Palladium(II) Catalyzed Aromatic Acetoxylation

III. Reaction between Pd(II) Complexes and Organic Electron Transfer Reductants

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Two compounds, 9,10-diphenylanthracene and tetra-*p*-anisyl-ethylene, known to undergo facile electron transfer oxidation, have been allowed to interact with $Pd(CH_3CN)_2(BF_4)_2$ in acetonitrile. For the former substrate no reaction was observed, whereas the latter gave a blue complex, presumably of the π-type. Treatment of this complex with 3,5-lutidine caused an intramolecular coupling process to occur (formation of a phenanthrene derivative), whereas addition of water regenerated the parent compound in a ligand displacement reaction. Thus, it appears improbable that the initial process in the oxidation by Pd(II) complexes is an electron transfer to give a cation radical.

The mechanism of the reaction between Pd(II) complexes and aromatics is discussed. It is proposed that a π-complex between Pd(II) and the aromatic substrate is first formed, followed by (1) attack of a nucleophile at a ring position to give an arylpalladium adduct, (2) attack of a base at an α hydrogen, if available, to form a benzylpalladium adduct, and/or (3) direct collapse to give a Wheland-type intermediate. These three possibilities appear to give a reasonably satisfactory picture of the reaction.

The first two papers of this series [1,2] have dealt with attempts to establish optimal reaction conditions for the Pd(II) catalyzed nuclear acetoxylation of the model compound, *p*-xylene,[1] and the application of these findings to other aromatic substrates.[2] It was shown that under the most favorable conditions nuclear acetoxylation is a fairly general reaction, albeit an impractically slow one, and that the isomer distribution of acetoxy products is *reversed* as compared to ordinary electrophilic substitutions. Part I also dealt in some detail with the problem of defining the oxidizing species present in the reaction mixture, and it was concluded that the Pd(II) acetate monomer (I) is the oxidizing species above 35° in acetic acid in the presence of tetra-

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butylammonium acetate or in the absence of excess acetate with a metal as the counterion, whereas in the presence of an alkali metal acetate Pd(II) is bound as a binuclear complex (II). We now wish to report some additional
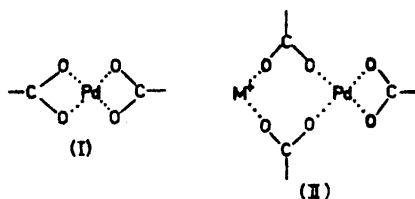
results with a bearing on the possible mechanism of Pd(II) oxidation of aromatics. The results from the two preceding papers [1,2] will be discussed in this context.

RESULTS

Our approach in this paper has been to subject compounds which are known to undergo *facile oxidation* via *electron transfer* to give either cation radicals or dications to oxidation by Pd(II) complexes in order to be able to compare the observed behavior with that of known processes. Two compounds were especially attractive from this point of view: 9,10-Diphenylanthracene (DPA) and tetra-*p*-anisylethylene (TAE), since their behavior upon electron transfer is well known from electrochemical investigations. Thus, DPA is oxidized anodically in $CH_3CN/LiClO_4$,[3] CH_2Cl_2/Bu_4NClO_4,[4] and $C_6H_5NO_2/Pr_4NClO_4$ [5] to form stable solutions of its cation radical (DPA$^{+\cdot}$), whereas TAE gives a reasonably stable solution of the corresponding dication, TAE^{2+}, in equilibrium with a low concentration of the cation radical in $CH_3CN/LiClO_4$.[6,7]

Given these characteristic reactions, it was of interest to use DPA and TAE as diagnostic tools for finding out whether Pd(II) complexes can act as electron transfer oxidants with the formation of radical cations or dications. Since both DPA$^{+\cdot}$ and TAE $^{2+}$ are sensitive toward nucleophiles, such as acetate ion, it was necessary to find a Pd(II) complex with less nucleophilic ligands. An accompanying favorable feature of such a complex would be its higher oxidation potential. A complex of this type is $Pd(CH_3CN)_2(BF_4)_2$ (III), reported a few years ago by Schramm and Wayland.[8] Acetonitrile is a very weak nucleophile and fluoroborate ion is virtually inert in this respect.

Treatment of DPA with complex III in CH_3CN solution gave no reaction, and the introduction of oxygen produced no change either. Thus no electron transfer from DPA to Pd(II) takes place. Oxidation of DPA with Pd(II) acetate in acetic acid at 115° under oxygen gave no 9,10-diacetoxy-9,10-dihydro-9,10-diphenylanthracene, the normal product from electron transfer oxidation of DPA in the presence of acetate ion.[9] Also here electron transfer from DPA to Pd(II) apparently does not take place.

