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Asymmetric 1,3-dipolar cycloaddition reactions between methacrylonitrile and nitrones catalysed by well-defined M(diphosphane) (M = Rh, Ir) complexes

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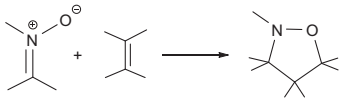
ABSTRACT

The cationic half-sandwich aqua-complexes $[(\eta^5\text{-}C_5Me_5)M(PP^*)(H_2O)][SbF_6]_2$ [M = Rh, Ir; PP* = (*R*)-Benphos, (*R*)-Cyphos, (2*R*,4*R*)-Norphos] catalyse the 1,3-dipolar cycloaddition reaction of nitrones with methacrylonitrile with perfect regioselectivity, low-to-perfect *endo*-selectivity and low-to-moderate enantioselectivity. The active species involved in the catalytic process, $[(\eta^5\text{-}C_5Me_5)M(PP^*)$(methacrylonitrile)$][SbF_6]_2$, have been isolated and characterised as mixtures of the (*S*)- and (*R*)-at-metal epimers. NMR measurements of these mixtures indicated that the (R_M)-isomers epimerise to the corresponding (S_M) counterparts. The molecular structure of the rhodium complex (S_{Rh},R_C)-$[(\eta^5\text{-}C_5Me_5)$Rh{(*R*)-Benphos}(methacrylonitrile)$][SbF_6]_2$ has been determined by X-ray diffraction methods. Diastereomerically pure (S_{Rh},R_C)-$[(\eta^5\text{-}C_5Me_5)$Rh(PP*)(methacrylonitrile)$][SbF_6]_2$ compounds catalyse stoichiometrically the above mentioned dipolar cycloaddition reaction with up to 90% enantiomeric excess, thus indicating the influence of the metal handeness on the catalytic stereochemical outcome. Catalysts can be recycled up to three times without a significant loss of either activity or selectivity.

1. Introduction

Cycloaddition reactions[1] are a fundamental class of processes in synthetic chemistry and among them 1,3-dipolar cycloadditions are atom-economic transformations that permit the construction of five-membered heterocycles. Moreover, enantioselective dipolar cycloaddition reaction versions allow for the creation of several adjacent stereogenic centres in a single step with stereochemical control.[2] Over the last few years, one of the most studied dipolar cycloaddition reactions has been the cycloaddition of nitrones with alkenes (Scheme 1).[3] The resulting isoxazolidines have been applied as valuable synthetic intermediates for the preparation of useful compounds such as alkaloids, β-lactams, amino acids or amino sugars by taking advantage of the easy cleavage of the N–O bond of these cyclic compounds under mild reducing conditions.[4]

The greatest challenge for the dipolar cycloaddition reactions of nitrones with alkenes is to control the enantioselectivity of the addition. For this purpose, the use of chiral transition-metal Lewis acids as catalysts is one of the most promising approaches. Typically, the coordination of a nitrone to the Lewis acid is more feasible than the coordination of an alkene.[5] For this reason, asymmetric catalytic reactions in which the dipolarophile is activated by a chiral Lewis acid (normal electron demand) were only successful for substrates such as alkenoyloxazolidinones that enable a bidentate coordination to the Lewis acid and preclude the coordination of the nitrone.[2,3] In fact, the first example of a transition-metal-catalysed asymmetric dipolar cycloaddition reactions between alkenes and nitrones exploits this feature, using chiral titanium compounds as catalysts.[6] In connection with this work, a catalytic intermediate featuring the *N*-cinnamoyloxazolidinone coordinated to the metal was isolated and characterised by X-ray crystallography (Scheme 2a).[7]



Scheme 1. Dipolar cycloaddition reaction between nitrones and alkenes.

However, over the last few years, only a few examples of one-point-binding catalysts for the asymmetric normal electron

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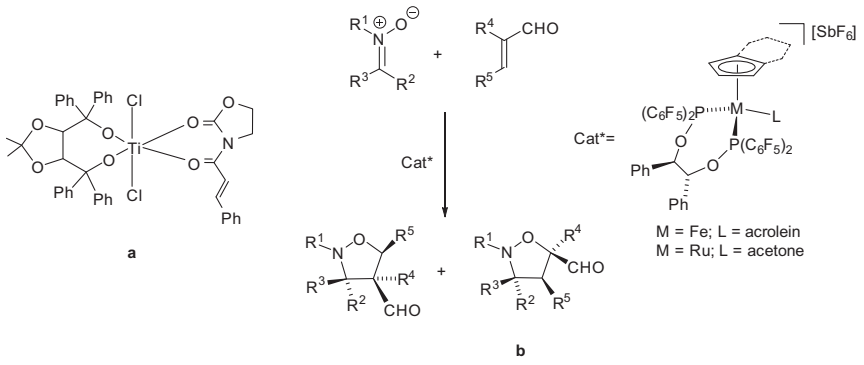
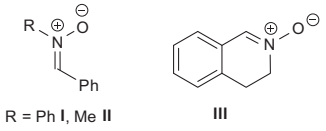
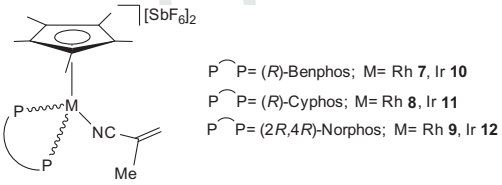


Scheme 2. Catalytic intermediate with coordinated *N*-cinnamoyloxazolidinone (**a**) and dipolar cycloaddition reactions catalysed by Binop-F complexes (**b**).



Scheme 3. Nitrones employed in the catalytic experiments.

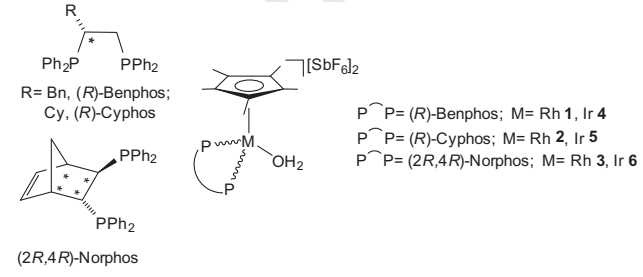


Scheme 5. Methacrylonitrile complexes **7**–**12**.

demand dipolar cycloaddition reactions of nitrones with electron-deficient monofunctionalised alkenes have been reported. Thus, in 2002, Kündig et al. developed catalytic dipolar cycloaddition reactions between nitrones and α,β-unsaturated aldehydes in the presence of Binop-F iron and ruthenium complexes as chiral Lewis-acid catalysts (Scheme 2b).[8] Since then, a number of reports dealing with this class of dipolar cycloaddition reactions have been published by Kündig et al.,[9] Yamada et al.,[10] Kanemasa et al.,[11] Maruoka et al.,[12] Doyle et al.[13] and ourselves.[5c,14] For this type of catalyst, the coordination of the aldehyde is favoured over the coordination of the nitrone either via the appropriate choice of the chiral Lewis acid or by keeping the nitrone concentration low by adding it slowly to the reaction medium.[8–14]

On the other hand, the problem of the competitive coordinations between nitrones and alkenes can be also circumvented by using alkenes with a good coordinating functionality such as a cyano group. In this context, we have shown that half-sandwich complexes of Rh(III) or Ir(III) containing the chiral fragment (η^5-C_5Me_5)M{(*R*)-Prophos} catalyse the dipolar cycloaddition reactions of nitrones and α,β-unsaturated nitriles.[15]

