CHEMISTRY LETTERS, pp. 69-72, 1981.

# REACTION OF IODOBENZENE WITH TRIMETHYLTIN CYANIDE IN THE PRESENCE OF TETRAKIS(TRIPHENYLPHOSPHINE)PALLADIUM : NEW COMPLEX FORMATION BETWEEN THE PALLADIUM AND THE CYANIDE

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*There were found to be another possible way producing benzonitrile in the reaction of PhI with* $Me_3SnCN$ *in the presence of* $Pd(PPh_3)_4$*, beside the ordinary one involving the oxidative addition of PhI to the Pd complex. Thus, the complexation of Pd complex with* $Me_3SnCN$ *gives a new complex* $[Pd(PPh_3)(Me_3SnCN)_2]_n$ *which reacts with PhI giving PhCN. This path is much faster than the former, but cannot make a catalytic cycle, because the palladium deposits during the reaction of the complex with PhI.*

While application of cyanosilane in organic synthesis is one of the current interests[1)], little attention was paid for the reaction of tin cyanide. Recently we reported the several coupling reactions of organic halides with organotin compounds in the presence of catalytic amounts of $Pd(PPh_3)_4$.[2)]

$$R\text{-}X + Bu_3SnR' \xrightarrow{[Pd]} R\text{-}R' + Bu_3SnX \qquad (1)$$

Since these results suggest that tin compounds bearing unsaturated R' group can react easily, the following reaction of organotin cyanide is expected to occur.

$$PhI + Me_3SnCN \xrightarrow{[Pd]} PhCN + Me_3SnI \qquad (2)$$

R': allyl, vinyl, phenyl, and ethynyl

However, the reaction of PhI with $Me_3SnCN$ in the presence of catalytic amounts of $Pd(PPh_3)_4$ did not proceed smoothly, but only a trace amount of PhCN was produced. Even using an equimolar amount of the Pd complex, the yield of PhCN was not higher than 40%. In order to get insight to the factors controlling the effectiveness of the coupling reaction, some mechanistic studies were conducted.

I. Initial Rate: The following data about initial rates of the reactions at 80°C in $CH_2Cl_2$ were obtained by GLC or spectroscopic methods. By analogy with the reaction of aryl halide with some other organotin compounds under similar conditions[2)], a possible way of the formation of PhCN may involve oxidative addition of PhI to $Pd(PPh_3)_4$ (4) and subsequent substitutions (5).

$$Pd(PPh_3)_4 + PhI + Me_3SnCN \longrightarrow PhCN + Me_3SnI + [Pd] \qquad (3)$$

$$\frac{d[PhCN]}{dt} = 4.5\times10^{-6}Msec^{-1}, \quad -\frac{d[PhI]}{dt} = 1.9\times10^{-5}Msec^{-1}$$

$$Pd(PPh\ ) + PhI \longrightarrow Ph\text{-}Pd\text{-}I \qquad (4)$$

$$-\frac{d[PhI]}{dt} = 6.1\times10^{-4}Msec^{-1}$$

$$Ph\text{-}Pd\text{-}I + Me_3SnCN \longrightarrow PhCN + Me_3SnI + [Pd] \qquad (5)$$

$$\frac{d[PhCN]}{dt} = 3.4\times10^{-4}Msec^{-1}$$

As shown in the rate-data obtained from the binary system ($[PhI]=[Pd(PPh_3)_4]=7\times10^{-3}M$), the oxidative addition of PhI to the Pd complex (4) and the subsequent reaction (5) ($[Ph\text{-}Pd\text{-}I]=[Me_3SnCN]=7\times10^{-3}M$) were found to proceed stoichometrically and quite easily. Nevertheless, under similar conditions the reaction of the ternary system (3) ($[PhI]=[Pd(PPh_3)_4]=7\times10^{-3}M$, $[Pd(PPh_3)_4]=6\times10^{-3}M$) was much slower than the reaction (4) and (5). These facts suggest that in the ternary system there are some other paths which prevent propagation of (4) and (5).

II. Complexation of $Pd(PPh_3)_4$ with $Me_3SnCN$: A solution of $Pd(PPh_3)_4$ in $CH_2Cl_2$ shows an absorption band at 340 nm. The band was found to diminish by adding not only PhI but also $Me_3SnCN$ to the solution. The pseudo first order rate constants of the reaction of $Pd(PPh_3)_4$ with $Me_3SnCN$ or PhI were obtained from the disappearance of the band at 340 nm.

| Reactant | $k_{obs.}\ sec^{-1}$ |
|---|---|
| $Pd(PPh_3)_4$, $Me_3SnCN$ | $1.25\times10^{-1}$ |
| $Pd(PPh_3)_4$, PhI | $1.82\times10^{-4}$ |

$[Pd(PPh_3)_4] = 2\times10^{-5}M$, $[Me_3SnCN] = [PhI] = 2\times10^{-4}M$
in $CH_2Cl_2$ at 25°C under Ar.

The complexation of $Pd(PPh_3)_4$ with $Me_3SnCN$ is $10^3$ times as fast as the oxidative addition of PhI to $Pd(PPh_3)_4$. In the ternary system, therefore, $Pd(PPh_3)_4$ may be consumed almost exclusively by the complexation with $Me_3SnCN$. This is possibly the reason why propagation of (4) and (5) does not take place.

