Planar Chirality in Tethered η^6:η^1-(Phosphinophenylenearene-*P*)ruthenium(II) Complexes and Their Potential Use as Asymmetric Catalysts

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Reaction of 2-dicyclohexylphosphinobiphenyl with [(η^6-benzene)$RuCl_2$]$_2$ yielded the tethered complex [Ru(η^6:η^1-2-dicyclohexylphosphinobiphenyl-*P*)Cl_2], **1**, rather than a bridge-splitting product, [(η^6-benzene)Ru(L)Cl_2], that is often observed. Treatment of [(η^6-benzene)$RuCl_2$]$_2$ with 2-dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl yielded the planar chiral, tethered complex [Ru(η^6:η^1-2-dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl-*P*)Cl_2], **2**. Abstraction of a chloride from **2** with $AgSbF_6$ and treatment with PPh_3 selectively gave the chiral-at-metal complex [*anti*-Ru(η^6:η^1-2-dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)-biphenyl-*P*)(PPh_3)Cl]SbF_6, **3a**, which underwent spontaneous resolution upon crystallization. The Me_2N group is coplanar with the η^6-phenyl ring in the cations and directs attack at the metal center, as well as determining the thermodynamic stability of *anti* versus *syn* epimers. The dication derived from enantiopure **3a** catalyzed the Diels−Alder reaction of methacrolein and cyclopentadiene with modest (19−23%) enantioselectivity. Analogues of **2** and **3a** containing 2-(dicyclohexylphosphino)-2′-methylbiphenyl were also prepared. We have found that epimerization at the metal center is slow in these compounds. Averaged NMR spectra at ambient temperatures are observed, however, due to rapid conformational interconversions that can be slowed at low temperature.

Introduction

In the development of effective catalysts for asymmetric synthesis there has been increasing attention paid to mixed donor ligands[1−3] coordinated to transition metal centers. We have previously focused on chelated η^2-P,S,[4] η^2-P,N,[5,6] and η^2-bisphosphine monoxide[7−12] ligand systems in the design of configurationally stable, chiral ruthenium Lewis acids. Thus far, the successful application of our ruthenium compounds containing mixed donor ligands to asymmetric reactions has generally required the use of ligands that were enantiopure prior to coordination to Ru.[6,9,11,12]

In our continuing efforts to utilize ligands that were not necessarily enantiopure before coordination to the metal, we have investigated 2-dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl, $\mathbf{L^A}$, which acted as an arene-tethered ligand instead of an η^2-P,N ligand. Analogues were also prepared from 2-(dicyclohexylphosphino)biphenyl, $\mathbf{L^B}$, and 2-(dicyclohexylphosphino)-2′-methylbiphenyl, $\mathbf{L^C}$, to yield a series of compounds based on the parent [Ru(η^6:η^1-2-dicyclohexylphosphino-biphenyl-*P*)Cl_2], **1**. Tethered ligands are a class of mixed donor ligands that involve an arene or cyclopentadienyl (Cp) ring linked to a pendant donor atom. There have been a moderate number of Cp-tethered (η^5:η^1) compounds,[13−15] but much fewer benzene-derived tethered (η^6:η^1) compounds, reported. Most of the (η^6:η^1) tethers that are known involve a phosphine as the pendant donor;[16−26] however, examples with pendant S,[27] O,[28] N, and As[29] are also known. The tethered donor can

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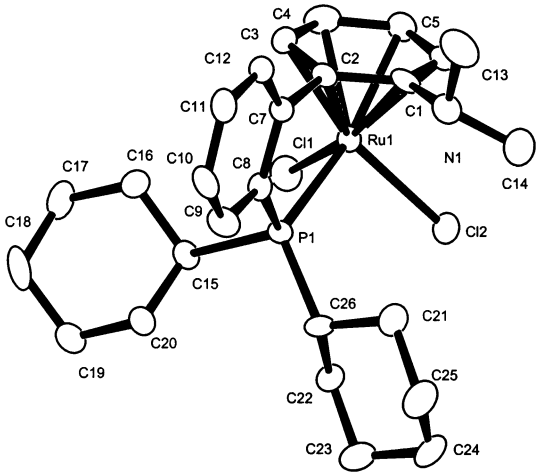


Figure 1. ORTEP view of [Ru(η^6:η^1-$Me_2NC_6H_4C_6H_4$-PCy_2-*P*)Cl_2]SbF_6, **2**, with 50% probability ellipsoids.

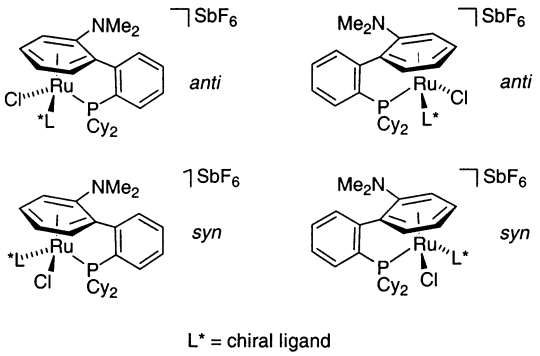
contribute to the chirality of a catalyst, like other mixed donor ligands, when two other different ligands are present, by producing a stereogenic metal center. In addition, a potential tethered ligand with substitution on appropriate arene carbon atoms can generate planar chirality upon coordination to the metal[16,17,19−21,29] that may potentially influence the stereochemical pathway of asymmetric reactions. In the case of $\mathbf{L^A}$ and $\mathbf{L^C}$, the ligands are conformationally dynamic and could exist as a pair of atropisomers if the barrier to biphenyl rotation were high enough. In a sense, the η^6:η^1 binding locks these conformations in place. Perhaps the most significant feature of tethered ligands is their potential contribution to the configurational stability at a catalyst's metal center, a requisite for avoiding low enantioselectivity in the products of asymmetric catalysis.

Herein we present a facile synthesis of tethered phosphinoarene, planar chiral ruthenium complexes from commercially available ligands and demonstrate their preliminary reactivity in an asymmetric carbon−carbon bond forming reaction.

Results and Discussion

The reaction of commercially available reagents [(benzene)$RuCl_2$]$_2$ and 2-dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl, $\mathbf{L^A}$, at 100 °C in DMF for 10−15 min yielded a product resulting from displacement of the benzene ligand. The ^{1}H and ^{31}P{^{1}H} NMR spectra indicated that the reaction had produced an η^6:η^1-tethered compound, [Ru(η^6:η^1-$\mathbf{L^A}$-*P*)Cl_2], **2**. Single-crystal X-ray diffraction verified the η^6:η^1-tethered coordination as shown in Figure 1. Removal of DMF by vacuum distillation and chromatography of the red-brown residue gave a 94% isolated yield of **2**. The synthesis of these η^6:η^1-tethered compounds is more attractive than those previously reported, in terms of time (18−72 h for others), temperature (120−140 °C for others), number of steps performed, and the commercial availability of reactants.[18−21,23,25,26,28,30,31] The analogues of [Ru(η^6:η^1-$\mathbf{L'}$-*P*)Cl_2], where $\mathbf{L'}$ = 2-(dicyclohexylphosphino)biphenyl, $\mathbf{L^B}$, or 2-(dicyclohexylphosphino)-2′-methylbiphenyl, $\mathbf{L^C}$, were prepared similarly, albeit in lower yields (31−45%).

Scheme 1. The Four Possible Diastereomers Resulting from Planar Chirality and Metal Chirality If the Ligand Is Chiral Nonracemic



Attempted Resolution of Enantiomers. The presence of the 2′-dimethylamino group in [Ru(η^6:η^1-$\mathbf{L^A}$-*P*)Cl_2] renders the molecule chiral; however, our attempts to resolve the planar chiral enantiomers of **2** by a variety of derivatization and crystallization experiments were unsuccessful. Owing to the presence of the basic dimethylamino group, the enantiomeric purity of **2** can be evaluated by addition of the chiral shift reagent europium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate, (+)-Eu(hfc)$_3$, to a CD_2Cl_2 solution of **2**. Shifts in the ^{1}H and ^{31}P{^{1}H} NMR spectra of *rac*-**2** show a 1:1 ratio of resonances due to the diastereomeric interactions. Possible resolutions via the cationic complexes [Ru(η^6:η^1-$\mathbf{L^A}$-*P*)(L*)Cl]SbF_6, where L* = a chiral nonracemic ligand, were considered. The abstraction of a chloride from **2** by $AgSbF_6$ and subsequent replacement by L creates a chiral metal center in addition to the planar chirality. If L is itself chiral, a maximum of four diastereomers may form, Scheme 1. If it is achiral (and not prochiral), a maximum of two diastereomers, each of which exists as a pair of enantiomers, could be obtained, Scheme 2. As denoted in Schemes 1 and 2, L may be situated either *anti* or *syn* to the NMe_2 substituent on the η^6-coordinated arene. Appropriate steric or electronic contributions from L could influence the diastereoselective formation of isomers shown in Schemes 1 and 2, which have the potential of being separated by classical methods (e.g., crystallization or chromatography).

