The Ir(PPh₃)₂ (CO)OClO₃ and Ir(PPh₃)₃N₂Cl Mediated Activation of Aldehyde C-H Bonds *via* Chelate-Assisted Oxidative Addition

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Hydrocarbon solution of Ir(PPh₃)₂(CO)OClO₃ reacts with Ph₂PC₆H₄-o-CHO and 3-methyl-2-aminopyridinyl aldimine to yield Ir(Ph₂PC₆H₄-o-CO) (PPh₃)₂(CO)(H)ClO₄(1) and Ir(NC₆H₄NCC₆H₅)(PPh₃)₂ (CO)(H) ClO₄(2), respectively. The compound Ir(PPh₃)₃N₂Cl also reacts with Ph₂PC₆H₄-o-CHO and 3-methyl-2-aminopyridinyl aldimine to give Ir(Ph₂PC₆H₄-o-CO) (PPh₃)₂(H)Cl(3) and Ir(NC₆H₅NCC₆H₅) (PPh₃)₂(H)Cl(4), respectively. Compounds 1, 2, 3, and 4 were characterized by infrared, ¹H NMR, ³¹P NMR, UV spectra, and conductivity measurements.

Introduction

The activation of aldehyde C-H bonds is currently attracting chemical interest since transition metal acyl hydride compounds are known or postulated to be key intermediates in catalyzed hydroformylation reactions[1] and metal-catalyzed carbonylation processes.[2]

Recently, we[3] reported the Pt PCy₃(C₂H₄)₂ mediated activation of aldehyde C-H bonds, which led to transition metal acyl hydride compounds. Acyl hydride compounds of rhodium (III)[4-6] and iridium (III)[7,8] have been prepared through chelate-assisted oxidative addition reaction. It was suggested that the reaction proceed by removing one phosphine ligand before the scission of C-H bond and the phosphines produced during reaction cause facile ligand-promoted reductive elimination back to the starting aldehyde.[9] The fact has obvious implications for the selection of transition metal reagents for carbon-hydrogen and carbon-carbon bond activation.

With this fact in consideration, the low-valent iridium compounds, Ir(PPh₃)₂ (CO) OClO₃,[10] **A**, and Ir(PPh₃)₃N₂Cl[11], **B**, were selected as candidates, because they are coordinatively unsaturated,they have readily displaceable ligands, and provide a nucleophilic metal center. As a counterpart, we have chosen the ligands, **C** and **D**, which are available to form a five-membered chelate.
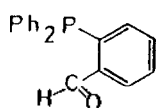
C   D

We describe here the reactions between **A**, **B** and **C**, **D**, which lead to C-H activation through formation of stable five-coordinate iridium (III) acyl hydride compounds.

Experimental

All synthetic procedures were carried out with use of standard Schlenk tube under a day and oxygen free atmosphere of N₂. The Ir(PPh₃)₂(CO)OClO₃, Ir(PPh₃)₂N₂Cl, Ph₂PC₆H₄-o-CHO[12], and 3-methyl-2-aminopyridinyl aldimine[13] were prepared according to literature methods. Benzene, hexane, and THF were dried over sodium, distilled under nitrogen from sodium/benzophenone, and deaerated by the freeze-thaw cycle technique before use. Infrared spectra were recorded on a Shimadzu IR-440 spectrophotometer from KBr pellet. ¹H NMR and ³¹P NMR spectra were measured on a Bruker WP 80 and WP 200, respectively. UV spectra were recorded on a Shimadzu UV 240. Conductivity measurement was conducted with an Industrial Instruments Model RC216B2. Elemental analyses were performed at the center of instrumental analysis, College of Engineering, Seoul National University, Seoul, Korea.

Preparation of complexes. Ir(Ph₂PC₆H₄-o-CO) (CO) (H) (PPh₃)₂ClO₄ (1). To a stirred benzene (3ml) solution of Ir(PPh₃)₂(CO)OClO₃ (0.9 mmol) Ph₂P C₆H₄-o-CHO(0.9 mmol) dissolved in benzene (8 *ml*) was added dropwise under nitrogen. Upon addition, the color changed immediately into orange, then pale yellow. The reaction was continued for 0.5h at room temperature. The volume was reduced to ca. 6 *ml* and hexane (10 *ml*) was added. The solution was left at room temperature for 2hr and the supernatant liquid was decanted from the solid with use of a curved Schlenk tube. The pale yellow solid was dried in vacuum. Yield: 82%. Anal. calcd for Ir C₅₆H₄₅P₃O₆Cl: C, 59.25; H, 4.00. Found: C, 58.61; H, 4.06. mp: 140-143°C.

