Reaction of Coordinated Phosphines. III. Reaction of Phenyl Compounds of Typical Groups V and VI Elements with Palladium(II) Salts in the Presence of Olefinic Compounds[1)]

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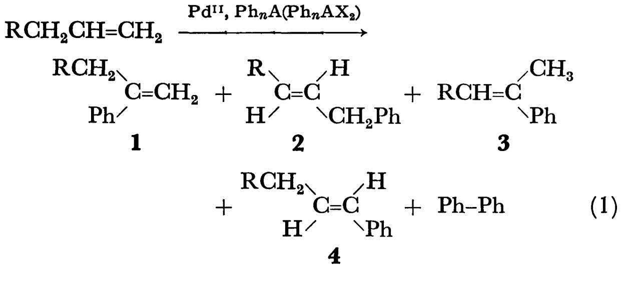
The reaction of phenyl compounds of typical groups V and VI elements, Ph_nA and Ph_nAX_2 (n=2, 3; A=P, As, Sb, Bi, S, Se, Te; X=Cl or X_2=O), with Pd(II) salts was studied in the presence of olefinic compounds (1-octene and ethyl acrylate) in acetonitrile. The phenyl migration from A to Pd to produce phenylpalladium species, which lead to the phenylation of olefin, was observed for all Ph_nA and Ph_nAX_2 (except for A=S and Ph_3PX_2) when $Pd(OAc)_2$ was utilized. The reaction, however, was inhibited or greatly suppressed for the compounds of P and As when $PdCl_2$ was used in place of $Pd(OAc)_2$. The compounds of Sb and Bi readily react with $PdCl_2$. Mechanistic discussion was given in terms of the extent of nucleophilic assistance by acetate ion when Pd(II) attacks the aromatic nucleus electrophilically at the carbon atom bonded to A.

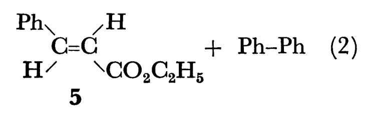
Previous observations on the migration of the aryl group from Ar_3P (coordinated to $Pd(OAc)_2$) to Pd under mild conditions,[2)] prompted us to examine other typical groups V and VI elements for similar reaction. Since the resulting phenylpalladium species is expected to show a similar reactivity to that derived from Ph_3P or phenylmercury(II) salts, the rate and extent of phenyl migration were assessed by the phenylation of added olefin. Asano *et al.* found that Ph_3As, Ph_3Sb and Ph_3Bi give *trans*-stilbine and biphenyl on reaction with $Pd(OAc)_2$ and styrene in refluxing dioxane–acetic acid.[3)] The present study deals with a more detailed aspect of the reactions under milder conditions with the aim of obtaining a general mechanistic insight into this type of phenyl migration.

Results

The reaction of Ph_nA with $Pd(OAc)_2$ in the presence of 1-octene or ethyl acrylate in acetonitrile is summarized in Table 1, and given in the following. The reaction was nearly complete within 5 h. It is seen that all the phenyl groups in Ph_3Sb, Ph_3Bi, and Ph_2Te can be mobilized under suitable conditions. Only one phenyl group of Ph_3As was mobilized in the 5 h reaction, but the final yield (24 h reaction) of the phenylated olefins and biphenyl indicates that two phenyl groups out of three could migrate from As to Pd. No phenyl of Ph_2S was mobilized in 5 h. However, a trace of phenylated olefins could be detected on GLC after 25 h. The time dependence of the reaction shows that the phenyl migration was especially rapid for Ph_3Sb, Ph_3Bi, and Ph_2Te as compared with Ph_3As or Ph_2Se. The variation



$$\mathrm{RCH_2CH{=}CH_2} \xrightarrow{\mathrm{Pd^{II},\ Ph_nA(Ph_nAX_2)}} \underset{\mathbf{1}}{\mathrm{RCH_2(Ph)C{=}CH_2}} + \underset{\mathbf{2}}{\mathrm{R(H)C{=}C(H)CH_2Ph}} + \underset{\mathbf{3}}{\mathrm{RCH{=}C(CH_3)Ph}} + \underset{\mathbf{4}}{\mathrm{RCH_2(H)C{=}C(H)Ph}} + \mathrm{Ph{-}Ph} \quad (1)$$



$$\mathrm{CH_2{=}CHCO_2C_2H_5} \xrightarrow{\mathrm{Pd^{II},\ Ph_nA(Ph_nAX_2)}} \underset{\mathbf{5}}{\mathrm{Ph(H)C{=}C(H)CO_2C_2H_5}} + \mathrm{Ph{-}Ph} \quad (2)$$

