

# Rhodium(I) Complexes of 1,1'-Bis(diphenylphosphino)-ferrocene as Efficient Catalysts in Regioselective Hydrogenation of Polynuclear Heteroaromatic Compounds

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Two rhodium(I) complexes of the types  $[\text{Rh}(\text{BPPF})(\text{NBD})]\text{ClO}_4$  (**10**) and  $[\text{Rh}(\text{BPPF})\text{Cl}]_2$  (**11**) (BPPF = 1,1'-bis(diphenylphosphino)-ferrocene) have been prepared and investigated as catalysts for the regioselective hydrogenation of polynuclear heteroaromatic nitrogen and sulfur compounds such as quinoline (**1**), acridine (**2**), phenanthridine (**3**), 7,8-benzoquinoline (**4**), benzothiophene (**5**), isoquinoline (**6**), indole (**7**), pyridine (**8**), and thiophene (**9**). Both complexes **10** and **11**, except for the cases of indole (**7**) and mononuclear heteroaromatics **8-9**, are very efficient in the selective reduction under quite mild hydrogenation conditions to give the corresponding saturated nitrogen and sulfur heterocyclic analogues of **1-6** in fast conversion rates and in excellent yields. Relative rate studies revealed that the reduction depends significantly on the steric and electronic effects of the substrates. Of the two complexes **10-11**, the dimeric species **11** gives faster reaction rates in all cases studied.

## Introduction

The various synthetic fuel products derived from coal, crude oil, or oil shale contain a wide variety of polynuclear heteroaromatic constituents and therefore require additional hydroprocessing to minimize their nitrogen and sulfur content through hydrodenitrogenation (HDN) and hydrodesulfurization (HDS), respectively.<sup>1-4</sup> It becomes, therefore, critical to understand the reactivity of model synthetic fuel compounds such as **1-9** (Figure 1) under various homogeneous catalytic hydrogenation conditions.

In this connection interest in the selective reduction of these model compounds has emerged in recent years. For example, Jardine and McQuillin<sup>5</sup> reported that **1** is reduced to 1,2,3,4-tetrahydroquinoline with  $\text{RhCl}_2(\text{py})_2(\text{dmf})\text{BH}_4$  as the catalyst. Fish<sup>6,7</sup> and Laine<sup>8,9</sup> also reported that various transition metal carbonyls,  $\text{M}_x(\text{CO})_y$  (M = Fe, Mn, Co, Ru), are catalytically active in the regioselective reduction of the model compounds **1-9** under water gas shift (Co,  $\text{H}_2\text{O}$ , base) and synthesis gas (1:1  $\text{CO}:\text{H}_2$ ) conditions as well as pure hydrogenation conditions ( $\text{H}_2$  alone). However, utility of these catalysts suffers from limited scope, drastic conditions, and poor yields.

Prompted by recent reports of  $\text{RhCl}(\text{PPh}_3)_3$ <sup>10</sup> and  $\text{HRuCl}(\text{PPh}_3)_3$ <sup>11</sup> catalyzed hydrogenation of the model compounds under rather mild conditions, we herein report our findings that two rhodium complexes of the types  $[\text{Rh}(\text{BPPF})(\text{NBD})]\text{ClO}_4$  and  $[\text{Rh}(\text{BPPF})\text{Cl}]_2$  are excellent catalysts for the regioselective reduction of the model compounds **1-6** under even milder conditions. We have chosen this particular ligand because the efficiency of this compound as ligand in a wide range of homogeneous catalysis is well established.<sup>12</sup> In this report the comparative rate studies are also described.

## Experimental

**Generals.** Unless otherwise stated air-sensitive reagents and products were manipulated in an argon atmosphere using a double manifold vacuum system and Schlenk techniques. All commercial reagents were of reagent grade and

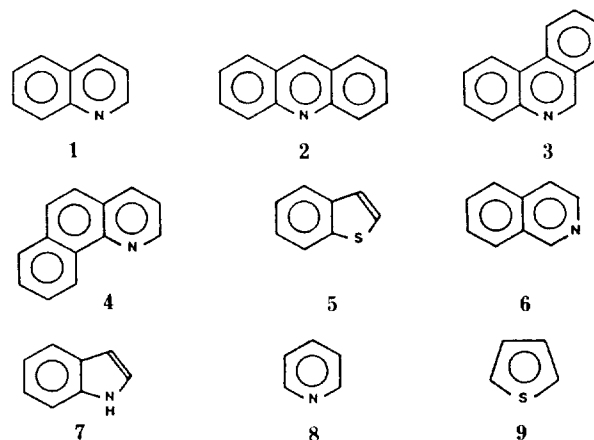


Figure 1. Model synthetic fuel compounds used in the homogeneous catalytic hydrogenation reactions.

were used as received unless otherwise mentioned. Solvents were purified by standard techniques,<sup>13</sup> and were freshly distilled prior to use.

