Formation of Ruthenium(II)−Bis(phosphine) Monoxide Complexes from the Bis(phosphine) Precursors: BINAP-Monoxide (BINAPO) as a Six-Electron (*P,O,*η^2-Naphthyl) Donor

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Aerobic oxidation of one P atom in *cis*-$RuCl_2$(P−P)(L_2) complexes (P−P = (*R*)-BINAP (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl) or dppb (1,4-bis(diphenylphosphino)butane), L_2 = bipy (2,2′-bipyridine) or phen (1,10-phenanthroline)) generates species such as [RuCl(BINAPO)(L_2)]PF_6 and *cis*-$RuCl_2$(dppbO)(L_2) containing the corresponding bis(phosphine) monoxide ligands [BINAPO = 2-(diphenylphosphinoyl)-2′-(diphenylphosphino)-1,1′-(binaphthyl), and dppbO = 1-(diphenylphosphinoyl)-4-(diphenylphosphino)butane)]. A novel coordination mode of BINAPO, involving the P^{III} atom, the O atom, and an η^2-naphthyl interaction proximate to the oxidized P atom, is identified by X-ray crystallography.

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Introduction

The synthesis and chemistry of Ru(II) complexes possessing a chelating, ditertiary phosphine ligand (P−P) remains a topic of interest in our group, the main impetus being the potential of such complexes as hydrogenation catalysts.[1−4] The use of chiral Ru(II)(P−P) complexes for asymmetric catalysis has been tremendously successful, especially in enantioselective hydrogenation,[5] and there has been much interest in the chemistry of Ru(II) complexes bearing chiral diphosphine ligands such as BINAP[4,6−9] and the related BIPHEP[10−12] ligands (Scheme 1). We have also studied Ru(II) complexes containing both P- and N-donor ligand sets, either with separate P- and N-donors[13] or in which the N-donor is incorporated into the phosphine ligand.[14] The use of Ru(II) systems with tetradentate "P_2N_2" ligands for catalytic hydrogenation[15] and epoxidation[16] reactions has also been reported. Of particular note, spectacular success has been achieved more generally in the use of chiral Ru(II) complexes with phosphine (either mono- or bidentate) and diamine (or amine-amido) ligands in catalytic enantioselective hydrogenation.[17] Recently we have been exploring the chemistry of a series of "Ru(P−P)(L_2)" complexes where P−P = dppb (1,4-bis(diphenylphosphino)butane) or (*R*)-BINAP,

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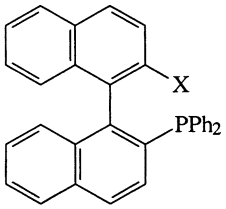
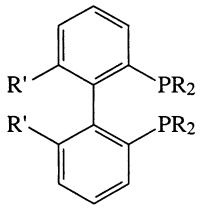
Scheme 1



X = PPh_2 (BINAP); $OPPh_2$ (BINAPO)



R = 3,5-di-^{t}Bu-Ph, R' = OMe (MeO-BIPHEP-Bu)

R = ^{i}Pr, R' = OMe (MeO-BIPHEP-Pr)

R = Ph, R' = Me (BIPHEMP)

and L_2 = a chelating bis(N-donor) ligand.[18,19] During our studies on the solution chemistry of these $RuCl_2(P-P)(L_2)$ complexes, we found that selective oxidation of one P atom occurs, and complexes containing the corresponding bis(phosphine) monoxide (BPMO) ligands are produced (specifically dppbO and BINAPO in this work).

The coordination chemistry of BPMO ligands remains of considerable interest, largely through studies to improve transition-metal-catalyzed transformations.[20] For example, a $Rh/Ph_2P(O)(CH_2)_2PPh_2$ catalyst system allows for far less forcing conditions (80 °C and 50 psi) compared to those typically employed (e.g., 200 °C and 500 psi) in the Monsanto acetic acid process using a Rh-chloro(carbonyl) catalyst.[21] Though BPMO ligands have been known for some time,[22] only more recently have the catalytic properties of their complexes been investigated. BPMO-based catalyst complexes have been studied, for example, for hydroformylation,[23−25a] hydrosilylation,[26] hydrovinylation,[27] oligomerization, and copolymerization.[28] Faller et al. have reported extensively on the chemistry of some arene complexes of Ru and Os with BPMO ligands (especially chiral ones), as well as their use as Lewis acid catalysts in Diels−Alder reactions.[29,30] Despite the interest, efficient general syntheses of BPMOs have remained problematic. The most general route involves a two-step process involving benzylation of a diphosphine, followed by base hydrolysis of the recrystallized phosphonium salt,[31] though this route seems limited to diphosphines bearing just simple alkyl (e.g., $-(CH_2)_n-$) bridges between phosphino groups. Grushin has reported a Pd-catalyzed synthesis of BPMO ligands from many commercially available diphosphines (P−P), including BINAP.[32] Other syntheses of BINAPO have appeared;[25b,26,27,33] however, with only one exception,[26] these have been low yielding and generally producing the monoxide as a byproduct. Gladiali et al. synthesized BINAPO from 1,1′-binaphthyl-2,2′-diol in a four-step procedure, followed by chiral resolution via a Pd-*C,N*-cyclometalated complex.[26] The coordination chemistry of BINAPO is largely undeveloped, considering the vast literature on transition metal complexes of BINAP and its derivatives.

In this paper, we report on the preparation of Ru(II)(dppbO) and Ru(II)(BINAPO) complexes directly from Ru(II)(P−P) precursors. In addition, we report a novel coordination mode of BINAPO in which the ligand acts as a six-electron donor, involving the P^{III} and O atoms, as well as an η^2-naphthyl interaction of the binaphthyl backbone with the Ru.

