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General Principles and Characteristics of Cyclopalladation Reactions

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The factors influencing the ease and mode of the reactions involving the direct intramolecular cyclopalladation of organic ligands at sp^2- and sp^3-carbon atoms are analysed and the principal requirements which must be met by the structure of the ligand, the characteristic features of the coordination intermediates, and the experimental reaction conditions are considered. The bibliography includes 232 references.

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I. INTRODUCTION

Cyclometallated complexes containing a comparatively reactive carbon–metal σ-bond stabilised by the additional coordination of the metal to a heterodonor atom of the same ligand are of great interest from several points of view. In the first place, cyclometallation processes are important as one of the ways of solving the most important current problems—that of the activation of the C–H bonds by transition metal compounds.[1,2] The study of the structures of stable cyclometallated complexes, which can be regarded as "frozen" intermediates in metal-catalysed chemical reactions, is a valuable source of information about the mechanisms of such catalytic processes.[3–5] The wide range of reactions with participation of cyclometallated compounds already known, which proceed with notable regio- and stereo-selectivity, leads to extensive possibilities for their synthetic application.[6–8] The cyclometallated compounds obtained in an optically active form can be used both for the synthesis of other chiral molecules,[9–12] and for the resolution of substrates with ligand properties,[13–18] and for the estimation of their optical purity.[19,20] Some of the cyclometallated complexes proved to be useful because of their liquid–crystal properties[21] or their high biochemical activity,[22,23] while others can be used to introduce heavy-atom and fluorescent labels into proteins and polypeptides.[24]

Since the synthesis of the first cycometallated complexes,[25] an enormous number of compounds of this class have been obtained (mono-, bi-, and tri-cyclic, mono-, di-, and trinuclear, and mono-, bis-, and tris-chelate) with metals having different electronic configurations (Pd, Pt, Ni, Rh, Ir, Ru, Re, Mn, Sn, etc.) and on the basis of a wide variety of ligands containing N, P, S, As, or O atoms as the heterodonors with M–C(sp^3) or M–C(sp^2) bonds involving an aliphatic, aromatic, olefinic, or acyl carbon atom; the complexes in which the M–C σ-bonds are stabilised by additional π-coordination can be formally also included in this class of compounds. A detailed discussion of each group of cyclometallated compounds is not of interest, especially since this has partly been done in review articles published previously,[26–42] which deal predominantly with data up to 1981. The analysis of the general principles of cyclometallation, which in the present review has been carried out in relation to the direct intramolecular cyclopalladation of ligands with heterodonor centres, is in our view of greater current interest.

Among all the known methods of synthesis of cyclopalladated complexes (CPC),[26] the direct palladation of a ligand coordinated beforehand via the heteroatom is the simplest and most convenient:



The terms "cyclopalladation"[43] or "*ortho*-palladation"—in the specific case of reactions involving the *ortho*-position in the aromatic ring of the ligand[44,45] were used to designate reactions of this type.

The ease and in many cases the very possibility of carrying out such processes depend on the structural features of the ligand and the intermediate coordination compounds and on the nature of the palladating agent and the reaction conditions. We have considered these factors in the present review.

II. PRINCIPAL REQUIREMENTS FOR THE STRUCTURE OF THE LIGAND

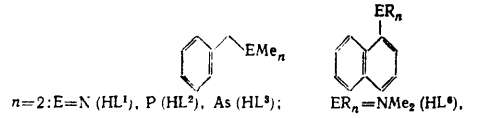
In order that the direct cyclopalladation of a particular ligand should be possible, its structure must satisfy a number of requirements concerning the nature of the heteroatom and its basicity, the possible size of the metallocycle, and the steric arrangement at the donor and metallated atoms within the chelate ring formed and outside it.

1. The Role of the Heteroatom

One of the necessary conditions for the successful palladation of a particular organic compound is the presence in the latter of a donor atom "directing" the reaction.[43,45–47] The formation of a transition metal–carbon σ-bond by direct metallation (without the preliminary coordination to the heteroatom) takes place in rare cases and is not characteristic of palladium. Intramolecular coordination to the heteroatom stabilises the C–Pd bond; the chelate effect is quite important in this connection. For example, the intramolecular cyclopalladation of azobenzene is 4×10^4 times faster than the intermolecular reaction of $PdCl_2$ with benzene;[48] the acceleration effect is associated with chelation via the azo-group, which converts the reaction from an intermolecular process to an entropically more favourable intramolecular process.

Preliminary coordination of the ligand to the transition metal atom is usually regarded as the first stage in the cyclometallation process.[45,48–51] It is therefore natural that the nature of the heteroatom should have a direct influence on the course of the reaction, which has in fact been confirmed by a whole series of facts.

The replacement of one heteroatom by another within the limits of the same general structure of the substrate can alter sharply its tendency to undergo cyclopalladation. For example, ligands of the types presented below form cyclopalladated complexes fairly readily (with $PdCl_4^{2-}$) only in the presence of a donor nitrogen atom—(HL^1) and (HL^6):[45,52–54]

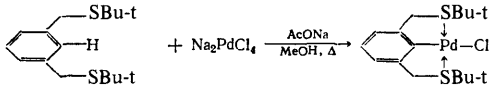


n=2:E=N (HL^1), P (HL^2), As (HL^3); n=1:E=O (HL^4), S (HL^5)

ER$_n$=NMe$_2$ (HL^6), PMe$_2$ (HL^7), SBu (HL^8)

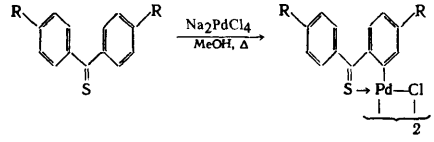
In the case of the dimethylphosphines (HL^2) and (HL^7) and arsine (HL^3), cyclopalladation does not occur and only coordination compounds of the type $[PdCl_2(HL)_2]$ are formed.[55–57] The introduction of oxygen, as in (HL^4), or sulphur, as in (HL^5) and (HL^8), as the donor atom also fails to stimulate metallation;[43,47,58] the thioether (HL^8) forms only a coordination compound. In their analysis of the failure of the attempts at the cyclopalladation of another *S*-donor ligand, namely benzyl phenyl sulphide, Takahashi et al.[59] concluded that the coordination of sulphur to palladium is so strong (compared with the analogous *N*-donor ligands) that it inhibits the further electrophilic substitution in the benzene ring under the influence of palladium(II). However, one should note that, when certain structural requirements and/or experimental conditions (see below) are observed, CPC based on phosphines[37] and thioethers[60,61] can be obtained.

In particular, the cyclopalladation process can be stimulated by doubling the number of thioether donor groups activating the *ortho*-position,[62,63] as happens, for example, in 1,3-di(*t*-butylthiomethyl)benzene:[63]



We may note that the monodentate analogue of this ligand is not metallated under the same conditions.

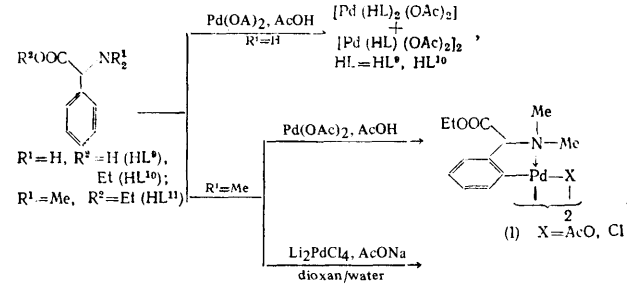
The degree of hybridisation of the donor atom has a significant influence on the ease of cyclopalladation. Thus, in contrast to the majority of thioethers (with the sulphur atom in the sp^3-hybrid state), which form only simple coordination compounds in the reactions with $PdCl_4^{2-}$ in methanol even on refluxing, thioketones[64–66] and thioamides[67–69] (containing a sulphur atom in the sp^2-hybrid state) undergo metallation comparatively readily under the same conditions. For example, CPC based on diaryl thioketones have been obtained:[66]



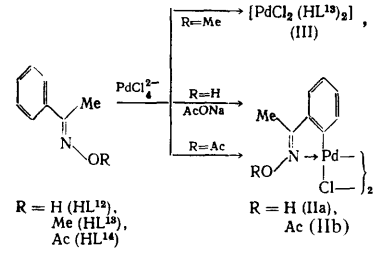
R=Me, MeO

The modification of the basicity of the initial ligand by altering the nature of the substituents at the heteroatom can also be significantly reflected in the rate and mode of the cyclopalladation reaction. For example, in view of the different reactivities of primary, secondary, and tertiary benzylamines, it has been suggested that the stronger *N*-coordination of the primary and secondary amines compared with the tertiary amine weakens the electrophilic properties of the metal to such an extent that this prevents the attack on the aromatic ring.[45]

Partly, for the same reason, it has not been possible to introduce into the *ortho*-palladation reaction either *C*-phenylglycine (HL^9) itself or its ethyl ester (HL^{10}), both containing a primary amino-group, while the *NN*-dimethyl derivative of the latter (HL^{11}) forms the CPC (I) both with palladium(II) acetate and with Li_2PdCl_4:[70,71]



This conclusion has also been confirmed by the comparative analysis of the reactivities of acetophenone oxime (HL^{12}), its *O*-methyl derivative (HL^{13}), and its *O*-acetyl derivative (HL^{14}) in the cyclopalladation reaction. The unsubstituted oxime (HL^{12}) undergoes *ortho*-palladation in the presence of sodium acetate with formation of compound (IIa), while its *O*-methyl analogue affords only the coordination compound (III) under these conditions:

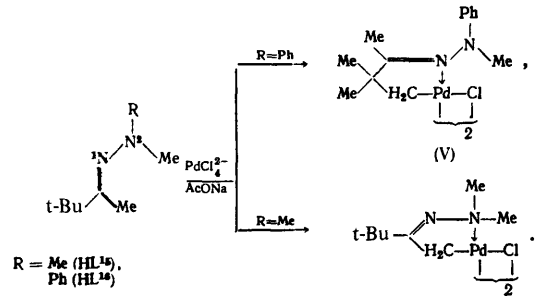


R = H (HL^{12}), Me (HL^{13}), Ac (HL^{14})

R = H (IIa), Ac (IIb)

The authors explained this by the fact that the stronger coordination of (HL^{13}) to palladium(II), induced by the presence of the electron-donating Me group, reduces the formal charge on Pd(2+), preventing the electrophilic attack by the latter on the aromatic ring. On the other hand, (HL^{14}), in which the coordinating capacity of the nitrogen atom is reduced owing to the introduction of the electron-accepting acetyl group, forms the *ortho*-palladised complex (IIb) even in the absence of a base.[72]

The study[73] of the causes of the regiospecificity of the cyclometallation of a number of hydrazones of aliphatic ketones provides a striking example of the influence of the comparative basicities of the heterodonor centres on the mode of cyclopalladation. In particular, it has been shown that the metallation of pinacolone dimethylhydrazone (HL^{15}) takes place at the methyl group attached to the azomethine fragment with coordination of the metal via the N(2) aminonitrogen atom [compound (IV)], which is unusual for hydrazones:

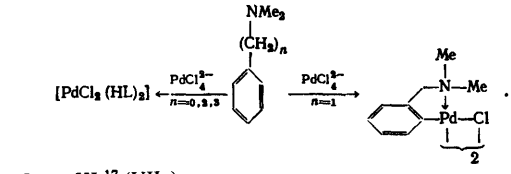


However, the introduction of the phenyl substituents at the N(2) atom, as in (HL^{16}), reduces its basicity (and hence its coordinating capacity), as a result of which the coordination of the metal via the azomethine N(1) atom becomes more favourable and, as a consequence of this type of preliminary coordination, the metallation of (HL^{16}) takes place at the methyl group in the t-Bu fragment [compound (V)].

Thus the presence of the heteroatom in the ligand is important for the stabilisation of the CPC formed, while the nature and the electron-donating properties of the heterocentre influence significantly both the reactivity of the metal and the mode of cyclopalladation.

