

## $\pi$ -LIGAND TRANSFER REACTIONS\*

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### I. INTRODUCTION

In 1956 Wilkinson, Cotton and Birmingham<sup>1</sup> reported the formation of ferrocene in the reaction between chromocene and ferrous chloride. This reaction represents the first known example of a  $\pi$ -ligand transfer reaction. The term  $\pi$ -ligand transfer was proposed originally by Maitlis and Games<sup>2</sup> for reactions involving a tetraphenylcyclobutadiene transfer from one transition metal to another. More recently, Rubezhov *et al.*<sup>3</sup> have suggested the terminology of  $\pi,\pi$ -transfer *versus*  $\pi,\sigma$ -transfer to distinguish between different types of allyl transfer processes. However, for the transition metal series alone, without considering main group elements this distinction is unnecessary since no  $\pi,\sigma$ -transfer processes have yet been encountered. In this review the term " $\pi$ -ligand transfer" will be used to describe reactions in which an organic  $\pi$ -ligand is transferred from one transition metal complex to another. The transition metals taking part in the transfer process can be either identical or different.

The practical aspects of  $\pi$ -ligand transfer reactions as a useful synthetic route to various  $\pi$ -complexes are obvious. The ultimate objectives in the development of this novel technique are aimed at one step, high yield and facile transfer processes starting from readily available and inexpensive reagents. This synthetic technique is of special importance when the free ligands are either extremely labile or totally unknown as with cyclobutadiene derivatives. To dramatize the potentiality of this novel technique in the latter case it is worth mentioning that more cyclobutadiene-metal complexes have been prepared by  $\pi$ -cyclobutadiene ligand transfer reactions than by any other procedure. Furthermore, in some cases,  $\pi$ -ligand transfer reactions represent the only known route by which certain  $\pi$ -complexes can be obtained. Unfortunately, in recent years, interest in this exciting field

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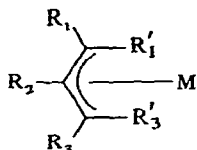
has subsided somewhat. Thus, it is hoped that this review, besides surveying and updating the substantial knowledge which has been accumulated throughout the years, will also stimulate further research in this novel and potentially important field. Some of the aspects of this subject were surveyed in part previously by Maitlis<sup>4</sup> and by Rubezhov and Gubin<sup>5</sup>.

To date, only three  $\pi$ -ligands (allyl, cyclobutadiene and cyclopentadienyl) have been successfully transferred from one transition metal complex to another. Unfortunately, these reactions usually occur under heterogeneous conditions and thus meaningful kinetic studies of them are not available. In spite of the lack of fundamental kinetic information, various mechanistic approaches were advanced to explain  $\pi$ -ligand transfer processes. Except for one case involving a  $\pi$ -allyl transfer from palladium to iron, in which a mechanism was proposed on the basis of comprehensive spectroscopic studies of the reaction in progress<sup>8</sup>, the  $\pi$ -ligand transfer mechanisms described below are tentative. At best, these speculative mechanisms explain the nature of the products formed.

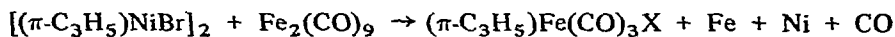
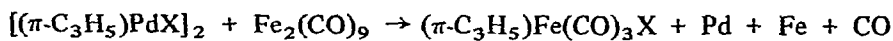
## II. $\pi$ -ALLYL TRANSFER REACTIONS

The  $\pi$ -allyl transfer reaction was discovered independently by two different groups of investigators: Nesmeyanov, Rubezhov and Gubin<sup>6</sup> and by Grindrod and Maitlis<sup>7</sup>. Both groups examined the same reaction that between the  $\pi$ -allylpalladium chloride dimer (1; X = Cl)\* and  $\text{Fe}_2(\text{CO})_9$  by which the  $\pi$ -allyl transfer product,  $\pi$ -allyliron tricarbonyl chloride (2; X = Cl), was obtained in 26%<sup>6</sup> and 39%<sup>7</sup> yield, respectively. Grindrod and Maitlis<sup>6</sup> also succeeded in transferring 2-methyl- $\pi$ -allyl from palladium to iron by a similar reaction. In 1969, Nesmeyanov *et al.*<sup>8</sup> reported what appears to be the most important and comprehensive study in this field. They described the transfer of  $\pi$ -allyl groups from nickel, palladium and platinum to iron. The reaction of various  $\pi$ -allylpalladium halide complexes (1; X = Cl, Br, I), (1;  $R_2 = \text{CH}_3$ ; X = Cl), (1;  $R_2 = \text{Ph}$ ; X = Cl) and (1;  $R_1 = \text{Ph}$ ; X = Cl) with  $\text{Fe}_2(\text{CO})_9$  in benzene solution at ambient temperature and over a period of 8 to 10 hours produced the respective  $\pi$ -allyliron tricarbonyl halide (2) complexes in yields up to 37%. The yield was calculated on the basis of consumption of the palladium complex (1). A similar reaction between the acetate derivative (1; X =  $\text{OCOCH}_3$ ) and  $\text{Fe}_2(\text{CO})_9$  carried out in the presence of tetramethylammonium iodide led to the formation of the  $\pi$ -allyliron iodide analogue (2; X = I). Interestingly, when  $\text{Fe}(\text{CO})_5$  was used instead of  $\text{Fe}_2(\text{CO})_9$  in the above reactions, the  $\pi$ -allyl transfer process slowed dramatically and required 8 to 10 days to complete. The  $\pi$ -allylnickel bromide dimer (3) has also been found to react with  $\text{Fe}_2(\text{CO})_9$  under similar conditions to give the  $\pi$ -allyliron complex (2; X = Br) but only in 12% yield. The halides of the  $\pi$ -allylpalladium complexes (1) appear to impose little if any influence on the  $\pi$ -allyl transfer process since the chloride,

\* For substituted  $\pi$ -allyl complexes the number of the compound will be followed by the description of the substituents and their positions according to the following scheme:



bromide and iodide products (2; X = Cl, Br, I) are isolated in approximately the same yield: 26%, 30% and 28%, respectively. By contrast, the nature and position of the substituents appear to affect the  $\pi$ -allyl transfer substantially. For instance, the  $\pi$ -allylpalladium



complexes (1) with 2-neopentyl and 2-(3-chloroisopropenyl) substituents did not react with  $\text{Fe}_2(\text{CO})_9$  and could be retrieved unchanged. At the same time, a total decay of  $\text{Fe}_2(\text{CO})_9$  was noticed and this was attributed to catalytic action of the  $\pi$ -allylpalladium chloride complexes (1). With respect to other substituted  $\pi$ -allyls, it has been demonstrated that transfer occurs satisfactorily with 2-methyl- $\pi$ -allyl, 2-phenyl- $\pi$ -allyl and 1-phenyl- $\pi$ -allyl<sup>8</sup>. Furthermore, comparison between the phenylallyl isomers revealed a slight enhancement in the transfer process with the 2-phenyl- $\pi$ -allyl ligand.

Spectroscopic studies were performed on the reaction of (1; X = Cl) and  $\text{Fe}_2(\text{CO})_9$ , in an attempt to elucidate the  $\pi$ -allyl transfer mechanism<sup>8</sup>. Nuclear Gamma Resonance (Mössbauer) studies revealed the fast disappearance of  $\text{Fe}_2(\text{CO})_9$ , the formation of one or several intermediates of the type  $\text{AFe}(\text{CO})_4$  and the gradual formation of the transfer product (2; X = Cl). Likewise, infrared measurements verified the rapid disappearance of the bridging carbonyls due to  $\text{Fe}_2(\text{CO})_9$ , in the reaction mixture. Most impressive were the PMR studies which showed broadening of the typical  $\pi$ -allyl resonances and the gradual appearance of a new symmetrical doublet at approximately  $\tau 6.25$ . Maximum line broadening was encountered approximately three hours into the reaction and from this point on, gradual sharpening of the resonance signals was observed. On the basis of above spectroscopic information, Nesmeyanov *et al.*<sup>8</sup> proposed the mechanism as shown in Fig. 1.

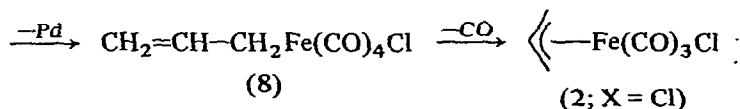
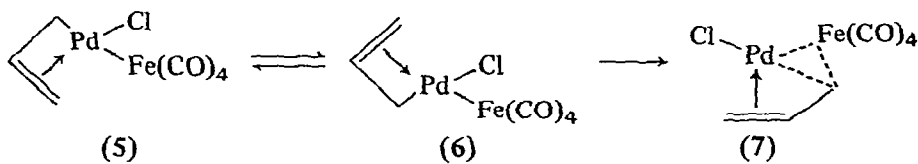
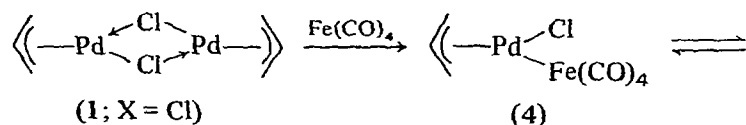
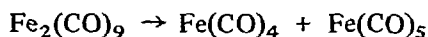


Fig. 1. The  $\pi$ -allyl transfer mechanism by Nesmeyanov *et al.*<sup>8</sup>.

This mechanism is based on the disproportionation of  $\text{Fe}_2(\text{CO})_9$  to  $\text{Fe}(\text{CO})_5$  and  $\text{Fe}(\text{CO})_4$  and the nucleophilic cleavage of the  $\mu$ -halide bridges in (1) by the latter, a process which forms the binuclear intermediate (4). The new doublet observed in the PMR spectra was attributed to the equivalent methylene protons in the equilibrating intermediates (5) and (6). Subsequent steps were discussed in terms of *cis* insertion<sup>9</sup> of  $\text{Fe}(\text{CO})_4$  into the Pd-C  $\sigma$ -bond as in (7), the formation of a  $\sigma$ -allyliron complex (8) and finally a  $\sigma, \pi$ -allyl rearrangement of (8) to (2) *via* loss of carbon monoxide. The mechanism of Nesmeyanov *et al.*<sup>8</sup> fails to explain some important features such as halide transfer and the formation of metallic iron which were encountered during the  $\pi$ -allyl transfer reactions. Moreover, the PMR spectra of the reaction in progress suggest the formation of diamagnetic (or nearly diamagnetic) intermediates while those conceived by Nesmeyanov *et al.*<sup>8</sup> are definitely paramagnetic. An alternative mechanism for the  $\pi$ -allyl transfer process which is in better agreement with the experimental and spectroscopic results is given in Fig. 2.

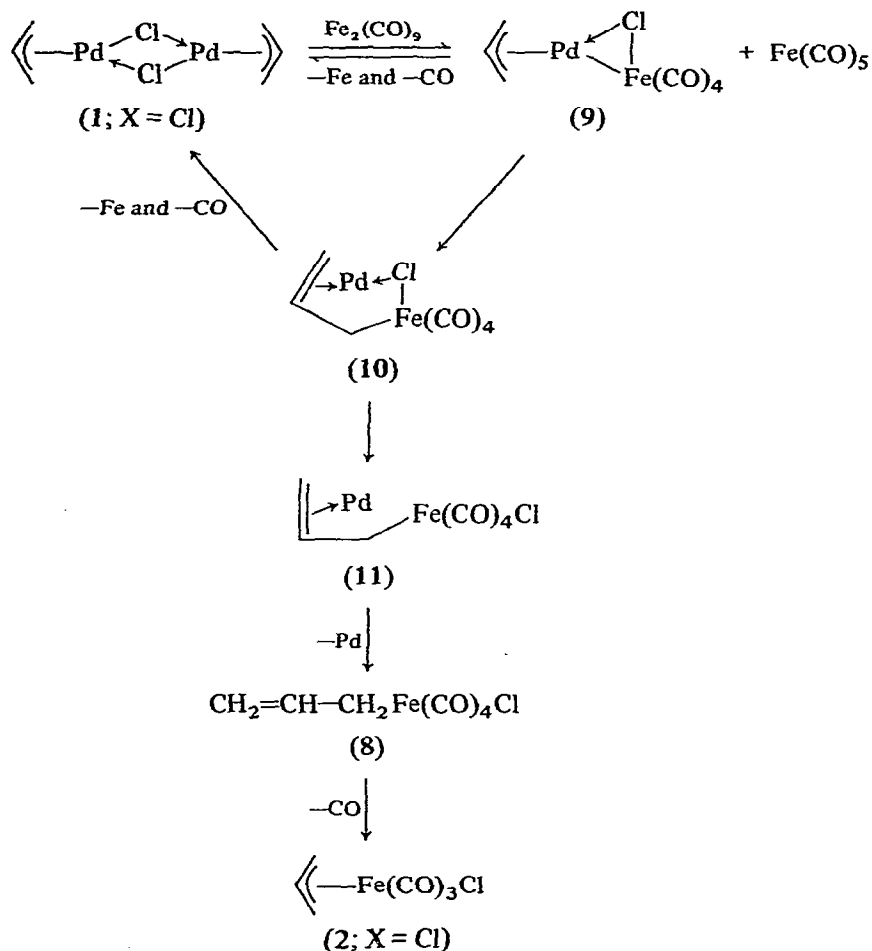
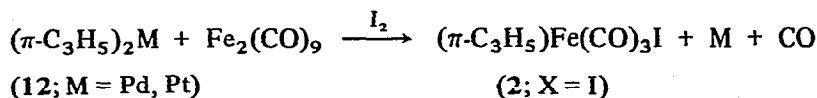
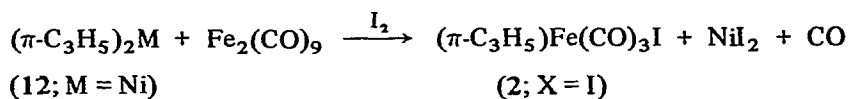


Fig. 2. An alternative  $\pi$ -allyl transfer mechanism.