With all these concerns in mind, we herein report on: (i) the catalytic asymmetric dipolar cycloaddition reactions of methacrylonitrile with nitrones **I**–**III** (Scheme 3) using the aqua-complexes (S_M,R_C)-[(η^5-C_5Me_5)M(PP*)(H_2O)][SbF_6]$_2$, [PP* = (*R*)-Benphos, (*R*)-Cyphos] and [(η^5-C_5Me_5)M{(2*R*,4*R*)-Norphos)}(H_2O)][SbF_6]$_2$, (M = Rh **1**–**3**, Ir **4**–**6**) (Scheme 4)[16] as catalyst precursors; (ii) the preparation and characterization of the corresponding catalytic intermediate complexes [(η^5-C_5Me_5)M(PP*)(methacrylonitrile)][SbF_6]$_2$ and [(η^5-C_5Me_5)M{(2*R*,4*R*)-Norphos)}(methacrylonitrile)][SbF_6]$_2$, (M = Rh **7**–**9**, Ir **10**–**12**) (Scheme 5), including the determination of the molecular structure by X-ray diffraction of the complex (S_{Rh},R_C)-[(η^5-C_5Me_5)Rh{(*R*)-Benphos}(methacrylonitrile)][SbF_6]$_2$ **7a**; and (iii) the use of the (S_M)-epimers of complexes **7**, **8**, **11** and **12** as stoichiometric catalysts for the above mentioned 1,3-dipolar cycloaddition reactions.



Scheme 4. Aqua-complexes **1**–**6**.

2. Results and discussion

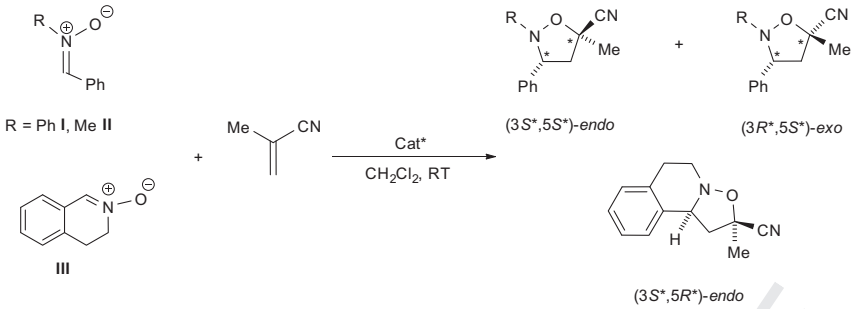
2.1. Catalytic studies

The aqua-complexes (S_M,R_C)-[(η^5-C_5Me_5)M(PP*)(H_2O)][SbF_6]$_2$, [PP* = (*R*)-Benphos, (*R*)-Cyphos] and [(η^5-C_5Me_5)M{(2*R*,4*R*)-Norphos}(H_2O)][SbF_6]$_2$, (M = Rh **1**–**3**, Ir **4**–**6**) were tested as catalyst precursors for the dipolar cycloaddition reactions reaction between methacrylonitrile and linear (*N*-benzylidenphenylamine *N*-oxide **I**, *N*-benzylidenmethylamine *N*-oxide **II**) and cyclic (2,3,4,5-dihydroisoquinoline *N*-oxide **III**) nitrones.

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 conversions, regio- and diastereoselectivities were determined by NMR spectroscopy while the enantioselectivity was determined by HPLC. With linear nitrones **I** and **II**, the rates were low (16–46% conversion, 90 h, entries 1–6). The reactions were faster with cyclic nitrone **III** (75–85% conversion, 16 h, entries 7–9). Iridium catalysts were less active (and selective) than the rhodium-based homologues (entries 10–12).

Perfect 3,5-regioselectivity was obtained in all cases and, as expected for Lewis acid-catalyzed dipolar cycloaddition reactions of nitrones with one-point binding alkenes, an *endo* preference was shown.[17] Linear nitrone **I** gave high diastereoselectivity in 3,5-*endo* with poor enantioselectivity (entries 1–3) while nitrone **II** afforded both 3,5-cycloadducts with poor diastereoselectivity and moderate enantioselectivity (entries 4–6). With nitrone **III**, perfect diastereoselectivity in the 3,5-*endo* cycloadduct was achieved with ee values around 65% (entries 7–9).

Table 1
Enantioselective dipolar cycloaddition reaction of methacrylonitrile with nitrones **I**–**III** catalysed by **1**–**6**[a]



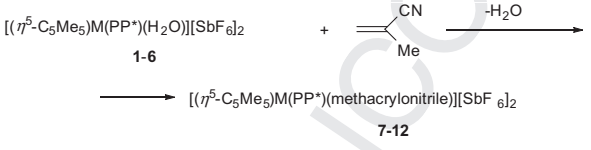
Entry	Catalyst	Nitrone	*t* (h)	Conv. (%)[b,c]	Isomer ratio (%) 3,5-*endo*/3,5-*exo*[c]	ee (%)[d] *endo*/*exo*
1	**1** (Rh/Benphos)	**I**	90	46	86/14	rac/6
2	**2** (Rh/Cyphos)	**I**	90	28	90/10	rac/7
3	**3** (Rh/Norphos)	**I**	90	30	85/15	rac/5
4	**1** (Rh/Benphos)	**II**	90	19	50/50	60/55
5	**2** (Rh/Cyphos)	**II**	90	18	52/48	65/69
6	**3** (Rh/Norphos)	**II**	90	16	56/44	63/67
7	**1** (Rh/Benphos)	**III**	16	83	100/—	61/—
8	**2** (Rh/Cyphos)	**III**	16	85	100/—	65/—
9	**3** (Rh/Norphos)	**III**	16	75	100/—	68/—
10	**4** (Ir/Benphos)	**III**	16	44	100/—	rac/—
11	**5** (Ir/Cyphos)	**III**	16	35	100/—	rac/—
12	**6** (Ir/Norphos)	**III**	16	37	100/—	6/—

[a] Reaction conditions: catalyst 0.03 mmol (10 mol %), methacrylonitrile 2.1 mmol, nitrone 0.30 mmol, in 4 mL of CH_2Cl_2, at RT.
[b] Based on nitrone.
[c] Determined by ^{1}H NMR.
[d] Determined by HPLC.

In order to obtain a better understanding of the catalytic reaction, we next investigated the intermediate complexes involved in the process.

2.2. Preparation of the complexes [(η^5-C_5Me_5)M(PP*)(methacrylonitrile)][SbF_6]$_2$ 7–12

The title complexes were prepared in nearly quantitative yield by the addition of methacrylonitrile to the corresponding aqua-complexes **1**–**6** (Eq. 1). The reaction afforded mixtures of the two possible epimers at the metal, namely S_M (which we will label with an **a**) and R_M (labelled **b**). The diastereomeric ratio of the formation is quoted in Eq. 1 and, as it can be seen, low diastereomeric excesses were achieved (⩽36%). The configuration at the metal centre was assigned by NOE measurements (see below).



(1)

PP* = Benphos; M = Rh **7a/7b** : 47/53, M = Ir **10a/10b** : 68/32
Cyphos; M = Rh **8a/8b** : 58/42, M = Ir **11a/11b** : 67/33
Norphos; M = Rh **9a/9b** : 56/44, M = Ir **12a/12b** : 53/47

The new complexes were characterised by analytical and spectroscopic methods including two-dimensional homo- and heteronuclear NMR correlations. In addition, the crystal structure of the rhodium methacrylonitrile complex **7a** was determined by X-ray diffractometric methods.

