Diastereoselectivity in Chiral Ruthenium Complexes of Bidentate Bisphosphine Monoxide Ligands: Controlling Epimerization in Aldehyde Complexes and 16-Electron Intermediates

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Heterobidentate and hemilabile ligands involving P,O-donor chelates produce chiral metal centers when bound to arene−ruthenium complexes. This chirality in cymene complexes produces diastereotopic methyl groups in the isopropyl ligand which serve as a detector of the chirality at the metal. [CyRu(η^2-chelate-*P,O*)Cl]$^+$ cations are precursors to strong 16-electron dicationic Lewis acids which have potential use in asymmetric catalysis. Sixteen-electron complexes of this type, however, provide a pathway with a low barrier to racemization or epimerization of the metal center in intermediates, such as [CyRu(η^2-chelate-*P,O*)(PhCHO)]$^{2+}$. Substitution of the central carbon in diphenylphosphinomethane monoxide (dppmO) forces the ligand to adopt a configuration with the substituent in an endo position, thus forcing the 16-electron intermediate to return diastereoselectively to its original configuration and prevents epimerization. Thus, an X-ray structure shows that (R^*_{Ru},R^*_C)-[CyRu(η^2- Ph_2PCHR)Ph_2PO-*P,O*)Cl]$^+$ is the preferred diastereomeric pair. In the parent, [CyRu(η^2-dppmO-*P,O*)(ligand)]$^{2+}$, racemization occurs at the metal center, since there is nothing driving the preferential formation of either the *R* or *S* ruthenium center. When the ligands are chiral, however, the metal center epimerizes to minimize steric interactions in the two diastereomers. The equilibrium between [(R_{Ru})-CyRu(η^2-dppmO-*P,O*)(R_C-ligand)]$^{2+}$ and [(S_{Ru})-CyRu(η^2-dppmO-*P,O*)(R_C-ligand)]$^{2+}$ reflects a 37% de for (1*R*)−(−)-myrtenal. Since a substituent on the central carbon prevents epimerization at the metal center, this diastereoselectivity is reflected in a preference for binding of (R_C)-ligand by either [(R_{Ru},R_C)-CyRu(η^2-Ph_2PCHPr)Ph_2PO-*P,O*)]$^{2+}$ or [(S_{Ru},S_C)-CyRu(η^2-Ph_2PCHPr)Ph_2PO-*P,O*)]$^{2+}$. An X-ray structure of *rac*-[(R_{Ru}*,R_C*)-CyRu(η^2-Ph_2PCHPr)Ph_2PO-*P,O*)(PhCHO]$^{2+}$ shows that the aldehyde assumes an orientation that would suggest one stereoface of the aldehyde may be more susceptible to attack.

Introduction

Owing in part to their mixed donor properties, heterobidentate phosphines have found wide use in catalysis as hemilabile ligands capable of generating open coordination sites for substrate binding. An equally important, yet less exploited, feature of these ligands is that they are unsymmetrical and upon chelation generate chirality and electronic asymmetry at the metal center in certain complexes. Of the following known motifs, η^2-P/N,[1] η^2-P/S,[2] η^2-P/Se,[3] η^2-P/C,[4] and η^2-P/O,[5] we have recently become interested in the latter, which can be obtained via ether phosphines, β-ketophosphines, phosphinocarboxylates, phosphino alcohols, phosphinosulfoxides, or bisphosphine monoxides. We are currently focusing on phosphinosulfoxides and bisphosphine monoxide ligand systems in our development of chiral ruthenium Lewis acids.[6] These studies are particularly relevant to maintaining the chirality at a metal center, which might otherwise undergo rapid racemization or epimerization via a free Lewis acid.

Herein, we describe the synthesis and characterization of a new series of ruthenium Lewis acid precursors containing chiral bisphosphine monoxide ligands based on the 1,1′-bis(diphenylphosphino)methane monoxide (dppmO, **1a**) skeleton. Although a number of metal complexes of **1a** are known, only a few are known that contain substitution on the backbone,[7,8] and the work reported here represents the first example that investigates the stereochemistry of complexes with the chiral derivatives $Ph_2PCH(R)P(O)Ph_2$ (R = CH_3, **1b**; Ph,

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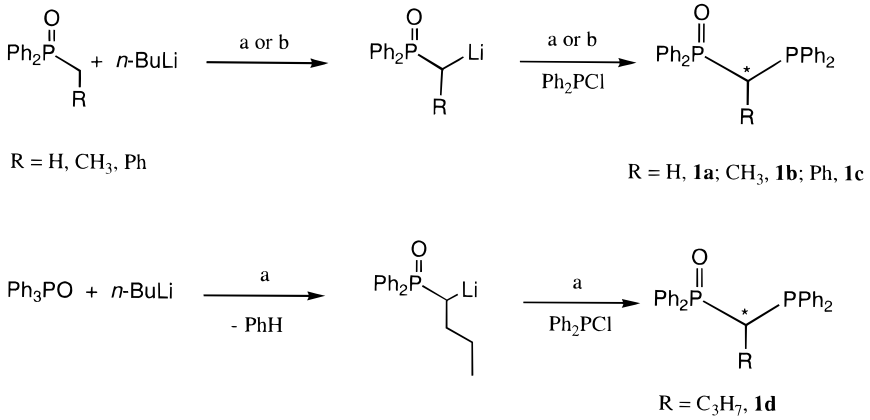
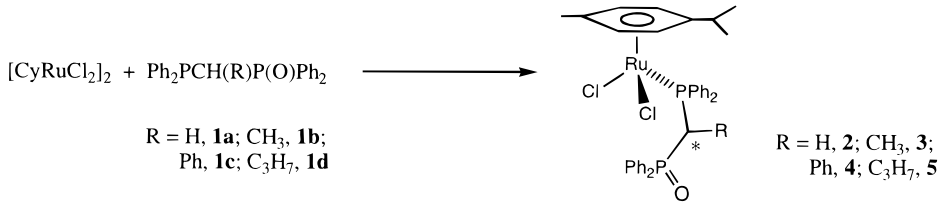
Scheme 1. Preparative Strategies for the Syntheses of Ligands 1a−1d: (a) Diethyl Ether, −78 °C; (b) THF, −78 °C



Scheme 2. Formation of η^1 Complexes 2−5



1c;C_3H_7, **1d**). The results described below suggest that the presence of the substituent and the chiral center in the backbone of **1b**−**1d** can influence their binding mode upon chelation, leading to high diastereoselectivity in the formation of the metal complexes.

Results

Ligand Synthesis. Procedures for the preparation of the bisphosphine monoxide ligands **1a**−**1d** are available in the literature (Scheme 1).[8−10] Except for the parent **1a**, the ligands were hygroscopic and were readily oxidized to the bisphosphine oxides, which often led to problems with isolation of pure ligand. We have adapted the procedures (Scheme 1) for preparation of the ligands in situ, but avoid the oxidation problem by complexation of the phosphine prior to isolation. One published procedure favors treatment of Ph_3PO with an alkyllithium, which serves to displace a phenyl as LiPh, which in turn lithiates the activated alkyl and provides a $Ph_2PCHRLi$ intermediate, as shown for the butyl derivative, **1d**. In our hands, starting with the diphenylalkylphosphine oxide produced cleaner products, particularly with ligands other than **1d**.

