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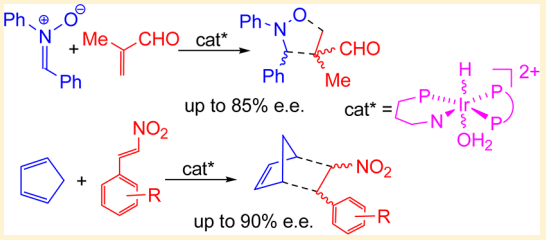
Chiral Octahedral Phosphano–Oxazoline Iridium(III) Complexes as Catalysts in Asymmetric Cycloaddition Reactions

Daniel Carmona,* Joaquina Ferrer,* Néstor García, Paola Ramírez, Fernando J. Lahoz, Pilar García-Orduña, and Luis A. Oro

Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC-Universidad de Zaragoza, Departamento de Química Inorgánica, Pedro Cerbuna 12, 50009 Zaragoza, Spain

Supporting Information

ABSTRACT: The synthesis and characterization of cationic iridium(III) aqua complexes of the formula $[IrH(H_2O)(PN^*)(PP)][SbF_6]_2$ (PN* = chiral phosphano–oxazoline ligand; PP = diphosphane) as well as that of the $OPOF_2$-containing complex $[IrH(OPOF_2)(PNiPr)(dppp)][SbF_6]$ (**10**) are reported. The X-ray molecular structures of $[IrH(H_2O)(PNInd)(dppe)][SbF_6]_2$ (**1**), $[IrH(H_2O)(PNInd)(dppen)][SbF_6]_2$ (**2**), and **10a** have been determined. Dichloromethane solutions of these aqua complexes efficiently catalyze the enantioselective 1,3-dipolar cycloaddition of the nitrone *N*-benzylidenephenylamine *N*-oxide to methacrolein and Diels–Alder reactions between cyclopentadiene and *trans*-β-nitrostyrenes. In the first case, the catalytic reaction occurs with excellent *endo* selectivity and ee up to 85%; the Diels–Alder reaction occurs rapidly at room temperature with good *endo*:*exo* selectivity and ee up to 90%. The dipolar cycloaddition intermediates $[IrH(methacrolein)(PNInd)(PP)][SbF_6]_2$ (PP = (*S*,*S*)-chiraphos (**11**), (*R*)-prophos (**12**)) have been characterized, and the molecular structure of **11** has been determined by an X-ray structural analysis.



INTRODUCTION

Asymmetric catalysis plays a decisive role in modern synthetic organic chemistry, and chiral metal complexes are frequently employed as effective homogeneous catalysts in order to achieve both high reactivity and control of the selectivity.[1] One of the most attractive methodologies to obtain optically active organic compounds involves cycloaddition reactions, in which several adjacent stereogenic centers can be created in a concerted fashion.[2] Among them, the enantioselective 1,3-dipolar cycloaddition (DC) reaction of an alkene and a nitrone affords five-membered isoxazolidines containing up to three contiguous asymmetric carbon atoms (Scheme 1a)[3] and the Diels–Alder (DA) reaction between an alkene and a diene can generate up to four contiguous stereogenic centers within a cyclohexene framework (Scheme 1b).[4]

To study these metal-catalyzed cycloadditions, alkenes that enable a bidentate coordination to the metallic Lewis acid, such as 3-alkenoyloxazolidinones (Scheme 1c), have been frequently employed as model substrates. In contrast, examples of activation of monofunctionalized alkenes are scarce. Only in the last years have some examples of the use of monodentate enals as dipolarophiles in enantioselective DC[5] reactions and as dienophiles in enantioselective DA reactions, the latter mostly catalyzed by half-sandwich complexes of Rh, Ir, and Ru,[6−9] been reported. However, other activated alkenes capable of linking one-point-binding metallic moieties in a monodentate fashion, such as nitroalkenes, remain almost unexplored. In particular, the only asymmetric DA processes studied involving nitroalkenes as dienophiles are their reactions with α,β-unsaturated ketones promoted by 2-substituted pyrrolidines.[10] Therefore, as far as we know, no metal-catalyzed asymmetric DA reactions with this type of dienophile have been reported so far.

On the other hand, chiral phosphano–oxazoline ligands (PN*) have proven to be useful in several metal-catalyzed reactions.[11] In some instances, for example, when Ir^I/PN* systems are applied to the asymmetric hydrogenation of unfunctionalized olefins,[12] they outperform P,P and N,N ligands.[13] In this context, we have reported the preparation and characterization of Ir(I) compounds with the (4*S*)-2-[2-(diphenylphosphanyl)phenyl]-4-isopropyl-4,5-dihydrooxazole (PN*i*Pr) ligand[14] and employed some of them as catalysts for asymmetric Michael additions.[14c] It is interesting to point out that although in many cases Ir(III) species are considered key intermediates in the catalytic processes involving PN* ligands, the use of well-defined Ir^{III}/PN* complexes as catalyst precursors is uncommon, with the exception of $(\eta^5\text{-}C_5Me_5)Ir^{III}$ derivatives.[9e]

With all these concerns in mind, in the present paper we disclose a general preparative route of octahedral iridium(III) aqua complexes containing chiral chelate phosphano–oxazolines and diphosphanes (PP) of general formula $[IrH(H_2O)(PN^*)(PP)][SbF_6]_2$ and their use as catalyst precursors in the asymmetric 1,3-dipolar cycloaddition of the nitrone *N*-benzylidenephenylamine *N*-oxide to methacrolein and in the

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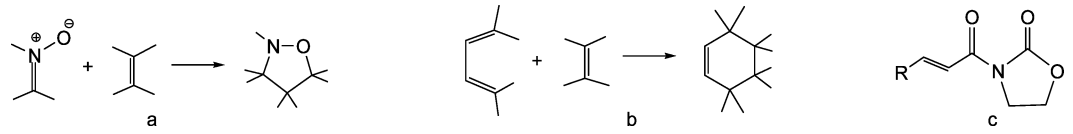
Scheme 1. DC of Nitrones and Alkenes (a), DA Reaction (b), and 3-Alkenoyloxazolidinones (c)

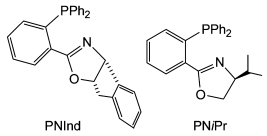


Diels–Alder reaction of *trans*-β-nitrostyrenes with cyclopentadiene. The complete analytical and spectroscopic characterization of the new complexes, including the molecular structure determination by X-ray diffraction of some representative examples, is also reported.

RESULTS AND DISCUSSION

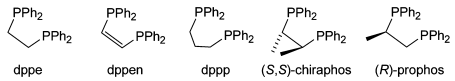
Preparation and Characterization of the Aqua Complexes $[IrH(H_2O)(PN^*)(PP)][SbF_6]_2$. The aqua complexes $[IrH(H_2O)(PN^*)(PP)][SbF_6]_2$ (**1**–**9**) were prepared in high yield by treating the corresponding chlorides[15] $[IrClH(PN^*)(PP)][SbF_6]$ with equimolar amounts of $AgSbF_6$ and excess of water in dichloromethane/acetone mixtures, according to eq 1.

$$[IrHCl(PN^*)(PP)][SbF_6] + AgSbF_6 + H_2O \longrightarrow [IrH(H_2O)(PN^*)(PP)][SbF_6]_2 + AgCl \quad (1)$$



PNInd PN*i*Pr

Complex	PN*	PP
1	PNInd	dppe
2	PNInd	dppen
3a,b	PNInd	dppp
4	PNInd	(*S*,*S*)-chiraphos
5a,a'	PNInd	(*R*)-prophos
6	PN*i*Pr	dppe
7	PN*i*Pr	dppen
8a,b	PN*i*Pr	dppp
9a,a'	PN*i*Pr	(*R*)-prophos

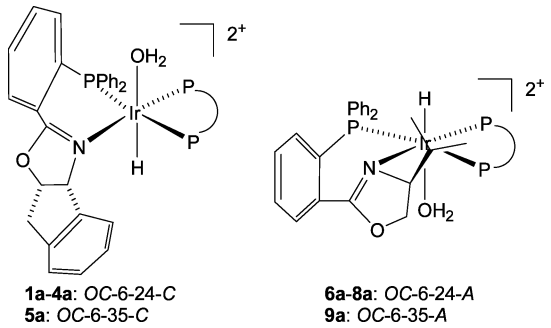


dppe dppen dppp (*S*,*S*)-chiraphos (*R*)-prophos

The preparative route employed is highly diastereoselective: complexes **1**, **2**, **4**, **6**, and **7** were obtained as a single isomer, while complexes containing dppp (**3**, **8**) and (*R*)-prophos (**5**, **9**) as diphosphanes were isolated as mixtures of two diastereomers (84:16 (**3**), 68:32 (**5**), 85:15 (**8**), and 62:38 (**9**) molar ratio mixtures). With labels **a** and **b** we represent a pair of epimers at the metal, and labels **a** and **a′** are used for coordination isomers (see below); in both cases label **a** refers to the major isomer.

The new complexes were characterized by mass spectrometry, IR and NMR spectroscopy, and microanalyses and, for compounds **1** and **2**, by X-ray crystal structure determinations. The NMR data were consistent with the presence of PN*, PP, hydride, and H_2O ligands in a 1:1:1:1 molar ratio (see the Experimental Section). Stereochemical assignments were accomplished through NOE experiments and two-dimensional homonuclear and heteronuclear ($^{13}C-^{1}H$, $^{31}P-^{1}H$) correlations. The presence of coordinated water was confirmed by an IR band in the 3600–3450 cm^{-1} region, along with a broad ^{1}H NMR signal at δ ranging from 3 to 5 ppm. The hydride ligand is denoted by a weak ν(Ir–H) band at high energy (2296–2326 cm^{-1}) and a ^{1}H NMR doublet of pseudotriplets at very high field (around −27 ppm). The δ value for the hydride resonance is indicative of a *trans* relationship between the hydride and the oxygen atom of the coordinated water.[16] For the PN*i*Pr-containing complexes **6**–**9**, very low chemical shift values were registered for the isopropyl methyl protons (from 0.65 to −0.58 ppm). We will turn to this point when discussing the molecular structure of the related complex **10**. On the other hand, the $^{31}P\{^{1}H\}$ NMR spectra of all compounds exhibit ABX or AMX patterns characteristic of a meridional arrangement around the metal with a large *trans* *J*(P,P) (about 320 Hz) and two smaller *cis* *J*(P,P) coupling constants.

