Tetrahedron Letters,Vol.25,No.41,pp 4599-4600,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

FORMATION OF DIARYL(ALLYL)PHOSPHINE IN π -ALLYL PALLADIUM(II) INDUCED CLEAVAGE OF TRIARYLPHOSPHINES

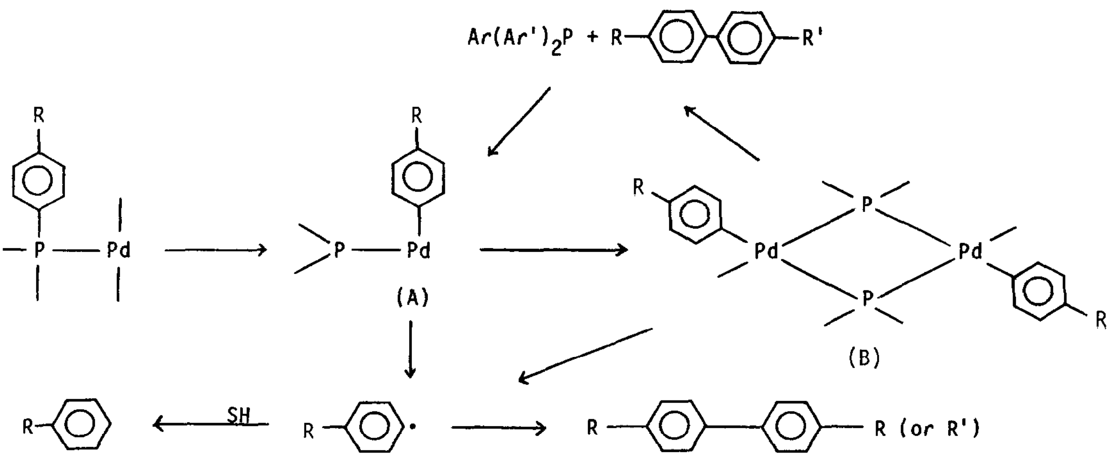
Anil B. Goel*
Ashland Chemical Company, Ventures Research and Development
P. O. Box 2219, Columbus, Ohio 43216, U.S.A.

ABSTRACT: A reverse migration of allylic group from palladium to phosphorus and the formation of diaryl(allyl)phosphine in the π -allyl palladium(II) induced cleavage of triarylphosphines has been demonstrated.

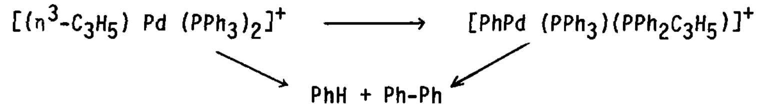
Studies concerning an undesired interaction of ligands with the metals leading to various by products in the course of homogeneous catalysis have become an important field of research in recent years[1-3]. Recently, we reported the cleavage of Ar-E (E = P or Sb and Ar = phenyl and p-substituted phenyl group) bonds of triarylphosphines and stibene in the palladium(II) salts catalyzed reactions and demonstrated the formation of a variety of aryl groups containing organic products under various reaction conditions[2]. Now I wish to report here for the first time the reverse migration of an allylic group from palladium to phosphorus and formation of diaryl(allyl)phosphine in the π -allyl palladium(II) induced cleavage of aryl-phosphorous bond of triarylphosphines.

In the palladium catalyzed reactions involving a mixture of two different but symmetrical triarylphosphines, formation of mixed aryl groups containing tertiary phosphines $Ar_2Ar'P$ and $ArAr'_2P$ along with homo- and hetro-aryl groups coupling products has been observed. When these reactions have been carried out for longer time, all the starting and the intermediate phosphines have been found to undergo Ar-P bond cleavage to produce organic products. In these reactions, migration of aryl groups from phosphine to palladium to form an organo-palladium intermediate of the type (A) has been proposed as the initial step. Formation of various coupling products and the exchange of aryl groups between triarylphosphines from this intermediate (A) can be the result of either a bimolecular mechanism[3] (intermediate B) or a radical process[4] (Scheme 1).

Scheme 1



The formation of mixed arylphosphines indicates the involvement of a reverse migration of an aryl group from palladium to the diarylphosphido-group. In view of this, a similar exchange of an organo-group of a preformed organo-palladium complex with an aryl group of triarylphosphine has been considered probable. In order to verify this, reactions of triarylphosphines, Ar_3P (Ar = phenyl or p-tolyl), with π-allyl palladium(II) complexes have been carried out and not surprisingly, exchange of an aryl group of triarylphosphine with the allyl group was noticed to produce a mixed diaryl(allyl)phosphine as an intermediate phosphine. Thus, when a cationic π-allyl palladium complex $[(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2]^+BF_4^-$ (1), was heated in toluene at >130°C in a closed reactor under inert atmosphere, formation of ~ 10% diphenyl(allyl)phosphine along with biphenyl (35%) and benzene (~ 7%) was noticed within 15 minutes (Scheme 2). The intermediate product, diphenyl(allyl)phosphine was confirmed by GC, GC/MS and ^1H NMR spectral analysis. In a similar reaction of Ar_3P with $[(\eta^3\text{-}C_3H_5)Pd(Cl)]_2$, about 5% diaryl(allyl)phosphine was detected by GC.



The above formation of mixed phosphines via the exchange of an aryl group of triarylphosphine with an allyl group at palladium, represents the first clear demonstration of the process of cleavage of aryl-phosphorus bond, transfer of the aryl group to the metal and reverse migration of the organic group from metal to phosphorus. Efforts are being made to further demonstrate such migration of alkyl or aryl groups from other group VIII transition metals to the phosphines and gather conclusive evidence in support of the involvement of either a bimolecular mechanism or a radical process.

REFERENCES:

1 D.R. Coulson, J.C.S. Chem. Commun., 1530 (1968); R. Cramer and D.R. Coulson, J. Org. Chem., 40, 2267 (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 Lett., 25, 391 (1984); A. B. Goel, Inorg. Chim. Acta, 84, L25 (1984).
3. "Formation of a Diphenylphosphido-Bridged Diplatinum Complex in the Platinum Catalyzed Cleavage of Ph_3P has recently been reported by A. Albinati," J. Jans, R. Naegeli and L.M. Venanzi, Presented at XI Int'l. Conf. on Organometal Chem., Pine Mountain, Georgia, Oct. 10-14, 1983.
4. P.M. Henry, "Palladium Catalyzed Oxidation of Hydrocarbons", Vol. 2, P. 312, D. Reidel Publication, Boston, MA U.S.A. (1981)

(Received in USA 2 July 1984)