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Asymmetric 1,3-Dipolar Cycloaddition Reaction between α,β-Unsaturated Aldehydes and Nitrones Catalyzed by Well-Defined Iridium or Rhodium Catalysts

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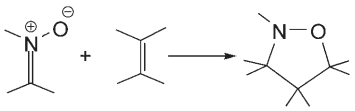
Abstract: Reaction of the complexes (S_M,R_C)-[$(\eta^5$-$C_5Me_5)$M{(*R*)-Prophos}(H_2O)]$(SbF_6)_2$ (M = Rh, Ir) with α,β-unsaturated aldehydes diastereoselectively gave complexes (S_M,R_C)-[$(\eta^5$-$C_5Me_5)$M{(*R*)-Prophos}-(enal)]$(SbF_6)_2$ which have been fully characterized, including an X-ray molecular structure determination of the complex (S_{Rh},R_C)-[$(\eta^5$-$C_5Me_5)$Rh{(*R*)-Prophos}(*trans*-2-methyl-2-pentenal)]$(SbF_6)_2$. These enal complexes efficiently catalyze the enantioselective 1,3-dipolar cycloaddition of the nitrones *N*-benzylideneaniline *N*-oxide and 3,4-dihydroisoquinoline *N*-oxide to the corresponding enals. Reactions occur with excellent regioselectivity, perfect *endo* selectivity and with enantiomeric excesses up to 94%. The absolute configuration of the adduct 5-methyl-2,3-diphenylisoxazolidine-4-carboxaldehyde was determined through its (*R*)-(−)-α-methylbenzylamine derivative.

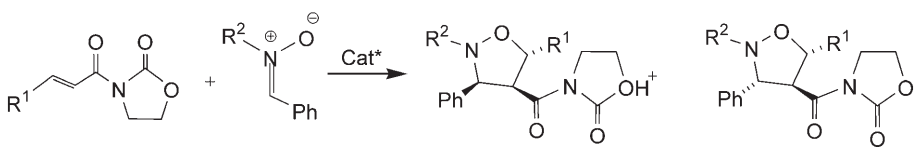
Keywords: asymmetric catalysis; 1,3-dipolar cycloaddition reactions; enals; iridium; nitrones; rhodium

Introduction

Cycloadditions are atom-economic processes that permit the creation of adjacents chiral centers in a concerted fashion.[1] In particular, the 1,3-dipolar cycloaddition reaction (DCR) of an alkene with a nitrone leads to the construction of up to three contiguous asymmetric carbon centers (Scheme 1). The resulting optically active isoxazolidines can easily be converted into biologically active amino alcohols, amino acids, alkaloids or β-lactams.[2] In this context, in 1994, Gothelf and Jørgensen reported the first example of a transition metal-catalyzed asymmetric DCR between alkenes and nitrones.[3] Chiral titanium compounds generated *in situ* from $[Ti(i\text{-}OPr)_2Cl_2]$ and chiral diols catalyzed the addition of 3-alkenoyl-2-oxazolidinones to benzylideneamine *N*-oxides (Scheme 2). As a nitrone can coordinate transition metals through its oxygen atom,[4] the necessity of using bidentate substrates, such as the 3-alkenoyl-2-oxazolidinones mentioned above, was discussed to avoid the competitive nitrone coordination. Consequently, most research in the field was concentrated



Scheme 1. DCR between nitrones and alkenes.



Scheme 2. DCR of 3-alkenoyl-2-oxazolidinones with nitrones.

on bidentate substrates and the use of simple non-chelating substrates was underexploited.[5]

However, in 2002, Kündig et al., by means of qualitative ^{31}P NMR experiments of competitive nitrone–aldehyde Lewis acid coordination, showed that crotonaldehyde coordinates a cationic ruthenium diphosphonite fragment preferentially to the nitrone *N*-benzylidenebenzylamine *N*-oxide. Subsequently, Kündig's group used this metallic fragment to catalyze the DCR between a series of nitrones and monodentate enals achieving excellent conversions and selectivities.[6] Since then, a few reports dealing with metal-catalyzed DCR between nitrones and enals have appeared. Yamada et al. published their work about β-ketoiminato cationic cobalt(III) complexes,[7] Kanemasa and co-workers reported on the use of chiral nickel(II), magnesium(II), or zinc(II) in the DCR of nitrones with α-alkyl- and α-arylacroleins[8] and Maruoka's group have reported the asymmetric DCR of nitrones and acrolein catalyzed by a bis-titanium binol complex.[9]