Table 1. Reaction of Ph_nA with $Pd(OAc)_2$ and olefins in acetonitrile (50 °C, 5 h)

Ph_nA. Molar ratio, A/Pd	Olefin[a)]	Yield of phenylated olefin, %[b)] (composition)[c)]	Yield of biphenyl, %[d)]	Total phenyl mobilized, %[e)]
Ph_3As				
0.5	O	33(17, 32, 2, 49)	23	79
2	O	13(32, 28, 1, 39)	2	17
0.5	E	21	10	41
1	E	48	21	90
2	E	8	4	16
Ph_3Sb				
1[f)]	O	113(16, 12, 15, 57)	70	253
0.5	E	120	15	150
1	E	203	20	243
2	E	208	30	268
3	E	195	60	315
Ph_3Bi				
1[f)]	O	48(11, 29, 8, 52)	120	288
0.5	E	43	43	129
1	E	80	100	280
2	E	73	240	553
3	E	47	260	567
Ph_2Se				
1	O	27(26, 29, 4, 41)	g)	(>27)
1	E	23	g)	(>23)
2	E	22	g)	(>22)
Ph_2Te				
0.5	E	90	h)	(>90)
1	E	147	h)	(>147)
2	E	194	h)	(>194)

a) O: 1-Octene; E: ethyl acrylate. b) (Mol of phenylated olefin/mol of $Pd(OAc)_2$)×100. c) % Composition of the phenylated octenes, **1**, **2**, **3**, and **4**, in this order. d) (Mol of biphenyl/mol of $Pd(OAc)_2$)×100. e) (Mol of phenyl group released from A/mol of $Pd(OAc)_2$)×100, calculated from (% value from b)) plus (% value from d))×2. f) Reaction at 25°C. g) Not determined, less than the phenylated olefin. h) Not determined.

in A/Pd ratio did not cause much difference in the reaction rate for the compounds of Bi, Sb, Te, and Se. However, the increase in As/Pd ratio over 1 considerably decreased the rate of phenyl migration. A similar observation was made for the reaction of Ph_3P.[2a] It is probable that as in the case of Ph_3P, the coordination of the second molecule of Ph_3As to Pd exercises some unfavorable effect on the phenyl migration process.

Some reaction systems show a marked tendency to form biphenyl rather than phenylated olefins. This is especially true for the system where the formation of the phenylpalladium species is rapid (*e.g.*, Ph_3Sb and Ph_3Bi). This is at least partially due to the fact that without sufficient supply of olefin the phenylpalladium species decompose to form biphenyl. A slight modification was made in experimental procedure for the reaction of Ph_3Sb and Ph_3Bi (Table 1). A mixture of the olefin and Ph_nA (A=Sb, Bi) was added to a solution of $Pd(OAc)_2$ in acetonitrile. When they were subjected to reaction by the standard procedure (prior reaction of $Pd(OAc)_2$ and Ph_3A in acetonitrile, see Experimental), most of the organic products were biphenyl. The reaction of PhHgOAc studied under comparative conditions indicates that the formation of biphenyl is unimportant (1—2% yield). The marked tendency of Ph_3Bi to form biphenyl seems to reflect a certain inherent nature of the compound.

The time-yield profiles for various Ph_nA are given in Fig. 1 to show the phenylation of ethyl acrylate under the same reaction conditions. Solid Ph_3A (0.50 mmol) was added to a solution of $Pd(OAc)_2$ (0.50 mmol) in a mixture of ethyl acrylate (5.0 mmol) and acetonitrile (3.0 g) at 50 °C. Some discrepancy in yields (at 5 h of reaction) from those in Table 1 reflects a subtle difference in the experimental procedure.[4]

Phenylation of olefins with $Ph_3P–Pd(OAc)_2$ under nitrogen proceeds much more slowly than that under ordinary atmosphere.[1] The aerobic reaction might remove excess phosphine ligand from the coordination sphere of Pd through oxidation. Thus, the reaction of Ph_3As is greatly suppressed under nitrogen, while no major effect is observed with the compounds of Sb, Bi, Te, and Se. The reaction of PhHgOAc with olefin under nitrogen was also shown not to differ from that under aerobic conditions.