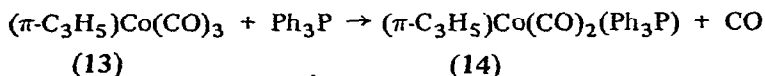
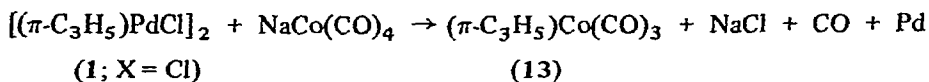
This mechanism suggests the formation of binuclear intermediates which are coordinatively and electronically saturated only with respect to one of the metals. The basic hypothesis is that the metal which remains coordinatively and electronically saturated in the reactant and product will tend to retain its configuration during the intermediate stages of the reaction. In this particular case, the iron atom is assumed to attain the favored rare gas, 18-electron configuration, throughout the transfer process while a stepwise reduction in the electronic configuration and coordination number of the palladium atom is taking place. For instance, the electronic configuration of the palladium atom in (1), (9), (10) and (11) is 16, 16, 14 and 12, respectively. In the penultimate step, the intermediate (11) disproportionates to give  $\text{Pd}^0$  and (8). Both Mössbauer and infrared spectra support the fast disappearance of  $\text{Fe}_2(\text{CO})_9$  and the formation of several intermediates of the type  $\text{AFe}(\text{CO})_4$ . The respective  $\pi$ -allyl protons in (1; X = Cl), (9) and (2; X = Cl) are all expected to resonate in similar regions. The same can also be said for the methylene protons in (10), (11) and (8) which could give rise to the new doublet at  $\tau 6.25$ . Therefore, the maximum line broadening observed after three hours of reaction could be the direct result of maximum accumulation of various interrelated intermediates as expected at approximately half reaction time. The sharpening of the PMR spectra lines and the increase in the intensity of the doublet at  $\tau 6.25$  towards the end of reaction probably reflect a decrease in the concentrations of (1; X = Cl), (9), (10) and (11) and an increase in the concentrations of (8) and (2; X = Cl). Disproportionation of the intermediates (9) and (10) neatly explains the irreversible formation of metallic iron as well as the evolution of carbon monoxide at an earlier stage than was conceived by Nesmeyanov *et al.*<sup>8</sup> Furthermore, the formation of intermediates such as (9) and (10) also explains the catalytic decomposition of  $\text{Fe}_2(\text{CO})_9$  in the presence of 2-neopentyl- and 2-(3-chloroisopropenyl)- $\pi$ -allylpalladium chloride dimers in which no  $\pi$ -allyl transfer processes were encountered. The much lower yield of  $\pi$ -allyl transfer found in the reaction between  $\pi$ -allylnickel bromide (3) and  $\text{Fe}_2(\text{CO})_9$  is also in accord with this mechanistic evaluation. The nickel halide bond, which is stronger than the palladium halide bond, would engage less favorable in the halide transfer process as envisioned above (Fig. 2). Undoubtedly, such an effect will reduce the efficiency of the  $\pi$ -allyl transfer process as well.

Nesmeyanov *et al.*<sup>8</sup> have also examined reactions between di- $\pi$ -allylnickel (12; M = Ni), -palladium (12; M = Pd) and -platinum (12; M = Pt) with  $\text{Fe}_2(\text{CO})_9$ . These reactions, carried out in ether solution and in the presence of iodine gave  $\pi$ -allyliron tricarbonyl iodide (2; X = I). Other products obtained were carbon monoxide,  $\text{NiI}_2$  with (12; M = Ni) and metallic palladium and platinum in the cases of (12; M = Pd, Pt). Vigorous evolution of carbon monoxide during the course of these reactions started only after the addition of iodine. Thus, it was concluded<sup>8</sup> that the  $\pi$ -allyl transfer processes from the di- $\pi$ -allylmetal

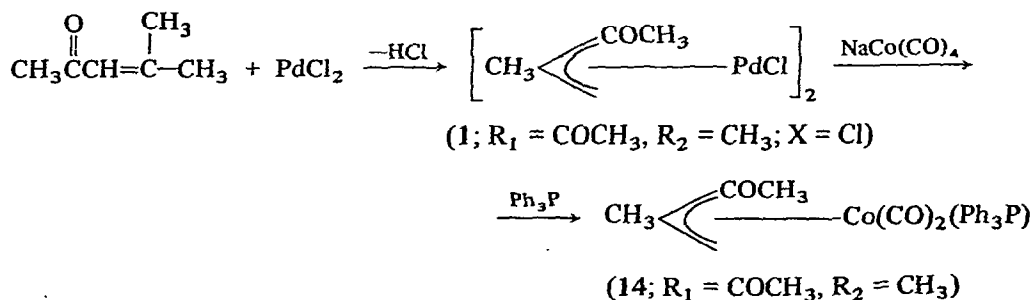
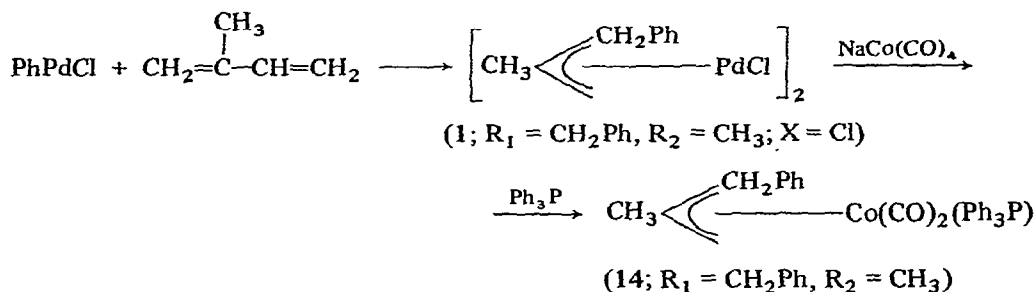


complexes (12) are fundamentally different from those involving the  $\pi$ -allylmetal halides (1).

An elegant  $\pi$ -allyl transfer from palladium to cobalt and *vice versa* was reported by Heck<sup>10</sup>.  $\pi$ -Allylpalladium chloride (1; X = Cl) has been shown to react with sodium tetracarbonylcobalt in ether solution at ambient temperature to afford  $\pi$ -allylcobalt tricarbonyl (13). The  $\pi$ -allylcobalt product was isolated and characterized as the monotriphosphine derivative (14), in 50% yield:



This interesting  $\pi$ -allyl transfer process enabled the preparation of several new  $\pi$ -allylcobalt complexes (14) which are unobtainable directly. For instance, (1-benzyl-2-methyl)- $\pi$ -allylpalladium chloride (1; R<sub>1</sub> = CH<sub>2</sub>Ph, R<sub>2</sub> = CH<sub>3</sub>; X = Cl), prepared from phenylpalladium chloride and isoprene, reacts with NaCo(CO)<sub>4</sub> and then with Ph<sub>3</sub>P to give the  $\pi$ -allylcobalt complex (14; R<sub>1</sub> = CH<sub>2</sub>Ph, R<sub>2</sub> = CH<sub>3</sub>) in 41% yield. Likewise, (1-acetyl-2-methyl)- $\pi$ -allylpalladium chloride (1; R<sub>1</sub> = CH<sub>3</sub>CO, R<sub>2</sub> = CH<sub>3</sub>; X = Cl) prepared from PdCl<sub>2</sub> and mesityl oxide, reacts with NaCo(CO)<sub>4</sub> and then with Ph<sub>3</sub>P to afford another exotic  $\pi$ -allylcobalt tricarbonyl complex, (14; R<sub>1</sub> = CH<sub>3</sub>CO, R<sub>2</sub> = CH<sub>3</sub>) in 35% yield. Interesting results have also been obtained by Heck<sup>10</sup> from the reaction of (1,1,2-trimethyl)- $\pi$ -allylpalladium chloride (1; R<sub>1</sub> = R<sub>1</sub>' = R<sub>2</sub> = CH<sub>3</sub>; X = Cl) and NaCo(CO)<sub>4</sub>. Addition of



$\text{Ph}_3\text{P}$  to the above reaction gave a low yield of an air-sensitive insoluble crystalline product. On the basis of its elemental composition and infrared spectrum (carbonyl region). This product was formulated as the binuclear complex (15). Heck<sup>10</sup> suggested that intermediates similar to (15) are also involved in the other  $\pi$ -allyl transfer processes which he studied and this led him to propose a detailed mechanism for the  $\pi$ -allyl transfer from palladium to cobalt (Fig. 3).

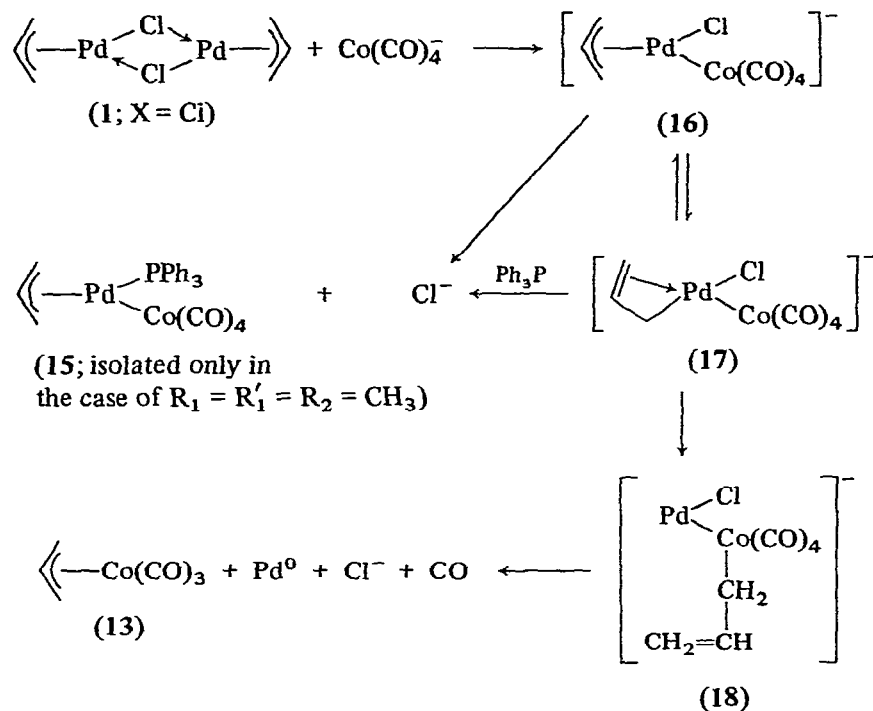


Fig. 3. The  $\pi$ -allyl transfer mechanism from palladium to cobalt by Heck<sup>10</sup>.

This mechanism is based on the formation of binuclear intermediates such as (16), (17) and (18) containing a palladium to cobalt bond. The actual transfer process involves *cis* migration and a 1,2-shift of the allyl group. When the  $\pi$ -allyl transfer process is inhibited, as with (1;  $\text{R}_1 = \text{R}'_1 = \text{R}_2 = \text{CH}_3$ ;  $\text{X} = \text{Cl}$ ) where steric factors are probably important, a facile reaction between the intermediate (16;  $\text{R}_1 = \text{R}'_1 = \text{R}_2 = \text{CH}_3$ ) and  $\text{Ph}_3\text{P}$  should lead to the formation of (15).

A reverse  $\pi$ -allyl transfer from cobalt to palladium was also demonstrated by Heck<sup>10</sup>. The  $\pi$ -allylcobalt complexes (13) and (13;  $\text{R}_1 = \text{R}_3 = \text{CH}_3$ ) when reacted with lithium trichloropalladate in acetonitrile solution at 0° afford the  $\pi$ -allylpalladium complexes (1;  $\text{X} = \text{Cl}$ ) and (1;  $\text{R}_1 = \text{R}_3 = \text{CH}_3$ ;  $\text{X} = \text{Cl}$ ) in 22 and 16% yield, respectively. Unfortunately, attempts to extend this novel technique to include other exotic  $\pi$ -allylcobalt complexes

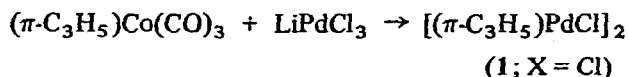


TABLE 1  
 $\pi$ -ALLYL LIGAND TRANSFER REACTIONS

Abbreviations: h = hour; min = minutes; aceto. = acetonitrile.