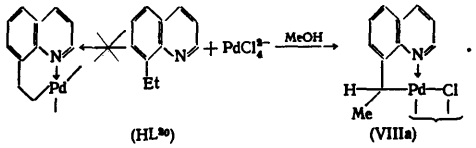
2. The Size of the Metallocycle

A clear-cut tendency towards the formation of a five-membered metallocycle is exhibited in the reactions involving the direct intramolecular cyclopalladation of the majority of organic ligands investigated. For example, in the series of amines of the type $Ph(CH_2)_nNMe_2$ (n = 0–3), only benzylamine (HL^1) is cyclopalladated, forming in this process the five-membered chelate ring (VIa);[45] the remaining ligands (HL^{17})–(HL^{19}) form only the simple coordination compounds (VIIIa–c):

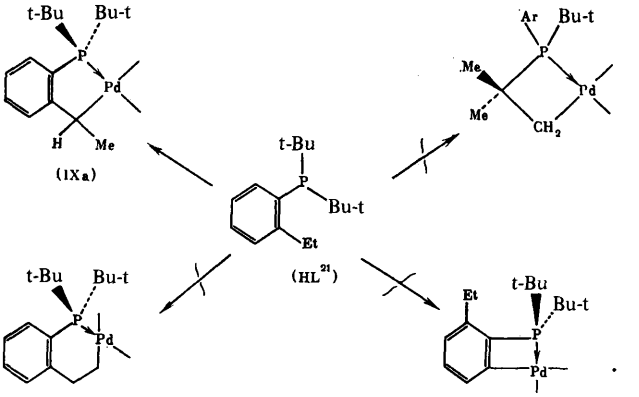


HL = HL^{17} (VIIa), HL^{18} (VIIb), HL^{19} (VIIc); n = 0 (HL^{17}), 1 (HL^1), 2 (HL^{18}), 3 (HL^{19})

In systems where there is a possibility of a choice between several modes of metallation, those leading to a five-membered metallocycle are as a rule realised. The dimeric CPC (VIIIa)[74–76] with a five-membered and not a six-membered metallocycle is formed in the palladation of 8-ethylquinoline (HL^{20}), despite the fact that a primary carbon atom is metallated more readily than a secondary carbon atom:[76]

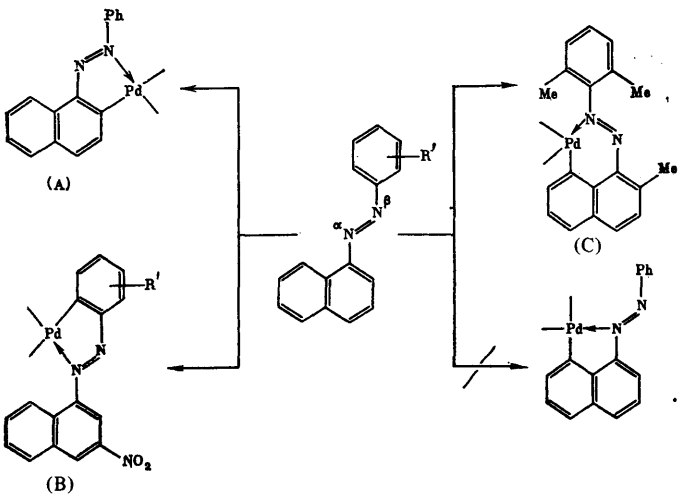


An analogous tendency has been observed also for *P*-donor ligands.[56,77,78] For example, several reaction pathways are possible for the cyclopalladation of the tertiary phosphine (HL^{21}): at the methyl group of the t-Bu fragment or in the free *ortho*-position in the benzene ring (with formation of four-membered metallocycles in both cases) and also the methyl or CH_2 group of the *ortho*-Et substituent (with formation of six- or five-membered rings respectively):



Despite the fact that the cyclopalladation at a secondary aliphatic carbon atom is more difficult than at a primary carbon atom (see below) or in an aromatic ring, the structure (IXa) with a five-membered metallocycle is produced in the experiment.[77]

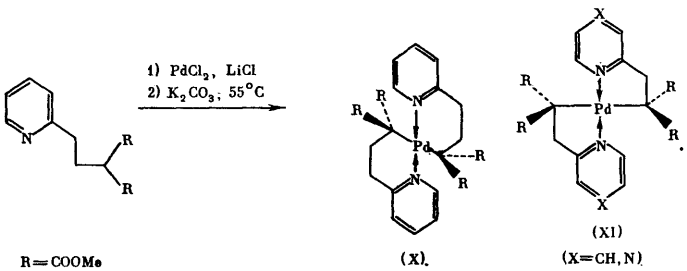
A marked tendency towards the formation of five-membered rings has been observed in a study of the behaviour of 1-arylazonaphthalenes under the conditions of the *ortho*-palladation reaction.[79–81] For ligands of this type, four versions of the closure of the metallocycle are possible, in principle, as a result of the presence of two donor nitrogen atoms and two aromatic rings suitable for metallation. In the absence of blocking groups, the reaction takes place preferentially via the C(2) atom of the naphthalene ring (A)[79] because of the greater accessibility of the N^{β} atom for preliminary coordination to the metal and the greater nucleophilicity of the naphthalene ring compared with the benzene ring; when strong electron-accepting substituents (the 3-NO_2 group) are introduced into the naphthalene ring and electron-donating substituents are introduced into the benzene ring, palladation at the benzene ring (B) becomes possible as a result of the change in the section involved in the preliminary coordination; a five-membered metallocycle is formed in both cases:



Only after the complete blocking by the methyl groups of all the sections suitable for the formation of five-membered rings (the 2′- and 6′-positions in the benzene ring and the 2-position in the naphthalene ring) is it possible to achieve

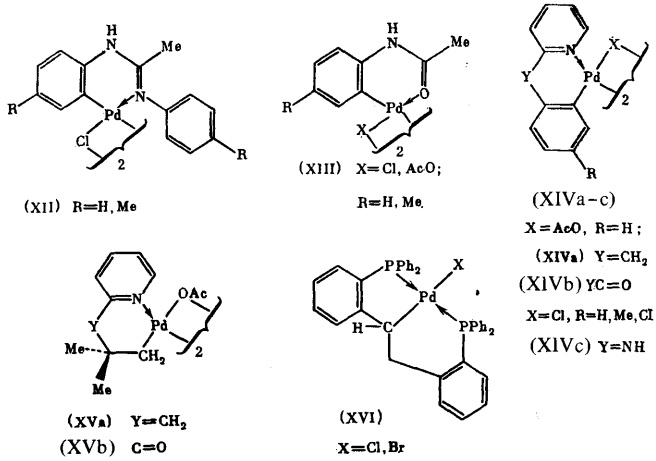
palladation in the *peri*-position in the naphthalene ring with formation of the six-membered metallocycle (C);[80] the involvement of the N^{β} atom in the structure (C) in coordination with the metal has been confirmed with the aid of ^{15}N NMR.[81]

It had been postulated earlier that the tendency by metals preferring the square-planar coordination to form five-membered metallocycles is associated with the necessity to maintain the ligand–metal–carbon intrachelate angle at a value near 90°.[82] The accumulated experimental data seem to confirm this "theory of five-membered rings". However, a recent comparison, based on X-ray diffraction analysis (XRA), of the structural features of complexes with five-membered[83,84] and six-membered[85] rings exhibiting the maximum structural similarity showed that the six-membered metallocycles can readily adjust to the requirement for a square planar environment of the metal; such complexes exhibit no unfavourable interactions and are obtained under the same conditions and with the same yields as their five-membered analogues.[85] The increase in the N–Pd–C intrachelate angle in structures of type (X) compared with (XI) is not accompanied by an appreciable loss of stability by the bis-chelates:[83-85]



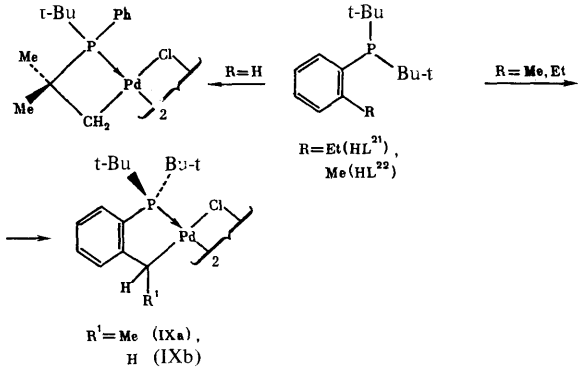
Fairly numerous CPC with six-membered metallocycles, based on different classes of ligands with N, O, and P donor atoms and obtained by the palladation at both sp^2- and sp^3-carbon centres, are known at the present time. Such complexes have been obtained from *N*-arylamidines (XII),[86] acid *N*-arylamides (XIII),[86-88] 2-benzylpyridine (XIVa),[89,90] 2-benzoylpyridine (XIVb),[90,91] 2-anilinopyridine (XIVc),[92] 2-neopentylpyridine (XVa),[93] 2-pivaloylpyridine (XVb),[94] and 2,2′-bis(diphenylphosphino)bibenzyl (XVI).[95,96]

It is noteworthy that in all the cases presented above the formation of six-membered metallocycles is enforced, since the ligand structures do not provide more favourable alternatives.

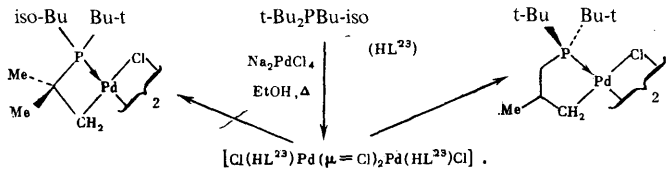


Four-membered metallocycles are also known—they are formed as a result of the direct intramolecular cyclopalladation of certain phosphines containing the t-butyl group.[97-100]

Nevertheless, here too the reaction pathway is enforced. When there is a possibility of the formation of a five-membered ring for ligands of this type, as happens, for example, in the case of (HL^{21})[77] or (HL^{22}),[78,101] the more favourable structure (IXa) or (IXb) respectively is in fact produced:



The cyclopalladation of di-t-butylisobutylphosphine (HL^{23}) also results in the formation of a five-membered and not a four-membered metallocycle:[102]



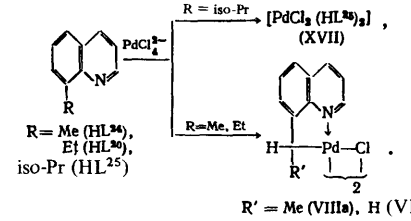
We may note that palladium(II) complexes with *N*-donor ligands, containing four-membered metallocycles, have not so far been isolated but the formation of such CPC has been postulated on the basis of spectroscopic data in a study of the mechanism of the amination of olefins in the presence of palladium compounds.[103]

Thus, despite the fact that the formation of five-membered metallocycles in CPC is in general preferred, there is no evidence, in principle, against the formation of either six-membered or four-membered metallocycles.

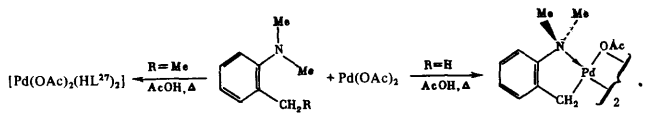
Analysis of the literature shows that the possibility of cyclopalladation and also the ease and mode of reaction are in many respects determined by the steric features of the initial substrate. Depending on their disposition in the molecule and the class of organic ligand, bulky substituents can neither promote or hinder the cyclopalladation reaction.

3. The State of the Palladated Carbon Atom

The problems of steric hindrance at the palladated carbon atom are especially acute in the direct metallation of aliphatic fragments. As was to be espected on the grounds of steric considerations, the ease of the cyclometallation of saturated carbon atoms decreases in the sequence primary > secondary > tertiary. For example, the palladation of 8-alkylquinolines takes place readily only when the 8-position contains a methyl group, as in (HL^{24}) and more slowly for the 8-ethyl derivative (HL^{20}); 8-isopropylquinoline (HL^{25}) forms only the coordination complex (XVII) under these conditions:[76,104]

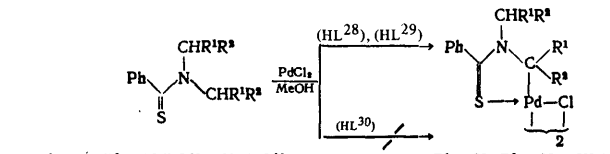


Whereas the metallation of a secondary carbon atom has been achieved in this system, albeit with difficulty, in the case of *o*-alkyl-*NN*-dimethylanilines, the CPC (XVIIIa) has been obtained only from the corresponding toluidine (HL[26]); palladation at the secondary carbon atom of the ethyl substituent in the ligand (HL[27]) has not been observed under any of the conditions used:[105]



R = H (HL[26]), Me (HL[27]) (XVIII)*a*

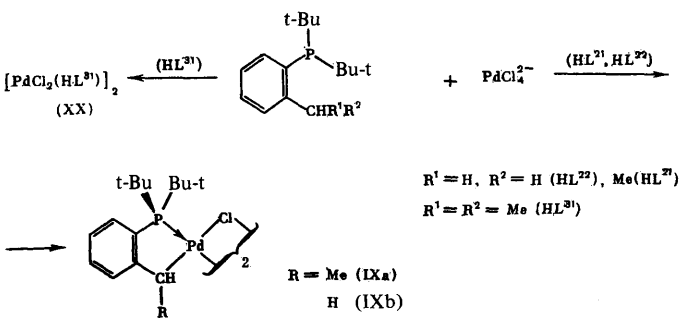
Analogous features have been observed in the series of S- and P-donor ligands. The study of the cyclopalladation of a series of *NN*-dialkylthiobenzamides demonstrated[67] a significantly greater reactivity of the *N*-Me group [the yield of the complex (XIXa) was 94%] compared with the *N*–Et group [the yield of compound (XIXb) was 13%], whereas the *N*-iso-Pr substituent in the ligand (HL[30]) could not be metallated at all:



$R^1 = H$, $R^2 = H$ (HL[28]), Me (HL[29]); $R^1 = R^2 = Me$ (HL[30])

$R^1 = H$, $R^2 = H$ (XIXa) Me (XIXb)