Synthesis of [(η^6-Cy)RuCl$_2$(η^1-Ph$_2$PCH(R)P(O)Ph$_2$)] Complexes. The ligands **1a** and **1b** readily cleaved the ruthenium dimer [(η^6-Cy)RuCl$_2$]$_2$ (Cy = cymene) in dichloromethane to yield [(η^6-Cy)RuCl$_2$(η^1-$Ph_2PCH_2P(O)Ph_2$)] (**2**) and [(η^6-Cy)RuCl$_2$(η^1-$Ph_2PCH(CH_3)P(O)Ph_2$)] (**3**), in which the phosphorus atom of the chelate was bound to the metal center (Scheme 2). In the $^{31}P\{^1H\}$ NMR spectrum this mode of coordination was marked by a large downfield shift in the P(III) resonance and a significant reduction in the $^2J_{PP}$ coupling constant. In the cases of **1c** and **1d**, these ligands also cleaved the ruthenium dimer in dichloromethane to initially yield [(η^6-Cy)RuCl$_2$(η^1-$Ph_2PCH(Ph)P(O)Ph_2$)] (**4**) and [(η^6-Cy)RuCl$_2$(η^1-$Ph_2PCH(C_3H_7)P(O)Ph_2$)] (**5**) in situ, but then reacted further by displacing a chloride ligand and chelating the metal center to produce their respective η^2- isomers, [(η^6-Cy)RuCl(η^2-$Ph_2PCH(Ph)P(O)Ph_2$)][Cl] (**4′**) and [(η^6-Cy)RuCl(η^2-$Ph_2PCH(C_3H_7)P(O)Ph_2$)][Cl] (**5′**). As a consequence, the η^1 compounds **4** and **5** were not isolable.

Coordination Isomerism in Complexes 2−5. We found that in moderately polar solvents (CH_2Cl_2 and $CHCl_3$) the η^1 complexes **3**−**5** readily form an equilibrium with their respective η^2 coordination isomers, [(η^6-Cy)RuCl(η^2-$Ph_2PCH(R)P(O)Ph_2$)][Cl] (R = CH_3, **3′**; Ph,

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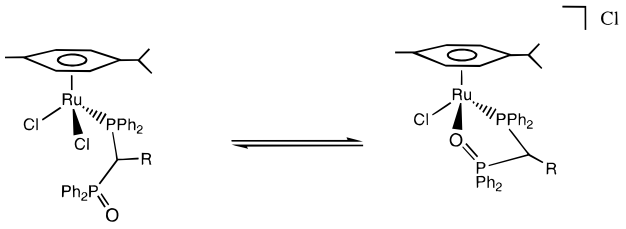
(10) $^{31}P\{^1H\}$ NMR (293 K, δ): **1a** (THF) 29.4 (d, $^2J_{PP}$ = 53 Hz, P(V)), −27.9 (d, $^2J_{PP}$ = 53 Hz, P(III)); **1b** ($CHCl_3$) 36.1 (d, $^2J_{PP}$ = 65 Hz, P(V)), −12.6 (d, $^2J_{PP}$ = 65 Hz, P(III)); **1c** ($CHCl_3$), 30.0 (d, $^2J_{PP}$ = 56 Hz, P(V)), −6.8 (d, $^2J_{PP}$ = 56 Hz, P(III)); **1d** ($CHCl_3$), 35.7 (d, $^2J_{PP}$ = 69 Hz, P(V)); −9.7 (d, $^2J_{PP}$ = 69 Hz, P(III)).

Scheme 3. Coordination Isomerism in Complexes 3−5



R = CH_3, **3**; Ph, **4**; C_3H_7, **5** R = CH_3, **3'**; Ph, **4'**; C_3H_7, **5'**

4′; C_3H_7, **5′**) (Scheme 3). In the case of **3**/**3′**, an ∼1:1 equilibrium was ultimately established at room temperature ($t_{1/2}$ − 30 min) in CH_2Cl_2. The rate of interconversion in ethyl acetate is considerably slower. The difference in charge between these two coordination isomers allowed for facile separation by column chromatography on silica gel and isolation of pure **3**. If pure **3** was redissolved in CD_2Cl_2, the equilibrium distribution was established over several hours. In contrast, under conditions similar to those described above, the η^1 coordination isomers of **4** and **5** converted quantitatively ($t_{1/2}$ of several minutes) in CH_2Cl_2 and $CHCl_3$ to **4′** and **5′**, respectively, and remained as the chelated η^2 isomers independent of solvent choice. As a result, compounds **4** and **5** could only be isolated as the η^2 coordination isomers **4′** and **5′**. Surprisingly this equilibrium was not observed for the parent compound [(η^6-Cy)$RuCl_2$(η^1-$Ph_2PCH_2P(O)Ph_2$)] (**2**), even after several days in dichloromethane. This suggests that the steric bulk in the ligand backbones of complexes **5** might be driving the chelation, in a rough analogy with the Thorpe−Ingold effect.[11] In most cases we converted the chloride salts to the SbF_6^- salts to allow purification and preparation of crystals suitable for X-ray diffraction.

Synthesis of [(η^6-Cy)$RuCl_2$(η^2-$Ph_2PCH(R)P(O)Ph_2$)][SbF_6] Complexes. The η^2 complexes [(η^6-Cy)RuCl(η^2-$Ph_2PCH_2P(O)Ph_2$)][SbF_6] (**6**) and [(η^6-Cy)RuCl(η^2-$Ph_2PCH(CH_3)P(O)Ph_2$)][SbF_6] (**7**) were prepared by reaction of the respective η^1 complexes, **2** and **3**, with 1 equiv of $AgSbF_6$ in dichloromethane at room temperature. The η^2 complexes [(η^6-Cy)$RuCl_2$(η^2-$Ph_2PCH(Ph)P(O)Ph_2$)][SbF_6] (**8**) and [(η^6-Cy)$RuCl_2$(η^2-$Ph_2PCH(C_3H_7)P(O)Ph_2$)][SbF_6] (**9**) were prepared under similar conditions except starting from the η^2 isomers, **4′** and **5′**. In all four complexes both phosphorus resonances in the $^{31}P\{^1H\}$ NMR spectra were shifted downfield, and we have tentatively assigned the resonance furthest downfield to the P(V) phosphorus.

X-ray Diffraction Study of Some Key Complexes. The structures of compound **3** and the SbF_6^- salts derived from **3′** and **5′**, **6** and **9** were determined by X-ray diffraction methods, and the data are summarized in are Table 1. The structure of an aldehyde complex, **10**, which is discussed later, is also included in the table. Figure 1 shows the structure of a typical η^1 complex, **3**.

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As shown in Figure 2, chelation of the ligand produces a chiral metal center. Consequently **6** is isolated and crystallized as a racemate. Upon chelation, in addition to the chiral environment at the metal centers in compounds **7**−**9**, the bridging carbon provides a second chiral center; thus diastereomeric complexes could form. Given that these ligands are capable of chelating the metal in two possible modes and therefore producing two distinct diastereomers in compounds **7**−**9**, we were pleased to note that only one set of resonances was observed in each of the $^{31}P\{^1H\}$ NMR spectra, indicating that only one diastereomer was present in solution in significant concentration. This suggests that there is a preferred mode of ligand chelation, which presumably arises from steric interactions of the R group in the ligand backbone with other ligands.

The Preferred Diastereomer of [(η^6-Cy)RuCl(η^2-$Ph_2PCH(C_3H_7)P(O)Ph_2$)][SbF_6] (9). Diffraction quality crystals of {**9**[$O(C_2H_5)_2$]}were grown from a dichloromethane/diethyl ether solution, and the structure was determined by the X-ray diffraction as shown in Figure 3. In support of the solution data, only the enantiomers of one diastereomer of **9** were observed in the solid state with the configurations of (R_{Ru}, R_C) and (S_{Ru}, S_C) or relative configurations of (R_{Ru}*, R_C*). The propyl chain in the backbone of the ligand was found to be oriented away from the chloride ligand, most likely as a result of steric effects. It follows that the same configuration would exist in all three η^2 compounds, **7**−**9**; thus the relative configuration of the metal center and carbon center of the single diastereomers observed in solution for **7** and **8** can be assigned by analogy to **9**. The presence of the chiral center in the backbone of these ligands gives rise to high diastereoselectivity in the formation of chelated complexes.

