HELVETICA chimica acta

201600139

Ruthenium *Lewis* Acid-Catalyzed Asymmetric *Diels–Alder* Reactions: Reverse-Face Selectivity for α,β-Unsaturated Aldehydes and Ketones

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Acrolein, methacrolein, methyl vinyl ketone, ethyl vinyl ketone, 3-methyl-3-en-2-one, and divinyl ketone were coordinated to a cationic cyclopentadienyl ruthenium(II) *Lewis* acid incorporating the electron-poor bidentate BIPHOP–F ligand. Analysis by NOESY and ROESY NMR techniques allowed the determination of conformations of enals and enones present in solution in CD_2Cl_2. The results were compared to solid-state structures and to the facial selectivities of catalytic asymmetric *Diels–Alder* reactions with cyclopentadiene. X-Ray structures of four Ru-enal and Ru-enone complexes show the α,β-unsaturated C=O compounds to adopt an *anti-s-trans* conformation. In solution, enals assume both *anti-s-trans* and *anti-s-cis* conformations. An additional conformation, *syn-s-trans*, is present in enone complexes. Enantioface selectivity in the cycloaddition reactions differs for enals and enones. Reaction products indicate enals to react exclusively in the *anti-s-trans* conformation, whereas with enones, the major product results from the *syn-s-trans* conformation. The alkene in *s-cis* conformations, while present in solution, is shielded and cannot undergo cycloaddition. A *syn-s-trans* conformation is found in the solid state of the bulky 6,6-dimethyl cyclohexanone-Ru(II) complex. The X-ray structure of divinyl ketone is unique in that the Ru(II) center binds the enone *via* a η^2 bond to one of the alkene moieties. In solution, coordination to Ru–C=O oxygen is adopted. A comparison of facial preference is also made to the corresponding indenyl *Lewis* acids.

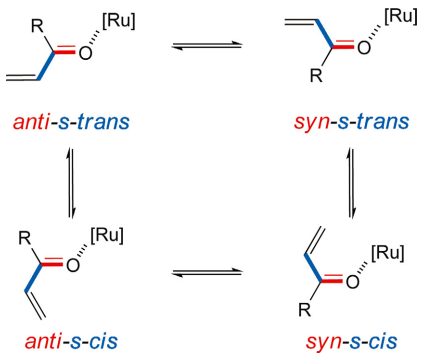
Keywords: Asymmetric cycloaddition, *Lewis* acid, Ruthenium, Enone conformation, NMR Analysis.

Introduction

Monocationic, one-point binding cyclopentadienyl-complexes of iron(II), and cyclopentadienyl and indenyl complexes of ruthenium(II) incorporating electron-poor pentafluorophenyl-diphosphinite ligands are efficient and selective homogeneous chiral *Lewis* acid catalysts for the inter- and intramolecular *Diels–Alder* (*DA*) reactions of dienes with enals[1] and enones,[2] dipolar cycloadditions between nitrones and enals,[3][4] arylnitrileoxides and enals,[5] as well as 1,4-additions of thiols to enones.[6] Following our initial report on these chiral transition-metal *Lewis* acids, several other pianostool type π-cyclopentadienyl and π-arene transition-metal *Lewis* acids were reported and used as catalysts in cycloaddition reactions. Explicitly, they are dicationic Cp^*ML_2 complexes of rhodium[7] and iridium,[7c][7d][7f][7g][7i][7j][8] and dicationic (arene)ML_2 complexes of ruthenium[9] and osmium[9l][10] incorporating bidentate phosphorus and/or N-ligands. When non-C_2-symmetric ligands are involved, a stereogenic metal atom results. Either on formation, or during catalysis, diastereomeric mixtures can form. High induction in cycloaddition reactions then is based on one diastereomer coordinating the enal selectively and/or catalyzing the cycloaddition reaction with a higher rate.

One point *Lewis* acids (LAs) activate α,β-unsaturated C=O compounds by binding to the C=O O-atom. LA coordination results in a lowering of the energy of the LUMO and hence being a better match for the diene HOMO in cycloaddition reactions. For asymmetric reactions, an additional requirement is a preferred conformation of the substrate in the chiral environment of the LA as different conformations lead to opposite product enantiomers. Excluding structures in which conjugation is interrupted due to the nonplanarity of the substrate, this results in four possible conformers (*Scheme 1*). When R = H (enals) *anti-s-trans* and *anti-s-cis* conformers dominate for steric reasons. With ketones, this selectivity is absent and preference of conformers depends on the size and nature of the R group.

†Deceased.



Scheme 1. Equilibrium of four possible conformers of Ru-dienophile complexes **1**.

For enals, the equilibrium between the *anti-s-trans* and *anti-s-cis* conformers and the effect of conformation on the transition energy of the *DA* reaction has been analyzed computationally. The *anti-s-trans* conformer with or without LA is computed to be more stable than the *anti-s-cis* conformer.[11] However, the energy barrier to interconversion of the two conformers is much lower than that for the cycloaddition reaction and a ground state preference does not allow a prediction for the reactive conformation in the cycloaddition reaction.[12] Both, the *anti-s-trans* and the *anti-s-cis* conformations have been proposed in transition-state models for *DA* reactions, sometimes even for the same catalyst.[13][14]

In this article, we present the results of a study of the coordination preferences of enals and enones to Ru(II) catalysts and their effect on the outcome of *DA* reactions. The conformational studies of the catalyst-dienophile complexes in solution were conducted using NOESY and ROESY NMR experiments in CD_2Cl_2 using chiral Ru *Lewis* acid catalyst precursors (*R,R*)-**1a** and (*S,S*)-**2a** (*Fig. 1*).

Results and Discussion

Conformation of Ru(II)-Enals: Ground State and DA *Transition State*

The *anti-s-trans* arrangement of enals coordinated to Ru(II) is found in the X-ray structures of [Ru((*S,S*)-BIPHOP–F)(Cp)(methacrolein)][SbF_6] (**1b**)[1c] and [Ru(acrolein)(Cp)((*S,S*)-Me_4BIPHOP–F)][SbF_6] (**1c**).[2a] The binding to the *Lewis* acid is enhanced by an interaction of the counteranion to both the aldehyde H and the Cp ligand in the solid state as well as in solution (tight ion pair),[1c][1f] reminiscent of *Corey* and *Lee*'s proposal of the formyl C–H···O(F) H-bond as a critical factor in enantioselective LA catalyzed reactions of aldehydes.[14]

Considering the discussions of transition-state conformations of enals and enones in *Lewis* acid catalyzed *DA* reactions mentioned in the introduction of this article, we investigated conformers of these reactants coordinated to the Ru(II) center in solution using the NOESY spectra of the coordinated acrolein and methacrolein. The NOE contacts are shown in *Fig. 2* and the spectra themselves are shown in the supporting information (*Figs. S1* and *S2*).

The BIPHOP–F ligand generates a very compact metal ligand environment that is unlikely to change in going from the solid state to solution.[1b] A surface model of [Ru((*S,S*)-BIPHOP–F)(Cp)(acrolein)]$^+$ obtained from combining the X-ray of the *Lewis* acid with an *anti-s-cis* bound acrolein is shown in *Fig. 3*. The views are perpendicular to the alkene moiety and show clearly that a *DA* reaction in the *anti-s-cis* conformation is not possible. This also holds for the methacrolein complex.

Comparing the ^{1}H-NMR of **1c** with free acrolein, we note that H–C(3) and H–C(4) are shifted from 6.50 to 7.03 ppm and 6.35 to 7.05 ppm, respectively. The shift of H–C(2) is from 6.37 to 6.72 ppm. These changes are characteristic of coordinated enals and they are observed for all enals used in this study.

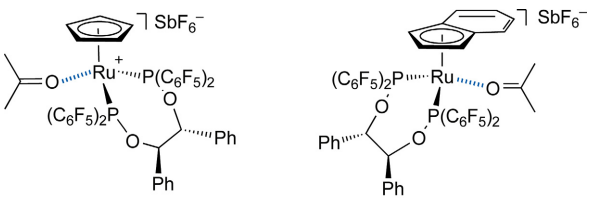


Figure 1. Chiral Ru *Lewis* acid precursors **1a** and **2a**.

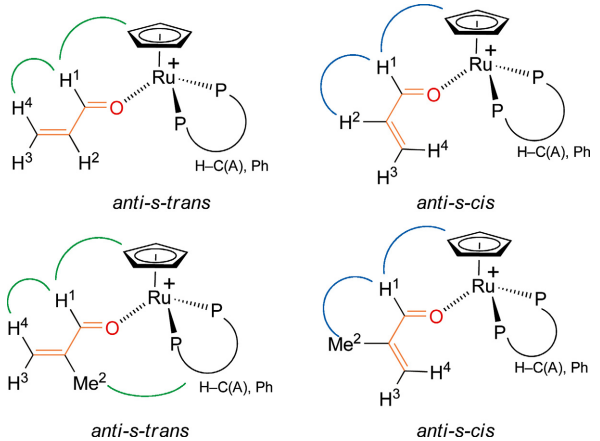


Figure 2. NOE contacts as seen in the NOESY spectra of [Ru(acrolein)(*R,R*)-BIPHOP–F)(Cp)][SbF_6][SbF_6] ((*R,R*)-**1c**) at −40 °C and of [Ru((*R,R*)-BIPHOP–F)(Cp)(methacrolein)][SbF_6] ((*R,R*)-**1d**) at r.t. in CD_2Cl_2. H–C(A) and Ph refer to Bn and Ph H-atoms of the chiral ligand. These symbols will also be used in other figures.