Ir (NC₆H₆NCC₆H₅) (PPh₃)₂(CO) (H)ClO₄ (2). To a stirred benzene (6 *ml*) solution of Ir (PPh₃)₂(CO)OClO₃(0.8 mmol) 3-methyl-2-aminopyridinyl aldimine (0.8 mmol) 3-methyl-2-aminopyridinyl aldimine (0.8 mmol) dissolved in THF was added under nitrogen. The temperature was raised to 50°C. The reaction was continued for 40 min. at that temperature. The solution was decanted into new vessel, followed by the reduction in volume to ca. 5 *ml*. Hexane (12 *ml*) was added

to the solution. The resulting pale yellow solid was filtered off and dried in vacuum overnight. Yield: 76%. mp: 128-132°C. Anal. Calcd for IrC₅₀H₄₂O₅N₂P₂ Cl: C, 57.72; H, 4.97. Found: C, 57.09; H, 3.98.

Ir(Ph₂PC₆H₄-o-CO) (PPh₃)₂(H)Cl(3). To a stirred benzene (6 ml) solution of Ir(PPh₃)₂N₂Cl (0.6 mmol) at 0°C Ph₂PC₆H-o-CHO (0.6 mmol) dissolved in benzene (8 ml) was added dropwise. The reaction was continued for 1h. The volume was reduced to ca. 6 ml and hexane (8 ml) was added. After filtering it off, the resulting beige solid was washed with cold hexane and dried in vacuum overnight. Yield: 88%. mp: 136-138°C(dec.). Anal. Calcd for Ir C₅₅H₄₈P₃OCl: C, 63.37; H, 4.35. Found: C, 62.96; H, 4.23.

Ir (NC₆H₆NCC₆H₃) (PPh₃)₂(H)Cl (4). To a stirred benzene solution of Ir(PPh₃)₂N₂Cl(0.8 mmol) at 0°C 3-methyl-2-aminopyridinyl aldimine (0.8 mmol) dissolved in THF was added dropwise. The temperature was raised to 60°C. After the reaction (3h) at that temperature, the volume was reduced and hexane was added. The resulting pale yellow solid was filtered off and dried in vacuum. Yield: 78%. mp: 122-124°C. Anal. Calcd for Ir C₄₉H₄₃N₂P₂Cl: C, 62.05; H, 4.42. Found: C, 62.61; H, 4.36.

Results and Discussion

The general preparation of the iridium acyl hydride proceeds through reactions between Ir (PPh₃)₂(CO)OClO₃, A, Ir (PPh₃₃)N₂Cl, B, and a molar equivalent amount of ligands C, D.

Ir(PPh₃)₂XY + RCHO or R'CHPh → [(PPh₃)₂XIr(EC_n H_mCO)(H)] Y

Where: R = Ph₂PC₆H₄-o-, R' = 3-methyl-2-aminopyridinyl, X = CO, Cl, Y = OClO₃, N₂, E = P, N.

The addition of equimolar quantity of C or D to a stirred benzene solution of A or B affords a pale yellow solution. The resulting pale yellow compounds, Ir(Ph₂PC₆H₄-o-CO) (PPh₃)₂(CO) (H)ClO₄(1), Ir(NC₆H₆NCC₆H₅) (PPh₃)₂(H) (CO) ClO₄ (2), Ir(Ph₂PC₆H₄-o-CO) (PPh₃)₂(H)Cl (3), and Ir(NC₆ H₆NCC₆H₅) (PPh₃)₂(H)Cl (4), were isolated as air stable solids in 76-88% yields. The structure of compounds 1, 2, 3, and 4, were deduced from their IR, ¹H NMR, ³¹P NMR and UV spectra,
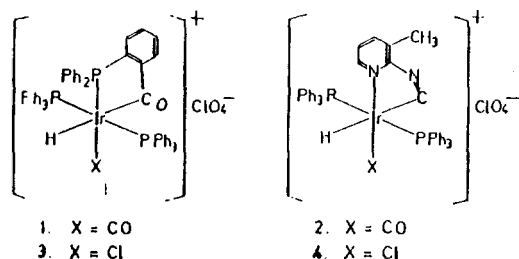
The key infrared features and UV absorption bands of these products are presented in Table 1.

