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The Application of Cyclopalladated Compounds in Synthesis

A.D.Ryabov

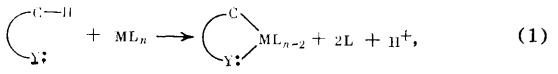
The review is devoted to the application in organic synthesis of organopalladium compounds with an intramolecular coordinate bond. Reactions with alkenes, alkynes, carbon monoxide, isocyanides, organolithium and organomagnesium compounds, and other reagents are examined. The mechanisms of these processes are discussed.
The bibliography includes 129 references.

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I. INTRODUCTION

The discovery of the reactions involving the cyclometallation of organic compounds by transition metal complexes,[1] leading to the formation of transition metal–carbon and metal–donor atom bonds, i.e.



(1)

initiated the wide-scale and comprehensive investigation of cyclometallated molecules. One of the causes of the continuous interest in these substances is the possibility of modelling many catalytic reactions involving transition metal complexes in which the formation of labile metal–carbon bonds has been postulated as the key stages.[2] A large number of cyclometallated complexes have been synthesised in recent years, which has been reflected in review articles.[3-7] The chemistry of cyclometallated compounds† soon outgrew the limits of purely model problems and these complexes have come to be used independently in organic synthesis. Their employment makes it possible to achieve absolute regioselectivity and, in the case of σ-aryl complexes and related compounds, *ortho*-substituted products, which are otherwise difficult to synthesise, can be obtained.

This review summarises the literature data concerning the application of cyclometallated complexes in organic synthesis. Since palladium(II) complexes are most widely used, attention has been naturally concentrated on the reactions of these compounds. The review also includes certain processes which are potentially important for organic synthesis. The methods of synthesis of cyclopalladated complexes as well as procedures for the cleavage of palladium–carbon bonds, leading to the liberation of the organic fragments of the complexes, are briefly described.

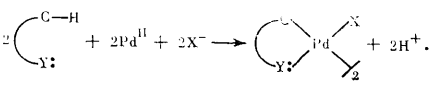
†Cyclopalladated compounds or cyclopalladated complexes have been recently referred to also as palladocycles. All these equivalent terms are used in this review.

II. THE SYNTHESIS AND DISSOCIATION OF PALLADOCYCLES

These problems have been examined in detail in a number of reviews.[3-7] Only general approaches to the synthesis of the cyclopalladated complexes used in organic synthesis are briefly described below. This is done, in particular, also in order to emphasise the availability of the initial compounds of the type of di-μ-chlorobis(cyclometallated ligand)dipalladium(II).

Direct Palladisation

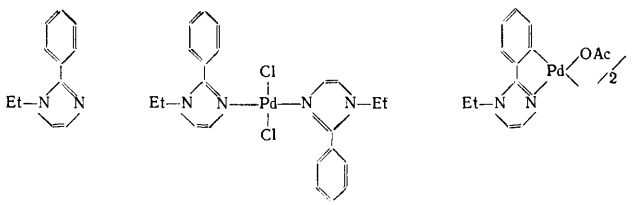
The reaction involves the direct interaction of the organic ligand with palladium(II) salts:



(2)

M_2PdCl_4, M_2PdCl_4–MOAc, and $Pd(OAc)_2$, where M = Li or Na, are used. The palladation is carried out in methanol, ethanol, acetone, dioxan, chloroform, acetic acid, and binary aqueous organic mixtures. As a rule, the palladation reaction takes place smoothly at room temperature, but in a number of instances heating is necessary. The "mildest" metallating agent is lithium or sodium tetrachloropalladate(II); the M_2PdCl_4–alkali metal acetate or amine system is frequently more effective. The acetate anion functions as a general base, which facilitates the dissociation of the C–H bond.[8]

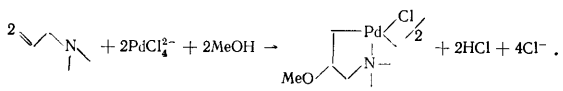
In those cases where the treatment of the ligand with M_2PdCl_4 does not lead to cyclopalladated products (the so-called bisadducts $PdCl_2L_2$ are then usually formed), palladium(II) acetate may prove to be effective. For example, Li_2PdCl_4 reacts with 1-ethyl-2-phenylimidazole(I), giving rise to the bisadduct (II), while the required cyclometallated complex (III) is obtained via the reaction of compound (I) with palladium(II) acetate in boiling acetic acid.[9]



(I) (II) (III)

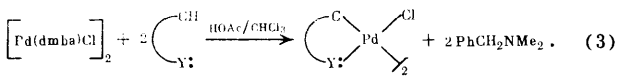
In a number of instances complexes of the type $PdCl_2L_2$ can be converted into cyclopalladated products of the type $[Pd(L-H)Cl]_2$ by heating or treatment with bases (see, for example, Shaw and co-workers[10,11]).

Direct palladation makes it possible to obtain complexes with aromatic, pseudoaromatic, and aliphatic ligands. The last can also be synthesised from allylamines[12] and allyl sulphides[13] by treating them with $PdCl_4^{2-}$ in the presence of nucleophiles:



Ligand Exchange

The essential feature of a recently proposed method[14] consists in the interaction of any *ortho*-palladated complex with the free ligand, which leads to a new palladocycle:



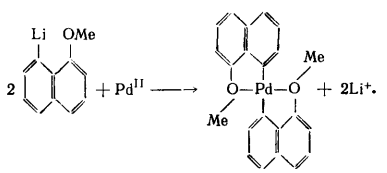
(3)

Here and henceforth $[Pd(dmba)Cl]_2$ represents di-μ-chlorobis(*NN*-dimethylbenzylamine-C^2,*N*)dipalladium(II) $[Pd(C_6H_4CH_2NMe_2)Cl]_2$. Acetic acid is an essential component of the reaction mixture; in its absence there is no exchange. The method makes it possible to obtain complexes with donor N and P atoms; ligands with oxygen-containing donor groups do not react.

This method is particularly convenient for the synthesis of compounds which can be obtained by the direct palladation of the corresponding ligands, in particular for the synthesis of di-μ-chlorobis(*N*,*N*-diethyl-4-nitrobenzylamine-C^2,*N*)-dipalladium(II).[14]

Transmetallation

The method consists in the treatment of the ligand with a suitable organolithium compound, which gives rise to the lithio-derivative of the latter, to which the metal salt is then added. Complexes of 1-methoxynaphthalene are synthesised in this way, for example:[15]



The use of organolithium compounds for such purposes has been considered in detail in a review.[5]

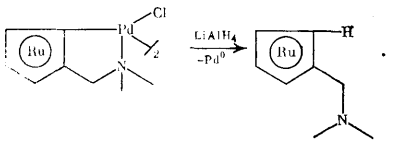
Another promising method involves the interaction of organomercury compounds with zerovalent palladium complexes of the type $Pd(PPh_3)_4$ or Pd_2(dibenzylideneacetone)$_3$.[16,17] These reactions proceed via the oxidative addition mechanism; two reviews are devoted to their characteristics.[18,19]

Thus it follows from the above discussion that cyclopalladated compounds are fairly readily available; they are stable in air and can be stored indefinitely. All these factors create conditions for the application of these complexes in organic synthesis.

Processes accompanied by the dissociation of the metal–carbon σ-bond in the metallocycle are no less important because in many instances the interaction of the initial complex with any substrate leads to the formation of a new complex with a modified cyclometallated organic ligand. In order to use such processes in synthesis, it is necessary to have at ones disposal selective methods which make it possible to decompose the metallocycles in such a way that the modified organic ligand can be readily isolated. Some of these methods are described below.

Reduction with Lithium Tetrahydroaluminate

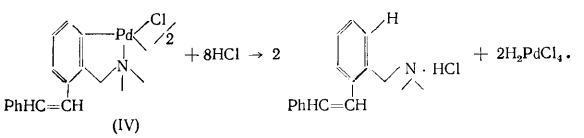
In organic solvents, for example in dry diethyl ether, the reduction of palladocycles by $LiAlH_4$ leads to the formation of the free ligand and zerovalent palladium, as happens, in particular, in the case of a ruthenocene derivative:[20]



The use of $LiAlD_4$ leads to selective deuteriation. $NaBH_4$ and H_2 are used as other reductants.

Acidolysis

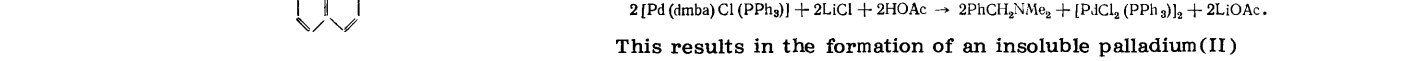
The palladium–carbon bond in the compounds considered dissociates in the presence of strong protic acids of the type of HCl, $HClO_4$, HNO_3, etc. For example, treatment of compound (IV) with hydrochloric acid in aqueous dioxan solution leads to the formation of the free ligand and the $PdCl_4^{2-}$ anion:[21]



(IV)

Acidolysis in Acetic Acid Induced by the Chloride Ion

As a rule, dimeric cyclopalladated compounds do not decompose in acetic acid. However, the monomeric complexes, i.e. the products of the cleavage of the chloride bridges by triphenylphosphine, undergo acidolysis in acetic acid in the presence of LiCl:[22,23]



This results in the formation of an insoluble palladium(II) complex and the free ligand. The *ortho*-deuteriated products are obtained in DOAc.[23]

III. REACTIONS WITH ALKENES

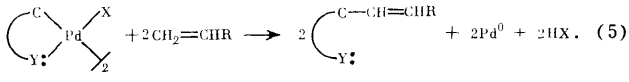
The possibility of the interaction of the cyclopalladated complexes with alkenes, involving the formation of the products of the formal substitution of palladium(II) by the vinyl group, was indicated for the first time in a review,[24] whose author concluded that styrene reacts readily with $[Pd(dmba)Cl]_2$ in acetic acid at room temperature with formation of 2-dimethylaminomethylstilbene:

$$[Pd(dmba)Cl]_2 + 2PhCH{=}CH_2 \rightarrow 2o\text{-}Me_2NCH_2C_6H_4CH{=}CHPh + 2Pd^0 + 2HCl. \quad (4)$$

This communication was followed by a large number of reports devoted to the reactions of palladocycles with alkenes; the results of these studies are summarised in Table 1.

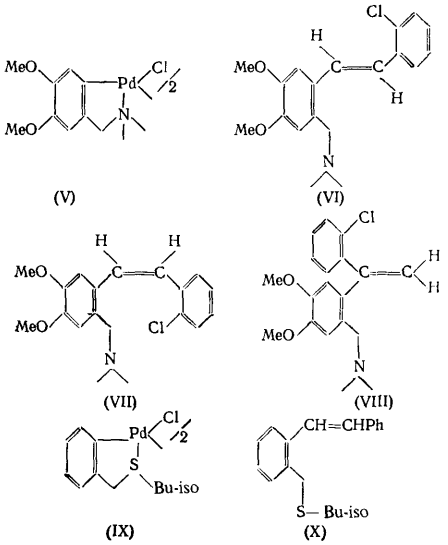
The Stoichiometry and Products of the Reaction

The reactants interact in molar proportions of 1 : 1, i.e. one palladocycle reacts with one alkene molecule:



$$+ 2CH_2{=}CHR \rightarrow 2 \quad + 2Pd^0 + 2HX. \quad (5)$$

Reactions of type (5) are oxidation-reduction processes and are accompanied by the reduction of palladium(II) to zerovalent palladium. Only α-olefins react. The process proceeds stereospecifically: palladium is substituted by the α-carbon atom of the alkene and the product has the *E*-configuration. This is indicated by the spin–spin coupling constants of the olefin protons $^3J(HH)$, which amount to 15–17 Hz.[25] The infrared spectra of the products contain the band due to the deformation vibrations of the *trans*-HC=CH bonds at 950–990 cm^{-1}.[21] The only exception known hitherto is that of the reaction of compound (V) with *o*-chlorostyrene.[25] In this case the *Z*-stilbene (VII) and 1,1-diarylethylene (VIII) are obtained together with the main product (VI). However, the amount of the last two impurities does not exceed 5% of the content of the main product (VI). The impurities can be readily removed by recrystallising the corresponding hydrochlorides from ethanol:



(V) (VI) (VII) (VIII) (IX) (X)

Table 1. Vinylation of cyclopalladated complexes.