Results and Discussion

Recent work in this group has investigated the solution chemistry of *cis*-$RuCl_2(P-P)(L_2)$ complexes (P−P = dppb or (*R*)-BINAP, L_2 = bidentate N-donor) and their potential in homogeneous catalytic hydrogenation of imines.[18,19] Catalytic hydrogenations employing "Ru(II)(P−P)" complexes are often performed in alcohol solvents, especially MeOH,[3,5] and thus we studied the nature of the species present in MeOH solutions of *cis*-$RuCl_2(P-P)(L_2)$. Conductivity studies have shown that dissociation of one Cl^- occurs, and signals assignable to the cationic species are readily detected by $^{31}P\{^1H\}$ NMR.[18,19b] However, such spectra

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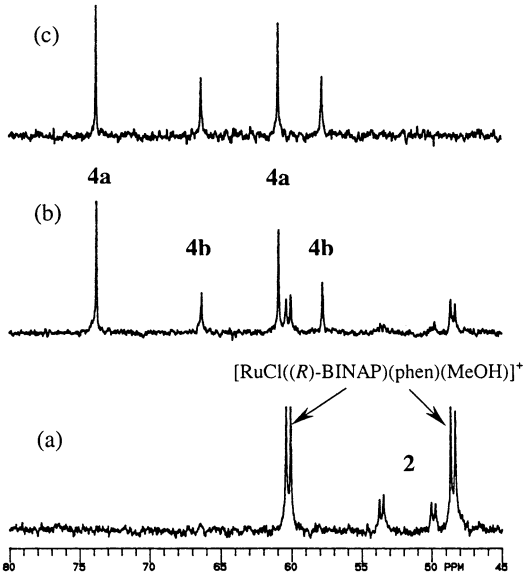

Figure 1. $^{31}P\{^1H\}$ NMR spectra of *cis*-$RuCl_2$((*R*)-BINAP)(phen) (**2**) in CD_3OD exposed to air at rt over (a) 2 h, (b) 5 days, (c) 14 days.

of CD_3OD solutions of *cis*-$RuCl_2$((*R*)-BINAP)(L_2) (L_2 = bipy (**1**), phen (**2**)) in air at room temperature (rt) change over time, as exemplified for **2** in Figure 1. Initially, the neutral species **2** and a monocationic complex thought to be[19b] [RuCl((*R*)-BINAP)(phen)(MeOH)]Cl are present (Figure 1a), but over days signals of these species disappear and four new singlets appear (Figure 1b,c) that result from BINAPO complexes. After ~14 days, no further changes occur in the spectra and the product ratios remain constant. The products are isolated as [RuCl(BINAPO)(L_2)]PF_6 (L_2 = bipy (**3**·PF_6), phen (**4**·PF_6)), after the addition of NH_4PF_6. The spectroscopic and analytical data are consistent with isomers (denoted **a** and **b**) of each of these formulations (see Experimental Section). Thus, aerobic oxidation of one of the P atoms has taken place. The two $^{31}P\{^1H\}$ NMR singlets for **3** and **4** are consistent with a relatively small or zero $^3J_{PP}$ value, as observed for Pd, Pt, and Rh complexes of BINAPO;[24−26] the assignments of the singlets (to P^{III} and P^V) are not obvious in view of the novel type of *P*,*O*,η^2-naphthyl bonding of the BINAPO discovered in the X-ray structures (see below). The complex [(*p*-cymene)RuCl(*P*,*O*-BINAPO)]$SbPF_6$ was originally reported to give rise to two $^{31}P\{^1H\}$ doublets,[30a] although a later publication reports no $^3J_{PP}$ values for this complex, the discrepancy being unmentioned.[29d]

Structures of 3a and 4a. The structures of **3a**·PF_6 and **4a**·PF_6 were determined by X-ray crystallography (Figures 2 and 3, respectively). The coordination environments of **3a** and **4a** are the same, including the stereochemistry, and the corresponding Ru−N, Ru−P, and Ru−Cl bond lengths are essentially identical (see Tables 1 and 2). The P═O bond distances are the same within error (av 1.516 Å) and are in the range typical for coordinated R_3P═O (1.49−1.52 Å).[34] Uncoordinated BINAPO has not been crystallographically characterized, although three reports of the structure of BINAP-$(O)_2$ have appeared.[8a,35,36] The one by Bunten et al.,[36] unlike the earlier ones,[8a,35] characterized $BINAP(O)_2$ in the absence of cocrystallized materials, and thus for structural comparison their data will be used. In the reported structures[25b,26,30a,b] and those here of coordinated BINAPO, the P═O bond length is greater than that in $BINAP(O)_2$ (av 1.4827 Å).[36]

In **3a** and **4a**, the two C atoms of the naphthyl ring proximate to the P═O group are η^2-coordinated to the Ru, and this leads to a substantial decrease in the

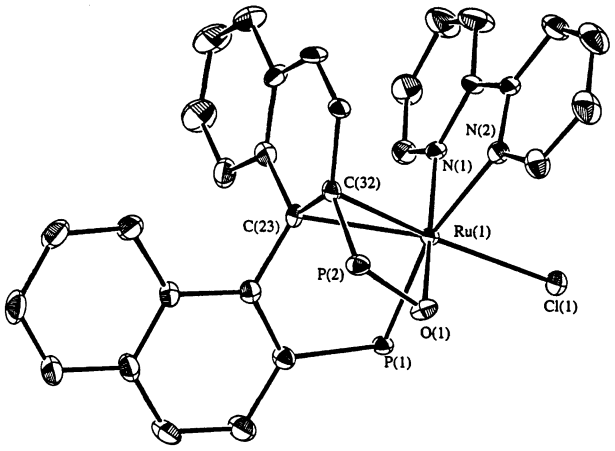

Figure 2. ORTEP representation of [RuCl(BINAPO)(bipy)]PF_6 (**3a**·PF_6). Thermal ellipsoids are drawn at 50% probability. The phenyl C atoms and the PF_6^- anion are omitted for clarity.

