Palladium(II) Catalyzed Cleavage of Aryl-Phosphorus Groups of Tertiary Arylphosphines

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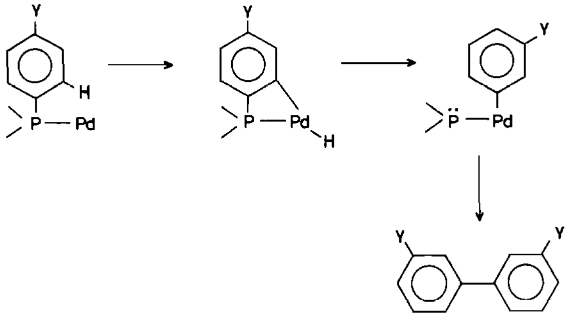
Received November 17, 1983

Although in transition metal catalyzed organic reactions, efforts have generally been focused on the evaluation of important mechanistic steps for major product formation from the substrates, the steps leading to by-products and often related to the catalyst decay probably occurring via an interaction of the metal with the ligands in some undesired fashion mostly remain unrecognized. For instance, the C–P bonds of tertiary phosphines used extensively in transition metal chemistry have been considered to be chemically stable under the usual conditions, yet recent studies have demonstrated the cleavage of these bonds in the cases of several transition metal complexes [1–5] in their lower oxidation states (mostly zero-valent). In a previous communication we reported the cleavage of phenyl–antimony groups of triphenylstibene catalyzed by palladium under various reaction conditions leading to several phenyl groups containing organic products. These investigations have been extended to various other systems and I wish to present here some of the preliminary results of the studies on the palladium catalyzed cleavage of aryl–phosphorus groups.

Reactions of palladium(II) acetate with one or two mol equivalents of triphenyl phosphine in toluene at room temperature result in the formation of $[Pd(OAc)_2(Ph_3P)]_2$ and $[Pd(OAc)_2(Ph_3P)_2]$. These complexes dissolved in organic solvents upon heating undergo decomposition yielding organic products such as biphenyl, benzene and phenyl acetate. The amounts of these products varied depending upon the reaction conditions. Typically, when a mixture of $Pd(OAc)_2$ and Ph_3P in 1:2 molar ratio was heated in toluene at 100 °C for 5 hours and the resulting solution was analyzed by GLC, it showed the formation of 60% biphenyl, 18% benzene and 5% phenyl acetate (based on palladium). None of the above organic products was formed when Ph_3P alone was heated in toluene. Since all the above organic products produced contained phenyl groups and the only source of phenyl groups was triphenyl phosphine, the formation of an intermediate palladium complex with phenyl–palladium bond is proposed. The decomposition of phenyl–palladium complexes is known to give biphenyl [7]. The formation of benzene in the above reactions probably suggests the formation of palladium–hydrogen bond in addition to the phenyl–palladium bond by the cleavage of phenyl carbon-hydrogen of Ph_3P (*ortho*-metalation, *i.e.*, oxidative addition mechanism). A similar oxidative addition mechanism has been proposed earlier in the thermal reaction of $IrCl(Ph_3P)_3$ in benzene yielding an *ortho*-metalated product, $IrH(Cl)(o\text{-}C_6H_4)Ph_2P(Ph_3P)_2$ [8] and also for the phenylation of styrene in the reaction of $(Ph_3P)_2Pd(OAc)_2$ with styrene [9]. If such a mechanism involving the *ortho*-metalation of triphenylphosphine is operative in the present studies then the reaction of $Pd(OAc)_2$ with a tri-*para*-substituted aryl phosphine (*e.g.*, tri-*p*-tolylphosphine) should produce 3,3′-disubstituted biphenyl (*e.g.*, 3,3′-dimethyl biphenyl) according to the reaction sequences shown in Scheme 1.



Scheme 1.

However, the reaction mixture of $Pd(OAc)_2$ with 2 equivalents of $(p\text{-}CH_3C_6H_4)_3P$ when heated in benzene produced 4,4′-dimethyl biphenyl and no 3,3′-dimethyl biphenyl was detected. Similarly, the reactions using tri(*p*-chlorophenyl) phosphine, $(p\text{-}ClC_6H_4)_3P$, and tri(*p*-methoxyphenyl)phosphine, $(p\text{-}CH_3OC_6H_4)_3P$, produced the 4,4′-dichlorobiphenyl and 4,4′-dimethoxy biphenyl respectively. These reactions also produced chlorobenzene and anisole. The formation of 4,4′-disubstituted biphenyl as the only coupling product rules out the possibility of the above described mechanism (Scheme 1) involving the *ortho*-metallation.

The other two possible ways for the cleavage of the phosphorus-aryl bond and the formation of Pd–aryl species are (i) nucleophillic attack on phosphorus coordinated to palladium by a nucleophile (Scheme 2) and (ii) electrophillic attack of a palladium species on the aromatic nucleus (Scheme 3).

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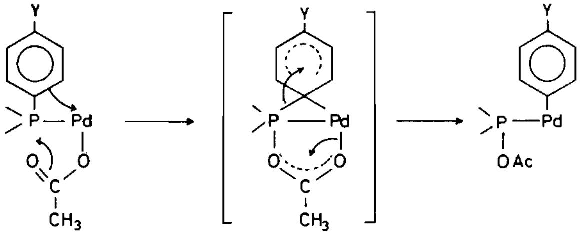
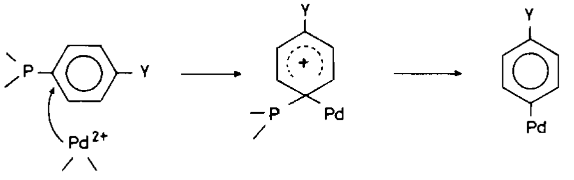


Scheme 2.



