Rhodium and Ruthenium Complexes with Optically Active Chelate Cyclopentadienyl-Phosphine Bidentate Ligands

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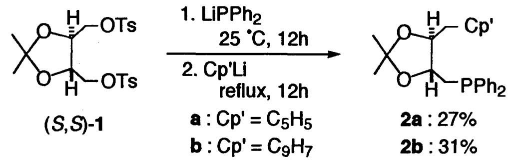
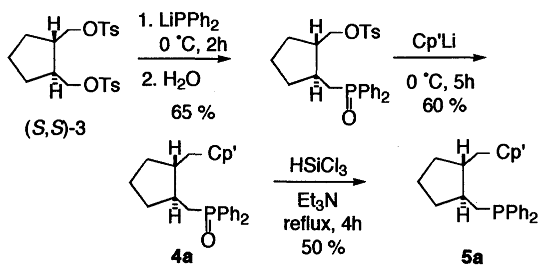
The first optically active cyclopentadienyl-phosphine bidentate ligands ([Cp-P]H ligands) in which a diphenylphosphino group and a cyclopentadienyl or an indenyl group are connected by an *L*-threitol derivative or an (*S,S*)-*trans*-1,2-dimethylenecyclopentane group have been prepared. The rhodium and ruthenium complexes of their anions have been prepared and characterized.

A variety of cyclopentadienyl and phosphine complexes of transition metals have been prepared and applied to stoichiometric organic reactions as well as homogeneous catalysis.[1] The hybrid ligands, possessing both a cyclopentadienyl and a tertiary phosphine group and connecting them by an appropriate spacer, [Cp-P]H ligand, attract much interest as heterodifunctional ligands effective for homogeneous catalysis. The chemistry of such complexes, however, is almost unexplored mainly due to a shortage of the desired ligands.[2] Although several achiral diphenylphosphino-alkylcyclopentadienes such as $Cp'(CH_2)_nPPh_2$ ($Cp'=C_5H_5$, n=2,3; $Cp'=C_5Me_4H$, n=3)[3,4] and the transition metal complexes of their anions have been reported,[3,5] a diversity of the ligand is lacking, especially no optically active analogues have been reported. Here we wish to report the preparation and the characterization of several optically active [Cp-P]H ligands and the rhodium and ruthenium complexes of their anions.



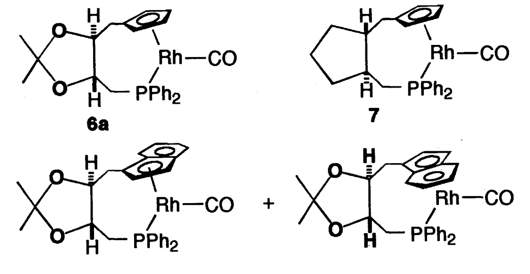
(1)



(2)

As optically active [Cp-P]H ligands, we describe those containing an *L*-threitol derivative or an (*S,S*)-1,2-*trans*-dimethylene-cyclopentane group as a chiral backbone. These optically active [Cp-P]H ligands were synthesized by successive introduction of a diphenylphosphino group and a cyclopentadienyl or an indenyl group into the symmetric and optically active ditosylate **1** or **3** (eq. 1, 2). Stepwise reactions of the ditosylate **1** with an equimolar amount of lithium diphenylphosphide and lithium cyclopentadienide gave the optically active [Cp-P]H ligand **2a**,[6] as an air-sensitive colorless oil in 27% yield based on **1**. The indenyl analogue **2b**[7] was similarly prepared in 31% yield based on **1**. The ligand **5a** was similarly obtained from the optically active ditosylate **3**[8] as an air-sensitive colorless oil in ca. 20% yield. The ligand **5a** was characterized as its phosphine oxide **4a**.[9]

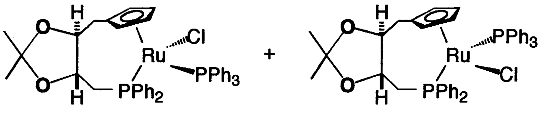
$$\tfrac{1}{2}\,[\mathrm{Rh(CO)_2Cl}]_2 + \overset{\substack{[\mathrm{Cp\text{-}P}]\mathrm{H} \\ \downarrow\ {}^{n}\mathrm{BuLi}}}{[\mathrm{Cp\text{-}P}]\mathrm{Li}} \xrightarrow[\mathrm{THF}]{} (\mathrm{Cp\text{-}P})\mathrm{RhCO} \qquad (3)$$



