# Resolution and Diels−Alder Catalysis with Planar Chiral Arene-Tethered Ruthenium Complexes

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Planar chiral arene-tethered ruthenium complexes were applied to the Diels−Alder reaction of methacrolein and cyclopentadiene, with enantiomeric excesses up to 70%. The influence of a chiral phosphoramidite ligand on the catalytic selectivity was examined, along with counterion effects. The potential of asymmetric activation using the mixture of diastereomers formed from a racemic tethered complex and an enantiopure phosphine directly in the catalysis was investigated.

## Introduction

Chiral pseudo-tetrahedral transition metal half-sandwich complexes have been used as asymmetric Lewis acid catalysts in Diels−Alder and Mukaiyama reactions[1−8] and in hydrogen transfer reactions for the reduction of ketones and aldehydes.[9−11] Half-sandwich compounds of the type $[(\eta^n\text{-}C_nH_n)ML^1L^2L^3]$ are chiral-at-metal, and pure enantiomers have been resolved in several cases.[12−15] A potential problem when such complexes are used as Lewis acid catalysts is that the metal center of the active catalyst can racemize. This is a process that can potentially have a detrimental effect on the enantioselectivity of the catalyses, as the computed and experimentally determined inversion barriers for the 16-electron Lewis acids are less than 15 kcal $mol^{-1}$.[16]

One strategy for imparting stereocontrol at the metal center of such compounds is to utilize tethered donor ligands, which are a class of mixed donor ligands in which an arene or cyclopentadienyl (Cp) ring is linked to a pendant donor group. There have been many cyclopentadienyl-derived versions of these compounds reported;[17−20] the arene analogues, however, are somewhat less common.[21−37] The use of tethered half-sandwich compounds in asymmetric catalysis has been limited to only a few cases so far.[38−40]

Recently, we reported the synthesis of a tethered ruthenium half-sandwich complex, [Ru($\eta^6$:$\eta^1$-2-dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl)$Cl_2$], **1**

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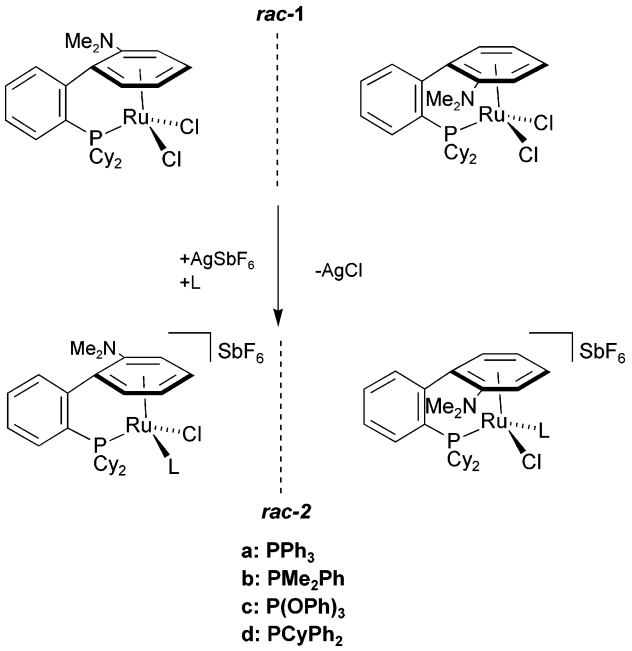


**Figure 1.** *anti*-Selective sythesis of racemic **2a**−**d** from racemic **1**.

(Figure 1),[41] which forms as a pair of planar chiral enantiomers. The tethered binding mode effectively locks the ligand chirality by halting the atropisomeric interconversion of the biphenyl moiety. Abstraction of a chloride ion from **1** with $AgSbF_6$ and treatment with phosphine (L) resulted in the highly selective formation of the chiral-at-metal complex [*anti*-Ru($\eta^6$:$\eta^1$-2-dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl)(L)Cl]-$SbF_6$, **2a**−**d** (Figure 1), as a pair of enantiomers. The high *anti* selectivity was attributed to the blocking effect of the $NMe_2$ group. It was shown that the *anti* isomer was the favored product both kinetically and thermodynamically. The $NMe_2$ group therefore can control the chirality of the metal center. This being the case, the dicationic complexes derived from enantiopure **2a**−**d**, formed by chloride abstraction with $AgSbF_6$, were used as Lewis acid catalysts for the Diels−Alder reaction of methacrolein and cyclopentadiene. To improve the selectivity and investigate a possible chiral poisoning/asymmetric activation approach to this system, the chiral phosphoramidite (*S*)-MonoPhos was also investigated as a ligand.

## Results and Discussion

**Resolution and Catalysis with 2a−d.** It was observed that **2a** and **2d** underwent spontaneous resolution upon crystallization and could be obtained in enantiomerically pure form via mechanical separation of the crystals. Samples of **2a** that were suitable for use in catalytic reactions were collected (the enantiopurity was verified with the specific rotation of **2a**, which was obtained from optical rotation measurements on a single crystal of the complex[42]). The spontaneous resolution of **2a** provides an effective starting point for the development of other catalysts, as treatment of enantiopure **2a** with an excess (>5 equiv) of another phosphine can readily displace the $PPh_3$ ligand. It was in this manner, for example, that single enantiomers of **2b** and **2c** could be obtained.

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(42) For **2a**: $[\alpha]_D$ ($c$ = 0.00175, $CH_2Cl_2$): 143°.

