

accelerating voltage of about 60 kV. The sample was kept at $-40\text{ }^{\circ}\text{C}$ and the inlet system and nozzle were at room temperature. The camera pressure never exceeded 5×10^{-6} Torr during the experiment. Two plates for each camera distance were analyzed by the usual procedures.¹⁸ The averaged molecular intensities in the ranges 0.014–0.17 and 0.08–0.35 pm^{-1} are presented in Figure 3.

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Registry No. AsF_5 , 7784-36-3; AsClF_4 , 94649-43-1; AsCl_2F_3 , 109278-32-2; AsCl_3F_2 , 95036-82-1; AsCl_4F , 87198-15-0; AsCl_5 , 22441-45-8.

(18) Oberhammer, H.; Gombler, W.; Willner, H. *J. Mol. Struct.* **1981**, *70*, 273.

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Cationic Iridium(I) Complexes of Unsaturated Aldehydes and Their Catalytic Activities

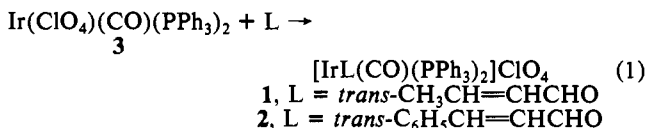
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The iridium complexes of unsaturated nitriles $[\text{Ir}^{\text{I}}\text{L}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ and $[\text{Ir}^{\text{III}}(\text{H})_2\text{L}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (L = unsaturated nitriles) have been prepared and investigated with respect to their catalytic activities for the hydrogenation and isomerization of L.¹ The rhodium(I) analogues $[\text{RhL}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ have also been prepared and studied for L being unsaturated nitriles² and unsaturated aldehydes.³

In this paper, we wish to report the synthesis of iridium(I) complexes of unsaturated aldehydes, $[\text{Ir}(\text{trans-CH}_3\text{CH}=\text{CHCHO})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (**1**) and $[\text{Ir}(\text{trans-C}_6\text{H}_5\text{CH}=\text{CHCHO})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (**2**), and their catalytic activities for the hydrogenation of *trans*- $\text{CH}_3\text{CH}=\text{CHCHO}$ and *trans*- $\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$, respectively. Catalytic hydrogenation of $\text{CH}_2=\text{CHCHO}$ with $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (**3**) is also included in this report.

Complexes **1** and **2** have been prepared according to eq 1. Attempts have been made to prepare a $\text{CH}_2=\text{CHCHO}$ complex of iridium without success, although the rhodium complex, $[\text{Rh}(\text{CH}_2=\text{CHCHO})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$, was previously prepared.²



Experimental Section

Caution. Perchlorate salts of transition-metal complexes containing organic ligands are potentially explosive.⁴

Materials. $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ was prepared by the literature method.⁵ $\text{CH}_2=\text{CHCHO}$ and *trans*- $\text{CH}_3\text{CH}=\text{CHCHO}$ (Aldrich) were distilled before use. *trans*- $\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$ (Aldrich) was used as purchased.

Physical Measurements. Electronic and infrared adsorption spectra were obtained with Shimadzu UV-240 and Shimadzu IR-440 instru-

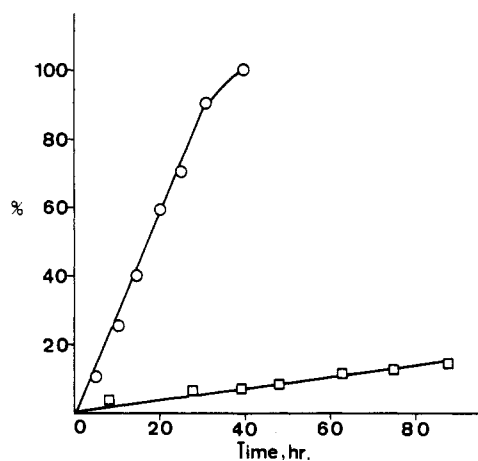


Figure 1. Hydrogenation of $\text{CH}_2=\text{CHCHO}$ (37 mmol) to $\text{CH}_3\text{CH}_2\text{CHO}$ with $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (**3**) (0.1 mmol) (O) and of *trans*- $\text{CH}_3\text{CH}=\text{CHCHO}$ (37 mmol) to $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ with $[\text{Ir}(\text{trans-CH}_3\text{CH}=\text{CHCHO})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (**1**) (0.1 mmol) (or **3**, 0.1 mmol) (□) at $25\text{ }^{\circ}\text{C}$ under hydrogen (P_{H_2} + vapor pressure of the solution = 1 atm).