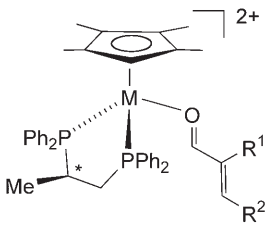
In this context, we have developed a catalytic system based on the chiral $(\eta^5\text{-}C_5Me_5)M\{(R)\text{-Prophos}\}$ (M = Ir, Rh) fragment which is well suited for the DCR between nitrones and methacrolein.[4c,10] A key point in this system is that methacrolein coordinates to the metallic fragment in a completely diastereoselective way and adopts a highly restricted geometry mostly due to the existence of CH/π interactions between the aldehyde proton and one of the phenyl groups of the Prophos ligand. Notably, because of this interaction, the aldehyde proton becomes very strongly shielded and resonates at about 2.5 ppm shifted to higher field with respect to free methacrolein, this strong shielding becoming a valuable structural diagnostic.[4c] In the present paper, we report the preparation and characterization of new (S_M,R_C)-$[(\eta^5\text{-}C_5Me_5)M\{(R)\text{-Prophos}\}(enal)](SbF_6)_2$ (M = Ir, Rh) complexes where enal represents acrolein, *trans*-crotonaldehyde, *trans*-2-methyl-2-butenal, *trans*-2-methyl-2-pentenal, 1-cyclohexene-1-carboxaldehyde or *trans*-cinnamaldehyde. The molecular structure of the rhodium derivative (S_{Rh},R_C)-$[(\eta^5\text{-}C_5Me_5)Rh\{(R)\text{-Prophos}\}(trans\text{-2-methyl-2-pentenal})](SbF_6)_2$ is also reported. In all cases, the CHO proton is strongly shielded (2.3 ppm on average). The establishment of the restricted conformation of the coordinated enals from spectroscopic and structural data indicates that these complexes are good catalyst candidates. Therefore, we tested them as catalysts for the DCR between the nitrones such as *N*-benzylideneaniline *N*-oxide and 3,4-dihydroisoquinoline *N*-oxide and the corresponding coordinated enals. Finally, to obtain information about the stereochemical course of the catalytic reaction, the absolute configuration of the adduct 5-methyl-2,3-diphenylisoxazolidine-4-carboxaldehyde was determined through the X-ray molecular analysis of its (*R*)-(−)-α-methylbenzylamine derivative.

Results and Discussion

Complexes of the formula (S_M,R_C)-$[(\eta^5\text{-}C_5Me_5)M\{(R)\text{-Prophos}\}(enal)](SbF_6)_2$ can be isolated by addition of the appropriate enal to the water complexes (S_M,R_C)-$[(\eta^5\text{-}C_5Me_5)M\{(R)\text{-Prophos}\}(H_2O)](SbF_6)_2$ in the presence of 4 Å molecular sieves according to Eq. (1). The new compounds have been characterized by the usual analytical and spectroscopic means (see Supporting Information). In addition, the molecular structure of the rhodium compound **7** has been determined by X-ray diffractometric methods. In these complexes the metal is a chiral center and the preparative reaction is completely diastereoselective: only S_M,R_C isomers were obtained in all cases (see below). The IR spectra exhibit an intense ν(CO) stretching band in the range 1570–1632 cm^{-1}. This band is shifted by around 100 cm^{-1} toward lower frequency with respect to the free ligands, indicating that, in accordance with *ab initio* calculations carried out on acrolein-Lewis acid models,[11] the double bond character of the C=O group has decreased after coordination to the metal.

The most interesting feature of the ^1H NMR spectra is the strong shielding of the aldehyde proton resonance after coordination. At −25 °C in CD_2Cl_2 solu-

$$(S_M,R_C)\text{-}[(\eta^5\text{-}C_5Me_5)M\{(R)\text{-Prophos}\}(H_2O)](SbF_6)_2 + \text{enal} \xrightarrow{4\text{Å MS}} (S_M,R_C)\text{-}[(\eta^5\text{-}C_5Me_5)M\{(R)\text{-Prophos}\}(enal)](SbF_6)_2 \quad (1)$$