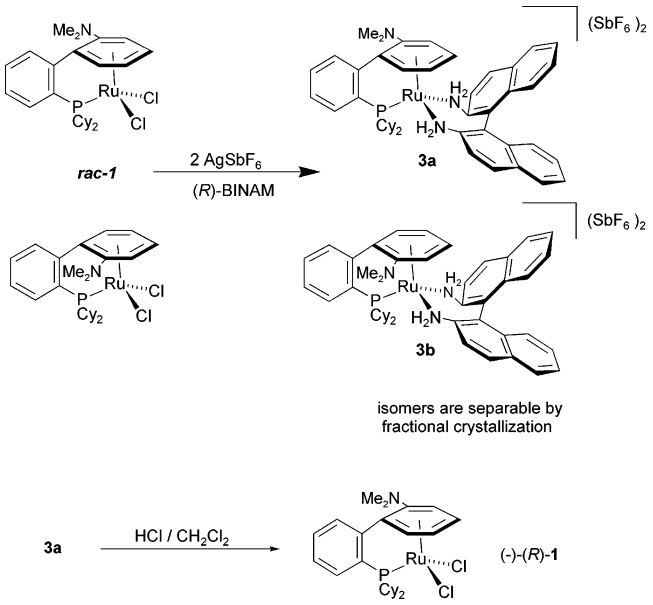



**Figure 2.** BINAM-based resolution.

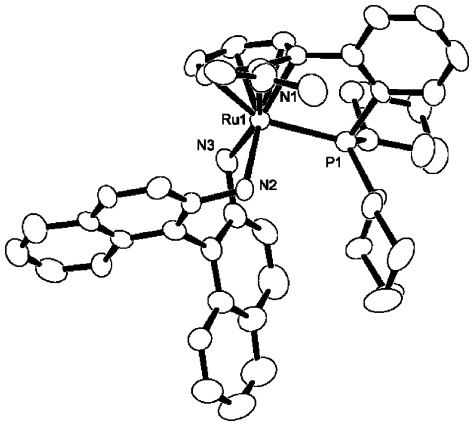
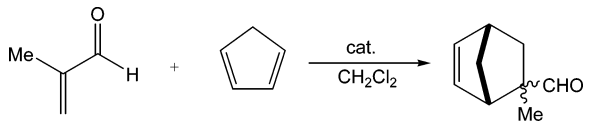



**Figure 3.** ORTEP drawing of the dication in (*R*,a*R*)-**3a**.

A more convenient resolution of the neutral complex **1** was developed utilizing the ligand (*R*)-BINAM. Abstraction of both chlorides with $AgSbF_6$ and treatment with this chiral ligand resulted in the formation of two diastereomeric complexes, **3a** and **3b**, which were separable by fractional crystallization. Specifically, complex **3a** was found to be more insoluble and could be obtained as a single diastereomer in up to 88% yield, leaving a supernatant that was enriched in **3b** (Figure 2). Though **3b** could not be isolated as a single diastereomer, repeated crystallizations from the supernatant solutions resulted in a product in up to 80% de. The absolute stereochemistry of (*R*,a*R*)-**3a** was confirmed by X-ray crystallography (Figure 3). The chirality descriptor references the planar chirality in the ring defined by the dimethylamino-substituted carbon atom in the ring and the axial chirality (a*R*) of the BINAM ligand.

Once separated, **3a** could be easily converted to enantiopure **1** by stirring in a solution of $HCl_{(aq)}$ and $CH_2Cl_2$. The ability to obtain these complexes in enantiopure form allowed investigation of their potential as precursors for asymmetric Lewis acid catalysts of the

**Table 1. Diels–Alder Catalysis with Dications Derived from 2a–d[a]**




| entry | ligand (L) | *exo*/*endo* | ee (%) |
|---|---|---|---|
| 1[b] | $PPh_3$ | 98/2 | 20 |
| 2 | $PPhMe_2$ | 96/4 | 26 |
| 3 | $P(OPh)_3$ | 97/3 | 13 |
| 4 | $PPh_2Cy$ | 94/6 | 40 |

[a] All reactions were carried out at 10% catalyst loading and at −25 °C. Greater than 95% conversions were observed in all cases. [b] This result was initially reported in ref 41.

Diels–Alder reaction of methacrolein and cyclopentadiene.The most selective of these was derived from **2d**, which catalyzed the reaction with 89% de (*exo*) and 40% ee. $PCyPh_2$ is a comparatively large and donating phosphine; however, bulkier phosphines (those with cone angles larger than 157°) do not readily coordinate. Although the selectivity is modest, these reactions illustrate that the chiral-at-metal complexes are capable of catalytic asymmetric induction.

**Tethered Complexes with (*S*)-MonoPhos.** The use of the chiral phosphoramidite (*S*)-MonoPhos in place of the achiral phosphines was also examined to evaluate the improved enantioselectivity that would be expected from a matched pair wherein the ligand chirality would enhance that of the metal-centered chirality. Starting from *rac*-**1**, the addition of 1 molar equiv each of (*S*)-MonoPhos and $AgSbF_6$ results in the formation of two diastereomers in equal amounts (**4a**, **4b**). Each diastereomer can be obtained individually by starting from resolved **1** or **2a**.

We were unable to obtain crystals of either **4a** or **4b** that were suitable for X-ray analysis; however, given the propensity for other phosphines to bind in the *anti* position, and the high diastereoselectivity observed in this case (over 90% de for both complexes), it is likely that (*S*)-MonoPhos also occupies the *anti* binding site. Given this, and knowing the absolute configuration of the planar chiral starting material, we can reasonably assign absolute configurations for **4a** and **4b**.

To investigate the diastereomeric preference elicited by (*S*)-MonoPhos in the absence of the $NMe_2$ directing group, [Ru($\eta^6$:$\eta^1$-2-dicyclohexylphosphino-2′-biphenyl)-((*S*)-MonoPhos)Cl]($SbF_6$) was synthesized as two diastereomers (**5a**, **5b**). The ratio of the two diastereomers was 58:42, and this ratio was unchanged in solution over extended periods.

The absence of planar chirality in the tethering ligand in this case means that it cannot influence the chirality at the metal center. Therefore, in this case the diastereoselectivity can be attributed solely to the binding arrangement preferred by (*S*)-MonoPhos. The modest diastereoselectivity exhibited by MonoPhos ensures that the $NMe_2$ group on the $\eta^6$ arene ring in **4** will determine the diasteromeric preference at the metal center.