The ^{1}H NMR spectra, apart from the typical peaks of the coordinated diphosphane and C_5Me_5 ligands, showed the presence of coordinated methacrylonitrile. A singlet in the 1.5–1.7 ppm region was assigned to the methyl group and two resonances in the 5.0–6.2 ppm region, that correlate with two ^{13}C NMR peaks in the 114–115 (NC—C=C) and 140–141 (NC—C=C) ppm intervals, are attributed to the olefinic protons. The CN carbon resonates at around 119 ppm, for the Benphos and Cyphos complexes and in the 126–131 ppm region for the Norphos complexes. In addition, a sharp IR band at around 2255 cm^{-1}, shifted approximately 26 cm^{-1} towards higher frequency with respect to free methacrylonitrile, was attributed to the C≡N functionality.

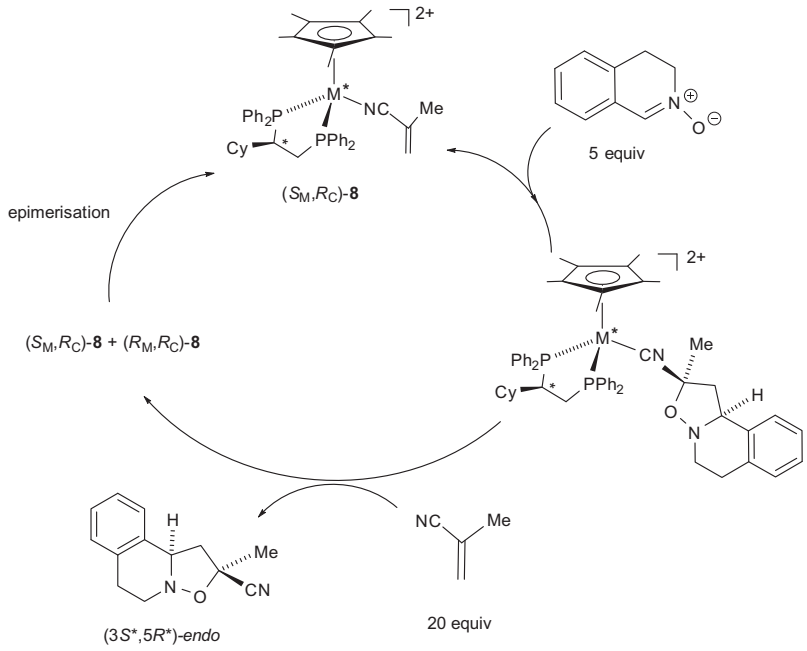
The ^{31}P NMR spectra consist of two doublets of doublets (Rh–P coupling constants of about 120–130 Hz and P–P couplings of about 40 Hz) for the rhodium complexes and two doublets for the iridium ones, with a P–P coupling of about 13 Hz.

An NOE correlation between the H_{11} (complexes **7**, **8**, **10** and **11**) or H_2 proton (complexes **9** and **12**) (see Scheme 7 for labelling) and the methyl protons of the coordinated methacrylonitrile strongly indicates an (*S*)-configuration at the metal (isomers labelled **a**).

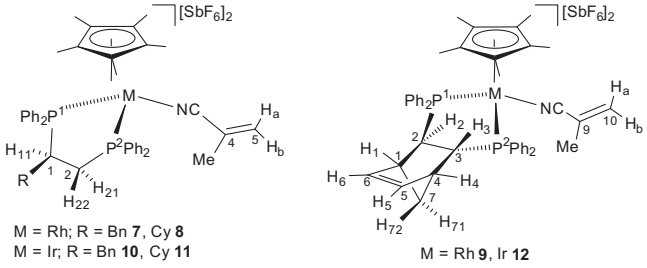
Mixtures of the (*R*)- and (*S*)-at-metal isomers epimerise to the (*S*)-at-metal epimer at different rates depending on both the metal and the phosphane. Thus, starting from slightly diastereoenriched samples of the Benphos and Cyphos rhodium compounds **7** and **8**, diastereopure **7a** and **8a** were obtained after 1 h of treatment at RT in acetone. However, in order to obtain the iridium analogues **10a** and **11a** in diastereopure form, it is necessary to reflux the starting epimeric mixtures in acetone over 6 h. Finally, mixtures of the Norphos isomers **9a**/**9b** (12% de) and **12a**/**12b** (6% de) evolve up to about 40% de in favour of the (*S*)-epimer, after refluxing in acetone for 6 h.

2.3. Molecular structure of compound 7a

Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of *n*-hexane into dichloromethane solutions of complex **7a**. A molecular representation of the complex is depicted in Figure 1 and the relevant structural parameters are summarized in Table 2. The metal atom exhibits a formal



Scheme 6. Recycling experiments.



Scheme 7. Labelling of the methacrylonitrile complexes **7**–**12**, for NMR assignments.

Table 2
Selected bond distances (Å) and angles (°) for the complex **7a**

Rh–P(1)	2.334(3)	P(1)–Rh–N	86.1(3)
Rh–P(2)	2.358(3)	P(1)–Rh–Ct[a]	130.8(2)
Rh–N	2.056(9)	P(2)–Rh–N	90.3(2)
Rh–Ct[a]	1.8520(2)	P(2)–Rh–Ct[a]	131.2(2)
N–C(44)	1.156(13)	N–Rh–Ct[a]	120.8(3)
C(44)–C(45)	1.447(15)	Rh–N–C(44)	174.8(9)
C(45)–C(46)	1.504(14)	N–C(44)–C(45)	176.7(12)
C(45)–C(47)	1.341(15)	C(44)–C(45)–C(46)	115.7(10)
P(1)–Rh–P(2)	83.49(10)	C(44)–C(45)–C(47)	116.7(10)

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

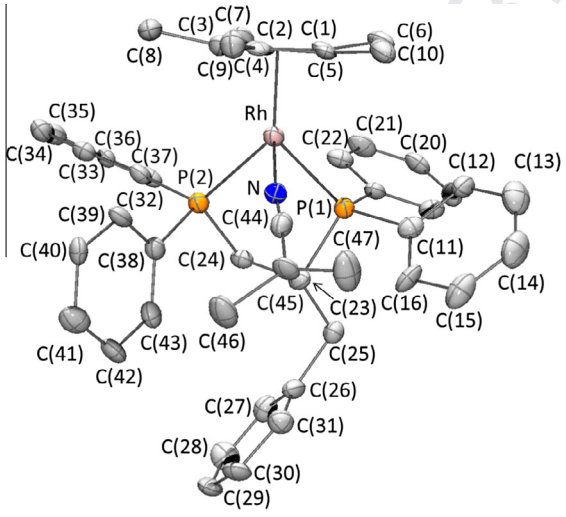


Figure 1. Molecular structure of the cation of **7a**.

