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Enantioselective Catalytic Diels–Alder Reactions with Enones As Dienophiles

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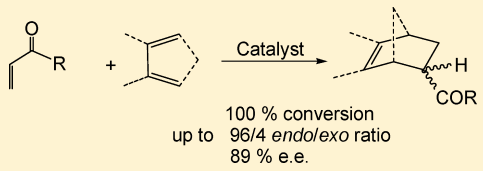
Supporting Information

ABSTRACT: The aqua complexes (S_M,R_C)-$[(\eta^5\text{-}C_5Me_5)M(PROPHOS)(H_2O)][SbF_6]_2$ [PROPHOS = (*R*)-propane-1,2-diylbis(diphenylphosphane); M = Rh (**1**), Ir (**2**)] are active catalysts for the asymmetric Diels–Alder reaction between ketones and dienes. At low temperatures, enantioselectivities of up to 89% ee are achieved. The intermediate Lewis acid–dienophile complexes (S_M,R_C)-$[(\eta^5\text{-}C_5Me_5)M(PROPHOS)(MVK)][SbF_6]_2$ (MVK = methyl vinyl ketone; M = Rh (**3**), Ir (**4**)) and (S_{Ir},R_C)-$[(\eta^5\text{-}C_5Me_5)Ir(PROPHOS)(EVK)][SbF_6]_2$ (EVK = ethyl vinyl ketone (**5**)) have been isolated and characterized by analytical and spectroscopic means, including the determination of the crystal structure of the iridium complexes **4** and **5** by X-ray diffractometric methods. Structural parameters indicate that the dispositions of the coordinated dienophiles are controlled by the CH/π attractive interactions established between a phenyl group of the PROPHOS ligand and the α-vinyl proton of the ketones. Proton NMR parameters indicate that these interactions are maintained in solution. From these data, the stereoselectivity of the catalytic reaction is discussed.



INTRODUCTION

Asymmetric catalysis is one of the most efficient synthetic methodologies for the preparation of enantioenriched compounds.[1] Among the wide variety of metal-catalyzed asymmetric processes, the Diels–Alder (DA) reaction is a powerful and versatile synthetic transformation that plays an important role in the construction of cyclohexene derivatives with up to four contiguous stereocenters.[2] In particular, cationic half-sandwich complexes of general formula $[(\eta^n\text{-ring})M(L^1L^2)*(Solv)]^{n+}$ [M = Rh, Ir, Ru; (L^1L^2)* = chiral bidentate ligand] have been used as chiral one-point-binding catalysts in enantioselective DA reactions by the groups of Kündig,[3] Faller,[4] Davies,[5] and ourselves.[6] Olefins with one carbonyl-containing substituent are well-suited dienophiles to which these catalysts can be applied: the electron-withdrawing carbonyl group activates the olefin toward a nucleophilic attack and, concurrently, provides the dienophile with an oxygen atom capable of linking the metal in an η^1-coordination mode. In fact, the reaction of enals (mostly methacrolein) with cyclopentadiene can be considered as the DA reaction model for this type of catalyst. However, enones, dienophiles that fulfill the two above-mentioned features, have been very scarcely employed as DA dienophiles. In 2002, MacMillan and Northrup reported the first enantioselective organocatalytic DA reaction with enones as dienophiles.[7] Subsequently, Corey et al.[8] and Shibatomi and Yamamoto[9] reported that activated chiral oxazaborolidines efficiently mediate the enantioselective cycloaddition of enones and dienes, Hawkins and co-workers published the application of a chiral aromatic alkyldichloroborane compound to the DA reaction between enones and cyclopentadiene,[10] and Harada's group reported that oxazaborolidinones are efficient catalysts for the asymmetric DA reaction of acyclic enones.[11] Notably, as far as we know, the only example of a chiral transition metal Lewis acid catalyst for asymmetric DA reactions of this type is the ruthenium complex $[(\eta^5\text{-}C_5H_5)Ru(R,R\text{-BIPHOP-F})(acetone)][SbF_6]$ (*R*,*R*-BIPHOP-F = 1,2-bis[bis(pentafluorophenyl)phosphanyloxy]-1,2-diphenylethane) recently reported by Kündig's group.[12]

Following our studies on enantioselective DA reactions of enals catalyzed by (S_M,R_C)-$[(\eta^5\text{-}C_5Me_5)M(PROPHOS)(H_2O)][SbF_6]_2$ [PROPHOS = (*R*)-propane-1,2-diylbis(diphenylphosphane); M = Rh (**1**), Ir (**2**)] complexes[6a,h,j,m,n] and taking into account the lack of examples of DA reactions of enones catalyzed by transition metal complexes, we envisaged the possibility of extending the application of our catalysts to DA reactions involving this type of dienophiles. In this paper, we report the results obtained in the reaction of vinyl ketones (MVK, EVK) with dienes (cyclopentadiene, 2,3-dimethylbutadiene, isoprene). The determination of the crystal structure by X-ray diffractometric methods of the intermediates (S_{Ir},R_C)-$[(\eta^5\text{-}C_5Me_5)Ir(PROPHOS)(MVK)][SbF_6]_2$ (**4**) and (S_{Ir},R_C)-$[(\eta^5\text{-}C_5Me_5)Ir(PROPHOS)(EVK)][SbF_6]_2$ (**5**), in which the dienophile is coordinated to the metal, allows us to discuss the observed asymmetric induction.