An interesting feature in the $^{31}P\{^1H\}$ NMR spectra that is common to each of the phosphoramidite-containing complexes (**4**, **5**) is the appearance of one broad resonance per diastereomer, indicative of some dynamic behavior, perhaps the interconversion of conformations

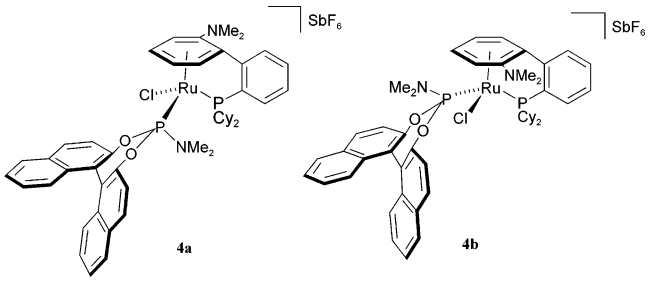



**Figure 4.** Two diastereomers, ($S_{Ru}$,*S*,a*S*)-**4a** and ($R_{Ru}$,*R*,a*S*)-**4b**, resulting from coordination of (*S*)-MonoPhos.

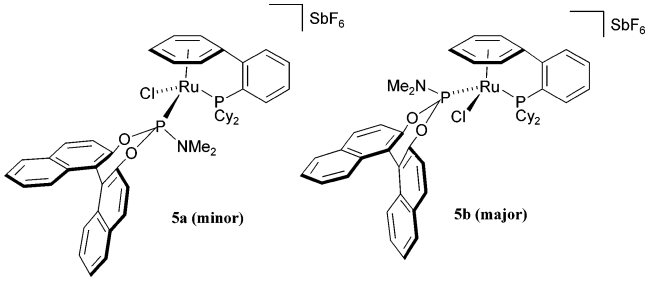



**Figure 5.** Without the controlling effect of the $NMe_2$ group, ($S_{Ru}$,a*S*)-**5a** and ($R_{Ru}$,a*S*)-**5b** form in a 42:58 ratio.

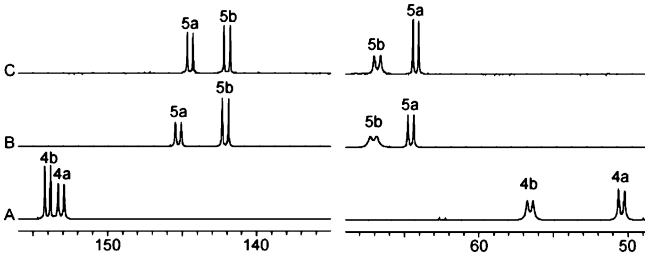



**Figure 6.** $^{31}P\{^1H\}$ NMR in $CD_2Cl_2$ of (A) **4a/4b**, (B) **5a/5b** at room temperature, and (C) **5a/5b** at 55 °C.

of the cyclohexyl groups (Figure 6). Each isomer contains two inequivalent phosphorus atoms coupled through ruthenium; one of the doublets is downfield (>140 ppm, corresponding to the phosphoramidite), and the other is in the region of 50–70 ppm. The spectra of **4a** and **4b** individually show that in one case (**4a**) it is the upfield resonance that is broad, while for the other isomer it is the more downfield resonance that is broad. The same can be said for **5**, as ascertained from integration of the resonances, as well as from the coupling constants. In addition, heating **5** to 55 °C sharpened the doublets, and it was apparent that the resonances of the minor isomer **5a** were sharpened to a greater extent. The spectrum for the major isomer **5b** is similar to that of **4b**, in that the broad resonance is the one further downfield, which could suggest that the metal chirality is the same for the two complexes.

The effect of the $NMe_2$ group in complexes derived from **1** is to direct the bulky phosphine ligand to the *anti* binding site. Consequently, the chirality of the tethered ligand controls the metal chirality to a large extent (greater than 95% de for both isomers of **4**). However, in the absence of the directing group, the chiral phosphoramidite (*S*)-MonoPhos also influences the metal chirality, though to a lesser extent (16% de for **5**). Therefore, the chirality of the tethered ligand has the greatest influence in determining the metal chiral-

**Table 2. Diels−Alder Catalysis with Dications Derived from 4a/4b[a]**

| entry | catalyst precursor | *exo*/*endo* | ee (%) [config] |
|---|---|---|---|
| 1 | mix **4a**,**4b**[b] | 92/8 | 27 [*R*] |
| 2 | **4b** | 93/7 | 47 [*R*] |
| 3 | **4a** | 92/8 | 19 [*R*] |

[a] All reactions were carried out at 10% catalyst loading and at −25 °C. Greater than 95% conversion was observed in all cases. [b] A 1:1 mixture of both isomers.

ity, and so the *anti* preference is likely retained, even in the case of **4a**, where it is in opposition to the preference of (*S*)-MonoPhos. In the case of **4b**, the controlling effects of both the tethered ligand and (*S*)-MonoPhos on the metal chirality are in conjunction and favor formation of the same diastereomer.

**Catalysis with 4a/4b.** The 1:1 mixture of both isomers catalyzed the reaction with modest enantioselectivity, indicating that the chiral phosphoramidite was affecting the asymmetric induction. When each pure diastereomer was used individually, it was observed that both yielded an enantiomerically enriched product with the same sense of chirality, although **4b** was more selective in doing so. It would appear that the selectivity induced by MonoPhos overrides the induction by the metal-centered chirality in **4a**, whereas in **4b** (the matched diastereomer) the induction by the ligand and metal center are acting in concert to produce a higher ee.

