

Stoichiometric and Catalytic Oxidation of BINAP by Dioxygen in a Rhodium(I) Complex

Kevin A. Bunten, David H. Farrar, Anthony J. Poë,* and Alan Lough

Department of Chemistry, University of Toronto, 80 St. George Street,
Toronto, Ontario, Canada M5S 3H6

Received March 28, 2002

The square planar complex (BINAP)Rh(CO)Cl (BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl) was synthesized from [Rh(COD)Cl]₂ (COD = 1,5 cyclooctadiene) and BINAP under a CO atmosphere. It reacts with oxygen to form the square planar (BINAP(O))Rh(CO)Cl in approximately 50% yield, along with molar equivalents of free BINAP dioxide (BINAP(O)₂) and CO₂. The oxygen atom of the BINAP(O) was shown crystallographically to be *trans* to the CO ligand. In the presence of excess BINAP under CO/O₂ gas mixtures, the reaction is catalytic with a TOF of 0.16 h⁻¹ at ambient temperature in chloroform. The kinetics of this transformation were investigated and conditions for optimum selectivity for BINAP(O) formation suggested. A stoichiometric mechanism is proposed that involves initial formation of an O₂ adduct, followed by oxygen atom transfer to both phosphorus atoms of BINAP or to one phosphorus atom and the CO ligand *trans* to it. These processes might be concerted, or stepwise with intermediate Rh=O species. To the best of our knowledge, this chemistry represents the first example of a reaction exhibiting oxygen atom addition from O₂ either to both phosphorus atoms in a bisphosphine ligand or to one phosphorus atom and a CO ligand in the same complex.

Introduction

Synthesis and properties of bisphosphine monoxide (BPMO) complexes are currently of interest. The combination of a hard oxygen moiety with a soft phosphorus center in the same ligand may lead to hemilabile^{1–7} behavior, resulting in the generation of potential coordination sites required for substrate activation. These unsymmetrical ligands can also generate chirality and electronic asymmetry at the metal center, and this may lead to efficient chiral catalysis.^{8–11}

Phosphorus ligands play an important role in determining the outcome of many catalytic processes, and complexes containing BPMO ligands have been successfully employed as catalysts for a variety of synthetic applications.^{12–17} BINAP (2,2'-bis(diphenylphosphino)-

1,1'-binaphthyl) rhodium and ruthenium complexes are well-studied catalysts for enantioselective hydrogenation^{18–22} of olefins and ketones. The presence of a mono-oxidized BINAP in an organometallic catalyst may have interesting consequences.⁹

Selective oxidation of bisphosphines to BPMOs is difficult,^{23–26} and general routes are very rare. Additionally, there is very little mechanistic research into this area of chemistry,²⁴ although Grushin has recently reported a full account²⁵ of his catalytic and selective oxidation of several bisphosphines by Pd(II) catalysts in the presence of alkali and 1,2-dibromoethane.

The syntheses of square planar complexes of the type RhL₂(CO)Cl are well documented in the literature.^{27–29} However, square planar complexes of chelating phosphine ligands are quite rare because many bisphosphine

* To whom correspondence should be addressed. E-mail: apoe@chem.utoronto.ca.

- (1) Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27.
- (2) Slone, C. S.; Weinburger, D. A.; Mirkin, C. A. *Prog. Inorg. Chem.* **1999**, *5*, 233.
- (3) Braunstein, P.; Frison, C.; Morise, X.; Adams, D. *J. Chem. Soc., Dalton Trans.* **2000**, 2205.
- (4) Coyle, R. J.; Slovokhotov, Y. L.; Antipin, M. Y.; Grushin, V. V. *Polyhedron* **1998**, *17*, 3059.
- (5) Brassat, I.; Englert, U.; Keim, W.; Keitel, D. P.; Killat, S.; Suranna, G.-P.; Wang, R. *Inorg. Chim. Acta* **1998**, *280*, 150.
- (6) Grim, S. O.; Walton, E. D. *Inorg. Chem.* **1980**, *19*, 1982.
- (7) Grim, S. O.; Satek, L. C.; Tolman, C. A.; Jesson, J. P. *Inorg. Chem.* **1975**, *14*, 656.
- (8) Faller, J. W.; Grimmond, B. J.; D'Allesio, D. G. *J. Am. Chem. Soc.* **2001**, *123*, 2525.
- (9) Gladiali, S.; Medici, S.; Kégl, T.; Kollar, L. *Monatsh. Chem.* **2000**, *131*, 1351.
- (10) Faller, J. W.; Parr, J. *Organometallics* **2000**, *19*, 1829.
- (11) Faller, J. W.; Liu, X.; Parr, J. *Chirality* **2000**, *12*, 325.
- (12) Roch-Neirey, C.; LeBris, N.; Laurent, P.; Clement, J.-C.; Abayes, H. *Tetrahedron Lett.* **2001**, 643.
- (13) Faller, J. W.; Patel, B. P.; Albrizzio, M. A.; Curtis, M. *Organometallics* **1999**, *18*, 3096.

- (14) Mecking, S.; Keim, W. *Organometallics* **1996**, *15*, 2656.
- (15) Wegman, R. W.; Abatjoglou, A. G. U.S. Patent 4670570, 1987.
- (16) Wegman, R. W.; Abatjoglou, A. G.; Harrison, A. M. *J. Chem. Soc., Chem. Commun.* **1987**, 1891.
- (17) Wegman, R. W. U.S. Patent 4563309, 1986.
- (18) Proctor, G. *Asymmetric Synthesis*; Oxford University Press: Oxford, 1996.
- (19) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley: New York, 1994.
- (20) *Catalytic Asymmetric Synthesis*; Ojima, I. Ed.; VCH: New York, 1993.
- (21) Abdur-Rashid, K.; Lough, A. J.; Morris, R. H. *Organometallics* **2001**, *20*, 1047.
- (22) James, B. R. *Catal. Today* **1997**, *37*, 209.
- (23) Cyr, P. W.; James, B. R. *Proceedings of the 83rd Canadian Society for Chemistry Conference*, Calgary, May 2000, Abstract no. 156.
- (24) Grushin, V. *J. Am. Chem. Soc.* **1999**, *121*, 5831.
- (25) Grushin, V. *J. Am. Chem. Soc.* **2001**, *123*, 3950, and references therein.
- (26) Abatjoglou, A. G.; Kapicak, L. A. U.S. Patent 4429161, 1984.
- (27) Vaska, L.; Peone, J. *J. Chem. Soc., Chem. Commun.* **1971**, 418.
- (28) Intille, G. M. *Inorg. Chem.* **1972**, *4*, 695.
- (29) Vallarino, L. *J. Chem. Soc.* **1957**, 2287.