Reaction	Yield (%)	Reaction conditions <sup>a</sup>	Reference
$(\pi\text{-C}_3\text{H}_5)_2\text{PdCl}_2 + \text{Fe}_2(\text{CO})_9 \rightarrow (\pi\text{-C}_3\text{H}_5)_2\text{Fe}(\text{CO})_3\text{Cl}$	26	Benzene, 8-10 h.	8, 6
$(\pi\text{-C}_3\text{H}_5)_2\text{PdCl}_2 + \text{Fe}_2(\text{CO})_9 \rightarrow (\pi\text{-C}_3\text{H}_5)_2\text{Fe}(\text{CO})_3\text{Cl}$	39	Hexane, 12 h.	7
$(\pi\text{-C}_3\text{H}_5)_2\text{PdBr}_2 + \text{Fe}_2(\text{CO})_9 \rightarrow (\pi\text{-C}_3\text{H}_5)_2\text{Fe}(\text{CO})_3\text{Br}$	30	Benzene, 8-10 h.	8
$(\pi\text{-C}_3\text{H}_5)_2\text{PdI}_2 + \text{Fe}_2(\text{CO})_9 \rightarrow (\pi\text{-C}_3\text{H}_5)_2\text{Fe}(\text{CO})_3\text{I}$	28	Benzene, 8-10 h.	8
$[(2\text{-CH}_3\text{-}\pi\text{-C}_3\text{H}_4)_2\text{PdCl}]_2 + \text{Fe}_2(\text{CO})_9 \rightarrow (2\text{-CH}_3\text{-}\pi\text{-C}_3\text{H}_4)_2\text{Fe}(\text{CO})_3\text{Cl}$	26	Benzene, 8-10 h.	8
$[(2\text{-CH}_3\text{-}\pi\text{-C}_3\text{H}_4)_2\text{PdCl}]_2 + \text{Fe}_2(\text{CO})_9 \rightarrow (2\text{-CH}_3\text{-}\pi\text{-C}_3\text{H}_4)_2\text{Fe}(\text{CO})_3\text{Cl}$	-	Hexane, 12 h.	7
$[(1\text{-Ph-}\pi\text{-C}_3\text{H}_4)_2\text{PdCl}]_2 + \text{Fe}_2(\text{CO})_9 \rightarrow (1\text{-Ph-}\pi\text{-C}_3\text{H}_4)_2\text{Fe}(\text{CO})_3\text{Cl}$	30	Benzene, 8-10 h.	8
$[(2\text{-Ph-}\pi\text{-C}_3\text{H}_4)_2\text{PdCl}]_2 + \text{Fe}_2(\text{CO})_9 \rightarrow (2\text{-Ph-}\pi\text{-C}_3\text{H}_4)_2\text{Fe}(\text{CO})_3\text{Cl}$	37	Benzene, 8-10 h.	8
$(\pi\text{-C}_3\text{H}_5)_2\text{PdOCOCCH}_3)_2 + \text{Fe}_2(\text{CO})_9 \rightarrow (\pi\text{-C}_3\text{H}_5)_2\text{Fe}(\text{CO})_3\text{I}$	7	Benzene, 10 h.	8
$(\pi\text{-C}_3\text{H}_5)_2\text{PdCl}_2 + \text{Fe}(\text{CO})_5 \rightarrow (\pi\text{-C}_3\text{H}_5)_2\text{Fe}(\text{CO})_3\text{Cl}$	-	Benzene, 8-10 days	8
$(\pi\text{-C}_3\text{H}_5)_2\text{NiBr}_2 + \text{Fe}(\text{CO})_9 \rightarrow (\pi\text{-C}_3\text{H}_5)_2\text{Fe}(\text{CO})_3\text{Br}$	12	Ether, 12 h.	8
$(\pi\text{-C}_3\text{H}_5)_2\text{Ni} + \text{Fe}_2(\text{CO})_9 + \text{I}_2 \rightarrow (\pi\text{-C}_3\text{H}_5)_2\text{Fe}(\text{CO})_3\text{I}$	-	Ether, 30 min.	8
$(\pi\text{-C}_3\text{H}_5)_2\text{Pd} + \text{Fe}_2(\text{CO})_9 + \text{I}_2 \rightarrow (\pi\text{-C}_3\text{H}_5)_2\text{Fe}(\text{CO})_3\text{I}$	-	Ether, 30 min.	8
$(\pi\text{-C}_3\text{H}_5)_2\text{Pt} + \text{Fe}_2(\text{CO})_9 + \text{I}_2 \rightarrow (\pi\text{-C}_3\text{H}_5)_2\text{Fe}(\text{CO})_3\text{I}$	-	Ether, 30 min.	8
$[(\pi\text{-C}_3\text{H}_5)_2\text{PdCl}]_2 + \text{NaCo}(\text{CO})_4 + \text{Ph}_3\text{P} \rightarrow (\pi\text{-C}_3\text{H}_5)_2\text{Co}(\text{CO})_2(\text{Ph}_3\text{P})$	50	Ether, 2 h.	10
$[(1\text{-CH}_2\text{Ph-}2\text{-CH}_3\text{-}\pi\text{-C}_3\text{H}_3)_2\text{PdCl}]_2 + \text{NaCo}(\text{CO})_4 + \text{Ph}_3\text{P} \rightarrow (1\text{-CH}_2\text{Ph-}2\text{-CH}_3\text{-}\pi\text{-C}_3\text{H}_3)_2\text{Co}(\text{CO})_2(\text{Ph}_3\text{P})$	41	Ether, 2 h.	10
$[(1\text{-COCH}_3\text{-}2\text{-CH}_3\text{-}\pi\text{-C}_3\text{H}_3)_2\text{PdCl}]_2 + \text{NaCo}(\text{CO})_4 + \text{Ph}_3\text{P} \rightarrow (1\text{-COCH}_3\text{-}2\text{-CH}_3\text{-}\pi\text{-C}_3\text{H}_3)_2\text{Co}(\text{CO})_2(\text{Ph}_3\text{P})$	35	Ether, 2 h.	10
$(\pi\text{-C}_3\text{H}_5)_2\text{Co}(\text{CO})_3 + \text{LiPdCl}_3 \rightarrow [(\pi\text{-C}_3\text{H}_5)_2\text{PdCl}]_2$	22	aceto. 12 h.	10
$(1,3\text{-(CH}_3)_2\text{-}\pi\text{-C}_3\text{H}_3)_2\text{Co}(\text{CO})_3 + \text{LiPdCl}_3 \rightarrow [(1,3\text{-(CH}_3)_2\text{-}\pi\text{-C}_3\text{H}_3)_2\text{PdCl}]_2$	16	aceto. 12 h.	10

<sup>a</sup> All of the reactions described were carried out at ambient temperature ( $\sim 25^\circ$ ).



such as 2,3-diethyl- $\pi$ -2,4-(penteno-4-lactonyl)cobalt tricarbonyl, 1-acetylmethyl- $\pi$ -allyl-cobalt tricarbonyl and 1-acetoxy- $\pi$ -allylcobalt tricarbonyl were unsuccessful.

Experimental details on all known  $\pi$ -allyl transfer reactions are given in Table 1.

### III. $\pi$ -CYCLOBUTADIENE TRANSFER REACTIONS

The most important methods for the preparation of cyclobutadiene-metal complexes involve reactions between acetylenes or various cyclobutenes (e.g., 3,4-dichloro-1,2,3,4-tetramethylcyclobutene<sup>11,12</sup>) with metal carbonyls or their derivatives, and  $\pi$ -cyclobutadiene ligand transfer from one transition metal complex to another. All the above procedures suffer from the disadvantage of being rather specific with regard to the metal, organic starting material and the conditions under which they are performed; thus, they are not easily extended to other cyclobutadiene ligands and metals. Although the major problems in developing a general synthetic route to cyclobutadiene-metal complexes have not yet been solved, the preparation of many known as well as new cyclobutadiene-metal complexes, in particular those with tetraphenylcyclobutadiene, was simplified greatly by the discovery of the  $\pi$ -cyclobutadiene ligand transfer reaction<sup>2</sup>. This novel technique led to the preparation of more new cyclobutadiene-metal complexes than did any other method. Furthermore, this interesting technique has also enabled the development of high yield, facile procedures for the preparation of many known cyclobutadiene-metal complexes. Undoubtedly, ligand transfer reactions contributed substantially to the expansion of this exotic field of cyclobutadiene-metal complexes.

The first successful transfer of a  $\pi$ -cyclobutadiene ligand was accomplished by Maitlis and Games<sup>2</sup> in the reactions between tetraphenylcyclobutadienepalladium bromide (**19**; R = Ph; X = Br) with Fe(CO)<sub>5</sub>, Ni(CO)<sub>4</sub> and Cp<sub>2</sub>Co.\* These reactions, performed in boiling aromatic solvents led to the isolation of Ph<sub>4</sub>C<sub>4</sub>Fe(CO)<sub>3</sub> (**20**; R = Ph), [Ph<sub>4</sub>C<sub>4</sub>NiBr<sub>2</sub>]<sub>2</sub> (**21**; R = Ph; X = Br) and Ph<sub>4</sub>C<sub>4</sub>CoCp (**22**; R = Ph) in 88, 47 and 12% yield, respectively. Other cyclobutadieneiron tricarbonyl complexes such as (**20**; R = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>), (**20**; R = *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub>) and (**20**; R = *p*-ClC<sub>6</sub>H<sub>4</sub>) were prepared analogously from Fe(CO)<sub>5</sub> and the respective cyclobutadienepalladium complexes (**19**)<sup>13</sup>. Tetraphenylcyclobutadieneiron tricarbonyl (**20**; R = Ph) has also been prepared by the  $\pi$ -ligand transfer reaction from the tetraphenylcyclobutadienenickel complex (**21**)<sup>13</sup> or tetraphenylcyclobutadieneplatinum diiodide dimer (**24**)<sup>15</sup> and Fe(CO)<sub>5</sub>. Similarly, the *p*-ClC<sub>6</sub>H<sub>4</sub> analogue (**20**; R = *p*-ClC<sub>6</sub>H<sub>4</sub>) was prepared from the catenated cyclobutadienepalladium complex (**23**) and Fe(CO)<sub>5</sub><sup>14</sup>. The formation of cyclobutadieneiron tricarbonyls (**20**) by  $\pi$ -ligand transfer reactions was successful not only with aryl but also with methyl substituents. Tetramethylcyclobutadienenickel chloride dimer (**21**; R = CH<sub>3</sub>; X = Cl), for instance, reacts with Fe(CO)<sub>5</sub>, Fe<sub>2</sub>(CO)<sub>9</sub> and Fe<sub>3</sub>(CO)<sub>12</sub> to afford tetramethylcyclobutadieneiron tricarbonyl (**20**; R = CH<sub>3</sub>) in 21, 6 and 35% yield, respectively<sup>16</sup>. The reactions discussed above describe facile  $\pi$ -cyclobutadiene transfer from nickel, palladium and platinum to iron. However, an example of a reverse transfer from iron to palladium is also known. Thus, bis(acetonitrile)-palladium dichloride reacts with tetraphenylcyclobutadieneiron tricarbonyl (**20**; R = Ph) in boiling benzene to give the catenated cyclobutadienepalladium complex (**25**)<sup>13</sup>. The latter

\* Cp =  $\pi$ -cyclopentadienyl.

complex, (25), was converted to the normal dimer (19; R = Ph; X = Br) on reaction with anhydrous HBr. The  $\pi$ -cyclobutadiene ligand transfer from palladium to iron has also been extended to the ruthenium system. Tetraphenylcyclobutadieniruthenium tricarbonyl (26) was isolated in 42% yield from the reaction between triruthenium dodecacarbonyl,  $\text{Ru}_3(\text{CO})_{12}$ , and the tetraphenylcyclobutadienepalladium complex (19; R = Ph; X = Br)<sup>13,17</sup>. Evidently, the reactions discussed above demonstrate that  $\pi$ -cyclobutadiene ligand transfer processes can be extended not only to rings with different substituents but also to related metals.

An important category of  $\pi$ -cyclobutadiene transfer reactions involves the formation of various aryl substituted cyclobutadienenickel halide complexes (21). The above mentioned<sup>2</sup>  $\pi$ -cyclobutadiene transfer reaction between the palladium complex (19; R = Ph; X = Br) and  $\text{Ni}(\text{CO})_4$  has also been extended to the preparation of the *p*-anisyl nickel analogue (21; R = *p*- $\text{CH}_3\text{OC}_6\text{H}_4$ ; X = Br)<sup>13</sup>. However, of even greater importance are the reactions between the aryl substituted cyclobutadienepalladium complexes (19) and bis(tri-*n*-butylphosphine)nickel halides (27; L = *n*- $\text{Bu}_3\text{P}$ ). These reactions, which are conveniently carried out in refluxing chlorobenzene, afford cyclobutadienenickel halides (21) and bis(tri-*n*-butylphosphine)palladium halides. By this route the cyclobutadienenickel complexes (21; R = Ph; X = Br), (21; R = Ph; X = Cl), (21; R = *p*- $\text{ClC}_6\text{H}_4$ ; X = Br), (21; R = *p*- $\text{CH}_3\text{C}_6\text{H}_4$ ; X = Br) and (21; R = *p*- $\text{CH}_3\text{C}_6\text{H}_4$ ; X = Br) have been prepared in 90, 82, 72, 77 and 73% yield, respectively<sup>18</sup>. It should be noted that preliminary experiments also indicated similar exchange processes with other bis(phosphine)nickel halides (*e.g.*, 27; L =  $\text{Ph}_3\text{P}$  or  $\text{L}_2 = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$ ; X = halogen). However, the products from these latter reactions are nearly impossible to separate.

The next category of reactions to be discussed are those involving  $\pi$ -cyclobutadiene transfer from palladium and nickel to cobalt. The tetraarylcyclobutadienepalladium halides (19; R = Ph, *p*- $\text{CH}_3\text{C}_6\text{H}_4$ ; X = Cl, Br, I) were found to react with  $\text{Co}_2(\text{CO})_8$  in dichloromethane solution at ambient temperature to afford the tetraarylcyclobutadienecobalt dicarbonyl halide complexes (28; R = Ph; X = Cl), (28; R = Ph; X = Br), (28; R = Ph; X = I) and (28; R = *p*- $\text{CH}_3\text{C}_6\text{H}_4$ ; X = Br) in 65, 59, 17 and 35% yield, respectively<sup>19,20</sup>. Interestingly, the yield of the transfer product is related to the nature of the halogen and decreases in the order  $\text{Cl} > \text{Br} \gg \text{I}$ . An analogous transfer reaction has been encountered between tetramethylcyclobutadienenickel diiodide (21; R =  $\text{CH}_3$ ; X = I) and  $\text{Co}_2(\text{CO})_8$ <sup>21</sup>. This reaction, performed in tetrahydrofuran solution at ambient temperature, affords a quantitative yield of tetramethylcyclobutadienecobalt dicarbonyl iodide (28; R =  $\text{CH}_3$ ; X = I) in a quantitative yield. Interestingly, the above reaction is the only known case of a quantitative  $\pi$ -ligand transfer process. The tetramethylcyclobutadienenickel chloride (21; R =  $\text{CH}_3$ ; X = Cl), unlike its iodo analogue, react with  $\text{Co}_2(\text{CO})_8$  to give the halogen free binuclear tetramethylcyclobutadienecobalt complex (29) in 55% yield<sup>21</sup>. The cobalt complex (29) was converted to the normal iodide (28; R =  $\text{CH}_3$ ; X = I) on reaction with iodine. The  $\pi$ -cyclobutadiene ligand transfer reactions mentioned above are described in Fig. 4.