If each diastereomer in the 1:1 mixture of diastereomers catalyzed the reaction at the same rate, then the ee's found for pure **4a** and **4b** would suggest an ee of ∼33% for the mixture. Since the mixture gives an ee of 27%, the reaction rate with **4a** is substantially faster (∼3×) than that with **4b**. Since in this case the matched diastereomer is more slowly reacting, this is not a good case for asymmetric activation[43] by forming the 1:1 mixture by adding the chiral phosphine to the racemic precursor. If, on the other hand, the matched diastereomer reacted much faster than the mismatched diastereomer, then the mixture would yield a high ee and could obviate the need to separate the diastereomers. Thus, one could use the asymmetric activation approach[43] successfully if a chiral ligand was developed in which the matched diastereomer reacted faster.

**Counterion Effects.** The counterion was also seen to play a role in the enantioselectivity of the catalysis. Different counterions could be introduced by using different silver salts when abstracting the chloride ligands. The optimal anion combination was $SbF_6^-$/$BF_4^-$, for which, when implemented along with the matched isomer, an ee of 70% was attained. The same catalyst at lower loading and at room temperature was less selective (59% ee). The use of triflate as a counterion at −25 °C slowed the reaction rate to such an extent that less than 5% conversion took place after 18 h. At room temperature, the reaction proceeded sluggishly and with modest selectivity.

To examine the possible cause for the observed counterion dependence, the catalyzed reaction rates were monitored with the different "noncoordinating" anions (Figure 7). In accordance with what has been previously observed,[8,44] the reaction rates are slowed

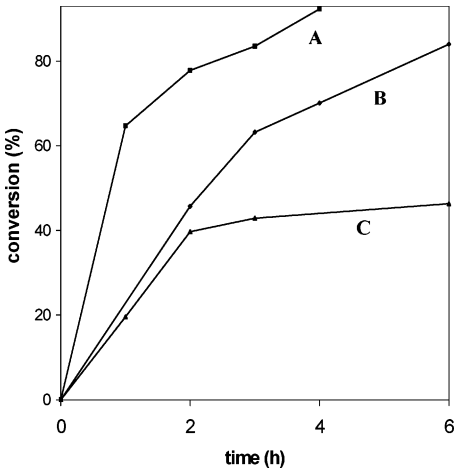



**Figure 7.** Plot of conversion as a function of time for the reaction of methacrolein and cyclopentadiene catalyzed by [Ru($\eta^6$:$\eta^1$-2-dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)-biphenyl)((*S*)-MonoPhos)](X)(Y). All reactions were done with a 1:1 mixture of the two *anti* isomers at 5% catalyst loading, with 0.025 mmol of catalyst in 10 mL of $CH_2Cl_2$ at −25 °C. Aliquots of 0.25 mL, taken at the specified time intervals, were quenched in precooled $Et_2O$ and analyzed by $^1$H NMR to determine conversion. (A) X = Y = $SbF_6$; (B) X = $SbF_6$, Y = $BF_4$; (C) X = Y = $BF_4$.

when $BF_4^-$ is used in place of $SbF_6^-$, which can be attributed to the more coordinating nature of $BF_4^-$. The variation in the reaction rate with the different anion combinations is potentially related to the differences in selectivity. In contrast to the previous examples, however, in this case the catalytic selectivity was greater with $BF_4^-$ than $SbF_6^-$. Kündig has postulated that C−H···F hydrogen bonding interactions between a ruthenium Lewis acid and various counterions were responsible for the observed differences in turnover frequency.[8] This type of hydrogen bonding, which is sensitive to the nature of the counterion, could also potentially be related to the differences in selectivity observed in our case. As an alternative explanation, recent PGSE-NMR measurements have shown that the $BF_4^-$ anion forms relatively strong ion pairs with ruthenium Lewis acids,[45] suggesting that the $BF_4^-$ anion could more effectively affect the approach of the diene. This could account for the observed slowing of the reaction rate, as well as the difference in selectivity, if, for example, the anion were slowing the rates of various diastereomeric intermediates to different extents.

**Epimerization of Metal Chirality.** The potential of epimerization at the various centers of chirality that exist in these catalysts needs to be considered if one wishes to understand the selectivity. The tethered binding mode effectively halts the atropisomeric interconversion of the ligand; therefore the resulting planar chirality is fixed upon the initial formation of **1**. Inversion of the planar chirality has not been observed in any of the complexes **1**−**4** during any of the manipulations performed in this study.

The cationic phosphine-containing complexes, such as **2a**−**d** and **4a**−**b**, have varying degrees of lability in

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(45) Kumar, P. G. A.; Pregosin, P. S. *Organometallics* **2004**, 23, 5410.

**Table 3. Diels−Alder Catalysis with [*anti*-Ru($\eta^6$:$\eta^1$-2-dicyclohexylphosphino-2′-(*N*,*N*-dimethylamino)biphenyl)((*S*)-MonoPhos)](A)(B)**

| entry | catalyst precursor | anion (A) | anion (B) | temp (°C) | % loading | *exo*/*endo* | ee (%) [config] |
|---|---|---|---|---|---|---|---|
| 1 | mix **4a**,**4b** | $SbF_6^-$ | $SbF_6^-$ | −25 | 10 | 92/8 | 27 [*R*] |
| 2 | mix **4a**,**4b** | $BF_4^-$ | $BF_4^-$ | −25 | 10 | 93/7 | 44 [*R*] |
| 3 | mix **4a**,**4b** | $SbF_6^-$ | $BF_4^-$ | −25 | 10 | 93/7 | 46 [*R*] |
| 4 | **4b** | $BF_4^-$ | $BF_4^-$ | −25 | 10 | 93/7 | 65 [*R*] |
| 5 | **4b** | $SbF_6^-$ | $BF_4^-$ | −25 | 10 | 93/7 | 70 [*R*] |
| 6 | **4b** | $SbF_6^-$ | $BF_4^-$ | 25 | 2 | 90/10 | 59 [*R*] |
| 7 | mix **4a**,**4b** | $SbF_6^-$ | $CF_3SO_3^-$ | 25 | 10 | 89/11 | 27 [*R*] |