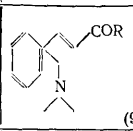
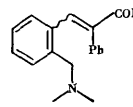
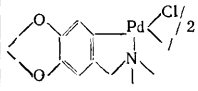
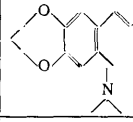
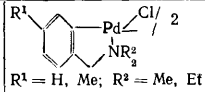
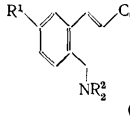
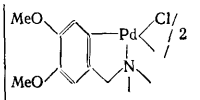
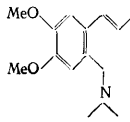
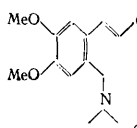
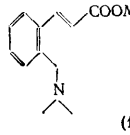
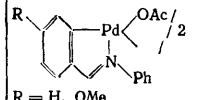
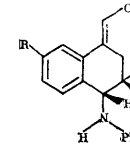
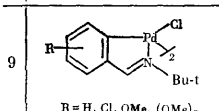
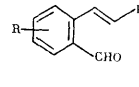
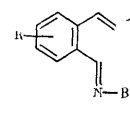
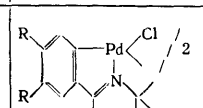
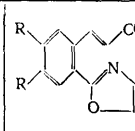
No.	Complex	Alkene	Product (yield, %)	Refs.
1	$[Pd(dmba)Cl]_2$	$H_2C{=}CHCOR$ R = Me, Et, C_6H_{11}	 (92–96)	[28]
2	ditto	$H_2C{=}C(Ph)COMe$	 (80)	[28]
3		$H_2C{=}CHCOMe$		[28]
4	 R^1 = H, Me; R^2 = Me, Et	$H_2C{=}CHC_6H_4R^3\text{-}n$ R^3 = H, Me, OMe, Cl, Br	 (30–60)	[21]
5		$H_2C{=}CHCOR$ R = Me, OEt	 (85–98)	[25]
6	ditto	$H_2C{=}CHC_6H_4R$ R = H, *p*-OMe, *o*-, *m*-, or *p*-Cl, *o*-, *m*-, or *p*-NO_2	 (32–94)	[25]
7	$[Pd(dmba)OAc]_2$	$H_2C{=}CHCOOMe$	 (17,5)	[37]
8	 R = H, OMe	ditto	 (10–11)	[37]
9	 R = H, Cl, OMe, $(OMe)_2$	$H_2C{=}CHPh$	 (67–91)	[43]
10	ditto	$H_2C{=}CHCN$	 (78)	[42]
11	 R = H, OMe	$H_2C{=}CHCOMe$	 (38–45)	[115]

Table 1 (cont'd).

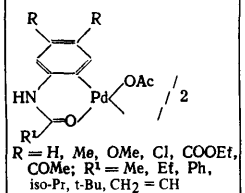
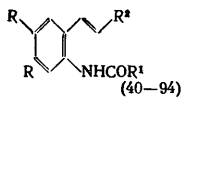
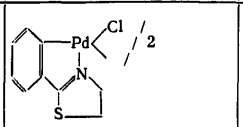
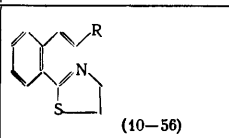
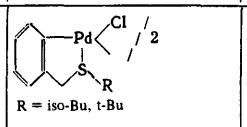
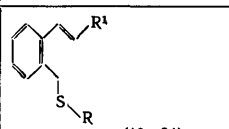
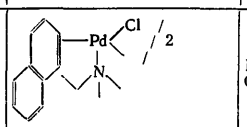
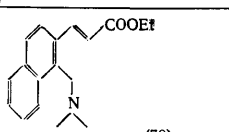
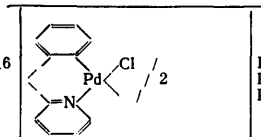
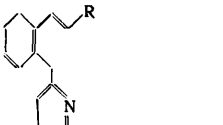
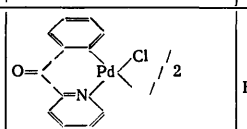
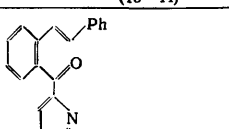
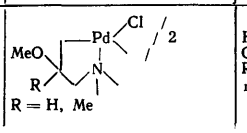
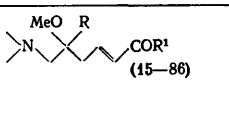
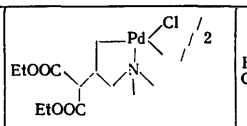
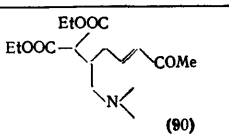
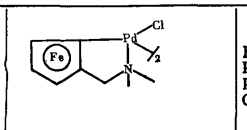
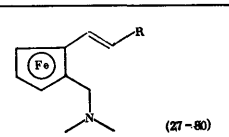
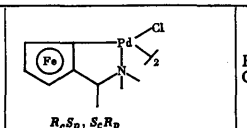
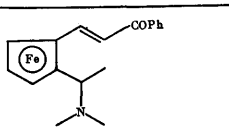
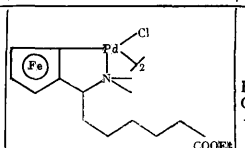
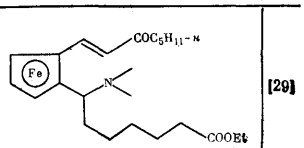
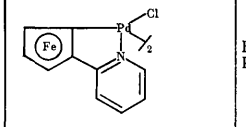
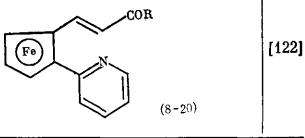
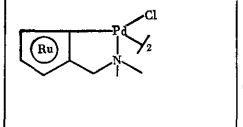
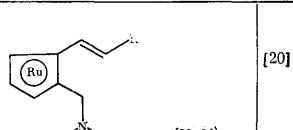
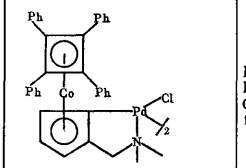
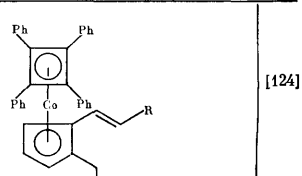
No.	Complex	Alkene	Product (yield, %)	Refs.
12	 R = H, Me, OMe, Cl, COOEt, COMe; R^1 = Me, Et, Ph, iso-Pr, t-Bu, CH_2 = CH	H_2C=CHR^2 R^2 = H, Ph, CN, COOMe, OAc, $CH(OEt)_2$, 3,4-$OCH_2OC_6H_3$, 3-AcO-4-MeO-C_6H_3	 (40—94)	[36, 116]
13		H_2C=CHR R = COMe, Ph	 (10—56)	[117]
14	 R = iso-Bu, t-Bu	H_2C=CHR^1 R^1 = COMe, Ph	 (10—21)	[26]
15		H_2C= CHCOOEt	 (70)	[118]
16		H_2C=CHR R = COMe, Ph	 (13—44)	[119]
17		H_2C=CHPh		[120]
18	 R = H, Me	H_2C= CHCOR¹ R^1 = Me, Et, n-C_6H_{13}, OEt	 (15—86)	[34]
19		H_2C= CHCOMe	 (90)	[121]
20		H_2C=CHR R = COMe, Ph, CN, CO_2Et, COPh	 (27—80)	[122, 123]
21	 R_cS_p, S_cR_p	H_2C= CHCOPh		[65]

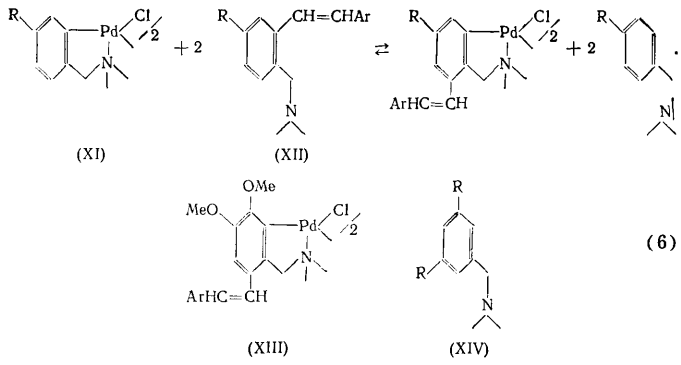
Table 1 (cont'd).

No.	Complex	Alkene	Product (yield, %)	Refs.
22		H_2C= $CHCOC_6H_{11}$-n	 (61)	[29]
23		H_2C=CHCOR R = Me, Ph	 (8-20)	[122]
24		H_2C=CHR R = COMe, COPh, Ph	 (89-94)	[20]
25		H_2C=CHR R = H, Ph, COMe, COPh, ferrocenyl	 (30-57)	[124]

The reaction of [Pd(ba)OAc]$_2$(di-μ-acetatobis(benzylidene-aniline-C^2,N)-dipalladium(II) [Pd(C_6H_4CH=NPh)OAc]$_2$ with methyl acrylate (Table 1, No. 8) exhibits a different stoichiometry, namely one palladocycle reacts with two molecules of the alkene. The structure of the reaction product was established in this case by X-ray diffraction.[37]

The side products in this reaction are most frequently the free ligands formed as a result of the dissociation of the initial complexes. For example, in the interaction of the complex (IX) with styrene in boiling *o*-xylene in the presence of NEt_3 the yields of *trans*-2-(isobutylthiomethyl)-stilbene (X) and $PhCH_2SBu$-iso are 21 and 76% respectively.[26] In acetic acid there is also a possibility of the secondary palladation of the arylolefins formed. Thus the reaction of compound (XI) with *para*-substituted styrenes in an acetic acid–benzene mixture involves the formation, together with the free stilbenes (Table 1, No. 4), of the palladation products of the latter (XII).[21] The complexes (XII) are obtained either as a result of the direct palladation of stilbenes by palladium(II) or as a result of the ligand exchange [reaction (6)]. The exchange reaction, whose nature is analogous to that of reaction (3), explains the

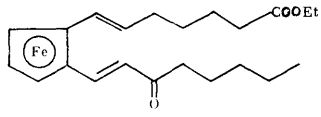
appearance of free ligands in acetic acid media:[21]



(6)

Reaction (6) leads to the non-productive consumption of the initial complex and to a decrease of the yield of the final product. Its suppression increases the yields of stilbenes.[25] In the reactions of compounds (V) with styrenes the hypothetical complex (XIII) can hardly exist for purely steric reasons, since the products of the palladisation of 3,5-dialkylbenzyl-*NN*-dimethylamines (XIV), containing Pd–C bonds in the *ortho*-position relative to the alkyl substituent, do not exist.[27]

The causes of the formation of the free ligands in the absence of acetic acid are less understandable. It has been assumed that[28] they are obtained as a result of the cleavage of the Pd–C bonds in the initial complexes under the influence of the hydrochloric acid liberated in the course of reaction (5), since in the presence of tertiary amines, which are potential HCl acceptors, the free ligands are not formed. However, subsequently, for example, in the study of Fuchita et al.[26], it was shown that the dissociation takes place also in the presence of amines. The role of the latter in reaction (5) remains altogether obscure. This is further confirmed by the formation of the product (XV) in 10% yield on ketovinylation of the ferrocene derivative (Table 1, No. 22) in the absence of NEt_3.[29]



(XV)

Overall, reaction (5) is a variant of the familiar reactions involving the arylation of olefins by hydrocarbons (the Fujiwara–Moritani reaction)[30,31] or organometallic compounds (the Heck reaction)[32,33] in the presence of palladium(II) salts:

$$ArM + H_2C{=}CHR + Pd^{II} \rightarrow ArHC{=}CHR + M^+ + H^+ + Pd^0, \qquad (7)$$

where M = H or HgX. As in reaction (5), the aryl group adds to the least branched carbon atom involved in the double bond and the product has the *E*-geometry. Thus reaction (5) can serve as a convenient model of the Fujiwara–Moritani or Heck processes, in which the initial complex contains a stable palladium–carbon bond.