ments. ^1H NMR spectra were recorded on a Varian 60-MHz instrument (Model EM-360A). Conductance measurements were performed in the corresponding aldehydes with a Wiss-Tech LBR conductivity meter at $25\text{ }^{\circ}\text{C}$ under nitrogen. Elemental analyses were carried out by Spang Microanalytical Laboratory, Eagle Harbor, MI.

Preparation. Standard vacuum-line and Schlenk-type glassware were used in handling metal complexes. Complexes **1** and **2** are stable in the solid state in air and in solution under nitrogen at $25\text{ }^{\circ}\text{C}$.

$[\text{Ir}(\text{trans-CH}_3\text{CH}=\text{CHCHO})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (1**).** Addition of *trans*- $\text{CH}_3\text{CH}=\text{CHCHO}$ (1 mL, ca. 12 mmol) to a benzene solution (35 mL) of **3** (0.42 g, 0.50 mmol) under nitrogen at $25\text{ }^{\circ}\text{C}$ immediately resulted in yellow crystals, which were collected by filtration, washed with benzene (20 mL), and dried under vacuum; yield 0.36 g (79% based on **1**). Anal. Calcd for $\text{IrC}_{41}\text{H}_{36}\text{O}_6\text{ClP}_2$: C, 53.86; H, 3.97; Cl, 3.88; P, 6.78. Found: C, 53.71; H, 3.89; Cl, 3.99; P, 6.92. Molar conductance = $105\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ ($[\text{Ir}] = 5.0 \times 10^{-5}\text{ M}$ in *trans*- $\text{CH}_3\text{CH}=\text{CHCHO}$).

$[\text{Ir}(\text{trans-C}_6\text{H}_5\text{CH}=\text{CHCHO})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (2**).** This compound was prepared in the same manner described for **1**. A 1-mL quantity (ca. 8.0 mmol) of *trans*- $\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$ and 0.42 g (0.50 mmol) of **3** were used; yield 0.40 g (82% based on **2**). Anal. Calcd for $\text{IrC}_{46}\text{H}_{38}\text{O}_6\text{ClP}_2$: C, 56.59; H, 3.92; Cl, 3.63; P, 6.34. Found: C, 57.01; H, 3.89; Cl, 3.71; P, 6.27. Molar conductance = $100\text{ ohm}^{-1}\text{ cm}^2\text{ mol}^{-1}$ ($[\text{Ir}] = 5.0 \times 10^{-5}\text{ M}$ in *trans*- $\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$).

Hydrogenation of $\text{CH}_2=\text{CHCHO}$ with $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (3**).** A 37-mmol sample of $\text{CH}_2=\text{CHCHO}$ and 0.1 mmol of **3** in a 25-mL round-bottomed flask were stirred at $25\text{ }^{\circ}\text{C}$ under hydrogen (P_{H_2} + vapor pressure of the solution = 1 atm). A part (ca. 0.5 mL) of the reaction mixture was taken out and analyzed by ^1H NMR spectroscopy at intervals. Disappearance of $\text{CH}_2=\text{CH}$ signals of $\text{CH}_2=\text{CHCHO}$ at 5.5–6.1 ppm (or appearance of CH_3 signals of $\text{CH}_3\text{CH}_2\text{CHO}$ at 0.7 ppm) was followed to obtain the data given in Figure 1.

