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Homogeneous Catalysis (IV). Hydrogenation of Acrylonitrile with *trans*-Chlorocarbonylbis(triphenylphosphine)rhodium(I)

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It has been found that the acrylonitrile solution of *trans*-$RhCl(CO)(Ph_3P)_2$ produces propionitrile catalytically at 90°C under $P_{H_2}=3$ atm. This catalytic hydrogenation proceeds only for a certain period of time producing *ca.* 50 moles of propionitrile per mole of the rhodium complex. The hydrogenation with *trans*-$RhCl(CO)(Ph_3P)_2$ in the presence of formaldehyde is much faster than in the absence of formaldehyde, and continues without a decrease in the rate for a prolonged period of time. It is suggested that the hydrogenation with *trans*-$RhCl(CO)(Ph_3P)_2$ proceeds through the unsaturated route initiated by the dissociation of CO from *trans*- $RhCl(CO)(Ph_3P)_2$ to give coordinatively unsaturated $RhCl(Ph_3P)_2$.

We recently reported the catalytic hydrogenation of acrylonitrile to propionitrile by a four coordinated iridium complex, *trans*-$IrCl(CO)(Ph_3P)_2$ (Ph_3P = triphenylphosphine) at 80°C under hydrogen ($P_{H_2}=3$ atm.).[1] We have subsequently become interested in the catalytic hydrogenation by the rhodium analog, *trans*-$RhCl(CO)(Ph_3P)_2$(**1**)[2]. In general, rhodium complexes are more active for the catalytic hydrogenation of olefins than the corresponding iridium complexes.[3] It is well established that the hydrogenation of an olefin with Wilkinson's catalyst, $RhCl(Ph_3P)_3$ (**1**) proceeds *via* two different routes, so-called the hydride route (eq. 1) and the unsaturated route (eq. 2), both of which involve the formation of the six coordinated dihydridoolefinrhodium(III) complex, $RhClH_2(olefin)(Ph_3P)_2$.[4-8] The intermediate ($RhClH_2(olefin)(Ph_3P)_2$) undergoes the intramolecular olefin insertion reaction into Rh-H bond to give the five coordinated RhClH (alkyl) $(Ph_3P)_2$ which finally produces alkane and the three coordinated intermediate $RhCl(Ph_3P)_2$(**3**) back into the catalytic cycle.[4-8] No investigation has been reported for the

$$\underset{\mathbf{2}}{RhCl(Ph_3P)_3} \underset{-H_2}{\overset{H_2}{\rightleftharpoons}} RhClH_2(Ph_3P)_3 \underset{Ph_3P}{\overset{-Ph_3P}{\rightleftharpoons}}$$

$$RhClH_2(Ph_3P)_2 \underset{-olefin}{\overset{olefin}{\rightleftharpoons}} RhClH_2(olefin)(Ph_3P)_2 \qquad (1)$$

$$\underset{2}{RhCl(Ph_3P)_3} \underset{Ph_3P}{\overset{-Ph_3P}{\rightleftharpoons}} \underset{3}{RhCl(Ph_3P)_2} \underset{-olefin}{\overset{olefin}{\rightleftharpoons}}$$

$$RhCl(olefin)(Ph_3P)_2 \underset{-H_2}{\overset{H_2}{\rightleftharpoons}} RhClH_2(olefin)(Ph_3P)_2 \qquad (2)$$

catalytic hydrogenation of olefins with **1** where a CO is coordinated in the place of a triphenylphosphine in **2**. It would be interesting to compare the catalytic activity of **1** with that of **2** with respect to the rate of hydrogenation as well as the reaction pathways.

In this article, we wish to describe the catalytic hydrogenation of acrylonitrile with **1** and suggest a reaction route. It has been found that the acrylonitrile solution of **1** under hy-

drogen ($P_{H_2}=3$ atm.) produces propionitrile catalytically at above 90 °C (eq. 3). whereas no evidence of the hydrogenation was observed at 25°C. The hydrogenation was followed by measuring the ^{1}H-NMR peaks of propionitrile produced during the reaction time by the same manner described in the previous paper.[1]

$$CH_2CHCN \xrightarrow[P_{H_2}=3\,atm,\ 90°C]{RhCl(CO)(Ph_3P)_2} CH_3CH_2CN \qquad (3)$$

