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# Role of Amine in Arylation of Ethylene with Iodobenzene Catalyzed by Rhodium Trichloride

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Rhodium trichloride effectively catalyzes the arylation of ethylene with iodobenzene in the presence of an amine to give styrene, although neither rhodium-powder nor chlorotris(triphenylphosphine)rhodium(I) is effective. The efficacy of the amine in increasing the yield of styrene is remarkable with tertiary and secondary amines but negligible with a primary amine. The difference among these amines in their interaction with rhodium trichloride is explained by their steric hindrance based on the isolation of the Rh(III)-amine complex only with primary amine.

The oxidative addition of an organic halide to Rh(I) complexes is well known. Alkyl, allyl, or acyl halide, for example, can be added to chlorotris(triphenylphosphine)rhodium(I) to give the corresponding σ-organorhodium(III) complex.[1] One of the well-known catalytic reactions using oxidative addition of an organic halide to Rh(I) complex is the acetic acid synthesis from methanol and carbon monoxide, of which the rate determining step is admittedly the oxidative addition of methyl iodide to Rh(I).[2] The oxidative addition of an aryl halide to Rh(I), however, is rarely found, except that iodobenzene reacts with methyltris(triphenylphosphine)rhodium(I) to give toluene.[3]

In the preceding paper, it was reported that, in the presence of a base, palladium-black effectively catalyzes the arylation of olefins with iodobenzene[4] as well as the carbonylation of iodobenzene.[5] These reactions are considered to take place *via* σ-arylpalladium(II) intermediate formed by the oxidative addition of iodobenzene to Pd(0) complex. As an extention of these studies, the oxidative addition of an aryl halide to rhodium has been examined. It has been found that the arylation of ethylene takes place smoothly in toluene when rhodium trichloride, $RhCl_3 \cdot 3H_2O$, is used as the catalyst together with a tertiary amine, whereas the primary amine is not very effective. The present paper is mainly concerned with the effect of the amine, and an interpretation is given for the reason why a tertiary amine is most effective in this catalytic reaction.

## Experimental

*Reaction Procedure.* Rhodium trichloride ($RhCl_3 \cdot 3H_2O$, 0.5 mmol), iodobenzene (30 mmol), amine (0∼30 mmol), and toluene (30 ml) were placed in a titanium-alloy autoclave (100 ml) equipped with a magnetic stirrer. Ethylene was introduced up to 20 kg/cm$^2$ at room temperature. The temperature was then raised up to 120 °C within 20 min, and kept constant for 3 hr. The autoclave was then cooled to room temperature with water, and the gaseous materials were discharged. The liquid products were quantitatively determined by gas chromatography, using a DC-550 column and bromobenzene as an internal standard.

*Preparation of Rhodium Complexes.* (a) Wilkinson's complex. $RhCl(P\phi_3)_3$ was prepared according to the literature[6] (Found: C, 70.46; H, 5.01; Cl, 4.23%. Calcd: C, 70.1; H, 4.9; Cl, 3.8%). (b) Penta(butylamine)chlororhodium(III)dichloride, $[RhCl(C_4H_7NH_2)_5]Cl_2$. $RhCl_3 \cdot 3H_2O$ (0.5 mmol) and butylamine (15 mmol) were placed in toluene (30 ml), and the solution was heated under reflux for 1 h. The solution turned yellow, giving a pale-yellow crystalline precipitate, which was recrystallized from methanol–water, and dried *in vacuo* (Found: C, 42.1; H, 10.0; N, 12.1; Cl, 19.3%. Calcd: C, 41.8; H, 9.58; N, 12.2; Cl 18.5%). (c) Tetra(butylamine)dichlororhodium(III)chloride, $[RhCl_2(C_4H_7NH_2)_4]Cl$. $[RhCl(C_4H_7NH_2)_5]Cl_2$ was treated with iodobenzene in the presence of butylamine under the conditions (Table 2) employed in the arylation of ethylene. No iodobenzene was consumed, while a precipitate was formed after the reaction. The precipitate was recrystallized from methanol and water (Found: C, 39.2; H, 9.6; N, 11.3; Cl, 19.0%. Calcd: C, 38.2; H, 8.8; N, 11.2; Cl 21.2%). (d) Tetra(benzylamine)dichlororhodium(III)chloride, $[RhCl_2(C_6H_5CH_2NH_2)_4]Cl$. The treatment of $RhCl_3 \cdot 3H_2O$ with benzylamine under the conditions employed in the arylation (Table 2) gave a crystalline yellow complex which was recrystallized from methanol and water (Found: C, 51.6, H, 5.9, N, 8.5, Cl, 17.5%. Calcd: C, 52.7, H, 5.7, N, 8.9, Cl, 16.7%). In this reaction, no arylation was observed, as in (c). (e) Phenyl rhodium(III) complex, $C_6H_5Rh(P\phi_3)_2(Cl)(I)$. $RhCl(P\phi_3)_3$ (1 mmol) and iodobenzene (30 mmol) were placed in dried and degassed toluene (40 ml) under nitrogen. The solution was heated under reflux for 4 h. $RhCl(P\phi_3)_3$ was gradually dissolved, and the solution changed from reddish brown to dark brown, giving a dark brown crystalline precipitate on cooling. The precipitate was washed with hexane and dried *in vacuo* (Found: C, 57.9; H, 4.3; Halogen, 17.6%. Calcd: C, 58.1; H, 4.0; Halogen 18.7%). By treating a toluene solution of this complex with atmospheric hydrogen at room temperature for 3 h, benzene was quantitatively obtained. $RhCl(P\phi_3)_3$, however, was practically inactive for the formation of styrene. (f) Phenylrhodium(III)carbonyl complex, $C_6H_5Rh(P\phi_3)_2(CO)(Cl)(I)$. A greenish yellow precipitate was obtained by treatment of iodobenzene (30ml) with a methanol solution (30 ml) of $RhCl_3 \cdot 3H_2O$ (0.5 mmol) in the presence of $P\phi_3$ (1.5 mmol) and butylamine (15 mmol) under ethylene pressure (20 kg/cm$^2$) at 120 °C for 3 h, although no styrene was detected. The precipitate was recrystallized from benzene and methanol, and a yellow crystal was obtained (Found: C, 57.2; H, 3.9; Halogen, 18.0%. Calcd: C, 57.8; H, 4.0; Halogen, 17.2%. $\nu_{CO}$ 1965 cm$^{-1}$). Treatment of a chlorobenzene solution of this complex with dry hydrogen chloride at room temperature gave benzene quantitatively.

