum (Appendix-II) showed a sharp A B quartet centred at 2.83τ (2.64τ; 2.78τ; 2.88τ; 3.02τ; J=8.2 c/s) due to the aromatic protons, and a sharp resonance at 7.73τ assigned to the methyl protons. The F^{19} N.M.R. spectrum (Appendix-II), relative to $CFCl_3$ as an internal standard, in dichloromethane solution, showed three multiplets centred at 107.1 p.p.m., 162.0 p.p.m. and 163.2 p.p.m. These were assigned to the ortho, para, and meta fluorines, respectively (Jo,m=22.8 c/s; Jm,p= 18.7 c/s).

[(π-Benzene)(π-tetraphenylcyclobutadiene)cobalt] bromide (91, R=Ph, Arene=benzene, X=Br)

(π-Tetraphenylcyclobutadiene)cobalt dicarbonyl bromide (0.70 g; 1.9 mmoles) and 2.8 g (2.1 mmoles) of aluminium chloride were refluxed in 30 ml benzene for 45 minutes. The reaction mixture was cooled to 25°C, 20 ml of a saturated KBr solution were added, and the heterogeneous system was stirred vigorously (to ensure efficient mixing of the two phases) for 30 minutes. The yellow, insoluble product was filtered off, extracted with dichloromethane, and the yellow solution obtained was filtered and evaporated to dryness on a rotary evaporator. Finally, the pure [(π-benzene)(π-tetraphenylcyclobutadiene)cobalt] bromide, m.p. 180-190°C (decomp.), was recrystallized from methanol-water and was vacuum dried at 80°C for 24 hours. Yield, 0.62 g, 55% based on the starting cobalt complex.

Analysis. Found: C,71.28; H,4.62; Co,9.75; Br,13.45. Calculated for

$C_{34}H_{26}CoBr$:, C,71.20; H,4.56; Co,10.02; Br 13.90. The infra-red spectrum (Appendix-I) was typical of the organic ligands present in the molecule and the H^1 N.M.R. spectrum showed two sharp resonances at 2.50τ and 3.35τ due to the phenyl and the π-bonded benzene protons, respectively.

[(π-Benzene)(π-Tetraphenylcyclobutadiene)cobalt] hexafluorophosphate
(91, R=Ph, Arene=benzene, X=PF_6)

A saturated methanol solution (1.0 ml) of ammonium hexafluorophosphate was added to a solution of 0.050 g (0.065 mmole) of [(π-benzene)(π-tetraphenylcyclobutadiene)cobalt] bromide in 10 ml of methanol. An immediate precipitate was formed, which was filtered off and vacuum dried at 80°C for 24 hours giving the anhydrous, yellow, [(π-benzene)(π-tetraphenylcyclobutadiene)cobalt] hexafluorophosphate, m.p. 370-378°C (decomp.). Yield, 0.039 g, 70%.

Analysis. Found: C,64.06; H,4.30. Calculated for $C_{34}H_{26}CoPF_6$: C,63.90; H,4.11. The infra-red spectrum (Appendix-I) showed a strong, rather broad, band at 850-840 cm^{-1} due to the hexafluorophosphate anion, otherwise the spectrum was identical to that of the bromide analogue (91, R=Ph, Arene= benzene, X=Br).

[(π-Benzene){π-tetrakis(p-tolyl)cyclobutadiene}cobalt] bromide
(91, R=To, Arene=benzene, X=Br)

{π-Tetrakis(p-tolyl)cyclobutadiene}cobalt dicarbonyl bromide (0.45 g; 0.74 mmole) and 0.20 g (1.5 mmoles) of aluminium chloride were refluxed in 50 ml benzene for 45 minutes. The yellow crystalline product [(π-benzene) {π-tetrakis(p-tolyl)cyclobutadiene} cobalt] bromide·monohydrate, m.p. 145-147°C (decomp.), was isolated by the same procedure used for (91, R=Ph, Arene=benzene, X=Br), except for the vacuum drying at 80°C. Yield, 0.40 g, 83% based on the starting cobalt complex.

Analysis. Found: C,70.56; H,5.43; Co,9.09. Calculated for $C_{38}H_{34}CoBr\cdot H_2O$: C,70.50; H,5.59; Co9.10. The anhydrous complex was obtained by vacuum drying the monohydrate $[(\pi\text{-}To_4C_4)Co(\pi\text{-}C_6H_6)]^+ Br^-\cdot H_2O$ at 60°C for 24 hours.

Analysis. Found: C,72.35; H,5.49. Calculated for $C_{38}H_{34}CoBr$: C,72.50; H,5.44. The infra-red spectrum of the anhydrous complex was very similar to that of (91, R=Ph, Arene=benzene, X=Br). The H^1 N.M.R. spectrum showed a sharp A B quartet centred at 2.74τ (2.57τ; 2.70τ; 2.78τ; 2.91τ; J= 8.0 c/s) due to the aromatic protons of the p-tolyl groups, and singlets at 3.51τ and 7.66τ assigned to the π-bonded benzene and to the methyl protons, respectively. The intensity ratio was the expected 16:6:12.

[(π-Toluene)(π-tetraphenylcyclobutadiene)cobalt] bromide (91, R=Ph, Arene=toluene, X=Br)

(π-Tetraphenylcyclobutadiene)cobalt dicarbonyl bromide (0.50; 0.91 mmole) and 0.23 g (1.7 mmoles) of aluminium chloride were refluxed in 50 ml toluene for 45 minutes. The yellow, crystalline product [(π-toluene)(π-tetraphenylcyclobutadiene)cobalt]bromide, m.p. 170-172°C (decomp.), was isolated by the same procedure used for (91, R=Ph, Arene= benzene, X=Br). Yield, 0.33 g, 62%, based on the starting cobalt complex.

Analysis. Found: C,71.60; H,4.89; Co, 10.21; Br,13.7. Calculated for $C_{35}H_{28}CoBr$: C,71.50; H,4.79; Co,10.00; Br 13.6. The infra-red spectrum was similar to that of (91, R=Ph, Arene=benzene, X=Br). The H^1 N.M.R. spectrum showed two sharp singlets at 2.50τ and 8.13τ due to the phenyl and methyl protons, respectively, and weak, rather diffuse resonances at 3.25τ and 3.50τ due to the aromatic protons on the π-bonded toluene. The intensity ratio was the expected 20:3:5.

[(π-p-Xylene)(π-tetraphenylcyclobutadiene)cobalt] bromide (91, R=Ph, Arene=p-xylene, X=Br)

(π-Tetraphenylcyclobutadiene)cobalt dicarbonyl bromide (0.52 g; 0.94 mmole) and 0.21 g (1.6 mmoles) of aluminium chloride were refluxed in 50 ml p-xylene for 45 minutes. The yellow crystalline product, [(π-p-xylene)(π-tetraphenylcyclobutadiene)cobalt] bromide, m.p. 215°C (decomp.), was isolated by the same procedure used for (91, R=Ph, Arene=benzene, X=Br). Yield, 0.30 g; 53% based on the starting cobalt complex.

Analysis. Found: C,72.20; H,5.02; Co,10.01; Br,13.29. Calculated for $C_{36}H_{30}CoBr$: C,72.00; H,5.03; Co,10.01; Br,13.29. The infra-red spectrum was similar to that of (91, R=Ph, Arene=benzene, X=Br). The H^1 N.M.R. spectrum showed three sharp singlets at 2.52τ, 3.48τ and 8.18τ assigned to the phenyl, π-bonded p-xylene and the methyl protons, with an expected intensity ratio of 20:4:6, respectively.

[(π-Mesitylene)(π-tetraphenylcyclobutadiene)cobalt] bromide (91, R=Ph, Arene=mesitylene, X=Br)

(π-Tetraphenylcyclobutadiene)cobalt dicarbonyl bromide (0.40 g; 0.72 mmole) and 0.15 g (1.1 mmoles) of aluminium chloride were heated in 40 ml mesitylene to a temperature of 125°C for 45 minutes. The yellow crystalline product [(π-mesitylene)(π-tetraphenylcyclobutadiene)cobalt] bromide, m.p. 160°C (decomp.), was isolated by the same procedure used for (91, R=Ph, Arene=benzene, X=Br). Yield, 0.32 g, 72% based on the starting cobalt complex.

Analysis. Found: C,72.10; H,5.40; Co,9.62; Br,12.88. Calculated for $C_{37}H_{32}CoBr$: C,72.20; H,5.20; Co,9.57; Br,12.98. The infra-red spectrum was similar to that of (91, R=Ph, Arene=benzene, X=Br). The H^1 N.M.R. spectrum showed three sharp singlets at 2.51τ, 3.76τ and 7.97τ, assigned to the phenyl, π-bonded mesitylene, and the methyl protons, with an expected intensity ratio of 20:3:9, respectively.

[(π-Biphenyl)(π-tetraphenylcyclobutadiene)cobalt] bromide (91, R=Ph, Arene=biphenyl, X=Br)

(π-Tetraphenylcyclobutadiene)cobalt dicarbonyl bromide (0.48 g, 0.88 mmole) and 0.17 g (1.3 mmoles) of aluminium chloride were heated in 17 g of biphenyl to a temperature of 120°C for 45 minutes. The product was isolated by the same procedure used for (91, R=Ph, Arene=benzene, X=Br), and was washed carefully with light petroleum and hot cyclohexane (to remove the excess of biphenyl present) to give [(π-biphenyl)(π-tetraphenylcyclobutadiene)cobalt] bromide, m.p. 138-140°C (decomp.). Yield, 0.23 g, 40% based on the starting cobalt complex.

Analysis. Found: C,73.87; H,4.81; Br,12.06. Calculated for $C_{40}H_{30}CoBr$: C,74.00; H,4.65; Br,12.30. The infra-red spectrum was similar to that of (91, R=Ph, Arene=benzene, X=Br), and the H^1 N.M.R. spectrum showed a rather broad singlet at 2.83τ assigned to the phenyl protons.

