THE REACTION OF π-ALLYL COMPOUNDS OF NICKEL, PALLADIUM AND PLATINUM WITH IRON NONACARBONYL

A. N. NESMEYANOV, S. P. GUBIN AND A. Z. RUBEZHOV

Institute of Organo-Element Compounds, Academy of Sciences, Moscow (USSR)

(Received September 2nd, 1968)

SUMMARY

The reaction of iron carbonyls with the π-allyl compounds of nickel, palladium and platinum has been studied. Bis(π-allylpalladium chloride), for example, has been shown to react first with fission of the μ-halide bridges in the dimeric molecule of $(\pi\text{-}C_3H_5PdCl)_2$. In the intermediate formed there is an intermolecular π–π-migration of the allyl ligand from palladium to the iron atom. The NMR study of the reaction mixture indicates that this migration is preceded by π–σ-perturbation in the π-allyl ligand. Thus, the migration of the C_3H_5-ligand takes place in three stages: coordination with the $Fe(CO)_4$-fragment, transformation of the ligand from the π- into the σ-bonded form, and finally the ligand migration itself, *i.e.*, the main stages responsible for the homogeneous catalysis by the transition-metal complexes.

INTRODUCTION

The reactions of migration of the π-bonded ligands are of considerable interest since they may be regarded as the reactions modelling the particular steps in the processes of homogeneous catalysis by the transition metal π-complexes[1]. So far, the migration reactions of only tetraphenylcyclobutadienyl-[2] and π-cyclopentadienyl-[3] ligands have been described. Their mechanism is practically unknown, and the schemes suggested by Maitlis *et al.* are of purely speculative nature.

We have shown that π-allylpalladium chloride reacts with iron nonacarbonyl, giving π-allyliron tricarbonyl chloride, *i.e.*, there is migration of the π-bonded allyl ligand from palladium to the iron atom (π̄–π-migration)[4]. Later, several groups of investigators reported the reactions of migration of the π-allyl group from one to another transition-metal atom[5,6]. In an earlier investigation a reaction of the π–σ-migration of the π-allyl group from palladium to the mercury atom was discovered and studied in detail[7,8].

As early as 1930, Nesmeyanov and Kocheshkov discovered the reaction of reductive transfer (σ–σ) of the aryl radical from diarylmercury to stannous chloride[9].

The present work is concerned with a detailed investigation of the iron nonacarbonyl reaction with the π-allyl derivatives of nickel, palladium and platinum. A mechanism of migration for π-allylpalladium chloride, for example, has been suggested, and the properties of the reaction intermediate have been studied.

RESULTS

Reaction of π-allylpalladium chloride with iron nonacarbonyl

We have found that the addition of iron nonacarbonyl to the benzene solution of $(\pi\text{-}C_3H_5PdCl)_2$ causes the gradual "dissolving" of iron nonacarbonyl with production of a green benzene solution of an intermediate compound. After several hours the latter gave $\pi\text{-}C_3H_5Fe(CO)_3Cl^*$, isolated at room temperature after precipitation of a black solid containing metallic iron and palladium. Iron pentacarbonyl also reacts with $(\pi\text{-}C_3H_5PdCl)_2$ under the same conditions but it requires 8–10 days to complete the reaction instead of 8–10 h. The reaction was shown to be complete when the black solid of the metallic mixture ceased to precipitate. Even a large excess of iron carbonyl (5–10 fold) leaves about half of the starting π-allylpalladium chloride unreacted and this was isolated unchanged. The reaction stoichiometry for several experiments carried out with both iron pentacarbonyl and iron nonacarbonyl is shown in Tables 1 and 2.

TABLE 1

REACTION OF $(\pi\text{-}C_3H_5PdCl)_2$ WITH IRON PENTACARBONYL

$(C_3H_5PdCl)_2$		$Fe(CO)_5$	Pd–Fe	$C_3H_5Fe(CO)_3Cl^c$	$(C_3H_5PdCl)_2{}^a$
(g)	1.0	1.2	0.8	0.2	0.3
(g-m)	0.0055	0.0061		0.0009	0.0017
(g(M))^b	0.59	0.35		0.05	0.17
(%)				26	30
(g)	1.0	1.2	0	0.2	0.3
(g-m)	0.0055	0.0061		0.0009	0.0017
(g(M))	0.59	0.35		0.05	0.17
(%)				26	31
(g)	5.0	6.0	1.8	0.2	4.3
(g-m)	0.025	0.030		0.0009	0.023
(g(M))	2.8	1.7		0.05	2.5
(%)			92	26	86
(g)	3.0	7.5	2.5	0.2	2.0
(g-m)	0.017	0.038		0.0009	0.011
(g(M))	1.7	2.1		0.05	1.2
(%)			98	17	66
(g)	3.0	3.5	1.2	0.2	2.0
(g-m)	0.017	0.018		0.0009	0.011
(g(M))	1.7	1.0		0.05	1.2
(%)			83	17	66

^{a} $(C_3H_5PdCl)_2$ unreacted. ^{b} g(M)—amount of metal in the complex. ^{c} The yields are given based on the reacted π-allylpalladium halide.

It can be seen from the Tables that in all cases the amounts of metals (Pd–Fe) precipitated correspond to the theoretical quantities. The consumption of iron

---

* The π-allyliron complexes obtained have been identified by means of m.p. determination and infrared, NMR and polarographic analyses. A similar identification procedure of the reaction products has been applied in all subsequent experiments.

