

Articles

Synthesis, Characterization, Diastereoselectivity, and Catalytic Activity of Complexes of Ruthenium with BINAP Monoxide

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The bisphosphine monoxides (*R*)- and (*S*)-BINPO, prepared by the monooxidation of (*R*)- and (*S*)-BINAP, respectively, form complexes [CyRuCl(η^2 -BINPO-*P,O*)]X (X = Cl[−], (*R*)-BINPO, **1**, (*S*)-BINPO, **1'**; or SbF₆[−], **2** and **2'**) and [CyRu(η^2 -BINPO-*P,O*)](SbF₆)₂, **3** and **3'**. The new compounds were characterized spectroscopically and in the case of **2'** by single-crystal X-ray diffraction. The BINPO ligand binds diastereoselectively, and one observes only a single thermodynamically stable diastereomer of the two possible isomers. Compound **3** is an efficient catalyst for the condensation of methacrolein and cyclopentadiene in moderate ee.

Introduction

There has been an increasing interest in chelating ligands that contain mixed donor sets. Complexes of such ligands offer a number of attractive features, especially in the case of complexes that have potential application in homogeneous catalysis. One feature is that the different donors can produce an electronic asymmetry at the metal. Another is that the ligands may be hemilabile. With this in mind, a number of groups have developed the use of bisphosphine monoxide (BPMO) ligands in coordination chemistry.¹

A report has appeared recently giving an efficient route to BPMO ligands derived from well-known bisphosphine ligands, including a number of commercially available chiral examples.² The monooxidized forms of these ligands offer some features not available to their unoxidized counterparts. First, upon chelation, they give rise to complexes that have a more pronounced steric asymmetry, as the organic substituents attached to the P(III) are very much closer to the metal center than those on the P(V). Second, the two donor atoms are now markedly dissimilar, and their different electronic properties may have a significant influence upon the bonding of other ligands coordinated to the metal center, thereby altering the stereochemistry of reaction inter-

mediates.^{3,4} Third, coordination of a BPMO to a fragment of the type [(arene)MX] (arene = η^6 -C₆H₆ or derivative, η^5 -(C₅H₅)[−] or derivative, M = transition metal, X = Cl[−], etc.) yields a chiral metal center,⁵ which may further enhance the selectivity of such a reagent.

As part of our continuing study of the application of heterobidentate ligands to homogeneous catalysis,⁶ we report here the preparation, characterization, and catalytic behavior of complexes of ruthenium(II) with BINPO (monooxidized BINAP).

Results and Discussion

The interaction of [CyRuCl₂]₂ with either (*R*)- or (*S*)-BINPO in dichloromethane gives a deep red solution with a complex ³¹P{¹H} NMR spectrum. Upon standing at room temperature for 48 h, the spectrum simplifies greatly to an AX pattern typical of η^2 coordination of a BPMO ligand. The chelation gives the complex [CyRuCl(η^2 -BINPO-*P,O*)]Cl (for (*R*)-BINPO, **1**; (*S*)-BINPO, **1'**), which is chiral at the metal center. Since only one set of resonances is observed in the NMR spectra of both **1** and **1'**, it seems that one of the two possible η^2 -isomers is thermodynamically preferred in each case (see Figure 1). This suggests that chelation proceeds diastereoselectively, Scheme 1. Anion metathesis of these compounds gives the hexafluoroantimonate salts **2** and **2'**; the latter was characterized crystallographically and is

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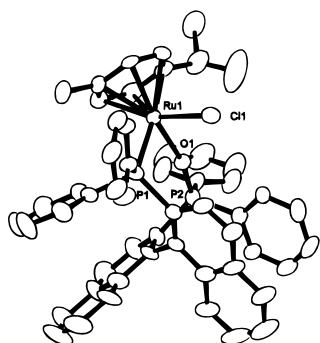
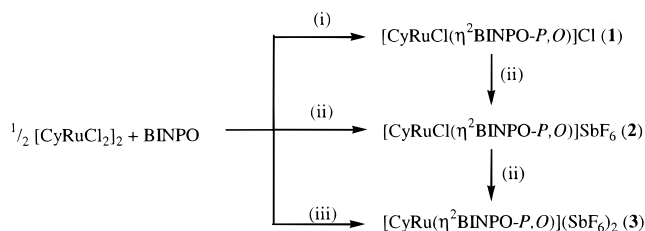


Figure 1. ORTEP view of the cation in (R_{Ru}) -[CyRuCl(η^2 -(*S*)-BINPO-*P,O*)]SbF₆, **2'**, with 50% probability ellipsoids.