A variety of chiral donor ligands, including amines (pyridine and (*R*)-(+)-α-methylbenzylamine) and sulfoxides ((*R*)-(+)-methyl-*p*-tolyl sulfoxide), failed to bind selectively to the [Ru(η^6:η^1-$\mathbf{L^A}$- *P*)Cl] moiety and yielded all possible diastereomers in nearly equal distributions that resisted separation. The chiral phosphines

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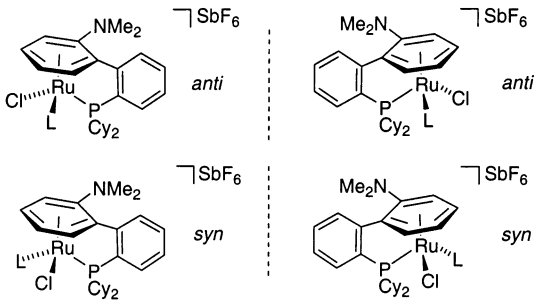
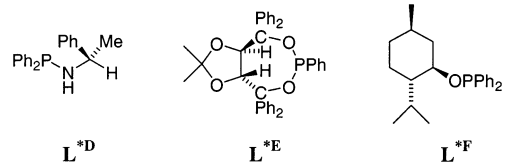
Scheme 2. The Pairs of Enantiomers for the Two Diastereomers Resulting from Planar Chirality and Metal Chirality If the Ligand Is Achiral



(*S*)-(−)-diphenyl(1-phenylethylamino)phosphine, **L*D**,[32] (1*R*,7*R*)-9,9-dimethyl-2,2,4,6,6-pentaphenyl-3,5,8,10-tetraoxa-4-phosphabicyclo[5.3.0]decane, **L*E**,[33] and (1*R*,2*S*,5*R*)-5-methyl-2-(1-methylethyl)cyclohexyl ester of diphenylphosphinous acid, **L*F**,[34] were prepared by reacting CH_2Cl_2 solutions of the appropriate nonracemic chiral alcohol or chiral amine with Ph_2PCl or $PhPCl_2$ in the presence of NEt_3 according to literature procedures. Each of these phosphines was stirred with **2** and 1 molar equiv of $AgSbF_6$ to give the cationic bisphosphine compounds [Ru(η^6:η^1-**L^A**-*P*)(L*)Cl]SbF_6, where L* = **L*D**, **L*E**, or **L*F**. Stirring the monodentate achiral phosphines, PPh_3, $PMePh_2$, PMe_2Ph, and PMe_3, with equimolar amounts of **2** and $AgSbF_6$ at room temperature yielded the cationic bisphosphine compounds [Ru(η^6:η^1-**L^A**-*P*)(L)Cl]SbF_6 (L = PPh_3, $PMePh_2$, PMe_2Ph, or PMe_3). Coordination of the new ligand was indicated by the presence of two doublets arising from phosphorus−phosphorus coupling in the $^{31}P\{^1H\}$ NMR spectrum. The presence of characteristic resonances in the ^1H NMR spectrum indicated that η^6-coordination of the arene of **L^A** was retained in the products.



L*D **L*E** **L*F**

For the compounds containing the chiral phosphorus-donor ligands, **L*D**, **L*E**, **L*F**, two isomers in an approximate 1:1 ratio rather than the four possible isomers form at room temperature. The ratio of products did not change significantly with time (>20 days) or variation in the stoichiometry of the reactants. For example, when 0.5 molar equiv of **L*E** or of $AgSbF_6$ was used to prepare [Ru(η^6:η^1-**L^A**-*P*)(**L*E**)Cl]SbF_6, the ratio remained the same. Also, the reaction of **2** with **L*D** without $AgSbF_6$ resulted in a 1:1 ratio of isomers for [Ru(η^6:η^1-**L^A**-*P*)(**L*D**)Cl]Cl. The $^{31}P\{^1H\}$ NMR spectra indicated that the ratio of the diastereomers of [Ru(η^6:η^1-**L^A**-*P*)(**L*D**)Cl]SbF_6 also remained the same from −80 to 80 °C. We were unable to find a convenient method for the separation of these diastereomers. Part of this difficulty can be traced to the failure of the diastereomers to crystallize separately. For example, the red-orange crystalline plates of [Ru(η^6:η^1-**L^A**-*P*)(**L*D**)Cl]SbF_6, obtained from recrystallization (CH_2Cl_2/hexanes), were quasi-racemates (verified by X-ray crystallography, Figure 2) having the same 1:1 ratio of *anti*-diastereomers in the unit cell as in the bulk material.

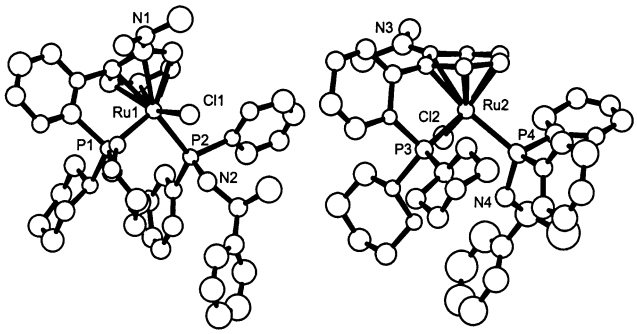


Figure 2. ORTEP view of [Ru(η^6:η^1-$Me_2NC_6H_4C_6H_4PCy_2$-*P*)(PPh_2(*S*)-1-phenylethyl)Cl]SbF_6 with 50% probability ellipsoids. A quasi-racemate is formed, and both diastereomers are found in the same unit cell and are related by a pseudocenter of symmetry.

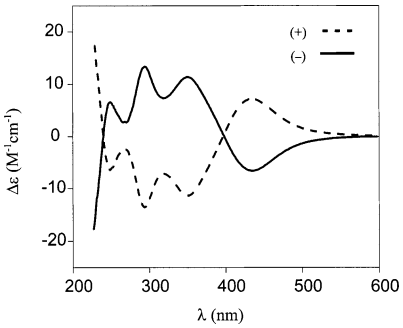


Figure 3. CD spectra of (+)- and (−)-[Ru(η^6:η^1-$Me_2NC_6H_4C_6H_4PCy_2$-*P*)(PPh_3)Cl]SbF_6, **3a**, in CH_2Cl_2.

Of the achiral phosphines, the PPh_3 derivative, [Ru(η^6:η^1-**L^A**-*P*)(PPh_3)Cl]SbF_6, **3a**, yielded a product that was the easiest to obtain as a pure diastereomer. Compound **3a** was purified by column chromatography and isolated as a single racemic diastereomer in 96% yield. It crystallized (CH_2Cl_2/ether) more readily than the chiral phosphine analogues, and fortunately, the enantiomers of **3a** underwent spontaneous resolution with a conglomerate forming upon crystallization. Mechanical separation of the crystals, determination of the sign of the optical rotation of individual crystals, and combination of solutions having similar rotations allowed separation of the pure enantiomers.

The mirror image relationship in the circular dichroism (CD) spectra (Figure 3) and the equivalent molar ellipticities of isolated (+) and (−)-**3a** illustrate that manual separation was an effective means of resolving this compound. Cutting a large single crystal allowed the determination of both the optical rotation of the dissolved crystal and the absolute configuration by X-ray diffraction study of a single crystal of (−)-**3a** (Figure 4). This showed that (−)-**3a** was the (R_{Ru},*R*)-enantiomer. Compound **3a** is a rare example of a planar chiral, tethered, late transition metal compound that has been isolated in enantiopure form.[21,35]

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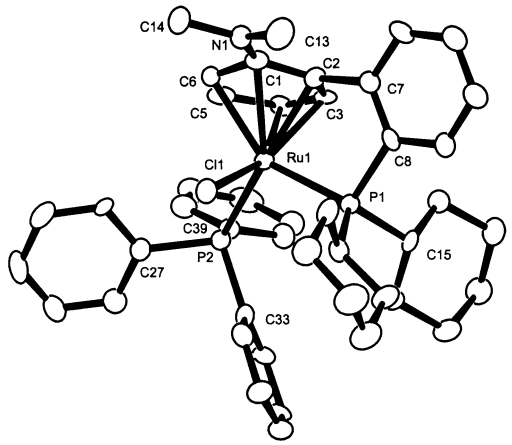

Figure 4. ORTEP view of (R_{Ru},*R*)-[Ru(η^6:η^1-$Me_2NC_6H_4C_6H_4$-PCy_2-*P*)(PPh_3)Cl]SbF_6, **3a**, with 50% probability ellipsoids. The descriptor for the metal center is determined by the priorities arene > Cl > P2 > P1. The descriptor for the ring chirality is determined by the chirality of the highest rank carbon atom in the ring, C1. Individual crystals contain either the (R_{Ru}, *R*) or the (S_{Ru}, *S*) enantiomer.

