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Enantioselective catalysts based on the chiral fragment (η^5-C_5Me_5)Ir(Prophos) for Diels–Alder reactions

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ABSTRACT

The aqua complex (S_{Ir},R_C)–[(η^5-C_5Me_5)Ir(Prophos)(H_2O)][SbF_6]$_2$ [Prophos = (*R*)-propane-1,2-diyl-bis(diphenylphosphane)] is an active precursor for the asymmetric Diels–Alder reaction of acyclic enals with cyclopentadiene, 2,3-dimethylbutadiene and isoprene. Enantioselectivities up to 78% ee are achieved. The intermediate Lewis acid-dienophile complex (S_{Ir},R_C)–[(η^5-C_5Me_5)Ir(Prophos)(ethyl acrolein)][SbF_6]$_2$ has been isolated and completely characterized, including the X-ray crystal structure determination. Structural parameters indicate that the disposition of the coordinated dienophile is controlled by CH/π attractive interactions established between a phenyl group of the Prophos ligand and the aldehyde proton of the coordinated enal. Proton NMR data indicate that these interactions are maintained in solution. From diffractometric and spectroscopic data, the origin of the enantioselectivity is discussed.

1. Introduction

Asymmetric catalysis is an indispensable and highly valuable tool for the synthesis of enantioenriched intermediates and products [1–3]. 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 [4–6]. In this methodology, coordination of the alkene to the metal lowers the barrier energy of the reaction and an enantiopure chiral ligand, also coordinated to the metal, is the source of chirality. In some instances, the metal becomes a chiral center after the coordination of the ligand as, for example, in half-sandwich three-legged piano stool complexes containing chiral bidentate ligands of C_1 symmetry (Scheme 1) [7].

During the last years, examples of one point binding catalysts for the asymmetric DA have been developed by the groups of Kündig [8–16], Faller [17–24] Davies [25–34] and ourselves [35–50]. When the alkene was an enal, the CHO group, apart from activating the double C=C bond, provides an anchoring atom able for the coordination to the metal. By far, the most studied system was the reaction between methacrolein and cyclopentadiene and, in particular, we have shown that the aquo complexes [(η^5-C_5Me_5)M(Prophos)(H_2O)][SbF_6]$_2$ [Prophos = (*R*)-propane-1,2-diyl-bis(diphenylphosphane); M = Ir (**1**), Rh (**2**)] are active catalyst precursors for this reaction [35–45]. However, the catalytic activity of half-sandwich complexes with acyclic α,β-unsaturated enals other than methacrolein has been much less studied. At this respect, we have investigated the reaction of acrolein with cyclopentadiene catalyzed by cations of formula [(η^5-C_5Me_5)Rh(N–N*)(H_2O)]$^{2+}$ or [(η^6-*p*-cymene)Ru(N–N*)(H_2O)]$^{2+}$, where N–N* is an enantiopure chiral pyridilimino ligand, obtaining good *exo:endo*-selectivity and poor enantioselectivity [38], Kündig's group has reported that the ruthenium complex [(η^5-C_5H_5)Ru(*R*,*R*-BIPHOP-F)(acetone)][SbF_6]$_2$ [(*R*,*R*-BIPHOP-F) = 1,2-bis[(pentafluorophenyl)phosphanyloxy]-1,2-diphenyl)] catalyzes efficiently the reaction between ethyl acrolein and cyclopentadiene [8] and Faller has achieved good yield and enantioselectivity for the latter reaction by using half-sandwich chiral Ru(II) and Os(II) complexes with (*S*)-BINPO [2,2′-(diphenyl phosphino-1,1′-binaphthyl)] ligand as catalyst [19,21].