Scheme 1^a



^a (i) 48 h, CH₂Cl₂, 25 °C. (ii) AgSbF₆, (–AgCl) CH₂Cl₂, 25 °C. (iii) 2 AgSbF₆ (–2 AgCl) CH₂Cl₂, 25 °C.

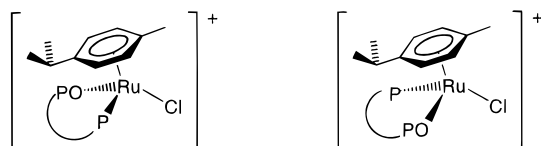


Figure 2. The two possible diastereomers of a [CyRuCl(η^2 -BINPO-*P,O*)]⁺ cation.

Table 1. Crystallographic Data for X-ray Diffraction Study of (R_{Ru}) -[CyRuCl(η^2 -(*S*)-BINPO-*P,O*)]SbF₆, **2'**

formula	SbRuClP ₂ F ₆ OC ₅₄ H ₄₆
cryst syst	monoclinic
space group	<i>P</i> 2 ₁ (No. 4)
<i>a</i> , Å	12.3028(2)
<i>b</i> , Å	15.2403(4)
<i>c</i> , Å	12.9278(2)
β , deg	97.600(1)
<i>V</i> , Å ³	2402.65(7)
fw	1145.17
ρ_{calcd} , g/cm ³	1.583 (<i>Z</i> = 2)
abs coeff (cm ^{−1})	10.60
cryst size, mm	0.17 × 0.07 × 0.02
diffractometer	Nonius KappaCCD
monochromator	graphite
radiatn	Mo K α (0.71073 Å)
max 2 θ , deg	55
no. of refl measured	32 346
no. of data used, $F^2 > 3\sigma(F^2)$	3584
no. of params refined	594
<i>p</i> factor	0.01
final residuals <i>R</i> , <i>R</i> _w	0.033, 0.036
convergence, largest shift/error	0.00
GOF	0.93
largest $\Delta(\rho)$, e Å ^{−3}	1.14

shown in Figure 2. Crystal data and solution parameters are given in Table 1 and metrical parameters in Table 2. The same compound can be prepared directly from the sequential addition of 2 equiv of BINPO and 2 equiv of AgSbF₆ to a solution of [CyRuCl₂]₂.

The (R_{Ru}) -[CyRuCl(η^2 -(*S*)-BINPO-*P,O*)]SbF₆ structure found for **2'** shows that the preferred diastereomer has

Table 2. Selected Bond Distances (Å) and Angles (deg) for [CyRuCl(η^2 -(*S*)-BINPO-*P,O*)]SbF₆, **2'**

Ru(1)–Cl(1)	2.388(2)	Ru(1)–P(1)	2.395(2)
Ru(1)–O(1)	2.138(4)	P(2)–O(1)	1.493(4)
Cl(1)–Ru(1)–P(1)	84.68(7)	Cl(1)–Ru(1)–O(1)	87.6(2)
P(1)–Ru(1)–O(1)	81.5(1)	Ru(1)–O(1)–P(2)	165.9(3)

Table 3. Catalysis of the Diels–Alder Reaction of Methacrolein and Cyclopentadiene by **3**

mol %	reaction time (h)	temperature (°C)	base	ee (%)	exo:endo
10	12	−12.0		5 (<i>R</i>)	5.6:1
10	12	−12.0	lutidine	19 (<i>R</i>)	10.4:1
10	18	−24.0		27 (<i>R</i>)	5.4:1
10	18	−24.0	lutidine	50 (<i>R</i>)	9.9:1
5	18	−24.0		24 (<i>R</i>)	5.5:1
5	18	−24.0	lutidine	47 (<i>R</i>)	9.8:1

the relative configuration of R^*S^* . Although there might be expected to be some modest flexibility from rotation about the bond connecting the naphthyl groups, they are approximately at right angles with a dihedral angle between them of 83.6°.