Aldehyde and Sulfoxide Complexes [(η^6-Cy)Ru(L)(η^2-$Ph_2PCH(R)P(O)Ph_2$)][SbF_6]$_2$. A series of aldehyde derivatives of complexes **7**−**9** were prepared in situ, and their $^{31}P\{^1H\}$ NMR data are summarized in Table 2. Complexes **7**−**9** were first treated with $AgSbF_6$, in dichloromethane, to produce complexes that we indicate as the free acid [(η^6-Cy)Ru(η^2-$Ph_2PCH(R)P(O)Ph_2$)][SbF_6]$_2$, but may either be solvates or aqua complexes or contain coordinated SbF_6. These precursors were then treated with excess quantities of the appropriate aldehyde. The critical observation in the $^{31}P\{^1H\}$ NMR spectra for the achiral aldehyde derivatives is the presence of only an AX pattern indicative of a single diastereomer. In the ^1H NMR spectra the arene protons and the isopropyl methyl protons are diastereotopic and free aldehyde is observed, which indicates that the complexes are not undergoing rapid equilibration. There is only a very small coordination shift of the CHO proton (0.02 ppm) so that ^{31}P spectra allow better characterization of binding. These spectra are similar to the spectra of the chloride complexes **7**−**9**, where only one diastereomer was observed in solution. In these aldehyde complexes, a single diastereomer with the substituent oriented away from the aldehyde is expected. The crystal structure data for [(η^6-Cy)Ru(PhCHO)(η^2-$Ph_2PCH(C_3H_7)P(O)Ph_2$)][SbF_6]$_2$, **10**, is given in Table 1. The endo propyl group of **10** is shown in Figure 4 and further illustrates this point. This structure also demonstrates that the carbonyl is σ-bonded rather than

Table 1. Crystallographic Data for [(η^6-Cy)RuCl$_2$(η-Ph$_2$PCH(CH$_3$)P(O)Ph$_2$)] (3), [(η^6-Cy)RuCl(η^2-Ph$_2$PCH$_2$P(O)Ph$_2$)][SbF$_6$] (6), [(η^6-Cy)RuCl(η^2-Ph$_2$PCH(C$_3$H$_7$)P(O)Ph$_2$)][SbF$_6$] (9), and [(η^6-Cy)Ru(PhCHO)(η^2-Ph$_2$PCH(C$_3$H$_7$)P(O)Ph$_2$)][SbF$_6$] (10)

	3	6	9	10
formula	$RuCl_2P_2OC_{36}H_{39}$	$SbRuClP_2F_6OC_{35}H_{36}$	$SbRuClP_2F_6OC_{38}H_{42}$	$Sb_2RuClP_{12}F_2OC_{45}H_{48}$
fw	721.63	906.88	948.96	1255.37
a, Å	31.82(4)	11.2691(7)	18.5995(4)	22.2276(4)
b, Å	9.686(5)	19.190(2)	14.2399(3)	10.7706(2)
c, Å	21.511(7)	16.958(1)	14.7627(2)	19.9741(3)
β (deg)	98.56(5)	96.316(4)	90	90
V, Å^3	6555(7)	3644.9(4)	3910.0(2)	4781.9(1)
Z	8	4	4	4
space group	*C*2/*c* (No. 15)	$P2_1/n$ (No. 14)	$Pna2_1$ (No. 33)	$Pna2_1$ (No. 33)
ρ_{calcd}, g cm^{-3}	1.462	1.652	1.612	1.708
μ (Mo Kα), cm^{-1}	7.67	13.73	12.84	15.50
temp, °C	−103	24	−90	−90
λ (Å)	0.71069	0.71069	0.71069	0.71069
$R(F_o)$	0.035	0.048	0.037	0.019
$R_w(F_o)$	0.037	0.047	0.040	0.023
GOF	1.65	1.73	1.63	1.06

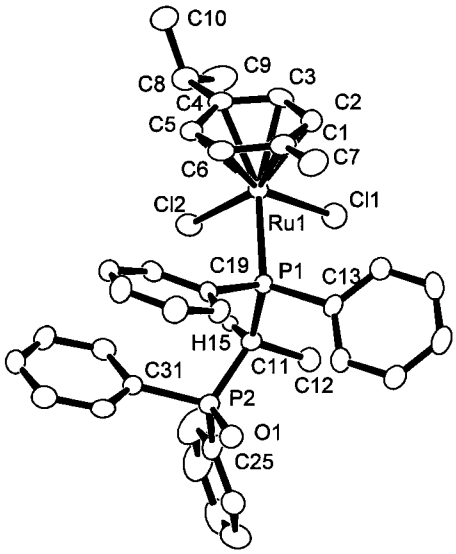

Figure 1. ORTEP representation of [(η^6-Cy)RuCl$_2$(η-Ph$_2$PCH(CH$_3$)P(O)Ph$_2$)] (**3**), with 50% probability ellipsoids.

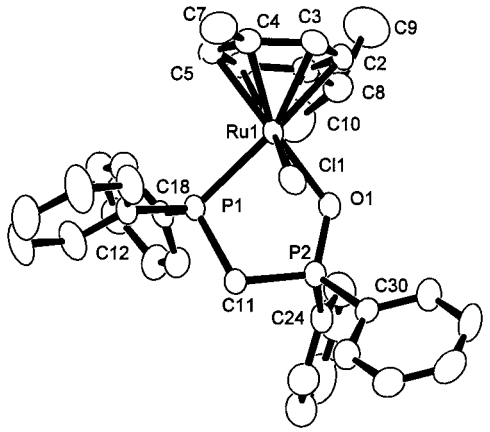

Figure 2. ORTEP representation of [(η^6-Cy)RuCl(η^2-Ph$_2$PCH$_2$P(O)Ph$_2$)][SbF$_6$] (**6**), with 30% probability ellipsoids.

π-bonded owing to the harder strong acid character of the dicationic Lewis acid. There is also a pronounced tilt of the aldehyde to allow preferential interaction of the π orbitals of the aldehyde carbonyl with specific d orbitals owing to a differential electronic effect of the P and O donors. The torsion angles are ϕ(P1−Ru1−O2−C39) = 153.4(2)° and ϕ(O1−Ru1−O2−C39) = 70.7(2)°,

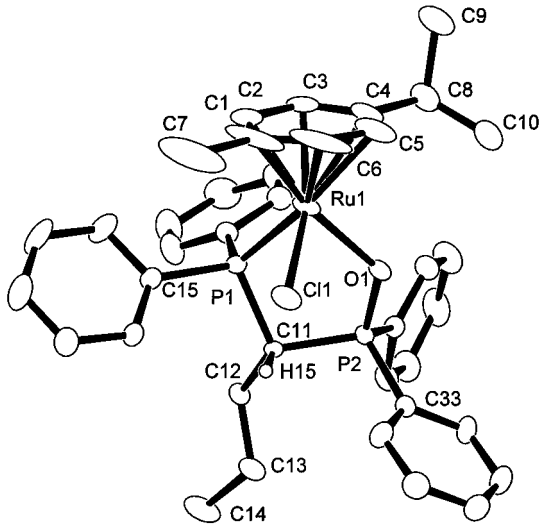

Figure 3. ORTEP representation of [(η^6-Cy)RuCl(η^2-Ph$_2$PCH(C$_3$H$_7$)P(O)Ph$_2$)][SbF$_6$] (**9′′**), with 30% probability ellipsoids. There is an unresolved disorder in the isopropyl group and orientation of the cymene ring.

and this has been observed in other systems[12] and interpreted theoretically.[21] This suggests that the system should give good selectivity in reactions on the

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Table 2. $^{31}P\{^1H\}$ NMR[a] Data of $[CyRuL(\eta^2\text{-}Ph_2PCH(R)P(O)Ph_2)][SbF_6]_2$ Complexes

L	P(III)	P(V)	$^2J_{PP}$ (Hz)	ΔP(III)	ΔP(V)
		R = CH_3			
solvento[b]	50.0	71.2	30		
Cl[c]	49.0	66.5	27	−4.6	−3.5
cinnamaldehyde	53.8	70.9	26	0.2	0.9
crotonaldehyde	53.6	70.0	25	0.0	0.0
methacrolein	55.7	72.3	24	2.1	2.3
benzaldehyde	55.8	72.3	25	2.2	2.3
		R = C_3H_7			
solvento[b]	50.9	72.3	34		
Cl[c]	50.1	68.2	28	−4.1	−5.9
cinnamaldehyde	54.8	74.2	27	0.3	0.1
crotonaldehyde	54.5	74.1	28	0.0	0.0
methacrolein	57.6	76.2	28	3.1	2.0
benzaldehyde	58.0	76.5	28	3.5	2.4
		R = Ph			
solvento[b]	58.4	65.3	34		
Cl[c]	57.1	60.3	30	−2.2	−3.6
cinnamaldehyde	59.3	65.0	30	0.0	0.1
crotonaldehyde	59.3	64.9	33	0.0	0.0
methacrolein	61.4	63.5	32	2.1	−1.5
benzaldehyde	61.3	64.4	31	2.0	-0.5

