Translated from *Uspekhi Khimii*, 52 244-267 (1983) U.D.C. 541.124

The Mechanism of the Oxidative Coupling of Unsaturated Hydrocarbons Under the Influence of Palladium(II) Complexes

I.V.Kozhevnikov

The results of studies on the mechanism of liquid-phase reactions involving the oxidative coupling of arenes to biaryls, of arenes and olefins to arylolefins, and of olefins to 1,3-dienes under the influence of palladium(II) complexes are surveyed. The bibliography includes 161 references.

CONTENTS

I. Introduction 138
II. The coupling of arenes 138
III. The arylation of olefins 145
IV. The oxidative coupling of olefins 147

I. INTRODUCTION

The liquid-phase reactions involving the oxidative coupling of unsaturated hydrocarbon to biaryls, arylolefins, and 1,3-dienes under the influence of palladium(II) complexes have been discovered and widely investigated in the course of the last twenty years[1-3]. In a general form, they can be represented by the equation

$$RH + R'H + Pd^{II} \rightarrow R{-}R' + Pd^{0} + 2H^{+}, \quad (1)$$

where R, R′ = aryl or alkenyl. These reactions involve the formation of a new C–C bond and as a rule give rise to products with a conjugated system of π-bonds. The oxidative coupling of hydrocarbons has come to be widely used synthetically because of its many advantages over traditional methods. These include simplicity, universality, and the possibility of carrying out catalytic reactions by oxidising zerovalent palladium to palladium(II) *in situ*. The importance of these reactions is indicated by the abundance of publications devoted to them[4-18].

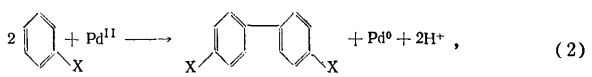
Qualitative hypotheses concerning the mechanism of the oxidative coupling of hydrocarbons and based on the fundamental reactions of organometallic chemistry were put forward a long time ago[4-18]. The formation of a new C–C bond is treated as a result of a sequence of π–σ transformations of the substrate in the coordination sphere of palladium(II). Here the key stage is the formation of the reactive intermediate RPdX with a C–Pd σ-bond. The hypothesis of the π–σ rearrangements proved useful in metal complex catalysis[19]. However, it does not provide a detailed picture of the reaction mechanism. The questions of the rate-limiting stage, the active form of palladium(II) compounds, the role of π-complexes of RH with palladium(II), and others remain obscure. An answer to these questions has been obtained only recently as a result of detailed kinetic studies of reaction (1) and also the synthesis of organopalladium compounds and the study of their reactions.

The aim of the present review is to survey the results of studies on the mechanism of the oxidative coupling of unsaturated hydrocarbons under the influence of palladium(II) complexes.

II. THE COUPLING OF ARENES

1. General Considerations

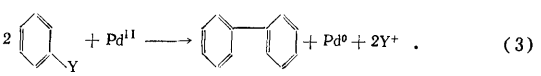
The coupling of arenes takes place under the influence of palladium(II) salts in organic and more rarely aqueous solutions at a temperature which does not usually exceed 120 °C:[1,16,20,21]



(2)

where X = H, alkyl, halogen, aryl, OR, CO_2R, OCOR,[1] NO_2,[22] OH,[23] etc. In the general case a mixture of all the theoretically possible biaryl isomers is formed (six isomers for PhX), their proportions being determined by the nature of the substituents in ArH.[1,21,24]

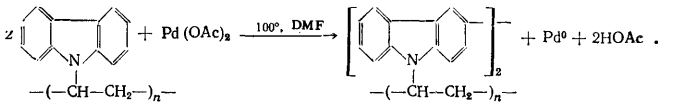
The coupling of organoelemental compounds takes place much more readily and selectively:



(3)

These include the aryl derivatives of mercury(II),[25-27] magnesium(II),[28] thallium(III),[29,30] tin(IV), lead(IV),[25] and boric[21] and sulphinic[31] acids. The mercury(II) compounds are most frequently used.

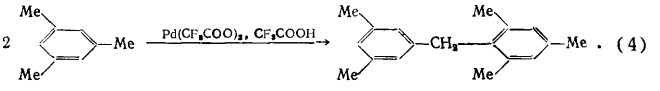
The coupling of arenes takes place in a large series of aromatic systems[16]. Derivatives of benzene[23-32] and napthalene[33,34], heterocyclic compounds[14,35-42], metallocenes[43,44], etc. undergo this reaction. The aromatic groups of polymers undergo intermolecular coupling[42]:



In the presence of oxidants capable of oxidising zerovalent palladium to palladium(II), catalytic coupling takes place[16]. Copper(II),[25,33,37-39] thallium(III),[29,30] and iron(III)[39,45]

salts, V_2O_5,[39] vanadium(V)-containing heteropolyacids[41,46,47], nitrogen oxides[48], and molecular oxygen[34,49-54] have been used as oxidants in homogeneous systems. Heterogeneous catalysts of the coupling of arenes are also known[16,55]. The yields of biaryls in the catalytic process reach hundreds of moles per mole of palladium(II).[52]

The pathway followed in the reactions of arenes depends on the nature of the ligands in the palladium(II) complexes. Inorganic acids, for example, $HClO_4$, catalyse the coupling of arenes[20,21,26,56]. The reaction of benzene and $Pd(ClO_4)_2$ in acetic acid takes place with a quantative yield of biphenyl[56]. In the presence of $Pd(OAc)_2$ in acetic acid, ArH undergoes acetoxylation in the ring and in the side chain as a side reaction[20,21,50,57-59]. In the presence of $Pd(CF_3COO)_2$, the contribution of these reactions is smaller[60]. Acetate ions promote the acetoxylation[20,57], while inorganic acids and oxygen suppress it[20,21,50]. The ring acetoxylation of ArH has been widely investigated as a potential method of synthesis of phenols[36,51,61-64]. There is reason to believe that the acetoxylation of methylbenzenes in the side chain is catalysed by palladium clusters[65,66]. When $Pd(NO_3)_2$ is used, the coupling is accompanied by the nitration of arenes[48,67,68]. In acid media the reaction of palladium(II) with methylbenzenes gives rise to diarylmethanes together with biaryls[21,22]:



(4)

Among promising reactions mention may be made of the coupling of polymethylbenzenes as a method of synthesis of biphenylpolycarboxylic acids, which are valuable monomers for polycondensation[18]. The coupling of phthalic acid esters is of interest from this standpoint. The coupling of furan derivatives can be used to synthesise long-chain α,ω-bifunctional compounds, for example, dicarboxylic acids. Thus, in the presence of $Pd(OAc)_2$ and $CuCl_2$, furfural and pyromucic acid esters are smoothly converted into 2,2′-bifuryl derivatives[38], from which sebacic acid can be obtained by the cleavage of the furan ring[69].

2. The Mechanism of the Coupling of Arenes

(a) *Palladium(II) acetate complexes.* Reaction (1) proceeds with different palladium(II) compounds, but preference is usually given to palladium(II) acetate. The latter is trimeric in the crystalline state[70]. In benzene at 37 °C and in acetic acid at 25 °C it is also trimerised, but depolymerises on heating[70-73]. At 80 °C in benzene, palladium(II) acetate is monomeric[70].

Palladium(II) salts of strong acids show a smaller tendency towards association. Thus $Pd(CF_3COO)_2$ is monomeric in benzene at 37° and 80 °C.[70]

On heating in acetic acid solution, the $Pd_3(OAc)_6$ trimer slowly dissociates to the monomer:

$$Pd_3(OAc)_6 \overset{K_{3,1}}{\rightleftarrows} 3Pd(OAc)_2 .$$

$K_{3,1} = 2.7 \times 10^{-10}$ mol^2 litre^{-2} at 75 °C.[71] In the presence of sodium or lithium acetate, palladium(II) acetate depolymerises even at 25 °C and the following equilibria are established:

$$2Pd_3(OAc)_6 + 6NaOAc \overset{K_{3,2}}{\rightleftarrows} 3Na_2Pd_2(OAc)_6 , \quad (5)$$

$$Na_2Pd_2(OAc)_6 + 2NaOAc \overset{K_{2,1}}{\rightleftarrows} 2Na_2Pd(OAc)_4 , \quad (6)$$

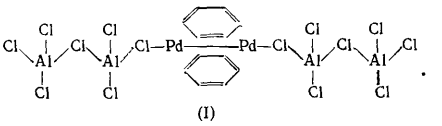
where $K_{3,2} = 7.77 \times 10^4$ litre^5 mol^{-5} and $K_{2,1} = 7.6 \times 10^{-4}$ litre mol^{-1} at 25 °C in acetic acid. In the presence of 0.2 M sodium acetate, the trimer is fully converted into the dimer $Na_2Pd_2(OAc)_6$.[72]

Palladium(II) acetate polymers readily decompose on treatment with ligands L such as pyridine, bipyridyl, Me_2SO, PPh_3, and $AsPh_3$ with formation of the complexes *trans*-$Pd(OAc)_2L_2$,[70] which undergo the *cis–trans* isomerisation in solution[74,75]. The slow interaction of $Na_2Pd_2(OAc)_6$ with olefins takes place similarly[76].

Palladium(II) acetate and chloride complexes have similar stability constants in aqueous solution[77] and for this reason palladium(II) chloride is converted into the acetate in the presence of an excess of sodium acetate.

The palladium(II) acetate monomer, dimer, trimer can have different reactivities[78,79]. If reactions (5) and (6) are used for their synthesis, then account must be taken of the possibility of base catalysis by the acetate ion in the determination of the relative reactivities of these species.

(b) *Arenes as ligands.* There is sufficient reason to assume that π-arene complexes of palladium(II) are intermediates in the oxidative coupling of arenes. π-Arene complexes are known for many metals, including palladium[80]. The diamagnetic complex $[Pd(C_6H_6)Al_2Cl_7]_2$, containing palladium in the formal +1 oxidation state, has been obtained by the Friedel–Crafts reduction. The complex has the structure



(I)

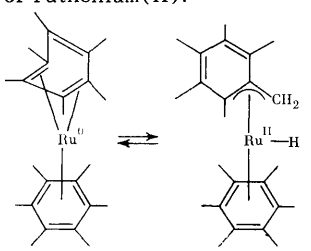
The lengths of the Pd–Pd and Pd–Cl bonds are 2.58 and 2.46 Å respectively and the Cl–Pd–Pd–Cl atoms are located virtually on a straight line[81].

When benzene was coupled under the influence of palladium(II) acetate in acetic acid in the presence of 0.5 M $HClO_4$ at 50 °C, the palladium(I) complex $[Pd(C_6H_6)(H_2O)ClO_4]_n$ where apparently $n = 2$ (Rudakov et al.[82]), was isolated[21], but its role in the reaction was not established. An analogous complex has been detected by NMR in the interaction of benzene with $PdSO_4$ in 90% sulphuric acid[82]. The complex Pd_2SO_4.(quinone).$3H_2O$ was isolated[83] in the oxidation of olefins to carbonyl compounds in an acid aqueous solution in the presence of quinone and $PdSO_4$. Virtually all the known palladium(I) complexes are diamagnetic and contain an even number of palladium atoms[84].