$R^1 = R^2 = H$	M = Rh (**1**), Ir (**2**)
$R^1 = H$, $R^2 = Me$	M = Rh (**3**), Ir (**4**)
$R^1 = R^2 = Me$	M = Rh (**5**), Ir (**6**)
$R^1 = Me$, $R^2 = Et$	M = Rh (**7**), Ir (**8**)
$R^1, R^2 = -(CH_2)_4-$	M = Rh (**9**), Ir (**10**)
$R^1 = H$, $R^2 = Ph$	M = Rh (**11**), Ir (**12**)

tion, this proton resonates in the range 6.93–7.50 ppm, shifted by about 2.3 ppm to higher field with respect to the corresponding free molecules. We have recently shown that a comparable shift, measured in the related (S_M,R_C)-[(η^5-C_5Me_5)M{(*R*)-Prophos}(methacrolein)]$(SbF_6)_2$ complexes, is due to the existence of CH/π interactions between the CHO proton and one of the phenyl rings of the Profos ligand.[4c] Therefore, it is likely that this type of interaction is also operating in complexes **1**–**12** (see the discussion of the structure of complex **7** below). In addition, NOESY experiments show enhancement patterns compatible only with an *s-trans* conformation for the coordinated enals and a λ conformation for the M–P–C–C–P five-membered metallacycle. In summary, the NMR data indicate that the conformations of both metallic fragment and enal are significantly hampered when the enal is coordinated to the metal into the chiral pocket defined by the (C_5Me_5)M{(*R*)-Prophos} moiety. To obtain additional structural information, the molecular structure of compound **7** has been determined by X-ray diffractometric methods.

Molecular Structure of Compound 7

Single crystals of complex **7** were obtained from dichloromethane/hexane solutions. An ORTEP representation of the cation is depicted in Figure 1 and selected structural parameters are listed in Table 1. The metal atom is pseudo-tetrahedral being coordinated to a η^5-C_5Me_5 ring, to the two phosphorus atoms of the (*R*)-Prophos ligand and to the oxygen atom of the

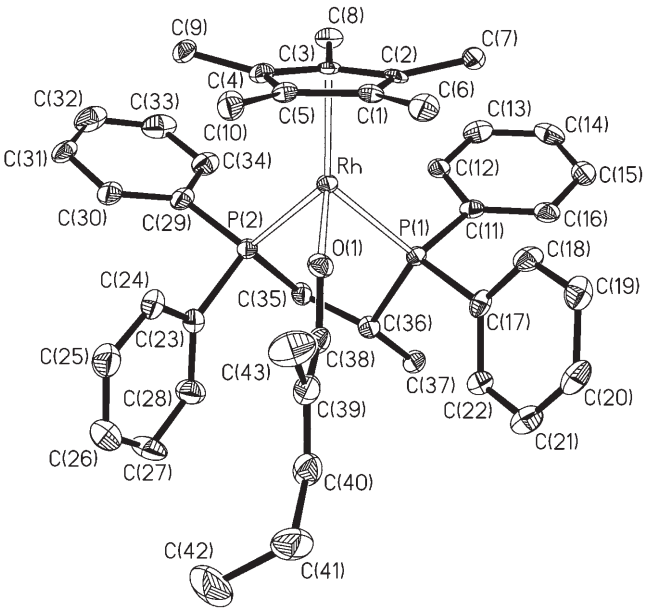


Figure 1. Molecular structure of the cationic complex of **7** (hydrogen atoms are omitted for clarity).

Table 1. Selected bond distances (Å) and angles (°) for the cationic metal complex of **7**.

Rh–P(1)	2.3276(11)	P(1)–C(36)	1.851(4)
Rh–P(2)	2.3273(12)	P(2)–C(35)	1.835(5)
Rh–O(1)	2.142(3)	C(35)–C(36)	1.543(6)
Rh–C(1)	2.236(4)	O(1)–C(38)	1.259(6)
Rh–C(2)	2.245(4)	C(38)–C(39)	1.429(7)
Rh–C(3)	2.189(4)	C(39)–C(40)	1.336(7)
Rh–C(4)	2.258(5)	C(39)–C(43)	1.484(8)
Rh–C(5)	2.235(4)	C(40)–C(41)	1.489(7)
Rh–G[a]	1.8666(19)	C(41)–C(42)	1.531(10)
P(1)–Rh–P(2)	83.78(4)	Rh–O(1)–C(38)	133.4(3)
P(1)–Rh–O(1)	90.66(9)	O(1)–C(38)–C(39)	123.2(4)
P(1)–Rh–G[a]	130.97(7)	C(38)–C(39)–C(40)	114.0(5)
P(2)–Rh–O(1)	94.63(9)	C(38)–C(39)–C(43)	118.8(5)
P(2)–Rh–G[a]	131.29(7)	C(40)–C(39)–C(43)	127.2(5)
O(1)–Rh–G[a]	114.31(10)	C(39)–C(40)–C(41)	128.9(5)