6b maior / minor = 69 /31

Reaction of the [Cp-P]H ligand, after being treated with an equimolar amount of butyllithium, with $[Rh(CO)_2Cl]_2$ in a 2:1 mole ratio in THF at 25 °C afforded mononuclear rhodium(I) complexes (eq. 3). The complex **6a** was isolated in 22% yield as an air-stable yellow powder, which was purified by column chromatography.[10] The presence of a terminal carbonyl group was confirmed by the ^{13}C NMR and the IR spectrum. The IR spectrum showed a CO stretching at 1960 cm^{-1} which is shifted to a lower wave number by ca. 100 cm^{-1} compared to that of the starting $[Rh(CO)_2Cl]_2$. The ^{13}C NMR of the coordinated CO group appeared as a doublet of doublet at δ 195.7 ($J_{C\text{-}Rh}$ = 86.8 and $J_{C\text{-}P}$ = 24.0 Hz). The chemical shifts and the coupling constants are reasonable for terminal Rh-CO groups.[11] The mass spectrum indicated the molecular ion at *m/e* 508 and the fragment peak due to the loss of a carbonyl group from the molecular ion at *m/e* 480. These spectral data showed the complex **6a** to be a mononuclear rhodium complex. The complex **6b** was obtained over 70% yield as an air-stable yellow powder, which was purified by recrystallization from hexanes at -78 °C.[12] The ^1H and ^{31}P NMR showed that the complex is comprised of two diastereomers in a 69:31 ratio. These two isomers could not be separated in a pure state. The complex **7** was obtained by a similar method in lower yield (<20%) as a hexane-soluble yellow solid. The spectral data indicated that the complex **7** is also a mononuclear rhodium complex analogous to **6a**.[13] In this case the main product was hexane-insoluble but toluene-soluble dark-brown powders, which may be a mixture of polynuclear rhodium complexes and could not fully be characterized.

Reaction of $RuCl_2(PPh_3)_3$ with a lithium salt of **2a** gave (Cp-P)$RuCl(PPh_3)$ **8** in 49% yield as an orange powder, which was purified by column chromatography.[14] Although complex **8** is air-stable in the solid state, it decomposes gradually in solution. The mass spectrum showed the parent ion at *m/e* 776 and the fragment peaks at *m/e* 741 (M$^+$-Cl) and 514 (M$^+$-PPh$_3$). ^{1}H and ^{31}P NMR revealed that the complex is a mixture of two diastereomers in a 59:41 ratio. The ^{1}H NMR spectrum showed the resonance of cyclopentadienyl protons at δ 5.21, 4.56, 3.91, 2.41 (the major isomer) and δ 4.97, 4.71, 4.06, 3.04 (the minor isomer). Appearance of one of the cyclopentadienyl protons at very high fields (δ 2.41 or 3.04) is presumably due to the shielding effect of a phenyl ring of the PPh$_3$.[15]



8 major / minor = 59 /41

The rhodium and ruthenium complexes having an optically active Cp-P ligand are expected to be effective for several asymmetric reactions.[16] Further investigation and their application for catalytic reaction are in progress.[17]

References and Notes

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6 **2a**: $[\alpha]_D^{23}$ -46.3° (*c* 1.02, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ = 1.35 (s, 3H), 1.40 (s, 3H,), 2.40-2.54 (m, 2H), 2.58-2.72 (m, 2H), 2.89 (s, 2H, Cp ring), 3.68-3.85 (m, 1H), 3.93-4.10 (m, 1H), 5.96-6.01 (m, 0.5 H, Cp ring), 6.11-6.15 (m, 0.6 H, Cp ring), 6.22-6.30 (m, 0.7 H, Cp ring), 6.36-6.42 (m, 1.2 H, Cp ring), 7.10-7.59 (m, 10H); ^{31}P NMR (CDCl$_3$) δ = -23.1 (s), -22.7 (s).

7 **2b**: $[\alpha]_D^{23}$ -35° (*c* 0.074, CHCl$_3$); ^{1}H NMR (CDCl$_3$) δ = 1.37 (s, 3H), 1.40 (s, 3H), 2.27 (d, *J* = 6.18 Hz, 2H), 2.86 (m, 2H), 3.27 (d, *J* = 1.48 Hz, 2H), 3.82-3.92 (m, 1H), 4.24 (m, 1H), 6.22 (s, 1H), 7.13-7.49 (m, 14H); ^{31}P NMR (CDCl$_3$) δ = 23.0 (s). HRMS: calcd. for $C_{28}H_{30}O_2P$ 429.1983 , found 429.1987.