Herein we report on: (i) the catalytic asymmetric DA reaction of enals **3**–**7** (Scheme 2) with cyclopentadiene using the aqua complex (S_{Ir},R_C)–[(η^5-C_5Me_5)Ir(Prophos)(H_2O)][SbF_6]$_2$ (**1**) as catalyst precursor; (ii) the DA reaction of other acyclic dienes with methacrolein (see Table 2) catalyzed by **1** and by the rhodium

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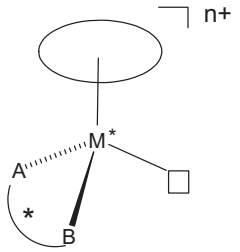


Scheme 1. Chiral fragment $[(\eta^n\text{-ring})M(AB^*)]^{n+}$.

analogue (S_{Ir},R_C)–$[(\eta^5\text{-}C_5Me_5)Rh(Prophos)(H_2O)][SbF_6]_2$ (**2**); (iii) the isolation and spectroscopic and diffractometric characterization of the intermediate (S_{Ir},R_C)–$[(\eta^5\text{-}C_5Me_5)Ir(Prophos)(ethyl\ acrolein)][SbF_6]_2$.

2. Experimental

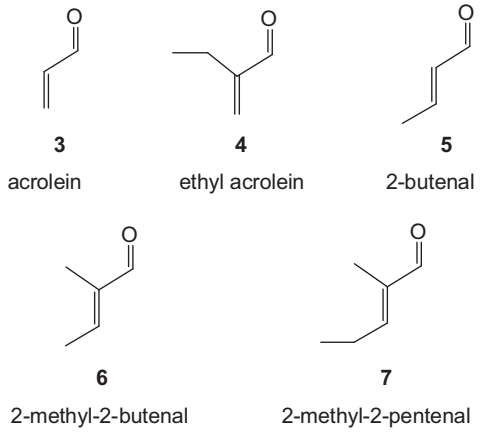
2.1. Material and instrumentation

All solvents were dried over appropriate drying agents, distilled under argon and degassed 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 240 B microanalyzer. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker AV-300, Bruker AV-400 or Bruker AV-500 spectrometers. Chemical shifts are expressed in ppm upfield from $SiMe_4$ or 85% H_3PO_4 (^{31}P). NOESY and ^{13}C, ^{31}P, ^{1}H correlation spectra were obtained using standard procedures. Gas chromatography was performed on Hewlet-Packard 3398 Series gas chromatograph equipped with a split-mode capillary injection system and flame ionization detectors using HP Ultra-1 (25 m × 0.32 mm).

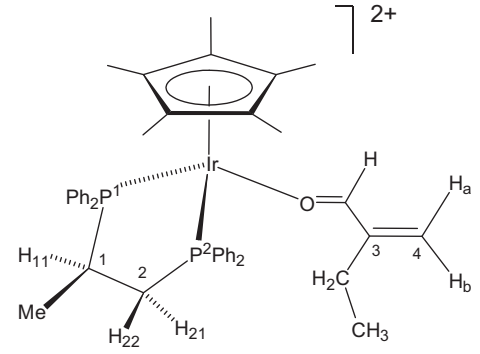
Complexes (S_M,R_C)–$[(\eta^5\text{-}C_5Me_5)M(Prophos)(H_2O)][SbF_6]_2$ (M = Ir (**1**), Rh (**2**)), were prepared using literature procedures [51,52].

2.2. Catalytic procedure

To the complex (S_{Ir},R_C)–$[(\eta^5\text{-}C_5Me_5)Ir(Prophos)(H_2O)][SbF_6]_2$ (0.025 mmol, 5 mol%) dissolved in CH_2Cl_2 (3 mL), 100 mg of activated 4 Å molecular sieves and the corresponding freshly distilled α,β-unsaturated enal (0.50 mmol) were added. The mixture was stirred for 15 min at −20 °C. Then it was introduced in a cryogenic bath at the appropriate temperature and a solution of the diene (3.00 mmol) in CH_2Cl_2 (1 mL) was added. The reaction was



Scheme 2. α,β-Unsaturated aldehydes employed.



Scheme 3. Labeling of the cation of **20** for NMR assignments.

monitored by gas chromatography (GC) and quenched, by addition of excess of Me_4NCl in CH_2Cl_2, at the specified times. Conversion and *exo*/*endo* 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/diethylether (9/1, v/v). Liquids were removed under vacuum before the determination of the enantiomeric purity. Enantioselectivity was determined as indicated in the footnote of Table 1.