ligands prefer a bridging orientation rather than an η^2 -binding mode as in $\text{Rh}(\eta^2\text{-dppe})(\text{CO})\text{Cl}$.^{30–32}

Reactions of metal carbonyl complexes of the type $\text{RhL}_2(\text{CO})\text{Cl}$ with oxygen have received relatively little attention. Foote et al.^{33,34} demonstrated that reaction of $\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}$ with singlet oxygen at -40°C forms an analogue of the well-known Vaska's adduct ($\eta^2\text{-O}_2$)- $\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}$,^{35–38} but the Rh complex rapidly loses its oxygen on warming to room temperature. When triplet oxygen is used, in the presence or absence of excess phosphine, reaction leads to the formation of phosphine oxide, CO_2 , and mixtures of rhodium complexes of the formula $\text{Rh}_4\text{Cl}_4(\text{CO})_4(\text{O}_2)_2\text{L}_2$ ($\text{L} = \text{PPh}_3$, PPhEt_2 , PEt_3 , and $\text{PPh}_2(\text{O}-i\text{Bu})$).^{39,40} Others have managed to prepare a variety of Rh dioxygen complexes using phosphines,^{41–44} iminophosphines,⁴⁵ and benzenethiolate ligands.⁴⁶

We report herein the synthesis, via $[\text{Rh}(\text{BINAP})\text{Cl}]_2$ (**1**) and $\text{Rh}(\text{BINAP})(\text{CO})\text{Cl}$ (**2**), of the square planar rhodium BPMO complex (BINAP(O)) $\text{Rh}(\text{CO})\text{Cl}$ (**3**), which is formed by O_2 oxidation of **2**. BINAP dioxide (BINAP(O)₂) and CO_2 are formed in equivalent amounts, and some unidentified products are also formed. In the presence of excess BINAP under CO/O_2 gas mixtures, **2** behaves as an oxygenation catalyst transforming BINAP quantitatively into a mixture of BINAP(O) and BINAP(O)₂. Kinetics for the formation of **3** from **2**, as well as for the catalytic oxidation of BINAP, are described.

Experimental Section

Summary. Details of all experimental procedures are given in the Supporting Information (SI). All chemical manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques⁴⁷ unless otherwise stated. Syntheses of compounds **1**, **2**, and **3** according to Scheme 1 are described in full in the SI pages. The products were characterized by solution FTIR and NMR spectroscopy, mass spectroscopy, and single-crystal X-ray crystallography.

X-ray data were collected on a Nonius Kappa CCD diffractometer using graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). A combination of $1^\circ \phi$ and ω (with κ offsets) scans were used to collect sufficient data. The data frames were

(30) Hughes, R. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, G., Abel, E., Eds.; Pergamon Press: Oxford, 1982; Vol. 5, pp 277–540.

(31) Dyer, G.; Wharf, R. M.; Hill, W. E. *Inorg. Chim. Acta* **1987**, 133, 137.

(32) Sanger, A. *J. Chem. Soc., Dalton. Trans.* **1977**, 120.

(33) Selke, M.; Foote, C. S. *J. Am. Chem. Soc.* **1993**, 115, 1166.

(34) Selke, M.; Foote, C. S.; Karney, W. L. *Inorg. Chem.* **1993**, 24, 5425.

(35) Vaska, L. *Acc. Chem. Res.* **1976**, 9, 175.

(36) Vaska, L. *Inorg. Chim. Acta* **1971**, 5, 295.

(37) Vaska, L.; Bath, S. S. *J. Am. Chem. Soc.* **1966**, 88, 1333.

(38) Vaska, L. *Science* **1963**, 140, 840.

(39) Cullen, W. R.; James, B. R.; Strukul, G. *Inorg. Chem.* **1978**, 17, 484.

(40) Geoffroy, G.; Denton, D. A.; Keeney, M. E.; Bucks, R. R. *Inorg. Chem.* **1976**, 15, 2382.

(41) Bennett, M. J.; Donaldson, P. B. *Inorg. Chem.* **1977**, 16, 1581.

(42) Bennet, M. J.; Donaldson, P. B. *J. Am. Chem. Soc.* **1971**, 93, 3307.

(43) Aresta, M.; Quartanta, E.; Ciccarese, A. *Chim. Mol. Chem.* **1985**, 1, 267.

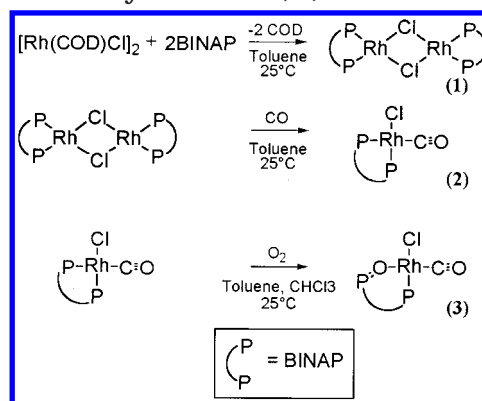
(44) Bennet, M. J.; Donaldson, P. B. *Inorg. Chem.* **1977**, 16, 1585.

(45) Ghilardi, C. A.; Midollini, S.; Moneti, S.; Orlandini, A.; Scapacci, G. *J. Chem. Soc., Dalton Trans.* **1992**, 3371.

(46) Oskada, K.; Hataya, K.; Yamamoto, T. *Inorg. Chem.* **1993**, 32, 2360.