[a] Spectra of solutions in CH_2Cl_2 were recorded on a GE-Omega 300 MHz spectrometer (121 MHz for ^{31}P) and chemical shifts are reported in δ relative to an 85% H_3PO_4 (aq) external standard. [b] The methylene chloride solvate is assumed, but coordinated SbF_6^- could be a ligand. [c] Complexes with chloro ligands have a charge of +1.

coordinated aldehyde, as has been observed with other chiral systems of this type having bound aldehydes.[12]

A comparison of selected bond lengths and angles is given in Table 3. One might note that there is an increase in all ligand angles involved in the five-membered chelate ring relative to the monodentate ligand. The bite angle is also rather small. Thus there is some strain introduced in forming the chelate, and factors that reduce it may account for the greater tendency to form chelates in some complexes.

Discussion

The 16-electron Lewis acid formed by abstraction of halide or the dissociation of an aldehyde might not be expected to be stable to racemization or epimerization.[13] Nevertheless, there are cases where racemization does not occur, such as with $CpRe(NO)(PPh_3)X$[14] or the intermediate in CpMo(NO)(allyl)X when halides are exchanged.[15] Empirically, the presence of a strong

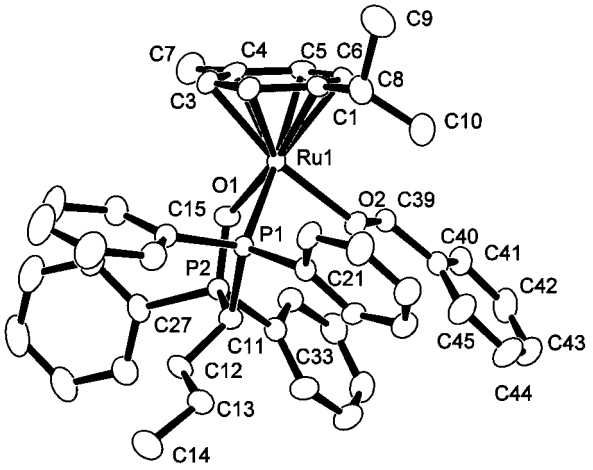

Figure 4. ORTEP representation of $[(\eta^6\text{-Cy})Ru(PhCHO)(\eta^2\text{-}Ph_2PCH(C_3H_7)P(O)Ph_2)][SbF_6]_2$ (**10**), with 50% probability ellipsoids.

Table 3. Comparison of Selected Bond Lengths (Å) and Angles (deg)

	3	**6**	**9**	**10**
Ru−Cl(1)	2.403(1)	2.403(1)	2.397(1)	
Ru−P(1)	2.374(1)	2.353(2)	2.329(1)	2.360(1)
Ru−O(1)	2.148(4)	2.154(3)	2.109(2)	
P(2)−O(1)	1.484(3)	1.517(4)	1.528(3)	1.520(2)
P(1)−Ru−O(1)	80.8(1)	81.2(1)	82.11(5)	
Ru−O(1)−P(2)	122.2(2)	125.2(2)	125.2(1)	
Ru−P(1)−C(11)	114.8(1)	103.5(2)	105.7(1)	106.9(1)
P(1)−C(11)−P(2)	119.6(2)	108.6(3)	105.1(2)	107.5(1)
O(1)−P(2)−C(11)	115.4(2)	109.2(2)	108.4(2)	110.0(1)

withdrawing group appears to be required for chiral stability, and this has been rationalized theoretically.[13] The 18-electron $CpRu(CO)(PPh_3)X$ system does not racemize, a feature also noted earlier using the neomenthyl-substituted cyclopentadienyl ligand.[16] However, when a chiral sulfoxide replaces the halide, epimerization can occur at the metal center, presumably via the 16-electron intermediate.[17] In our CyRu(P,O-ligand)$^{2+}$ intermediate, the unsymmetrical "two-legged piano stool" might be expected to have a low barrier to conversion to a form of the CyRuPO moiety having a plane of symmetry. In fact some 16-electron CpRuLX complexes have been characterized crystallographically and found to have a "planar" Ru.[18] Hence, moderately rapid epimerization or racemization might be anticipated when weak bonding of a ligand is involved. Scheme 4 depicts two possible mechanisms by which the diastereomers in either the solvento or aldehyde complexes could interconvert.

The cymene ligand is particularly diagnostic of rapid racemization. The methyl groups of the isopropyl and the aromatic cymene protons are diastereotopic when the Ru chiral center is maintained on the NMR time scale. For example, if $[(\eta^6\text{-Cy})RuCl(\eta^2\text{-}Ph_2PCH_2P(O)Ph_2)][SbF_6]$, **6**, racemized rapidly, a single isopropyl methyl doublet would be observed, rather than the two actually observed at δ 1.19 and δ 1.04.[19] The benzaldehyde complex also shows two isopropyl resonances at δ 1.32 and δ 1.13. The solvento complex also shows two isopropyl resonances at δ 1.42 and δ 1.23. Thus, even for more weakly bound ligands, the racemization rate is slow on the NMR time scale ($t_{1/2} > 1$ s). The dimethyl sulfoxide complex derived from **6** also shows diaste-

(19) Although racemization of the complex, involving a rapid interconversion of R_{Ru} and S_{Ru}, would average the methyls in **6**, the presence of the stereogenic centers in the Me-, Ph-, and Bu-substituted ligands would not allow averaging of the environments and the isopropyl methyls and cymene aromatics would remain diastereotopic. As shown in **3**, the methyl substituent in the backbone favors twisting of the phenyls, which creates a chiral environment close to the metal, even though the chiral center is remote. This results in cymene aromatic shifts ranging over 1.6 ppm and diastereotopic isopropyl methyls differing by 0.35 ppm. An unusual downfield shift of ~1 ppm of one pair of phenyl protons to δ 8.86 is also indicative of the differential interaction of the nonequivalent phenyls.

(20) At this time, it is not known which atom of the sulfoxides acts as the donor; however it is clear from ^{31}P NMR that coordination occurs preferentially to one or the other because only diastereomers of one complex were formed. Sulfur binding is preferred in cyclopentadienyl-ruthenium cation analogues;[17] however, the higher acidity in the arene complexes may well promote O binding.

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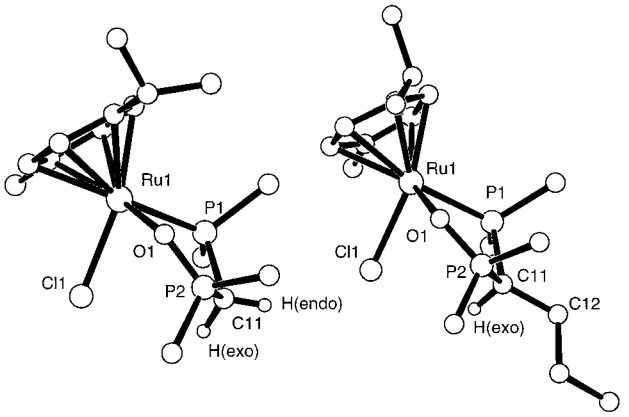


Figure 5. Comparison of ring conformations in **6** and **9**. Only the *ipso* carbons of the phenyls are shown.

reotopic methyls indicative of slow exchange and slow racemization.[20]

The methylene protons in the ligand in **6** also are nonequivalent, which further indicates that racemization is slow. An interesting feature here is that the $^{31}P-^{1}H$ couplings to the nonequivalent protons are substantially different: $J_{H-P} = 10.2$ and 17.3 Hz for the resonance at δ 3.71 and $J_{H-P} = 0.9$ and 12.8 Hz for the proton resonance at δ 3.23. Since the methyl-substituted analogue (**7**) shows a single methylene proton with $J_{H-P} = 12.1$ and 21.1 Hz, this suggests that the exo proton has the larger couplings, and the assignments would be δ 3.71 for H_{exo} and δ 3.23 for H_{endo} in **6**. The couplings are a sensitive function of angle and vary substantially for ligands other than chloride.