[a] G represents the centroid of the C_5Me_5 ring.

enal molecule. The metal atom has the *S* absolute configuration in accordance with the ligand priority sequence[12] η^5-C_5Me_5 > P(1) > P(2) > O and the Rh–P–C–C–P metallacycle a λ conformation[13] [Cremer and Pople parameters $Q_2 = 0.485(5)$ Å, $\phi_2 = 90.9(2)°$].[14]

The O(1)–C(38)–C(39)–C(40) skeleton of the 2-methyl-2-pentenal ligand is essentially planar with an *s-trans* conformation and an *E*-configuration around the carbonyl double bond. The bond distances along the conjugated system O(1)–C(38)–C(39)–C(40) [O=C = 1.259(6), C–C = 1.429(7), C=C = 1.336(7) Å] clearly evidence the partial delocalization of the π-electron density and account for the ν(CO) frequencies measured.

The relative disposition of the 2-methyl-2-pentenal ligand within the metal coordination sphere could be characterized by the torsion angle C_5Me_5(centroid)–M–O(1)–C(38) that relates its molecular plane to that of the sterically demanding C_5Me_5 ligand; while values close to 0° (or 180°) imply a perpendicular disposition between C_5Me_5 and enal planes, an approximate figure to 90° reflects a roughly parallel disposition. The observed value, −179.2(4)°, clearly indicates a perpendicular disposition. It is interesting to point out that in the related methacrolein compounds (S_M,R_C)-[(η^5-C_5Me_5)M{(*R*)-Prophos}(methacrolein)]-$(SbF_6)_2$ (M = Rh, Ir) the methacrolein plane is closer to a parallel disposition to the C_5Me_5 plane [mean value −65.2(4)°].[4c]

An analysis of the intramolecular interatomic distances clearly shows the existence of a CH/π attractive interaction between the CHO proton, H(38), and the *pro-R* phenyl ring bonded to the P(2) atom of the (*R*)-Prophos ligand. This interaction is characterized by the short H••••Ph(plane) distance, 2.799 Å, and the low γ angle, 27.3° (angle between the centroid-H vector and the normal to the phenyl ring). Although

the conformation of the enal ligand is significantly different to those observed in the methacrolein analogues, these CH/π parameters are very similar to those determined in the previously reported methacrolein complexes [mean values H••••Ph(plane) 2.76 Å, γ angle 22.3°].[4c]

The conformation of the enal ligand is mostly retained in dichloromethane solution. Thus, the maintenance of the CH/π interactions explains the strong field shielding observed in the ^{1}H NMR spectrum for the involved CHO proton. Furthermore, NOESY measurements are also in good agreement with the solid state geometry: the CHO proton shows an NOE relationship with *ortho* protons belonging to each one of the two PPh_2 groups of the (*R*)-Prophos ligand. Only a nearly perpendicular disposition of the enals accounts for this observation.

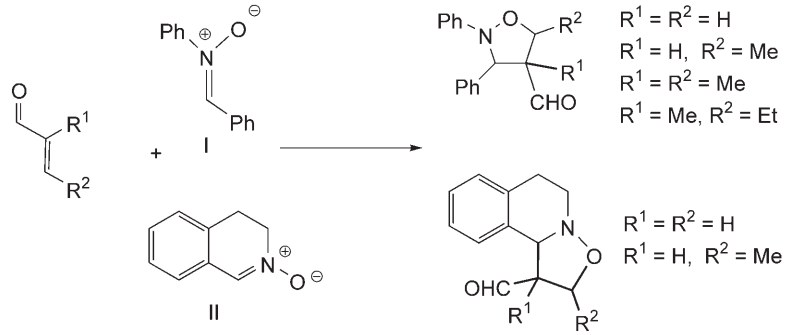
A strong shielding is observed for the CHO proton in all the enal complexes and the NOE relationship with both PPh_2 moieties is also a general feature for all the complexes we are describing. Thus, it can be concluded that, in complexes **1**–**12**, the unsaturated functionalities of the enals lay in a plane almost perpendicular to that of the C_5Me_5 ligand and adopt an *s-trans* conformation. Furthermore, the configuration around the C=O double bond is *E* and CH/π interactions between the CHO proton and the *pro-R* phenyl ring strongly restrict the conformation around the M–O bond. The most significant difference with respect to the methacrolein homologues is a twist of nearly 120° in the coordination plane of the enals.