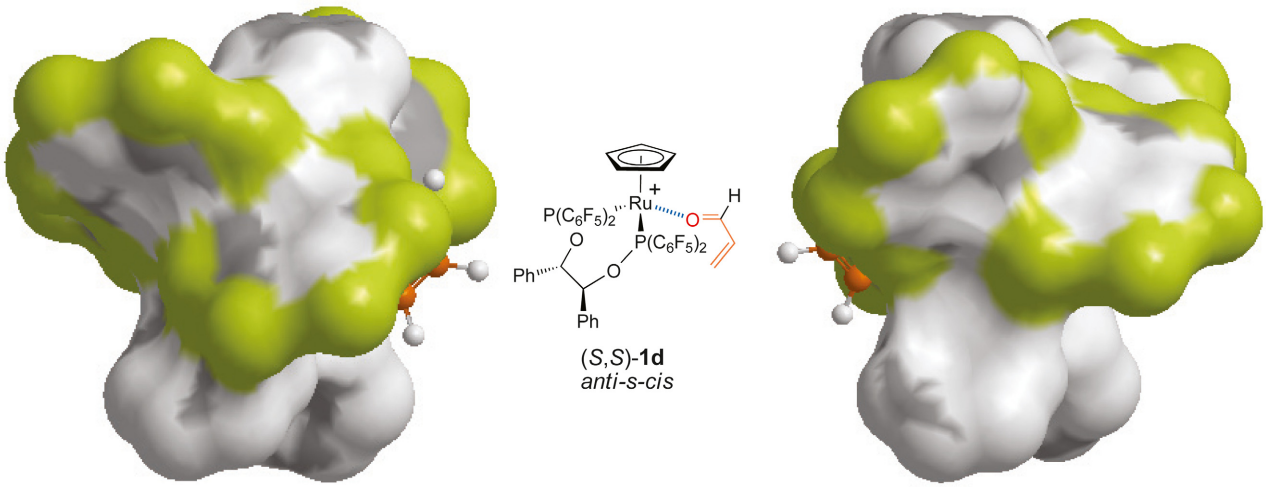


Figure 3. Models of *anti-s-cis* coordinated acrolein in complex (*S,S*)-**1d** showing the blocked alkenyl function both for the *Si*- and *Re* faces.

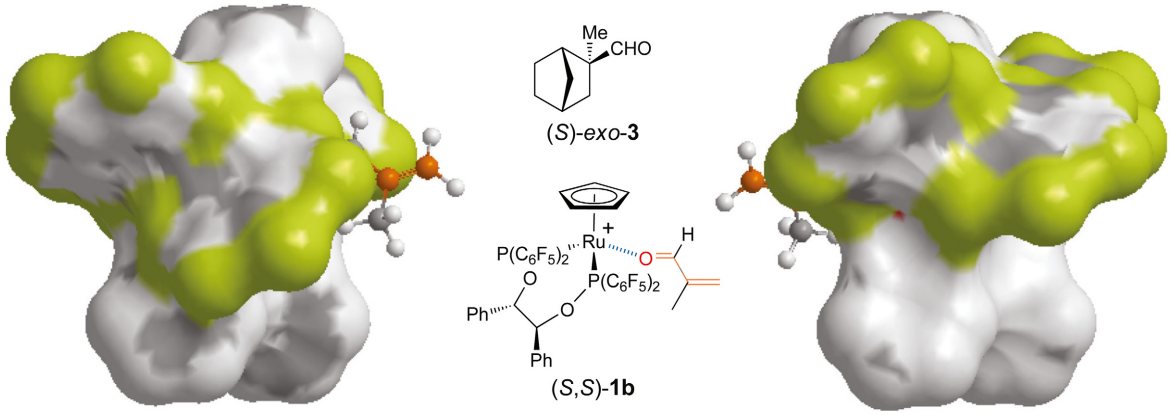
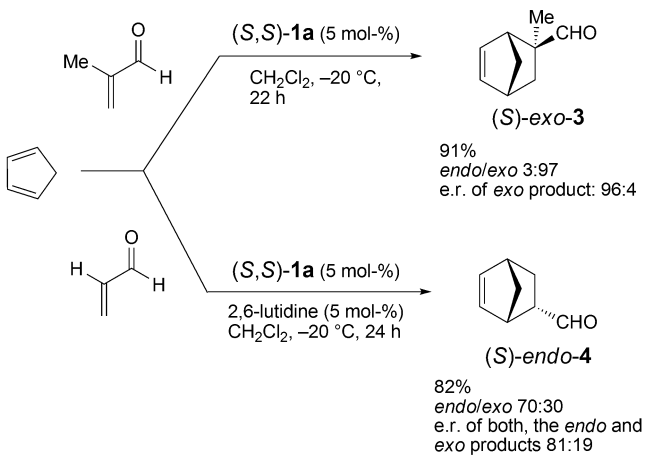


Figure 4. X-ray structure of (*S,S*)-**1b** containing an *anti-s-trans* coordinated methacrolein. Projection vertical on alkene faces.



Scheme 2. Aymmetric *Diels–Alder* reactions of cyclopentadiene with methacrolein and acrolein catalyzed by (*S,S*)-CpRu **1a**.

The correlations between the Cp–H signal and H–C(1) indicate *anti*-geometries in both Ru-acrolein and methacrolein complexes. In keeping with literature precedent of *Lewis* acids coordinating enals on the less hindered *anti*-side, there are no signals indicating the presence of a *syn*-conformer. The *s-trans* and *s-cis* conformers are observed by the cross peaks of H–C(1) and H–C(4) marked in green, and H–C(1) and Me(2) (H–C(2) for acrolein) marked in blue, respectively (*Fig. 2*). NOE contact between H–C(A) and Me(2) confirms the *anti-s-trans* coordinated methacrolein (Spectra in *Supplementary Material*) and the lowering of the ν_{CO} stretching mode from 1700 to 1606 cm^{-1} in the methacrolein complex indicates a LA–O=C coordination.

The X-ray structure of the methacrolein complex (*S,S*)-**1b** shows that the C_α-*Re* face of the *anti-s-trans* coordinated methacrolein (in orange) is more accessible for an approaching diene than the C_α-*Si* face (*Fig. 4*). In keeping with this observation, the reaction with cyclopentadiene yields as major enantiomer (*S*)-*exo*-**3** with methacrolein and (*S*)-*endo*-**4** with acrolein (*Scheme 2*).[1a – 1c]

Table 1. Carbonyl stretching frequencies in [Ru(Cp)L_2(CO)][X] complexes

L	X^-	ν_{CO} [cm^{-1}]	Solvent	Lit.
PMe_3	PF_6	1961	Nujol	[15]
PPh_3	BPh_4	1980	$CHCl_3$	[16]
MeCN	BF_4	2000	CH_2Cl_2	[17]
$P(OMe)_3$	BF_4	2022	CH_2Cl_2	[18]
BIPHOP–F (L_2)	SbF_6	2029	CH_2Cl_2	This work
BIPHOP–F (L_2)	SbF_6	2031	KBr	This work

Table 2. ^{1}H-NMR Shift differences of H–C(3) of LA-crotonaldehyde *vs.* free crotonaldehyde[a]

LA	$\Delta\delta$ (H–C(3))	Lit.
[FeCp(CO)(PPh_3)][BF_4]	0.16	[19]
[FeCp(CO)($P(OMe)_3$)][BF_4]	0.33	[19]
[Ru(chiraphosO)(*p*-cymene)][SbF_6]	0.41	[20]
[FeCp$(CO)_2$][BF_4]	0.54	[21]
$AlEt_3$	0.63	[22]
[MoCp$(CO)_3$][PF_6]	0.70	[21]
[FeCp(CYCLOP-F)][BF_4]	0.74	[23]
[Ru(BIHOP-F)Cp][SbF_6]	0.86	This work
$SnCl_4$	0.87	[22]
$AlEt_2Cl$	0.91	[22]
$TiCl_4$	1.03	[22]

[a] Selected data. For additional *Lewis* acids see ref. [22].

Table 3. ^{13}C-NMR Shift of acetone in selected LA-acetone complexes[a]

LA	δ(C) (acetone)	$\Delta\delta$(C)	Lit.
$MgCl_2$	221	14	[24]
[Ru($Me_2N(CH_2)_2NMe_2$)Tp][BPh_4]	227	20	[25]
ZnI_2	227	20	[24]
[RuCp(BIHOP-F)][SbF_6]	229	22	This work
$ZnCl_2$	230	23	[24]
[ReCp(NO)(PPh_3)][BF_4]	232	25	[26]
$ScOTf_3$	239	32	[24]
$AlCl_3$	245	38	[24]

[a] Selected data. For additional data see ref. [24].

Changing the catalyst from CpRu **1a** to IndRu **2**, the product stereochemistry again indicates the enal to react in the *anti-s-trans* conformation. However, it causes a turnaround of the incoming diene leading to an *exo* preference in the acrolein/cyclopentadiene reaction.[1d] We ascribe the switch of *endo*- to *exo*-selectivity to an unfavorable diene approach due to the extended catalyst roof.[1d] A control of *endo/exo*-selectivity of catalyzed *DA* reactions *via* this roof effect appeared very promising at first. It turned out, however, that the cationic Ru(BIPHOP–F)(indenyl) *Lewis* acid was too weak to overcome *endo* selectivity in less reactive enal/diene reactions and instead of a *DA* reaction with reversal of the diene approach, no *DA* product was formed. IR, ^{1}H-, and ^{13}C-NMR spectral properties were used to probe the *Lewis* acidity of [Ru(BIPHOP–F]Cp]$^+$ (*Tables 2 – 4*). The data shows that BIPHOP–F is a poorer σ-donor / better π-acceptor than $P(OMe)_3$ (*Table 1*) but, because of the strong donor properties of the Cp ligand, the *Lewis* acid strength of the cationic Ru-complex is no stronger than $SnCl_4$ or $ZnCl_2$ (*Tables 3* and *4*). Attempts to synthesize dicationic Ru-arene (benzene, *o*-xylene) complexes incorporating BIPHOP–F unfortunately did not meet with success.

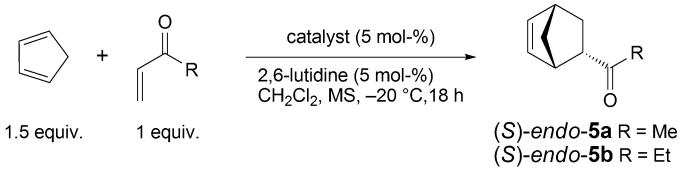
Conformation of Ru(II)-Enones: Ground State and DA *Transition State*

The *syn-s-trans* arrangement of enones is present in the X-ray structures of (S_{Ir},*R*)-[Ir(η^5-C_5Me_5)(prophos)(methyl vinyl ketone)][SbF_6]$_2$ and of (S_{Ir},*R*)-[Ir(η^5-C_5Me_5)(prophos)(ethyl vinyl ketone)][SbF_6]$_2$.[8e] Conversely, the *anti-s-trans* arrangement of enones is found in the X-ray structures of [Ru((*R,R*)-BIPHOP–F)(Cp)(methyl vinyl ketone)][SbF_6](**1e**)[2a] and of [Ru((*R,R*)-BIPHOP–F)(Cp)(2-cyclohexenone)][SbF_6](**1f**).[6] In the following, the [Ru]-enone conformation in the solid state and in solution will be analyzed. The superposition of the acrolein complex (*R,R*)-**1c** (red) and the methyl vinyl ketone (MVK) complex (*R,R*)-**1e** (blue) shows that the olefin of MVK is bent down to reduce steric interaction of the Me group and the Cp roof of the catalyst (*Fig. 5*). The C_α-*Si* face of the olefin is slightly less accessible compared with the coordinated enals. Nevertheless, we expected that in analogy to the *DA* reactions with enals, the main product of the reaction between CpH and MVK would be (*R*)-*endo*-**5a** with catalyst (*R,R*)-**1a**.