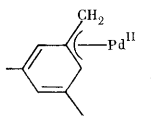
The less stable arene complexes of palladium(II) have not been isolated, but their formation in reaction (1) has been detected by kinetic methods. The coupling of thiophen to bithienyl under the influence of $Pd_3(OAc)_6$ in acetic acid obeys the Michaelis equation; the stability constant of the thiophen complex of palladium(II) $K = 0.2$ litre mol^{-1} at 70 °C.[40] The arylation of styrene on treatment with $Pd_3(OAc)_6$ in acetic acid at 70 °C was similarly found to have $K = 0.11$ and 4.6 litre mol^{-1} for benzene and naphthalene; in both cases ΔH is close to zero[85]. In the oxidative coupling of benzene in 90% sulphuric acid under the influence of $PdSO_4$, the π-complex $(C_6H_6)Pd(II)$ with $K = 17$ litre mol^{-1} at 23 °C was detected by NMR.[82]

Both all the π-electrons of ArH and only some of them can participate in the formation of the bond between the metal ion and the arene[18]. Thus, in the complex $(Me_6C_6)_2Ru(0)$ one ring is involved in complex formation symmetrically (η^6), while the other is involved with participation of two double

bond (η^4) and the free C–C bond is located to one side of Ru(0) and has the usual length of 1.33 Å.[86] It is assumed that in solution there is equilibrium with the π-benzyl hydrido-complex of ruthenium(II):[87]



It has been suggested[22] that the formation of diarylmethanes in the oxidative coupling of methylbenzenes [reaction (4)] proceeds via π-benzyl complexes:



(c) *Stoichiometric mechanism.* It is generally accepted that the oxidative coupling of arenes proceeds via electrophilic substitution as the rate-limiting stage[4,5,10,11,16,88,89],

$$ArH + PdX_2 \rightleftarrows \pi\text{-}ArH \cdot PdX_2 \rightarrow ArPdX + HX\,, \qquad (7)$$

which constitutes a π–σ reaction of ArH in the coordination sphere of palladium(II). The coupling of arenes is in fact accelerated by electron-donating and retarded by electron-accepting substituents in ArH; the isomeric composition of the biaryls is characteristic of electrophilic substitution reactions, at any rate for coupling in acid media[1,21,22,24,47]. The reaction proceeds in accordance with the kinetic equation[1,21,40,56]

$$W = k[Pd^{II}][ArH]\,, \qquad (8)$$

is catalysed by bases[40], and exhibits a powerful isotope effect: $k_H/k_D = 5.0$.[21,24] Certain azo-coupling reactions, which are typical examples of electrophilic aromatic substitution, possess analogous properties[90]:

$$ArN_2^+ + Ar'H \rightarrow ArN{=}NAr' + H^+\,.$$

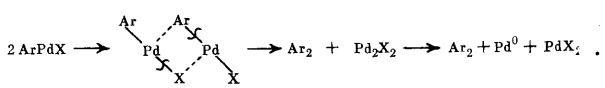
Reaction (7) is confirmed also by the finding that the coupling of arenes proceeds much more readily when one uses aromatic organoelemental compounds in which the element can be substituted by palladium(II), for example ArHgX (Eqn.(3)).[26]

Several pathways have been suggested for subsequent rapid reactions of ArPdX.[1,10,14,16,21,22,89,91] The mechanism involving the symmetrisation of ArPdX with formation of Ar_2Pd and subsequent reductive elimination of biaryl from Ar_2Pd is best supported by evidence[16]:

$$2ArPdX \rightarrow Ar_2Pd + PdX_2\,, \qquad (9)$$

$$Ar_2Pd \rightarrow Ar_2 + Pd^0\,. \qquad (10)$$

One cannot rule out the synchronous formation of biaryl in a dinuclear complex:



The possibility of reactions (9) and (10) has been demonstrated by the occurrence of similar reactions when aryl and alkyl derivatives of palladium(II), stabilised by phosphine ligands, are used[92–95].

Aryl derivatives of platinum(IV) without phosphine ligands and functioning as intermediates in the oxidative coupling of arene under the influence of platinum(IV) have been obtained recently[96]:



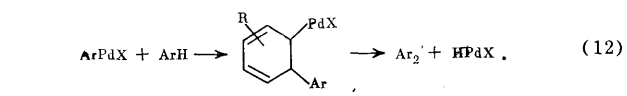
The structure of β-naphthylplatinum(IV) has been determined.

Repeated electrophilic substitution, which proceeds via an aryl-arene complex with palladium(II), has been considered as another pathway leading to the formation of biaryls[13,18,26,54]:

$$ArPdX + ArH \rightarrow [ArPd \cdot ArH] \rightarrow Ar_2 + Pd^0 + H^+\,. \qquad (11)$$

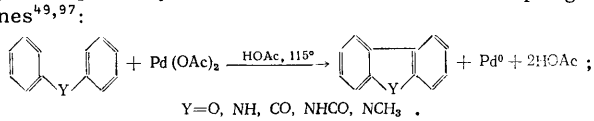
Stage (11) is possible in individual instances, for example, in the coupling of organoelemental compounds, but it is not apparently a stage in the general mechanism of the coupling of arene[16].

It is believed[22] that the coupling of arenes can proceed via the arylpalladisation of ArH and the β-elimination of palladium hydride:



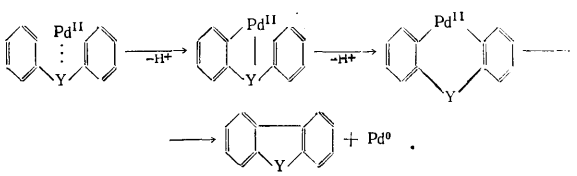
The choice between stage (9), on the one hand, and stages (11) and (12) on the other, can be made on the basis of the relative rates k/k_0 (relative to benzene) and the isotope effects k_H/k_D in the coupling of arenes[24]. It has been found that the values of k/k_0 for the coupling of toluene, measured in separate and competing reactions of benzene and toluene, agree. The isotope effects in the rates and products of the coupling of C_6H_6 and C_6D_6 have also proved to be equal. This confirms the mechanism involving stages (7), (9), and (10) but disagrees with the involvement of stages (11) and (12), because in the separate reactions the ratios k/k_0 and k_H/k_D depend on the rate-limiting stage (7), while in the competing reactions they depend on all the stages in which ArH participates and the dissociation of a C–H bond takes place.

Stage (11) probably occurs in the intramolecular coupling of arenes[49,97]:



Y=O, NH, CO, NHCO, NCH_3 .

The reaction takes place with a high yield of 2,2′-coupling products (60–90%) and apparently involves the *ortho*-palladisation of the arene by a palladium(II) complex with an *n*-donor group Y. The structure of ArPdX is favourable for the repeated intramolecular electrophilic substitution:



The *ortho*-metallation of aryl derivatives of nitrogen and phosphorus by Group VIII metal salts and complexes is well known[98].

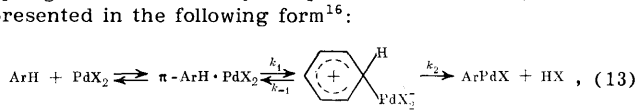
In the coupling of arenes the formation of free radicals is ruled out because phenol has not been found in the products of the coupling of benzene in an atmosphere of O_2,[1] the inhibitors of free radicals have no effect[49], and there is no H–D exchange between the arene and the solvent[21].

The detection of palladium(I) compounds in the coupling products[21] raises the question of the possible involvement of the reduced forms of palladium as intermediates in this reaction[21,82,99]. Many instances of catalysis by palladium(I) complexes and palladium clusters of liquid-phase oxidation reactions have been discovered recently[65,66,100–104]. In such reactions the initial compounds may be palladium(II) derivatives. The active reduced forms of palladium are formed in the course of the reaction, which leads in certain instances to the appearance of an inductive period[100,101]. In contrast to palladium(II) compounds, palladium clusters do not usually play the role of stoichiometric oxidants but act as catalysts in the presence of O_2.[100,104]

The question of the role of palladium(I) in oxidative coupling reactions has been investigated inadequately. However, a number of data show that palladium(I) compounds have only an indirect bearing on such reactions, at least under the most typical conditions—in aqueous acetic acid media. Indeed, the coupling of arenes can proceed both stoichiometrically and catalytically—in the presence of oxidants capable of oxidising the reduced forms of palladium [Pd(0), Pd(I), and Pd(II)].[37–39,47]. The stoichiometric reaction takes place without an inductive period, obeying the kinetic equation (8) up to the complete conversion of palladium(II),[1,40] which shows that palladium(II) is responsible for the coupling of arenes. Palladium(I) compounds are probably formed in a side reaction of zerovalent palladium with palladium(II) and are stabilised as a result of the coordination of the arene. This applies equally to other oxidative coupling reactions of unsaturated hydrocarbons considered here.

The mechanism of reactions (7), (9), and (10) is examined in detail below.

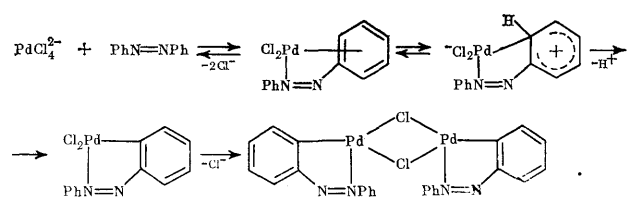
(d) *Palladisation of arenes.* The rate-limiting stage in the coupling of arenes, namely the palladisation of ArH, can be represented in the following form[16]:



(13)

where the cyclohexadienylpalladium(II) derivative is the usual intermediate in electrophilic aromatic substitution[90]. The palladisation of ArH is probably a common stage in many oxidation reactions of arenes catalysed by palladium(II), such as the arylation of olefins, the acetoxylation and nitration of ArH, etc. The mechanism of reaction (13) is therefore of considerable interest.

Direct data on reaction (13) have been obtained for the *ortho*-palladisation of azobenzenes, which leads to the formation of stable cyclic metal-containing compounds. The following mechanism has been proposed for this reaction[98]:



Metallation in the *ortho*-position has been confirmed by X-ray diffraction, the synthesis of deutero-derivatives of arenes in the reduction of palladisation products by $LiAlD_4$, and the analysis of the products of the insertion of CO in the Ar–Pd bond[98]. That *ortho*-palladisation is a kind of electrophilic substitution is indicated by the influence of the substituents in the aromatic ring on the rate of reaction[98].

ortho-Palladisation is catalysed by bases (amines, carboxylate ions, and OH^-), which facilitate the elimination of a proton[98,105]. The dependence of the rate of this reaction on the concentration of the base B is of the type $W = a[B]/\{[B] + c\}$, where a and c are constants[105]. Certain azo-coupling reactions are characterised by a similar relation[90].

The majority of data on the mechanism of the palladisation of arenes, which are discussed below, have been obtained indirectly in the study of the oxidative coupling of arenes[24,88]. In stages (9) and (10) the initial location of palladium(II) in the aromatic ring is retained, which is confirmed by numerous data concerning reaction (3). Thus in the coupling of both 4-tolylmercuroacetate and 4,4′-ditolylmercury(II) under the influence of palladium(II) and under conditions which rule out the isomerisation of the substrate, only 4,4′-bitolyl is formed[26]. Thus the rate of coupling of arenes and the isomeric composition of the biaryls correspond unambiguously to the rate and selectivity of reaction (13).[24,88]

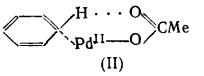
The palladisation of ArH proceeds in conformity with the kinetic equation (8) and is catalysed by strong acids ($HClO_4$)[21,26,56,88] and bases[40]. Eqn.(8) holds for both monomeric palladium(II) complexes[1,21,56] and under the conditions corresponding to the existence of palladium acetate dimers and trimers[40].

