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Palladium Catalyzed Cleavage of Phenyl–Antimony Groups of Triphenylstibine

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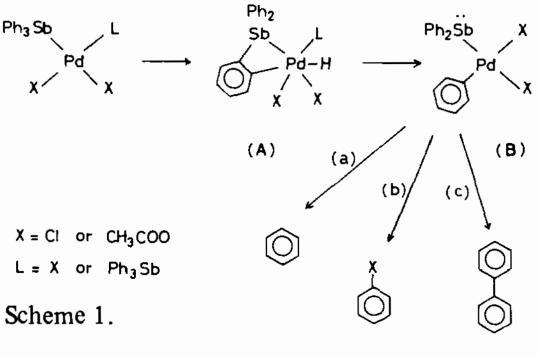
In transition metal catalyzed organic reactions, efforts have generally been concentrated mainly on the evaluation of important mechanistic steps leading from reactants to major products, and the steps leading to by-products often remain unrecognized. This latter process is often related to the catalyst decay probably occurring *via* an interaction of the metal with the ligands in some undesired manner and therefore such ractions should be explored carefully. For example, it has recently been observed that triphenylphosphine, most commonly used in the metal catalyzed reactions, can undergo a reversible oxidative addition to zerovalent nickel and palladium complexes [1].

Although several tertiary phosphine and arsine complexes of palladium(II) and platinum(II) have been known for quite some time and have frequently been used in many homogeneously catalyzed reactions, the corresponding stibine complexes have only recently received some attention [2–5]. Furthermore, although metalation and the oxidative addition reactions of triphenylphosphine in the palladium and platinum complexes have been documented [1, 6], no such process of triphenylstibine in palladium(II) complexes has ever been reported. Here we wish to report for the first time the palladium catalyzed cleavage of phenyl–antimony groups of Ph$_3$Sb and some reactions leading to formation of various organic products.

Reactions of palladium(II) acetate with one or two mol equivalents of triphenylstibine in solvents such as toluene at room temperature have been found to result in the formation of complexes of the type [Pd(OCOCH$_3$)$_2$(Ph$_3$Sb)]$_2$ and [Pd(OCOCH$_3$)$_2$(Ph$_3$Sb)$_2$] in solution [7]. The solution of these complexes in toluene upon heating at 100 °C or higher, resulted in the formation of organic products such as biphenyl, phenyl acetate and relatively smaller amounts of benzene. The amounts of these organic products have been found to be dependent on reaction conditions such as reaction time and temperature. In a typical experiment at 100 °C for 5 hr, about 70% biphenyl, 17% phenyl acetate and 5% benzene (based on palladium) were determined by GLC analysis. In a similar reaction, when triphenylstibine was treated with palladium(II) chloride at high temperatures (>100 °C), benzene, biphenyl and chloro-benzene were the observed products. It has further been observed that phenyl groups containing organic products were formed even when palladium(II) complexes were used in catalytic amounts and catalytic turnover numbers greater than 2 have been observed in ~5 hr. None of the above organic products was formed when triphenylstibine alone was refluxed in toluene. Since all the organic products obtained have been observed to contain phenyl groups and the only source of phenyl groups was triphenylstibine, we propose the formation of phenyl–palladium and palladium–hydrogen bonds by the cleavage of phenyl carbon–hydrogen bonds. Such a process involving carbon–hydrogen bond cleavage by metal and formation of carbon–metal and metal–hydrogen bonds (more commonly known as metalation process) has been well characterized [1, 8, 9]. Recently, biphenyl formation has been reported in the thermal decomposition of a triphenylphosphine complex of zerovalent nickel [1].

A probable reaction scheme describing the formation of these organic products is proposed (Scheme 1). In this, the migration of the phenyl groups from antimony to the palladium followed by the reductive elimination or by a coupling process would result in the formation of phenyl acetate (or chlorobenzene) and biphenyl, respectively.



Scheme 1.

(a) Reaction or some interaction with A
(b) Reductive elimination
(c) Coupling of two molecules of B or from a bimolecular intermediate.

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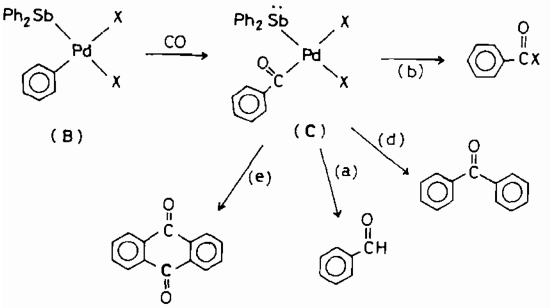
When the above reaction of triphenylstibine with palladium(II) chloride was conducted in toluene under carbon monoxide atmosphere at temperatures > 150 °C, in addition to small amounts of benzene and biphenyl, other products such as benzoyl chloride, benzophenone, benzaldehyde and anthraquinone were also obtained. The formation of these products can be described by the reaction sequences in Scheme 2.



Scheme 2.

(d) Interaction of C with B or similar interaction involving the reductive elimination of a benzoyl and a phenyl group

(e) *via* cyclocarbonylation of benzophenone with palladium catalyst [10]

In conclusion, we have demonstrated that the triphenylstibine ligand, in the presence of palladium(II) salts, undergoes cleavage of phenyl–antimony bonds and a series of organic products can be obtained under various reaction conditions. Our preliminary work on the reactions of triphenylstibine with salts of various metals including cobalt, nickel and platinum also result in the similar cleavage of phenyl–antimony bonds yielding biphenyl and other organic products. Studies to determine the mechanisms of the reactions leading to the above various products are in progress.

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