This was not the case as shown by the results in *Table 4*. Although the C_α-*Si* face is exposed in the ground state of complex **1e**, it is the C_α-*Re* face of the enone that undergoes cycloaddition. In the *anti-s-trans* conformation this is not possible, but coordination of MVK in either the *syn-s-trans* or the *anti-s-cis* conformation would expose the C_α-*Re* face of the enone and lead to the observed product stereochemistry. As with enals, the alkene is not accessible to an incoming diene when in an *s-cis* conformation and, therefore, it is likely that it is the dienophile in the *syn-s-trans* conformation that undergoes reaction.

In contrast to enals, the *syn*- and *anti*-conformations of enones coordinated to *Lewis* acids have similar steric constraints. Referring to *Scheme 1*,

Table 4. Asymmetric *Diels–Alder* reactions of cyclopentadiene with enones catalyzed by (*R,R*)-CpRu **1a** and (*S,S*)-IndRu **2a**[a]



Entry	Catalyst	R	Yield[b] [%]	*Endo/exo*[c]	e.r.[d]	Config.[2a]
1	(*R,R*)-**1a**	Me	74	93:7	77:23	(*S*)
2	(*R,R*)-**1a**	Et	79	96:4	91:9	(*S*)
3	(*S,S*)-**2a**	Me	76	93:7	88:12	(*R*)
4	(*S,S*)-**2a**	Et	67	91:9	65:35	(*R*)

[a] Scale 0.50 mmol, 1 equiv. of MVK. Results shown are the average of two or more experiments. [b] Yield of isolated products. [c] Determined by ^{1}H-NMR. [d] Determined by chiral GC.

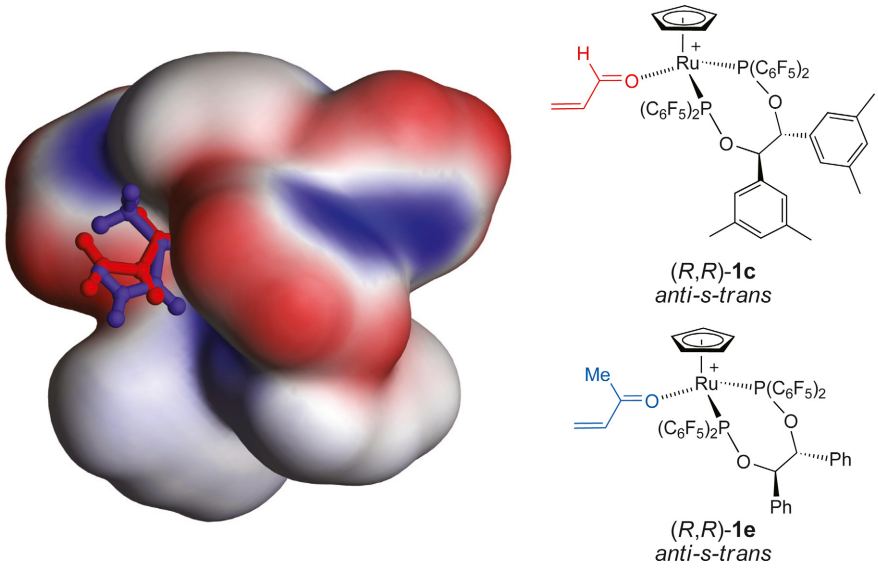


Figure 5. Superposed surface filled X-ray structures of (*R,R*)-**1c** (red) and (*R,R*)-**1e** (blue).

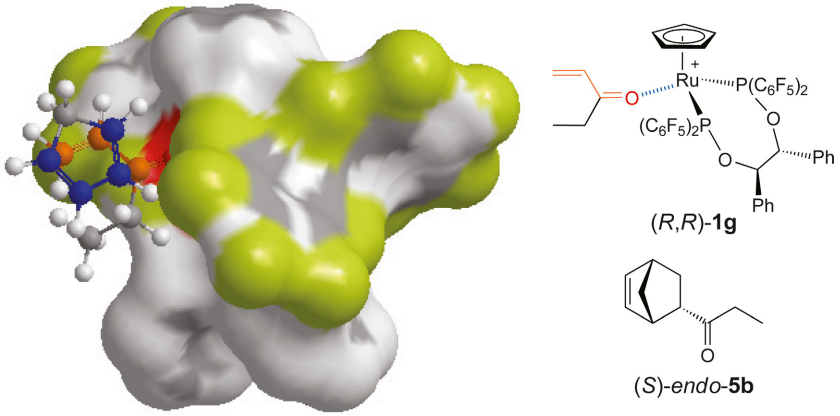


Figure 6. Modeled approach of CpH in *endo* fashion to C_α-*Re* face of *syn-s-trans* coordinated EVK in (*R,R*)-**1g** providing (*S*)-endo-**5b**.

enantioselection with a chiral LA will be the same in *anti-s-trans* and *syn-s-cis* conformations and opposite from either *anti-s-cis* or *syn-s-trans* conformations. This conformational flexibility has delayed the development of efficient chiral LAs for cycloaddition reactions of α,β-unsaturated ketones.[2][8e][23]

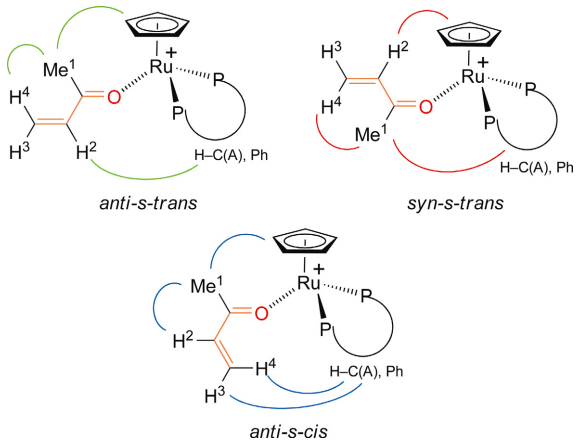


Figure 7. Observed NOESY correlations of [Ru((*R,R*)-BIPHOP–F)(Cp)(methyl vinyl ketone)][SbF_6] ((*R,R*)-**1e** [SbF_6]) in CD_2Cl_2.

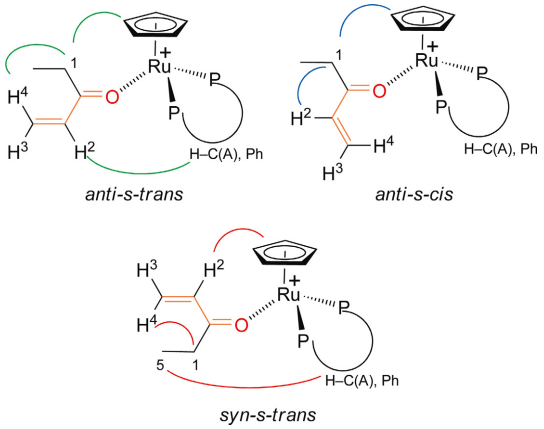


Figure 8. Observed ROESY correlations in [Ru((*R,R*)-BIPHOP–F)(Cp)(ethyl vinyl ketone)][BArF] ((*R,R*)-**1g** [BArF]) in CD_2Cl_2.

The hypothesis of an *anti-s-trans* ground-state conformation but a *syn-s-trans* reactive conformation for α,β-unsaturated ketones catalyzed by **1a** was first formulated on finding that reactions with ethyl vinyl ketone (EVK) afforded products with higher enantioselectivities (*Table 4*, *Entry 2*) than with MVK (*Entry 1*). This was the case not only with cyclopentadiene, but also with a range of acyclic dienes where e.r.'s often exceeded 95:5.[2] In an *anti-s-trans* conformation, the orientation of the terminal Me group of EVK in the catalyst site poses problems. There is no room at the top because of the Cp ring, no room at the back because of the pentafluorophenyl ring, unfavorable when in the same plane as the vinyl group (allylic strain), and hence the best orientation of the terminal Me group would be at the front. This, however, is in the trajectory of an incoming diene and would seem to bar the cycloaddition reaction. These constraints and the finding that product stereochemistry indicated attack on the C_α-*Re* face firmed up the hypothesis of a *syn-s-trans* reactive conformation for reactions of α,β-unsaturated ketones (*Fig. 6*).

Reactions catalyzed by the indenyl complex **2a** were slower, perhaps because of a more hindered approach due to the extended catalyst roof (*Entry 3*). We also note low asymmetric induction with the indenyl complex in the reaction with EVK (*Entry 4*).

The NOESY spectrum confirms the advanced hypothesis of a *syn-s-trans* reactive conformation. Three conformers (*Fig. 7*) of the MVK complex (*R,R*)-**1e** were present in solution (spectrum shown in *Fig. S3*). In addition to the two conformers observed for the enal complex, a third conformer having the *syn-s-trans* (red) arrangement was present as indicated by the correlations between Me^1 and the ligand backbone H-atom H–C(A), and H–C(2) and the Cp roof. The same conformers were also observed in solutions of the analogous EVK complex **1g** (*Figs. 8* and *S4*).

NMR Spectroscopic conformational studies of [Ru((*R,R*)-BIPHOP–F)(indenyl)(enone)]$^+$ complexes were attempted at various temperatures, but none of the spectra was suitable for 2D-NMR analysis. Therefore, conformations present in IndRu-enone complexes in solution cannot be discussed.