Reaction (13) with palladium(II) acetate in acetic acid has a strong primary isotope effect $k_H/k_D = 5.0$ (at 50 °C),[21] which does not change when the concentration of perchloric acid in the reaction mixture is varied from 0 to 0.86 M.[24] It has been noted that there is no isotope exchange between ArH and the solvent[21,106]. Hence it follows that the rate of palladisation of arenes is limited by the irreversible stage (k_2) involving the elimination of a proton from the cyclohexadienyl intermediate; the stage governed by the constants k_1 and k_{-1} involved rapid equilibration. It is noteworthy that mercuration of benzene by mercury acetate in acetic acid is to some extent limited by the stage with k_1 and k_{-1}. This is indicated by the increase of k_H/k_D from 3.2 to 6.0 with increase of perchloric acid concentration from 0 to 0.32 M.[107]

The catalysis by $HClO_4$ can be explained by the increase of k_1 as a result of the formation of more reactive palladium(II) perchlorate complexes[26] and also by the increase of k_2 as a consequence of the increase of the inductive effect of palladium(II) in the cyclohexadienyl intermediate on substitution of $X = OAc^-$ by ClO_4^-.

In the reaction of benzene with palladium(II) acetate in 94% acetic acid at 50 °C, the solvent was found to have the isotope effect $k_{DOAc}/k_{HOAc} = 2.7$; in the presence of 0.43 M perchloric acid, it is smaller (1.3).[24] These data apparently show that, in aqueous acetic acid in the absence of perchloric acid, the active form of palladium(II) acetate is the monomer PdOAc(OH), formed on dissociation of the trimer: $Pd_3(OAc)_6 + H_2O \rightleftharpoons PdOAc(OH) + Pd_2(OAc)_4 + HOAc$. Since the acid DOAc in D_2O is weaker than HOAc in H_2O ($K_H/K_D = 3.2$ at 25 °C [108]), the dissociation equilibrium of $Pd_3(OAc)_6$ in DOAc–D_2O is more displaced to the right compared with the equilibrium in HOAc–H_2O. In the presence of perchloric acid, palladium(II) exists predominantly in the form of monomeric perchlorate complexes and for this reason a weak isotope effect is observed.

It has been suggested that the palladisation of arenes proceeds in a single stage via the transition state



(II)

in which there is simultaneous formation of the C–Pd bond and proton transfer to the acetate ligand[56]. However, in reality there is no grounds for ruling out the generally accepted two-stage electrophilic substitution mechanism involving a cyclohexadienyl intermediate[90].

The possibility of proton transfer to the ligand in the cyclohexadienyl intermediate had been suggested previously in the mercuration of arenes[107,109]. This mechanism probably operates in the palladisation of arenes in weakly basic media, for example, in the arylation of arenes in benzene. In aqueous and aqueous organic solutions in the presence of strong inorganic acids, the solvent is more likely to be the proton acceptor, because its basicity is higher than that of the ligand. The linear dependence of the rate of coupling of benzene under the influence of $Pd(ClO_4)_2$ in 70% acetic acid on the perchlorate acid concentration is consistent with this postulate[56]. When a proton is transferred to the ligand, a linear dependence of the rate of coupling on the Hammett function h_0 would be expected[110].

Table 1 presents data on the site of substitution, the relative rates k/k_0, and the partial rate factors f_o, f_m, and f_p for the palladisation of arenes in acetic acid. They were obtained by analysing the products of the competitive coupling of arenes[24]. In acid media, in the presence of $HClO_4$ or other strong acids, the site of substitution is characteristic of electrophilic substitution, although the positional selectivity (the selectivity of attack on different positions in the ring) is much lower than for other reactions of this class[24,88]. The Hammett equation $\lg f_p = \rho\sigma^+$ holds (Fig. 1).[24] The values $\rho = -0.7 - -2.2$ [24,88] are significantly higher than for typical electrophilic aromatic substitution reactions: $\rho = -5 - -11$, [111] i.e. palladisation has a low substrate selectivity.

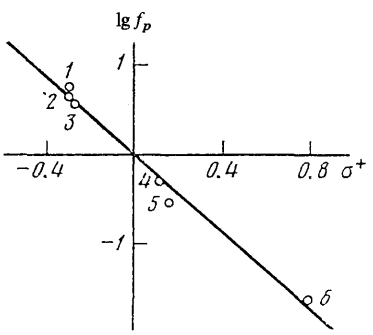


Figure 1. Dependence of $\lg f_p$ on σ^+ for the palladisation of arenes by palladium(II) acetate in acetic acid in the presence of 0.25 M $HClO_4$ at 20 °C; $\rho = -2.22$: *1*) PhMe; *2*) PhEt; *3*) iso-PrPh; *4*) PhCl; *5*) PhBr; *6*) $PhNO_2$.[24]

The selectivity in palladisation decreases with decrease of perchloric acid concentration, although its mechanism does not change under these conditions, since k_H/k_D is independent of the perchloric acid concentration[24]. An unexpected result was obtained for the reaction of toluene with palladium acetate in the absence of added strong acids: the relative contents of the *o*-, *m*-, and *p*-isomers are 5.8, 62, and 32%, i.e. the usual mode of electrophilic substitution is reversed. The yields of the *m*- and *p*-isomers are nearly statistical[24,88]. This anomaly is discussed below (see also Refs. 1, 14, and 22).

The palladisation in the *ortho*-position in a monosubstituted arene is controlled to a greater extent by the steric influence of the substituent than by its electronic influence. This can be seen from the decrease of f_o in the sequence PhMe > PhEt > iso-PrPh (Table 1). The bulk of the attacking species is also important in the *ortho*-attack. Thus in the palladisation of toluene in acetic acid, the yield of *o*- and *p*-isomers decreases with decrease of the perchloric acid concentration from 0.86 M to zero. However, f_p decreases only by a factor of 3, while f_o decreases by a factor of 8. The state of palladium(II) in solution changes under these conditions: the monomer $Pd(ClO_4)_2$ is converted into the trimer $Pd_3(OAc)_6$. The latter is evidently subjected to a stronger steric hindrance in attack on the *ortho*-position of toluene[24].

Table 1. The mode of substitution and the partial rate factors *f* for the palladisation of arenes in acetic acid {[ArH] = 2.5 M, $[Pd(OAc)_2]$ = 0.050 M, $[H_2O]$ = 0.95 M, 20 °C}.[24]

ArH	$[HClO_4]$	Content of isomers, %			k/k_0^*	f_o	f_m	f_p
		ortho	*meta*	*para*				
PhMe **	—	5.8	62	32	0.90	0.16	1.7	1.7
PhMe **	0.017	7.6	49	43	1.08	0.25	1.6	2.8
PhMe **	0.086	15	39	46	1.44	0.65	1.7	4.0
PhMe **	0.43	19	32	49	1.74	1.0	1.7	5.1
PhMe **	0.86	23	30	47	1.76	1.2	1.6	5.0
PhMe	0.25	23	29	48	1.93	1.3	1.7	5.5
PhEt	0.25	12	38	50	1.44	0.52	1.6	4.4
iso-PrPh	0.25	3.8	45	51	1.21	0.14	1.6	3.7
PhCl	0.25	27	29	44	0.18	0.14	0.16	0.46
PhBr	0.25	34	31	35	0.13	0.13	0.16	0.28
$PhNO_2$	0.25	0	71	29	0.013	0	0.028	0.023

*k_0 corresponds to the reaction of benzene.
**At 50 °C and for [ArH] = 1.5 M and $[H_2O]$ = 3.4 M.

The increase of f_p in the sequence iso-PrPh < EtPh < MePh is remarkable, illustrating the influence of hyperconjugation in the palladisation of arenes[24].

The palladisation reaction is compared in Fig. 2 with other aromatic substitution reactions in relation to the reactions of toluene in terms of the Brown selectivity ratios $\lg f_p = a \lg (f_p/f_m)$ (for toluene, $a = 1.31$).[111] The selectivity ratio characterises the relation between the substrate selectivity f_p and the positional selectivity f_p/f_m of the substitution in the ring of ArH. Evidently, palladisation is the least selective reaction in the series of electrophilic aromatic substitution processes, its selectivity approaching that of radical substitution, which is nearly statistical with respect to *m*- and *p*-isomers.[88]

The low selectivity in the palladisation of arenes indicates the compensation of the polar (electronic) effects of the substituents in the ArH ring[88]. Such compensation is possible as a result of the $d\pi-p\pi$ binding in the π-arene complex of palladium(II). The π-ArH.PdX_2 linkage is achieved as a result of the transfer of electron density from the occupied $p\pi$ orbitals of arene to the unoccupied *s*, *p*, and *d* orbitals of palladium(II) and in the reverse direction from the occupied *d* orbitals of palladium(II) to the vacant antibonding π orbital of ArH (dative bond). The operation of two mechanisms of the transfer of electron density creates conditions for the compensation of the polar influence of the substituent on the reaction centre[88]. With increase of the

"rigidity" of the ligand environment of palladium(II), for example, following the introduction of the electron-accepting ligand ClO_4^-, the efficiency of the compensation diminishes as a consequence of the weakening of the dative bond. Both the selectivity of the palladisation and its rate then increase. These qualitative ideas make it possible to explain the anomalous mode of substitution in the palladisation of arenes. However, they require a more rigorous quantum-chemical justification.

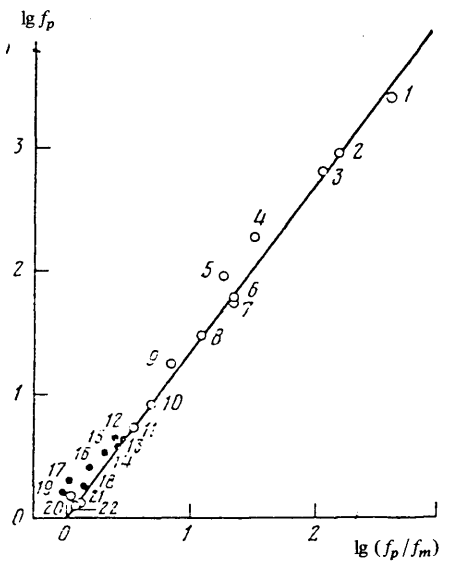


Figure 2. The ratio of selectivities for substitution in the toluene ring[88]; filled circles—reactions with palladium(II): *1*) bromination (Br_2 in 85% acetic acid, 25 °C);[111] *2*) chlorination (Cl_2 in acetic acid, 25 °C);[111] *3*) benzoylation (PhCOCl in nitrobenzene, 25 °C);[111] *4*) thallation [$Tl(CF_3COO)_3$ in trifluoroacetic acid, 10 °C];[112] *5*) ditto, 73 °C;[112] *6*) nitration (HNO_3 in 90% acetic acid, 45 °C);[111] *7*) thallation [$Tl(OAc)_3$ + H_2SO_4 in acetic acid, 70 °C];[114] *8*) mercuration [$Hg(OAc)_2$ + $HClO_4$ in acetic acid, 50 °C];[111] *9*) ditto [$Hg(OAc)_2$ in acetic acid, 50 °C];[111] *10*) sulphonation ($MeSO_2Cl$ + $AlCl_3$, 100 °C);[111] *11*) iso-propylation (iso-PrBr + Ga_2Br_6, 25 °C);[111] *12*) palladisation [$Pd(OAc)_2$ + H_2SO_4 in acetic acid, 95 °C];[88] *13*) ditto [$Pd(OAc)_2$ + $HClO_4$ in acetic acid, 55 °C];[88] *14*) ditto, 95 °C;[88] *15*) ditto ($PdCl_2$ + NaOAc in acetic acid, 90 °C;[88] *16*) ditto [$Pd(OAc)_2$ + CF_3COOH in acetic acid, 95 °C];[88] *17*) ditto [$Pd(OAc)_2$ + NaOAc in acetic acid, 95 °C];[88] *18*) catalytic coupling [$Pd(OAc)_2$ in ArH, 25 atm O_2, 150 °C];[53] *19*) palladisation [$Pd(OAc)_2$ in acetic acid, 95 °C];[88] *20*) radical arylation (attacking radical *p*-$NO_2C_6H_4^{\bullet}$, 20 °C);[113] *21*) ditto (*p*-$MeC_6H_4^{\bullet}$);[113] *22*) ditto ($Ph^{\bullet}$).[113]

It is of interest to compare the palladisation of arenes with their mercuration. It is generally accepted that the mercuration of ArH, at least in polar media, is a type of electrophilic substitution[90]. The palladisation and mercuration of arenes are characterised by a profound similarity of the mechanisms, which is confirmed by the clear-cut correlation between their rates (Fig.3).[24] Both reactions proceed in conformity with the kinetic equation (8) and have a powerful primary isotope effect[107,109,115]. The rate and selectivity of mercuration increase following the addition of $HClO_4$,[109,115] which indicates the compensation of the polar influence of the substituents. The effect of compensation is weaker than in the palladisation of arenes, because it does not lead to the reversal of the mode of substitution. This is apparently due to a weaker $d\pi-p\pi$ bonding in the π-$ArH.HgX_2$ complex as a consequence of the lower energy of the *d* electrons of mercury(II) compared with palladium(II).