## Results

*General Features of the Reaction.* From the reaction of iodobenzene (30 mmol) with ethylene (20 kg/cm$^2$) at 120 °C for 3 h in methanol (30 ml) using $RhCl_3 \cdot 3H_2O$ (0.5 mmol) as the catalyst in the presence of butylamine (15 mmol) or tributylamine (15 mmol), a small amount of styrene (8.0 and 0.96 mmol, respectively) was obtained; most of the catalyst was found in the form of metallic rhodium after the run. The addition of triphenylphosphine (1.5 mmol, $P\phi_3/Rh=3$ in mol) to this catalyst system completely inhibited the formation of styrene, and no iodobenzene was consumed. From the reaction mixture, σ-phenylrhodium(III)-carbonyl complex, $C_6H_5Rh(P\phi_3)_2(CO)(Cl)$(I), as described in the experimental section, was isolated. Carbon monoxide seems to be supplied from methanol.

Table 1. Arylation of ethylene catalyzed by Rh-catalyst

Catalyst 0.5 mmol, Iodobenzene 30 mmol, Tributylamine 15 mmol, Toluene 30 ml, $P_{C_2}'$ 20 kg/cm$^2$ at room temp, Temp, 120 °C, and Time 3 h.

| Rh-Catalyst | $P\phi_3$ (mmol) | Conv[a] (%) | Select (%) |
|---|---|---|---|
| Rh-powder | 0 | 0 | 0 |
| $RhCl(P\phi_3)_3$ | 0 | 61 | 4 |
| $RhCl_3\cdot 3H_2O$ | 0 | 86 | 80 |
| $RhCl_3\cdot 3H_2O$ | 0.75 | 72 | 78 |
| $RhCl_3\cdot 3H_2O$ | 1.5 | 7 | 0 |
| $RhCl_3\cdot 3H_2O$ | 3 | 5 | 0 |

a) Based on iodobenzene.

The yield of styrene, however, was considerably increased by using a toluene–tributylamine mixture instead of methanol as the solvent. The results are summarized in Table 1. Rh-powder[7] showed no activity, and $RhCl(P\phi_3)_3$ gave only a small amount of styrene in spite of a considerable consumption of iodobenzene. Even in the case of $RhCl_3\cdot 3H_2O$, which proved to be effective for the arylation, the addition of triphenylphosphine($P\phi_3/Rh\geq 3$ in mol) also inhibited almost completely the formation of styrene.

*The Effect of Amine.* The effect of the amount of tertiary amines on the conversion of iodobenzene and selectivity to styrene is shown in Fig. 1. In the absence of tertiary amine, no styrene was formed and a substantial amount of metallic rhodium was found after the run. It is clear in Fig. 1 that the conversion of iodobenzene increases with increase in the amount of tertiary amine, while the selectivity to styrene decreases when a larger amount of the amine is added. Neither stilbene nor 1,1-diphenylethylene was detected.

