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# Reaction of Coordinated Phosphines. V. Aryl and Alkyl Transfer from Tertiary Phosphine to Transition Metal[1]

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A carbon–phosphorus bond cleavage was observed in the reaction of $MCl_2(PR_3)_2$ (M=Ni, Co, or Pd, R=Ph, $n$-$C_8H_{17}$) with *p*-tolyllithium, *p*-tolylmagnesium halide, lithium aluminum hydride, or magnesium amalgam, and the reactivity was most pronounced with Ni followed by Co and Pd. Reaction of $NiCl_2(PPh_3)_2$ with *p*-tolyllithium gave biphenyl and 4-methylbiphenyl, along with 4,4′-dimethylbiphenyl. Phenyllithium was formed in the reaction mixture, and the recovered tertiary phosphine contained tri-*p*-tolylphosphine, di-*p*-tolylphenylphosphine, and *p*-tolyldiphenylphosphine as well as triphenylphosphine. 1-Octene was formed in the reaction of $NiCl_2\{P(n\text{-}C_8H_{17})_3\}_2$ with *p*-tolyllithium. Thermal decomposition of $Ni(mesityl)X(PEt_3)_2$ (X=mesityl or Br) and $Co(mesityl)_2(PPhEt_2)_2$ at 30 °C gave vinyl mesitylene.

Tertiary phosphine is a ligand frequently used in organotransition metal complexes due to its versatility in donor-acceptor properties, and its carbon–phosphorus bonds had been considered to be chemically stable under usual reaction conditions. However, the decomposition of triarylphosphines in which the aryl group transfers from phosphorus to transition metal has become recently known for reactions of palladium,[1,2–4] nickel,[5–8] osmium[9] and other metal complexes.[10] Low-valent metals are involved in most of them, but there is a case where divalent palladium is undoubtedly responsible for the activation of aryl–P bond.[1,2b,11] Though a transition metal-assisted C–P bond fission still remains to be rather uncommon reaction in organotransition metal chemistry, it deserves serious attention, not only concerning the basic mechanism involved but also with regards to the scope of the practical occurrence of this type of reaction, since it may have some relevance to the process such as catalyst decay or induction of side reactions in certain catalytic processes. In the present study, a system in which aryl–P bond is cleaved and re-formed under the influence of low-valent Ni, Co, and Pd is described. Evidences are also collected for the alkyl–P bond cleavage facilitated by Ni, Co, and Pd complexes.

## Results and Discussion

*Reaction of Dichlorobis(triphenylphosphine)metal(II) with* p-*Tolyllithium and* p-*Tolylmagnesium Bromide.* The reaction of tertiary phosphine-coordinated transition metal halides with organic derivatives of lithium, magnesium or sodium has been widely used in the synthesis of low-valent transition metal complexes, in which the tertiary phosphines remained on the metal without any chemical transformations in themselves. However, $NiCl_2(PPh_3)_2$ (**1**), $CoCl_2(PPh_3)_2$ (**2**), and $PdCl_2(PPh_3)_2$ (**3**) reacted with *p*-tolyllithium or *p*-

TABLE 1. REACTION OF $MCl_2(PPh_3)_2$ WITH *p*-TOLYLLITHIUM (ArLi)[a)]