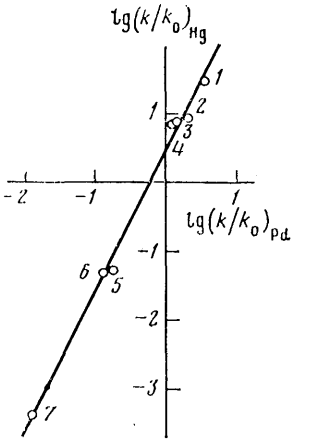
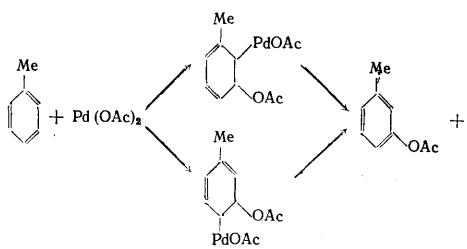


Figure 3. Relation between the rates of palladisation and mercuration of arenes in acetic acid in the presence of $HClO_4$: *1*) *o*-xylene; *2*) PhMe; *3*) PhEt; *4*) iso-PrPh; *5*) PhCl; *6*) PhBr; *7*) $PhNO_2$.[24]

The thallation of arenes probably has a similar mechanism[112,114,116]. The ratio k_H/k_D = 3.7 has been found for the reaction of $Tl(CF_3COO)_3$ with C_6H_6 and C_6D_6 in CF_3.$COOH$.[112] The electrophilic character of the metallation of arenes increases in the sequence Pd(II) < Hg(II) < Tl(III) (the corresponding values of *p* are −2.2,[24] −5.3,[115] and −7.5 [112]).

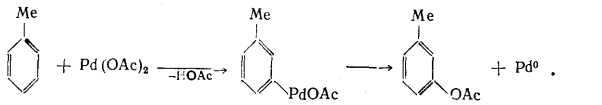
An anomalous selectivity has also been observed in the acetoxylation[51,64,89] and nitration[48,68] of arenes in the ring under the influence of palladium(II), but this phenomenon has not been attributed to electrophilic substitution in ArH. The reaction of arenes with $Pd(NO_3)_2$ in acetic acid at 90 °C involves simultaneous acetoxylation (ρ = −1.2) and nitration (ρ = −1.4). MeC_6H_4OAc and $MeC_6H_4NO_2$ with the relative proportions of isomers *meta* > *para* have been obtained from toluene. In the presence of a strong acid (Cl_3CCOOH) the acetoxylation is suppressed and the normal relative isomeric composition (*para* > *meta*) is restored for nitration, as in the oxidative coupling of arenes[68].

In order to account for the anomalous selectivity in the acetoxylation reaction, a mechanism involving the acetoxypalladisation of ArH has been proposed[51,64,89]:



(14)

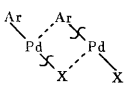
However, from the above considerations, the mechanism involving electrophilic substitution and reductive elimination is more probable for these reactions. For example, we have for *meta*-acetoxylation:



This mechanism provides a good explanation of the acceleration of the ring acetoxylation of arenes in the presence of strong oxidants[14], since they facilitate the reductive elimination from ArPdOAc as a result of the increase of the effective positive charge on the palladium atom.

It is remarkable that the hypothesis of the influence of the $d\pi-p\pi$ bonding in the arene complexes of palladium(II) on the selectivity in the coupling of arenes was already put forward in a pioneer investigation[1]. Similar ideas have received wide currency for the reactions of olefins catalysed by metal complexes[117,118]. However, the picture for the reactions of olefins is complicated as a result of the superposition on the compensation effect of the steric influence of substituents acting in the same direction. In the palladisation of arenes, the steric effects play no role for *meta*- and *para*-substitution. The conclusion that the polar influence is compensated therefore appears more justified. The unusual nature of this phenomenon from the standpoint of the general treatment of electrophilic aromatic substitution must be emphasised[90]. The use of the compensation effect to control the selectivity in the palladisation of arenes is of practical interest.

(e) *The symmetrisation of ArPdX.* The symmetrisation of ArPdX [Eqn.(9)] probably proceeds via a mechanism involving the synchronous dissociation of old bonds and the formation of new bonds in the transition state[16]



(III)

This mechanism has been proposed for the symmetrisation of stable aryl and alkyl derivatives of metals, for example ArHgX.[119]

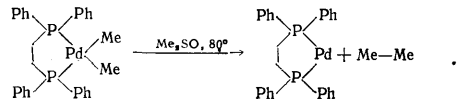
Information about reaction (9) has been obtained by analysing the distribution of aryl groups in the arene coupling products[16,88]. By analogy with the symmetrisation of ArHgX, the preferential formation of the asymmetric biaryls Ar–Ar' as a result of the synergistic effect of the Ar groups of different polarity in the transition state (III) is to be expected in the interaction of ArPdX and Ar'PdX.[119] In reality the distribution of the Ar groups in biaryls is usually close to the statistical distribution. Only in the case of very powerful directing groups ($ArNO_2$, the 2- and 3-positions in thiophen) are asymmetric biaryls formed preferentially[16,88]. This can be explained by the compensation of the polar influence of the substituents in the transition state (III) as a result of the $d\pi-p\pi$ interaction of palladium(II) with the Ar groups[88].

The distribution of the aryl groups in biaryls has been put forward as a justification of reaction (12).[22] However, in reality the available data[22] indicate a statistical distribution of the Ar groups with the exception of the coupling of nitrobenzene, for which the synergistic effect indicated above takes place[88].

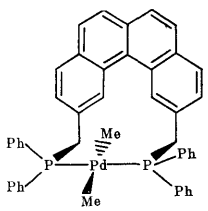
(f) *Reductive elimination.* Considerable advances have been made recently in the understanding of the mechanism of the reductive elimination of hydrocarbons from σ-diorganopalladium(II) in reactions of dialkyl and diaryl compounds of palladium(II), stabilised by phosphine ligands, taking place at a measureable rate[92–95]. These compounds are usually obtained by the oxidative addition of organic halogeno-derivatives to zerovalent palladium or by an exchange reaction:

$$ArX + Pd(PPh_3)_4 \rightarrow ArPdX(PPh_3)_2 + 2PPh_3 ,$$
$$PdCl_2(PPh_3)_2 + 2MeLi \rightarrow Me_2Pd(PPh_3)_2 + 2LiCl .$$

It has been established that palladium(II) complexes containing organic groups in the *cis*-position undergo reductive elimination[95]:



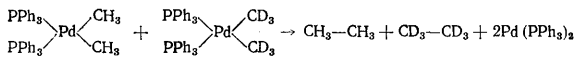
The complexes *trans*-$Me_2Pd(PPh_3)_2$ and *trans*-$Me_2Pd.(PPh_2Me)_2$ undergo the reductive elimination of ethane only after isomerisation to the *cis*-derivatives, which can be clearly observed by ^1H and ^{31}P NMR.[95] On the other hand, the complex (IV), which cannot isomerise, is stable as regards the elimination reaction.



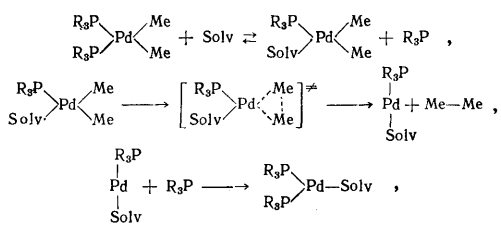
(IV)

Polar solvents [dimethyl sulphoxide (DMSO), dimethylformamide (DMF), and tetrahydrofuran (THF)] promote the elimination reaction in contrast to non-polar solvents (benzene and tetrachloroethane). The same may be said about the oxidative coupling of arenes under the influence of palladium(II). A polar solvent facilitates both *cis–trans* isomerisation of diorganopalladium(II) and the reductive elimination from *cis*-complexes [the latter via the substitution of σ-donor phosphine ligands in the coordination sphere of palladium(II), which results in an increase of the effective positive charge on the palladium ion].

The reductive elimination proceeds as an intramolecular process. This is clearly indicated by the absence of a redistribution of deuterium in the competing reaction



and by the first order of the elimination reaction with respect to diorganopalladium(II). The addition of phosphine ligands inhibits the reaction, which indicates its dissociative mechanism[95]:



where Solv is a solvent molecule.

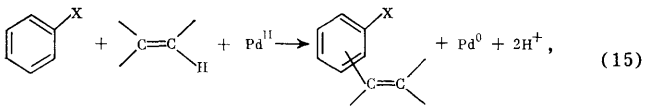
The reductive elimination is greatly accelerated in the presence of organic halogeno-derivatives capable of undergoing the oxidative addition reaction ($PhCH_2Br$, MeI, etc.). It has been suggested that in this case the elimination proceeds via palladium(IV) compounds[93–95].

The absence of free radicals in the reductive elimination is confirmed by the retention of optical activity in α-deuteroethylbenzene obtained by the reaction of the optically active α-deuterobenzyl bromide with *cis*-$Me_2Pd(PPh_3)_2$.[93]

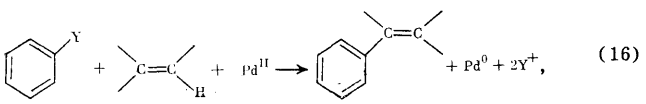
III. THE ARYLATION OF OLEFINS

1. General Considerations

The reaction involving the coupling of arenes with olefins, also referred to as the arylation of olefins, can be represented by the equations



(15)

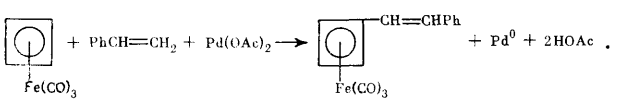


(16)

which are analogous to Eqns.(2) and (3). Here X and Y are in the main the same substituents as in reactions (2) and (3).[8,9,25,120] Reaction (15) is much faster than reaction (2) and reaction (16) is much faster than reaction (3). In the presence of olefins, biaryls are apparently hardly formed. The arylation reaction (15) is usually carried out in the presence of $Pd(OAc)_2$ in solution in acetic acid or in an arene at about 100 °C, ArH being introduced in excess relative to the olefin and palladium(II).[9] As in the coupling of arenes, reaction (16) takes place under milder conditions and more selectively than reaction (15).[25] Very effective methods have been developed using aryl derivatives of mercury(II).[25,121-123] The arylation of olefins by organosilicon compounds is promising[7].