Interaction of TAE with III in acetonitrile at 20° under argon resulted in the slow appearance of a blue colour (λ_{max} at 568 and 300 nm, compared to

those of TAE and III alone, 315 and 280 nm) which is slowly converted to a
yellow one (λ_{max} 482 nm). TAE^{2+} is known to possess a characteristic blue
colour with λ_{max} at 575 nm in ethylene chloride,[10,11] but that the blue colour
is not due to the dication in the Pd(II) case is shown by cyclic voltammetry
of the blue solution produced from TAE and III. The cyclic voltammogram
in $CH_3CN/LiClO_4$ has the appearance shown in Fig. 1, which clearly indicates

Fig. 1. Cyclic voltammogram of the
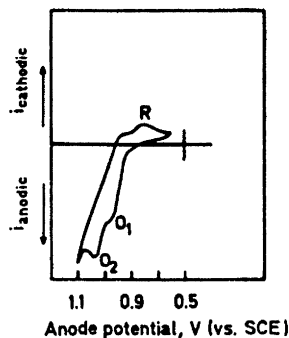TAE − Pd(II) complex in $CH_3CN/LiClO_4$
at a Pt button anode.

that a species different from TAE^{2+} must be present. The TAE/TAE^{2+} system
displays an almost perfectly reversible single-step cyclic voltammogram under
the same conditions. Instead we interpret the voltammogram as being due to
a complex between Pd(II) and TAE, for simplicity referred to as IV in the
following. This complex undergoes two oxidation steps at O_1 and O_2 and a
reduction step at R, the latter presumably being due to reduction of a com-
pound formed at O_1 or O_2. We do not wish to speculate further about the
nature of these redox processes, since for the purpose at hand it is sufficient
to establish that TAE^{2+} is not present.

In line with the assumption that IV is formed from III and TAE in
acetonitrile solution, addition of water caused the blue colour to disappear
immediately and TAE to precipitate. This must be due to a displacement of
TAE in IV by water. Also by addition of 3,5-lutidine the colour disappeared,
but in this case TAE was not recovered unchanged. Instead the phenanthrene
derivative V could be isolated, together with unchanged starting material.
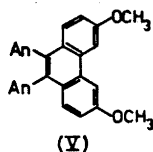
An = p-anisyl

(V)

This type of behavior is known from the anodic oxidation of TAE in $CH_3CN/$
Et_4NClO_4.[12] Apparently proton abstraction by lutidine from IV or a similar
complex can cause intramolecular coupling in a way at least formally resem-
bling that proposed earlier[13] for intermolecular coupling of aromatics by Pd(II)
chloride in the presence of acetate ion (see also Discussion).

Oxygen had an interesting effect upon the formation of the blue complex and its conversion into the yellow one, in that the reactions were speeded up considerably. Thus the blue colour appeared after a few minutes (in argon after 6 h), turned blue-greenish after 3 h, and yellow after standing overnight. In argon the blue colour persists for several days. Attempts to study these transformations quantitatively by UV spectrophotometry failed due to side-reactions between III and acetonitrile.

Finally, p-xylene, as a representative of a compound that is much more oxidation-resistent than DPA or TAE, was refluxed with III with no solvent, whereupon a small amount of N-(p-methylbenzyl)acetamide, together with 2,5,4'-triphenyldiphenylmethane as the major product, was isolated. This reaction is formally analogous to a similar electrode process, anodic oxidation of p-xylene in $CH_3CN/NaClO_4$, in which the same compounds are formed and postulated to originate via a mechanism involving a sequence of electron transfer and chemical steps.[14,15]

DISCUSSION

Previous mechanistic proposals. It is appropriate to start the discussion of the results described in this series of papers (in the following to be referred to as Parts I, II, and III) by bringing to mind Maitlis' general statement [16] about organic reactions catalyzed by transition metals:

"A curious feature of reactions catalyzed by transition metals is the relative lack of evidence for the typical reactive intermediates of organic chemistry, carbanions and carbonium ions. This probably arises from the metal acting both as a source and a sink of electrons and making such ionic intermediates energetically unfavorable. Although organic free radical intermediates have been postulated as intermediates in metal-catalyzed reactions, there is again little evidence for them. Most reactions should, therefore, on present evidence, be regarded as occurring largely within the coordination sphere of the metal."