[(π-n-Butylbenzene)(π-tetraphenylcyclobutadiene)cobalt] bromide (91, R=Ph, Arene=n-butylbenzene, X=Br)

(π-Tetraphenylcyclobutadiene)cobalt dicarbonyl bromide (0.16g, 0.29 mmole) and 0.10 g (0.75 mmole) of aluminium chloride were refluxed in 10 ml. n-butylbenzene for 45 minutes. The yellow crystalline product [(π-n-butylbenzene)(π-tetraphenylcyclobutadiene)cobalt] bromide was isolated by the same procedure used for (91, R=Ph, Arene=benzene, X=Br). Yield, 0.13 g, 73% based on the starting cobalt complex. The H^1 N.M.R. spectrum showed a sharp singlet at 2.59τ due to the phenyl protons, two unresolved multiplets centred at 3.36τ and 3.64τ due to the π-phenyl protons and three unresolved multiplets centred at 8.05τ, 8.80τ and 9.28τ assigned to n-butyl protons.

[(π-n-Butylbenzene)(π-tetraphenylcyclobutadiene)cobalt] hexafluorophosphate (91, R=Ph, Arene=n-butylbenzene, X=PF_6)

A saturated methanol solution (10 ml) of ammonium hexafluorophosphate was added to a solution of 0.050 g (0.079 mmole) of [(π-n-butylbenzene)(π-tetraphenylcyclobutadiene)cobalt] bromide in 10 ml of methanol. An immediate precipitate was formed, which then was filtered off and vacuum dried at 80°C for 24 hours to give yellow crystals of [(π-n-butylbenzene)(π-tetraphenylcyclobutadiene)cobalt] hexafluorophosphate, m.p. 229-233°C (decomp.). Yield, 0.047 g, 85% based on the starting cobalt complex.

Analysis. Found: C,65.70; H,4.75. Calculated for $C_{38}H_{34}CoPF_6$: C,65.70; H,4.96. The infra-red spectra showed a strong, rather broad, band at 850-840 cm^{-1} due to the hexafluorophosphate anion, otherwise the spectrum was identical to that of (91, R=Ph, Arene=n-butylbenzene, X=Br).

(π-2.4-Cyclohexadienyl)(π-tetraphenylcyclobutadiene)cobalt (96)

A solution of 0.13 g (3.3 mmoles) sodium borohydride in 2 ml of water was added dropwise to a solution of 0.20 g (0.35 mmole) of [(π-benzene)(π-tetraphenylcyclobutadiene)cobalt] bromide in 20 ml of methanol at 25°C. A red precipitate, formed immediately, was filtered off and then extracted with light petroleum to give a red solution. This solution was filtered, the filtrate was stripped to dryness on a rotary evaporator and the orange-red crystalline product obtained was recrystallized from light petroleum-methanol to give (π-2.4-cyclohexadienyl)(π-tetraphenylcyclobutadiene)cobalt, m.p. 134-135°C. Yield, 0.035 g; 20% based on the starting cobalt complex.

Analysis. Found: C,82.91; H,5.70; mol. wt. 494. Calculated for $C_{34}H_{27}Co$: C,82.70; H,5.50; mol. wt. 494. The compound had a low νCH 2762 cm^{-1} assigned to the methylene group on the π-bonded cyclohexadienyl ligand. (see INTRODUCTION), additional νCH was found at 3030 cm^{-1}. The H^1 N.M.R. spectrum showed a strong, rather broad, peak centred at 2.73τ due to the phenyl protons, and five multiplets centred at 4.09τ; 5.40τ; 6.14τ; 7.68τ and 8.52τ assigned to the Ha; Hb; Hc; $>CH_2$ and $>CH_2$ protons of the π-bonded cyclohexadienyl ligand, respectively.

Conversion of the (π-2,4-cyclohexadienyl)(π-tetraphenylcyclobutadiene)cobalt into the [(π-benzene)(π-tetraphenylcyclobutadiene)cobalt] hexafluorophosphate

N-Bromosuccinimide (0.0045 g; 0.025 mmole) was added to a solution of 0.0070 g (0.014 mmole) of (π-2.4-cyclohexadienyl)(π-tetraphenylcyclobutadiene)cobalt in 30 ml light petroleum and 4 ml methanol, over a period of 5 minutes at 25°C. The yellow solution formed was filtered, and 5 ml of saturated methanol solution of ammonium hexafluorophosphate were added to the filtrate to give an immediate precipitate of [(π-benzene)(π-tetraphenylcyclobutadiene)cobalt] hexafluorophosphate, m.p. 355-368°C (decomp.), mixed m.p. with an authentic sample 370-375° (decomp). Yield, 0.0074 g, 82% based on the starting cobalt complex. The infra-red spectrum was identical with that of the authentic sample.

(π-1-n-Butyl-2.4-cyclohexadienyl)(π-tetraphenylcyclobutadiene)cobalt

(97, R=PH)

A solution of n-butyllithium (27 mmoles) in 15 ml n-hexane was added to a suspension of 0.10 g (0.17 mmole) of [(π-benzene)(π-tetraphenylcyclobutadiene)cobalt] bromide in 10 ml n-hexane at 25°C. The reaction mixture was left to stir for 3 hours, then 2.0 g (37 mmoles) of ammonium chloride were added (to destroy excess of n-butyllithium) and the solvent removed on a rotary evaporator. The solid obtained was washed with water, dried under vacuum and then extracted with n-hexane to give an orange-red solution. This solution was filtered, the filtrate was stripped to dryness, and the orange-red crystalline product obtained was recrystallized from hexane-methanol to give (π-1-n-butyl-2.4-cyclohexadienyl)(π-tetraphenylcyclobutadiene)cobalt, m.p. 140°C (decomp.). Yield, 0.050 g, 53% based on the starting cobalt complex.

Analysis. Found: C,82.81; H,6.49; mol. wt. 550. Calculated for $C_{38}H_{35}Co$: C,82.90; H,6.42; mol. wt. 556. The infra-red spectrum (Appendix -I) was appreciably different from that of the starting cobalt complex. The H^1 N.M.R. spectrum showed a fairly broad, unresolved multiplet centred at 2.79τ due to the phenyl protons, three unresolved multiplets centred at 4.50τ, 5.70τ and 7.20τ assigned to the Ha, Hb and Hc cyclohexadienyl protons, respectively, and a broad unresolved multiplet centred at 9.10τ assigned to the n-butyl and the saturated cyclohexadienyl protons.

(π-1-n-Butyl-2.4-cyclohexadienyl){π-tetrakis(p-tolyl)cyclobutadiene}cobalt

(97, R=To)

A solution of n-butyllithium (17 mmoles) in 10 ml n-hexane was added to a suspension of 0.11 g (0.17 mmole) of [(π-benzene){π-tetrakis (p-tolyl)cyclobutadiene} cobalt] bromide in 10 ml n-hexane at 25°C. The reaction mixture was left to stir for 3 hours, then 2.0 g (37 mmoles) of ammonium chloride were added (to destroy excess of n-butyllithium), and the solvent removed on a rotary evaporator. The orange-red crystalline product (π-1-n-butyl-2.4-cyclohexadienyl){π-tetrakis(p-tolyl)cyclobutadiene}cobalt, m.p. 129-131°C, was isolated by the same procedure used for (97, R=Ph). Yield, 0.045 g, 42% based on the starting cobalt complex.

Analysis. Found: C,83.16; H,7.29. Calculated for $C_{42}H_{43}Co$: C,83.20; H,7.31. The H^1 N.M.R. spectrum showed a sharp A B quartet centred at 2.82τ (2.59τ; 2.72τ; 2.93τ; 3.06τ; J=8.0c/s) due to the aromatic protons and a sharp singlet at 7.70τ due to the methyl protons. In addition the spectrum also showed three unresolved multiplets centred at 4.52τ, 5.76τ and 7.28τ assigned to the Ha, Hb and Hc cyclohexadienyl protons, respectively, and a broad unresolved multiplet centred at 9.10τ assigned to the n-butyl and the saturated cyclohexadienyl protons.

Conversion of the (π-1-n-butyl-2.4-cyclohexadienyl)(π-tetraphenylcyclobutadiene)cobalt into the [(π-n-butylbenzene)(π-tetraphenylcyclobutadiene)cobalt] hexafluorophosphate

N-Bromosuccinimide (0.030 g; 0.17 mmole) was added to a solution of 0.050 (0.091 mmole) of (π-1-n-butyl-2.4-cyclohexadienyl)(π-tetraphenylcyclobutadiene)cobalt in 10 ml light petroleum and 20 ml methanol over a period of 5 minutes at 25°C. The yellow solution formed was filtered and 10 ml of saturated methanol solution of ammonium hexafluorophosphate were added to the filtrate to give an immediate precipitate of [(π-n-butylbenzene)(π-tetraphenylcyclobutadiene)cobalt] hexafluorophosphate, m.p. 229-230°C (decomp.), mixed m.p. with an authentic sample 228-230°C (decomp.). Yield, 0.040 g, 63% based on the starting cobalt complex. The infra-red spectrum was identical with that of the authentic sample.

[(π-Aniline)(π-tetraphenylcyclobutadiene)cobalt] bromide (92, X=Br)

(π-Tetraphenylcyclobutadiene)cobalt dicarbonyl bromide (0.50 g; 0.91 mmole) and 0.45 g (4.8 mmoles) of aniline were refluxed in 30 ml isooctane for 50 minutes in the presence of 0.72 g (5.6 mmoles) of aluminium chloride. The yellow crystalline product, [(π-aniline)(π-tetraphenylcyclobutadiene)cobalt] bromide, m.p. 220-230°C (decomp.), was isolated by the same procedure used for (91, R=Ph, Arene=benzene, X=Br). Yield, 0.32 g, 60% based on the starting cobalt complex.

Analysis. Found: C,69.17; H,4.96. Calculated for $C_{34}H_{27}NCoBr$: C,69.40; H,4.64.