Soluble copper(II) [25,121-124] and silver(I) [2] salts, heteropolyacids,[125] and O_2 [126] are used as oxidants in the catalytic coupling. Platinum metals on carbon are known as heterogeneous catalysts of the gas-phase arylation of ethylene[127].

The arylation of olefins is characterised by a high yield of products and a notable universality with respect to arenes and olefins. The coupling reaction takes place with aromatic carbocyclic[8,9,25] and heterocyclic[9,124,128] compounds, metallocenes[44], etc. Coordinated cyclobutadiene reacts[129,130]:



Olefins from C_2 upwards[9], cyclo-olefins[131], butadiene[123,132], alkenyl derivatives with the substituents Ar, Cl, Br, OAc, CN,[9] NO_2,[133] OR, OCOR,[122] and CH_2OH,[121] styrene, and norbornadiene in their complexes with palladium(II) [9,134], and other compounds[135,136] undergo the reaction. Acetylenes enter into an analogous reaction with formation of arylacetylenes[137].

Substituents at the double bond lower the reactivity of the olefin. In arylation by arylmercury(II) in the presence of $PdCl_2$ and $CuCl_2$ at 20 °C, the reactivity of the olefins decreases in the following sequence: ethylene (14000) > methyl acrylate (970) > propene (220) > styrene (42) > 1-methylstyrene (1).[25] The reaction is accompanied by the isomerisation with respect to the position of the double bond[25,131]. The arylation of methylolefins takes place both at the double bond of the olefin and in the allyl position[15,136].

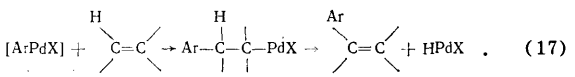
In the arylation of olefins containing an electronegative substituent (for example, a halogen) in the allyl position, aromatic allyl-substituted compounds are formed and the reaction proceeds catalytically with respect to palladium(II).[121] The arylation of olefins has a high stereoselectivity[138].

The phenylation of ethylene by benzene has been investigated as a possible method of synthesis of styrene[126,139-141]. The reaction takes place catalytically in the presence of $Pd(OAc)_2$ in benzene at 80 °C and an O_2 pressure of 10 atm.[126] However, owing to its low selectivity, it has no advantages over the traditional method of synthesis of styrene.

The selectivity in the coupling of arenes with olefins is determined by the competition with side reactions involving the oxidation, acetoxylation, and oxidative dimerisation (coupling) of olefins[126,141]. Reaction (16) of the aryl derivatives of mercury(II), tin(IV), and lead(IV) in the presence of $CuCl_2$ is accompanied by the formation of organochlorine compounds[142].

2. The Mechanism of the Coupling of Arenes with Olefins

The coupling of arenes with olefins proceeds via the π–σ rearrangement of the arene and olefin π-complexes of palladium(II). Several mechanisms of the arylation of olefins have been proposed[9,10,85]. The mechanism involving the arylpalladisation of olefins and the subsequent β-elimination of palladium hydride is most thoroughly justified[10,130,134,143-149]:

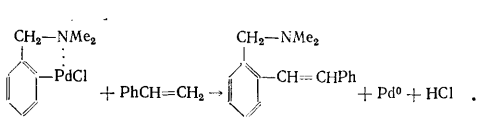


(17)

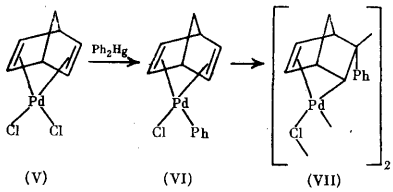
As in the coupling of arenes, the active intermediate ArPdX is formed via the electrophilic substitution in ArH, which is the rate-limiting stage of the reaction.

The arylation of olefins is accelerated by electron-donating and retarded by electron-accepting substituents in ArH. Like the coupling of arenes, the reaction has a low substrate and positional selectivity with respect to the arene as a consequence of the compensation of the electronic influence of the substituents. Thus $\lg f_p = 0.48$, $\lg (f_p/f_m) = 0.33$,[141] and $\rho = -1.4$ [130] for the reaction of toluene with styrene under the influence of palladium(II) acetate. This is consistent with the arylation of olefins via palladised ArH. At the same time the activation of palladium(II) by the olefin plays a major role in the arylation of olefins because the rate of arylation is higher by several orders of magnitude than the rate of coupling of arenes to give biaryls[85].

The involvement of ArPdX as an intermediate has been confirmed by the arylation of styrene by the palladium(II) complex of benzyldimethylamine, which has a C–Pd σ-bond:[146]



Stereochemical studies have shown that the arylpalladisation is in fact *cis*-addition[134,147]. Thus the phenylation of dichloro-η^4-norbornadienepalladium(II) by Ph_2Hg and $NaBPh_4$ in solution in CH_2Cl_2 or acetone at 20 °C gives rise to the *endo*-addition product (VII) in 79% yield:



(V) (VI) (VII)

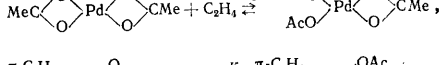
The structure of compound (VII) has been established by ^{1}H NMR and X-ray diffraction. It is suggested that the complex (VI) is an intermediate in the phenylation of compound (V); it has been possible to isolate its stable platinum analogue[134].

The *cis*-addition of ArPdX to the double bond of the olefin is controlled to a greater extent by steric factors than electronic factors[143]. The compensation of the electronic effects of the substituents in the olefin in its π-complex with ArPdX prior to the arylpalladisation reaction (17) probably plays an appreciable role in this process. A large organic group usually adds contrary to the Markovnikov rule, to the least substituted carbon atom involved in the double bond, while palladium(II) adds to the most substituted carbon atom. Thus the phenylation of propene by PhHgOAc in the presence of palladium(II) acetate in acetic acid yields 70% of 1-phenylprop-1-ene, 14% of allylbenzene, and 16% of 1-methylstyrene, i.e. the ratio of the yields of the products of the addition of PhPdOAc to the terminal and inner carbon atoms of propene is 5.3.[143] A similar result was obtained in the phenylation of propene by benzene[141].

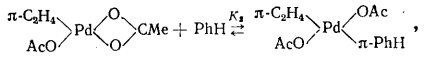
The phenylation of olefins (Ol) under the influence of the monomeric $Pd(OAc)_2$ complexes in benzene proceeds in accordance with the kinetic equation

$$W = k\,[Pd(OAc)_2]\,[Ol]\,[PhH]\ . \qquad (18)$$

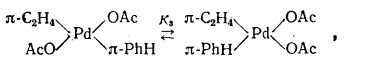
For the reactions of ethylene and styrene, the values of $k[PhH] \times 10^3$ are respectively 2.2 and 0.196 $mol^{-1}\ s^{-1}$ at 95 °C. For the reaction of ethylene, E = 68.7 kJ mol^{-1}.[141,145] The phenylation of styrene and ethylene by benzene and deuterobenzene-d_6 is characterised by the kinetic isotope effect k_H/k_D = 5.0; for the reaction of C_2D_4 and styrene-β,β-d_2 with benzene, k_H/k_D = 1.2. The isotope effects in the reaction rates and products are the same[141,144,145]. Taking into account these data, the mechanism of the arylation of olefins by the monomeric $Pd(OAc)_2$ in benzene has been represented as follows[144,145]:



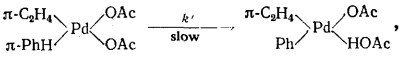
(19)



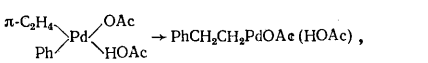
(20)



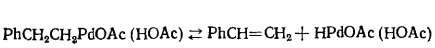
(21)



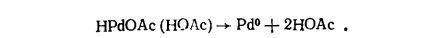
(22)



(23)

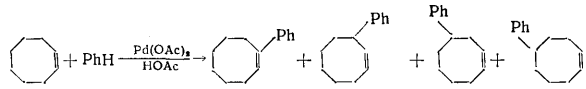


(24)

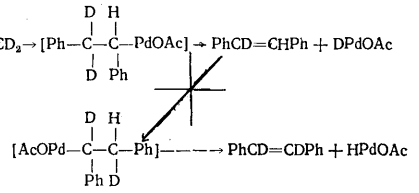


(25)

Stages (19)–(21) involve rapid equilibration. The coordination of the olefin facilitates the partial substitution of the bidentate acetate ion in the *trans*-position by an arene molecule as a consequence of the strong *trans*-effect of the olefin. The isomerisation [reaction (21)] to the favourable *cis*-configuration can proceed via the five-coordinated intermediate as a result of the addition of a second phH molecule[74,75] or with participation of the bidentate acetate ion. The rate-limiting stage (22), analogous to reaction (13), involves the π–σ rearrangement of the arene in the coordination sphere of palladium(II). It is irreversible because there is no H–D exchange between ArH and the solvent in the arylation of olefins[144]. There is a probability of proton transfer to the ligand in the reaction in benzene; in more basic media, the solvent may be the proton acceptor (see above). Since the introduction of additional π ligands into the coordination sphere of the metal ion promotes the π–σ rearrangement as a result of the destabilisation of the existing π ligands[19], the higher rate of arylation of olefins compared with the coupling of arenes to biaryls becomes understandable[141]. The *cis*-arylpalladisation stage (23) is apparently rapid and irreversible. In the general case the β-elimination reaction (24) is fast and reversible[131,143], as shown by the isomerisation of the products of the arylation of cyclo-olefins via the repeated addition-elimination of palladium hydride[131]:



However, in the arylation of styrene stage (24) is almost irreversible, which is confirmed by the absence of a hydride shift in the reaction of styrene-β,β-d_2:[128,148]



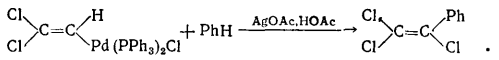
The kinetic equation

$$W = \frac{k'K_1K_2K_3\,[Pd(OAc)_2]\,[Ol]\,[PhH]}{1 + K_1[Ol]\,\{1 + K_2[PhH]\,(1 + K_3)\}}\ ,$$

which is the same as Eqn.(18) for $K_1[Ol]\{1 + K_2[PhH].(1 + K_3)\} \ll 1$, where $k = k'K_1K_2K_3$, follows from reactions (19)–(25).[141,145] The olefin activity series obtained $C_2H_4 >$ $PhCH = CH_2$ [141,145] is consistent with the sequence of the stabilities of the π-complexes of olefins with palladium(II) acetate[76].

The trimer $Pd_3(OAc)_6$ and the dimer $Na_2Pd_2(OAc)_6$ are active in the arylation of olefins in acetic acid[85]. The kinetics of the arylation of olefins in acetic acid under the conditions of the association of palladium(II) acetate are more complex than the kinetics of the reaction with monomeric $Pd(OAc)_2$ in benzene and depend significantly on the nature of the arylating agent. The phenylation of styrene by benzene in acetic acid is of zero order with respect to the olefin and of first and 0.5 order with respect to the palladium(II) acetate dimer and trimer respectively. The dependence of the rate on the concentration of PhH is consistent with the Michaelis equation, which indicates the formation of π-arene complexes of palladium(II). The arylation of styrene by naphthalene and PhHgOAc proceeds via two parallel pathways of zero and first order with respect to the olefin. In order to account for these data, a mechanism involving the oxidative addition of ArH to palladium(II) has been proposed at the rate-limiting stage[85,150]. However, one cannot rule out the possibility that the process may be limited by the dissociation of polymeric palladium(II) species under the influence of ArH to give more active monomeric palladium(II) complexes.

