(4) The values of the enthalpy change ratios of isotropization to melting, $\Delta H_i/\Delta H_c$, were about twice those of compounds having only one mesogenic unit.
(5) Judging by the ΔS_i values, the compounds with even n's seemed to form more highly ordered liquid crystal phases than those with odd n's.

Acknowledgement. The authors are grateful to the Korea Science and Engineering Foundation and to the NSF-sponsored Materials Research Laboratory of the University of Massachusetts for the support of this work.
J.-I. Jin wishes to thank Dr. Robert Ausubel for his many useful suggestions in the preparation of this article.

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Homogeneous Catalysis (VI). Hydride Route with Chloro Ligand Dissociation for the Hydrogenation of Acrylonitrile with *trans*-Chlorocarbonylbis(triphenylphosphine)iridium(I)

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The reaction of $IrClH_2(CO)(Ph_3P)_2$ (Ph_3P=triphenylphosphine) with acrylonitrile (AN) produces a stoichiometric amount of propionitrile (PN) at 100°C under nitrogen, which suggests that the catalytic hydrogenation of AN to PN with $IrCl(CO)(Ph_3P)_2$ proceeds through the hydride route where the formation of the dihydrido complex, $IrClH_2(CO)(Ph_3P)_2$ is the initial step. The rate of the hydrogenation of AN to PN with $IrCl(CO)(Ph_3P)_2$ is decreased by the presence of excess Cl^- in the reaction system, which suggests that Cl^- is the dissociating ligand in the catalytic cycle. It has been also found that the rate of the hydrogenation increases with increase both in hydrogen pressure and in concentration of free Ph_3P, and with decrease in AN concentration in the reaction system.

Introduction and Objectives

Wilkinson's catalyst, $RhCl(Ph_3P)_3$ is a very active catalyst for hydrogenation of various olefins even at room temperature,[1~7] while the iridium analog, $IrCl(Ph_3P)_3$ catalyzes only certain terminal olefins with very slow rates.[8] It is well known that the high catalytic activity of $RhCl(Ph_3P)_3$ results in part from the significant dissociation of a Ph_3P from $RhCl(Ph_3P)_3$ in solution,[1~7] whereas the dissociation of a Ph_3P from $IrCl(Ph_3P)_3$ is so small that the concentration of the catalytically active species, $IrCl(Ph_3P)_2$ is very low.[8] On the other hand, the rhodium carbonyl complex, $RhCl(CO)(Ph_3P)_2$ is practically inactive for the hydrogenation of olefins at room temperature, but catalyzes the hydrogenation of various olefins at above 80°C.[10~12] It is already known that $RhCl(CO)(Ph_3P)_2$ dissociates CO (but not Ph_3P) at elevated temperature.[13] We also found that the dissociation of CO from $RhCl(CO)(Ph_3P)_2$ initiates the catalytic hydrogenation of AN to PN at above 80°C.[12] Consequently, we have become interested in the nature of the dissociating ligand in the catalytic cycle for the hydrogenation of AN with the iridium analog, $IrCl(CO)(Ph_3P)_2$ (1) (which is known not to dissociate any ligand

at all at room temperature[14] and practically inactive for the hydrogenation of olefins at room temperature) which is active for the hydrogenation of olefins at above 80°C.[11,15~18] During our investigation for the hydrogenation of AN with complex **1** at above 80°C, it has been found that the addition of excess Ph_3P in the catalytic system increases the rate of the hydrogenation. This observation contradicts the assumption made by James[15] and Onoda[16] that a Ph_3P dissociates from **1** to allow an olefin to the active site, iridium. We, therefore, have decided to look into the details of the ligand effects on the hydrogenation of AN with complex **1** and find out the dissociating ligand.