solution depending on the nature of the phosphine.[41] The complexes with larger phosphines, such as **2a**, are relatively labile in solution. This was evidenced by the generation of a nonequilibrium mixture of *anti*/*syn* isomers by extraction of the chloride with $AgSbF_6$ and subsequent attack by $Cl^-$.[41] It was observed that equilibrium for **2a** was reestablished in solution ($t_{1/2} \approx 25$ h), while no equilibration was observed for **2b**, which has a smaller and more donating phosphine ligand.[41] Further evidence of the lability of **2a** is the ability to exchange $PPh_3$ with other phosphines (e.g., MonoPhos, $P(OPh)_3$) by heating a $CH_2Cl_2$ solution under reflux with an excess of the other phosphine. These reactions yield *anti* isomers as the product presumably owing to the steric effect of the $NMe_2$ group. It would appear that more weakly bound ligands allow equilibration to the more stable *anti* isomer at faster rates.

The active catalyst for the Diels−Alder reaction is a dicationic species generated by extraction of the chloride ligand with a silver salt and then subsequent addition of an excess (10 equiv) of methacrolein. $^{31}P$ NMR studies were performed on the species formed from the treatment of either **4a** or **4b** with $AgSbF_6$ and methacrolein. In the case of **4a**, two isomers in a ratio of 89:11 are formed, and this ratio did not change over time. Likewise, for **4b**, two isomers were again observed, this time in a ratio of 98:2, and once again this ratio remained constant over time. Lowering the temperature to −25 °C did not cause an observable change in either of these ratios. To determine whether the ratios were kinetically controlled or equilibrium values, THF was added to the solution so as to change the polarity of the solvent environment. Indeed, the ratios were changed immediately (<5 min) upon the addition of THF; the isomers corresponding to **4a** now had a ratio of 68:32, whereas in the case of **4b** a new ratio of 95:5 was observed. These ratios did not change over extended periods of time in solution at room temperature, showing that the change in polarity had perturbed the equilibrium isomer ratios and that equilibration was achieved in less than 5 min.

The isomers are presumably a mixture of *syn* and *anti* complexes with opposite chirality at the metal. The equilibration would likely occur by dissociation of methacrolein, generating a 16-electron species or one with a weakly bound solvent ligand, followed by reassociation of methacrolein. The observation of two isomers (for both **4a** and **4b**) in the $^{31}P$ NMR spectrum indicates that the interconversion is slow on the NMR time scale, and so a barrier greater than 15 kcal/mol is expected for this process. However, the equilibrium is reached quickly, and so the slower catalyses reported herein were performed where equilibration of isomers occurs rapidly relative to the Diels−Alder reaction. The higher amount of minor isomer in the case of the dication derived from **4a** could account for the lower selectivity for this catalyst with respect to that derived from **4b**.

## Conclusion

We have demonstrated that arene-tethered ligands can provide an effective means for controlling metal-centered chirality. This approach can be extended to the design of asymmetric catalysts; the tethered complexes reported herein were used to catalyze the Diels−Alder reaction between methacrolein and cyclopentadiene, giving products with high *exo* selectivity and with ee's up to 70%.

## Experimental Section

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. All solvents were distilled under nitrogen using standard desiccating agents. $AgSbF_6$, $AgBF_4$, $PCyPh_2$, (*S*)-MonoPhos, (*R*)-BINAM, $NMe_2$-$C_6H_4C_6H_4PCy_2$, $C_6H_4C_6H_4PCy_2$ (Strem), $PPh_3$, $P(OPh)_3$, $PMe_2$-Ph, P(*i*Pr)$Ph_2$, methacrolein, dicyclopentadiene, and (+)-Eu(hfc)$_3$ (Aldrich) were used as received. The preparation of [Ru(benzene)$Cl_2$],[46] **1**, **2a**, and **2b**[41] was done according to respective literature procedures. NMR spectra were recorded on a Bruker 400 MHz (operating at 162 MHz for $^{31}P$), a Bruker 500 MHz (operating at 202 MHz for $^{31}P$), or a GE Omega 300 MHz (operating at 122 MHz for $^{31}P$) spectrometer. Chemical shifts are reported in ppm relative to solvent peaks ($^1H$) or an $H_3PO_4$ external standard. Elemental analyses were carried out by Atlantic Microlabs.

**General Procedure for Synthesis of [Ru($\eta^6$:$\eta^1$-$NMe_2$-$C_6H_4C_6H_4PCy_2$)(L)(Cl)]$SbF_6$. Method A.** A flame-dried flask was charged with 1 molar equiv each of **1**, $AgSbF_6$, and a phosphine (L) under a stream of nitrogen. The flask was evacuated and refilled with nitrogen, and then $CH_2Cl_2$ (5 mL) was added. The resulting mixture was stirred in the dark until the reaction was complete, as monitored by $^{31}P\{^1H\}$ NMR, at which point it was filtered through Celite and dried under vacuum. Crystals were obtained by slow diffusion of $Et_2O$ into a $CH_2Cl_2$ solution.

**Method B.** A flame-dried flask was charged with 1 equiv of **2a**, 5 equiv of ligand (L), and $CH_2Cl_2$ (5 mL) under a stream of nitrogen. The resulting solution was subjected to a freeze/pump/thaw cycle and then was heated under reflux for 16 h. The volume of solvent was reduced to 1 mL, and $Et_2O$ (5 mL) was added. A yellow solid formed, and the liquid was decanted from it. An additional 5 mL of $Et_2O$ was added, then decanted, and the solid was dried under vacuum.