Catalytic Reactions

Structural data demonstrate that complexes **1**–**12** consist of a sole epimer at metal with a fixed λ conformation for the M–P–C–C–P five-membered metallacycle and with the corresponding enals showing also an unique conformation into the $(C_5Me_5)M\{(R)$-Prophos$\}$ chiral pocket. Thus, they are excellent candidates to be tested as catalysts for cycloaddition reactions: the enals present a restricted conformation and, furthermore, they are activated by coordination to the metal. In fact, most of them efficiently catalyze the cycloaddition reaction of the nitrones *N*-benzylideneaniline *N*-oxide (I) and 3,4-dihydroisoquinoline *N*-oxide (II) to the corresponding enals (Scheme 3). Table 2 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. Catalysts were prepared *in situ* by treating the aqua precursors (S_M,R_C)-$[(\eta^5$-$C_5Me_5)M\{(R)$-Prophos$\}(H_2O)](SbF_6)_2$ with the corresponding enals in the presence of 4 Å MS. The 1-cyclohexene-1-carboxaldehyde (**9**, **10**) and *trans*-cinnamaldehyde (**11**, **12**) derivatives were not active. The cyclic nitrone II was added slowly to avoid undesired nitrone coordination. In general, iridium-based catalysts are a little more reactive and selective than the rhodium-based homologues. Typically, quantitative conversions are obtained after some hours at −25 °C with the former catalysts. Perfect diastereoselectivity for the *endo* isomer was observed in all cases and the 3,4 regioisomer was the sole adduct (nitrone I) or the major one (more than 90 %, nitrone II). The *ee* values achieved ranged from 66 to 94 %, enantioselectivity increasing as temperature decreases (compare entries 8 and 10 with 9 and 11, respectively).

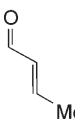
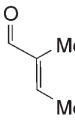
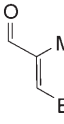
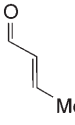
Determination of the Absolute Configuration

The absolute configuration of the major adduct obtained from the reaction of *trans*-crotonaldehyde with nitrone I was determined as depicted in Scheme 4. The isolated enantioenriched product was converted into a diastereomeric mixture of amines through condensation with (*R*)-(−)-α-methylbenzylamine followed by *in situ* reduction of the resulting imine with sodium borohydride in methanol. The most abundant diastereomer (**13**) was separated by chromatography. Crystals of **13** suitable for X-ray analysis were obtained from dichloromethane/hexane and its molecular structure was determined. An ORTEP diagram of the compound is shown in Figure 2. The absolute con-



Scheme 3. Cycloaddition reactions.

Table 2. Enantioselective DCR of enals with nitrones I and II.[a]

Entry	Catalyst	Enal	Nitrone	T [°C]	t [h][b]	Yield [%][c,d]	*ee* [%][e]
1[f]	**1** (Rh)		I	−25	16	100	78
2[f]	**2** (Ir)		I	−25	16	100	90
3[f]	**3** (Rh)		I	−25	72	98	68.5
4[f]	**4** (Ir)		I	−25	25	100	84.5
5	**5** (Rh)		I	−10	63	35	86
6	**5** (Rh)		I	−25	120	18	89
7	**6** (Ir)		I	−25	72	96.5	92
8	**7** (Rh)		I	−10	72	31	80
9	**7** (Rh)		I	−25	96	10	90.5
10	**8** (Ir)		I	−10	72	100	84.5
11	**8** (Ir)		I	−25	72	55	94
12	**1** (Rh)		II	−25	25	49	77
13	**2** (Ir)		II	−25	25	69	66
14	**3** (Rh)		II	−25	25	100	74
15	**4** (Ir)		II	−25	25	100	70

[a] *Reaction conditions:* catalyst 0.06 mmol (10.0 mol%), enal 4.2 mmol, 50 mg of 4 Å molecular sieves, and nitrone 0.6 mmol in 4 mL of CH_2Cl_2.
[b] Total reaction time; addition of the cyclic nitrone II was accomplished over 24 h.
[c] Based on nitrone.
[d] Determined by ^{1}H NMR.
[e] Determined by HPLC.
[f] Catalyst 0.03 mmol (5.0 mol%).

figurations of the stereogenic centers were established unambiguously as 3*S*,4*R*,5*S* corresponding to the 3*S*,4*R*,5*S* catalytic adduct. Accordingly, the *Re* face of the coordinated *trans*-crotonaldehyde has to be much more accessible to the nitrone than its *Si* face during the chirality induction step.