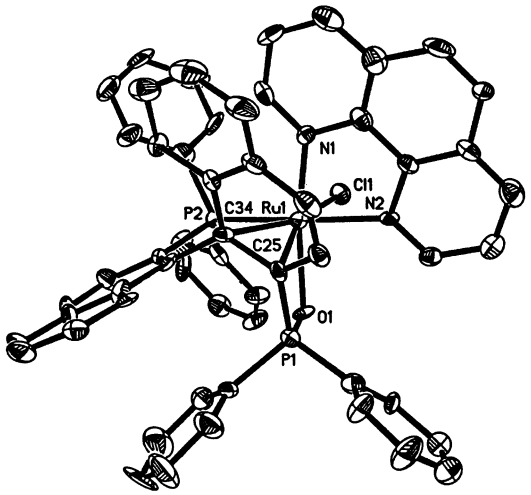

Figure 3. ORTEP representation of [RuCl(BINAPO)(phen)]PF_6 (**4a**·PF_6). Thermal ellipsoids are drawn at 50% probability. The PF_6^- anion is omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for [RuCl(BINAPO)(bipy)]PF_6 (3a·PF_6)

Ru(1)−Cl(1)	2.384(1)	Ru(1)−P(1)	2.320(1)
Ru(1)−O(1)	2.212(3)	Ru(1)−N(1)	2.057(3)
Ru(1)−N(2)	2.113(4)	Ru(1)−C(23)	2.346(4)
Ru(1)−C(32)	2.255(4)	P(1)−O(1)	1.518(3)
C(23)−C(32)	1.444(6)		
P(1)−Ru(1)−O(1)	86.79(8)	Ru(1)−O(1)-P(2)	97.2(1)
Cl(1)−Ru(1)−C(23)	161.4(1)	Cl(1)−Ru(1)-C(32)	161.1(1)
dihedral of naphthyl planes		96.6	

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Table 2. Selected Bond Distances (Å) and Angles (deg) for [RuCl(BINAPO)(phen)]PF_6 (4a·PF_6)

Ru(1)−Cl(1)	2.377(2)	Ru(1)−P(2)	2.311(2)
Ru(1)−O(1)	2.196(4)	Ru(1)−N(1)	2.051(5)
Ru(1)−N(2)	2.137(6)	Ru(1)−C(25)	2.281(7)
Ru(1)−C(34)	2.356(7)	P(1)−O(1)	1.515(4)
C(25)−C(34)	1.463(9)		
P(2)−Ru(1)−O(1)	87.71(12)	Ru(1)−O(1)−P(1)	98.6(2)
Cl(1)−Ru(1)−C(25)	161.5(2)	Cl(1)−Ru(1)−C(34)	160.6(2)
dihedral of naphthyl planes	81.6		

P═O−Ru angle in **3a** and **4a** (97.2(1)° and 98.6(2)°, respectively) relative to the heterobidentate *P*,*O*-chelating mode of BINAPO, where the P═O−M angles are 125.1(2)° (M = Pd),[26] 165.9(3)° (M = Ru),[30a] and 161.5(5)° (M = Os).[30b] Also, the P−Ru−O bite angle of BINAPO in **3a** and **4a** (av 87.2°) is greater than that in [(*p*-cymene)RuCl(*P*,*O*-BINAPO)]$^+$ (81.5(1)°).[30a]

Coordination of the naphthyl group in **3a** and **4a** leads to an elongation of the Ru-bonded C−C bond, 1.444(6) and 1.463(9) Å, respectively, relative to the corresponding uncoordinated C−C bond in [(*p*-cymene)RuCl(*P*,*O*-BINAPO)]$^+$ of 1.39(1) Å,[30a] which is identical to that in $BINAP(O)_2$.[36] These C−C bond distances in **3a** and **4a** are close to those in [(Cp)Ru(BINAP)]$^+$ (1.464(14) Å), which possesses BINAP coordinated in a related *P*,*P*′,η^2-mode.[37] Coordination of the naphthyl ring in **3a** and **4a** causes significant disruption of the aromaticity of the naphthyl moiety, and inspection of the C−C bond lengths in the separate naphthyl groups suggests localization of double bonds in the coordinated rings (Supporting Information). Such disruption of the aromaticity of the η^2-coordinated aromatic rings of BINAP[37] and MeO-BIPHEP[12a] ligands in related coordination modes has been noted. The average Ru−C bond lengths in **3a** (2.300 Å) and **4a** (2.318 Å) are relatively long compared to the analogous Ru−C(naphthyl) bonds in [(Cp)Ru(BINAP)]$^+$ (av 2.270 Å)[37] and to conventional Ru−C bonds in Ru(arene) and Ru(olefin) complexes (2.10−2.30 Å).[34] The Ru−C bond distances within both **3a** and **4a** are unequal. In **3a**, the Ru−C(23) bond length is longer than the Ru−C(32) length (2.346(4) vs 2.255(4) Å, respectively), and in **4a** the Ru−C(34) bond distance is greater than that of Ru−C(25) (2.356(7) vs 2.281(7) Å, respectively). In contrast, the Ru−C bond lengths in [(Cp)Ru(BINAP)]$^+$ are very similar to each other (within twice their esd's) at 2.258(7) and 2.281(9) Å,[37] as are those of the related complex [Ru(η^6-indole)(MeO-BIPHEP-Bu)]$^{2+}$ (2.34(3) and 2.31(3) Å).[38] However, noticeably different Ru−C bond lengths are present in the related [(η^5-C_8H_{11})Ru(MeO-BIPHEP-Pr)]-CF_3CO_2 (2.299(5) and 2.366(5) Å).[12a] While the two Ru−C bond distances within each of **3a** and **4a** are different, the nearly identical Cl−Ru−C angles (av 161°) suggest a symmetric displacement of the bound "olefinic" moiety.