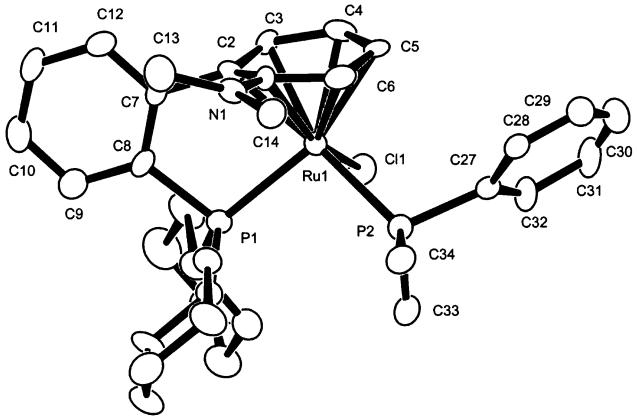

Figure 5. ORTEP view of (R_{Ru},*S*)-[Ru(η^6:η^1-$Me_2NC_6H_4C_6H_4$-PCy_2-*P*)(PMe_2Ph)Cl]SbF_6, **4**, with 50% probability ellipsoids. The descriptor for the metal center is determined by the priorities arene > Cl > P2 > P1. The descriptor for the ring chirality is determined by the chirality of the highest rank carbon atom in the ring, C1. Individual crystals contain both the (R_{Ru}, *S*) and the (S_{Ru}, *R*) enantiomer.

Diastereomeric Preferences. The compounds containing the achiral phosphines exhibit a preference for the initial formation of the *anti*-diastereomer shown in Scheme 2, but only in the case of PPh_3 is the reaction essentially completely diastereoselective. The observed de at room temperature for each [Ru(η^6:η^1-$\mathbf{L^A}$-*P*)(L)Cl]-SbF_6 is as follows: L = PPh_3 (>96% de); $PMePh_2$ (91% de); PMe_2Ph (86% de); PMe_3 (90% de). These diastereomeric ratios are unchanged when the compounds are left in solution over several days. The compounds containing the achiral phosphines tend to crystallize (CH_2Cl_2/ether) more readily than the analogues containing chiral phosphines. The X-ray diffraction study of a single crystal of [Ru(η^6:η^1-$\mathbf{L^A}$-*P*)(PPh_3)Cl]SbF_6, **3a** (Figure 4), which is observed as one diastereomer in NMR spectra, confirmed the assignment as the *anti* isomer, Scheme 2. Repeated recrystallizations from CH_2Cl_2/ether allowed isolation of the minor isomer of [Ru(η^6:η^1-$\mathbf{L^A}$-*P*)(PMe_2Ph)Cl]SbF_6, **4**. An X-ray crystal structure determination (Figure 5) confirmed that the minor isomer had the *syn* arrangement, Scheme 2. When *syn*-**4** was dissolved in dichloromethane, no interconversion to the *anti* isomer was observed over extended periods.

The observed ratio of the diastereomers containing achiral phosphines appears to be kinetically controlled since the ratios remain constant in solution for extended periods. The diastereomer ratio can, however, be altered upon repeated crystallization, as observed for **4**. The degree of diastereoselectivity in the formation apparently depends on the steric and electronic influences exerted on the achiral phosphine by the dimethylamino group in the η^6-ring. PMe_2Ph in **4** is a less sterically demanding and a better donating ligand than PPh_3 in **3a**. As a result, the *syn* arrangement in **4** is less sterically disfavored, and some of this diastereomer can be observed in the product. On the other hand, the greater bulk of PPh_3 prevents the formation of a significant amount of the *syn* diastereomer. Comparison of the crystal structures of *syn*-**4** and *anti*-**3a** illustrates how the PMe_2Ph ligand conformation can adjust to minimize interactions with the dimethylamino group, whereas PPh_3 does not have an option for rotating around the Ru−P bond to reduce the Ph−NMe_2 interactions.

It would appear that the principal factor controlling conformational preferences and diastereomeric preferences are steric interactions of the ligand with the dimethylamino group. In this context, it is interesting to note that the lone pair of the dimethylamino group has significant donation to the ring in the positively charged aryl-ruthenium moiety. This should result in significant double-bond character in the N-aryl bond, thus making it a relatively rigid structure. The structures of the cations show that the nitrogen atom in the dimethylamino group is essentially planar and all of its atomic constituents are in the same plane as the arene. This contrasts with the neutral compound (Figure 1), where the nitrogen atom in the dimethylamino function is pyramidal and furthermore the methyl groups are rotated out of the plane of the arene.

Interactions with the dimethylamino group should direct the initial formation of the diastereomers of complexes with a particular ligand and then influence the final thermodynamic equilibrium populations. With the more basic phosphines that have smaller cone angles, (i.e., PMe_3 and PMe_2Ph), the Ru−P bond appears to be so strong that the thermodynamic equilibrium ratio is established so slowly that we were unable to measure the rate.

Presumably *syn*−*anti* interconversion would occur via loss of a phosphine ligand. This dissociation is slow with PMe_3 and PMe_2Ph; however it appears that PPh_3 is more labile and should allow more rapid equilibration. In fact, in the presence of an excess (>5 molar equiv) of PMe_2Ph, interconversion of the single isomer of **3a** to both diastereomers of **4** having a reduced de (67%) occurs with a half-life of approximately 37 h. Thus it appears that the >90% de represents a thermodynamic equilibrium for **3a**, whereas the equilibrium value for **4** is still uncertain. This diastereomeric preference in the formation of *anti*-**3a** apparently results from the incoming PPh_3 being directed to a particular coordination site on Ru by steric interaction with the NMe_2 substituent on the coordinated arene ring.

The single, isolated diastereomer of **3a** is apparently the preferred thermodynamic and kinetic product of the reaction. A nonequilibrium mixture of *syn* and *anti* isomers of **3a** can be prepared by abstraction of chloride from *anti*-**3a**, giving [Ru(η^6:η^1-$\mathbf{L^A}$-*P*)(PPh_3)](SbF_6)$_2$, **5**, followed by addition of lithium chloride. A kinetic ratio of 2:1 (33% de) for *anti:syn* isomers equilibrates over 150 h to a ratio of 25:1 (92% de) ($t_{1/2} \approx 25$ h). Thus, both the kinetic and thermodynamic preference in diastereomer formation in the reaction of [Ru(η^6:η^1-$\mathbf{L^A}$-*P*)Cl_2] with PPh_3 is determined by interactions with the dimethylamino group.

Similarly, the dication [Ru(η^6:η^1-$\mathbf{L^A}$-*P*)(PMe_2Ph)](SbF_6)$_2$, **6**, is formed by chloride abstraction from **4** using $AgSbF_6$. Addition of excess Cl^- in the form of LiCl to **6** regenerates **4**; however this reaction favors formation of the *syn* isomer (*anti:syn* = 10:90, 80% de). This outcome contrasts with the addition of PMe_2Ph to [Ru(η^6:η^1-$\mathbf{L^A}$-*P*)Cl]SbF_6 that preferentially yields *anti*-**4** (*anti:syn* = 93:7, 86% de) and suggests that the kinetic product in the addition of LiCl to **6** is determined by a sterically favorable approach for the incoming nucleophilic chloride.

With the less bulky methyl substituent in the tethered complex formed from 2-(dicyclohexylphosphino)-2′-methylbiphenyl, **3c**, reaction with PPh_3 yields both diastereomers in the kinetic product (88% de). Hence, even a methyl group can significantly influence the preferred direction of attack of the PPh_3.

Conformations and Diastereomeric Configurations. Brunner[36] has pointed out that there have been a number of errors in interpretation of diastereomeric ratios based on room-temperature NMR observations. That is, high diastereoselectivity (100% de) has been claimed in some cases when only a single set of resonances was observed in the NMR spectra at ambient temperatures. Careful study at low temperature indicated that both diastereomers were present; however, an averaged spectrum was observed at higher temperatures owing to rapid equilibration between the diastereomers. Since **3a** was isolated as a single diastereomer, VT NMR spectra were examined to determine if there were potential problems arising from stereochemical nonrigidity.