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9 **4**: $[\alpha]_D^{23}$ 29.4° (*c* 1.03, CHCl$_3$). ^{31}P NMR (CDCl$_3$) δ = 30.8 (s), 30.9 (s). Anal. Found: C, 79.01; H, 7.66%. Calcd for $C_{24}H_{27}OP$: C, 79.53; H, 7.51%.

10 **6a**: $[\alpha]_D^{23}$ -57.3 (*c* 0.26, CHCl$_3$); mp 100-103 °C (dec.); IR 1960 cm^{-1} (br, ν_{CO}); ^{1}H NMR (C_6D_6) δ = 1.29 (s, 3H), 1.43 (s, 3H), 2.17-2.33 (m, 1H), 2.58-2.73 (m, 1H), 3.08-3.23 (m, 1H), 3.47-3.64 (m, 1H), 3.79-3.93 (m, 1H), 4.01-4.14 (m, 1H), 5.11 (brs, 1H), 5.17 (brs, 1H), 5.33-5.39 (m, 1H), 5.42-5.48 (m, 1H), 6.97-7.18 (m, 6H), 7.44-7.55 (m, 2H), 7.90-8.03 (m, 2H); ^{31}P NMR (C_6D_6) δ = 38.0 (d, $J_{P\text{-}Rh}$ = 196.8 Hz); ^{13}C NMR (C_6D_6) δ = 195.7 (dd, $J_{C\text{-}Rh}$ = 86.8 Hz, $J_{C\text{-}P}$ = 24.0 Hz, *C*O); FABMS *m/e* 508 (M$^+$), 480 (M$^+$-CO)

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12 **6b**: mp 168-173 °C; IR 1968 cm^{-1} (br, ν_{CO}); ^{31}P NMR (CDCl$_3$) δ = 30.3 (d, *J* = 198.7 Hz, minor), 32.0 (d, *J* = 196.8 Hz, major); ^{13}C NMR (CDCl$_3$) δ = 192.9 (dd, $J_{C\text{-}Rh}$ = 89.1 Hz, $J_{C\text{-}P}$ = 20.6 Hz, *C*O, minor), 193.4 (dd, $J_{C\text{-}Rh}$ = 89.7 Hz, $J_{C\text{-}P}$ = 21.8 Hz, *C*O, major); FABMS *m/e* 558 (M$^+$), 530 (M$^+$-CO). Found: C, 61.92; H, 5.09%. Calcd for $C_{29}H_{28}O_3PRh$: C, 62.38; H, 5.05%.

13 **7**: mp 57-60°C; IR 1960 cm^{-1} (br, ν_{CO}); ^{31}P NMR (CDCl$_3$) δ = 43.7 (d, $J_{P\text{-}Rh}$ = 194.8 Hz); ^{13}C NMR (CDCl$_3$) δ = 195.2 (dd, $J_{C\text{-}Rh}$ = 87.7, $J_{C\text{-}P}$ = 22.9 Hz). FABMS *m/e* 476 (M$^+$), 448 (M$^+$-CO).

14 **8**: mp 152-154 °C (dec.); ^{31}P NMR (CDCl$_3$) δ = 28.6 (d, $J_{P\text{-}P}$ = 44.1 Hz, major), 31.8 (d, $J_{P\text{-}P}$ = 42.2 Hz, minor), 36.80 (d, $J_{P\text{-}P}$ = 42.2 Hz, minor) 36.83 (d, $J_{P\text{-}P}$ = 44.1 Hz, major); FABMS *m/e* 776 (M$^+$), 741 (M$^+$-Cl), 514 (M$^+$-PPh$_3$), 479 (M$^+$-Cl-PPh$_3$).

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16 We have found that the ruthenium complex **8** was an effective catalyst for asymmetric condensation. For example, reaction of 1-dodecyne with 3-butene-2-ol in the presence of complex **8** (10 mol%) and NH_4PF_6 (20 mol%) gave the optically active β,γ-unsaturated ketone, 3-methyl-1-pentadecen-4-one, $[\alpha]_D^{23}$ -5.04° (*c* 0.853, CHCl$_3$), see; Y. Saito, T. Yamagata, Y. Kataoka, and K. Tani, The 41st Symposium on Organometallic Chemistry, Japan, **1994**, abstr. PA109.

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