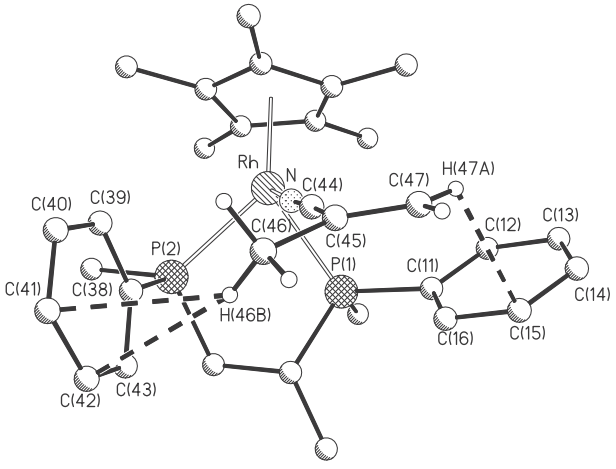


Figure 2. CH/π interactions in complex **7a**.

pseudo-tetrahedral environment coordinated to an η^5-C_5Me_5 group, to the two phosphorus atoms of the (*R*)-Benphos ligand and to the nitrogen atom of the nitrile. The absolute configuration at the metal is *S*, in accordance with the ligand priority sequence η^5-C_5Me_5 > P(1) > P(2) > N.[18] The M–P(1)–C(23)–C(24)–P(2) metallacycle exhibits a λ conformation with highly puckered ^{3}E envelope conformation (Cremer and Pople parameters $Q = 0.570(9)$ Å, $\phi = 75.3(5)°$).[19]

Table 3
Selected geometrical parameters (Å, °) concerning CH/π interactions for complex **7a**

	H···G[a]	H···Ph[b] (plane)	γ angle[c]	C–H···C[d]	C–H···C(Ph)[e]
C(47)–H(47A)···C(11)/C(16)	3.45	2.74	37.5	C(15): 2.85	3.17–4.43
C(46)–H(46B)···C(38)/C(43)	2.88	2.78	15.5	C(41): 2.89 C(42): 2.89	3.16–3.54

[a] H···G: separation between hydrogen atom and the centroid of the phenyl ring.
[b] H···Ph (plane) represents the distance from the H atom to the mean plane of the phenyl ring of the reported C–H···π interaction.
[c] γ angle: angle between the G–H vector and the normal to the phenyl ring.
[d] CH···C: distance between H atom and the phenyl carbon atom under the assumed criterium (3.05 Å).
[e] CH···C(Ph): range of distances between H atom and the rest of the carbon atoms of the π system.

The bond lengths and angles in the metal coordination sphere match with those reported in closely related complexes. For instance, Rh–P and Rh–Ct (C_5Me_5 centroid) bond lengths do not significantly differ from the values found in [(η^5-C_5Me_5)Rh{(*R*)-Benphos}(methacrolein)]$^{+2}$ complex (Rh–P(1): 2.331(2), Rh–P(2): 2.360(2) and Rh–Ct: 1.854(9) Å)[16] while Rh–N bond length nicely agrees with that reported in [(η^5-C_5Me_5)Rh{(*R*)-Prophos}(methacrylonitrile)]$^{+2}$ complex (Rh–N: 2.067(7) Å).[15a]

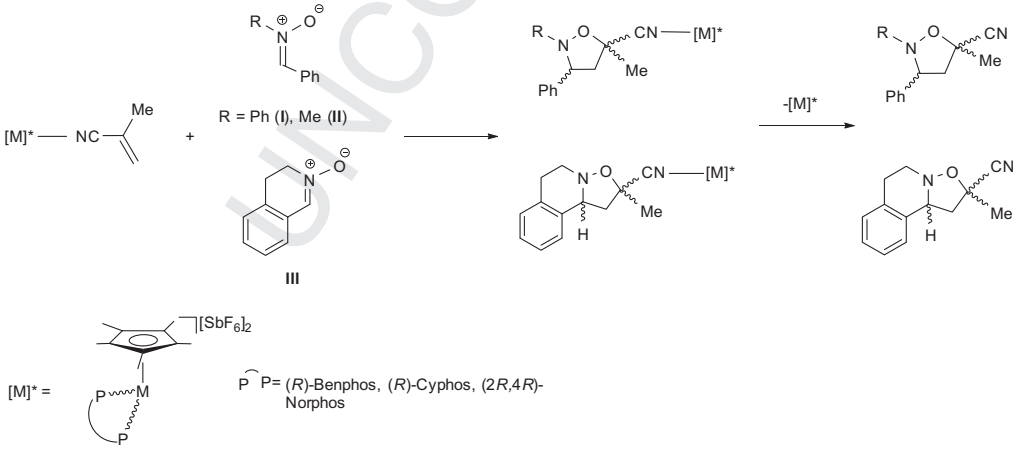
The unsaturated nitrile fragment N–C(44)–C(45)–C(47) is essentially planar. The bond distances along this conjugated system, [N–C(44) 1.156(13), C(44)–C(45) 1.447(15), C(45)–C(47) 1.341(15) Å], indicate the partial delocalisation of the π-electron density and justify the decrease of the *ν*(CN) frequency measured in the IR of these complexes.[20]

Due to the linearity of the Rh–N–C(44)–C(45) moiety [Rh–N–C(44) = 174.8(9)°, N–C(44)–C(45) = 176.7(12)°], the relative disposition of the methacrylonitrile ligand within the metal coordination sphere could be characterised by the Ct–Rh···C(45)–C(47) torsion angle that relates the nitrile and C_5Me_5 planes. While angles close to 90° indicate a parallel arrangement for both planes, values close to 0° (or 180°) point to a relative perpendicular disposition between them. The measured value, −68.4(9)°, identifies an intermediate disposition. The absolute value of this angle is comparable to that reported (74.5°) for the homologue (*R*)-Prophos methacrylonitrile rhodium compound.[15a] This arrangement favours the establishment of CH/π interactions[21] between an olefinic proton of the methacrylonitrile [H(47A)] and the C(15)–C(16) bond of the *pro-S* phenyl ring of the P(1)PPh_2 group, as well as between a hydrogen of the CH_3 group of the methacrylonitrile [H(46B)] and the C(41)–C(42) double bond of the *pro-R* phenyl ring of the P(2) Ph_2 fragment (Fig. 2). These interactions are characterised by short H···phenyl plane ring separations and H···C interatomic distances, that are clearly shorter than the sum of the van der Waals radii (Table 3).

In the encountered conformation, the *Si* face of the coordinated nitrile becomes shielded by the *pro-S* phenyl ring of the P(1)PPh_2 group involved in the CH/π interactions and, therefore, the attack of the nitrone would preferentially occur through the *Re* face of this substrate.

2.4. Stoichiometric reactions

The preparation of complexes **7**–**12** according to Eq. 1, clearly establishes that both epimers at the metal are present during the catalytic reactions reported. Assuming that both are active in catalysis, enantioselectivity could decrease if they induce divergently. By taking advantage of the observed epimerization of the **b** isomers to the corresponding **a** epimers (see above), we prepared pure samples of the (S_M)-diastereomers for the Benphos and Cyphos containing compounds **7**, **8**, **10** and **11**. In an attempt to improve the enantioselectivity, we carried out stoichiometric reactions between the enantiopure (S_M)-isomers **7a**, **8a**, **10a** and **11a** and nitrones **I**–**III** (Eq. 2). We also performed stoichiometric CDR reactions using as catalyst mixtures of the Norphos compounds **9a**,**b** and **12a**,**b** enriched in the **a** epimer (40% de in both cases). Table 4 shows a selection of the results obtained along with the reaction conditions.