Palladation at a tertiary carbon atom in phosphines could not be achieved even in the presence of bulky substituents stimulating cyclometallation. Thus, whereas the cyclopalladation of di(t-butyl)-*o*-methylphenylphosphine (HL[22]) and di(t-butyl)-*o*-ethylphenylphosphine (HL[21]) takes place comparatively readily [structures (IXb) and (IXa)[77,78,101]], the ligand (HL[31]), containing the o-iso-Pr substituent, forms only the coordination complex (XX) under these conditions and the attempt to cyclopalladate it at elevated temperatures leads only to decomposition:[77]

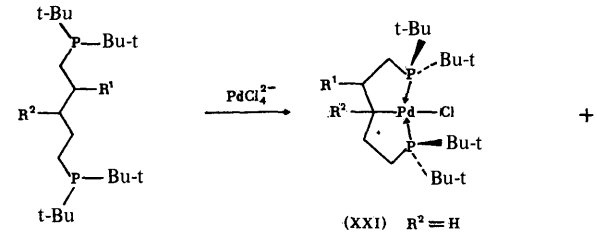


$R^1 = H$, $R^2 = H$ (HL[22]), Me(HL[21])

$R^1 = R^2 = Me$ (HL[31])

R = Me (IXa) H (IXb)

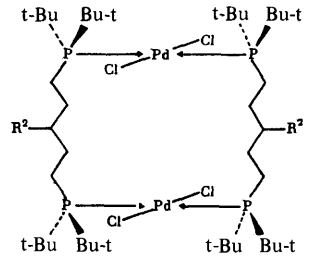
Similar features have been observed also in the formation of bicyclic CPC from a series of long-chain diphosphines. CPC could not be obtained from 1,5-bis(di-t-butylphosphino)-3-methylpentane (HL[32]) apparently precisely because of the difficulty of metallating a tertiary carbon atom; in the case of the unsubstituted derivative (HL[33]) and the 2-methyl derivative (HL[34]), where the metallation takes place at the methylene group, the CPC are formed, although in a low yield. The main product of the reaction with (HL[33]) and the only product in the case (HL[32]) is the dinuclear *trans*-complex (XXII) with bridging diphosphine ligands.[106–108]



(XXI) $R^2 = H$

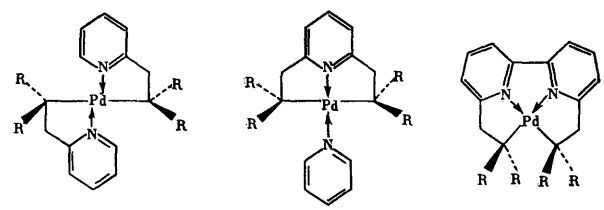
$R^1 = H$, $R^2 = Me$ (HL[32]), H (HL[33]);

$R^1 = Me$, $R^2 = H$ (HL[34])



(XXII) $R^2 = H$, Me

Cyclopalladation at a tertiary carbon atom takes place comparatively readily provided that the carbanionic centre thus produced is stabilised by electron-accepting substituents; this results in the formation of bis-chelate compounds (XXIII), bicyclic compounds (XXIV), or tricyclic compounds (XXV):[22,23,83,84]

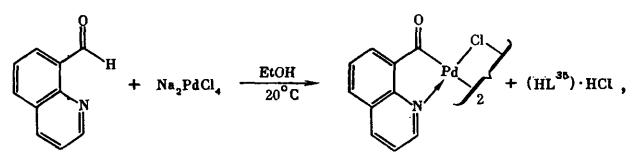


(XXIII) R = COOMe

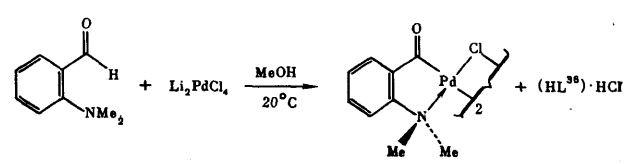
(XXIV) R = COMe, COOEt, CN

(XXV) R = COOMe, COOEt COOPr-iso

The ease with which the aldehyde functional group is palladised at the carbon atom is also noteworthy: acyl complexes are formed from aldehydes containing an additional donor group, in alcohol at room temperature without the introduction of an additional base:[109,110]



(HL[35]) (XXVI)

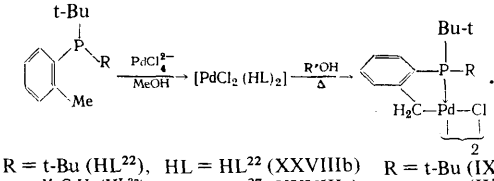


(HL[36]) (XXVII)

Thus a common feature is a decrease in the tendency towards cyclopalladation after the introduction of substituents at the carbon atom to be palladised; however, when such substituents are strongly electron-accepting, metallation is facilitated as a result of the increase in the acidity of the residual C–H bond and the resonance stabilisation of the carbanionic ligand.

4. Substituents at the Donor Heteroatom

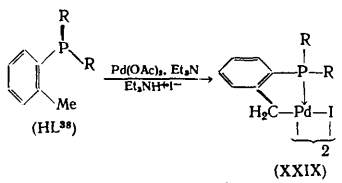
The steric hindrance at the donor heteroatom of the ligand can both promote and hinder its cyclopalladation. For tertiary phosphines, this process is greatly facilitated when bulky substituents are present at the phosphorus atom; for many of these compounds, an obligatory condition for successful cyclometallation is the presence of the t-butyl group.[56,77,78,97–101,111–113] This requirement refers to cyclopalladation both in the aromatic ring and in the aliphatic fragment. A far-reaching study of the cyclometallation of bulky phosphines has been carried out by Shaw and co-workers.[56,57,77,78,101,114–118] Comparison of the ease of the intramolecular palladation of the two phosphine ligands (HL^{22}) and (HL^{37}) in the coordination compounds (XXVIIIb, c) isolated beforehand showed that the rate of metallation of the ligand (HL^{22}), containing two t-butyl substituents at the phosphorus atom, is much higher than for the phosphine (HL^{37}), containing only one such bulky substituent:[78]



R = t-Bu (HL^{22}), o-MeC_6H_4 (HL^{37}); HL = HL^{22} (XXVIIIb), HL^{37} (XXVIIIc); R = t-Bu (IXb), o-MeC_6H_4 (IXc)

As an illustration of the lower tendency towards the cyclopalladation of arsines (compared with phosphines), we may note that ligands with an As donor atom, analogous to those described above, of the type $(t\text{-Bu})_n As(C_6H_4Me\text{-}o)_{3-n}$ (where $n = 1, 2$) do not undergo intramolecular metallation under the same conditions despite the introduction of even two bulky t-butyl substituents; heating of the *trans*-bis-complexes formed as intermediates with arsines coordinated as monodentate ligands via the heterodonor centre leads only to the segregation of zerovalent palladium.[119]

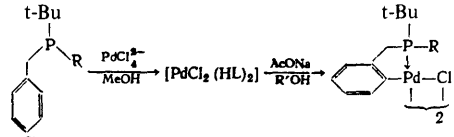
The cyclopalladation of tri(*o*-tolyl)phosphine (HL^{38}), which contains no t-butyl group, was considered for a long time to be impossible.[120] However, the formation of such CPC with (HL^{38}) (as a side product) was recently unexpectedly observed in the catalytic arylation reactions of conjugated polyenes, where the catalyst was the $Pd(OAc)_2$–(HL^{38})–Et_3N–$Et_3NH^+I^-$ system; the dimeric structure of the CPC (XXIX) with iodide bridges has been confirmed by X-ray diffraction analysis:[121]



(XXIX)

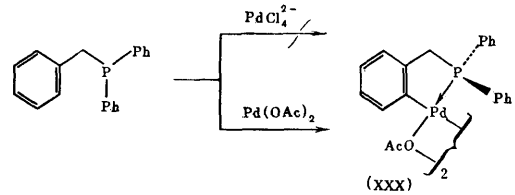
R = *o*-tolyl

An analogous stimulating effect of steric compression has been observed in the *ortho*-palladation of a series of benzylphosphines.[56] The rate of reaction decreases appreciably on passing from (HL^{39}) to (HL^{40}):



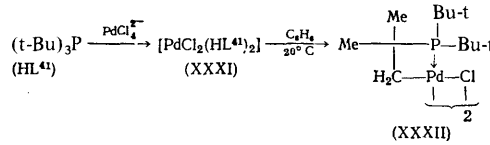
R = t-Bu (HL^{39}), $PhCH_2$ (HL^{40})

The *ortho*-palladation of phosphines not containing t-butyl substituents, for example, Me_2PCH_2Ph,[55] Ph_2PCH_2Ph, and $PhP(CH_2Ph)_2$,[122] does not occur at all under the same conditions. We may note that the *ortho*-palladated complex (XXX) based on Ph_2PCH_2Ph can be obtained only by using a more effective palladating agent—palladium(II) acetate:[112]



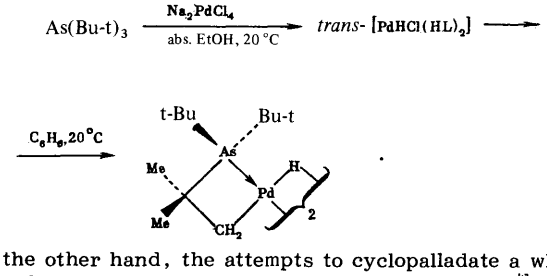
(XXX)

As was to be expected, in the case of tri(t-butyl)phosphine (HL^{41}), containing three bulky substituents, cyclopalladation takes place extremely readily: the bis-complex (XXXI) isolated beforehand is slowly converted into the cyclometallated compound (XXXII) even at room temperature in benzene,[98] the structure of the cyclometallated compound having been confirmed by X-ray diffraction analysis (XRA):[123]



(XXXII)

When three bulky t-butyl groups are introduced at the donor atom, intramolecular palladation of even an arsine ligand analogous to (HL^{41}) becomes possible, although in this case the reaction proceeds via a fundamentally different pathway with the intermediate formation of a stable hydride complex and its final product is the unusual hydrido-bridged dimeric cyclopalladated complex:[124]



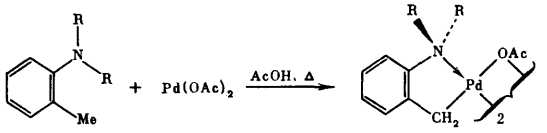
On the other hand, the attempts to cyclopalladate a whole series of less sterically hindered, compared with (HL^{41}), phosphines of the type of $R_2P(Bu\text{-}t)$ and $RP(Bu\text{-}t)_2$ (where R = Pr, Ph, or *p*-tolyl) were unsuccessful.[115] It follows from the calculation of the "cone angle" for such phosphines[98,115] that the steric compression in mixed alkylarylphosphines is much smaller than in (HL^{41}) and is insufficient to stimulate the formation of a four-membered metallocycle.

In his analysis of the causes of the effect of bulky substituents, which stimulate cyclometallation, Shaw[115] put forward several possible explanations. In the first place, we have the removal on metallation of unfavourable interactions between the phosphine and the adjoining ligand—for example, the halide in complexes of the type $[PdHal_2.(HL)_2]$. From the thermodynamic standpoint, the metallation

of bulky phosphines is accompanied by only a slight loss of rotational entropy, since rotation is strongly hindered even in ligands coordinated as monodentate species. If this is a kinetic effect, then one can assume that the free energy of activation for the metallation of sterically hindered phosphines is much lower than for the unhindered ligands as a consequence of entropic factors.

The "*gem*-dimethyl effect" is known in organic chemistry for small carbon rings ($n \leq 7$);[118] in the case of metallocycles involving larger atoms (phosphorus and metal) larger substituents are required for the stabilisation and easier formation of the rings, which results in the "*gem*-di-t-butyl effect".[118]

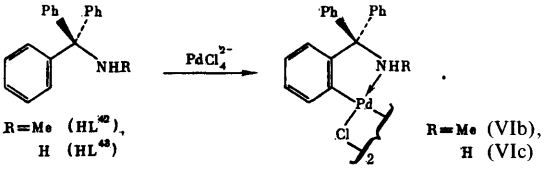
The characteristic features of the cyclopalladation of tertiary phosphines described above are not apparently characteristic of all types of ligands. Thus it is known[105] that the presence of bulky substituents at the nitrogen atom in *o*-alkylanilines hinders cyclopalladation: the replacement of *N*-methyl substituents by *N*-ethyl substituents decreases appreciably the yield of the CPC (XVIIIb) compared with (XVIIIa):



R=Me (XVIIIa) 70%
R=Et (XVIIIb) 8%

5. The Influence of Substituents in Other Fragments of the Ligand

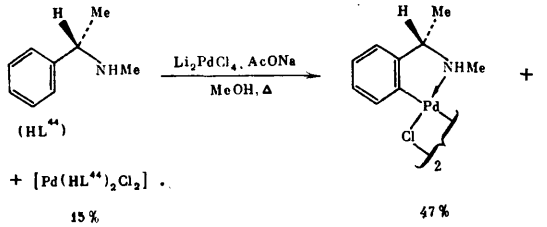
Steric effects due to the presence of bulky substituents at non-donor atoms of the ligand have a significant influence both on the rate of the cyclopalladation reaction and on its mode. Bulky substituents at the carbon atoms forming part of the metallocycle as a rule accelerate the reaction.[52,59,98,125,126] A striking illustration of this conclusion is provided by the results of a study of the cyclopalladation of benzylamines.[52] It is known that primary and secondary benzylamines do not form CPC under the conditions of the Cope–Friedrich reaction.[45] However, when two phenyl substituents were introduced in the α-position in the benzyl ligand, it was possible to obtain the CPC (VIb, c) from not only the secondary amine (HL^{42}) but also from the primary amine (HL^{43}):[52]



R=Me (HL^{42}), H (HL^{43})

R=Me (VIb), H (VIc)

Later it was established[127,128] that a substituent in the α-position as small as the methyl group is quite sufficient for the successful cyclopalladation of secondary benzylamines:



(HL^{44})

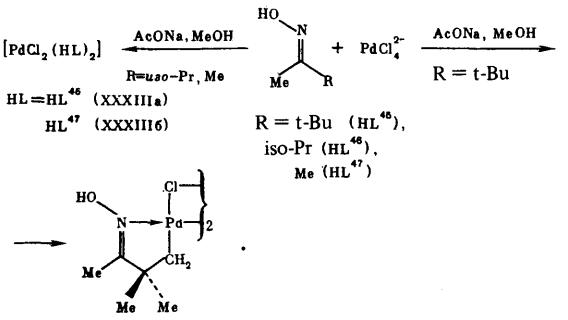
+ $[Pd(HL^{44})_2Cl_2]$.