2.3. Preparation of (S_{Ir},R_C)–$[(\eta^5\text{-}C_5Me_5)Ir(Prophos)(ethyl\ acrolein)][SbF_6]_2$ (**20**)

Under argon, to a solution of **1** (114.0 mg, 0.091 mmol) in CH_2Cl_2 (4 mL), excess of ethyl acrolein (88.1 μL, 0.900 mmol) and 4 Å molecular sieves (100.0 mg) were added. The resulting yellow suspension was stirred for 20 min, at −20 °C and then was filtered through a cannula. The filtrate was concentrated to ca. 1 mL. The slow addition of 10 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 yields pure of **20**. Yield: 62.5 mg, 59% (Scheme 3).

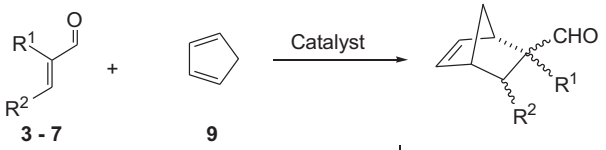
^{1}H NMR (400 MHz, CD_2Cl_2, −50 °C): δ = 7.90–7.22 (m, 20H, Ph), 7.28 (s, 1H, CHO), 6.23 (s, 1H, H_b), 5.73 (s, 1H, H_a), 3.56 (dddd, J = 48.3, 15.6, 11.2, 4.8 Hz, 1H, H_{22}), 2.80 (m, 1H, H_{11}), 2.67 (m, 1H, H_{21}), 1.42 (m, 18H, C_5Me_5, Me) 1.37 (m, 2H, CH_2CH_3). 0.71 ppm (t, J = 7.4 Hz, 3H, CH_2CH_3). ^{13}C NMR (100.61 MHz, CD_2Cl_2, −50 °C): δ = 209.25 (CHO), 149.69 (C^3), 147.43 (C^4), 134.05–101.32 (Ph), 101.43 (t, J(P,C) = 1.7 Hz, C_5Me_5), 34.36 (dd, J(P,C) = 40.7, 12.3 Hz, C^2), 31.60 (dd, J(P,C) = 36.9, 7.7 Hz, C^1), 19.67 (CH_2CH_3), 15.16 (dd, J(P,C) = 17.4, 4.3 Hz, Me), 10.68 (CH_2CH_3), 8.77 ppm (C_5Me_5). ^{31}P NMR (161.96 MHz, CD_2Cl_2, −25 °C): δ = 48.17 (d, $J(P^1P^2)$ = 8.3 Hz, P^1), 27.64 ppm (d, P^2). IR (KBr pellets, cm^{-1}): ν(CO) 1585m, $\nu(SbF_6)$ 659s. Anal. Calcd for $C_{42}H_{49}F_{12}IrOP_2Sb_2$: C, 38.9; H, 3.8. Found: C, 39.3; H, 3.6.

2.4. X-ray crystallography

X-ray diffraction data for **20** were collected at 100(2) K using narrow ω rotation (0.3°) on a Bruker SMART APEX CCD diffractometer (Mo-Kα graphite-monochromated radiation, λ = 0.71073 Å). Images were processed with SAINT+ [53] and data were corrected for absorption by numerical methods based on the crystal face indexing.

The structure was solved by direct methods with SHELXS-97 [54]. Refinement, by full-matrix least-squares on F^2, was performed with SHELXL-97 [55]. Anisotropic displacement parameters were included for all non-H non disordered atoms. Hydrogen atoms were included in calculated positions and refined with displacement and positional riding parameters. Additionally to the internal configuration reference of the Prophos ligand, the Flack parameter has

Table 1
DA reaction of α,β-unsaturated enals with cyclopentadiene catalyzed by **1**[a].



