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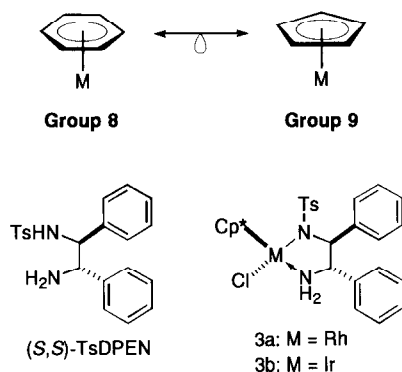
(Received August 3, 1998; CL-980589)

of **3a** and **3b** exhibited one set of signals due to a single isomer, two NH<sub>2</sub> protons being observed as an ABX pattern due to the chiralities of the metal and the ligand.

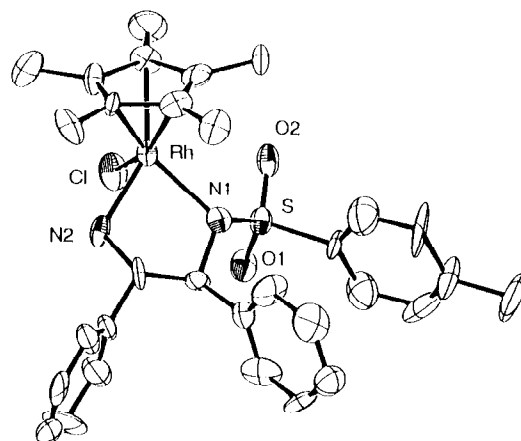
Figure 1 shows the crystal structure of the rhodium complex **3a** which adopts pseudo-tetrahedral and three-legged piano stool geometry where Cp\* is a capping ligand and two nitrogen atoms of the ligand and a chloro ligand are legs.<sup>15</sup> The (*R*)-configuration around the rhodium center is the result of the chirality of (*S,S*)-TsDPEN, which forms a  $\delta$ -five-membered chelation. Such a diastereoselective complexation of a half-metallocene complex with a chiral auxiliary has been reported for Cp\*Ir<sup>16</sup> and ( $\eta^6$ -arene)Ru<sup>2f</sup> complexes.

The goal for homogeneous catalysis, especially asymmetric catalysis, is the achievement of high activity and selectivity for the target reactions.<sup>1</sup> Development in this field has been based on the design of the phosphine ligand coordinated to the catalytically active metal center. Nitrogen-containing optically active compounds have recently been utilized as a chiral auxiliary for various transition metals such as ruthenium,<sup>2-4</sup> cobalt,<sup>5</sup> rhodium,<sup>6-8</sup> iridium,<sup>9,10</sup> and so on. Among them, Noyori's ruthenium catalyst, ( $\eta^6$ -arene)RuCl complex (**1**) of (1*S*,2*S*)-*N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine (abbr. (*S,S*)-TsDPEN), has attracted much interest in view of its high catalytic ability and the exposition of the reaction mechanism which involves a 16-electron ( $\eta^6$ -arene)RuL<sub>2</sub>-type complex and a hydride complex, both complexes being characterized crystallographically.<sup>2f</sup>

We conceived that  $(\eta^6\text{-arene})\text{M}$  ( $\text{M}$  = Group 8 metals) fragments are isolobal with  $(\eta^5\text{-C}_5\text{R}_5)\text{M}$  ( $\text{M}$  = Group 9 metals) ones<sup>11</sup> through the comparison of the structure and the reactivity of our ruthenium—thiolate complexes  $(\eta^6\text{-arene})\text{Ru}(\text{SR})_2$ <sup>12</sup> with those of the reported iridium—thiolate complexes  $\text{Cp}^*\text{Ir}(\text{SAr})_2$  ( $\text{Cp}^*$  = pentamethylcyclopentadienyl).<sup>13</sup> Thus, these prompted us to prepare new  $\text{Cp}^*\text{MCl}$  complexes ( $\text{M}$  = Rh, Ir) of (*S,S*)-TsDPEN and their application to asymmetric transfer hydrogenation of ketonic substrates. The results of these investigations are the subject of the present contribution.



Treatment of  $[\text{Cp}^*\text{MCl}_2]_2$  (**2a**: M = Rh; **2b**: M = Ir) with two equiv. of (*S,S*)-1'SDPEN in dichloromethane in the presence of four equiv. of triethylamine resulted in the formation of **3a** and **3b**, respectively, in modest yield.<sup>14</sup> The  $^1\text{H}$  NMR spectra



**Figure 1.** Molecular structure of complex **3a** with the numbering scheme. Selected bond lengths (Å) and angles (degree): Rh—Cl = 2.421(5), Rh—N1 = 2.18(1), Rh—N2 = 2.09(2); Cl—Rh—N1 = 94.1(4), Cl—Rh—N2 = 84.0(4), N1—Rh—N2 = 77.5(5).