**2c:** 91% yield. $^1H$ NMR (400 MHz, $CDCl_3$): 7.81 (1H, d, $J$ = 7.2 Hz, $C_6H_4P$), 7.71−7.57 (3H, m, $C_6H_4P$), 7.38 (6H, dd, $J$ = 8.0 Hz, 7.6 Hz, $POC_6H_5$), 7.27 (3H, t, $J$ = 7.6 Hz, $POC_6H_5$), 7.19 (6H, d, $J$ = 8.0 Hz, $POC_6H_5$), 5.34 (1H, d, $J$ = 8.0 Hz, $\eta^6$-$C_6H_4N$), 5.23 (1H, m, $\eta^6$-$C_6H_4N$), 5.04 (1H, m, $\eta^6$-$C_6H_4N$), 4.89 (1H, t, $J$ = 6.0 Hz, $\eta^6$-$C_6H_4N$), 2.941 (3H, s, $\eta^6$-$C_6H_4N$-$(CH_3)_2$), 2.936 (3H, s, $\eta^6$-$C_6H_4N(CH_3)_2$), 2.85 (1H, m, $C_6H_{11}$),

(46) Bennett, M. A.; Smith, A. K. *J. Chem. Soc., Dalton Trans.* **1974**, *2*, 233.

2.57 (1H, m, $C_6H_{11}$), 2.15 (2H, m, $C_6H_{11}$), 1.92 (4H, m, $C_6H_{11}$), 1.76−1.15 (13H, m, $C_6H_{11}$), 1.10 (1H, m, $C_6H_{11}$). $^{31}$P NMR (161.914 MHz, $CDCl_3$): 123.8 (d, $^2J_{PP}$ = 66 Hz), 67.6 (d, $^2J_{PP}$ = 66 Hz). Anal. Calcd for $C_{44}H_{51}ClF_6NO_3P_2RuSb$: C, 49.11; H, 4.78; N, 1.30. Found: C, 49.16; H, 4.73; N, 1.39.

**2d:** 94% yield. $^1$H NMR (400 MHz, $CDCl_3$): 7.90−7.81 (2H, m), 7.73 (1H, m), 7.70−7.52 (8H, m), 7.49−7.35 (3H, m), ($C_6H_4$P and CyP($C_6H_5$)$_2$), 5.92 (1H, m, $\eta^6$-$C_6H_4$N), 5.81 (1H, d, $J$ = 6.8 Hz, $\eta^6$-$C_6H_4$N), 4.83 (1H, m, $\eta^6$-$C_6H_4$N), 3.55 (1H, m, $\eta^6$-$C_6H_4$N), 3.07 (6H, s, $\eta^6$-$C_6H_4$N($CH_3$)$_2$), 2.76 (1H, m), 2.64 (1H, m), 2.49 (1H, m), 2.15−0.96 (28H, m), 0.83 (1H, m), 0.69 (1H, m), ($PPh_2$-($C_6H_{11}$) and P($C_6H_{11}$)$_2$). $^{31}$P NMR (121.650 MHz, $CDCl_3$): 51.1 (d, $^2J_{PP}$ = 38 Hz), 27.3 (d, $^2J_{PP}$ = 38 Hz). Anal. Calcd for $C_{44}H_{57}$-$ClF_6NP_2RuSb$: C, 51.10; H, 5.56; N, 1.35. Found: C, 51.09; H, 5.55; N, 1.35.

**Synthesis of Ru($\eta^6$:$\eta^1$-$NMe_2C_6H_4C_6H_4PCy_2$)($\eta^2$-(*R*)-BINAM)](SbF$_6$)$_2$.** A flame-dried flask was charged with **1** (164.2 mg, 0.29 mmol), $AgSbF_6$ (200 mg, 0.58 mmol), (*R*)-BINAM (84.5 mg, 0.30 mmol), and 5 mL of $CH_2Cl_2$ under a stream of nitrogen. The resulting solution was subjected to a freeze/pump/thaw cycle and was then stirred at room temperature for 1 h. After filtration through Celite, the product was dried under vacuum, resulting in a red powder (344 mg, 95%). Anal. Calcd for $C_{46}H_{52}F_6N_3PRuSb$: C, 44.45; H, 4.19; N, 3.36. Found: C, 44.44; H, 4.58; N, 3.17. Crystallization was done under a nitrogen atmosphere in a Schlenk tube, by slow diffusion of an $Et_2O$ layer (9 mL) into a solution of the product in 9 mL of $CH_2Cl_2$.

**3a.** $^1$H NMR (500 MHz, $CDCl_3$): 8.30 (d, 1H, $J$ = 8.5 Hz), 8.04 (d, 1H, $J$ = 8.5 Hz), 7.95 (dd, 1H, $J$ = 6.5, 6.0 Hz), 7.25−7.77 (m, 11H), 7.05 (d, 1H, $J$ = 8.0 Hz), 6.82 (d, 1H, $J$ = 8.5 Hz), ($C_{20}H_{12}N_2H_4$ and $C_6H_4$P); 6.62 (br d, 1H, $J$ = 10 Hz, N*H*), 6.32 (d, 1H, $J$ = 6.5 Hz, $\eta^6$-$C_6H_4$N), 6.12 (dd, 1H, $J$ = 5.0, 5.5 Hz, $\eta^6$-$C_6H_4$N), 5.96 (br d, 1H, $J$ = 10 Hz, N*H*), 5.75 (m, 2H, N*H* and $\eta^6$-$C_6H_4$N), 5.15 (d, 1H, $J$ = 5.5 Hz, $\eta^6$-$C_6H_4$N), 4.86 (br d, 1H, $J$ = 10 Hz, N*H*), 2.92 (s, 6H, N($CH_3$)$_2$), 0.29−2.54 (m, 21H, $C_6H_{11}$), −0.45 (br s, 1H, $C_6H_{11}$). $^{31}$P NMR (161.9 MHz, $CDCl_3$): 58.4 (s). $[\alpha]_D$ (*c* 0.00169, $CH_2Cl_2$): −192°.