Another consequence of the naphthyl coordination of BINAPO in **3a** and **4a** is a change in the orientation of the Ph rings, from the usual axial/equatorial alternating arrangement as seen in [(*p*-cymene)RuCl(*P*,*O*-BINAPO)]$^+$,[30a] to one in which three of the Ph rings occupy more pseudoequatorial positions. A similar arrangement of the Ph rings has also been observed in Ru(II) complexes of related diphosphine ligands that coordinate via the two P atoms and two C atoms of a biaryl group.[38] The dihedral angles between the planes of the naphthyl rings of the binaphthyl backbone of BINAPO in **3a** and **4a** are 96.6° and 81.6°, respectively. The value of this angle for **4a** is similar to that in BINAPO complexes of Pd (82.1(1)°),[26] Ru (83.6°),[30a] and Os (81(1)°),[30b] in which only *P*,*O*-coordination occurs, and is also similar to that for *P*,*P*′,η^2-coordinated BINAP bound to Ru (80°).[37] However, the dihedral angle in **3a** is larger than that typically observed in BINAP[7a,e,f] and BINAPO[26,30a,b] systems and is even greater than that in $BINAP(O)_2$ (94.17°).[36] Upon changing from *P*,*P*′- to *P*,*P*′,η^2-naphthyl coordination, the dihedral angle of BINAP increases from 66° to 80° ((Cp)RuI(BINAP) vs [(Cp)Ru(BINAP)]$^+$).[37] Similarly, this dihedral angle in **4a** (81.6°) is greater than that in *cis*-$RuCl_2$((*R*)-BINAP)-(phen), **2** (77.37°),[19] although the oxidation of the phosphine may also be a factor; the dihedral angle of the binaphthyl rings in uncoordinated BINAP (88.3°)[39] is substantially less than that in $BINAP(O)_2$ (94.17°).[36] The reason for the large difference of this angle in **3a** and **4a** is not obvious and may be a result of crystal-packing effects.

To summarize then the structural findings, **3a** and **4a** represent the first characterized *P*,*O*,η^2-naphthyl coordination mode of the new class of biaryl-bridged bis(phosphine) monoxide ligands. *P*,*P*′,η^2-naphthyl coordination of BINAP is known,[37,38] and similar bonding in some Ru(MeO-BIPHEP) complexes has been reported.[12a,38] A related novel coordination mode of PPh_3, via the P atom and an η^2-phenyl interaction, has also been reported.[40] Worth noting is that Faller et al. have prepared [(*p*-cymene)M(BINAPO)]$^{2+}$ in situ (M = Ru, Os), which they formulate as solvated species;[30] it is not impossible that the corresponding isolated complexes might exhibit the *P*,*O*,η^2- coordination mode of BINAPO found in **3a**·PF_6 and **4a**·PF_6 in order to compensate for coordinative unsaturation.

Synthesis of 3 and 4. The ratio of the isomers of **3** and **4** formed (**a**:**b**, cf. Figure 1) varied depending on reaction conditions. Thus, refluxing a MeOH solution of *cis*-$RuCl_2$((*R*)-BINAP)(bipy), **1**, in air for 48 h, followed by addition of NH_4PF_6, yielded **3a**·PF_6 and **3b**·PF_6 in a 1:9 ratio, compared to a 3:2 ratio obtained after 14 days for the rt reaction. Complexes **3**·PF_6 and **4**·PF_6 may also be prepared by aerobic oxidation of the corresponding [RuCl((*R*)-BINAP)(L_2)]PF_6 species which are produced in situ by reaction of *cis*-$RuCl_2$((*R*)-BINAP)(L_2) with $AgPF_6$ in CH_2Cl_2.[19b] These cationic complexes presumably possess BINAP bound in a *P*,*P*′,η^2-naphthyl mode, as evidenced from the ^{31}P NMR data, which show one signal shifted well upfield, this being a recognized characteristic of "tridentate" BINAP.[37,38] For example, a CD_2Cl_2 solution of **1** plus 1.2 equiv of $AgPF_6$ gives an AX pattern in the $^{31}P\{^1H\}$ spectrum (δ_A = 68.0, δ_X = 10.6, $^2J_{AX}$ = 30.6 Hz), very different from the $^{31}P\{^1H\}$ data for **1** (δ 47.2 (s)).[19] The η^2-naphthyl binding in [RuCl(BINAP)(L_2)]$^+$ is only

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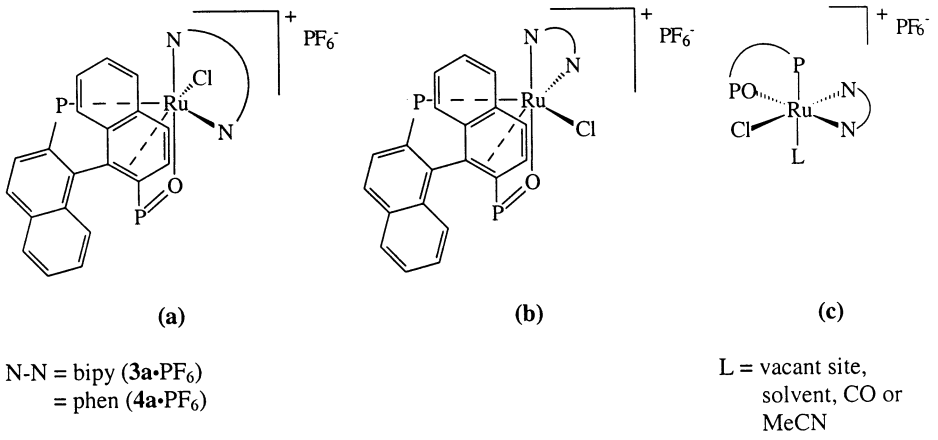
Scheme 2[a]



[a] In **c**, P−PO = BINAPO.

present in noncoordinating or weakly coordinating solvents, as the solvento complexes $[RuCl(BINAP)(L_2)(solvent)]^+$ exist in solvents such as MeOH or MeCN (cf. Figure 1).[19b]

The addition of base (e.g., NEt_3, aqueous NaOH, or KO^{t}Bu) markedly accelerates the formation of the BINAPO species from *cis*-$RuCl_2$(BINAP)(L_2) and gives a single product isomer. For example, the $^{31}P\{^1H\}$ NMR spectrum of a CD_3OD solution of **1**, 2 h after addition of ~10 equiv of NaOH, consists solely of two singlets (δ 70.9 and 58.9), which are assigned to **3a**·Cl; for the isolated **3a**·PF_6 in CD_2Cl_2 the singlets are seen at δ 69.8 and 56.6 (see Experimental Section). Similar results were also obtained with the other bases; however, isolation of clean products from these reactions was difficult.