(47) Shriver, D. F.; Drezdson, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

Scheme 1. General Reaction Scheme for the Synthesis of **1**, **2**, and **3**



integrated and scaled using the Denzo-SMN package.⁴⁸ Data were corrected for absorption effects by the program Denzo-SMN, which uses the high redundancy of the data to apply a scale to each frame of data. The structures were solved and refined on F^2 using the SHELXTL/PC V5.03 package.⁴⁹

Concentrations of oxygen in chloroform were estimated by the method of Wilhelm et al.⁵⁰ and corrected for solvent vapor pressure.⁵¹ They were based on tabulated solubilities⁵² in chloroform, and solubilities in 1,2-dichloroethane were assumed to be the same. Concentrations of CO_2 were based on molar absorbances estimated from solutions of known concentration of $\text{Ru}_3(\text{CO})_{12}$ to which an excess of $[\text{n-Bu}_4][\text{OH}]$ had been added, so generating an exact equivalent of CO_2 .⁵³

Reactions **2** \rightarrow **3**, in chloroform at various temperatures and under atmospheres of pure O_2 or O_2/N_2 mixtures, were monitored by IR spectrophotometry in thermostated cells, and rate constants were obtained from single-exponential analysis of absorbance changes of the C–O stretching bands of the complexes involved. Corresponding reactions in 1,2-dichloroethane at 25°C were carried out in Schlenk tubes with continuous bubbling of the O_2 or O_2/N_2 gases and with periodic sampling and IR spectral measurements.

Catalytic Reactions in Chloroform and Toluene. Catalytic reactions using excess BINAP were all performed in a similar manner. In a typical experiment, mixtures of **2** and a 10-fold or greater excess of BINAP in chloroform or toluene were reacted under a CO/O_2 gas mixture controlled by gas-flow meters. After a predetermined time, the IR spectrum was recorded and the solvent was subsequently evaporated. The residue was extracted into CDCl_3 and the solution $^31\text{P}\{^1\text{H}\}$ NMR spectrum was recorded and integrated to give yields of BINAP, BINAP(O), and BINAP(O)₂.

Results

Synthesis and Structure. Synthesis. Complex **2** was prepared from **1** by the well-known bridge splitting method^{29–32} (Scheme 1) and undergoes slow oxidation in solution or in the solid state forming (BINAP(O)) $\text{Rh}(\text{CO})\text{Cl}$ (**3**) in up to ca. 50% yield. However, in the presence of a 2-fold excess of BINAP, under a CO/O_2 (1:1) gas mixture, **3** is formed quantitatively, as observed by monitoring the intensity of the infrared

(48) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, 276, 307.

(49) Sheldrick, G. M. *SHELXTL/PC V5.1*; Bruker Analytical X-ray Systems: Madison, WI, 1997.

(50) Wilhelm, E.; Battino, R. *Chem. Rev.* **1973**, 73, 1.

(51) Timmermans, J. *Physicochemical Constants of Pure Organic Compounds*; Elsevier: Amsterdam, 1950; pp 218–221.

(52) *Solubilities of Inorganic and Organic Compounds*; Stephen, H., Stephen, T., Eds.; The MacMillan Company: New York, 1963; Vol. 1, pp 574–575.

(53) Gross, D. C.; Ford, P. *J. Am. Chem. Soc.* **1985**, 107, 585.

Table 1. Infrared ν_{CO} (cm^{-1}) Absorbance Bands for Compounds **2 and **3****

solvent	2	3
CHCl_3	2018	1986
CH_2Cl_2	2010	1979
$\text{ClCH}_2\text{CH}_2\text{Cl}$	2007	1977

Table 2. $^{31}\text{P}\{^1\text{H}\}$ NMR Data for Selected Compounds

compound	$^{31}\text{P}\{^1\text{H}\}$ NMR (δ ppm)
1 ^a	50 (d, $J_{\text{RhP}} = 195$ Hz)
2 ^b	46.1 (d of d, $J_{\text{RhP}} = 163$ Hz, $J_{\text{PP}} = 44$ Hz), 24.9 (d of d, $J_{\text{RhP}} = 128$ Hz, $J_{\text{PP}} = 44$ Hz)
3 ^b	48.6 (d, $J_{\text{RhP}} = 175$ Hz), 41.5 (s)
$\text{BINAP}(\text{O})$ ^b	28.1 (s), -14.3
$\text{BINAP}(\text{O})_2$ ^b	29.3 (s)

^a C_6D_6 , ^b CDCl_3

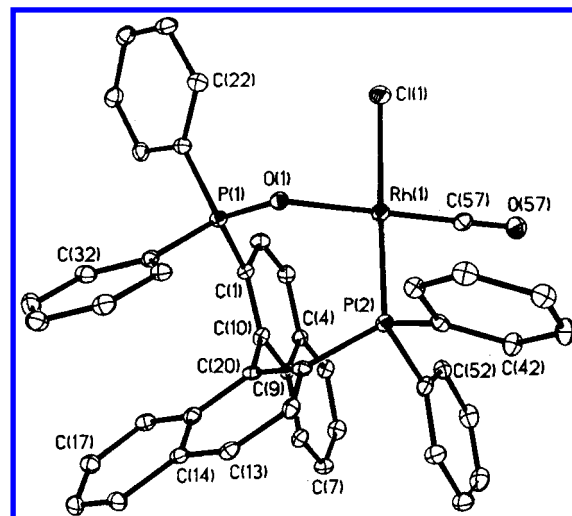
carbonyl stretching bands. The addition of excess BINAP to solutions of **3** leads to rapid and quantitative re-formation of **2**. Compounds **1**, **2**, and **3** were characterized by X-ray crystallography (Table S1), solution FTIR analysis of the ν_{CO} stretching frequencies (Table 1), solution $^{31}\text{P}\{^1\text{H}\}$ NMR (Table 2), and mass spectrometry. The purity of the compounds was demonstrated by the sharpness of the bands in the NMR spectra and the absence of any that were attributable to possible significant impurities (Figures S1–S3). The IR spectra of **2** and **3** also showed sharp single bands with no shoulders, and the presence of the 789–28 and 805–28 mass unit bands in the mass spectra provided additional support. These represent the expected molecular masses minus the mass of the CO ligands that are evidently easily displaced in the mass spectrometric measurements.

X-ray Crystallography. The dimeric nature of **1** was confirmed by its X-ray structure, and two molecules of THF were cocrystallized in the lattice. An ORTEP plot of its structure is given in Figure S4. The two BINAP ligands exhibit unexceptional bite angles and Rh–Cl–Rh angles (Table S2). Lengths of the Rh(1 or 2)–Cl and Rh(1 or 2)–P bonds are also unexceptional (Table S3). This dimer is not perfectly flat, as the molecule is bent to an angle of 124.8° , the bending angle being defined as the angle between the two squares of the rhodium subunits.⁵⁴

Complexes **2** and **3** (Figures S5 and 1) are square planar Rh(I) monomers. Complex **2** shows disorder in the placement of the CO and Cl ligands with 87% of the unit cells having the CO group *trans* to P(1) and the Cl *trans* to P(2). The bite angle of the BINAP ligand is quite normal, and other bond angles are typical for a square planar complex (Table S2). Bond lengths are also unexceptional (Table S3).

