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# Solid State Reactions of Iridium-1,5-Cyclooctadiene Compounds with Hydrogen and Carbon Monoxide

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Solid-gas reactions of [Ir(COD)(PhCN)L]ClO<sub>4</sub> (1), [Ir(COD)L<sub>2</sub>]ClO<sub>4</sub> (2), [Ir(H)<sub>2</sub>(COD)(PhCN)L]ClO<sub>4</sub> (3), [Ir(H)<sub>2</sub>(COD)L<sub>2</sub>]ClO<sub>4</sub> (4), [Ir(COD)(CO)<sub>2</sub>L]ClO<sub>4</sub> (5), [Ir(COD)(CO)L<sub>2</sub>]ClO<sub>4</sub> (6) and [Ir(COD)(PhCN)<sub>2</sub>]ClO<sub>4</sub> (7) (COD=1,5-cyclooctadiene; L=PPh<sub>3</sub> (a), AsPh<sub>3</sub> (b)) with H<sub>2</sub> and CO have been investigated to find the differences in reactivities from those in solution. Ir(H)<sub>n</sub> moiety and cyclooctene (COE) are detected in the solid-gas reactions of 1 and 2 with H<sub>2</sub> while they are not observed in the reactions in solution. Complexes, 3 and 4 lose H<sub>2</sub> in the solid state while they undergo hydride transfer to COD in solution to produce COE and cyclooctane (COA). Solid-gas reaction of 5 and 6 with H<sub>2</sub> produce only COE at 25°C while their reactions in solution produce COA. The reaction of CO with 3a in the solid state gives quantitative amount of 5a while in solution it gives only unknown product. Both reactions of 7 in the solid state and in solution with CO give unidentified brown solid which further reacts with CO/H<sub>2</sub> to give Ir<sub>4</sub>(CO)<sub>12</sub>.

#### Introduction

Heterogeneous reactions of solid transition metal complexes with gaseous molecules in the absence of a solvent have been attracted by some chemists since they often occur via different reaction pathways from those of homogeneous ones and provide synthetic methods for new compounds that can not be readily prepared from the reactions in solution. We have recently prepared new iridium(I) complexes, [Ir (COD)(CO)<sub>2</sub>L]ClO<sub>4</sub> and [Ir(COD)(CO)L<sub>2</sub>]ClO<sub>4</sub> (COD=1,5-cy-clooctadiene; L=PPh<sub>3</sub>, AsPh<sub>3</sub>) from the reactions of [Ir(COD) (PhCN)L]ClO<sub>4</sub> and [Ir(COD)L<sub>2</sub>]ClO<sub>4</sub> with CO, respectively in the absence of a solvent<sup>3</sup> which are not prepared from the reactions in solution. We now wish to report solid-gas reactions of some Ir-COD complexes with H<sub>2</sub> and CO including some unique reactions that are not observed for reactions in solution.

## Results and Discussion

Reactions of [Ir(COD)(PhCN)L]Cl<sub>4</sub> (1) and [Ir(COD)-L<sub>2</sub>]ClO<sub>4</sub> (2) (L=PPh<sub>3</sub> (a), AsPh<sub>3</sub> (b)) with H<sub>2</sub>. Cyclooctane (COA) is quantitatively produced from the reactions of 1 and 2 with H<sub>2</sub> at 25°C in the absence of a solvent. Solid samples obtained at the early stage of these reactions showed strong infrared absorptions at 850-950 and 2100-2250 cm<sup>-1</sup> due to p(Ir-H) and v(Ir-H), respectively which slowly disappeared as the reactions proceed. On the other hand, <sup>1</sup>H-NMR spectral measurements confirmed a considerable amount of the initial hydrogenation product, cyclooctene (COE) at the early stage of the reactions which was further hydrogenated