(2)

Table 4
Stoichiometric dipolar cycloaddition reaction of methacrylonitrile catalysed by **7**–**12**[a]

Entry	Catalyst	Nitrone	Isomer ratio 3,5-*endo*/3,5-*exo* (%)[b]	ee (%)[c] *endo*/*exo*
1	**7** (Rh/Benphos)	**I**	77/23	26/30
2	**8** (Rh/Cyphos)	**I**	77/23	40/47
3	**9** (Rh/Norphos)	**I**	82/18	29/26
4	**7** (Rh/Benphos)	**II**	39/61	77/80
5	**8** (Rh)/Cyphos)	**II**	42/58	84/82
6	**9** (Rh/Norphos)	**II**	44/56	72/70
7	**7** (Rh/Benphos)	**III**	100/—	72/—
8	**8** (Rh/Cyphos)	**III**	100/—	90/—
9	**9** (Rh/Norphos)	**III**	100/—	86/—
10	**10** (Ir/Benphos)	**III**	100/—	51/—
11	**11** (Ir/Cyphos)	**III**	100/—	56/—
12	**12** (Ir/Norphos)	**III**	100/—	22/—

[a] Reaction conditions: catalyst, a 7.5×10^{-2} M solution in 4 mL of CH_2Cl_2; nitrone, 5 equiv in 1 mL of CH_2Cl_2; 3 h at RT.
[b] Determined by ^{1}H NMR.
[c] Determined by HPLC.

A slight decrease in the diastereoselectivity was observed for the reaction between the rhodium complexes and the linear nitrones **I** and **II** (compare entries 1–6 in Table 4 with the corresponding entries in Table 1). The perfect selectivity, in favour of the 3,5-*endo* cycloadduct for the cyclic nitrone **III**, was not affected (entries 7–12).

In these stoichiometric reactions, a notable and generalised increase in the ee values was observed in relation to those obtained in substoichiometric runs. Thus, for example, whereas employing a mixture of the two Rh/Cyphos epimers **8a**/**8b** as catalyst gave no significant ee for the reaction between methacrylonitrile and nitrone **I** (entry 2, Table 1), using enantiopure **8a** gives, for the same reaction, 40% and 47% ee in the 3,5-*endo* and in the 3,5-*exo* cycloadducts, respectively (entry 2, Table 4). Similarly, 90% ee in the 3,5-*endo* adduct was obtained in the reaction between methacrylonitrile and nitrone **III** when stereopure complex **8a** was employed as the catalyst (entry 8, Table 4), in contrast to the 65% ee obtained when **8a**/**8b** mixtures were used (entry 8, Table 1). Employing diastereomerically enriched mixtures of the Norphos complexes **9** and **12** in a stoichiometric manner also improved the ee; in particular, 86% ee was achieved for nitrone **III** (entry 9, Tables 1 and 4). These results strongly indicate that changing the metal configuration reverses the induction sign and renders antipode adducts; i.e., the metal configuration governs the stereoselectivity.

2.5. Recycling experiments

Finally, in an attempt to increase the ratio adduct/catalyst without a loss of ee, we carried out recycling experiments using the reaction between nitrone **III** and methacrylonitrile catalysed by complex **8** as the model reaction. Scheme 6 shows the reaction procedure. In the first step, 5 equivalents of nitrone were added to diastereomerically pure (S_M,R_C)-**8**. After the required reaction time, excess nitrone was extracted in Et_2O/CH_2Cl_2 to avoid the simultaneous presence of nitrone, alkene, and catalyst in the reaction medium. The adduct was dissociated from the rhodium complex by adding 20 equivalents of alkene with concomitant formation of a mixture of the (S_M,R_C)-**8** and (R_M,R_C)-**8** epimers. The adduct and the excess nitrile were extracted in Et_2O/CH_2Cl_2, and from the extract, the adduct was isolated and characterised. The (S_M,R_C)-**8** and (R_M,R_C)-**8** mixture was allowed to epimerise to (S_M,R_C)-**8**, which after the addition of new nitrone, restarted a further catalytic run. Following this procedure, **8a** renders the 3,5-*endo* cycloadduct in 88% yield and with 80% ee and in 90% yield and with 78% ee in the second and third run, respectively.

3. Conclusions

Catalysts based on the chiral Lewis acid fragment (η^5-C_5Me_5)M(PP*) (M = Rh, Ir; PP* = enantiopure chiral diphosphane) generate efficient systems for the 1,3-dipolar cycloaddition reaction between methacrylonitrile and nitrones. The employment of alkenes containing a good coordinating functionality allowed for the complete characterization of the substrate-catalyst intermediates formed during catalysis, as well as the optimization of the catalytic system performance. The ee achieved in the stoichiometric reactions compared to those in substoichiometric catalytic runs, strongly indicate that the enantioselectivity is controlled by the metal centre. Finally, catalysts can be recycled up to three times without a significant loss of activity or selectivity.

4. Experimental section

4.1. Material and instrumentation

All solvents were dried over appropriate drying agents, distilled under argon and degassed prior to use. All preparations were 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. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Bruker AV-500 (500.13 MHz), AV-400 (400.16 MHz) or ARX-300 (300.10 MHz) spectrometers. Chemical shifts are expressed in ppm up field from $SiMe_4$ or 85% H_3PO_4 (^{31}P). NOESY and ^{13}C, ^{31}P and ^{1}H correlation spectra were obtained using standard procedures. Optical rotations were recorded on a Perkin–Elmer 241 polarimeter (10 cm cell, 589 nm). Analytical high performance liquid chromatography (HPLC) was performed on an Alliance Waters (Waters 2996, PDA detector) instrument using a chiral column Daicel Chiralcel OD-H (0.46 cm × 25 cm) with OD-H guard (0.46 cm × 25 cm) or Chiralpak AD-H (0.46 cm × 25 cm) columns. Complexes **1**–**6** were prepared using literature procedures.[16]

4.2. Catalytic procedure

At −25 °C, the corresponding aqua-complex [(η^5-C_5Me_5)M(PP*)(H_2O)][SbF_6]$_2$ **1**–**6** (0.03 mmol, 10 mol %), NC(Me)C=CH_2 (2.10 mmol) and CH_2Cl_2 (3 mL) were stirred for 30 min. To the resulting solution, nitrone (0.30 mmol) in CH_2Cl_2 (1 mL) was added. After stirring at the indicated temperature for the appropriate reaction time, 20 mL of *n*-hexane were added. After filtration over Celite, the solution was evaporated to dryness. The conversion and regioselectivity were determined in $CDCl_3$ solutions of the crude mixture by ^{1}H NMR. The residue was purified by chromatography (SiO_2) to provide the corresponding isoxazolidine. The enantiomeric excess was determined by HPLC (for details see Supplementary material).

4.3. Preparation of [(η^5-C_5Me_5)M(PP*)(NC(Me)C=CH_2)][SbF_6]$_2$ 7–12

At −25 °C under argon, to a solution of the corresponding complex [(η^5-C_5Me_5)M(PP*)(H_2O)][SbF_6]$_2$ (0.13 mmol) in CH_2Cl_2 (5 mL), NC(Me)C=CH_2 (0.26 mmol) was added. The resulting yellow solution was stirred for 5 min and then the solvent was vacuum-evaporated to dryness. The diastereomeric composition of the residue was determined by NMR. The residue was re-dissolved in a minimum amount of CH_2Cl_2 (about 1 mL) and the addition of

20 mL of dry *n*-hexane afforded a yellow solid that was filtered off, washed with *n*-hexane and vacuum-dried.

4.3.1. Compound 7, R = Bn

Yield: 87%. IR (cm^{-1}): *ν*(CN) 2255 (m), *ν*(SbF_6) 651 (s). Anal. Calcd for $C_{47}H_{50}F_{12}RhNP_2Sb_2$: C, 44.6; H, 4.0; N, 1.1. Found: C, 44.1; H, 3.7; N, 1.1.