**3b.** $^1$H NMR (400 MHz, $CDCl_3$): 8.18 (d, 1H, $J$ = 8.8 Hz), 8.11 (d, 1H, $J$ = 8.4 Hz), 7.98 (t, 1H, $J$ = 7.6 Hz), 7.90 (d, 1H, $J$ = 8.4 Hz), 7.25−7.77 (m, 10H), 6.96 (d, 1H, $J$ = 8.4 Hz), 6.82 (d, 1H, $J$ = 8.4 Hz), ($C_{20}H_{12}N_2H_4$ and $C_6H_4$P); 6.39 (m, 2H, N*H* and $\eta^6$-$C_6H_4$N), 6.24 (br d, 1H, $J$ = 10 Hz, N*H*), 6.19 (br d, 1H, $J$ = 11 Hz, N*H*), 5.78 (d, 1H, $J$ = 4.8 Hz, $\eta^6$-$C_6H_4$N), 5.72 (m, 1H, $\eta^6$-$C_6H_4$N), 5.06 (d, 1H, $J$ = 6.4 Hz, $\eta^6$-$C_6H_4$N), 4.22 (br d, 1H, $J$ = 10 Hz, N*H*), 2.68 (br s, 6H, N($CH_3$)$_2$), 0.29−2.54 (m, 21H, $C_6H_{11}$), −0.94 (br s, 1H, $C_6H_{11}$). $^{31}$P NMR (161.9 MHz, $CDCl_3$): 56.3 (s).

**Conversion of 3a into (−)-1.** A flask was charged with 6% $HCl_{(aq)}$ (10 mL), and to this was added a solution of **3a** (78 mg in 5 mL of $CH_2Cl_2$). The resulting mixture was stirred vigorously for 30 min. The organic layer was separated and washed with an additional 10 mL of 6% $HCl_{(aq)}$ and then collected and dried under vacuum, resulting in quantitative recovery of (−)-**1**. $[\alpha]_D$ (*c* 0.00195, $CH_2Cl_2$): −986°.

**Synthesis of [Ru($\eta^6$:$\eta^1$-$NMe_2C_6H_4C_6H_4PCy_2$)((*S*)-MonoPhos)(Cl)]SbF$_6$.** A flame-dried flask was charged with **1** (75.7 mg, 0.13 mmol), $AgSbF_6$ (46 mg, 0.13 mmol), and (*S*)-MonoPhos (49 mg, 0.14 mmol) under a stream of nitrogen. The flask was evacuated and refilled with nitrogen, and then $CH_2Cl_2$ (5 mL) was added. The resulting mixture was stirred in the dark for 2 h, at which point it was filtered through Celite. The volume was reduced to 1 mL, $Et_2O$ (5 mL) was added to precipitate the yellow powder, and the liquid was decanted. An additional 5 mL of $Et_2O$ was added, then decanted, and the solid was dried under vacuum (135 mg, 90%). Anal. Calcd for $C_{48}H_{54}ClF_6N_2O_2P_2RuSb$: C, 51.24; H, 4.84; N, 2.49. Found: C, 51.22; H, 4.91; N, 2.44.

**4a.** $^1$H NMR (400 MHz, $CD_2Cl_2$): 8.08 (1H, d, $J$ = 9.2 Hz), 8.01 (1H, d, $J$ = 8.0 Hz), 7.90 (1H, d, $J$ = 8.0 Hz), 7.77 (1H, dd, $J$ = 6.8 Hz, 8.0 Hz), 7.68 (1H, dd, $J$ = 8.0 Hz, 7.2 Hz), 7.59−7.19 (10H, m), ($C_6H_4$P and $C_{20}H_{12}O_2$P), 6.07 (1H, dd, $J$ = 6.8 Hz, 6.4 Hz, $\eta^6$-$C_6H_4$N), 5.89 (1H, d, $J$ = 8.8 Hz, $C_{20}H_{12}O_2$P), 5.78 (1H, m, $\eta^6$-$C_6H_4$N), 5.57 (1H, m, $\eta^6$-$C_6H_4$N), 5.15 (1H, d, $J$ = 6.8 Hz, $\eta^6$-$C_6H_4$N), 2.88 (6H, s, $\eta^6$-$C_6H_4$N-($CH_3$)$_2$), 2.59 (6H, d, $^3J_{PH}$ = 10.0 Hz, PN($CH_3$)$_2$), 2.46−0.83 (20H, m, $C_6H_{11}$), 0.75 (1H, m, $C_6H_{11}$), 0.48 (1H, m, $C_6H_{11}$). $^{31}$P NMR (161.914 MHz, $CD_2Cl_2$): 154.0 (d, $^2J_{PP}$ = 65 Hz), 51.6 (d, $^2J_{PP}$ = 65 Hz).

**4b.** $^1$H NMR (400 MHz, $CD_2Cl_2$): 8.07 (1H, d, $J$ = 8.8 Hz), 8.02 (1H, d, $J$ = 8.4 Hz), 8.01 (2H, m), 7.81−7.20 (13H, m), ($C_6H_4$P and $C_{20}H_{12}O_2$P), 6.23 (1H, t, $J$ = 6.0 Hz, $\eta^6$-$C_6H_4$N), 5.67 (2H, m, $\eta^6$-$C_6H_4$N), 4.98 (1H, d, $J$ = 4.8 Hz, $\eta^6$-$C_6H_4$N), 2.983 (3H, s, $\eta^6$-$C_6H_4$N($CH_3$)), 2.979 (3H, s, $\eta^6$-$C_6H_4$N($CH_3$)), 2.40 (6H, d, $^3J_{PH}$ = 10.0 Hz, PN($CH_3$)$_2$), 2.75−2.46 (4H, m, $C_6H_{11}$), 2.23−1.09 (16H, m, $C_6H_{11}$), 0.96−0.83 (2H, m, $C_6H_{11}$). $^{31}$P NMR (161.914 MHz, $CD_2Cl_2$): 154.8 (d, $^2J_{PP}$ = 62 Hz), 58.5 (br d).

