

Cationic Iridium(I) Complex of Ethyl Cinnamate and Hydrogenation of Unsaturated Esters with Iridium(I)-Perchlorato Complex

Kyung Joon Yang and Chong Shik Chin*

Department of Chemistry, Sogang University, Seoul 121. Received August 30, 1986

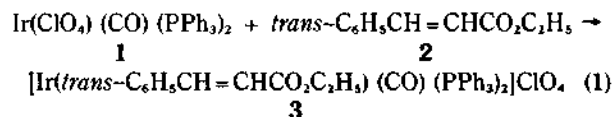
Reaction of $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ with $\text{trans-C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$ produces a new cationic iridium(I) complex, $[\text{Ir}(\text{trans-C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5)(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$, where $\text{trans-C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$ seems to be coordinated through the carbonyl oxygen rather than through the π -system of the olefinic group according to the spectral data. It has been found that $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ catalyzes the hydrogenation of $\text{CH}_2=\text{CHCO}_2\text{C}_2\text{H}_5$, $\text{trans-CH}_3\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$ and $\text{trans-C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$ to $\text{CH}_3\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$ and $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$, respectively at room temperature under the atmospheric pressure of hydrogen. The relative rates of the hydrogenation of the unsaturated esters are mostly understood in terms of steric reasons.

Introduction

The hydrogenation of unsaturated esters¹ and soybean oil (a mixture of unsaturated esters)² to the corresponding saturated esters has been known to be catalyzed with a rhodium(I) perchlorato complex, $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ at room temperature. The iridium(I) analogue, $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (**1**) has been found to react with unsaturated compounds to form cationic iridium(I) complexes, $[\text{IrL}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (L = unsaturated nitriles^{3,4} and unsaturated aldehydes⁵ coordinated through the nitrogen and oxygen atom, respectively, but not through the olefinic group) which show the catalytic activities for the hydrogenation of L to the corresponding saturated nitriles and saturated aldehydes. In this paper, we wish to report the synthesis of a cationic iridium(I) complex of an unsaturated ester and the catalytic hydrogenation of unsaturated esters to the corresponding saturated esters with $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (**1**) at room temperature under the atmospheric pressure of hydrogen.

Results and Discussion

Reaction of **1** with $\text{trans-C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$ (**2**) produces a new cationic iridium (I) complex $[\text{Ir}(\text{trans-C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5)(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (**3**) according to equation 1. Attempts to isolate any iridium complexes of $\text{CH}_2=\text{CHCO}_2\text{C}_2\text{H}_5$ (**4**) and $\text{trans-CH}_3\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$ (**5**) have been unsuccessful. Complex **3** is soluble in polar solvents such as chloroform,



dichloromethane and chlorobenzene but insoluble in non polar solvents such as hexane and benzene. It is stable in the solid state in air and in solution under nitrogen at room temperature. **Bonding between iridium and trans-C₆H₅CH=CHCO₂C₂H₅ (2) in [Ir(trans-C₆H₅CH=CHCO₂C₂H₅)(CO)(PPh₃)₂ClO₄ (3).** Electronic absorption spectrum of **3** in the visible region (Table 1) suggests that **3** is a four coordinated iridium(I) complex where **2** is coordinated through the oxygen atom to iridium but not through the π -system of the olefinic group. It is well-established that the related four coordinated iridium(I) complex, $\text{IrA}(\text{CO})(\text{PPh}_3)_2$ (A = OH, Cl, Br, I, CN,