As mentioned earlier, the *syn-s-trans* arrangement of enones is found in the solid-state structures of (S_{Ir},*R*)-[Ir(η^5-C_5Me_5)(PROPHOS)(methyl vinyl ketone)][SbF_6]$_2$ and of (S_{Ir},*R*)-[Ir(η^5-C_5Me_5)(PROPHOS)(ethyl vinyl ketone)][SbF_6]$_2$.[8e] Product stereochemistry indicated cyclopentadiene addition to the C_α-*Re* face of MVK to give the *endo* C(2)-(*S*) norbornene product. As shown in *Fig. 9*, the C_α-*Re* face of MVK is not accessible in the *syn-s-trans* conformation and we hypothesize that the reactive conformation in this catalytic system is that of the enone in the *anti-s-trans* conformation – a reversal of the situation in the Ru *Lewis* acid reaction. The change can be ascribed readily to the different chiral environments generated by the PROPHOS and BIPHOP–F ligands, respectively.

We next looked at α-Me-methyl vinyl ketone (αMeMVK). Here, as state earlier in the EVK complex, only the ROESY spectrum of the BArF complex allowed the differentiation of signals to be sufficient for the identification of all relevant interactions. These are shown in *Fig. 10* (modelled CpH approach see *Fig. S5*, spectra see *Fig. S6*).

Although three conformers are present in solution, inspection of models and access to the alkene clearly favor the *anti-s-trans* conformation for the *DA* reaction. The results shown in *Table 5* bear this out. We note, however, the long reaction times and the poor *exo*-selectivity in these reactions when compared to those obtained with methacrolein (*Scheme 2*).

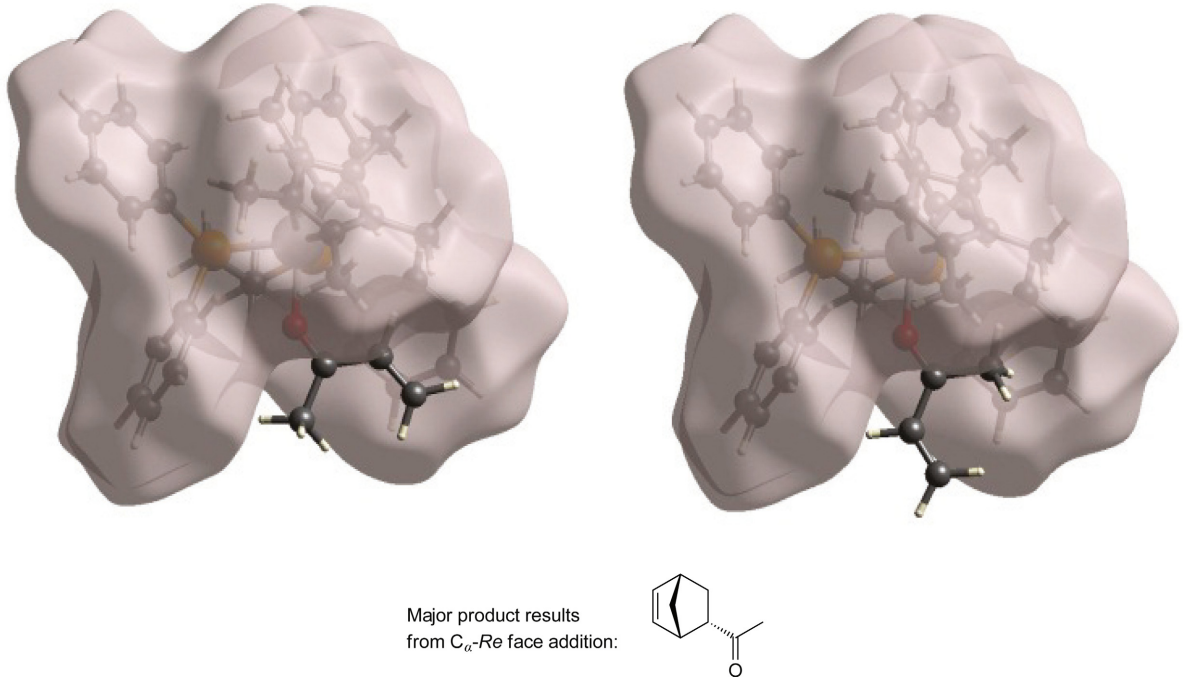


Figure 9. Left image: X-ray structure of (S_{Ir},*R*)-[Ir(η^5-C_5Me_5)(PROPHOS)(MVK)][SbF_6]$_2$ showing the *syn-s-trans* coordinated MVK. The C_α-*Re* face of the alkene is completely shielded in this conformation, but it would be readily accessible in the *anti-s-trans* conformation (model on right).

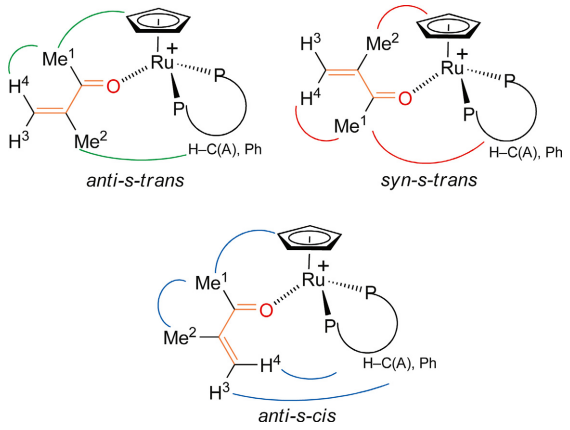
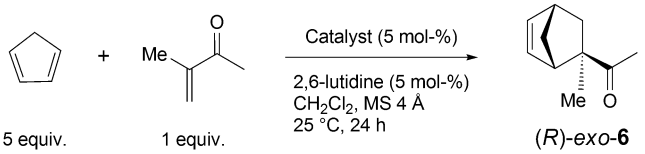


Figure 10. Observed ROESY correlations in [Ru((*R*,*R*)-BIPHOP–F)(Cp)(αMeMVK)][BArF] ((*R*,*R*)-**1h** [BArF]) in CD_2Cl_2.

Table 5. Aymmetric *Diels–Alder* reactions of cyclopentadiene with α-Me-methyl vinyl ketone catalyzed by (*R*,*R*)-CpRu **1a** and (*S*,*S*)-IndRu **2a**



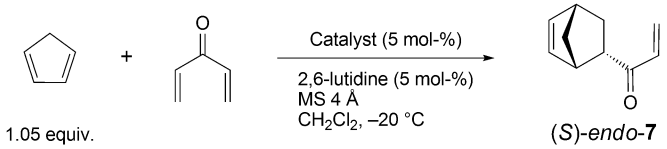
Entry	Catalyst	Yield[a] [%]	*Endo/exo*[b]	e.r.[c]
1	(*R*,*R*)-**1a**	80	33:67	90:10 ((*R*)-*exo*) 85:15 ((*R*)-*endo*)
2	(*S*,*S*)-**2**	70	33:67	87:13 ((*S*)-*exo*) 85:15 ((*S*)-*endo*)

[a] Yield of isolated products. [b] Determined by ^{1}H-NMR. [c] Determined by chiral GC.

With the changes observed in conformations of coordinated enals and enones undergoing *DA* reactions, it was of interest to investigate reactions of divinyl ketone. Both *anti-s-trans* and *syn-s-trans* conformations are present in the *Lewis* acid adduct of this substrate. *Table 6* summarizes the results obtained. The (*S*)-*endo* adduct **7** was obtained as the major product in reactions catalyzed by either catalyst (*R*,*R*)-CpRu **1a** or (*S*,*S*)-IndRu **2a**. This shows the C=C bond undergoing cycloaddition reaction to be different in the two catalyst sites. The *syn-s-trans* alkene reacts when the precatalyst is (*R*,*R*)-CpRu **1a**, whereas with (*S*,*S*)-IndRu **2a**, it is the *anti-s-trans* alkene that undergoes cycloaddition (*Fig. 11*).

The activation of α,β-unsaturated C=O compounds for cycloadditions involves coordination of the C=O O-atom to a *Lewis* acid as shown in *Scheme 1* and found in the crystal structures of RuCp and RuInd complexes mentioned earlier in this article. A Ru(II) complex fragment can, however, also bind to the alkene portion of enals and enones. This, in fact, is the preferred mode

Table 6. Asymmetric *Diels–Alder* reactions of cyclopentadiene with divinyl ketone catalyzed by (*R,R*)-CpRu **1a** and (*S,S*)-IndRu **2a**



Entry	Catalyst	Time [h]	Yield[a] [%]	*Endo/exo*[b]	e.r.[c]	Config.
1[d]	(*R,R*)-**1a**	24	90	95:5	77:23	(*S*)
2	(*R,R*)-**1a**	19	75	94:6	87:13	(*S*)
3	(*S,S*)-**2a**	40	72	92:8	79:21	(*S*)

[a] Yield of isolated products. [b] Determined by ^{1}H-NMR. [c] Determined by chiral GC. [d] With 1.5 equiv. of CpH, no MS, data from ref. [2a].