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RESULTS AND DISCUSSION

Diels–Alder Reactions of Vinyl Ketones with Dienes.

We first tested the catalytic activity of the complexes (S_M,R_C)-$[(\eta^5\text{-}C_5Me_5)M(PROPHOS)(H_2O)][SbF_6]_2$ [M = Rh (**1**), Ir (**2**)] in the DA reaction between the ketones MVK (**6**) and EVK (**7**) and cyclopentadiene (**8**), 2,3-dimethylbutadiene (**9**), and isoprene (**10**). As specified in Scheme 1, two pairs of enantiomers can be formed when cyclopentadiene or isoprene are used as diene (a, c), but only two enantiomers can be obtained for 2,3-dimethylbutadiene (b).

Scheme 1. Possible Cycloadducts for the DA Reaction between the Vinyl Ketones 6 and 7 and the Dienes 8–10

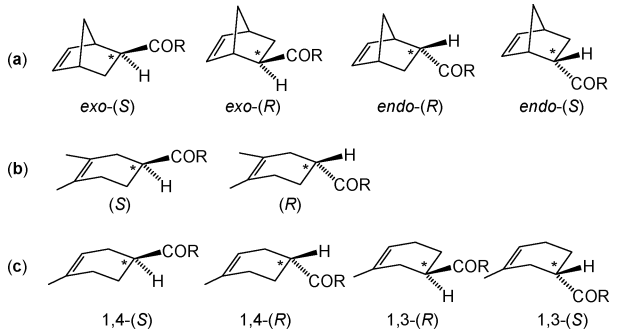
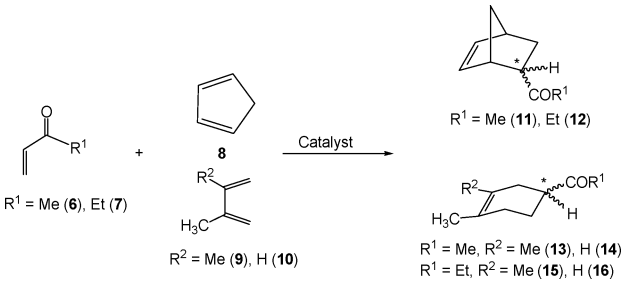


Table 1 lists the results obtained and the reaction conditions employed. All the reactions were carried out at room temperature, and the collected results are the average of at least two comparable reaction runs. Catalyst precursors **1** and **2** are treated with the corresponding vinyl ketone, in the presence of 4 Å MS, before the addition of the diene to generate the complexes $[(\eta^5\text{-}C_5Me_5)M(PROPHOS)(enone)]^{2+}$ (see below). Both rhodium and iridium systems are very active for the reaction of the vinyl ketones **6** and **7** with cyclopentadiene, conversions higher than 75% being achieved in 15 min in all cases (entries 1, 4, 7, and 10); however with dienes **9** and **10**, under the same conditions, low conversions (≤36%) are obtained after 6 days of reaction. For both metals, good *endo* selectivities are obtained in the reactions with cyclopentadiene (entries 1, 4, 7, and 10), and the 1,4-isomers are obtained preferentially in the reactions with isoprene (entries 3, 6, 9, and 12); however the enantioselectivities achieved are modest (≤27% ee).

The high activity shown by vinyl ketones **6** and **7** with cyclopentadiene at room temperature together with the possibility of improving the low ee obtained prompted us to study these reactions at lower temperatures (Table 2). For comparative purposes, the values registered at room temperature (RT) are also included. The catalytic systems remain active at low temperatures. Thus, for example, at −50 °C, after 24 h of reaction, quantitative conversions are achieved with both catalysts (entries 6, 10, and 13) and, as expected, the *endo*/*exo* selectivity slightly increases when temperature decreases. For the dienophile MVK, the major adduct obtained is the *endo*-(*S*) isomer, which implies a diene addition to the C*α*-*re* face. Notably, while for the enone MVK the ee value increases when temperature decreases (entries 1–4 and 7–11), unexpectedly, this value remains almost unchanged for the enone EVK and, furthermore, the *endo*-(*R*) product is slightly more abundant (entries 5, 6 and 12, 13). We will be back to this point later, when discussing the molecular structures in the solid state of the enone-containing intermediates **4** and **5**. It is interesting to point out that the enantioselectivity achieved for the enone MVK, with both catalytic systems, is the highest reported so far for a metallic catalytic system.[12]