The Nature of the Cyclopalladised Complex and the Olefin

Table 1 shows that a whole series of palladocycles with chelating donor atoms of different types (Table 1, Nos. 1–17) react with olefins. Derivatives of *NN*-dialkylbenzylamines (Table 1, Nos. 1–7), benzylideneamines, and anilines (Nos. 8–10) have been studied in greatest detail. The donor atoms in the reacting complexes are those of nitrogen, oxygen, and sulphur. Five- and six-membered palladocycles react. The aliphatic complexes with a nitrogen donor atom also enter into the reaction (Table 1, Nos. 18 and 19), while the analogous complexes with an S donor atom in the ring are unreactive.[34] Palladocycles such as ferrocene, ruthenocene, and cyclopentadienyltetraphenylcyclobutadienecobalt derivatives (Table 1, Nos. 20–25) also react readily with olefins. The possibility of the asymmetric palladation of these compounds[35] creates conditions for the synthesis of enantiomeric and diastereoisomeric vinyl compounds (Table 1, Nos. 21 and 22).

As mentioned above, only α-olefins undergo reaction (5). Branched alkenes, for example pent-3-en-2-one, do not interact with $[Pd(dmba)Cl]_2$. On the other hand, the terminal alkene 3-phenylbut-3-en-2-one reacts and the yield is 80%.[28] Substituents at the double bond exert a weak influence on the yields of the vinylation products (see, for example, Horino and Inoue[36]). On the whole, the yields are determined more by the nature of the initial complex than by that of the alkene. As a rule, if reaction (5) involving any alkene proceeds with a satisfactory yield then it also proceeds fairly smoothly with other alkenes of different types. The exceptions are the $[Pd(dmba)Cl]_2$ analogues already mentioned. These complexes react readily with vinyl ketones (Table 1, Nos. 1–3 and 5) in boiling benzene or toluene in the presence of tertiary amines but under these conditions they are inert with respect to olefins without keto-groups.[21,25,37]

The vinylation of *NN*-dialkylbenzylamine complexes by these alkenes can be carried out only in the presence of carboxylic acids; it has been noted that the reaction is significantly accelerated in the presence of sodium or lithium perchlorate.[21]

Reaction Conditions

Reaction (5) is usually carried out with an aromatic hydrocarbon as the solvent (benzene, toluene, and xylenes) in the presence of a tertiary amine, usually NEt_3 (method A), or in acetic acid to which benzene or methylene chloride are added to increase the solubility of the initial complexes (method B). The reaction is performed at 75 °C and above by method A and at lower temperatures by method B. The reaction time is determined by the nature of the initial palladocycle and can vary within wide limits. As a rule,[21,25,28] the vinylation of benzylamine derivatives is accelerated in the presence of acetic acid but sometimes the reaction does not proceed in this solvent.[34]

The rates of reactions catalysed by acetic acid increase markedly when lithium, sodium, or magnesium perchlorate is added to the acetic acid solutions.[21,38] Their catalytic effect consists in the fact that they react with acetic acid via reaction (8) and the real catalyst of reaction (5) is

perchloric acid:

$$MClO_4 + HOAc \overset{K_8}{\rightleftharpoons} MOAc + HClO_4. \quad (8)$$

The equilibrium in Eqn. (8) is strongly displaced to the left: for $[NaClO_4] = 0.1$ M, the $HClO_4$ concentration is only $\sim 2 \times 10^{-5}$ M ($K_8 = 4.3 \times 10^{-9}$ M). The cyclopalladised complexes are stable at such low $HClO_4$ concentrations and do not decompose under these conditions. The addition of small amounts of $HClO_4$ to the reaction mixture also increases the rate of reaction.[38]

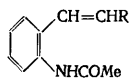
The Synthesis of Analogues of Prostaglandins

Table 1 presents examples of the reactions of alkenes with cyclopalladated complexes isolated beforehand in a pure state. At the same time, it is possible to carry out the vinylation of the palladocycles formed *in situ*. Holton[39] used this approach to synthesise prostaglandins. The palladisation of the enamine (XVI) in a mixture of ethylene-chlorohydrin and dimethyl sulphoxide (DMSO) leads to the bicyclic cyclometallated complex (XVII) with a five-membered palladocycle; without being isolated in a pure state, the latter is treated with n-pentyl vinyl ketone. The vinyl ketone (XVIII) was obtained as a result. It can then be converted by traditional chemical methods[39] into Corey's lactone-diol (XIX), which is a precursor of prostaglandin $PGF_{2\alpha}$.[40]

The ketovinylation of the products of the asymmetric palladation of ferrocene derivatives is also a key stage in the synthesis of models of natural prostaglandins.[29] The metallation of 2-(6-ethoxycarbonyl-1-dimethylaminohex-1-yl)-1-(3-oxo-oct-1-en-1-yl)ferrocene (Table 1, No. 22) with subsequent mild reduction to the methiodide (XX) with $NaBH_4$ leads to compound (XXI).

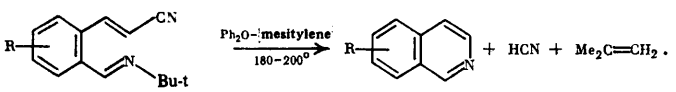
The Synthesis of Heterocycles

The vinylation of *ortho*-palladised compounds, which leads, in particular, to *ortho*-substituted stilbenes, is a convenient method of synthesis of compounds of this class (see, for example, Becker[41]). However, there is an additional interest in analogous products owing to the possibility of their employment to synthesise heterocyclic compounds. Several examples are presented below. Treatment of compound (XXIIa) with concentrated HCl for several minutes results in the formation of quinoline in high yields.[36] Quinaldine and carbostyril respectively have been obtained analogously from compounds (XII, b and c):[36]

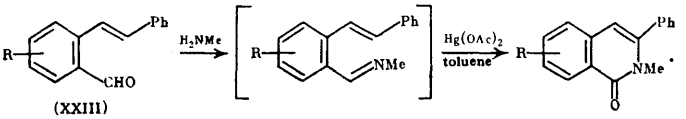


(XXII): a) R=CH(COEt)$_2$; b) R=COMe; c) R=COOMe.

A synthetic approach to substituted isoquinolines, starting with the products of the reactions of *ortho*-palladised Schiff bases with acrylonitrile (Table 1, No. 10), has been proposed recently:[42]

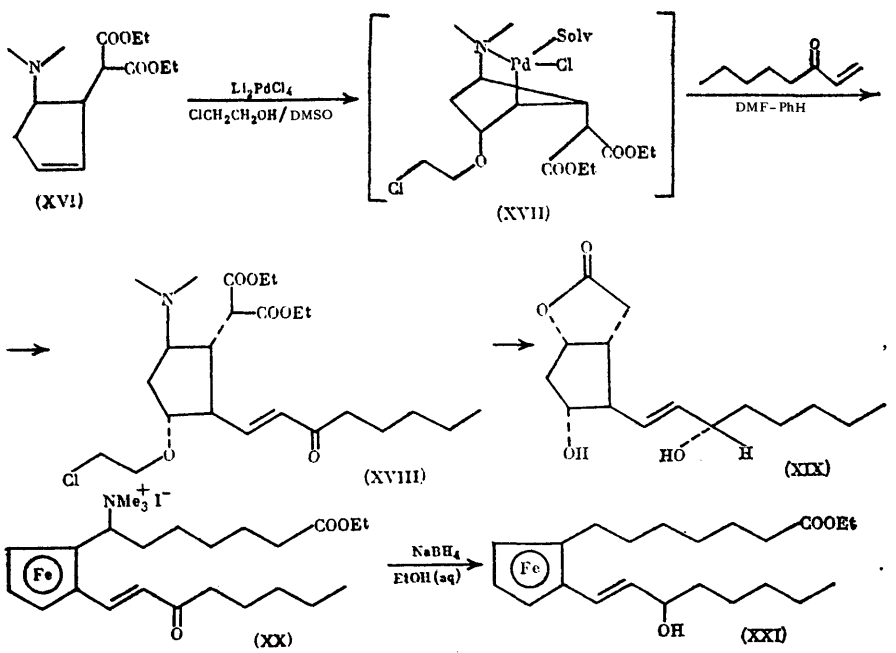


3-Arylisoquinolones can be obtained[43] in accordance with the scheme



(XXIII)

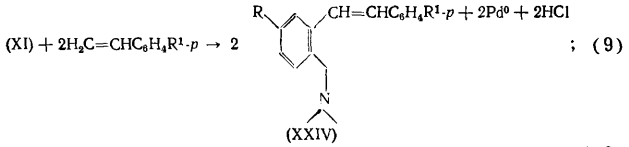
The starting compounds are synthesised as shown in Table 1 (No. 9). The above methods are attractive,



because of their simplicity and the high yield of the required products.

The Reaction Mechanism

The kinetics of the reactions of cyclopalladated complexes with alkenes have been investigated in relation to the interaction of the complex (XI) with *para*-substituted styrenes in acetic acid:[38,44]



$$(XI) + 2H_2C{=}CHC_6H_4R^1\text{-}p \rightarrow 2\ (XXIV) + 2Pd^0 + 2HCl \quad ; \quad (9)$$

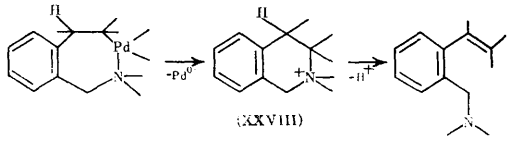
$$d[(XXIV)]/dt = k_2[(XI)][H_2C{=}CHC_6H_4R^1\text{-}p]. \quad (10)$$

The rate of reaction is described by the kinetic equation (10). An interesting feature of reaction (9) is the large positive salt effect. In the presence of tetrabutylammonium, sodium, lithium, and magnesium perchlorates, k_2 increases sharply. The catalytic effect increases in the above series of cations from left to right and the increase reaches almost two orders of magnitude for $[Mg(ClO_4)_2] = 0.1$ M.