The reactions involving  $\pi$ -cyclobutadiene transfer from palladium to molybdenum, tungsten and vanadium are limited in scope and generally give poor to moderate yields. However, in most cases these transfer reactions represent the only route by which the products can be prepared. The first  $\pi$ -cyclobutadiene transfer reactions in this category to be studied were those between tetraphenylcyclobutadienepalladium halides (19) and the

hexacarbonyls of molybdenum and tungsten<sup>22</sup>. The products of these reactions were originally formulated as the tetraphenylcyclobutadienemetal tricarbonyl halide dimers (30; M = Mo; R = Ph; X = Br), (30; M = Mo; R = Ph; X = I) and (30; M = W; R = Ph; X = I)

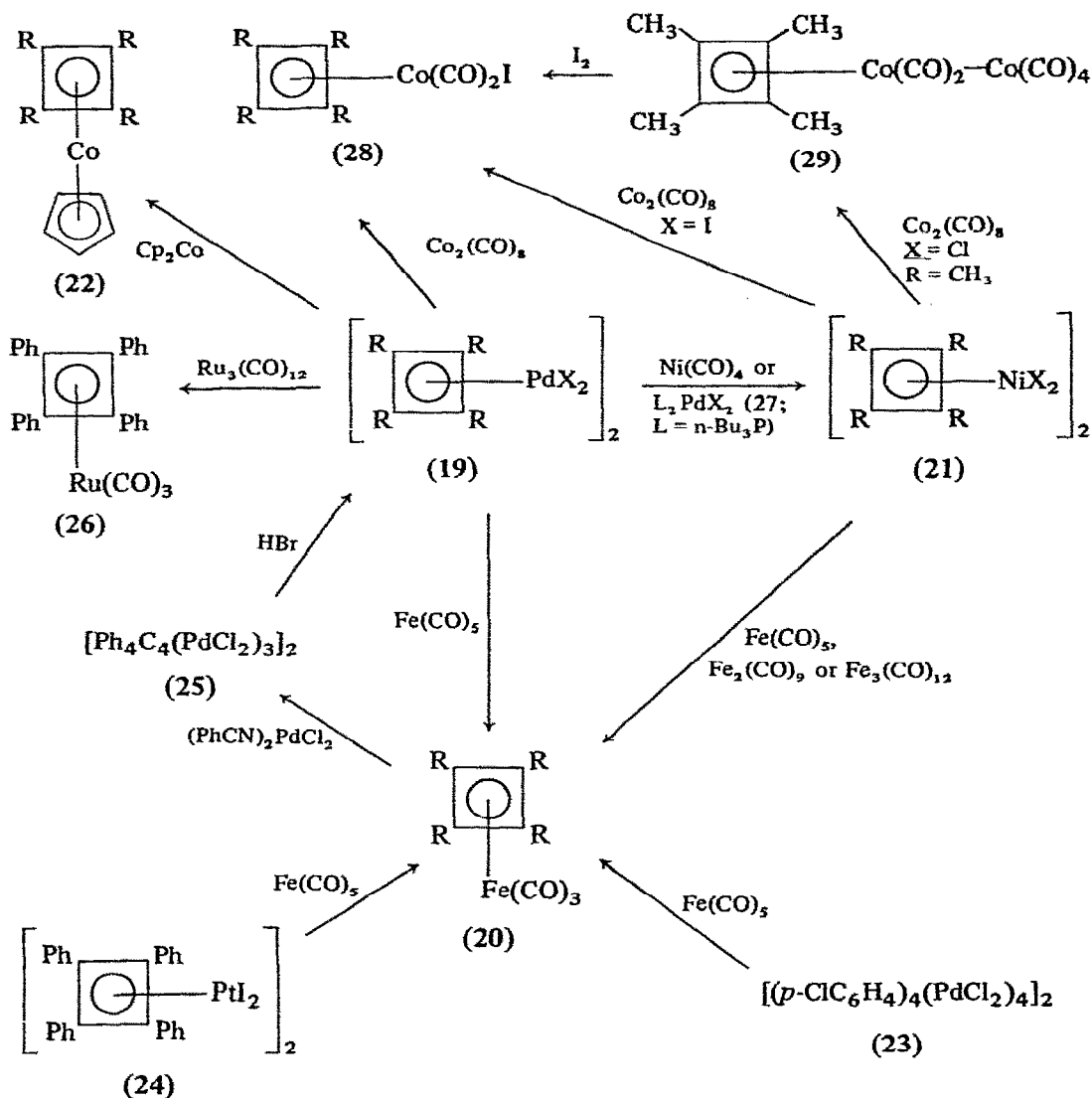


Fig. 4. π-Cyclobutadiene transfer reactions involving nickel, palladium, platinum, ruthenium, iron and cobalt.

and were isolated in 7%, 9%, and trace amounts yield, respectively. The molybdenum complexes mentioned above<sup>22</sup>, including a new *p*-tolyl bromide analogue were subjected to a reexamination and, as a result, their structures were reformulated as the tetraarylcyclobutadienemolybdenum dicarbonyl halide dimers (31; M = Mo; R = Ph, *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; X = Br, I)<sup>24</sup>.

Subsequent X-ray analysis of the molybdenum complex (**31**; R = Ph; X = Br) confirmed the new structural assignment<sup>27</sup>. A somewhat improved synthesis of the molybdenum complex (**31**; M = Mo; R = Ph; X = Br) has been achieved in the transfer reaction between the palladium complex (**19**; R = Ph; X = Br) and  $\pi$ -benzenemolybdenum tricarbonyl (**32**)<sup>23</sup>. Similar  $\pi$ -cyclobutadiene transfer processes were encountered in the reactions between the tetraphenylcyclobutadienepalladium complexes (**19**; R = Ph) and the cyclopentadienyl-metal tricarbonyl dimers (**33**) of molybdenum and tungsten<sup>24,25</sup>. The products of these reactions, the ( $\pi$ -cyclobutadiene)( $\pi$ -cyclopentadienyl)metal carbonyl halides complexes (**34**; M = Mo; R = Ph; X = Cl), (**34**; M = Mo; R = Ph; X = Br), (**34**; M = Mo; R = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; X = Br) and (**34**; M = W; R = Ph; X = Br) were isolated in 18, 7, 6 and 0.7% yield, respectively. All the above reactions involving  $\pi$ -cyclobutadiene transfer from palladium to molybdenum and tungsten are carried out either in boiling benzene over prolonged periods (up to 67 h) or in refluxing xylene for about 10 minutes. Frequently, the latter procedure gave a somewhat improved yield.

Nesmeyanov *et al.*<sup>26</sup> reported an interesting  $\pi$ -cyclobutadiene transfer process, from palladium to vanadium. The reaction of tetraphenylcyclobutadienepalladium bromide (**19**; R = Ph; X = Br) and cyclopentadienylvanadium tetracarbonyl (**35**), carried out in refluxing toluene for 10 minutes, gave ( $\pi$ -cyclobutadiene)( $\pi$ -cyclopentadienyl)vanadium dicarbonyl (**36**) in 15% yield. The  $\pi$ -cyclobutadiene ligand transfer reactions discussed above are given in Fig. 5. Experimental details pertaining to all known  $\pi$ -cyclobutadiene transfer reactions are given in Table 2.

$\pi$ -Cyclobutadiene ligand transfer reactions usually occur under heterogeneous conditions and, to date, no meaningful kinetic studies have been performed. Consequently the various mechanistic approaches advanced to explain these novel reactions are basically intuitive. In spite of the obvious limitations, and in order to complete the discussion of  $\pi$ -cyclobutadiene ligand transfer reactions, some of the basic mechanistic approaches will be introduced below. Early attempts to explain  $\pi$ -cyclobutadiene ligand transfer processes relied on a dissociative type mechanism and the postulation of transient free cyclobutadiene intermediates. This approach was mentioned in conjunction with  $\pi$ -cyclobutadiene transfer from palladium to iron and nickel as observed in the reactions of (**19**; R = Ph) with Fe(CO)<sub>5</sub><sup>2</sup> and (**27**)<sup>18</sup>. However, at present, it is commonly agreed that a dissociative free cyclobutadiene mechanism is out of the question. The formation of highly reactive transient intermediates as free cyclobutadienes would, in all likelihood, lead to the formation of various organic by-products rather than to transfer products. An alternative and more feasible mechanism for these transfer reactions involving binuclear or polynuclear intermediates in which the metal atoms are bridged by halogen and the cyclobutadiene ring was postulated. In this scheme, originally proposed by Maitlis<sup>4</sup>, two main steps were envisioned for the  $\pi$ -cyclobutadiene transfer from the palladium complexes (**19**) to other metals; the first involved complex formation between the metal carbonyl and (**19**), possibly with loss of CO and the second was the actual  $\pi$ -cyclobutadiene transfer, with loss of CO and some reorganization (Fig. 6).

In none of these reactions was the  $\pi$ -cyclobutadiene ligand assumed to become completely free of the metal. According to Maitlis<sup>4</sup>, the formation of organic side products (especially when the yield of the transfer product is low) such as octaphenylcyclooctatetraene (**37**) and tetraphenylcyclopentadienone (**38**) suggests that while the first step

leading to the breakup of the palladium complex (19) is always efficient, the second step involving the actual  $\pi$ -cyclobutadiene transfer is sometimes very difficult and thus could lead to the formation of the organic side products (37) and (38). This mechanism accounts for all products formed in these reactions and in addition explains the halogen transfer which in many cases accompanies  $\pi$ -cyclobutadiene ligand transfer. Rubezhov and Gubin<sup>5</sup>

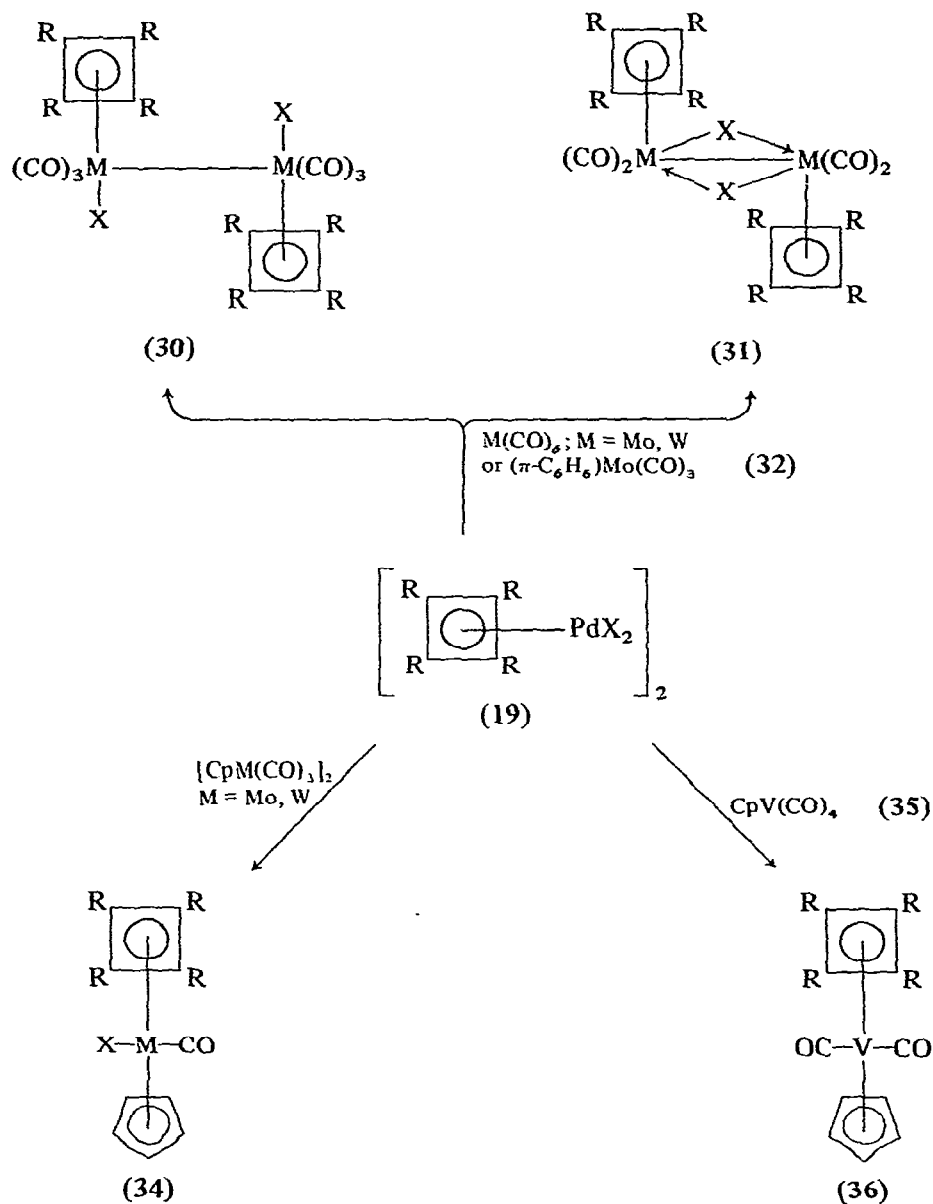


Fig. 5.  $\pi$ -Cyclobutadiene transfer reactions from palladium to molybdenum, tungsten and vanadium.