15%

47%

It is noteworthy that the cyclopalladation of secondary amines is also facilitated with increase in the bulk of the substituent at the nitrogen atom: the *N*-isopropyl derivatives of α-methylbenzylamine and α-(2-naphthyl)ethylamine form CPC in 84 and 73% yields respectively.[127,128]

An obligatory condition in the cyclopalladation of oximes is the presence of the bulky t-butyl substituents at the keto-group,[125,126] for example, as in (HL^{45}); in its absence, as in (HL^{46}) and (HL^{47}), only the coordination compounds (XXIIIa, b) are formed:

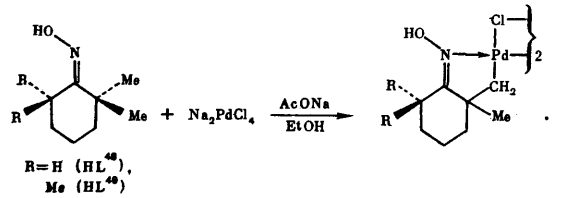


$HL = HL^{45}$ (XXXIIIa)

HL^{47} (XXXIIIб)

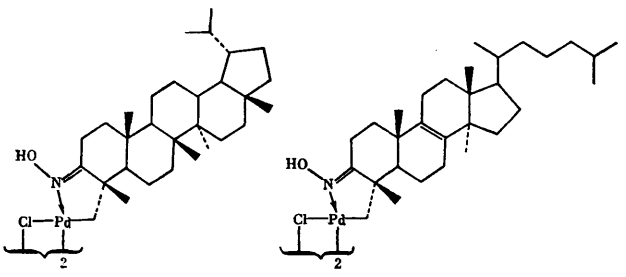
R = t-Bu (HL^{45}), iso-Pr (HL^{46}), Me (HL^{47})

Analogous features have been observed also for the oximes of cyclic ketones: (*E*)-2,2-dimethylcyclohexanone oxime (HL^{48}) and the strongly sterically hindered 2,2,6,6-tetramethylcyclohexanone oxime (HL^{49}) form CPC under standard conditions and in a high yield (~85%),[129] while the less sterically hindered 2-methylcyclohexanone oxime does not form cyclopalladation products:



R=H (HL^{48}), Me (HL^{49})

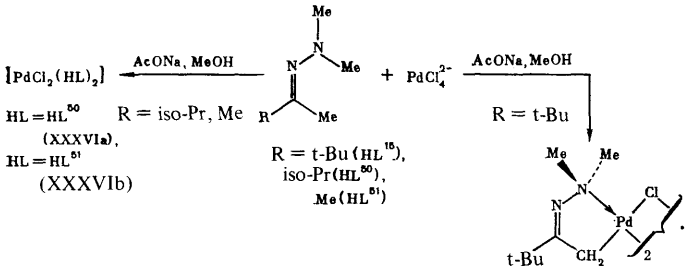
The possibility of the cyclopalladation of such fragments at the methyl group has been used successfully for the introduction of various functional groups into the non-activated methyl group in certain natural products, for example (*E*)-lupanone oxime[129] and lanost-8-en-3-one oxime[130] via the reactions of the corresponding CPC (XXXIV) and (XXXV):



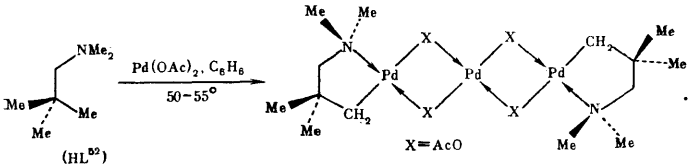
(XXXIV) (XXXV)

The presence of the t-butyl group at the carbonyl carbon atom is also necessary for the cyclopalladation of hydrazones,[125,126] but under these conditions the methyl group of the –N=C– fragment is metallated as a result of the preliminary coordination via the nitrogen atom of the amino-group and not via the imino-nitrogen atom of the ligand (HL^{15}). The less sterically hindered ligands (HL^{50}) and

(HL[51]) form only the coordination compounds (XXXVIa, b):

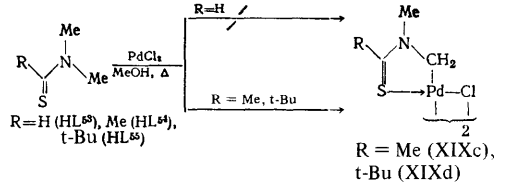


The successful cyclopalladation of dimethylneopentylamine (HL[52]) is apparently in fact caused by the presence in the ligand molecule of the bulky t-butyl fragment (and also by the possibility of the closure of the preferred five-membered metallo-cycle); it is of interest to note that the reaction product is in this instance an unusual trinuclear complex:[131]



The successful cyclopalladation of 2-neopentylpyridine[93] and 2-pivaloylpyridine[94] with formation of the CPC (XVa,b) is accounted for by analogous causes; here the stimulating influence of the steric hindrance overcomes the unfavourable closure of six-membered metallocycles (see Section 2).

Bulky groups at non-donor carbon atoms promote the cyclopalladation reaction also in the case of *S*-donor ligands—thioamides[67,68] and thioketones.[64] For example, whereas it was impossible to introduce *NN*-dimethylthioformamide (HL[53]) into this reaction under any conditions, the corresponding thioacetyl derivative (HL[54]) is converted into the dimer (XIXc) after refluxing with $PdCl_2$ in methanol for 10 h in 49% yield; the replacement of the methyl group in the acid residue by the t-butyl group, as in (HL[55]), makes it possible to obtain the CPC (XIXd) in 94% yield after 1 h:[67]



R = Me (XIXc), t-Bu (XIXd)

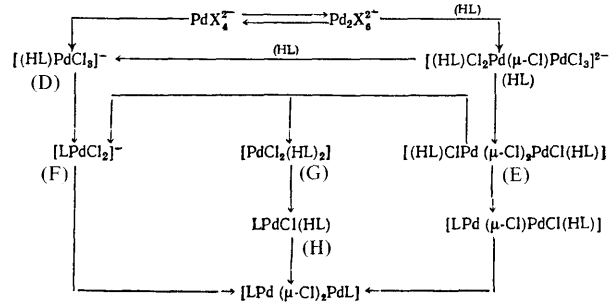
Thus the presence of bulky substituents at non-donor atoms in the ligands as a rule facilitates their cyclopalladation. The cause of this effect is analogous to the causes of the influence of the substituents at the donor phosphorus atoms in tertiary phosphines discussed previously (see above). Furthermore, the presence of bulky substituents in the ligand can lead to an enforced close approach by one of the protons to the metal atom within the framework of a simple coordination compound. Such interactions have been frequently confirmed by X-ray diffraction (see Section III).

III. STRUCTURAL CHARACTERISTICS OF THE COORDINATION INTERMEDIATES

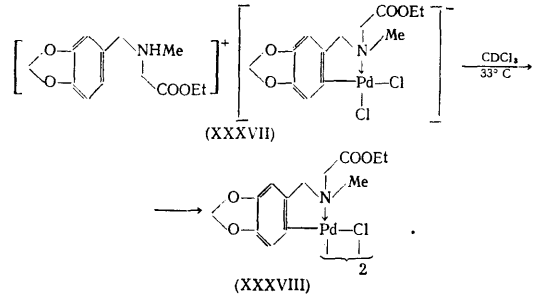
It has come to be assumed that the first stage in the cyclopalladation process is the coordination of the ligand to the transition metal atom. The alternative reaction **mechanism—direct electrophilic metallation of the aromatic** ring (analogously to the very familiar mercuration reaction) with subsequent chelation—is unlikely for metals in a low oxidation state to which palladium(II) belongs.[132]

The preliminary coordination of the initial ligand to the metal is acknowledged by the majority of investigators but the question of the specific structure of such coordination intermediates remains controversial. It apparently depends to a large extent both on the structure of the ligand and on the reaction conditions. For example, a study of the cyclopalladation of tertiary benzylamines[133] led to the postulation of several possible reaction pathways involving intermediates having different structures (Scheme 1):

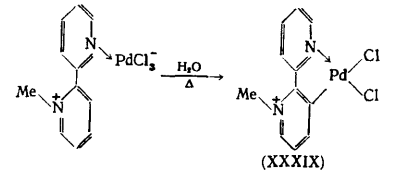
Scheme 1



Here X = Cl and (HL) and (L^-) are respectively the *NN*-dimethylaminobenzylamine ligands coordinated as a monodentate species and a 2*C*,*N*-chelated species. Some of the intermediate cyclopalladated and coordination compounds presented in Scheme 1 have been detected by spectroscopic methods or isolated in a pure state in the given and other ligand systems. For example, the mononuclear CPC (XXXVII) of type (F) has been isolated after treating the corresponding *NN*-disubstituted glycine ester with LiCl and $PdCl_2$ in methanol;[133] this compound is unstable and is converted already on dissolution in chloroform into the usual dimeric *ortho*-palladated complex (XXXVIII):

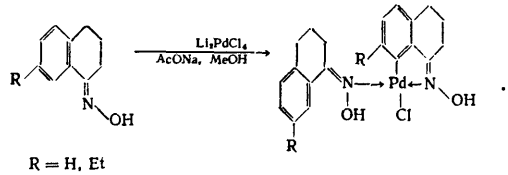


Stable mononuclear cyclopalladated compounds of type (F) are encountered comparatively rarely, but such a structure has been proposed, for example, for the product of the *ortho*-palladation of a cationic ligand—*N*-methyl-2,2′-bipyridylium (XXXIX):[134,135]



Complexes containing both a cyclopalladated ligand and a ligand bound as a monodentate species via the heteroatom [structure (H) in Scheme 1] have been isolated for certain reactant ratios in the *ortho*-palladation reactions of 1-tetralone

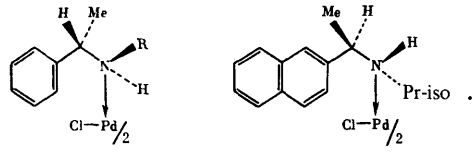
oximes:[136]



R = H, Et

Coordination compounds of type (G) belong to the class of the most typical stable intermediates—they have been isolated in a pure state in the cyclopalladation reactions of a wide variety of ligands: azobenzene,[50] hydrazones,[73] oximes,[72] aromatic primary amines,[137] sulphides,[60] thioamides,[69] tertiary phosphines,[78,98] and other ligands.[51,138] The isolation of coordination intermediates with tertiary benzylamines is hindered by the ready cyclometallation, but their 1:1 stoichiometry has been established with the aid of ^{1}H NMR even for the ratio $PdCl_4^{2-}$: $(HL^1) = 1:2$. Only one ligand is coordinated to the metal, while the other remains free.[139] It has been suggested that the first coordination intermediate is in this instance a dimeric coordination compound of type (E); the existence of the same type of intermediate has been suggested in the $Pd(OAc)_2$–(HL^1) system in $CDCl_3$.[133] However, kinetic and spectroscopic studies of the latter system in the presence of an excess of the ligand established[140] the rapid formation of a *trans*-bis-complex of type (G) (X = AcO), which is regarded as the initial state in the *ortho*-palladation reaction of (HL^1) in the given solvent.

