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Regioselective catalytic hydrogenation of nitrogen rings of fused heteroaromatic compounds with an iridium–triphenylphosphine complex

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Catalytic hydrogenation of fused heteroaromatic compounds, acridine, quinoline and quinaldine, selectively occurs at the nitrogen containing rings to give 9,10-dihydroacridine, 1,2,3,4-tetrahydroquinoline and 1,2,3,4-tetrahydroquinaldine in the homogeneous solution prepared from the reaction of $[Ir(COD)(PPh_3)(PhCN)]ClO_4$ (COD = 1,5-cyclooctadiene) with H_2 (5 atm) at 50°C, while isoquinoline and indole are not hydrogenated under the same experimental conditions. In the presence of the rhodium analog $[Rh(COD)(PPh_3)(PhCN)]ClO_4$ however, both isoquinoline and indole are also hydrogenated at the nitrogen containing rings, which is understood in terms of heterogeneous catalysis by metallic rhodium powders produced in the reduction of the rhodium compound under the same experimental conditions (50°C, 5 atm of H_2).

Keywords: hydrogenation; heteroaromatic compounds; iridium complex

1. Introduction

Hydrogenation of fused heteroaromatic nitrogen compounds has been studied to understand and develop the catalytic systems effective for hydrodenitrogenation of coal compounds [1–4]. A number of rhodium and ruthenium complexes [1–4] have been found to catalyze the hydrogenation of a variety of fused heteroaromatic nitrogen compounds at relatively low temperature (as low as 40°C) and under low pressure of hydrogen (as low as 2 atm) while a single iridium complex, $[Ir(COD)(PPh_3)_2]ClO_4$ (COD = 1,5-cyclooctadiene), to our knowledge, has been reported to be active for the hydrogenation of one binuclear heteroaromatic nitrogen compound, quinoline, at high temperature, 150°C [4].

In this paper, we report regioselective hydrogenation of fused heteroatomic nitrogen compounds catalyzed by the homogeneous solution obtained from the reaction of $[Ir(COD)(PPh_3)(PhCN)]ClO_4$ with H_2 under relatively mild conditions (50°C, 5 atm of H_2) and related data obtained with the rhodium analog, $[Rh(COD)(PPh_3)(PhCN)]ClO_4$.

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2. Experimental

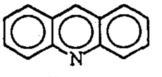
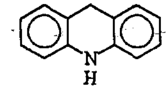
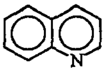
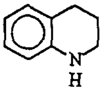
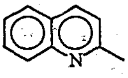
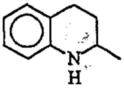
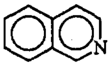
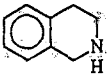
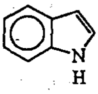
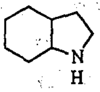
Metal complexes, $[Ir(COD)(PPh_3)(PhCN)]ClO_4$ (denoted by Ir-1), $[Rh(COD)(PPh_3)(PhCN)]ClO_4$ (Rh-1), $[Ir(COD)(PhCN)_2]ClO_4$ (Ir-2), and $[Rh(COD)(PhCN)_2]ClO_4$ (Rh-2), were prepared by the similar manner as described in the literature [5]. All the fused heteroaromatic nitrogen compounds were purchased from Aldrich and used without further purification. All the experiments were carried out in the same manner described below for the hydrogenation of acridine with Ir-1. The CH_2Cl_2 solution (5.0 ml) of Ir-1 (0.1 mmol, 77 mg) and acridine (3.0 mmol, 550 mg) under H_2 (5 atm) in a bomb reactor (Parr 1341, volume 360 ml) was put in an oven maintained at 50°C for a planned period of time (1–10 h) and cooled down to room temperature at intervals. Then, the reaction mixture was analyzed by ^1H-NMR measurements in $CDCl_3$, as it was done previously [1–3], after CH_2Cl_2 was removed by blowing nitrogen through the reaction mixture. ^1H-NMR ($CDCl_3$, 60 MHz, ppm): acridine, 7.2–8.5 (m, 9H); 9,10-dihydroacridine, 4.0 (s, 2H), 5.7–6.3 (s, 1H), 6.5–7.4 (m, 8H); quinoline, 7.2–9.0 (m, 7H); 1,2,3,4-tetrahydroquinoline, 4.0 (s, 1H), 3.3 (t, 2H), 2.9 (t, 2H), 2.0 (m, 2H), 7.2–8.5 (m, 4H); octahydroquinoline, 2.5–3.5 (m, 2H), 0.8–2.0 (m, 13H); quinaldine, 2.7 (s, 3H), 7.1–8.1 (m, 6H); 1,2,3,4-tetrahydroquinaldine, 1.1 (d, 3H), 1.3–2.0 (m, 2H), 2.5–2.9 (m, 2H), 3.0–3.5 (m, 1H), 6.4–7.0 (m, 5H); octahydroquinaldine, 1.0–2.5 (m, 16H), 2.5–4.0 (m, 1H); isoquinoline, 7.5–8.0 (m, 5H), 8.6 (d, 1H), 9.3 (s, 1H); 1,2,3,4-tetrahydroisoquinoline 2.8–3.3 (m, 4H), 4.0 (s, 1H), 7.0 (s, 4H); octahydroisoquinoline, 1.5–2.5 (m, 9H), 2.5–3.1 (m, 3H); indole, 6,5 (s, 1H), 7.0–7.8 (m, 6H); 2,3-dihydroindole (indoline), 2.7–3.7 (m, 4H), 6.8–7.3 (m, 4H); hexahydroindole (indolidine), 0.8–3.0 (two broad signals).