Reactivity of 3 and 4. Methanolic solutions of **3**·PF_6 and **4**·PF_6 are air-stable for weeks. However, in CD_2Cl_2 or $CDCl_3$ solution, exposure to air causes a color change from yellow to green within 48 h. $^{31}P\{^1H\}$ NMR analysis of the resulting solutions indicates that **3a**·PF_6 and **4a**·PF_6 do not decompose, but **3b**·PF_6 and **4b**·PF_6 do. Thus, the nonstructurally characterized **b** isomers are more reactive than the **a** isomers. While **3**·PF_6 and **4**·PF_6 do not react with H_2, reactivity with CO or MeCN occurs, but only with the **b** isomers. For example, reaction of **3**·PF_6 with 10 equiv of MeCN in CD_2Cl_2 results in the disappearance of the signals due to **3b**·PF_6 and generation of a new set of signals (δ 54.5 s, 50.7 s) proposed to be due to [RuCl(*P*,*O*-BINAPO)(bipy)(MeCN)]PF_6. The ratio of this new nitrile species to **3a**·PF_6 is the same as the **3b**:**3a** ratio prior to MeCN addition. These ratios remain unchanged for 7 days, showing that any possible equilibrium between **3a**·PF_6 and **3b**·PF_6 is exceedingly slow to establish. Similarly, a solution of **4**·PF_6 under 1 atm of CO shows signals due to **4a**·PF_6 and [RuCl(*P*,*O*-BINAPO)(phen)(CO)]PF_6 (δ 54.2 s, 13.3 s).[19b] The upfield signal, relative to those of **4b**·PF_6 (δ 64.9 s, 59.9 s), is indicative of a P atom trans to CO,[41] and the magnitude of the shift suggests that CO is trans to the P^{III} atom, as greater sensitivity of the ^{31}P chemical shift of the unoxidized P atom, compared to that of the P^V atom, has been demonstrated from ligand substitution reactions of Pt(II)−BINAPO systems.[24]

The $^{31}P\{^1H\}$ NMR data suggest that the products of reaction of **3b**/**4b** with simple donor ligands have structure **c** (L = MeCN or CO) as shown in Scheme 2. The stability of **3a**/**4a** shows that the facial *P*,*O*,η^2-coordination of BINAPO is kinetically stable (structure **a**, Scheme 2), in contrast to the ready displacement of the η^2-naphthyl moiety observed for complexes with *P*,*P*′,η^2-bonding modes of BINAP and MeO−BIPHEP.[12a,37,38] Two structures for **3b**/**4b** seem plausible: **b** in Scheme 2, in which the η^2-naphthyl moiety is coordinated trans to a N atom, or **c**, in which L is a vacant site trans to the coordinated P atom. In solution, a weakly coordinated solvent molecule may occupy this vacant site. The instability of **3b**/**4b** in noncoordinating or weakly coordinating solvents and the $^{31}P\{^1H\}$ evidence that reaction with MeCN or CO gives products with the incoming ligand trans to the P atom favor structure **c**.

Synthesis and Reactivity of dppbO Complexes. Aerobic oxidation of phosphine in *cis*-$RuCl_2$(dppb)(L_2) (L_2 = bipy (**5**), phen (**6**)) to give complexes containing dppbO also occurs, although this reaction is much slower relative to those with the analogous BINAP complexes. Again, addition of base markedly increases the rate of formation of the BPMO species. Thus, while formation of *cis*-$RuCl_2$(dppbO)(bipy) (**7**) is incomplete after 30 days at rt in MeOH, the reaction is quantitative in <1 h in the presence of ~10 equiv of base, as judged by $^{31}P\{^1H\}$ NMR. As for **3**·PF_6 and **4**·PF_6, the $^{31}P\{^1H\}$ NMR spectra of **7** and **8** consist of a singlet for each P atom (**7**: δ 53.4, 32.2; **8**: δ 53.7, 32.0), and only one product is observed for the dppbO species (i.e., only one geometric isomer is formed). As **5** and **6** are formed as a racemic mixture,[18] it is assumed that **7** and **8** are also prepared as racemates. On the basis of the NMR and IR spectroscopic data, **7** and **8** are proposed to be neutral, six-coordinate, *cis*-dichloro complexes in which dppbO is *P*,*O*-coordinated. Within *cis*-dichloro species, the P^V atom can be trans to N or Cl, while the P^{III} atom will be correspondingly trans to Cl or N. Though the dppbO ligand in these complexes might be expected to be hemilabile,[20,29] displacement of the coordinated phosphine oxide "arm" to give η^1-dppbO is not facile. For

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example, the $^{31}P\{^1H\}$ NMR spectrum of **7** remains unchanged after the addition of 100 equiv of MeCN or 1 atm of CO to a $CDCl_3$ solution of the complex.