The $^{31}P\{^1H\}$ NMR spectrum of **3a** was recorded at various temperatures in three different solvents: dichloromethane-d_2 (Figure 6), acetone-d_6, and chloroform-*d*. In each solvent only one diastereomer, having a doublet for each coordinated phosphine, was observed between 60 and −20 °C. At −40 °C the doublets broadened, and from −60 and −80 °C a major and minor set of doublets was visible. Although this might have been attributed to *syn*−*anti* interconversion, the slow exchange of phosphine in **3a** and the extremely slow diastereomeric interconversions in **4** suggest otherwise. A more likely alternative is that the two sets of doublets observed at low temperature were due to the slowing of a conformational interconversion process, such as interconversion of phenyl group conformations on PPh_3.[37−39] To evaluate this rationale, the analogues [Ru(η^6:η^1-L′-*P*)(PPh_3)Cl]SbF_6, where L′ = $\mathbf{L^B}$ or $\mathbf{L^C}$, were prepared in the one-step reaction of [Ru(PPh_3)$_3Cl_2$], L′, and $AgSbF_6$ in refluxing chlorobenzene. [Ru(η^6:η^1-$\mathbf{L^B}$-*P*)(PPh_3)Cl]-

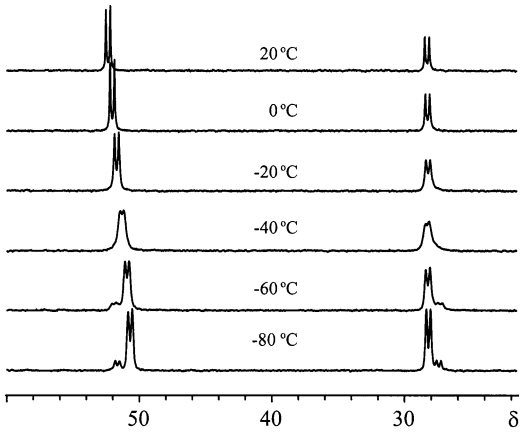

Figure 6. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of [Ru(η^6:η^1-$Me_2NC_6H_4C_6H_4PCy_2$-*P*)(PPh_3)Cl]SbF_6, **3a**, in CD_2Cl_2.

SbF_6, **3b**, possesses a chiral metal center and no planar chirality and exists as a racemate of only one possible diastereomer. Thus, there is no possibility of *syn*−*anti* interconversion. The variable-temperature $^{31}P\{^1H\}$ NMR spectrum of **3b** was similar to that of **3a**; a second small set of doublets was observed at −80 °C. Because the single possible diastereomer of **3b** also exhibited additional resonances at low temperature, interconversion of either phenyl or cyclohexyl conformers is a viable explanation. The variable-temperature $^{31}P\{^1H\}$ NMR spectrum of the methyl-substituted analogue [Ru(η^6:η^1-$\mathbf{L^C}$-*P*)(PPh_3)Cl]SbF_6, **3c**, which has planar as well as central metal chirality like **3a**, contributed additional insight. As a result of the different steric and electronic influences offered by the methyl- versus the dimethylamino-substituted arene, both diastereomers were observed in the $^{31}P\{^1H\}$ NMR spectrum from −80 to 80 °C. Nevertheless, an additional pair of doublets was still observed at lower temperatures associated with the major diastereomer. The low concentration of the second diastereomer precluded observation of another set of doublets associated with the weaker doublet. Presumably, if a greater fraction of the minor diastereomer had been present, a total of four pairs of doublets attributable to four diastereomers would have been observed at low temperature.

The VT $^{31}P\{^1H\}$ NMR spectrum of the PMe_2Ph derivative **4**, which shows both diastereomers in significant concentrations, shows two pairs of doublets in the same ratio from −80 to 80 °C but no additional set of doublets at −80 °C. This further suggests that the low-temperature interconversions involve conformational changes. One rationale is that phenyl conformers on PPh_3 are involved and could cause the additional resonances for **3a**, **3b**, and **3c**, since the only obvious difference between **4** and **3a** is the smaller number of phenyl groups on PMe_2Ph versus PPh_3. Alternatively, the greater steric interactions with PPh_3 could affect the conformational preferences for the cyclohexyl groups and (cyclohexyl)−C−P bond rotation conformations

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could be involved. The important feature is that the low-temperature phenomenon is associated with a ligand conformational effect, not an epimerization at the metal center that interconverts *syn* and *anti* isomers.

Potential Control of Bidentate Ligand Coordination. The formation of a particular diastereomer appears to be controlled by the bulk (cone angle) of a particular donor. This should thus allow selective coordination of chelating ligands that have significant differences in steric bulk at the termini of the chelates. Two qualitative tests of this aspect were carried out. Coordination of the chiral bidentate bisphosphine, (*R*)-(+)-1,2-bis(diphenylphosphino)propane, (*R*)-PROPHOS, to the [Ru(η^6:η^1-**L^A**-*arene, P*)] fragment, effected by abstraction of both chlorides from *rac*-**2** using $AgSbF_6$ at room temperature, did not exhibit differentiation between the two phosphine termini, as four diastereomers were observed. This system has only modest steric differences between the termini, but offered potential as a resolving agent if it had been more selective.

On the other hand, the heterobidentate ligand 1,1′-bis(diphenylphosphino)methane monoxide, dppmO, has termini with large differences in steric requirements. The coordination of both P and O to the metal, which was established by coupling patterns and characteristically shifted $^{31}P\{^1H\}$ NMR resonances,[7] gave only one of the two possible diastereomers. It appears that steric interactions determine bonding site selectivity, and thus the phosphine terminus of dppmO presumably occupied the less congested site *anti* to NMe_2 and allowed the phosphine oxide to occupy the more hindered site. This result illustrates the potential of using planar chiral ligands to control the relative stereochemistry of the remaining ligands on the metal. We will report on further studies in this area in the future.

Asymmetric Catalysis with 3a. The availability of the enantiopure tethered precatalyst **3a** permits testing its application in an asymmetric Lewis-acid-catalyzed reaction. The catalytically active dication [Ru(η^6:η^1-**L^A**-*P*)(PPh_3)](SbF_6)$_2$, **5**, is prepared by chloride abstraction from enantiopure **3a**. Few late transition metal catalysts containing tethers[40,41] and, to our knowledge, only one other containing a planar chiral tether[15] have been applied as catalysts in asymmetric reactions. The preliminary catalytic reaction in which we applied **5** as a catalyst was the asymmetric Diels−Alder reaction of methacrolein with cyclopentadiene. Using 10 mol % catalyst, the enantioselectivity was modest (19% ee) at −24 °C, though conversion (95%) and diastereoselectivity (96% *exo*) were high. Lowering the temperature to −78 °C made a modest improvement in the enantioselectivity (23% ee), though the conversion (96%) and diastereoselectivity (91% *exo*) remained high. Use of precatalyst (+)-(S_{Ru},*S*)-**3a** generated the (*S*)-*exo* Diels−Alder product predominantly, while (−)-(R_{Ru},*R*)-**3a** generated the (*R*)-*exo* product.

A brief comment on the nature of the active catalyst is appropriate. The unsolvated dication is formally a 16-electron complex and may effectively yield a planar [(arene)Ru(P)(PPh_3)] metal center. Interaction with adventitious water or a substrate would yield a stereogenic ruthenium center, the stereochemistry of which would probably be controlled by steric interactions that would place the PPh_3 *anti* to the NMe_2 group (Scheme 2). Interpretation of the NMR spectra of the adducts of **5** is complicated by multiple equilibria, as well as conformational interconversions that are temperature dependent. A future publication will address the complex equilibria in these systems.

Conclusions

Commercially available ligands **L^A**, **L^B**, and **L^C** were found to form η^6-arene complexes with tethered donors when coordinated to ruthenium. Ligands **L^A** and **L^C** contribute planar chirality upon coordination owing to the presence of their NMe_2 and Me substituents. Chiral-at-metal **3a** spontaneously resolved upon crystallization and allowed separation of the enantiomers. The dication derived from enantiopure **3a** catalyzed an asymmetric Diels−Alder reaction, giving products in modest ee. Analogues of **3a** were also prepared for structural comparison. We are currently considering approaches to enhance these features of analogous compounds for application to other catalytic reactions.