Such a generalization, based as it is upon a scrutiny of hundreds of mechanistic suggestions for transition metal mediated reactions,[17] should carry great weight in any discussion of Pd(II) catalyzed processes, and it is therefore a suitable starting point to review previous mechanistic proposals for reactions between Pd(II) complexes and aromatics with this statement in mind.

Van Helden and Verberg [13] studied the biaryl coupling reaction that takes place when aromatics are treated with sodium acetate and Pd(II) chloride (ratio 5:1, no reaction was observed in the absence of acetate) in acetic acid at 90°. The reaction was found to be first order in benzene and in Pd(II) chloride, and independent of [NaOAc]. The isomer distribution of biaryls was that characteristic for an electrophilic process, and electron-withdrawing substituents had a weak rate-decreasing effect, whereas the opposite was true for electron-donating substituents. Sterically demanding substituents had an adverse effect upon the yield of biaryl(s). A mechanism involving a rate-determining electrophilic attack of Pd(II) chloride on the aromatic ring to form a σ-complex (VI), as exemplified in eqn. (1) for benzene, was proposed. VI would then react with acetate ion in a fast reaction to form a π-cyclo-

hexadienyl complex (VII), which dimerizes rapidly to binuclear complex VIII. Breakdown of VIII gives the products shown in eqn. (2).

$$\text{(1)}$$

$$\text{(2)}$$
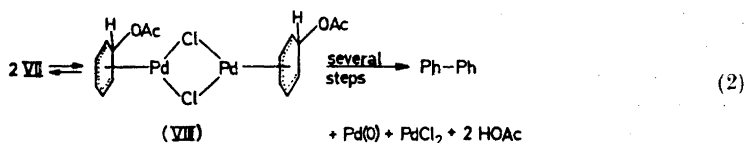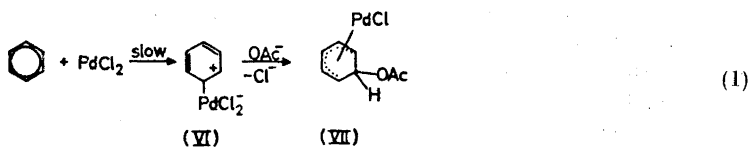
In the oxidation of toluene, an increase in the $[NaOAc]/[Pd(II)]$ ratio (Na/Pd ratio) from 5 to a value between 10 and 15, under otherwise identical conditions, changes the nature of the product, in that side-chain (α) acetoxylation becomes the predominant process.[18],[19] Use of Pd(II) acetate instead of the chloride in this reaction gives acetoxylation also at *low* Na/Pd ratios and in the absence of added acetate.[20] It was suggested [19] that the coupling reaction requires an aggregate of two or more palladium ions connected by a bridging ligand. Such polynuclear complexes should be easily broken down by acetate ion in the case of Pd(II) acetate but less easily so when chloride ion, a more effective bridging ligand, is present. However, this mechanism does not account for the necessity [13] of having a moderate amount of NaOAc present in order to obtain biaryls. On the contrary, if only the good bridging ligand, chloride ion, is necessary, optimal yields of biaryls would be expected without NaOAc. Moreover, it is difficult to explain the strong favorable effect of perchloric acid upon biaryl coupling [19],[23] *via* Pd(II) acetate, since no good bridging ligand is present in this case (see below).

In this context it is important to note that two stable benzylpalladium complexes (IX and X) have been isolated and characterized.[21] Both compounds on treatment with KOAc in HOAc at 100° give benzyl acetate, whereas with AgOAc under identical conditions benzyl acetate and benzylidene acetate are formed.
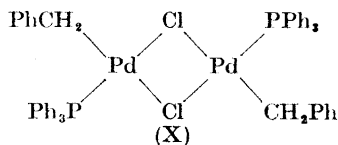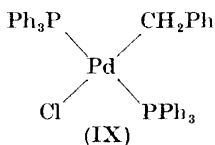
Oxygen strongly influences the ratio between acetoxylation and biaryl coupling. Under 100 atmospheres of oxygen, a reaction mixture containing toluene as substrate, which would normally give essentially only acetoxyla-

tion product, gave almost exclusively biaryl coupling, apparently by suppression of acetoxylation and a slight acceleration of coupling.[19] Complete absence of solvents like acetic acid and a high oxygen pressure in the Pd(II) acetate catalyzed oxidation of aromatics has actually turned out to be the best conditions hitherto found to effect biaryl coupling.[22] Nuclear acetoxylation is also almost completely suppressed at high oxygen pressure,[19] the biaryl coupling being again slightly accelerated.