The molecular structure determination by X-ray diffraction methods for the unique isomer of compounds **1** and **2** confirms the solution structural data and reveals a *C* configuration[17] for these diastereomers. Taking advantage of the similarity of the NMR data for all the major isomers of the PNInd-containing compounds **1**–**5**, we propose for all of them a *C* configuration (Figure 1), according to the stereochemical rules.[17] For the major isomer (labeled **a**) of the PN*i*Pr-containing complexes, the configuration at the metal was determined by NOE measurements. Thus, irradiation of the hydride resonance induces NOE enhancement on the CH proton of the *i*Pr group. This NOE relationship is only compatible with an *A* configuration for these complexes (Figure 1).



1a-4a: *OC*-6-24-*C*
5a: *OC*-6-35-*C*

6a-8a: *OC*-6-24-*A*
9a: *OC*-6-35-*A*

Figure 1. Proposed structures for the cations of the major diastereomers of **1**–**9**.

By analogy with the related chloride isomers (see ref 34), we assign an *A* configuration to the minor isomer of complex **3** (**3b**) and a *C* configuration to the **b** isomer of the PN*i*Pr-containing complex **8**. It is interesting to note that only for dppp derivatives are both epimers at metal obtained. Most probably, the higher conformational flexibility of the three-carbon chain connecting the P atoms of the diphosphane (only two carbons in the remaining cases)[18] allows for the accommodation of the water molecule at both sides of the equatorial plane defined by the two phosphorus atoms of the diphosphane and the phosphorus and nitrogen atoms of the PN* ligand.

On the other hand, assignment of the stereochemistry to the **a**, **a′** pair of isomers of the (*R*)-prophos-containing compounds **5** and **9** was accomplished by comparison of the ^{13}C NMR resonance of the asymmetric carbon of the (*R*)-prophos ligand

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with that of the corresponding chlorides (see ref 34). The phosphorus atom nearest to the asymmetric carbon of the diphosphane is *trans* to the phosphorus atom of the PN* ligand in isomers **a**′ and *cis* in the corresponding **a** isomers (Figure 2).

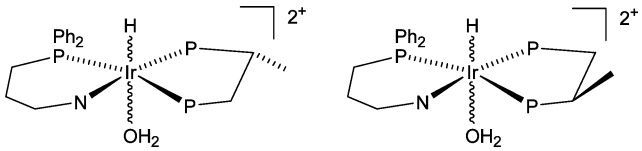

Figure 2. Proposed structures for the cations of **5a**′ and **9a**′.

In an attempt to obtain single crystals of complex **8**, we carried out the reaction depicted in eq 1 but using $AgPF_6$ as halogen scavenger instead of $AgSbF_6$ (eq 2). From the reaction medium a pale yellow solid was isolated that, according to analytical and spectroscopic data, was formulated as the $OPOF_2$-containing complex $[IrH(OPOF_2)(PNiPr)(dppp)][SbF_6]$ (**10**). The difluorophosphate anion most probably derives from partial hydrolysis of the PF_6 anion.[9g,19] Complex **10** was obtained as a 92:8 molar ratio mixture of the two isomers **10a**,**b**. Their spectroscopic properties are comparable to those of **8a**,**b**, respectively (see the Experimental Section). Single crystals of the major isomer, **10a**, were obtained, and its molecular structure was solved by X-ray diffraction.

$$[IrHCl(PNiPr)(dppp)][SbF_6] + AgPF_6 + H_2O \rightarrow \underset{\mathbf{10}}{[IrH(OPOF_2)(PNiPr)(dppp)][SbF_6]} + AgCl \quad (2)$$

Molecular Structures of Complexes 1, 2, and 10a. Single crystals suitable for X-ray diffraction analysis of the three complexes were obtained by slow diffusion of diethyl ether into dichloromethane solutions of the compounds. Views of the three cations are depicted in Figure 3. Selected structural parameters are summarized in Table 1.

All the three cations display an octahedral coordination around the iridium, with a hydride *trans* to the oxygen atom of coordinated water (**1** and **2**) or to one of the two oxygens of a difluorophosphate anion (**10a**); a phosphano−oxazoline, coordinated through its nitrogen and phosphorus atoms, and a diphosphane, coordinated through the two phosphorus atoms, occupy an equatorial plane of the octahedron. According to stereochemical nomenclature rules,[17] the three cations are *OC*-6-24 isomers. The PNInd-containing cations (compounds **1** and **2**) present a *C* configuration; however, the PN*i*Pr-containing cation (complex **10a**) adopts an *A* configuration, in good agreement with the observed NOE relationship (see above). As a consequence of the *trans* influence of the hydride ligand, the Ir−O bond distances, 2.238(7) Å (**1**), 2.258(6) Å (**2**), and 2.231(5) Å (**10a**), are elongated in comparison to the values observed in octahedral Ir complexes in which the oxygen atom is not *trans* to an hydride ligand (mean value 2.134(7) Å).[20] The Ir−P(1) and Ir−P(2) bond distances are in the range

Table 1. Selected Bond Distances (Å) and Angles (deg) for 1, 2, and 10a

	1	2	10a
Ir−P(1)	2.353(2)	2.341(2)	2.3599(18)
Ir−P(2)	2.287(2)	2.286(2)	2.294(2)
Ir−P(3)	2.345(2)	2.335(2)	2.3235(18)
Ir−O(2)	2.238(7)	2.258(6)	2.231(5)
Ir−N	2.145(7)	2.143(7)	2.120(6)
Ir−H	1.6036	1.599(10)	1.589(10)
N−C(45)	1.283(11)	1.312(11)	1.269(9)
N−C(54)/C(47)[a]	1.496(11)	1.489(11)	1.524(9)
P(1)−Ir−P(2)	83.52(7)	83.79(8)	87.38(8)
P(1)−Ir−P(3)	174.68(10)	174.73(8)	174.49(8)
P(1)−Ir−N	94.4(2)	95.5(2)	92.83(18)
P(1)−Ir−O(2)	90.8(2)	92.9(2)	90.03(13)
P(1)−Ir−H	90.2	93(5)	89(3)
P(2)−Ir−P(3)	100.60(8)	97.22(8)	98.09(8)
P(2)−Ir−N	172.6(2)	173.8(2)	172.78(18)
P(2)−Ir−O(2)	103.47(19)	103.53(16)	101.94(18)
P(2)−Ir−H	84.3	77(3)	86(3)
P(3)−Ir−N	81.1(2)	83.0(2)	81.67(18)
P(3)−Ir−O(2)	91.53(19)	91.9(2)	89.48(13)
P(3)−Ir−H	86.9	82(4)	91(3)
N−Ir−O(2)	83.7(3)	82.7(2)	85.3(2)
N−Ir−H	88.6	97(3)	87(3)
O(2)−Ir−H	172.3	174(5)	172(3)
Ir−N−C(45)	125.6(6)	125.9(6)	129.8(5)
Ir−N−C(54)	126.2(6)	128.0(5)	123.6(5)
C(45)−N−C(54)	107.9(7)	106.0(7)	106.4(6)

[a]Label C(47) corresponds to **10a**.

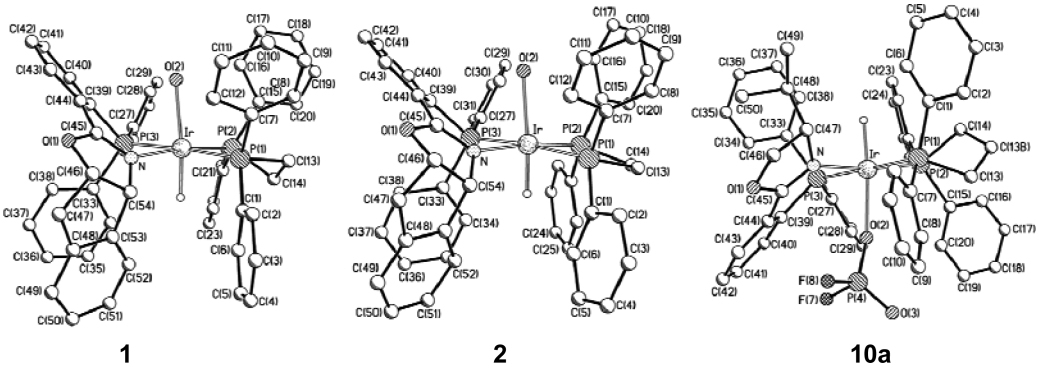

Figure 3. Molecular representations of the cations of **1**, **2**, and **10a.** Selected bond distances (Å) and angles (deg) for the $OPOF_2$ moiety in complex **10a**: O(2)−P(4), 1.459(5); O(3)−P(4), 1.449(5); P(4)−F(7), 1.537(5); P(4)−F(8), 1.538(5). Ir−O(2)−P(4), 167.1(4); O(2)−P(4)−O(3), 121.1(4); O(2)−P(4)−F(7), 108.2(3); O(2)−P(4)−F(8), 106.7(4); O(3)−P(4)−F(7), 110.3(3); O(3)−P(4)−F(8), 109.0(3); F(7)−P(4)−F(8), 99.3(3).