Experimental Section

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk techniques. All solvents were distilled under nitrogen with standard desiccating agents. $AgSbF_6$, **L^A**, **L^B**, **L^C** (Strem), PPh_3, $PMePh_2$, PMe_3, PMe_2Ph, *R*-PROPHOS, methacrolein, dicyclopentadiene, and (+)-Eu(hfc)$_3$ (Aldrich) were used as received. [Ru(benzene)Cl_2]$_2$,[42,43] **L*^{D}**,[32] **L*^{E}**,[33] **L*^{F}**,[34] and dppmO[44] were prepared according to literature methods. NMR spectra were recorded at room temperature, unless otherwise noted, on a GE Omega 300 MHz (operating at 122 MHz for ^{31}P), Bruker 400 MHz (operating at 162 MHz for ^{31}P), or Bruker 500 MHz (operating at 202 MHz for ^{31}P) spectrometer. Chemical shifts are reported in ppm relative to residual solvent peaks (^1H, ^{13}C) or an 85% H_3PO_4 external standard (^{31}P). Optical rotations were measured on a Perkin-Elmer model 341 polarimeter at 589 nm and 25 °C, using a 1 dm path length. CD spectra were recorded on an AVIV model 202 spectrometer. CD spectra were recorded in dichloromethane at 25 °C from 600 to 200 nm in 1.0 nm intervals with a 10 s averaging time, using a 1 mm path length quartz cell. Elemental analyses were carried out by Atlantic Microlabs.

Preparation of [Ru(η^6:η^1-L^A-*P*)Cl_2], 2. [Ru(benzene)Cl_2]$_2$ (171.4 mg, 0.34 mmol) and **L^A** (272.4 mg, 0.69 mmol) were stirred in DMF (12 mL) at 100 °C for 12−15 min. After cooling to room temperature, the solvent was removed by reduced pressure distillation. The dark red-brown residue was purified by flash chromatography (silica gel, $(CH_3)_2CO$), affording **2** in 94% yield (363.8 mg, 0.64 mmol). The product was recrystallized from CH_2Cl_2/ether. ^1H NMR (400 MHz, $CDCl_3$, δ): 7.80 (1 H, m, C_6H_4P); 7.63 (1 H, m, C_6H_4P); 7.59 (2 H, m, C_6H_4P); 6.25 (1 H, m, η^6-C_6H_4N); 5.87 (1 H, d, J = 6.4 Hz, η^6-C_6H_4N); 5.75 (1 H, t, J = 5.5 Hz, η^6-C_6H_4N); 4.76 (1 H, d, J = 5.5 Hz, η^6-C_6H_4N); 2.70 (1 H, m, C_6H_{11}); 2.55 (6 H, s, NCH_3); 2.51 (1 H, m, C_6H_{11}); 1.98 (1 H, m, C_6H_{11}); 1.78 (7 H, m, C_6H_{11}); 1.63 (5 H, m, C_6H_{11}); 1.25 (5 H, m, C_6H_{11}); 1.11 (1 H, m, C_6H_{11}); 0.88 (1 H, m, C_6H_{11}). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 145.82

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(d, J = 20 Hz, C_6H_4P); 142.26 (d, J = 38 Hz, C_6H_4P); 131.54 (s, C_6H_4P); 130.44 (d, J = 2 Hz, C_6H_4P); 129.10 (d, J = 21 Hz, C_6H_4P); 129.01 (d, J = 16 Hz, C_6H_4P); 116.56 (s, η^6-C_6H_4N); 103.20 (d, J = 2 Hz, η^6-C_6H_4N); 96.21 (d, J = 2 Hz, η^6-C_6H_4N); 85.95 (d, J = 14 Hz, η^6-C_6H_4N); 83.35 (d, J = 5 Hz, η^6-C_6H_4N); 76.34 (s, η^6-C_6H_4N); 44.00 (s, NCH_3); 35.51 (d, J = 20 Hz, C_6H_{11}); 34.18 (d, J = 22 Hz, C_6H_{11}); 28.10 (s, C_6H_{11}); 27.60 (d, J = 12 Hz, C_6H_{11}); 27.50 (d, J = 9 Hz, C_6H_{11}); 27.41 (d, J = 9 Hz, C_6H_{11}); 27.17 (s, C_6H_{11}); 27.09 (d, J = 11 Hz, C_6H_{11}); 26.69 (d, J = 8 Hz, C_6H_{11}); 26.16 (d, J = 9 Hz, C_6H_{11}). $^{31}P\{^1H\}$ NMR (122 MHz, $CDCl_3$, δ): 58.79 (s). Anal. Calcd for $C_{26}H_{36}Cl_2NPRu$: C, 55.22; H, 6.42; N, 2.48. Found: C, 55.50; H, 6.47; N, 2.41.

Preparation of [Ru(η^6:η^1-L^A-*P*)(PPh_3)Cl]SbF_6, 3a. [Ru(η^6:η^1-$\mathbf{L^A}$-*P*)Cl_2] (50.8 mg, 0.090 mmol), $AgSbF_6$ (31 mg, 0.090 mmol), and PPh_3 (24.4 mg, 0.093 mmol) were stirred in CH_2Cl_2 (5 mL) for 2 h. The solvent was then removed under reduced pressure, giving an orange residue. After purification by flash chromatography (silica gel, CH_2Cl_2/$(CH_3)_2CO$ (1:1)), **3a** was isolated in 96% yield (88.2 mg, 0.086 mmol). Crystals suitable for X-ray diffraction were obtained by slow diffusion of ether into a dichloromethane solution. *anti*-**3a**: ^1H NMR (400 MHz, CD_2Cl_2, δ): 7.71 (1 H, m, C_6H_4P); 7.65 (1 H, m, C_6H_4P); 7.61 (2 H, m, C_6H_4P); 7.46 (15 H, m, C_6H_5P); 6.00 (1 H, d, J = 6.8 Hz, η^6-C_6H_4N); 5.82 (1 H, m, η^6-C_6H_4N); 5.08 (1 H, m, η^6-C_6H_4N); 3.89 (1 H, m, η^6-C_6H_4N); 3.095 (3 H, s, NCH_3); 3.091 (3 H, s, NCH_3); 2.61 (1 H, m, C_6H_{11}); 2.14 (1 H, m, C_6H_{11}); 1.81 (3 H, m, C_6H_{11}); 1.67 (3 H, m, C_6H_{11}); 1.56 (3 H, m, C_6H_{11}); 1.44 (2 H, m, C_6H_{11}); 1.22 (3 H, m, C_6H_{11}); 1.11 (3 H, m, C_6H_{11}); 0.85 (1 H, m, C_6H_{11}); 0.77 (2 H, m, C_6H_{11}). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 53.79 (d, J = 40 Hz); 29.65 (d, J = 40 Hz). One diastereomer (*anti*) was isolated. Anal. Calcd for $C_{44}H_{51}ClF_6NP_2RuSb$: C, 51.40; H, 5.00, N, 1.36. Found: C, 51.46; H, 5.01; N, 1.40.

A sample with an enrichment of the *syn* isomer was obtained in situ by treating *anti*-**3a** with $AgSbF_6$ and quenching with 5 equiv of LiCl (vide infra preparation of **5**). This showed an initial *anti*:*syn* ratio of ~2:1. *syn*-**3a**: $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ): 58.98 (d, J_{PP} = 44 Hz); 28.86 (d, J_{PP} = 44 Hz). The ratio decayed from a 33% de after 1 h to 92% de after 150 h.

Preparation of [Ru(η^6:η^1-L^A-*P*)(L^{*D})Cl]SbF_6. [Ru(η^6:η^1-$\mathbf{L^A}$-*arene*, *P*)Cl_2] (11.2 mg, 0.020 mmol) and $AgSbF_6$ (7 mg, 0.020 mmol) were stirred in CD_2Cl_2 (0.9 mL). Ligand $\mathbf{L^{*D}}$ (66 mg, 0.22 mmol) was added, and the solution was stirred for 1.5 h. The compound was purified by column chromatography (silica gel, CH_2Cl_2/$CH_3COOC_2H_5$ (1:1)). Orange crystalline plates of quasi-racemates were obtained by diffusion of hexanes into a dichloromethane solution. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, δ): 69.96 (d, J = 44 Hz, minor isomer); 66.93 (d, J = 44 Hz, major isomer); 57.81 (*pseudo*-t, J = 44 Hz, overlapped major and minor isomers). The ratio of isomers was 1.1:1.

Preparation of [Ru(η^6:η^1-L^A-*P*)(L^{*E})Cl]SbF_6. [Ru(η^6:η^1-$\mathbf{L^A}$-*P*)Cl_2] (17.2 mg, 0.030 mmol) was stirred with $AgSbF_6$ (10 mg, 0.029 mmol) in CD_2Cl_2 (0.85 mL). As $\mathbf{L^{*E}}$ (17.6 mg, 0.031 mmol) was stirred into the purple solution for 2 h, the color changed to red-orange. Purification was achieved by column chromatography (silica gel, CH_2Cl_2/$(CH_3)_2CO$ (1:1)). $^{31}P\{^1H\}$ NMR (122 MHz, CD_2Cl_2, δ): 151.50 (d, J = 51 Hz, major isomer); 150.29 (d, J = 46 Hz, minor isomer); 59.95 (br, major isomer); 57.04 (d, J = 46 Hz, minor isomer). The ratio of isomers was 1.4:1.