Table 1. DA Reactions of Vinyl Ketones 6 and 7 and Dienes 8, 9, and 10[a]



entry	catalyst	R^1	diene/R^2	time (h)	conv[b] (%)	selectivity[b,c] (molar ratio)	ee[d] (%)
1	**1**	Me (**6**)	HCp (**8**)	0.25	77	90/10	27 (*S*)
2	**1**	Me (**6**)	Me (**9**)	144	32		2 (*S*)
3	**1**	Me (**6**)	H (**10**)	144	11	70/30	2/1
4	**1**	Et (**7**)	HCp (**8**)	0.25	89	92/8	1 (*R*)
5	**1**	Et (**7**)	Me (**9**)	144	30		0
6	**1**	Et (**7**)	H (**10**)	144	17	75/25	0/0
7	**2**	Me (**6**)	HCp (**8**)	0.25	96	93/7	17 (*S*)
8	**2**	Me (**6**)	Me (**9**)	144	36		5 (*S*)
9	**2**	Me (**6**)	H (**10**)	144	14	72/28	3/1
10	**2**	Et (**7**)	HCp (**8**)	0.25	91	93/7	1 (*R*)
11	**2**	Et (**7**)	Me (**9**)	144	32		0
12	**2**	Et (**7**)	H (**10**)	144	28	80/20	1/0

[a]Reaction conditions: catalyst 0.025 mmol (5 mol %), ketone 0.5 mmol, diene 2.5 mmol, and 100 mg of 4 Å molecular sieves in 4 mL of CH_2Cl_2. [b]For diene **8** determined by GC; for dienes **9** and **10** determined by ^{1}H NMR. [c]For diene **8**, *endo*/*exo* molar ratio; for diene **10**, 1,4/1,3 adducts molar ratio. [d]Absolute configuration of the major adduct established by comparison with literature data (*S* at C_2)[12]

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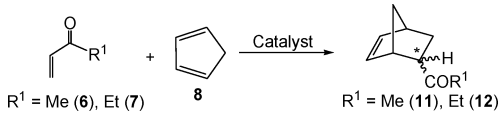
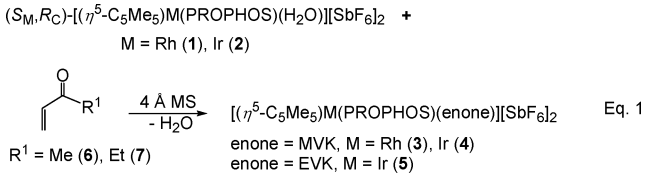
Table 2. DA Reaction of Vinyl Ketones 6 and 7 with Cyclopentadiene at Low Temperatures[a]



entry	catalyst	R^1	T (°C)	time (h)	conv[b] (%)	isomer ratio[b] (*endo*/*exo*) (%)	ee[b,c] (%)
1	**1**	Me (**6**)	RT	0.25	77	90/10	27 (*S*)
2	**1**	Me (**6**)	0	0.5	76	91/9	47 (*S*)
3	**1**	Me (**6**)	−20	6	82	92/8	56 (*S*)
4	**1**	Me (**6**)	−50	24	80	92/8	71 (*S*)
5	**1**	Et (**7**)	RT	0.25	89	92/8	1 (*R*)
6	**1**	Et (**7**)	−50	24	100	92/8	4 (*R*)
7	**2**	Me (**6**)	RT	0.25	96	93/7	17 (*S*)
8	**2**	Me (**6**)	0	0.5	100	93/7	45 (*S*)
9	**2**	Me (**6**)	−20	6	91	93/7	74 (*S*)
10	**2**	Me (**6**)	−50	24	100	94/6	88 (*S*)
11	**2**	Me (**6**)	−70	165	85	94/6	89 (*S*)
12	**2**	Et (**7**)	RT	0.25	91	93/7	1 (*R*)
13	**2**	Et (**7**)	−50	24	100	96/4	4 (*R*)

[a]Reaction conditions: catalyst 0.025 mmol (5 mol %), ketone 0.5 mmol, diene 2.5 mmol, and 100 mg of 4 Å molecular sieves in 4 mL of CH_2Cl_2. [b]Determined by GC. [c]Absolute configuration of the major adduct established by comparison with literature data (*S* at C_2).[12]

Enone Compounds (S_M,R_C)-[(η^5-C_5Me_5)M(PROPHOS)(enone)][SbF_6]$_2$. To obtain information about the catalytic outcome, we have isolated and characterized the enone-containing complexes (S_M,R_C)-[(η^5-C_5Me_5)M(PROPHOS)(enone)][SbF_6]$_2$ (enone = MVK, M = Rh (**3**), Ir (**4**); enone = EVK, M = Ir (**5**)). Addition of an excess of enone to dichloromethane solutions of the aqua complexes (S_M,R_C)-[(η^5-C_5Me_5)M(PROPHOS)(H_2O)][SbF_6]$_2$, in the presence of 4 Å molecular sieves as water scavenger, affords the corresponding enone complexes **3**−**5** (eq 1).

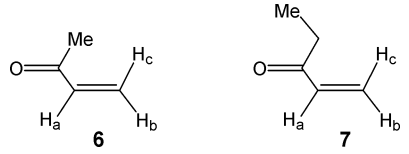


In the new complexes, the metal is a stereogenic center and the preparative reaction is completely diastereoselective because from −70 °C to RT only one set of sharp resonances was observed in the ^{1}H, ^{13}C, and ^{31}P NMR spectra. The complexes have been characterized by the usual analytical and spectroscopic means, including the molecular structure determination of compounds **4** and **5**.