The configuration of the binaphthyl portion of the ligand apparently forces a configuration of the Ph₂P fragment that sterically controls the preference for direction of chelation. The ligand backbone requires an unusually large Ru–O–P angle of 165.9(3)°. Even though there is an eight-membered chelate ring, it produces a quite small bite angle of 81.5(1)°.

Although the coordination about the metal can be considered pseudotetrahedral, one should note that all of the angles between the P, O, and Cl are less than 90°. Comparison with the dppmO analogue, which has a five-membered chelate ring, produces only a slightly smaller bite angle of 80.8°. ^{1a} The chiraphosO analogue, with six-membered chelate rings, has larger bite angles of 82.2(4)° or 83.8(3)° depending upon the diastereomer. ⁶

Further treatment of **2** or **2'** with AgSbF₆ or sequential reaction of 2 equiv of BINPO and 4 equiv of AgSbF₆ with [CyRuCl₂]₂ gives the doubly charged complex ions [CyRu(η^2 -BINPO-*P,O*)](SbF₆)₂, **3** and **3'**. The likelihood of the cation in **3** or **3'** existing as coordinatively unsaturated species as written is limited, especially in solution, where they probably exist as solvates, but since the exact nature of the compounds is uncertain, they are written here as the “free” Lewis acids.

This dipositive cation is a strong Lewis acid, and **3** can be used to catalyze the condensation of cyclopentadiene and methacrolein. ⁶ We had observed very modest enantioselectivity in this reaction with the chiraphosO analogue; however, [CyRuX(η^2 -chiraphosO-*P,O*)]²⁺ complexes are not formed with as high diastereoselectivity at the metal center⁷ as found for the BINPO complex. The six-membered chelate ring for the chiraphos derivative assumes a boat conformation in one diastereomer and a chair conformation and thus accommodates the steric interactions associated with the (R_{Ru}) and (S_{Ru}) more readily than BINPO, which does not have the same options. This suggested that the BINPO derivative should yield better enantioselectivity. Some results for this reaction with **3** are presented in Table 3. Compound **3** is the first example of a BINPO-supported Lewis acid used to catalyze a Diels–Alder

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reaction. The enantiomeric excess observed in the product is enhanced by the addition to the catalytic reaction of half an equivalent of 2,6-lutidine (with respect to the ruthenium), as is the exo:endo ratio. The influence of a noncoordinating base on the course of the reaction is most likely the suppression of any catalysis by other competing Lewis acids in solution, such as unligated metal ions or protons arising from adventitious water in the reaction mixture.⁸ Since the incorporation of base into the catalytic reaction system results in an increase in selectivity, for both ee and exo:endo, it can be inferred that the nonenantioselective production of the bicyclic aldehyde is promoted by such stray acid. The origin of the decreased formation of the endo isomer is less obvious. The α -substituent on the methacrolein favors exo isomer formation, even for the thermal reaction (exo:endo \approx 5:1), and acid catalysis usually results in larger exo:endo ratios. Kundig et al.^{7a} have suggested that hydrogen bonding to anions has a significant effect on rate and to some minor extent on ee. The addition of base could possibly compete for hydrogen-bonding sites and alter the ion pairing. In the crystal structure of **2** there are several close contacts between fluoride and H on the ligands, which might be considered weak hydrogen bonds,⁹ for example there is a 2.25 Å distance between a cymene C–H (at 1.09 Å) and an F on the SbF_6^- . There certainly would be ion pairing in solution, regardless of the nature of the interactions, and it could be altered by additives. Alternatively, donor–acceptor interactions of the lutidine with the reactants could be the source of the variation in exo:endo ratio, unrelated to a proton-catalyzed path.