NCS, ClO_4)⁶ and $[\text{IrL}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (L = unsaturated nitriles^{3,4} and unsaturated aldehydes⁵ coordinated through the nitrogen and oxygen atom, respectively) show the very similar three bands in the same region. It is also well-known that $\text{IrX}(\text{L})(\text{CO})(\text{PPh}_3)_2$ (X = Cl, Br, I; L = $\text{CH}_2=\text{CHCN}$, $\text{trans-(CN)-CH}=\text{CH(CN)}$, $(\text{CN})_2\text{C}=\text{C(CN)}$)⁷ and $[\text{IrL}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (L = $\text{trans-(CN)CH}=\text{CH(CN)}$)⁸ where L is coordinated through the π -system of the olefinic group, show no absorption bands in the visible region. Infrared spectral data in Table 1 support the bonding between the carbonyl oxygen and iridium in **3**. The significant decreases in $\nu_{\text{C=O}}$ of the ester group in **2** upon coordination are indicative of the bonding between the carbonyl oxygen and the metal. There has been no report on the transition metal complexes of esters where an ester is coordinated through the oxygen of C-O-C group. The data for $\nu_{\text{C=O}}$ of **2** would provide valuable information on the nature of the bonding between **2** and **3**. The absorption band due to $\nu_{\text{C=O}}$ of **2**, however, is not resolved due to the strong absorption of $\nu_{\text{C=O}}$ near it. A strong and broad band at ca. 1100 cm^{-1} observed for **3** (not given in Table 1) is attributable to the tetrahedral (Td) anion ClO_4^- ,⁹ which supports that **3** is an 1:1 electrolyte as confirmed by the conductance measurements (see Experimental). The slight upfield shifts have been observed for the protons of **2** upon coordination to $\text{Ir}(\text{CO})(\text{PPh}_3)_2^+$ (Table 1), and practically no changes in coupling constants have been found for the protons of **2** in **3** from those of free **2** (not given in Table 1).

Catalytic hydrogenation of unsaturated esters with Ir(ClO₄)(CO)(PPh₃)₂ (1). It has been found that complex **1** catalyzes the hydrogenation of $\text{CH}_2=\text{CHCO}_2\text{C}_2\text{H}_5$ (**4**), $\text{trans-CH}_3\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$ (**5**) $\text{trans-C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$ (**2**) to the corresponding saturated esters, $\text{CH}_3\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$ and $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CO}_2\text{C}_2\text{H}_5$, respectively. The catalytic hydrogenation of **2** with **3** gives the same results shown in Figure 1 obtained using **1** in place of **3**, which is readily understood since the reaction of **1** with **2** could give **3** immediately in the reaction mixture under the catalytic conditions. This catalytic hydrogenation of **2**, **4** and **5** with **1** is certainly an evidence that there is an interaction between the olefinic group of the unsaturated esters and the iridium in **1**. The hydrogenation is relatively slow, but it does not show any decrease in the rates for a considerably long period of time (see Figure 1). The slowness of the hydrogenation of the unsaturated esters, **2**, **4** and **5** with **1** is probably due to the in-

Table 1. Electronic Absorption (CH₂Cl₂), Infrared (Nujol) and ¹H-NMR (CDCl₃) Spectral Data for *trans*-C₆H₅CH=CHCO₂C₂H₅ (2**) and [Ir(*trans*-C₆H₅CH=CHCO₂C₂H₅)(CO)(PPh₃)₂](ClO₄)(**3**)**

Compound	electronic absorption, nm ^a	
	3	437 (530), 382 (2240), ca. 320 ^b
	infrared absorption, cm ⁻¹	
	$\nu_{C=O}$	$\nu_{C=C}^c$
2	1634, 1709	
3	1580, 1625 1962	
	¹ H-NMR, δ (ppm) ^d	
2	1.29(t, CH ₃ , 3H), 4.20(q, CH ₂ , 2H), 6.35(d, CHCO ₂ , 1H), 7.36(d, C ₆ H ₅ CH=, 1H), 7.62(m, C ₆ H ₅ , 5H)	
3	1.24(t, CH ₃ , 3H), 4.05(q, CH ₂ , 2H), 6.33(d, CHCO ₂ , 1H), ca. 7.50(m, C ₆ H ₅ CH, C ₆ H ₅ CH, PC ₆ H ₅ , 36H)	

^a Under nitrogen at 25°C. Extinction coefficients are given in parentheses. ^b A shoulder due to the strong absorption by the ligands at ca. 300 nm. ^c CO coordinated directly to iridium. ^d Under nitrogen at 25°C at 60 MHz. Chemical shifts are relative to Me₄Si.