Mechanism of Oxidation. While oxidation of a coordinated phosphine to phosphine oxide is well-known, and indeed catalytic systems employing transition metal complexes have been developed for such oxidations,[32,42−44] examples of aerobic oxidation of a coordinated chelating diphosphine to give a coordinated phosphine oxide group are relatively rare.[25b,45] There are examples of reaction of coordinated BINAP in Ru(II) systems to give complexes in which P−O bonds have formed; however, these also involve cleavage of a P−C(naphthyl) bond and, for example, subsequent hydrolysis to give the 2-diphenylphosphino-1,1′-binaphthyl ligand, either coordinated in a *P*,η^4-naphthyl (with Ph_2P═O co-ligand)[46] or a *P*,η^6-naphthyl (with $Ph_2P(OH)$ co-ligand)[47] fashion. Similar reactivity also occurs with related MeO−BIPHEP complexes.[47,48] Subsequent oxidation of the coordinated P atom in the $Ph_2P(OH)$ fragment, which was cleaved from the original BINAP or MeO−BIPHEP ligands, in the presence of H_2O has also been reported.[49]

Our preliminary investigations on the mechanism of formation of the BPMO complexes from the *cis*-$RuCl_2(P-P)(L_2)$ species have not been conclusive. The enhancement of reaction rate by base could indicate the involvement of OH^-, as in the well-established chemistry shown in eq 1.[42,50] To investigate the source of the

$$P^{III} + OH^- \rightarrow P^V{=}O + H^+ + 2e \qquad (1)$$

O atom in the BPMO products, the effects of H_2O and O_2 on the reaction were examined. A CD_3OD solution of **1** and ∼250 equiv of H_2O exposed to air was monitored by $^{31}P\{^1H\}$ NMR. The initial spectrum was notably different from that obtained without the added water, which is similar to that shown in Figure 1. In the presence of excess water, signals due to **1** were absent, and the more upfield signal of the cationic species is substantially broadened while the downfield signal remains unchanged. The broadening likely results from coordinative competition of H_2O and MeOH, and similar broadening due to such solvent exchange has been observed in the $^{31}P\{^1H\}$ NMR spectra of Ru(II),[51] as well as Rh(I) and Ir(I) complexes.[52] At −60 °C, the solution spectrum consists of signals due to **1**, [RuCl((*R*)-BINAP)(bipy)$(CD_3OD)]^+$, and an AX pattern that we assign to [RuCl((*R*)-BINAP)(bipy)$(H_2O)]^+$ ($\delta_A = 58.5$, $\delta_X = 49.8$, $^2J_{AX} = 37.8$ Hz). The oxidation of the phosphine occurs slower in the presence of the added H_2O, being only ∼75% complete after 14 days at rt, compared to 100% completion in the absence of added H_2O. Also, under an Ar atmosphere, low conversion of **1** to **3** occurs in a MeOH solution with >50 equiv of H_2O added, even in the presence of added base: after 1 h, <10% conversion to **3** is observed, and the same reaction in air gives 100% conversion after this time. Of note, a solution of **2** in CD_3OD under 1 atm of O_2 showed no conversion to the BINAPO species **4** after 1 week, relative to ∼70% conversion obtained when the reaction is performed in air (cf. Figure 1). The available data implicate the necessity of both O_2 and H_2O for the formation of the BPMO complexes. No reduced coproduct has been identified (cf. eq 1), although the high yields of the isolated complexes indicate that sacrificial reduction of Ru does not occur; reduction of O_2 with involvement of peroxide (or superoxide) is plausible (see below). Labeling experiments using $H_2{}^{18}O$ were inconclusive in IR studies because of a preponderance of bands present in the ν(P═O) region for **3** and **4**, while mass spectrometry data showed no detectable incorporation of ^{18}O into these complexes.

The direct use of peroxides as oxidant was also examined. Addition of ∼5 equiv of H_2O_2 (30% aqueous) to a CD_3OD solution of **1** caused immediate effervescence, and the $^{31}P\{^1H\}$ spectrum of this solution obtained within 5 min shows the presence of a Ru(BINAPO) species (δ 74.3 s, δ 59.9 s), probably **3a**·Cl and free $BINAP(O)_2$ (δ 36.1 s) in a 1:3 ratio. Complete oxidation to $BINAP(O)_2$ occurred within 15 min. The $^{31}P\{^1H\}$ spectrum of a CD_3OD solution of **1** with 1 equiv of cumene hydroperoxide after 15 min shows the presence of **1**, [RuCl((*R*)-BINAP)(bipy)$(CD_3OD)]^+$, and another species ($\delta_A = 50.7$, $\delta_X = 42.5$, $^2J_{AX} = 35.1$ Hz), possibly an alkylperoxide-containing complex, in a 1:2:4 ratio, respectively. Within 3 h, the formation of **3** is detected, and within 5 days there is complete conversion to **3a** and **3b** in the same 3:2 ratio produced in the absence of added peroxide. Oxidation of coordinated PPh_3 via platinum metal−OOH species (including those of Ru) has also been documented.[45d,53]

The oxidation of the diphosphine ligand in some Ru(II)(P−P) systems under catalytic epoxidation conditions using PhIO has been noted.[54,55] Related to the *cis*-$RuCl_2(P-P)(L_2)$ complexes discussed here are the [RuCl$(P_2N_2)]^+$ complexes, where P_2N_2 = a chiral tetradentate

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diphosphine-diimine or -diamine ligand; these catalyze asymmetric epoxidation of olefins with H_2O_2, and phosphine oxide-containing species are considered to be formed by reaction of the $[RuCl(P_2N_2)]^+$ complexes with H_2O_2.[16]

Conclusions

The aerobic oxidation of one P atom of the bis(phosphine) ligand in *cis*-$RuCl_2(P-P)(L_2)$ complexes (L_2 = bipy or phen) generates products containing the corresponding bis(phosphine) monoxide ligands (P−P═O), and complexes of the type $[RuCl(BINAPO)(L_2)]PF_6$ and $RuCl_2(dppbO)(L_2)$ have been synthesized. A novel *P,O,*η^2-coordination mode of BINAPO involving the unoxidized P atom, the O atom, and an η^2-naphthyl interaction has been established.