The ^{1}H NMR spectra indicate the presence of the C_5Me_5, PROPHOS, and enone ligands in a 1:1:1 molar ratio. In particular, three groups of signals in the 4.4−6.3 ppm region together with one ^{13}C resonance around 215−220 ppm and a band at ca. 1670 cm^{-1} in the IR spectra denote the presence of the coordinated enone. The ^{31}P NMR spectra consist of two double doublets (**3**) or two doublets (**4**, **5**) with ^{103}Rh−^{31}P (∼130 Hz) and ^{31}P−^{31}P (∼40 Hz (**3**) and ∼11 Hz (**4**, **5**)) couplings.

The most striking feature of the ^{1}H NMR spectra is the strong shielding observed for the H_a and methyl protons of the coordinated enones (Scheme 2). The α vinyl proton resonance

Scheme 2. Labeling of Selected Protons of the Enones



appears about 1.7 ppm and the methyl protons about 0.8 ppm shifted in both cases toward high field with respect to the corresponding free molecule. The solid-state molecular structure satisfactorily explains these data (see below).

From a catalytic point of view, the conformation of the coordinated enone is an important feature, and in this regard, NOESY data give valuable information (Figure 1). NOE

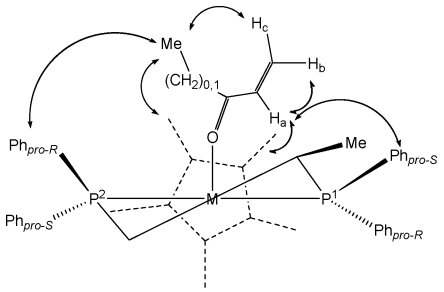


Figure 1. Selected NOEs for the enone complexes.

enhancements between the alkyl and the H_c protons as well as between H_a and H_b confirm an *s-trans* conformation for the enone ligand. On the other hand, a NOE relationship of H_a with the C_5Me_5 and the *ortho* protons of the *pro-S* phenyl ring of the P^1Ph_2 group, together with an enhancement of the *ortho* protons of the *pro-R* phenyl ring of the P^2Ph_2 group when the methyl enone protons are irradiated, indicates a *Z* configuration around the C═O bond, in an *S* configuration at the metal center with a λ conformation for the M-(PROPHOS) metallacycle. In this context, it is interesting to point out that an *E* configuration around the carbonyl bond of coordinated MVK was found in the ruthenium compound [(η^5-C_5H_5)Ru-(*R*,*R*-BIPHOP-F)(MVK)][SbF_6] recently reported by Kündig et al.[12] Finally, another NOE interaction was detected between the methyl group of the EVK ligand and the methyl protons of the C_5Me_5 ring.

Molecular Structure of Compounds 4 and 5. An X-ray structural analysis of complexes **4** and **5** was undertaken. A molecular representation of the cationic complexes is shown in Figure 2. Selected bond lenghts and angles are summarized in Table 3. In spite of the limited data quality of **5**, it can be clearly established that both cationic structures show similar general characteristics. In both half-sandwich complexes, the metals adopt the common pseudotetrahedral coordination mode, with the metal coordinated to the η^5-C_5Me_5 ring, to the two phosphorus atoms of the chelate PROPHOS diphosphine, and to the oxygen atom of the enone ligand. According to the ligand priority sequence,[13] the absolute configuration at the metal is *S* in both complexes. The five-membered metallacycle Ir−P(1)−C(24)−C(23)−P(2) adopts a λ conformation. Cremer and Pople ring puckering parameters (Q_2 = 0.487(3)

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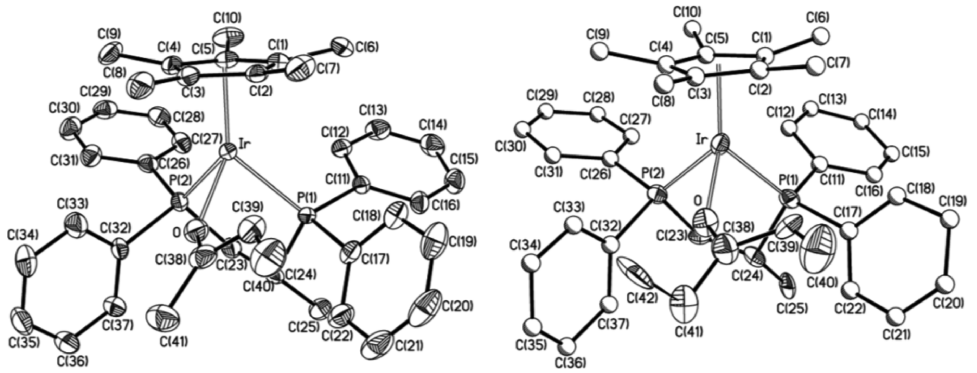

Figure 2. Molecular structures of the cation in complexes **4** and **5**. Hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Legnths (Å) and Angles (deg) for Complexes 4 and 5