It has been shown[38,44] that the effect of the salt is associated with the existence of equilibrium (8) in acetic acid. Perchloric acid catalyses the process in conformity with a kinetic equation of the type $k_2 = k_3 + k_4[HClO_4]$, i.e. the reaction proceeds via two parallel pathways—the "solvolytic" pathway (k_3) and the acid-catalysed pathway (k_4). Since reaction (9) does not occur in the absence of acetic acid, it is assumed that the solvolytic pathway is promoted by acetic acid. The electrophilic catalyst E (acetic and perchloric acids for the k_3 and k_4 pathways respectively) interacts with the bridging chloro-ligands of the initial complex [Eqn. (11)], which facilitates the coordination of palladium(II) to the alkene molecule:

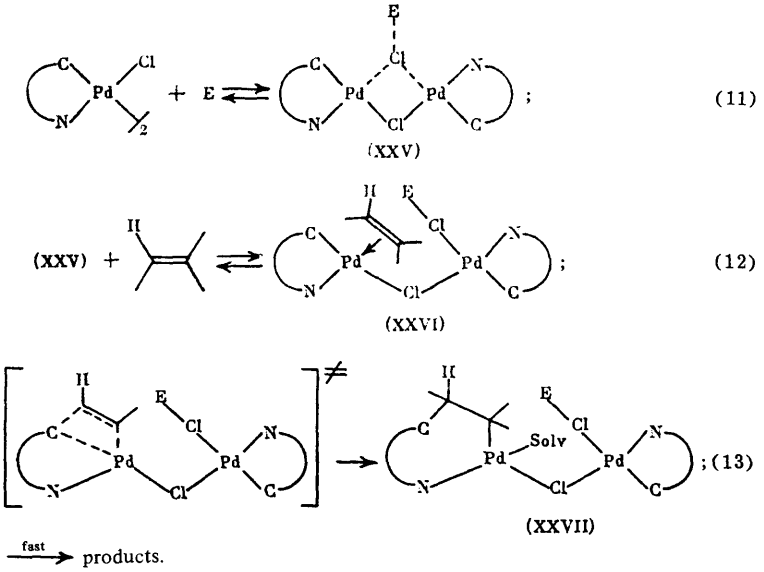
Generally speaking the intermediate complex (XXV) can have only one bridging ligand: similar compounds have been recently characterised by X-ray diffraction methods.[45] Subsequently compound (XXV) reacts reversibly with the alkene to form the π-complex (XXVI). The latter undergoes the rate-limiting π-σ rearrangement via a cyclic four-centre transition state. This is indicated by the low absolute values of the Hammett parameters $\rho(R^1)$ and $\rho(R)$ obtained, which do not exceed unity, and also by the low enthalpies of activation $\Delta H^{\neq}$.[38]

The elimination of hydrogen from the intermediate complex (XXVII), which leads to the final products, is a rapid stage. This is indicated by the kinetic isotope effect $k_2(PdCHCH_2)/.k_2(PhCHCD_2) = 1$. It has been suggested[25,38] that hydrogen is removed in the form of palladium hydride HPd^+ as a result of 1,3-elimination. The same mechanism operates in the Fujiwara–Moritani and Heck reactions [see Eqn. (7)].[46–48] Another possibility for the conversion of the complex (XXVII) into the reaction product involves the reductive elimination of zerovalent palladium, which leads to tetrahydroisoquinoline derivatives of type (XXVIII). The latter are fairly labile and readily undergo the Hofmann rearrangement to arylolefins in the presence of bases:[49]



(XXVIII) (14)

The mechanism (11)–(13) is probably valid in broad outline also for other palladocycles. There may be differences in the method of incorporation of the alkene in the coordination sphere of palladium(II). The olefin can in principle substitute the donor atom in cyclopalladated complexes, which results in their dechelation. Unfortunately, it is difficult to distinguish this possibility by direct kinetic methods from the reaction pathway examined above.



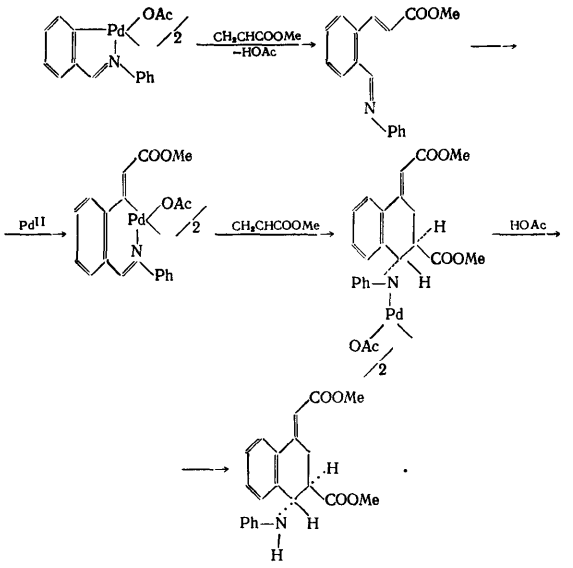
(XXV) (11)

(XXVI) (12)

(XXVII) (13)

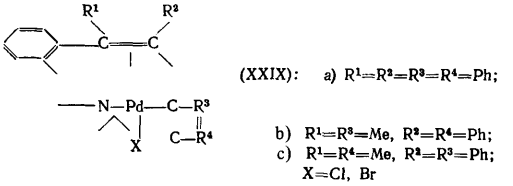
(XXVII) $\xrightarrow{fast}$ products.

In conclusion we shall consider the "double" insertion mechanism[37] (Table 1, No. 8). The usual formation of the arylolefin is followed by its secondary vinyl palladation. Next comes the insertion of a second methyl acrylate molecule and intramolecular addition of the palladium–carbon bond to the C=N double bond. Finally the Pd–N covalent bond formed undergoes homolysis or acidolysis by the acetic acid, which appears in the course of the first vinylation stage:[37]

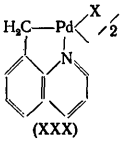


IV. REACTIONS WITH ALKYNES

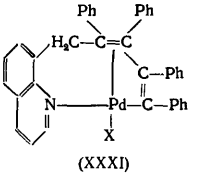
Cyclopalladised compounds readily react with disubstituted alkynes of the type $RC{\equiv}CR'$ ($R = R' = Ph$; $R = Ph$, $R' = Me$), forming double insertion products.[50] For example, $[Pd(dmba)Cl]_2$ is then converted into the complex (XXIXa) with a rarely encountered nine-membered palladocycle. The asymmetric alkyne PhC_2Me gives rise to a mixture of the isomeric complexes (XXIXb) and (XXIXc), each of which has been isolated in a pure state:



(XXIX): a) $R^1=R^2=R^3=R^4=Ph$;
b) $R^1=R^3=Me$, $R^2=R^4=Ph$;
c) $R^1=R^4=Me$, $R^2=R^3=Ph$;
X=Cl, Br

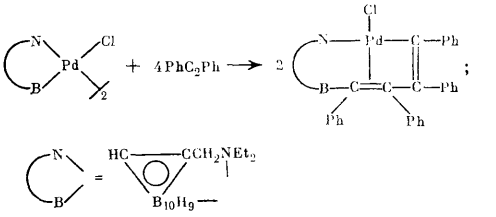


(XXX)

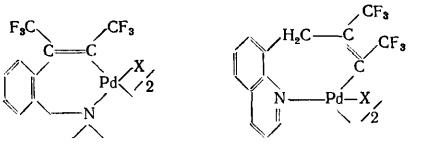


(XXXI)

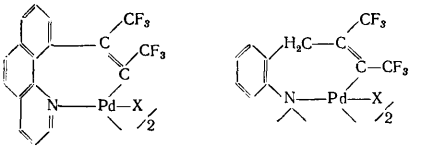
The structure of compounds (XXIXb, X = Br) and (XXIXc, X = Cl) has been established by X-ray diffraction. Tolane reacts with compound (XXX), also giving rise to the double insertion product (XXXI); hexaphenylbenzene is formed as a side product. The yield of compound (XXXI) depends on the reaction time and it has been assumed on this basis[50] that the complex (XXXI) can be an intermediate in the trimerisation of tolane. The reaction of compound (XXX) with PhC_2Me leads to a mixture of 1,2,4-trimethyl-3,5,6-triphenylbenzene and 1,3,5-trimethyl-2,4,6-triphenylbenzene in proportions of 7:3; the yield of the analogue (XXXI) does not exceed 1% in this case.[50] Double insertion products are also formed in the interaction of tolane with the *B*-palladated *o*-carbaborane:[51]



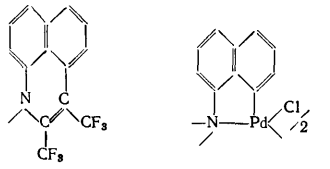
Cyclopalladised derivatives of benzo[*h*]quinoline, azobenzene, and *NN*-dimethyl-1-naphthylamine do not react with PhC_2Ph.[50] Nor has it been possible to obtain the products of the insertion in the Pd–C bond of one PhC_2Ph molecule. On the other hand, in the case of hexafluorobut-2-yne the monoinsertion products (XXXII)–(XXXV) are formed exclusively.[50,52,53]



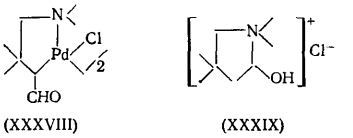
(XXXII) (XXXIII)



(XXXIV) (XXXV)



(XXXVI) (XXXVII)



(XXXVIII) (XXXIX)

The unusual compound (XXXVI), obtained as a result of the dissociation of the N–Me bond, has been isolated in the reaction of compound (XXXVII) with $CF_3C_2CF_3$.[50] Tolane does not react with the aliphatic cyclopalladated complex (XXXVIII), but treatment of the latter with phenylacetylene leads to 3,3-dimethyl-4-dimethylaminobutanal, whose hydrochloride has the cyclic structure (XXXIX).[54]

The reactions examined in this Section lead in most cases to new palladocycles and only sometimes to new free organic compounds. However, all these processes are extremely promising, since their products are difficult to obtain by other methods. We may note that, whereas the vinylation of palladated ligands (Section III) is characteristic of palladium(II) compounds only, the insertion of alkynes is also observed for other cyclometallated complexes of platinum group metals. In particular PhC_2Ph gives rise to the complex $\{\overline{Rh[(PhC=CPh)_2C_6H_4PPh_2]}PPh_3\}$,[55,56] while $CF_3C_2CF_3$ produces $\{\overline{Ru[(CF_3C=CCF_3)_2C_6H_4PPh_2](\eta\text{-}C_5H_5)}\}$,[57] i.e. complexes with eight-membered metallocycles are formed.

There are no data concerning the mechanisms of the interaction of alkynes with palladocycles. However, the mechanism of the double insertion of PhC_2Ph, leading to compounds of type (XXIX), is probably of special interest. The fact that it has not been possible[50] to detect the mono-insertion products suggests the possibility of the synchronous addition of two alkyne molecules to the palladium–carbon bond.