| Complex | ArLi/M[b)] | Reaction time/h | Product, mol % based on M | | | Tertiary phosphine recovered, mol % based on $PPh_3$ in the complex | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | Ph–Ph | Ph–Ar | Ar–Ar | $PPh_3$ | $PPh_2Ar$ | $PPhAr_2$ | $PAr_3$ |
| **1** | 1 | 40 | 6.9 | 8.9 | 17 | — | — | — | —[c)] |
| | 2 | 40 | 26 | 23 | 46 | 34 | 5.1 | trace | 0 |
| | 4 | 40 | 86 | 93 | 69 | 16 | 9.8 | 3.5 | 0.14 |
| | 8 | 40 | 82 | 210 | 140 | 0.7 | 0.5 | 0.1 | 0.4 |
| | 2[d)] | 35 | 17 | 22 | 58 | — | — | — | —[c)] |
| **2** | 1 | 35 | 1.6 | 3.4 | 27 | — | — | — | —[c)] |
| | 2 | 35 | 14 | 11 | 59 | 20 | 2.9 | 0 | 0 |
| | 4 | 35 | 27 | 35 | 79 | 22 | 1.5 | 0.1 | 0 |
| | 2[d)] | 35 | 5.1 | 10 | 54 | — | — | — | —[c)] |
| **3** | 1 | 48 | 4.9 | 8.6 | 34 | — | — | — | —[c)] |
| | 2 | 48 | 9.3 | 19 | 74 | 45 | 1.3 | 0 | 0 |
| | 4 | 48 | 2.5 | 12 | 150 | — | — | — | —[c)] |
| | 20[e)] | 48 | trace | 5 | 210 | — | — | — | —[c)] |
| $PPh_3$ only | 2[f)] | 23 | 0.04[g)] | 0.2[g)] | 0[g)] | — | — | — | —[c)] |

a) One mmol of complex in ether at room temperature. b) Molar ratio. c) Not determined. d) $MCl_2\{1,2\text{-bis(diphenylphosphino)ethane}\}$ was used instead of $MCl_2(PPh_3)_2$. e) A half mmol of **3** was used. Reaction temperature was raised to 25 °C, 3 min afetr the addition of ArLi at −70 °C. f) Molar ratio: $(ArLi/PPh_3)\times 0.5$. g) (mol of biaryl/mol of $PPh_3$ used) $\times 0.5 \times 100$.

TABLE 2. REACTION OF $MCl_2(PPh_3)_2$ WITH *p*-TOLYLMAGNESIUM BROMIDE (ArMgBr)[a]

| Complex | Reaction time/h | Product, mol % based on the complex[b] | | |
|---|---|---|---|---|
| | | Ph–Ph | Ph–Ar | Ar–Ar |
| **1** | 62 | 8 | 19 | 54 |
| **2** | 88 | 8 | 16 | 26 |
| **3** | 153 | 0.9 | 2.6 | 13 |

a) Five mmol of complex in ether at room temperature. Molar ratio; ArMgBr/M=2.
b) A considerable amount of $PPh_2Ar$ was detected in all cases.

tolylmagnesium bromide at room temperature to give the organic products including biphenyl, 4-methylbiphenyl, tri-*p*-tolylphosphine, di-*p*-tolylphenylphosphine, and *p*-tolyldiphenylphosphine, indicating that the aryl–P bond was cleaved and reformed by the influence of transition metal. Typical results are summarized in Tables 1 and 2. Total yield of biaryls and the amount of phenyl group carried into biaryls are shown in Figs. 1 and 2, respectively. The yield of biaryls increased with the increase of molar ratio of *p*-tolyllithium to $MCl_2(PPh_3)_2$ for all of the three transition metals (Fig. 1). The amount of phenyl group transferred into biaryls increased excepting for Pd as the yield of biaryls increased (Fig. 2). Excess organolithium reagent decreased the amount of recovered tertiary phosphines markedly, only 1 to 2% of triarylphosphines being recovered when 8-fold *p*-tolyllithium over nickel complex was used.