[(π-Aniline)(π-tetraphenylcyclobutadiene)cobalt] hexafluorophosphate.

(92, X=PF_6)

A saturated methanol solution (15 ml) of ammonium hexafluorophosphate was added to a solution of 0.050 g (0.085 mmole) of [(π-aniline) (π-tetraphenylcyclobutadiene)cobalt] bromide in 10 ml of methanol. On standing, the yellow crystalline product [(π-aniline)(π-tetraphenylcyclobutadiene)cobalt] hexafluorophosphate, m.p. 330-334°C (decomp.), precipitated. Yield, 0.051 g, 91% based on the starting cobalt complex.

Analysis. Found: C,62.87; H,4.05; N,1.95. Calculated for $C_{34}H_{27}NCoPF_6$: C,62.50; H,4.16; N,2.14. The infra-red spectrum (Appendix-I) was identical to that of (92, X=Br) except for the strong, rather broad, band at 850-840 cm^{-1} due to the hexafluorophosphate anion. The spectrum (nujol) also showed two νNH bands at 3390 cm^{-1} and 3497 cm^{-1} assigned to the free amino group.

Potentiometric pKa measurements on [(π-aniline)(π-tetraphenylcyclobutadiene)cobalt]bromide in (50%) aqueous methanol

Hydrochloric acid (o.1 N, 5 ml) was added to a solution of 0.12 g (0.21 mmole) of [(π-aniline)(π-tetraphenylcyclobutadiene)cobalt] bromide in 50 ml methanol and 45 ml water. This solution was titrated with equal volumes of sodium hydroxide (0.1 N) and methanol (to keep the composition of the solvent constant) and the pH was measured at 24.6°C under nitrogen on a Radiometer pH meter-4. The aniline (0.0227 g, 0.244 mmole) and the reference solutions were prepared and titrated in an identical way. The results obtained were:

titration		p_aH reference solution	$[(\pi\text{-}Ph_4C_4)Co(\pi\text{-}C_6H_5NH_2)]^+Br^-$		$C_6H_5NH_2$	
NaOH(0.1N)ml	methanol ml		p_aH	pKa	p_aH	pKa
0.00	0.00	2.360	2.295		2.648	
0.40	0.40	2.440	2.435		2.715	
0.80	0.80	2.480	2.500		2.800	
1.20	1.20	2.522	2.554		2.905	
1.60	1.60	2.574	2.610		3.025	
2.00	2.00	2.633	2.671		3.195	
2.40	2.40	2.695	2.745		3.400	
2.80	2.80	2.775	2.835		3.690	
3.00	3.00	2.820	2.888		3.810	
3.20	3.20	2.867	2.945	2.891	3.950	
3.40	3.40	2.919	3.010	2.885	4.100	
3.60	3.60	2.984	3.090	2.928	4.232	
3.80	3.80	3.062	3.180	2.968	4.386	4.475
4.00	4.00	3.148	3.291	2.976	4.528	4.456
4.20	4.20	3.269	3.445	3.035	4.700	4.484
4.40	4.40	3.406	3.681	3.213	4.885	4.487
4.60	4.60	3.600	4.142		5.140	4.538
4.80	4.80	4.160	4.427		5.510	
5.00	5.00	7.685	8.345		9.110	
5.20	5.20	10.278	9.510		10.400	
5.40	5.40		10.384		10.665	

* For calculations see Appendix-III

The average pKb of [(π-aniline)(π-tetraphenylcyclobutadiene)cobalt] bromide, calculated from several points of the titration curve (Appendix-III), was 11.00 ± 0.10. Under similar conditions the pKb of aniline was found to be 9.51 ± 0.04. The decrease in basicity on complexing of the aniline is, therefore, about 1.5 pK units.

[(π-Cycloheptatriene)(π-tetraphenylcyclobutadiene)cobalt] bromide•1.1 cobaltous bromide (93, R=Ph, X=Br•1.1 $CoBr_2$)

(π-Tetraphenylcyclobutadiene)cobalt dicarbonyl bromide (0.22 g; 0.39 mmole) was refluxed in 15 ml of cycloheptatriene for 30 minutes. The reaction mixture was cooled to 25°C, 30 ml of light petroleum were added and the green precipitate which formed was filtered off, washed with light petroleum and vacuum dried to give [(π-cycloheptatriene)(π-tetraphenylcyclobutadiene)cobalt] bromide•1.1 cobaltous bromide, m.p. 254-256°C (decomp.). Yield, 0.093 g, 25% based on the starting cobalt complex.

Analysis. Found: C,50.69; H,3.69; Br,31.00; Co,14.80. Calculated for $C_{35}H_{28}CoBr$•1.1 $CoBr_2$: C,50.77; H,3.41; Br,30.88; Co,14.94. This complex was insoluble in solvents which did not decompose it. The presence of the π-cycloheptatriene and π-tetraphenylcyclobutadiene ligands was inferred by comparison of its infra-red spectrum with those of analogous compounds (see below).

[(π-Cycloheptatriene)(π-tetraphenylcyclobutadiene)cobalt] iodide (93, R=Ph, X=I)

A saturated methanol solution (2.0 ml) of potassium iodide was added to a solution of 0.10 g (0.12 mmole) of [(π-cycloheptatriene)(π-tetraphenylcyclobutadiene)cobalt] bromide ·1.1 cobaltous bromide in 10 ml of methanol. The yellow-orange crystalline product formed was filtered off, then was washed with methanol and vacuum dried at 25°C to give [(π-cycloheptatriene)(π-tetraphenylcyclobutadiene)cobalt] iodide, m.p. 195-205°C (decomp.). Yield, 0.031 g, 44% based on the starting cobalt complex.

Analysis. Found: C,66.52; H,4.48. Calculated for $C_{35}H_{28}CoI$: C,66.30; H,4.45. The infra-red spectrum (Appendix-I) was identical to that of (93, R=Ph, X=Br·1.1 $CoBr_2$) indicating the presence of the same cation in both.

[(π-Cycloheptatriene)(π-tetraphenylcyclobutadiene)cobalt] hexafluorophosphate (93, R=Ph, X=PF_6)

A saturated methanol solution (2.0 ml) of ammonium hexafluorophosphate was added to a solution of 0.080 g (0.10mmole) of [(π-cycloheptatriene)(π-tetraphenylcyclobutadiene)cobalt] bromide·1.1 cobaltous bromide in 15 ml of methanol. The yellow crystalline product formed was filtered off, then washed with methanol and vacuum dried at 60°C to give [(π-cycloheptatriene)(π-tetraphenylcyclobutadiene)cobalt] hexafluorophosphate, m.p. 284-288°C (decomp.). Yield, 0.036 g, 56% based on the starting cobalt complex.

Analysis. Found: C,64.28; H,4.19. Calculated for $C_{35}H_{28}CoPF_6$: C,64.41; H,4.33. The infra-red spectrum (Appendix-I) was identical to that of (93, R=Ph, X=I), except for the strong, rather broad, band at 850-840 cm^{-1} due to the hexafluorophosphate anion.

[(π-Cycloheptatriene)(π-tetraphenylcyclobutadiene)cobalt] tetrathiocyanato cobaltat. (93, R=Ph, X=$\frac{1}{2}$Co(NCS)$_4$

Potassium thiocyanate (0.30 g; 3.1 mmoles) was added to a solution of 0.035 g (0.043 mmole) of [(π-cycloheptatriene)(π-tetraphenylcyclobutadiene)cobalt] bromide•1.1 cobaltous bromide in 10 ml of methanol. The original yellow-orange solution turned green and was filtered, 5 ml of water were added to the filtrate, and the green crystalline product formed was filtered off, washed with water and vacuum dried at 25°C to give [(π-cycloheptatriene)(π-tetraphenylcyclobutadiene)cobalt] tetrathiocyanatocobaltat, m.p. 110-120°C (decomp.). Yield, 0.015 g, 27% based on the starting cobalt complex.

Analysis. Found: C,68.55; 68.74; H,4.42; 4.43. Calculated for $C_{74}H_{56}N_4S_4Co_3$: C,68.10; H,4.43. The infra-red spectrum was identical to that of (93, R=Ph, X=I), except for the strong band at 2066 cm^{-1} due to a terminal NCS group (Appendix-I).

[(π-Cycloheptatriene){π-tetrakis(p-tolyl)cyclobutadiene} cobalt] bromide• 1.5 cobaltous bromide (93, R=To, X=Br•1.5 CoBr$_2$)

{π-Tetrakis(p-tolyl)cyclobutadiene} cobalt dicarbonyl bromide (0.22 g; 0.37 mmole) was refluxed in 10 ml of cycloheptatriene for 30 minutes. The green [(π-cycloheptatriene) {π-tetrakis(p-tolyl)cyclobutadiene} cobalt] bromide•1.5 cobaltous bromide, m.p. 238-242°C (decomp.) was isolated by the same procedure used for (93, R=Ph, X=Br•1.1 CoBr$_2$). Yield, 0.08 g, 40% based on the starting cobalt complex.

Analysis. Found: C,48.18; H,412. Calculated for $C_{39}H_{36}CoBr\cdot 1.5\,CoBr_2$: C,48.21; H,3.74.

[(π-Cycloheptatriene) {π-tetrakis(p-tolyl)cyclobutadiene} cobalt] hexafluorophosphate (93, R=To, X=PF_6)

A saturated methanol solution (2.0 ml) of ammonium hexafluorophosphate was added to a solution of 0.05 g (0.051 mmole) of [(π-cycloheptatriene) {π-tetrakis(p-tolyl)cyclobutadiene} cobalt] bromide•1.5 cobaltous bromide in 10 ml of methanol. The yellow crystalline product formed was filtered off, then was washed with methanol and vaccum dried at 25°C to give [(π-cycloheptatriene) {π-tetrakis(p-tolyl)cyclobutadiene} cobalt] hexafluorophosphate, m.p. 248-251°C (decomp.). Yield, 0.0090 g, 25% based on the starting cobalt complex.