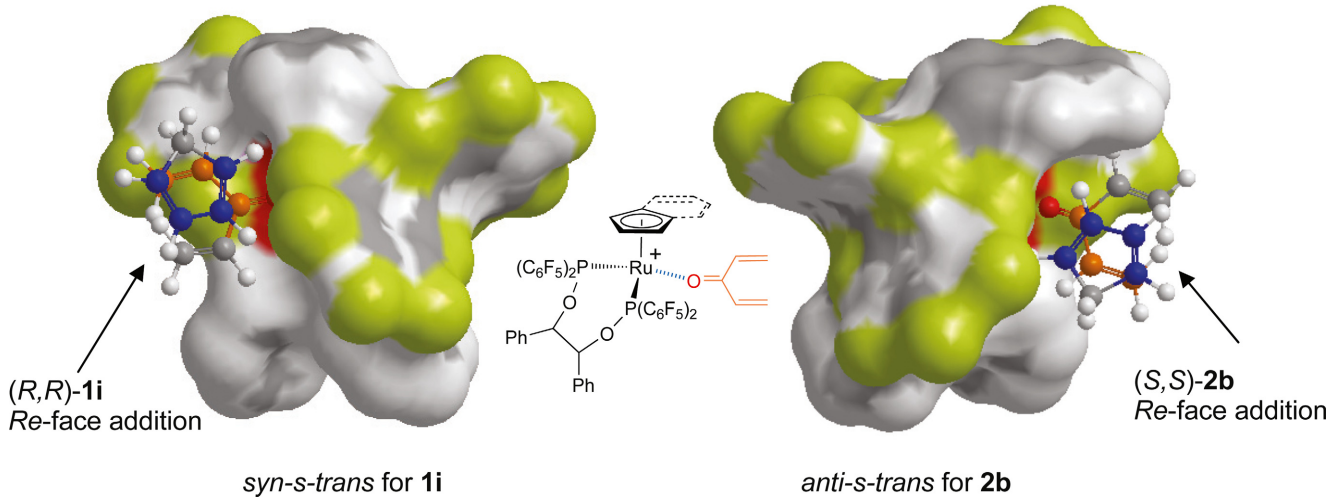


Figure 11. Modeled approach of CpH in *endo* fashion to the C_α-*Re* face of divinyl ketone in Ru((*R,R*)-BIPHOP–F)(Cp)(divinyl ketone)$^+$ (*R,R*)-**1i** and Ru((*S,S*)-BIPHOP–F)(divinyl ketone)(indenyl)$^+$ (*S,S*)-**2b** complexes providing (*S*)-endo-**7**.

of coordination in Ru(II) complexes with more electron-rich phosphine ligands. To quote from an article by *Bosnich* and coworkers: 'The [CpRu(PR_3)$_2$(CH_2=CH_2)] PF_6 species incorporates a basic ruthenium atom, which tends to prefer olefin to dienophile carbonyl coordination. Thus this complex does not promote the classical *DA* reaction and this aspect is not circumvented by replacing one of the phosphines by a carbonyl ligand. . .'.[27] The above quote came to mind when it was found that the crystal structure of [Ru((*R,R*)-BIPHOP–F)(Cp)(divinyl ketone)][SbF_6] ((*R,R*)-**1i**[SbF_6]) shows binding to the alkene, rather than to the ketone function (*Fig. 12*).[1] This contrasts with the solution structure, where, as in other O-bound enones, only the C=O-Ru coordinated isomer is apparent (IR ν_{CO} = 1640 cm^{-1}).

Although the crystal quality is not optimal (see *Supplementary Material*), the structure shows unambiguously the binding of the Ru to the alkene, with a coordinated C=C bond length of 1.36 Å and Ru–C distances of 2.22 and 2.29 Å, respectively. The torsion angle C(1)–C(2)–C(9)–O is 68°, and, hence, the alkene is twisted out of conjugation with the C=O bond. Remarkably, two alkene C–H bonds (H positions calculated geometrically) are inclined toward, rather than away from the Ru center.

Our hypothesis is that this is because binding the alkene in a plane normal to the Ru-alkene bonds would require the C=O bond to be more deeply imbedded in the catalyst groove. This is not possible as apparent from the *Hirshfeld* surface of the catalyst groove (*Fig. 12*, bottom). Contacts shown in red on

[1] CCDC-1473049 and 1473050 contain the supplementary crystallographic data for (*R,R*)-**1j**[SbF_6] and for (*R,R*)-**1i**[SbF_6], resp. These data can be obtained free of charge *The Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

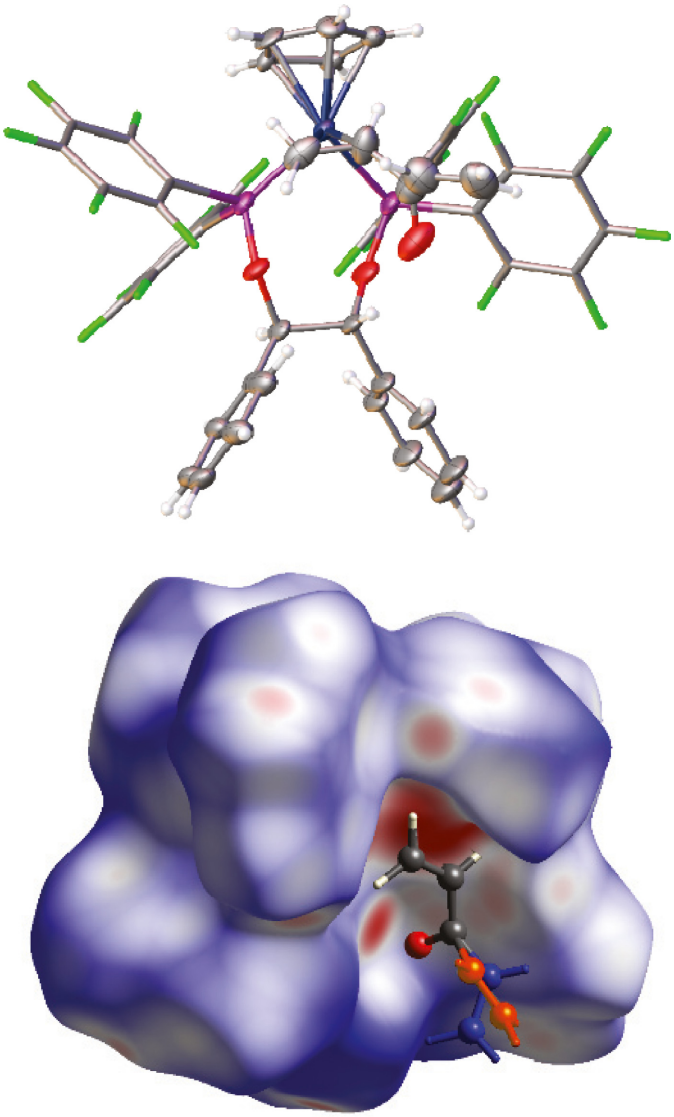


Figure 12. Top: ORTEP plot of the crystal structure of [Ru((*R,R*)-BIPHOP–F)(Cp)(divinyl ketone)][SbF_6] ((*R,R*)-**1i**[SbF_6] showing a η^2 bound enone. SbF_6 anion and disordered free alkene omitted for clarity. Ellipsoids at 30% probability levels. Bottom: Normalized contact distance dnorm mapped on the *Hirshfeld* surface of the catalyst groove. The ketone is represented as balls and sticks. The nonbonded alkene is disordered over two positions in the crystal structure (shown in orange and blue, resp.). See also *Fig. S9*.

this surface highlight the intermolecular interactions with distances closer than the sum of the *van der Waals* radii.[28] In addition to the bonding of the alkene to the Ru center, the ketone O-atom is also the receptor of a C–H···O bond, which may help to stabilize this unusual geometry. The noncoordinated C=C bond is disordered over two positions (red and blue parts in *Fig. 12*, bottom).

As mentioned earlier, X-ray structures showed MVK and cyclohexenone to bind to the CpRu(BIPHOP–F)$^+$ *Lewis* acid in the *anti-s-trans* conformation while cycloaddition products indicated a *syn-s-trans* conformation of the enone undergoing reaction. We argued that a bulky alkyl group on the enone may switch the ground-state conformation from *anti-s-trans* to *syn-s-trans* in order to avoid conflict with the Cp roof of the catalyst. This hypothesis was proved correct.

Ketone exchange of acetone in **1a** for 6,6-dimethylcyclohex-2-en-1-one provided the corresponding complex **1j**. Its ROESY spectrum (*Fig. S7*) indicated again the presence of both conformers in solution. However, in contrast to previous structures, the X-ray of complex **1j** showed for the first time in this series the *syn-s-trans* conformation of the enone. (*Fig. 13*).[1]

Conclusions

Enals always bind the Ru(II)(BIPHOP–F) *Lewis* acids *via* coordination to the C=O O-atom and both *anti-s-trans*

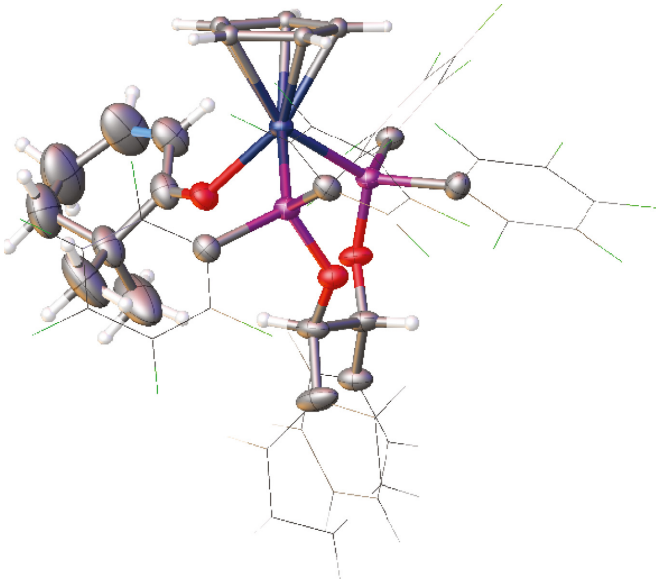


Figure 13. ORTEP plot of the crystal structure of [Ru((*R,R*)-BIPHOP–F)(Cp)(6,6-dimethylcyclohex -2-en-1-one)][SbF_6] ((*R,R*)-**1j** [SbF_6]) showing the *syn-s-trans* conformation of the coordinated enone (alkene in blue). Ellipsoids at 50% probability levels. See also *Fig. S8*.

and *anti-s-cis* conformations are present in solution. The *anti-s-trans* conformation is preferred in the solid state and it is also the conformation undergoing cycloaddition reaction with cyclopentadiene. In the *anti-s-cis* conformation, the alkene is shielded by the chiral BIPHOP–F ligand. A third conformation, *syn-s-trans*, is present in the corresponding Ru-enone complexes. Small alkyl vinyl ketones adopt an *anti-s-trans* conformation in the solid state, but reactions involve the *syn-s-trans* conformation giving rise to products of opposite chirality compared to enals. Increasing bulk of the enone as in 6,6-dimethylcyclohexenone switches the ground state conformation (X-ray) from *anti-s-trans* to *syn-s-trans*. The X-ray structure of [Ru(BIPHOP–F)Cp(divinyl ketone)][SbF_6] reveals a η^2-alkene-Ru bond. In solution, this enone is activated toward cycloaddition *via* a C=O-Ru *Lewis* acid coordination. In solution, divinyl ketone is O-bound, activated for cycloadditions and presents both a *syn-s-trans* as well as an *anti-s trans* alkene. The (*S*)-*endo* cyclopentadiene cycloadduct from reactions of divinyl ketone and cyclopentadiene catalyzed by (*R,R*)-**1a** shows that it is the C_α-*Re* face undergoing cycloaddition. This is the *syn-s-trans* alkene. When the catalyst roof is changed to indenyl, the *anti-s-trans* alkene is engaged because the *syn-s-trans* alkene is now too close to the catalyst roof to engage in cycloadditions.