Davidsson and Triggs [19,23] noted a strong accelerating effect by perchloric acid upon biaryl coupling by Pd(II) acetate in acetic acid. Kinetic studies [23] with benzene as the substrate showed the reaction to be first order in monomeric Pd(II) and first order in benzene. For hexadeuteriobenzene, a large primary isotope effect, $k_H/k_D = 5.0$, was determined in analogy to that found in the mercuration of benzene. At 100° Pd metal is the product of reduction, whereas at temperatures below 60°, Pd(I) is formed. The results for the acid-catalyzed reaction were interpreted in terms of a rate-determining electrophilic palladation reaction to form an arylpalladium complex (eqn. (3)), followed by a fast, bimolecular concerted recombination step, giving biaryl and Pd(0) or Pd(I) complex (eqn. 4).[23] The role of perchloric acid would then presumably

$$Ar - H + Pd^{2+} \rightarrow Ar - Pd^+ + H^+ \tag{3}$$

$$2 Ar - Pd^+ \rightarrow Ar - Ar + 2 Pd^+ \tag{4}$$
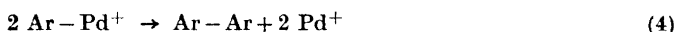
be to increase the electrophilicity of Pd(II), although it was not stated how this would take place in molecular terms. Since the strongly acidic conditions mean that no acetate ion can be present, the only remaining ligands are HOAc and perchlorate ion. Formation of $Pd(ClO_4)_2$ was actually suggested later.[24]

More support for the formation of arylpalladium intermediates stems from the fact that aromatic organometallics, e.g. organomercury compounds [24] and arylboronic acids [23] undergo biaryl coupling upon treatment with Pd(II) acetate. Substitution of the metal by Pd(II) to form Ar–Pd(II) species is a well-established mechanism [17] in palladium chemistry.
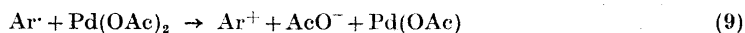
Even more complicated systems have been shown to give good yields of biaryls. Thus, complexes of the type olefin-Pd(II) chloride gave biaryls from aromatics when treated with silver nitrate in acetic acid.[25] If no silver nitrate was present, biaryl coupling was not observed. The olefins used were ethylene, styrene, and cyclohexene, and the yields of biphenyl from benzene were 99, 68, and 3 %, respectively; with no olefinic ligand present, the yield was 40 %. Incidentally, this experiment seems to contradict the necessity for the presence of sodium acetate.[13] This sequence of yields is consistent with the order of stability of the three complexes, and it was therefore suggested that the reactivity is dependent upon the rate at which the olefin ligand exchanges with benzene. The role of silver nitrate was presumably that of an oxidant, since nitrogen dioxide was evolved in the reaction. A mechanism involving σ-arylpalladium complexes was again invoked.

Using Pd(II) nitrate as an oxidant, it was established [26] that in acetic acid, benzene is converted primarily to phenyl acetate, with nitrobenzene [27] and biphenyl as by-products. Certain additives, such as perchloric acid or water, made the biaryl become the major product. Chloride ion inhibited

both processes completely. It was concluded that acetoxylation takes place *via* a mononuclear π-complex between Pd(II) salts and aromatics (eqn. (5)), whereas biaryl coupling occurs *via* a binuclear complex (as in eqns. (1) and (2)). Nitration was also assumed to proceed through an arene π-complex (eqn. (6)), since the product distribution was very much different from that of ordinary nitration processes (*meta* orientation!).

$$\text{(diagram)} \tag{5}$$
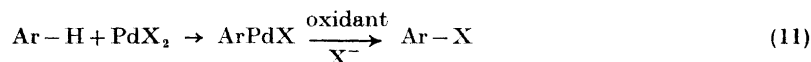
$$\text{(diagram)} \tag{6}$$
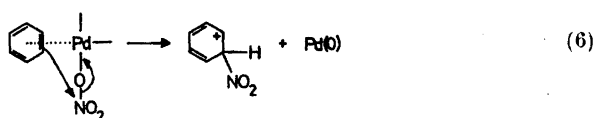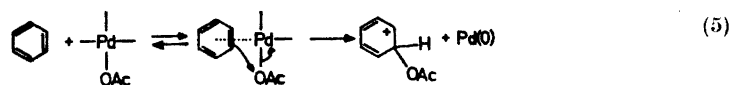
This acetoxylation mechanism is, however, not the only one suggested. Davidson and Triggs,[19] referring to the fact that Pd(II) acetate acetoxylation is inhibited by oxygen in a way similar to lead tetraacetate oxidation processes, proposed a radical chain mechanism in which initially a univalent Pd(OAc) species is formed in a concerted reaction from Pd(II) acetate. The Pd(I) species would then act as an electron transfer oxidant toward the aromatic compound, giving a radical cation as an intermediate. Loss of a proton from the radical cation would give a neutral aryl radical which would be further oxidized by Pd(II) acetate to give an aryl cation and a new Pd(I)OAc species, *etc.* (eqns. (7) − (9)).
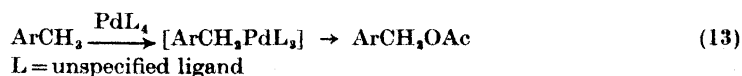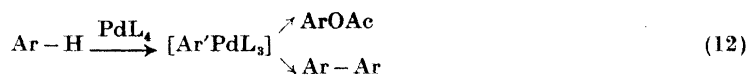
$$Pd(OAc) + Ar - H \;\rightarrow\; ArH^{+\cdot} + AcO^- + Pd(0) \tag{7}$$