V. REACTIONS WITH CARBON MONOXIDE

The ability of carbon monoxide to react with compounds containing metal–carbon bonds is well known (see, for example, the relevant reviews[58,59]). Cyclopalladated complexes, to the reactions of which with CO this Section is devoted, are not exceptional.

Table 2. Carbonylation of cyclopalladated complexes.

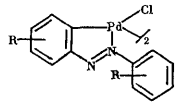
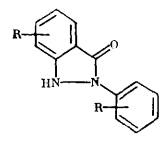
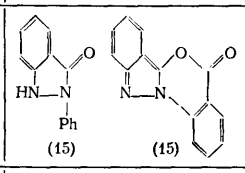
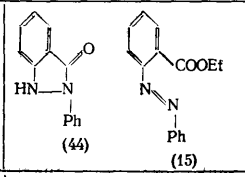
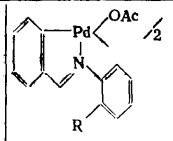
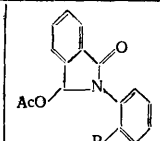
No.	Complex	Product (yield, %)	Solvent (p_{CO}, atm)	Refs.
1	 R = H; 2-, 3-, 4-Me; 3-, 4-Cl; 4-OMe	 (55–97)	EtOH, H_2O (30–150)	[61]
2	$[Pd(azb)Cl]_2$	ditto (17)	MeOH (2.8)	[125]
3	$[Pd(azb)OAc]_2$	 (15) (15)	PhCl (1)	[60]
4	ditto	 (44) (15)	EtOH (1)	[60]
5	 R = H, Me	 (65–66)	xylene (1)	[60]

Table 2 (cont'd).

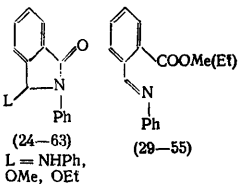
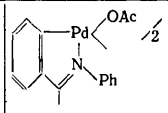
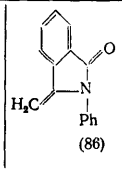
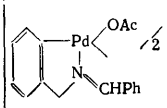
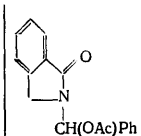
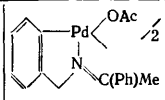
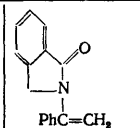
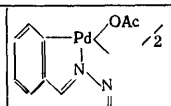
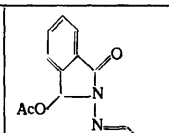
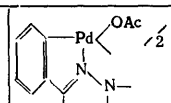
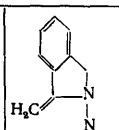
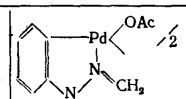
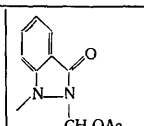
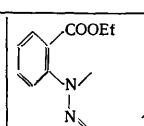
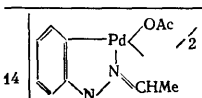
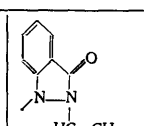
No.	Complex	Product (yield, %)	Solvent (p_{CO}, atm)	Refs.
6	$[Pd(ba)OAc]_2$	 (24–63) L = NHPh, OMe, OEt (29–55)	xylene–aniline, MeOH, EtOH (1)	[60]
7		 (86)	xylene (1)	[60]
8		 (48)	ditto	[60]
9		 (49)	ditto	[60]
10		 (48)	ditto	[60]
11		 (61)	ditto	[60]
12		 (53)	ditto	[60]
13	ditto	 (38) (13)	EtOH	[60]
14		 (68)	PhH	[60]

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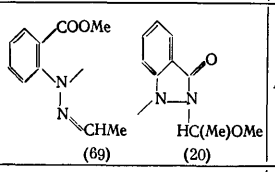
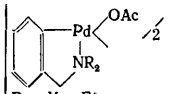
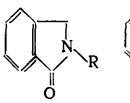
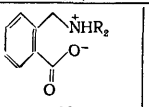
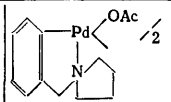
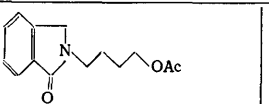
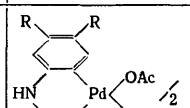
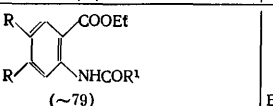
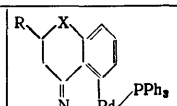
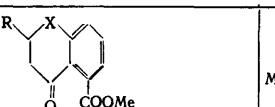
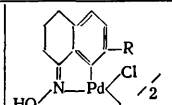
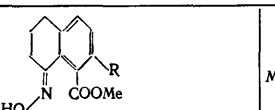
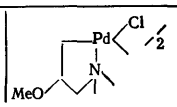
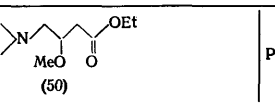
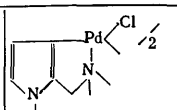
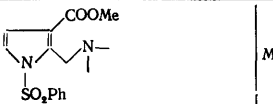
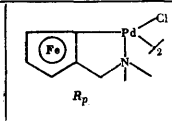
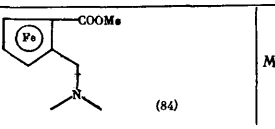
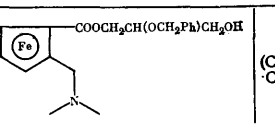
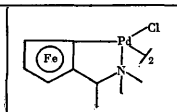
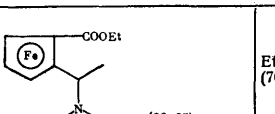
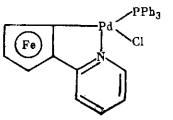
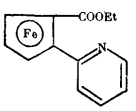
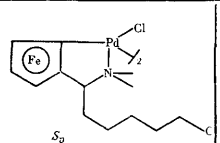
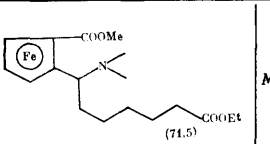
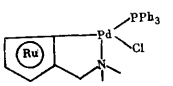
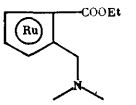
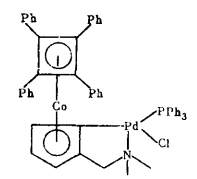
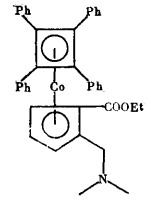
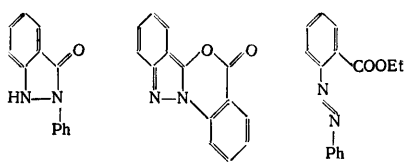
No.	Complex	Product (yield, %)	Solvent (p_{CO}, atm)	Refs.
15	ditto	 (69) (20)	MeOH	[60]
16	 R = Me, Et	 (27—72)  (5—36)	xylene	[60]
17		 (51)	ditto	[60]
18	 R = H, Me, OMe, Cl, COOEt, COMe, COOMe; R^1 = Me, Et, t-Bu	 (~79)	EtOH (1)	[36]
19	 X = O, S; R = H, Me, Ph	 (28—45)	MeOH (60)	[67]
20	 R = H, Et	 (32—73)	MeOH (7)	[63]
21		 (50)	PhH—EtOH	[126]
22		 (69)	MeOH	[128]
23		 (84)	MeOH	[92]
24	ditto		$(CH_2OH)_2$· ·$CH(OCH_2Ph)$	[35]
25		 (20-25)	EtOH, PPh_3 (70)	[65]

Table 2 (cont'd).

No.	Complex	Product (yield, %)	Solvent (p_{CO}, atm)	Refs.
26		 (37)	EtOH (60)	[66]
27		 (71.5)	MeOH	[127]
28		 (40)	EtOH (80)	[20]
29		 (42)	EtOH (50)	[124]

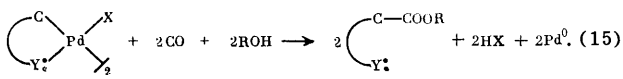
The Stoichiometry and Products of the Reactions

Examples of the reactions of cyclopalladated complexes with carbon monoxide are presented in Table 2. As a rule, one palladocycle absorbs one CO molecule. The carbonylation is accompanied by the reduction of palladium(II) to zerovalent palladium. In contrast to the reactions with alkenes, which yield isotypical compounds, the structure of the products of the carbonylation of palladocycles cannot always be predicted unambiguously. For example, depending on the carbonylation conditions, the products (XL)–(XLII) are formed from the *o*-metallated azobenzene[60,61] (Table 2, Nos. 2–4).



(XL) (XLI) (XLII)

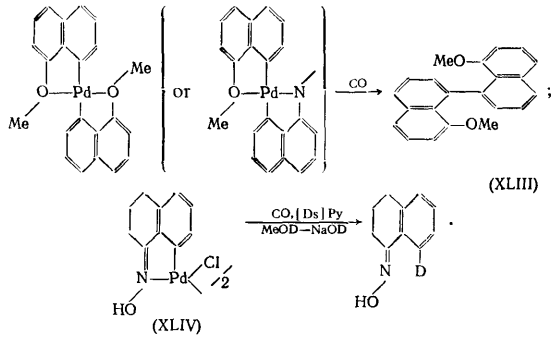
We may note that the formation of the lactone (XLI) is a fairly rare instance of a reaction with the stoichiometry palladocycle : CO = 1 : 2. The same large assortment of products is formed from palladated derivatives of benzilideneaniline (Table 2, Nos. 5–7). Table 2 shows that specific products are formed as a rule from each concrete complex. The most characteristic carbonylation pathway involves the formation of esters in alcohols:



(15)

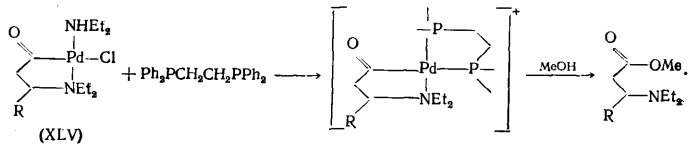
Esters are obtained from cyclopalladated azobenzenes (Table 2, No.4), benzylideneanilines (No.6), the 1-methyl-1-phenylhydrazones of formaldehyde (No.13) and acetaldehyde (No.15), acetanilides (No.18), certain oximes (Nos.19 and 20), aliphatic compounds (No.21), pyrroles (No.22), ferrocene (Nos.23–27), ruthenocene (No.28), and cyclopentadienyltetraphenylcyclobutadienecobalt (No.29).