Conclusions

The unusually large metal–P–O bond angle in the BINPO complex provides a particularly low steric requirement at the P=O donor site, compared to that of the Ph_2P donor site. We anticipate that this steric differential, in addition to the electronic asymmetry provided by the P,O-donor set, may be ultimately useful in a broader set of catalytic Lewis acid reactions, and we are currently investigating the use of this and other metal–BINPO complexes as Lewis acid catalysts.

Experimental Section

All manipulations were performed under an atmosphere of nitrogen using standard Schlenk and drybox techniques. Solvents were dried and distilled before use according to published protocols.¹⁰ AgSbF_6 and BINAP were obtained from a commercial source (Aldrich) and used as received. $[\text{CyRuCl}_2]_2$ was prepared according to literature methods.¹¹ (*R*)-BINPO and (*S*)-BINPO were prepared by a recently published litera-

ture method.² The NMR spectra were recorded of solutions in CDCl_3 at 500.08 MHz (^1H) or 202.43 MHz (^{31}P) on a GE Omega 500 spectrometer. Chemical shifts are reported in ppm relative to residual protio solvent resonances (^1H) or external 85% H_3PO_4 (^{31}P). Microanalyses were performed by Atlantic Microlabs. For brevity, details of the preparation and characterization of **1–3** only are given.

Preparation of $[\text{CyRuCl}(\eta^2\text{-BINPO-}P,O)]\text{Cl}$, **1.** (*R*)-BINPO (27 mg, 0.042 mmol) was added as a solid to a dichloromethane solution (5 mL) of $[\text{CyRuCl}_2]_2$ (13 mg, 0.021 mmol). The solution darkened to a deep red over a period of 2 h. After 48 h, the solvent was removed and the residue recrystallized in quantitative yield from dichloromethane–diethyl ether. ^1H NMR (CDCl_3 , 293 K, δ): 8.15–6.48 (32 H, m, aromatic) 6.10 (1H, d, $J = 6$ Hz, CyC-H) 5.98 (1H, d, $J = 6$ Hz, CyC-H) 5.72 (1H, d, $J = 6$ Hz, CyC-H) 5.40 (1H, d, $J = 6$ Hz, CyC-H) 2.46 (1H, septet, $J = 7$ Hz $\text{CyCH}(\text{CH}_3)_2$) 1.29 (3H, s, CyCH_3) 1.18 (3H, d, $J = 7$ Hz, $\text{CyCH}(\text{CH}_3)-\text{CH}_3$) 0.98 (3H, d, $J = 7$ Hz, $\text{CyCH}(\text{CH}_3)-\text{CH}_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR: P(V) 40.01 (d, $^3J^{31}\text{P}$ 63 Hz) P(III) 24.77 (d, $^3J^{31}\text{P}$ 63 Hz). Anal. Calcd for $\text{C}_{54}\text{H}_{46}\text{O}_2\text{P}_2\text{Cl}_2\text{Ru}$: C, 68.64; H, 4.91. Found: C, 68.40; H, 5.07. $\nu(\text{P=O})$ (KBr): 1094 cm^{-1} .

Preparation of $[\text{CyRuCl}(\eta^2\text{-BINPO-}P,O)]\text{SbF}_6$, **2.** (*R*)-BINPO (27 mg, 0.042 mmol) was added as a solid to a dichloromethane solution (5 mL) of $[\text{CyRuCl}_2]_2$ (13 mg, 0.021 mmol). The solution darkened to a deep red over a period of 2 h. AgSbF_6 was added (14 mg, 0.042 mmol) as a solution in dichloromethane (1 mL). A white precipitate of AgCl formed immediately, and after 10 min of stirring, the reaction mixture was centrifuged and the supernatant removed by syringe. The solvent was removed from the supernatant fraction and the residue recrystallized in quantitative yield from dichloromethane–diethyl ether. ^1H NMR (CDCl_3 , 293 K, δ): 8.15–6.50 (32 H, m, aromatic) 6.12 (1H, d, $J = 6$ Hz, CyC-H) 5.99 (1H, d, $J = 6$ Hz, CyC-H) 5.68 (1H, d, $J = 6$ Hz, CyC-H) 5.44 (1H, d, $J = 6$ Hz, CyC-H) 2.48 (1H, septet, $J = 6.5$ Hz $\text{CyCH}(\text{CH}_3)_2$) 1.25 (3H, s, CyCH_3) 1.14 (3H, d, $J = 6.5$ Hz, $\text{CyCH}(\text{CH}_3)-\text{CH}_3$) 0.98 (3H, d, $J = 6.5$ Hz, $\text{CyCH}(\text{CH}_3)-\text{CH}_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR: P(V) 40.10 (d, $^3J_{\text{P-P}} = 61$ Hz) P(III) 26.14 (d, $^3J_{\text{P-P}} = 61$ Hz). Anal. Calcd for $\text{C}_{54}\text{H}_{46}\text{OF}_6\text{P}_2\text{ClRuSb}$: C, 56.64; H, 4.05. Found: C, 56.14; H, 4.34. $\nu(\text{P=O})$ (KBr): 1096 cm^{-1} .