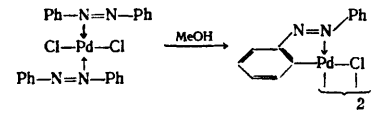
In the case of secondary benzylamines, whose tendency to undergo metallation is significantly reduced,[127,128] their coordination compounds of the *trans*-bis-type were isolated together with the cyclometallation products and were characterised by both spectroscopic and XRA methods:[141–143]



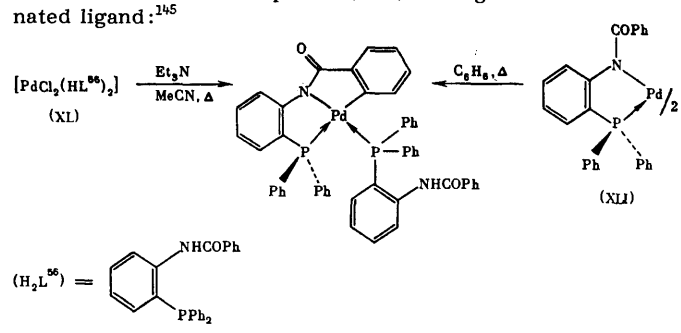
R = Me, iso-Pr

In the cyclopalladation of 1-tetralone oxime, the 1:1 stoichiometry of the intermediate was established by the ^{1}H NMR method and a dinuclear structure of type (E) and not an anionic structure of type (D) was attributed to it.[136] The formation of a similar dinuclear intermediate with the ligand coordinated as a monodentate species in the interaction of *trans*-$[PdCl_2(PhCN)_2]$ with the *N*-methyl-*N*-phenylhydrazone of pinacolene[73] even when a large excess of the ligand is used was attributed by the authors to the steric hindrance generated by the bulky substituents in the ligand. In other systems, there is a possibility of the formation of both mononuclear and dinuclear coordination intermediates depending on the reactant ratio. For example, complexes of types (E) and (G) have been isolated in the cyclopalladation reactions of di-t-butylisobutylphosphine[102] and pinacolone *NN*-dimethylhydrazone[73] for metal:ligand ratios of 1:1 and 1:2 respectively.

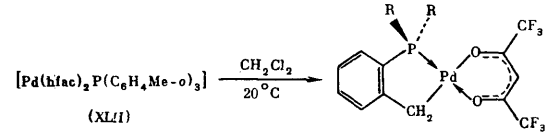
The most convincing evidence showing that the formation of coordination compounds with a monodentate ligand is one of the intermediate stages in the cyclopalladation process is provided by their ready conversion into CPC.[48,51,73,78,98,115,138,144], etc. Thus dichlorobis(azobenzene)palladium(II) can be readily converted into a cyclopalladated compound on heating[51] or by its simple dissolution in polar solvents (ethanol, methanol, aqueous dioxan):[48]



Several examples may be quoted to illustrate the wide variety of forms in which the first stage of the cyclopalladation process can take place (coordination via the heteroatom). Thus the *ortho*-palladation of the amidophosphine ligand (H^2L^{56}) can take place starting both with the traditional bis-complex comprising the ligand P-coordinated as a monodentate species, as in compound (XL), and with the bis-chelate compound (XLI) having an *NP*-coordinated ligand:[145]

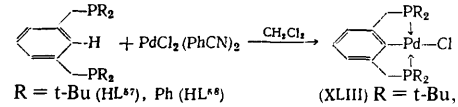


When palladium(II) bis(β-diketonates) are used to cyclopalladate bulky phosphines, pentacoordinated adducts of the type $Pd(hfac)_2(PR_3)$ (hfacH = 1,1,1,5,5,5-hexafluoropentane-2,4-dione) are formed as intermediates, one of which, formed in the reaction with tri(*o*-tolyl)phosphine, has not only been isolated but has also been characterised by XRA.[146] This phosphine is cyclopalladated by simply allowing a solution of the adduct (XLII) in dichloromethane to stand at room temperature:[146]



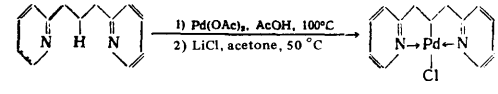
R = *o*-tolyl 47%

The ease and sometimes the very possibility of cyclopalladation depends significantly on the geometry of the complex with the ligand coordinated solely via the heteroatom. Thus it has been shown that complexes of the type *cis*-$[PdX_2(HL)]$ with the bidentate phosphines (HL^{57}) and (HL^{58}) are not converted into cyclometallated products, while the corresponding *trans*-complexes, in which the C–H bond has been activated in the vicinity of the metal atom, readily form CPC of type (XLIII):[147,148]



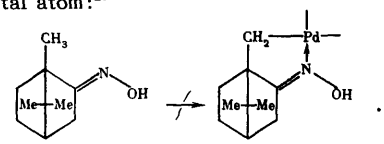
R = t-Bu (HL^{57}), Ph (HL^{58}) (XLIII) R = t-Bu, Ph

It may be that such activation of the central methylene group occurs also in the cyclopalladation of 1,3-di(2-pyridyl)-propane:[149]



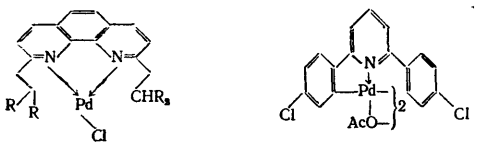
On the other hand, when the geometry of the coordination intermediate rules out for some reason a sufficiently close approach to the metal atom by the section to be metallated,

the metallation reaction becomes impossible. Thus, despite the formally close structural similarity of D-camphor oxime (HL^{59}) to the readily palladated pinacolone oxime,[125,126] all attempts to stimulate the conversion of its coordination complex *trans*-$[PdCl_2(HL^{59})_2]$ into the cyclopalladated derivative under various conditions were unsuccessful.[150] XRA of this complex established that the geometrical features of the molecule (especially the rigidity of the skeleton and the large Pd–N–C angles) prevent the methyl group from being close to the metal atom:[150]



(HL^{59}) (XLV)

The impossibility of the repeated metallation of substituted phenanthroline ligands in the monometallated complexes (XLIV), although their bipiridyl analogues do form doubly metallated derivatives fairly readily, has been explained by the increased rigidity of the central heteroaromatic fragment:[23]

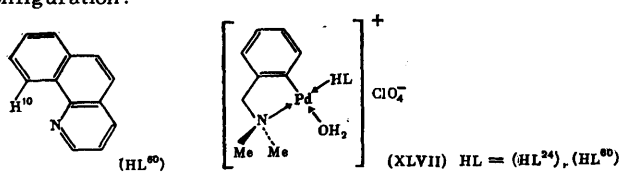


(XLIV) R = COOPr-iso (XLVI)

In their analysis of the causes of the failure of the attempt at the repeated palladation of 2,6-diarylpyridines, Selbin et al.[151] concluded on the basis of the XRA of the monopalladated dimer (XLVI) that, following the formation of the first strong, and therefore shortened, Pd–C σ-bond and also as a result of the increase in the Pd–C–C and C–C–C angles in the metallocycle with sp^2-carbon atoms, the metal "recedes" too far from the second aromatic ring and its metallation becomes impossible.

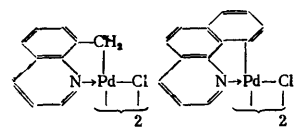
Analysis of the geometries of a number of coordination compounds on the basis of X-ray diffraction data demonstrated the occurrence in many palladium(II)[50,152] and also platinum(II)[153,154] complexes of specific intramolecular interactions which in fact make it possible to regard these complexes as possible intermediates in the cyclometallation of the corresponding ligands. A characteristic feature of the structure of the coordination compound of palladium(II) with azobenzene is an extremely close intramolecular contact of one of the chlorine atoms with the *ortho*-proton of the benzene ring and also fairly close contact (above and below the coordination plane) of the palladium atom with the *ortho*-protons of all four benzene rings of the ligands (two of these contacts are shortened).

Deeming and co-workers carried out a detailed study of the coordination chemistry of 8-alkylquinolines and benzo[*h*]-quinoline (HL^{60}) from the standpoint of the geometry of possible intermediates in the cyclopalladation reactions of these ligands.[86,104,155] In particular, they selected as test models the mononuclear *ortho*-palladated complexes of type (XLVII), in which the ligands investigated (HL^{24}) and (HL^{60}) are coordinated as monodentate species in the *trans-NN*-configuration:[155]



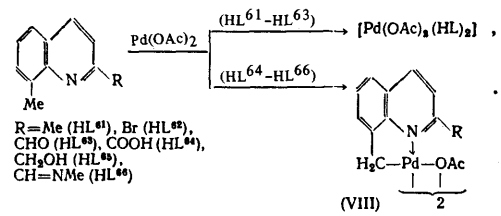
(HL^{60}) (XLVII) HL = (HL^{24}), (HL^{60})

It has been shown with the aid of ^1H NMR and also on the basis of the XRA of certain models that, in complexes of this type, one of the protons of the ligand coordinated as a monodentate species approaches the metal extremely closely: H(10) in the case of (HL^{60}) and the methyl group in the case of (HL^{24}). Such specific axial interactions in complexes with ligands coordinated as monodentate species are fully correlated in many cases with the pathway followed in the subsequent metallation: in the given instance, the ligands (HL^{24}) and (HL^{60}) are cyclopalladated in precisely the positions indicated above with formation of the dimers (VIIIa) and (XLVIII) respectively:[75,156]



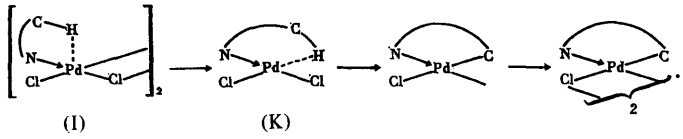
(VIIIa) (XLVIII)

However, despite the convincingly demonstrated reality of the axial interactions in the coordination compounds, it is still not clear for what position of the palladatable C–H bond relative to the coordination plane can its activation be the most effective. It has been suggested[155] that in square planar complexes of d^8 metals certain hydrogen atoms of the ligand are located above or below the coordination plane not as a result of bonding interactions but as a consequence of the endeavour to fill the unoccupied axial site, which reduces the repulsion. In particular, the much greater stability of the 7-methylquinoline complex compared with the analogous 8-methylquinoline compound clearly indicates the destabilising character of the enforced Pd...H–C interaction with the 8-methyl group of the ligand (HL^{20}). Further studies by these[76,86,104,156] and other[157] workers showed that the close axial approach by one of the protons of the ligand coordinated as a monodentate species does not always lead to the cyclometallation in this particular section. It is believed[104] that, under conditions where it behaves as an electrophile (which is in fact postulated in *ortho*-palladation reactions), the palladium atom should employ an unoccupied $d_{x^2-y^2}$ orbital, which requires cyclometallation in the coordination plane. The possibility of the activation of the C–H bond of the initial ligand in the coordination plane of the metal in cyclopalladation processes has been investigated by Deeming and co-workers,[76,104,156] who observed that the introduction of a substituent R in the 2-position in 8-methylquinoline can significantly modify the reactivity of the coordinated ligand. In the presence of groups such as Me, Br, and CHO in this position in the (HL^{61})–(HL^{63}) ligands, cyclopalladation does not take place, whereas for R=COOH, CH_2OH, or CH=NMe in the (HL^{64})–(HL^{66}) ligands, the latter are readily cyclopalladated at the 8-methyl group by palladium(II) acetate with formation of CPC of type (VIII):[158]



The authors suggest that the palladation of the 8-methyl group occurs only when the substituent R contains a [illegible] tive donor centre capable of participating in the [illegible] of the quinoline ligand (together with the quinolin[illegible] atom) and which thereby forces the 8-methyl group to approach the palladium atom in the coordination plane.

Spectroscopic analysis of the course of the *ortho*-palladation reactions of 1-tetralone oxime[136] and benzyldimethylamine[139] using low-temperature ^1H NMR spectra established that the axial and equatorial (within the coordination plane) orientations of the palladated C–H bond constitute two consecutive steps in the intramolecular metallation of these ligands:



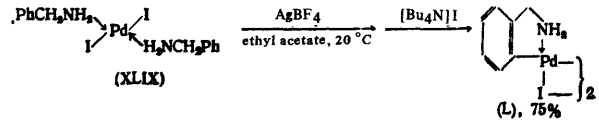
(I) (K)

In the case of tetralone oxime, it was possible to isolate from the aqueous medium at a reduced temperature (0 °C) the intermediate and most unstable (as regards cyclometallation) complex *cis*-$[PdCl_2(HL)].3H_2O$, whose spectroscopic characteristics indicate the location of the *ortho*-proton of the aromatic ring of the organic ligand in the coordination plane of the metal or close to it, which corresponds to a type (K) intermediate.[136]

The conversion of the intermediate (I) with an axial orientation of the C–H group into the intermediate (K) within the plane requires the liberation of one coordination site outside the metal. Pathways leading to the liberation of a coordination vacancy (in the given case apparently via the opening of the halide bridges) are not altogether clear, but there is no doubt about the importance of this stage in the cyclopalladation process.

Analysis of the kinetics of the cyclopalladation reactions of a series of substituted benzyldimethylamines by $Pd_2(OAc)_6^{2-}$ in acetic acid, led Sakodynskaya et al.[140] to the conclusion that the rate-limiting stage of the reaction is the formation of the coordination vacancy as a result of the dissociation of one of the acetate bridges in the adduct of the type $[(HL)(AcO)Pd(\mu\text{-}AcO)_2Pd(OAc)_2]^-$.