In a number of instances the "carbonylation products" of palladocycles do not contain carbon monoxide at all. Thus the carbonylation of derivatives of 1-methoxynaphthalene results in the quantitative formation of 8,8′-dimethoxy-1,1′-binaphthyl (XLIII).[15] The study of the interaction of palladated oximes with CO showed[62,63] that the free ligand is formed under certain conditions. This "reductive carbonylation" reaction has served as the basis of a method of synthesis of selectively deuteriated vinyl[62] and aryl[63] oximes. For example, the reaction of the palladocycle (XLIV) with CO in solution in MeOD in the presence of $[D_5]$pyridine leads to the selective formation of the oxime of 8-deuterio-1-tetralone.[63] This method has advantages over the traditional procedure involving the reduction of $LiAlD_4$ in which the palladised oximes are reduced to amines:[64]



Carbonylation Conditions

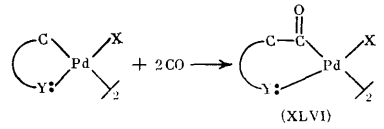
Depending on the nature of the initial palladocycle and the character of the products expected, the following solvents are used: benzene, chlorobenzene, xylenes, methanol, ethanol, water, and a xylene–aniline mixture. A wide range of carbon monoxide pressures are used: from simple bubbling with CO at atmospheric pressure to 150 atm. The reaction time and temperature are also varied within wide limits. The carbonylation is carried out under homogeneous and heterogeneous (when the solubility of the initial complex is low) conditions, sometimes in the presence of triphenylphosphine. It might have been supposed that PPh_3 is necessary to increase the solubility of the initial palladocycles as a result of the formation of soluble monomeric complexes of the type $[Pd(L-H)Cl(PPh_3)]$;[65] however, in a number of instances even homogeneous carbonylation does not take place in the absence of the PPh_3 [66,67] and the conversion of the acyl complex (XLV) into an ester in MeOH takes place only in the presence of $Ph_2PCH_2CH_2PPh_2$.[68] These examples show that phosphines can play an important role in the carbonylation process.



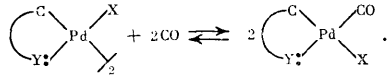
The Reaction Mechanisms

The kinetics of the carbonylation of cyclopalladated compounds have been investigated. The majority of the mechanisms of the interaction with CO postulated are based on the structure of the final products, i.e. the proposed schemes merely clarify the pathways leading to the formation of the final compounds. However, since the majority of similar stages with participation of CO have been thoroughly investigated for other related systems (see, for example, Refs.58, 59, and 69), the reaction mechanisms appear on the whole to be fairly convincing.

Evidently the key stage in all the reactions listed in Table 2 is the insertion of CO in the palladium–carbon σ-bond, which results in the formation of a six-membered cyclic acyl complex (XLVI).



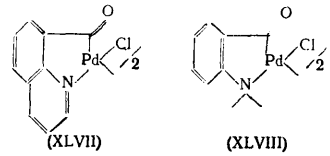
(16)



(17)

The insertion can be preceded by the equilibrium stage involving the rupture of the bridging ligands in accordance with Eqn.(17). Such monomeric cyclopalladated complexes with CO have been described for derivatives of certain oximes and 8-methylquinoline.[70–72] However, in these cases they are not converted further either into compound (XLVI) or into carbonylation products.

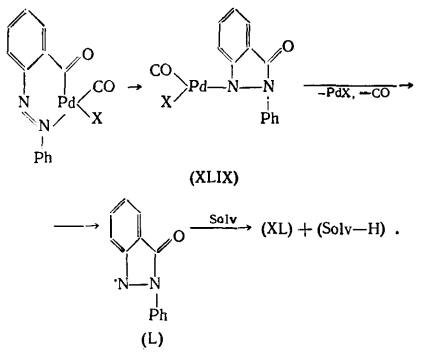
The five-membered acyl complexes (XLVII) and (XLVIII) are known and are obtained by the direct palladisation of the corresponding aldehydes on treatment with Na_2PdCl_4 in ethanol.[73] The reactions of the alkenes $RHC=CH_2$ ($R=H$, Me, or Et) with $PdCl_2(PhCN)_2$ in the presence of CO and diethylamine lead to the analogous complexes (XLV).[68,74] The increased stability of the complexes (XLV), (XLVII), and (XLVIII) can be accounted for by the presence of the stable five-membered palladocycle:



In particular, compound (XLV) undergoes further reactions only under special conditions[68] (see above). Six- and seven-membered acyl complexes of palladium(II) are significantly less stable and spontaneously enter into further reactions whose sequence is determined by the nature of the initial complex and the medium. Thus stage (16), which is common to all the complexes, is followed by processes typical for the compounds of the given type. We shall consider certain examples.

1. *Palladated azobenzenes.* At high CO pressures (up to 150 atm) in ethanol, 2-aryl-3-indazolinones (XL) are formed preferentially, apparently as a result of the intramolecular addition of the palladium–acyl fragment to the N=N double bond in the intermediate acyl complex, which leads to the amide complex (XLIX).[61] The latter can be converted into the final product (XL) either in the course of the protolysis of the Pd–N bond by ethanol or during

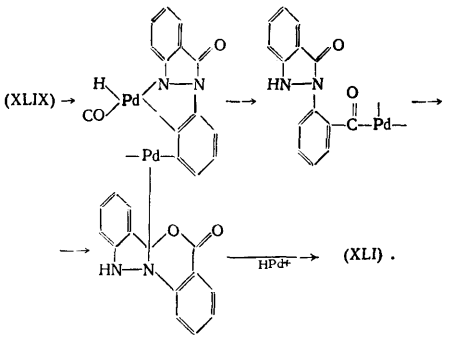
the "oxidative homolysis" of this bond with formation of the radical (L), which is capable of abstracting hydrogen from the solvent molecule. Examples of oxidative homolysis are well known. [75,76]



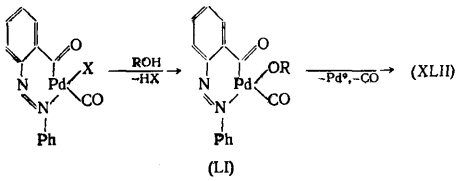
(XLIX)

(L)

The formation of the lactone (XLI), the product of the "double insertion" of CO, can be explained by the repeated palladation of the neighbouring aromatic ring. The key stage in this sequence of reactions is the intramolecular addition of acylpalladium to the carbonyl oxygen of the amide group. The subsequent 1,4-elimination of palladium hydride leads to a lactone (XLI):

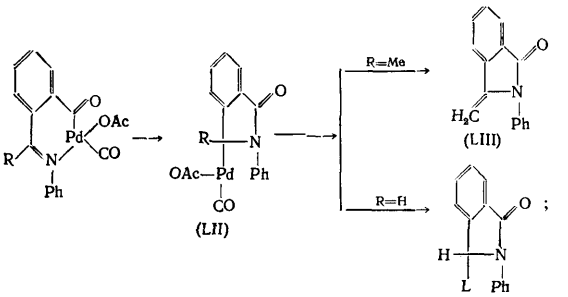


The esters (XLII) are formed as a result of the ethanolysis of compound (XL) [60] or, and we believe this to be more probable, in the course of the reductive decomposition of the complex (LI). We may note that compounds (XL) and (XLII) are also formed in the carbonylation of the analogous azobenzene complexes of platinum(II): [77]



(LI)

2. *Palladated Schiff bases.* The structure of the carbonylation products of these compounds (Table 2, Nos. 5–7) is determined by the presence of the azomethine double bond to which the palladium–acyl group adds. [60] The pathways leading to the further transformation of the σ-derivative (LII) depend on the nature of the substituent R at the C=N double bond and on the presence of an extraneous nucleophile. When R = H, palladium(II) is formally substituted by the nucleophile: by the acetoxy- or carboxy-group, when the reaction is carried out in an inert solvent or in alcohol respectively, and also by the PhNH group when the reaction is carried out in the presence of aniline. When R = Me, the reaction pathway changes and the alkene (LIII) is formed in the course of the 1,3-elimination of palladium:



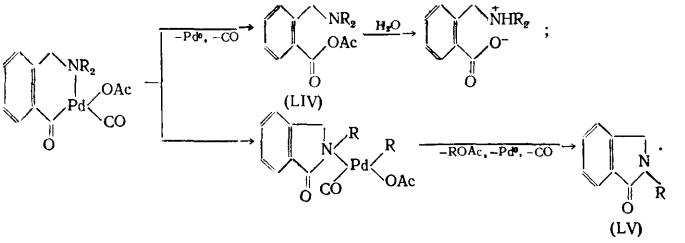
(LII)

(LIII)

L = OAc, OR', NHPh.

The carbonylation of other cyclopalladated complexes containing the N=N and C=N double bonds proceeds analogously to the carbonylation of azobenzene and azomethine derivatives. The principal stages considered above obtain in the reactions of other related complexes and, in conformity with the structure of the final carbonylation products, it is easy to determine the entire sequence of reactions of CO with the given specific palladocycle.

3. *Complexes of NN-dialkylbenzylamines.* Zwitter-ionic products (Table 2, No. 16) are formed in the hydrolysis of the mixed anhydrides (LIV). The formation of the phthalimidine (LV) is accompanied by the dissociation of the N–Me bond. It has been suggested [60] that the nitrogen–carbon bond is ruptured as a result of the 1,2-alkyl shift from nitrogen to palladium. It is of interest that the formation of compound (XXXVI) examined above can involve exactly the same mechanism.

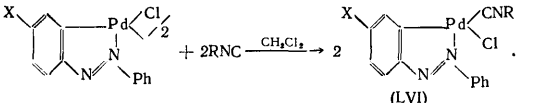


(LIV)

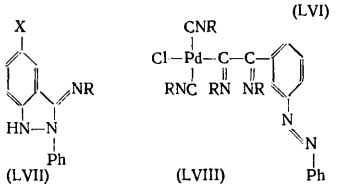
(LV)

VI. REACTIONS WITH ISOCYANIDES AND CARBON DIOXIDE

The reactivity of the isocyanides (CNR) with respect to the transition metal–carbon bond [78] is in many respects analogous to that of carbon monoxide, which is isoelectronic with isocyanides. Under mild conditions, isocyanides, taken in stoichiometric amounts, react [79] with dimeric o-palladised derivatives of azobenzenes, forming the monomeric complexes (LVI):



(LVI)



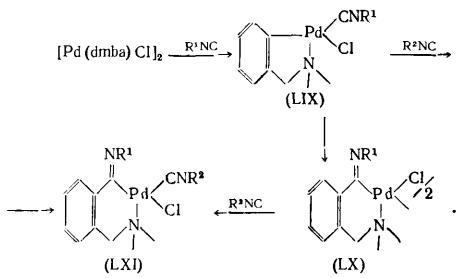
(LVII)

(LVIII)

X = H, OMe; R = Bu-t, C_6H_{11}, C_6H_4Me-o

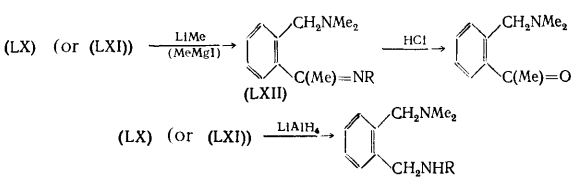
Heating of compounds (LVI) in toluene (at 100–130 °C) leads to 3-imino-2-phenylindazolines (LVII) in 67–90% yields and the process involves the reduction of palladium(II) to zero-valent palladium. The product (LVII) is not formed in the reaction with an excess of *o*-tolyl isocyanide and the complex $[Pd(C_6H_4N{=}NPh)(o\text{-}MeC_6H_4NC)_4Cl]$ is obtained.[79] A similar product has been isolated[80] in the interaction of an excess of cyclohexyl isocyanide with di-μ-chlorobis(azobenzene-C^2,N)dipalladium(II), i.e. $[Pd(azb)Cl]_2$ or $[Pd(C_6H_4N{=}NPh)Cl]_2$. It has been suggested[80] that two molecules of the isocyanide are inserted during the reaction in the Pd–C bond, which results in the formation of compound (LVIII).