The infrared spectra of compounds 1(see Figure 1), 2, 3, and 4, in KBr pellet clearly indicate the presence of the Ir-H bond. The intense peak at 2108cm⁻¹ of 1 is assigned to the Ir-H stretching mode, which is expected to exhibit a band with stretching frequency in the region 2200-2000cm⁻¹.[7,8] It is interesting to note that the Ir-H stretching frequency of 1 is relatively high, compared with the compound PCy₃ Pt P(C₆H₄-o-CO)(H)³, which occurs near 2023cm⁻¹. The low value of the compound PCy₃ Pt P(C₆H₄-o-CO)(H) was assumed to be related to the slight interaction between the oxygen of the carbonyl group (C≈0) and the hydride, as shown in the longer C-O bond length. It, so-called multicenter interaction,[4] gives rise to the cis geometry of both ligands. However, the high value of 1 can be assumed to be no interaction between two groups. It may be related to the trans geometry of both ligands, as discussed in the NMR spectra. On the other hand,
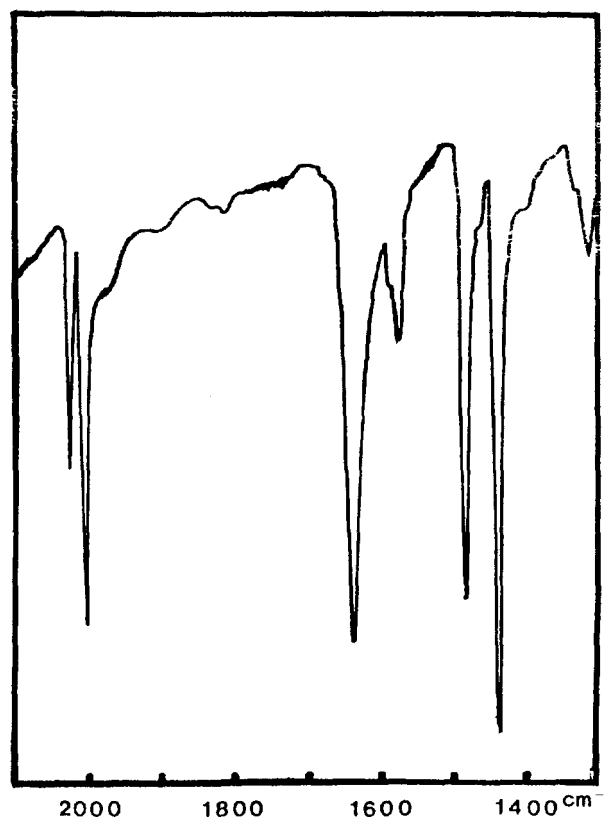

Figure 1. The infrared spectrum of Ir(Ph₂PC₆H₄-o-CO) (PPh₃)₂ (CO)(H)ClO₄(2500-1500 cm⁻¹).

1. X = CO
3. X = Cl

2. X = CO
4. X = Cl

Table 1. Infrared, and UV Spectral Data

| Complex | IR absorption band (cm⁻¹)[a] | | | | | UV absorption(nm)[b] |
	c νIr-H	d νC≡O	d νC=O	c νC=C	e νC=N	max(logε)
1	2108	2003	1638	1572		290(1.8), 422(0.4)
2	2058	1990		1575	1595	371(1.2), 442(0.8)
3	2120		1622	1576		295(1.6), 415(0.3)
4	2065			1570	1589	362(1.1), 431(0.7)

[a]KBr pellet. [b]Recorded in CH₂Cl₂ Solution. [c]Strong. [d]Very strong. [e]Very strong. [f]medium.

the infrared spectrum of **2** gave a low value for the hydride stretching frequency compared with that of the compound **1**. It may be related to the increase of ionic character of hydride by substituting the $C = N$ group for the $C = 0$ group. The peak at $2003 cm^{-1}$ of **1** is assigned to $\nu(C \equiv 0)$, which is shifted to a higher frequency than that found for the compound Ir $(PPh_3)_2(CO)OClO_3$ due primarily to the change in oxidation state. The peak at $1608 cm^{-1}$ of **1** is assigned to $\nu(C = 0)$. The low value compared with that found for the free ligand, $1685 cm^{-1}$, may be attributed to the back bonding of the Ir to the carbonyl.

The electronic absorption spectra of these complexes show two bands. The two bands of compound **2** which are due to the d–d transitions in the octahedral crystal field appear at 442 nm and 371 nm. The peak at 442 nm can be assigned as the spin allowed transition from $^1A_{1g}$ to $^1T_{1g}$ and the peak at 371nm from $^1A_{1g}$ to $^1T_{2g}$, which is characteristic of the low spin d^6 configuration.