3. Results and discussion

It has been already known that the reaction of $[Ir(COD)(PPh_3)(PhCN)]ClO_4$ (Ir-1) with H_2 produces a homogeneous solution that catalyzes nitriles to give amines [6]. This homogeneous solution is catalytically active also for the hydrogenation of some selected fused heteroaromatic nitrogen compounds, and the hydrogenation occurs regioselectively at the nitrogen containing rings.

The hydrogenation can be monitored for several days without a significant decrease in rate. It is seen in table 1 that only the nitrogen containing rings of the substrates are hydrogenated leaving the non-heteroaromatic rings intact as observed before by others [1–4]. The relative rates of the hydrogenation may not be clearly understood until the detailed mechanism is established. It may be said, however, that steric effects on the interactions between the iridium metal and the nitrogen atoms of the substrates play a role in determining the rates of the hydrogenation since it is noticed that the hydrogenation is faster for the more hindered nitrogens of quinaldine and acridine than for the less hindered one of quinoline, while the even more less hindered nitrogen of isoquinoline is not hydrogen-

Table 1
Hydrogenation of fused heteroatomic nitrogen compounds (3.0 mmol) with $[Ir(COD)(PPh_3)(PhCN)]ClO_4$ (Ir-1, 0.1 mmol), $[Rh(COD)(PPh_3)(PhCN)]ClO_4$, (Rh-1, 0.1 mmol), $[Ir(COD)(PhCN)_2]ClO_4$ (Ir-2, 0.1 mmol), and $[Rh(COD)(PhCN)_2]ClO_4$ (Rh-2, 0.1 mmol), respectively, in CH_2Cl_2 (5.0 ml) at 50°C under 5 atm of hydrogen

Substrate	Product	Turnover number (sub/M h) [a]			
		Ir-1	Rh-1	Ir-2	Rh-2
 acridine		7.5	2.0	15	4.2
 quinoline		1.1	0.5	3.3	5.2
 quinaldine		6.3	0.4	5.7	1.2
 isoquinoline		–	0.2	–	–
 indole		–	0.3	4.0	4.6

[a] Disappearance of substrate (in mole) per metal (in mole) per hour.

