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Palladium(II) Catalyzed Aryl Groups Exchange between Triarylphosphines

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Studies focusing the process of catalyst degradation in the course of homogeneous transition metal catalyzed organic synthesis have become a very important field of research in recent years [1, 2]. Such a catalyst deactivation process has been shown to occur generally via an interaction of the metal with the ligands in some undesired manner leading to various by-products. Recently we reported a similar unexpected interaction of palladium(II) salts with triphenyl stibene and triarylphosphines under various reaction conditions resulting in the cleavage of phenyl–antimony and aryl–phosphorus bonds and yielding various organic products [2]. The cleavage reactions of Ph_3Sb and Ph_3P under CO_2 or (NO + CO) pressure resulted in the formation of benzoic acid as the major product. Now we wish to report here for the first time the palladium(II) catalyzed aryl groups exchange between triarylphosphines and also the redistribution of aryl groups of mixed arylphosphines.

We have earlier reported that the reaction of Ph_3P and Ph_3Sb with $Pd(OAc)_2$ in toluene at >80 °C produce phenyl groups containing organic products such as biphenyl (coupling product), benzene and phenyl acetate. Similarly the reactions of *para*-substituted triarylphosphine afforded the organic products, however, the coupling products were found to be the 4,4′-disubstituted biaryls, thus ruling out the possible *ortho*-metalation of C–H bonds of arylphosphines as the reaction pathway for the Ar–P cleavage process [3].

When the above reaction was carried out by reacting a mixture of two different triarylphosphines with $Pd(OAc)_2$, formation of three different coupling products (two homo-coupling and one hetero-aryl coupling) was observed [2] which suggested the possible involvement of either a bimolecular or a radical process [4] in the product formation step. Now we have found that in these reactions involving a mixture of two different but symmetrical triarylphosphines with $Pd(OAc)_2$, exchange of aryl groups between the phosphines occurs resulting in the formation of two new mixed aryl groups containing unsymmetrical phosphines. The amounts of these mixed aryl groups containing phosphines were found to be dependent on the starting triarylphosphines and with time all of them were converted to the organic products (Scheme 1). In a typical example,

$$(Ar)_3P + (Ar')_3P \overset{Pd(II)}{\rightleftharpoons} (Ar)(Ar')_2P + (Ar)_2(Ar')P$$

$$Ar{-}Ar' + Ar{-}Ar + Ar'{-}Ar' + ArH + Ar'H$$

(where Ar or Ar′ = phenyl, *p*-tolyl, *p*-chlorophenyl, *p*-methoxyphenyl)

Scheme 1.

when triphenylphosphine, Ph_3P, and tri-*p*-tolylphosphine, $(p\text{-}CH_3C_6H_4)_3P$, were allowed to react with $Pd(OAc)_2$ in toluene at 100 °C for 15 minutes, in addition to the three coupling products (biphenyl, 4,4′-dimethyl biphenyl and 4-methylbiphenyl), the two mixed phenyl and *p*-tolyl groups containing phosphines, *i.e.*, $Ph_2(p\text{-}CH_3C_6H_4)P$ and $Ph(p\text{-}CH_3C_6H_4)_2P$ were also formed. Such palladium(II) catalyzed exchange of aryl groups was also observed between triphenylstibene and triarylphosphine, although to a lesser extent. For example, in the reaction of a mixture of Ph_3Sb and $(p\text{-tolyl})_3P$ with $Pd(OAc)_2$, formation of mixed phenyl (*p*-tolyl) phosphines was identified. This lower exchange reactivity may be due to the fact that the cleavage of Ph–Sb bonds occurs at a much faster rate than that of *p*-tolyl–P bonds of $(p\text{-tolyl})_3P$ thus yielding biphenyl as the major product. Interestingly, the redistribution of aryl groups was observed in the reaction of $Pd(OAc)_2$ with mixed aryl groups containing phosphine, $(Ar)_n(Ar')_{3-n}P$, to give the corresponding two triarylphosphines and a mixed arylphosphine (eqn. 2) along with other organic products.

$$(Ar)_n(Ar')_{3-n}P \overset{Pd(II)}{\rightleftharpoons} (Ar)_3P + (Ar')_3P + (Ar)_{3-n}(Ar')_nP$$

(where Ar = Ph and Ar′ = *p*-tolyl and *p*-chlorophenyl)

Scheme 2.