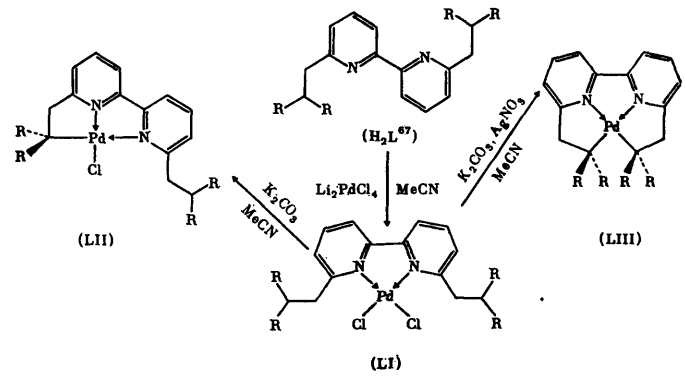
The most striking illustration of the importance of this stage in the cyclopalladation process is provided by the ready formation of the *ortho*-palladated dimer (L) with a high yield from the coordination complex (XLIX) when the latter is treated with two equivalents of $AgBF_4$, which effectively extracts iodide ions from the coordination sphere of the metal in the form of AgI:[159]



(XLIX) (L), 75%

This is particularly important because we are dealing with the palladation of the primary benzylamine which was for a long time believed to be impossible (see above). Naturally, the removal of halide ligands from the coordination sphere of the metal in the intermediate coordination compounds stimulates cyclometallation so effectively not only because of the liberation of the coordination vacancies but also as a result of the generation in this process of a stronger electrophile (Pd^{2+}), which is necessary for the second stage of the reaction—the electrophilic attack.

An analogous procedure has been used successfully to synthesise tricyclic CPC with two Pd–C(sp^3) σ-bonds in the *cis*-positions.[23] In the presence of sufficiently bulky substituents R in ligands of the type (H_2L^{67}), the coordination compounds (LI), isolated beforehand, are converted by bases only into monometallated derivatives (LII), while the introduction of $AgNO_3$ makes it possible to metallate both side chains with formation of compound (LIII):



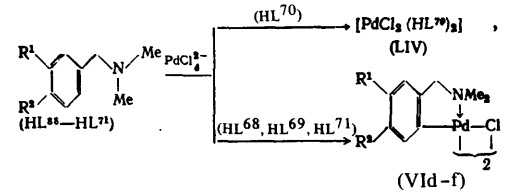
(LII) (LI) (LIII)

Compounds of type (LIII) with the *cis*(C)-geometry exhibit a high biochemical activity in relation to DNA,[160,161] while their *trans*(C)-analogues (LIII) have no biochemical activity.[22]

Although the studies discussed above do not provide a complete answer to the question of the mechanism of the activation of the C–H bond in the cyclopalladation process, they leave no doubt about the exceptional importance of the analysis of the structural features of the coordination compounds arising in the first stage of this process. The second stage of the process, the palladation proper, depends to a large extent on the electronic effects of the substituents in the ligand.

IV. ELECTRONIC EFFECTS IN CYCLOPALLADATION REACTIONS

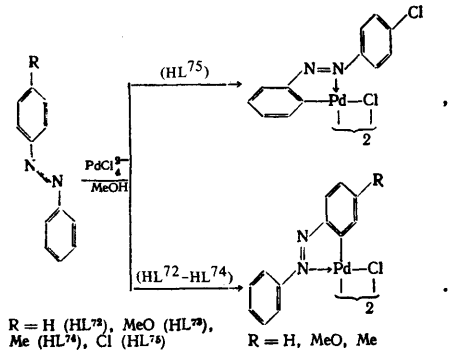
The electrophilic character of palladium(II) in the *ortho*-palladation reactions of various aromatic substrates is generally accepted and has been demonstrated experimentally. Electron-donating substituents (for example the methoxy- or methyl groups) greatly stimulate the *ortho*-palladation, while electron-accepting groups (for example, the nitro-group) partially or completely deactivate the aromatic ring. Such effects have been observed in the *ortho*-palladation reactions of benzylamines,[5,76,77,89] benzyl sulphides,[61] Schiff bases[162] and hydrazones,[163] and asymmetrically substituted azobenzenes[49,164] and 1-arylazonaphthalenes.[79,80] As an example, one may quote the results of a study of the behaviour of a number of benzyldimethylamines substituted in the aromatic ring.[45,165] While the ligands (HL^{68}) and (HL^{69}) with electron-donating substituents readily undergo *ortho*-palladation, the 3-nitro-derivative (HL^{70}) forms only the coordination compound (LIV). As an illustration of the marked acceleration of the reaction by several electron-donating substituents, one may recall the experimental conditions for the *ortho*-palladation of the ligand (HL^{71}): this benzylamine gives rise to the dimeric CPC (VIf) almost instantaneously at −78 °C in 95% yield:[165]



(VId-f)

$R^1 = H$, $R^2 = MeO$ (HL^{68}, VId), Me (HL^{69}, VIe), NO_2 (HL^{70}); $R^1 = MeO$, $R^2 = MeSCH_2O$ (HL^{71}, VIf)

The study of the *ortho*-palladation of asymmetrically substituted azobenzenes,[49,164] 1-arylazonaphthalenes,[80] and dibenzyl sulphides[61] showed that both $PdCl_4^{2-}$ and $Pd(OAc)_2$ are electrophiles in these processes. The fact that palladation takes place preferentially in the aromatic ring of (HL^{73}) and (HL^{74}) having an electron-donating substituent and that of *p*-chloroazobenzene (HL^{75}) takes place exclusively in the unsubstituted phenyl group shows that the *ortho*-palladation occurs predominantly in that of the two aromatic rings which is more enriched in electrons:



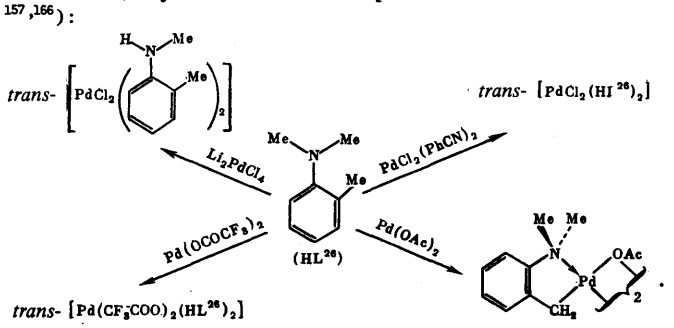
As was to be expected, the rate of *ortho*-palladation of compounds (HL^{72})–(HL^{74}) diminishes as a function of the nature of the substituent R in the sequence MeO > Me > H.[164]

V. EXPERIMENTAL CONDITIONS IN THE DIRECT CYCLOPALLADATION REACTIONS

Apart from the large number of structural factors influencing the ease and mode of cyclopalladation reactions, their success depends to a large extent also on the choice of conditions in the synthesis, namely on the nature of the palladating agent, the presence and nature of the base, the nature of the solvent, and the temperature and duration of the reaction.

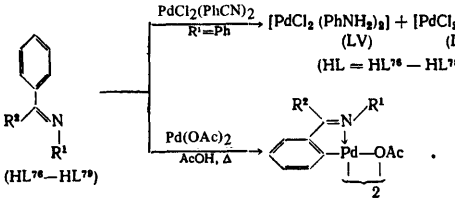
1. Palladating Agents

Both simple palladium(II) salts, namely $PdCl_2$ and $\{Pd(OAc)_2\}_3$, and coordination and chelate compounds of palladium(II), i.e. $M_2[PdCl_4]$ (M = Li, Na or K), $[PdCl_2(RCN)_2]$ (R = Ph or Me), $[Pd(acac)_2]$ (acacH = acetylacetone), and $[Pd(hfac)_2]$ are used as metallating agents in cyclopalladation reactions. The dependence of the reaction pathway on the nature of the metallating agents is clearly demonstrated by the reaction scheme for *NN*-dimethyl-*o*-toluidine (HL^{26}) under various conditions (only the main reaction products are indicated[105,157,166]):



Historically the first method, proposed by Cope and Friedlich,[45] which is based on the interaction of the corresponding organic ligand with alkali metal tetrachloropalladate in the presence or absence of a base, is still used fairly widely for the synthesis of CPC.[44,45,52,165,167–169] Sometimes, the readily available palladium(II) coordination complex of benzonitrile *trans*-$[PdCl_2(PhCN)_2]$ is used for the cyclopalladation of organic compounds.[95,100,144,170] However, this method is not apparently distinguished by any advantages and does not always lead to the desired results.

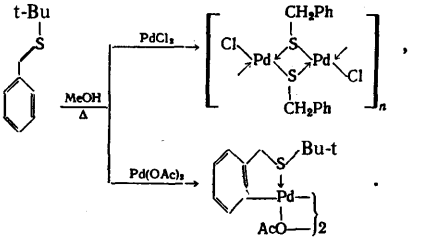
Palladium(II) acetate, which is regarded as the best electrophile in aromatic substitution reactions[176] and is a milder reagent for readily hydrolysable ligands, frequently proves to be a more effective palladating agent.[89,91,104,112,166,171–175] For example, it is known that Schiff bases, especially the aniline derivatives (HL^{76})–(HL^{78}), are extremely sensitive to hydrolysis, which is appreciably accelerated when they are coordinated to a metal.[172,177] Thus, in the attempts to orthopalladate the ligands (HL^{76}) and (HL^{77}) with the aid of $[PdCl_2(PhCN)_2]$ in methanol[172] or of the ligand (HL^{76}) with $PdCl_2$ in aqueous dioxan,[177] the coordination compound of aniline (LV), formed as a result of the hydrolysis of the Schiff bases, was isolated as the main reaction product together with only small amounts of the coordination compounds (LVI) of the initial azomethines. The *ortho*-palladated compounds (LVIIa–d), based on the corresponding Schiff bases, were obtained only when $\{Pd(OAc)_2\}_3$ was used as the metallating agent in glacial acetic acid:[172]



(LVIIa–d)

R^1 = Ph, R^2 = H (HL^{76}, LVIIa), Me (HL^{77}, LVIIb), Ph (HL^{78}, LVIIc); R^1 = Me, R^2 = H (HL^{79}, LVIId)

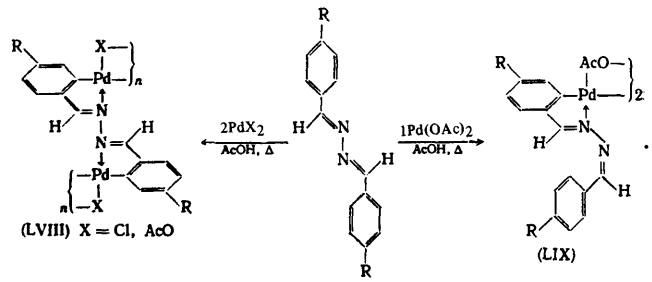
The *ortho*-palladation of benzyl t-butyl sulphide was achieved with the aid of palladium(II) acetate,[60] whilst all the attempts to cyclopalladate this ligand by treatment with Na_2PdCl_4 in alcohol (in the presence and absence of AcONa) or with $PdCl_2(PhCN)_2$ in dichloromethane or toluene were unsuccessful;[63] the use of $PdCl_2$ as the metallating agent leads to the dealkylation of the thioether ligand with formation of the polymeric complex $[\{Pd(\mu\text{-}Cl)(\mu\text{-}SCH_2Ph)\}_n]$:[60]



The successful *ortho*-palladation also of a series of less sterically hindered thioether ligands, namely benzyl izobutyl sulphide,[178] certain dibenzyl sulphides, and also dibenzyl sulphoxide,[61,179] with the aid of palladium(II) carboxylates as metallating agents is evidence for their high effectiveness.

By varying the palladating agent, it is possible to attain different degrees of metallation of ligands which provide several potential regions for this purpose. For example, in the reaction of benzylideneazines with $PdCl_2$, only the polymeric dicylcopalladised compounds (LVIII) are formed,[163] while in the reaction using $Pd(OAc)_2$ it is possible to isolate both the monometallated derivatives (LIX) and the dimetallate

derivatives (LVIII) depending on the conditions:[180,181]

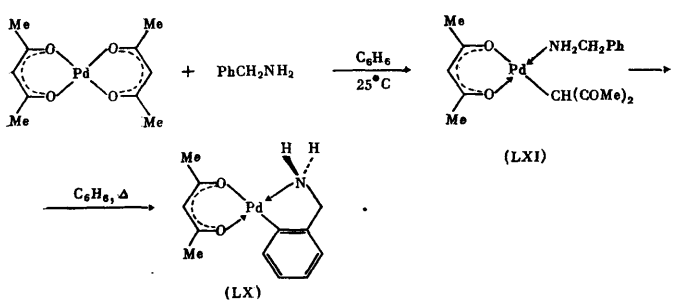


(LVIII) X = Cl, AcO (LIX)

The advantages of palladium(II) acetate as a palladating agent are especially evident in cyclometallation with participation of aliphatic fragments. For example, *NN*-dimethyl-*o*-toluidine (HL^{26}) is metallated by $Pd(OAc)_2$ with an almost quantitative yield, while under the conditions of the Cope–Friedrich reaction, the chloro-bridged analogue is formed in only 8% yield; the main process in the latter case becomes the dealkylation of the amine (HL^{26}) and the formation of the corresponding coordination compound.[105] When $Pd(OAc)_2$ was used, it was possible to synthesise the CPC (XVIIIb) from *NN*-diethyl-*o*-toluidine (see above), while on treatment with Li_2PdCl_4 the above ligand is not cyclopalladated at all.