The conformational study presented reveals many details on the ground state and reactive conformation of dienophiles in the cavity of a chiral *Lewis* acid and maps the pathway of catalyzed asymmetric *DA* reactions.

Experimental Section

General

All glassware and syringes were oven-dried and further dried by placing under vacuum and heating with a heat gun for *ca.* 5 min (3×). Purification of THF, Et_2O, toluene, and CH_2Cl_2 was carried out using a *Solvtek*© purification system. Acetone was distilled from drierite before use. Dicyclopentadiene was cracked at 170 °C and CpH was either used immediately or stored under N_2 at −40 °C. Commercial chemicals were used as supplied unless otherwise stated. MS 4 Å was activated at 170 °C under reduced pressure for 15 h. Catalysts **1a** – **1c**, **3e**, **3f**, and **2a** were prepared by published procedures.[1c][1d][2a][5][6] Flash chromatography (FC) was performed using a *Brunschwig* silica gel (60 Å, 32 – 63 mesh; *Art. 7736*). Thin-layer chromatography was performed on precoated aluminum plates (*Fluka* silica *60F*$_{254}$), and visualized using UV light or staining with cerium ammonium molybdate, basic $KMnO_4$ soln. IR Spectra were recorded on a *PerkinElmer Spectrum One* spectrophotometer using a diamond *ATR Golden Gate* sampling. ^{1}H-, ^{13}C-, ^{31}P-, ^{19}F-NMR spectra were recorded on *Bruker ARX-500*, *AMX-400*, or *ARX-300* FT spectrometers in the solvent indicated. ^{1}H- and ^{13}C-NMR chemical shifts (δ) are quoted in parts per million [ppm] relative to TMS. Coupling constants (*J*) are in Hertz [Hz]. ^{31}P- and ^{19}F-NMR chemical shifts are referenced to H_3PO_4 and C_6F_6 as external standard, resp. MS spectra were obtained on a *Varian CH4* or *SM1* spectrometer; ionizing voltage 70 eV; *m/z*. HR-EI-MS were obtained using a *Finningan MAT 95* operating at 70 eV. HR-ESI-MS analyses were measured on a *VG analytical7070E* instrument (data system *11250*, resolution *7000*).

Preparation of Ru-Substrate Complexes. General Procedure. All solvents used were taken directly from the solvent purification system. Activated powdered MS (4 Å) was first added to dried *Schlenk* tubes. Under an N_2 atmosphere, the Ru-complex **1a** (1 equiv.) was dissolved in CH_2Cl_2 (*ca.* 1 ml/0.03 mmol catalyst), and the freshly dried and distilled enal or enone (10 – 20 equiv.) was added. After 5 – 10 min, the volatiles were removed under vacuum. This procedure was repeated twice. The mixture was filtered through a *Celite 545* plug to remove MS. The volatiles were concentrated under vacuum to *ca.* 1 ml. Hexanes (*ca.* 8 ml/0.03 mmol catalyst) were added in

order to precipitate the complex. The solvents were removed by syringe and the complex was washed with hexanes (2× *ca.* 4 ml/0.03 mmol catalyst) and dried under vacuum for 1 – 2 h. The residue was dissolved in dry CD_2Cl_2 and transferred to an NMR tube under an N_2 atmosphere.

[Ru((R,R)-BIPHOP–F)(Cp)(methacrolein)][SbF_6]((*R,R*)-**1b**[SbF_6]). The *General Procedure* was applied using (*R,R*)-**1a** (0.03 mmol, 42 mg, 1 equiv.) and methacrolein (0.6 mmol, 42 mg, 49 μl, 20 equiv). (*R,R*)-**1b**[SbF_6] was obtained as a yellow solid. IR (CH_2Cl_2): 1606. ^{1}H-NMR (500 MHz, CD_2Cl_2, r.t.): 9.69 (*s*, CHO, 1 H); 7.30 – 7.07 (*m*, 7 arom. H); 6.95 – 6.40 (br. *s*, 1 arom. H); 6.86 (*s*, =CH_2, 2 H); 6.73 (*d*, *J* = 7.6, 2 arom. H); 5.20 (*dd*, *J* = 7.8, 13.8, POCH); 5.03 (app. *t*, *J* = 8.0, POCH); 4.96 (*s*, Cp); 1.90 (*s*, Me). ^{1}H-NMR (500 MHz, CD_2Cl_2, −40 °C): 9.69 (*d*, *J* = 4.1, CHO, 1 H); 7.03 – 7.07, 7.10 – 7.18, 7.30 – 7.39 (3 *m*, 2 arom. H each); 6.86 (*s*, 1 H of =CH_2); 6.81 (*s*, 1 H of =CH_2); 6.76 (app. *t*, *J* = 7.5, 1 arom. H); 6.69 (*d*, *J* = 7.6, 2 arom. H); 5.76 (*d*, *J* = 7.5, 1 arom. H); 5.14 (*dd*, *J* = 7.6, 14.7, POCH); 5.00 (app. *t*, *J* = 7.6, POCH); 4.91 (*s*, Cp); 1.84 (*s*, Me). ^{31}P-NMR (202 MHz, CD_2Cl_2, −40 °C): 129.4 (*d*, *J* = 65.2, 1 P); 125.9 (*dd*, *J* = 67.0, 20.7, 1 P).

[Ru((*R,R*)-BIPHOP–F)(Cp)(acrolein)][SbF_6] ((*R,R*)-**1d**[SbF_6]). The *General Procedure* was applied using (*R,R*)-**1a** (0.03 mmol, 42 mg, 1 equiv.) and acrolein (1.5 mmol, 84 mg, 0.1 ml). (*R,R*)-**1d**[SbF_6] was obtained as a yellow solid. IR (CH_2Cl_2): 1626. ^{1}H-NMR (500 MHz, CD_2Cl_2, −40 °C): 9.71 (*d*, *J* = 8.5, CHO, 1 H); 7.34 – 7.28 (*m*, 2 arom. H); 7.08 – 7.17 (*m*, 4 arom. H); 7.05 (*d*, *J* = 17.0, =CHH_{trans}); 7.03 (*d*, *J* = 10.0, =CH_{cis}H); 6.76 – 6.81 (*m*, 3 arom. H); 6.72 (*ddd*, *J* = 8.5, 10.0, 17.0, C*H*=CH_2); 5.95 (br. *d*, *J* = 5.7, 1 arom. H); 5.18 (*dd*, *J* = 7.9, 14.3, POCH); 4.95 (*dd*, *J* = 7.9, 9.3, POCH); 4.90 (*s*, Cp). ^{31}P-NMR (202 MHz, CD_2Cl_2, −40 °C): 129.2 (*d*, *J* = 63.0, 1 P); 125.1 (*dd*, *J* = 66.3, 16.2, 1 P).

[Ru((*R,R*)-BIPHOP–F)(Cp)(MVK)][SbF_6] ((*R,R*)-**1e**[SbF_6]). The *General Procedure* was applied using (*R,R*)-**1a** (0.03 mmol, 42 mg, 1 equiv.) and methyl vinyl ketone (MVK, 0.6 mmol, 42 mg, 51 μl).[29] The yellow residue was dissolved in CD_2Cl_2, and the ^{1}H-NMR spectrum showed (*R,R*)-**1e**[SbF_6]) together with small amounts of the aqua complex, free MVK, and traces of hexanes. IR (CH_2Cl_2): 1643. ^{1}H-NMR (500 MHz, CD_2Cl_2, r.t.): 7.23 – 6.99 (*m*, 7 arom. H); 6.85 – 6.60 (br. *s*, 1 arom. H); 6.76 (*d*, *J* = 17.2, =CH_{cis}H); 6.74 (br. *d*, *J* = 6.3, 2 arom. H); 6.67 (*d*, *J* = 10.8, =CH_{trans}H); 6.41 (*dd*, *J* = 17.5, 10.8, 1 H, C*H*=CH_2); 5.28 (*dd*, *J* = 16.9, 8.8, POCH); 4.99 (*dd*, *J* = 14.1, 5.9, POCH); 4.94 (*s*, Cp); 2.61 (*s*, Me). ^{1}H-NMR (500 MHz, CD_2Cl_2, −20 °C): 7.31 (br. *s*, 2 arom. H); 7.18 – 7.12 (*m*, 2 arom. H); 7.11 – 7.05 (*m*, 2 arom. H); 6.81 (br. *s*, 2 arom. H); 6.77 (*d*, *J* = 17.4, =CH_{cis}H); 6.71 (br. *d*, *J* = 7.4, 2 arom. H); 6.67 (*d*, *J* = 10.7, =CH_{trans}H); 6.37 (*dd*, *J* = 17.4, 10.7, C*H*=CH_2); 5.97 (br. *s*, 1 arom. H); 5.24 (*dd*, *J* = 14.2, 8.1, POCH); 4.95 (app. *t*, *J* = 8.1, POCH); 4.91 (*s*, Cp); 2.58 (*s*, Me). ^{31}P-NMR (202 MHz, CD_2Cl_2, −20 °C): 130.0 (*d*, *J* = 67.0, 1 P); 124.2 (*dd*, *J* = 68.1, 20.6, 1 P).

[Ru((*R,R*)-BIPHOP–F)(Cp)(EVK)][SbF_6] ((*R,R*)-**1g**[SbF_6]). The *General Procedure* was applied using (*R,R*)-**1a** (0.03 mmol, 42 mg, 1 equiv.) and ethyl vinyl ketone (EVK, 0.6 mmol, 50 mg, 60 μl, 20 equiv.; dried over $CaCl_2$ for 1 h at r.t.). NMR showed a mixture of the EVK-complex **1g**[SbF_6], accompanied by small quantities of the corresponding aqua complex, free EVK, and hexanes. IR (CH_2Cl_2): 1642. ^{1}H-NMR (500 MHz, CD_2Cl_2, r.t.): 7.30 – 6.90 (*m*, 8 arom. H); 6.79 (*d*, *J* = 17.5, =CH_{cis}H); 6.73 (*d*, *J* = 7.4, 2 arom. H); 6.70 (*d*, *J* = 1, =CHH_{trans}); 6.26 (*dd*, *J* = 10.6, 17.7, C*H*=CH_2); 5.26 (*dd*, *J* = 14.8, 8.3, POCH); 4.96 (app. *t*, *J* = 8.5, POCH); 4.93 (*s*, Cp); 3.08 (app. *quint.*, *J* = 7.4, CH_2Me); 1.23 (*t*, *J* = 7.3, Me). ^{31}P-NMR (162 MHz, CD_2Cl_2, r.t.): 130.6 (br. *d*, *J* = 66.2, 1 P); 126.0 (br. *d*, *J* = 63.3, 1 P).