Hydrogenation of *trans*- $\text{CH}_3\text{CH}=\text{CHCHO}$ with $[\text{Ir}(\text{trans-CH}_3\text{CH}=\text{CHCHO})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (1**) (or $\text{Ir}(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ (**3**)).** This reaction was carried out in the same manner described above, using 37 mmol of *trans*- $\text{CH}_3\text{CH}=\text{CHCHO}$ and 0.1 mmol of **1** (or **3**). After a certain period of time, the volatile materials were separated from the nonvolatile materials by using a dry ice/acetone bath trap. *trans*- $\text{CH}_3\text{CH}=\text{CHCHO}$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO}$ in the volatile materials were analyzed by ^1H NMR spectroscopy. The nonvolatile materials (oily oligomers of *trans*- $\text{CH}_3\text{CH}=\text{CHCHO}$ and iridium complex) were dissolved in CDCl_3 and analyzed by ^1H NMR spectroscopy.

Bonding between Iridium and Unsaturated Aldehydes

Spectral data suggest that *trans*- $\text{CH}_3\text{CH}=\text{CHCHO}$ in **1** and *trans*- $\text{C}_6\text{H}_5\text{CH}=\text{CHCHO}$ in **2** are coordinated through the oxygen atom to iridium. It is well-known that the related four-coordinated iridium(I) complexes, $\text{IrA}(\text{CO})(\text{PPh}_3)_2$ (A = monodentate ligand coordinated through oxygen and nitrogen atom), show the three bands very similar to those for **1** and **2** (Table I) in the visible region.^{1,6} With the exception of $[\text{Ir}(\text{C}_2\text{H}_4)_2-$

(1) Park, S. H.; Park, H.-K.; Chin, C. S. *Inorg. Chem.* **1985**, *24*, 1120.
(2) Lee, M. K.; Kim, I. B.; Chin, C. S. *J. Organomet. Chem.* **1985**, *290*, 115.
(3) Kim, I. B.; Chin, C. S. *Polyhedron* **1984**, *3*, 1151.
(4) See: *J. Chem. Educ.* **1978**, *55*, A355. *Chem. Eng. News*, **1983**, *61* (Dec 5), 4; **1970**, *53*, 55; **1963** (July 8), *41*, 47 and ref 5.
(5) Peone, J.; Vaska, L. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 511.

(6) Brady, R.; Flynn, B. R.; Geoffroy, G. L.; Gray, H. B.; Peone, J.; Vaska, L. *Inorg. Chem.* **1976**, *15*, 1485.

Table I. Spectroscopic Data for $[\text{Ir}(\text{trans-CH}_3\text{CH}=\text{CHCHO})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (**1**) and $[\text{Ir}(\text{trans-C}_6\text{H}_5\text{CH}=\text{CHCHO})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (**2**)

compd	electronic abs, ^a nm	
1	438 (630), 383 (2670), 329 (3760)	
2	437 (610), 381 (2960), ca. 320 ^b	
IR, abs, ^c cm ⁻¹		
compd	$\nu(\text{C}=\text{O})$	$\nu(\text{C}\equiv\text{O})$
<i>trans-CH</i> ₃ <i>CH</i> =CHCHO	1689, 1642	
1	1631, 1604	2003
<i>trans-C</i> ₆ <i>H</i> ₅ <i>CH</i> =CHCHO	1674, 1626	
2	1612, 1580	1981
¹ H NMR, ^d ppm		
<i>trans-CH</i> ₃ <i>CH</i> =CHCHO	9.58 (d, CHO), 6.96 (m, CH ₃ CH), 6.14 (m, CHCHO), 2.02 (dd, CH ₃)	
1	8.31 (d, CHO), 7.50 (m, PC ₆ H ₅), 6.76 (m, CH ₃ CH), 5.46 (m, CHCHO), 1.80 (dd, CH ₃)	
<i>trans-C</i> ₆ <i>H</i> ₅ <i>CH</i> =CHCHO	9.67 (d, CHO), 7.30 (m, C ₆ H ₅ CH, C ₆ H ₅ CH), ^e 6.52 (m, CHCHO)	
2	8.64 (d, CHO), 7.50 (m, C ₆ H ₅ CH, C ₆ H ₅ CH, PC ₆ H ₅), ^f 6.02 (m, CHCHO)	

^a Under nitrogen at 25 °C in CH₂Cl₂ solution. Extinction coefficients are given in parentheses. ^b Shoulder due to the strong band near 300 nm. ^c Nujol mull. ^d Under nitrogen at 25 °C at 60 MHz, CDCl₃ solution. Chemical shifts are relative to Me₄Si. ^e Multiplets centered at 7.30 ppm. ^f Multiplets centered at 7.50 ppm.