TABLE 2

REACTIONS OF π-ALLYLPALLADIUM COMPOUNDS WITH IRON NONACARBONYL

		(AllPdCl)$_2$	Fe$_2$(CO)$_9$	Pd–Fe	AllFe(CO)$_3$Cl	(AllPdCl)$_2$ [a]
Crotyl	(g)	2.24	4.1	1.0	0.24	1.17
	(g-m)	0.012	0.012		0.0011	0.006
	(g(M))[b]	1.25	1.3		0.05	0.46
	(%)			65	25	52
Cinnamyl	(g)	2.04	2.89	0.65	0.2	1.1
	(g-m)	0.008	0.009		0.0008	0.004
	(g(M))	0.86	1.05		0.05	0.46
	(%)			46	30	54
2-Phenyl	(g)	2.7	4.93	1.3	0.4	0.81
	(g-m)	0.011	0.13		0.0016	0.003
	(g(M))	1.1	1.5		0.10	0.33
	(%)			60	30	30
Neo-C$_5$H$_{11}$	(g)	0.7	0.97	0.38	—	0.7
	(g-m)	0.0028	0.0028			
	(g(M))					
	(%)			quantit.		quantit.
2-Chloro-	(g)	2.43	4.07	1.65	—	2.29
isopropenyl	(g-m)	0.001	0.001			
	(g(M))		1.2			
	(%)			quantit.		quantit.
Allyl	(g)	4.62	8.47	3.1	0.5	2.91
	(g-m)	0.23	0.023		0.0022	0.015
	(g(M))	2.5	2.6		0.12	1.6
	(%)			92	25	63
Allyl	(g)	2.8	5.5	2.3	0.6	1.3
	(g-m)	0.015	0.015		0.0028˙	0.007
	(g(M))	1.64	17		0.15	0.76
	(%)			95	25	47

^{a} (AllPdCl)$_2$ unreacted. ^{b} g(M), amount of metal in the complex.

carbonyl is quantitative while about half of the starting palladium compounds remains unreacted. These results indicate that iron nonacarbonyl generates two particles: the first participating in the reaction, the second decomposing into metallic iron and carbon monoxide. The evolution of carbon monoxide commences only 4–5 h after the beginning of the reaction *i.e.*, the dissolving of iron nonacarbonyl which starts immediately after the mixing of the reagents, does not result in evolution of carbon monoxide. A regular decay of iron nonacarbonyl should be evident in the last case:

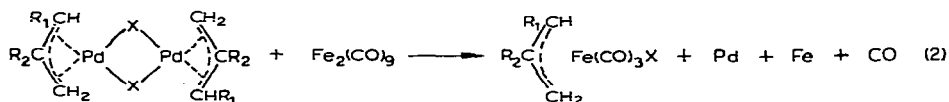$$Fe_2(CO)_9 \rightarrow Fe(CO)_4 + Fe(CO)_5 \qquad (1)$$

A considerable quantity of iron pentacarbonyl was shown by both gas chromatography and polarography to be present in the solution. The complete dissolving of iron nonacarbonyl is first manifested by the green colour, then in the slow precipi-

tation of metallic palladium and finally by the precipitation of iron and evolution of carbon monoxide.

Reaction of the substituted π-allylpalladium chlorides with iron nonacarbonyl

It follows from the data of Tables 1 and 2 that the introduction of substituents into the π-allyl group of π-allylpalladium halides does not affect the stoichiometric ratios, and the reaction with iron nonacarbonyl proceeds according to the scheme:

$$
\begin{array}{c}
R_1CH \diagdown \diagup CH_2 \\
R_2C\!\!\diagup\!\!\diagdown Pd \diagup \diagdown Pd\!\!\diagup\!\!\diagdown CR_2 \\
CH_2 \quad X \quad CHR_1
\end{array}
+ Fe_2(CO)_9 \longrightarrow
\begin{array}{c}
R_1CH \\
R_2C\!\!\diagup Fe(CO)_3X \\
CH_2
\end{array}
+ Pd + Fe + CO \quad (2)
$$

The nature and position of a substituent substantially influence the reaction course. 2-neopentyl- π-allylpalladium chloride and 2-(3-chloroisopropenyl)-π-allylpalladium chloride, for example, do not react with iron nonacarbonyl, no evolution of carbon monoxide and no precipitation of metallic palladium were observed and the starting palladium derivative remains unchanged*. At the same time, there was a complete decay of iron nonacarbonyl, probably due to a catalytic action of the π-allylpalladium complexes.

The normal reaction course is inhibited by such substituents in the π-allyl ligand as 2-chloromethyl- or 1-acetyl-groups. The relevant π-allyliron tricarbonyl derivatives seem to be unstable under the reaction conditions, and cannot be isolated from the solution.