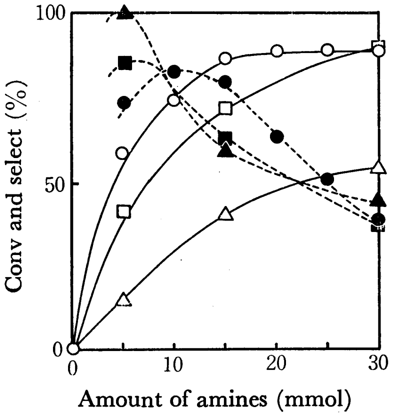


Fig. 1. Effect of the amount of tertiary amines. $RhCl_3\cdot 3H_2O$ 0.5 mmol, toluene 30 ml, iodobenzene 30 mmol, $P_{C_2}'$ 20 kg/cm$^2$, Temp. 118 °C, and Time 3 h.

— Conv and --- Select

○ Tributylamine, □ Tripropylamine, and △ Triethylamine.

Separate experiments showed that iodobenzene remained unchanged in the absence of $RhCl_3\cdot 3H_2O$ under the condition specified in Fig. 1, while a considerable amount of iodobenzene was consumed even in the absence of ethylene when $RhCl_3\cdot 3H_2O$ was added. Although the reaction products were unidentified, this suggests that the rhodium catalyst catalyzes also a reaction of iodobenzene with the tertiary amine.

The effects of primary, secondary, and tertiary amines are summarized in Table 2. The yield of styrene decreases in the order, tertiary≥secondary≫primary amine. Practically no arylation takes place when primary amine or pyridine is added. The steric effect of primary amine was examined under the same

Table 2. Effect of amines (1)

$RhCl_3\cdot 3H_2O$ 0.5 mmol, Iodobenzene 30 mmol, Toluene 30 ml, $P_{C_2}'$ 20 kg/cm$^2$ at room temp, Amine 15 mmol, Temp 120 °C, and Time 3 h.

| Amine | $pK_b$ | Conv[a] (%) | Select (%) |
|---|---|---|---|
| None | — | 0 | 0 |
| Diethylamine | 3.02 | 42 | 89 |
| Triethylamine | 3.35 | 40 | 60 |
| Propylamine | 3.47 | 0 | — |
| Dipropylamine | 3.00 | 53 | 90 |
| Tripropylamine | 3.35 | 71 | 63 |
| Butylamine | 3.41 | 0 | — |
| Dibutylamine | 2.75 | 58 | 86 |
| Tributylamine | 3.11 | 86 | 80 |
| Octylamine |  | 0 | — |
| Dioctylamine |  | 47 | 93 |
| Trioctylamine |  | 92 | 84 |
| Aniline | 9.42 | 23 | 29 |
| Pyridine | 8.85 | 0 | — |

a) Based on iodobenzene.

Table 3. Effect of amine (2)

$RhCl_3\cdot 3H_2O$ 0.5 mmol, Iodobenzene 30 mmol, Toluene 30 ml, $P_{C_2}'$ 20 kg/cm$_2$ at room temp, Temp 120 °C, and Time 3 h.

| Tributylamine (mmol) | Butylamine (mmol) | Conv.[d] (%) | Select. (%) |
|---|---|---|---|
| 15 | 0 | 86 | 80 |
| 15 | 3.75 | 38 | 95 |
| 15 | 5 | 12 | 100 |
| 15 | 7.5 | 0 | — |
| 15 | 15 | 0 | — |
| 5[a] | 0 | 51 | 88 |
| 5[a),b] | 0 | 38 | 84 |
| 5[a] | 30[c] | 36 | 71 |

a) $RhCl_3\cdot 3H_2O$ was used 0.75 mmol. b) Reaction time is 1 h. c) Butylamine was injected after 1 h and the temperature was kept constant furthermore for 2 h. d) Based on iodobenzene.

reaction condition. Monotertiarybutylamine and 1,1,3,3-tetramethylbutylamine selectively gave styrene, although the conversions were low (9 and 10% respectively). The arylations in the presence of both tributylamine and butylamine were carried out to define their effects more clearly. The results are described in Table 3. It is clear that even when a large amount of tributylamine is present, the addition of butylamine remarkably decreases the yield of styrene. When butylamine was added through a high pressure injector during the course of arylation in the presence of tributylamine, it also terminated the formation of styrene (the last line of Table 3).