	4	5		4	5
Ir−P(1)	2.3250(10)	2.326(8)	P(1)−Ir−G[a]	131.29(11)	132.6(6)
Ir−P(2)	2.3443(10)	2.346(9)	P(2)−Ir−O	81.67(9)	81.4(4)
Ir−O	2.145(2)	2.140(13)	P(2)−Ir−G[a]	130.32(11)	130.2(6)
Ir−G[a]	1.879(3)	1.857(18)	O−Ir−G[a]	128.64(13)	125.2(7)
O−C(38)	1.229(5)	1.24(3)	Ir−O−C(38)	138.6(3)	140(2)
C(38)−C(39)	1.468(7)	1.52(4)	O−C(38)−C(39)	120.2(4)	120(2)
C(39)−C(40)	1.293(7)	1.32(4)	C(38)−C(39)−C(40)	124.3(5)	126(3)
C(38)−C(41)	1.497(6)	1.52(3)	O−C(38)− C(41)	118.7(4)	117(3)
C(41)−C(42)		1.61(4)	C(39)−C(38)−C(41)	121.1(4)	123(2)
P(1)−Ir−P(2)	84.06(3)	84.0(2)	C(38)−C(41)−C(42)		106(2)
P(1)−Ir−O	83.10(8)	86.4(4)			

[a]G represents the centroid of the η^5-C_5Me_5 ring.

Å and ϕ_2 = 79.6(2)° in **4** and Q_2 = 0.45(2) Å and ϕ_2 = 78(1)° in **5**) are characteristic of a mixture between ^3E and $^3T_4$ conformations.[14] Puckering amplitude values (Q_2) are very similar and close to those observed in other [(η^5-C_5Me_5)M(PROPHOS)(L)] half-sandwich complexes.[6l,15]

The relative disposition of the enone groups within the metal coordination sphere, characterized by the G−Ir−O−C(38) torsion angle (−52.3(5)° in **4** and −53(3)° in **5**), corresponds to an intermediate situation between a parallel and an orthogonal arrangement of the enone and cyclopentadienyl planes. This disposition is suitable for the establishment of intramolecular CH/π interactions involving the α vinyl proton (H(39) in Figure 3) of the MVK and EVK ligands, in **4** and **5**, respectively, and the *pro-S* phenyl ring of the P(1)Ph_2 group. Table 4 collects the values of the structural parameters characteristic for CH/π interactions.[16] These interactions fix the M−O enone rotamer and place the α vinyl proton of the enone inside the electronic diamagnetic ring current of the

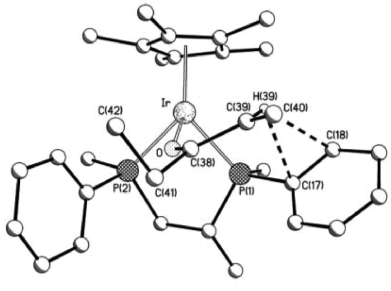

Figure 3. CH/π interactions in complex **5**.

Table 4. Selected Structural Parameters (Å, deg) Concerning CH/π Interactions for Complexes 4 and 5[a]

complex	H···G(Ph)	H···Ph (plane)	γ angle	C−H···C(17)/ C(18)	C− H···C(Ph)
4	3.12	2.89	22.2	2.99/2.95	3.39−3.82
5	2.87	2.70	29.6	2.77/2.81	3.13−3.56

[a]H···G(Ph) represents the distance from the H(39) atom to the centroid of the phenyl ring G(Ph); H···Ph is the separation from the H atom to the mean plane of the phenyl ring; γ angle is the angle between the G(Ph)−H vector and the normal to the phenyl ring; C−H···C is the contact distances between H atom and phenyl carbon atoms (≤3.05 Å); C−H···C(Ph) is the separation between H and the rest of the carbon atoms of the phenyl ring.

phenyl ring of the P(1)Ph_2 group (Figure 3), and most probably, they are also operating in solution, giving rise to the strong shielding observed for this proton in the ^{1}H NMR spectra. Furthermore, in this conformation the enone Cα-*si* face becomes shielded by the phenyl ring involved in the CH/π interactions.

On the other hand, the shift to higher energy of the enone methyl protons' resonance can be accounted for by assuming that these protons are affected by the electronic diamagnetic ring current of the *pro-R* phenyl ring of the P(2)Ph_2 group. The structural parameters observed in the solid state exclude any significant CH/π interaction between these two fragments.

The conformation proposed in solution for the coordinated enones, on the basis of NOE measurements, is comparable to that determined in the solid state by means of the X-ray diffraction structural study. Thus, both enones adopt an *s-trans* conformation and the configuration around the CO carbonyl bond is *Z*, placing the M(C_5Me_5) and vinyl groups at the same

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side of the double bond. In this disposition and with the M−O rotamer fixed by the CH/π interactions, the Cα-*si* face of the enone is shielded by the *pro*-*S* phenyl ring of the P^1Ph_2 group, and therefore, the diene attack would take place preferentially through the *re*-face, in good agreement with the catalytic outcome for the MVK/HCp reaction. The comparison of the structural parameters of the EVK ligand in **5** to those of its analogue MVK in **4** sheds light on the different catalytic behavior of **5**. The MVK ligand in **4** is essentially planar. The maximum deviation from the mean plane, 0.030(5) Å, corresponds to C(40). However, although the O−C(38)−C(39)−C(40)−C(41) skeleton of the EVK ligand in **5** is also essentially planar, the remaining CH_3 fragment significantly deviates from planarity (Figure 3). In fact, the C(41)−C(42) bond is almost perpendicular to the above-defined plane, the angle between the C(41)−C(42) vector and the normal to this plane being only 16(1)°. Probably, this methyl fragment adopts a similar disposition in solution because we have measured a NOE relationship between these protons and those of the C_5Me_5 ring (see above). In this conformation, this methyl hinders the approach of the diene through the Cα-*re* face, and therefore, both faces are similarly accessible by the diene. Consequently, even at low temperature, enantioselectivity is eroded and, according to the catalytic outcome, the attack via the Cα-*si* face is slightly preferred for this complex.