Melting points were determined using a Gallenkamp Melting Point apparatus and are reported without correction. Micro-analyses were performed by the Microanalytical Department of Korea Advanced Institute of Science and Technology. <sup>1</sup>H-, <sup>13</sup>C-, and <sup>31</sup>P-NMR spectra were recorded on a Bruker AM-300 spectrometer operating at 200 MHz, 80.15 MHz, and 121.5 MHz, respectively. The capillary gas chromatography analyses were performed on a HP 5890A instrument with a 30m × 0.53mm HP-5 capillary column and flame-ionization detection. The ligand BPPF<sup>14</sup> and the complex **10**<sup>15,16</sup> were prepared according to the literature procedures.

**Catalytic Hydrogenation.** The catalytic reactions were run in a Parr type-4565 pressure reactor. To the 100-ml reactor cup was added the substrate (2.12 mmol) and the rhodium complex ( $2.12 \times 10^{-2}$  mmol) in a degassed solvent (40 ml) under a stream of argon, along with a stirring bar. After being flushed, the reactor was then pressurized to the desired

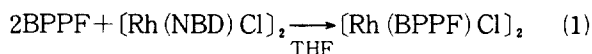
value with hydrogen and placed in a stirred thermostated oil bath ( $60^{\circ}\text{C} \pm 2^{\circ}\text{C}$ ) and the temperature allowed to equilibrate (approximately 5 min). For comparative rate studies, typically five samples were removed via syringe from the reactor at regular intervals of 30-60 min and were analyzed by GC with the following conditions:  $50\text{-}250^{\circ}\text{C}$  with 1.5-min initial hold at  $50^{\circ}\text{C}$  and  $10^{\circ}\text{C}/\text{min}$  to  $250^{\circ}\text{C}$  with a 10 min hold at  $250^{\circ}\text{C}$ . The conversion vs. time data were plotted, and for conversion of up to about 80% the plots were linear providing a pseudozero-order rate by least-squares analysis.

**Synthesis of  $[\text{Rh}(\text{BPPF})\text{Cl}]_2$  (11).** This previously unknown compound was prepared according to the literature procedures<sup>17,18</sup> with minor modification.  $[\text{Rh}(\text{NBD})\text{Cl}]_2$  (300 mg, 0.65 mmol) was dissolved in THF (15 ml) in a Schlenk tube. To the stirred solution was added BPPF (7.92 mg, 1.4 mmol) in toluene (10 ml). The solution was further stirred for 1 h during which time a fine yellow precipitate deposited. This was isolated on a Schlenk filter, washed with diethyl ether (20 ml), dissolved in dichloromethane (15 ml), and filtered to remove any solid impurity. The filtrate was reduced in volume to about 10 ml to which was added hexane (7 ml) without disturbing the dichloromethane layer. This solution was allowed to stand at room temperature to give orange microcrystals (60% yield): mp  $232\text{-}234^{\circ}\text{C}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.39-7.82(m, 40H, -Ph), 4.17(brs, 8H,  $-\text{C}_5\text{H}_4$ ), 4.80(brs, 8H,  $-\text{C}_5\text{H}_4$ );  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  -5.51(d,  $J_{\text{Rh}} = 164\text{Hz}$ ). Anal. Calcd. for  $\text{C}_{68}\text{H}_{56}\text{Cl}_2\text{P}_2\text{Fe}_2\text{Rh}_2$ : C, 59.17; H, 4.25. Found: C, 58.94; H, 4.05.

**Synthesis of  $[\text{Rh}(\text{BPPF})(\text{CH}_3\text{CN})_2]\text{ClO}_4$  (12).** The complex **10** (200 mg,  $2.4 \times 10^{-4}$  mol) was dissolved in acetonitrile (10 ml) in a Schlenk tube and the solution was degassed by the freeze-and-thaw method. To the evacuated system hydrogen was then bubbled until no further color change from deep orange to bright yellow was observed. The resulting solution was allowed to stand at room temperature under an atmosphere of hydrogen to deposit yellow crystals (70% yield): mp  $203\text{-}205^{\circ}\text{C}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.40-7.77(m, 20H, -Ph), 4.32(s, 4H,  $-\text{C}_5\text{H}_4$ ), 4.21(s, 4H,  $-\text{C}_5\text{H}_4$ );  $^{31}\text{P}$  NMR ( $\text{CDCl}_3$ )  $\delta$  11.43(d,  $J_{\text{Rh}} = 177\text{Hz}$ ). Anal. Calcd. for  $\text{C}_{38}\text{H}_{34}\text{N}_2\text{O}_4\text{P}_2\text{ClFeRh}$ : C, 54.90; H, 4.29; N, 3.34. Found: C, 54.37; H, 4.26; N, 3.32.