The reaction proceeds satisfactorily only in the case of the alkyl- and aryl-substituted π-allylpalladium halides. Thus, the substituted π-allyliron compounds

TABLE 3

SUBSTITUTED π-ALLYLIRON COMPOUNDS OBTAINED BY THE REACTION OF (π-C₃H₅PdCl)₂ WITH IRON NONACARBONYL

Compound	M.p.	Yield[a] (%)	Analysis							
			Found				Calcd.			
			C	H	Fe	Hal	C	H	Fe	Hal
π-C₃H₅Fe(CO)₃Cl	83–84	26	33.29	2.79	25.84	10.71	33.33	2.31	25.92	16.20
π-C₃H₅Fe(CO)₃Br	85–86	30	—	—	—	—	—	—	—	—
π-C₃H₅Fe(CO)₃I	79–80	28	—	—	—	—	—	—	—	—
π-C₄H₇Fe(CO)₃Cl	34–35	26	—	—	—	—	—	—	—	—
π-(I-C₆H₅C₃H₄)Fe(CO)₃Cl	88–88.5	30	49.68	3.29	18.65	11.88	49.32	3.10	13.03	12.12
π-(2-C₆H₅-C₃H₄)Fe(CO)₃Cl	93	37	49.32	3.22	19.53	12.72	49.32	3.10	13.09	12.12

[a] Yields are given basing on the reacted π-allylpalladium halide.

listed in Table 3 have been prepared. The yields of the π-allyliron compounds are as high as 25–30%. In some cases, the preparation of substituted π-allyliron complexes

---

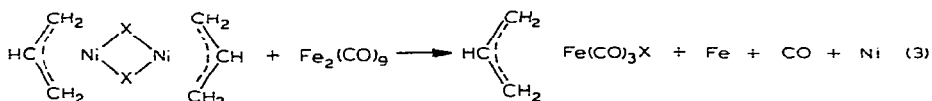* An X-ray study of 2-neopentyl-π-allylpalladium chloride indicated no essential difference in structure from that of unsubstituted bis(π-allylpalladium chloride) which may adequately explain the inability of this compound to exchange its π-allyl group. This explanation is still under review.

by this procedure may be preferable to other known methods since the relevant π-allylpalladium complexes are readily available[10].

Reaction of iron nonacarbonyl with bis(π-allylnickel halides)

We have investigated the reaction of iron nonacarbonyl with bis(π-allylnickel chloride) and bis(π-allylnickel bromide). The reaction is carried out under normal conditions in an argon atmosphere and requires an ether–benzene medium. The corresponding allyl derivatives of iron were prepared and other reaction products, metallic nickel and iron, and carbon monoxide were isolated.

Thus, the reaction of bis(π-allyl-nickel halides) with iron nonacarbonyl is described by the equation:

$$
\begin{array}{c}
\text{(bis-π-allylnickel halide)} + \text{Fe}_2\text{(CO)}_9 \longrightarrow \text{(π-allyl)Fe(CO)}_3\text{X} + \text{Fe} + \text{CO} + \text{Ni} \quad (3)
\end{array}
$$

The behaviour of allylnickel halides in the reaction with iron nonacarbonyl is essentially the same as that of the respective palladium derivatives.

Reaction of the bis-π-allyl compounds of nickel, palladium and platinum with iron nonacarbonyl

All bis-π-allyl compounds investigated react readily and rapidly with iron nonacarbonyl. Thus, when iron nonacarbonyl is added in slight excess to a solution of bis(π-allyl)nickel, the mixture darkens. If after several minutes a solution of iodine in ether is added, carbon monoxide is freely evolved, π-allyliron tricarbonyl iodide and nickel iodide (insoluble in benzene) being the reaction products. The reaction may be described by the following equation:

$$
\begin{array}{c}
\text{(bis-π-allyl)Ni} + \text{Fe}_2\text{(CO)}_9 \xrightarrow{+\text{I}_2} \text{(π-allyl)Fe(CO)}_3\text{I} + \text{NiI}_2 + \text{CO} \quad (4)
\end{array}
$$
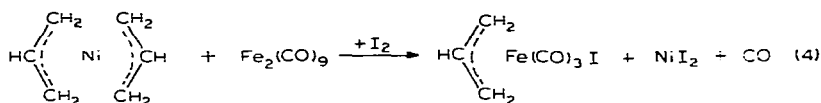
The reaction with bis(π-allyl)platinum or -palladium compounds follows an analogous scheme but, unlike the nickel derivative, metallic palladium or platinum are obtained. It should be noted that in all three cases carbon monoxide is freely evolved only after the addition of halogen to the mixture. This indicates that the reactions of bis-π-allyl compounds and those of the corresponding π-allylmetal-halides are fundamentally different, since the latter gives an intermediate decomposing spontaneously with time to give the final reaction product.

Physico-chemical properties of solutions containing the intermediate compound. Investigation of reaction mechanism for interaction between (π-C$_3$H$_5$PdCl)$_2$ and iron nonacarbonyl

In order to understand the mechanism of the π-allyl ligand migration from palladium to the iron atom it is necessary to investigate the following: (i) the reaction state of iron carbonyl; (ii) the nature of the bonding between the active iron carbonyl fragment and the π-allylpalladium chloride molecule and (iii) the nature of the migration stage itself if there are some prior changes in the π-bonded ligand, etc. To

resolve these questions we have investigated the physico-chemical properties of the green solutions of the reaction intermediate. The prolonged stability of the solutions enables all stages of the reaction course to be studied.