Scheme 3.

For the nucleophillic attack reaction (Scheme 2), the rate of the aryl groups migration should be slower in the cases of aryl phosphines containing electron releasing substitutes at the *para*-position (*e.g.*, Me or MeO) compared to that containing electron withdrawing substituents (*e.g.*, Cl). On the other hand, for the mechanism involving electrophillic attack of palladium species on the aromatic nucleus (Scheme 3), the rate of the aryl groups migration should be slower for the aryl phosphines containing electron withdrawing substituents at the *para*-position. In order to determine the mechanism, several experiments were carried out where an equimolar mixture of two different aryl phosphines having variable electronic parameters, *i.e.*, different *para*-substituents, was allowed to react with $Pd(OAc)_2$.

When an equimolar mixture of tri(*p*-tolyl)phosphine, $(p\text{-}CH_3C_6H_4)_3P$, tri(*p*-chlorophenyl)phosphine, $(p\text{-}ClC_6H_4)_3P$ and $Pd(OAc)_2$ were allowed to react in refluxing benzene for 2 hrs, three biaryl products, *i.e.*, 4,4′-dimethylbiphenyl (homo coupling of *p*-tolyl groups), 4-methyl-4′-chloro biphenyl (mixed coupling of *p*-tolyl and *p*-chlorophenyl groups) and 4,4′-dichlorobiphenyl (homo coupling of *p*-chlorophenyl groups) were observed in approximately 1:2:3 ratio. Thus the rate of *p*-chlorophenyl group migration was observed to be twice as fast as that of the *p*-methylphenyl (*p*-tolyl) group. Similarly in the reaction of $Pd(OAc)_2$ with equimolar amounts of Ph_3P and $(p\text{-}CH_3C_6H_4)_3P$, three coupling products were formed: *i.e.*, biphenyl (homo coupling of phenyl groups), 4,4′-dimethylbiphenyl (homo coupling of *p*-tolyl groups) and methyl biphenyl (hetero coupling of phenyl and *p*-tolyl groups). The amount of phenyl groups in these products was about 10% higher than that of *p*-tolyl groups. The reaction of $Pd(OAc)_2$ with an equimolar mixture of tri(*p*-chlorophenyl) phosphine and tri(*p*-methoxy phenyl)phosphine, $(p\text{-}CH_3OC_6H_4)_3P$, also produced higher amounts of dichlorobiphenyl compared to that of dimethoxybiphenyl (>2:1 ratio). The reaction also produced the mixed chloromethoxy biphenyl. These results are supportive of the mechanism involving the nucleophillic attack of a nucleophile on the coordinated phosphine (Scheme 2), for the migration of aryl groups from the phosphines to the palladium center.

In order to confirm that no other factors such as steric parameters (if any) of the different para substituted aryl groups of various above aryl phosphines are involved in the aryl group migration from phosphorus to palladium, reaction of a mixed phosphine, *i.e.*, diphenyl(*p*-tolyl)phosphine, was carried out with $Pd(OAc)_2$. Since it contains phenyl and *p*-tolyl groups in 2:1 ratio, the probability of obtaining phenyl group containing products is two times higher to that of tolyl group containing product provided no other effects are involved. Indeed, the products observed were biphenyl, methylbiphenyl and 4,4′-dimethyl biphenyl in the ratio 4.1:4.2:1.0 making phenyl:*p*-tolyl groups in 2:1 ratio.

Formation of the homo- and hetero-aryl groups coupling products from the aryl–palladium intermediate, formed in these reactions via the mechanism outlined in Scheme 2, is either the consequence of a bimolecular mechanism [10] or more likely of a radical process [11]. A bimolecular process, however, does not explain the formation of the hydrocarbon products such as benzene, toluene, chlorobenzene, anisole, *etc.* in these reactions since no Pd–H bond is formed. On the other hand, the radical process where aryl radicals are formed *via* the decomposition of aryl–palladium bonds does explain the formation of aromatic hydrocarbons by hydrogen atoms abstraction. Preliminary experiments where spin-trapping agent (e.g., N-*tert*-butyl-α-phenylnitrone) was added in the reactions of tertiary arylphosphines with $Pd(OAc)_2$, showed the formation of radicals in the ESR spectra. The amount of radicals varied depending upon the phosphine used and higher amounts were observed in the cases of the electron withdrawing substituents at the *para*-position. Further efforts are being made to prove conclusively the generation of radicals in these reactions.

The reaction of triphenylphosphine with $PdCl_2$ under carbon monoxide pressure (≥2000 psig) at >160 °C also resulted in the formation of products such as benzophenone, anthraquinone, benzaldehyde, benzoylchloride, in addition to benzene and biphenyl. The probable reaction sequences involved here have been described earlier [6].

In conclusion, the cleavage of aryl–phosphorus groups in the tri-arylphosphine catalyzed by palladium(II) salts has been demonstrated to produce a series of organic products under various reaction conditions. Evidence against the earlier proposed mechanism [6, 9] involving the probable *ortho*-metalation by oxidative addition process and in support of a mechanism involving the nucleophillic attack of a nucleophile on the coordinated phosphorus and migration of aryl group (or groups) to the palladium have been presented. A radical process for the cleavage of aryl–palladium yielding coupling biaryl products and the aromatic hydrocarbons by hydrogen atoms abstraction has been proposed.

Acknowledgements

The author is grateful to Professor J. C. Bailer, Jr., of the University of Illinois at Urbana-Champaign, Illinois for some very valuable suggestions.

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