## Results and Discussion

**Synthesis.** Addition of 2 equivalents of BPPF to a benzene or THF solution of  $[\text{Rh}(\text{NBD})\text{Cl}]_2$  results in the facile displacement of the NBD ligand to give a new bimetallic rhodium(I) complex **11** as orange crystals after usual workups (equation 1).



This compound is only sparingly soluble in most hydrocarbon solvents and soluble to some extent in polar chlorinated solvents such as  $\text{CH}_2\text{Cl}_2$  and  $\text{CHCl}_3$ . From the analytical and NMR data in the experimental section, the formulations of these two rhodium complexes can be easily confirmed. The  $^1\text{H}$  NMR spectra of both **10** and **11** show, in addition to the multiplets for the phenyl groups, a pair of broad lines for the cyclopentadienyl ring protons. The square planar geometry around the rhodium metals are easily confirmed by the  $^{31}\text{P}$

**Table 1.** Catalytic Regioselective Hydrogenation of Polynuclear Heteroaromatic Compounds by the Rh(I) Complexes<sup>a</sup>

| Substrate | Catalyst | Product                          | Yield (%) | Turnover Rate <sup>b</sup> |
|-----------|----------|----------------------------------|-----------|----------------------------|
| 1         | 10       | 1,2,3,4-tetrahydroquinoline      | 100       | $7.60 \times 10^{-2}$      |
|           | 11       | 1,2,3,4-tetrahydroquinoline      | 100       | $2.40 \times 10^{-1}$      |
| 2         | 10       | 9,10-dihydroacridine             | 100       | $1.59 \times 10^{-1}$      |
|           | 11       | 9,10-dihydroacridine             | 100       | $2.08 \times 10^{-1}$      |
| 3         | 10       | 9,10-dihydrophenanthridine       | 100       | $1.67 \times 10^{-1}$      |
|           | 11       | 9,10-dihydrophenanthridine       | 100       | $1.75 \times 10^{-1}$      |
| 4         | 10       | 1,2,3,4-tetrahydrobenzoquinoline | 100       | $6.29 \times 10^{-2}$      |
|           | 11       | 1,2,3,4-tetrahydrobenzoquinoline | 100       | $7.75 \times 10^{-2}$      |
| 5         | 10       | 2,3-dihydrobenzothiophene        | 82        | $2.89 \times 10^{-1}$      |
|           | 11       | 2,3-dihydrobenzothiophene        | 88        | $3.74 \times 10^{-1}$      |
| 6         | 10       | 1,2,3,4-tetrahydroisoquinoline   | 5         | $6.85 \times 10^{-3}$      |
|           | 11       | 1,2,3,4-tetrahydroisoquinoline   | 8         | $8.65 \times 10^{-3}$      |

<sup>a</sup>Reaction conditions:  $\text{P}(\text{H}_2) = 200$  psi;  $t = 60^{\circ}\text{C}$ ; [Substrate] =  $5.3 \times 10^{-2}\text{M}$  in 40 ml of solvent; [Catalyst] =  $5.3 \times 10^{-4}\text{M}$ . <sup>b</sup>mol of substrate consumed/mol of Rh/min for 30% conversion.

NMR spectra consisting of sharp doublets indicative of equivalent phosphorus nuclei coupled to rhodium-103 ( $^{103}\text{Rh}$ , 100% natural abundance, spin 1/2). An unusual feature of the  $^{31}\text{P}$  NMR spectrum of the compound **11** is the appearance of the phosphorus signal in an exceptionally high field as compared with its analogues incorporating other chelating phosphines such as  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$  and  $(\text{C}_6\text{H}_{11})_2\text{PCH}_2\text{-CH}_2\text{P}(\text{C}_6\text{H}_{11})_2$ .<sup>17,18</sup> The increased electron density on the phosphorus atoms exerted by the cyclopentadienyl groups may be responsible for this small coordination shift found in **11**.

