

- 66, 676 (1980).  
 24. R. S. Weening, D. Roos, and R. Wever, *J. Lab. Clin. Med.*, **85**(2), 245 (1975).

25. S. A. Weitzmann and T. P. Stossel, *J. Immunol.*, **128**(6), 2770 (1982).

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

Chong Shik Chin\*, Byeongno Lee, and Youngik Kim

Department of Chemistry, Sogang University, Seoul 121-742

Received January 13, 1993

Solid-gas reactions of  $[\text{Ir}(\text{COD})(\text{PhCN})\text{L}]\text{ClO}_4$  (**1**),  $[\text{Ir}(\text{COD})\text{L}_2]\text{ClO}_4$  (**2**),  $[\text{Ir}(\text{H})_2(\text{COD})(\text{PhCN})\text{L}]\text{ClO}_4$  (**3**),  $[\text{Ir}(\text{H})_2(\text{COD})\text{L}_2]\text{ClO}_4$  (**4**),  $[\text{Ir}(\text{COD})(\text{CO})_2\text{L}]\text{ClO}_4$  (**5**),  $[\text{Ir}(\text{COD})(\text{CO})\text{L}_2]\text{ClO}_4$  (**6**) and  $[\text{Ir}(\text{COD})(\text{PhCN})_2]\text{ClO}_4$  (**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>.

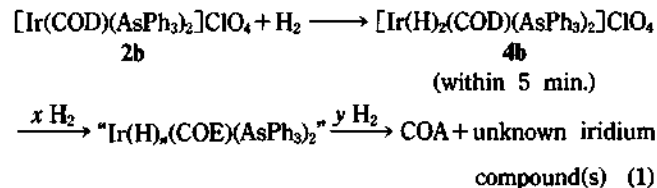
### Introduction

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.<sup>1,2</sup> We have recently prepared new iridium(I) complexes,  $[\text{Ir}(\text{COD})(\text{CO})_2\text{L}]\text{ClO}_4$  and  $[\text{Ir}(\text{COD})(\text{CO})\text{L}_2]\text{ClO}_4$  (COD=1,5-cyclooctadiene; L=PPh<sub>3</sub>, AsPh<sub>3</sub>) from the reactions of  $[\text{Ir}(\text{COD})(\text{PhCN})\text{L}]\text{ClO}_4$  and  $[\text{Ir}(\text{COD})\text{L}_2]\text{ClO}_4$  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  $[\text{Ir}(\text{COD})(\text{PhCN})\text{L}]\text{Cl}_4$  (**1**) and  $[\text{Ir}(\text{COD})\text{L}_2]\text{ClO}_4$  (**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  $\nu(\text{Ir-H})$  and  $\nu(\text{Ir-H})$ , 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)<sub>n</sub> moiety nor COE is detected by IR and <sup>1</sup>H-NMR measurements during the reactions of **1** and **2** with H<sub>2</sub> (1 atm) in solution at 25°C where the conversion of the coordinated COD to COA is rapid. Dihydridoiridium(III) complex,  $[\text{Ir}(\text{H})_2(\text{COD})(\text{PhCN})(\text{PPh}_3)]\text{ClO}_4$  (**3a**),<sup>4</sup>  $[\text{Ir}(\text{H})_2(\text{COD})(\text{PhCN})(\text{AsPh}_3)]\text{ClO}_4$  (**3b**),<sup>5</sup>  $[\text{Ir}(\text{H})_2(\text{COD})(\text{PPh}_3)_2]\text{ClO}_4$  (**4a**)<sup>6</sup> and  $[\text{Ir}(\text{H})_2(\text{COD})(\text{AsPh}_3)_2]\text{ClO}_4$  (**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.<sup>7</sup> A similar observation was previously reported: the solid-gas reaction of  $[\text{Ir}(\text{COD})-(\text{PPh}_3)_2]_3\text{PW}_{12}\text{O}_{40}$  with D<sub>2</sub> gives COA containing up to 16 deuterium atoms, which was explained to occur *via* (H)<sub>2</sub>Ir-COE and (H)<sub>3</sub>Ir-<sup>3</sup>η-cyclooctenyl species.<sup>1c</sup>