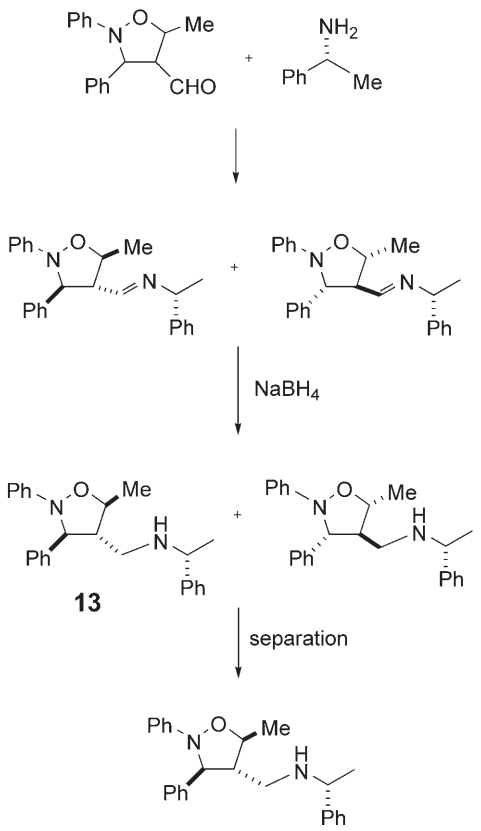
Conclusions

We have synthesized and characterized a series of cationic complexes containing α,β-unsaturated aldehyde ligands of formula (S_M,R_C)-[(η^5-C_5Me_5)M{(*R*)-Prophos}(enal)]$(SbF_6)_2$ (M = Rh, Ir). From structural studies we have shown that, in these complexes, the enal ligand is confined into the chiral pocket formed by the metal surrounded by the η^5-C_5Me_5 and the (*R*)-Prophos ligands. Notably, its geometry is highly restricted: *s-trans* conformation, *E*-configuration around the C=O bond and the rotation about the M–O bond is anchored by CH/π interactions. Therefore, such complexes are excellent candidates for asymmetric reactions involving the C=C bond. Consequently, we have also shown that they catalytically add nitrones I and II with excellent regioselectivity, perfect *endo* selectivity and enantiomeric excesses up to 94%.

Experimental Section

General Remarks

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 a Bruker AV-300 spectrometer (300.13 MHz) , Brucker AV-400 (400.16 MHz) or Brucker AV-500 (500.13 MHz). Chemical shifts are expressed in ppm upfield from $SiMe_4$. NOEDIFF and ^{1}H correlation spectra were obtained using standard procedures. Analytical high performance liquid chromatography (HPLC) was performed on an Alliance Waters (Water 2996 PDA detector) instrument using a chiral column Daicel Chiralpack OD-H (0.46 cm × 25 cm) and OD-H guard (0.46 × 5 cm) or AD-H (0.46 cm × 25 cm).



Scheme 4. Derivatization of the isoxazolidines.

