Palladium-Catalyzed Cleavage of P-C Bonds in Quaternary Phosphonium Salts and Its Applications to Organic Synthesis

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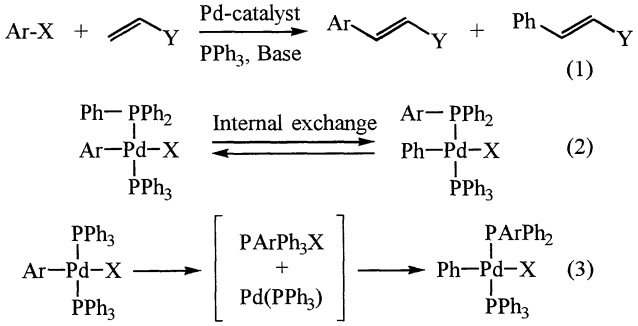
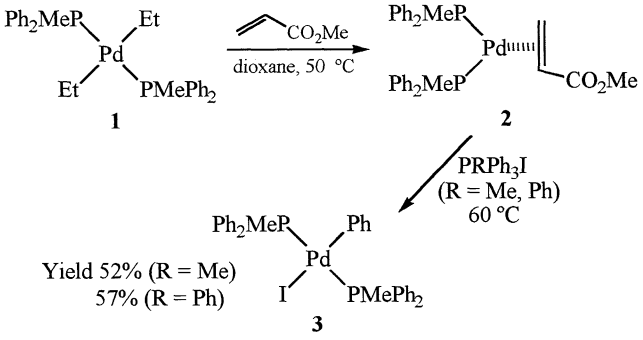
(Received September 5, 1995)

Phosphonium salts, PPh_4I and $PMePh_3I$, oxidatively add to Pd(methyl acrylate)$(PMePh_2)_2$ to give *trans*-[PdPhI$(PMePh_2)_2$] in moderate yields with cleavage of the P-phenyl bond. Conversely thermolysis of *trans*-$PdPhIL_2$ (L = $PMePh_2$ and PPh_3) reductively eliminates $PMePh_3I$ and PPh_4I, respectively. Application of the P-C bond cleavage process in phosphonium salts to olefination, carbonylation and hydrogenation reactions has been explored.

The objectives of the present study are twofold: one is to explore the applicability of the P-C bond cleavage reaction to organic synthesis and the other is to clarify the reason for the occurrence of an unwanted side reaction in Heck type reaction (olefination of aryl halides) to cause involvement of the phenyl group in PPh_3 ligand into the product olefin (Eq. 1).[1,2] Formation of the undesired product was accounted for by internal exchange of the aryl ligand in the intermediate complex with the phenyl group in the PPh_3 ligand (Eq. 2).[3] We considered an alternative route to the exchange process involving the reductive elimination of aryl halide and its subsequent combination with the PPh_3 to give quaternary phosphonium salt.[4] Oxidative addition of the phosphonium salt with the coordinatively unsaturated Pd(0) species with cleavage of the P-phenyl bond would produce a phenylpalladium halide complex (Eq. 3).[5]

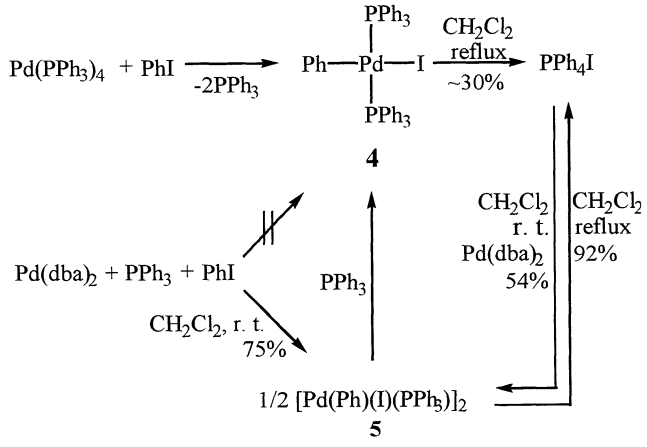


In fact treatment of a coordinatively unsaturated Pd(0) complex, Pd(methyl acrylate)$(PPh_2Me)_2$ **2**, with $PMePh_3I$ at 60 °C induced the cleavage of the P-phenyl bond in the phosphonium salt to produce *trans*-[PdPhI$(PMePh_2)_2$] **3** in 52% yield. Similarly the reaction of **2** with PPh_4I gave **3** in 57% yield (Scheme 1). Complex **3** can be prepared also by the reaction of **2** with phenyl iodide. Thermolysis of **3** at 80 °C in CD_3CN liberated $PMePh_3I$ and palladium black containing unidentified species having the $PMePh_2$ ligand. Similar behavior can be observed with PPh_3-coordinated palladium complexes. Thus, *trans*-[PdPhI$(PPh_3)_2$] **4**, which can be prepared by oxidative addition of phenyl iodide with $Pd(PPh_3)_4$, liberates ca. 30% of PPh_4I by refluxing **4** in CH_2Cl_2. Conversely, treatment of $Pd(dba)_2$ (dba = dibenzylideneacetone) with PPh_4I in CH_2Cl_2 in a 1 : 1 ratio at room temperature, as monitored by ^{31}P-NMR, formed the known phenylpalladium complex **5**[6] in 54% yield. The phenylpalladium complex **5** can be also prepared in 75% yield by treatment of $Pd(dba)_2$ with 1 equiv. of PhI in the presence of 1



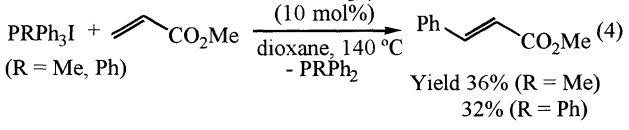
Scheme 1.

equiv. of PPh_3 in CH_2Cl_2 at room temperature with concomitant formation of PPh_4I (11%). The dimeric complex **5** containing one PPh_3 ligand per palladium seems to be more susceptible than **4** having two PPh_3 ligands to loss of the phosphonium salt PPh_4I. Refluxing **5** in CH_2Cl_2 liberated PPh_4I in 92% yield.