The possibility of the formation of not only the usual dinuclear but also of trinuclear cyclopalladated compounds should be noted as one of the complications associated with the use of the trimeric palladium(II) acetate for cyclopalladation. Thus, in a more detailed study of the structure of the primary product of the palladation of *NN*-dimethyl-*o*-toluidine, to which a dimeric formula had been attributed earlier[105,106] using mass-spectrometry, ^1H and ^{13}C NMR, and also specific synthesis, it was shown that the true structure of the complex formed in the reaction of (HL^{26}) with $\{Pd(OAc)_2\}_3$ in acetic acid is trinuclear with two pairs of bridging acetate ligands linking three palladium(II) atoms, two of which (the terminal atoms) are *CN*-chelated by the ligand (L^{26}).[182] This type of trinuclear structure was first established for the products of the cyclometallation of dimethylneopentylamine,[131] whose molecular weight in benzene corresponds to the trimer.

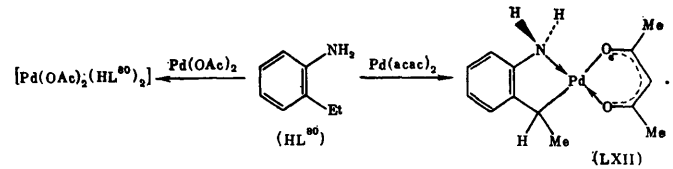
The use of the palladium(II) bis(acetylacetonate) complex as the palladating agent yielded unique results. In particular, with the aid of this reagent it has been possible to obtain the cyclopalladated complex (LX) based on the primary benzylamine,[137] whose metallation presents considerable difficulties:[45]



(LXI) (LX)

It has been suggested[137] that one of the causes of the successful cyclopalladation of this ligand may be the fact that $Pd(acac)_2$ fixes only one amine molecule. Furthermore, the intermediate (LXI) formed in the first stage contains a fairly labile C-bound acetylacetonate ligand, which functions as an effective proton acceptor, stimulating thereby the cyclopalladation reaction.

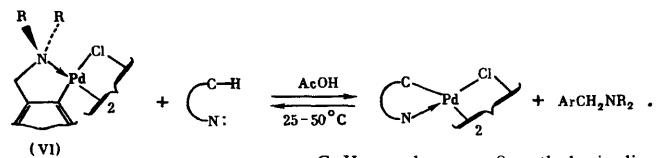
The cyclopalladation of primary *o*-alkylanilines presents special difficulties, since these ligands contain a "poor" coordinating centre (the primary aromatic amino-group) and an aliphatic fragment (the *o*-alkyl group—see above) which is difficult to metallate. Nevertheless, when palladium(II) acetylacetonate was used, it proved possible to achieve the cyclopalladation of *o*-ethylaniline (HL^{80}) at the secondary carbon atom with formation of the CPC (LXII):[137,157]



(HL^{80}) (LXII)

We may note that palladium(II) bis(hexafluoroacetylacetonate) has also been used successfully as a palladating agent[138] with the aid of which it has been possible to obtain CPC based on a wide variety of ligands: tertiary arylalkylamines, Schiff bases, thioamides, thioketones, and also thioethers, especially benzyl methyl sulphide, whose cyclopalladation presents certain difficulties[58] (see above).

A new method of synthesis of CPC, proposed by Yatsimirskii and Ryabov[90,183] and based on the ligand exchange reaction, is of undoubted interest. The fundamental difference from the procedures involving the direct cyclopalladation examined above consists in the use as the palladating agent of any available soluble *ortho*-palladated dimeric complex [for example, compounds (VIa, g)]:



(VI)

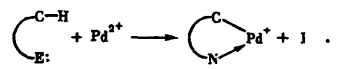
Ar = Ph, R = Me (VIa), or Et (VIg);
Ar = ferrocenyl, R = Me

C–H = azobenzene, 8-methylquinoline, N: benzylideneaniline, 2-benzoylpyridine, *NN*-diethyl-4-nitrobenzylamine

The ligand exchange reactions proceed under comparatively mild conditions (25–50 °C) but have to be carried out in the presence of acetic acid as the cosolvent. Among the CPC obtained by this method, compounds based on 2-benzyl- and 2-benzoyl-pyridine, containing six-membered metallocycles, and the complex with *NN*-diethyl-4-nitrobenzylamine merit special attention. The *ortho*-palladation of the last ligand, containing a benzene ring deactivated by an electron-accepting substituent, was achieved for the first time; this result makes it possible to regard the ligand exchange method as promising for the synthesis of metallocycles which are difficult to obtain under the conditions of the standard methods.

2. The Role of the Base in the Cyclopalladation Process

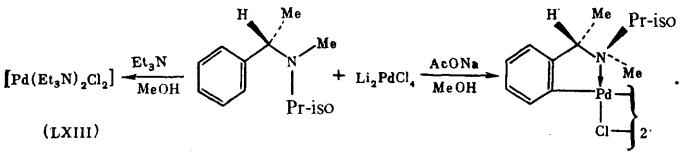
Cyclometallation in the reactions of the type considered here is coupled with the elimination of a proton from the ligand molecule:



When the proton is evolved in the form a strong acid such as HCl, the problem of its neutralisation becomes especially acute. Sodium acetate[46,56,169,184–186] or aliphatic tertiary amines (for example, Et_3N and Bu_3N)[13,45,165] are usually

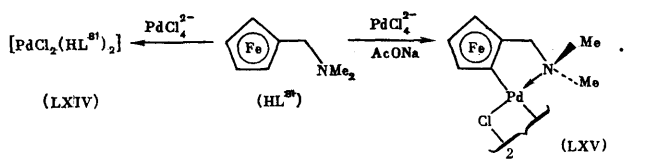
employed as the acceptor; in the cyclometallation of compounds with activated tertiary carbon atoms, K_2CO_3 has been used successfully as the base;[23] if the ligand has very marked basic properties, then an excess of this type of organic substrate is used to neutralise the HCl.[13,45,75]

Tertiary amines are apparently less universal as bases than sodium acetate. For example, in the cyclopalladation of sterically hindered tertiary α-arylalkylamines using triethylamine as the base, the latter competes successfully with the basic substrate for the metal and the main reaction product is its coordination compound (LXIII);[187] we may note that in the presence of sodium acetate such amines readily form CPC:[128,188]



(LXIII)

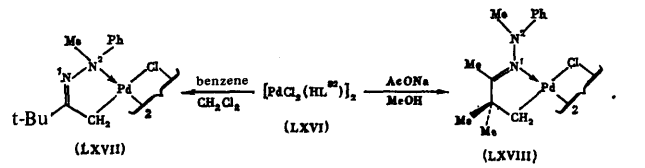
Many systems are known in which the formation of cyclopalladated products in the absence of a base takes place with extremely low yields or the reaction does not occur at all. For example, the cyclopalladation of ferrocenyl ligands in the cyclopentadiene ring can in many cases be achieved only in the presence of sodium acetate despite the fact that this type of ring is more enriched in electrons than the corresponding phenyl derivatives.[46,169,184] Thus, whereas benzyldimethylamine forms the *ortho*-palladation product on treatment with Li_2PdCl_4 in the absence of a base (albeit with a low yield of 35%[45]), its ferrocenyl analogue (HL^{81}) affords under these conditions only the coordination compound (LXIV),[169,189] while the CPC (LXV) is formed only after the introduction of an additional base—sodium acetate:



(LXIV) (HL^{81}) (LXV)

Analogous features have been observed when the results of the cyclopalladation reactions of 2-phenylpyridine[190] and 2-ferrocenylpyridine[184] were compared. Only in the presence of a base (sodium acetate), was it possible to obtain the CPC from a series of acetylhydrazones,[185,191] oximes,[72,125,126] pyrazoles,[192] and phosphines.[56,144]

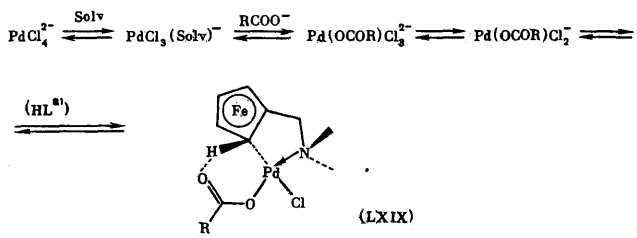
In the cyclopalladation of the pinacolone *N*-methyl-*N*-phenylhydrazone (HL^{82}), the introduction of the base not only accelerates the metallation reaction but also alters its pathway. The intermediate dinuclear coordination compound (LXVI) with the *N*(1)-coordinated hydrazone in the absence of a base in non-polar solvents (benzene, dichloromethane) is slowly and spontaneously metallated at the CMe group and is converted into the CPC (LXVII), while in the presence of a base (sodium acetate) in methanol, the isomeric complex (LVIII) with a metallated t-butyl group is formed (in this case the reaction is faster):[73]



(LXVII) (LXVI) (LXVIII)

The structure of the two isomeric compounds (LXVII) and (LXVIII) has been confirmed by XRA.[193] The authors explained the change in the regioselectivity of this process as a function of experimental conditions by assuming that the complex (LXVI) with the *N*(1)-coordinated ligand (most of the initial hydrazone is bound in this form) participates in the reaction in the presence of a base; in the absence of a base, only the complex with the *N*(2)-coordinated ligand (present in the equilibrium mixture in a small amount) reacts, since the palladation then proceeds at the more active C–CH_3 group adjoining the azomethine bond.[73]

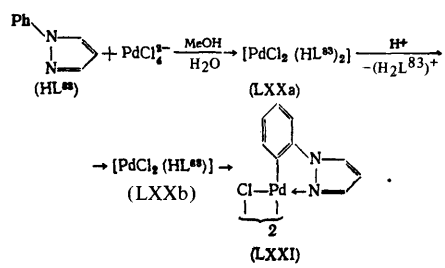
The role of sodium acetate in the cyclometallation reaction is apparently not limited to the simple neutralisation of HCl. When optically active salts of *N*-acetyl-α-aminoacids are used as bases, the cyclopalladated complex derived from *NN*-dimethyl-aminomethylferrocene (HL^{81}) is produced in an optically active form.[46] This example of the enantioselective introduction of planar chirality demonstrates unambiguously that the acid anion is directly involved in the transition state of the cyclopalladation reaction. It has been suggested[46] that the chiral carboxylate ion is inserted in the metallating agent during the cyclopalladation process and then enters into the composition of the bicyclic transition state (LXIX):



(LXIX)

Such asymmetric cyclopalladation reactions have found application in the synthesis of chiral di- and tri-substituted ferrocene derivatives[194] including ferrocenyl analogues of prostaglandins.[12]

There are exceptions to every rule and among cyclopalladation reactions there exists one which does not require the introduction of a base but does proceed in the presence of strong acids. Thus the cyclopalladation of 1-phenylpyrazole (HL^{83}) takes place in methanol in the presence of HCl or $HClO_4$.[43] The authors suggest that the acid is necessary in this case to remove (via protonation) one ligand molecule from the rapidly formed bis-complex (XXIIa). This is accompanied by the formation of the coordination-unsaturated intermediate (LXXb), which is then cyclopalladated with formation of compound (LXXI):



(LXXI)

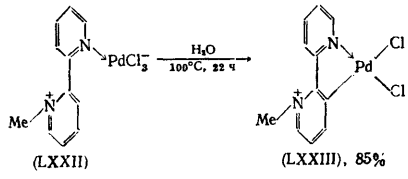
3. Other Experimental Conditions

Reaction conditions such as the nature of the solvent, temperature, and reaction time are quite important in the cyclopalladation of various organic ligands.

The solvent most widely used in reactions of the type considered is methanol.[45,67,72,76,77] Its role does not apparently reduce solely to increasing the solubility of the reactants, in particular, Li_2PdCl_4 and $PdCl_2(PhCN)_2$. The advantages

of polar solvents are probably based on the fact that they promote the creation of vacant sites in the coordination sphere of palladium(II) as a result of solvation. To illustrate this solvent effect, manifested in the stage involving the transition from the coordination compound to the cyclopalladated compound, one may recall the *ortho*-palladation of azobenzene[48] (see above), whose coordination complex is stable in non-polar solvents but is converted into the cyclopalladated compound after the simple addition of alcohol or aqueous dioxan.

The conversion of the palladium(II) coordination complex with a cationic ligand—*N*-methyl-2,2′-bipyridylium (LXXII)—into the cyclopalladated compound (LXXIII) requires a still more polar (aqueous) medium:

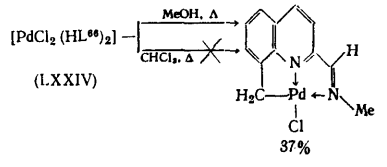


(LXXII) (LXXIII), 85%

Cyclometallation does not occur on refluxing in alcohols (ethanol, 2-methoxyethanol).[134,135]

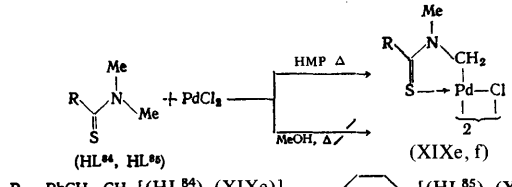
This reaction is especially surprising, since the positively charged pyridinium ring of the ligand is in this instance subjected to *ortho*-palladation (which is traditionally regarded as an electrophilic process).