Compound **3** is best described as a mono-oxidized phosphine bound to the rhodium center with the carbonyl group *trans* to the oxygen. This complex has a P–Rh–O bite angle of $90.69(8)^\circ$ and internal angles near 90° (Table S2). The complex has Rh–P and Rh–O bond lengths of 2.242(1) and 2.123(3) Å, respectively. The rhodium–carbonyl bond is considerably shorter than in **2** (1.774(5) vs 1.905(5) Å) (Table S3).

Infrared Spectroscopy. The carbonyl infrared stretching regions for **2** and **3** were recorded in chloroform, dichloromethane, and 1,2-dichloroethane (Table 1). Both compounds exhibit a single ν_{CO} band, at 2018

**Figure 1.** ORTEP plot of the X-ray structure of **3** showing 30% thermal ellipsoids.

and 1978 cm^{-1} , respectively, in chloroform. There is a shift of ca. 10 cm^{-1} to lower carbonyl stretching frequencies as the solvents are changed to dichloromethane and 1,2-dichloroethane.

Phosphorus NMR Spectroscopy. The solution $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in C_6D_6 of **1** exhibits a single doublet at 50 ppm ($J_{\text{RhP}} = 195$ Hz). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2** in CD_6D_6 consists of a doublet of doublets at 46.5 and 26.0 ppm ($J_{\text{Rh-P}} = 162$ and 128 Hz, $J_{\text{P-P}} = 44$ Hz), and **3** exhibits a doublet at 49.2 ppm ($J_{\text{Rh-P}} = 175$ Hz) and a singlet at 41.9 ppm. No phosphorus–phosphorus coupling was observed for complex **3** (Table 2).

Reactions and Kinetics. Reactions of **2** with oxygen in chloroform were monitored by infrared spectroscopy (Figure 2A), using a temperature-controlled infrared cell. A clear isosbestic point is visible for 90% of the reaction, and very weak peaks are observed growing and decreasing at 2080 and 2070 cm^{-1} . After the oxidation is complete, the 2080 cm^{-1} peak is gone, but some of the 2070 cm^{-1} absorbance remains. After separation from an unidentified solid residue, this minor product was isolated by precipitation with hexanes, but no crystals suitable for crystallographic analysis could be isolated. The compound exhibits infrared bands at 2070 and 1991 cm^{-1} . No phosphorus peaks were observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum.

In the absence of added CO, compound **3** was formed from **2** in up to ca. 50% yield as estimated from the intensity of the carbonyl infrared stretching bands and the measured molar absorbance coefficients (see SI pages). The solution $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of the reaction mixture obtained after stirring **2** with oxygen clearly indicates that $\text{BINAP}(\text{O})_2$ and **3** are formed in nearly 1:1 ratios. The rate of reaction of **2** with oxygen (monitored at 2018 cm^{-1}) followed first-order behavior and was accompanied by growth of infrared bands at 2338 and 1986 cm^{-1} corresponding to CO_2 and **3**, respectively (Figure 2A). Rate constants for the loss of **2** are shown in Table 3. Rate constants for growth of product bands were generally in agreement. Plots of k_{obs} vs $[\text{O}_2]$ (Figure 3) for reactions at 25°C were linear with

(54) Aullón, G.; Ujaque, G.; Lledós, A.; Alvarez, S.; Alemany, P. *Inorg. Chem.* **1998**, *37*, 804.

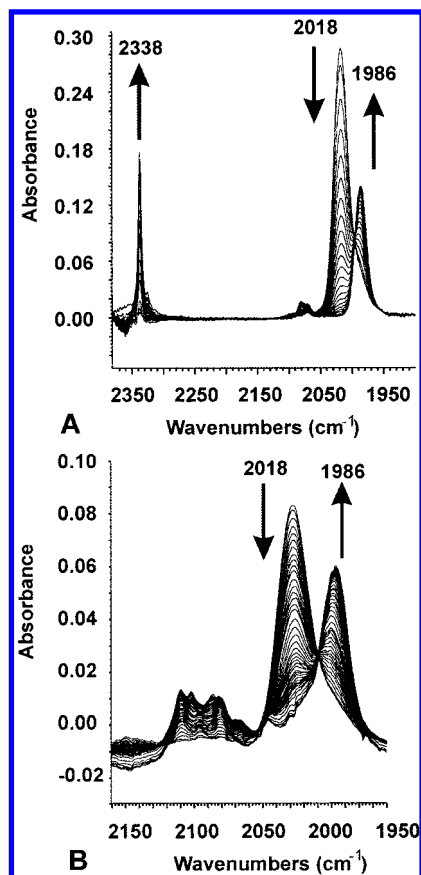


Figure 2. Spectroscopic changes for kinetic runs in chloroform: (A) pure O₂; (B) CO/O₂ (1:1).

Table 3. Kinetic Data for Reactions of 2 in Pure O₂, N₂/O₂, and CO/O₂ Saturated Chloroform Solutions

temp (°C)	10 ³ [O ₂] (M)	10 ⁴ k _{obs} (s ⁻¹)	10 ² k _{obs} /[O ₂] (M ⁻¹ s ⁻¹)
40 ^a	4.81	7.64 ± 0.06	15.89
25 ^a	6.74	3.41 ± 0.02	5.84
25 ^a	6.74	4.05 ± 0.03	5.06
25 ^a	6.74	4.15 ± 0.12	6.64
25 ^a	6.74	4.48 ± 0.04	6.16
14.9 ^a	7.39	1.34 ± 0.003	1.82
8.3 ^a	8.06	0.93 ± 0.004	1.15
25 ^b	3.39	2.07 ± 0.04	
25 ^b	3.39	1.93 ± 0.04	
25 ^b	3.39	1.95 ± 0.03	
25 ^c	3.39	2.60 ± 0.04	
25 ^c	3.39	1.87 ± 0.01	
25 ^c	3.39	1.93 ± 0.02	
25 ^d	1.35	1.03 ± 0.01	