The time course of the reaction was studied for nickel system by direct GLC analysis of the reaction mixture for biaryls. The analysis was also made after the mixture had been treated with excess acetone or iodine to determine the amount of aryllithium present. The results obtained in the reaction at room temperature indicated that most of the biaryls and phenyllithium were formed within 10 min after the addition of the lithium reagent to the metal complex. A slow reaction then followed, and the mixture reached an apparent equilibrium after 10 h, which persisted at least for 5 days. The reaction is illustrated by:

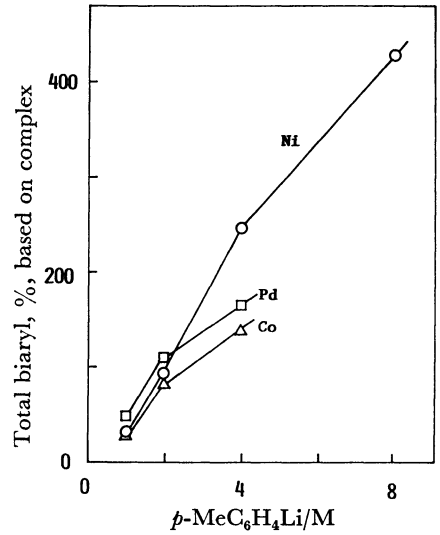

Fig. 1. Reaction of $MCl_2(PPh_3)_2$ with *p*-tolyllithium. Total yield of biaryls as a function of *p*-tolyllithium/M. Ordinate: (total mol of biaryls/mol of $MCl_2(PPh_3)_2$ employed) × 100. See Table 1 for conditions.

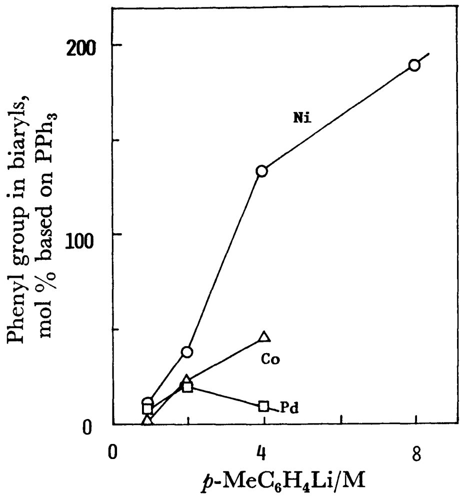

Fig. 2. Reaction of $MCl_2(PPh_3)_2$ with *p*-tolyllithium. Amount of phenyl group found in biaryls.
Ordinate: (total mol of phenyl group found in biaryls/mol of $PPh_3$ employed as metal complex) × 100.

$$\mathrm{NiCl_2(PPh_3)_2}\ (\mathbf{1}) + 8\mathrm{ArLi} \xrightarrow{\text{ether, r.t., 10 h—4 days}}$$
$$1.0\mathrm{ArLi} + 0.5\mathrm{PhLi} + 0.8\mathrm{Ph{-}Ph} + 1.5\mathrm{Ph{-}Ar} + 1.9\mathrm{Ar{-}Ar} + 0.008\mathrm{PPh_3} + 0.008\mathrm{PPh_2Ar} + 0.004\mathrm{PPhAr_2} \quad (\mathrm{Ar}{=}p\text{-tolyl}) \tag{1}$$

The relative yield of each biaryl varied from run to run, but the combined yield remained constant under specified reaction conditions. Similar study at Dry Ice–methanol temperature gave the result:

$$\underset{0.5}{\mathbf{1}} + \underset{4.0\ \text{mmol}}{8\mathrm{ArLi}} \xrightarrow[-70\ ^\circ\mathrm{C}]{\text{1) 55 min in ether}} \xrightarrow{\text{2) 5 ml of acetone}} \xrightarrow{\text{3) 16 h, room temp, then aq } \mathrm{NH_4Cl}}$$
$$\underset{0.0}{\mathrm{Ph(CH_3)_2OH}} + \underset{5.5}{\mathrm{ArC(CH_3)_2OH}} + \underset{0.024}{\mathrm{Ph{-}Ph}} + \underset{0.032}{\mathrm{Ph{-}Ar}} + \underset{1.0\ \text{mmol}}{\mathrm{Ar{-}Ar}} \quad (\mathrm{Ar}{=}p\text{-tolyl}) \tag{2}$$