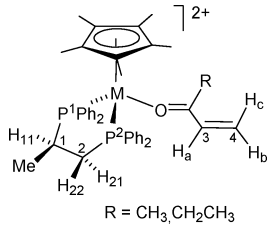
CONCLUSION

In summary, the aqua complexes **1** and **2** generate active systems that efficiently catalyze the Diels−Alder reaction between the vinyl ketones MVK and EVK and dienes in good *endo*/*exo* ratio and moderate to good enantioselectivity. From **1** and **2**, the catalyst−substrate intermediates (S_M,R_C)-$[(\eta^5\text{-}C_5Me_5)M(PROPHOS)(enone)][SbF_6]_2$ can be prepared in a completely diastereoselective manner. From detailed structural information about these catalyst−substrate intermediates, in both the solid state and solution, it is possible to explain the catalytic outcome. The coordinated enone adopts an *s*-*trans* conformation and the configuration around the CO double bond is *Z*. Particularly relevant is the existence of CH/π intramolecular interactions in the solid state that, according to NMR solution data, most probably remain in solution. These interactions fix the M−O enone rotamer and conform the disposition of the enone inside the chiral pocket of the catalyst defined by the $(C_5Me_5)M(PROPHOS)$ moiety. As a result, the Cα-*si* face of both MVK and EVK intermediates becomes hindered by a PROPHOS phenyl and, additionally, the CH_3 fragment of the enone EVK hampers approach of the diene through the opposite enantioface. All these structural data are in good agreement with the experimental catalytic results: while 89% ee's are achieved for the MVK/HCp reaction, only 4% ee is obtained for the related EVK/HCp system.

EXPERIMENTAL SECTION

General Comments. All solvents were dried over appropriate drying agents, distilled under argon, and degassed prior to use. Dienes and dienophiles were distilled prior to use. All preparations have been carried out under argon. Infrared spectra were obtained as KBr pellets with a Perkin-Elmer Spectrum One FT-IR spectrophotometer. Carbon, hydrogen, and nitrogen analyses were performed using a Perkin-Elmer 240C microanalyzer. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AV 500 (500.13 MHz), AV-400 (400.16 MHz), or 300 ARX (300.10 MHz) spectrometer. Chemical shifts are expressed in ppm upfield from $SiMe_4$ or 85% H_3PO_4 (^{31}P). NOESY and ^{13}C, ^{31}P, ^1H correlation spectra were obtained using standard procedures. Gas chromatography was performed on Hewlet-Packard 3398 and 6890 Series gas chromatographs equipped with a split-mode capillary injection system and flame ionization detectors using HP Ultra-1 (25 m × 0.32 mm), CP-Chirasil-DEX CB (25 m × 0.25 mm), and Beta Dex 120 (30 m × 0.25 mm) columns. (S_M,R_C)-$[(\eta^5\text{-}C_5Me_5)M(PROPHOS)(H_2O)][SbF_6]_2$ (M = Rh (**1**), Ir (**2**)) were prepared according to published procedures.[17]

Scheme 3. Labeling of the Cation of the Complexes for NMR Assignments



Preparation of (S_M,R_C)-$[(\eta^5\text{-}C_5Me_5)M(PROPHOS)(MVK)][SbF_6]_2$ (M = Rh (3), Ir (4)) and (S_M,R_C)-$[(\eta^5\text{-}C_5Me_5)Ir(PROPHOS)(EVK)][SbF_6]_2$ (5). At −20 °C, under argon, to a solution of the corresponding (S_M,R_C)-$[(\eta^5\text{-}C_5Me_5)M(PROPHOS)(H_2O)][SbF_6]_2$ (0.09 mmol) complex in CH_2Cl_2 (4 mL) were added enone (0.9 mmol) and 4 Å molecular sieves (100.0 mg). The resulting suspension was stirred for 20 min and then was filtered through a cannula. The filtrate was concentrated to ca. 3 mL. The slow addition of 20 mL of dry *n*-hexane afforded yellow crystals, which were filtered off, washed with *n*-hexane, and vacuum-dried. Recrystallization from CH_2Cl_2/*n*-hexane yielded pure samples of the complexes.