A comparison of chelated ligands **1a** and **1d** as found in **6** and **9** is shown in Figure 5. The chelate ring is slightly puckered with the methylene backbone away from the cymene ring. This provides virtually no steric interaction of the endo methylene substituent with the cymene ring, but a potential interaction of the exo substituent with halide or ligand. As shown in Figure 5, the exo methylene hydrogen in **6** is 2.88 Å from the Cl (assuming a 1.09 Å C−H length) at approximately the sum of the van der Waals radii (~2.90 Å). This H- - - Cl distance decreases to 2.67 Å in **9** owing to steric interactions in the ring upon introduction of the propyl group. If the exo methylene H were replaced by a methyl group and the conformation of the ring remained the same, then the H- - - Cl distance would decrease to 1.46 Å, which would create a severe repulsion problem.

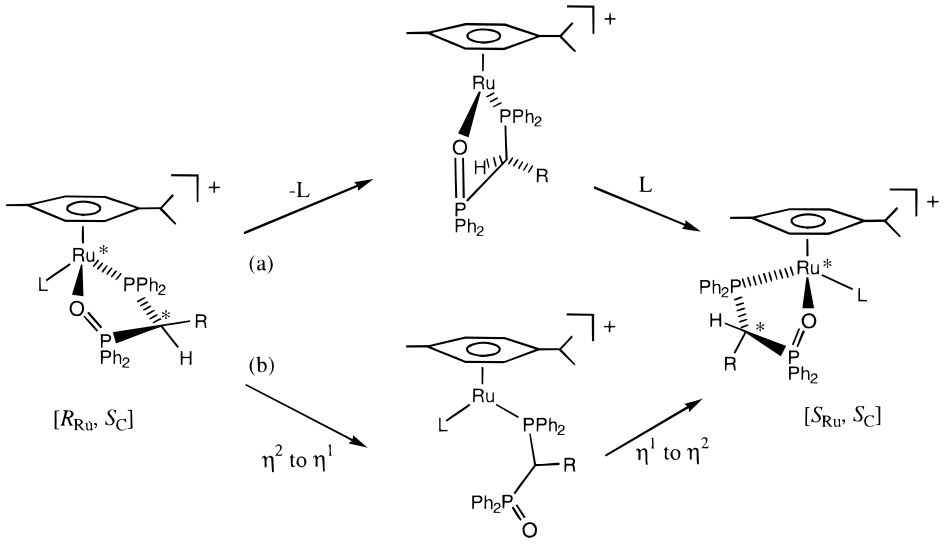
The complexes with a substituent on the backbone have the potential of selectively returning to a specific metal chirality after forming a 16-electron intermediate, but those based on the dppmO ligand would racemize with an achiral aldehyde or solvent. One can then assess the potential for epimerization at the metal center by observing the effects with chiral aldehydes.

Synthesis of [CyRuL(η^2-$Ph_2PCH(R)P(O)Ph_2$)][SbF_6]$_2$ Complexes Where L = (1*R*)-(−)-myrtenal, *t*-BuS(O)Me, Me_2SO, (*R*)-(+)-(*p*-C_6H_4Me)S(O)Me. The generation of an open coordination site on the complexes [CyRuCl(η^2-$Ph_2PCH(R)P(O)Ph_2$)][Cl] and $CyRuCl_2$(η^1-$Ph_2PCH_2P(O)Ph_2$) was accomplished by removal of chloride via AgCl formation upon the addition of AgSbF_6. We will refer to the intermediate formed as the 16-electron Lewis acid, [CyRu(η^2-$Ph_2PCH(R)P(O)Ph_2$)][SbF_6]$_2$; however, it is more likely to be a solvento complex or involve coordinated SbF_6.

The potential problem of displacing the phosphine oxide portion of the chelate with sulfoxides was investigated by adding a large excess of Me_2SO to [CyRu(Me_2SO)(η^2-$Ph_2PCH_2P(O)Ph_2$)][SbF_6]$_2$; the η^1 complex was not detected. The ^{31}P NMR data for the sulfoxide and myrtenal complexes are presented in Table 4.

The addition of (1*R*)-(−)-myrtenal to [CyRuL(η^2-$Ph_2PCH_2P(O)Ph_2$)]$^{2+}$ yields two diastereomers (Scheme 5). Since there is no substituent on the bridging carbon to constrain epimerization at the metal center, epimeriza-

Scheme 4. Two Possible Mechanisms for the Interconversion of Diastereomers in the Aldehyde Derivatives of Complexes 7−9: (a) Dissociation of L, Followed by Inversion of Chelate and Recoordination of L; (b) Hemidissociation of Chelate P(O) Moiety, Followed by Rotation about Ru−P Bond and Rechelation of Ligand



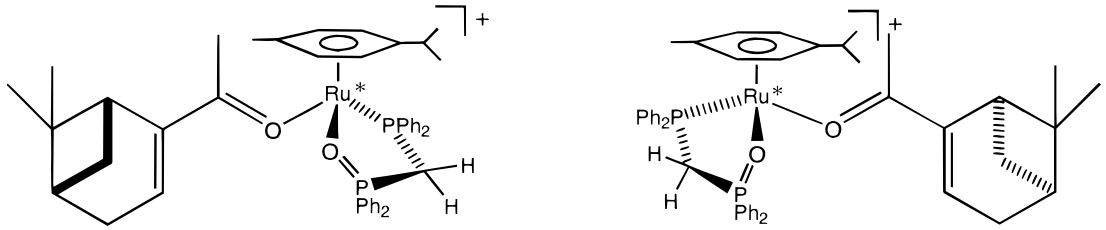
R = H, **6**; CH_3, **7**; Ph, **8**; C_3H_7, **9**
L = H_2O or aldehyde

Table 4. $^{31}P\{^1H\}$ NMR[a] Data of [CyRuL(η^2-$Ph_2PCH(R)P(O)Ph_2$)][SbF_6]$_2$ Complexes

	major diastereomer			minor diastereomer			
	P(III)	P(V)	$^2J_{PP}$ (Hz)	P(III)	P(V)	$^2J_{PP}$ (Hz)	de
			R = H				
(1*R*)-(−)-myrtenal	48.1	73.4	20	47.7	74.3	22	37[b]
(*R*)-(+)-(*p*-tol)S(O)Me	48.9	72.0	20	45.3	70.4	18	<2[b]
rac-*t*-BuS(O)Me	44.8	72.0	22	44.6	72.1	23	20[b]
Me_2SO	45.6	70.8	18				
			R = CH_3				
(1*R*)-(−)-myrtenal	56.3	71.8	25	57.3	72.2	28	40[c]
(*R*)-(+)-(*p*-tol)S(O)Me	52.4	69.4	26	55.1	71.9	27	<4[c]
rac-*t*-BuS(O)Me	51.4	70.8	28	51.7	69.6	29	25[c]
Me_2SO	51.4	69.8	26				

[a] Spectra were recorded at 121 MHz for ^{31}P, and chemical shifts are reported in ppm downfield from an 85% H_3PO_4 (aq) external standard. [b] Diastereomeric excess values do vary significantly with Ru:L ratio. [c] Diastereomeric excess values vary with Ru:L ratio and were interpolated for 5:1 Ru:L.

Scheme 5. Diastereomers of the Complex of (1*R*)-Myrtenal with [CyRu(η^2-dppmO-*P*,*O*)]$^{2+}$



[R_{Ru}] [S_{Ru}]

tion at the metal occurs to yield a 37% de with a $t_{1/2}$ < 1 min. The addition of *t*-BuS(O)Me also produces a modest de of 20%.