Analysis. Found: C, 66.00; H, 5.12. Calculated for $C_{32}H_{28}CoPF_6$: C, 66.20; H, 5.12. The infra-red spectrum was identical to that of (93, R=To, X=Br•1.5 $CoBr_2$) except for the strong, rather broad band at 850-840 cm^{-1} due to the hexafluorophosphate anion.

(π-3.5-Cycloheptadienyl)(π-tetraphenylcyclobutadiene)cobalt (95, R=Ph, X=H)

A solution of 0.10 g (2.3 mmoles) of sodium borohydride in 0.6 ml of water was added dropwise to a solution of 0.14 g (0.17 mmole) of [(π-cycloheptatriene)(π-tetraphenylcyclobutadiene)cobalt] bromide•1.1 cobaltous bromide in 50 ml methanol. The red precipitate of the product, formed immediately, was filtered off and then extracted with n-hexane to give a red solution. This solution was filtered, the filtrate was stripped to dryness on a rotary evaporator, and the orange-red crystalline product obtained was recrystallized from n-hexane-methanol to give (π-3.5-cycloheptadienyl) (π-tetraphenylcyclobutadiene)cobalt, m.p. 187-188°C (decomp.). Yield, 0.014 g, 16% based on the starting cobalt complex.

Analysis. Found: C,82.76; H,5.90; Co,11.50; mol. wt. 507. Calculated for $C_{35}H_{29}Co$: C,82.64; H,5.75; Co,11.60; mol. wt. 508. The H^1 N.M.R. spectrum showed a strong, rather broad peak centred at 2.80τ due to the phenyl protons and five multiplets centred at 4.20τ; 5.13τ; 5.89τ; 7.46τ and 8.40τ assigned to the Ha; Hb(=H^1b); Hc(=H^1c); $>CH_2$ and $>CH_2$ protons of the π-bonded cycloheptadienyl ligand, respectively, (for infra-red spectrum see Appendix-I).

Conversion of the (π-3.5-cycloheptadienyl)(π-tetraphenylcyclobutadiene) cobalt into the [(π-cycloheptatriene)(π-tetraphenylcyclobutadiene)cobalt] hexafluorophosphate

N-Bromosuccinimide (0.030 g; 0.17 mmole) was added slowly to a mixture of 0.030 g (0.059 mmole) of (π-3.5-cycloheptadienyl)(π-tetraphenylcyclobutadiene)cobalt and 0.050 g (0.33 mmole) of ammonium hexafluorophosphate in 2.0 ml light petroleum and 5.0 ml methanol. The reaction mixture was stirred at 25°C for 5 minutes, and the yellow precipitate formed was filtered off and washed with water. The product was recrystallized from dichloromethane-light petroleum to give [(π-cycloheptatriene)(π-tetraphenylcyclobutadiene)cobalt] hexafluorophosphate, m.p. 272-282°C (decomp.), mixed m.p. with an authentic sample [of m.p. 284-289°C (decomp.)] was 281-285°C (decomp.). Yield, 0.0070 g 18% based on the starting cobalt complex. The infra-red spectrum was identical with that of the authentic sample.

(π-2-Hydroxy-3.5-cyclohexadienyl)(π-tetraphenylcyclobutadiene)cobalt

(95, R=Ph, Y=OH)

A suspension of 0.21 g (0.26 mmole) of [(π-cycloheptatriene)(π-tetraphenylcyclobutadiene)cobalt] bromide·1.1 cobaltous bromide in 20 ml wet benzene and 10 ml triethylamine was heated for 10 minutes on a steam bath. The orange solution formed was filtered, the filtrate was stripped to dryness on a rotary evaporator, and the orange product obtained was recrystallized from ether-light petroleum to give (π-2-hydroxy-3.5-cycloheptadienyl)(π-tetraphenylcyclobutadiene)cobalt, m.p. 135-137°C (decomp.). Yield, 0.086 g, 64% based on the starting cobalt complex.

Analysis. Found: C,79.94; H,5.70; Co,11.03. Calculated for $C_{35}H_{29}OCo$: C,80.20; H,5.58; Co,11.25. (for infra-red spectrum see Appendix-I)

(π-2-Methoxy-3.5-cycloheptadienyl)(π-tetraphenylcyclobutadiene)cobalt

(95, R=Ph, $Y=OCH_3$)

A solution of 0.054 g (1.0 mmole) of sodium methoxide in 2 ml methanol was added to a solution of 0.27 g (0.33 mmole) of [(π-cycloheptatriene)(π-tetraphenylcyclobutadiene)cobalt] bromide·1.1 cobaltous bromide in 20 ml of methanol at 25°C. The orange solid which precipitated was filtered off and then extracted with n-hexane to give an orange-red solution. This solution was filtered; the filtrate was evaporated to dryness on a rotary evaporator and the orange-red crystalline product obtained was recrystallized from dichloromethane and methanol to give (π-2-methoxy-3.5-cycloheptadienyl)(π-tetraphenylcyclobutadiene)cobalt, m.p. 190-195°C(decomp.). Yield 0.090 g 62% based on the starting cobalt complex.

Analysis. Found: C,80.08; H,5.95; mol. wt. 536. Calculated for $C_{36}H_{31}O\,Co$: C,80.30; H,5.80; mol. wt. 538. The H^1 N.M.R. spectrum showed two peaks at 2.43τ and 6.73τ due to the phenyl and methyl protons with the expected intensity ratio of 20:3, respectively. In addition the spectrum showed seven multiplets centred at 4.10(triplet)τ; 5.00τ; 5.50τ; 6.25τ; 6.90τ; 7.90τ; and 8.90τ assigned to the unequivalent cycloheptadienyl protons. The low field triplet was assigned to the coupling of Ha with Hb and H^1b (Jab $\sim$ Jab^1 = 7 c/s) (For infra-red spectrum see Appendix-I)

(π-2-Methoxy-3.5-cycloheptadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} cobalt (95, R=Ph, Y=OCH_3)

A solution of 0.054 g (1.0 mmole) of sodium methoxide in 2.0 ml methanol was added to a solution of 0.26 g (0.27 mmole) of [(π-cycloheptatriene) {π-tetrakis(p-tolyl)cyclobutadiene} cobalt] bromide·1.5 cobaltous bromide in 30 ml of methanol at 25°C. The orange crystalline product (π-2-methoxy-3.5-cycloheptadienyl) {π-tetrakis(p-tolyl)cyclobutadiene} cobalt, m.p. 175-178° (decomp.) was isolated by the same procedure used for $(\pi\text{-}Ph_4C_4)Co(\pi\text{-}C_7H_8OMe)$. Yield, 0.070 g, 43% based on the starting cobalt complex.

Analysis. Found: C,80.67; H,6.45; mol. wt. 616. Calculated for $C_{40}H_{39}OCo$: C,80.80; H,6.6; mol. wt. 594. The H^1 N.M.R. spectrum showed a sharp A B quartet centred at 2.83τ (2.63τ; 2.77τ 2.90τ; 3.03τ; J=8.0 c/s) and singlets at 6.88τ and 7.73τ assigned to the aromatic, methoxy and methyl protons, respectively. The intensity ratio was the expected 16:3:12.

Attempted synthesis of (π-allyl)(π-tetraphenylcyclobutadiene)carbonyl cobalt

A suspension of allylmagnesium chloride [prepared at 25°C from 0.40 g (5.25 mmoles) allylchloride and 0.30 g of magnesium in 30 ml ether] was added to a suspension of 0.50 g (0.91 mmole) of (π-tetraphenylcyclobutadiene)cobalt dicarbonyl bromide in 40 ml toluene at 0°C. The reaction mixture was warmed to 25°C, stirred for 4 hours, and the solvent was removed on a rotary evaporator. The residual solid was dried and extracted with n-hexane to give a red-orange solution. This solution was filtered, the filtrate was evaporated to dryness and the orange-red crystalline product obtained was recrystallized from light petroleum-methanol to give (π-allyl)(π-tetraphenylcyclobutadiene)carbonyl cobalt, m.p. 63-64°C (decomp.). Yield, 0.040 g, 9.0% based on the starting cobalt complex.

Analysis. Found: C,80.72; 80.64; H,5.92, 6.02; mol. wt. 466. Calculated for $C_{32}H_{25}OCo$, C,79.40; H,5.20; mol. wt. 484. The infra-red spectrum (Appendix-I) showed a single strong terminal carbonyl stretching frequency at 1988 cm^{-1}, the other bands in the spectrum, were similar to those of the other π-tetraphenylcyclobutadiene complexes. This compound was extremely unstable in solution and all attempts to prepare a pure sample failed.

Attempted synthesis of (σ-methallyl)(π-tetraphenylcyclobutadiene)dicarbonyl cobalt (88)

A suspension of methallylmagnesium chloride [prepared at 25°C from 0.40 g (4.4 mmoles) of methallylchloride and 0.30 g of magnesium in 30 ml ether] was added to a suspension of 0.50 g (0.91 mmole) of (π-tetraphenylcyclobutadiene)cobalt dicarbonyl bromide in 30 ml toluene at 0°C. The yellow crystalline product (σ-methallyl)(π-tetraphenylcyclobutadiene) dicarbonyl cobalt, m.p. 173-175°C (decomp.) was isolated by the same procedure used for (90). Yield, 0.10 g, 21% based on the starting cobalt complex.