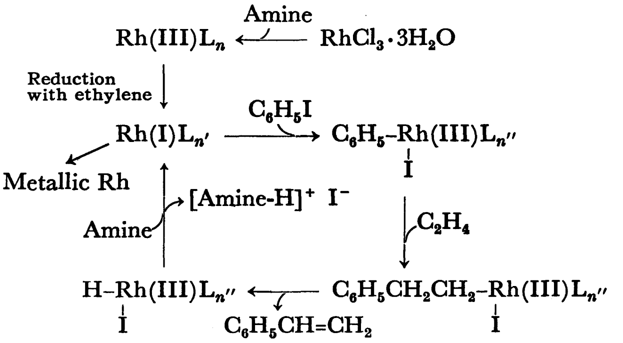
The isolation of rhodium–amine complex was carried out as described in the experimental section. The treatment of $RhCl_3\cdot3H_2O$ with butylamine gave $[RhCl(C_4H_9NH_2)_5]Cl_2$, which changed into another complex, $[RhCl_2(C_4H_9NH_2)_4]Cl$, under the arylation condition. The treatment of $RhCl_3\cdot3H_2O$ with benzylamine under the arylation condition gave $[RhCl_2(C_6H_5CH_2NH_2)_4]Cl$, which has an analogy with the Rh(III)–butylamine complex. The primary amine is known to give stable Rh(III) complexes.[8] Practically no metallic rhodium was formed after the arylation in the presence of tertiary amine; all attempts to isolate a rhodium–tertiary amine complex, however, were unsuccessful.

## Discussion

The treatment of $RhCl(P\phi_3)_3$ with iodobenzene in toluene under reflux gives a stable σ-phenylrhodium(III) complex, $C_6H_5Rh(P\phi_3)_2(Cl)(I)$, as described in the experimental section. $RhCl(P\phi_3)_3$ is catalytically inactive for the arylation of ethylene in spite of a considerable consumption of iodobenzene by the reaction with amine, as shown in Table 1. This suggests that the oxidative addition of iodobenzene to Rh(I) takes place readily, while $P\phi_3$ prevents the coordination of ethylene. When $RhCl_3\cdot3H_2O$ is used as the catalyst, the addition of a catalytic amount of $P\phi_3$ prevents not only the formation of styrene, but also the consumption of iodobenzene, as shown in Table 1. In this case, $P\phi_3$ presumably stabilizes the Rh(III) complex as $RhCl_3(P\phi_3)_3$,[6] because, if Rh(I) were formed during the reaction, iodobenzene should be consumed, as observed with $RhCl(P\phi_3)_3$. In the absence of $P\phi_3$, however, $RhCl_3\cdot3H_2O$ is fairly active for the arylation of ethylene with iodobenzene in the presence of tertiary amine. From the above consideration, it is postulated that the arylation reaction proceeds *via* a Rh(I) complex which is formed by reduction of a Rh(III) complex, although all attempts to isolate the Rh(I) complex in the absence of $P\phi_3$ were unsuccessful. Possible reducing agents were separately examined for their effectiveness under relevant conditions. Practically no reduction of Rh(III) was observed with amine or toluene. The treatment of $RhCl_3\cdot3H_2O$ with ethylene in the absence of iodobenzene, however, gave a black precipitate, presumably metallic rhodium, demonstrating some reducing ability for ethylene. Accodingly, it seems likely that Rh(III) is reduced by ethylene[9] during the course of arylation.

A question arises why the primary amines are almost ineffective for the arylation in spite of the fact that their basicities are almost the same as those of the secondary and tertiay amines, as shown in Table 2. The most plausible explanation may be a steric hindrance of the amine, because a bulky primary amine, for example, monotertiarybutylamine or 1,1,3,3-tetramethylbutylamine, gave styrene selectively, although the conversion was low. The less crowded primary amine tightly coordinates to Rh(III) to give a highly stable Rh(III)–primary amine complex, thus stabilizing the Rh(III) state. On the other hand, tertiary amines, which are sterically more crowded, are likely to coordinate weakly to Rh(III), giving rise to only slight inhibition of the reduction from Rh(III) to Rh(I). In fact, no Rh(III)–tertiary amine complexes have been isolated.

The active species may be a weakly bonded Rh(I)–tertiary amine complex, to which iodobenzene is oxidatively added to give σ-phenylrhodium(III) complex, followed by insertion of ethylene and elimination of β-hydrogen to give styrene as follows:



L: Hologen, Amine, Olefin, and Solvent.

Scheme.

The more tight coordination of the primary amine to Rh(III) than of the tertiary amine is also supported by the result that the formation of styrene is almost completely inhibited by the injection of butylamine during the course of the arylation described in Table 3. This means that the primary amine stabilizes the Rh(III) intermediate, resulting in a lack of regeneration of Rh(I) complex.

Since iodobenzene is consumed in the interaction with $RhCl_3\cdot3H_2O$–tributylamine mixture even in the absence of ethylene, σ-phenylrhodium(III) complex seems to react with tributylamine to give $[C_6H_5N(C_4H_9)_3]^+I^-$, although its isolation was unsuccessful. This may be the reason why the selectivity to styrene decreases with the increase in the amount of tributylamine, as shown in Fig. 1.

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