	10	11	12	13	14
R^1	H	Et	H	Me	Me
R^2	H	H	Me	Me	Et

Entry	Enal	Adduct	T (°C)	t (h)	Conv. (%)[b,c]	Isomer ratio (*exo*/*endo*) (%)[c]	ee (%)[d,e]
1	**3**	**10**	RT	0.5	70	55/45	14(−)/10(*S*)
2	**3**	**10**	0	1	82	50/50	14(−)/5(*S*)
3	**3**	**10**	−20	1	70	46/54	10(−)/rac
4	**3**	**10**	−50	7	85	30/70	rac/6(*R*)
5	**4**	**11**	0	1	91	97/3	64(*S*)/(−)
6	**4**	**11**	−20	1	87	97/3	71(*S*)/(−)
7	**4**	**11**	−50	24	87	98/2	78(*S*)/(−)
8	**5**	**12**	0	24	92	70/30	18(−)/rac
9	**5**	**12**	−20	66	88	71/29	15(−)/10(*R*)
10	**6**	**13**	RT	48	92	97/3	57/(−)
11	**6**	**13**	0	102	74	98/2	58/(−)
12	**6**	**13**	−20	120	56	99/1	64/(−)
13	**7**	**14**	0	168	69	98/2	41/(−)
14	**7**	**14**	−20	148	21	98.5/1.5	48/(−)

[a] Reaction conditions: catalyst 0.025 mmol (5% mol), enal 0.5 mmol, 100 mg of 4 Å molecular sieves and HCp 3 mmol, in 4 mL of CH_2Cl_2.
[b] Based on enal.
[c] Determined by GC.
[d] Determined by acetalization with (−)-(2R,4R)-2,4-pentanediol and ^{1}H NMR analysis.
[e] The absolute configuration was established by comparison with literature data [57,58].

been refined as a check on the correct absolute structure determination [56]. Static disorder has been observed in a phenyl group, in the dichloromethane solvent molecule and in the terminal methyl group of the ethyl acrolein. Disordered atoms have been included in the model in two different positions with complementary occupancy factors, and have been refined with isotropic thermal parameters. Bond lengths in the two disordered C–C bonds of the ethyl acrolein ligand (C(41)–C(42A) and C(41)–C(42B)) have been restrained to be identical. Hydrogen atoms of the solvent molecule have not been included in the model. Information concerning crystallographic data collection and structure refinement is summarized in Table 1S (Supplementary material). CCDC-969379 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

3. Results and discussion

3.1. Diels–Alder reaction of the α,β-unsaturated enals 3–7 with cyclopentadiene

The complex (S_{Ir},R_C)–$[(\eta^5\text{-}C_5Me_5)Ir(Prophos)(H_2O)][SbF_6]_2$ (**1**) was tested as catalyst precursor for the DA reaction between the α,β-unsaturated enals **3**–**7** (Scheme 2) and cyclopentadiene (**9**). Table 1 lists a selection of the results together with the reaction conditions employed. The collected results are the average of at least two comparable reaction runs.

The iridium complex efficiently catalyzes the DA reactions; high conversions were achieved in all cases. However, the reaction is sensible to the enal, β-unsubstituted enals being much more reactive than β-substituted ones. Thus, for example, while for enal **4** a conversion of 91% was achieved after 1 h of reaction (entry 5) for enal **5**, 24 h of treatment, under similar conditions, were necessary to achieve 92% of conversion (entry 8). On the other hand, α-substitution strongly affects the *exo*–*endo* selectivity: *exo* isomers were readily favored for α-substituted enals **4**, **6**, and **7** (entries 5–7 and 10–14) while for α-unsubstituted enals **3** and **5** smaller or no *exo* preference was observed (entries 1–4 and 8, 9). Poor to good enantomeric excesses were achieved. Again, the substitution pattern strongly affects the catalytic outcome. Thus while α-substituted ethyl acrolein (**4**), 2-methyl-2-butenal (**6**), and 2-methyl-2-pentenal (**7**) give ee values ranging from 48% to 78% (−20 °C, entries 5, 11, and 14) enantioselectivities smaller than 18% ee were obtained for the α-unsubstituted enals acrolein (**3**) and 2-butenal (**5**). As expected, lowering temperature slows down reaction rates and, in general, increases ee. However, the influence of temperature changes on the ee for enals **3** and **5** is more complex, inversion of the configuration of the *endo* isomer occurring in some cases (entry 4). The reasons of this influence remain unclear.