The most useful information on the state of iron in the intermediate complex (p- and s- electron density, and complex symmetry) may be obtained[11] by analysing a series of successive samples of the reaction mixture by nuclear gamma resonance spectroscopy (the Mössbauer effect). The results of such an investigation are shown in Fig. 1 and Table 4. The data given show that the first test already contains a significant
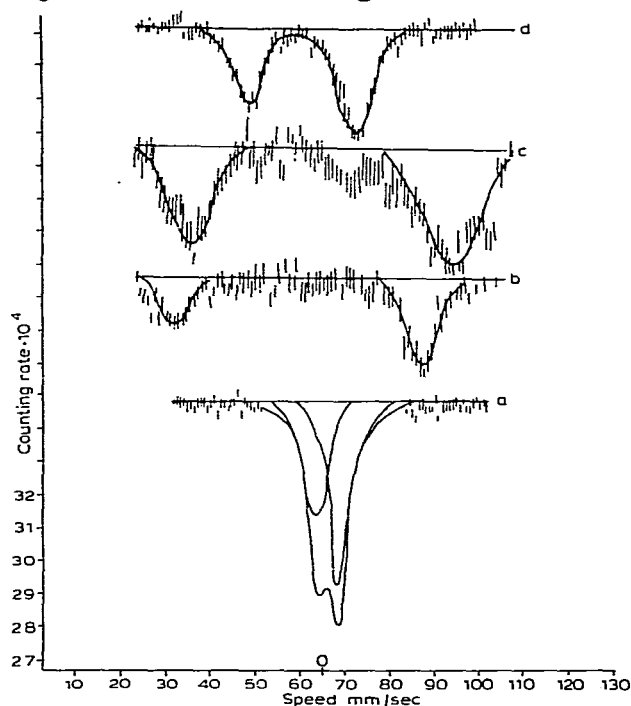
Fig. 1. Nuclear gamma resonance spectra of successive samples taken from the reaction mixture, $(C_3H_5-PdCl)_2 + Fe_2(CO)_9$: (a) $Fe_2(CO)_9$; (b) 15 min after mixing the reagents; (c) after 4 h; (d) $C_3H_5Fe(CO)_3Cl$.

amount of iron; but this is not iron nonacarbonyl, since the spectrum parameters are essentially different from those of $Fe_2(CO)_9$[12].

Further analysis shows that δ and ΔE are practically invariant during the reaction. The broad lines in the spectrum of the last test testify that one or several other compounds of iron may be present in the reaction mixture. A comparison of our parameters with the data described in ref. 12 suggests a zerovalent iron compound of trigonal bipyramid structure. In the given case, besides iron pentacarbonyl, this may be a compound of structure $AFe(CO)_4$, where A is the π-allylpalladium chloride fragment. A similar compound may be a result of fission of the μ-halide bridge in the molecule of π-allylpalladium chloride by the nucleophilic $Fe(CO)_4$-fragment. The latter is formed under the reaction conditions (eqn. (1)). According to the data described[13] such a fission may occur at 80–95°, or at room temperature at a lower rate.

It is more convenient to discuss the bonding between the $Fe(CO)_4$-fragment

TABLE 4

PARAMETERS OF THE NUCLEAR GAMMA RESONANCE SPECTRUM OF THE REACTION MIXTURE

Compound	Solvent	$T(^{\circ}K)$	δ^b (mm/sec)	ΔE (mm/sec)
$Fe_2(CO)_9$	benzene	80	0.41	0.45
Test No. 1[a]			0.18	2.48
No. 2			0.19	2.62
No. 3			0.19	2.54
No. 4			0.18	2.48
No. 5			0.19	2.48
No. 6			0.22	2.58
π-$C_3H_5Fe(CO)_3Cl$			0.37	1.46
$Fe(CO)_5 + C_3H_5PdCl$ after 2 h			0.15	2.52
$Fe(CO)_5$			0.15	2.58

[a] Test No. 1 was taken 15 min after mixing the reagents and the others after every hour. [b] With respect to sodium nitroprusside.

and π-allylpalladium chloride radical in the intermediate compound using the infrared spectral data.

Figure 2 shows the carbonyl regions in the spectra of iron nonacarbonyl, π-allyliron tricarbonyl chloride (final product), and the successive samples taken
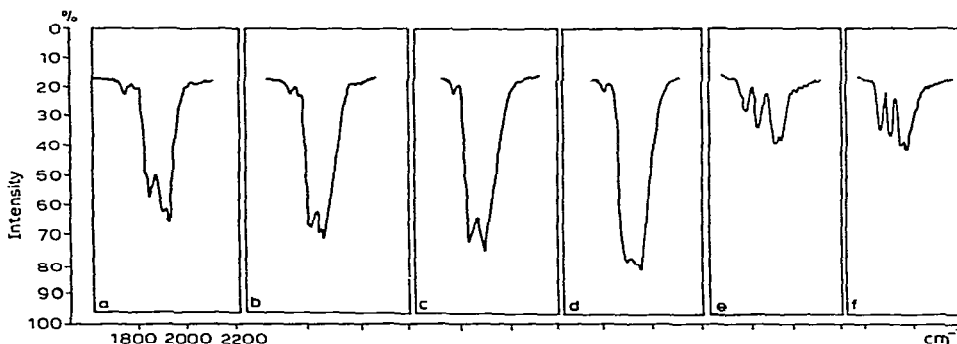

Fig. 2. Infrared spectra (carbonyl region) of successive samples taken from reaction mixture, $(C_3H_5PdCl)_2 + Fe_2(CO)_9$: (a) 15 min after mixing the reagents; (b, c, d) after every hour; (e, f) after 16 h.

