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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 $[\text{Ir}(\text{COD})(\text{PhCN})\text{L}]\text{ClO}_4$ (**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=PPh₃ (a), AsPh₃ (b)) with H₂ and CO have been investigated to find the differences in reactivities from those in solution. Ir(H)_n moiety and cyclooctene (COE) are detected in the solid-gas reactions of **1** and **2** with H₂ while they are not observed in the reactions in solution. Complexes, **3** and **4** lose H₂ 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 H₂ 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/H₂ to give Ir₄(CO)₁₂.

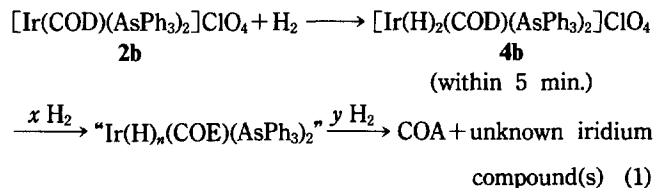
Introduction

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.^{1,2} 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=PPh₃, AsPh₃) 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 solvent³ which are not prepared from the reactions in solution. We now wish to report solid-gas reactions of some Ir-COD complexes with H₂ 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=PPh₃ (a), AsPh₃ (b)) with H₂.** Cyclooctane (COA) is quantitatively produced from the reactions of **1** and **2** with H₂ 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⁻¹ due to $\rho(\text{Ir-H})$ and $\nu(\text{Ir-H})$, respectively which slowly disappeared as the reactions proceed. On the other hand, ¹H-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)_n moiety nor COE is detected by IR and ¹H-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, $[\text{Ir}(\text{H})_2(\text{COD})(\text{PhCN})(\text{PPh}_3)]\text{ClO}_4$ (**3a**),⁴ $[\text{Ir}(\text{H})_2(\text{COD})(\text{PhCN})(\text{AsPh}_3)]\text{ClO}_4$ (**3b**),⁵ $[\text{Ir}(\text{H})_2(\text{COD})(\text{PPh}_3)_2]\text{ClO}_4$ (**4a**)⁶ and $[\text{Ir}(\text{H})_2(\text{COD})(\text{AsPh}_3)_2]\text{ClO}_4$ (**4b**)⁵ have been prepared from the reaction of **1** and **2** with H₂ 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 H₂ 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 H₂ 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 $[\text{Ir}(\text{COD})-(\text{PPh}_3)_2]_3\text{PW}_{12}\text{O}_{40}$ with D₂ gives COA containing up to 16 deuterium atoms, which was explained to occur *via* (H)₂Ir-COE and (H)₃Ir-³η-cyclooctenyl species.^{1c}



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)_n moiety and both by ¹H-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 ¹H-NMR measurements, measurements have been carried out at low temperature (−60°C) under N₂.

[Ir(H)₂(COD)(PhCN)L]ClO₄ (3) and [Ir(H)₂(COD)-L₂]ClO₄ (4) in the solid state under vacuum or N₂ to eliminate H₂. All experiments were carried out in the same manner as described below for the reaction of [Ir(H)₂(COD)(PhCN)(PPh₃)]ClO₄ (**3a**). Beige solid of **3a** (0.2 g) was kept in a 25 ml round bottom flask under vacuum (or under N₂) at 25°C in the absence of a solvent for 5 hours during which time the solid slowly turned reddish orange. Hydrogen (H₂) 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)(PPh₃)]ClO₄) by infrared and electronic absorption spectrum measurements.

Reactions of [Ir(COD)(CO)₂(PhCN)L]ClO₄ (5) and [Ir(COD)(CO)L₂]ClO₄ (6) with H₂. All experiments have been carried out in the same manner as described below for the reaction of [Ir(COD)(CO)₂(PPh₃)]ClO₄ (**5a**) with H₂. Beige solid of **5a** (*ca.* 0.2 g) in a 25 ml round bottom flask was exposed to H₂ (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 H₂, cold (−60°C) CDCl₃ (3 ml) was added to the reaction mixture under N₂ at −60°C where ¹H-NMR spectrum of the mixture shows only the signals due to COD, COE and PPh₃ but no signals due to COA.

Reactions of [Ir(COD)(PhCN)₂]ClO₄ (7) with H₂. Yellow micro-crystals of **7** (*ca.* 0.1 g) in a 25 ml round bottom flask exposed to H₂ (1 atm) at 25°C for 3 hours turned black. A 2 ml of cold (−60°C) CDCl₃ was added after removal of H₂ from the reaction mixture. The ¹H-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.⁵

Reactions of [Ir(COD)(PhCN)₂]ClO₄ (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^{−1} (Nujol). This brown solid was found to be quantitatively converted into Ir₄(CO)₁₂⁸ under H₂ (7 atm) and CO (2 atm) in CDCl₃ 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)(PPh₃)]ClO₄ (**1a**) and [Ir(COD)(CO)₂(PPh₃)]ClO₄ (**5a**), respectively by ¹H-NMR, infrared and electronic absorption spectra measurements.

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