Preparation of [Ru(η^6:η^1-L^A-*P*)(L^{*F})Cl]SbF_6. [Ru(η^6:η^1-$\mathbf{L^A}$-*P*)Cl_2] (17.4 mg, 0.031 mmol), $AgSbF_6$ (11 mg, 0.032 mmol), and $\mathbf{L^{*F}}$ (11.9 mg, 0.035 mmol) were stirred in CH_2Cl_2 (2.5 mL), giving an orange solution with a white suspension within 4 h. The mixture was then filtered through Celite, the solvent was removed, and the orange residue was dried in vacuo. The compound was purified by column chromatography (silica gel, CH_2Cl_2/$CH_3COOC_2H_5$ (2:1)). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, δ): 122.74 (d, J = 44 Hz, overlapped major and minor isomers), 61.48 (br d, J = 42 Hz, major isomer), 59.99 (br, minor isomer). The ratio of isomers was 1.1:1.

Preparation of [Ru(η^6:η^1-L^B-*P*)Cl_2]. [Ru(benzene)Cl_2]$_2$ (96.2 mg, 0.19 mmol) and $\mathbf{L^B}$ (150 mg, 0.43 mmol) were heated overnight in 90−100 °C DMF (12 mL), giving a red solution. The product was washed through a chromatography column (silica gel) with $CH_3COOC_2H_5$. Isolated yield: 45% (90.6 mg, 0.17 mmol). Recrystallization involved slow diffusion of ether into a CH_2Cl_2 solution. ^1H NMR (500 MHz, CD_2Cl_2, δ): 7.79 (1 H, m, C_6H_4P); 7.61 (3 H, m, C_6H_4P); 6.35 (1 H, td, J = 6 Hz, 2.5 Hz, η^6-C_6H_5); 6.02 (2 H, t, J = 6 Hz, η^6-C_6H_5); 4.99 (2 H, d, J = 5.5 Hz, η^6-C_6H_5); 2.60 (2 H, m, C_6H_{11}); 1.82 (6 H, m, C_6H_{11}); 1.73 (2 H, m, C_6H_{11}); 1.69 (4 H, m, C_6H_{11}); 1.40 (2 H, m, C_6H_{11}); 1.25 (6 H, m, C_6H_{11}). $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, δ): 62.64 (s). Anal. Calcd for $C_{24}H_{31}Cl_2PRu$: C, 55.17; H, 5.98. Found: C, 55.24; H, 5.99.

Preparation of [Ru(η^6:η^1-L^C-*P*)Cl_2]. [Ru(benzene)Cl_2]$_2$ (56.7 mg, 0.113 mmol) and $\mathbf{L^C}$ (84.2 mg, 0.231 mmol) were stirred in DMF (6 mL) at 100 °C for 10 min. A bright red solution resulted. The solvent was removed by vacuum distillation, and the residue was dried in vacuo overnight. The product was chromatographed (silica gel) with $(CH_3)_2CO$. Isolated yield: 31% (37 mg, 0.069 mmol). Crystals were obtained by diffusion of hexanes into an ether solution. ^1H NMR (300 MHz, CD_2Cl_2, δ): 7.78 (1 H, m, C_6H_4P); 7.62 (2 H, m, C_6H_4P); 7.62 (1 H, m, C_6H_4P); 6.22 (1 H, m, η^6-C_6H_4Me); 5.95 (1 H, d, J = 6.3 Hz, η^6-C_6H_4Me); 5.73 (1 H, *pseudo*-t, J = 5.7 Hz, η^6-C_6H_4Me); 4.99 (1 H, d, J = 6.0 Hz, η^6-C_6H_4Me); 2.70 (1 H, m, C_6H_{11}); 2.48 (1 H, m, C_6H_{11}); 1.89 (6 H, m, C_6H_{11}); 1.75 (3 H, s, CH_3); 1.64 (6 H, m, C_6H_{11}); 1.22 (7 H, m, C_6H_{11}); 0.85 (1 H, m, C_6H_{11}). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, δ): 61.26 (s).

Preparation of [Ru(η^6:η^1-L^B-*P*)(PPh_3)Cl]SbF_6, 3b. To [Ru(PPh_3)$_3Cl_2$] (53.6 mg, 0.056 mmol) in chlorobenzene (5 mL) was added $AgSbF_6$ (19 mg, 0.055 mmol) and $\mathbf{L^B}$ (20 mg, 0.057 mmol). There was a color change in the solution from dark red-brown to yellow-orange as the mixture was refluxed. After 2 h, the solvent was removed by vacuum distillation. The residue was stirred in ether to remove excess PPh_3, then washed through a chromatography column (silica gel) with $(CH_3)_2CO$. Yield was 75% (41 mg, 0.041 mmol). ^1H NMR (400 MHz, CD_2Cl_2, δ): 7.71−7.38 (19 H, m, C_6H_5P and C_6H_4P); 6.36 (1 H, m, η^6-C_6H_5); 5.94 (1 H, d, J = 5.6 Hz, η^6-C_6H_5); 5.85 (1 H, m, η^6-C_6H_5); 5.76 (2 H, m, η^6-C_6H_5); 2.67 (1 H, m, C_6H_{11}); 2.04 (2 H, m, C_6H_{11}); 1.69 (5 H, m, C_6H_{11}); 1.42 (6 H, m, C_6H_{11}); 1.24 (4 H, m, C_6H_{11}); 0.86 (1 H, m, C_6H_{11}); 0.72 (1 H, m, C_6H_{11}); 0.51 (2 H, m, C_6H_{11}). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, δ): 61.05 (d, J = 45 Hz); 28.53 (d, J = 45 Hz).

Preparation of [Ru(η^6:η^1-L^C-*P*)(PPh_3)Cl]SbF_6, 3c. To [Ru(PPh_3)$_3Cl_2$] (26.6 mg, 0.028 mmol) in chlorobenzene (5 mL) was added $AgSbF_6$ (9 mg, 0.026 mmol) and $\mathbf{L^C}$ (16.5 mg, 0.045 mmol). There was a color change in the solution from red-brown to yellow as the mixture was refluxed. After 3 h, the solvent was removed by vacuum distillation, then the residue was stirred in ether and dried in vacuo. Yield was 78% (20 mg, 0.020 mmol). ^1H NMR (400 MHz, CD_2Cl_2, δ): *anti* isomer: 7.60 (19 H, m, C_6H_5P and C_6H_4P); 6.35 (1 H, d, J = 5.5 Hz, η^6-C_6H_4Me); 5.97 (1 H, m, η^6-C_6H_4Me); 5.41 (1 H, d, J = 5.5 Hz, η^6-C_6H_4Me); 4.60 (1 H, m, η^6-C_6H_4Me); 2.64 (1 H, m, C_6H_{11}); 2.11 (3 H, d, J = 3.0 Hz, CH_3); 1.87 (1 H, m, C_6H_{11}); 1.65 (12 H, m, C_6H_{11}); 1.13 (6 H, m, C_6H_{11}); 0.96 (1 H, m, C_6H_{11}); 0.82 (1 H, m, C_6H_{11}); *syn* isomer: not distinguishable. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, δ): 57.99 (d, J = 42 Hz, *syn* isomer); 55.46 (d, J = 42 Hz, *anti* isomer); 27.05 (d, J = 42 Hz, major *anti* isomer); 25.42 (d, J = 42 Hz, *syn* isomer). At room temperature, there were two isomers present in a 16:1 (*anti*:*syn*) ratio.

Preparation of [Ru(η^6:η^1-L^A-*P*)($PMePh_2$)Cl]SbF_6. To [Ru(η^6:η^1-$\mathbf{L^A}$)Cl_2] (29.4 mg, 0.052 mmol) in CH_2Cl_2 (2 mL) was added $AgSbF_6$ (18 mg, 0.052 mmol). The solution darkened in color. Centrifugation removed the precipitated AgCl. $PMePh_2$ (0.012 mL, 0.064 mmol) was then added, slowly turning the

solution orange. After ~3 h, the solvent was removed and the orange residue was washed with ether to remove excess $PMePh_2$. Small red crystals were obtained by diffusion of ether into a CH_2Cl_2 solution. ^1H NMR (400 MHz, CD_2Cl_2, δ): *anti* isomer: 7.76−7.34 (14 H, m, C_6H_5P and C_6H_4P); 5.93 (1 H, d, J = 6.8 Hz, η^6-C_6H_4N); 5.55 (1 H, br, C_6H_5P and η^6-C_6H_4N); 5.19 (1 H, br, C_6H_5P and η^6-C_6H_4N); 4.98 (1 H, br, C_6H_5P and η^6-C_6H_4N); 3.04 (6 H, s, NCH_3); 2.21 (3 H, d, J = 9.2 Hz, PCH_3); 2.67 (1 H, m, C_6H_{11}); 2.04 (1 H, m, C_6H_{11}); 1.85 (4 H, m, C_6H_{11}); 1.51 (12 H, m, C_6H_{11}); 0.88 (3 H, m, C_6H_{11}); 0.65 (1 H, m, C_6H_{11}); *syn* isomer: not distinguishable. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, δ): 61.35 (d, J = 46 Hz, *syn* isomer); 59.13 (d, J = 45 Hz, *anti* isomer); 14.49 (d, J = 45 Hz, *anti* isomer); 13.24 (d, J = 46 Hz, *syn* isomer). The observed ratio of the *anti* to *syn* isomer was 22:1.