3.2. Diels–Alder reactions of methacrolein with acyclic dienes

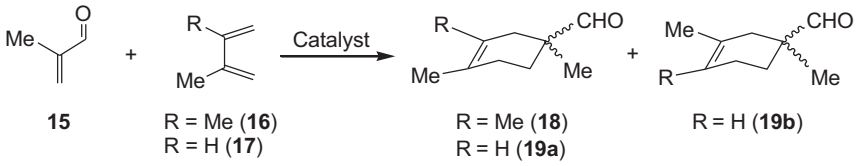
We also tested the DA reaction between methacrolein (**15**) and acyclic dienes 2,3-dimethylbutadiene (**16**) and isoprene (**17**), using the aqua complexes $[(\eta^5\text{-}C_5Me_5)M(Prophos)(H_2O)][SbF_6]_2$ (M = Ir (**1**), Rh (**2**)) as catalyst precursors. A list of the obtained results is collected in Table 2. Both complexes are active but to get good conversions, at −20 °C, reactions take several days. At this temperature, moderate enantioselectivities are obtained (about 60% ee). Lowering temperature slightly improves enantioselectivity (63%, 68% ee, entries 2 and 5, respectively). For asymmetrical isoprene (**17**) the 1,4-dimethyl regioisomer **19a** is preferentially obtained (95%).

Under the reaction conditions depicted in Table 1, neither **1** nor **2** catalyze the DA reaction between methacrolein and cyclohexadiene.

3.3. Isolation of the intermediate (S_{Ir},R_C)–$[(\eta^5\text{-}C_5Me_5)Ir(Prophos)(ethyl\ acrolein)][SbF_6]_2$ (20)

It is commonly assumed that the pathway for the DA reaction between enals and dienes catalyzed by one-point-binding half-sandwich transition metal complexes (Scheme 4) involves the diene attack to the coordinated enal (step 1) followed by displacement of the coordinated adduct by the enal (step 2). Therefore, to

Table 2
DA reaction of methacrolein with acyclic dienes[a].



15 R = Me (**16**), R = H (**17**) R = Me (**18**), R = H (**19a**) R = H (**19b**)

Entry	Catalyst	Diene	Adduct	T (°C)	t (h)	Conv. (%)	(ee) (%)
1	**1**	**16**	**18**	−20	72	92	60
2	**1**	**16**	**18**	−50	337	74	68
3	**1**	**17**	**19**	−20	72	91.5[b]	42
4	**2**	**16**	**18**	−20	95	85	60
5	**2**	**16**	**18**	−50	353	65	63

[a] For reaction conditions and determination of results, see footnote in Table 1.
[b] Isomer ratio **19**a/**19**b:95/5.

get a deeper insight into the mechanism of the catalytic reaction, we attempted to characterize the involved metal–enal intermediate complex.

At −20 °C, addition of an excess of ethyl acrolein to a solution of the aqua-complex **1** in dichlorometane, in the presence of 4 Å molecular sieves as water scavenger, affords complex **20** in good yield (Eq. 1).

$$[(\eta^5\text{-}C_5Me_5)]Ir(Prophos)H_2O)][SbF_6]_2 + \underset{\mathbf{4}}{\text{ethyl acrolein}} \xrightarrow[-H_2O]{CH_2Cl_2,\,4\text{Å MS}} \underset{\mathbf{20}}{[(\eta^5\text{-}C_5Me_5)]Ir(Prophos)(\mathbf{4})][SbF_6]_2} \quad (1)$$

The preparative route is completely diastereoselective: from −70 °C to RT only one set of sharp resonances was observed in the ^{1}H, ^{13}C and ^{31}P NMR spectra of complex **20**, indicating that only one diastereomer was obtained. The complex was characterized by analytiscal and spectroscopic means, including two dimensional homonuclear (COSY, NOESY) and heteronuclear (^{31}P–H, ^{13}C–H) correlations. In addition, its crystal structure was determined by X-ray diffractometric methods (see below).