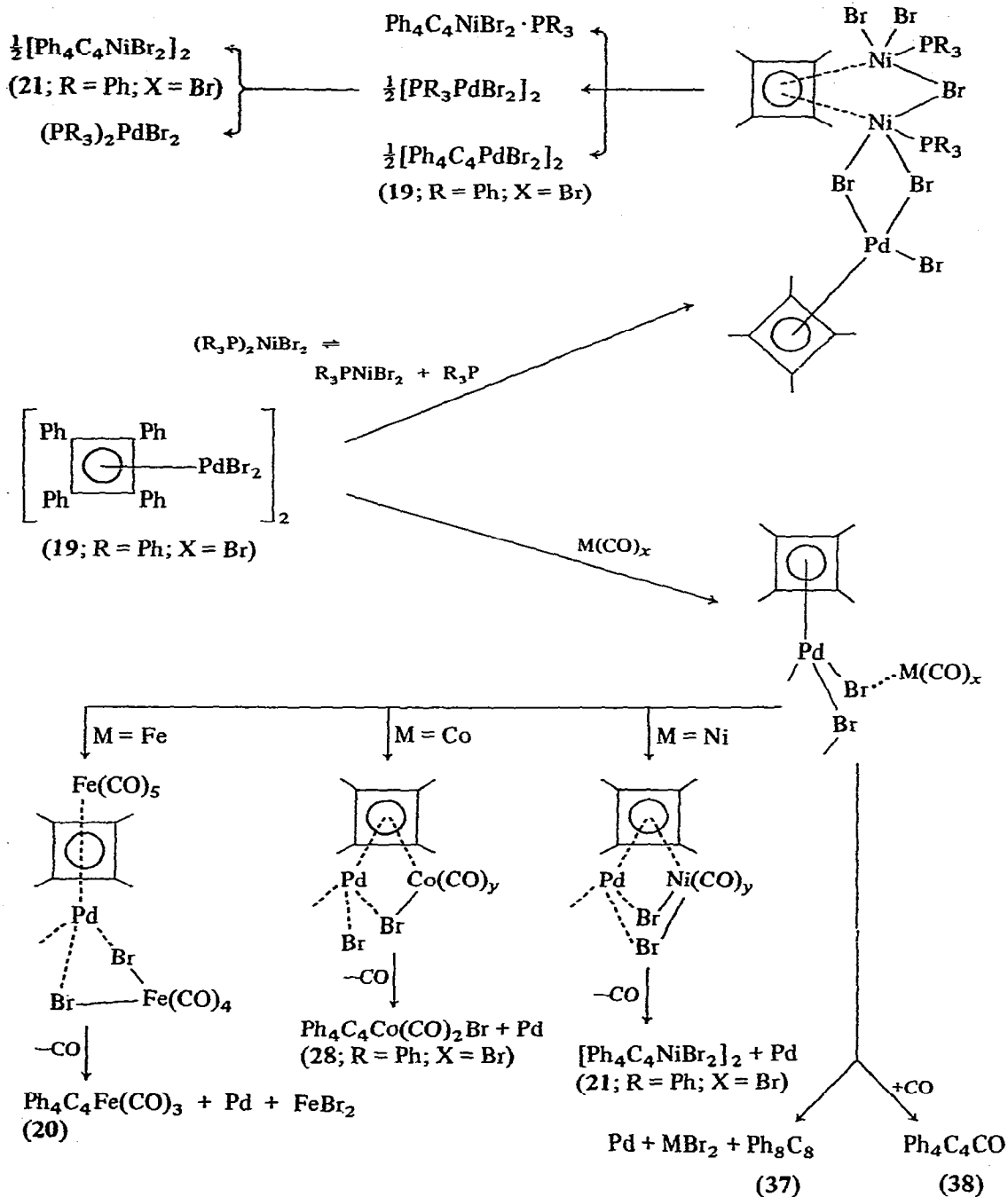


Fig. 6. The mechanisms proposed for the  $\pi$ -cyclobutadiene transfer from palladium to iron, cobalt and nickel<sup>4</sup>.

also postulated a mechanism for the  $\pi$ -cyclobutadiene transfer process in the reaction between (19) and  $\text{Fe}(\text{CO})_5$ . By analogy with the  $\pi$ -allyl transfer reaction mechanism (Fig. 1) they suggested as the first step a nucleophilic attack of  $:\text{Fe}(\text{CO})_4$  on (19). The intermediate formed by this process could then undergo intramolecular ligand transfer to afford the final product (20) according to the scheme in Fig. 7.

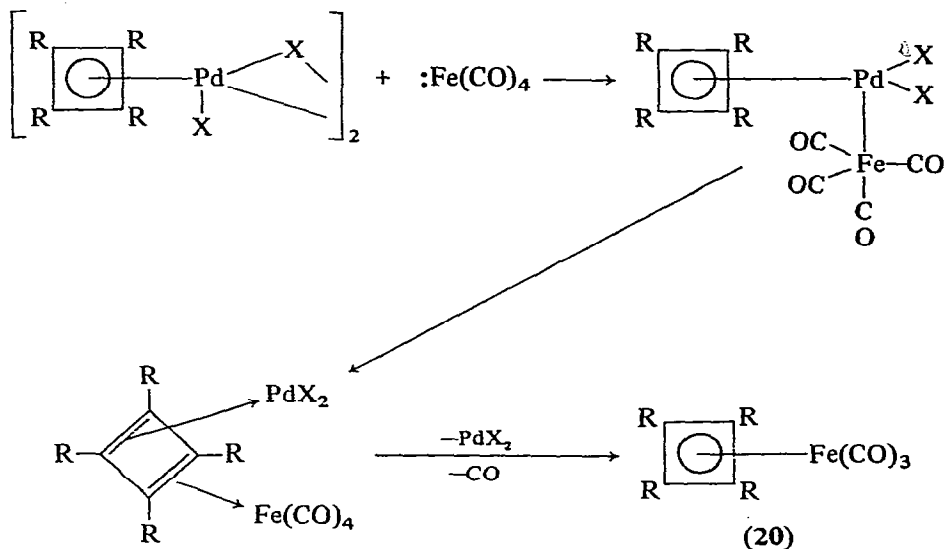
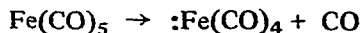


Fig. 7. A mechanism proposed for a  $\pi$ -cyclobutadiene transfer from palladium to iron<sup>5</sup>.

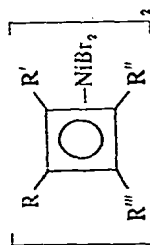
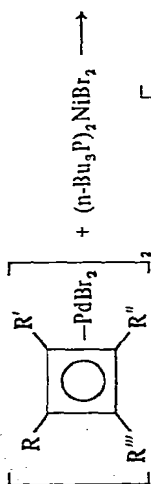
Whatever the correct transfer mechanism is it appears almost certain that these complex reactions proceed *via* a multistep process involving the formation of bi- or polynuclear intermediates which are probably halogen bridged. Furthermore, it is believed that the cyclobutadiene ring never becomes completely free of the metals. Perhaps, the actual  $\pi$ -cyclobutadiene transfer could be best explained in terms of an intramolecular rearrangement involving a 1,2,3-shift by which a stepwise ring transfer is taking place while at no time becoming completely free of the metals. This approach is illustrated in Fig. 8 for the transfer which was encountered between the palladium complex (19) and  $\text{Fe}(\text{CO})_5$  or  $\text{Ni}(\text{CO})_4$ . This proposed mechanism is based on the hypothesis that the metal which attains a favored rare gas, 18-electron, configuration in the reactant and product will also retain its electronic configuration during the intermediate stages of the reaction. In other words, one of the metals is assumed to remain coordinatively and electronically saturated throughout the transfer process. The halogen bridges, besides connecting the metal atoms in binuclear (or polynuclear) intermediates, also function as electron-density modifiers. This would facilitate charge transfer from one metal to another *via* a  $\mu, \sigma$  metal-halogen bond rearrangement so that one of the metals could remain coordinatively and electronically saturated at all times. During the final stages of the reaction, the halogens could either be retained by, or migrate from the metal to which they were originally attached. With the

(continued on p. 19)

TABLE 2  
 $\pi$ -CYCLOBUTADIENE LIGAND TRANSFER REACTIONS  
 Abbreviations: amb. = ambient temp. ( $\sim 25^\circ$ ); h = hour; min = minutes; THF = tetrahydrofuran.

Reaction	Yield (%)	Reaction conditions	Reference
$[\text{Ph}_4\text{C}_4\text{PdBr}_2]_2 + \text{Fe}(\text{CO})_5 \rightarrow \text{Ph}_4\text{C}_4\text{Fe}(\text{CO})_3$	88	Xylene, reflux, 20 min.	2
$[\text{Ph}_4\text{C}_4\text{PdBr}_2]_2 + \text{Ni}(\text{CO})_4 \rightarrow [\text{Ph}_4\text{C}_4\text{NiBr}_2]_2$	47	Benzene, reflux, 2.5 h.	2
$[\text{Ph}_4\text{C}_4\text{PdBr}_2]_2 + \text{Cp}_2\text{Co} \rightarrow \text{Ph}_4\text{C}_4\text{CoCp}$	12	Xylene, reflux, 2.5 h.	2
$[\text{R}_4\text{C}_4\text{PdX}_2]_2 + \text{Fe}(\text{CO})_5 \rightarrow \text{R}_4\text{C}_4\text{Fe}(\text{CO})_3$			
R = Ph; X = Br	78	Benzene, reflux, 2 h.	13
R = <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	47	Benzene, reflux, 2 h.	13
R = <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	17	Benzene, reflux, 2 h.	13
R = <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ; X = Br	46	Benzene, reflux, 10 min.	14
$[\text{Ph}_4\text{C}_4\text{NiX}_2]_2 + \text{Fe}(\text{CO})_5 \rightarrow \text{Ph}_4\text{C}_4\text{Fe}(\text{CO})_3$	90	Benzene, reflux, 2 h.	13
$[\text{Ph}_4\text{C}_4\text{Pt}_2]_2 + \text{Fe}(\text{CO})_5 \rightarrow \text{Ph}_4\text{C}_4\text{Fe}(\text{CO})_3$	-	Benzene, reflux, 10 min.	15
$[\text{p-ClC}_6\text{H}_4]_4\text{C}_4(\text{PdCl}_2)_4]_2 + \text{Fe}(\text{CO})_5 \rightarrow (\text{p-ClC}_6\text{H}_4)_4\text{C}_4\text{Fe}(\text{CO})_3$	44	Benzene, reflux, 10 min.	14
$[\text{Ph}_4\text{C}_4\text{Fe}(\text{CO})_3 + (\text{PhCN})_2\text{PdCl}_2 \rightarrow [\text{Ph}_4\text{C}_4(\text{PdCl}_2)_3]_2$	-	Benzene, reflux, 12 h.	13
$[(\text{CH}_3)_4\text{C}_4\text{NiCl}_2]_2 + \text{Fe}_3(\text{CO})_{12} \rightarrow (\text{CH}_3)_4\text{C}_4\text{Fe}(\text{CO})_3$	35	THF, reflux, 20 min.	16
$[(\text{CH}_3)_4\text{C}_4\text{NiCl}_2]_2 + \text{Fe}_2(\text{CO})_9 \rightarrow (\text{CH}_3)_4\text{C}_4\text{Fe}(\text{CO})_3$	6.3	THF, reflux, 17 h.	16
$[(\text{CH}_3)_4\text{C}_4\text{NiCl}_2]_2 + \text{Fe}(\text{CO})_5 \rightarrow (\text{CH}_3)_4\text{C}_4\text{Fe}(\text{CO})_3$	21	Dry benzene, reflux, 25 h.	16
$[\text{Ph}_4\text{C}_4\text{PdBr}_2]_2 + \text{Ru}_3(\text{CO})_{12} \rightarrow \text{Ph}_4\text{C}_4\text{Ru}(\text{CO})_3$	42	Chlorobenzene, reflux, 12 h.	13, 17
$[(\text{p-CH}_3\text{OC}_6\text{H}_4)_4\text{C}_4\text{PdBr}_2]_2 + \text{Ni}(\text{CO})_4 \rightarrow [(\text{p-CH}_3\text{OC}_6\text{H}_4)_4\text{C}_4\text{NiBr}_2]_2$	77	Various solvents, 40°	13
$[\text{R}_4\text{C}_4\text{PdX}_2]_2 + (\text{n-Bu}_3\text{P})_2\text{NiX}_2 \rightarrow [\text{R}_4\text{C}_4\text{NiX}_2]_2 + (\text{n-Bu}_3\text{P})_2\text{PdX}_2$			
R = Ph; X = Br	90	Chlorobenzene, reflux, 2 h.	18
R = Ph; X = Cl	82	Chlorobenzene, reflux, 2 h.	18
R = <i>p</i> -ClC <sub>6</sub> H <sub>4</sub> ; X = Br	72	Chlorobenzene, reflux, 2 h.	18
R = <i>p</i> -CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub> ; X = Br	77	Chlorobenzene, reflux, 2 h.	18
R = <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ; X = Br	73	Chlorobenzene, reflux, 2 h.	18





Chlorobenzene, reflux, 2 h. 18

a mixture of R = R' = o-anisyl, R'' = R''' = phenyl and R = R'' = o-anisyl,

R' = R''' = phenyl isomers

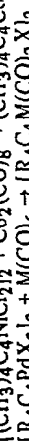
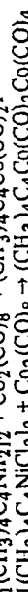


R = Ph; X = Cl

R = Ph; X = Br

R = Ph; X = I

R = p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; X = Br



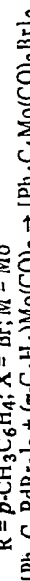
R = Ph; X = Br; M = Mo

R = Ph; X = Br; M = Mo

R = Ph; X = I; M = Mo

R = Ph; X = I; M = W

R = p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; X = Br; M = Mo



R = Ph; X = Cl; M = Mo

R = Ph; X = Cl; M = Mo

R = Ph; X = Br; M = Mo

R = Ph; X = Br; M = Mo

R = p-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>; X = Br; M = Mo

R = Ph; X = Br; M = W



65	CH <sub>2</sub> Cl <sub>2</sub> , amb., 45 h.	20
59	CH <sub>2</sub> Cl <sub>2</sub> , amb., 45 h.	20
17	CH <sub>2</sub> Cl <sub>2</sub> , amb., 45 h.	20
35	CH <sub>2</sub> Cl <sub>2</sub> , amb., 45 h.	20
100	THF, 25°C, 14 h.	21
55	THF, 25°C, 3 h.	21
7	Benzene, reflux, 67 h.	22
18	Xylene, reflux, 10 min.	23
9	Benzene, reflux, 67 h.	22
Traces	Benzene, reflux, 67 h.	22
18	Xylene, reflux, 5 min.	24
14	Benzene, reflux, 15 h.	23
55	Benzene, reflux, 50 h.	25
18	Xylene, reflux, 10 min.	25
7	Xylene, reflux, 10 min.	25
4.5	Benzene, reflux, 5 h.	25
6	Xylene, reflux, 5 min.	24
0.7	Benzene, reflux, 50 h.	25
15	Toluene, reflux, 10 min.	26