$$ArH^{+\cdot} \;\rightarrow\; Ar^{\cdot} + H^+ \tag{8}$$

$$Ar^{\cdot} + Pd(OAc)_2 \;\rightarrow\; Ar^+ + AcO^- + Pd(OAc) \tag{9}$$

While this mechanism would in principle be feasible for α acetoxylation of *easily* oxidizable methylaromatic substrates ($ArCH_2$ instead of Ar in eqns. (7) − (9)), we think it rather improbable in the case of nuclear acetoxylation, since such high-energy species as aryl cations[28] are postulated as intermediates. Moreover, the inhibition by oxygen is not complete even under 50 atmospheres of oxygen; hence the similarity with the radical chain mechanism proposed for lead tetraacetate oxidation is only superficial, since here inhibition is complete even with traces of oxygen.[29] Our own results regarding acetoxylation under oxygen (Parts I and II) fully confirm that oxygen does not perceptibly inhibit acetoxylation at atmospheric pressure. The Pd-catalyzed air oxidation of methylbenzenes to give benzyl acetates[30] is another demonstration that oxygen is not deleterious to acetoxylation. For the latter process it was proposed that a mononuclear Pd(II) species is the reagent responsible for α acetoxylation.

Finally, Henry [31] has made a very interesting study of the nuclear acetoxylation of benzene and benzene derivatives with Pd(II) acetate in acetic acid in the presence of a co-oxidant. The best one was found to be potassium dichromate, but $Pb(OAc)_4$, $KMnO_4$, CrO_3, and $KClO_3$ also worked reasonably well. In the absence of co-oxidant, biphenyl was the major product from benzene. Both benzene and phenylmercury acetate worked well as substrates, and for the latter a number of other oxidative nucleophilic substitutions became possible, e.g. chlorination in the presence of Cl^- and cyanation in the presence of CN^-. Similar halogenations [32] and cyanations [33] have been reported also with nonmetallic oxidants. Toluene gave predominantly nuclear acetate in this reaction, in contrast to most of the acetoxylation reactions already mentioned above, and with methanesulphonic acid present, the isomer distribution of cresyl acetates was $o:m:p = 19:62:19$, the same striking preponderance of *meta* substitution as found for other aromatics in Part II. The mechanism of nuclear acetoxylation under these conditions was proposed to involve attack by either a Pd(IV) species, formed by oxidation of Pd(II) by the co-oxidant (eqn. (10)), or a Pd(II) species to form an arylpalladium intermediate (eqn. (1)). The role of the co-oxidant would then be to substitute the -PdX moiety oxidatively by the nucleophile, since control experiments showed that the nucleophile will not attack the arylpalladium compound in the absence of co-oxidant. The latter type of mechanism was deemed the more likely one for various reasons.

$$PdX_2 + \text{oxidant} \xrightarrow{\;2\;X^-\;} PdX_4 \xrightarrow{\;Ar-H\;} Ar-X + PdX_2 + X^- \qquad (10)$$

$$Ar-H + PdX_2 \rightarrow ArPdX \xrightarrow[X^-]{\text{oxidant}} Ar-X \qquad (11)$$