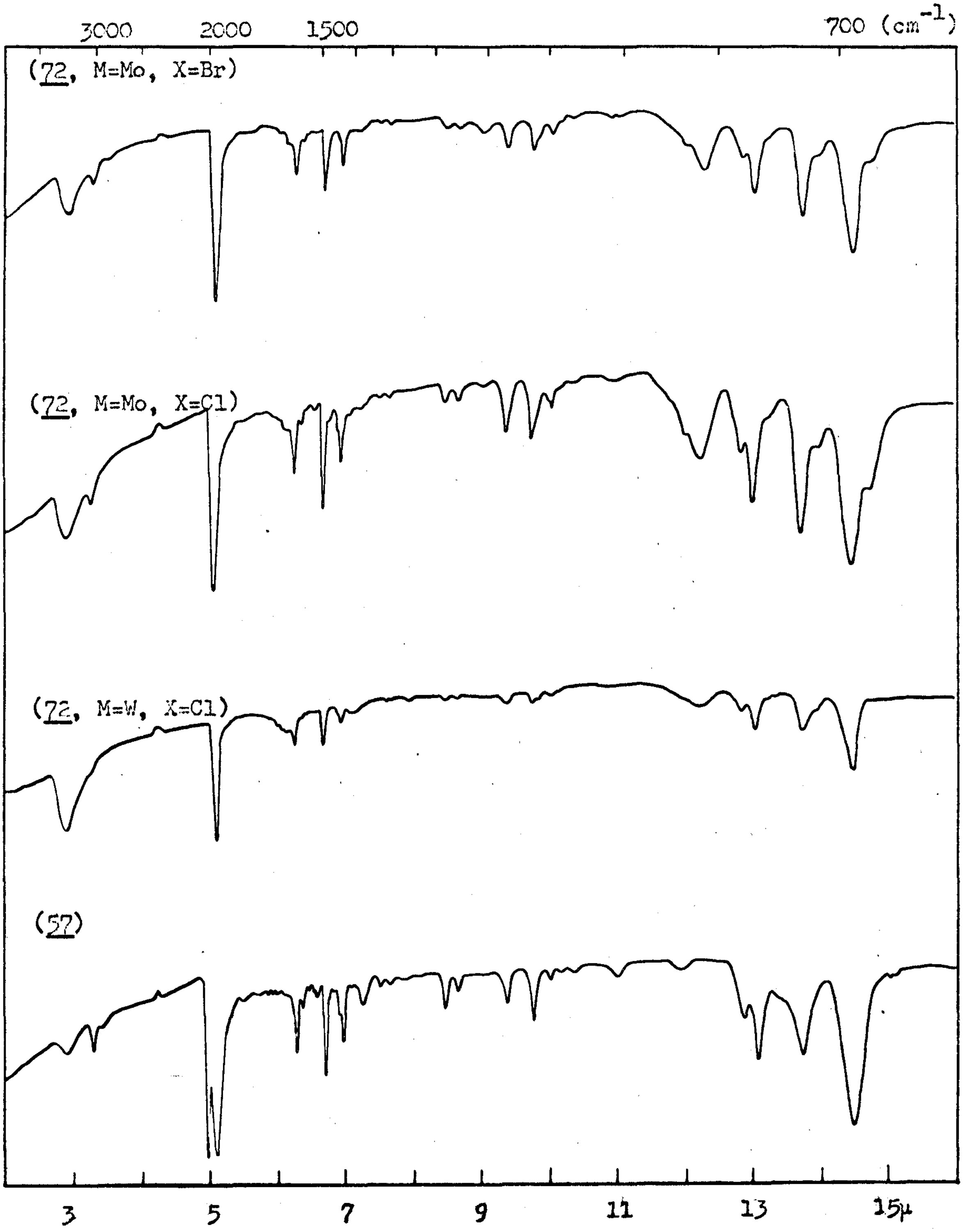
Analysis. Found: C,77.42; H,5.10; O,5.99; mol. wt. 510. Calculated for $C_{34}H_{27}O_2Co$: C,77.40; H,5.18; O,6.08; mol. wt. 526. The infra-red spectrum (Appendix-I) showed two strong terminal carbonyl stretching frequencies at 2028 cm^{-1} and 1976 cm^{-1}; the other bands in the spectrum were similar to those of the other π-tetraphenylcyclobutadiene complexes. Although this compound was expected to be diamagnetic, the presence of some undetectable paramagnetic impurities gave a very diffuse and uninterpretable H^1 N.M.R. spectrum. All attempts to prepare the (π-methallyl)(π-tetraphenylcyclobutadiene)carbonyl cobalt from (σ-methallyl)(π-tetraphenylcyclobutadiene)dicarbonyl cobalt by either refluxing in benzene or through ultra-violet irradiation in n-hexane failed.

APPENDIX

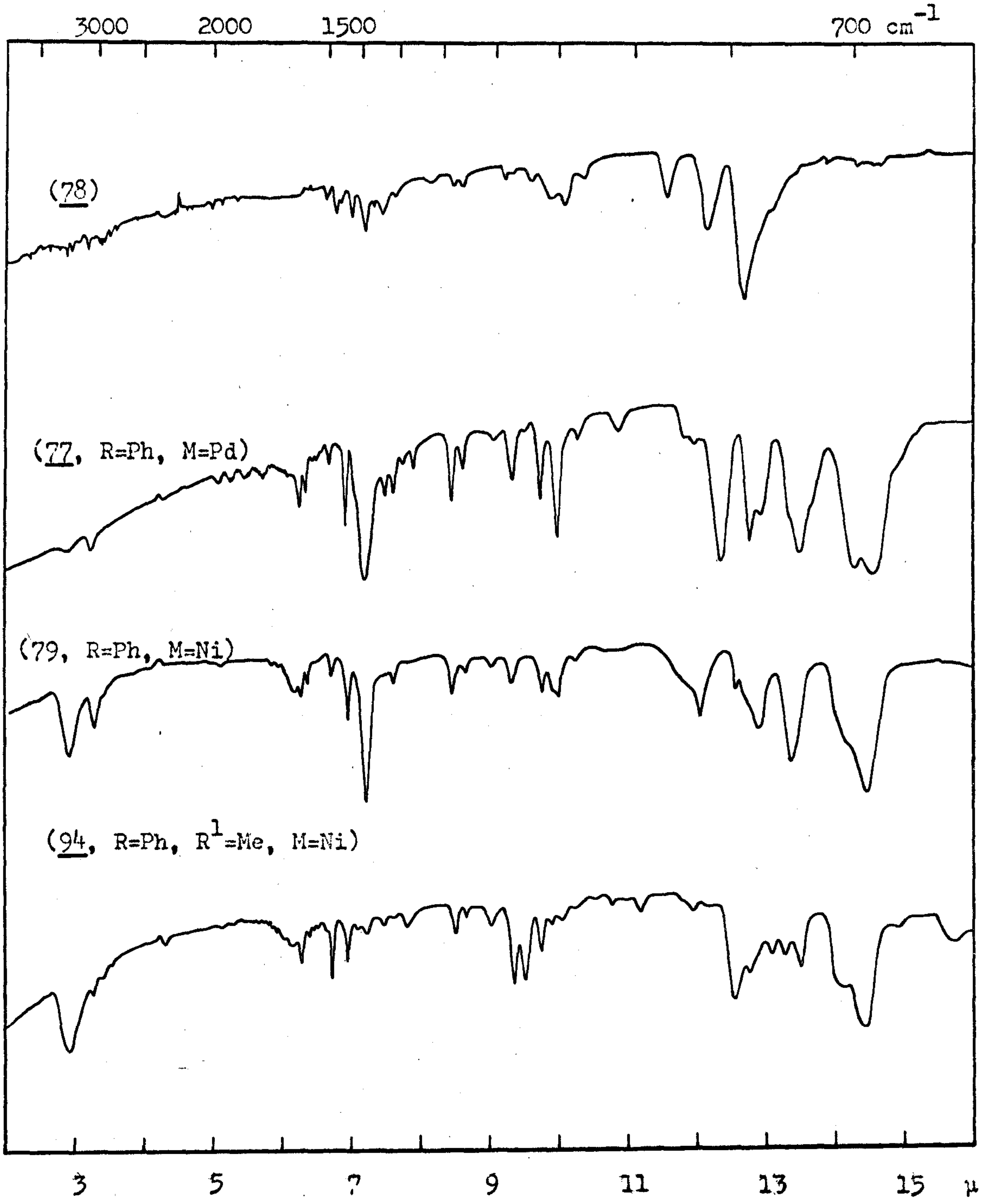
APPENDIX

Appendix - I

Infra-red spectra of typical cyclobutadiene-metal complexes.