from the reaction mixture. Very strong absorption bands in the spectrum of iron nonacarbonyl at 2090 cm^{-1} and 2025 cm^{-1} are assigned to the vibrations of the terminal carbonyl groups, and the band at 1830 cm^{-1} is the vibration of the bridged CO-ligand[14]. The spectrum of the first test already shows no bands relating to the bridged carbonyl group vibration. There are two strong bands at 2000 cm^{-1} and 1980 cm^{-1} with intensities increasing with time indicating an increasing amount of an intermediate. In the spectrum of the sixth test and those following, the weak band shows up in the high frequency region at 2075 cm^{-1} with a gradually increasing intensity. The last two tests were taken 15–16 h after the reagents were mixed and show that an appreciable part of an intermediate product had decomposed by that

time. In the infrared spectrum of the last test there are three bands of nearly equal intensities at 2075, 2025 and 1985 cm^{-1}. These bands also appear in the spectra of the π-allyliron tricarbonyl complexes[15]. Thus, the FeCO$_4$-fragment and palladium atom are not bonded through the carbonyl bridge but a direct bond may exist between iron and palladium. Increasing ability of the Fe(CO)$_4$-fragment to participate in the metal–metal bonding supports this[13]. Summarizing the data of the infrared and nuclear gamma resonance spectral investigation we conclude that the intermediate complex has the following structure:

(I)
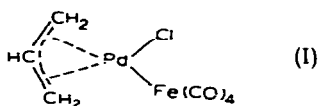
This complex is responsible for the migration of the π-allyl ligand from palladium to the iron atom. The transformation of the π-allyl ligand into the σ-bonded form should evidently precede the migration. The NMR spectra of the successive samples taken during the reaction of (π-C$_3$H$_5$PdCl)$_2$ with iron nonacarbonyl are shown in Fig. 3 : the lower spectrum recorded 1 h after mixing the reagents and that of
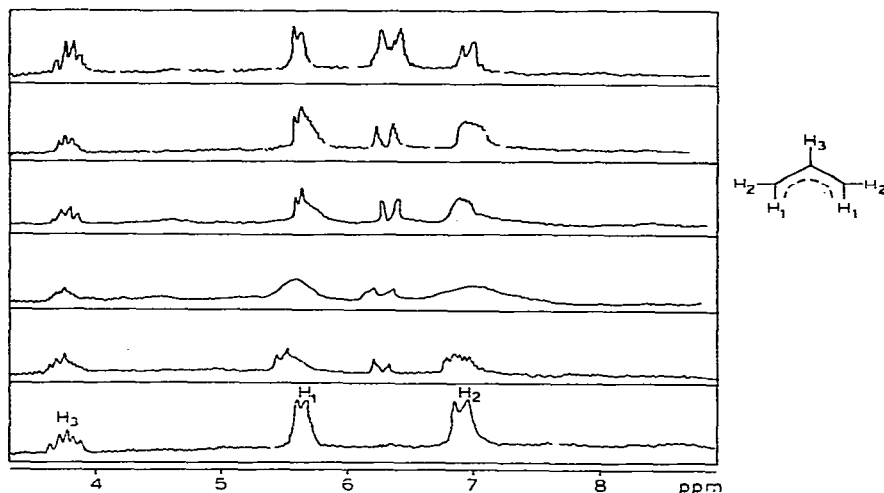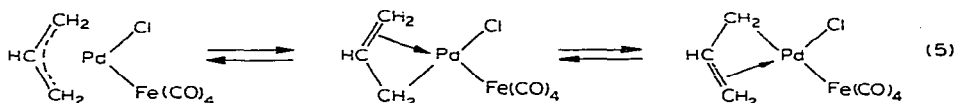

Fig. 3. NMR spectra of successive samples taken from the reaction mixture, (π-C$_3$H$_5$PdCl)$_2$ + Fe$_2$(CO)$_9$ (every hour after mixing the reagents) (C$_6$H$_6$).

π-allylpalladium chloride are practically analogous. The broadening of signals from H$_1$,H$_2$ and H$_3$,H$_4$ protons and decrease in intensities can be observed.

Furthermore, there is a doublet showing between signals from the methylene protons, and its intensity increases with time. These data as well as those of the infrared spectra indicate that an intermediate product is accumulating in the mixture. The doublet appearing almost in the middle between the methylene proton signals testifies to their magnetic equivalence. This may be a result of a fast equilibrium in the solution:

$$\begin{array}{ccc}
\underset{HC}{\overset{CH_2}{\diagdown}}\overset{Cl}{\underset{Pd}{\diagup}}\overset{}{\diagdown}Fe(CO)_4 \quad\rightleftharpoons\quad & HC\overset{CH_2}{\diagdown}Pd\overset{Cl}{\diagup}\diagdown Fe(CO)_4 \quad\rightleftharpoons\quad & HC\overset{CH_2}{\diagdown}Pd\overset{Cl}{\diagup}\diagdown Fe(CO)_4 \quad (5)
\end{array}$$

leading to the π,σ-bonded allyl group on the palladium atom. In general, the picture is qualitatively similar to that of the well-known π-C_3H_5PdClL, where L is a σ-donor ligand (PPh_3, for example)[16].