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Scheme 2. DC of *N*-Benzylidenephenylamine *N*-Oxide and Methacrolein

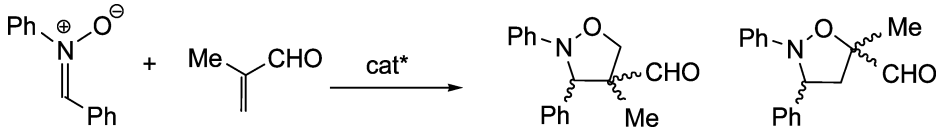

Table 2. Catalytic Results[a] for the DC Reaction

entry	precatalyst	*T* (°C)	time (h)	conversn (%)[b]	3,4-*endo* (%)[c]	3,5-*endo* (%)[c]	ee (%)[d]
1	**1**	room temp	1.5	47	9	91	−22/−21
2	**1**	−25	96	29	8	92	−31/−25
3	**2**	room temp	1.5	85	8	90[e]	−23/−12
4	**2**	−25	48	20	22	78	−32/−31
5	**3a,b** (84:16)	room temp	1.5	45	37	63	−72/−6
6	**3a,b** (84:16)	−25	96	34	41	59	−85/−14
7	**4**	room temp	48	98	5	93[e]	−53/−26
8	**4**	−25	96	20	7	93	−71/−22
9	**5a,a′** (68:32)	−25	96	87	60	40	77/38
10	**6**	room temp	3	82	7	91[e]	19/10
11	**6**	−25	96	36	15	85	5/32
12	**7**	room temp	1.5	47	14	86	18/2
13	**7**	−25	96	54	25	75	27/18
14	**8a,b** (85:15)	room temp	1.5	47	13	87	8/8
15	**8a,b** (85:15)	−25	96	38	17	83	25/25
16	**9a,a′** (62:38)	room temp	1.5	29	11	89	13/18
17	**9a,a′** (62:38)	−25	96	22	12	88	22/35

[a]Reaction conditions: catalyst 0.030 mmol, (5.0 mol %), methacrolein 4.2 mmol, nitrone 0.60 mmol, 4 Å molecular sieves (100 mg), in CH_2Cl_2 (2.5 mL). [b]Based on nitrone. [c]Determined by ^{1}H NMR spectroscopy. [d]Determined by integration of the ^{1}H NMR signals of the diastereomeric (*R*)-methylbenzylimine derivatives. Positive ee values correspond to the (3*R*,4*R*)-*endo* adduct. For the 3,5-*endo* adduct, positive ee values are arbitrarily assigned to the ee in the lower field 3-H proton ^{1}H NMR signal. [e]Exo adducts, 2%.

found for Ir(III) hydride complexes containing diphosphanes,[21] the former being longer than the second, probably due to the higher *trans* influence of the P(3) phosphorus atom. The bond distances and angles of PN* ligands are in good agreement with those of previously reported PN*/iridium(III) complexes.[9e] The difference of the two N−C bond distances clearly indicates the localization of the N═C double bond on the N−C(45) pair, with no evident electron density delocalization. The bidentate coordination of these ligands leads to the formation of a six-membered Ir−N−C(45)−C(44)−C(39)−P(3) metallacycle that, according to the Cremer and Pople parameters,[22] adopts a highly puckered slightly twisted screw-boat $^1S_6$ (**1** and **2**) or an analogous inverted $^6S_1$ conformation (**10a**). This structural feature, together with the close values of dihedral angles between NIrP and N−C(45)−C(44)−C(39)−P planes (130.8(2)° (**1**), 136.7(2)° (**2**), and 135.1(2)° (**10a**)) seems to be characteristic of these phosphano−oxazoline fragments. We have already pointed out the marked rigidity of these ligands and their coordination toward the metal (see ref 34). In particular, this conformation forces the *pro-R* (C(33)−C(38)) and *pro-S* (C(27)−C(32)) phenyl groups of the PPh_2 moiety of the PN* ligand to occupy pseudo-axial and pseudo-equatorial positions, respectively. This puckering is most probably maintained in solution, as evidenced by the shielding of the methyl isopropyl groups of **10a** (see above), due to the diamagnetic electronic current of the pseudo-axial PPh ring.

It is interesting to note that substitution of chlorine atom by a water molecule (eq 1) seems to hardly alter the structural parameters of the metal coordination sphere, as shown by the very similar geometrical values of **2** and its parent chloride [IrClH(PNInd)(dppen)]$^+$. However, when intermolecular interactions are considered, the ability of the coordinated water to act as a potential hydrogen bond donor should be taken into account. In this context, **1** and **2** cations interact through O−H···O hydrogen bonds with water and diethyl ether solvent molecules, respectively (O···O distances 2.613(14) Å (**1**) and 2.701(11) Å (**2**)).

1,3-Dipolar Cycloaddition of *N*-Benzylidenephenylamine *N*-Oxide and Methacrolein. Complexes **1**−**9** were tested as catalyst precursors for the 1,3-dipolar cycloaddition between methacrolein and *N*-benzylidenephenylamine *N*-oxide (Scheme 2). Table 2 gives a selection of the results obtained together with the reaction conditions employed. The collected results are the average of, at least, two comparable reaction runs. Before the addition of the nitrone, the precursors were treated with methacrolein, in the presence of molecular sieves (see the Experimental Section). Under these conditions, the formation of active methacrolein complexes is favored at the expense of the initial aqua complexes (see below). All complexes generate active systems for the essayed reaction. An *endo* preference was showed in all cases, and most of the reactions occur with perfect *endo* selectivity. Moderate to good enantioselectivity was obtained, the PNInd derivatives **1**−**5** being more enantioselective. Strikingly, the highest ee values were achieved when mixtures of diastereomers were employed as precatalysts (entries 5, 6, and 9). Lowering the reaction temperature had very little effect on the diastereoselectivity, but significant improvements in the enantioselectivity were achieved.

Methacrolein Complexes [IrH(methacrolein)(PNInd)(PP)][SbF_6]$_2$ (PP = (*S*,*S*)-chiraphos (11), (*R*)-prophos (12)). To get a better insight into the catalytic reaction, we have

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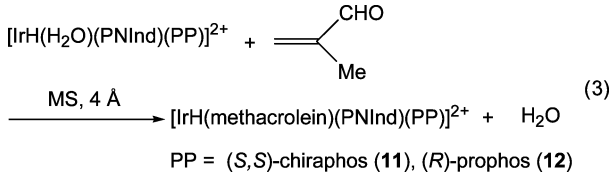
studied, by NMR spectroscopy, the solution behavior of complexes **1**−**9** in the presence of an excess of methacrolein. In most cases, complex mixtures of unidentified compounds are formed, but when at 0 °C 5 equiv of methacrolein was added to dichloromethane solutions of the PNInd-containing aqua complexes $[IrH(H_2O)(PNInd)(PP)]^{2+}$ (PP = (*S*,*S*)-chiraphos (**4**), (*R*)-prophos (**5**)), the clean formation of the corresponding new cation $[IrH(methacrolein)(PNInd)(PP)]^{2+}$ was observed, according to ^1H and ^{31}P NMR measurements (eq 3). At this temperature, the aqua and methacrolein complexes



(3)

are in equilibrium, but this equilibrium can be completely shifted to the right by the addition of 4 Å molecular sieves. In fact, from these solutions the methacrolein cations can be isolated as the hexafluoroantimonate salts $[IrH(methacrolein)(PNInd)(PP)][SbF_6]_2$ (PP = (*S*,*S*)-chiraphos (**11**), (*R*)-prophos (**12**)). Complex **11** was obtained as the sole diastereomer; however, due to the C_1 symmetry of the (*R*)-prophos ligand, two diastereomers, **12a** and **12a′**, in the molar ratio 74:26 were isolated for complex **12**.[23]

The complexes were characterized by spectroscopic means and by the X-ray molecular structure determination of compound **11**. One large and two short P,P couplings and three *cis*-type P,H couplings in the NMR spectra strongly indicated a meridional arrangement for the three phosphorus atoms. Additionally, the chemical shift of the hydride, about −26 ppm, close to those observed for this ligand in the parent aqua compounds, is indicative of a *trans* relationship between the hydride and the oxygen atom of the methacrolein ligand. The ^1H and ^{13}C NMR data show resonances attributable to coordinated methacrolein. In particular, a ^{13}C NMR peak around 207 ppm (CHO) and two new ^1H NMR resonances at about 6 ppm (olefinic protons) denote the presence of this ligand in the molecule. While in complex **11** the aldehyde CHO proton resonates at 7.39 ppm, about 2.1 ppm shifted to higher field with regard to the corresponding free methacrolein resonance (9.53 ppm), the aldehyde proton in **12a** and **12a′** is only shielded by ca. 0.5 and 1.3 ppm, respectively. Finally, in complex **11**, enhancement of the CHO proton resonance when the olefinic proton at 5.80 ppm was irradiated is only compatible with an s-*trans* conformation for the coordinated methacrolein.

Although the structural parameters obtained from the X-ray analysis of **11** are of limited accuracy as a consequence of the weakly diffracting sample, we present the refined structure as it supports—together with the spectroscopic data commented on above—the connectivity and conformation of the complex and allows rationalization of the catalytic results (see below).

In the asymmetric unit, two isostructural independent molecules (**11** and **11′**) were present with no significant differences in their geometrical parameters. A view of the cation of **11** is depicted in Figure 4. The iridium atom displays a distorted-octahedral geometry, coordinated to the PNInd and (*S*,*S*)-chiraphos chelate ligands (κ^2P,N and κ^2P,P coordination, respectively), to one hydride, and to a methacrolein fragment (η^1 coordinated through its oxygen atom). The hydride and the oxygen atoms are mutually *trans*, the resulting diastereomer adopting an *OC*-6-24-*C* stereochemistry. The aldehyde coordinates as a planar molecule with an s-*trans* conformation and an *E* configuration around the carbonylic double bond. This molecular structure is compatible with the reported spectroscopic data, indicating that the solid-state structure is essentially maintained in solution.

The puckering amplitude of the six-membered PN* metallacycle is very similar to that of complexes **1**, **2** and **10a**; it exhibits the same $^1S_6$ screw-boat conformation already noted.[22] In contrast, significant differences have been observed in the deviation from planarity and in the conformation of the PP metallacycles of the complexes reported in this paper (and in ref 34), reflecting their flexibility.[24] In **11** the five-membered Ir−P(1)−C(13)−C(14)−P(2) metallacycle adopts a twisted $^4T_3$ conformation. This disposition seems to be suitable for the establishment of intramolecular CH/π interactions involving the CHO proton and the *pro-R* phenyl ring connected to the P(1) atom of the (*S*,*S*)-chiraphos ligand (Figure 4) of potential relevance for its catalytic behavior.[5o] From the calculated positions of the hydrogen atoms, short H···Ph interatomic distances—shorter than the sum of van der Waals radii (H−C)—have been estimated.[25] These interactions fix the Ir−O rotamer and place the aldehydic proton inside the electronic diamagnetic current of the involved phenyl ring. Most probably, the CH/π interactions are also operating in solution, giving rise to the strong shielding observed for the CHO proton in the ^1H NMR spectrum of **11**.