INFRA-RED SPECTRA



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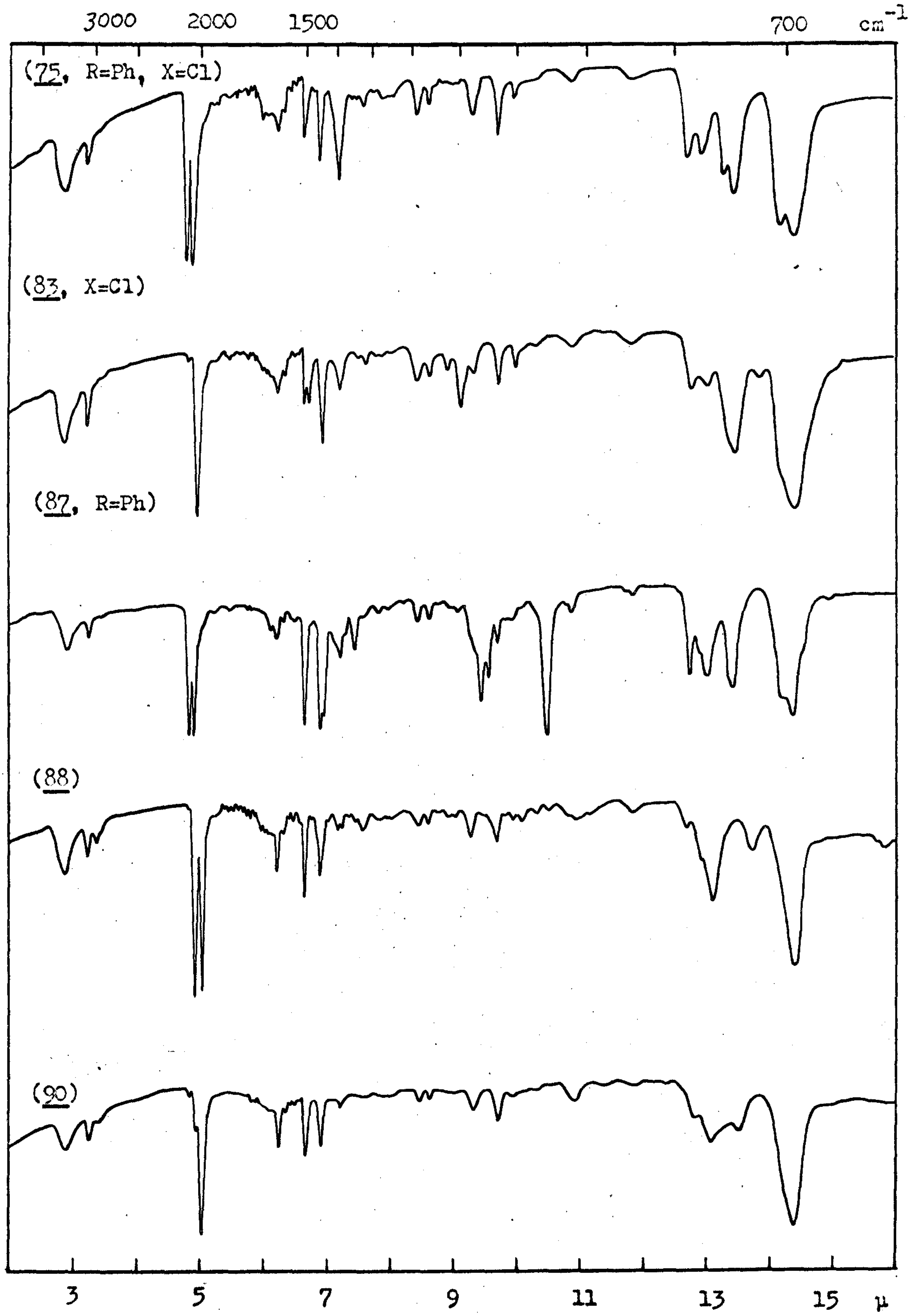

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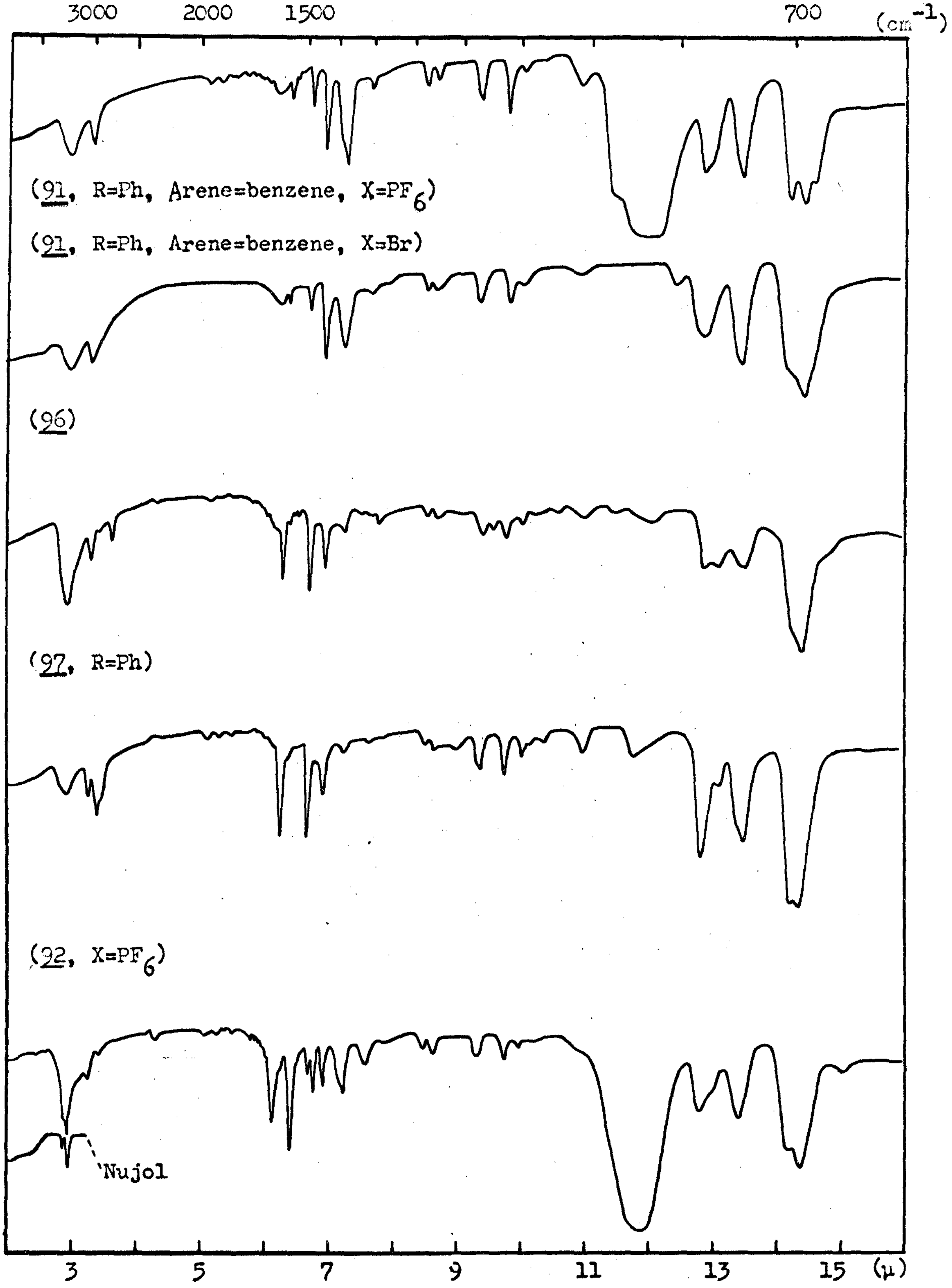
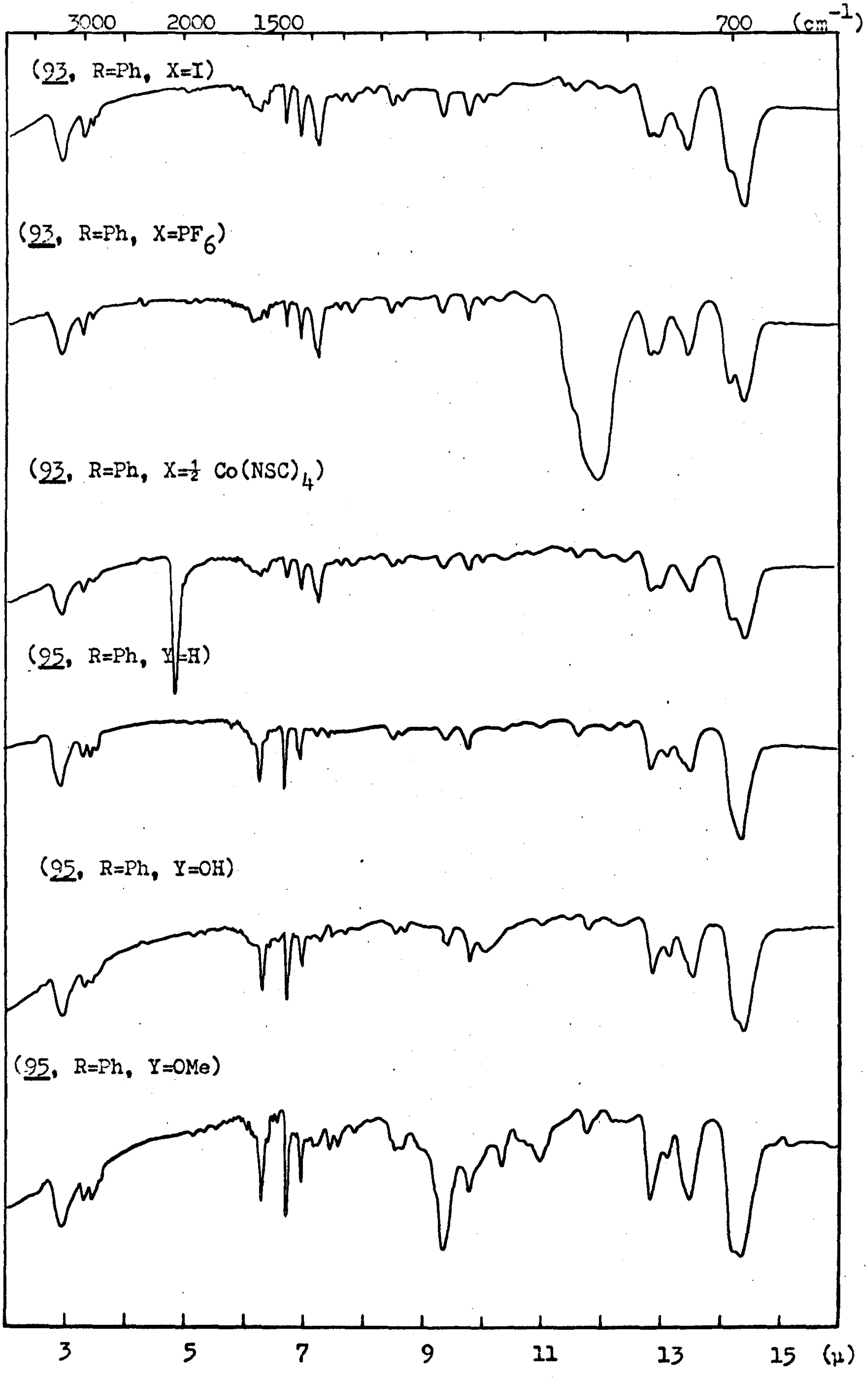