**Synthesis of [Ru($\eta^6$:$\eta^1$-$C_6H_4C_6H_4PCy_2$)((*S*)-MonoPhos)-(Cl)]SbF$_6$ (5).** A flame-dried flask was charged with Ru($\eta^6$:$\eta^1$-$C_6H_4C_6H_4PCy_2$)$Cl_2$ (72.5 mg, 0.13 mmol), (*S*)-MonoPhos (50 mg, 0.14 mmol), and $AgSbF_6$ (48 mg, 0.14 mmol) under a stream of nitrogen. The flask was evacuated and refilled with nitrogen, and the $CH_2Cl_2$ (5 mL) was added. The resulting mixture was stirred in the dark for 6 h, at which point it was filtered through Celite. The volume of solvent was reduced to 1 mL, and $Et_2O$ (5 mL) was added. A yellow solid formed, and the supernatant was decanted from it. An additional 5 mL of $Et_2O$ was added, then decanted. The solid was purified on silica gel eluting with $CH_2Cl_2$ and dried under vacuum (105 mg, 76%).

**Minor Isomer (5a).** $^1$H NMR (400 MHz, $CDCl_3$): 8.26 (1H, d, $J$ = 9.2 Hz), 8.15−7.09 (15H, m), ($C_6H_4$P and $C_{20}H_{12}O_2$P), 6.66 (1H, m, $\eta^6$-$C_6H_5$), 6.30 (1H, dd, $J$ = 6.8 Hz, 6.4 Hz, $\eta^6$-$C_6H_5$), 6.08 (2H, m, $\eta^6$-$C_6H_5$), 5.40 (1H, d, $J$ = 5.6 Hz, $\eta^6$-$C_6H_5$), 2.52 (6H, d, $^3J_{PH}$ = 11.2 Hz, N($CH_3$)$_2$), 2.83−0.58 (22H, m, $C_6H_{11}$). $^{31}$P NMR (161.914 MHz, $CDCl_3$): 146.1 (d, $^2J_{PP}$ = 63 Hz), 65.6 (d, $^2J_{PP}$ = 63 Hz).

**Major Isomer (5b).** $^1$H NMR (400 MHz, $CDCl_3$): 8.15−7.09 (16H, m, $C_6H_4$P and $C_{20}H_{12}O_2$P), 6.34 (1H, dd, $J$ = 6.0 Hz, 6.4 Hz, $\eta^6$-$C_6H_5$), 6.00 (1H, d, $J$ = 6.0 Hz, $\eta^6$-$C_6H_5$), 5.93 (1H, br s, $\eta^6$-$C_6H_5$), 5.64 (1H, br s, $\eta^6$-$C_6H_5$), 5.47 (1H, d, $J$ = 5.2 Hz, $\eta^6$-$C_6H_5$), 2.49 (6H, d, $^3J_{PH}$ = 10.4 Hz, N($CH_3$)$_2$), 2.83−0.58 (22H, m, $C_6H_{11}$). $^{31}$P NMR (161.914 MHz, $CH_2Cl_2$): 143.3 (d, $^2J_{PP}$ = 69 Hz), 68.2 (br d).

**General Procedure for Diels−Alder Catalysis.** A flame-dried flask was charged with 0.025 mmol of the cationic ruthenium precatalyst and 0.023 mmol of AgX (X = $SbF_6$, $BF_4$, OTf) under a stream of nitrogen. $CH_2Cl_2$ (3 mL) was added, and the mixture was stirred for 30 min, followed by filtration through Celite to remove the precipitated AgCl. The filtrate was added to a fresh flame-dried flask and was then subjected to a freeze/pump/thaw cycle, and the flask was backfilled with nitrogen. Methacrolein (20 uL, 0.25 mmol) was added at this point, and the flask was then transferred to a freezer, where it was allowed to cool to −25 °C for 1 h before the addition of Cp (0.2 mL). The reactions were allowed to proceed at this temperature for 16 h, at which point the volatiles were removed under vacuum, and the resulting residue was passed through a short plug of silica gel in $Et_2O$ in order to remove the inorganic material. Conversion and diastereoselectivity were determined by $^1$H NMR, and the enantioselectivity was determined with the use of (+)-Eu(hfc)$_3$ as a chiral shift agent.

**Epimerization Studies on Dicationic Species.** A flame-dried flask was charged with **4a** or **4b** (36 mg, 0.032 mmol) and $AgSbF_6$ (11 mg, 0.032 mmol) under a stream of nitrogen, followed by $CH_2Cl_2$ (1.25 mL). The mixture was stirred for 30 min, at which point methacrolein (26 uL, 0.32 mmol) was added by syringe, and the resulting solution was syringed into a sealed NMR tube under nitrogen. The $^{31}$P NMR studies were performed directly. Species derived from **4a**: $^{31}$P NMR (161.914 MHz, $CH_2Cl_2$): major isomer, 149.6 (d, $^2J_{PP}$ = 61 Hz), 49.8 (d,

$^2J_{PP}$ = 61 Hz), minor isomer, 151.2 (d, $^2J_{PP}$ = 63 Hz), 49.1 (d, $^2J_{PP}$ = 63 Hz); ratio 89:11. Species derived from **4b**: $^{31}$P NMR (161.914 MHz, $CH_2Cl_2$): major isomer, 151.5 (d, $^2J_{PP}$ = 57 Hz), 49.6 (d, $^2J_{PP}$ = 57 Hz), minor isomer, 153.5 (d, $^2J_{PP}$ = 60 Hz), 48.7 (d, $^2J_{PP}$ = 60 Hz); ratio 98:2.

These equilibrium values could be perturbed to new ones over a time < 10 min by adding THF (0.05 mL) by syringe to the NMR tube: **4a** 68:32; **4b** 95:5.

**Supporting Information Available:** A listing of X-ray crystallographic data, atomic positions, thermal parameters, bond distance and angles for **3a**. Also $^{13}$C spectra for selected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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