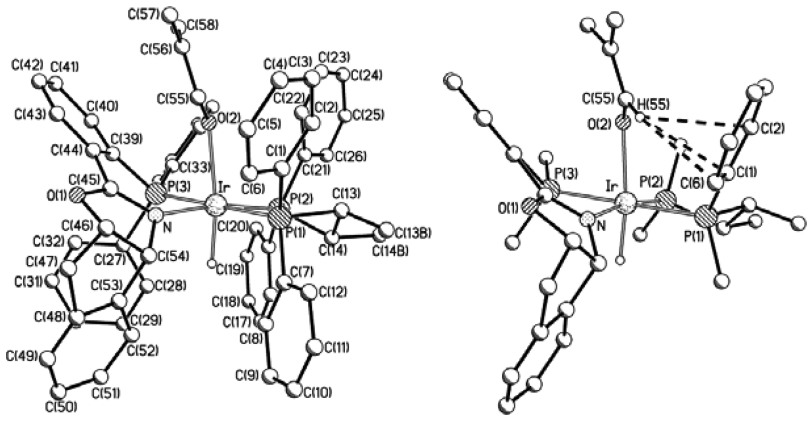


Figure 4. Molecular representations of the cation of complex **11** showing the CH···π interaction.

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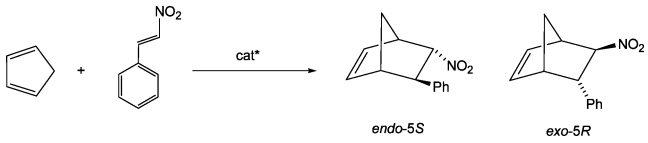
In the conformation observed for the coordinated enal, its *Si* face becomes shielded by the phenyl ring involved in the CH/π interaction and, therefore, nitrone attack would preferentially occur through the *Re* face of this substrate. In particular, a 3,4-*endo* nitrone attack will give (3*S*,4*S*)-*endo* enantiomers which are the major isomers experimentally obtained. Similarly, a 3,5-*endo* nitrone attack through the enal *Re* face would render (3*R*,5*S*)-*endo* adducts as the major enantiomers.

Diels–Alder Reaction between Cyclopentadiene and Nitrostyrenes. As stated in the Introduction, as far as we know, no metal-catalyzed asymmetric DA reactions involving nitroalkenes as dienophiles have been reported so far. As we have shown, the coordinated molecule of water in complexes **1**–**9** can be readily displaced by oxygen-donor substrates such as methacrolein. Then, we considered the possibility of activating the commercially available nitrostyrene toward the DA reaction with cyclopentadiene.[26] Indeed, complexes **1**–**9** catalyze this reaction. Table 3 gathers a selection of the results

Table 3. Catalytic Results[a] for the DA Reaction of Cyclopentadiene with Nitrostyrene



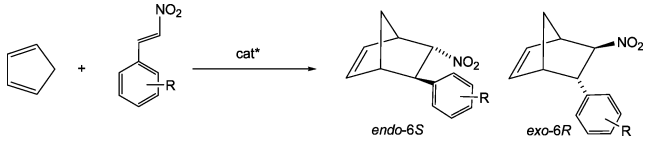
entry	precat.	time (h)	conversn (%)[b,c]	isomer ratio[c] *endo*:*exo* (%)	ee (%)[d]
1		2	1		
2		18.5	15	96:4	
3	**1**	4	100	97:3	59
4	**2**	4.5	100	96:4	44
5	**3a,b** (84:16)	8	43	96:4	20
6	**5a,a′** (68:32)	0.75	100	100:0	84
7[e]	**5a,a′** (68:32)	45	23	100:0	90
8	**6**	5	97	97:3	53
9	**7**	6	100	96:4	46
10	**8a,b** (85:15)	8	25	94:6	4
11	**9a,a′** (62:38)	7	62	95:5	25

[a]Reaction conditions: catalyst 0.030 mmol, (5.0 mol %), nitrostyrene 0.6 mmol, cyclopentadiene 3.60 mmol, 4 Å molecular sieves (100 mg), in CH_2Cl_2 (4 mL), at room temperature. [b]Based on nitrostyrene. [c]Determined by ^{1}H NMR spectroscopy. [d]Determined by HPLC. [e]At −25 °C.

obtained at room temperature, together with the remaining reaction conditions employed. The collected results are the average of at least two comparable reaction runs. In almost all cases, quantitative conversions were achieved after a few hours of treatment at room temperature. The catalyzed reaction shows *endo* preference and for complex **5** occurs with perfect *endo* selectivity. Moderate to good ee values were achieved, and as expected, the enantioselectivity increases when the temperature decreases (entries 6 and 7).

As complex **5** gives the best results, i.e. quantitative conversion in 45 min, perfect *endo* selectivity, and 84% ee, at room temperature, we tested this catalyst precursor in the reaction of substituted nitrostyrenes with cyclopentadiene. Table 4 gives the results obtained operating at room temperature. As in the preceding examples, the collected results are the average of at least two comparable reaction runs. The catalytic system admits both electron-withdrawing and electron-donor substituents into the aromatic ring of the

Table 4. Catalytic Results[a] for the DA Reaction of Cyclopentadiene with Substituted Nitrostyrenes Catalyzed by Complex 5



entry	R	time (h)	conversn (%)[b,c]	isomer ratio[c] *endo*:*exo* (%)	ee (%)[d]
1	H	0.75	100	100:0	84
2	2-OMe	1.5	100	99:1	79
3	2,3-$(OMe)_2$	17	100	98:2	79
4	2,4-$(OMe)_2$	71	82	99:1	67
5	2-CF_3	1	100	91:9	87
6	2-Cl	0.5	100	97:3	77
7[e]	2-Cl	144	49	98:2	86
8	2,3-Cl_2	144	98	87:13	70
9	2,4-Cl_2	143	59	99:1	71

[a]Reaction conditions: catalyst 0.030 mmol, (5.0 mol %), nitrostyrene 0.6 mmol, cyclopentadiene 3.60 mmol, 4 Å molecular sieves (100 mg), in CH_2Cl_2 (4 mL), at room temperature. [b]Based on nitrostyrene. [c]Determined by ^{1}H NMR spectroscopy. [d]Determined by HPLC. [e]At −25 °C.

nitroalkene, although two substituents in this ring strongly slow down the reaction rate. Taking into account the electrophilic character of the dienophile in DA reactions, this rate deceleration has to be based on steric grounds because it is even stronger for electron-withdrawing groups (entries 8 and 9). In general, excellent *endo* selectivity was observed and good ee values were obtained for both types of substituents.

CONCLUSIONS

In summary, we have prepared phosphano–oxazoline/iridium(III) complexes of the formula $[IrH(H_2O)(PN^*)(PP)][SbF_6]_2$ through a highly stereoselective synthetic route. The new complexes have been completely characterized, including the assignment of the cationic absolute configuration. The high *trans* influence of the hydride ligand originates in the long, and potentially labile, Ir–O bond distances. The PN* metallacycles always showed a highly puckered conformation, apparently quite rigid, internally and in their coordination to the metal. These aqua complexes are active precursors for the 1,3-dipolar cycloaddition between the nitrone *N*-benzylidenephenylamine *N*-oxide and methacrolein. The reaction occurs with excellent diasteroselectivity toward the *endo* isomers and ee values up to 85%. The methacrolein intermediates $[IrH(methacrolein)(PNInd)(PP)][SbF_6]_2$ (**11** and **12**) have been isolated and characterized. The structural analysis has confirmed the planar coordination of the methacrolein molecule, with a common *s-trans* conformation and *E* configuration, and the presence of the catalytic relevant CH/π interaction. The aqua compounds also generate active and selective systems for the Diels–Alder reaction of *trans*-β-nitrostyrenes with cyclopentadiene, exhibiting high diastereoselectivity toward the *endo* isomers and ee values up to 90%. This is the first example reported up to now of a metal-catalyzed asymmetric Diels–Alder reaction involving nitroalkenes as dienophiles.

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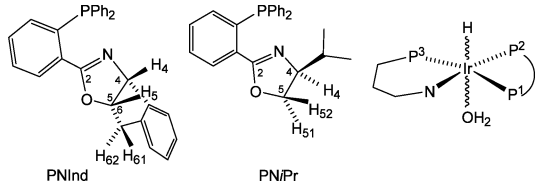
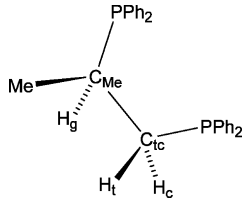
EXPERIMENTAL SECTION

General Comments. 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 Nujol mulls 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 (300.13 MHz), Bruker AV-400 (400.16 MHz), and Bruker AV-500 (500.13 MHz) spectrometers. In both ^{1}H NMR and ^{13}C NMR measurements the chemical shifts are expressed in ppm downfield from $SiMe_4$. The ^{31}P NMR chemical shifts are relative to 85% H_3PO_4. J values are given in Hz. NOESY and ^{13}C, ^{31}P, ^{1}H correlation spectra were obtained using standard procedures. MALDI-TOF$^+$ (dithranol) mass spectra were recorded on a Bruker Autoflex III spectrometer. Analytical high-performance liquid chromatography (HPLC) was performed on an Alliance Waters 2695 (Waters 2996 PDA detector) instrument using a chiral column Chiralpack AD-H (0.46 cm ×25 cm) or Daicel Chiralcel OJ-H (0.46 × 25 cm) and OJ-H guard (0.46 cm × 5 cm). Phosphano−oxazolines PNInd and PN*i*Pr[27a] and the nitrone *N*-benzylidenephenylamine *N*-oxide[27b] were prepared using literature procedures. For the preparation of the starting chloride complexes [IrClH(PN*)(PP)][SbF_6] see ref 34. General labeling for NMR assignments is given in Scheme 3, and labeling of the (*R*)-prophos ligand for NMR assignments is given in Scheme 4.