to cyclooctane (COA). Neither Ir(H), moiety nor COE is detected by IR and <sup>1</sup>H-NMR measurements during the reactions of 1 and 2 with H2 (1 atm) in solution at 25°C where the conversion of the coordinated COD to COA is rapid. Dihydridoiridium(III) complex, [Ir(H)2(COD)(PhCN)(PPh3)]  $ClO_4$  (3a),<sup>4</sup> [Ir(H)<sub>2</sub>(COD)(PhCN)(AsPh<sub>3</sub>)]ClO<sub>4</sub> (3b),<sup>5</sup> [Ir(H)<sub>2</sub> (COD)(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> (4a)<sup>6</sup> and [Ir(H)<sub>2</sub>(COD)(AsPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> (4b)<sup>5</sup> have been prepared from the reaction of 1 and 2 with H<sub>2</sub> in solution at low temperature where the corresponding solid-gas reactions do not occur. Complex 4b could be obtained in good purity from the solid-gas reaction of 2b with H<sub>2</sub> at room temperature when the reaction is stopped at the early stage (within 5 minutes) (Eq. 1) while none of other dihydrides (3a, 3b, 4a) were isolated from the solid-gas reactions at room temperature. These observations suggest that the production of COA from the solid-gas reactions of 1 and 2 with H<sub>2</sub> may also occur through the well-known reaction pathways (via either metal-hydride or metal-olefin route) established from the homogeneous catalytic hydrogenation of olefins with metal complexes.7 A similar observation was previously reported: the solid-gas reaction of [Ir(COD) -(PPh<sub>3</sub>)<sub>2</sub>]<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> with D<sub>2</sub> gives COA containing up to 16 deuterium atoms, which was explained to occur via (H)2Ir-COE and (H)<sub>3</sub>Ir-<sup>3</sup>η-cyclooctenyl species.<sup>1c</sup>

$$[Ir(COD)(AsPh_3)_2]CIO_4 + H_2 \longrightarrow [Ir(H)_2(COD)(AsPh_3)_2]CIO_4$$
2b
4b
(within 5 min.)
$$\xrightarrow{x H_2} \text{"Ir(H)_s(COE)(AsPh_3)_2"} \xrightarrow{y H_2} COA + unknown iridium$$
compound(s) (1)

The differences in reactivities between the reactions in the solid state and in solution are striking for dihydridoiridium(III) complexes, 3 and 4. These compounds simply lose H<sub>2</sub> in solid state either under vacuum or N<sub>2</sub> at room temperature while in solution, they undergo hydride transfer to COD to produce a significant amounts of COE, COA (up to 20%), unknown Ir-COD compounds(s) and small amounts of 1 and 2 (Eq. 2). Very small amounts of unknown compound(s) are also produced in solid-gas reactios. These observations suggest that solid-gas reactions are recommended to be carried out when multi-step intra-moleuclar rearrangements (inter-molecular reactions may as well be included) should be repressed for some reason.

$$[Ir(H)_2(COD)A]ClO_4 \xrightarrow{N_2 \text{ or vacuum}} [Ir(COD)A]ClO_4 + H_2$$

$$\downarrow 3, 4 \qquad \text{solid-gas reaction} \qquad 1, 2$$

$$\downarrow N_2 \text{ or vacuum} \qquad COE + COA + \text{unknown Ir-COD} + 1, 2$$
in solution
$$(2)$$

$$A = (PhCN)(PPh_3) \quad (3a), \quad (PhCN)(AsPh_3) \quad (3b), \quad (PPh_3) \quad (4a), \quad (AsPh_3)_2 \quad (4b)$$

Reactions of [lr(COD)(CO)<sub>2</sub>L]ClO<sub>4</sub> (5) and [lr(COD)  $(CO)L_2$ CiO<sub>4</sub> (6) (L=PPh<sub>3</sub> (a), AsPh<sub>3</sub> (b)) with H<sub>2</sub>. The 18 electron complexes, 5a and 5b slowly react with H2 (1 atm) to produce COE which is further hydrogenated to COA in solution at 25°C while the solid-gas reactions quantitatively produce COE which is not further hydrogenated even under increased pressure of H<sub>2</sub> (5 atm). The solid-gas reactions, however, give COA when temperature was increased to 50°C (Eq. 3). The other 18 electron Ir(I)-(COD)-(CO) complexes. 6a and 6b also show the differences in reactivities that 5a and 5b showed in reactions in the solid state and in solution. This certainly indicates that increasing the reaction temperature of solid-gas reaction could bring their reactivities similar to those in solution. Reactions of 5 and 6 with H<sub>2</sub> are very slow both in the solid state and in solution as expected for 18 electron compounds since dissociation of either CO or L from 5 and 6 should occur before the interactions between the Ir in 5 and 6 with H2 take place to give COE and COA. It is worth-while to notice that 18 electron complexes such as 5 and 6 also undergo multi-step reactions such as the production of COE and COA in the absence of a solvent as observed in solution reactions.