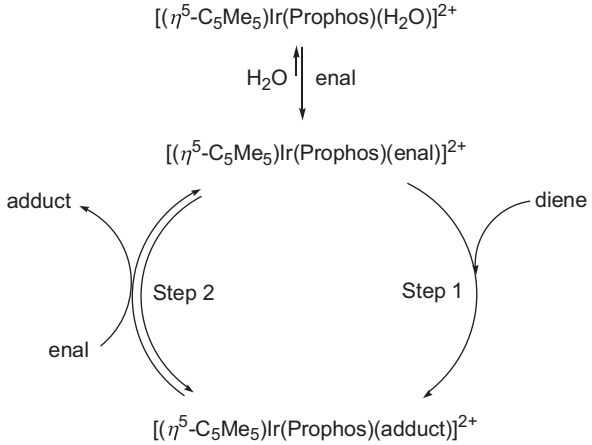
The ^{1}H and ^{13}C NMR spectra, besides the peaks of the Prophos and C_5Me_5 groups, show resonances corresponding to coordinated ethyl acrolein. Notably, the aldehyde proton is strongly shielded: it resonates at 7.28 ppm, about 2.3 ppm shifted to higher field with respect to the corresponding free molecule resonance. A peak at 209.25 ppm, in the ^{13}C NMR spectrum, is attributed to the formyl carbon. Moreover, an intense υ(CO) band at ca. 1585 cm^{-1}, in the IR spectrum, confirms the presence of coordinated enal. The ^{31}P NMR spectrum consists of two doublets centered at 27.64 and 48.17 ppm with a $J(P^1P^2)$ of 8.3 Hz.

On the other hand, the ^{1}H–^{1}H NOESY spectrum of complex **20** give us important stereochemical information. It shows NOE relationships between the H_a and formyl protons and between the H_b and CH_3 protons of the ethyl group of the coordinated ethyl acrolein (see Scheme 3). These correlations strongly indicate an *s-trans* conformation for the enal ligand. Moreover, irradiation of the H_{11} proton enhances the formyl and methylene ethyl group protons. With the ethyl acrolein in an *s-trans* conformation, the latter NOE relationships are only compatible with a λ conformation for the Ir–P^1–C^1–C^2–P^2 metallacycle together with an *S* configuration for the iridium atom, according to the priority sequence η^5-C_5Me_5 > P^1 > P^2 > O [59], and an *E* configuration around the carbonyl double bond of the enal.

3.4. Molecular structure of compound *20*

Single crystals, suitable for X-ray diffraction analysis, were obtained from CH_2Cl_2/*n*-hexane solutions of complex **20**. Fig. 1 shows a view of the cation of the complex and the most relevant bond lengths and angles are collected in Table 3.

The metal environment exhibits the "three-legged piano-stool" geometry commonly encountered for half-sandwich d^6 cations: an η^5-C_5Me_5 ring occupies three *fac* coordination positions and the two phosphorous atoms of the Prophos and the oxygen atom of the ethyl acrolein ligand complete the coordination sphere. According to the ligand priority sequence η^5-C_5Me_5 > P(1) > P(2) > O [59] the absolute configuration at the metal is *S*. The five-membered metallacycle Ir–P(1)–C(24)–C(23)–P(2) exhibits a λ conformation.



Scheme 4. Plausible catalytic cycle.

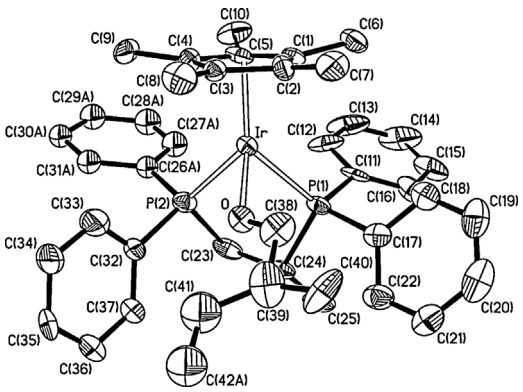


Fig. 1. Molecular structure of the cation of **20**. Only one position of disordered parts (C(26)–C(32) phenyl ring and C(42) atom) has been represented. Hydrogen atoms have been omitted for clarity.