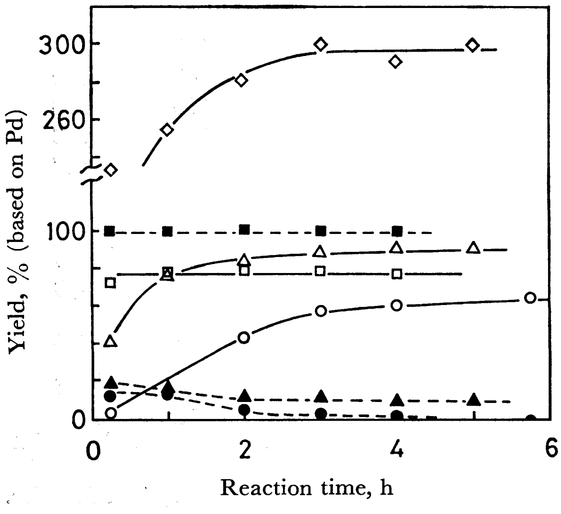


Fig. 1. The reaction of Ph_3A with $Pd(OAc)_2$ in the presence of ethyl acrylate (50 °C). Ph_3A, 0.50 mmol; $Pd(OAc)_2$, 0.50 mmol; ethyl acrylate, 5.0 mmol; acetonitrile, 3.0 g. ——, **5**; ----, biphenyl. A: P(○,●), As (△,▲), Sb(◇), Bi(□,■).

$Ph_3P–PdCl_2$ does not phenylate olefins in the absence of added sodium acetate.[2a] A similar study indicates that the compounds of P, As, and Se are completely or almost inactive without acetate ion. The compounds of Sb, Bi, and Te, on the other hand, exhibit somewhat decreased reactivity, but still phenylate ethyl acrylate effectively. Phenylmercury(II) chloride coupled with $PdCl_2$ has been utilized as an effective phenylating agent for olefin.[6] Hg requires no assistance by acetate ion in the migration of phenyl group from Hg to Pd. These observations indicate an essential difference in the mechanism of phenyl migration according to the nature of elements. If the nucleophilic attack by acetate ion on the coordinated A atom[2a] is important for the reaction of Ph_3P, Ph_3As, and Ph_2Se with bivalent Pd, we might expect that the reaction is suppressed for quinquevalent P and As (or with quadrivalent Se), since the coordination through A atom is impossible. The reactions of Ph_3PO or Ph_3PCl_2 were completely inhibited, those of Ph_3AsO or Ph_3AsCl_2 being suppressed a great deal. The reactions of Ph_2SeCl_2 were slightly suppressed. On the other hand, no major influence on the phenyl transfer activity was observed for Ph_3SbCl_2 and Ph_3BiCl_2. These observations are in line with the idea that the mechanism of phenyl migration can vary among elements A.

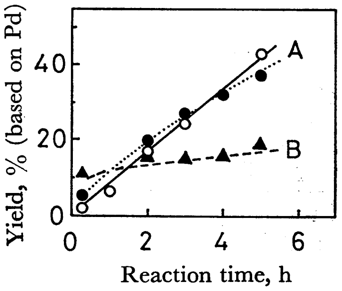
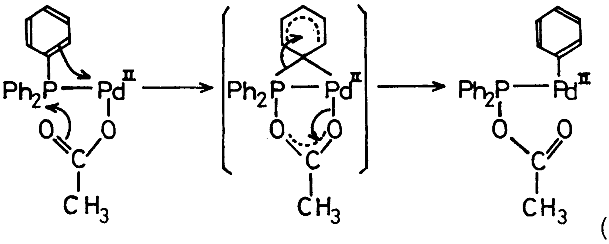


Fig. 2. The phenyl transfer from P to Pd as assessed by quenching with bromine (A) and by phenylation of ethyl acrylate (B) (25 °C).
A: Ph_3P, 2.0 mmol; $Pd(OAc)_2$, 2.0 mmol; acetonitrile, 30 g; ○, ●, duplicate runs.
B: Ph_3P, 0.50 mmol; $Pd(OAc)_2$, 0.50 mmol; ethyl acrylate, 5.0 mmol; acetonitrile, 3 g.
yield: (mol of bromobenzene or **5**/mol of $Pd(OAc)_2$) × 100.