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>2</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°C 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)<sub>2</sub>]ClO<sub>4</sub> (7) with H<sub>2</sub>.** Yellow micro-crystals of 7 (ca. 0.1 g) in a 25 ml round bottom flask exposed to H<sub>2</sub> (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<sub>2</sub> 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)<sub>2</sub>]ClO<sub>4</sub> (7) with CO.** Yellow micro-crystals of 7 (ca. 0.1 g) in a 25 ml 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<sub>4</sub>(CO)<sub>12</sub><sup>8</sup> under H<sub>2</sub> (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)<sub>2</sub>(COD)(PhCN)(PPh<sub>3</sub>)ClO<sub>4</sub> (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 <sup>1</sup>H-NMR, infrared and electronic absorption spectra measurements.

**Acknowledgement.** Authors wish to acknowledge that this study was supported by "Non Directed Research Fund", the Korea Research Foundation, 1992.

## References

- (a) A. R. Siedle and R. A. Newmark, *J. Am. Chem. Soc.*, **111**, 2058 (1989) and *Organometallics*, **8**, 1442 (1989); (b) A. R. Siedle, R. A. Newmark, K. A. Brown-Wensley, R. P. Skarjune, L. C. Hadded, K. O. Hodgson, and A. L. Roe, *Organometallics*, **7**, 2078 (1988); (c) A. R. Siedle, R. A. Newmark, M. R. V. Sahyun, P. A. Lyon, S. L. Hunt, and R. P. Skarjune, *J. Am. Chem. Soc.*, **111**, 8346 (1989).
- (a) J. A. McCleverty and G. Wilkinson, *Inorg. Synth.*, **8**, 211 (1966); (b) B. R. Flynn and L. Vaska, *Chem. Commun.*, 703 (1974); (c) C. Bianchini, A. Meli, M. Peruzzini, A. Vacca, F. Vizza, and A. Albinati, *Inorg. Chem.*, **31**, 3841 (1992); (d) C. Bianchini, C. Mealli, M. Peruzzini, and F. Zanobini, *J. Am. Chem. Soc.*, **114**, 5905 (1992); (e) C. Bianchini and F. Zanobini, *Organometallics*, **10**, 3415 (1991); (f) C. Bianchini, M. Peruzzini, A. Vacca, and F. Zanobini, *Organometallics*, **10**, 3697 (1991).
- C. S. Chin, B. Lee, and S. Kim, *Organometallics*, in press: solid-gas reactions of [Ir(COD)(PhCN)L]ClO<sub>4</sub> and [Ir(COD)L<sub>2</sub>]ClO<sub>4</sub> (L=PPh<sub>3</sub>, AsPh<sub>3</sub>) with CO quantitatively give [Ir(COD)(CO)<sub>2</sub>L]ClO<sub>4</sub> and [Ir(COD)(CO)L<sub>2</sub>]ClO<sub>4</sub>, respectively which are not prepared from the same reactions in solution except that [Ir(COD)(CO)<sub>2</sub>(PPh<sub>3</sub>)Cl<sub>4</sub> could be obtained at low temperature (-20°C) when the reaction is stopped at the early stage.
- C. S. Chin and B. Lee, *J. Chem. Soc. Dalton Trans.*, 1323 (1991).
- Unpublished results which will be published elsewhere.
- R. H. Crabtree, H. Felkin, and G. E. Morris, *Chem. Commun.*, 716 (1976).
- (a) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 5th Ed., Wiley, p. 1244 (1988); (b) J. P. Collman, L. S. Hegeudus, J. R. Norton, and R. Finke, "Principles and Applications of Organotransition Metal Chemistry", University Science Book, p. 523 (1987).
- L. Malatesta, G. Caglio, and M. Angoletta, *Inorg. Synth.*, **13**, 95 (1971).