It is of interest that the arylation of olefins can be carried out with participation of σ-vinyl complexes of palladium(II):[9]

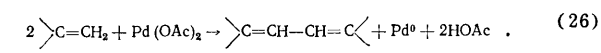


However, this mechanism has no general importance. This is demonstrated by data concerning the oxidative dimerisation of α-olefins to 1,3-dienes which proceeds via σ-vinyl derivatives of palladium(II) (see below). Since ethylene and linear olefins do not enter into this reaction, there is no reason to assume that their arylation proceeds via σ-vinylpalladium(II) compounds. Furthermore, the stage involving the substitution of the vinyl hydrogen atom by palladium(II) should be partily reversible, since it precedes the rate-limiting stage in which ArH is palladised. However, this is inconsistent with the absence of H–D exchange between olefins and the solvent under the conditions of the arylation reaction[128,148].

IV. THE OXIDATIVE COUPLING OF OLEFINS

1. Conditions and Products of the Reaction

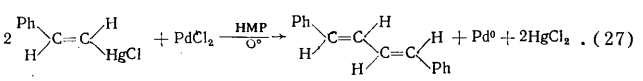
The coupling of olefins (another commonly used term is oxidative dimerisation) takes place in solutions of palladium(II) salts, usually $Pd(OAc)_2$, with formation of derivatives of 1,3-dienes:[3,151,152]



(26)

Olefins substituted at the double bond, for example, styrene, 1-methylstyrene, 1,1-diphenylethylene, vinyl acetate, etc., undergo this reaction[151,152]. Ethylene, the β-unbranched olefins $R-CH_2-CH=CH_2$, and β-chloroolefins are inactive. The coupling is exclusively of the "head to head" type, i.e. a C–C bond involving the least substituted carbon atoms of the double bonds is formed[152].

Alkenylmercury(II) derivatives, obtained by the addition of mercury(II) salts to acetylenes, undergo stereospecific coupling under the influence of $PdCl_2$:[153]



(27)

In the presence of copper(II) and iron(III) salts[154] or oxygen[126], reaction (26) takes place catalytically. Both homogeneous[126] and heterogeneous[155,156] catalysts based on palladium compounds are known.

The oxidation and acetoxylation of olefins[3,126,141] as well as their non-oxidative dimerisation[5] compete with the coupling of olefins. In the presence of arenes, olefins are arylated[141].

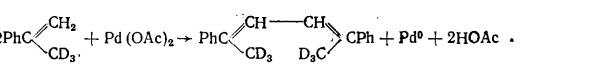
2. The Mechanism of the Coupling of Olefins

The available experimental data can be generalised within the framework of the hypothesis that the oxidative coupling of olefins proceeds via a slow π–σ transformation stage with formation of vinylpalladium(II) derivatives[5,10,14,157]:

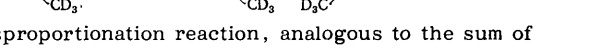


(28)

Next, as in the non-oxidative dimerisation of olefins[117,158], rapid insertion of the olefin in the C–Pd bond and β-elimination of palladium hydride take place[5,10,157]:



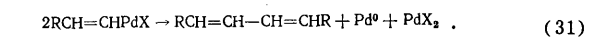
(29)



(30)

The involvement of π-allylpalladium(II) complexes and free radicals is ruled out in view of the high selectivity of the "head to head" coupling and the retention of deuterium in the products of the coupling of 1-methyl-d_3-styrene:[152]

A disproportionation reaction, analogous to the sum of reactions (9) and (10) for the coupling of arenes, has been proposed as a second pathway leading to the formation of the C–C bond[10,14,157]:



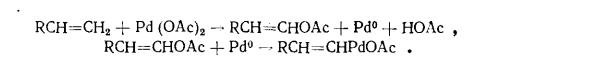
(31)

Reaction (27) of vinylmercury(II) derivatives confirms the possibility of such a pathway. However, stage (29) is more probable in the coupling of olefins. It should be fairly rapid, because it is an analogue of the chain propagation stage in the Ziegler–Natta polymerisation[117,158]. The occurrence of reaction (29) is promoted by the condition $[RCH=CHPdX] \ll [RCH=CH_2]$. An example of the faster insertion of an olefin in the C–Pd bond compared with the disproportionation of the σ-organopalladium(II) may be provided by the arylation of olefins, since biaryls are hardly formed in this reaction. The involvement of stage (29) in the coupling of olefins is also confirmed by the formation of non-oxidative dimerisation side products[5,141].

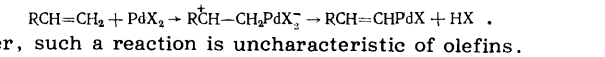
The high selectivity of the "head to head" coupling cannot serve as a justification of the involvement of stage (31) in the process, because, as mentioned above, the insertion of olefins in the C–Pd bond is subject to rigid steric control[138,143]. Furthermore, examples are known of non-oxidative "head to head" dimerisation of olefins catalysed by palladium(II) complexes with nearly 100% selectivity[158].

The mechanism (28)–(30) has been confirmed by kinetic data. Polymeric forms of palladium(II) acetate are active in the oxidative dimerisation of styrene in acetic acid: $Pd_3(OAc)_6 > Na_2Pd_2(OAc)_6 \gg Na_2Pd(OAc)_4$. The reaction is of first order with respect to the palladium(II) acetate dimer and trimer and in the latter case also of first order with respect to the olefin[157]. The formation of fairly stable π-complexes $Na_2Pd_2(OAc)_5(Ol)$ in a system containing $Na_2Pd_2(OAc)_6$ has been demonstrated by kinetic and spectroscopic methods[76,157].

The detailed mechanism of the π–σ reaction (28) has not been elucidated. The reaction is irreversible, because the products of the oxidative dimerisation of olefins in DOAc do not contain deuterium[152]. It has been suggested that the vinylpalladium(II) derivative is formed via the acetoxylation of the olefin and subsequent oxidative addition of alkenyl acetate to zerovalent palladium[5]:

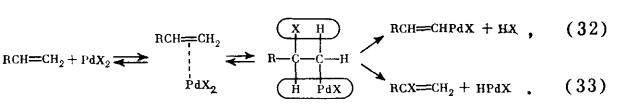


A scheme has been proposed for the direct electrophilic substitution of vinyl hydrogen by palladium(II), by analogy with the palladisation of arenes[14,157]:



However, such a reaction is uncharacteristic of olefins.

The electrophilic substitution of vinyl hydrogen via an addition–elimination mechanism is more probable[141]:



(32)

(33)

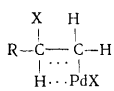
(VIII)

This mechanism agrees well both with oxidative dimerisation data and with the general ideas concerning the reactivity of olefins. The addition of PdX_2 in accordance with the Markovnikov rule leads to the coupling of olefins; otherwise, acetoxylation takes place. The probability of the latter is evidently smaller for β-disubstituted olefins as a consequence of the concerted steric and electronic influence of substituents in the olefin. β-Unbranched olefins are inactive in oxidative dimerisation, probably as a consequence of their acetoxylation in the allyl position and the formation of inert π-allyl-palladium(II) complexes. β-Chloro-olefins are apparently preferentially acetoxylated via the elimination of palladium chloride.

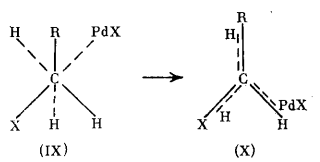
The addition of palladium(II) to olefins is reversible. This is indicated by the catalysis by palladium(II) compounds of reactions such as the transesterification of vinyl esters of carboxylic acids[159], the isotope exchange of chloride ions between $Li^{36}Cl$ and vinyl chloride[160], the isomerisation of *trans*-ethylene-1,2-d_2,[161] etc. The acetoxypalladisation of olefins in acetic acid solution proceeds via the *trans*-attack on the olefin by a solvent molecule[14].

The elimination from the intermediate (VIII) takes place via the two competing reactions (32) and (33). Reaction (32), which leads to the formation of vinyl-palladium(II), belongs to the class of the well known olefin 1,2-elimination processes in which the mode of substitution and the effects of substituents have been investigated in detail[90]. For X = OAc, the 1,2-elimination of olefins usually proceeds via a bimolecular E2 mechanism involving the synchronous removal of X^- and proton transfer to a base, which may be a nucleophilic solvent[90]. The influence of the substituent R on the rate of reaction (32) is determined by its inductive and mesomeric effects; steric effects do not usually play a significant role. The introduction of alkyl substituents in the α-position relative to X accelerates reaction (32). The effect of α-aryl substituents is much stronger; they promote reaction (32) as a result of conjugation with the double bond formed in the transition state[90].

The β-elimination of palladium hydride [reaction (33)] probably takes place intramolecularly via a cyclic transition state[117]:



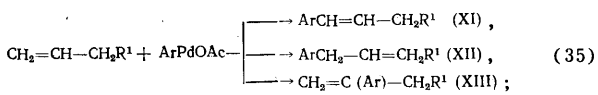
The activation process apparently involves the transition of the system from a more stable inhibited conformation, for example, of type (IX), to the eclipsed conformation (X):



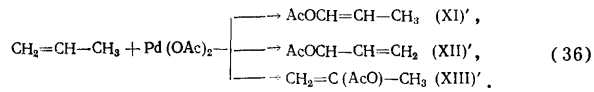
(34)

(IX) (X)

The mode of substitution and the effect of substituents in the β-elimination of palladium(II) hydride have been hardly investigated although they are undoubtedly of great interest. Certain conclusions can be reached from data concerning the products of the reactions involving the arylation and acetoxylation of olefins considered below, which have been studied in detail under conditions which rule out the migration of the double bond[78,138,143]:

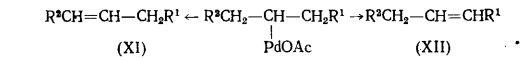


(35)



(36)

The ratio of the products (XI) and (XII) [and correspondingly (XI)′ and (XII)′] yields information about the influence of the nature of the substituents in the β-position relative to palladium(II) on the mode of β-elimination of HPdOAc:



These data are presented in Table 2. In the first place it is seen that the polar influence of the substituents on the β-elimination of HPdX agrees with the fact that in this reaction hydrogen is split off from the carbon atom in the form of the hydride ion and palladium is split off in the form of XPd^+. Thus electron-accepting substituents hinder the abstraction of an α-hydrogen atom, while electron-donating substituents facilitate it [cf. R^1 = OAc or CN and R^2 = Ph, R^1 = H and R^2 = *p*-$MeOC_6H_4$, Ph, or *p*-$AcOC_6H_4$, and R^1 = H or n-Pr and R^2 = Ph in reaction (35)]. In these series the steric effects of the substituents R^1 and R^2 are either of the same order of magnitude or do not change when the substituents are varied. The data for reaction (36) permit the same conclusion, although here the role of the steric factors may prove to be more significant. This is indicated by the dependence of the yields of the products (XI)′ and (XII)′ on the sodium acetate concentration, which determines the degree of association of palladium(II) acetate (see Section II, Subsection 2). The mode of elimination of palladium hydride is influenced by both the inductive and mesomeric effects of the substituent. The aryl group promotes the formation of a double bond which is conjugated with it. The directing effect of the aryl group is much stronger than that of the alkyl group (see R^1 = n-Pr, R^2 = Ph).

Table 2. The mode of β-elimination of palladium hydride in olefin arylation and acetoxylation reactions under the influence of palladium(II) acetate.