It is well established that the hydrogenation of olefins with $RhCl(Ph_3P)_3$ proceeds through the two routes, hydride route and olefin route.[1~7] We have lately suggested that the hydrogenation of AN with $RhCl(CO)(Ph_3P)_2$ is initiated by the dissociation of CO from $RhCl(CO)(Ph_3P)_2$ to give $RhCl(Ph_3P)_2$ which is certainly an intermediate of the olefin route.[12] Although no reaction mechanism has been suggested for the hydrogenation with $IrCl(Ph_3P)_3$,[8] the olefin routes (eq. (1-a, b)) were suggested for the hydrogenation with **1**.[15,16] Unlike the rhodium analog, $RhCl(CO)(Ph_3P)_2$ which does not reacts with an olefin before it

$$\underset{\mathbf{2}}{IrClH_2(CO)(Ph_3P)_2} \underset{H_2}{\overset{-H_2}{\rightleftharpoons}} \underset{\mathbf{1}}{IrCl(CO)(Ph_3P)_2} \underset{-olefin}{\overset{olefin}{\rightleftharpoons}}$$

$$IrCl(olefin)(CO)(Ph_3P)_2 \underset{Ph_3P}{\overset{-Ph_3P}{\rightleftharpoons}} IrCl(olefin)(CO)(Ph_3P)$$

$$\underset{-H_2}{\overset{H_2}{\rightleftharpoons}} IrClH_2(olefin)(CO)(Ph_3P) \longrightarrow IrCl(CO)(Ph_3P) + alkane \quad (1\text{-a})^{15}$$

oefin = maleic anhydride

$$\underset{\mathbf{2}}{IrClH_2(CO)(Ph_3P)_2} \underset{H_2}{\overset{-H_2}{\rightleftharpoons}} \underset{\mathbf{1}}{IrCl(CO)(Ph_3P)_2} \underset{Ph_3P}{\overset{-Ph_3P}{\rightleftharpoons}}$$

$$IrCl(CO)(Ph_3P) \underset{-olefin}{\overset{olefin}{\rightleftharpoons}} IrCl(olefin)(CO)(Ph_3P) \underset{-H_2}{\overset{H_2}{\rightleftharpoons}}$$

$$IrClH_2(olefin)(CO)(Ph_3P) \longrightarrow IrCl(CO)(Ph_3P) + alkane \quad (1\text{-b})^{16}$$

olefin = dimethyl maleate

dissociates a ligand,[12] complex **1** readily reacts with some olefins to give stable olefin adducts, $IrCl(olefin)(CO)(Ph_3P_2)$[19] (eq. (1-a)). The equilibrium between complex **1** and $IrClH_2(CO)(Ph_3P)_2$ (**2**) is involved even in the olefin route (eq. (1)) since complex **1** reacts with H_2 at room temperature to give stable dihydrido complex **2**.[19] It is well known that complex **2** is much stabler than the AN adduct, $IrCl(AN)(CO)(Ph_3P)_2$ (**3**) at 30°C.[19] Therefore, one might expect that the hydrogenation of AN with **1** may also proceed through the hydride route (see eq. (3) below). We, in this report, intend to give some evidence of the hydride route for the hydrogenation of of AN with **1**.

Results and Discussion

We have found that the reaction of **2** with AN produces a stoichiometric amount of PN (eq. (2)). This observation suggests that the hydrogenation of AN to PN with **1**[18] proceeds through the hydride route (eq. (3), see below for the dissociating ligand being Cl^-), since the hydrogen pressure in the reactor developed from the reaction, **2**⟶**1**+H_2, would not be high enough for the hydrogenation to proceed through the olefin route (eq. (1-a)[20]) under our experimental conditions (see Experimental). The above observation (eq. (2)) does not exclude the possible

$$\underset{\mathbf{2}}{IrClH_2(CO)(Ph_3P)_2} + CH_2CHCN \xrightarrow[8\,hr.]{100\,^\circ C,\ N_2} \underset{\mathbf{1}}{IrCl(CO)(Ph_3P)_2} + CH_3CH_2CN \quad (2)$$

olefin route for the hydrogenation of AN with **1**. The hydrogenation may occur through the olefin route in the presence of excess AN and H_2. The reaction of **3** with H_2 in the absence of free AN and in the presence of excess H_2 may give some information on whether the hydrogenation occurs through the olefin route or not. Unfortunately, the AN adduct, **3** can not be isolated in good purity since in readily loses AN in the absence of excess AN.