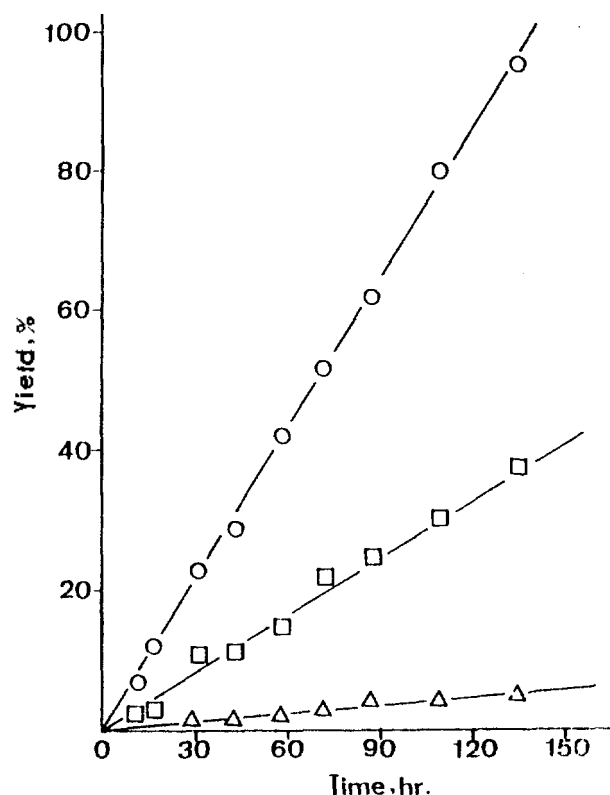


Figure 1. Hydrogenation of unsaturated esters (37 mmol) with Ir(ClO₄)(CO)(PPh₃)₂ (0.1 mmol) at 25°C under hydrogen (P_{H₂} + vapor pressure of the solution = 1 atm).

—○—○—, CH₂=CHCO₂C₂H₅; —□—□—, *trans*-CH₃CH=CHCO₂C₂H₅; —△—△—, *trans*-C₆H₅CH=CHCO₂C₂H₅.

interaction of the catalyst metal with the carbonyl oxygen of the ester group as observed for **3** (see text). The extremely

slow rate observed for **2** may be understood in terms of the stability of **2** due to the extended conjugated system as well as the steric reason since the bulk phenyl group may interfere the interaction between the olefinic group of **2** and the catalyst. It may be also said that the hydrogenation of **2** with **1** is very slow partly because the bond between the iridium and the carbonyl oxygen of **2** in **3** is so stable that the interaction between the catalyst and the olefinic group of **2** is somewhat less likely to occur. The faster rate observed for **4** than for **5** is probably explained also by a steric effect that the interaction of the olefinic group with the metal catalyst is more facile for **4** than for **5**. It is interesting to notice that the hydrogenation of the unsaturated esters (**2**, **4** and **5**) with **1** (Figure 1) is much faster than that of unsaturated nitriles coordinated through the nitrogen atom) which are formed by the reactions of **1** with L,³ while it is comparable with that of unsaturated aldehydes with **1** whose reactions with unsaturated aldehydes show good evidences for the interaction between the iridium and carbonyl oxygen of the aldehydes.⁵

Experimental

Infrared, electronic absorption and proton NMR spectra were obtained on Shimadzu IR-440, Shimadzu UV-240 and Varian 60MHz (EM-360A). Conductance measurements were carried out with Wiss-Tech. Werkstätten Weinheim/Obb. conductometer. Elemental analyses were performed at Spang Microanalytical Laboratory, Eagle Harbor, Michigan, U.S.A. A standard vacuum line and Schlenk-type glassware were used in handling metal complexes. CH₂=CHCO₂C₂H₅ (Aldrich), *trans*-CH₃CH=CHCO₂C₂H₅ (Fluka) and *trans*-C₆H₅CH=CHCO₂C₂H₅ (Fluka) were used after distillation. Ir(ClO₄)(CO)(PPh₃)₂ was prepared by the literature method.⁹ Nitrogen and hydrogen were extra pure grade from Dong Yang Argon in Korea.