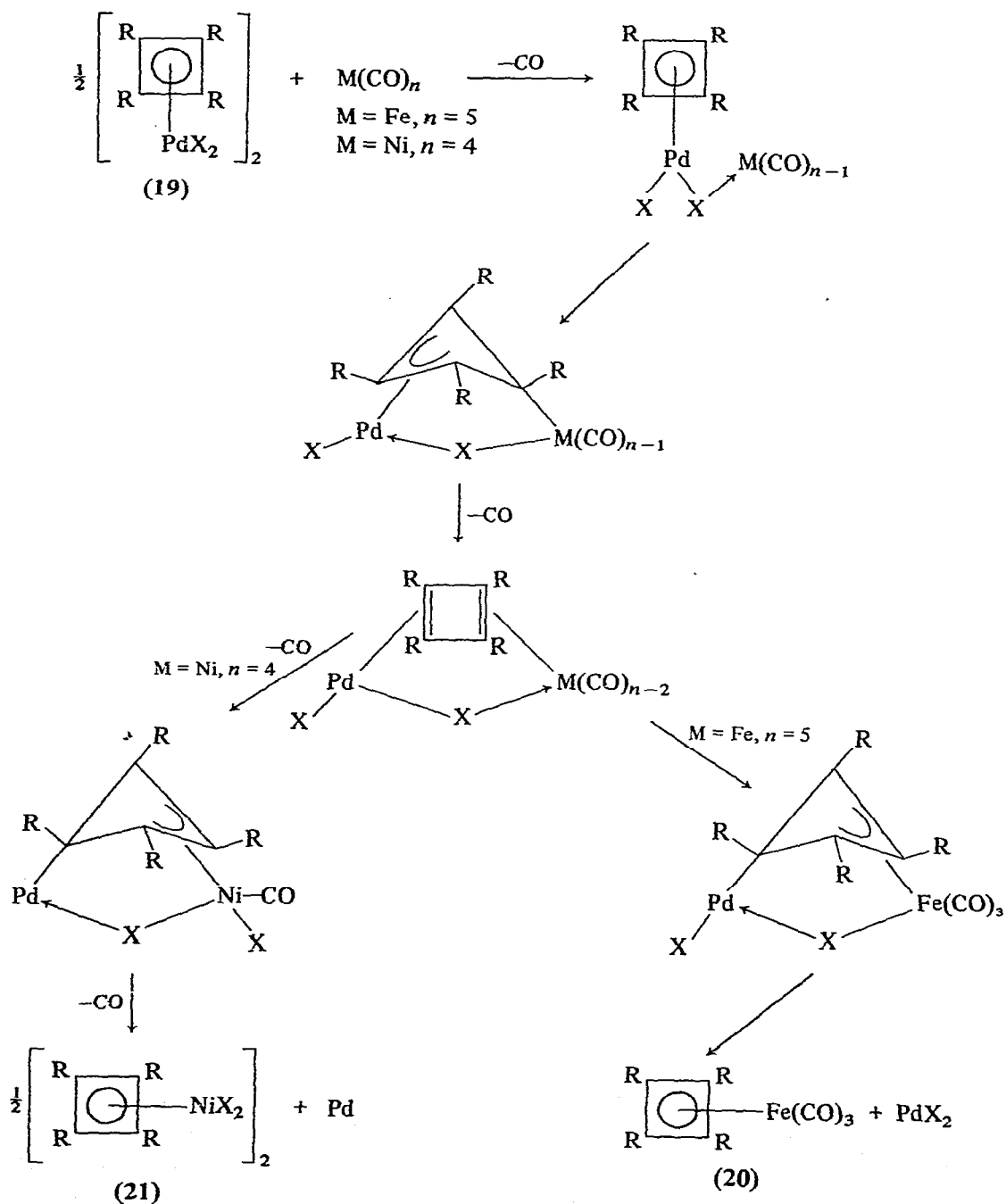


Fig. 8. The mechanisms proposed for the  $\pi$ -cyclobutadiene transfer from palladium to nickel and iron.

same ground rules in mind, this mechanistic approach, which was already mentioned in conjunction with  $\pi$ -allyl transfer reactions, could easily be extended to include most of the other known  $\pi$ -ligand transfer reactions.

#### IV. $\pi$ -CYCLOPENTADIENYL TRANSFER REACTIONS

$\pi$ -Cyclopentadienyl ligand transfer reactions in organometallic chemistry are interesting; however, their practical applications are rather limited in scope. The synthetic feasibility of these reactions was demonstrated only in a few cases. For instance, the basic organonickel reagent,  $[\text{CpNi}(\text{CO})]_2$ , is best prepared by the transfer reaction between nickelocene and  $\text{Ni}(\text{CO})_4$ <sup>28</sup>. The reason why these interesting reactions constitute only a minor synthetic technique is because  $\pi$ -cyclopentadienylmetal complexes can be prepared in high yield by other convenient methods which require readily available and inexpensive starting materials such as sodium and thallium cyclopentadienides or directly from free cyclopentadiene and its dimer<sup>29,30</sup>. However, in some cases  $\pi$ -cyclopentadienyl transfer reactions represent the only known technique by which certain cyclopentadienylmetal complexes can be prepared.

The most important cyclopentadienylating agent for  $\pi$ -transfer reactions is cyclopentadienyliron dicarbonyl bromide (39). The transfer of the cyclopentadienyl ring from cyclopentadienyliron dicarbonyl dimer (40) is also possible except that in this case the transfer process generally is less efficient since the transfer products are obtained in poorer yields. Use of the iron bromide (39) and the iron dimer (40) as cyclopentadienylating agents is discussed below. The cyclopentadienyliron dicarbonyl bromide (39) was found to react with tetraphenylcyclobutadienenickel bromide (21; R = Ph; X = Br) and tetraphenylcyclobutadienepalladium bromide (19; R = Ph; X = Br) in boiling benzene to afford the  $[(\pi\text{-cyclobutadiene})(\pi\text{-cyclopentadienyl})\text{metal}]\text{-tetrabromoferrate}$  complexes (41; M = Ni; R = Ph; Y =  $\text{FeBr}_4$ ) and (41; M = Pd; R = Ph; Y =  $\text{FeBr}_4$ ) in 77 and 85% yield, respectively<sup>31,32,33</sup>. Likewise, 1,5-cyclooctadienepalladium bromide (42) has been found to react with the iron bromide (39) under analogous conditions to give  $[(\pi\text{-1,5-cyclooctadiene})(\pi\text{-cyclopentadienyl})\text{palladium}]\text{-tetrabromoferrate}$  (43) in 61% yield<sup>33</sup>. Interestingly, the tetrabromoferrate complexes (41; M = Pd; R = Ph; Y =  $\text{FeBr}_4$ ) and (43) have also been prepared by the  $\pi$ -cyclopentadienyl transfer reactions from the iron dimer (40) but only in 42 and 8% yield, respectively. When the cyclopentadienyliron dicarbonyl dimer (40) rather than the iron bromide (39) is used as a cyclopentadienylating agent, yields of the tetrabromoferrates (41) and (43) are much lower since all of the bromide in  $\text{FeBr}_4^-$  now must come from the other reactant. It has also been noted that at higher temperatures (above 81°) the transfer reaction between the palladium complex (19; R = Ph; X = Br) and the iron dimer (40) affords small quantities of a second  $\pi$ -transfer product, tetraphenylcyclobutadieneiron tricarbonyl (20; R = Ph)<sup>33</sup>. The *p*-tolyl derivatives (41; M = Ni; R = *p*- $\text{CH}_3\text{C}_6\text{H}_4$ ; Y =  $\text{FeBr}_4$ ) and (41; M = Pd; R = *p*- $\text{CH}_3\text{C}_6\text{H}_4$ ; Y =  $\text{FeBr}_4$ ) are obtained by analogous reactions from the iron bromide (39)<sup>23</sup>. All of the paramagnetic tetrabromoferrate complexes (41; Y =  $\text{FeBr}_4$ ) were characterized as the diamagnetic bromides (41; Y = Br). Attempts to convert the 1,5-cyclooctadienepalladium complex (43) to a diamagnetic form (e.g., with  $\text{Br}^-$ ,  $\text{I}^-$  or  $\text{PF}_6^-$ ) were unsuccessful and resulted in total decomposition<sup>23</sup>.

Cyclopentadienylation reactions with the iron bromide (39) and iron dimer (40) have also been encountered with cyclobutadienecobalt dicarbonyl halides (28)<sup>20,23</sup>. For instance, tetraphenylcyclobutadienecobalt dicarbonyl bromide (28; R = Ph; X = Br) was found to react with both the iron bromide (39) and iron dimer (40) in boiling benzene to afford ( $\pi$ -tetraphenylcyclobutadiene)( $\pi$ -cyclopentadienyl)cobalt (22; R = Ph) in 78 and 73% yield, respectively. The *p*-tolyl derivative (22; R = *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>) is prepared analogously from the iron bromide (39) in 71% yield. A similar reaction between tetramethylcyclobutadienecobalt dicarbonyl iodide (28; R = CH<sub>3</sub>; X = I) and the iron dimer (40) in boiling benzene affords (22; R = CH<sub>3</sub>) but only in 18% yield<sup>21</sup>. Another example of a low yield (~5%)  $\pi$ -cyclopentadienyl transfer is the reaction of the cyclopentadienylating agent (40) with TiCl<sub>4</sub><sup>31,33</sup> in boiling xylene solution. The product, cyclopentadienyltitanium trichloride (44), was characterized as the oxychloride tetramer (CpTiOCl)<sub>4</sub>. The titanium trichloride complex (44) has also been obtained in 84% yield from the reaction between dicyclopentadienyltitanium dichloride and TiCl<sub>4</sub>, again in boiling xylene<sup>34</sup>. The reactions mentioned above are described in Fig. 9.

The next category of  $\pi$ -cyclopentadienyl transfer processes to be discussed include the reactions between metallocenes and metal carbonyl or metal phosphine derivatives. In these reactions, transfer takes place between either identical or different transition metal atoms. One of the best explored  $\pi$ -transfer reactions of this type pertains to nickelocene (Fig. 10). The reaction of nickelocene (45) with Fe(CO)<sub>5</sub> in boiling benzene solution gave three different  $\pi$ -transfer products the iron dimer (40), the cyclopentadienylnickel carbonyl dimer (46) and an interesting binuclear complex (47) containing both iron and nickel atoms<sup>35</sup>. Similarly, the reaction of nickelocene (45) and Ni(CO)<sub>4</sub> in benzene solution at 70° led to the formation of two different  $\pi$ -transfer products, the dimer (46) and the trimer (48) obtained in 50 and 40% yield, respectively<sup>36,37</sup>. Except with metal carbonyls, nickelocene (45) has also been shown to undergo  $\pi$ -cyclopentadienyl transfer reactions with phosphinenickel halides and related complexes. These reactions were carried out in three different ways according to the ligands involved. Nickelocene (45) has been shown to react with the bisphosphinenickel halides (27; L = Ph<sub>3</sub>P; X = Cl), (27; L = Bu<sub>3</sub>P; X = Cl) and (27; L = Ph<sub>2</sub>MeP; X = Br) to afford the cyclopentadienylnickel phosphine halide complexes (49; L = Ph<sub>3</sub>P; X = Cl), (49; L = Bu<sub>3</sub>P; X = Cl) and (49; L = Ph<sub>2</sub>MeP; X = Br) in 90, 67 and 79% yield, respectively<sup>38,39</sup>. Similarly, a mixture of nickelocene and Ni(CO)<sub>4</sub> reacted with (PhO)<sub>3</sub>P, Ph<sub>3</sub>As and Ph<sub>3</sub>Sb in the presence of iodine to give the cyclopentadienylnickel iodide derivatives (49; L = (PhO)<sub>3</sub>P; X = I), (49; L = Ph<sub>3</sub>As; X = I) and (49; L = Ph<sub>3</sub>Sb; X = I) in 39, 53 and 52% yield, respectively<sup>38</sup>. The arsine bromide analogue (49; L = Ph<sub>3</sub>As; X = Br) has also been prepared by a similar route from nickelocene (45), NiBr<sub>2</sub> and Ph<sub>3</sub>As<sup>38</sup>. The cyclopentadienylnickel of phosphine, phosphite, arsine and stibine halide derivatives were prepared in tetrahydrofuran solution either at ambient temperature or under reflux conditions. The yields of the products in all these reactions were good to excellent. The cyclopentadienyl transfer reactions from nickelocene discussed above are illustrated in Fig. 10.

