

Application of Chiral Bidentate Ligands to the $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ System: Unusual Isomerism Derived from the Chiral Ligands

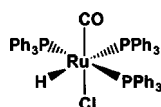
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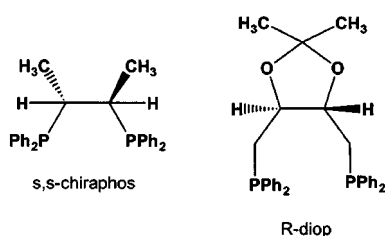
Catalytic asymmetric reactions using organometallic reagents have been convenient ways to produce useful levels of enantioselectivity on both naturally occurring and non-naturally occurring organic compounds.¹ For higher enantiomeric excess and selectivity, many chiral ligands and catalyst systems using transition metals have been studied and structurally characterized.² The use of well known transition metal catalysts (e.g. Vaska's complex etc.) and chiral bidentate ligands having C_2 symmetry component are widely accepted for this purpose. Among many transition metal catalyst systems, utilization of the ruthenium(II) complexes in homogeneous reactions appears to grow exponentially. And there have been tremendous advances in the area for a wide range of reactions including unsaturated organics.³

The complex, $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$, first reported by Vaska and Diluzino in 1961,⁴ has attracted continuous attention. Interests in the complex $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ and related species have been further increased by their catalytic activity in a number of important reactions such as olefin migration and hydrogenation of carbon-carbon double bond, aldehydes, ketones, α,β unsaturated aldehydes, nitroarenes, and N- and S-hetero cycles.⁵



We previously reported that the ruthenium(II) hydrido carbonyl complexes containing chelating bidentate diphosphine ligands showed effective catalytic activities in homogeneous hydrogenation of aldehydes and cyclohexene,^{6(a),(b)} and other research groups reported similar results.^{6(c)} However, there have been no examples about utilization and application of chiral bidentate ligands in the $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ system, though a variety of chiral bidentate phosphine ligands have been designed and synthesized.

This document describes the application of chiral bidentate phosphine ligands (*s,s*-chiraphos and R-diop) to the synthesis of ruthenium(II) hydrido carbonyl complexes and the



unusual isomerism observed during the synthesis of these complexes.

Experimental Section

All synthetic reactions were carried out under the N_2 stream using the Schlenk technique. PPh_3 , $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ and *s,s*-chiraphos were purchased from Aldrich Co. and these materials were used without further purification. R-diop was synthesized from the literature method¹⁴ with slight modifications (Li metal was used instead of K and Na metal). $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ and $[\text{RuH}(\text{CO})(\text{NCMe})_2(\text{PPh}_3)_2]\text{BF}_4$ were prepared following the literature method.⁷ All solvents were purified by the standard procedure. ^1H NMR spectra were recorded on a Bruker 500 MHz spectrometer. The IR spectra was recorded on a Nicolet Avatar spectrometer and Elemental Analysis was performed at the Korea Basic Science Institute, Seoul Branch Lab.

Preparation of $\text{RuHCl}(\text{CO})(\text{PPh}_3)(\text{L-L})$ (1) and (2); (L-L = *s,s*-chiraphos (1) and R-diop (2)). $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (0.1 mmol) and ligand (0.1 mmol) were dissolved in toluene (10 mL) and heated at ca. 80 °C for 5 h. After cooling to room temperature, this solution was filtered and the filtrate was concentrated to ca. 2 mL, to which *n*-pentane (50 mL) was added. The resulting pale yellow precipitate was collected on a sintered glass and washed with *n*-pentane (10 mL) and ethylether (10 mL), and dried *in vacuo*. Yield: (*s,s*-chiraphos 65%, R-diop 72%) EA: For *s,s*-chiraphos $\text{C}_{47}\text{H}_{44}\text{ClO}_3\text{Ru}$ Calcd. C; 66.08, H; 5.19 Found. C; 66.40, H; 5.75. For R-diop $\text{C}_{50}\text{H}_{48}\text{ClO}_3\text{Ru}$ Calcd. C; 64.83, H; 5.22 Found. C; 65.10, H; 5.61.

Preparation of $[\text{RuH}(\text{CO})(\text{NCMe})(\text{PPh}_3)(\text{L-L})]\text{BF}_4$ (3) and (4); (L-L = *s,s*-chiraphos (3) and R-diop (4)). $[\text{RuH}(\text{CO})(\text{NCMe})(\text{PPh}_3)_2]\text{BF}_4$ (0.1 mmol) and ligand (0.1 mmol) were dissolved in toluene (10 mL) and heated at ca. 80 °C for 5 h. After cooling to room temperature, this solution was filtered and the filtrate was concentrated to ca. 2 mL, to which *n*-pentane (50 mL) was added. The resulting pale yellow precipitate was collected on a sintered glass and washed with *n*-pentane (10 mL) and ethylether (10 mL), and dried *in vacuo*. Yield: (*s,s*-chiraphos 65%, R-diop 72%) EA: For *s,s*-chiraphos $\text{C}_{47}\text{H}_{44}\text{ClO}_3\text{Ru}$ Calcd. C; 66.08, H; 5.19 Found. C; 66.40, H; 5.75. For R-diop $\text{C}_{50}\text{H}_{48}\text{ClO}_3\text{Ru}$ Calcd. C; 64.83, H; 5.22 Found. C; 65.10, H; 5.61.