(CO)(PPh₃)₂]⁺, whose spectral data were not reported,⁷ there have been no reports on $[\text{IrL}(\text{CO})(\text{PPh}_3)_2]^+$ in which L is coordinated through the π system of the olefinic group of L. The significant decreases in $\nu(\text{C}=\text{O})$ of *trans-CH*₃*CH*=CHCHO and *trans-C*₆*H*₅*CH*=CHCHO upon coordination to $\text{Ir}(\text{CO})(\text{PPh}_3)_2^+$ also suggest that the unsaturated aldehydes in **1** and **2** are coordinated through the oxygen atom but not through the olefinic group. The $\nu(\text{C}=\text{C})$ bands of the unsaturated aldehydes are obscured by the very strong absorption bands of $\nu(\text{C}=\text{O})$ in all spectra of the free unsaturated aldehydes and iridium complexes. A strong and broad absorption band observed at 1100 cm⁻¹ for **1** and **2** (not listed in Table I) is attributable to the tetrahedral (Td) anion ClO₄⁻,⁵ and in agreement, **1** and **2** are 1:1 electrolytes as shown by the conductance measurements (see Experimental Section). The fact that the olefinic protons of *trans-CH*₃*CH*=CHCHO and *trans-C*₆*H*₅*CH*=CHCHO do not show significant changes in the chemical shifts upon coordination to $\text{Ir}(\text{CO})(\text{PPh}_3)_2^+$ (see Table I) also suggests that the coordination of the unsaturated aldehydes in **1** and **2** does not occur through the π system of the olefinic group. It should be mentioned that the reactions of **3** with saturated aldehydes such as CH₃CH₂CH₂CHO and CH₃CH₂CHO did not afford the products analogous to **1** and **2**. The isolated greenish products seem to be mixtures of **3** and a small amount of uncharacterized iridium complexes that do not contain the saturated aldehydes.

Catalytic Activities

It is known that the complexes $[\text{IrL}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (L = unsaturated nitriles coordinated through the nitrogen atom) react with H₂ to give dihydrido-iridium(III) complexes $[\text{Ir}(\text{H})_2\text{L}(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ and that they catalyze hydrogenation of the unsaturated nitrile (L) to the corresponding saturated nitrile at elevated temperature (100 °C).¹ Reactions of **1** and **2** with H₂ would provide valuable information for the catalytic hydrogenation of *trans-CH*₃*CH*=CHCHO and *trans-C*₆*H*₅*CH*=CHCHO with **1** and **2**, respectively. It has been found that $\text{Ir}(\text{H})_2(\text{ClO}_4)(\text{CO})(\text{PPh}_3)_2$ ⁸ is the only product of the reactions of **1** and **2** with H₂.

Complex **1** catalyzes the hydrogenation of *trans-CH*₃*CH*=CHCHO to CH₃CH₂CH₂CHO at 25 °C (see Figure 1). The same results as shown in Figure 1 have been obtained by using