Preparation of [Ir(*trans*-C₆H₅CH=CHCO₂C₂H₅)(CO)(PPh₃)₂](ClO₄)(3**).** Addition of *trans*-C₆H₅CH=CHCO₂C₂H₅ (20 drop, ca. 6 mmole) into the benzene solution of Ir(ClO₄)(CO)(PPh₃)₂ (0.27 g, 0.3 mmole) under nitrogen at 25°C immediately resulted in precipitation of pale yellow microcrystals which were collected by vacuum filtration, washed with hexane (30 ml) and dried under vacuum. The yield was 0.20 g (65% based on **3**). *Anal.* Calcd. for IrC₄₈H₄₂O₂ClP₂: C, 56.50; H, 4.15; Cl, 3.47; P, 6.07. Found: C, 55.98; H, 4.59; Cl, 3.54; P, 6.19. Molar conductance = 100 ohm⁻¹cm²mol⁻¹ ([Ir] = 5.0 × 10⁻⁵ M in *trans*-C₆H₅CH=CHCO₂C₂H₅ at 25°C under nitrogen). The molar conductance of the standard 1:1 electrolyte, (n-Bu)₄NClO₄ was measured to be 110 ohm⁻¹cm²mol⁻¹ in *trans*-C₆H₅CH=CHCO₂C₂H₅ at 25°C under nitrogen ([n-Bu)₄NClO₄] = 5.0 × 10⁻⁵ M).

Catalytic hydrogenation of unsaturated esters with Ir(ClO₄)(CO)(PPh₃)₂. The following procedure was followed in all experiments using 0.1 mmole of Ir(ClO₄)(CO)(PPh₃)₂ (**1**) and 37 mmoles (ca. 5.0 ml) of the corresponding unsaturated ester. Complex **1** was dissolved in the corresponding unsaturated ester in a 25 ml round-bottomed flask under nitrogen at 25°C. Then the reaction mixture was flushed with hydrogen several times and stirred under hydrogen (P_{H₂} + vapor pressure of the reaction mixture = 1 atm). A portion of the reaction mixture was taken out of reactor and analyzed by proton NMR measurements at intervals. Hydrogenation of

$\text{CH}_2=\text{CHCO}_2\text{C}_2\text{H}_5$, was followed by measuring the disappearance of the signals due to $\text{CH}_2=\text{CH}$ - at 5.2-6.2 ppm (relative to Me_4Si). The quartet due to $-\text{CO}_2\text{CH}_2\text{CH}_3$ at 4.0 ppm was employed as an internal standard. Hydrogenation of *trans*- $\text{CH}_3\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$ was followed by measuring the disappearance of the signals at 6.3-6.5 ppm due to $-\text{CH}=\text{CH}-$ and using the quartet at 4.0 ppm due to $-\text{CO}_2\text{CH}_2\text{CH}_3$ as an internal standard. Hydrogenation of *trans*- $\text{C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$ was followed by measuring the disappearance of the signals at 6.3-6.4 ppm due to $-\text{CH}=\text{CHCO}_2-$ and using the quartet at 4.2 ppm due to $-\text{CO}_2\text{CH}_2\text{CH}_3$ as an internal standard.