EXPERIMENTAL

The preparation of the bis-π-allyl compounds of nickel, palladium and platinum may be carried out by a modification of the method of Wilke[17] from the anhydrous metal halides and allylmagnesium bromide in ether. Bis(π-allylnickel halides) are synthesized from bis-π-allylnickel and the corresponding allyl halides[18].

Bis(π-allylpalladium halides) are prepared by published methods[19].

The bis-π-allyl compounds of nickel, palladium and platinum, and the bis-(π-allyl halide) complexes of nickel were not isolated in crystalline form but used as solutions in ether or benzene.

The nickel complexes have been analysed quantitatively by complexometric titration with EDTA[20].

(1) *Reaction of iron nonacarbonyl with the bis-π-allyl derivatives of nickel, palladium and platinum*

General procedure. 100 ml of an ethereal solution containing about 1.0 g (0.007–0.004 mole) of the corresponding bis-π-allyl compound was stirred with 1.0–1.5 g (0.003–0.004 mole) of iron nonacarbonyl for 30 min at room temperature. The mixture darkened. After the solution of iodine in ether had been added to the mixture, there was vigorous evolution of carbon monoxide (the absorption of gaseous reaction products by the palladium chloride solution causes precipitation of metallic palladium). When the evolution of carbon monoxide was complete, the solvent was evaporated *in vacuo*. and the residue extracted with n-pentane. The extract was evaporated, and the residue crystallized from n-pentane. π-Allyliron tricarbonyl iodide crystallised out at $-80°$; m.p. 84–85°; lit. m.p.[10] 84–85°.

(2) *Reaction of iron nonacarbonyl with bis(π-allylnickel bromide)*

100 ml of an ethereal solution, containing 1.0 g (0.007 mole) of bis(π-allylnickel bromide) was stirred with 2.5 g (0.007 mole) of iron nonacarbonyl for 12 h at room temperature. The reaction mixture was evaporated *in vacuo* and extracted with hexane. The hexane solution was evaporated *in vacuo* and the residue crystallized from pentane by cooling to $-80°$ 0.1 g (12%) of π-allyliron tricarbonyl bromide was obtained; m.p. 85–86° (dec.); lit.[10] m.p. 85–86° (dec.).

(3) *Reaction of iron nonacarbonyl with bis(π-allyl halides) of palladium*

General procedure. 1.0 g (0.005 mole) of the corresponding palladium compound and 1.6 g (0.005 mole) of iron nonacarbonyl were stirred at room temperature

for 8 h. A black solid was precipitated during the reaction. The evolution of carbon monoxide started 4–5 h after mixing the reagents (tested with a solution of palladium chloride). The solvent was evaporated *in vacuo* and the residue extracted with pentane. The pentane extract was evaporated *in vacuo* and the residue crystallized from pentane at −80°.

The following compounds have been obtained.

(a) π-Allyliron tricarbonyl chloride. Yield 26%; m.p. 83–84°; lit.[10] m.p. 83–84°. (Found: C, 33.29; H, 2.79; Cl, 16.71; Fe, 25.84. $C_6H_5ClO_3Fe$ calcd.: C, 33.33; H, 2.31; Cl, 16.20; Fe, 25.92%).

(b) π-Crotyliron tricarbonyl chloride. Yield 26%; m.p. 34–35°; lit.[10] m.p. 34.5°. (Found: C, 36.40, 36.28; H, 2.98, 2.95; Cl, 15.47, 15.54; Fe, 24.87, 24.79. C_7H_7-$ClFeO_3$ calcd.: C, 36.52; H, 3.06; Cl, 15.21; Fe, 24.36%).

(c) 1-Phenyl-π-allyliron tricarbonyl chloride. Yield 30%; m.p. 88–88.5°. (Found: C, 49.68; H, 3.29; Cl, 11.98; Fe, 18.65. $C_{12}H_9ClFeO_3$ calcd.: C, 49.32; H, 3.10; Cl, 12.12; Fe, 19.09%).

(d) 2-Phenyl-π-allyliron tricarbonyl chloride. Yield 37%; m.p. 93°. (Found: C, 49.32; H, 3.22; Cl, 12.72; Fe, 19.53. $C_{12}H_9ClFeO_3$ calcd.: C, 49.32; H, 3.10; Cl, 12.12; Fe, 19.09%).

(4) *Reaction of iron nonacarbonyl with bis(π-allylpalladium acetate)*

1.0 g (0.005 mole) of bis(π-allylpalladium acetate) and 1.6 g (0.005 mole) of iron nonacarbonyl were stirred at room temperature for 10 h; 1.0 g (0.005 mole) of tetramethylammonium iodide was added. The mixture was stirred for 30 min, the solvent evaporated *in vacuo*, and the residue extracted with hexane. The hexane extract evaporated *in vacuo*, and the residue crystallized from pentane at −80°. 1.0 g (7%) of π-allyliron tricarbonyl iodide was obtained; m.p. 79–80°; lit. m.p. 79–80°.

(5) *Reaction of iron nonacarbonyl with 2-neopentyl-π-allylpalladium chloride.*

0.7 g (0.003 mole) of 2-neopentyl-π-allylpalladium chloride and 1.0 g (0.003 mole) of iron nonacarbonyl were stirred in benzene at room temperature; no black solid precipitated; carbon monoxide was evolved and an amorphous precipitate formed; 0.4 g of metallic iron was obtained. The yield, based on iron nonacarbonyl taken in the reaction, was quantitative.