The interaction of $[Pd(dmba)Cl]_2$ with isocyanides[81] is presented schematically below:

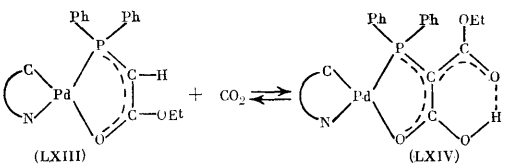


Treatment of the initial complex with a stoichiometric amount of *o*-tolyl isocyanide affords the monomer (LIX). When compound (LIX) is heated in tetrahydrofuran (THF), the coordinated isocyanide is inserted intramolecularly in the Pd–C bond with formation of the iminoacyl complex (LX). The monomer (LIX) can react with an isonitrile of another type with formation of compound (LXI). The ease of insertion of the isocyanides CNR as a function of the nature of the substituent R diminishes in the sequence *o*-tolyl > phenyl > t-butyl. This series shows that the reactivity of the isocyanide is determined by electronic and not steric factors.[81]

The new six-membered iminoacyl palladocycles (LX) and (LXI) are obtained in high yields and this has stimulated their employment as important intermediates for the synthesis of a number of *ortho*-substituted compounds. In particular, the reaction with methyl-lithium or methyl-magnesium iodide leads to the Schiff bases (LXII),[81] whose acid hydrolysis gives rise to the corresponding ketones and reduction with $LiAlH_4$ affords the corresponding diamines:

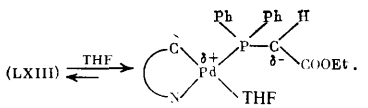


Instances of the insertion of CO_2 in the Pd–C bond in cyclopalladated complexes have not so far been described in the literature. Nevertheless, it is useful to consider one interesting reaction of carbon dioxide. It has been shown recently that the complexes (LXIII) are capable of binding CO_2 reversibly.[82,83] Bubbling of dry CO_2 through their solutions in THF for several seconds leads to the insertion of CO_2 in the PC–H bond and the formation of new complexes of type (LXIV) in which chelation via the oxygen atom of the ester has been replaced by chelation via an oxygen atom of carbon dioxide:



C N = benzyldimethylamine (a) or 8-methylquinoline (b)

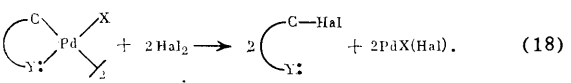
The structure of one of these complexes (LXIVb) has been established by X-ray diffraction.[83] The addition of CO_2 is fully reversible: the initial complex (LXIII) is reformed in a stream of argon and the process can be repeated several times. Despite the fact that the palladocycle is not involved directly in the reaction, in its absence, for example in the case of *cis*-$Pt[Ph_2PCHC(O)OEt]_2$, there is no binding of CO_2. It is believed[83] that the strong *trans*-influence of the σ-linked carbon of the metallocycle has a labilising effect on the Pd–O bond and the carbanionic carbon atom of the reactive 1,3-dipolar form of the complex attacks a carbon dioxide molecule:



VII. HALOGENATION

The reactions of halogens with aromatic hydrocarbons as a rule lead preferentially to *para*-substituted aryl halides.[84] The use of *ortho*-metallated complexes makes it possible to alter radically the halogenation selectivity of and to obtain *ortho*-substituted compounds exclusively.

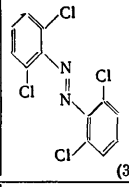
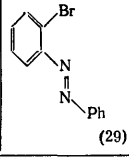
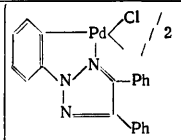
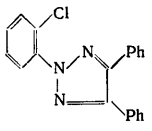
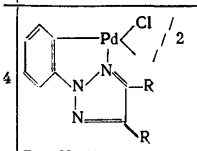
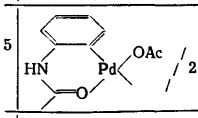
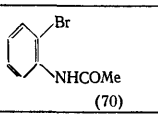
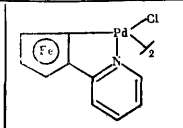
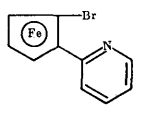
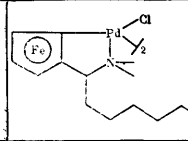
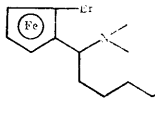
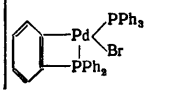
Examples of the action of halogens (Cl_2, Br_2) on cyclopalladated complexes are summarised in Table 3. The reactions proceed in conformity with the equation



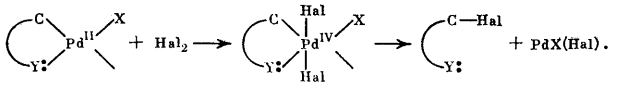
The solvents are aqueous dioxan, methylene chloride, and chloroform. Palladium(II) is not reduced during the reaction. As a result, repeated palladation of the halogenated ligand is possible, which is the cause of the appearance of the 2,6,2′,6′-tetrachloroazobenzene.[85,86] When the reaction time is reduced, 2-chloro-, 2,6-dichloro-, and 2,6,2′-trichloro-azobenzenes are obtained. In contrast to chlorination, polysubstituted products are not formed on bromination.[86]

Only palladium(II) complexes enter into a reaction of type (18). Di-μ-chlorobis(azobenzene-C^2,N)diplatinum(II) is resistant to the action of halogens and the Pt–C bond is not ruptured.[86] In the interaction with halogens of other cyclometallated complexes of platinum group metals, in particular iridium(III) and rhodium(III),[87–89] only the C–H bonds of the metallocycles are chlorinated or brominated, while the M–C bonds remain unchanged. For example, the chlorination of the doubly metallated complex $\{IrCl[P(OC_6H_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)](PEt_3)_2\}$ proceeds with formation of $\{IrCl[P(OC_6Cl_3Me\text{-}o)_2(OC_6H_4Me\text{-}o)](PEt_3)_2\}$.[89]

Table 3. Halogenation of cyclopalladated complexes.

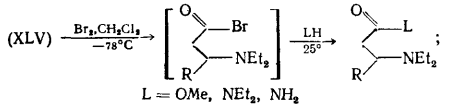
No.	Complex	Halogen	Product (yield, %)	Solvent	Refs.
1	$[Pd(azb)Cl]_2$	Cl_2	 (39)	water–dioxan	[86]
2	То же	Br_2	 (29)	ditto	[86]
3		Cl_2	 (60)	ditto	[129]
4	 R = H, Me	Cl_2	mixture of mono-, di-, and poly-chlorinated products	ditto	[129]
5		Br_2	 (70)	CH_2Cl_2	[36]
6		Br_2	 (35)	$CHCl_3$	[36]
7		Br_2	 (43)	CH_2Cl_2	[29]
8		Br	$\{PdBr_2[PPh_2(C_6H_4Br)]_2\}$, $PdBr_2(PPh_3)_2$	PhH	[91]

The mechanism of the halogenation of palladocycles has not been specially investigated. It may be that the reaction proceeds via the oxidative addition of the halogen to palladium(II) with formation of an octahedral palladium(IV) complex (see, for example, Murenik and Pross[90]), while reductive elimination affords the final products:



The mechanism involving the electrophilic attack by the halogen directly on the palladium–carbon bond might serve as an alternative.

The bromination of acyl derivatives of the palladocycles (XLV) is used to synthesise amides and esters.[68] The intermediate acyl bromides are not isolated; the yield of the final reaction products is quantitative.



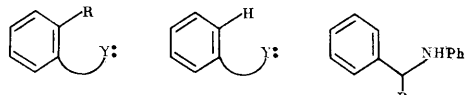
L = OMe, NEt_2, NH_2

Fenton[91] demonstrated the possibility of the chlorination of palladocycles by CCl_4. He obtained the complex $[Pd(o\text{-}ClC_6H_4PPh_2)(PPh_3)Cl_2]$ with an *ortho*-chlorinated ligand from the complex $[Pd(C_6H_4PPh_2)Cl(PPh_3)]$ with a four-membered ring.

Examples of the effective iodination of palladocycles are so far lacking. A report of the possibility of the iodination of dimethylaminomethylferrocene has been reported recently,[92] but the reaction conditions and yields of products are not indicated.

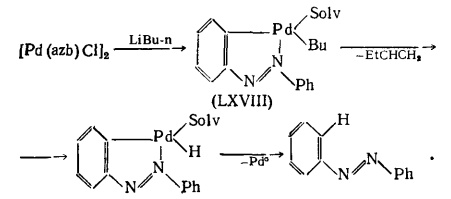
VIII. ALKYLATION, ACYLATION, AND PHOSPHINATION

The *ortho*-alkylated products of the general type (LXV) have been obtained in yields of 22–76% by treating $[Pd(azb)Cl]_2$, $[Pd(dmba)Cl]_2$, and $[Pd(ba)Cl]_2$ with organolithium compounds of the type LiR, where R = Me or Ph, in ether at 0–5 °C.[93,94] The free ligands (LXVI) are formed as side products (up to 38%), while in the case of the benzylideneaniline derivative, compound (LXVII) is formed in addition.



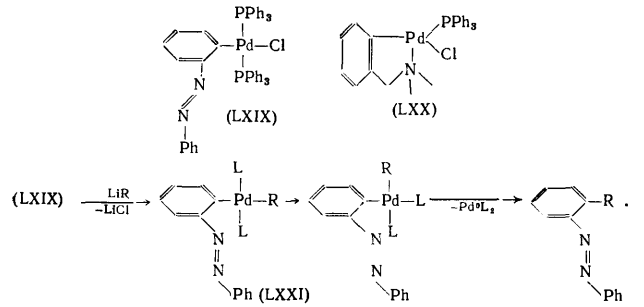
(LXV) (LXVI) (LXVII)

If the group R in the organolithium compound contains β-hydrogen atoms, then the fraction of the reduction products (LXVI) increases significantly. In particular, in the reaction of LiBu-n with $[Pd(azb)Cl]_2$ the yields of compounds (LXV) and (LXVI) are 5 and 89% respectively and in the case of $[Pd(ba)Cl]_2$ the yields of compounds (LXV) and (LXVII) are 1 and 64% respectively. The appearance of reduction products in large amounts when the hydrocarbon group R contains a β-hydrogen atom is associated with the intermediate formation of hydride complexes,[94] whose decomposition leads to compounds (LXVI).