(S_{Rh},R_C)-$[(\eta^5\text{-}C_5Me_5)Rh(PROPHOS)(MVK)][SbF_6]_2$ (3). Yield: 85%. Anal. Calcd for $C_{41}H_{47}F_{12}RhOP_2Sb_2$: C, 41.3, H, 3.9. Found: C, 41.4; H, 3.9. IR (KBr, cm^{-1}): ν(CO) 1664 (m), $\nu(SbF_6)$ 659 (s). ^1H NMR (400.16 MHz, CD_2Cl_2, −50 °C): δ 7.91−7.26 (m, 20H, Ph), 6.07 (d, J = 17.7 Hz, 1H, H_c), 6.03 (d, J = 10.8 Hz, 1H, H_b), 4.65 (dd, J = 17.6, 10.8 Hz, 1H, H_a), 3.37 (dt, J = 53.2, 14.2 Hz, 1H, H_{22}), 2.59 (m, 1H, H_{11}), 2.55 (m, 1H, H_{21}), 1.48 (s, 3H, $COCH_3$), 1.42 (m, 15H, C_5Me_5), 1.19 ppm (m, 3H, Me). ^{13}C NMR (100.61 MHz, CD_2Cl_2, −50 °C): δ 215.57 (CO), 141.87 (C^4), 131.83 (C^3), 134.44−119.42 (24C, Ph), 99.17 (C_5Me_5), 31.91 (Me), 31.02 (dd, J(PC) = 37.0, 6.8 Hz, C^1), 30.35 (dd, J(PC) = 38.0, 13.5 Hz, C^2), 26.20 ($COCH_3$), 14.36 (dd, J(PC) = 18.0, 3.0 Hz, Me), 10.07 ppm (C_5Me_5). ^{31}P NMR (161.96 MHz, CD_2Cl_2, −20 °C): δ 74.51 (dd, $J(RhP^1)$ = 130.2 Hz, $J(P^1P^2)$ = 39.8 Hz, P^1), 50.71 ppm (dd, $J(RhP^2)$ = 131.3 Hz, P^2).

(S_{Ir},R_C)-$[(\eta^5\text{-}C_5Me_5)Ir(PROPHOS)(MVK)][SbF_6]_2$ (4). Yield: 79%. Anal. Calcd for $C_{41}H_{47}F_{12}IrOP_2Sb_2$: C, 38.4, H, 3.7. Found: C, 38.3; H, 3.9. IR (KBr, cm^{-1}): ν(CO) 1676 (m) $\nu(SbF_6)$ 659 (s). ^1H NMR (400.16 MHz, CD_2Cl_2, −70 °C): δ 7.91−7.23 (m, 20H, Ph), 6.14 (d, J = 17.1 Hz, 1H, H_c), 6.07 (d, J = 10.7 Hz, 1H, H_b), 4.62 (dd, J = 18.1, 11.2 Hz, 1H, H_a), 3.26 (dt, J = 53.9, 10.8 Hz, 1H, H_{22}), 2.51 (m, 1H, H_{11}), 2.42 (m, 1H, H_{21}), 1.56 (s, 3H, $COCH_3$), 1.44 (m, 15H, C_5Me_5), 1.20 ppm (m, 3H, Me). ^{13}C NMR (100.61 MHz, CD_2Cl_2, −50 °C): δ 216.60 (CO), 141.92 (C^4), 132.90 (C^3), 134.81−118.43 (24C, Ph), 99.17 (C_5Me_5), 30.98 (dd, J(PC) = 36.8, 7.7 Hz, C^1), 30.35 (m, C^2), 26.37 (Me), 14.48 ($COCH_3$), 9.66 ppm (C_5Me_5). ^{31}P NMR (161.96 MHz, CD_2Cl_2, −50 °C): δ 45.74 (d, $J(P^1P^2)$ = 11.6 Hz, P^1) 28.49 ppm (d, P^2).

(S_{Ir},R_C)-$[(\eta^5\text{-}C_5Me_5)Ir(PROPHOS)(EVK)][SbF_6]_2$ (5). Yield: 83%. Anal. Calcd for $C_{42}H_{49}F_{12}IrOP_2Sb_2$: C, 38.9, H, 3.8. Found: C, 39.0; H, 3.3. IR (KBr, cm^{-1}): ν(CO) 1677 (m) $\nu(SbF_6)$ 652 (s). ^1H NMR (400.16 MHz, CD_2Cl_2, −70 °C): δ 7.86−7.20 (m, 20H, Ph), 6.29 (d, J = 17.7 Hz, 1H, H_c), 6.03 (d, J = 10.8 Hz, 1H, H_b), 4.42 (dd, J = 17.7, 11.1 Hz, 1H, H_a), 3.28 (dt, J = 53.2, 14.2 Hz, 1H, H_{22}), 2.43 (m, 1H, H_{11}), 2.37 (q, J = 8.7 Hz, 2H, $COCH_2$), 2.34 (m, 1H, H_{21}), 1.41 (m, 15H, C_5Me_5), 0.83 (t, J = 7.0 Hz, 3H, Me), 0.23 ppm (t, J = 7.3 Hz, 3H, $COCH_2CH_3$). ^{13}C NMR (100.61 MHz, CD_2Cl_2, −50 °C): δ 220.54 (CO), 140.79 (C^4), 131.16. (C^3), 136.60−118.34 (24C, Ph), 99.68 (C_5Me_5), 33.12 (dd, J(PC) = 40.6, 7.7 Hz, C^1), 33.16

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(CH_2CH_3), 31.41 (dd, J(PC) = 38.3, 9.2 Hz, C^2), 14.34 (Me), 9.07 (CH_2CH_3), 8.74 ppm (C_5Me_5). ^{31}P NMR (161.96 MHz, CD_2Cl_2, −50 °C): δ 45.88 (d, $J(P^1P^2)$ = 11.0 Hz, P^1), 28.99 ppm (d, P^2).