The filtrate was evaporated; 0.7 g of the starting 2-neopentyl-π-allylpalladium chloride was obtained; m.p. 204° (dec.); lit.[19] m.p. 204° (dec.).

(6) *Reaction of iron nonacarbonyl with bis[(2-chloroisopropenyl)π-allylpalladium chloride]*

2.43 g (0.001 mole) of bis[(2-chloroisopropenyl)-π-allylpalladium chloride] and 4.07 g (0.001 mole) of iron nonacarbonyl were stirred at room temperature; no black solid precipitated; carbon monoxide was evolved and an amorphous substance precipitated. The latter was filtered off, washed and dried and 1.65 g of metallic iron obtained. The yield, based on iron nonacarbonyl taken in the reaction, was quantitative.

The filtrate was evaporated; 2.3 g of the starting bis[(2-chloroisopropenyl)-π-allylpalladium chloride] was obtained, m.p. 165–170° (dec.); lit[19] m.p. 165–170° (dec.).

INVESTIGATION OF THE REACTION MECHANISM

A 3–5-fold excess of iron nonacarbonyl was added to the benzene solution of $(\pi\text{-}C_5H_5PdCl)_2$. Samples were taken periodically, filtered off in a stream of pure argon and the solutions obtained studied by different physico-chemical methods.

The infrared spectra were recorded using the UR-10 model spectrophotometer in the region, 2200–1700 cm^{-1}. The NMR spectra were taken by means of the Jeol apparatus with an operating frequency of 100 Mc using hexamethyldisiloxane as internal standard.

For the nuclear gamma resonance study, the specimens were frozen in liquid nitrogen in the special camera in which the measurements were carried out. The spectra were recorded with the apparatus of the Institute of Chemical Physics of the USSR Academy of Sciences.

DISCUSSION

The reaction of the π-allyl compounds of nickel, palladium and platinum with iron nonacarbonyl may be discussed from two points of view.

First, this reaction is the migration of the π-allyl ligand from palladium to the iron atom; on the other hand, this is also a substitution of the carbonyl ligand in the ion nonacarbonyl molecule. Such reactions are the most characteristic of the metal-carbonyl reactions. These reactions, in general, have been carried out for dienes, polyenes, and aromatic systems.

Iron carbonyl, however, does not participate in exchange with the labelled carbon monoxide under normal conditions, although such an exchange was established at 25°, and even lower temperatures, in the presence of catalysts[21]. Metallic nickel and platinum have the best catalytic properties. The carbon monoxide exchange may occur by both probable mechanisms: associative (S_N2) and dissociative (S_N1). The attraction of the d-electrons by some acceptors (by catalyst, for example, (Ni, Pt)) stimulates the carbon monoxide exchange according to an associative mechanism, postulated by the authors of the paper cited. The bridged iron carbonyl has the vacant orbitals which facilitate exchange with the labelled carbon monoxide in the presence of catalysts according, probably, to the associative mechanism. Thus, the iron carbonyl molecules act as electron donors with respect to the catalysts, i.e., they display nucleophilic reactivity.

Iron carbonyl is also a nucleophilic reagent in reactions with nickelocene[22].

Maitlis suggested[23] that the migration of hydrocarbon ligands (e.g., tetraphenylcyclobutadienyl (TPCB) ligand) from palladium to some other metal atoms, as well as of the cyclopentadienyl fragment from iron to cobalt and palladium, or the reaction of nickelocene with iron carbonyl, follow an analogous mechanism.

According to Maitlis[2], in the migration of the TPCB ligand the latter should exist as an independent particle, although neither the TPCB dimer or tolane have been found among the reaction products. Nonetheless, Maitlis et al. attempted first to discuss the reactions in the light of metal carbonyl chemistry. He suggests, for example[2], that iron pentacarbonyl gives $Fe(CO)_4Br$ (the reaction being characteristic of the metal carbonyls with a covalently-bonded halogen); the latter compound reacts with excess TPCB in the usual manner through substitution of carbon monoxide.

Thus in the papers cited, iron pentacarbonyl behaved in these reactions either as a nucleophilic reagent, forming carbonyl bridges with the nickel atom, or as a halogen acceptor. We assume that the nucleophilic properties of iron pentacarbonyl play a predominant part in reactions with such electron-deficient compounds as the π-allyl complexes of the platinum group metals.