$\pi$ -Cyclopentadienyl transfer reactions have also been encountered with other metallocenes. For instance, chromocene reacts with ferrous chloride in boiling tetrahydrofuran solution to afford ferrocene in 10% yield<sup>1</sup>, and ferrocene when reacted with ruthenium trichloride under similar conditions gives ruthenocene in 42% yield<sup>5</sup>. A somewhat related

reaction between dicyclopentadienylytitanium dichloride and  $\text{Fe}(\text{CO})_5$  in boiling xylene solution led to the formation of ferrocene in 10% yield<sup>31</sup>. A different sandwich complex  $(\pi\text{-allyl})(\pi\text{-cyclopentadienyl})\text{palladium}$  has also been shown to undergo  $\pi\text{-cyclopentadienyl}$

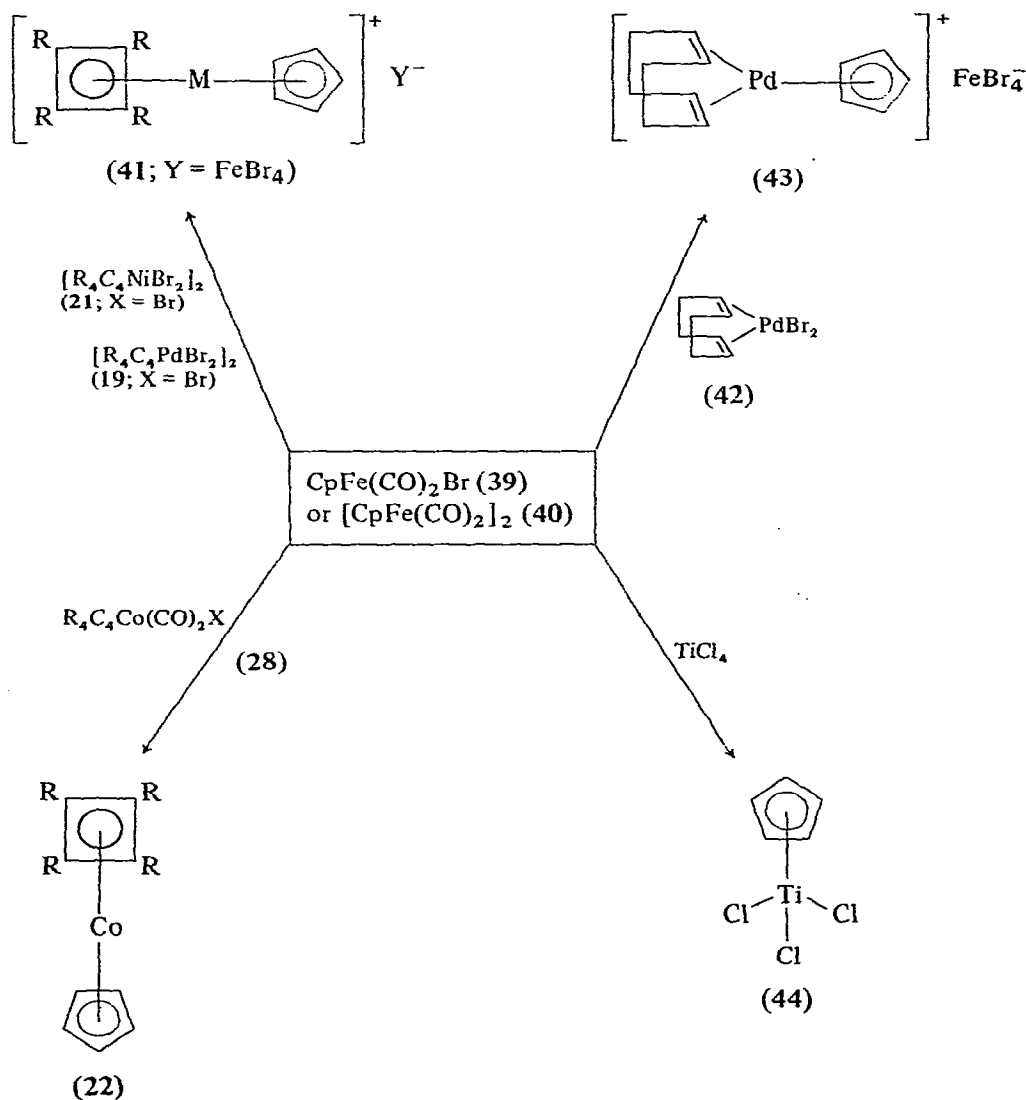


Fig. 9. The  $\pi\text{-cyclopentadienyl}$  transfer reactions from iron to nickel, palladium, cobalt and titanium.

transfer. This palladium complex reacts with ferrous chloride to afford ferrocene<sup>40</sup>, while with  $\text{Fe}(\text{CO})_5$ , two transfer products, ferrocene and the iron dimer (40) are isolated.<sup>5</sup>

In an attempt to determine the nature of the  $\pi\text{-cyclopentadienyl}$ -titanium bond, Nesmeyanov *et al.*<sup>41,42</sup> have studied the  $\pi\text{-cyclopentadienyl}$  transfer reactions between various cyclopentadienylytitanium complexes of the type  $\text{CpTi}(\text{OR})_{3-n}\text{X}_n$  ( $\text{R} = \text{Et}, i\text{-Pr}$ ,

t-Bu, Ph, COCH<sub>3</sub>; X = Cl, Br, I) and ferrous chloride or ferrous acetylacetonate. These reactions carried out in tetrahydrofuran solution at an elevated temperature led to the formation of ferrocene in up to 74% yield. The  $\pi$ -methylcyclopentadienyltitanium

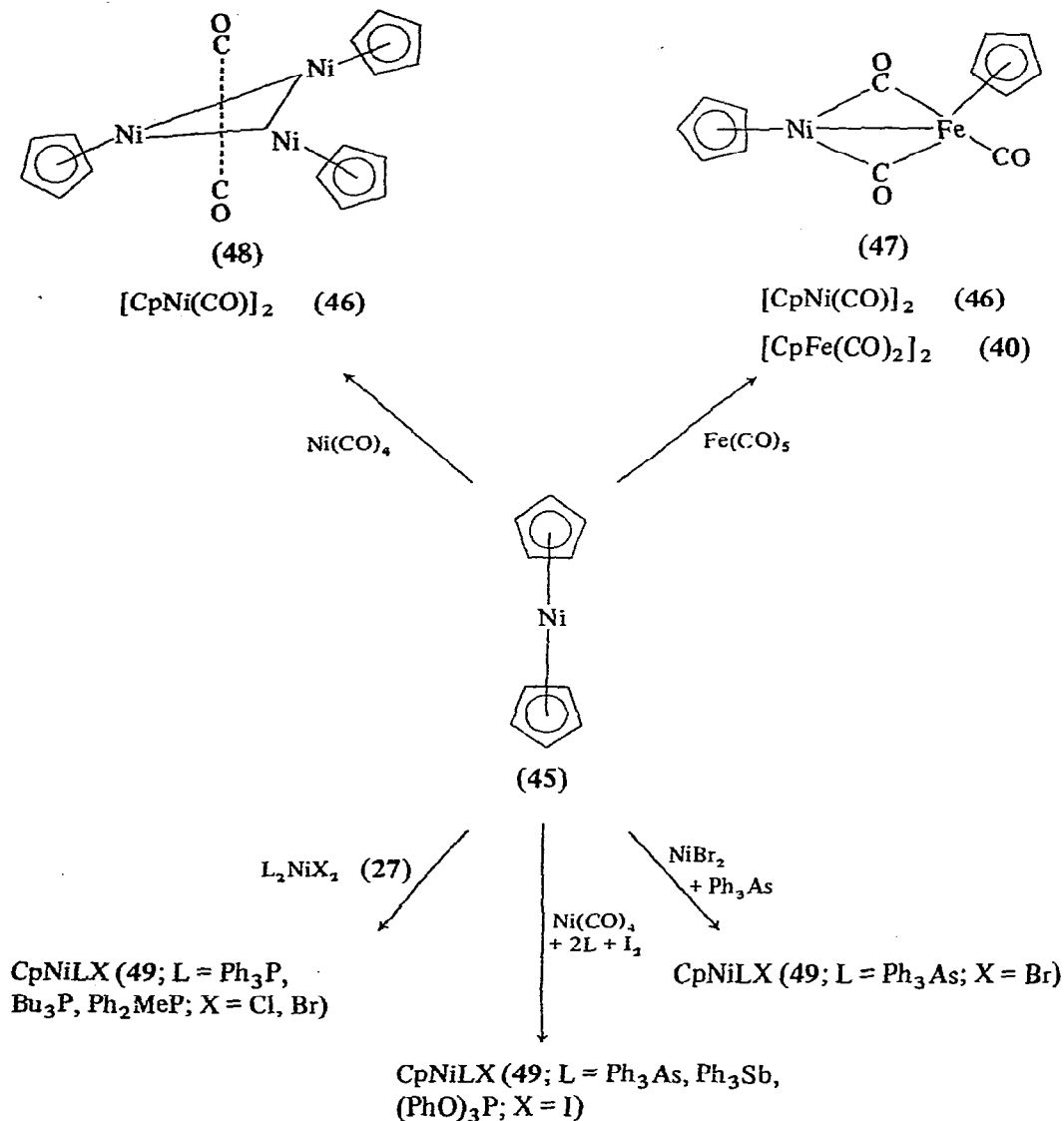


Fig. 10. The  $\pi$ -cyclopentadienyl transfer reactions involving nickelocene.

triethoxide complex,  $(\pi\text{-CH}_3\text{C}_5\text{H}_4)\text{Ti(OC}_2\text{H}_5)_3$ , has been reported to react analogously with ferrous chloride<sup>41</sup>. Similar  $\pi$ -cyclopentadienyl transfer reactions have also been encountered between the dicyclopentadienyltitanium derivatives,  $\text{Cp}_2\text{TiXY}$  ( $\text{X} = \text{Y} = \text{OCOCH}_3$ ;  $\text{X} = \text{Y} = \text{OCOC}_2\text{H}_5$ ;  $\text{X} = \text{OC}_2\text{H}_5$ ,  $\text{Y} = \text{Cl}$ ), and ferrous chloride or ferrous acetyl-

acetate. Again, these reactions led to the formation of ferrocene<sup>42,5</sup>. Experimental details pertaining to the reactions discussed in this section are presented in Table 3.

No mechanistic studies have yet been carried out on any of the π-cyclopentadienyl transfer reactions. However, despite the lack of experimental results in this area, a few attempts to suggest a reasonable mechanism have been made. To explain the π-cyclopentadienyl transfer process in the reaction between the iron bromide (39) and the cyclobutadiene or 1,5-cyclooctadienepalladium and -nickel complexes (19; R = Ph; X = Br), (21; R = Ph; X = Br) and (42) Maitlis *et al.*<sup>33</sup> proposed a two part mechanism (Fig. 11). The

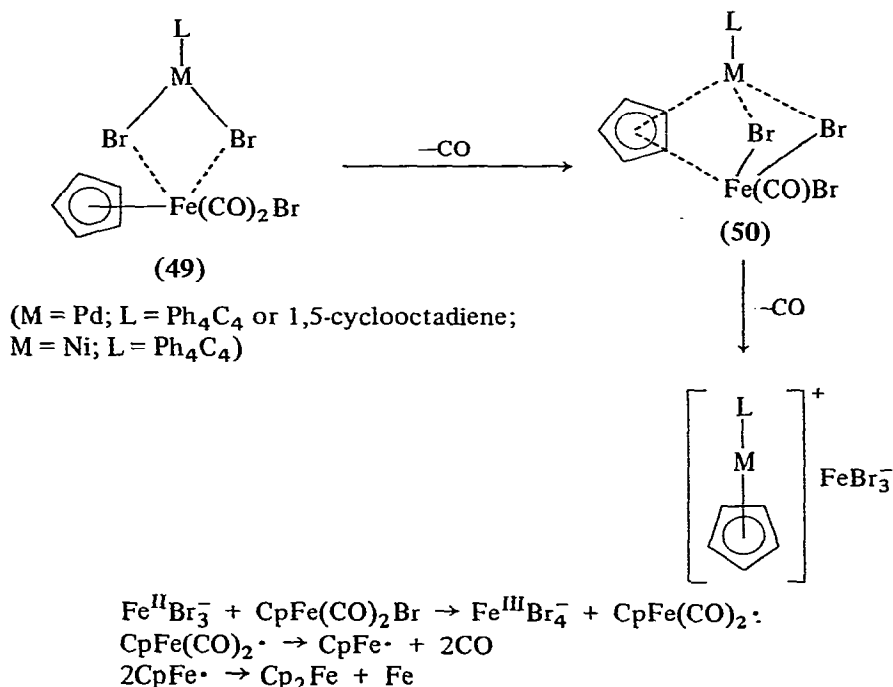
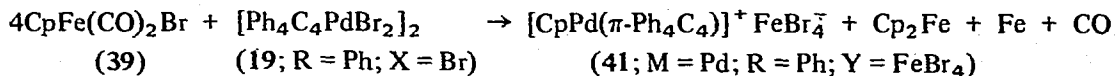


Fig. 11. The mechanism proposed for the π-cyclopentadienyl transfer reactions from iron to nickel and palladium<sup>33</sup>.

first part involved the formation of cyclopentadienyl and/or bromide bridged binuclear intermediates such as (49) and (50). In the second part, the ferrous tribromide anion is oxidized to tetrabromoferrate by an excess of cyclopentadienyliron dicarbonyl bromide (39) via a process involving free radical intermediates. This mechanistic scheme explained the formation of ferrocene and metallic iron as by-products. These by-products were actually separated and identified in the transfer process between the iron bromide (39) and the cyclobutadienepalladium complex (19). Rubeshov and Gubin<sup>5</sup> found it hard to believe that the coordinatively and electronically saturated iron atom in (39) could associate with



(continued on p. 26)

TABLE 3

 $\pi$ -CYCLOPENTADIENYL LIGAND TRANSFER REACTIONSAbbreviations: h = hour; min = minute; amb. = ambient temperature ( $\sim 25^\circ$ ); 1,5-COD = 1,5-cyclooctadiene; THF = tetrahydrofuran.