Experimental Section

General Procedures. Unless stated otherwise, manipulations were carried out under Ar using standard Schlenk techniques. Reagent grade solvents (Fisher Scientific) were distilled from Na (Et_2O, hexanes), CaH_2 (CH_2Cl_2), or Mg/I_2 (MeOH) under N_2. Deuterated solvents ($CDCl_3$, CD_2Cl_2, CD_3OD) were obtained from Cambridge Isotope Laboratories and dried if necessary over activated molecular sieves (Fisher: type 4 Å), deoxygenated, and stored under Ar. Other reagents were used as supplied by commercial vendors. Ruthenium was obtained as $RuCl_3 \cdot 3H_2O$ on loan from Johnson Matthey Ltd. or Colonial Metals Inc., and (*R*)-BINAP was a gift from Dr. S. King (formerly of Merck). The $RuCl_2(P-P)(L_2)$ complexes **1**, **2**, **5**, and **6** were prepared by our reported methods.[18,19] Solution NMR spectra were recorded on a Varian XL300 FT-NMR spectrometer (299.94 MHz for ^1H, 121.42 MHz for ^{31}P), using residual solvent proton (^1H) or external $P(OMe)_3$ (^{31}P: δ 141.0 vs external 85% aqueous H_3PO_4) as reference. All *J* values are given in Hz. ^{31}P chemical shifts are reported with respect to 85% aqueous H_3PO_4, downfield shifts being taken as positive. UV−vis spectra were recorded on a Hewlett-Packard diode array spectrophotometer and are given as λ (nm) [ϵ (M^{-1} cm^{-1})], sh = shoulder. IR spectra were recorded on KBr pellets using an ATLI Mattson Genesis Series FTIR spectrophotometer. Mass spectrometry studies were performed by the Mass Spectrometry Facility, and elemental analyses were performed by P. Borda of the Microanalyis Facility, at the University of British Columbia.

Preparation of $[RuCl(BINAPO)(bipy)]PF_6$ (3·PF_6). An orange solution of *cis*-$RuCl_2$((*R*)-BINAP)(bipy) (**1**) (49 mg, 0.051 mmol) in MeOH (6 mL) was stirred in air for 14 days at rt, when the solution became deep red. Solid NH_4PF_6 (85 mg, 0.52 mmol) was added to the solution, and the mixture stirred for 5 h. The solvent was removed in vacuo, and the dark red residue then dissolved in CH_2Cl_2 (5 mL) and filtered through Celite with washings of CH_2Cl_2 (4 × 4 mL). The filtrate was concentrated under vacuum to ∼5 mL, and the product was precipitated by addition of Et_2O (10 mL) and hexanes (15 mL), collected by filtration, washed with hexanes (2 × 3 mL) and Et_2O (4 × 3 mL), and dried in vacuo. Yield (as a mixture of PF_6 salts of isomers **3a** and **3b**): 40 mg (73%). Anal. Calcd for $C_{54}H_{40}N_2ClF_6OP_3Ru$: C, 60.26; H, 3.75; N, 2.60. Found: C, 60.22; H, 3.76; N, 2.74. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): for **3a**, δ 69.8 s, 56.6 s, and for **3b**, δ 62.7 s, 59.2 s; −144.0 m J_{PF} = 710. ^1H NMR (CD_2Cl_2): δ 4.20−10.20 (br m, BINAPO and bipy protons). IR (KBr, cm^{-1}): ν(PO) 1129 (w, **3a**) and 1150 (w, **3b**), ν(PF) 841. UV−vis (CH_2Cl_2): 422 [4,800]. LRMS [+LSIMS]: 931 (M^+), 896 (M^+ − Cl), 739 (M^+ − Cl − bipy). X-ray quality, orange crystals of **3a**·PF_6 were obtained by slow aerobic evaporation of a $CHCl_3$ solution of the product obtained from the reaction of **1** with 1 equiv of $AgPF_6$.

Table 3. Crystallographic Data for $[RuCl(BINAPO)(bipy)]PF_6$ (3a·PF_6) and $[RuCl(BINAPO)(phen)]PF_6$ (4a·PF_6)

	3a·PF_6·$2CHCl_3$	**4a**·PF_6·CH_3OH
chemical formula	$C_{56}H_{42}N_2Cl_7F_6OP_3Ru$	$C_{57}H_{44}N_2ClF_6O_2P_3Ru$
fw	1315.11	1132.37
space group	$P2_12_12_1$ (No. 19)	$P4_32_12$ (No. 96)
Z	4	8
a, Å	13.2409(3)	11.8013(3)
b, Å	20.0499(5)	11.8013(3)
c, Å	20.387(1)	71.073(2)
V, Å^3	5412.2(3)	9898.3(4)
D_{calcd}, g cm^{-3}	1.614	1.520
μ, cm^{-1}	7.88	5.37
λ, Å	0.71069	0.71073
T, °C	−100	−100
R; R_w (on F^2, all data)[a]	0.077, 0.111	0.1103; 0.1242

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum[w(F_o^2 - F_c^2)^2/\sum[w(F_o^2)^2]]^{1/2}$.

Preparation of $[RuCl(BINAPO)(phen)]PF_6$ (4·PF_6). Compound **4**·PF_6 was prepared in a manner analogous to that used for **3**·PF_6. Thus, after a MeOH solution of *cis*-$RuCl_2$((*R*)-BINAP)(phen) (**2**) (33 mg, 0.034 mmol) was stirred in air for 17 days at rt, NH_4PF_6 (58 mg, 0.36 mmol) was added and the resulting mixture stirred for 1.5 h. After workup, the yellow product was isolated and dried in vacuo. Yield (as a mixture of PF_6 salts of isomers **4a** and **4b**): 32 mg (88%). Anal. Calcd for $C_{56}H_{40}N_2ClF_6OP_3Ru$: C, 61.13; H, 3.66; N, 2.55. Found: C, 61.10; H, 3.74; N, 2.69. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): for **4a**, δ 69.5 s, 57.3 s, and for **4b**, δ 64.9 s, 59.9 s; −144.0 m J_{PF} = 710. ^1H NMR (CD_2Cl_2): δ 4.20−10.50 (br m, BINAPO and phen protons). IR (KBr, cm^{-1}): ν(PO) 1126 (w, **4a**) and 1159 (w, **4b**), ν(PF) 841. UV−vis (CH_2Cl_2): 416 [5,700]. LRMS [+LSIMS]: 955 (M^+), 919 (M^+ − Cl), 739 (M^+ − Cl − phen). Slow evaporation in air of the MeOH solution containing **2** and excess NH_4PF_6 gave orange crystals of **4a**·PF_6 suitable for X-ray analysis.