Preparation of [Ru(η^6:η^1-L^A-*P*)(PMe_3)Cl]SbF_6, 7. [Ru(η^6:η^1-L^A-*P*)Cl_2] (22.6 mg, 0.040 mmol), $AgSbF_6$ (14 mg, 0.040 mmol), and PMe_3 (1.0 M in toluene, 0.04 mL, 0.040 mmol) were stirred in CD_2Cl_2 (0.9 mL) for 3 h. The purple color of the dicationic solution slowly turned more orange-brown as the reaction proceeded. After centrifugation to remove AgCl, the NMR spectra were recorded. Small red crystals were obtained by diffusion of ether into a CH_2Cl_2 solution. ^1H NMR (400 MHz, CD_2Cl_2, δ): *anti* isomer: 7.76 (2 H, m, C_6H_4P); 7.67 (2 H, m, C_6H_4P); 6.01 (1 H, m, η^6-C_6H_4N); 5.97 (1 H, m, η^6-C_6H_4N); 5.66 (1 H, m, η^6-C_6H_4N); 4.79 (1 H, m, η^6-C_6H_4N); 2.84 (6 H, s, NCH_3); 2.19 (1 H, m, C_6H_{11}); 1.71 (9 H, d, J = 10 Hz, PCH_3); 1.65 (20 H, m, C_6H_{11}); 0.52 (1 H, m, C_6H_{11}); *syn* isomer: not distinguishable. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, δ): 64.46 (d, J = 51 Hz, *syn* isomer); 62.84 (d, J = 47 Hz, *anti* isomer); 2.09 (d, J = 47 Hz, *anti* isomer); −0.24 (d, J = 51 Hz, *syn* isomer). The initial ratio of the *anti* to *syn* isomer was 18:1.

Preparation of [Ru(η^6:η^1-L^A-*P*)(PMe_2Ph)Cl]SbF_6, 4. [Ru(η^6:η^1-**L^A**-*P*)Cl_2] (21.0 mg, 0.037 mmol) and $AgSbF_6$ (13 mg, 0.038 mmol) were stirred in CD_2Cl_2 (0.9 mL) for 20 min. PMe_2Ph (0.007 mL, 0.049 mmol) was added, and the color of the solution turned red-orange. After stirring for 3 h, the solution was centrifuged, dried, and washed with ether. Yield was 89% (30 mg, 0.033 mmol). Small red crystals were obtained by diffusion of ether into a CH_2Cl_2 solution. ^1H NMR (300 MHz, CD_2Cl_2, δ): *anti* isomer: 7.64 (9 H, m, C_6H_4P and C_6H_5P); 5.83 (1 H, d, J = 7.2 Hz, η^6-C_6H_4N); 5.39 (1 H, m, η^6-C_6H_4N); 5.24 (1 H, m, η^6-C_6H_4N); 4.80 (1 H, d, J = 5.2 Hz, η^6-C_6H_4N); 2.903 (3 H, s, NCH_3); 2.901 (3 H, s, NCH_3); 2.79 (1 H, m, C_6H_{11}); 2.19 (1 H, m, C_6H_{11}); 2.00 (3 H, d, J = 10 Hz, PCH_3); 1.95 (3 H, d, J = 10 Hz, PCH_3); 1.52 (19 H, m, C_6H_{11}); 0.67 (1 H, m, C_6H_{11}); *syn* isomer (partial): 5.86 (1 H, obstructed m, η^6-C_6H_4N); 5.56 (1 H, d, J = 6.0 Hz, η^6-C_6H_4N); 5.37 (1 H, obstructed m, η^6-C_6H_4N); 5.20 (1 H, obstructed m, η^6-C_6H_4N); 2.50 (6 H, s, NCH_3); 2.10 (3 H, d, J = 10 Hz, PCH_3); 2.07 (3 H, d, J = 10 Hz, PCH_3). $^{31}P\{^1H\}$ NMR (122 MHz, CD_2Cl_2, δ): 61.79 (d, J = 49 Hz, *syn* isomer); 60.42 (d, J = 46 Hz, *anti* isomer); 2.01 (d, J = 46 Hz, *anti* isomer); −0.79 (d, J = 49 Hz, *syn* isomer). The initial ratio of *anti* to *syn* isomer was 13:1. Anal. Calcd for $C_{34}H_{47}ClF_6NP_2RuSb$: C, 45.18; H, 5.24; N, 1.55. Found: C, 45.14; H, 5.28; N, 1.53. (Note that the X-ray structure was from a sample obtained by fractional crystallization from CH_2Cl_2/ether that gave only the *syn* isomer.)

[Ru(η^6:η^1-L^A -*P*)(η^2-(*R*)-PROPHOS-*P*,*P*)]$(SbF_6)_2$. [Ru(η^6:η^1-**L^A**-*P*)Cl_2] (30.9 mg, 0.055 mmol), (*R*)-PROPHOS (23.6 mg, 0.057 mmol), and $AgSbF_6$ (38 mg, 0.11 mmol) were stirred in CD_2Cl_2 (0.9 mL) for 3 h. After centrifuging to remove the AgCl precipitate, an NMR spectrum was recorded of the red supernatant. $^{31}P\{^1H\}$ NMR (122 MHz, CD_2Cl_2, δ): 76.95 (*pseudo*-t, J = 30 Hz); 73.74 (*pseudo*-t, J = 27 Hz); 73.06 (*pseudo*-t, J = 31 Hz); 64.83 (*pseudo*-t, J = 29 Hz); 58.44 (m); 54.90 (*pseudo*-t, J = 30 Hz); 53.11 (m); 44.98 (*pseudo*-t, J = 31 Hz); 39.63 (*pseudo*-t, J = 27 Hz). Four diastereomers in nearly equal ratios were formed.

[Ru(η^6:η^1-L^A-*P*)(η^2-dppmO-*P*,*O*)]$(SbF_6)_2$. [Ru(η^6:η^1-**L^A**-*P*)Cl_2] (24.3 mg, 0.043 mmol), dppmO (20.3 mg, 0.049 mmol), and $AgSbF_6$ (30 mg, 0.087 mmol) were stirred in CD_2Cl_2 (0.9 mL) for 3.5 h, giving an orange solution. Yield was 92% (54 mg, 0.040 mmol). Orange-yellow crystals were obtained by slow ether diffusion into a CH_2Cl_2/MeOH solution. ^1H NMR (400 MHz, CD_2Cl_2, δ): 7.96−6.65 (24 H, m, C_6H_5P and C_6H_4P); 6.12 (1 H, m, η^6-C_6H_4N); 5.61 (1 H, d, J = 7.2 Hz, η^6-C_6H_4N); 4.98 (1 H, m, η^6-C_6H_4N); 4.48 (1 H, m, η^6-C_6H_4N); 4.25 (1 H, m, C*H*); 3.53 (1 H, ddd, J = 16, 16, 10 Hz, C*H*); 2.96 (6H, s, NCH_3); 2.85 (1 H, m, C_6H_{11}); 2.41 (1 H, m, C_6H_{11}); 1.66 (16 H, m, C_6H_{11}); 0.76 (2 H, m, C_6H_{11}); 0.41 (1 H, m, C_6H_{11}); 0.13 (1 H, m, C_6H_{11}). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, δ): 72.39 (d, J = 27 Hz, $P(O)Ph_2$); 52.57 (dd, J = 27, 43 Hz, PPh_2); 49.78 (d, J = 43 Hz, PCy_2). One diastereomer was isolated.

In Situ Preparation of [Ru(η^6:η^1-L^A-*P*)(PPh_3)]$(SbF_6)_2$, 5. [Ru(η:$^6\eta^1$-**L^A**-*P*)(PPh_3)Cl]SbF_6 (19.7 mg, 0.0192 mmol) and $AgSbF_6$ (6 mg, 0.02 mmol) were stirred in CD_2Cl_2 (0.9 mL) for 1 h 20 min. After centrifuging to remove precipitated AgCl, the supernatant was transferred to an NMR tube. $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, δ): +60 °C: 58.54 (d, J_{PP} = 36 Hz); 35.53 (d, J_{PP} = 36 Hz). *20 °C*: 58.17 (br); 35.58 (br). −40 °C: 57.66 (d, J_{PP} = 36 Hz); 34.46 (d, J_{PP} = 36 Hz).