Nature of the product-forming intermediate. Transient arylpalladium complexes have frequently been postulated as intermediates in Pd(II) mediated reactions.[18,34] As can be seen from the review given above, most proposals concerning biaryl coupling and nuclear acetoxylation also involve this kind of intermediate. The high reactivity of arylmercury [23,24,31] and arylboron [23] compounds toward Pd(II) complexes as compared to the parent aromatics, and the similarity in the product distribution from both types of starting material, supports this postulate in a very convincing way. In the following discussion, we shall assume the intervention of C–Pd bonded intermediates both for reactions on the ring (arylpalladium species) and at the α position (benzylpalladium species). In the latter case the finding that isolatable benzylpalladium complexes can be converted into benzyl acetate [21] carries strong weight as evidence for this assumption. Thus, a crude mechanistic picture for these processes would appear as in eqns. (12) and (13):

$$Ar-H \xrightarrow{PdL_4} [Ar'PdL_3] \begin{array}{c} \nearrow ArOAc \\ \searrow Ar-Ar \end{array} \qquad (12)$$

$$ArCH_3 \xrightarrow{PdL_4} [ArCH_2PdL_3] \rightarrow ArCH_2OAc \qquad (13)$$
L = unspecified ligand

The remaining and by far most difficult task in outlining a detailed mechanism is now to try to understand how the nature of L influences (a) the mode of formation of organopalladium complexes, and (b) the further reactions of $Ar'PdL_3$ and $ArCH_2PdL_3$.

Nature of the initial step. Certain metal ion oxidations with ions of high oxidizing power (*e.g.*, Mn(III),[35] Co(III),[36] and Pb(IV)[37]) in acetic acid produce acetoxylation products from aromatics *via* an initial one-electron transfer from the substrate to the metal ion to produce a radical cation as the product-forming intermediate. Such a mechanism has also been proposed for Pd(II) mediated reactions [23] (see above), but appears less likely in view of the weak oxidizing power of Pd(II) and/or Pd(I) compounds as compared to the ions mentioned. In fact, as shown in Part III, compounds that easily undergo electron transfer oxidation (DPA, TAE) show no signs of reacting with Pd(II) (as III) to give products characteristic of such a process. For DPA no reaction is observed, and with TAE a complex is formed (IV, below formulated as a π-complex). Likewise, in the reaction between Pd(II) acetate and DPA, none of the products to be expected from electron transfer oxidation is obtained.

Thus we can see no compelling reason for assuming that Pd(II) oxidation of aromatics occurs *via* an initial electron transfer to give a radical cation, which would then react to form products in subsequent chemical and/or electron transfer steps. Instead, the results referred to above and those reported in Part III are in agreement with the assumption that electron transfer takes place *within* the coordination sphere of the metal ion, presumably with assistance of a base/nucleophile within or outside the coordination sphere (as exemplified in eqns. (5) and (6)). A very striking illustration of this behavior is afforded by IV, which on attack by a weak nucleophile/base, such as water, gives back the π-donor (TAE), whereas with the stronger base, lutidine, electron transfer within the complex takes place and an oxidation product is formed. This is formulated as in eqn. (14), in which IV is shown as the usual type of π-donor-acceptor resonance hybride, although with only one of the resonance forms given. Assuming that an intramolecular attack between two rings occurs in a fast reversible step, the removal of the proton by a base would then be rate-determining and eventually lead to the phenanthrene derivative V and Pd(0). Similar additions across a double bond of the donor of a purely organic charge-transfer complex have been reported.[38]

(14)

An = p-anisyl
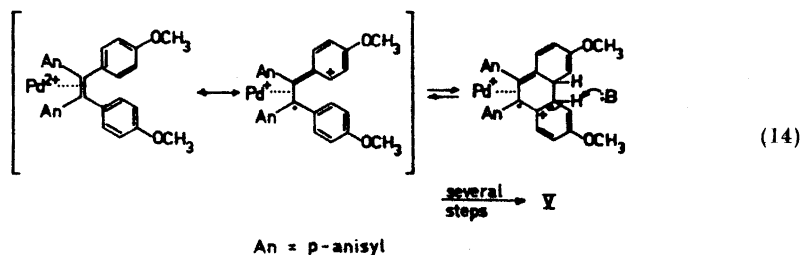
We now postulate that the first step in the reaction between aromatics and Pd(II) complexes is the formation of a π-complex (XI), which according to its structure and the prevailing reaction conditions can undergo: (1) nucleophilic attack at the ring to form an arylpalladium *adduct* [39] (XII), (2) attack of a base at an α hydrogen, if available, to form a benzylpalladium *substitution* intermediate (XIII), or (3) direct collapse to a Wheland-type intermediate (XIV, see eqn. (15)).