The ability of $Fe(CO)_4$ to trimerization and formation of bonds with other elements during the reaction, as well as the absence of absorption in the region of the bridged carbonyl group, support the formation of the intermediate I. A facile fission of the μ-halide bridge in the molecule of dimeric π-allylpalladium chloride by basic and nucleophilic agents is well known[24]. The electron density on the palladium atom varies, but the latter compensates this change (in a given case this is an increase in electron density) for other ligands. since the double bonding between palladium and iron is difficult to understand. According to Kettle and Mason[25] the π-allyl ligand is unable to attract electrons from the palladium atom; thus the system is inclined to exist in the more stable state in which the olefinic fragment of allyl ligand participates in a contribution into back-donation. This means the presence of some intermediate complexes with the π,σ-bonded allyl group[11] in the mixture:
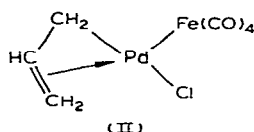
A subsequent reaction may be supposed as a cis-migration[26] of the π,σ-bonded allyl group from palladium to the iron atom. Here there is migration of the chlorine atom from palladium to the $Fe(CO)_4$-fragment with evolution of carbon monoxide, precipitation of metallic palladium and formation of π-allyliron tricarbonyl chloride. This may be illustrated by the following scheme:
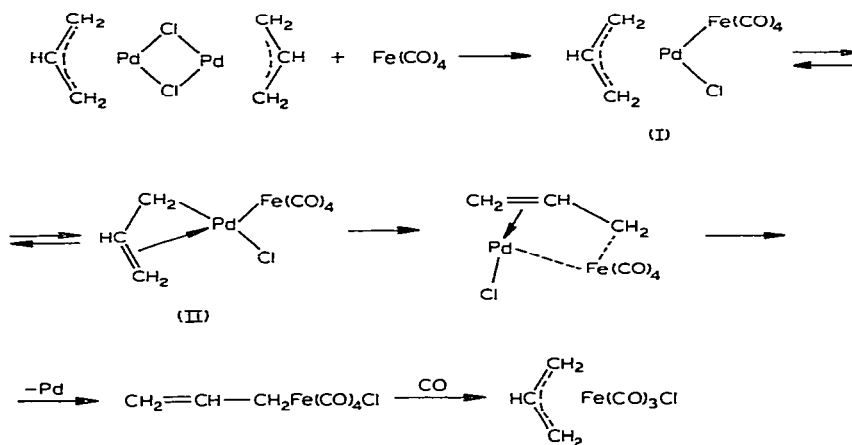
Thus, this reaction is the π–π migration of the allyl ligand from one to another transition-metal atom.

REFERENCES

1 B. A. DOLGOPLOSK, I. I. MOISEEV AND E. I. TINYAKOVA, Dokl. Akad. Nauk SSSR, 173 (1967) 1087.
2 P. M. MAITLIS AND M. L. GAMES, J. Amer. Chem. Soc., 85 (1963) 1887.
3 P. M. MAITLIS AND M. L. GAMES, Can. J. Chem., 42 (1964) 183.
4 A. N. NESMEYANOV, A. Z. RUBEZHOV AND S. P. GUBIN, Izv. Akad. Nauk SSSR, Ser. Khim., (1966) 149.
5 R. F. HECK, J. Amer. Chem. Soc., 90 (1968) 159.
6 J. POWELL AND B. L. SHOW, J. Chem. Soc., (1968) 159.
7 S. P. GUBIN, A. Z. RUBEZHOV, L. I. DENISOVICH AND A. N. NESMEYANOV, Izv. Akad. Nauk SSSR, Ser. Khim., (1960) 1680.
8 A. N. NESMEYANOV, A. Z. RUBEZHOV, L. A. LEITES AND S. P. GUBIN, J. Organometal Chem., 12 (1968) 187.
9 A. N. NESMEYANOV AND K. A. KOCHESHKOV, Ber., 63 (1930) 2496; 64 (1931) 628; Zh. Obshch. Khim., 1 (1931) 219.
10 E. O. FISHER AND H. WERNER, Z. Chem., 2 (1962) 174.
11 V. I. GOL'DANSKI, The Mössbauer Effect and its Application in Chemistry, USSR Acad. of Sci. Publ. House, Moscow, 1963.
12 R. A. STUKAN, Thesis, Institute of Chem. Physics, Moscow, 1965.
13 N. A. BELOZERSKI, Metal Carbonyls, Metallurg. Publ. House, Moscow, 1958, p. 40.
14 H. ZEISS (Ed.), Organometallic Chemistry, Reinhold, New York, Chapman and Hall, London, 1960.
15 F. J. IMPASTATO AND K. G. IHRMAN, J. Amer. Chem. Soc., 85 (1961) 3726.
16 K. VRIEZE, P. COSSEE, A. P. PRAAT AND C. W. HILBERS, J. Organometal. Chem., 11 (1968) 353.
17 G. WILKE, B. BOGDANOVIC, P. HARDT, P. HEIMBACH, W. KEIM, M. KRÖNER, W. OBERKIRCH, K. TANAKA, E. STEINRÜCKE, D. WALTER AND A. ZIMMERMANN, Angew. Chem. Intern. Ed. Engl., 5 (1966) 151.
18 V. A. VASHKEVICH, A. M. LAZUTKIN AND B. I. MITSNER, Zh. Obshch. Khim., 37 (1967) 1926.
19 M. I. LOBACH, B. D. BABITSKI AND V. A. KORMER, Usp. Khim., 36 (1967) 1158.
20 G. SCHWARZENBACH AND H. FLASCHKA, Die Komplexometrische Titration, 5th ed., Enke, Stuttgart, 1965 (Die Chemische Analyse, Band 45).
21 A. N. WEBB AND J. MITCHELL, J. Phys. Chem., 63 (1959) 1878.
22 J. F. TILNEY-BASSETT, J. Chem. Soc. (1963) 4784.
23 P. M. MAITLIS, A. EFRATY AND M. L. GAMES, J. Amer. Chem. Soc., 87 (1965) 719.
24 M. L. GREEN AND P. L. NAGY, Advan. Organometal. Chem., 2 (1964) 325.
25 S. F. A. KETTLE AND R. MASON, J. Organometal. Chem., 5 (1966) 573.
26 P. COSSEE, Rec. Trav. Chim., 85 (1966) 1151.