In Situ Preparation of [Ru(η^6:η^1-L^A-*P*)(PMe_2Ph)]$(SbF_6)_2$, 6. [Ru(η^6:η^1-**L^A**-*P*)(PMe_2Ph)Cl]SbF_6 (17 mg, 0.019 mmol) and $AgSbF_6$ (6 mg, 0.02 mmol) were stirred in CD_2Cl_2 (0.9 mL) for 1 h. After centrifuging to remove precipitated AgCl, the supernatant was transferred to an NMR tube. $^{31}P\{^1H\}$ NMR (122 MHz, CD_2Cl_2, δ): 62.26 (br, minor isomer); 56.71 (br, major isomer); 5.09 (br, major isomer); 0.23 (br, minor isomer). The ratio of the isomers was 4:1.

General Procedure for the Catalyzed Diels−Alder Reaction.[11] To enantiopure (−)-(R_{Ru},*R*)-[Ru(η^6:η^1-**L^A**-*P*)(PPh_3)Cl]SbF_6 (9.8 mg, 0.0095 mmol) in CH_2Cl_2 (2 mL) was added $AgSbF_6$ (3 mg, 0.0087 mmol). Additional CH_2Cl_2 (1 mL) washed any $AgSbF_6$ from the walls of the centrifuge tube into the mixture. After stirring for 35 min, the solution was centrifuged. The orange supernatant was transferred to a precooled −20 °C vial. Methacrolein (8 μL, 0.097 mmol) was added, and the mixture was allowed to cool to −78 °C for 40 min. An aliquot of freshly distilled CpH (0.08 mL, 0.97 mmol) was then added by syringe to the reaction mixture. After 17 h at −78 °C, the solution was transferred to a flask, where the solvent was removed under reduced pressure to give an orange residue. Conversion of methacrolein (96%) and diastereomeric excess (de, 91% *exo*) were determined by ^1H NMR spectroscopy. The shift reagent (+)-Eu(hfc)$_3$ was used to determine an enantiomeric excess of 23% (*R*).

When (+)-(S_{Ru},*S*)-[Ru(η^6:η^1-**L^A**-*P*)(PPh_3)Cl]SbF_6 was used as the precatalyst at −20 °C, the conversion of methacrolein was 95% and the diastereomeric excess was 96% (*exo*), as determined by ^1H NMR spectroscopy. The shift reagent (+)-Eu(hfc)$_3$ was used to determine an enantiomeric excess of 19% (*S*).

Structure Determination and Refinement of 2, 3a, 4, and 7. Data were collected on a Nonius KappaCCD (Mo Kα radiation) and corrected for absorption (SORTAV).[45] The structures were solved by direct methods (SIR92)[46] and refined on *F* for all reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included at calculated positions. Relevant crystal and data parameters are presented in Table 1. A sample was cut from a large crystal of **3a**, and the absolute configuration of that portion was determined by inverting coordinates and noting a difference in *R* and R_w of 0.0373 and 0.0389 compared to 0.0343 and 0.0355 of the correct configuration. The remainder of the crystal was dissolved, and the optical rotation and CD spectrum were recorded to correlate chiroptical properties with absolute configuration. ORTEP views are shown in Figures 1,

(45) (a) Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33. (b) Blessing, R. H. *J. Appl. Crystallogr.* **1997**, *30*, 421.
(46) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr.* **1993**, *26*, 343.

Table 1. Crystallographic Data for Complexes Containing a Tethered Phosphine Moiety [Ru(η^6:η^1-$Me_2NC_6H_4C_6H_4PCy_2$-*P*)(L)Cl]

	2 (L = Cl)	*anti*-**3a** (L = PPh_3)	*anti*-**7** (L = PMe_3)	*syn*-**4** (L = $PPhMe_2$)
color, shape	red-orange plate	orange block	yellow plate	orange needle
empirical formula	$C_{26}H_{36}Cl_2NPRu$	$C_{44}H_{51}ClF_6NP_2RuSb$	$C_{29}H_{45}ClF_6NP_2RuSb$	$C_{35}H_{49}Cl_3F_6NP_2RuSb$
fw	565.53	1028.10	841.89	988.90
radiation/Å		Mo K α (monochr.) 0.71073		
T/K	183	183	296	183
cryst syst	monoclinic	orthorhombic	monoclinic	orthorhombic
space group	$P2_1/n$ (No. 14)	$P2_12_12_1$ (No. 19)	$P2_1/n$ (No. 14)	$Pca2_1$(No. 29)
unit cell dimens				
a/Å	11.7759(5)	10.9480(3)	14.0169(5)	15.1594(5)
b/Å	10.7780(5)	14.1398(5)	16.2724(6)	14.1727(5)
c/Å	20.5862(10)	27.1255(9)	15.2783(6)	18.2768(5)
β/deg	103.178(3)	90	100.333(2)	90
V/Å^3	2544.0(2)	4199.1(2)	3428.3(2)	3926.8(2)
Z	4	4	4	4
D_{calc}/g cm^{-3}	1.476	1.626	1.631	1.673
μ/cm^{-1} (Mo Kα)	9.03	12.02	14.51	14.12
cryst size/mm	0.05 × 0.12 × 0.14	0.07 × 0.07 × 0.010	0.05 × 0.12 × 0.17	0.05 × 0.05 × 0.12
total reflns, unique reflns	19583, 6077	16673, 9974	19048, 6870	22071, 11213
R_{int}	0.117	0.048	0.099	0.066
no. obsd ($I > n\sigma(I)$)	2556, 2	3302, 3	2449, 3	3228, 2
transmn range	0.917−0.963	0.865−0.919	0.794−1.000	0.847−0.935
params, constrnts	280, 0	505, 0	370, 0	441, 0
R,[a] R_w,[b] GOF	0.040, 0.035, 0.67	0.034, 0.036, 0.90	0.042, 0.048, 1.09	0.042, 0.040, 0.084
resid density/e Å^{-3}	−0.49 < 0.51	−0.47 < 0.54	−0.67 < 0.63	−0.62 < 0.068

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, for all $I > n(I)$. [b] $R_w = [\sum[w(|F_o| - |F_c|)^2]/\sum[w(F_o)^2]]^{1/2}$.

4, and 5 for **2**, **3a**, and **4**, respectively. An ORTEP view of **7** is similar to that of **3a** and is included in the Supporting Information.

Structure Determination and Refinement of [Ru(η^6:η^1-$Me_2NC_6H_4C_6H_4PCy_2$-*P*)(PPh_2(*S*)-1-phenylethylamino)Cl]SbF_6, 8. An orange plate suitable for analysis was obtained by diffusion of hexane into a methylene chloride solution of a 1:1 mixture of diastereomers. Data were collected on a Nonius KappaCCD (Mo Kα radiation) and corrected for absorption (SORTAV).[45] A triclinic cell with $Z = 2$ was found with cell constants of $a = 10.7371(3)$ Å; $b = 11.7416(3)$ Å; $c = 19.5736(5)$ Å; $\alpha = 86.531(2)°$; $\beta = 75.512(2)°$; $\gamma = 77.1560(13)°$; $V = 2329.38(11)$ Å^3. The structure was solved by direct methods (SIR92)[46] and refined on *F* for all reflections. A solution could be found for either centrosymmetric $P\bar{1}$ or noncentrosymmetric *P*1. In the $P\bar{1}$ solution, there was a disorder in the phenethylamine moiety corresponding to both chiralities being present. Since the phenethylamine was not racemic, it followed that the two ruthenium moieties were epimeric and the appropriate space group was *P*1 with two independent cations and anions. Owing to the pseudosymmetry, the movements of the two independent molecules were correlated and the atom movements during refinement had to be dampened. There was also a ∼4:1 disorder in one of the SbF_6 ions. Heavy atoms (Sb, Ru, Cl, P, F) were refined with anisotropic displacement parameters, and the remaining non-hydrogen atoms were refined with isotropic parameters. Since the heavy atoms are related by a pseudocenter, there are not sufficient anomalous dispersion differences to determine the polarity using the Flack parameter or differences in *R* upon inversion. The polarity was fixed by using the known *S*-configuration of the amine. For data > $3\sigma(I)$, and 6239 observations with 566 variables, the final residuals were $R = 0.052$ and $R_w = 0.063$.

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Supporting Information Available: A listing of atomic positions, thermal parameters, and bond distances and angles for **2**, **3a**, **4**, **7**, and **8**, as well as an ORTEP view of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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