$$(15)$$
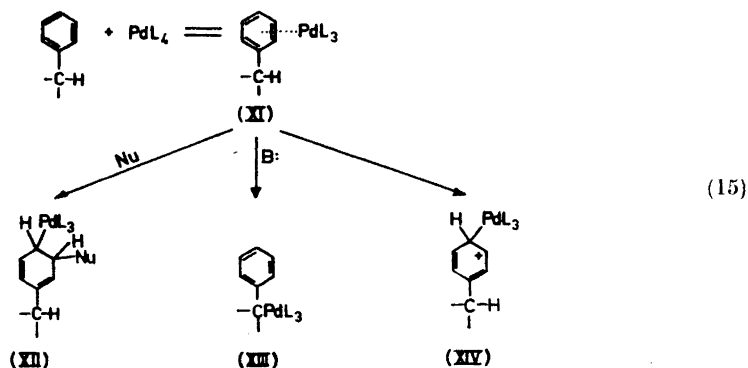
As shown in Part I and pointed out at the beginning of Part III, nuclear acetoxylation of *p*-xylene presumably takes place *via* Pd(II) acetate monomer (I), whereas binuclear species II is the active complex under conditions leading to α acetoxylation.[40] Since the nature of the alkali metal acetate added has a strong effect on the rate of formation of the α acetoxylation product from *p*-xylene (Part I, Figs. 7 and 8), we find it reasonable to assume that the corresponding π-complexes (XI) also have different structures and that this is the reason that the reaction takes a different course in the two cases. To suggest a definite structure for either of the two types of complexes is at present only a matter of speculation; it may be that the complex leading to α acetoxylation is less susceptible to attack on the ring by an external nucleophile for reasons of steric hindrance, or that, if the attacking nucleophile is bound to the π-complex (XI) as a ligand, the structure of a given complex is such as to favor only one of the two processes. The fact that added triphenylphosphine favors α acetoxylation (Part I) might be cited as supporting the former assumption, since triphenylphosphine would act both as a bulky ligand and as an aid in the removal of acetate ligand from Pd(II). Similarly, only α acetoxylation is observed in the case of the sterically hindered higher methylbenzenes (Part II).

Given conditions that lead to nuclear acetoxylation, the intervention of arylpalladium adduct (XII), affords a satisfactory explanation for the observation of the inverse isomer distribution pattern reported in Part II. Then Pd(II) will simply become attached to ring positions susceptible to electrophilic attack, and removal of PdHX from the adduct will lead to the "wrong" isomer.
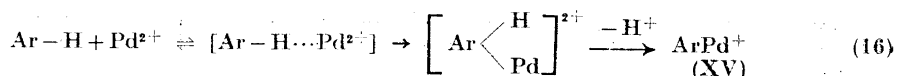
The induction period observed at low Na/Pd ratios for α acetoxylation (Part I, Figs. 1 and 3) is difficult to reconcile with the mechanism given above

(eqn. (15)). The end of the induction period appears to coincide with the appearance of Pd metal, but since the induction period disappears at high Na/Pd ratios, we believe this to be fortuitous. This is supported by the fact that added triphenylphosphine, which keeps Pd(0) in solution as a complex, actually favors α acetoxylation, showing that a heterogeneous step involving Pd metal is not required for this reaction to occur. The possibility that a radical chain mechanism is responsible for α acetoxylation is excluded by the fact that the induction period is observed both under argon and oxygen.

The effect of oxygen on Pd(II) mediated reactions presents several puzzling problems, as discussed above. It appears to increase the rate of biaryl coupling and decrease the rate of acetoxylation; in our own investigation we have also noted that aldehydes are among the major products from methylbenzenes when oxygen is present (Parts I and II). We have no consistent explanation for this behavior, but would like to suggest that dioxygen complexes of Pd(II) [41] and/or Pd(0) [42] play an important role in the phenomena observed. Dioxygen complexes of Pd(II) are known to cause peroxidation reactions,[41] which might be the reason that aldehydes are formed from methylbenzenes under oxygen. The role of dioxygen complexes in these reactions merits further attention.

Nature of the follow-up reactions of organopalladium species. Having postulated the general mechanism shown in eqn. (15) to account for the formation of organopalladium intermediates it now remains to explain how the arylpalladium species are diverted between biaryl coupling and nuclear acetoxylation, assuming that α acetoxylation occurs *via* benzylpalladium complex XIII. As discussed earlier, the presence of a good bridging ligand, such as chloride ion, has often been considered a prerequisite for biaryl formation. However, this is really not necessary, since Pd(II) acetate in the presence of perchloric acid [19,23] effects biaryl coupling in a fast, reasonably efficient process.