In those cases where the group R contains no β-hydrogen atoms, the possibility of the homolysis of the Pd–C bond in the initial complexes has been postulated[94] to account for the formation of compounds (LXVI), although cyclopalladated compounds show no tendency towards spontaneous homolytic decomposition. From our point of view, it is more likely that in this case the homolysis is induced by the groups R

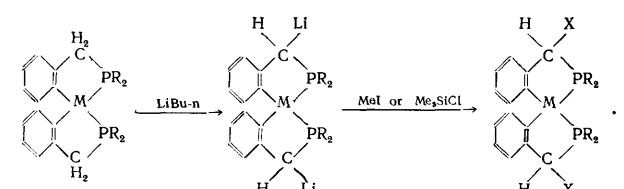
in the intermediate aryl-alkyl or aryl-aryl complex of type (LXVIII). The stability of such compounds increases in the presence of phosphine ligands and it has been found, in conformity with this fact, that the formation of side products in the alkylation of palladocycles is suppressed in the presence of PPh_3; the yields of compound (LXV) increase to 90%.[94] The optimum results are obtained for the ratio $PPh_3 : Pd = 4$. Under these conditions, $[Pd(azb)Cl]_2$ and $[Pd(dmba)Cl]_2$ exist in the forms (LXIX) and (LXX) respectively.[95,96] The mechanism of the alkylation reaction [in relation to compound (LXIX) with $L = PPh_3$] involves the formation of compound (LXXI),[94] its *trans–cis* isomerisation, and reductive elimination:[97,98]



Other phosphorus-containing ligands, for example $P(Bu\text{-}n)_3$, $Ph_2PCH_2CH_2PPh_2$, and $P(OPh)_3$, are less effective as inhibitors of side processes than PPh_3. Apart from organolithium compounds, the Grignard reagents MeMgBr, PhMgBr, and $H_2C=CHMgBr$ have been used. In the last case *o*-substituted arylolefins, analogous to those obtained in the reactions of palladocycles with alkenes (see Section III), are formed.[94]

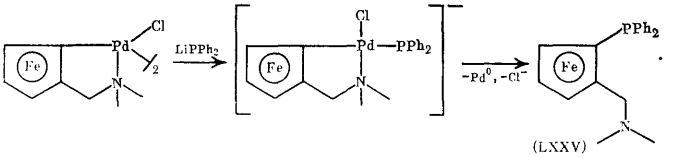
The alkylation of $[Pd(ba)Cl]_2$ by secondary organolithium compounds leads to compounds (LXV) in low yields even in the presence of PPh_3 and is accompanied by the secondary–normal isomerisation of the alkyl group.[99] We may note that the "double" alkylation of $[Pd(ba)Cl]_2$, i.e. the repeated palladation of compound (LXV) and treatment with LiR followed by the acid hydrolysis of the reaction products, leads to 2,6-disubstituted aromatic aldehydes which are difficult to obtain by other methods.[94] Treatment of palladised 2-pyridylferrocene in benzene with LiBu-n and LiPh afforded o-substituted products in yields of 34 and 27% respectively.[66] The alkylation of the iminoacyl complexes (LX) and (LXI) was considered above.

The interaction of n-butyl-lithium with the complexes (LXXII) proceeds via a different pathway.[100] The M–C bond is not then involved, the methylene groups of the complexes being substituted by lithium. Treatment of compound (LXIII) with methyl iodide or trimethylsilyl chloride results in the modification of the cyclometallated ligands in the complexes (LXXIV):

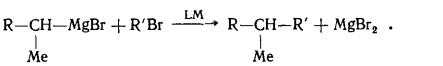


M = Pd, Pt; R = Me, Ph;
X = Me, Me_3Si

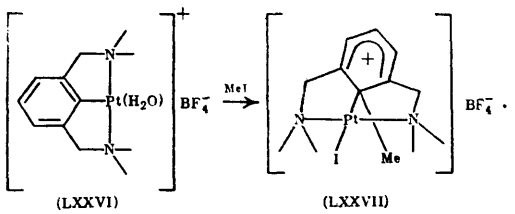
The phosphination of palladocycles is on the whole carried out analogously to alkylation, but in this case the complex is treated with $LiPPh_2$.[101] If the initial cyclopalladation of the substituted ferrocene is carried out asymmetrically, then the enantiomeric ligand (LXXV) with planar chirality is formed:



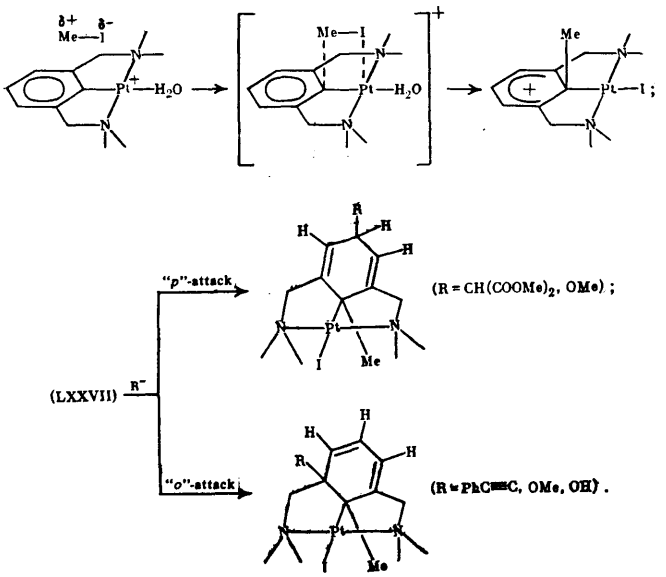
Such ligands have found extensive applications, particularly in the asymmetric cross-coupling reactions of Grignard reagents and organic halogeno-derivatives catalysed by palladium and nickel complexes.[102,103] The highest stereoselectivity is ensured when the ligands L contain elements of planar chirality.[103]



Direct alkylation of cyclometallated complexes by alkyl halide is so far known for platinum(II) complexes.[104] The reaction of compound (LXXVI) with an excess of methyl iodide in acetone leads to the unusual product (LXVII) whose structure has been established by X-ray diffraction. The central atom of the complex had a slightly distorted square-planar configuration, while the aryl ligand has the boat form.

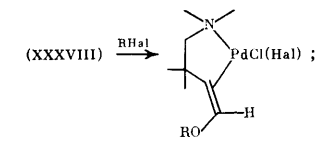


The addition of MeI is reversible: in the presence of NaX (X = Cl, Br, or I) the product is $\{PtX[C_6H_3(CH_2NMe_2)_2\text{-}oo']\}$ in aqueous solutions, while the initial complex (LXXVI) is regenerated in boiling water or aqueous acetone solution. An excess of NaCN decomposes the complex (LXXVII) with formation of $oo'\text{-}(Me_2NCH_2)_2C_6H_3Me$.[105] It is most likely that the mechanism of the formation of compound (LXXVII) involves the direct addition of methyl iodide to compound (LXXVI):[104]



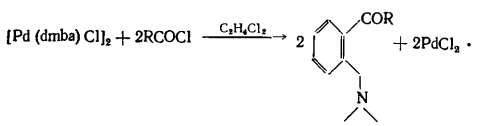
The cationic complex (LXXVII) gives rise to *para*- and *ortho*-addition products on reaction with the strong bases $CH(COOMe)_2^-$, $PhC \equiv C^-$, MeO^-, and HO^-.[105] Depending on the reaction conditions, the "*para*"- or "*ortho*"-attack may be made to predominate. Treatment of these complexes with powerful non-coordinating acids (except for $R = PhC_2^-$) leads to a high yield of the initial compound (LXXVII).

In the interaction of compound (XXXVIII) with allyl bromide and benzyl chloride the hydrocarbon fragment attacks the carbonyl oxygen atom of the complex, which results in the formation of a complex without a palladium–carbon σ-bond:[54]

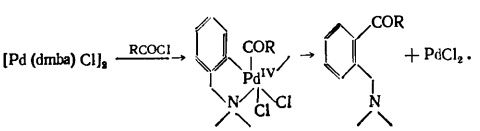


$R = CH_2CH{=}CH_2, CH_2Ph$; Hal = Cl, Br.

The acylation of dimers of type $[Pd(dmba)Cl]_2$ leads to aryl ketones:[106]



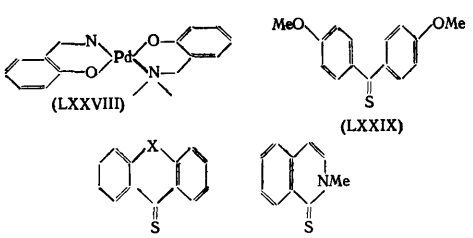
On the one hand, acyl and benzoyl chlorides and, on the other, unsubstituted *ortho*-palladised *NN*-dialkylbenzylamines as well as their analogues with electron-donating substituents enter into the reaction. The yields of aryl ketones are 25–93%. Palladocycles with a chlorine atom in the ring are unreactive. The acylation mechanism[106] involves oxidative addition with the intermediate formation of palladium(IV) and the subsequent reductive elimination of palladium(II) chloride:

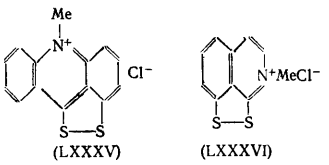


The interaction of palladocycles with acyl halides has also been described by Clark et al.[107]

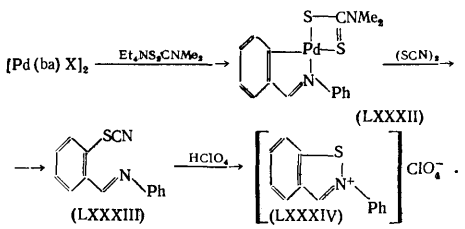
IX. OTHER REACTIONS

The anodic oxidation of $[Pd(azb)OAc]_2$ and $[Pd(dmba)OAc]_2$ does not result in the formation of any isolatable organic products.[108] On the other hand, the oxidation of $[Pd(dmba)Cl]_2$ with *m*-chloroperbenzoic acid in methylene chloride at 0 °C followed by treatment with $NaBH_4$ in methanol leads to a palladium(II) complex of salicylaldimine (LXXVIII) in 35% yield.[109]





Cyclopalladation is a key stage in the syntheses of derivatives of isothiazoles and 1,2-dithiols[110] from metallated benzylideneaniline, 2-pyridylbenzene, benzo[*h*]-quinoline, and the sulphur-containing arenes (LXXIX)–(LXXXI). The pathway leading to isothiazoles is illustrated below using as an example the reaction of palladised benzylideneaniline. The initial complexes are treated with tetraethylammonium *NN*-dialkyldithiocarbamate, which converts them into the monomers (LXXXII):



On treatment with thiocyanogen in chloroform, the latter give rise to the thiocyanates (LXXXIII) and the very sparingly soluble complex $[Pd(Me_2NCSS)SCN]_2$. Compounds (LXXXIII) are stable only in the case of 2-pyridylbenzene and benzo[*h*]quinoline, but treatment of even unstable intermediates with perchloric acid leads to isothiazoles of type (LXXXIV). In the case of compounds (LXXXb) and (LXXXI) best results are achieved when the analogues (LXXXII) react with *N*-sulphenylmorpholine chloride, which results in the formation of the 1,2-dithiols (LXXXV) and (LXXXVI). The yields of isothiazoles and 1,2-dithiols are 25–90 and 81–91% respectively.

A pathway to *ortho*-deuteriated aromatic ketones has been proposed by Alper.[111] Refluxing of the *ortho*-palladated compounds (LXXIX) and $O{=}C(C_6H_4Me\text{-}p)_2$ in MeOD for 18 h leads to $O{=}C(C_6H_4X\text{-}p)(C_6H_4D\text{-}o\text{-}X\text{-}p)$, where X = OMe or Me, in yields of 82 and 84% respectively. The transamination of complexes of Schiff bases has been described.[112]

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The reactions considered indicate the extensive possibilities of the application of cyclopalladated compounds and also the related complexes of other transition metals in organic sythesis. Their use is of greatest interest in the preparation of organic compounds which are difficult to obtain by other procedures and also of enantiomeric and diastereoisomeric molecules. Bearing in mind that chiral palladocycles are also used for the separation of racemates, for example, those of tertiary phosphines,[113,114] one may hope that this field of chemistry, which is developing at the frontier between organic and organometallic chemistry as well as metal complex catalysis, will undergo further natural development.

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