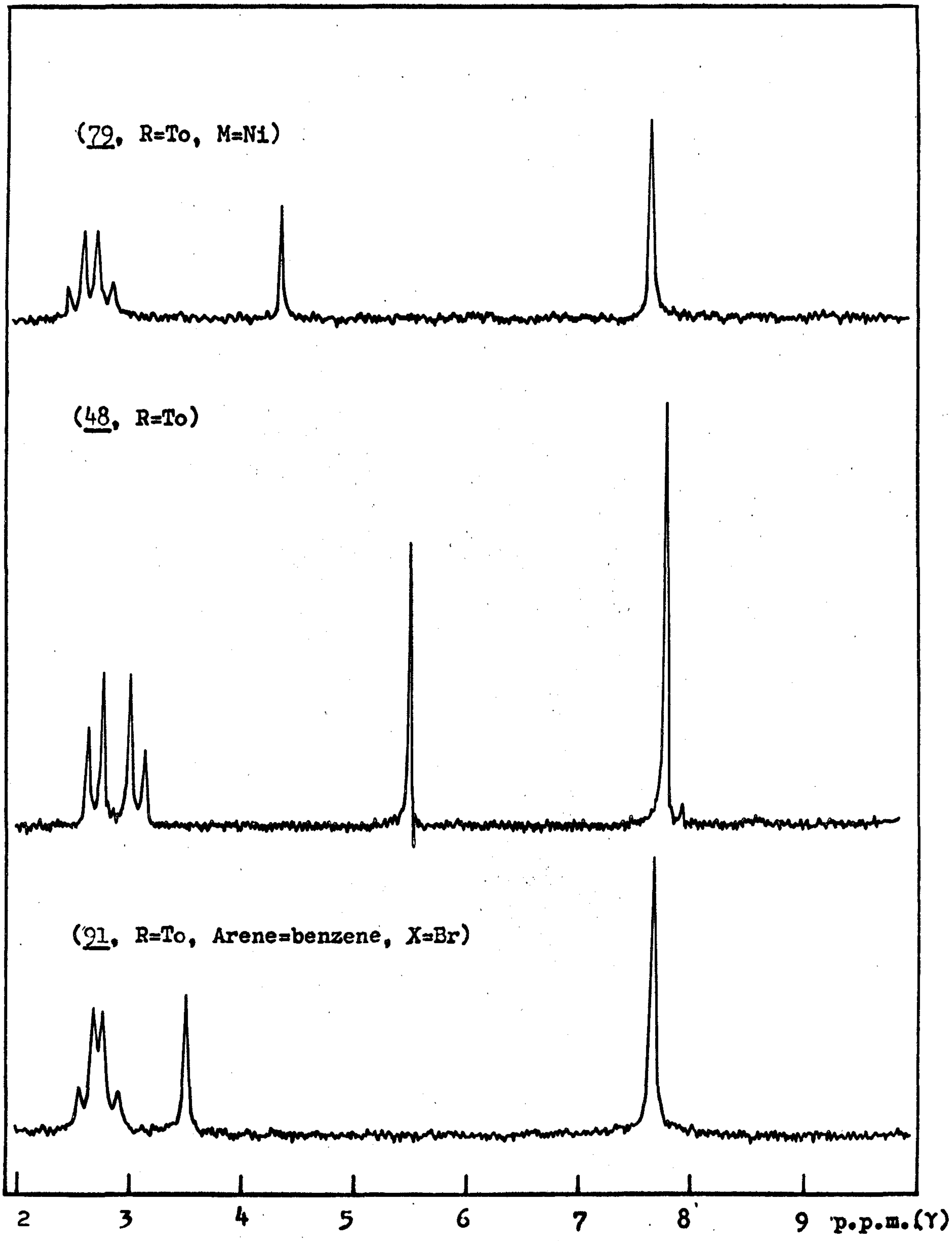
INFRA-RED SPECTRA



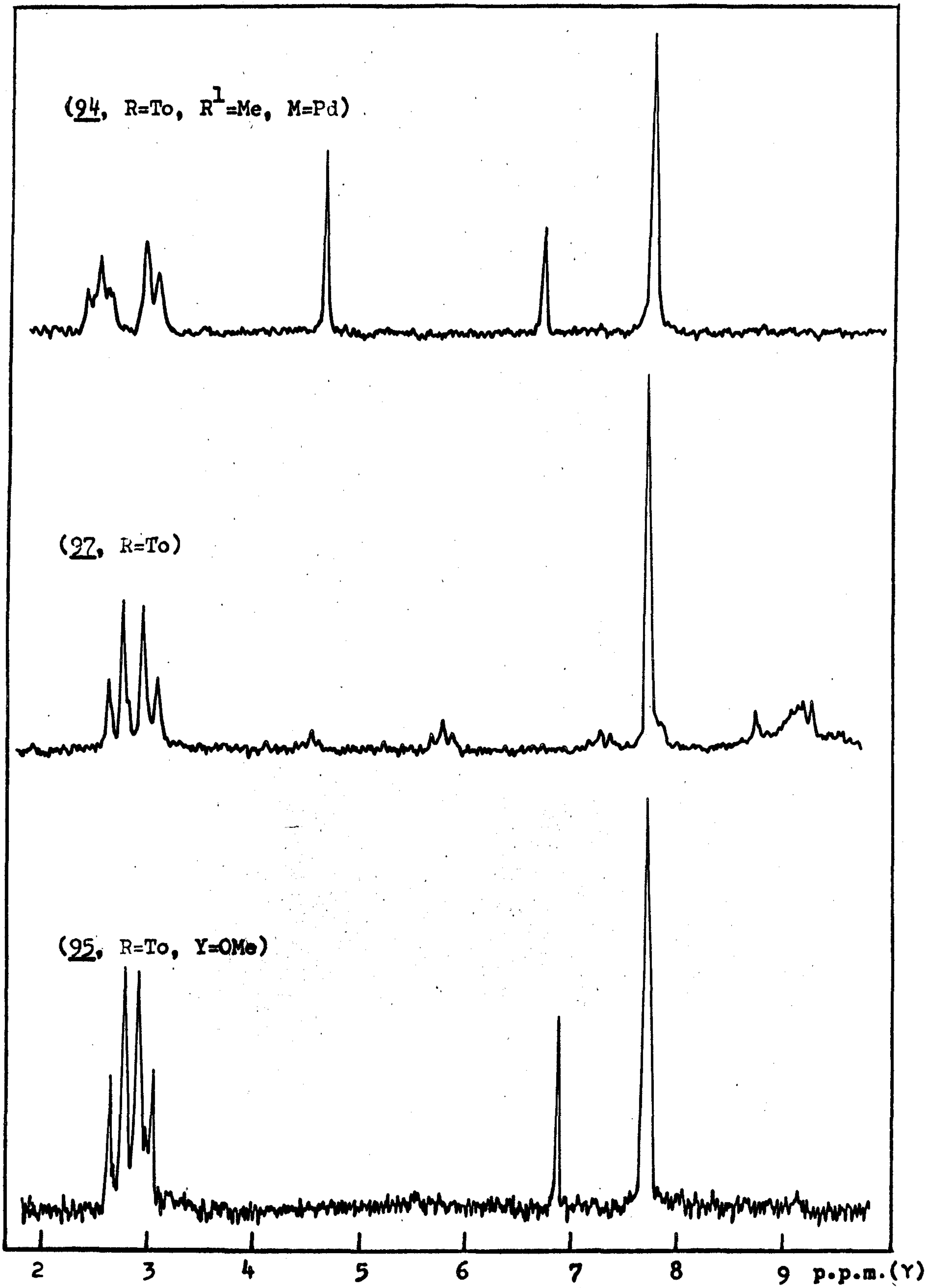
INFRA-RED SPECTRA

Appendix - II

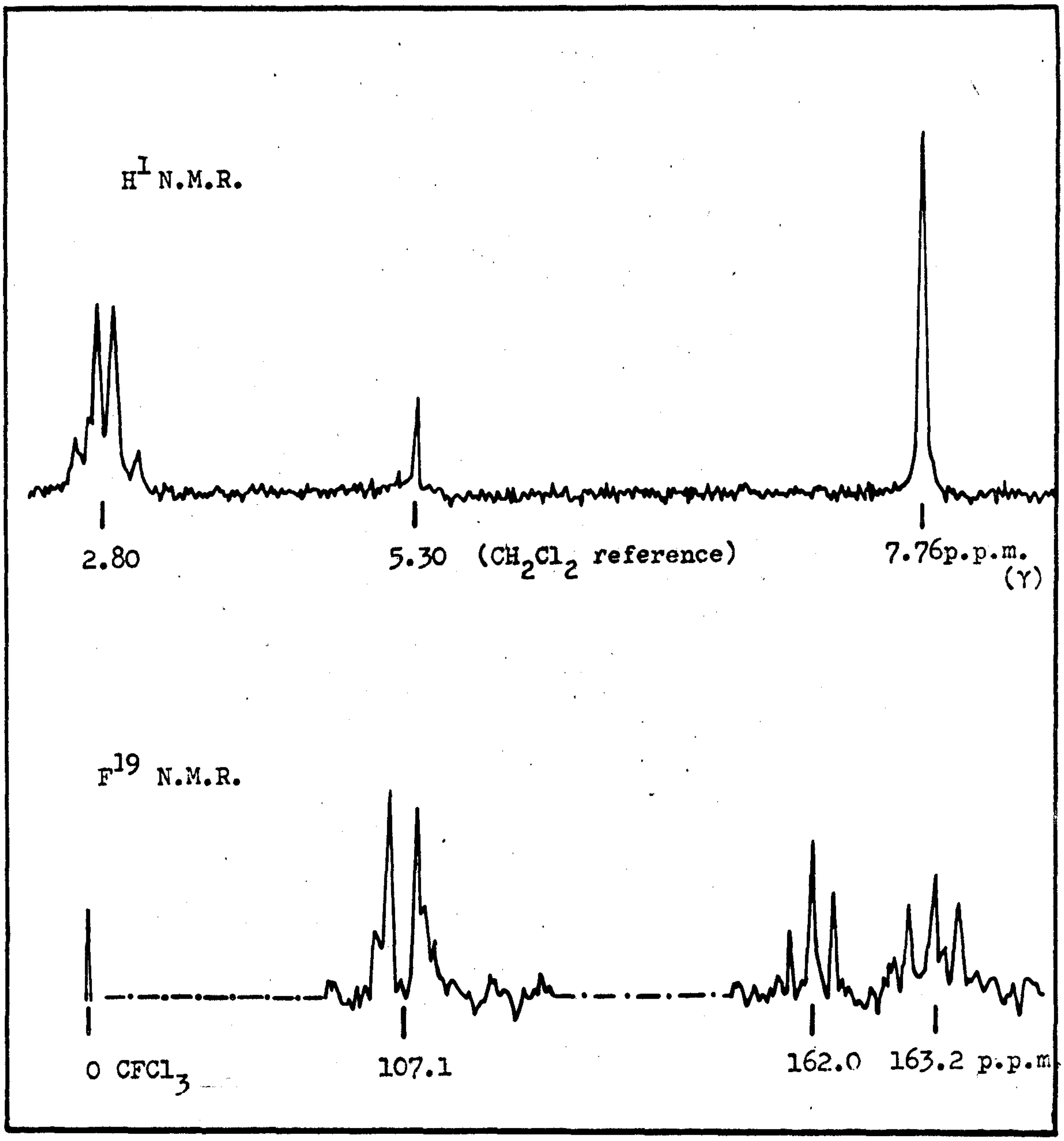
N.M.R. spectra of typical cyclobutadiene-metal complexes.