Scheme 2.

Upon finding the ready cleavage of the P-aryl bond in the phosphonium salt on its interaction with Pd(0) complexes we explored the applicability of the P-C bond cleavage reaction to organic synthesis. Treatment of quaternary phosphonium salt $PRPh_3I$ (R = Me or Ph) with methyl acrylate and triethylamine in the presence of $Pd(PPh_3)_4$ (10 mol%) in dioxane at 140 °C gave methyl cinnamate in 36% (R = Me) and 32% (R = Ph) yields, respectively (Eq. 4).



The aryl group in $PRAr_3I$ can be carbonylated in the presence of a palladium catalyst and an amine to give an amide **6** in excellent

Table 1. Palladium-Catalyzed Carbonylation of Quaternary Phosphonium Salts.[a]

Run	R	Ar	X	Yield of **6** /%	Yield of **7** /%
1[b]	Ph	Ph	I	< 7	10
2[c]	Ph	Ph	Cl	96	trace
3[c]	Ph	Ph	Br	99	trace
4[c]	Ph	Ph	I	67	trace
5[d]	Me	*p*-Tol	I	< 10	——
6[c]	Me	Ph	I	79	——

[a]All the yields were determined by GLC except for run 1 and 4, where the yields were determined by isolation. Catalyst used: [b]$PdCl_2(PPh_3)_2$ (5 mol%). [c]$Pd(PPh_3)_4$ (10 mol%). [d]$Pd(dba)_2$ (10 mol%).

to good yields and an α-keto amide **7** in low yields (Eq. 5 and Table 1).

$$PRAr_3X + CO \xrightarrow[\text{dioxane, 130 °C}]{\text{(50 ~70 atm)}} \underset{\textbf{6}}{ArCNEt_2} + \underset{\textbf{7}}{ArCCNEt_2} \quad (5)$$

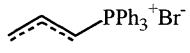
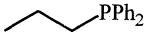
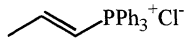
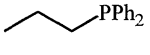
It is noteworthy that the reactivities of PPh_4X (X=I, Br, and Cl) in the carbonylation reaction are independent of the nature of X, whereas those of ArX are significantly dependent on X (reactivity: I~Br>>Cl).[7]

As an application of the P-C bond cleavage in the phosphonium salts combined with hydrogenation we examined the feasibility of preparation of mixed tertiary phosphines catalyzed by palladium catalysts (Eq. 6 and Table 2). Various phosphonium salts $PRPh_3I$ can be prepared readily by treatment of PPh_3 with alkyl and alkenyl iodides. Palladium-catalyzed hydrogenation of the phosphonium salts in the presence of diethylamine afforded alkyldiphenylphosphines as shown in Table 2. The reaction proceeds only in the presence of palladium catalysts and amine. In these cases, preferential cleavage of the P-aryl bond over the P-alkyl bond is recognized, although P-allyl and P-1-propenyl bonds are more reactive than P-aryl bonds (see run 5 and 6 in Table 2). The phosphonium salts, P^iPrPh_3I and P^nBuPh_3I, show lower reactivity, possibly because of steric reasons (see run 7 and 8 in Table 2). Further substitution of the tertiary phosphine $PRPh_2$ with an alkyl group(s) caused decrease in reactivity of the phosphonium salts. No reaction was observed when PMe_2Ph_2I or PMe_3PhI was employed.

$$PPh_3 + R\text{-}I \longrightarrow PRPh_3{}^+I^- \xrightarrow[\text{dioxane}]{\text{Pd-catalyst, } H_2 \text{ (100 atm)}, Et_2NH} PRPh_2 + Ph\text{-}H \quad (6)$$
$$130\ °C$$

This study was supported by grant from Nippon Zeon Co.

Table 2. Palladium-Catalyzed Hydrogenation of Various Phosphonium Salts

Run	Phosphonium Salt	Product	Yield/%[a]
1[b]	$PMePh_3{}^+I^-$	$PMePh_2$	96
2	$PMePh_3{}^+I^-$	$PMePh_2$	0[c]
3[b]	$PMePh_3{}^+I^-$	$PMePh_2$	0[d]
4[b]	$PEtPh_3{}^+I^-$	$PEtPh_2$	30
5[e]		PPh_3[f], 	66, 18
6[e]		PPh_3[f], 	29, 18
7[e]	$P^iPrPh_3{}^+I^-$	P^iPrPh_2	~5
8[e]	$P^nBuPh_3{}^+I^-$	P^nBuPh_2	11

[a]Determined by GLC. [b]$Pd(PPh_3)_4$ (1.0 mol%) was used. [c]Blank test without the palladium complex. [d]Blank test without Et_2NH. [e]$Pd(dba)_2$ (1.0 mol%) was used. [f]Formation of propene was observed.

and the Grant-in-Aid for Scientific Reserch on Priority Area of Reactive Organometallics No. 05236106 from the Ministry of Education, Science and Culture, Japan.

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