Preparation of Solutions of $[\text{CyRu}(\eta^2\text{-BINPO-}P,O)]\text{-(SbF}_6)_2$, **3.** Compound **3** was prepared in situ for catalytic reactions and was characterized spectroscopically. BINPO (27 mg, 0.042 mmol) was added as a solid to a dichloromethane solution (5 mL) of $[\text{CyRuCl}_2]_2$ (13 mg, 0.021 mmol). The solution darkened to a deep red over a period of 2 h. AgSbF_6 was added (29 mg, 0.084 mmol) as a solution in dichloromethane (1 mL). A white precipitate of AgCl formed immediately, and after 10 min of stirring, the reaction mixture was centrifuged and the supernatant removed by syringe. The solution was used directly for the catalytic reactions. ^1H NMR (CDCl_3 , 293 K, δ): 8.12–6.4 (32H, m, aromatic) 6.28 (1H, d, $J = 5.9$ Hz, CyC-H) 6.10 (1H, d, $J = 5.9$ Hz, CyC-H) 5.88 (1H, d, $J = 5.9$ Hz, CyC-H) 5.61 (1H, d, $J = 5.9$ Hz, CyC-H) 2.61 (1H, septet, $J = 7$ Hz $\text{CyCH}(\text{CH}_3)_2$) 1.41 (3H, s, CyCH_3) 1.22 (3H, d, $J = 7$ Hz, $\text{CyCH}(\text{CH}_3)-\text{CH}_3$) 1.08 (3H, d, $J = 7$ Hz, $\text{CyCH}(\text{CH}_3)-\text{CH}_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR: P(V) 66.37 (s) P(III) 52.18 (s). $\nu(\text{P=O})$ 1022 cm^{-1} .

X-ray Crystallography. Single crystals suitable for X-ray analysis were formed by vapor diffusion of diethyl ether into a methanol solution of **2'**. Crystallographic data are summarized in Table 1. The structure of **2'** was determined from data collected with a Nonius KappaCCD at -90°C . Lorentz and polarization corrections were applied to all data. An empirical absorption correction was applied using SORTAV.¹²

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Intensities of equivalent reflections, excluding Friedel pairs, were averaged. The structure was solved by direct methods (SIR92¹³) using the teXan crystal structure analysis package, and the function minimized was $\sum w(|F_o| - |F_c|)^2$ in all cases. Hydrogen atoms were placed at calculated positions before each refinement and were included in the refinement, but were not refined. Large thermal parameters for the cymene isopropyl group were observed, indicating a small disorder in the orientation of the isopropyl group. The absolute configuration was determined by reference to the configuration of the (S)-

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BINPO. This was confirmed by refinement of the inverted structure, which gave $R = 0.035$ and $R_w = 0.040$; whereas the reported coordinates gave $R = 0.033$ and $R_w = 0.036$. This (+)-(R_{Ru})-[CyRuCl(η^2 -(S)-BINPO-*P,O*)]SbF₆ shows a positive CD band at 490 nm and a negative CD band at 392 nm.

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Supporting Information Available: Tables of crystal data, positional and thermal parameters, and bond lengths and angles for **2'**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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