$$\underset{\mathbf{3}}{IrCl(AN)(CO)(Ph_3P)_2} \underset{AN}{\overset{-AN}{\rightleftharpoons}} \underset{\mathbf{1}}{IrCl(CO)(Ph_3P)_2} \underset{-H_2}{\overset{H_2}{\rightleftharpoons}}$$

$$\underset{\mathbf{2}}{IrClH_2(CO)(Ph_3P)_2} \underset{Cl^-}{\overset{-Cl^-}{\rightleftharpoons}} [IrH_2(CO)(Ph_3P)_2]^+ \underset{-AN}{\overset{AN}{\rightleftharpoons}}$$

$$[IrH_2(AN)(CO)(Ph_3P)_2]^+ \longrightarrow [Ir(CO)(Ph_3P)_2]^+ + PN \quad (3)$$

In order to find out the dissociating ligand in equation (3), the hydrogenation of AN to PN with **1** have been carried out in the presence of excess free Cl^- or Ph_3P. It had been already known that CO is not the dissociating ligand in the catlytic cycle for the hydrogenation of AN to PN with **1**.[18]

It is seen in Table 1 that the presence of Cl^- ($(n\text{-}Bu)_4NCl$) in the catalytic system suppresses the hydrogenation, which suggests that the dissociating ligand in the catalytic cycle is Cl^-. The presence of Cl^- in the catalytic system would depress the dissociation of Cl^- from **2** to give $[IrH_2(CO)(Ph_3P)_2]^+$, and consequently lower the rate of the hydrogenation. Even if the olefin route is also applicable for the hydrogenation of AN with **1**, the formation of $[Ir(AN)(CO)(Ph_3P)_2]^+$ (confer eq. (1-a)) would be inhibited by the presence of Cl^-, and consequently the lower hydrogenation rate would be observed. Table 1 also shows that the addition of Ph_3P into the catalytic system increases the rate of hydrogenation. This observation evidently contradicts that Ph_3P is the dissociating ligand,, which was suggested in the hydrogenation of maleic anhydride[15] and dimethyl maleate.[26] The effect of Ph_3P on the rate of the hydrogenation is not clearly understood thus far, and is under investigation.

Table 2 summarizes the effects of AN, H_2 and **1** on the rate of the hydrogenation. It is seen in Table 2 that the decrease in AN concentration increases the rate of the hydrogenation. This is probably due to the equilibrium between **1** and **3**:

TABLE 1: Ligand Effects on the Hydrogenation of Acrylonitrile (AN) to Propionitrile (PN) with IrCl (CO)(Ph_3P)$_2$ (0.15 mmole), obtained for the First 4 Hours at 100°C under Hydrogen Pressure of 4 atm

AN mmole (m*l*)	benzene (m*l*)	(n-Bu)$_4$NCl (mmole)	Ph_3P (mmole)	PN (mmole)
37.5(2.5)	7.5			8.4
37.5(2.5)	7.5	3.0		2.5
150(10)				4.4
150(10)			0.15	7.8
150(10)			0.30	9.1
150(10)			0.45	11.5

TABLE 2: Effects of Acrylonitrile (AN), Hydrogen (H_2) and IrCl (CO) (Ph_3P)$_2$ on the Hydrogenation of Acrylonitrile to Propionitrile (PN) with IrCl (CO) (Ph_3P)$_2$, obtained for the First 4 Hours at 100°C