ated at all under the same experimental conditions. Strong interactions between the metal and the nitrogen seem to depress the rate of the hydrogenation. Fish and co-workers found somewhat different relative rates with a rhodium complex from our results in table 1: hydrogenation rate decreases in the following order, acridine > quinoline > isoquinoline in the presence of $[RhCp^*(CH_3CN)_3]^{2+}$ ($C_p^* = C_5Me_5^-$), which they explained as the results of both steric and electronic effects on the interactions between the metal and substrates [1,2]. The catalytically active species present in the solution obtained from the reaction of Ir-1 and H_2 should contain the moiety of "$Ir(PPh_3)(PhCN)(ClO_4)$" according to the following equation[#1]

$$\underset{\text{Ir-1}}{[Ir(COD)(PPh_3)(PhCN)]ClO_4} + 2H_2 \rightarrow \text{"}Ir(PPh_3)(PhCN)(ClO_4)\text{"} + C_8H_{16}. \tag{1}$$

[#1] Unpublished results: the reaction of $[Ir(COD)(PPh_3)(PhCN)]ClO_4$ with H_2 (5 atm) at 50°C in CH_2Cl_2 produces C_8H_{16} and a brown solution which contains PPh_3, PhCN and ClO_4^-.

Since both PhCN and ClO_4^- are well known to be labile ligands which are readily replaced by other ligands, the ligands around the iridium of the catalytically active species may not entirely control the interactions between the iridium and the nitrogen atoms of substrates.

The rhodium analog, $[Rh(COD)(PPh_3)(PhCN)]ClO_4$ (Rh-1), shows different reactivities from those of the iridium complex Ir-1. All of five substrates in table 1 are found to be slowly hydrogenated in the presence of Rh-1 at 50°C under 5 atm of hydrogen (see table 1). It should be mentioned here that metallic rhodium powders are slowly produced during the catalytic hydrogenation with Rh-1 in CH_2Cl_2 at 50°C under 5 atm of hydrogen according to

$$\underset{\text{Rh-1}}{[Rh(COD)(PPh_3)(PhCN)]ClO_4} + \tfrac{9}{2}H_2 \rightarrow$$
$$Rh + C_8H_{16} + PhCH_2NH_2 + PPh_3 + HClO_4\,. \qquad (2)$$

A small amount of rhodium metallic fine powders can be separated by filtration of the catalytically active reaction mixture. Therefore, the hydrogenation data with Rh-1 in table 1 are probably due to, at least in part, the catalytic activities of the metallic rhodium powders present in the reaction mixture. We have found in this study that metallic powders of both iridium and rhodium (see below) show much higher catalytic activities for the hydrogenation of those substrates in table 1 than those with Ir-1 and Rh-1 shown in table 1.

We have also found that (i) significant amounts of metallic powders of both iridium [6] and rhodium were produced from the reactions of non-phosphine complexes, $[M(COD)(PhCN)_2]ClO_4$ (M = Ir (Ir-2), Rh (Rh-2)) with H_2 according to the following equation:

$$[M(COD)(PhCN)_2]ClO_4 + \tfrac{13}{2}H_2 \rightarrow M + C_8H_{16} + 2PhCH_2NH_2 + HClO_4\,, \qquad (3)$$

and (ii) the catalytic hydrogenation of those heteroaromatic nitrogen compounds is considerably faster in the presence of non-triphenylphosphine complexes, Ir-2 and Rh-2, than that with triphenylphosphine complexes, Ir-1 and Rh-1, respectively. These observations may suggest that the higher rates with Ir-2 and Rh-2 are, in part, due to those metallic iridium and rhodium powders. In fact, the fine metallic powders separated from the reactions of Ir-2 and Rh-2 with H_2 show much higher catalytic activities for hydrogenation of those heteroatomic compounds in the absence of $PhCH_2NH_2$ and $HClO_4$. For example, the turnover numbers could be as high as 22 acridine/Ir h (mole acridine per mole iridium per hour), 8.0 acridine/Rh h, and 5.2 quinoline/Rh h with metallic powders separated under the same experimental conditions, at 50°C under 5 atm of H_2.

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