Reaction*	R^1	R^2	Relative contents, %		
			XI, (XI),	XII, (XII),	XIII, (XIII),
(35)	H	*p*-$MeOC_6H_4$	53	4	43
(35)	H	Ph	62	12	26
(35)	H	*p*-$AcOC_6H_4$	58	18	24
(35)	n-Pr	Ph	47	7	18
(35)	CN	Ph	45	0	0
(35)	OAc	Ph	94	0	5
(36)	H	OAc	2	2	96
(36) **	H	OAc	0.5	13	86.5
(36) ***	H	OAc	3	71	26
(36) ****	H	OAc	<0.5	94	2

*Reaction (35)—in acetonitrile at 20–30 °C;[138] reaction (36)—in acetic acid at 25 °C.[78] The reactions were carried out in the absence of chloride ions; there is then no migration of the double bond.

**[NaOAc] = 0.098 M.

***[NaOAc] = 0.49 M.

****[NaOAc] = 0.90 M.

It follows from the foregoing that the electronic effect of the substituent R acts in the same direction on reactions (32) and (33) and apparently does not affect their competition.

However, the steric effect of R differentiates these reactions. As already mentioned, the steric factor usually does not play a significant role in reaction (32). On the other hand, in the β-elimination of HPdX the rate of the activated process (34) depends greatly on the bulk of the substituent R. For bulky substituents, for example Ar, the formation of the eclipsed conformation (X) is difficult and reaction (32), leading ultimately to the olefin coupling products, therefore take place preferentially. For β-disubstituted olefins, reaction (33) is altogether ruled out. Thus the addition–elimination mechanism (32) and (33) is fully consistent with the experimental data on the coupling of olefins.

In conclusion one should note that the oxidative coupling reactions of unsaturated hydrocarbons under the influence of palladium(II) compounds have common fundamental elements in their mechanisms. They all proceed via a sequence of $\pi-\sigma$ reactions in the coordination sphere of palladium(II) and include the electrophilic substitution of hydrogen by palladium(II) at a trigonal carbon atom as the rate-limiting stage. The intermediate $d\pi-p\pi$ binding of palladium(II) as a "soft" acid to "soft" bases (arenes of olefins) plays an important role in these reactions. As a result of this, the mode of palladisation of the substrate is inconsistent in many instances with the traditional ideas concerning the ratio of the electronic and steric factors in reactions of unsaturated hydrocarbons with electrophiles. This phenomenon is of significant interest for metal complex catalysis as a method of controlling the selectivity of reactions and merits detailed study.

REFERENCES

1. R.Van Helden and G.Verberg, Rec.Trav.Chim., 1965, **84**, 1263.
2. Y.Fujiwara, I.Moritani, S.Danno, R.Asano, and S.Teranishi, J.Amer.Chem.Soc., 1969, **91**, 7166.
3. R.Hüttel, J.Kratzer, and M.Bechter, Chem.Ber., 1961, **94**, 766.
4. P.M.Maitlis, "The Organic Chemistry of Palladium", Acad.Press, New York, 1971.
5. E.V.Stern, Uspekhi Khim., 1973, **42**, 232 [Russ. Chem.Rev., 1973(2)].
6. R.Hüttel, Synthesis, 1970, 225.
7. L.G.Volkova, I.Ya.Levitin, and M.E.Vol'pin, Uspekhi Khim., 1975, **44**, 1217 [Russ.Chem.Rev., 1975(7)].
8. R.Jira and W.Freiesleben, "Organometallic Reactions", 1972, Vol.3, p.1.
9. I.Moritani and Y.Fujiwara, Synthesis, 1973, 524.
10. P.M.Henry, Adv.Organometal.Chem., 1975, **13**, 363.
11. H.-W.Krause, R.Selke, and H.Pracejus, Z.Chem., 1976, **16**, 465.
12. R.A.Sheldon and J.K.Kochi, Adv.Catal., 1976, **25**, 272.
13. I.I.Moiseev, Zhur.Vses.Khim.Obshch.im.Mendeleeva, 1977, **22**, 30.
14. P.M.Henry, "Palladium Catalyzed Oxidation of Hydrocarbons", D.Reidel Publ.Co., Dordrecht, 1980.
15. R.F.Heck, Adv.Catal., 1977, **26**, 323.
16. I.V.Kozhevnikov and K.I.Matveev, Uspekhi Khim., 1978, **47**, 1231 [Russ.Chem.Rev., 1978(7)].
17. R.F.Heck, Accounts Chem.Res., 1979, **12**, 146.
18. G.W.Parshall, "Homogeneous Catalysis", Wiley-Interscience, New York, 1980.
19. B.Gorewit and M.Tsutsui, Adv.Catal., 1978, **27**, 227.
20. J.M.Davidson and C.Triggs, Chem.Ind.(London), 1966, 457.
21. J.M.Davidson and C.Triggs, J.Chem.Soc.A, 1968, 1324.
22. F.R.S.Clark, R.O.C.Norman, C.B.Thomas, and J.S.Wilson, J.Chem.Soc., Perkin Trans.I, 1974, 1289.
23. N.F.Gol'dshleger and M.L.Khidekkel', Izv.Akad. Nauk SSSR, Ser.Khim., 1969, 675.
24. I.V.Koshevnikov, React.Kinet.Catal.Letters, 1981, **17**, 233.
25. R.F.Heck, J.Amer.Chem.Soc., 1968, **90**, 5518.
26. M.O.Unger and R.A.Fouty, J.Org.Chem., 1969, **34**, 18.
27. R.A.Kretchmer and R.Glowinski, J.Org.Chem., 1976, **41**, 2661.
28. S.T.Ioffe and A.N.Nesmeyanov, in "Metody Elementoorganicheskoi Khimii" (Methods of Organoelemental Chemistry), Izd.Akad.Nauk SSSR, Moscow, 1963, p.372.
29. P.M.Henry, J.Org.Chem., 1970, **35**, 3083.
30. S.Uemura, Y.Ikeda, and K.Ichikawa, Chem.Comm., 1971, 390.
31. K.Garves, J.Org.Chem., 1970, **35**, 3273.
32. Y.Fujiwara, I.Moritani, K.Ikegami, R.Tanaka, and S.Teranishi, Bull.Chem.Soc.Japan, 1970, **43**, 863.
33. G.G.Arzoumanidis and F.C.Frank, J.Org.Chem., 1973, **38**, 4443.
34. H.Iataaki and H.Yoshimoto, J.Org.Chem., 1973, **38**, 76.
35. T.Izumi, T.Iino, and A.Kasahara, Bull.Chem.Soc. Japan, 1973, **46**, 2251.
36. L.Eberson and L.Gomez-Gonzalez, Acta Chem. Scand., 1973, **27**, 1249.
37. I.V.Kozhevnikov, React.Kinet.Catal.Letters, 1976, **4**, 451.
38. I.V.Kozhevnikov, React.Kinet.Catal.Letters, 1976, **5**, 415.
39. I.V.Kozhevnikov, React.Kinet.Catal.Letters, 1977, **6**, 401.
40. I.V.Kozhevnikov, Yu.V.Burov, and K.I.Matveev, React.Kinet.Catal.Letters, 1977, **6**, 35.
41. V.E.Taraban'ko, I.V.Kozhevnikov, and K.I.Matveev, React.Kinet.Catal.Letters, 1978, **8**, 77.
42. I.V.Kozhevnikov, S.A.Tuzovskaya, V.P.Lopatinskii, V.M.Sutyagin, O.V.Rotar, and K.I.Matveev, React. Kinet.Catal.Letters, 1978, **9**, 287.
43. A.Kasahara, T.Izumi, and S.Ohnishi, Bull.Chem. Soc.Japan, 1972, **45**, 951.
44. A.Kasahara, T.Izumi, G.Saito, M.Yodono, R.Saito, and Y.Goto, Bull.Chem.Soc.Japan, 1972, **45**, 895.
45. R.Nakajima and T.Hara, Chem.Letters, 1972, 523.
46. G.U.Mennenga, A.I.Rudenkov, K.I.Matveev, and I.V.Kozhevnikov, React.Kinet.Catal.Letters, 1976, **5**, 401.
47. A.I.Rudenkov, G.U.Mennenga, L.N.Rachkovskaya, K.I.Matveev, and I.V.Kozhevnikov, Kinetika i Kataliz, 1977, **18**, 915.
48. R.O.C.Norman, W.J.E.Parr, and C.B.Thomas, J.Chem.Soc., Perkin Trans.I, 1974, 369.
49. H.Yoshimoto and H.Itatani, Bull.Chem.Soc.Japan, 1973, **46**, 2490.
50. J.M.Davidson and C.Triggs, Chem.Ind.(London), 1967, 1361.
51. L.Eberson and L.Gomez-Gonzalez, J.Chem.Soc.D, 1971, 263.
52. H.Itatani and H.Yoshimoto, Chem.Ind.(London), 1971, 674.
53. H.Yoshimoto and H.Itatani, J.Catal., 1973, **31**, 8.
54. M.Kashima, H.Yoshimoto, and H.Itatani, J.Catal., 1973, **29**, 92.