Scheme 3. Labeling for NMR Assignments



Scheme 4. Labeling of the (*R*)-Prophos Ligand for NMR Assignments



Preparation of the Complexes [IrH(H_2O)(PN*)(PP)][SbF_6]$_2$ (1−9). Under argon at room temperature, in the absence of light, to a solution of the corresponding chloride [IrHCl(PN*)(PP)][SbF_6] (0.25 mmol) in 15 mL of a mixture of CH_2Cl_2 and $(CH_3)_2CO$ (95/5, v/v) was added 85.9 mg (0.25 mmol) of $AgSbF_6$ and 10 μL (0.55 mmol) of H_2O. The suspension was stirred for 1 h (5 h at −25 °C for compounds **3** and **8**), and the AgCl that formed was filtered through a cannula. The resulting filtrate was partially concentrated under reduced pressure to ca. 2 mL, and the slow addition of *n*-hexane led to the precipitation of a pale yellow solid which was washed with *n*-hexane and vacuum-dried.

1: yield 87%. Anal. Calcd for $C_{54}H_{49}F_{12}IrNO_2P_3Sb_2$: C, 43.2; H, 3.3; N, 0.9. Found: C, 43.3; H, 3.1; N, 0.9. IR (Nujol, cm^{-1}): ν(OH) 3600 (b), ν(IrH) 2296 (w), ν(CN) 1599 (w), ν(SbF_6) 666 (m). MS: *m*/*z* (%) 1010.3 (100) [M$^+$ − H_2O − H]. ^{1}H NMR (300.13 MHz, CD_2Cl_2, room temperature): δ 8.2−6.1 (38H, Ar); 5.32 (d, *J* = 5.8 Hz, 1H, H_4); 5.28 (pt, *J* = 4.8 Hz, 1H, H_5); 4.1 (bs, 2H, H_2O); 3.45, 3.28 (AB part of an ABX system, *J*(AB) = 17.9 Hz, H_{61}, H_{62}); 2.64 dt, *J*(PH) = 41.5 Hz, *J*(HH) = 11.1 Hz, 2.54 dt, *J*(PH) = 36.5 Hz, *J*(HH) = 11.7 Hz, 2.37 m, 2.30 m (4H, $(CH_2)_2$); −26.86 (dpt, *J*(PH) = 22.6, 10.3 Hz, 1H, Ir−H). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, room temperature): δ 167.64 (t, *J* = 6.1 Hz, C^2); 138.6−123.6 (48C, Ar); 87.38 (C^5); 80.77 (d, *J* = 2.0 Hz, C^4); 36.25 (C^6); 33.64 bd, *J* = 42.9, 9.1 Hz, 26.92 dd, *J* = 36.9, 7.1 Hz (2C, $(CH_2)_2$). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, room temperature): δ 36.48 (d, *J*(P^3,P^1) = 317.7 Hz, P^1); 12.11 (d, *J*(P^3,P^2) = 13.7 Hz, P^2); 2.04 (dd, P^3).

2: yield 86%. Anal. Calcd for $C_{54}H_{47}F_{12}IrNO_2P_3Sb_2$: C, 43.3; H, 3.2; N, 0.9. Found: C, 43.1; H, 3.6; N, 0.7. IR (Nujol, cm^{-1}): ν(OH) 3600 (b), ν(IrH) 2310 (w), ν(CN) 1598 (w), ν(SbF_6) 666 (m). MS: *m*/*z* (%) 1008.2 (100) [M$^+$ − H_2O − H]. ^{1}H NMR (300.13 MHz, CD_2Cl_2, room temperature): δ 8.3−6.0 (38 H, Ar); 7.3 (bm, 2H, CH═CH); 5.61 (pt, *J* = 5.1 Hz, 1H, H_5); 5.35 (d, *J* = 5.1 Hz, 1H, H_4); 3.3 (bs, 2H, H_2O); 3.42, 3.21 (AB part of an ABX system, *J*(AB) = 18.4 Hz, *J* = 4.6 Hz, H_{61}, H_{62}); −27.69 (dpt, *J*(PH) = 23.6, 12.3 Hz, 1H, Ir−H). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, room temperature): δ 167.41 (t, *J* = 6.1 Hz, C^2); 151.85 ddd, *J* = 55.2, 23.9, 4.6 Hz, 141.06 dd, *J* = 53.8, 15.3 Hz (2C, CH═CH); 138.4−121.3 (48C, Ar); 86.56 (C^5); 79.41 (bs, C^4); 36.44 (C^6). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, room temperature): δ 44.86 (bd, *J* = 325.2 Hz, P^1); 17.05 (pt, *J* = 13.4 Hz, P^2); 1.20 (dd, P^3).

3a:**3b**: 86:14 molar ratio. Yield: 88%. Anal. Calcd for $C_{55}H_{51}F_{12}IrNO_2P_3Sb_2$: C, 43.6; H, 3.4; N, 0.9. Found: C, 43.4; H, 3.3; N, 0.8. IR (Nujol, cm^{-1}): ν(OH) 3600 (b), ν(IrH) 2302 (w), ν(CN) 1598 (m), ν(SbF_6) 655 (m). MS: *m*/*z* (%) 1024.4 (100) [M$^+$ − H_2O − H].

3a: ^{1}H NMR (300.13 MHz, CD_2Cl_2, −25 °C): δ 8.0−6.5 (38H, Ar); 5.36 (d, *J* = 5.7 Hz, 1H, H_4); 4.56 (pt, *J* = 8.1 Hz, 1H, H_5); 4.0 (bs, 2H, H_2O); 3.31, 3.12 (AB part of an ABX system, *J*(AB) = 18.1 Hz, *J* = 4.8 Hz, 2H, H_{61}, H_{62}); 3.2−2.8, 2.7−2.3, 1.9−1.5 (3 × bm, 6H, $(CH_2)_3$); −27.05 (dpt, *J*(PH) = 23.4, 10.0 Hz, 1H, Ir-H). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, −25 °C): δ 167.12 (bs, C^2); 138.6−123.5 (48C, Ar); 87.71 (C^5); 80.95 (C^4); 36.19 (C^6); 28.28 bdd, *J* = 42.7, 18.2 Hz, 22.85 dd, *J* = 34.8, 12.7 Hz, 16.55 s (3C, $(CH_2)_3$). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, −25 °C): δ −0.22, −8.30 (AB part of an ABX system, *J*(AB) = 322.2 Hz, *J* = 23.6, 15.0 Hz, 2P, P^1, P^3); −30.20 (dd, P^2).

3b: ^{1}H NMR (300.13 MHz, CD_2Cl_2, −25 °C): δ −24.93 (dpt, *J*(PH) = 29.6, 14.8 Hz, 1H, Ir-H). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, −25 °C): δ −0.48, −10.88 (AB part of an ABX system, *J*(AB) = 319.3 Hz, *J* = 22.6, 16.0 Hz, 2P, P^1, P^3); −15.09 (dd, P^2).

4: yield 76%. Anal. Calcd for $C_{56}H_{53}F_{12}IrNO_2P_3Sb_2$: C, 44.0; H, 3.5; N, 0.9. Found: C, 43.9; H, 3.4; N, 0.7. IR (Nujol, cm^{-1}): ν(OH) 3500 (b), ν(IrH) 2301 (w), ν(CN) 1600 (w), ν(SbF_6) 666 (m). MS: *m*/*z* (%) 1038.3 (100) [M$^+$ − H_2O − H]. ^{1}H NMR (300.13 MHz, CD_2Cl_2, room temperature): δ 8.2−5.85 (38H, Ar); 5.40 (pt, *J* = 5.1 Hz, 1H, H_5); 5.30 (d, *J* = 5.6 Hz, 1H, H_4); 3.4 (bs, 2H, H_2O); 3.44, 3.27 (AB part of an ABX system, *J*(AB) = 18.4 Hz, *J* = 4.6 Hz, 2H, H_{61}, H_{62}); 2.62 (bs, 2H, C*H*Me); 0.90 (dd, *J* = 13.6, 5.4 Hz, 3H, Me); 0.79 (dd, *J* = 14.1, 5.1 Hz, Me); −27.11 (dt, *J* = 22.70, 11.44 Hz; 1H; Ir-H). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, room temperature): δ 167.37 (C^2); 138.5−120.9 (48C, Ar); 87.17 (C^5); 79.55 (d, *J* = 3.2 Hz, C^4); 40.11 (bdd, *J* = 42.2, 16.7 Hz, CHMe); 36.34 (C^6); 32.69 (dd, *J* = 35.6, 10.3 Hz, CHMe); 13.37 (d, *J* = 4.0 Hz, Me); 13.15 (d, *J* = 3.2 Hz, Me). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, room temperature): δ 38.37 (bd, *J* = 314.8 Hz, P^1); 11.73 (pt, *J* = 13.4 Hz, P^2); 2.11 (dd, P^3).

5a:**5a′**: 68:32 molar ratio. Yield: 77%. Anal. Calcd for $C_{55}H_{51}F_{12}IrNO_2P_3Sb_2$: C, 43.6; H, 3.4; N, 0.9. Found: C, 43.55; H, 3.4; N, 0.8. IR (Nujol, cm^{-1}): ν(OH) 3500 (b), ν(IrH) 2310 (w), ν(CN) 1613 (w), ν(SbF_6) 660 (m). MS: *m*/*z* (%) 1024.2 (100) [M$^+$ − H_2O − H].