GLC analysis of the reaction mixture for sample solutions extracted at earlier reaction stage gave the result illustrated in Fig. 3. The reaction mixture at −70 °C was a yellow-brown solution, and on raising the temperature it quickly darkened to give a blackish, turbid mixture. Since the extracted sample solutions were brought to high temperature during analysis, it was conceivable that the 100% yield of 4,4′-dimethylbiphenyl at 1.5 h reaction in Fig. 3 was an artifact from the thermal decomposition of $Ni(p\text{-tolyl})_2(PPh_3)_2$. It is obvious from Fig. 3 and Reaction 2 that aryl–P bond rearrangement takes place not at −70 °C but only at elevated temperatures around 0 °C or above. The presence of excess lithium reagent is important for this

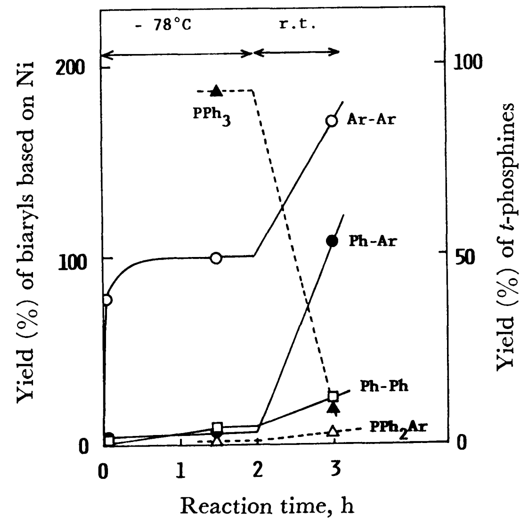

Fig. 3. Time course of the reaction of $NiCl_2(PPh_3)_2$ with *p*-tolyllithium.
Left ordinate: (total mol of biaryls/mol of Ni complex employed) × 100. Right ordinate: (mol of recovered $PAr_3$/mol of $PPh_3$ employed as Ni complex) × 100.

process since the yield of biphenyl or 4-methylbiphenyl is low at a low ratio of *p*-tolyllithium to **1**.

*Reaction of $MCl_2(PPh_3)_2$ with Magnesium Amalgam and $LiAlH_4$.* Similar C–P bond cleavage was observed in the reaction of **1**, **2** and **3** with magnesium amalgam or $LiAlH_4$. The reaction with the amalgam took place in THF but not in ether. Typical results are summarized in Table 3, Ni and Co complexes being much active than Pd complex. A considerable decomposition of triphenylphosphine in the Reaction 1 seem ssomewhat contradictory to the report[12)] that reduction of the corresponding bromide complex with sodium amalgam in acetonitrile produced bis(triphenylphosphine)nickel(0). A difference in solvent combined with a longer reaction time would be responsible for this discrepancy.

Table 3. Reaction of $MCl_2(PPh_3)_2$ with $LiAlH_4$ or magnesium amalgam[a)]

| | Complex | Solvent | Reaction time/h | Product/% Ph-Ph | Product/% Benzene |
|---|---|---|---|---|---|
| $LiAlH_4$ | **1** | ether | 24 | trace | 31 |
| | **2** | ether | 77 | trace | 22 |
| | **3** | ether | 24 | 0 | 6.1 |
| Mg(Hg) | **1** | ether[b)] | 42 | 0 | — |
| | **1** | THF | 25 | 40 | — |
| | **2** | THF | 19 | 49 | — |
| | **3** | THF | 43 | 0.2 | — |
| $PPh_3$ only | | THF | 40 | 0.4 | — |

a) To 5 mmol of the complexes in the solvent, 2.5 mmol of $LiAlH_4$ or 14 mg-atom of Mg was used, respectively, at room temperature. b) The complex was scarcely soluble in ether.