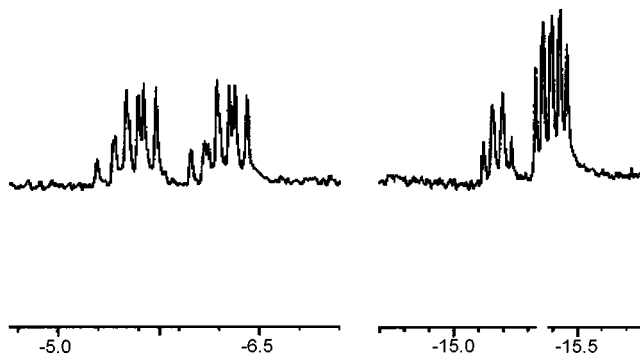


Figure S1. 500 MHz ^1H -NMR spectra for (1). Hydrido region only

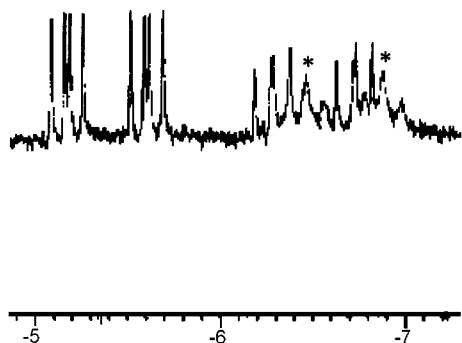
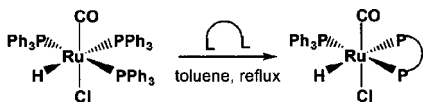


Figure S2. 500 MHz ^1H -NMR spectra for (2). Hydride region only. Impurities are marked as a asterisks.

(CO)(NCMe) $_2$ (PPh $_3$) $_2$ BF $_4$ (0.1 mmol) were suspended in toluene (10 mL) and to this reaction mixture was added the solution of ligand (0.1 mmol) in toluene (5 mL) and heated at *ca.* 80 °C for 5 h. After cooling to room temperature, this solution was filtered and the filtrate was concentrated to *ca.* 2 mL and *n*-pentane (50 mL) were added. The resulting pale yellow precipitates were collected on a sintered glass, washed with *n*-pentane (10 mL) and ethylether (10 mL) and dried in *vacuo*. Yield (*s,s*-chiraphos 70%, *R*-diop 73%). EA: For *s,s*-chiraphos C $_{49}$ H $_{47}$ BF $_4$ NO $_3$ P $_3$ Ru Calcd. C; 62.17, H; 5.00, N; 1.48 Found. C; 62.65, H; 5.23, N; 1.94 For *R*-diop C $_{52}$ H $_{51}$ BF $_4$ NO $_3$ P $_3$ Ru Calcd. C; 61.31, H; 5.05, N; 1.37 Found. C; 61.93, H; 5.25, N; 1.87. Attempt to synthesis in methylenechloride yields too many isomers (see Results and Discussion).

Results and Discussion

RuHCl(CO)(PPh $_3$) $_3$ reacts readily with an equivalent amount of the achiral bidentate chelating ligand to form complexes of the type RuHCl(CO)(PPh $_3$)(L-L') (L-L' = dppm, dppe, dppp, dppb, dppv, dppf).^{6,10}



In a similar way, RuHCl(CO)(PPh $_3$)(*s,s*-chiraphos) (1) and RuHCl(CO)(PPh $_3$)(*R*-diop) (2) have been synthesized in our work with moderately good yields.