The conductance measurements (112–118 ohm^{-1} cm^2 mol^{-1}) ^{1}H NMR spectrum of **1** taken in CDCl$_3$ at room temperature for **1–2**) indicate that the complexes are 1:1 electrolytes. ex-

hibits resonances of Ir–H centered at $\delta - 8.48$(1H, d of t, $J_{P_1-H} = 7.50HZ$, $J_{P_2-H} = 10.23HZ$), as shown in Table 2. Its pattern consists of doublets of triplets, due to the spin coupling between the phosphorus and hydride, corresponding to the AMX$_2$ spin system. The value is very close to that of the compound $(PPh_3)Ir(Ph_2PC_6H_4$-o-$CO)(Cl)(H)(CO)$ reported by Rauchfuss.[8] The spin system indicates that two phosophorus ligands (2) are made equivalent by a molecular mirror plane of symmetry. Additionally, the spectrum shows that one phosphorus (1) occupied in the mirror plane with hydride, with both types of hydride coupling to two equivalent phosphine ligands. These data are best explained by two possible octahedral structure **E** and **F** in which two phosphorus ligands have the trans configuration. The structure is analogous to that of ditriphenyl phosphine chloro quinoline carboxyl rhodium hydride, except the nitrogen ligand replacing one axial phosphine. The next problem is to decide which of two possible structure **E** and **F** is correct. If the structure is **F**, in which the hydride and the phosphine ligand have trans configuration, the coupling constant between them is expected to be relatively large (50–150HZ)[15-16] compared with that be-

Table 2. ^{1}H NMR, ^{31}P{H} Spectral Data, and Molar Conducivity

Complex	^{1}H NMR[a] Ir –H	–CH$_3$	P{H} NMR[b]	Molar Conductivity[c] (Ohm^{-1}cm^{2}mol^{-1})
1	-8.48(d of t, $J_{P_1-H} - 7.50$, $J_{P_2-H} = 10.23HZ$)		4.93(t), 23.66(d,$J_{P_1P_2} = 253.4HZ$)	118
2	-12.34(t, $J_{P_1-H} = 12.81HZ$)	2.46		112
3	-19.38(d of t, $J_{P_1-H} = 6.3, J_{P_2-H} = 15.5HZ$)		24.51(t), 37.52(d, $J_{P_1-P_2} = 336.2HZ$)	
4	-22.21(t, $J_{P-H} = 11.70AZ$)	2.39		

[a]Recorded in CDCl$_3$ solution; reported in ppm from TMS. [b]Reported in ppm from 85% H$_3$PO$_4$ at 80.96MHZ. [c]Recorded in 0.012g/25ml of acetone solution.
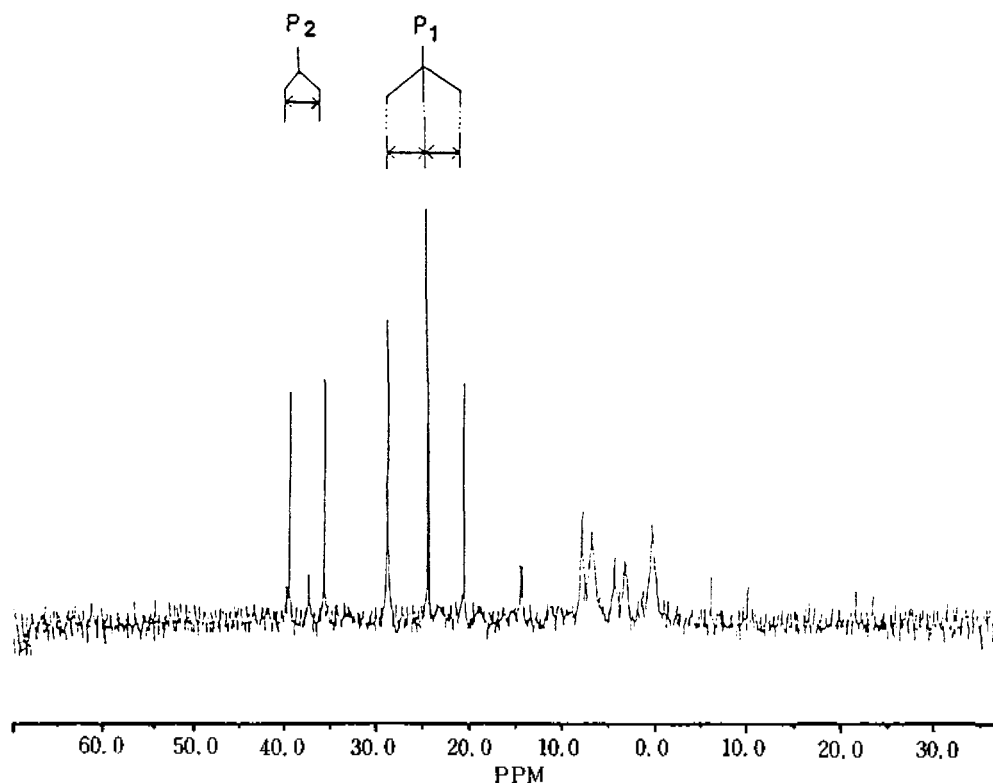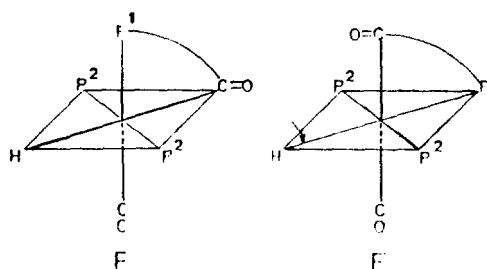