55. A.M.Osipov, L.P.Metlova, and Yu.V.Semenenko, React.Kinet.Catal.Letters, 1978, **9**, 407.
56. A.K.Yatsimirskii, A.D.Ryabov, and I.V.Berezin, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 1493.
57. D.R.Bryant, J.E.McKeon, and B.C.Ream, Tetrahedron Letters, 1968, 3371.
58. J.M.Davidson and C.Triggs, J.Chem.Soc.A, 1968, 1331.
59. D.J.Rawlinson and G.Sosnovsky, Synthesis, 1973, 567.
60. M.K.Starchevskii, M.N.Vargaftik, and I.I.Moiseev, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 242.
61. H.-J.Arpe and L.Hörnig, Erdöl und Kohle-Erdgas-Petrochem., 1970, **23**, 79.
62. L.N.Rachkovskaya, K.I.Matveev, G.N.Il'inich, and N.K.Eremenko, Kinetika i Kataliz, 1977, **18**, 1040.
63. L.Eberson and L.Jönsson, Acta Chem.Scand., 1976, **30**, 579.
64. L.Eberson and L.Jönsson, Annalen, 1977, 223.
65. M.K.Starchevskii, M.N.Vargaftik, and I.I.Moiseev, Kinetika i Kataliz, 1979, **20**, 1163.
66. M.K.Starchevskii, M.N.Vargaftik, and I.I.Moiseev, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 2639.
67. K.Itikawa, S.Uemura, and T.Okada, J.Chem.Soc. Japan, Pure Chem.Sect., 1969, **90**, 212; Ref.Zhur. Khim., 1969, 20zh141.
68. M.Tanaka, T.Yoneyama, J.Yamashita, and H.Hashimoto, Technol.Repts Tohoku Univ., 1978, **43**, 105; Ref.Zhur.Khim., 1979, 11zh178.
69. I.F.Bel'skii and V.M.Shestakovskii, "Kataliz v Khimii Furana" (Catalysis in the Chemistry of Furan), Izd.Nauka, Moscow, 1972.
70. T.A.Stephenson, S.M.Morehouse, A.R.Powell, J.P.Heffer, and G.Wilkinson, J.Chem.Soc., 1965, 3632.
71. A.K.Yatsimirskii and A.D.Ryabov, Zhur.Neorg. Khim., 1977, **22**, 1863 [Russ.J.Inorg.Chem., 1977(7)].
72. R.N.Pandey and P.M.Henry, Canad.J.Chem., 1974, **52**, 1241.
73. L.Eberson and L.Gomez-Gonzalez, Acta Chem.Scand., 1973, **27**, 1162.
74. D.A.Redfield, J.H.Nelson, R.A.Henry, D.W.Moore, and H.B.Jonassen, J.Amer.Chem.Soc., 1974, **96**, 6298.
75. A.D.Ryabov and A.K.Yatsimirskii, Kinetika i Kataliz, 1979, **20**, 106.
76. R.N.Pandey and P.M.Henry, Canad.J.Chem., 1975, **53**, 1833.
77. A.K.Yatsimirskii and I.V.Berezin, Izv.Akad.Nauk SSSR, Ser.Khim., 1976, 1490.
78. S.Winstein, J.McCaskie, H.-B.Lee, and P.M.Henry, J.Amer.Chem.Soc., 1976, **98**, 6913.
79. A.K.Yatsimirskii, A.D.Ryabov, and I.V.Berezin, Dokl.Akad.Nauk SSSR, 1966, **232**, 1130.
80. M.L.H.Green, "Organometallic Compounds", Vol.2, "The Transition Elements" (Translated into Russian), Izd.Mir, Moscow, 1972.
81. G.Allegra, A.Immirzi, and L.Porri, J.Amer.Chem. Soc., 1965, **87**, 1394.
82. E.S.Rudakov, V.L.Lobachev, and R.I.Rudakova, React.Kinet.Catal.Letters, 1979, **10**, 1.
83. N.B.Shitova, L.I.Kuznetsova, and K.I.Matveev, Kinetika i Kataliz, 1974, **15**, 72.
84. M.N.Vargaftik, T.A.Stromnova, and I.I.Moiseev, Zhur.Neorg.Khim., 1980, **25**, 236 [Russ.J.Inorg. Chem., 1980(1)].
85. A.K.Yatsimirsky, A.D.Ryabov, and I.V.Berezin, J.Mol.Catal., 1979, **5**, 399.
86. G.Huttner and S.Lange, Acta Cryst., 1972, **B28**, 2049.
87. J.W.Johnson and E.L.Muettertis, J.Amer.Chem. Soc., 1977, **99**, 7395.
88. I.V.Kozhevnikov, Dokl.Akad.Nauk SSSR, 1980, **252**, 915.
89. L.Eberson and L.Gomez-Gonzalez, Acta Chem.Scand., 1973, **27**, 1255.
90. C.K.Ingold, "Theoretical Foundations of Organic Chemistry" [Structure and Mechanism in Organic Chemistry?] (Translated into Russian), Izd.Mir, Moscow, 1973.
91. J.L.Garnett and J.C.West, Austral.J.Chem., 1974, **27**, 129.
92. G.W.Parshall, J.Amer.Chem.Soc., 1974, **96**, 2360.
93. D.Milstein and J.K.Stille, J.Amer.Chem.Soc., 1979, **101**, 4981.
94. D.Milstein and J.K.Stille, J.Amer.Chem.Soc., 1979, **101**, 4992.
95. A.Gillie and J.K.Stille, J.Amer.Chem.Soc., 1980, **102**, 4933.
96. G.B.Shul'pin, A.E.Shilov, A.N.Kitaigorodskii, and J.V.Z.Krevor, J.Organometal.Chem., 1980, **201**, 319.
97. B.Akermark, L.Eberson, E.Jonsson, and E.Pettersson, J.Org.Chem., 1975, **40**, 1365.
98. G.W.Parshall, Acc.Chem.Res., 1970, **3**(3), 139.
99. E.S.Rudakov and V.M.Ignatenko, Dokl.Akad.Nauk SSSR, 1978, **241**, 148.
100. M.K.Starchevskii, M.N.Vargaftik, and I.I.Moiseev, Kinetika i Kataliz, 1980, **21**, 1451.
101. I.I.Moiseev, M.N.Vargaftik, O.I.Gentosh, N.M.Zhavoronkov, I.V.Kalechits, Yu.A.Pazderskii, T.A.Stromnova, and L.S.Shcherbakova, Dokl.Akad. Nauk SSSR, 1977, **237**, 645.
102. T.A.Stromnova, M.N.Vargaftik, G.Ya.Mazo, Ya.V.Salyn', V.I.Nefedov, and I.I.Moiseev, Izv. Akad.Nauk SSSR, Ser.Khim., 1977, 1205.
103. T.A.Stromnova, L.G.Kuz'mina, M.N.Vargaftik, G.Ya.Mazo, Yu.T.Struchkov, and I.I.Moiseev, Izv.Akad.Nauk SSSR, Ser.Khim., 1978, 720.
104. I.P.Stolyarov, M.N.Vargaftik, S.F.Politanskii, O.M.Nefedov, and I.I.Moiseev, "Tezisy Dokladov Vsesoyuznoi Konferentsii po Metalloorganicheskoi Khimii" (Abstracts of Reports at the All-Union Conference on Organometallic Chemistry), Moscow, 1979, Vol.2, p.318.
105. A.K.Yatsimirskii, Zhur.Neorg.Khim., 1979, **24**, 2711 [Russ.J.Inorg.Chem., 1979(10)].
106. M.Preece and S.D.Robinson, Inorg.Chim.Acta, 1978, **29**, L199.
107. A.J.Kresge and J.F.Brennan, J.Org.Chem., 1967, **32**, 752.
108. "Spravochnik Khimika" (The Chemist's Handbook), Izd.Khimiya, Moscow–Leningrad, 1964, Vol.3, p.95.
109. A.J.Kresge, M.Dubeck, and H.C.Brown, J.Org. Chem., 1967, **32**, 745.
110. F.A.Long and M.A.Paul, Chem.Rev., 1957, **57**, 935.
111. L.M.Stock and H.C.Brown, Adv.Phys.Org.Chem., 1963, **1**, 35.
112. G.Olah, I.Hashimoto, and H.C.Lin, Proc.Nat. Acad.Sci.USA, 1977, **74**, 4121.
113. T.C.Nonhebel and J.C.Walton, "Free-Radical Chemistry: Structure and Mechanism" (Translated into Russian), Izd.Mir, Moscow, 1977.
114. J.M.Briody and R.A.Moore, J.Chem.Soc., Perkin Trans.II, 1972, 179.

115. A.J.Kresge and H.C.Brown, J.Org.Chem., 1967, **32**, 756.
116. K.R.Yan, L.M.Stock, and T.L.Wright, J.Org.Chem., 1979, **44**, 2309.
117. G.Henrici-Olive and S.Olive, "Coordination and Catalysis" (Translated into Russian), Izd.Mir, Moscow, 1980.
118. I.I.Moiseev, "π-Kompleksy v Zhidkofaznom Okislenii Olefinov" (π-Complexes in the Liquid-Phase Oxidation of Olefins), Izd.Nauka, Moscow, 1970.
119. O.A.Reutov, I.P.Beletskaya, and V.I.Sokolov, "Mekhanizmy Reaktsii Metalloorganicheskikh Soedinenii" (The Mechanism of the Reactions of Organometallic Compounds), Izd.Khimiya, Moscow, 1972, Chapter 1.
120. T.Spencer and F.G.Thorpe, J.Organometal.Chem., 1975, **99**, C8.
121. R.F.Heck, J.Amer.Chem.Soc., 1968, **90**, 5531.
122. R.F.Heck, J.Amer.Chem.Soc., 1968, **90**, 5535.
123. R.F.Heck, J.Amer.Chem.Soc., 1968, **90**, 5542.
124. I.V.Kozhevnikov, React.Kinet.Catal.Letters, 1976, **5**, 439.
125. V.E.Taraban'ko, I.V.Kozhevnikov, and K.I.Matveev, Kinetika i Kataliz, 1978, **19**, 1160.
126. R.S.Shue, J.Catal., 1972, **26**, 112.
127. K.Shimizu, H.Suga, K.Kurita, J.Imamura, and N.Ohota, J.Chem.Soc.Japan, Chem.and Ind. Chem., 1973, 999.
128. A.Kasahara, T.Izumi, M.Yodono, R.Saito, T.Takeda, and T.Sugawara, Bull.Chem.Soc.Japan, 1973, **46**, 1220.
129. Y.Fujiwara, R.Asano, I.Moritani, and S.Teranishi, Chem.Letters, 1975, 1061.
130. Y.Fujiwara, R.Asano, I.Moritani, and S.Teranishi, J.Org.Chem., 1976, **41**, 1681.
131. M.Yamamura, I.Moritani, A.Sonoda, S.Teranishi, and Y.Fujiwara, J.Chem.Soc., Perkin Trans.I, 1973, 203.
132. Y.Fujiwara, R.Asano, and S.Teranishi, Isr.J.Chem., 1976–1977, **15**, 262.
133. K.Yamamura and S.Watarai, Bull.Chem.Soc.Japan, 1975, **48**, 3757.
134. A.Segnitz, E.Kelly, S.H.Taylor, and P.M.Maitlis, J.Organometal.Chem., 1977, **124**, 113.
135. K.Yamamura, J.Org.Chem., 1978, **43**, 724.
136. K.Yamamura, J.Chem.Soc., Perkin Trans.I, 1975, 988.
137. R.F.Heck, US P.3751446 (1971).
138. R.F.Heck, J.Amer.Chem.Soc., 1969, **91**, 6707.
139. A.P.Kotlobai, E.B.Perova, and M.D.Navalikhina, Khim.Prom., 1973, 147.
140. W.W.Kaeding, Catal.Rev., 1973, **8**, 307.
141. I.V.Kozhevnikov, S.Ts.Sharapova, and L.I.Kurteeva, Kinetika i Kataliz, 1982, **23**, 352.
142. R.F.Heck, J.Amer.Chem.Soc., 1968, **90**, 5538.
143. R.F.Heck, J.Amer.Chem.Soc., 1971, **93**, 6896.
144. R.S.Shue, J.Amer.Chem.Soc., 1971, **93**, 7116.
145. I.V.Kozhevnikov and S.T.Sharapova, React.Kinet. Catal.Letters, 1980, **15**, 49.
146. J.Tsuji, Accounts Chem.Res., 1969, **2**, 144.
147. H.Horino, M.Arai, and N.Inoue, Tetrahedron Letters, 1974, 647.
148. S.Danno, I.Moritani, Y.Fujiwara, and S.Teranishi, J.Chem.Soc.B, 1971, 196.
149. J.Tsuji, "Organic Synthesis by Means of Transition Metal Complexes" (Translated into Russian), Izd. Khimiya, Moscow, 1979.
150. A.K.Yatsimirskii, A.D.Ryabov, and I.V.Berezin, Dokl.Akad.Nauk SSSR, 1979, **243**, 707.
151. C.F.Kohll and R.Van Helden, Rec.Trav.Chim., 1967, **86**, 193.
152. H.C.Volger, Rec.Trav.Chim., 1967, **86**, 677.
153. R.C.Larock, J.Org.Chem., 1976, **41**, 2241.
154. Japanese P.5522 (1972); Ref.Zhur.Khim., 1973, 4N152.
155. M.N.Vasil'eva, A.A.Andreev, and D.M.Shopov, Kinetika i Kataliz, 1979, **20**, 896.
156. A.K.Yatsimirskii, A.S.Erokhin, and I.V.Berezin, Izv.Akad.Nauk SSSR, Ser.Khim., 1980, 42.
157. A.K.Yatsimirsky, A.D.Ryabov, and I.V.Berezin, J.Mol.Catal., 1978, **4**, 151.
158. G.Lefebvre and Y.Chauvin, in "Aspects of Homogeneous Catalysis" (Translated into Russian), Izd.Mir, Moscow, 1973, p.158.
159. R.N.Pandey and P.M.Henry, Canad.J.Chem., 1975, **53**, 2223.
160. P.M.Henry, J.Org.Chem., 1972, **37**, 2443.
161. B.Hudson, D.E.Webster, and P.B.Wells, J.Chem. Soc., Dalton Trans., 1972, 1204.

Institute of Catalysis,
Siberian Division of the USSR Academy
of Sciences, Novosibirsk