7a, (S_{Rh})-Isomer, 47%: $[\alpha]_D^{25}$ = 11.0 (*c* 0.60, CH_2Cl_2). ^1H NMR (500.10 MHz, CD_2Cl_2, 25 °C): *δ* = 8.00–7.15 (m, 25H, Ph), 5.96 (s, 1H, H_b), 5.16 (s, 1H, H_a), 3.29 (d, *J* = 13.0 Hz, 1H, CH*H*Ph), 3.10 (dt, *J* = 53.5, 13.6 Hz, 1H, H_{22}), 2.80 (m, 1H, H_{11}), 2.39 (m, 1H, H_{21}), 1.96 (t, *J* = 13.0 Hz, 1H, *CH*HPh), 1.52 (t, *J* = 2.2 Hz, 15H, C_5Me_5), 1.49 ppm (s, 3H, Me). ^{13}C NMR (125.77 MHz, CD_2Cl_2, 25 °C): *δ* = 140.29 (C^5), 137.72–123.74 (25C, Ph), 119.96 (CN), 114.69 (C^4), 107.74 (d, *J* = 4.8 Hz, C_5Me_5), 38.74 (dd, *J* = 29.0, 10.3 Hz, C^1), 36.01 (d, *J* = 16.4, 4.1 Hz, CH_2Ph), 29.03 (dd, *J* = 29.0, 10.3 Hz, C^2), 19.02 (Me), 9.20 ppm (C_5Me_5). ^{31}P NMR (202.46 MHz, CD_2Cl_2, 25 °C): *δ* = 68.81 (dd, *J*(Rh,P^1) = 123.2 Hz, *J*(P^1,P^2) = 38.1 Hz, P^1), 41.75 ppm (dd, *J*(Rh,P^2) = 125.8 Hz, P^2).

7b, (R_{Rh})-Isomer, 53%: ^1H NMR (300.10 MHz, CD_2Cl_2, −25 °C): *δ* = 5.81 (d, *J* = 1.5 Hz, 1H, H_b), 5.16 (s, 1H, H_a), 3.02 (m, 1H, CH*H*Ph), 1.51 (t, *J* = 2.2 Hz, 15H, C_5Me_5), 1.49 ppm (s, 3H, Me). ^{31}P NMR (121.48 MHz, CD_2Cl_2, −25 °C): *δ* = 67.00 (dd, *J*(Rh,P^1) = 126.3 Hz, *J*(P^1,P^2) = 33.6 Hz, P^1), 57.60 ppm (dd, *J*(Rh,P^2) = 123.4 Hz, P^2).

4.3.2. Compound 8, R = Cy

Yield: 91%. IR (cm^{-1}): *ν*(CN) 2257 (m), *ν*(SbF_6) 653 (s). Anal. Calcd for $C_{46}H_{54}F_{12}RhNP_2Sb_2$: C, 43.9; H, 4.3; N, 1.1. Found: C, 43.6; H, 4.0; N, 1.1.

8a, (S_{Rh})-Isomer, 58%: $[\alpha]_D^{25}$ = 5.8 (*c* 1.02, CH_2Cl_2). ^1H NMR (400.16 MHz, CD_2Cl_2, 25 °C): *δ* = 7.96–7.33 (m, 20H, Ph), 5.90 (br s, 1H, H_b), 5.17 (br s, 1H, H_a), 3.38 (dt, *J* = 54.3, 12.4 Hz, 1H, H_{22}), 2.49 (m, 1H, H_{21}), 2.44 (m, 1H, H_{11}), 1.60–0.70 (m, 11H, Cy), 1.50 (t, *J* = 3.5 Hz, 3H, Me), 1.46 ppm (t, *J* = 3.5 Hz, 15H, C_5Me_5). ^{13}C NMR (100.61 MHz, CD_2Cl_2, 25 °C): *δ* = 140.02 (C^5), 135.02–121.32 (24C, Ph), 120.74 (CN), 114.72 (C^4), 107.60 (d, *J* = 4.8 Hz, C_5Me_5), 42.38–25.51 (6C, Cy), 38.18 (dd, *J*(P,C) = 14.1, 5.3 Hz, C^1), 26.56 (q, *J* = 14.9 Hz, C^2), 18.98 (Me), 9.11 ppm (C_5Me_5). ^{31}P NMR (161.96 MHz, CD_2Cl_2, 25 °C): *δ* = 73.73 (dd, *J*(Rh,P^1) = 121.8 Hz, *J*(P^1,P^2) = 37.8 Hz, P^1), 44.91 ppm (dd, *J*(Rh,P^2) = 126.4 Hz, P^2).

8b, (R_{Rh})-Isomer, 42%: ^1H NMR (400.16 MHz, CD_2Cl_2, −25 °C): *δ* = 5.85 (d, *J* = 1.6 Hz, 1H, H_b), 5.25 (br s, 1H, H_a), 3.28 (m, 1H, H_{22}), 2.85 (m, 1H, H_{21}), 2.77 (m, 1H, H_{11}), 1.46 (s, 3H, Me), 1.41 ppm (t, *J* = 3.3 Hz, 15H, C_5Me_5). ^{31}P NMR (161.96 MHz, CD_2Cl_2, −25 °C): *δ* = 59.56 (dd, *J*(Rh,P^1) = 123.8 Hz, *J*(P^1,P^2) = 37.7 Hz, P^1), 53.58 ppm (dd, *J*(Rh,P^2) = 121.9 Hz, P^2).

4.3.3. Compound 9

Yield: 91%. IR (cm^{-1}): *ν*(CN) 2253 (m), *ν*(SbF_6) 652 (s). Anal. Calcd for $C_{45}H_{48}F_{12}RhNP_2Sb_2$: C, 43.6; H, 3.9; N, 1.1. Found: C, 43.8; H, 4.0; N, 1.1.

9a, (S_{Rh})-Isomer, 56%: ^1H NMR (300.10 MHz, CD_2Cl_2, 25 °C): *δ* = 7.96–7.17 (m, 20H, Ph), 6.16 (dd, *J* = 5.4, 3.0 Hz, 1H, H_5), 6.01 (s, 1H, H_b), 5.39 (s, 1H, H_a), 4.92 (dd, *J* = 5.4, 3.0 Hz, 1H, H_6), 3.44 (s, 1H, H_1), 3.21 (br s, 1H, H_2), 3.10 (s, 1H, H_4), 3.08 (m, 1H, H_3), 2.12 (m, 2H, H_{71}, H_{72}), 1.64 (s, 3H, Me), 1.56 ppm (t, *J* = 3.7 Hz, 15H, C_5Me_5). ^{13}C NMR (75.50 MHz, CD_2Cl_2, 25 °C): *δ* = 140.94 (d, *J* = 7.3 Hz, C^5), 140.30 (C^{10}), 135.33–123.13 (24C, Ph), 130.75 (C^6), 127.03 (CN), 115.09 (C^9), 106.39 (d, *J* = 5.5 Hz, C_5Me_5), 52.81 (m, C^7), 51.00 (dd, *J* = 26.7, 17.7 Hz, C^3), 45.17 (dd, *J* = 35.6, 17.5 Hz, C^2), 43.96 (dd, *J* = 9.0, 7.5 Hz, C^1), 41.88 (dd, *J* = 13.2, 7.8 Hz, C^4), 18.99 (Me), 9.39 ppm (C_5Me_5). ^{31}P NMR (121.48 MHz, CD_2Cl_2, 25 °C): *δ* = 39.86 (dd, *J*(Rh,P^1) = 124.3 Hz, *J*(P^1,P^2) = 41.2 Hz, P^1), 30.60 ppm (dd, *J*(Rh,P^2) = 131.1 Hz, P^2).