III. Trial for Catalytic Reaction: If the above considerations are correct, the catalytic coupling through the propagation of (4) and (5) would be expected to take place, when the concentration of $Me_3SnCN$ could be kept much lower than PhI by adding a solution of $Me_3SnCN$ very slowly to the solution of PhI containing a catalytic amount of $Pd(PPh_3)_4$.

TABLE Catalytic Reaction of PhI with $Me_3SnCN$

| solvent | temp. | time | PhI(mmol) | $Me_3SnCN$(mmol) | [Pd](mmol) | Yield of PhCN* |
|---|---|---|---|---|---|---|
| $CH_2Cl_2$ | 40°C | 24h | 0.55 | 0.44 | 0.1 | 200% |
| PhH | 80°C | 20h | 0.52 | 0.55 | 0.02 | 950% |

* based on $Pd(PPh_3)_4$

As shown in Table, adding dropwisely a solution of $Me_3SnCN$ (1/2000∿1/3000 mol/min) during 20-24h., PhCN was produced in about 40% yield, which is a 2-10 molar amount on the basis of $Pd(PPh_3)_4$ employed. This indicates that propagation of (4) and (5) actually took place although the chain length was not so long. Such restriction about the cyanide concentration has been also observed in the reaction of PhI and sodium or potassium cyanide in the presence of Pd(0) or Ni(0)[3].

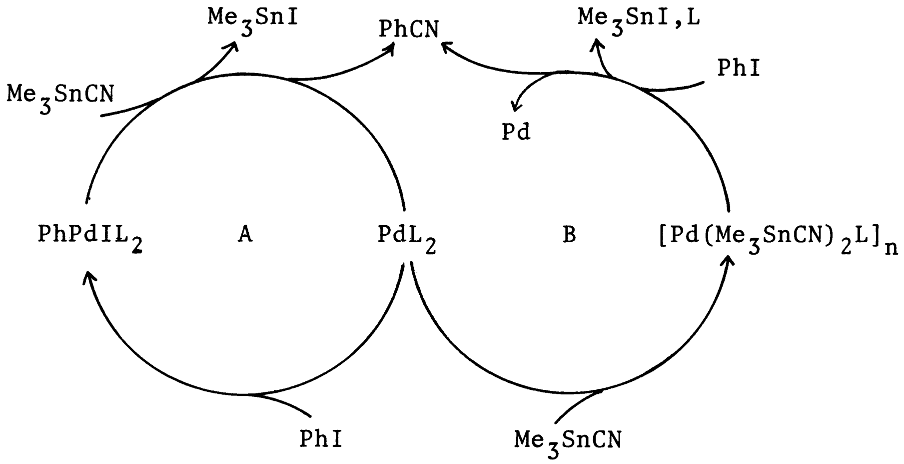
IV. A New Complex of $Pd(PPh_3)_4$ with $Me_3SnCN$: A solution of $Pd(PPh_3)_4$(0.4 mmol) and $Me_3SnCN$(1.1 mmol) in $CH_2Cl_2$(3 ml) was allowed to react for 2 h at 80°C to give precipitates. The precipitates were filtered, washed with $CH_2Cl_2$, EtOH, and $Et_2O$, and dried. Elemental analysis showed the composition of this new complex as $[Pd(PPh_3)(Me_3SnCN)_2]_n$.[4,5] The isolated complex is hardly soluble in common solvents. Quite interestingly, addition of PhI into the suspension of this complex in $CH_2Cl_2$ gave PhCN almost about quantitatively based on the following stoichiometrical equation, and depositing palladium, although produced $PPh_3$ and Pd were not determined.

$$[Pd(PPh_3)(Me_3SnCN)_2]_n + 2nPhI \longrightarrow 2nPhCN + 2nMe_3SnI + n[PPh_3, Pd] \qquad (6)$$

The infrared spectrum (KBr, KR-S5) of $[Pd(PPh_3)(Me_3SnCN)_2]_n$ showed the characteristic bands for a cyano group at 2110 $cm^{-1}$ and for a trimethyltin group at 2910, 790, and 553 $cm^{-1}$. At present, however, the refined structure is not known.

V. Mechanism: From these observations, formation of PhCN in the reaction of the equimolar ternary mixture of PhI, $Me_3SnCN$, and $Pd(PPh_3)_4$ is considered to involve process B, but not A. The process B, however, cannot construct a catalytic cycle, because of deposition of metallic Pd. As a result, the catalytic coupling could not be attained, unless the concentrations of $Me_3SnCN$ were kept very low.

Mechanism



L: $PPh_3$

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4) Found: C, 41.79: H, 4.48; N, 3.78% Calcd. for $C_{26}H_{33}N_2P_3Sn_2Pd$: C, 41.82, H, 4.42 N. 3.75%.
5) The complexation of $Pd(PPh_3)_4$ with $Me_3SnCN$ seems to be a two-step process, because by the addition of $Me_3SnCN$ into the solution of $Pd(PPh_3)_4$, a new characteristic band at 475 nm was found to growth and reach the maximum intensity after 30 sec., then to diminish completely after 10 min.

(Received September 26, 1980)