Reactions of [Ir(H)<sub>2</sub>(COD)(PhCN)(PPh<sub>3</sub>)]ClO<sub>4</sub> (3a) with CO. Reaction of 3a with CO (1 atm) in solution at 25°C gives unknown iridium compound(s) whose infrared spectrum shows absorptions due to coordinated CO and PPh<sub>3</sub> while the reaction in the solid state initially gives 1a quantitatively and then slowly 5a (Eq. 4). We also found in separate experiments that H<sub>2</sub> elimination from 3a in the solid state

becomes significantly faster in the presence of CO even at low temperature ( $-30^{\circ}$ C) than that in the absence of CO (under N<sub>2</sub> or vacuum), which has not been unambiguously understood yet.

Reactions of [Ir(COD)(PhCN)<sub>2</sub>]ClO<sub>4</sub> (7) with CO and H<sub>2</sub>. Non phosphine Ir(I)-(COD) complex, [Ir(COD)(PhCN)<sub>2</sub>]ClO<sub>4</sub> (7) behaves in the similar way toward CO and H<sub>2</sub> both in solution and in the solid state. Reaction of 7 with CO produce unidentified brown solid both in the presence and absence of a solvent while those with H<sub>2</sub> give COA and iridium metal powders. The brown solid obtained from the reaction with CO further reacts with CO (2 atm)/H<sub>2</sub> (7 atm) in solution at 100°C to give Ir<sub>4</sub>(CO)<sub>12</sub>.

## Conclusion

It may be said that while the solid-gas reaction of Ir-COD complexes, 1-7 with H<sub>2</sub> and CO are somewhat slower and require higher temperature to occur than those reactions in solution, they seem in general to follow the same reaction pathways both in the solid state and in solution. Solid-gas reactions could be utilized when the reactions in solution are too rapid to be investigated in detail.

## **Experimental**

### Instruments

<sup>1</sup>H-NMR, infrared and electronic absorption spectra were measured by a Varian Gemini at 300 MHz spectrometer, Shimadzu IR-440 and Shimadzu UV-240 spectrophotometer, respectively. A Varian 3700 and Hewlett Packard HP 5890A gas chromatogragh were used for analysis of the reaction mixtures.

### **Materials**

Precautions must be taken in handling the complexes, 1-7 since perchlorate salts are potentially explosive. Standard vacuum line and Schlenk type glassware were used in handling metal complexes. Complexes, [Ir (COD)(PhCN)L]ClO<sub>4</sub>45 [Ir(COD)L<sub>2</sub>]ClO<sub>4</sub>45 [Ir(H)<sub>2</sub>(COD)(PhCN)L]ClO<sub>4</sub>5 [Ir(H)<sub>2</sub>(COD)L<sub>2</sub>], 66 [Ir(COD)(CO)<sub>2</sub>L]ClO<sub>4</sub>3 and [Ir (COD)(CO)L<sub>2</sub>]ClO<sub>4</sub>3 were prepared by the known methods. Hydrogen (H<sub>2</sub>) was ultra pure grade from Hankook Gas and carbon monoxide (CO) was extra pure grade from Alphagaz, Laforte, Texas, U.S.A. (purchased through the Korean importer, Union Gas).

Reactions of [Ir(COD)(PhCN)L]ClO<sub>4</sub> (1) and [Ir (COD)L<sub>2</sub>]ClO<sub>4</sub> (2) with H<sub>2</sub>. All reactions in the solid state were carried out in the same manner as described below for the reaction of [Ir(COD)(PhCN)(PPh<sub>3</sub>)]ClO<sub>4</sub> (1a). Red-orange micro-crystals of 1a (0.6 g, 0.78 mmol) in a 25 ml round bottom flask was reacted with H<sub>2</sub> (1 atm) as 25°C

in the absence of a solvent for 6 hours during which time the solid slowly turned brown. A part of the solid (0.05 g) was taken out of the flask at interval and analyzed by infrared spectrum measurements (in KBr) for Ir(H)<sub>n</sub> moiety and both by <sup>1</sup>H-NMR and GC measurements for COE and COA. In order to prevent the reaction (e.g., hydride transfer from Ir to coordinated COD) form occurring in solution during the <sup>1</sup>H-NMR measurements, measurements have been carried out at low temperature (-60°C) under N<sub>2</sub>.