When R = Me, there are three chiral centers in the complex with a chiral aldehyde. One would not expect a significant difference in the preference for having the methyl oriented away from L, and thus the metal chirality could not adapt to steric interactions with a chiral ligand in the same way as found for [CyRuL(η^2-$Ph_2PCH_2P(O)Ph_2$)]$^{2+}$. Hence, one would expect the diastereoselectivity to be expressed for the enantiomers of a chiral ligand. As observed with the achiral aldehydes, the backbone substituent forces a particular configuration at the metal. The selectivity for the chiral ligands, i.e., aldehydes or sulfoxides, is that due to the difference in K_{eq}'s for (*R*)-ligand and the [R_{Ru}, R_C] or [S_{Ru}, S_C] Lewis acid. The relative amounts of the two complexes will vary with the concentration of free [R_{Ru}, R_C] or [S_{Ru}, S_C] Lewis acid that is available, and thus the de varies with relative concentration. The highest selectivity is observed when the $[Ru]_{total} \gg [L]_{total}$ ratio is high; that is, when [R_{Ru}, R_C]:[S_{Ru}, S_C] for the free acid is ~1:1. As $[Ru]_{total}$ approaches $[L]_{total}$, the de decreases as both enantiomers of the Lewis acid effectively become ligated. To provide a standard reference point, the de given for R = Me was interpolated for the ratio of 5:1 for Ru:L. (We are currently investigating more quantitative determinations of the equilibrium constants.) The data in Table 4 demonstrate that there is a significant selectivity in the binding of the chiral aldehyde.

Conclusion

We have shown that the chirality of a metal center can be retained by appropriate substitution of backbone in the ligand, even if there is the potential for epimerization via the formation of a 16-electron intermediate. We are currently exploring the use of these ligands for use in asymmetric Lewis acid catalysis. In addition, we are developing the use of these racemic bisphosphine monoxides in chiral poisoning/acceleration strategies.[21]

Experimental Section

General. All synthetic manipulations were carried out using standard Schlenk techniques under inert atmosphere. Reagent grade diethyl ether and dichloromethane were dried over benzophenone ketyl and CaH_2, respectively, and thoroughly degassed by pump/thaw techniques prior to use to prevent oxidation of the ligands. Absolute methanol and ethyl acetate, and Silica-60 (EM Separation Technologies) used for chromatography, were reagent grade and used without further purification. The ligands **1a**−**1d** and the ruthenium dimer $[CyRuCl_2]_2$ were prepared according to published procedures.[8] The solution of 1.6 M *n*-BuLi in hexanes was used as received. *trans*-Cinnamaldehyde, 99+% (Aldrich), crotonaldehyde, 99+% (Aldrich), methacrolein, 95% (Aldrich), (1*R*)-(−)-myrtenal (Aldrich), (*R*)-(+)-(*p*-tol)S(O)Me (Aldrich), dimethyl sulfoxide, and $AgSbF_6$ were used without further purification. The racemate of *t*-BuS(O)Me was prepared according to a published procedure.[22] ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker 500 MHz or a GE Omega 300 MHz (operating at 121 MHz for ^{31}P) spectrometer, and chemical shifts are reported in ppm relative to residual solvent peaks (^1H) or an 85% H_3PO_4 (aq) external standard (^{31}P). Elemental analyses were carried out by Robertson Microlit Labs, Patterson, NJ, or Atlantic Microlabs.

Preparation of [(η^6-Cy)$RuCl_2$(η^1-$Ph_2PCH_2P(O)Ph_2$)] (2). Ligand **1a** (157 mg, 0.39 mmol) was dissolved in 10 mL of dry degassed dichloromethane. An equivalent of the $[CyRuCl_2]_2$ dimer (120 mg, 0.196 mmol) was added, and the mixture was stirred for 2 h. The solvent was removed, and the red solid residue was recrystallized from a dichloromethane/diethyl ether solution in nearly quantitative yield. ^1H NMR ($CDCl_3$,

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293 K, δ): 7.98 (m, 4 H, Ph), 7.37 (m, 4 H, Ph), 7.26 (m, 8 H, Ph), 7.18 (m, 4 H, Ph), 5.25 (d, 2 H, J = 6.3 Hz, Cy C*H*), 5.11 (d, 2 H, J = 6.3 Hz, Cy C*H*), 3.87 (apparent t = dd, 2 H, J_{H-P} = 9.9, 9.9 Hz, P−CH_2−P), 2.48 (spt, 1H, J = 6.8 Hz, Cy C*H*$(CH_3)_2$), 1.82 (s, 3 H, Cy CH_3), 0.80 (d, 6 H, J = 6.8 Hz, Cy $(CH_3)_2$CH). $^{31}P\{^1H\}$ NMR: 23.6 (d, J_{P-P} =33.0 Hz, P(III)), 25.7 (d, J_{P-P} =33.0 Hz, P(V)). Anal. Calcd for $C_{35}H_{36}Cl_2OP_2Ru$: C, 59.49; H, 5.14. Found: C, 59.33; H, 5.26.

Preparation of [(η^6-Cy)RuCl$_2$(η^1-Ph$_2$PCH(CH$_3$)P(O)Ph$_2$)] (3). One equivalent of the ligand **1b** (680 mg, 1.6 mmol) was dissolved in 10 mL of dry degassed dichloromethane, along with a stoichiometric amount of the $[CyRuCl_2]_2$ dimer (500 mg, 0.8 mmol). The resulting deep red solution was stirred at room temperature under nitrogen for 30 min. Removal of the solvent under vacuum typically produced a red-orange oil, which was transferred to a silica gel chromatography column (2 × 5 cm) and eluted with ethyl acetate under nitrogen pressure. The second fraction typically eluted a deep red-orange band, followed by several colorless to pale yellow fractions. A deep red-orange band remained on top of the column and could only be eluted using absolute methanol. The early colored band contained the η^1 coordination isomer of **3**; when this fraction was left to stand overnight in air, large red crystals of **3** formed (∼40% yield). The deep red band which was eluted with methanol contained the η^2 coordination isomer [CyRuCl(η^2-Ph$_2$PCH(CH$_3$)P(O)Ph$_2$)][Cl] (**3′**), which was isolated as an red-orange air-stable solid after removing the methanol under vacuum (typically ∼40% yield). ^{1}H NMR ($CDCl_3$, 293 K, δ) for **3**: 8.86 (2 H, m, Ph), 7.8−7.1 (18H, m, Ph), 5.63 (1 H, d, J = 5.9 Hz, Cy C*H*), 4.98 (1 H, d, J = 6.1 Hz, Cy C*H*), 4.96 (1 H, qdd obscured, P_2CH-CH_3), 4.92 (1 H, d, J = 5.9 Hz, Cy C*H*), 4.04 (1 H, d, J = 6.1 Hz, Cy C*H*), 3.04 (1 H, spt, J = 6.9 Hz, Cy C*H*$(CH_3)_2$), 1.53 (3 H, s, Cy CH_3), 1.38 (3 H, d, J = 6.9 Hz, Cy CH_3−CHCH$_3$), 1.23 (3 H, d, J = 6.9 Hz, Cy CH$_3$CH−CH_3), 0.88 (3 H, ddd, J = 7.5 Hz; $^2J_{P-H}$ = 16.4 Hz; $^2J_{P-H}$ = 16.8 Hz P_2C-CH_3). $^{31}P\{^1H\}$ NMR for **3**: 32.8 (d, 29 Hz), 33.8 (d, 29 Hz). Anal. Calcd for $C_{36}H_{38}Cl_2OP_2Ru$: C, 60.00; H, 5.31. Found: C, 59.89; H, 5.10.