9b, (R_{Rh})-Isomer, 44%: ^1H NMR (300.10 MHz, CD_2Cl_2, 25 °C): *δ* = 6.74 (dd, *J* = 5.4, 3.1 Hz, 1H, H_5), 6.11 (s, 1H, H_b), 6.09 (dd, *J* = 5.4, 3.1 Hz, 1H, H_6), 5.56 (s, 1H, H_a), 3.46 (br s, 1H, H_2), 3.27 (s, 1H, H_1), 2.90 (s, 1H, H_4), 2.45 (t, *J* = 13.8 Hz, 1H, H_3), 1.78 (m, 1H, H_{72}), 1.73 (s, 3H, Me), 1.58 (s, 15H, C_5Me_5), 0.41 ppm (d, *J* = 9.2 Hz, 1H, H_{71}). ^{13}C NMR (75.50 MHz, CD_2Cl_2, 25 °C): *δ* = 142.15 (d, *J* = 8.0 Hz, C^5), 140.54 (C^{10}), 133.40 (C^6), 127.22 (CN), 115.16 (C^9), 106.67 (d, *J* = 5.5 Hz, C_5Me_5), 52.07 (d, *J* = 10.9 Hz, C^7), 48.58 (dd, *J* = 33.9, 19.2 Hz, C^3), 47.21 (dd, *J* = 27.9, 15.8 Hz, C^2), 43.65 (C^1), 41.30 (dd, *J* = 11.8, 6.6 Hz, C^4), 19.02 (Me), 9.40 ppm (C_5Me_5). ^{31}P NMR (121.48 MHz, CD_2Cl_2, 25 °C): *δ* = 39.86 (dd, *J*(Rh,P^1) = 124.3 Hz, *J*(P^1,P^2) = 41.2 Hz, P^2), 30.81 ppm (dd, *J*(Rh,P^2) = 131.0 Hz, P^1).

4.3.4. Compound 10, R = Bn

Yield: 95%, IR (cm^{-1}): *ν*(CN) 2257 (m), *ν*(SbF_6) 652 (s). Anal. Calcd for $C_{47}H_{50}F_{12}IrNP_2Sb_2$: C, 41.7; H, 3.7; N, 1.0. Found: C, 41.5; H, 3.5; N, 0.9.

10a, (S_{Ir})-Isomer, 68%: $[\alpha]_D^{25}$ = −10.2 (*c* 0.46, CH_2Cl_2). ^1H NMR (400.16 MHz, CD_2Cl_2, 25 °C): *δ* = 7.99–7.12 (m, 25H, Ph), 5.93 (s 1H, H_b), 5.17 (s, 1H, H_a), 3.30 (m, 1H, CH*H*Ph), 3.18 (m, 1H, H_{22}), 2.87 (m, 1H, H_{11}), 2.42 (m, 1H, H_{21}), 2.01 (m, 1H, *CH*HPh), 1.62 (t, *J* = 2.3 Hz, 15H, C_5Me_5), 1.50 ppm (s, 3H, Me). ^{13}C NMR (100.61 MHz, CD_2Cl_2, 25 °C): *δ* = 141.13 (C^5), 137.96–118.84 (30C, Ph), 119.57 (CN), 114.37 (C^4), 102.20 (C_5Me_5), 38.70 (dd, *J* = 34.2, 7.9 Hz, C^1), 35.33 (d, *J* = 16.5, 3.3 Hz, C^3), 29.78 (dd, *J* = 42.0, 12.8 Hz, C^2), 19.12 (Me), 8.54 ppm (C_5Me_5). ^{31}P NMR (161.96 MHz, CD_2Cl_2, 25 °C): *δ* = 35.99 (d, *J*(P^2,P^1) = 13.1 Hz, P^1), 11.76 ppm (d, P^2).

10b, (R_{Ir})-Isomer, 32%: ^1H NMR (300.10 MHz, CD_2Cl_2, −25 °C): *δ* = 5.76 (d, *J* = 1.7 Hz, 1H, H_b), 5.14 (s, 1H, H_a), 1.59 (s, 15H, C_5Me_5), 1.37 ppm (s, 3H, Me). ^{31}P NMR (121.48 MHz, CD_2Cl_2, −25 °C): *δ* = 35.13 (d, *J*(P^2,P^1) = 9.5 Hz, P^1), 25.04 ppm (d, P^2).

4.3.5. Compound 11, R = Cy

Yield: 90%. IR (cm^{-1}): *ν*(CN) 2254 (m), *ν*(SbF_6) 652 (s). Anal. Calcd for $C_{46}H_{54}F_{12}IrNP_2Sb_2$: C, 41.0; H, 4.0; N, 1.0. Found: C, 41.0; H, 4.1; N, 0.9.

11a, (S_{Ir})-Isomer, 67%: $[\alpha]_D^{25}$ = −19.1 (*c* 0.67 in CH_2Cl_2). ^1H NMR (400.16 MHz, CD_2Cl_2, 25 °C): *δ* = 7.93–7.31 (m, 20H, Ph), 5.83 (br s, 1H, H_b), 5.06 (br s, 1H, H_a), 3.34 (dt, *J* = 51.7, 11.6 Hz, 1H, H_{22}), 2.43 (m, 1H, H_{21}), 2.39 (m, 1H, H_{11}), 1.73–0.76 (m, 11H, Cy), 1.56 (t, *J* = 2.3 Hz, 15H, C_5Me_5), 1.40 ppm (t, *J* = 1.3 Hz, 3H, Me). ^{13}C NMR (100.61 MHz, CD_2Cl_2, 25 °C): *δ* = 140.88 (C^5), 135.02–120.64 (24C, Ph), 119.91 (CN), 114.46 (C^4), 102.10 (C_5Me_5), 42.28–25.52 (6C, Cy), 37.35 (dd, *J*(P,C) = 13.4, 4.3 Hz, C^1), 27.07 (m, C^2), 19.10 (Me), 8.49 ppm (C_5Me_5). ^{31}P NMR (161.96 MHz, CD_2Cl_2, 25 °C): *δ* = 40.46 (d, *J*(P^2,P^1) = 13.0 Hz, P^1), 14.60 ppm (d, P^2).

11b, (R_{Ir})-Isomer, 33%: ^1H NMR (400.16 MHz, CD_2Cl_2, −10 °C): *δ* = 5.86 (br s, 1H, H_b), 5.11 (br s, 1H, H_a), 3.50 (m, 1H, H_{22}), 2.87 (m, 1H, H_{21}), 2.79 (m, 1H, H_{11}), 1.53 (t, *J* = 2.2 Hz, 15H, C_5Me_5), 1.35 ppm (s, 3H, Me). ^{31}P NMR (161.96 MHz, CD_2Cl_2, 20 °C): *δ* = 28.51 (d, *J*(P^2,P^1) = 13.9 Hz, P^1), 20.51 ppm (d, P^2).

4.3.6. Compound 12

Yield: 82%. IR (cm^{-1}): *ν*(CN) 2254 (m), *ν*(SbF_6) 654 (s). Anal. Calcd for $C_{45}H_{48}F_{12}IrNP_2Sb_2$: C, 40.7; H, 3.6; N, 1.0. Found: C, 41.3; H, 3.3; N, 1.1.