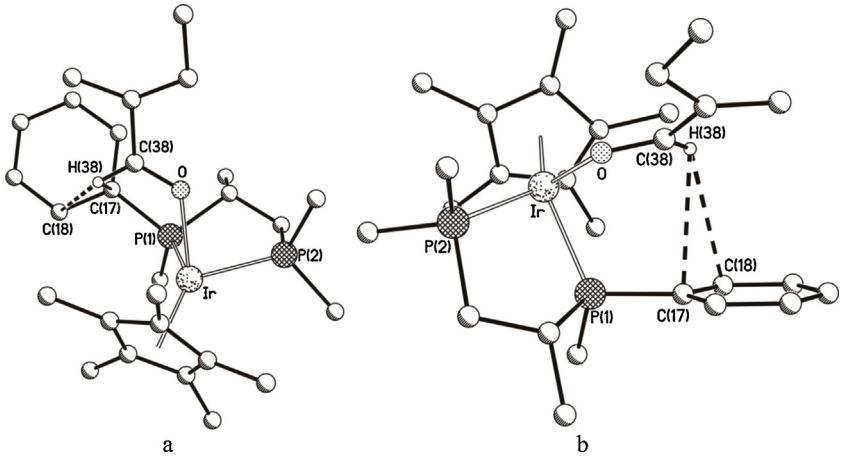
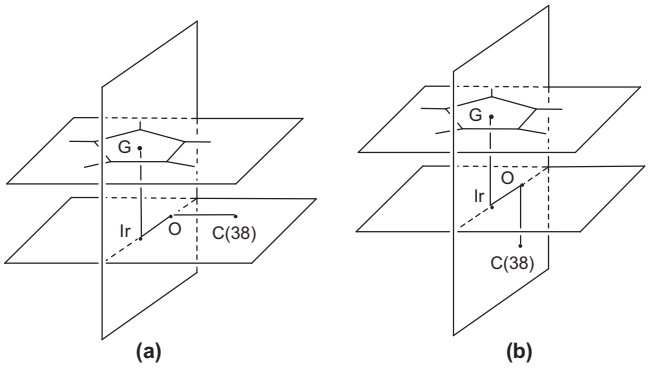


Fig. 2. Schematic representation of CH/π interactions observed in complex **20**: (a) view perpendicular to the phenyl plane; (b) view nearly parallel to the phenyl plane.

Cremer and Pople ring puckering parameters (Q_2 = 0.466(9) Å and ϕ_2 = 75.5(6)°) [60] are characteristic for an envelope ^3E conformation. The observed puckering amplitude value (Q_2) is close to those reported in other related [(η^5-C_5Me_5)Ir(Prophos)L]$^{2+}$ half-sandwich complexes with coordinated methacrolein [52] or enones [49].

The conformation proposed in solution for the ethyl acrolein, on the basis of NOESY measurements, is identical to that determined in the solid state. Thus, the enal adopts an *s-trans* conformation with respect to the C(38)–C(39) single bond and an *E* configuration around the double O–C(38) bond. The O–C(38)–C(39)–C(40) skeleton of the ethyl acrolein is essentially planar. The terminal methyl group (C(42)) is disordered over two positions with complementary occupancy factors; one of them corresponds to a planar disposition while the other position lies 1.11(2) Å out of the mean plane determined by the remaining O, C(38), C(39), C(40) and C(41) atoms. The relative disposition of the enal fragment within the metal coordination sphere can be characterized by the G–Ir–O–C(38) torsion angle that relates the plane of the ethyl acrolein to that of the sterically demanding C_5Me_5 ligand. Values close to 0 (or 180°) point to a relative perpendicular disposition, while angles close to ±90° indicate a parallel arrangement (Scheme 5). The measured value of −59.2(10)° indicates an intermediate disposition, close to those found in related methacrolein cations [(η^n-arene)M(PP*)(methacrolein)]$^{2+}$ (absolute values in the range 45.5(6)–65(2)°) [47,48,51,52]. This intermediate arrangement favors the establishment of intramolecular CH/π interactions between the *pro-S* phenyl ring of P(1) and the formyl proton of the organic substrate. In **20**, a small H. . .phenyl plane distance (2.80 Å), shorter than the sum of van der Waals radii (3.05 Å), evidences the existence of this interaction between the CHO proton, H(38), and the *pro-S* phenyl ring linked to the P(1) atom of the Prophos ligand



Scheme 5. G–Ir–O–C(38) torsion angle for enal dispositions: (a) −90°, (b) 180°.