Preparation of [(η^6-Cy)RuCl(η^2-Ph$_2$PCH$_2$P(O)Ph$_2$)][SbF$_6$] (6). Silver hexafluoroantimonate (49 mg, 0.14 mmol) was added to **2** (100 mg, 0.14 mmol) in 6 mL of dichloromethane. The solution was stirred for 20 min in the dark and filtered through Celite to remove the precipitated silver chloride. The solvent was removed, and the product was recrystallized from a dichloromethane/diethyl ether solution, 88% yield. ^{1}H NMR (CD_2Cl_2, 293K, δ): 7.10−7.73 (20 H m, Ph), 5.83 (1 H, d, J = 6.0 Hz, Cy C*H*), 5.56 (1 H, d, 6.0 Hz, Cy C*H*), 5.54 (s, 2 H, Cy C*H*, Cy C*H*), 3.71 (1 H, ddd, J = 14.6 Hz, $^2J_{H-P}$ =10.2 Hz, 17.3 Hz, P−(*H*C)H−P), 3.23 (1H, ddd, J = 14.6 Hz, $^2J_{H-P}$ =12.8 (CH_{exo})−P, $^2J_{H-P}$ = 0.9 (CH_{endo})−P), 2.56 (1 H, spt, J = 7.0 Hz, Cy C*H*$(CH_3)_2$), 1.94 (3 H, s, Cy CH_3), 1.19 (3 H, d, J = 7.0 Hz, Cy CH_3−CHCH$_3$)), 1.04 (3 H, d, J = 7.0 Hz, Cy CH$_3$−CH−CH_3). $^{31}P\{^1H\}$ NMR: 44.8 (d, J_{P-P} =15.8 Hz, P(III)), 68.5 (d, J_{P-P} =15.8 Hz, P(V)). Anal. Calcd for $[C_{35}H_{36}ClOP_2Ru][SbF_6]$: C, 46.36; H, 4.00. Found: C, 46.13; H, 3.95.

Preparation of [(η^6-Cy)RuCl(η^2-Ph$_2$PCH(CH$_3$)P(O)Ph$_2$)][SbF$_6$] (7). Compound **7** was prepared as the SbF_6 salt by reaction of **3** (100 mg, 0.14 mmol) with 1 equiv of $AgSbF_6$ in dichloromethane at room temperature. The reaction was complete within minutes, and the precipitated AgCl was filtered before the solvent was removed under vacuum. The product was recrystallized from dichloromethane and diethyl ether (80−90% yield). ^{1}H NMR ($CDCl_3$, 293 K, δ): 7.8−7.3 (20H, m, Ph), 5.91 (1 H, d, J = 6.1 Hz, Cy C*H*), 5.72 (1 H, d, J = 5.7 Hz, Cy C*H*), 5.67 (1 H, d, J = 6.1 Hz, Cy C*H*), 5.51 (1 H, d, J = 5.7 Hz, Cy C*H*), 4.42 (1 H, qdd, q, J = 7.4 Hz, d, $^2J_{P-H}$ = 12.1 Hz; d, $^2J_{P-H}$ = 21.1 Hz, P_2CH-CH_3), 2.47 (1 H, spt, J = 6.9 Hz, Cy C*H*$(CH_3)_2$), 2.08 (3H, s, Cy CH_3), 1.50 (1H, ddd, d, J = 7.4 Hz; d, $^2J_{P-H}$ = 11.4 Hz; d, $^2J_{P-H}$ = 18.3 Hz P_2C-CH_3), 1.02 (3 H, d, J = 6.9 Hz, Cy CH_3−CHCH$_3$), 0.91 (3 H, d, J = 6.9 Hz, Cy CH$_3$CH$_2$−CH_3). $^{31}P\{^1H\}$ NMR: 49.0 (d, $^2J_{PP}$ = 28 Hz), 66.5 (d, $^2J_{PP}$ = 27 Hz). Anal. Calcd for $[C_{36}H_{38}ClOP_2Ru][SbF_6]$: C, 46.95; H, 4.16. Found: C, 46.53; H, 4.31.

Preparation of [(η^6−Cy)RuCl(η^2-Ph$_2$PCH(Ph)P(O)Ph$_2$)][SbF$_6$] (8). Ligand **1c** (930 mg, 1.95 mmol) was dissolved in 10 mL of dry degassed CH_2Cl_2, and 1 equiv of the [(η^6-Cy)$RuCl_2$]$_2$ dimer (600 mg, 0.98 mmol) was added. The resulting deep red solution was stirred at room temperature under nitrogen for 30 min. Removal of the solvent under vacuum typically produced a red-orange oil, which was transferred to a silica gel chromatography column (2 × 5 cm) and eluted with ethyl acetate under nitrogen pressure. Typically after 100 mL of ethyl acetate a deep red-orange band remained on top of the column and could only be eluted using absolute methanol. This band contained the η^2 coordination isomer [CyRuCl(η^2-Ph$_2$PCH(CH$_3$)P(O)Ph$_2$)][Cl] (**4′**), which was isolated as an orange, air-stable solid after removing the methanol under vacuum, but not further purified. Compound **8** was prepared by reaction of **4′** (200 mg, 0.26 mmol) with 1 equiv of $AgSbF_6$ (88 mg) in dichloromethane at room temperature. The precipitated AgCl, which formed immediately, was filtered from the solution, and the solvent was removed under vacuum. The product was recrystallized from dichloromethane and diethyl ether in 80−90% yield. ^{1}H NMR ($CDCl_3$, 293 K, δ):7.8−6.8 (25 H, m, Ph), 6.03 (2 H, overlapped doublets, J = 5.8 Hz, Cy C*H*) 5.91 (1 H, d, J = 5.8 Hz, Cy C*H*), 5.62 (1 H, d, J = 5.8 Hz, Cy C*H*), 5.47 (1 H, dd, $^2J_{P-H}$ = 5.8 Hz; P−(*H*C)Ph-P; $^2J_{P-H}$ = 11.6 Hz,), 2.82 (1 H, spt, J = 6.9 Hz, Cy C*H*$(CH_3)_2$), 1.96 (3 H, s, Cy CH_3), 1.26 (3 H, d, J = 6.9 Hz, Cy CH_3−CHCH$_3$), 1.17 (3 H, d, J = 6.9 Hz, Cy CH$_3$CH$_2$−CH_3). $^{31}P\{^1H\}$ NMR: 57.1 (d, $^2J_{PP}$ = 30 Hz), 60.3 (d, $^2J_{PP}$ = 30 Hz). Anal. Calcd for $[C_{41}H_{40}ClOP_2Ru][SbF_6]\cdot CH_2Cl_2$: C, 47.24; H, 3.96. Found: C, 47.74; H, 3.87.

Preparation of [CyRuCl(η^2-Ph$_2$PCH(C$_3$H$_7$)P(O)Ph$_2$)][SbF$_6$] (9). The same procedure was used as described for **8** except **1d** was used. ^{1}H NMR ($CDCl_3$, 293K, δ): 7.8−7.3 (20 H, Ph), 5.98 (1 H, d, 5.7 Hz, Cy C*H*), 5.71 (2 H, d, 5.7 Hz, Cy C*H*), 5.62 (1 H, d, 5.7 Hz, Cy C*H*), 4.35 (1 H, m, P−prC*H*−P), 2.36 (1 H, spt, 6.9 Hz, Cy CH$_3$C*H*CH$_3$), 2.08 (3 H, s,Cy CH_3), 1.6−1.1 (4 H, br m CH_2CH_2CH$_3$), 0.99 (3 H, d, 6.9 Hz CH_3−CHCH$_3$), 0.74 (3 H, d, 6.9 Hz, CH$_3$−CHCH_3), 0.65 (3 H, t, 7.1 Hz, CH$_2$CH$_2$CH_3). $^{31}P\{^1H\}$: 50.1 (d, $^2J_{PP}$ = 29 Hz), 68.2 (d, $^2J_{PP}$ = 28 Hz). The compound was ground finely and kept under vacuum overnight before analysis to remove ether. Anal. Calcd for $[C_{38}H_{42}ClOP_2Ru][SbF_6]$: C, 48.10; H, 4.46. Found: C, 48.31; H, 4.24.

General Procedure for the in Situ Observation of Aldehyde and Sulfoxide Complexes, [CyRu(η^2-Ph$_2$PCH(R)P(O)Ph$_2$)(L)][SbF$_6$]$_2$. These experiments were carried out in air for all systems. A 10 mL round-bottom flask was charged with 200 mg of an η^2-$[SbF_6]^-$ complex (either **7**, **8,** or **9**) and 5 mL of freshly distilled dichloromethane in air. To the orange solutions were added 1.1 equiv of $AgSbF_6$, which caused the immediate precipitation of AgCl as a fluffy white solid; stirring was continued for 1 h before the AgCl was filtered. The bright orange solution was divided into portions. Each portion was treated with a ligand in several additions so that the resonances of the product and starting acid could be identified by $^{31}P\{^1H\}$ NMR. Ultimately10 equiv of the appropriate aldehyde was added. When necessary, anhydrous $MgSO_4$ was added to remove water from the solvent. Phosphorus NMR are given in Table 2. Proton NMR for some representative complexes are given below.