[Ru((*R,R*)-BIPHOP–F)(Cp)(EVK)][BArF] ((*R,R*)-**1g**[BArF]). The *General Procedure* was applied using (*R,R*)-**1a** (0.035 mmol, 50 mg) and EVK (0.7 mmol, 58 mg, 70 μl, 20 equiv.; dried over $CaCl_2$ for 1 h at r.t.) followed by the addition of NaBArF (0.038 mmol, 34 mg, 1.1 equiv.). NMR showed a mixture of the EVK-complex **1g**[BArF] and free EVK. IR (CH_2Cl_2): 1641. ^{1}H-NMR (500 MHz, CD_2Cl_2, r.t.): 7.78 – 7.71 (*m*, 8 *o-H* of BArF); 7.57 (*s*, 4 *p-H* of BArF); 7.24 – 6.90 (*m*, 7 arom. H); 6.74 (*d*, *J* = 7.4, 3 arom. H); 6.71 (*d*, *J* = 17.9, =CH_{cis}H); 6.51 (*d*, *J* = 11.1, =CHH_{trans}); 6.17 (*dd*, *J* = 17.7, 11.1, C*H*=CH_2); 5.35 (*dd*, *J* = 11.2, 4.8, POCH); 5.04 (*t*, *J* = 8.4, POCH); 4.84 (*s*, *J* = 6.6, Cp); 3.04 (*q*, *J* = 7.2, CH_2Me); 1.22 (*t*, *J* = 8.0, Me). ^{31}P-NMR (162 MHz, CD_2Cl_2, r.t.): 130.4 (br. *d*, *J* = 68.4, 1 P); 126.0 (br. *d*, *J* = 66.5, 1 P). ^{19}F-NMR (376.4 MHz, CD_2Cl_2): 99.01 (*s*, CF_3 of BArF).

[Ru((*R,R*)-BIPHOP–F)(Cp)(MeMVK)][SbF_6] ((*R,R*)-**1h**[SbF_6]). The *General Procedure* was applied using (*R,R*)-**1a** (0.03 mmol, 42 mg) and 3-methylbut-3-en-2-one (MeMVK, 0.6 mmol, 50 mg, 59 μl; dried over powdered $CaCl_2$ for 2 h at r.t.). The dried yellow precipitate was not completely soluble in CD_2Cl_2. The ^{1}H-NMR showed MeMVK-complex **1h**[SbF_6] along with free MeMVK and small impurities. IR (CH_2Cl_2): 1641. ^{1}H-NMR (500 MHz, CD_2Cl_2, r.t.): 7.00 – 7.22 (*m*, 8 arom. H); 6.67 (br. *d*, *J* = 7.6, 2 arom. H); 6.44 (*s*, =CH_{cis}H); 6.30 (*s*, =CHH_{trans}); 5.29 (*dd*, *J* = 8.8, 15.1, POCH); 4.98 (*s*, Cp); 4.93 – 5.03 (*m*, POCH); 2.57 (*s*, COMe); 1.91 (*s*, =CMe). ^{31}P-NMR (202 MHz, CD_2Cl_2, r.t.): 130.4 (br. *d*, *J* = 61.6); 125.0 (br. *dd*, *J* = 67.2, 21.8).

[Ru((*R,R*)-BIPHOP–F)(Cp)(MeMVK)][BArF] ((*R,R*)-**1h**[BArF]). The *General Procedure* was applied using

(*R,R*)-**1a** (0.035 mmol, 50 mg) and MeMVK (0.7 mmol, 58 mg, 69 μl, dried over $CaCl_2$ for 1 h at r.t.) followed by the addition of NaBArF (0.038 mmol, 34 mg, 1.1 equiv.). NMR showed a mixture of the MeMVK-complex **1h**[BArF] and free MeMVK. IR (CH_2Cl_2): 1642. ^{1}H-NMR (500 MHz, CD_2Cl_2): 7.82 – 7.68 (*m*, 8 *o-H* of BArF); 7.57 (br. *s*, 4 *p-H* of BArF); 7.25 – 6.90 (*m*, 8 arom. H); 6.67 (*d*, *J* = 7.5, 2 arom. H); 6.37 (*s*, =CH_{cis}H); 6.27 (*s*, =CHH_{trans}); 5.29 (*dd*, *J* = 14.3, 8.0, POCH); 5.02 (*t*, *J* = 8.4, POCH); 4.89 (*s*, 1 H of Cp); 2.48 (*s*, COMe); 1.90 (*s*, =CMe). ^{31}P-NMR (162 MHz, $CDCl_3$): 130.8 (br. *d*, *J* = 65.3, 1 P); 125.4 (br. *d*, *J* = 69.4, 1 P).^{19}F-NMR (376.4 MHz, CD_2Cl_2): 99.01 (*s*, CF_3 of BArF).

[Ru((*R,R*)-BIPHOP–F)(Cp)(DVK)][SbF$_6$] ((*R,R*)-**1i**[SbF_6]). The *General Procedure* was applied using (*R,R*)-**1a** (0.035 mmol, 50 mg) and divinyl ketone[30] (DVK, 0.72 mmol, 60 mg, 68 μl). Crystals for X-ray analysis were grown in a cut NMR tube (*ca.* 50 mg of **1i**[SbF_6]) in CH_2Cl_2 (0.5 ml) by two-chamber diffusion of a 5:1 mixture of hexane/toluene (*Schlenk* tube) under N_2 atmosphere at r.t.

[Ru((*R,R*)-BIPHOP–F)(Cp)(DVK)][BArF] ((*R,R*)-**1i**[BArF]). The *General Procedure* was applied using (*R,R*)-**1a** (0.035 mmol, 50 mg) and DVK (0.36 mmol, 30 mg, 34 μl, 10 equiv.) followed by the addition of NaBArF (0.038 mmol, 34 mg, 1.1 equiv.). NMR showed a mixture of the DVK-complex and free DVK. IR (CH_2Cl_2): 1640. ^{1}H-NMR (400 MHz, CD_2Cl_2, r.t.): 7.74 (*m*, 8 *o-H* of BArF); 7.56 (br. *s*, 4 *p-H* of BArF); 7.30 – 6.82 (*m*, 7 arom. H); 6.70 (*d*, *J* = 7.7, 2 arom. H); 6.57 (*dd*, *J* = 16.8, 10.5, C*H*=CH_2 and 1 arom. H); 6.47 (*d*, *J* = 7.7, =CHH_{trans}); 6.44 (*d*, *J* = 14.4, =CH_{cis}H); 5.29 (*dd*, *J* = 14.3, 8.0, POCH); 5.00 (*t*, *J* = 8.0, POCH); 4.90 (*s*, Cp). ^{31}P-NMR (162 MHz, CD_2Cl_2, r.t.): 130.0 (*d*, *J* = 65.9, 1 P); 124.5 (*d*, *J* = 67.9, 1 P). ^{19}F-NMR (376.4 MHz, CD_2Cl_2, r.t.): 99.03 (*s*, CF_3 of BArF).

Synthesis of ((R,R)-**1j**[SbF_6])

6,6-Dimethyl 2-cyclohexenone. A soln. of 6-methyl 2-cyclohexenone[31] (0.36 g, 3.3 mmol, 1 equiv.) in HMPA (1.00 ml) was added dropwise to a THF soln. of LDA (3.6 mmol in THF) at −78 °C. This light green soln. was stirred at −78 °C for 1 h followed by addition of MeI (0.31 ml, 4.95 mmol, 1.5 equiv.). The resulting mixture was slowly warmed up to r.t. and stirred for 2 h. Sat. aq. NH_4Cl (10 ml) was added. The mixture was extracted with Et_2O (3 × 10 ml), and the combined extracts were washed with brine and dried (anh. $MgSO_4$). The residue was chromatographed (5% Et_2O in pentanes, R_f = 0.33) to give a colorless oil (0.35 g, 2.82 mmol, 85% yield). IR (neat): 2926*s*, 1707*s*, 1677*s*, 1452*w*, 1385*w*, 1224*w*, 1150*w*. ^{1}H-NMR (400 MHz, $CDCl_3$): 6.86 (*dt*, *J* = 9.9, 3.9, C*H*=CHCO); 5.91 (*dt*, *J* = 10.0, 1.9, CH=C*H*CO); 2.37 (*tdd*, *J* = 6.0, 4.0, 2.0, =CHCH_2); 1.82 (*t*, *J* = 6.1, CCH_2); 1.11 (br. *s*, 2 Me). ^{13}C-NMR (101 MHz, $CDCl_3$): 204.7 (CO); 148.7 (CH); 128.3 (CH); 41.4 (C); 36.2 (CH_2); 24.1 (2 Me); 23.4 (CH_2). HR-ESI-MS (TOF): 125.0967 ($C_{20}H_{31}N_2O_5^+$; calc. 125.0960).