^a $\Delta H^\ddagger = 14.6 \pm 1.1$ kcal mol⁻¹; $\Delta S^\ddagger = -15.3 \pm 3.8$ cal mol⁻¹ K⁻¹; $\sigma(k_2) = 17\%$, pure O₂. ^b CO/O₂ (1:1). ^c N₂/O₂ (1:1). ^d N₂/O₂ (80:20).

an intercept close to zero. The second-order rate constant was determined from a linear least-squares analysis of the dependence of k_{obs} on [O₂], using proportional weighting, and $10^2 k_2 = 5.35 \pm 0.53$ M⁻¹ s⁻¹, the intercept being given by $10^5 \text{int} = 2.88 \pm 1.76$ s⁻¹, with $\sigma(k_{\text{obs}}) = 14\%$. Activation parameters, also shown in Table 3, were determined from rate constants for reactions under pure O₂ with second-order rate constants estimated from $k_2 = k_{\text{obs}}/[\text{O}_2]$; that is, it was assumed the contribution of the intercept to k_{obs} was negligible.

Oxygenation kinetics were also measured in 1,2-dichloroethane by taking aliquots of solution from a

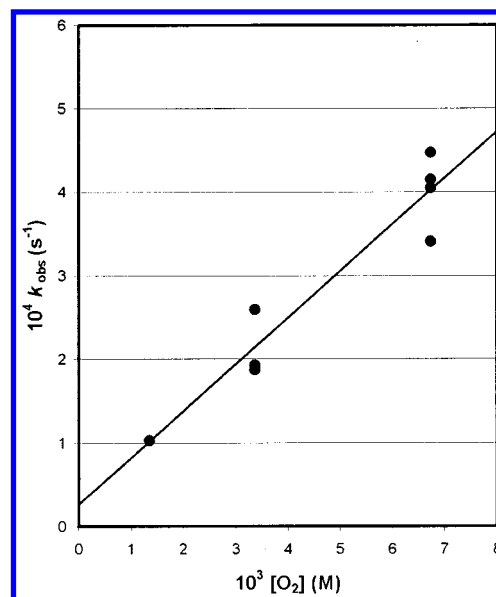


Figure 3. Plot of k_{obs} vs [O₂] for the reaction of **2** at 25 °C in the presence of pure O₂ and N₂/O₂ gas mixtures.

Schlenk flask containing the reaction mixture, which was subject to continuous bubbling with pure O₂ or O₂/N₂ mixtures. The second-order rate constant was determined as before from k_{obs} vs [O₂] plots: $10^2 k_2 = 9.37 \pm 1.26$ M⁻¹ s⁻¹.

Effect of Carbon Monoxide. Oxidation of **2** in chloroform under CO/O₂ (1:1) gas mixtures results in the formation of new carbonyl bands in the infrared spectrum at 2099, 2087, 2070, 2055, and 2020 cm⁻¹ (Figure 2B), and no isosbestic points are observed in this region. Yields of **3** were generally higher (65–70%) under CO/O₂ (1:1) than in reactions under N₂/O₂ (1:1), but the rate of reaction of **2** is unaffected by the presence of CO (Table 3).

Effect of Added BINAP. When reaction of **2** with an O₂/CO mixture is carried out in the presence of 1 molar equiv of BINAP, **2** is completely converted into BINAP(O)Rh(CO)Cl and none of the high-energy bands mentioned above for reaction under CO are formed.

Reactions of 3 with Carbon Monoxide. A sample of pure **3** reacts reversibly but incompletely with CO in chloroform, giving infrared bands at 2090 and 2020 cm⁻¹ with 10% the intensity of the initial absorbance of **3**. Solutions of **3** and the other oxidation products of reactions of **2** give spectra similar to Figure 2B upon treatment with CO. Mixtures of **3** and these unidentified products react quantitatively and rapidly with BINAP, forming **2** exclusively.

Catalytic Oxidation of BINAP. Reactions of **2** with as much as a 50-fold excess of BINAP in chloroform or toluene were followed under CO/O₂ gas mixtures, with varied temperatures and reaction times. Using large excesses of BINAP was impractical, as it results in extremely long reaction times, spanning several weeks, before all the BINAP was consumed. Infrared monitoring of the reaction indicated no degradation of **2** until all of the BINAP had been consumed. The yields of BINAP, BINAP(O), and BINAP(O)₂ were estimated from integration of their ³¹P{¹H} NMR spectra (Figure S6). The product yields were dependent on solvent, temperature, gas ratios, and reaction time. Thus, suit-

able reaction conditions can be inferred to optimize product yields and minimize reaction times. Reaction of BINAP with oxygen in the absence of **2** in chloroform shows no appreciable oxidation after 24 h, but reactions using a 10-fold excess of BINAP relative to catalyst show no traces of unoxidized BINAP after periods as short as 72 h. The approximate yield ratios [BINAP(O)₂]/[BINAP(O)] were ~2:1 and 1:1 in chloroform and toluene, respectively (Figure S6). Turnover frequencies for the catalytic reaction in chloroform and toluene are 0.16 and 0.12 h⁻¹, with turnover numbers of at least 70 and 10, respectively. Attempts to get larger turnover numbers were impractical because of the long reaction times involved at ambient pressures. Reactions under CO/O₂ (3:1) mixtures in both solvents result in higher monoxide formation, but the turnover frequency is drastically reduced to 0.016 h⁻¹, making the process very slow. Reactions under pure O₂ lead to incomplete BINAP oxidation, even after long reaction times, and consequently very low yields of BINAP(O) and BINAP-(O)₂ were observed. Elevated temperatures increase the overall rate of reaction, but the ratios of BINAP(O)₂ to BINAP(O) are significantly increased.

Use of Other Ligands. Attempts to use ligands other than CO for the catalytic reactions were unsuccessful. Reactions with 10-fold excess of BINAP and 100-fold excesses of norbornylene or cyclohexylisocyanide lead to incomplete oxidation of BINAP. The former produced only trace amounts of norcamphor and norborneneol, whereas the latter reacts rapidly with **2** to form mixtures of isocyanide complexes,^{55,56} as evidenced by changes in the infrared frequencies of the ν_{CN} bands.

Use of dpmm in place of the excess BINAP led to similar catalytic formation of the monoxide and dioxide products in CDCl₃, but reactions with dppe gave less clear results. No further studies were undertaken.