The rate of hydrogenation is very slow as shown in Figure 1[9] where the apparent induction period (*ca.* 8 hours) is noticed. It is also seen that the hydrogenation proceeds for no more than 35 hours (including the induction period) giving *ca.* 50 moles of propionitrile per mole of the rhodium complex, *i. e.*, propionitrile production is completely suppressed after 35 hours. The brownish-yellow solid[10] isolated from the reaction mixture (after 45 hours of heating under the catalytic conditions) did not show any absorption bands attributable to the coordinated CO in its infrared spectrum.[11] The infrared spectra of the isolated solid samples[10] at intervals during the catalysis showed that the intensity of the ν_{CO} of **1** at 1955 cm^{-1} (KBr) decreases both with the reaction time and with the decrease in the rate of hydrogenation. These observations may suggest that the dissociation of CO from **1** causes the deterioration of the catalytic activity of **1**. It is known that **1** eliminates CO to give **3** at high temperature (eq. 4).[12] The concentration of CO in the reaction mixture (20 ml) in the reactor (400 ml) at 90 °C would be negligible even after the complete dissociation of CO from **1** (0.3 mmol). Therefore, the formation of **1** from the reaction of **3** with CO (the reverse reaction of eq. 4) would be negligible under our experimental conditions. It is well known that **3** plays an very important role in the catalytic cycle when **2** is used as catalyst (see eq. 1 and 2), but loses the catalytic activity in the absence of triphenylphosphine due to the self-dimerization to give

$$\underset{\mathbf{1}}{RhCl(CO)(Ph_3P)_2} \xrightarrow{\Delta} \underset{\mathbf{3}}{RhCl(Ph_3P)_2} + CO \qquad (4)$$

$[RhCl(Ph_3P)_2]_2$ (**4**).[13] Accordingly, the deterioration of the catalytic activity of **1** after 35 hours (see Figure 1) is understood in terms of the formation of the dimer, **4** due to the lack of CO in the reaction mixture. In the presence of sufficient CO, the three coordinated **3** would readily react with CO to give **1**, and the hydrogenation would not occur due to the lack of the catalytic species **3** in the reaction mixture. In fact, it has been found that the hydrogenation does not proceeds under the same experimental conditions described above except that CO($P_{CO}=0.5$ atm.) was added into the reaction mixture.

The search for the system that supplies CO to **3** to prevent the formation of the dimer(**4**) but does not produce free CO[14] in the reaction mixture under the catalytic conditions, has led us to the preparation of **1**. The complex **1** is prepared by the reaction of $RhCl_3\cdot 3H_2O$ with triphenylphosphine in formaldehyde solution.[2] In other words, formaldehyde is the source of CO in **1**. The complex **1**, however, does not abstract CO from formaldehyde.

In a separate experiment, the hydrogeration of acrylonitrile was carried out in the presence of formaldehyde (10 ml of 37 % solution in H_2O) under the same conditions employed for the data shown in Figure 1. It has been found that the hydrogenation proceeds much faster in the presence of formaldehyde (140 moles of propionitrile per mole of the rhodium complex for 25 hours) than in the absence of formaldehyde (40 moles of propionitrile per mole of rhodium complex for 25 hours), and the catalytic hydrogenation of acrylonitrile continues without a decrease in the rate for a prolonged period of time. This observation clearly suggests that formaldehyde, as does triphenylphophine in the hydrogenation with Wilinson's catalyst (see eq. 2), prevents the dimerization of **3**. Based on the data shown in Figure 1, the infrared spectral data discussed above and the experiment in the presence of formaldehyde, it is suggested that the hydrogenation of acrylonitrile with **1** proceeds *via* the unsaturated route (cf. eq. 2) initiated by the dissociation of CO from **1** (see eq. 5 and 6). In the absence of formaldehyde, all the rhodium species in the reaction mixture would be converted to the catalytically inactive dimer (**4**) by the irreversible dimerization of **3** (see eq. 5), and the catalysis would eventually stop as seen in Figure 1. In the presence of formaldehyde, the dimerization of **3** is prevented by the reaction of **3** with HCHO (see eq. 6). The concentration of **3**, however, would be sufficient for the catalytic reaction to be observed since the concentration of free CO in the reaction mixture is not enough to suppress the dissociation of CO from **1** and there is a equilibrium between **1** and **3** (see eq. 6).