IrCl(CO)(Ph_3P)$_2$ mmole	AN mmole(m*l*)	benzene m*l*	P_{H_2} atm	PN mmole	TN*
0.15	150(10)		4.0	4.4	7.32
0.15	37.5(2.5)	7.5	4.0	8.4	
0.15	150(10)		2.0	2.3	
0.15	150(10)		3.0	3.7	
0.15	150(10)		6.0	6.8	
0.30	150(10)		4.0	8.7	7.25

*TN (turnover number) = CH_3CH_2CN/Ir/hr.

the higher concentration of AN would shift the equilibrium in favor of **3** which is inactive for the hydrogenation through the hydride route (see eq. (3)). Other reaction steps (i. e., except the equilibrium between **1** and **3**) involving AN in both the olefin route and hydride route are in favor of decreasing the rate of the hydrogenation with decrease in AN concentration in the reaction system.

Table 2 shows that the rate of the hydrogenation increases with increasing the hydrogen (H_2) pressure. This observation is expected in the hydrogenation proceeding through the hydride route (eq. (3)). In the olefin route (eq. (1-a)), however, there are two equilibria involving H_2, which would affect the the rate of the hydrogenation to the opposite directions each other. The equilibrium between **1** and the dihydrido complex, **2** would be shifted to the direction of **2** by increasing hydrogen pressure, and consequently the rate of the hydrogenation through the olefin route may decrease with increasing hydrogen pressure of the reaction system. On the other hand, the formation step of dihydrido-acrylonitrile complex, [IrH_2 (AN) (CO) (Ph_3P)$_2$]$^+$ would be in favor of increasing the rate of the hydrogenation with increasing hydrogen pressure of the reaction system (confer eq. (1-a)). Therefore, whether the hydrogenation of AN to PN with **1** proceeds through the hydride route (eq. (3)) only or through both the hydride route and the olefin route simultaneously, remains obscure.

It is seen in Table 2 that as expected, the rate of the hydrogenation increases linearly with increasing the concentration of **1** in the region of 15 m*M* – 30 m*M* giving practically the same turnover numbers (CH_3CH_2CN/Ir/hr.), 7.32 and 7.25 (see Table 2).

Conclusions

The hydrogenation of acrylonitrile to propionitrile with IrCl (CO) (Ph_3P)$_2$ proceeds mainly through the hydride route where the formation of the dihydrido complex, $IrClH_2$ (CO) (Ph_3P)$_2$ is followed by the ligand (Cl^-) dissociation to give [IrH_2(CO) (Ph_3P)$_2$]$^+$ to which an acrylonitrile is coordinated to produce dihydrido-acrylonitrile iridium complex, [IrH_2 (AN) (CO) (Ph_3P)$_2$]$^+$ which finally gives a propionitrile and [Ir(CO) (Ph_3P)$_2$]$^+$. It is not unequivocal whether the hydrogenation also proceeds through the olefin route where the formation of the acrylonitrile adduct, IrCl (AN) (CO) (Ph_3P)$_2$ would be the initial step.

Experimental

Compounds. IrCl(CO) (Ph_3P)$_2$[21] and $IrClH_2$ (CO) (Ph_3P)$_2$[22] were prepared by the literature methods.

Instrument. A Varian EM 360A ^{1}H-NMR spectrometer was used to measure the amounts of AN and PN in the reaction mixture.

Reactor. A stainless steel reactor (Part 1341 type oxygen bomb with a self-closing gas inlet valve, internal volume of 360 m*l*) was used as a reaction vessel for the reaction of $IrClH_2$(CO) (Ph_3P)$_2$ with AN and the hydrogenation of AN with IrCl(CO) (Ph_3P)$_2$.