The formation of phenylpalladium species has hitherto been studied by the phenylation of olefins. As a more direct method for characterizing the unstable intermediate, the quenching experiments with bromine were attempted for the reaction of Ph_3P and $Pd(OAc)_2$ at 25 °C (Fig. 2). The aliquots withdrawn at appropriate time intervals were allowed to react with excess bromine in carbon tetrachloride. Bromobenzene which seems to be formed by the "bromodepalladation reaction"[7] of the phenylpalladium salts increased approximately linearly with the reaction time, supporting the formation of the chemical species containing the phenyl-palladium bond. Phenylation of ethyl acrylate under similar conditions was obviously slow as compared to the formation of phenylpalladium species. A problem remains in the quenching practice as to a satisfactory way for standardizing the analytical method. In the reaction of $PhPd(Ph_3P)_2I$ with excess bromine, 67% of bromobenzene was obtained along with 4% of iodobenzene, indicating that the bromodepalladation of the complex is not quantitative.

Discussion

The results could be rationalized by two extreme reaction mechanisms for the phenyl transfer from A to Pd. The first is represented by Ph_3P given in Scheme 3 where only the relevant ligands on Pd are shown. PPh_3 coordinated to bivalent Pd is in effect phosphonium ion, which is attacked by acetate ion on P, and concurrently, the phenyl group on P migrates to the vacant coordination site on Pd. Thus, the mechanism is an electrophilic aromatic substitution of P by Pd (or a 1,2-shift of phenyl group from P to Pd) promoted by nucleophilic assistance by acetate ion. It is not at all certain, however, whether the acetate ion which attacks P requires a prior coordination to Pd (Scheme 3). The process of phenyl migration from an electron rich to electron deficient center (1, 2-shift of aryl group[8]) and the ability of acetoxyl group for anchimeric assistance[9] are familiar in organic chemistry. On the other hand, the reaction of the compounds of Bi seems neither to require the prior coordination of A to Pd nor necessitate the nucleophilic assistance by acetate ion. Thus, a simple electrophilic aromatic substitution by bivalent Pd would be enough to describe the reaction (Scheme 4). Phenylmercury (II) salts might react with bivalent Pd in a similar way.



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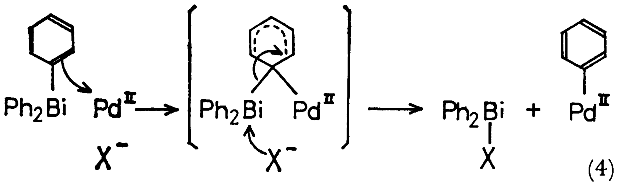

(4)

For the elements other than P and Bi, the entity of the reaction would be somewhere between the two extremes, and no discontinuous change in mechanism seems to be involved. The reactions of As are more related to those of P, while the reactivity of Sb and Te seems to be close to that of Bi or Hg. The factors responsible for these varying reactivities of Ph_3A would be the decreasing A–C bond energy in the order $Bi<Sb<As<P$[3] coupled with the decreasing electronegativity $Bi<Sb<P<As$,[10] both facilitating the electrophilic aromatic substitution on the carbon atom bonded to Bi or Sb. In order to cleave the more stable P–C bond *via* electrophilic process on carbon, a prior coordination of phosphorus to palladium is required, which not only brings the reactants into close proximity but also enables the nucleophilic assistance by acetate ion on the coordinated P atom. The donor ability of Ph_3A increases in the order $P>As>Sb\gg Bi$.[11]

Experimental

Materials. $Pd(OAc)_2$ was prepared by the method of Stephenson *et al.*[12] Commercial transition metal salts were used. The following phenyl derivatives of groups V and VI typical elements were synthesized according to the reported procedures and identified by elemental analyses as well as by comparison of IR and melting points; Ph_3Sb,[13] Ph_3Bi,[14] Ph_2Se,[15] Ph_2Te,[16] Ph_3PCl_2,[17] Ph_3AsCl_2,[17,18] Ph_3AsO,[19] Ph_3SbCl_2,[14] Ph_3BiCl_2,[20] Ph_2SO,[21] Ph_2SeCl_2.[22] Commercial Ph_3P and Ph_3As were used with or without further purification. Phenylpalladium complex, $PhPd(Ph_3P)_2I$, was prepared[23] and identified by elemental analysis.