(C(17)–C(22) ring) (Fig. 2). The geometrical parameters characterizing this interaction in **20** are collected in Table 4.

As it has been suggested in other closely related Ir or Rh complexes [47,51,52], these attractive intramolecular interactions hinder the rotation of the organic substrate within the chiral pocket conformed into the (η^5-C_5Me_5)Ir(Prophos) fragment and, consequently, they stabilize a preferential conformation for the coordinated aldehyde. Most probably, this interaction is also operating in solution and explains the strong shielding observed for the formyl proton in the ^{1}H NMR spectrum. In this conformation, the C_α-*si-face* of the enal is sheltered by the phenyl ring involved in the CH/π interactions and, therefore, the cyclopentadiene attack would take preferentially through the C_α-*re-face*, in good agreement with the catalytic outcome.

Table 3
Selected bond lengths (Å) and angles (°) for complex **20**.

Ir–P(1)	2.319(2)	P(1)–Ir–O	84.11(17)
Ir–P(2)	2.319(2)	P(1)–Ir–G[a]	133.2(3)
Ir–O	2.158(6)	P(2)–Ir–O	86.85(18)
Ir–G[a]	1.871(8)	P(2)–Ir–G[a]	130.4(3)
P(1)–C(24)	1.854(8)	O–Ir–G[a]	122.3(3)
P(2)–C(23)	1.826(11)	Ir–O–C(38)	127.2(8)
O–C(38)	1.196(13)	O–C(38)–C(39)	123.6(13)
C(38)–C(39)	1.484(18)	C(38)–C(39)–C(40)	110.8(13)
C(39)–C(40)	1.365(18)	C(38)–C(39)–C(41)	113.9(13)
C(39)–C(41)	1.41(2)	C(40)–C(39)–C(41)	134.4(14)
P(1)–Ir–P(2)	83.99(8)		

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

Table 4
Selected structural parameters (Å, deg) concerning CH/π interactions for complex **20**[a].

H. . .G(Ph)	H. . .Ph plane	γ angle	C–H. . .C	C–H. . .C(Ph)
3.04	2.80	23.0	C17: 2.80 C18: 3.08	3.08–3.79

[a] H. . .G(Ph): distance between the H(38) atom and the centroid of the phenyl ring G(Ph); H. . .Ph plane: separation between the hydrogen atom and the phenyl ring mean plane; γ angle: angle between the G(Ph)–H vector and the normal to the phenyl ring; C–H. . .C: contact distances between hydrogen atom and the phenyl carbon ring under the assumed criterion ≤3.05 Å for CH/π interaction; C–H. . .C(Ph): distances between the hydrogen atom and the rest of the carbon atoms of the phenyl ring.

4. Conclusions

In summary, the aqua-complex (S_{Ir},R_C)–[(η^5-C_5Me_5)Ir(Prophos)(H_2O)][SbF_6]$_2$ efficiently catalyzes the Diels–Alder reaction of simple acyclic enals with cyclopentadiene. The catalyst-substrate intermediate (S_{Ir},R_C)–[(η^5-C_5Me_5)Ir(Prophos)(ethyl acrolein)][SbF_6]$_2$ can be prepared and isolated in a completely diastereoselective manner. From the stereochemistry of the coordinated enal in this intermediate, it is possible to explain the catalytic outcome. In particular, the existence of CH/π intramolecular interactions in both solid state and solution, hinders the Ir–O enal rotation essentially accounting for the encountered enantioselectivity.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molcata.2014.01.021.

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