Table 4. Thermal decomposition of **4**, **5** and **6**[a)]

| Complex | Solvent | Product, mol % based on complex[b)] **7** | **8** | **9** | **10** | **11** |
|---|---|---|---|---|---|---|
| **4** | ether | trace | 8 | 3 | 5 | — |
| | benzene | 4 | 40 | 3 | 9 | — |
| | $CCl_4$ | trace | 5 | trace | 12 | 5 |
| **5** | ether | 2 | 15 | 2 | — | — |
| | benzene | 7 | 33 | 9 | — | — |
| | $CCl_4$ | 0.2 | 9 | 90 | — | 0 |
| **6** | ether | 0.4 | 30 | 36 | — | — |
| | benzene | trace | 13 | 60 | — | — |
| | $CCl_4$ | trace | 2 | 95 | — | trace |

a) At 30 °C for 3 h. b) Balance was mostly the unreacted complex.

*Alkyl-P Bond Cleavage of Coordinated Trialkylphosphine.* The C–P bond fission is not limited to triarylphosphines but trialkylphosphines, though to a smaller extent. When *trans*-bis(triethylphosphine)mesitylnickel(II) bromide (**4**), *trans*-bis(triethylphosphine)dimesitylnickel(II) (**5**), and *trans*-bis(diethylphenylphosphine)dimesitylcobalt(II) (**6**) was stirred in ether, benzene or carbon tetrachloride at 30 °C, 2,4,6-trimethylstyrene (**7**) was formed together with mesitylene (**8**), bimesityl (**9**), mesityl bromide (**10**) or mesityl chloride (**11**) (Table 4). The compound **7** presumably resulted *via* ethyl transfer from phosphorus to metal. Reaction of $NiCl_2\{P(n\text{-}C_8H_{17})_3\}_2$ with an 8-fold molar excess of *p*-tolyllithium gave 1-octene (5% on molar basis on the phosphine used) along with 4,4′-dimethylbiphenyl (≈100% on molar basis on the complex used).

Alkyl–P bond fission using Pd complex was not successful under the similar reductive conditions, but had been achieved under oxidative conditions. Thus, simply by heating the equimolar mixture of trialkylphosphine and $Pd(OAc)_2$ in acetic acid at 90 °C, a considerable amount of olefins and carbonyl compounds were formed.[1)]

*Mechanism.* Though the present report concerns with factual description rather than discussion of mechanism operating in the current reactions, some idea on the mechanism is invoked in the following in order to help a correlation among the experimental facts. Typical C–P bond cleavage disclosed in this study is those of $MCl_2(PPh_3)_2$–*p*-tolyllithium system, and seems to be more complicated than that of $PAr_3$–$Pd(OAc)_2$ system previously reported.[1)] The reaction of 1 mol of **1** with 2 mol of *p*-tolyllithium produced nearly stoichiometric amount (0.95 mol) of biaryls on the basis that the diarylnickel compound decomposes into biaryl and zero-valent nickel (Table 1). However, on increasing the ratio of *p*-tolyllithium/**1** more biaryl is formed, the amount exceeding 4 mol per mol of **1** when the ratio is 8, and the recovery of tertiary phosphines decreased concurrently. These observations combined with the results in Reactions 1 and 2 suggest that the Reaction 3 was effected under the catalysis of low (probably zero) valent nickel. The examination of the amount of

$$\mathrm{Ph_3P + ArLi \xrightarrow{Ni(0)} Ph_2PLi + Ar\text{-}Ph} \qquad (3)$$

biaryl formed indicates that the resulting $Ph_2PLi$ further reacted with excess ArLi, giving Ph–Ar and presumably $PhPLi_2$. Direct evidence for the formation of $Ph_2PLi$ or $PhPLi_2$ was not obtained because of its strong tendency to associate with nickel. It should be noted that the reaction like 3 does not proceed in the absence of Ni complex (Table 1, the last low).