Reaction of $IrClH_2(CO)(Ph_3P)_2$ with AN. A 0.47 g (0.6 mole) of $IrClH_2$(CO)(Ph_3P)$_2$ was dissolved in the mixture of AN (2.0 m*l*, ca. 30 mmole) and benzene (8.0 m*l*) in the reactor under nitrogen at room temperature. Then the reactor was covered with a vacuum-tight cap, heated in oven maintained at 100°C for 8 hours, cooled on ice bath, and opened. A part of the resulting yellow solution was transferred into an NMR tube for ^{1}H-NMR measurement. The ratio of AN (ABC pattern centered at δ= 6.0 ppm) to PN (a quartet at δ= 2.38 ppm, a triplet at δ= 1.22 ppm) was ca. 50:1.

Hydrogenation of AN with IrCl(CO)(Ph_3P)$_2$. Experimental m*l*details are given for one typical experiment since all the experiments were carried out in the same manner described below. A 0.117g(0.15 mmole) of IrCl(CO)(Ph_3P)$_2$ was dissolved in 10 (150 mmol) of AN in the reactor under atmospheric pressure of hydrogen at room temperature. Then the reactor was covered with a vacuum-tight cap and connected with a hydrogen cylinder through a connection tube with a pressure gauge on it. Hydrogen was introduced into the reactor from the cylinder through the connection tube until the pressure gauge showed 4 atm. The hydrogen cylinder with the connection tube was disconnected from the reactor whose self-closing inlet valve maintains the pressure of the reactor. Then the reactor was heated at 100°C in an oven for 4 hours, cooled on ice bath, and opened for ^{1}H-NMR measurement. The ratio of AN to PN in the reaction mixture was found to be ca. 145:4.4. It should be noted that the hydrogen pressure would be somewhat higher than 4 atm at 100 °C.

Acknowledgment. This study in a part of the "Selective Reduction" supported by the Korean Ministry of Education.

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(20) It is well know that complex **1** reacts with H_2 and AN to give **2** and **3**, respectively.[19] Therefore, the possible olefin route for the hydrogenation of AN would be similar to eq. (1–a) where the dissociation of L occurs after the formation of the olefin adduct, $IrCl(olefin)(CO)(Ph_3p)_2$.
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Polyacetylene Compounds from Panax Ginseng C. A. Meyer

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(*Received April 19, 1983*)

Two major and two minor polyacetylenes were isolated from fresh white Korean ginseng roots. The petroleum ether–ethyl ether fractions containing the polyacetylene compounds were collected through solvent fractionation, partition and silica gel column chromatography. Further separation of polyacetylenic fractions was proceeded by bonded normal phase HPLC utilizing a moderately nonpolar microparticulate column. The low pressure liquid chromatography was used for the semi-preparative separation. The chemical structures of the two major polyacetylenes separated were determined by UV, IR, ^1H NMR, ^{13}C NMR, mass spectra and elemental analysis. One of them is identified to be heptadeca-1-en-4, 6-diyne-3, 9, 10-triol, a new structure, and the other is heptadeca-1, 9-dien-4, 6-diyn-3-ol, known as panaxynol.

Introduction

Panax ginseng C. A. Meyer (Araliaceae) has been known for many years as the most valued among all herbal medicines and plants having mysterious effects in Korea, China and Japan. Since the saponin components from American ginseng (Panax quinquefolium L.) were isolated for the first time by Garriques in 1854,[1] much interest has been generated for the chemical, biochemical and pharmacological studies on ginsengs.

Recently, it was reported[2,3] that the petroleum ether fraction extracted from Korean ginseng roots inhibits the growth of murine leukemia L5178Y and murine Sarcoma 180 cells *in vitro*, and also inhibits DNA, RNA and protein synthesis in murine ascitic Sarcoma 180 cells *in vitro*. The petroleum ether-etheral extracts from ginseng roots contain fatty acids, hydrocarbons, steroids, polyacetylene compounds, and glycosides. However, since it has not been known which of the components described above shows the cytotoxicity for the carcinoma cells, Panax ginseng has been investigated to determine the chemical composition of the plant root.

A polyacetylene compound from ginseng roots was isolated by Takahashi *et al.* in 1964.[4,5] The chemical structure of the compound was turned out to be identical with falcarinol