[Ru((*R,R*)-BIPHOP–F)(Cp)(6,6-Dimethyl-2-cyclohexenone)][SbF$_6$] ((*R,R*)-**1j**[SbF_6]). The *General Procedure* was applied using (*R,R*)-**1a** (0.035 mmol, 50 mg) and a soln. of 6,6-dimethyl 2-cyclohexenone (DCH; 0.35 mmol, 43 mg, 10 equiv.) in CH_2Cl_2 (0.5 ml). Complex **1j** was isolated as a yellow solid. The ^{1}H-NMR showed **1j** and the corresponding aqua complexes along with free DCH. Crystals for spectral, elemental, and X-ray analysis were grown in a cut NMR tube (*ca.* 30 mg of **1j**[SbF_6]) in CH_2Cl_2 (0.5 ml) by two-chamber diffusion of a 5:1 mixture of hexane/toluene (*Schlenk* tube) under N_2 atmosphere at r.t. M.p. 147 – 149 °C. IR (CH_2Cl_2): 1642. ^{1}H-NMR (500 MHz, CD_2Cl_2): 7.57 (*dt*, *J* = 9.7, 3.7, 1 H, C*H*=CHCO), 7.33 (br. *s*, 1 arom. H); 7.20 – 7.03 (*m*, 7 arom. H); 6.96 (*d*, *J* = 7.4, CH=C*H*CO); 6.79 (*d*, *J* = 7.5, 2 arom. H); 5.92 (*d*, *J* = 10.1, 2 POCH); 5.27 (*dd*, *J* = 13.7, 7.1, POCH); 5.02 (*t*, *J* = 8.4, POCH); 4.88 (*s*, Cp); 2.70 (*s*, =CHCH_2); 2.08 (*dt*, *J* = 14.0, 6.9, CC*H*H); 1.96 (*dt*, *J* = 13.6, 4.5, CCH*H*); 1.19 (*s*, 4 H); 1.16 (*s*, 2 Me). ^{31}P-NMR (162 MHz, $CDCl_3$): 130.8 (*d*, *J* = 68.9, 1 P); 126.9 (*d*, *J* = 68.8, 1 P). Anal. calc. for $C_{51}H_{29}O_3F_{26}P_2RuSb$ (1468.51): C, 41.71; H, 1.99; found C, 41.63; H, 1.87.

Diels–Alder *Reactions of Keto Dienophiles*. *General Procedure*. The Ru-catalyst (0.05 equiv.) and *ca.* 100 – 130 mg of activated powdered MS 4 Å were added to a dried *Schlenk* tube under N_2. 2,6-Lutidine (3 μl, 0.025 mmol, 0.05 equiv.) and CH_2Cl_2 (0.7 ml/1 mmol of enone) were added at r.t. The mixture was brought to the reaction temp. (−20 °C or r.t.). After 15 min, the enone (1 equiv.) was added, followed by cyclopentadiene (1.05, 1.5, or 5.0 equiv.). The reaction was followed by removing aliquots (analysis by ^{1}H-NMR). The reaction was quenched by precipitation of the catalyst by the addition of hexanes (for **1a**) or pentanes (for **2a**; 8 – 10 ml). The mixture was filtered over *Celite*. Volatiles were evaporated and the residue was analyzed by ^{1}H-NMR to give the ratio of *endo*/*exo* isomers. The residue was purified by FC. The precipitated catalyst was recovered from the *Celite* pad with acetone, Bu_4NI was added, and the mixture was stirred for 5 min. The solvent was removed *in vacuo*, and the residue was analyzed by ^{31}P-NMR and collected in order to recover the catalyst (CpRuI, 85 – 90% yield and IndRuI, 60 – 65% yield).[1c][1d][5]

1-Bicyclo[2.2.1]hept-5-en-2-yl-ethanone (**5a**).[2a] The *General Procedure* was followed using (*R*,*R*)-**1a** (46 mg, 0.033 mmol), MVK (58 μl, 0.66 mmol), and CpH (84 μl, 1.0 mmol) at −20 °C for 24 h. The crude product (*endo*/*exo* 93:7) was purified by FC (SiO_2, 7% Et_2O in pentane) to give (−)-(1*S*,2*S*,4*S*)-*endo*-**5a** (66.2 mg, 0.49 mmol, 74%) as a colorless oil. e.r. 77:23.

Using (*S*,*S*)-**2a** as catalyst, the reaction was run on the same scale for 48 h to afford (−)-(1*S*,2*S*,4*S*)-*endo*-**5a** (*endo*/*exo* 93:7, 68.4 mg, 76%). e.r. 93:7.

1-Bicyclo[2.2.1]hept-5-en-2-yl-propanone (**5b**).[2a] The *General Procedure* was followed using (*R*,*R*)-**1a** (36 mg, 0.025 mmol), EVK (50 μl, 0.50 mmol), and CpH (63 μl, 0.75 mmol). The crude product (*endo*/*exo* 96:4) was purified by FC (SiO_2, 5% Et_2O in pentane) to give (−)-(1*S*,2*S*,4*S*)-*endo*-**5b** (59 mg, 79%) as a colorless oil. e.r. 91:9.

Using (*S*,*S*)-**2a** as catalyst, the reaction was run on the same scale for 48 h to afford (+)-(1*R*,2*R*,4*R*)-*endo*-**5b** (*endo*/*exo* 91:9, 47 mg, 63%). e.r. 65:35.

1-(2-Methyl-bicyclo[2.2.1]hept-5-en-2-yl)-ethanone (**6**).[2a]2 The *General Procedure* was followed using (*R*,*R*)-**1a** (36 mg, 0.025 mmol), MeMVK (50 μl, 0.50 mmol), and CpH (63 μl, 0.75 mmol). The crude product (*endo*/*exo* 33:67, 81% conv.) was purified by FC (SiO_2, 5% Et_2O in pentane) to give (−)-(1*S*,2*R*,4*S*)-*exo*-**6** (34 mg) and a mixture of *endo* and *exo* (26 mg) product as a colorless oil (0.40 mmol, 80% yield).

Data of the endo-*Isomer*: ^{1}H-NMR ($CDCl_3$, 400 MHz): 6.11 (*dd*, *J* = 5.8, 3.1, CCHCH=C*H*); 6.00 (*dd*, *J* = 5.6, 2.8, CCHC*H*=CH); 2.82 (br. *s*, =CHC*H*C); 2.77 (br. *s*, =CHC*H*CH_2); 2.09 (*s*, COMe); 1.98 (*dd*, *J* = 12.1, 2.7, C*H*HC); 1.64 (br. *d*, *J* = 8.6, CHC*H*HCH); 1.48 (*ddd*, *J* = 8.6, 4.4, 1.8, CHCH*H*CH); 1.36 (*s*, C*Me*); 1.35 (*dd*, *J* = 11.8, 3.6, 1 H, CH*H*C). e.r. 85:15.

Data of the exo-*Isomer*: ^{1}H-NMR ($CDCl_3$, 400 MHz): 6.25 (*dd*, *J* = 5.6, 3.0, CCHCH=C*H*); 6.11 (*dd*, *J* = 5.6, *J* = 3.0, CCHC*H*=CH); 2.98 (br. *s*, =CHC*H*C); 2.80 (br. *s*, =CHC*H*CH_2); 2.40 (*dd*, *J* = 11.8, 3.9, C*H*HCCHO); 2.22 (*s*, COMe); 1.41 (*dd*, *J* = 8.6, 2.1, CHC*H*HCH); 1.21 (br. *d*, *J* = 8.6, CHCH*H*CH); 1.08 (*s*, C*Me*); 0.77 (*dd*, *J* = 11.9, 2.7, CH*H*CCHO). e.r. 90:10.

Using (*S*,*S*)-**2a** as catalyst, the reaction was run on the same scale for 24 h to afford (+)-(1*R*,2*S*,4*R*)-*exo*-**6** (*endo*/*exo* 33:67, 70%). e.r. (*exo*): 87:13, e.r. (*endo*): 85:15.

1-[Bicyclo[2.2.1]hept-5-en-2-yl]prop-2-en-1-one (**7**).[2a] The *General Procedure* was followed using (*R*,*R*)-**1a** (36 mg, 0.025 mmol), DVK (55 μl, 0.50 mmol), and CpH (45 μl, 0.52 mmol). The crude product (*endo*/*exo* 95:5) was purified by FC (SiO_2, 7% Et_2O in pentane) to give (−)-(1*S*,2*S*,4*S*)-*endo*-**7** (56 mg, 76%) as a colorless oil. ^{1}H-NMR (400 MHz, $CDCl_3$) of *endo*-isomer: 6.46 (*dd*, *J* = 17.5, 10.5, 1 H of =CH_2); 6.23 (*dd*, *J* = 17.5, 1.3, 1 H of =CH_2); 6.14 (*dd*, *J* = 5.6, 3.2, =CH); 5.81 (*dd*, *J* = 5.6, 2.5, =CH); 5.72 (*dd*, *J* = 10.5, 1.3, COCH=); 3.22 – 3.28 (*m*, COCH); 3.23 (br. *s*, =CHC*H*); 2.91 (br. *s*, =CHC*H*); 1.81 (*ddd*, *J* = 11.8, 8.5, 3.5, COCHC*H*H); 1.54 (*ddd*, *J* = 11.8, 3.9, 2.8, COCHCH*H*); 1.46 (br. *d*, *J* = 8.1, COCHCHC*H*H); 1.36 (br. *d*, *J* = 8.1, COCHCHCH*H*). Chiral GC (*Hydrodex-β*, H_2, 100 °C, isothermal): t_R of *endo*-isomer = 20.11 (minor)/21.01 (major) min, e.r. 87:13.

Using (*S*,*S*)-**1b**, the reaction was run on the same scale for 40 h to afford (+)-(1*S*,2*S*,4*S*)-*endo*-**7** (*endo*/*exo* 92:8; t_R of *endo*-isomer = 20.30 (minor)/21.31 (major) min): 53 mg, 72%, e.r. 79:21.

Supplementary Material

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/hlca.201600139.

Acknowledgements

Bettina Ludwig (née *Bressel*) thanks the *Deutsche Forschungsgemeinschaft* (*DFG*) for a Postdoctoral Research Fellowship. *Damien Jeannerat* and *André Pinto* are thanked for their help with the NMR measurements, *Patrick Romanens* for technical expertise, and the *University of Geneva* and the *Swiss National Science Foundation* for financial support.

Author Contribution Statement

Sirinporn Thamapipol: Much of the data in this article are taken from *S.T.*'s PhD Thesis, University of Geneva: 'One Point Binding Chiral Ruthenium *Lewis* Acid Catalysts: Asymmetric Intramolecular *DA* Reactions and Conformational Studies'. *Bettina Ludwig* (née *Bressel*): Postdoc University of Geneva: 'NMR analyses of Ru-enone complexes, syntheses and catalytic reactions'. *Céline Besnard*: X-ray structure analyses. *Christophe Saudan*: PhD Thesis, University of Geneva: 'Syntheses of Ru-*Lewis* acids, chiral ligands, determination of *Lewis* acid strengths'. *E. Peter Kündig*: Thesis Director, Project initiator.

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Received May 5, 2016
Accepted June 2, 2016