The BINAP in complex **1** is oxidized by O₂ to BINAP-(O)₂, but not catalytically.

Discussion

Synthesis and Characterization. Reactions and Products. The reaction of [Rh(COD)Cl]₂ with 2 equiv of (*R*)-BINAP leads to the formation of **1** in high yield.⁵⁷ This complex is characterized as a bis bridged dimer and is bent by an angle θ of 124.8°. Such bending is common for this class of compounds ([L₂RhCl]₂), and a large variety of bending angles ranging from practically planar (160° < θ < 180°) or strongly bent (θ < 150°) are observed.^{54,58–64} Bond lengths and angles for **1** are characteristic for this class of complex.

Complex **2** (Figure S5) is a rare example of a crystallographically characterized square planar chelate bisphosphine complex of rhodium. A search of the Cambridge Structure Database (CSD)⁶⁵ yielded only two chelated bisphosphine structures where L = carbonylchloro((2,2'-biphenyl-1,1'-diyl)bis(6,6'-di-*tert*-butyl-4,4'-dimethoxy-2,2'-biphenyl-1,1'-diyl)diphosphite), which crystallized in two different space groups.⁶⁶ However, other *cis*-chelate complexes, where L = bis(diphenylphosphino)ethane (dppe) and three *o*-carborane phosphino derivatives,^{67,68} Ph₂P(C₂B₁₀H₁₀)PPh₂, Ph₂P-(C₂B₁₀H₁₀)P(NMe₂)₂, and (Me₂N)P(C₂B₁₀H₁₀)P(NMe₂)₂, have been isolated and characterized by infrared and ³¹P{¹H} NMR spectroscopy,³² but not by X-ray crystallography. Phosphorus–rhodium bond lengths in **2** (2.341(1), 2.250(1) Å) are close to the average value (2.320 Å) for a sample of 38 structures with the fragment RhP₂-(CO)Cl found on the CSD. Of these complexes, 24 contained *trans*-monophosphine ligands, 7 contained bridging bisphosphine ligands, 9 incorporated *trans*-chelating bisphosphine ligands, and 2 were the *cis*-chelate complexes mentioned above.

The action of oxygen on **2** results in the formation of **3** in approximately 50% yield, along with approximately equivalent yields of BINAP(O)₂ and CO₂ and trace amounts of an unidentified CO-containing product. The crystal structure proved the existence of the mono-oxidized BINAP coordinated to the rhodium center. A search of the CSD revealed only two similar structures published with BPMP ligands in Rh(I) complexes, the ligands being [bis(isopropoxy)phosphoryl(diphenylphosphino)methane-*O,P*] ((*O*-*i*-Pr)₂P(O)CH₂PPh₂)⁶⁹ and [(diphenylphosphinomethylene)diphenylphosphineoxide-*O,P*] (dpmm(O)).¹⁶ Both complexes have Rh–P and Rh–O bond lengths and phosphorus–oxygen bite angles that are similar to those found for **3**. Another interesting feature of these complexes is the strong *trans* effect of the oxygen donor on the carbonyl ligand. Rh–C bond lengths are significantly shortened from 1.905(5) to 1.774(5) Å when changing from **2** to **3**. Similar Rh–C bond lengths of 1.79(1)⁶⁹ and 1.787¹⁶ Å are observed for the above analogous complexes. Infrared spectroscopy of **3** in the C–O stretching region show a significant decrease in ν_{CO} of 31 cm⁻¹ in all solvents (Table 1). Analogous complexes containing dppe(O),¹⁶ dpmm(O),¹⁶ ((*O*-*i*-Pr)₂P(O)CH₂PPh₂), and ((*O*-Et)₂P(O)CH₂PPh₂)⁶⁹ ligands exhibit similar ν_{CO} stretching frequencies of 1995, 1985, 1990, and 1990 cm⁻¹ in CH₂Cl₂, respectively. The first compound shows a decrease in ν_{CO} of 15 cm⁻¹ (Nujol) when going from dppe to dppe(O). The decrease in Rh–C bond length and ν_{CO} stretching frequencies of the BPMP complexes are conventionally attributed to increased π -back-bonding from the metal to the carbonyl carbon as a result of π -electron donation of electrons from the oxygen to the metal. Gladiali et al.⁹ have isolated some BINAP(O) complexes of Rh(I) such as [{BINAP(O)}Rh(diolefine)][BF₄], and labiliza-

(55) Jones, W. D. J.; Hessel, E. T. *Organometallics* **1990**, *9*, 718.

(56) Jones, W. D.; Hessel, E. T. *New J. Chem.* **1990**, *14*, 481.

(57) Although (*R*)-BINAP was used, the primary interest was in the oxidation reactions and not the stereochemistry of the BINAP complex.

(58) Feiken, N.; Pregosin, P.; Trabesinger, G. *Organometallics* **1998**, *17*, 4510.

(59) Roucoux, A.; Thieffry, L.; Carpentier, J.-F.; Devocelle, M.; Meliet, C.; Agbossou, F.; Mortreux, A.; Welch, A. J. *Organometallics* **1996**, *15*, 2440.

(60) Wang, K.; Goldman, M. E.; Emge, T. J.; Goldman, A. S. *J. Organomet. Chem.* **1996**, *518*, 55.

(61) Hofmann, P.; Meir, C.; Hiller, W.; Heckel, M.; Riede, J.; Schmidt, M. U. *J. Organomet. Chem.* **1995**, *490*, 51.

(62) Binger, P.; Haas, J.; Glaser, G.; Goddard, R.; Krüger, C. *Chem. Ber.* **1994**, *127*, 1927.

(63) Schnabel, C. R.; Roddick, D. M. *Inorg. Chem.* **1993**, *32*, 1513.

(64) Curtis, D. M.; Butler, W. M.; Greene, J. *Inorg. Chem.* **1978**, *17*, 2928.

(65) 3D Search and Research Using the Cambridge Structural Database. Allen, F. H.; Kennard, O. *Chem. Des. Automat. News* **1993**, *8* (1), 1 and 31–37.