[Ir(H)<sub>2</sub>(COD)(PhCN)L]ClO<sub>4</sub> (3) and [Ir(H)<sub>2</sub>(COD)-L<sub>2</sub>]ClO<sub>4</sub> (4) in the solid state under vacuum or N<sub>2</sub> to eliminate H<sub>2</sub>. All experiments were carried out in the same manner as described below for the reaction of [Ir(H)<sub>2</sub> (COD)(PhCN)(PPh<sub>3</sub>)]ClO<sub>4</sub> (3a). Beige solid of 3a (0.2 g) was kept in a 25 ml round bottom flask under vacuum (or under N<sub>2</sub>) at 25℃ in the absence of a solvent for 5 hours during which time the solid slowly turned reddish orange. Hydrogen (H<sub>2</sub>) was confirmed by gas chromatographic analysis for the gas mixture of the reactor, and the reddish orange solid was identified as 1a ([Ir(COD)(PhCN)(PPh<sub>3</sub>)]ClO<sub>4</sub>) by infrared and electronic absorption spectrum measurements.

Reactions of [Ir(COD)(CO)<sub>2</sub>(PhCN)L]ClO<sub>4</sub> (5) and [Ir(COD)(CO)L<sub>2</sub>]ClO<sub>4</sub> (6) with H<sub>2</sub>. All experiments have been carried out in the same manner as described below for the reaction of [Ir(COD)(CO)<sub>2</sub>(PPh)<sub>3</sub>)]ClO<sub>4</sub> (5a) with H<sub>2</sub>. Beige solid of 5a (ca. 0.2 g) in a 25 ml round bottom flask was exposed to H<sub>2</sub> (5 atm) in the absence of a solvent for 24 hours at 25°C during which time the solid slowly became brown. After the removal of H<sub>2</sub>, cold (-60°C) CDCl<sub>3</sub> (3 ml) was added to the reaction mixture under N<sub>2</sub> at -60°C where <sup>1</sup>H-NMR spectrum of the mixture shows only the signals due to COD, COE and PPh<sub>3</sub> but no signals due to COA.

Reactions of  $[Ir(COD)(PhCN)_2]CIO_4$  (7) with  $H_2$ . Yellow micro-crystals of 7 (ca. 0.1 g) in a 25 ml round bottom flask exposed to  $H_2$  (1 atm) at 25°C for 3 hours turned black. A 2 ml of cold (-60°C) CDCl<sub>3</sub> was added after removal of  $H_2$  from the reaction mixture. The <sup>1</sup>H-NMR spectrum of the soluble materials in the reaction mixture showed signals due to COA and PhCN, and the insoluble black solid was identified as iridium powders.<sup>5</sup>

Reactions of  $[Ir(COD)(PhCN)_2]CIO_4$  (7) with CO. Yellow micro-crystals of 7 (ca. 0.1 g) in a 25 m/ round bottom flask exposed to CO (1 atm) for 24 hours at 25°C turned brown. This brown solid is insoluble in most organic solvents and shows no infrared absorption except very weak ones at 2000-2100 cm<sup>-1</sup> (Nujol). This brown solid was found to be quantitatively converted into  $Ir_4(CO)_{12}^{-6}$  under  $H_2$  (7 atm) and CO (2 atm) in CDCl<sub>3</sub> in a bomb type reactor at 100°C for 20 hours.

Reactions of [Ir(H)2(COD)(PhCN)(PPh3)]ClO4 (3a)

with CO. Beige solid of 3a (ca. 0.2 g) in a 25 ml round bottom flask turned reddish orange within 1 hour which further turned beige within 24 hours under CO (1 atm) at 25°C in the absence of a solvent. The red-orange and beige solid were identified as [Ir(COD)(PhCN)(PPh<sub>3</sub>)]ClO<sub>4</sub> (1a) and [Ir (COD)(CO)<sub>2</sub>(PPh<sub>3</sub>)]ClO<sub>4</sub> (5a), respectively by 'H-NMR, infrared and electronic absorption spectra measurements.

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