H^1 N.M.R. SPECTRA



H^1 N.M.R. SPECTRA



N.M.R. SPECTRA OF (87, R=To)

Appendix - III

pKa Calculations for the π-complexed aniline in $\left[(\pi\text{-}Ph_4C_4)Co(\pi\text{-}C_6H_5NH_2)\right]^+Br^-$.

In the system under consideration the following six species are present:

H^+, OH^-, Cl^-, Na^+, X^*, XH^+

The concentrations of these species, at any instant, are defined by the following equations:

(1) $$Ka = \frac{[X][H^+]}{[XH^+]}$$

(2) $$K_w = [H^+][OH^-]$$

(3) $$C_x \text{ (sum of all X species)} = [X] + [XH^+]$$

(4) $$[H^+] + [Na^+] + [XH^+] = [OH^-] + [Cl^-]$$

$[Cl^-]$ is the stoichiometric concentration of the acid present

$[Na^+]$ is calculated from the concentration of the base added

$$\left.\begin{array}{lll} \dfrac{Ka}{[H^+]} = \dfrac{[X]}{[XH^+]} & & \text{from (1)} \\ & & \\ [X] = C_x - [HX^+] & & \text{from (3)} \end{array}\right\} \quad \frac{Ka}{[H^+]} = \frac{C_x - [XH^+]}{[XH^+]}$$

$$[XH^+] = [OH^-] + [Cl^-] - [H^+] - [Na^+] \quad \text{from (4)}$$

Since $[OH^-]$ can be neglected

$$[XH^+] = [Cl^-] - [H^+] - [Na^+] = S$$

* $X = [(\pi\text{-}Ph_4C_4)Co(\pi\text{-}C_6H_5NH_2)]^+ \ Br^-$

$$\frac{Ka}{[H^+]} = \frac{C_x - S}{S} \quad \text{or} \quad Ka = \left\{ [H^+] \; \frac{C_x - S}{S} \right\}$$

$$pKa = -\log [H^+] - \log \frac{C_x - S}{S}$$

$$pKa = p_cH - \log \frac{C_x - S}{S}$$

The factor p_cH is the corrected p_aH value for the mixed solvent system (methanol-water):

$$p_cH = p_aH + \text{Constant.}$$

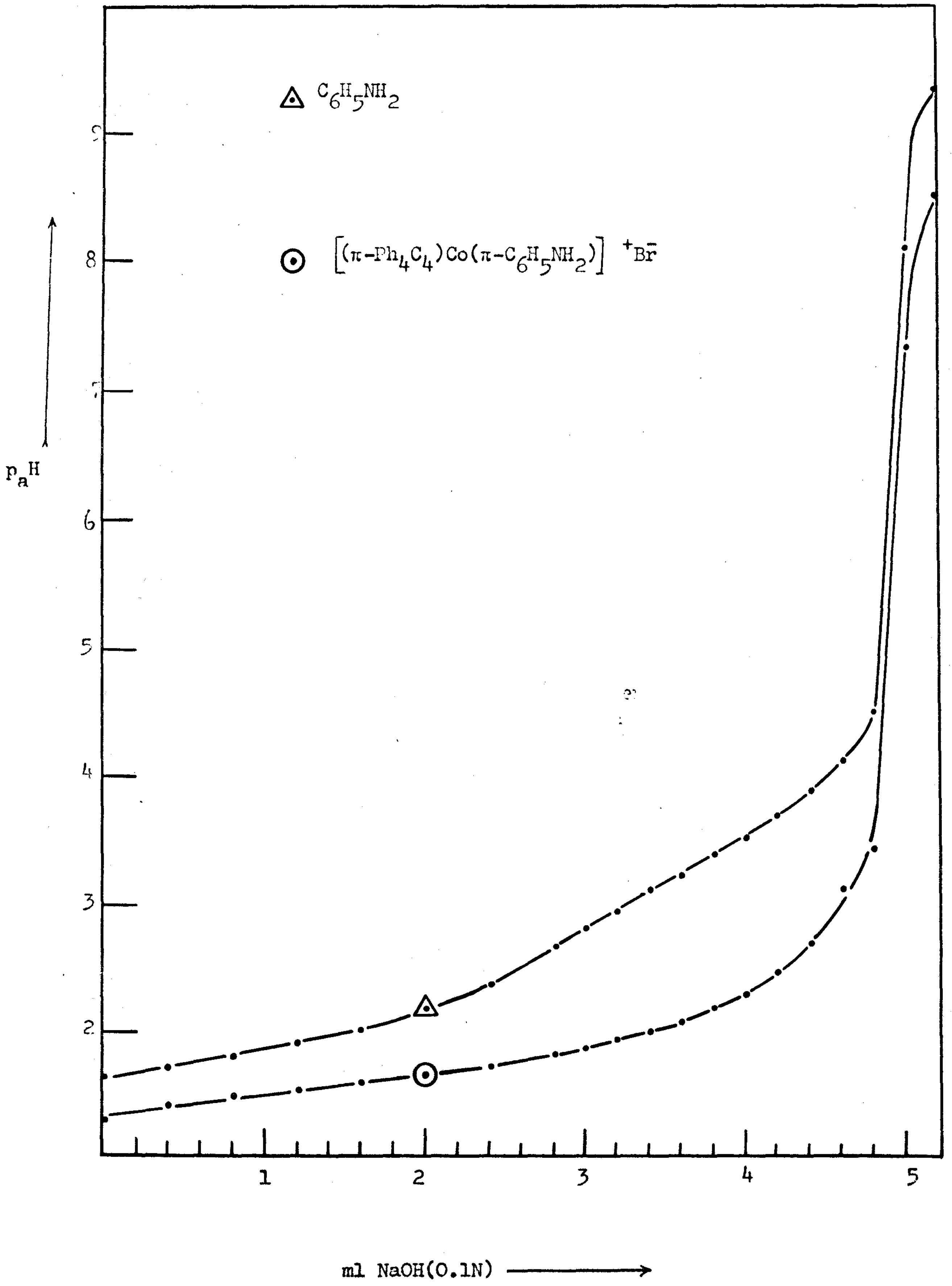
On the basis of the calibration titration, it was found that the Constant = 0.100.

The pKa values for $[(\pi\text{-}Ph_4C_4)Co(\pi\text{-}C_6H_5NH_2)]^+ Br^-$ were calculated as illustrated in the following table.

The pKa value for aniline was calculated in an identical way to that of $[(\pi\text{-}Ph_4C_4)Co(\pi\text{-}C_6H_5NH_2)]^+Br^-$. The titration curves for the aniline complex (<u>92</u>, X=Br) and the free aniline are given below.

Vol. of NaOH(0.1N) added (ml)	Vol. of CH_3OH added (ml)	Total Vol. (ml)	$[Cl^-]^*$ x 10^3	$[Na^+]^*$ x 10^3	p_aH	p_cH	$[H^+]^*$ x 10^4	S x 10^3	C_x^* x 10^3	C_x-S x 10^3	log $\frac{C_x - S}{S}$	pKa
3.20	3.20	106.40	4.71	3.01	2.945	3.045	9.02	0.800	1.940	1.140	0.1548	2.891
3.40	3.40	106.80	4.69	3.19	3.010	3.110	7.76	0.720	1.932	1.212	0.2253	2.885
3.60	3.60	107.20	4.67	3.35	3.090	3.190	6.45	0.680	1.925	1.245	0.2625	2.928
3.80	3.80	107.60	4.65	3.50	3.180	3.280	5.25	0.630	1.922	1.292	0.3118	2.968
4.00	4.00	108.00	4.62	3.69	3.291	3.391	3.99	0.530	1.914	1.384	0.4150	2.976
4.20	4.20	108.40	4.61	3.87	3.445	3.545	2.85	0.450	1.906	1.456	0.5105	3.035
4.40	4.40	108.80	4.60	4.05	3.681	3.781	1.65	0.390	1.900	1.510	0.5877	3.213

* $[Cl^-]$, $[Na^+]$, $[H^+]$ and C_x concentrations are given in moles/liter.


△ $C_6H_5NH_2$
⊙ $[(\pi\text{-}Ph_4C_4)Co(\pi\text{-}C_6H_5NH_2)]^+Br^-$
p_aH
9
8
7
6
5
4
3
2
1
2
3
4
5
ml NaOH(0.1N)

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