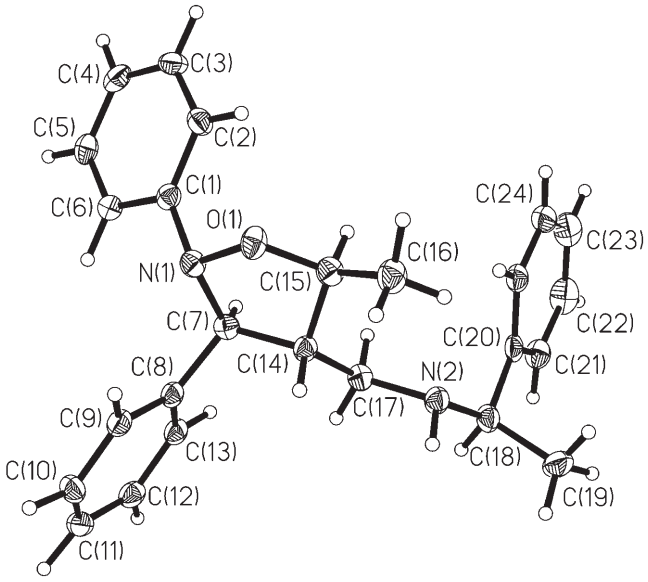


Figure 2. Molecular drawing of the organic adduct **13**. Selected bond distances (Å) and angles (°) in the isoxazolidine ring are: O(1)–N(1) 1.445(3), O(1)–C(15) 1.446(3), N(1)–C(1) 1.418(3), N(1)–C(7) 1.497(3), C(7)–C(8) 1.512(3), C(7)–C(14) 1.528(4), C(14)–C(15) 1.518(4), C(14)–C(17) 1.523(4), C(15)–C(16) 1.506(4), N(1)–O(1)–C(15) 107.19(17), O(1)–N(1)–C(7) 107.29(18), N(1)–C(7)–C(14) 104.3(2), C(7)–C(14)–C(15) 102.1(2), O(1)–C(15)–C(14) 102.38(19).

The complexes (S_M,R_C)-[(η^5-C_5Me_5)M{(*R*)-Prophos}-(H_2O)](SbF_6)$_2$ (M = Rh, Ir) were prepared using literature procedures.[4c]

Preparation of (S_M,R_C)-[(η^5-C_5Me_5)M{(*R*)-Prophos}-(enal)](SbF_6)$_2$ (M = Rh, Ir) (1–12)

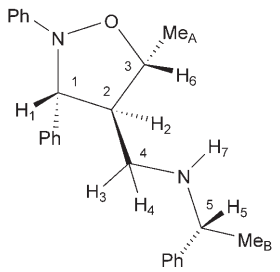
At −25 °C, under argon, to a solution of (S_M,R_C)-[(η^5-C_5Me_5)M{(*R*)-Prophos}(H_2O)](SbF_6)$_2$ (0.122 mmol) in CH_2Cl_2 (20 mL) the corresponding enal (0.610 mmol) and 4 Å molecular sieves (200.0 mg) were added. The solution was stirred for 20 min and the 4 Å MS was separated by filtration. Addition of 20 mL of dry hexane to the yellow filtrate afforded a yellow solid that was filtered off, washed with hexane and vacuum-dried.

Catalytic Procedure

At −25 °C, the metallic complex (S_M,R_C)-[(η^5-C_5Me_5)M{(*R*)-Prophos}(H_2O)](SbF_6)$_2$ (0.03 or 0.06 mmol, 5 or 10 mol %) was dissolved in CH_2Cl_2 (3 mL). Freshly distilled aldehyde (4.20 mmol) and 50 mg of activated 4 Å molecular sieves were added and the suspension stirred for 30 min. A solution of nitrone I (0.6 mmol) in CH_2Cl_2 (1 mL) was added. Nitrone II (0.6 mmol, 1 mL CH_2Cl_2) was added dropwise with a syringe pump for 24 h. After stirring at −25 or −10 °C for the appropriate reaction time, 20 mL of hexane were added. After filtration over Celite, the solution was evaporated to dryness. The residue was purified by chromatography (SiO_2) to provide the corresponding isoxazolidines. Conversion and regioselectivity were determined on a $CDCl_3$ solution of the crude mixture by ^{1}H NMR analysis. The enantiomeric excess was determined by HPLC analysis (for details see Supporting Information).

Synthesis of (1*R*)-*N*-[(5-Methyl-2,3-diphenylisoxazolidin-4-yl)methyl]-1-phenylethanamine (13)

The product (358.0 mg, 1.43 mmol) of the catalytic reaction between *trans*-crotonaldehyde and *N*-benzylideneaniline *N*-oxide [entry 4, Table 2, (3*S*,4*R*,5*S*)- and (3*R*,4*S*,5*R*)-5-methyl-2,3-diphenylisoxazolidine-4-carboxaldehyde, in 92.25/7.75, molar ratio] was dissolved in benzene (10 mL) and treated with (*R*)-(−)-α-methylbenzylamine (190.1 mg, 1.57 mmol). The resulting mixture was stirred at ambient temperature for 24 h and the solvent was evaporated under reduced pressure. The residue was extracted in methanol (5 mL) and treated with $NaBH_4$ (60.0 mg, 1.59 mmol) at 0 °C. After 15 min the reaction was quenched with methanolic HCl (1 mL, 0.1 M). The solvent was evaporated under reduced pressure and the residue was partitioned between ethyl acetate (10 mL) and saturated aqueous ammonium chloride (10 mL). The organic layer was separated, washed with brine (1 × 10 mL), dried over $MgSO_4$ and evaporated under reduced pressure. From the residue the most abundant component of the mixture (compound **13**) was separated by chromatography (SiO_2, dichloromethane/diethyl ether, 98:2) as a colorless oil. Crystals suitable for X-ray analysis were obtained by crystallization from dichloromethane/hexane. ^{1}H NMR (400 MHz, C_6D_6, 25 °C, Scheme 5): δ = 6.73–7.38 (15 H, Ar), 4.31 (d, J = 7.2 Hz, 1 H, H_1), 3.91 (dq, J = 8.05, 5.9 Hz, 1 H, H_6), 3.28 (q, J = 6.6 Hz, 1 H, H_5), 2.36 (dd, J = 12.1, 5.5 Hz, 1 H, H_3), 2.23 (dd, J = 7.5 Hz, 1 H, H_4),