In the absence of formaldehyde,

$$\underset{\mathbf{1}}{RhCl(CO)(Ph_3P)_2} \xrightarrow{-CO} \underset{\mathbf{3}}{RhCl(Ph_3P)_2} \longrightarrow \underset{\mathbf{4}}{[RhCl(Ph_3P)_2]_2}$$

$$\Big\downarrow \text{catalytic cycle}, \ H_2,\ CH_2{=}CHCN \qquad (5)$$

$$\underset{\mathbf{3}}{RhCl(Ph_3P)_2} + CH_3CH_2CN$$

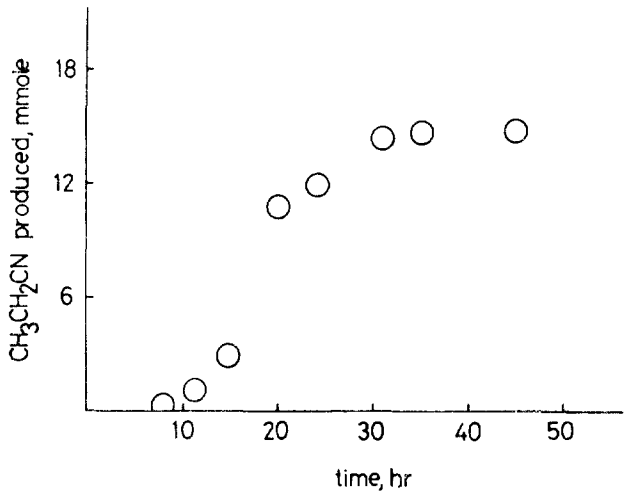

Figure 1. Production of propionitrile from the acrylonitrile (20 ml) solution of RhCl (CO) $(Ph_3P)_2$ (0.208 g, 0.30 mmole) under $P_{H_2}=3$ atm. at 90 °C.

In the presence of formaldehyde.

$$\underset{1}{RhCl(CO)(Ph_3P)_2} \underset{HCHO}{\overset{-CO}{\rightleftharpoons}} \underset{3}{RhCl(Ph_3P)_2} \xrightarrow[\text{catalytic cycle}]{H_2,\ CH_2=CHCN} RhCl(Ph_3P)_2 + CH_3CH_2CN \quad (6)$$

It is yet to be investigated whether the hydrogenation with **1** also proceeds *via* the hydride route (cf. eq. 1) initiated by the formation of the oxidative addition of H_2 to give $RhClH_2(CO)(Ph_3P)_2$.

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Syntheses of Phosphonamides Containing Aminobenzylphosphonic Acid and Aminopenicillanic Acid

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This paper reports new phosphonamide derivatives which contain diethyl aminomethylphosphonate, diethyl DL-1-aminobenzylphosphonate and 6-aminopenicillanic acid; N-(ethyl phthalimidomethylphosphonyl)-L-methionine methyl ester, N-(ethyl phthalimidomethylphosphonyl)-L-valine ethyl ester, N-[ethyl N-(methoxycarbonylmethyl)benzylphosphonamido]-2-phthalimidoacetamide, N-[ethyl N-(diethyl phosphonylbenzyl)methylphthalamido] phthalimide, N-[ethyl {ethyl N-(diethyl phosphonylbenzyl)aminomethylphosphonamido} phosphonylmethyl] phthalimide, N-[ethyl N-(diethyl phosphonylbenzyl)methylphosphonamido]-2-phthalimidoacetamide, N, N'-bis (ethyl phthalimidomethylphosphonyl)ethylene diamine, 6-(ethyl DL-1-aminobenzylphosphonamido) penicillanic acid, ethyl N-(ethoxycarbonylmethyl)-1-aminobenzylphosphonamide, ethyl N-(diethyl phosphonylbenzyl)aminomethylphosphonamide and N,N'-bis (ethyl aminomethylphosphonyl) ethylene diamine.

Introduction

It is well known that penicillins have been one of the most useful and least toxic antibiotics, since it was isolated in 1929 by Fleming.

All of naturally occuring penicillins contains the bicyclic ring, 6-aminopenicillanic acid (6-APA) as main structure, but they have different substituents at C-6.[1-2]

Although these drugs have revolutionized the medical world, still they have some serious problems. One of these is the lowering of activity against gram-negative bacteria on long term application in chemotherapy.[3] Hence many medicinal chemists have attempted to modify these compounds through the introduction of amido group into C-6 position in the penicillin nucleus. Consequently many semisynthetic penicillins were reported in the literatures.