Reaction of Ph_nA with Pd(II) Salt in the Presence of Olefinic Compounds. The reaction was carried out in the following way with slight modifications. In a reaction cell fitted with a constant-temperature water jacket were placed 0.50 mmol of Ph_nA (or Ph_nAX_2), desired amount (0.25—1.0 mmol) of Pd(II) salt and 3.0 g of acetonitrile. After the mixture had been stirred for 5 min, 5.0 mmol of olefin (1-octene or ethyl acrylate) and an internal standard (diethylene glycol dibutyl ether or 1,2-diphenylethane) were added. The reaction was monitored by analyzing the phenylated olefins and biphenyl, until the precipitation of palladium black was complete (usually 24 h). Identification of the reaction products was reported.[2]

Reaction of Ph_3P with $Pd(OAc)_2$, Quenching with Bromine. $Pd(OAc)_2$ (0.50 mmol) was dissolved in acetonitrile (3.0 g, with chlorobenzene as an internal standard) in a thermostatted cell at 25 °C. Ph_3P (0.50 mmol) was then added. Samples were withdrawn from the reaction mixture and added to the excess bromine ($\approx$2 mmol) dissolved in carbon tetrachloride. The mixture was shaken with 10% aq $Na_2S_2O_3$, and the organic layer was separated. The latter solution was analyzed by GLC after being dried with $MgSO_4$. The use of iodine in place of bromine proved inadequate, since the reaction of Ph_3P with iodine did not reach completion and the phenyl transfer reaction continued to take place. The reaction of $PhPd(Ph_3P)_2I$ with bromine was carried out in a similar way. The complex was dissolved in acetonitrile or in a mixture of acetonitrile and dichloromethane and treated with 4—5 folds molar excess bromine in carbon tetrachloride.

References

1) Presented at 21st (Sendai, 1973) and 22nd (Kyoto, 1974) Symposium on Organometallic Chemistry. The lectures 205 and 205B, respectively, in the Abstract.

2) a) T. Yamane, K. Kikukawa, M. Takagi, and T. Matsuda, *Tetrahedron*, **29**, 955 (1973); b) K. Kikukawa, T. Yamane, M. Takagi, and T. Matsuda, *Chem. Commun.*, **1972**, 695.

3) R. Asano, I. Moritani, Y. Fujiwara, and S. Teranishi, *Bull. Chem. Soc. Jpn.*, **46**, 2910 (1973).

4) The yield of biphenyl decreases with time (Fig. 1). Control experiments showed that most of the biphenyl detected at the early stage of the reaction is an artifact induced by direct GLC analysis.

5) R. F. Heck, *J. Am. Chem. Soc.*, **93**, 6896 (1971) and Refs. cited therein.

6) R. F. Heck, *J. Am. Chem. Soc.*, **90**, 5518 (1968).

7) The halodemetallation reaction of various arylmetal compounds is summarized in R.O.C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier, New York, N.Y. (1965), Chap. 10.

8) R. Muneyuki and H. Tanida, "Theoretical Organic Chemistry, Structural Part," (in Japanese), ed by M. Nakagawa, Kagaku-dojin, Kyoto (1974), p. 50.

9) "Molecular Rearrangements, Part One, ed by P. de Mayo, Interscience Publishers, New York, N.Y. (1963), p. 1244.

10) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry, A Comprehensive Text," 2nd ed, Interscience Publishers, New York, N.Y. (1966), p. 486.

11) S. Murahashi, "Yukikinzoku Handobukku," Asakura Shoten, Tokyo (1967), p. 706.

12) T. A. Stephenson, S. M. Morehouse, A. R. Powell, T. P. Heffer, and G. Wilkinson, *J. Chem. Soc.*, **1965**, 3632.

13) G. S. Hiers, *Org. Synth.*, Coll. Vol. I, 550 (1956).

14) W. J. Lile and R. C. Menzies, *J. Chem. Soc.*, **1950**, 617.

15) H. M. Leicester, *Org. Synth.*, Coll. Vol. II, 238 (1950).

16) a) O. Steiner, *Ber.*, **34**, 570 (1901); b) K. Lederer, *ibid.*, **48**, 1345 (1915).

17) L. Horner, H. Oediger, and H. Hoffmann, *Justus Liebigs Ann. Chem.*, **626**, 26 (1959).

18) A. Michaelis, *Justus Liebigs Ann. Chem.*, **321**, 162 (1902).

19) A. W. Johnson, *J. Org. Chem.*, **25**, 183 (1960).

20) G. Wittig and K. Clauss, *Justus Liebigs Ann. Chem.*, **578**, 136 (1952).

21) C. E. Colby and C. S. McLoughlin, *Ber.*, **20**, 195 (1887).

22) H. M. Leicester, *Org. Synth.*, Coll. Vol. II, 240 (1950).

23) P. Fitton, M. P. Johnson, and J. E. McKeon, *Chem. Commun.*, **1968**, 6.