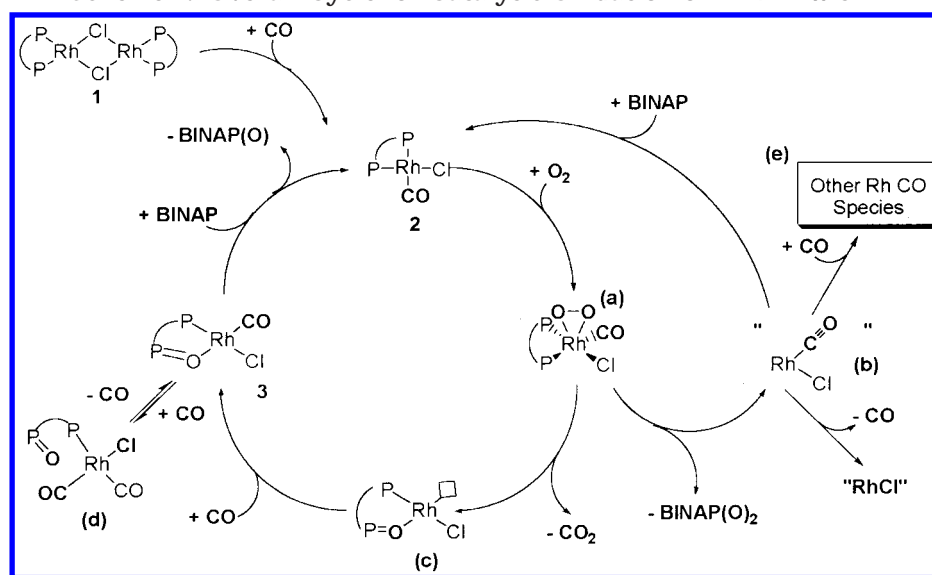
(66) Paciello, R.; Siggel, L.; Kneuper, H.-J.; Walker, N.; Roper, M. *J. Mol. Catal. A: Chem.* **1999**, *143*, 85.

(67) Hill, W. E.; Silva-Trivino, L. M. *Inorg. Chem.* **1979**, *18*, 361.

(68) Hill, W. E.; Silva-Trivino, L. M. *Inorg. Chem.* **1978**, *17*, 2495.

(69) Le Gall, I.; Laurent, P.; Soulier, E.; Salaun, J.-Y. *J. Organomet. Chem.* **1998**, *567*, 13.

Scheme 2. Overall Cycle for Catalytic Oxidation of BINAP with 2



tion of groups *trans* to the oxygen atom of some Pt(II) BINAP(O) complexes was observed.⁷⁰

Kinetics. Reaction of (BINAP)Rh(CO)Cl with Oxygen. The sharp isosbestic point between the 2018 and 1986 cm^{-1} bands shows the cleanness of this transformation in chloroform and 1,2-dichloroethane. The rate constants in Table 3 show good reproducibility with standard deviations of the averages being about 5%. The reactions of **2** follow the rate equation $k_{\text{obs}} = \text{int} + k_2[\text{O}_2]$, where the intercept is statistically almost indistinguishable from zero. This, combined with a negative entropy of activation ($\Delta S^\ddagger = -15.3 \text{ cal mol}^{-1} \text{ K}^{-1}$), indicates that the first step of the mechanism most likely involves dioxygen coordination to the rhodium complex, forming a short-lived η^2 -rhodium dioxygen intermediate. The kinetics of similar reactions of analogous iridium complexes were studied in detail by Vaska^{36,71–73} and Halpern.⁷⁴ These exhibit highly negative ΔS^\ddagger values between -24 and $-50 \text{ cal mol}^{-1} \text{ K}^{-1}$,⁷² but the Ir complexes do not activate the oxygen toward phosphine oxidation, simple oxidative addition being preferred. Oxygen adducts of Rh(I) complexes are only observed when the electron density on the Rh atom is made high enough, usually by the presence of three or more P-donor ligands.^{36,41,73,75} The presence of the strong π -acid CO ligand precludes adduct formation unless it is by addition of singlet oxygen.³⁴

Effect of Carbon Monoxide. In the absence of excess BINAP and CO, the reaction yields roughly equimolar amounts of **3** and $\text{BINAP}(\text{O})_2$, together with an equivalent amount of CO_2 . This result suggests there are two reaction pathways after initial O_2 coordination (Scheme 2). The dioxygen in the adduct can proceed to either form two phosphorus–oxygen bonds (right-hand path) or bond to one phosphorus atom and to the CO

ligand (left-hand path), yielding “(BINAP(O))RhCl” (c in Scheme 2) with a vacant coordination site and 1 mol of CO_2 . This intermediate must in turn react very rapidly with any CO in solution to form **3**. In the absence of added CO, the only source must be the short-lived species “Rh(CO)Cl” (b in Scheme 2). This must supply the needed CO quite effectively because the yield of **3** can be as high as $\sim 50\%$, which is the maximum possible if it is generated by CO released in forming $\text{BINAP}(\text{O})_2$. The resulting “RhCl” must be the insoluble uncharacterized residue found after these reactions.

The presence of excess CO has no effect on the rate of disappearance of **2**, but the increased yield of **3** (to $\sim 60\text{--}70\%$) reflects the fact that its yield is no longer dependent on the generation of CO from “Rh(CO)Cl”. Of the high-energy peaks observed in the infrared spectrum of reaction mixtures containing CO/O_2 (1:1), two can be attributed to the reaction of **3** with CO and the others may be attributed to side products formed by complexation of the “Rh(CO)Cl” species with CO. In the presence of excess BINAP, none of these bands are detected, and “Rh(CO)Cl” and these other products must react with BINAP to re-form **2** (Scheme 2). The yield of **3** is then 100% with respect to the amount of added **2**.

Catalytic Oxidation of BINAP. In the presence of excess BINAP and under a CO/O_2 (1:1) gas mixture, **2** will behave as an oxygenation catalyst to form $\text{BINAP}(\text{O})$ and $\text{BINAP}(\text{O})_2$. Solvent plays a role in determining the extent of monoxide and dioxide formation. The use of toluene favors $\sim 50\%$ monoxide formation, and chloroform results in $\sim 30\%$ monoxide yields. Thus, the solvent has an ability to control the relative rates of the two competing reaction pathways of the O_2 adduct.