**Hydrogenation.** Table 1 contains the product yields and turn-over rates for the regioselective hydrogenation of the heterocyclic rings in compounds **1-6** catalyzed by the two rhodium(I) complexes **10-11** under a standard set of conditions. Most reaction of polynuclear heteroaromatics except for isoquinoline (**6**) and indole (**7**) go to completion within approximately 20 h with turnover rates (Rh/h) ranging from 22 to 4. These numbers are, to our knowledge, the highest among those reported in the literature. For example, they are in general 10-100 times greater than those obtained with  $\text{RhCl}(\text{PPh}_3)_3$ <sup>10</sup> and  $\text{HRuCl}(\text{PPh}_3)_3$ <sup>11</sup> even under milder conditions. The order of individual rate is  $5 > 3 > 2 > 1 > 4 > 6$  with the complex **10**, while it becomes  $5 > 2 > 1 > 3 > 4 > 6$  with the complex **11**. Although we did not make any effort to study the effects of the variation of substrates on the turnover

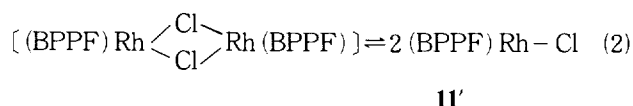
**Table 2.** Turnover rates of Reduction of Quinoline with **10** and **11** in Various Solvents<sup>a</sup>

| Catalyst  | Solvent                         | Turnover Rate <sup>b</sup> |
|-----------|---------------------------------|----------------------------|
| <b>10</b> | EtOH                            | $7.60 \times 10^{-2}$      |
|           | THF                             | $2.36 \times 10^{-2}$      |
|           | CH <sub>3</sub> CN              | $1.71 \times 10^{-2}$      |
|           | CH <sub>2</sub> Cl <sub>2</sub> | $4.82 \times 10^{-2}$      |
| <b>11</b> | EtOH                            | $2.36 \times 10^{-1}$      |
|           | THF                             | $7.67 \times 10^{-2}$      |
|           | CH <sub>3</sub> CN              | $3.68 \times 10^{-2}$      |
|           | CH <sub>2</sub> Cl <sub>2</sub> | $3.42 \times 10^{-2}$      |

<sup>a</sup> Reaction conditions: P(H<sub>2</sub>) = 200 psi; *t* = 60 °C; [Quinoline] =  $5.3 \times 10^{-2}$  M in 40 ml of solvent; [Catalyst] =  $5.3 \times 10^{-4}$  M. <sup>b</sup> Turnover rate = mol of substrate consumed/mol of Rh/min for 30% conversion.

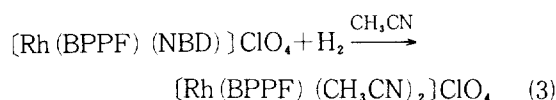
rates, both electronic and steric effects seem to be important. For the reduction of **1** and its benzoderivatives **2-4**, the compound **4**, which is the most sterically hindered at nitrogen is the slowest to be reduced. On the other hand, a comparison of reduction rates of **5** and **7** shows that the rate difference is due to electronic effects caused most likely by the coordinating ability of the heteroatom, since these two molecules differ only in the identity of heteroatom. In this connection it is of interest to note the low activity of the compound **6**, which may have been caused by inability of nitrogen in this molecule to coordinate on the metal center. The mononuclear heteroaromatics **8** and **9** were totally inactive toward the reduction.

When a comparison of reduction rates is made between the two catalysts **10-11**, the dimeric species **11** gives higher rates in all cases. It seems likely that the 14-electron monomer **11'** produced by the chloride bridge cleavage reaction (equation 2) is responsible for the catalytic properties of **11**.

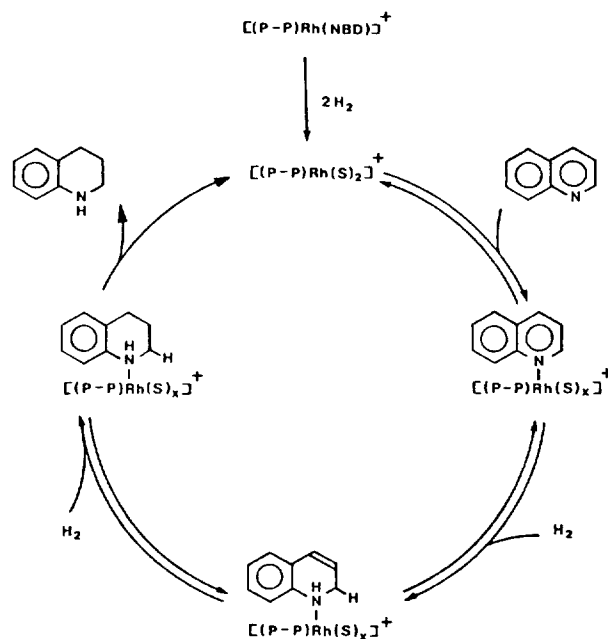


The increased activity of this complex may also stem from the increased concentration of the active catalytic species **11'** as can be seen from equation 2.