General Procedure for Catalytic Diels−Alder Reactions between Enones and Dienes. The corresponding (S_M,R_C)-[(η^5-C_5Me_5)M(PROPHOS)(H_2O)][SbF_6]$_2$ complex (0.025 mmol, 5 mol %) was dissolved in 3 mL of dry CH_2Cl_2 under argon at −20 °C, and 100 mg of activated 4 Å molecular sieves and the enone (0.500 mmol) were added. After 15 min the mixtures were introduced in a cryogenic bath at the appropriate temperature, and diene (2.5 mmol) in 1 mL of CH_2Cl_2 was added. The reaction was monitored by gas chromatography (GC) and quenched, by addition of 0.1 mL of MeCN, at the specified times. Yields and *endo/exo* ratios were determined by GC analysis. Finally, the mixture was concentrated to ca. 0.3 mL, filtered through silica gel, and washed with *n*-pentane/diethyl ether (9:1). Liquids were removed under vacuum (ice bath) before the determination of the enantiomeric purity. Enantiomeric excesses were determined by gas chromatography (for detailed procedures see the Supporting Information). The absolute configuration of the major adduct was assigned by comparison with literature data.[12]

Crystal Structure Determination of Complexes 4 and 5. X-ray diffraction data were collected at 100(2) K with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using narrow ω rotation (0.3°) on a Bruker SMART APEX CCD diffractometer. Intensities were integrated and corrected for absorption effects with the SAINT-PLUS program.[18] The structures were solved by direct methods with SHELXS-97.[19] Refinement, by full-matrix least-squares on F^2, was performed with SHELXL-97.[20] Hydrogen atoms were included in calculated positions and defined with displacement and positional riding parameters. In both structures, in addition to the internal configuration reference of the (*R*)-PROPHOS ligand, the Flack parameter has been refined as a check of the correct absolute structure determination.[21] Particular details concerning the presence of solvent and specific refinement are listed below.

Crystal data for **4**: $C_{41}H_{47}F_{12}IrOP_2Sb_2{\cdot}CH_2Cl_2$; M = 1366.35; yellow prismatic block, 0.201 × 0.168 × 0.158 mm^3; monoclinic; $P2_1$; a = 13.1907(7) Å, b = 12.8417(7) Å, c = 14.1613(8) Å; β = 99.1190(10)°; Z = 2; V = 2368.5(2) Å^3; D_c = 1.916 g/cm^3; μ = 4.195 mm^{-1}; min. and max. absorption correction factors 0.845 and 1.000; $2\theta_{max}$ = 57.12°; 38 771 collected reflections, 11 150 unique reflections [R_{int} = 0.018]; number of data/restraints/parameters 11 150/1/566; final GoF 1.037; R1 = 0.0233 [11 029 reflections, $I > 2\sigma(I)$]; wR2 = 0.0594 for all data; Flack parameter x = 0.003(2); largest difference peak 2.34 e/Å^3.

Crystal data for **5**: $C_{42}H_{49}F_{12}IrOP_2Sb_2{\cdot}CH_2Cl_2$; M = 1380.38; yellow prism 0.094 × 0.047 × 0.023 mm^3; monoclinic; $P2_1$; a = 13.132(4) Å, b = 13.166(4) Å, c = 14.039(5) Å, β = 96.429(5)°; Z = 2; V = 2412.0(13) Å^3; D_c = 1.901 g/cm^3; μ = 4.120 mm^{-1}; min and max. absorption correction factors 0.634 and 0.846; $2\theta_{max}$ = 50.78°; 13 405 collected reflections, 6380 unique reflections [R_{int} = 0.091]; number of data/restraints/parameters 6380/23/341; final GoF 1.047; R1 = 0.0733 [4329 reflections, $I > 2\sigma(I)$]; wR2 = 0.175 for all data; Flack parameter x = 0.025(17). Complex **5** tends to form twinned crystals, not very appropriate for X-ray diffraction; unfortunately, several crystals were tested with no success. Finally a tiny anisotropic crystal allows us to solve the structure. However, the high value of the second parameter of the weighting scheme and the presence of some very negative reflections point out that the chosen sample was also partially twinned. The limited quality of the data does not allow proper anisotropic refinement of all non-hydrogen atoms; carbon atoms of C_5Me_5 ligands and methyl groups, and fluorine atoms of the counterions have been refined only with isotropic thermal parameters. Geometrical restraints were included for SbF_6 counterions. A maximal residual density peak of 3.26 e/Å^3 was observed at the end of the refinement; it was located close to the metal atom and has no chemical sense.

■ ASSOCIATED CONTENT

Supporting Information

Analytical procedures, data of adducts, and X-ray crystallographic information files containing full details of the structural analysis of complexes **4** and **5** (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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