Reaction	Yield (%)	Reaction conditions	Reference
$[R_4C_4MBr_2]_2 + CpFe(CO)_2Br \rightarrow [R_4C_4MCp] + FeBr_4$ R = Ph; M = Ni	77	Benzene, reflux, 3 h.	33, 23
R = <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ; M = Ni	57	Benzene, reflux, 3 h.	23
R = Ph; M = Pd	85	Benzene, reflux, 3 h.	33, 23
R = <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ; M = Pd	55	Benzene, reflux, 3 h.	23
$[Ph_4C_4PdBr_2]_2 + [CpFe(CO)_2]_2 \rightarrow [Ph_4C_4PdCp] + FeBr_4$	42	Benzene, reflux, 3 h.	33
$(1,5-COD)PdBr_2 + CpFe(CO)_2Br \rightarrow [(1,5-COD)PdCp] + FeBr_4$	61	Benzene, reflux, 2.5 h.	33, 23
$(1,5-COD)PdBr_2 + [CpFe(CO)_2]_2 \rightarrow [(1,5-COD)PdCp] + FeBr_4$	8	Benzene, reflux, 2.5 h.	33, 23
$R_4C_4Co(CO)_2Br + CpFe(CO)_2Br \rightarrow R_4C_4CoCp$ R = Ph	78	Benzene, reflux, 2.5 h.	20, 23
R = <i>p</i> -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	71	Benzene, reflux, 2.5 h.	20, 23
$Ph_4C_4Co(CO)_2Br + [CpFe(CO)_2]_2 \rightarrow Ph_4C_4CoCp$	73	Benzene, reflux, 2.5 h.	20, 23
$(CH_3)_4C_4Co(CO)_2I + [CpFe(CO)_2]_2 \rightarrow (CH_3)_4C_4CoCp$	18.5	Benzene, reflux, 19 h.	21
$TiCl_4 + [CpFe(CO)_2]_2 \rightarrow CpTiCl_3$	5	Benzene, reflux, few min.	31, 33
$TiCl_4 + CpTiCl_2 \rightarrow CpTiCl_3$	84	<i>p</i> -Xylene, 115–120°, 24 h.	34
$Cp_2Ni + Fe(CO)_5 \rightarrow [CpFe(CO)_2]_2 + CpNi(CO)_2Cp + [CpNi(CO)]_2$	—	Benzene, reflux, 8 h.	35
$Cp_2Ni + Ni(CO)_4 \rightarrow [CpNi(CO)]_2 + Cp_3Ni_3(CO)_2$	50	Benzene, 70°, 12 h.	36, 37
40			
$Cp_2Ni + L_2NiX_2 \rightarrow 2CpNiLX$ L = Ph <sub>3</sub> P; X = Cl	90	THF, amb., 30 min.	38
L = (C <sub>4</sub> H <sub>9</sub> ) <sub>3</sub> P; X = Cl	67	THF, amb., 30 min.	38
L = Ph <sub>2</sub> MeP; X = Br	79	THF, amb., 30 min.	38
$Cp_2Ni + Ni(CO)_4 + 2L + I_2 \rightarrow 2CpNiLI$ L = (PhO) <sub>2</sub> P	39	THF, 30 min., at 25° and	38, 39
L = Ph <sub>3</sub> As	53	30 min. of reflux.	38
L = Ph <sub>3</sub> Sb	52		38



$\text{Cp}_2\text{Ni} + \text{NiBr}_2 + 2\text{Ph}_3\text{As} \rightarrow 2\text{CpNi}(\text{Ph}_3\text{As})\text{Br}$	66	THF, 50°, 3 h.	38
$\text{Cp}_2\text{Cr} + \text{FeCl}_2 \rightarrow \text{Cp}_2\text{Fe}$	10	THF, reflux, 6 h.	1
$\text{Cp}_2\text{Fe} + \text{RuCl}_3 \rightarrow \text{Cp}_2\text{Ru}$	42	250°	5 <sup>a</sup>
$\text{Cp}_2\text{TiCl}_2 + \text{Fe}(\text{CO})_5 \rightarrow \text{Cp}_2\text{Fe}$	10	Xylene, reflux, few min.	40
$\text{CpPd}(\pi\text{-C}_3\text{H}_5) + \text{FeCl}_2 \rightarrow \text{Cp}_2\text{Fe}$	65	THF, reflux, 4 h.	5 <sup>a</sup>
$\text{CpPd}(\pi\text{-C}_3\text{H}_5) + \text{Fe}(\text{CO})_5 \rightarrow \text{Cp}_2\text{Fe} + [\text{CpFe}(\text{CO})_2]_2$	-	Benzene, amb.	5 <sup>a</sup>
$\text{CpTi}(\text{OC}_2\text{H}_5)_2\text{Cl}_2 + \text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_2 \rightarrow \text{Cp}_2\text{Fe}$	9	THF, 150°, 8 h.	5 <sup>a</sup>
$\text{CpTi}(\text{OC}_2\text{H}_5)_2\text{Cl} + \text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_2 \rightarrow \text{Cp}_2\text{Fe}$	70	THF, 150°, 8 h.	5 <sup>a</sup>
$\text{CpTi}(\text{OC}_2\text{H}_5)_3 + \text{FeCl}_2 \rightarrow \text{Cp}_2\text{Fe}$	Traces	THF, reflux, 1 h.	42
$\text{CpTi}(\text{OC}_2\text{H}_5)_3 + \text{FeCl}_2 \rightarrow \text{Cp}_2\text{Fe}$	70	THF, reflux, 15 min.	5 <sup>a</sup>
$\text{CpTi}(\text{OC}_2\text{H}_5)_3 + \text{FeCl}_2 \rightarrow \text{Cp}_2\text{Fe}$	74	Nitromethane, 100°, 1 h.	5 <sup>a</sup>
$\text{CpTi}(\text{OC}_2\text{H}_5)_3 + \text{FeCl}_2 \rightarrow \text{Cp}_2\text{Fe}$	66	THF, reflux, 1 h.	42
$\text{CpTi}(\text{OC}_2\text{H}_5)_3 + \text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_2 \rightarrow \text{Cp}_2\text{Fe}$	Traces	THF, 150°, 8 h.	5 <sup>a</sup>
$\text{CpTiBr}_3 + \text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_2 \rightarrow \text{Cp}_2\text{Fe}$	9	150°, 8 h.	5 <sup>a</sup>
$\text{CpTi}(\text{OC}_2\text{H}_5)_2\text{Br} + \text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_2 \rightarrow \text{Cp}_2\text{Fe}$	11	THF, 150°, 3 h.	5 <sup>a</sup>
$\text{CpTi}(\text{OC}_2\text{H}_5)_2\text{I} + \text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_2 \rightarrow \text{Cp}_2\text{Fe}$	4	THF, 150°, 3 h.	5 <sup>a</sup>
$\text{CpTi}(\text{OC}_3\text{H}_7\text{-i})\text{Cl}_2 + \text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_2 \rightarrow \text{Cp}_2\text{Fe}$	11	THF, 150°, 3 h.	5 <sup>a</sup>
$\text{CpTi}(\text{OC}_3\text{H}_7\text{-i})\text{Cl} + \text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_2 \rightarrow \text{Cp}_2\text{Fe}$	56	THF, reflux, 1 h.	5 <sup>a</sup>
$\text{CpTi}(\text{OC}_3\text{H}_9\text{-tert})_3 + \text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_2 \rightarrow \text{Cp}_2\text{Fe}$	25	THF, 150°, 6 h.	41
$(\pi\text{-CH}_3\text{C}_5\text{H}_4)\text{Ti}(\text{OC}_2\text{H}_5)_3 + \text{FeCl}_2 \rightarrow (\pi\text{-CH}_3\text{C}_5\text{H}_4)_2\text{Fe}$	55	THF, reflux, 1 h.	5 <sup>a</sup>
$\text{CpTi}(\text{OCOCH}_3)_3 + \text{FeCl}_2 \rightarrow \text{Cp}_2\text{Fe}$	51	THF, reflux, 1 h.	5 <sup>a</sup>
$\text{CpTi}(\text{OPh})_3 + \text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_2 \rightarrow \text{Cp}_2\text{Fe}$	46	THF, reflux, 1 h.	42
$\text{Cp}_2\text{Ti}(\text{OCOCH}_3)_2 + \text{FeCl}_2 \rightarrow \text{Cp}_2\text{Fe}$	44	THF, reflux, 1 h.	5 <sup>a</sup>
$\text{Cp}_2\text{Ti}(\text{OCOCH}_3)_2 + \text{FeCl}_2 \rightarrow \text{Cp}_2\text{Fe}$	36	Nitromethane, 100 h.	5 <sup>a</sup>
$\text{Cp}_2\text{Ti}(\text{OCOC}_2\text{H}_5)_2 + \text{FeCl}_2 \rightarrow \text{Cp}_2\text{Fe}$	4	THF, reflux, 1 h.	5 <sup>a</sup>
$\text{Cp}_2\text{Ti}(\text{OC}_2\text{H}_5)\text{Cl} + \text{FeCl}_2 \rightarrow \text{Cp}_2\text{Fe}$	4	THF, reflux, 1 h.	5 <sup>a</sup>
$\text{Cp}_2\text{Ti}(\text{OC}_2\text{H}_5)\text{Cl} + \text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_2 \rightarrow \text{Cp}_2\text{Fe}$	4	THF, reflux, 1 h.	5 <sup>a</sup>

<sup>a</sup> These experimental details were quoted in the review by Rubezhov and Gubin<sup>5</sup>. Some of the data could not be traced to the original papers.

nucleophiles via additional bridge bonds. They suggested the dissociation of either CO or Br from (39) so that the intermediates generated could then react with the substrate.

Another mechanistic approach which has already been mentioned in conjunction with  $\pi$ -allyl and  $\pi$ -cyclobutadiene transfer reactions is also feasible here. This approach assumes the formation of poly- or bi-nuclear intermediates in which one of the metals retains its rare gas, 18-electron configuration while the other undergoes changes and becomes coordinatively and electronically unsaturated. A typical example to illustrate the  $\pi$ -cyclopentadienyl transfer in the reaction between the bromide (39) and the cyclobutadienecobalt dicarbonyl bromide (28) is shown in Fig. 12. The actual transfer process is envisioned to take place through a  $\pi$ -bonded allyl to olefin rearrangement. In this process, the cobalt

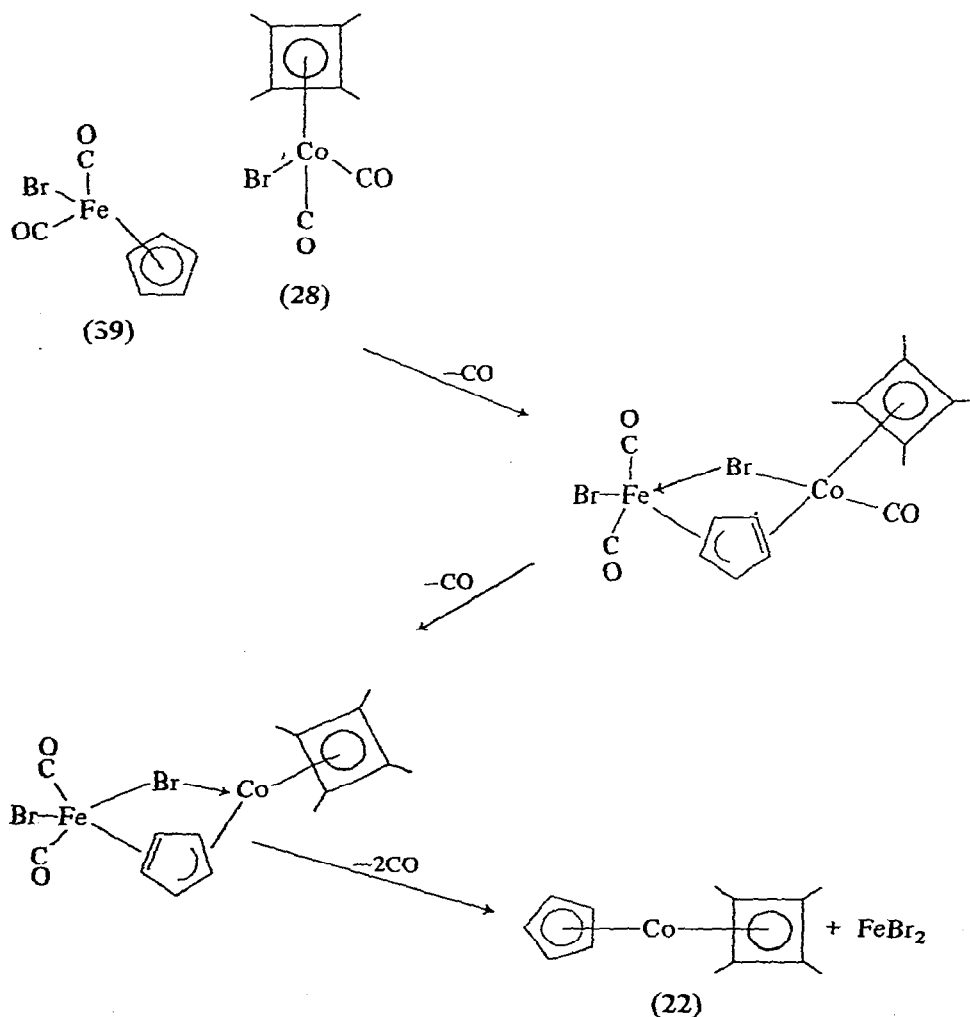


Fig. 12. The mechanism proposed for the  $\pi$ -cyclopentadienyl transfer in the reaction between (39) and (28).

atom is assumed to remain coordinatively and electronically saturated while at the same time the iron atom becomes unsaturated in both respects. Other  $\pi$ -cyclopentadienyl transfer reactions can be described in a similar fashion.

## V. MISCELLANEOUS $\pi$ -LIGAND TRANSFER REACTIONS AND CONCLUSION

In 1957 Fischer and Öfele<sup>43</sup> reported the reaction between dibenzenechromium and  $\text{Cr}(\text{CO})_6$  by which  $\pi$ -benzenechromium tricarbonyl was obtained in 25% yield. This reaction was carried out in benzene solution at 220° for 12 hours. Under the above conditions, the product obtained could have resulted from a direct reaction between  $\text{Cr}(\text{CO})_6$  and the solvent although conceivably some  $\pi$ -benzene transfer could have taken place as well.

A dramatic example of a double  $\pi$ -ligand transfer reaction was reported by Maitlis and Efraty<sup>20</sup> in the reaction between the tetraphenylcyclobutadienepalladium complex (41;  $\text{M} = \text{Pd}$ ;  $\text{R} = \text{Ph}$ ;  $\text{Y} = \text{Br}$ ) and  $\text{Co}_2(\text{CO})_8$ . This reaction, carried out in boiling benzene solution for one hour, gives ( $\pi$ -tetraphenylcyclobutadiene)( $\pi$ -cyclopentadienyl)cobalt (22;  $\text{R} = \text{Ph}$ ) in 10% yield. This novel reaction is the only known example of a simultaneous transfer of two  $\pi$ -bonded ligands from one metal complex to another.

This review work was purposely aimed at surveying the  $\pi$ -ligand transfer reactions which were proven successful with ligands such as  $\pi$ -allyl,  $\pi$ -cyclobutadiene and  $\pi$ -cyclopentadienyl. However, there are no apparent reasons why this interesting technique could not be extended to include other  $\pi$ -ligands. Generally,  $\pi$ -ligand transfer reactions are carried out in one step and require only simple apparatus which are commonly available in most synthetic laboratories. With only a few exceptions, the reactions take anywhere from few minutes to few hours to complete. Unfortunately, no kinetic studies have yet been performed on any of these reactions. Consequently, very little is known about their mechanisms. It is currently believed that these transfer processes proceed via the formation of poly- or bi-nuclear intermediates in which halogens and/or the  $\pi$ -ligand bridge the metal atoms. More precise mechanistic evaluations should await further studies. It is hoped that future investigations in this field will emphasize the mechanistic aspects of the  $\pi$ -ligand transfer reactions.

## ACKNOWLEDGMENT

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