Table 2 shows solvent effects. Of various coordinating solvents acetonitrile gives the slowest rates probably due to the fact that this solvent competes more effectively with the substrate for the coordination site on the rhodium atom. In fact, when the catalyst **10** was hydrogenated in CH<sub>3</sub>CN, a disolvated rhodium(I) intermediate **12** was formed and isolated as stable yellow crystals according to equation 3.



No uptake of H<sub>2</sub> further than 2 equivalents was observed, and the formulation of **12** was confirmed by the analytical and NMR data (See Experimental). These observations, coupled with other well documented facts concerning the mechanism of hydrogenation by the cationic rhodium com-

**Figure 2.** A possible catalytic cycle for hydrogenation of quinoline via an olefin route by the complex **10** (P-P = BPPF; S = solvent).

plexes of the type **10**, suggest that an "olefin route"<sup>19,21</sup> is in operation in the reduction by the complex **10** in the solvents like EtOH, THF, and CH<sub>3</sub>CN as depicted in Figure 2.

Finally, in connection with mechanism of hydrogenation by the compound **11**, it is of interest to note from Table 2 that the rate also drops significantly in CH<sub>2</sub>Cl<sub>2</sub>. This may be due to the fact that the equilibrium of equation 3 lies far to the left in this solvent. In a better coordinating solvent such as EtOH, however, the equilibrium may lie in favor of the monomer **11'**. This can then react with hydrogen to generate a dihydridorhodium(III) species, (BPPF)Rh(H)<sub>2</sub>Cl.<sup>18</sup> Thus it may be implied that an "hydride route"<sup>19,22</sup> is being operative to complete the hydrogenation cycle. Obviously, the isolation and spectroscopic studies of the intermediate species that can be involved in the catalytic cycles mentioned above would help to understand these reactions. Such studies are underway to clarify these points.

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## Numerical Model Simulation of DF-CO<sub>2</sub> Transfer Chemical Laser

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Theoretical analysis of DF-CO<sub>2</sub> transfer chemical laser is performed through simple kinetic model consisting of 30 chemical reactions. In this model, we calculate the power theoretically by solving the rate equations, which are related to the D<sub>2</sub> + F<sub>2</sub> chain reaction and the DF-CO<sub>2</sub> resonance energy transfer, combined with both the gain processes and the stimulated emission processes. The calculated powers are verified with previously reported results in good agreements. The output energy rises linearly with the increase in pressure, and the duration time of output pulse show the inverse dependence on pressure. Through the detailed calculation of temperature and concentrations of reactants as a function of time, it is found that the deactivation processes of DF(v) can be neglected in low pressure, but they have to be considered in high pressure. From the parametric study for the variation on [D<sub>2</sub>]/[F<sub>2</sub>] and [CO<sub>2</sub>]/[D<sub>2</sub> + F<sub>2</sub>] at several constant total pressure, the optimum lasing conditions are found to be in a range of 1/3 to 1 and 2 to 4, respectively.

### Introduction

A chemical laser which operates on a population inversion produced in the course of an exothermic chemical reaction has many advantages<sup>1</sup>. It provides a direct conversion of chemical energy into electromagnetic energy. And it generates high output power due to available large energy released from chemical reaction. On the other hand, the molecule which is excited by chemical reaction can induce the population inversion in other molecule through the vibrational energy transfer. It is called transfer chemical laser(TCL). The first observations of this type of laser operation were

made by Gross<sup>2</sup> and Chen *et al.*<sup>3</sup>, for the DF-CO<sub>2</sub> system. With their efforts to increase power of CO<sub>2</sub> laser, they found efficient pulse CO<sub>2</sub> laser operation at 10.6 μm when CO<sub>2</sub> was added to pulsed DF chemical laser. It gives a strong laser output by excited CO<sub>2</sub> whose energy is transferred from excited DF formed by chain chemical reactions<sup>1</sup>. Because population inversion of CO<sub>2</sub> is obtained from the chemical reaction, it is classified into chemical laser and it does not have to maintain the flash photolysis or electric discharges continuously.

The phenomena occurring in the chemical laser system are very complicated, and have not been well understood. In