5a: ^{1}H NMR (400.16 MHz, $CDCl_3$, room temperature): δ 8.3−6.0 (38H, Ar); 5.20 (m, 1H, H_5); 4.28 (d, *J* = 7.7 Hz, 1H, H_4); 3.49 (m, 1H, H_g); 3.40 (bs, 2H, H_2O); 3.30, 3.13 (AB part of an ABX system, *J*(AB) = 18.4 Hz, *J* = 5.1 Hz, 2H, H_{61}, H_{62}); 3.15 (m, 1H, H_c); 2.17 (m, 1H, H_t); 1.15 (dd, *J*(PH) = 14.3 Hz, *J*(HH) = 6.7 Hz, 3H, Me); −27.85 (dpt, *J*(PH) = 22.5, 11.8 Hz, 1H, Ir-H). ^{13}C{^{1}H} NMR (75.5 MHz, CD_2Cl_2, room temperature): δ 166.3 (t, *J* = 4.3 Hz, C^2); 138.3−121.5 (48C, Ar); 85.45 (C^5); 75.67 (C^4); 41.60 (bdd, *J* = 36.3, 13.7 Hz, C_{tc}); 36.61 (C^6); 38.12 (bd, *J* = 42.1 Hz, C_{Me}); 14.95 (dd, *J* = 13.5, 3.9 Hz, Me). ^{31}P{^{1}H} NMR (162.0 MHz, CD_2Cl_2, room temperature): δ 38.72 (bd, *J* = 323.7 Hz, P^1); 2.60 (pt, *J* = 11.9 Hz, P^2); 2.24 (dd, P^3).

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5a′: ^{1}H NMR (400.16 MHz, $CDCl_3$, room temperature): δ 5.40 (pt, J = 6.7 Hz, 1H, H_5); 5.07 (d, J = 6.7 Hz, 1H, H_4); 3.4−3.0 (bm, 4H, H_{61}, H_{62}, H_2O); 3.10 (m, 1H, H_t), 2.74 (m, 1H, H_c), 2.50 (m, 1H, H_g); 1.34 (dd, J(PH) = 14.3 Hz, J(HH) = 6.7 Hz, 3H, Me); −27.66 (dpt, J(PH) = 25.1, 13.8 Hz, 1H, Ir-H). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, room temperature): δ 167.0 (bs, C^2); 86.01 (C^5); 77.73 (C^4); 41.60 (m, C_{Me}); 37.57 (bs, C_{tc}); 36.61 (C^6); 13.98 (dd, J = 15.9, 4.4 Hz, Me). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, room temperature): δ 22.30 (d, $J(P^3,P^1)$ = 317.8 Hz, P^1); 15.50 (d, $J(P^3,P^2)$ = 13.4 Hz, P^2); 1.29 (dd, P^3).

6: yield 93%. Anal. Calcd for $C_{50}H_{51}F_{12}IrNO_2P_3Sb_2$: C, 41.3; H, 3.5; N, 1.0. Found: C, 41.0; H, 3.6; N, 0.9. IR (Nujol, cm^{-1}): ν(OH) 3605 (b), ν(IrH) 2325 (w), ν(CN) 1606 (w), $\nu(SbF_6)$ 659 (m). MS: m/z (%) 964.3 (100) [$M^+ - H_2O - H$]. ^{1}H NMR (400.16 MHz, CD_2Cl_2, room temperature): δ 8.3−6.7 (34H, Ar); 4.42 (d, J = 9.2 Hz, 1H, H_{52}); 4.29 (pt, J = 9.2 Hz, 1H, H_{51}); 3.90 (d, J = 8.2 Hz, 1H, H_4); 3.80 (bs, 2H, H_2O); 2.56 m, 2.17 m (4H, $(CH_2)_2$); 1.65 (bs, 1H, MeMeC*H*); 0.11 (d, J = 6.6 Hz, 3H, Me*Me*CH); −0.43 (d, J = 6.6 Hz, 3H, *Me*MeCH); −26.98 (dpt, J(PH) = 22.0, 10.2, 1H, Ir-H). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, room temperature): δ 166.20 (C^2); 135.8−125.3 (42C, Ar); 78.07 (C^4); 68.52 (C^5); 33.91 ddd, J = 44.3, 11.1, 2.4 Hz, 26.97 dd, J = 37.2, 6.3 Hz (2C, $(CH_2)_2$); 29.17 (MeMeCH); 17.68 (Me*Me*CH); 11.59 (*Me*MeCH). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2, room temperature): δ 36.58 (bd, J = 320.1 Hz, P^1); 14.88 (bs, P^2); 6.51 (bd, P^3).

7: yield 85%. Anal. Calcd for $C_{50}H_{49}F_{12}IrNO_2P_3Sb_2$: C, 41.3; H, 3.4; N, 1.0. Found: C, 41.2; H, 3.8; N, 1.0. IR (Nujol, cm^{-1}): ν(OH) 3605 (b), ν(IrH) 2324 (w), ν(CN) 1604 (w), $\nu(SbF_6)$ 659 (m). FMS: m/z (%) 962.4 (100) [$M^+ - H_2O - H$]. ^{1}H NMR (300.13 MHz, CD_2Cl_2, room temperature): δ 8.3−6.6 (34H, Ar); 7.1 (m, 2H, CH═CH); 4.45 (pt, J = 9.2 Hz, 1H, H_{51}); 4.35 (dd, J = 9.5, 7.7 Hz, 1H, H_{52}); 4.04 (bd, J = 8.6 Hz, 1H, H_4); 3.50 (bs, 2H, H_2O); 1.29 (bs, 1H, MeMeC*H*); −0.15 (d, J = 6.7 Hz, 3H, Me*Me*CH); −0.52 (d, J = 6.7 Hz, 3H, *Me*MeCH); −27.46 (dpt, J(PH) = 21.3, 11.6 Hz, 1H, Ir-H). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, room temperature): δ 166.38 (C^2); 151.09 bdd, J = 55.6, 23.4 Hz, 142.04 dd, J = 52.0, 16.1 Hz (2C, CH═CH); 135.6−125.0 (42C, Ar); 77.64 (C^4); 68.26 (C^5); 28.86 (MeMeCH); 17.39 (Me*Me*CH); 11.41 (*Me*MeCH). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, room temperature): δ 44.63 (dd, J = 325.2, 13.4 Hz, P^1); 17.29 (pt, P^2); 3.15 (dd, J = 13.4 Hz, P^3).

8a:**8b**: 85:15 molar ratio. Yield: 72%. Anal. Calcd for $C_{51}H_{53}F_{12}IrNO_2P_3Sb_2$: C, 41.7; H, 3.6; N, 1.0. Found: C, 41.5; H, 3.9; N, 0.7. IR (Nujol, cm^{-1}): ν(OH) 3604 (b), ν(IrH) 2325 (w), ν(CN) 1607 (w), $\nu(SbF_6)$ 659 (m). MS: m/z (%) 978.3 (100) [$M^+ - H_2O - H$].

8a: ^{1}H NMR (300.13 MHz, CD_2Cl_2, room temperature): δ 8.3−6.0 (34H, Ar); 4.29 (d, J = 9.5 Hz, 1H, H_{52}); 3.95 (d, J = 7.6 Hz, 1H, H_4); 3.52 (pt, J = 9.1 Hz, 1H, H_{51}); 3.30 (bs, 2H, H_2O); 3.15, 2.67, 2.46, 1.69 (4 × m, 6H, $(CH_2)_3$); 2.07 (psp, J = 6.7 Hz, 1H, MeMeC*H*); 0.65 (d, J = 6.7 Hz, 3H, Me*Me*CH); −0.50 (d, J = 6.7 Hz, 3H, *Me*MeCH); −26.77 (dpt, J(PH) = 22.5, 10.0 Hz, 1H, Ir-H). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, room temperature): δ 165.82 (t, J = 4.7 Hz, C^2); 135.9−123.0 (42C, Ar); 77.96 (C^4); 69.18 (C^5); 28.24 (dd, J = 43.7, 16.8 Hz), 23.25 (dd, J = 34.1, 12.7 Hz), 16.51 (3C, $(CH_2)_3$); 29.87 (MeMeCH); 18.43 (Me*Me*CH); 11.87 (*Me*MeCH). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, −25 °C): δ 4.07, −7.61 (AB part of an ABX system, J(AB) = 321.2 Hz, J = 23.5, 16.0 Hz, 2P, P^1, P^3); −28.23 (dd, P^2).

8b: ^{1}H NMR (300.13 MHz, CD_2Cl_2, room temperature): δ −26.05 (m, 1H, Ir-H). ^{31}P NMR (121.5 MHz, CD_2Cl_2, −25 °C): δ −1.82, −10.81 (AB part of an ABX system, J(AB) = 319.5 Hz, J = 23.1, 14.6 Hz, 2P, P^1, P^3); −15.83 (dd, P^2).

9a:**9a′**: 62:38 molar ratio. Yield: 74%. Anal. Calcd for $C_{51}H_{51}F_{12}IrNO_2P_3Sb_2$: C, 41.7; H, 3.6; N, 0.9. Found: C, 42.2; H, 3.9; N, 1.0. IR (Nujol, cm^{-1}): ν(OH) 3600 (b), ν(IrH) 2326 (w), ν(CN) 1607 (m), $\nu(SbF_6)$ 658 (m). MS: m/z (%) 978.5 (100) [$M^+ - H_2O - H$].

9a: ^{1}H NMR (400.16 MHz, CD_2Cl_2, room temperature): δ 8.05−6.4 (34H, Ar); 4.31 (bs, H_{52}); 4.18 (pt, J = 9.0 Hz, 1H, H_{51}); 3.13 (bs, 2H, H_2O); 2.53 (m, 1H, H_g); 2.47, 2.24 (2 × m, 2H, H_c, H_t); 3.83 (bd, J = 8.4 Hz, 1H, H_4); 1.56 (m, MeMeC*H*); 0.80 (m, 3H, Me); 0.03 (d, J = 6.9 Hz, 3H, *Me*MeCH); −0.58 (d, J = 6.4 Hz, 3H, Me*Me*CH); −27.11 (dpt, J(PH) = 20.5, 9.1 Hz, 1H, Ir-H). $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_2Cl_2, room temperature): δ 166.1 (t, J = 4.9 Hz, C^2); 136.0−120.9 (42C, Ar); 7.06 (C^4); 8.64 (C^5); 41.39 (bdd, J = 47.5, 16.0 Hz, C_{tc}); 29.78 (bd, J = 30.8 Hz, C_{Me}); 28.93 (MeMeCH); 17.88 (*Me*MeCH); 14.56 (dd, J = 22.7, 3.7 Hz, Me); 13.85 (Me*Me*CH). $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, room temperature): δ 38.17 (dd, J = 315.4, 6.8 Hz, P^1); 12.26 (dd, J = 14.6 Hz, P^2); 2.17 (dd, P^3).