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Reactions, Hydrogenation and Isomerization of Unsaturated Esters with a Rhodium(I)-Perchlorato Complex

Hyun Mok Jeong and Chong Shik Chin*

Department of Chemistry, Sogang University, CPO Box 1142, Seoul 121. Received August 30, 1986

The isolated products from the reactions of $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (**1**) with $\text{CH}_2=\text{CHCO}_2\text{C}_2\text{H}_5$ (**2**) and *trans*- $\text{CH}_3\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$ (**3**) contain 80~90% of $[\text{Rh}(\text{CH}_2=\text{CHCO}_2\text{C}_2\text{H}_5)(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (**4**) and $[\text{Rh}(\text{trans-CH}_3\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5)(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (**5**), respectively where **2** and **3** seem to be coordinated through the carbonyl oxygen. It has been found that complex **1** catalyzes the isomerization of $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{CO}_2\text{C}_2\text{H}_5$ (**6**) to $\text{CH}_3(\text{CH}_2)_{n-1}\text{CH}=\text{CH}(\text{CH}_2)_{n-2}\text{CO}_2\text{C}_2\text{H}_5$ ($n=0\sim 7$) under nitrogen at 25°C. The isomerization of **6** is slower than that of $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{CH}_3$ to $\text{CH}_3(\text{CH}_2)_{n-1}\text{CH}=\text{CH}(\text{CH}_2)_{n-2}\text{CH}_3$ ($n=0\sim 8$), which is understood in terms of the interactions between the carbonyl oxygen of **6** and the catalyst. It has been also observed that complex **1** catalyzes the hydrogenation of **2**, **3**, **6**, *trans*- $\text{C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$ (**7**), $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{C}_2\text{H}_5$ (**8**) and $\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{CH}_3$ (**9**), and the isomerization (double bond migration) of **6** and **9** under hydrogen at 25°C. The interactions between the carbonyl oxygen of the unsaturated esters and the catalyst affect the hydrogenation in such a way that the hydrogenation of the unsaturated esters becomes slower than that of simple olefins.

Introduction

Perchlorato ligand (ClO_4) in $\text{M}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ ($\text{M}=\text{Rh}, \text{Ir}$) is so labile that it is readily replaced even by various solvent molecules.¹ We recently reported that ClO_4 group in $\text{M}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ ($\text{M}=\text{Rh}, \text{Ir}$) is replaced with unsaturated nitriles,² unsaturated aldehydes³ and unsaturated alcohols⁴ to give cationic complexes, $[\text{ML}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ ($\text{L}=\text{unsaturated nitriles, unsaturated aldehydes and unsaturated alcohols}$) which show catalytic activities for the hydrogenation, isomerization and oligomerization of the corresponding unsaturated compounds (L). We also found that $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (**1**) catalyzes the hydrogenation and isomerization of soybean oil which is a mixture of unsaturated esters and saturated esters.⁵ The interactions between the rhodium in **1** and the carbonyl oxygen of soybean oil, however, could not be established in that study.⁵

Accordingly, we have decided to investigate the interaction between pure unsaturated esters and **1**. In this paper, we

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wish to report the formation of cationic rhodium(I) complexes of unsaturated esters and the catalytic activities of **1** for the hydrogenation and isomerization of unsaturated esters.

Results and Discussion

Reactions of $\text{Rh}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (1**) and unsaturated esters.** Interaction is apparent between the rhodium in **1** and the carbonyl oxygen of the ester group in the unsaturated esters chosen in this study (see below) although pure complexes have not been isolated from the reactions of **1** and the unsaturated esters. The reactions of **1** with $\text{CH}_2=\text{CHCO}_2\text{C}_2\text{H}_5$ (**2**) and *trans*- $\text{CH}_3\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$ (**3**) yield pale yellow solids, respectively (see Experimental for details), while no rhodium complexes have been isolated from the reactions of **1** with other unsaturated esters, *trans*- $\text{C}_6\text{H}_5\text{CH}=\text{CHCO}_2\text{C}_2\text{H}_5$, $\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{CO}_2\text{C}_2\text{H}_5$ and $\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{C}_2\text{H}_5$. The products obtained from the reaction of **1** with **2** and **3** lose **2** and **3**, respectively when they are dissolved