3 in place of **1**. Complex **2** does not show catalytic activity for the hydrogenation of *trans-C*₆*H*₅*CH*=CHCHO even at 100 °C. The olefinic group of *trans-C*₆*H*₅*CH*=CHCHO may be too stable due to the extended conjugate system to undergo the hydrogenation reaction. It is interesting to see that complex **3** is active for the hydrogenation of CH₂=CHCHO to give CH₃CH₂CHO at 25 °C (see Figure 1), although a CH₂=CHCHO complex of iridium has not been isolated from the reaction of **3** and CH₂=CHCHO. Decarbonylation products (alkane and alkene) have not been detected in the reactions of CH₂=CHCHO with **3** and *trans-CH*₃*CH*=CHCHO with **1** under N₂ and H₂ at 25 °C for several days. The hydrogenation of CH₂=CHCHO is much faster than that of *trans-CH*₃*CH*=CHCHO and proceeds to completion without formation of oligomers whereas a considerable amount of nonvolatile oligomers is obtained during the hydrogenation of *trans-CH*₃*CH*=CHCHO with **1** at 25 °C. Approximately the same number of moles of *trans-CH*₃*CH*=CHCHO is converted into oligomers as is hydrogenated to CH₃CH₂CH₂CHO in the presence of **1** at 25 °C. A small amount of oligomers is also produced in the absence of H₂; less than 1% of *trans-CH*₃*CH*=CHCHO is converted into oligomers when 37 mmol of *trans-CH*₃*CH*=CHCHO is stirred under N₂ at 25 °C for 48 h in the presence of 0.1 mmol of **1**. The hydrogenation of CH₂=CHCHO with **3** is somewhat different from the results obtained with the rhodium complex, $[\text{Rh}(\text{CH}_2=\text{CHCHO})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$, which converts more CH₂=CHCHO into the oligomers than to the hydrogenation product, CH₃CH₂CHO.⁵

The fact that the hydrogenation with **3** and **1** occurs at the olefinic group of CH₂=CHCHO and *trans-CH*₃*CH*=CHCHO requires an interaction between the olefinic group of the unsaturated aldehydes and the iridium in some part of the catalytic cycle. It still remains uncertain whether the hydrogenation occurs by the well-established mechanism through the olefinic π -bonded complexes or by 1,4-addition of Ir-H to the unsaturated aldehydes.

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Registry No. **1**, 109150-66-5; **2**, 109124-71-2; **3**, 32356-67-5; CH₂=CHCHO, 107-02-8; *trans-CH*₃*CH*=CHCHO, 123-73-9.

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Iron(II) Aryldiazene Complexes as Precursors of New Derivatives of the Type $[\text{FeL}(\text{CO})\{\text{P}(\text{OEt})_3\}_4]^{2+}$: Synthesis and Characterization

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In previous reports¹ we described the synthesis of the first aryldiazene iron(II) derivatives of the type $[\text{Fe}(\text{ArN}=\text{NH})(\text{CO})\text{P}_4]^{2+}$ [P = P(OEt)₃], which showed the ArNNH ligand to be a good leaving group in the complexes. The facile substitution of this ligand should therefore make the diazene compound a suitable starting material for the synthesis of new mono derivatives of iron(II) with unusual ligands. In this paper, as part of our studies on the chemistry of Fe(II) phosphite complexes,² we report an extensive study on the reactivity of the $[\text{Fe}(\text{ArN}=\text{NH})(\text{CO})\text{P}_4]^{2+}$ cations with several ligands, which allowed the synthesis of aldehyde, sulfide, and arylhydrazine complexes containing the

(7) Clark, H. C.; Reimer, K. J. *Inorg. Chem.* **1975**, *14*, 2133.

(8) Vaska, L.; Peone, J. *Suom. Kemistil. B* **1971**, *44*, 317.

(1) (a) Albertin, G.; Antoniutti, S.; Bordignon, E. *J. Chem. Soc., Chem. Commun.* **1984**, 1688. (b) Albertin, G.; Antoniutti, S.; Lanfranchi, M.; Pelizzi, G.; Bordignon, E. *Inorg. Chem.* **1986**, *25*, 950.

(2) (a) Albertin, G.; Bordignon, E. *Inorg. Chem.* **1984**, *23*, 3822. (b) Albertin, G.; Baldan, D.; Bordignon, E. *J. Chem. Soc., Dalton Trans.* **1986**, 329. (c) Albertin, G.; Antoniutti, S.; Pelizzi, G.; Vitali, F.; Bordignon, E. *J. Am. Chem. Soc.* **1986**, *108*, 6627.