9a′: ^{1}H NMR (300.13 MHz, CD_2Cl_2): δ 4.33 (bs, 1H, H_{52}); 4.18 (pt, J = 9.0 Hz, 1H, H_{51}); 3.76 (bd, J = 8.4 Hz, 1H, H_4); 3.35 (bs, 2H, H_2O); 2.83 (m, 1H, H_g); 2.48, 2.36 (2 × m, 2H, H_c, H_t); 1.56 (m, MeMeC*H*); 0.80 (m, 3H, Me); 0.08 (d, J = 6.9 Hz, 3H, *Me*MeCH); −0.57 (d, J = 5.7 Hz, 3H, Me*Me*CH); −27.43 (bm, 1H, Ir-H). $^{13}C\{^1H\}$ (75.5 MHz, CD_2Cl_2): δ 166.05 (t, J = 4.9 Hz, C^2); 77.74 (C^4); 68.54 (C^5); 36.13 (C_{Me}); 33.14 (C_{tc}); 29.20 (MeMeCH); 17.76 (*Me*MeCH); 14.20 (dd, J = 18.7, 4.6 Hz, Me); 11.45 (Me*Me*CH). $^{31}P\{^1H\}$ (121.5 MHz, CD_2Cl_2, room temperature): δ 20.47 (dd, J = 315.7, 9.3 Hz, P^1); −0.05 (dd, J = 7.4 Hz, P^2); 2.17 (dd, P^3).

Preparation of the Complex [IrH(OPOF$_2$)(PN*i*Pr)(dppp)][SbF$_6$] (10). Under argon in the absence of light, to a solution of [IrClH(PN*i*Pr)(dppp)][SbF_6] (60.0 mg, 0.050 mmol) in 10 mL of a mixture of $CH_2Cl_2/(CH_3)_2CO$ (95/5, v:v) were added 12.1 mg (0.050 mmol) of $AgPF_6$ and 2 μL (0.11 mmol) of H_2O. The suspension was stirred for 45 min and filtered through Celite. The resulting filtrate was concentrated until ca. 1 mL, and addition of *n*-hexane afforded a pale yellow solid which was filtered off, washed with *n*-hexane, and vacuum-dried. The solid was recrystallized from CH_2Cl_2/Et_2O.

10a:**10b**: 92:8 molar ratio. Yield: 53%. Anal. Calcd for $C_{51}H_{51}F_8IrNO_3P_4Sb$: C, 46.6; H, 3.9; N, 1.1. Found: C, 46.6; H, 3.9; N, 1.0. IR (Nujol, cm^{-1}):ν(IrH) 2320 (w), ν(CN) 1611 (m), ν(PO) 1306 (s), $\nu(SbF_6)$ 654 (m).

10a: ^{1}H NMR (400.16 MHz, CD_2Cl_2, room temperature): δ 8.4−6.4 (34H, Ar); 4.05 (dd, J = 9.0, 1.4 Hz, 1H, H_{52}); 3.83 (bd, J = 8.1 Hz, 1H, H_4); 2.88 (pt, J = 8.6 Hz, 1H, H_{51}); 3.40, 2.93, 2.33, 2.07, 1.90, 1.61 (6 × m, 6H, $(CH_2)_3$); 1.86 (sp, J = 6.7 Hz, 1H, MeMeC*H*); 0.63 (d, J = 6.7 Hz, 3H, Me*Me*CH); −0.51 (d, J = 6.7 Hz, 3H, *Me*MeCH); −27.09 (ddt, J(PH) = 38.4, 21.0, 10.5 Hz, 1H, Ir-H). $^{13}C\{^1H\}$ NMR (100.6 MHz, CD_2Cl_2, room temperature): δ 165.82 (t, J = 4.4 Hz, C^2); 135.3−125.8 (42C, Ar); 78.30 (d, J = 4.4 Hz, C^4); 68.06 (C^5); 29.91 (MeMeCH); 26.70 dd, J = 41.6, 18.6 Hz, 22.02 dd, J = 33.6, 10.6 Hz, 16.77 s (3C, $(CH_2)_3$); 18.39 (Me*Me*CH); 11.96 (*Me*MeCH). $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2, room temperature): δ 2.62, −7.19 (AB part of an ABX system, J(AB) = 345.7 Hz, J = 24.5, 16.9 Hz, P^1, P^3); −19.52 (t, J(PF) = 957.9 Hz, PO_2F_2); −33.44 (dd, P^2).

10b: ^{1}H NMR (400.16 MHz, CD_2Cl_2, room temperature): δ −26.50 (m, 1H, Ir-H). $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_2Cl_2, room temperature): δ −4.28, −19.85 (AB part of an ABX system, J(AB) = 353.2 Hz, J = 28.3 Hz, J = 15.1 Hz, P^1, P^3); −14.85 (dd, P^2); −17.27 (t, J(FP)= 954.8 Hz, PO_2F_2).

Catalytic Procedure for the 1,3-Dipolar Cycloaddition Reaction. At −25 °C, under argon, the complexes [IrH(H_2O)(PN*)(PP)][SbF_6]$_2$ (0.030 mmol, 5 mol %) were dissolved in CH_2Cl_2 (1.5 mL). Activated molecular sieves (4 Å, 100.0 mg) and freshly distilled methacrolein (0.35 mL, 4.2 mmol) were added. The suspension was stirred for 30 min, and then a solution of the nitrone *N*-benzylidenephenyl *N*-oxide (118.25 mg, 0.60 mmol) in CH_2Cl_2 (1 mL) was added. After the mixture was stirred at the appropriate temperature for the reaction time indicated, *n*-hexane (15 mL) was added. The suspension was filtered through Celite and the solution concentrated to ca. 0.3 mL. The resulting residue was purified by chromatography (SiO_2), and a mixture of the corresponding isomers was obtained. Conversion and regio- and diastereoselectivity were determined by ^{1}H NMR spectroscopic analysis. Enantioselectivity was determined as indicated in the footnote of Table 2.

Preparation of the Complexes [IrH(methacrolein)(PNInd)(PP)][SbF$_6$]$_2$ (PP = (*S*,*S*)-chiraphos (11), (*R*)-prophos (12)). At 0 °C under argon, to a solution of the appropriate aqua complex [IrH(H_2O)(PNInd)(PP)][SbF_6]$_2$ (**4**, **5**; 0.070 mmol) in CH_2Cl_2 (10 mL) were added methacrolein (30.0 μL, 0.36 mmol) and molecular

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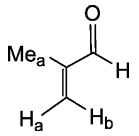
sieves (4 Å, 100.0 mg). The solution was stirred for 90 min and then filtered through a cannula. The solvent was partially evaporated, and the slow addition of *n*-hexane (20 mL) afforded a pale yellow solid which was washed with *n*-hexane and vacuum-dried. Labeling of the methacrolein ligand for NMR assignments is given in Scheme 5.

Scheme 5. Labeling of the Methacrolein Ligand for NMR Assignments



11: yield 57%. Anal. Calcd for $C_{60}H_{57}F_{12}IrNO_2P_3Sb_2$: C, 45.6; H, 3.6; N, 0.9. Found: C, 45.2; H, 3.9; N, 1.2. IR (Nujol, cm^{-1}): ν(IrH) 2324 (w); ν(CO) 1566 (w); ν(CN) 1607 (s); $\nu(SbF_6)$ 658 (m). MS: *m*/*z* (%): 1038.3 (100) [M^+ − methacrolein − H]. ^{1}H NMR (400.16 MHz, CD_2Cl_2, −25 °C): δ 8.3−5.9 (38H, Ar); 7.39 (s, 1H, CHO); 6.40 (s, H_a); 5.80 (s, H_b); 5.67 (pt, J = 5.4 Hz, 1H, H_5); 5.23 (d, J = 5.8 Hz, 1H, H_4); 3.41, 3.22 (AB part of an ABX system, J(AB) = 17.9 Hz, J = 4.6 Hz, 2H, H_{61}, H_{62}); 2.63, 2.50 (2 × m, 2H, 2 × C*H*Me); 1.41 (s, 3H, Me_a); 0.77 (bm, 6H, 2 × CH*Me*); −26.05 (dpt, J(PH) = 23.8, 9.9 Hz, 1H, Ir-H). ^{13}C NMR (100.61 MHz, CD_2Cl_2, −25 °C): δ 205.96 (CHO); 166.90 (t, J = 5.1 Hz, C^2); 148.77 (CH_aH_b); 143.51 (CHOC); 139.2−120.5 (48C, Ar); 88.04 (C^5); 78.94 (C^4); 39.43 (ddd, J = 42.5, 11.7, 4.1 Hz, *C*HMe); 35.91 (C^6); 31.96 (dd, J = 35.9, 9.5 Hz, *C*HMe); 13.80 (Me_a); 13.50, 13.33 (2C, 2 × CH*Me*). ^{31}P NMR (161.98 MHz, CD_2Cl_2, −25 °C): δ 37.19 (dd, J = 314.4, 13.8 Hz, P^1); 13.77 (pt, J = 13.8 Hz, P^2); 1.04 (dd, P^3).