12a, (S_{Ir})-Isomer, 53%: ^1H NMR (300.10 MHz, CD_2Cl_2, 25 °C): *δ* = 7.95–7.15 (m, 20H, Ph), 6.15 (m, 1H, H_5), 5.97 (br s, 1H, H_b), 5.30 (br s, 1H, H_a), 4.89 (dd, *J* = 5.3, 2.7 Hz, 1H, H_6), 3.45 (s, 1H, H_1), 3.30 (m, 1H, H_2), 3.11 (s, 1H, H_4), 3.08 (m, 1H, H_3), 2.36 (m, 1H, H_{71}), 2.18 (m, 2H, H_4, H_{72}), 1.68 (s, 3H, Me), 1.61 ppm (t, *J* = 2.4 Hz, 15H, C_5Me_5). ^{13}C NMR (75.50 MHz, CD_2Cl_2, 25 °C): *δ* = 141.17 (C^{10}), 140.88 (d, *J* = 7.7 Hz, C^5), 134.96–121.73 (24C, Ph), 130.29 (C^6), 126.25 (CN), 114.78 (C^9), 101.03 (t, *J* = 1.6 Hz, C_5Me_5), 53.24 (m, C^7), 51.11 (dd, *J* = 33.9, 14.7 Hz, C^3), 45.41 (dd, *J* = 42.5, 14.8 Hz, C^2), 43.60 (dd, *J* = 8.3, 6.6 Hz, C^1), 40.89 (dd,

J = 12.2, 6.8 Hz, C^4), 19.10 (Me), 8.78 ppm (C_5Me_5). ^{31}P NMR (121.48 MHz, CD_2Cl_2, 25 °C): δ = 6.00 (d, $J(P^2,P^1)$ = 27.0 Hz, P^1), −1.41 ppm (d, P^2).

12b, (R_{Ir})-Isomer, 47%: ^1H NMR (300.10 MHz, CD_2Cl_2, 25 °C): δ = 6.78 (m, 1H, H_5), 6.15 (m, 1H, H_6), 6.07 (s, 1H, H_b), 5.46 (s, 1H, H_a), 3.45 (m, 1H, H_1), 3.26 (s, 1H, H_3), 2.88 (s, 1H, H_4), 2.53 (m, 1H, H_2), 2.01 (m, 1H, H_{72}), 1.65 (t, J = 2.5 Hz, 15H, C_5Me_5), 1.59 (s, 3H, Me), 0.41 ppm (d, J = 9.4 Hz, 1H, H_{71}). ^{13}C NMR (75.50 MHz, CD_2Cl_2, 25 °C): δ = 142.03 (d, J = 7.8 Hz, C^6), 141.40 (C^{10}), 114.86 (C^9), 133.58 (C^5), 126.35 (CN), 101.28 (t, J = 1.6 Hz, C_5Me_5), 52.58 (C^7), 49.08 (dd, J = 41.5, 16.3 Hz, C^2), 47.26 (dd, J = 33.4, 13.5 Hz, C^1), 43.08 (dd, J = 9.6, 7.8 Hz, C^3), 40.49 (dd, J = 11.4, 5.4 Hz, C^4), 19.13 (Me), 8.79 ppm (C_5Me_5). ^{31}P NMR (121.48 MHz, CD_2Cl_2, 25 °C): δ = 5.94 (d, $J(P^2,P^1)$ = 27.5 Hz, P^2), −1.61 ppm (d, P^1).

4.4. Epimerisation reactions

Mixtures of (*S*) and (*R*) at the metal epimers were dissolved in acetone. After stirring at RT for 1 h (rhodium complexes **7** and **8**) or refluxing for 6 h (iridium complexes **10** and **11**) the solution was concentrated to approximately 1 mL and then hexane (10 mL) was added. The resulting yellow solids were characterised by NMR as the corresponding diastereopure (*S*) at metal epimers.

On the other hand, after refluxing for 6 h in acetone 56/44 (rhodium complex **9**) or 53/47 (iridium complex **12**) molar ratio mixtures of the corresponding (*S*) and (*R*) at metal epimers, diastereomeric mixtures with 40% de in favour of the (*S*) at the metal epimer were recovered in both cases.

4.5. Stoichiometric catalytic reactions

At room temperature, to a dichloromethane solution of the corresponding diastereopure methacrylonitrile complex **7a**, **8a**, **10a** and **11a** or 70/30 molar ratio mixtures of the **9a**/**9b** and **12a**/**12b** complexes (4 mL, ca. 7.5×10^{-2} mol L^{-1}), five equivalents of nitrone were added. The solution was stirred for 3 h and then an excess of $^nBu_4NBr$ (ca. 5 equiv) in CH_2Cl_2 (1 mL) was added. The solvent was evaporated under vacuum to dryness and the residue was extracted with diethyl ether/CH_2Cl_2: 5/1 (3 × 5 mL). The solvents of the combined extracts were evaporated and the resulting colourless oil was analysed and characterised by NMR and HPLC techniques.

4.6. Recycling experiments

To diastereopure (S_{Rh},R_C)-[(η^5-C_5Me_5)Rh{(*R*)-Cyphos}(NC(Me)C = CH_2)] $[SbF_6]_2$ **8a** (93.5 mg, 0.075 mmol) in CH_2Cl_2 (4 mL), 3,4-dihydroisoquinoline *N*-oxide (55.2 mg, 0.375 mmol) in CH_2Cl_2 (1 mL) was added. The resulting solution was stirred for 3 h, at RT, and then vacuum-evaporated to dryness. The residue was washed with an Et_2O/CH_2Cl_2, 9/1, v/v mixture (10 × 7 mL) to eliminate the excess nitrone. To the remaining solid dissolved in CH_2Cl_2 (4 mL), methacrylonitrile (125.7 μL, 1.500 mmol) was added. After stirring for 4 h at 0 °C, the solution was concentrated under reduced pressure to dryness. The residue was extracted with an Et_2O/CH_2Cl_2, 9/1, v/v mixture (10 × 7 mL) and the obtained solution was concentrated under vacuum to dryness. The yield and enantiomeric purity of this solid were determined by the usual methods. The remaining solid after extraction, which consisted of **8a**/**8b** mixtures, was dissolved in CH_2Cl_2 (4 mL) and the solution was stirred at room temperature to complete epimerization to **8a** (about 3 h). The addition of 3,4-dihydroisoquinoline *N*-oxide (55.2 mg, 0.375 mmol) to this solution initiated the next catalytic reaction.

4.7. X-ray structure determination of compound 7a

The X-ray diffraction data were collected at 100(2) K on a Bruker SMART APEX CCD area detector diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using narrow ω rotations (0.3°). Intensities were integrated with SAINT-PLUS program[21] and corrected from absorption effects with SADABS.[22] The structure was solved by direct methods with SHELXS-2013[23] and refined, by full-matrix least-squares method on F^2, with SHELXL-2013,[24] included in WinGX package.[25] All non-hydrogen atoms allowed anisotropic thermal motion. Hydrogen atoms were observed in Fourier differences maps and refined with a riding model from calculated. Additionally to the internal configuration reference of the (*R*)-Benphos ligand, the Flack parameter was refined as a check of the correct absolute structure determination.[26] Information concerning crystallographic data collection and structure refinement is summarized in Supplementary material. CCDC-1443435 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.

Uncited reference

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetasy.2016.04.006.

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