It is noteworthy that analogous RuHCl(CO)(PPh $_3$)(L-L') complexes usually have two structural isomers, *cis*- and *trans*-isomers, with respect to CO and Cl, except for RuHCl(CO)(PPh $_3$)(dppv) and RuHCl(CO)(PPh $_3$)(dppf), which have shown to yield the *trans* isomer only. For dppm, dppe and dppp, the complexes in boiling toluene or stirring at room temperature in methylene chloride have shown to possess

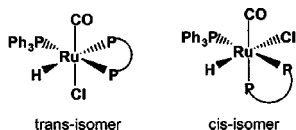


Table 1. Selected Spectroscopic Data

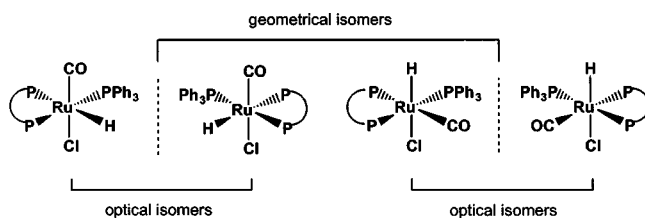
compound	^1H NMR ^a			IR ^b
	δ (Ru-H) ppm	$^2J(\text{H,P})_{\text{trans}}$ Hz	$^2J(\text{H,P})_{\text{cis}}$ Hz	ν (CO) cm $^{-1}$
(1)	-6.2 ddd	111	21, 15	1937
	-6.3 ddd	115	21, NA ^c	
	-15.1 dt		15	
	-15.3 dt		12	
(2)	-5.3 ddd	108	25, 18	1938
	-6.5 ddd	111	26, 22	
(3)	many isomers			1953
(4)	major resonance at -7.1 and unidentified resonance			1948

^ain CDCl $_3$. ^bKBr pallet. ^cNA = Not available (overlapped)

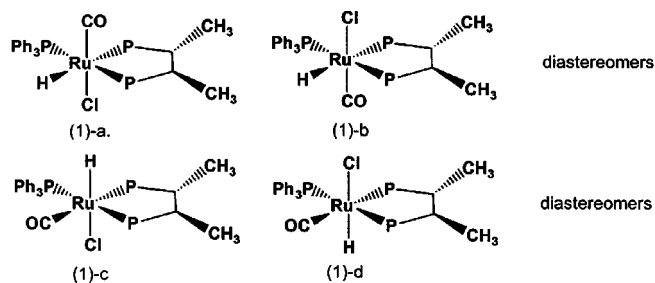
different isomer ratio.^{6,10}

We were initially interested in characterizing the geometry of the ruthenium hydrido-carbonyl complexes containing chiral bidentate ligands, which may give only the same isomers that produced for achiral ligands due to their well defined C $_2$ symmetry. Initially, we have expected that at least two isomers existed, *cis* and *trans* for compound (1) and (2). However, in the case of compound (1), we have found four sets of hydride resonance signals around -6 ppm and -15 ppm and compound (2), two sets of hydride resonance signals around -5 ~ -6 ppm region from the ^1H nmr spectra. Selected ^1H nmr data and IR data are collected in Table 1.

To elucidate this unexpected isomers observed in the solution, we have re-examined the isomerism in the RuHCl(CO)(PPh $_3$)(L-L) system. Finally we have realized that the compound RuHCl(CO)(PPh $_3$)(L-L) have theoretically not only two geometrical isomers but also two additional optical isomers. However, these additional isomers could not have been detected through routine nmr spectroscopy, because two additional isomers are in the enantiomeric relationship. To observe this isomers, chiral bidentate ligands are needed to convert enantiomers to diastereomers.



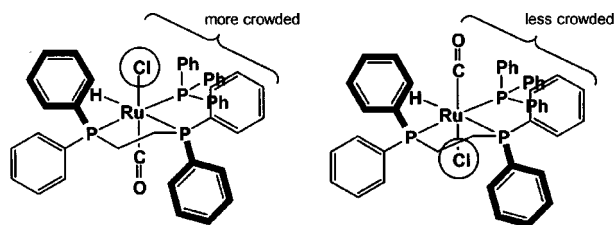
To our best knowledge, no other research groups involved in the study of RuHCl(CO)(PPh $_3$)(L-L') systems have so far pointed out the existence of such optical isomers. From the basis of optical isomerism and the relationship between coupling constant and ligand geometry of hydride phosphine metal complexes,¹¹ the RuHCl(CO)(PPh $_3$)(*s,s*-chiraphos) complex seem to have four distinct isomers in solution due to a chiral bidentate ligand making two enantiomers and two diastereomers possible.



For compound (1), the metal hydride signals have been detected at -6.2 ppm as a doublet of doublet of doublet ($^2J_{\text{H-P}}$ 111, 21, 15 Hz), -6.3 ppm as a doublet of doublet of doublet ($^2J_{\text{H-P}}$ 115, 21, (NA = see Table 1) Hz), -15.1 ppm as a overlapped doublet of triplet ($^2J_{\text{H-P}}$ 15 Hz) and -15.3 ppm as a doublet of triplet ($^2J_{\text{H-P}}$ 12 Hz). The two sets of hydride resonance signals around -6.2 ppm are consistent with one phosphorous atom being trans to hydride as represented in (1)-a and (1)-b. The remaining two sets around -15.1 ppm are consistent with all phosphorous atoms being cis to hydride in (1)-c and (1)-d. Although the alternative stereochemistry cannot rigorously be excluded, our assignment is reasonable on the basis of the interpretation of Santos *et al.*¹⁰

IR spectra have not been able to distinguish these four types of isomers, while at least two isomer, which have very similar carbonyl environments, are expected to exist in solid state, since only one band of carbonyl stretching frequency (CO) is observed.

