The Half-sandwich Hydride and 16-Electron Complexes of Rhodium and Iridium Containing (1*S*,2*S*)-*N*-(*p*-Toluenesulfonyl)-1,2-diphenylethylenediamine: Relevant to the Asymmetric Transfer Hydrogenation

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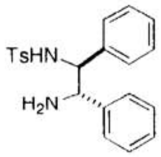
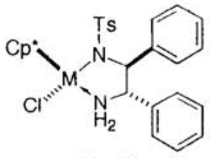
We prepared the half-sandwich hydride and 16-electron complexes of rhodium and iridium bearing an anion of (1*S*,2*S*)-*N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine: for the iridium catalyst system, a 16-electron complex **2b** and an 18-electron, hydride complex **3b** were synthesized, while only a 16-electron complex **2a** was detected for the rhodium catalyst.

Recently, asymmetric transfer hydrogenation has been developed by using transition metal catalysts possessing a nitrogen-containing chiral auxiliary;[1] the metal center being ruthenium,[2-4] cobalt,[5] rhodium,[6-8] iridium,[9,10] and so on. We have designed and actually prepared the rhodium and iridium Cp*MCl complexes (**1a**: M = Rh; **1b**: M = Ir) (Cp* = pentamethylcyclopentadienyl) of (1*S*,2*S*)-*N*-(*p*-toluenesulfonyl)-1,2-diphenylethylenediamine (abbr. (*S*,*S*)-TsDPEN)[11] since (η^6-arene)M (M = Ru, Os) fragments are isolobal with (η^5-C_5R_5)M (M = Rh, Ir) ones,[12] and the Noyori's ruthenium(II) catalyst has an (η^6-arene)RuCl fragment. Herein we report on the preliminary results focused on the preparation of the half-sandwich hydride and 16-electron complexes of rhodium and iridium relevant to the asymmetric transfer hydrogenation catalyzed by the rhodium and iridium complexes **1**.

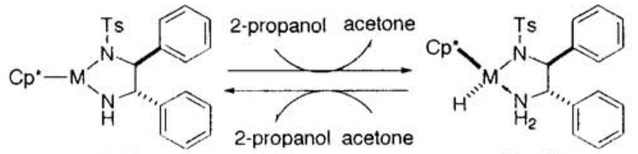


(*S*,*S*)-TsDPEN



1a: M = Rh
1b: M = Ir

In the case of the iridium complex, both of the 16-electron complex **2b**[13] and the hydride complex **3b**[14] were isolated and characterized. These complexes were prepared as follows. To a solution of [Cp*IrCl$_2$]$_2$ and two equiv. of (*S*,*S*)-TsDPEN in dichloromethane, was added dropwise an excess of aqueous solution of KOH, which is the same operation as the catalytic reaction in 2-propanol.[11] Complex **2b** was obtained in 80% yield as deep purple powder; the color proved **2b** to be 16-electron species (*vide infra*).[13] The complex **2b** was also derived from treating **1b** with excess of aqueous KOH in dichloromethane. It is an important feature that **2b** reacted with 2-propanol to afford a pale yellow hydride complex **3b** in quantitative yield.[14] The ^{1}H NMR spectrum of **3b** consists of a singlet (δ 1.76) due to the pentamethylcyclopentadienyl ligand and a singlet hydride resonance (δ -9.94) together with one set of signals due to the anion of (*S*,*S*)-TsDPEN. A weak broad band at 2078 cm^{-1} in the infrared spectrum of **3b** is assigned to the metal-hydride stretching frequency. Thus, these data indicated that **3b** was obtained as a single isomer.



2a: M = Rh
2b: M = Ir
3a: M = Rh
3b: M = Ir

A reverse reaction of **3b** with acetone occurred smoothly to regenerate **2b**. As the catalytic reaction was carried out in excess 2-propanol, the color of the reaction mixture remained pale yellow due to the presence of the hydride complex **3b**.

In sharp contrast to the iridium catalyst, for the rhodium catalyst we could detect only a 16-electron complex **2a**, but its hydride derivative **3a** was not detected. Treatment of the reaction mixture of [Cp*RhCl$_2$]$_2$ and two equiv. of (*S*,*S*)-TsDPEN in dichloromethane with an excess of aqueous KOH solution resulted in the formation of deep green powder of **2a**.[15] The complex **2a** was highly air-sensitive; hence its isolation and characterization were hampered. However, the UV spectrum of **2a** strongly suggested the formation of a coordinatively unsaturated 16-electron complex **2a** similar to **2b** (*vide infra*). During the catalytic reaction using the rhodium catalyst, we observed the distinctive green color due to the 16-electron complex **2a** even though the reaction was operated in excess 2-propanol. Although it is not clear what mechanism is operating for the rhodium catalyst, it is definitely shown that the rhodium center favors a 16-electron species, whereas the iridium center favors a hydride species in the reaction conditions.