The successful cyclopalladation of 8-methylquinoline-2-carboxaldimine (HL^{66}), forming part of the composition of the coordination compound (LXXIV), in methanol and the absence of metallation products in chloroform (even at elevated temperatures) has been explained[76] as follows: by liberating a vacant site in the coordination sphere of palladium(II), methanol promotes the bidentate coordination of the ligand to the metal, which ensures the equatorial position of the 8-methyl group, necessary for the cyclopalladation in this fragment:



(LXXIV) 37%

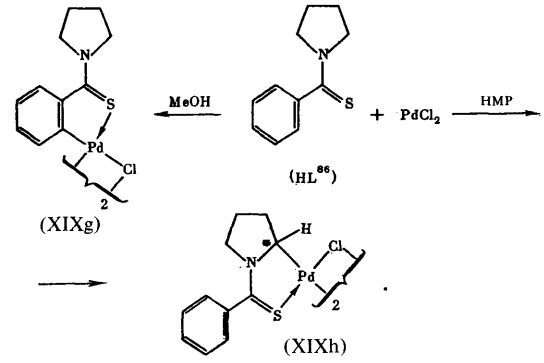
A similar solvation effect is probably the basis of the ready cyclopalladation in hexamethylphosphoramide (HMP) of certain thioamide ligands [for example, (HL^{84}) and (HL^{85})], which do not enter into this reaction in other solvents, especially in methanol:[67]



(HL^{84}, HL^{85}) (XIXe, f)

R = PhCH=CH [(HL^{84}), (XIXe)], —[(HL^{85}), (XIXf)]

The nature of the solvent can influence not only the yield of the final product but also the pathway in the cyclopalladation reaction. For example, the cyclopalladation of *N*-thiobenzoylpyrrolidine (HL^{86}) in methanol takes place in the aromatic ring with formation of the *ortho*-palladated complex (XIXg), whereas in HMP the α-methylene group of the pyrrolidine ring is subjected to metallation, affording compound (XIXh):[67,195,196]

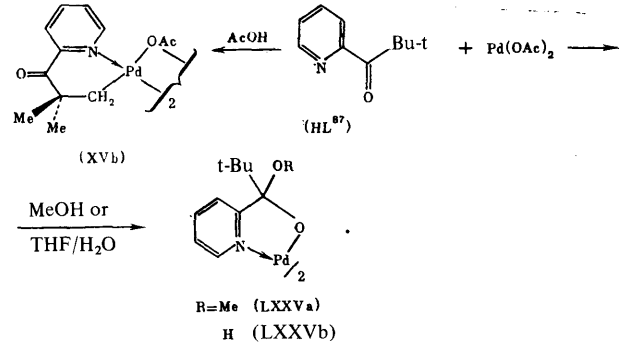


(XIXg) (HL^{86}) (XIXh)

The successful resolution of the latter complex into enantiomers constitutes the best proof that the aliphatic fragment of the (HL^{86}) is cyclopalladated.[195,196]

Apart from methanol and HMP, which have already been mentioned, some workers use aqueous dioxan[48,197] or 2-methoxyethanol[102] as effectively solvating solvents. Despite all the advantages of polar solvents, certain ligands are sufficiently reactive to enter into the cyclopalladation reaction even in weakly solvating solvents of low polarity such as benzene[137] and chloroform;[75,156] the reactions with palladium(II) acetate are carried out as a rule in glacial acetic acid.[89,172,173,198]

The importance of the correct selection of the solvent is illustrated by the following example. When the reaction of 2-pivaloylpyridine (HL^{87}) with $Pd(OAc)_2$ is carried out in acetic acid, the usual dimeric cyclopalladation product (XVb) is formed,[94] whereas in methanol and in aqueous tetrahydrofuran (THF) the bis-chelates (LXXVa) and (LXXVb) are formed respectively as a result of the nucleophilic attack by the methoxide or hydroxide ions on the coordinated acyl fragment of the ligand (HL^{87}):[199]



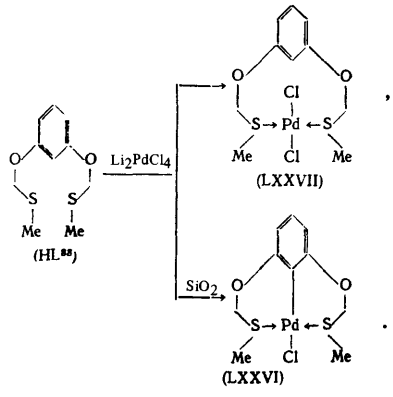
(XVb) (HL^{87})

R=Me (LXXVa)
H (LXXVb)

The required cyclometallation reaction time and temperature are determined by many factors: the class of ligand, its stereochemical characteristics, the nature of the palladating agent and solvent, etc. For example, whereas the *ortho*-palladation of the substituted benzylamine (HL^{71}) in the aromatic ring activated by donor substituents takes place almost instantaneously even at −78 °C[165] (see Section IV), the cyclopalladation of *NN*-diethylthiobenzamide (HL^{29}) is possible only after prolonged heating in HMP.[67] It is noteworthy that the increase in the reaction temperature and time frequently does not produce the desired result owing to the progressive formation of palladium black or the occurrence of other side processes.

Yet another way whereby the cyclopalladation reaction can be accelerated significantly and which is based on the catalytic action of silica gel merits mention.[62] As an example,

we shall quote the results of two attempts at the cyclopalladation of the bis-thioether ligand (HL^{88}): when the reaction with Li_2PdCl_4 is carried out in the presence of silica gel, the CPC (LXXVI) is formed in 95% yield, whereas in the absence of the Lewis acid under the same conditions the main reaction product is the coordination complex (LXXVII):[62]



Thus analysis of the literature data indicates a wide variety of factors influencing the mode and ease of the cyclopalladation reactions and also the structure of the cyclopalladated complex formed. However, a more far-reaching and detailed study of the causes of such effects and the mechanisms of reactions of the given type constitutes at the present time a task of fairly considerable current interest.

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During the preparation of the manuscript for publication, a number of communications having a direct bearing on the topic of this review appeared in the literature.

Apart from the annual compilations of articles on the chemistry of palladium compounds,[200,201] Omae's monograph, summarising a series of review articles by the author published previously,[28,30,37-42] was published;[202] a review of this book[203] contains a series of serious critical comments.

Recently, there has been some progress in the research into the mechanisms of cyclopalladation reactions. It has been demonstrated by spectroscopic and kinetic studies of the *ortho*-palladation of a series of ring-substituted *NN*-dialkylbenzylamines that the reaction mechanism depends significantly on the nature of the solvent: in acetic acid, the rate-limiting stage is the opening of the acetate bridges in the polynuclear palladium acetate, while in chloroform the palladation proper of the amine takes place in the rate-determining stage within the framework of a pseudotricoordinate 14-electron intermediate.[204] The study of the kinetics and mechanism of the ortho-palladation of a series of 3,2′-annelated 2-phenylpyridines with bridges of different lengths by palladium bis(diketonates) suggested that the rate-determining stage of the process is not the attack by palladium(II) on the benzene ring but the subsequent deprotonation.[205]

The cyclopalladated ligand exchange reactions are finding increasing application in the synthesis of CPC of various types;[206-209] an advantage of this method is the preferential palladation of the more electron-accepting of the two ligands in the equilibrium process.[210,211] However, the ideas about the reaction mechanisms still remain contradictory: together with the dissociative mechanism, proposed on the basis of the study of the kinetics and thermodynamics of the reactions,[211,212] the possibility of the formation of mixed-ligand mononuclear bis-chelate CPC as key intermediates has also been discussed.[210] The final result is determined in both cases by the comparative stabilities of the Pd–C σ-bonds of the two palladium-containing heterocycles in relation to protonolysis.[213]

The problem of estimating the influence of various structural factors on the ease of cyclopalladation remains of current interest. Comparison of the behaviour of 1-phenyl- and 1-benzyl-substituted pyrazoles[214] and bornanopyrazoles[215] in the *ortho*-palladation reactions confirms the greater ease of formation of complexes with five-membered metallocycles: the 1-phenyl derivatives readily form CPC by reaction not only with palladium(II) acetate but also with Li_2PdCl_4, while 1-benzyl-substituted ligands afford only the coordination complexes. At the same time an increasing number of communications contradicting the idea of the absolute preference for five-membered palladium-containing heterocycles have been published. Thus the cyclopalladation of *N*-phenylbenzamidine by both $Pd(OAc)_2$ and Li_2PdCl_4 results in the formation of CPC with six-membered metallocycles as a result of metallation in the aniline ring and not the benzamidine ring, which might have led to the formation of a five-membered palladium-containing metallocycle; it has been suggested that this reaction pathway is caused by the greater electron density in the benzene ring of the aniline fragment.[216] For comparison, we may note that the *ortho*-palladation of substituted benzylideneanilines takes place in the aromatic ring of the benzylidene fragment.[217-219] An even more surprising result has been obtained in a study of the cyclopalladation of a series of benzylideneamines of the type $2,4,6\text{-}Me_3C_6H_2CH = N(CH_2)_nPh$ ($n = 0,1,2$),[220] which make it possible to compare simultaneously the tendencies towards metallation at the sp^2- and sp^3-centres and to estimate the importance of the size of the palladium-containing metallocycle formed. It was shown that in all the systems the metallation takes place at the *ortho*-methyl group (sp^3-centre) with formation of a six-membered palladium-containing metallocycle even if the alternative pathway involving metallation in the *ortho*-position in the benzene ring of the amine fragment (sp^2-centre) should have led to the formation of a five-membered ring (for $n = 1$). The nature of the factors which can compensate for the five-membered ring being preferred (compared with the six-membered ring) and for the preferred metallation of the sp^2-centre (compared with the sp^3-centre) remains obscure.[220]

The formation of six-membered metallocycles can be stimulated by introducing an additional (second) heterodonor centre: in contrast to the potentially bidentate 2-(1-methylbenzyl)pyridine, which is not metallated by $PdCl_4^{2-}$, the corresponding 2,2′-bipyridyl derivative readily forms a CPC with a tridentate *NNC*-coordinated ligand on treatment with Na_2PdCl_4 in aqueous HCl;[221] the structure of the complex has been confirmed by X-ray diffraction. It is suggested that the ready formation of CPC with six-membered palladium-containing metallocycles by potentially tridentate ligands of the NCN type {for example, 1,3-bis[1-(2-pyridinyl)ethyl]benzene} is stimulated by the fact that metallation removes the stresses arising in the stage involving simple coordination via the terminal heterodonor centres.[222] We may note, within the framework of tricyclic systems with ligands of the CNNC type, the formation of not only six-membered but also seven-membered palladium-containing metallocycles proved to be possible.[223]

The possibilities arising from the modification of the cyclopalladation conditions for ligands with unfavourable structural features have been demonstrated in a number of investigations. As an illustration of the greater effectiveness of palladium(II) acetate compared with tetrachloropalladates,

one may mention that with its aid it has been possible to achieve the *ortho*-palladation of sterically unhindered benzyl methyl sulphide[224] and methyl α-naphthyl sulphide[225] and also the cyclopalladation in the aliphatic carbon centres of 2-t-butylbenzothiazole[226] and substituted benzylideneazine $(2,4,6\text{-}Me_3C_6H_2CH{=}N)_2$;[207] six-membered palladium-containing metallocycles are formed in the last case. Cyclopalladated complexes belonging to the series of substituted benzylidenebenzylamines have been synthesised in satisfactory yields by reaction with Li_2PdCl_4 only for a 1:1 reactant ratio, while in the case where a twofold excess of the ligand was used only the coordination complexes of the corresponding benzylamines were isolated as a result of hydrolysis.[227] With the same 1:1 stoichiometry and using $PdCl_2$ as the palladating agent, it has been possible to synthesise the CPC of substituted benzoylbenzylideneanilines.[228] An interesting example of the change in the metallation pathway as a function of the nature of the solvent is provided by two investigations:[211,212] when the reaction of the dibenzylamine ligand having two potential metallation regions, i.e. $3,4\text{-}(MeO)_2C_6H_3CH_2N(Me)CH_2C_6H_4NO_2\text{-}4$, with palladium(II) acetate is carried out in chloroform, the electron-enriched benzene ring is palladated, while in acetic acid the reaction involves the benzene ring containing the electron-accepting nitro-group. In the *ortho*-palladation reaction of α-phenyl-α-(2-pyridyl)toluene on treatment with palladium(II) acetate, a CPC with a six-membered palladium-containing metallocycle is formed only in acetic acid, while in benzene the reaction stops after the formation of the simple coordination *trans*-bis-complex.[229] The conversion of such coordination intermediates into CPC can be achieved either by heating in a suitable solvent—for example, chloroform[230] or ethanol[221]—or by introducing an additional equivalent of the palladating agent—for example, Li_2PdCl_4[215] or $PdCl_2$.[231] The synthesis of unusual dinuclear CPC with a single halide bridge from the *NCN*-chelated 2,6-bis(dimethylaminomethyl)phenyl ligand deserves to be mentioned.[232]

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