It is conceivable that the catalysis of nickel in Reaction 3 resides in the oxidative addition of Ph–P bond to zero-valent Ni (Reaction 4). A further reaction of the resulting Ni complex with ArLi gives $Ph_2PLi$ and ArPhNi, and the decomposition of the latter affords Ar–Ph with reproduction of zero-valent Ni (Reactions 5 and 6). The formation of the mixed tertiary phosphines suggests that the Reactions 4 and 5 are reversible, and phenyllithium may be produced *via* the Reaction 7.

$$Ph_3P + Ni \rightleftarrows Ph_2P\text{–}Ni\text{–}Ph \tag{4}$$

$$Ph_2P\text{–}Ni\text{–}Ph + ArLi \rightleftarrows Ph_2PLi + Ar\text{–}Ni\text{–}Ph \tag{5}$$

$$Ar\text{–}Ni\text{–}Ph \longrightarrow Ar\text{–}Ph + Ni \tag{6}$$

$$Ph_2P\text{–}Ni\text{–}Ph + ArLi \rightleftarrows Ph_2P\text{–}Ni\text{–}Ar + PhLi \tag{7}$$

The oxidative addition of $Ar_2P$–Ar bond to Ni(0) or Ni(I) has been claimed in the literature.[5,6] Coordinative unsaturation on the metal seems to be one of the essential factors for this type of reactions to take place. The complex $Ni(Ph_3P)_3$ is unstable in solution, and the structure containing $Ph_2P$–Ni bond has been suggested for the decomposition product.[13] With regard to the use of excess organolithium reagent in our study, a possible involvement of the ate-type complex of Ni(0)[14] may not be overlooked, but its importance in the C–P bond cleavage[7] is yet to be investigated.

## Experimental

*Materials.* Bis(tertiary phosphine) complexes of transition metal dichlorides were prepared by conventional methods from the corresponding metal chlorides and phosphine ligands and characterized by elemental analysis as well as by ordinary spectroscopic methods. Diaryl transition metal complexes; **4**, **5** and **6**, were prepared from the corresponding dichloro complexes according to the literatures.[15,16]

*Reaction of $MCl_2(PPh_3)_2$ with p-Tolyllithium.* An ethereal 0.6—0.7 M organolithium solution was prepared by a conventional method from *p*-tolyl bromide and lithium. The solution was standardized by acid titration, and the amount of by-product (4,4′-dimethylbiphenyl) was determined by GLC with hexadecane as an internal standard. A calculated amount of the organolithium reagent was added under stirring to a suspension of $MCl_2(PPh_3)_2$ (1 mmol) in 10 ml ether containing hexadecane (internal standard). After stirred for several hours under dry nitrogen, the mixture was treated with aqueous ammonium chloride and excess potassium cyanide. The organic layer was worked up in a conventional manner and analyzed by GLC. Since some portion of tertiary phosphines had been converted into the oxides during the work-up, the product was reduced with trichlorosilane–triethylamine in benzene before the analysis for phosphines. Eicosane was employed as an internal standard. All the products were characterized either by direct comparison on GLC with authentic samples or by isolation from a large-scale run followed by a conventional spectroscopic study. By the addition of acetone or iodine to the reaction mixture, aryllithium were converted to 2-aryl-2-propanol or aryl iodides, respectively. They were analyzed by GLC after conventional work-up.

*Other Reactions.* Reaction of $MCl_2(PPh_3)_2$ with *p*-tolylmagnesium bromide was conducted in a similar manner as with *p*-tolyllithium. The reaction with magnesium amalgam (0.34 g of magnesium in 30 g of mercury) was carried out with 5 mmol of $MCl_2(PPh_3)_2$ in 100 ml of THF or ether. Benzene obtained from the reaction with $LiAlH_4$ was analyzed by GLC with toluene as an internal standard. The thermal decomposition of aryl transition metal complexes **4**, **5**, and **6** was conducted as described in the literature. The products from these reactions were characterized in a usual manner either by comparison with authentic samples or by isolation followed by instrumental study and elemental analysis.

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