Scheme 5. Atom labeling for the NMR assignments.

2.08 (m, 1H, H_2), 1.33 (d, 3H, Me_A), 1.01 (d, 3H, Me_B), 0.65 (bs, 1H, N*H*); ^{13}C NMR (100.62 MHz, C_6D_6, 25 °C): δ = 152.8–114.17 (18 C, Ar), 78.76 (s, C_3), 75.07 (s, C_1), 61.99 (s, C_2), 58.60 (s, C_5), 47.85 (s, C_4), 24.52 (s, *Me*$_B$), 18.26 (s, Me_A).

X-Ray Structure Analyses of Compounds 7 and 13

Single crystals of both compounds were mounted on a glass fiber and intensity data were collected at low temperature [100(2) K] on a CCD Bruker SMART APEX diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) using ω rotations (0.3°). Instrument and crystal stability were evaluated by measuring equivalent reflections at different times; no significant decay was observed.

Crystal data for **7** (from 9275 reflections, $2.2 < \theta < 25.7°$): $C_{43}H_{51}F_{12}OP_2RhSb_2 \cdot 2(CH_2Cl_2)$, monoclinic, space group $P2_1$; a = 13.2118(8), b = 13.0218(8), c = 16.1363(10) Å, β = 106.023 (10)°, V = 2668.3(3) Å^3, Z = 2, ρ_{cald} = 1.730 Mg m^{-3}, μ(Mo-Kα) = 1.646 mm^{-1}; crystal size 0.19 × 0.13 × 0.07 mm; max. 2θ = 55.2°; 32220 measured reflections, 12153 unique (R_{int} = 0.0363).

Crystal data for **13** (from 1422 reflections, $2.3 < \theta < 20.6°$): $C_{25}H_{28}N_2O$, orthorhombic, space group $P2_12_12_1$; a = 8.5475(14), b = 9.4444(15), c = 25.245(4) Å, V = 2037.9(6) Å^3, Z = 4, ρ_{cald} = 1.214 Mg m^{-3}, μ(Mo-Kα) = 0.074 mm^{-1}; crystal size 0.34 × 0.11 × 0.06 mm; max. 2θ = 52.1°; 11228 measured reflections, 4008 unique (R_{int} = 0.0558).

Data were integrated with Bruker SAINT-PLUS software.[15] Absorption corrections were applied by using SADABS program.[16] Structures were solved by direct methods and completed by subsequent difference Fourier techniques. Refinement on F^2 was carried out for both structures by full-matrix least-squares (SHELXL-97).[17] In **7**, two dichloromethane solvent molecules were found in the crystal structure. In both structures, all non-hydrogen atoms were refined with anisotropic displacement parameters. For **7**, hydrogen atoms were included in calculated positions and refined with riding positional and thermal parameters. In the case of **13**, hydrogens were included in the model from the residual density maps and refined as free isotropic atoms. The absolute configuration for both compounds were determined on the basis of previously known internal references and, for **7**, this assignment was confirmed using the Flack parameter[18] (−0.002(15)). Conventional final agreement factors[17] were: R_1 = 0.0378 [for 11135 reflections with $F^2 > 4\sigma(F^2)$], ωR_2 = 0.0907 and S = 1.037 for all independent reflections of **7**; R_1 = 0.0546 [for 3207 reflections with $F^2 > 4\sigma(F^2)$], ωR_2 = 0.1065 and S = 1.042 for all independent reflections of **13**.

CCDC-632053 and 632054 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge on application to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [fax: + 44 1223/336–033; e-mail: deposit@ccdc.cam.ac.uk].

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