Returning to eqn. (15), adduct XII is assumed to be formed in the slow step from the π-complex (XI). As mentioned above, removal of PdHX from the adduct gives the nuclear acetate; since a co-oxidant strongly favors this mode of reaction, it appears reasonable to assume that the oxidant operates in assisting this stage of the reaction. Under our conditions for favoring nuclear acetoxylation, Pd(II) acetate alone in acetic acid under oxygen, oxygen probably plays this oxidative role in the removal of PdHX. However, under strongly acidic conditions ($HClO_4$ present), two additional factors are introduced. In the first place, acetate ion will be removed from the solution, giving a much less strongly coordinated Pd(II) complex with a concomitant increase in electrophilic reactivity. This appears to be the case also for the addition of the strong Lewis acid, $AlCl_3$; see Part I. Hence an arylpalladium species (XV) may be formed directly from the π-complex (eqn. (16)) in an ordinary electrophilic mechanism with the same high k_H/k_D ratio as observed for mercuration. In the second place, any adduct (XII) formed would immediately solvolyze under acidic conditions to produce the arylpalladium substitution product (XV) *via* XIV.

$$Ar-H + Pd^{2+} \rightleftharpoons [Ar-H\cdots Pd^{2+}] \rightarrow \left[Ar\!\!<^{H}_{Pd} \right]^{2+} \xrightarrow{-H^+} \underset{(XV)}{ArPd^+} \qquad (16)$$

This reasoning leads to the assumption that an arylpalladium substitution product (XV) is the critical intermediate in biaryl coupling, at least under acidic conditions, but probably also under others. The problem of how the coupling reaction takes place is not easy to solve, but we suggest that a mixed arene-arylpalladium complex is involved (eqn. (17)).

$$[Ar-Pd^+\cdots ArH] \rightarrow Ar-Ar+H^+ + Pd(0) \tag{17}$$
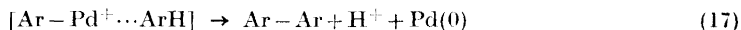
EXPERIMENTAL

Materials. Solvents and inorganic chemicals used were of reagent grade quality. $Pd(CH_3CN)_2(BF_4)_2$ (III) was prepared according to the procedure given by Schramm and Wayland,[8] DPA was a recrystallized specimen of commercial origin (Aldrich), and TAE was obtained through the courtesy of Dr. Klas Nyberg.[6]

Attempted reaction between DPA and Pd(II) complexes. (a) DPA (0.091 mmol) was dissolved in acetonitrile (5 ml) and III (0.094 mmol) dissolved in acetonitrile (0.2 ml) was added. No reaction took place, the starting material being recovered unchanged after standing overnight. In a similar experiment, bubbling with oxygen had no effect.

(b) DPA (2.1 mmol) was dissolved in acetic acid (50 ml). The solution was thermostated at 115° and oxygen was bubbled through it. After 30 min Pd(II) acetate (1.0 mmol) was added and the solution kept at 115° under oxygen for 4 h. The usual work-up [1] gave a crystalline material which lacked the characteristic IR spectral bands of 9,10-diacetoxy-9,10-dihydro-9,10-diphenylanthracene [43] (1760, 1255, 770, 760, 750, and 710 cm^{-1}). Most of this sample was unchanged starting material.

Reaction between TAE and III. (a) To prepare solutions of the blue complex no special precautions were taken to avoid contact with oxygen from the air. Thus, TAE (0.066 mmol) was dissolved in acetonitrile (5 ml) and III (0.094 mmol in 0.2 ml of acetonitrile) was added. After 1 h the solution was strongly blue-colored, and its UV spectrum exhibited λ_{max} at 300 and 568 nm. After standing for several days, the solution attained a yellow colour (λ_{max} 482 nm).

(b) To demonstrate the effect of oxygen, solutions 1 mM in TAE and containing 0.188 mmol of III were shaken in stoppered flasks under either oxygen or argon. The following colour changes were noticeable:

Time lapse	Under O_2	Under Ar
10 min	Blue colour appears	No change
3 h	Blue-greenish	No change
6 h	Blue-greenish	Blue colour appears
7 h	Green	Blue
20 h	Yellow	Blue

Thus, oxygen appears to catalyze the changes that take place in solutions of TAE and III. Attempts to follow the kinetics of these processes failed due to side-reactions, probably between acetonitrile and III.

(c) Cyclic voltammograms (Heath EUW 19 A operational amplifier with polarography module EUA-19-2 and a Moseley 7035 B x,y-recorder) were determined at a Beckman platinum button electrode (No. 39273), using a solution made up according to the procedure given under (a) above.

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