The reactions are also dependent on CO/O_2 gas ratios. Reactions in 3:1 CO/O_2 mixtures yield more $\text{BINAP}(\text{O})$ vs $\text{BINAP}(\text{O})_2$, but the decreased $[\text{O}_2]$ results in very low yields even after long reaction times. Increasing temperature increases the relative yields of $\text{BINAP}(\text{O})_2$, but decreasing O_2 levels must lower the overall turnover frequency of the process. Reaction under pure O_2 leads to low yields of BINAP oxides, presumably due to catalyst degradation resulting from CO_2 loss and formation of uncharacterized rhodium species. Reactions

(70) Kollár, L.; Gladiali, S.; Tenorio, M. J.; Weissensteiner, W. *J. Clust. Sci.* **1998**, *9*, 321.

(71) Vaska, L.; Chem, L. S.; Miller, W. V. *J. Am. Chem. Soc.* **1971**, *93*, 6671.

(72) Vaska, L.; Chen, L. S.; Senoff, C. V. *Science* **1971**, *174*, 587.

(73) Vaska, L.; Chen, L. S. *J. Chem. Soc., Chem. Commun.* **1971**, 1081.

(74) Chock, P. B.; Halpern, J. *J. Am. Chem. Soc.* **1966**, *88*, 3512.

(75) McGinney, J. A.; Payne, N. C.; Ibers, J. A. *J. Am. Chem. Soc.* **1969**, *91*, 6301.

under high pressures of O₂/CO mixtures and low temperatures would therefore be needed to produce improved selectivity of the monoxide product with reasonable turnover frequencies.

The Intimate Mechanism of the Oxidation. Although the stoichiometric mechanism outlined in Scheme 2 is well established by the nature and yields of the various products and by the kinetics, the details of how the putative dioxygen adduct reacts with two phosphorus atoms, or one phosphorus atom and the CO ligand *trans* to it, remain obscure. Coordination of the oxygen will have the effect of homolytically weakening the O–O bond, and the P-donor atoms and the CO ligand share a thermodynamic tendency to accept oxygen atoms which are available from the weakened oxygen molecule. One possibility is that they do this in an unusual concerted manner that effectively involves five-member transition states, and another is that stepwise processes are involved in which one oxygen atom remains attached to the Rh atom while the other attaches to a phosphorus or carbon atom. The oxygen atom from the rhodium then completes the process. The transition state for the first of these two steps would resemble the four-member transition states of alkene metathesis.⁷⁶

Summary. (i) A mechanism for the stoichiometric or catalytic conversion of **2** to **3** (Scheme 2) is proposed partly on the basis of the following observations. The negative entropy of activation and a linear dependence of k_{obs} on oxygen concentration are indicative of an initial addition of oxygen to **2**, forming a short-lived analogue of Vaska's complex ($\eta^2\text{-O}_2$)Ir(PPh₃)₂(CO)Cl. The cleanness of the overall reaction from **2** to **3** is evidenced by a clear isosbestic point; so there are no side reactions not specified in Scheme 2. Reactions of **2** with oxygen proceed cleanly to form **3** but in up to ca. 50% yield, along with equivalent amounts of BINAP(O)₂ and CO₂, and two minor unidentifiable species shown in the IR spectrum. Thus, after initial reaction of **2** with O₂, the dioxygen complex can react via two independent pathways. One route involves oxidation of both P atoms on BINAP, forming BINAP(O)₂ and the reactive intermediate "Rh(CO)Cl" (right-hand path). Alternatively, the oxygen ligand can add to one P atom on BINAP and to CO, forming CO₂ and the coordinatively unsaturated intermediate "(BINAP(O))RhCl" (left-hand path), which can efficiently scavenge any free CO to form **3**. It is not possible to decide whether the oxidations proceed by single concerted steps or via two-step processes that involve Rh=O intermediates.

(ii) Other reactions of the species involved in Scheme 2 support the proposed scheme. Addition of CO does not affect the rate of decay of **2**, but the presence of excess

CO can raise the overall yield of **3** by ~20%. The implication is that the added CO rapidly fills the vacant coordination site on "(BINAP(O))RhCl" made available after loss of CO₂. The observation of additional peaks in the IR spectrum for reactions under CO suggests the formation of (η^1 -BINAP(O))Rh(CO)₂Cl (d in Scheme 2) and other dicarbonyl rhodium species in solution (e in Scheme 2).

(iii) In the presence of excess BINAP, **3** was shown to react quantitatively to form **2** and thus complete the catalytic cycle. The reaction must be conducted under CO/O₂ gas mixtures, thus ensuring the quantitative regeneration of **2** because, in the absence of CO, the catalyst would degrade by 50% per cycle. Under catalytic conditions, no higher energy IR bands, normally found under noncatalytic conditions, are observed, thus lending support to the idea that BINAP will rapidly scavenge the short-lived "Rh(CO)Cl" and other Rh carbonyl species that may exist in solution so as to reform **2** (Scheme 2).

Conclusions

The complex (BINAP)Rh(CO)Cl is an active, albeit nonselective, oxygenation catalyst for the formation of BINAP(O) and BINAP(O)₂ from solutions of excess BINAP under CO/O₂ gas mixtures at ambient pressures, and a probable mechanism is proposed for this transformation. The TOF and TON for this process are 0.16 h⁻¹ and 70, respectively, in chloroform at 25 °C. The rather low reactivity of this process provides an opportunity to identify the key species in the catalytic cycle, but conditions can be envisaged that would improve the rates and selectivity. To our knowledge, this is the first example of a catalytic cycle that occurs with both oxidation of the two phosphorus atoms on a chelating bisphosphine ligand and oxidation of one phosphorus atom and a CO ligand. However, because of the need to form the relatively unusual mononuclear chelate complexes, this catalytic reaction cannot easily be generalized.

Acknowledgment. The support of the Natural Science and Engineering Research Council, Ottawa, is gratefully acknowledged. We also thank Professors Warren Giering and Alfred Prock (Boston University) for the loan of two gas flow meters and Digital Specialty Chemicals for the gift of (*R*)-BINAP.

Supporting Information Available: Experimental details and crystallographic data tables of all bond lengths, angles, atomic coordinates, and thermal parameters, along with ³¹P{¹H} NMR spectra for complexes **1**, **2**, and **3** (Figures S1–S3), ORTEP drawings for **1** and **2** (Figures S4 and S5), and figures showing yields of BINAP(O) and BINAP(O)₂, are available free of charge via the Internet at <http://pubs.acs.org>.

OM020241A

(76) Cotton, F. A.; Wilkinson, G. In *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; Chapter 28, pp 1265–1269.