Preparation of $RuCl_2(dppbO)(bipy)$ (7). NEt_3 (0.08 mL, 0.57 mmol) was added to a stirred solution of *cis*-$RuCl_2(dppb)$(bipy) (**5**) (44 mg, 0.058 mmol) in MeOH (15 mL) in air, and the resulting solution was stirred at rt for 22 h, when the solution changed from orange to dark red. The solvent was removed under vacuum, and the residue was taken up in CH_2Cl_2 (2 mL). Addition of Et_2O (25 mL) precipitated the product that was collected by filtration, washed with Et_2O (4 × 2 mL), and then dried in vacuo. Yield: 35 mg (77%). Anal. Calcd for $C_{38}H_{36}N_2Cl_2OP_2Ru$: C, 59.23; H, 4.71; N, 3.64. Found: C, 59.26; H, 4.82; N, 3.80%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 53.4 s (P^{III}), 32.2 s (P^V). ^1H NMR ($CDCl_3$): δ 0.90−2.52 (br m, 8H, CH_2), 6.70−7.80 (br m, 26H: 20H for Ph protons, and 6H for $H_{3/3'}$-$H_{5/5'}$ of bipy), 8.12 (m, 1H, H_6 of bipy), 8.91 (m, 1H, $H_{6'}$ of bipy). IR (KBr, cm^{-1}): ν(PO) 1121 (m). UV−vis (CH_2Cl_2): 494 [4200], 344 [5000].

Preparation of $RuCl_2(dppbO)(phen)$ (8). Compound **8** was prepared in a manner similar to that used for **7**, using *cis*-$RuCl_2(dppb)$(phen) (**6**) (29 mg, 0.037 mmol) and NEt_3 (0.05 mL, 0.036 mmol) in MeOH (15 mL). The mixture was stirred in air for 18 h and then worked up as described for **7**. Yield: 23 mg (76%). Anal. Calcd for $C_{40}H_{36}N_2Cl_2OP_2Ru$: C, 60.46; H, 4.57; N, 3.52. Found: C, 59.38; H, 4.90; N, 3.64. Several attempts to obtain a better microanalysis were unsuccessful. Anal. Calcd for a monohydrate: C, 59.11; H, 4.71; N, 3.45. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 53.7 s (P^{III}), 32.0 s (P^V). ^1H NMR ($CDCl_3$): δ 1.00−2.50 (br m, 8H, CH_2), 6.52−8.80 (br m, 27H: 20H for Ph protons and 7H for H_2-H_8 of phen), 9.43 (m, 1H, H_9 of phen). IR (KBr, cm^{-1}): ν(PO) 1120 (m). UV−vis (CH_2Cl_2): 490 [5,600], 456 [5,000] (sh).

X-ray Crystallography. Crystallographic data for **3a**·PF_6 and **4a**·PF_6 are summarized in Table 3. The structure of

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3a·PF_6 that crystallized with two $CHCl_3$ solvates was determined using data collected on a Rigaku/ADSC CCD diffractometer at −100 °C. The data, corrected for Lorentz and polarization effects, were collected and processed,[56] and the structure was solved by direct methods and expanded using Fourier techniques. Of 44 345 reflections collected, 11 493 were unique ($R_{int} = 0.055$); equivalent reflections were merged. The final cycle of full-matrix least-squares refinement was based on 11 466 observed reflections ($I > 0/00\sigma(I)$) and 685 variable parameters. All non-hydrogen atoms were refined anisotropically; H atoms were included but not refined. All calculations were performed using the teXsan crystallographic software package.[56a]

The structure of **4a**·PF_6 that crystallized with an MeOH solvate was determined from data collected on a Siemens SMART Platform CCD diffractometer at −100 °C. Most non-hydrogen atoms were located using a direct methods solution, and several least squares/difference Fourier cycles were performed to locate the remainder. All H atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Of the 80 682 reflections collected, 8740 were independent ($R_{int} = 0.0650$). Due to the high-symmetry Laue class, an investigation was performed to show that the crystal was not twinned. The length of the *c* cell constant led to repositioning of the CCD detector, setting it at 8.0 cm to collect data in two swaths. The Flack *x* parameter (0.02(4)) was used to identify the correct space group ($P4_32_12$) from its enantiomorph ($P4_12_12$). To aid the refinement of C(13)−C(18) and C(25)−C(34), 43 restraints (DELU and ISOR) were added. All calculations were performed using the SHELXTL suite of programs.[57]

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Supporting Information Available: Tables of crystallographic data for **3a**·PF_6 and **4a**·PF_6, including positional and thermal parameters, complete bond lengths and angles, anisotropic displacement parameters, and ORTEP figures showing the entire molecules with full numbering schemes. This material is available free of charge via the Internet at http://pubs.acs.org.

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(56) (a) *teXsan: Crystal Structure Analysis Package*; Molecular Structure Corporation: The Woodlands, TX, 1997. (b) *d*TREK: Area Detector Software*; Molecular Structure Corporation: The Woodlands, TX, 1997.

(57) *SHELXTL-Plus, Version 5.0*; Siemens Industrial Automation, Inc.: Madison, WI, 1994.

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