The absorption bands of **2a** and **2b** observed at λ_{max} 575 and 538 nm, respectively, in the electronic spectra are assigned to the LMCT bands in which a filled pπ-orbital of nitrogen atoms donates some electrons to a vacant d-orbital of the electron deficient metal center;[16] in good accordance with the MO description for 16-electron, two-legged piano stool complexes.[17] Such a unique donation of pπ-electron of the diamine ligand may be a reason for stabilizing the 16-electron species.

In summary, we demonstrated the isolation and characterization of the new rhodium and iridium complexes, *i.e.*, 16-electron complexes as well as a hydride complex. The equilibrium between the 16-electron species and the hydride one depends on the kind of the metal center; the rhodium complex predominantly favors the 16-electron species. More detailed studies to elucidate the reaction mechanism are in progress.

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11 Synthesis of the rhodium and the iridium complexes **1** and their application to asymmetric transfer hydrogenation of ketonic substrates are preliminary reported in: K. Mashima, T. Abe, and K. Tani, *Chem. Lett.*, **1998**, the previous paper.

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13 **2b**: 80% yield, mp >82 °C (dec). ^{1}H NMR (300 MHz, toluene-d_8, 35 °C): δ 1.62 (s, 15H, C_5Me_5), 2.01 (s, 3H, CH_3 in *p*-Ts), 4.07 (s, 1H, C*H*NH), 4.53 (s, 1H, C*H*N-*p*-Ts), 4.99 (br s, 1H, N*H*), 6.60, 7.44 (each d, *J* = 8.2 Hz, 4H, aromatic protons due to *p*-Ts), 6.97—7.67 (m, 10H, Ph). UV—vis (dichloromethane): λ_{max} 538 (ε 3.7 x 10^3), 429 (ε 3.4 x 10^3), 379 (ε 2.9 x 10^3) nm. FAB-MS: 693 (MH^+). Found: C, 54.08; H, 5.08; N, 4.10%. Anal. Calcd for $C_{31}H_{35}IrN_2O_2S$: C, 53.81; H, 5.10; N, 4.05%.

14 **3b**: 98% yield, mp 115—118 °C (dec). ^{1}H NMR (300 MHz, toluene-d_8, 35 °C): δ -9.94 (s, 1H, Ir-H), 1.76 (s, 15H, C_5Me_5), 2.09 (s, 3H; CH_3 in *p*-Ts), 3.34 (br d, 1H, N*H*H), 3.65 (m, 1H, C*H*NH_2), 4.15 (br t, 1H, NH*H*), 4.52 (d, *J* = 8.2 Hz, 1H, C*H*N-*p*-Ts), 6.75, 7.74 (each d, *J* = 8 Hz, 4H, aromatic protons due to *p*-Ts), 6.83—7.23 (m, 10H, Ph). UV—vis (2-propanol): λ_{max} 302 (ε 5.1 x 10^4) nm. FAB-MS : 694 (M^+). IR (KBr): 2078 br cm^{-1} ν(Ir-H). Found: C, 53.45; H, 5.43; N, 3.90%. Anal. Calcd for $C_{31}H_{37}IrN_2O_2S$: C, 53.66; H, 5.37; N, 4.04%.

15 **2a**: 89%, mp 154—158 (dec). ^{1}H NMR (400 MHz, CD_2Cl_2, 35 °C): δ 1.77 (s, 15H, C_5Me_5), 2.38 (s, 3H; CH_3 in *p*-Ts), 3.02 (br d, $J_{Rh\text{-}H}$ = 11 Hz and $J_{H\text{-}H}$ = 2.4 Hz, 1H, N*H*), 3.7—3.8 (ABX pattern, *J* = 11.0 Hz, 2H, C*H*NH and C*H*N-*p*-Ts), 6.76—7.39 (m, 14H, Ph). UV—vis (dichloromethane): λ_{max} 575 (ε 3.1 x 10^2), 346 (ε 3.7 x 10^3) nm.

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