Figure 2. The ^{31}p{H} NMR spectrum of Ir (Ph$_2$P C$_6$H$_4$-o-CO) (PPh$_3$)$_2$(H)Cl.

tween hydride and cis phosophorus (3-20HZ). The small coupling constants of **1** indicate that the hydride is cis to the phosphorus. Therefore, the possible structure of **F** will be eliminated.

The $^{31}P\{H\}$ NMR spectrum (See Figure 2) provides additional information on the structure of **3**. It consists of one doublet and one triplet due to the spin coupling between the chemically equivalent two phosphine ligands and one phosphine ligand, corresponding to the AX_2 spin system. This pattern is very similar to that of the compound Os (PMe₂Ph)₃ Cl₂(MeCN)[17], which has the mirror plane formed by one phosphine, MeCN and two chlorine. Accordingly, from our experimental observations, the correct structure of the compound **3** appears to favor the structure E. The complexes of **1, 2,** and **4** can be similarly assigned as the complex **3**.

In further studies, we are investigating the possibility of carbon–carbon bond cleavage under the same condition.

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Transport Mechanisms and Defect Structures of the System α-Fe₂O₃-CoO

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The electrical conductivity of the system α-Fe₂O₃-CoO was measured in the temperature range 200–1000°C and P_{O_2} range 10^{-7}–2×10^{-1} atm. Possible defect models were suggested on the basis of conductivity data, which were measured as a function of temperature and of oxygen partial pressure. The observed activation energies were 0.50 eV and 1.01 eV in the low- and high-temperature regions, respectively. The observed conductivity dependences on P_{O_2} were $\sigma \propto P_{O_2}^{-1/6}$ in the P_{O_2} range 10^{-7}–10^{-4} atm and $\sigma \propto P_{O_2}^{-1/4}$ at P_{O_2}'s of 10^{-4}–2×10^{-1} atm at temperatures from 300–1000°C. An extrinsic electron conduction due to an Vö defect and an intrinsic electron conduction due to an $Fe_i^{\cdot}$ defect were suggested at different temperature and oxygen partial pressure regions, respectively.

Introduction

Fe₂O₃ is known to be metal excess,[1,2] oxygen deficient[3], and an intrinsic semiconductor,[4,5] while FeO and Fe₃O₄ are metal deficient p-type semiconductors, represented as $Fe_{1-x}O^{6-8}$ and $Fe_{3-x}O_4^{1-9}$, respectively. Salmon[1] suggested that predominant defects in Fe₂O₃ are oxygen vacancies or interstitial iron ions.

Two surface sites, probably an Fe^{2+} interstitial and an ox-

ygen vacancy were suggested by Kim *et al*[10] from the kinetic measurements of the oxidation of CO on α-Fe₂O₃ which was prepared by FeCl₂ and KOH according to the Balz method.[11] The oxygen vacancy was also found from the measurements of conductivities on α-Fe₂O₃[12], Ni-doped α-Fe₂O₃[13], and Cd-doped α-Fe₂O₃[14,15] at temperatures from 250 to 460°C under various P_{CO}, P_{SO_2}, and P_{O_2} conditions. The conductivity data showed that the adsorption of O₂ on pure and doped α-Fe₂O₃ withdraws the conduction electrons from an