Thus, when a solution of $Ph_2(p\text{-tolyl})P$ and $Pd(OAc)_2$ was heated, formation of two symmetrical triarylphosphines, *i.e.*, Ph_3P and $(p\text{-}CH_3C_6H_4)_3P$ along with a mixed phenyl di-*p*-tolyl phosphine, $Ph(p\text{-}CH_3C_6H_4)_2P$, was observed.

Preliminary experiments using salts of other group VIII metals in their lower as well as higher oxidation states also result in the exchange of aryl groups on phosphines. If such exchange and redistribution of the aryl groups on phosphines is catalyzed by most commonly used metals, it raises a serious question about the actual effect of various ligands in studies such as electronic effect of ligands.

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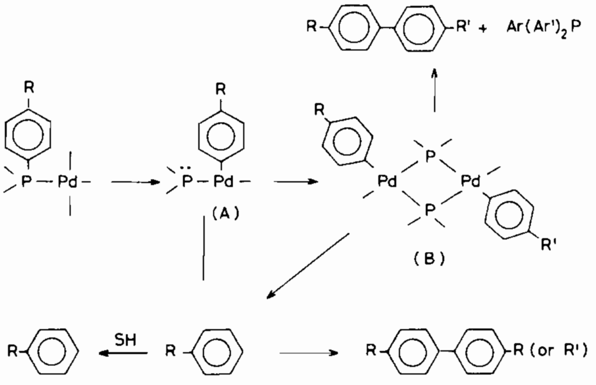
It is important to note that in all the aryl groups exchange or redistribution reactions of triarylphosphines with one or more *para*-substituted aryl groups, the resulting new phosphine products also contained the substituents at the *para*-position. Therefore, it appears that the entire process of cleavage and reformation does not involve the *ortho*-metallation of C–H bonds of triarylphosphines that would have resulted in the formation of *meta*-substituted aryl groups products. Formation of various coupling products and the exchange of aryl groups between triarylphosphines from an intermediate of the type (*A*) can be the result of either a bimolecular mechanism or a radical process (Scheme 3).



Scheme 3.

Recently Albinati *et al.* [5] have observed the cleavage of Ph–P bond of Ph$_3$P and the formation of a phosphido-bridged diplatinum complex in the thermally induced reductive elimination of benzene from the complex $[(Ph_3P)_2Pt(\mu\text{-}H)_2Pt(Ph)(Ph_3P)_2]^+$. Our preliminary experiments where a spin-trapping agent (*e.g.* N-tert-butyl-α-phenylnitrone) was added in the reactions of triarylphosphine with $Pd(OAc)_2$, showed the formation of radicals in the EPR spectra. Further efforts are being made to prove conclusively the involvement of a radical process either partially or exclusively and also to extend these studies to other group VIII metal complexes.

References

1 D. R. Coulson, *J.C.S. Chem. Commun.*, 1530 (1968); R. Cramer and D. R. Coulson, *J. Org. Chem.*, *40*, (1975); C. W. Bradford, R. S. Nyholm, G. J. Gainsford, J. M. Guss, P. R. Ireland and R. Mason, *J.C.S. Chem. Commun.*, *87* (1972); C. W. Bradford and R. S. Nyholm, *J. Chem. Soc., Dalton Trans.*, 529 (1973); D. R. Fahey and J. E. Mahan, *J. Am. Chem. Soc.*, *98* (1976); J. R. Blickensderfer and H. D. Kaesz, *J. Am. Chem. Soc.*, *97*, 2681 (1975); T. Yamane, K. Kikukawa, M. Takagi and T. Matsuda, *Tetrahedron*, *29*, 955 (1973); K. Kikukawa, T. Yamane, Y. Ohbe, M. Takagi and T. Matsuda, *Bull. Chem. Soc. Jpn.*, *52*, 1187 (1979).

2 A. B. Goel, H. J. Richards and J. H. Kyung, *Inorg. Chim. Acta*, *76*, L95 (1983); Tetrahedron Letters (in press).

3 A. D. Ryabov and A. K. Yatsimirsky, *J. Mol. Cat.*, *4*, 449 (1978).

4 P. M. Henry, 'Palladium Catalyzed Oxidation of Hydrocarbons', Vol. 2, p. 312, D. Reidel Publication, Boston, MA, U.S.A. (1981).

5 A. Albinati, J. Jans, R. Naegeli and L. M. Venanzi, Presented at XI Int. Conf. on Organomet. Chem. Pine Mountain, Georgia, Oct. 10–14, 1983.