[CyRu(η^2-Ph$_2$PCH(H)P(O)Ph$_2$)(solvent)][SbF$_6$]$_2$. ^{1}H NMR (CD_2Cl_2, 293 K, δ) 7.9−7.1 (20 H, m, Ph), 6.23 (1 H, d, J = 6.0 Hz, Cy C*H*) 5.78 (1 H, d, J = 5.7 Hz, Cy C*H*), 5.61 (1 H, d, J = 6.0 Hz, Cy C*H*), 5.49 (1 H, d, J = 5.7 Hz, Cy C*H*), 3.56 (1 H, ddd, J = 15.7 Hz, P−(*H*C)H−P; $^2J_{P-H}$ = 5.6 Hz; $^2J_{P-H}$ = 13.0 Hz), 3.40 (1 H, ddd, J = 15.7 Hz, P−(HC)*H*−P; $^2J_{P-H}$ = 9.5 Hz; $^2J_{P-H}$ = 11.1 Hz), 2.81 (1 H, spt, J = 6.9 Hz, Cy C*H*$(CH_3)_2$),

2.07 (3 H, s, Cy CH_3), 1.42 (3 H, d, J = 6.9 Hz, Cy CH_3−CHCH$_3$), 1.23 (3 H, d, J = 6.9 Hz, Cy CH$_3$CH$_2$−CH_3).

[CyRu(η^2-Ph$_2$PCH(H)P(O)Ph$_2$)(PhCHO)][SbF$_6$]$_2$. ^{1}H NMR (CD_2Cl_2, 293 K, δ) 9.95 (1 H, s, PhC(O)H), 7.9−7.1 (25 H, m, Ph), 6.23 (1 H, d, J = 6.5 Hz, Cy CH) 5.88 (1 H, d, J = 6.5 Hz, Cy CH), 5.64 (1 H, d, J = 7.0 Hz, Cy CH), 5.63 (1 H, d, J = 6.5 Hz, Cy CH), 3.67 (1 H, ddd, J = 16.0 Hz, P−(HC)H−P; $^2J_{P-H}$ = 8.8 Hz; $^2J_{P-H}$ = 12.7 Hz), 3.49 (1 H, ddd, J = 16.0 Hz, P−(HC)H−P; $^2J_{P-H}$ = 9.8 Hz; $^2J_{P-H}$ = 11.1 Hz), 2.70 (1 H, spt, J = 6.9 Hz, Cy CH(CH$_3$)$_2$), 2.07 (3 H, s, Cy CH_3), 1.32 (3 H, d, J = 6.9 Hz, Cy CH_3−CHCH$_3$), 1.13 (3 H, d, J = 6.9 Hz, Cy CH$_3$CH$_2$−CH_3).

[CyRu(η^2-Ph$_2$PCH(H)P(O)Ph$_2$)(DMSO)][SbF$_6$]$_2$. ^{1}H NMR (CD_2Cl_2, 293 K, δ 8.1−7.0 (20 H, m, Ph), 6.32 (1 H, d, J = 5.7 Hz, Cy CH) 5.79 (1 H, d, J = 6.0 Hz, Cy CH), 5.58 (1 H, d, J = 5.7 Hz, Cy CH), 5.41 (1 H, d, J = 6.0 Hz, Cy CH), 3.47−3.44 (2H, overlapped ddd, P−(HC)H−P), 2.86 (1 H, spt, J = 6.9 Hz, Cy CH(CH$_3$)$_2$), 2.35 (3 H, s, CH_3S(O)CH$_3$), 2.21 (3 H, s, CH$_3$S(O)CH_3), 2.07 (3 H, s, Cy CH_3), 1.36 (3 H, d, J = 6.9 Hz, Cy CH_3−CHCH$_3$), 1.12 (3 H, d, J = 6.9 Hz, Cy CH$_3$CH$_2$−CH_3).

[CyRu(η^2-Ph$_2$PCH(CH$_3$)P(O)Ph$_2$)(DMSO)][SbF$_6$]$_2$. ^{1}H NMR (CD_2Cl_2, 293 K, δ 7.9−7.1 (20 H, m, Ph), 6.07 (1 H, d, J = 5.7 Hz, Cy CH) 6.05 (1 H, d, J = 6.0 Hz, Cy CH), 5.71 (1 H, d, J = 6.0 Hz, Cy CH), 5.41 (1 H, d, J = 5.7 Hz, Cy CH), 3.91 (1 H, qdd: q, 7.4 Hz, CHCH$_3$; d, $^2J_{P-H}$ = 12.1 Hz; $^2J_{P-H}$ = 19.7 Hz), 2.62 (1 H, spt, J = 7.0 Hz, Cy CH(CH$_3$)$_2$), 2.57 (3 H, s, CH_3S(O)CH$_3$), 2.21 (3 H, s, CH$_3$S(O)CH_3), 2.06 (3 H, s, Cy CH_3), 1.21 (3 H, d, J = 7.0 Hz, Cy CH_3−CHCH$_3$), 1.13 (3 H, ddd, J = 7.4 Hz, CHCH_3, J_{P-H} = 12.2 Hz, J_{P-H} = 17.3), 0.83 (3 H, d, J = 7.0 Hz, Cy CH$_3$CH$_2$−CH_3).

Crystallization of [(η^6-Cy)RuCl$_2$(η^1-Ph$_2$PCH(CH$_3$)P(O)Ph$_2$)], 6. Crystals for X-ray diffraction were grown by slow evaporation of solvent from a solution of the complex in ethyl acetate at room temperature.

Crystallization of [(η^6-Cy)RuCl$_2$(η^1-Ph$_2$PCH$_2$P(O)Ph$_2$)], 3, {[CyRuCl(η^2-Ph$_2$PCH(C$_3$H$_7$)P(O)Ph$_2$)][SbF$_6$]·[O(C$_2$H$_5$)$_2$]}, 9″, and [CyRu(PhCHO)(η^2-Ph$_2$PCH(C$_3$H$_7$)P(O)Ph$_2$)][SbF$_6$]$_2$, 10. Crystals for X-ray diffraction were grown at room temperature by slow vapor diffusion of diethyl ether into a dichloromethane solution of the compound in a closed concentric vial system. An ether molecule crystallized with compound **9** to yield **9″**.

X-ray Crystallography. Crystallographic data are listed in Table 1. The structure of **3** was determined at −103 °C from data collected with a serial diffractometer (Rigaku AFC5S), whereas data for **6** were collected on a Nonius KappaCCD at room temperature. Data for **9″** and **10** were collected on a Nonius KappaCCD at −90 °C. The CCD data were collected with one φ scan, followed by at least one ω scan to get a data set as nearly complete as possible (less than 10 reflections remaining to fill the Ewald sphere). The structures were solved by direct methods (SIR92) 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. An empirical absorption correction (DIFABS) was applied for **3**, and SORTAV was applied to the CCD data. Large thermal parameters for portions of the cymene ring and the isopropyl groups were observed in several structures, indicating disorder in orientation of the isopropyl group and to some extent the arene ring. Satisfactory disorder models could not be found, but the disorders were minor and did not appear to affect the important features of the structure involving other ligands as judged from thermal parameters. Structures **9** and **10** are in polar space groups ($Pna2_1$)and were also refined with the coordinates inverted to establish the polarity. The number of observations with $I > 3\sigma(I)$, the number of variables, and the reflection/parameter ratios were as follows: **3** 4434, 379, 11.7; **6** 4477, 424, 10.6; **9″**, 5009, 450, 11.1; **10**, 7126, 576, 12.4.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, anisotropic thermal parameters, interatomic distances and angles, and hydrogen atom coordinates for **3**, **6**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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