In the compound (1), two geometrical isomers sets for (1)-a, (1)-b and (1)-c, (1)-d are clearly separated in the chemical shift of the hydride resonance because there are definitely different chemical environments (all phosphorous *cis* to hydride and one phosphorus trans to hydride) around hydride. However between diastereomers, the chemical shift differences become very small (*ca.* ppm = 0.1). These very small differences derived from the diastereomeric relationship can be visualized from the view of the steric crowdedness as shown below.

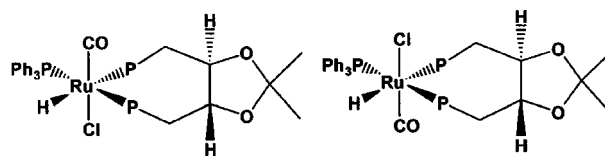


In general, a chiral bidentate phosphine ligand imposes a rigid C_2 symmetric environment to the metal center *via* fixing the conformation of the diphosphine- and metal containing chelating ring. This conformational rigidity in turn determines the chiral dispositions of the four phenyl rings on the phosphorous atoms: two phenyl rings are oriented in axial directions and the others in equatorial directions. These equatorial phenyls play a major role to the environment around the metal center.¹²

The diastereomeric differentiation of the two sets of quad-

rant space sectors is made in a way that one diastereomer is more crowded in their PPh_3 containing quadrant space sector. However the chemical shift data to those isomers could not be precisely assigned because of the similarity of the chemical environment on the hydride.

In the case of the complex $\text{RuHCl}(\text{CO})(\text{R-diop})$ (2), it is very interesting to observe that there are only two hydride resonance peaks at -5.3 ppm ($^2J_{\text{P-H}}$ 108, 25, 18 Hz) and -6.5 ppm ($^2J_{\text{P-H}}$ 111, 26, 22 Hz) as a doublet of doublet of doublet, respectively. The geometry of the compound (2) is assigned from the same logic¹¹ as that used for the $\text{RuHCl}(\text{CO})(\text{PPh}_3)(\text{s,s-chiraphos})$. IR spectra also support such assignment for compound (2). Slight shift of $\nu(\text{CO})$ after substitution shows that the trans position of the chloride to the carbonyl group is occupied by good π -accepting ligand such as PPh_3 or chelating $-\text{PPh}_2$ moiety, Ru (d-orbital) $\text{P}(\pi^*$ orbital) back-donation should result in higher $\nu(\text{CO})$ frequency. The reason why two isomers at upper field are suppressed is unclear.



For the analogous $[\text{RuH}(\text{CO})(\text{NCMe})_2(\text{PPh}_3)_2]\text{BF}_4$ cationic complexes of *s,s*-chiraphos and R-diop, they show too many isomers in the solution regardless of the reaction condition, though in solid state they exhibit only one band of $\nu(\text{CO})$. As we reported earlier, the cationic $[\text{RuH}(\text{CO})(\text{NCMe})_2(\text{PPh}_3)_2]\text{BF}_4$ complex gives several isomers when reacted with bidentate phosphine ligand. Furthermore, they also have the isomerization process in the solution.¹³

The chiral bidentate ligands used in this study have yielded quite interestingly more than two isomers during the preparation of ruthenium(II) complexes except for R-diop ruthenium(II) hydrido carbonyl system. These observations could be interpreted as a way that the additional chirality in the ruthenium hydrido carbonyl system *via* chiral bidentate ligands acts as a plane that discriminate carbonyl-side and chloride-side of the complex. Therefore the *s,s*-chiraphos ruthenium(II) hydrido carbonyl system results in four isomers compared to the analogous dppe ruthenium hydrido carbonyl system, which gives only two geometrical isomers. Interestingly, the R-diop ruthenium(II) hydrido carbonyl system, unlike the *s,s*-chiraphos ruthenium(II) hydrido carbonyl system, suppresses the up-field isomers. In this case, the large seven-membered ring of the diop-ruthenium(II) chelation may play a crucial role. Other ruthenium(II) cationic complexes give more complicated results which may be due to their labile nature of the nitrile ligands causing many coordination modes. This phenomenon would show negative results as a catalyst for asymmetric synthesis, but generally the "usual catalyst" is a not an 18 electron species but a 16 electron species *via* one ligand dissociation.¹¹ Under

these circumstances, the disruption of the molecular symmetry should give another species which have different ligand geometry around a central metal atom.

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