Asymmetric transfer hydrogenation of acetophenone by using complexes **3** and one equiv. of aq. KOH in 2-propanol proceeded under the conditions with a substrate/catalyst molar ratio of 100, giving (*S*)-1-phenylethanol in up to 88% *ee* (enantiometric excess) and in moderate yield: one equiv. of aq. KOH was enough to generate the active species and two equiv. of aq. KOH somewhat decreased the catalyst activity. In the same reaction conditions, the rhodium catalyst **3a** was much active than the iridium catalyst **3b**. The same catalyst system using one equiv. of aq. KOH hydrogenated 2-acetonaphthone, 1-tetralone, and 1-indanone to give (*S*)-1-(2-naphthyl)ethanol (85% *ee*), (*S*)-1-tetralol (97% *ee*), and (*S*)-indanol (99% *ee*), respectively. The correlation between the chirality of the ligand and the configuration of the alcohols was found to be the same as that found for **1**, though the catalytic activity and enantioselectivity of **3** were less than those of the ruthenium catalyst **1** [97% *ee*, 95% yield for transfer hydrogenation of acetophenone (S/C = 200) for 15 h at room temperature].<sup>2b</sup>

**Table 1.** Asymmetric transfer hydrogenation of prochiral ketones catalyzed by **3a** and **3b**<sup>a</sup>

run	cat. <sup>b</sup>	ketone	KOH <sup>c</sup>	yield <sup>d</sup> %	ee <sup>e</sup> %	config <sup>f</sup>
1	<b>3a</b>	acetophenone	2	80	90	(S)
2	<b>3a</b>		1	95	84	(S)
3	<b>3b</b>		2	58	90	(S)
4	<b>3b</b>		1	89	88	(S)
5	<b>3a</b>	2-acetonaphthone	1	82	85	(S)
6	<b>3b</b>		1	67	81	(S)
7	<b>3a</b>	1-tetralone	1	79	97	(S)
8	<b>3a</b>		2	28	95	(S)
9	<b>3b</b>		1	68	96	(S)
10	<b>3b</b>		2	27	90	(S)
11	<b>3a</b>	1-indanone	1	47	99	(S)
12	<b>3b</b>		1	41	91	(S)

<sup>a</sup>The reaction was carried out at room temperature for a period of 48 h using a 0.1 M solution of ketone in 2-propanol. <sup>b</sup>Ketone:[**3**] = 100:1. <sup>c</sup>Molar ratio of KOH:[**3**].

<sup>d</sup>Determined by HPLC analysis. <sup>e</sup>Determined by HPLC analysis using DAICEL CHIRALCEL OD. <sup>f</sup>Configuration (in parenthesis) was determined from the sign of rotation of the isolated product.

In summary, we demonstrate that rationally designed rhodium and iridium complexes bearing both a Cp\* and a chiral diamine ligand are excellent catalyst precursors for the asymmetric transfer hydrogenation of ketonic substrates; the rhodium complex proves to be superior to the iridium complex. Application of new catalyst systems to asymmetric transfer hydrogenation of various C=X bonds and, moreover, the mechanistic study<sup>17</sup> are in progress.

We appreciate Dr. N. Sayo (Takasago International Corporation) for his fruitful discussion. This work was financially supported by the Grant-in-Aid for Scientific Research on Priority Areas (No. 283, "Innovative Synthetic Reactions") from the Ministry of Education, Science, Sports and Culture, Japan.

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- 3a**: 70% yield, mp (dec) 129–131 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 35 °C): δ 1.84 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 2.21 (s, 3H, CH<sub>3</sub> of *p*-Ts), 3.26 (br d, 1H, *NHH*), 3.69 (m, 1H, CHNH<sub>2</sub>), 3.95 (d, *J* = 10.7 Hz, 1H, CHN-*p*-Ts), 3.97 (br t, 1H, *NHH*), 6.65–7.44 (14H, aromatic protons). UV–vis (dichloromethane): λ<sub>max</sub> 352 (ε 4.0 × 10<sup>3</sup>) nm, FAB-MS: 639 (MH<sup>+</sup>), 603 (M<sup>+</sup> - Cl). Found: C, 57.95; H, 5.64; N, 4.41%. Anal. Calcd for C<sub>31</sub>H<sub>36</sub>ClN<sub>2</sub>O<sub>2</sub>RhS: C, 58.26; H, 5.68; N, 4.38%. **3b**: 87% yield, mp >205 °C (dec). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 35 °C): δ 1.82 (s, 15H, C<sub>5</sub>Me<sub>5</sub>), 2.24 (s, 3H, CH<sub>3</sub> in *p*-Ts), 3.70 (m, 1H, HCNH<sub>2</sub>), 4.00 (br d, 1H, *NHH*), 4.29 (d, *J* = 10.7 Hz, 1H, CHN-*p*-Ts), 4.51 (br t, 1H, *NHH*), 6.66–7.47 (14H, aromatic protons). UV–vis (dichloromethane): λ<sub>max</sub> 315 (ε 1.7 × 10<sup>3</sup>) nm. FAB-MS: 728 (M<sup>+</sup>), 693 (M<sup>+</sup> - Cl). Found: C, 51.01; H, 5.06; N, 4.03%. Anal. Calcd for C<sub>31</sub>H<sub>36</sub>ClIrN<sub>2</sub>O<sub>2</sub>S: C, 51.12; H, 4.98; N, 3.85%.
- Crystal data for **3a**: formula = C<sub>31</sub>H<sub>36</sub>ClN<sub>2</sub>O<sub>2</sub>RhS, FW = 639.06, orthorhombic space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> (# 19), *a* = 16.45(1), *b* = 21.63(1), *c* = 8.38(2) Å, *V* = 2980(5) Å<sup>3</sup>, *D*<sub>calcd</sub> = 1.424 g cm<sup>-3</sup>, μ(MoKα) = 7.61 cm<sup>-1</sup>, 2θ<sub>max</sub> = 65.0°, *R* (*R*<sub>w</sub>) = 0.056 (0.067) and GOF = 1.66 for 1802 reflection data with *I* > 3σ(*I*) and 343 variables.
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