12a:**12a′**: 74:26 molar ratio.[23]

12a: ^{1}H NMR (400.16 MHz, CD_2Cl_2, −25 °C): δ 9.05 (s, 1H, CHO); 8.2−5.9 (m, 38H, Ar); 6.50, 6.34 (2 × s, 2H, H_a, H_b); 5.35 (m, 1H, H_5); 3.78 (d, J = 9.1 Hz, 1H, H_4); 3.7 (m, 1H, H_g); 3.3, 1.8 (2 × m, 2H, H_c, H_t); 2.40, 3.02 (AB part of an ABX system, J(AB) = 18.3 Hz, J = 4.7 Hz, 2H, H_{61}, H_{62}); 1.69 (s, 3H, Me_a); 1.16 (dd, J(PH) = 13.3 Hz, J(HH) =5.7 Hz, 3H, Me); −26.00 (dpt, J(PH) = 21.9, 12.0 Hz, 1H, Ir-H). ^{13}C NMR (125.77 MHz, CD_2Cl_2, −25 °C): δ 209.46 (CHO); 165.70 (t, J = 4.2 Hz, C^2); 148.39 (CH_aH_b); 143.90 (CHOC); 143.9−119.9 (48C, Ar); 84.45 (C^5); 73.38 (C^4); 40.23 (bdd, J = 44.9, 11.5 Hz, C_{tc}); 39.25 (C^6); 37.90 (dd, J = 37.4, 3.5 Hz, C_{Me}); 14.07 (Me); 14.05 (Me_a). ^{31}P NMR (121.98 MHz, CD_2Cl_2, −25 °C): δ 37.48 (dd, J = 331.6, 9.4 Hz, P^1); 3.79 (bd, P^3); 1.28 (pt, J = 13.0 Hz, P^2).

12a′: ^{1}H NMR (400.16 MHz, CD_2Cl_2, −25 °C): δ 8.2−5.9 (m, 38H, Ar); 8.20 (s, 1H, CHO); 6.43, 5.83 (2 × s, 2H, H_a, H_b); 2.9−2.6 (m, 3H, H_g, H_c, H_t); 1.49 (s, 3H, Me_a); 1.26 (dd, J(PH) = 14.7 Hz, J(HH) = 6.2 Hz, 3H, Me); −26.00 (bm, 1H, Ir-H). ^{13}C NMR (125.77 MHz, CD_2Cl_2, −25 °C): δ 207.09 (CHO); 166.73 (C^2); 148.80 (CH_aH_b); 143.9−119.9 (49C, Ar, CHOC); 86.72 (C^5); 77.75 (C^4); 35.96 (C^6); 14.07 (Me); 14.05 (Me_a). ^{31}P NMR (121.98 MHz, CD_2Cl_2, −25 °C): δ 26.79 (bd, J = 320.3 Hz, P^1); 19.08 (bs, P^2); 2.07 (bd, P^3).

Catalytic Procedure for the Diels−Alder Reaction between Cyclopentadiene and *trans*-β-Nitrostyrenes. Under argon at −25 °C, in a Schlenk flask, the appropriate catalyst (0.030 mmol), 3 mL of CH_2Cl_2, molecular sieves (4 Å, 100.0 mg), and the corresponding *trans*-β-nitrostyrene (0.60 mmol) were added. After 15 min of stirring, freshly distilled cyclopentadiene (3.6 mmol) in 1 mL of CH_2Cl_2 was added and the system was stirred at the indicated temperature. The reaction was monitored by TLC chromatography. After the reaction time, a solution of 19.3 mg (0.125 mmol) of N^nBu_4Br in 0.1 mL of methanol was added. The resulting suspension was concentrated, and Et_2O (15 mL) was added to precipitate the catalyst. The suspension was filtered through Celite and the resulting solution concentrated to ca. 0.3 mL. The conversion and *endo*:*exo* ratio were determined by ^{1}H NMR. Enantiomeric excesses were determined by HPLC.

Crystal Structure Determination of Complexes 1, 2, 10a, and 11. X-ray diffraction data were collected at 100(2) K with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), using narrow ω rotation (0.3°) on a Bruker SMART APEX CCD diffractometer. Intensities were integrated and corrected for absorption effect with the SAINT-PLUS program.[28] The structures were solved by direct methods with SHELXS-97.[29] Refinement, by full-matrix least squares on F^2, was performed with SHELXL-97.[30] Hydrogen atoms were included in calculated positions and refined with displacement and positional riding parameters. The hydride ligand was included from electrostatic potential calculations (HYDEX program)[31] and refined with a geometrical restraint in Ir−H distance (except in **1**, where its position was fixed). The absolute configuration was determined on the basis of previously known internal references, and this assignment was confirmed using the Flack parameter.[32] Particular details concerning the presence of solvent and specific refinements are listed below.

Crystal data for ***1****:* $C_{54}H_{49}F_{12}IrNO_2P_3Sb_2{\cdot}2C_4H_{10}O{\cdot}H_2O$, M = 1666.81; colorless plate, 0.077 × 0.064 × 0.009 mm^3; monoclinic, $P2_1$; a = 11.6736(8), b = 23.6185(17), c = 11.8942(8) Å; β = 94.5270(10)°; Z = 2; V = 3269.2(4) $Å^3$; D_c = 1.693 g/cm^3; μ = 3.006 mm^{-1}, minimum and maximum absorption correction factors 0.802 and 0.974; $2\theta_{max}$ = 54.12°; 25174 collected reflections, 14045 unique (R_{int} = 0.0538); number of data/restraints/parameters 14045/97/773; final GOF 1.046; R1 = 0.0605 (11624 reflections, $I > 2\sigma(I)$); wR2 = 0.1170 for all data; Flack parameter x = 0.002(6); largest difference peak 2.107 e/$Å^3$. One of the diethyl ether solvent molecules has been found to be highly disordered. It has been included in the model in two different positions, with complementary occupancy factors and refined with geometrical restraints. Some constraints have been included to avoid unrealistic thermal parameters.

Crystal data for ***2****:* $C_{54}H_{47}F_{12}IrNO_2P_3Sb_2{\cdot}C_4H_{10}O{\cdot}CH_2Cl_2$, M = 1657.58; colorless block, 0.220 × 0.080 × 0.040 mm^3; monoclinic, $P2_1$; a = 13.102(5), b = 16.399(5), c = 14.495(5) Å; β = 109.079(5)°; Z = 2; V = 2943.3(18) $Å^3$; D_c = 1.870 g/cm^3; μ = 3.423 mm^{-1}, minimum and maximum absorption correction factors 0.521 and 0.875; $2\theta_{max}$ = 57.76°; 36442 collected reflections, 13985 unique (R_{int} = 0.0527); number of data/restraints/parameters 13985/21/746; final GOF 1.117; R1 = 0.0592 (12765 reflections, $I > 2\sigma(I)$); wR2 = 0.1221 for all data; Flack parameter x = 0.018(6); largest difference peak 1.575 e/$Å^3$. Static disorder was observed in one SbF_6^- anion and in the dichloromethane and diethyl ether solvent molecules; they have been modeled in each case with two sets of positions with complementary occupancy factors and refined with some geometrical restraints.

Crystal data for ***10a****:* $C_{51}H_{51}F_8IrNO_3P_4Sb{\cdot}4C_4H_{10}O$, M = 1612.31; colorless prism, 0.110 × 0.096 × 0.074 mm^3; orthorhombic, $P2_12_12_1$, a = 14.003(3), b = 18.597(4), c = 22.965(5) Å; Z = 4; V = 5980(2) $Å^3$; D_c = 1.791 g/cm^3; μ = 2.843 mm^{-1}, minimum and maximum absorption correction factors 0.716 and 0.823; $2\theta_{max}$ = 57.66°; 60679 collected reflections, 14653 unique (R_{int} = 0.1273); number of data/restraints/parameters 14653/1/628; final GOF 0.918; R1 = 0.0532 (10043 reflections, $I > 2\sigma(I)$); wR2 = 0.1073 for all data; Flack parameter x = 0.004(6); largest difference peak 1.097 e/$Å^3$. At the last steps of refinement, there were very large solvent-accessible voids in the structure and two different zones where residual density peaks were observed. The solvent was highly disordered, and it cannot be modeled even assuming several restraints. Therefore, SQUEEZE[33] corrections have been applied. The total potential solvent accessible void volume (1400 $Å^3$) and the number of electrons (636 e in the unit cell) have been interpreted with the presence of 16 ether molecules.

Crystal data for ***11****:* weakly diffracting single crystals of this compound were obtained by slow diffusion of *n*-hexane into dichloromethane solutions; $C_{60}H_{57}F_{12}IrNO_2P_3Sb_2{\cdot}0.5CH_2Cl_2{\cdot}$-$1.5C_6H_{14}$, M = 1752.49; yellow plate, 0.220 × 0.157 × 0.058 mm^3; orthorhombic, $P2_12_12$, a = 25.703(3), b = 26.433(3), c = 21.329(2) Å; Z = 8; V = 14491(2) $Å^3$; D_c = 1.619 g/cm^3; μ = 2.749 mm^{-1}, minimum and maximum absorption correction factors 0.505 and 0.744; $2\theta_{max}$ = 40.28°; 68844 collected reflections, 13738 unique (R_{int} = 0.107); number of data/restraints/parameters 13738/37/615; final GOF 1.060; R1 = 0.086 (10041 reflections, $I > 2\sigma(I)$); wR2 = 0.2468 for all data; Flack parameter x = 0.057(13); largest difference peak 1.871 e/$Å^3$. Several crystals were tested before selecting the one used for data collection. In general, they were slightly twinned samples with

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highly irregular mosaic structure. Eventually, a very weakly diffracting crystal was selected, showing no detectable intensity over $2\theta > 40°$. Due to the limited quality of data, only Ir, Sb, P, and O atoms have been refined with a thermal anisotropic model, and several geometrical restraints have been applied. At this point, two very large voids were observed in the structure, with several significant residual peaks. Unfortunately, no clear model of disordered solvent could be established. Therefore, SQUEEZE[33] corrections have been applied. The solvent-accessible void volumes (2×1081 Å^3) and the estimated number of electrons (2×370 e) have been interpreted with the presence of six *n*-hexane molecules in each of these two apparently empty regions.

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, and CIF files giving X-ray crystallographic data for the structural analysis of complexes **1**, **2**, **10a**, and **11**, scanned HPLC traces and spectroscopic data of the Diels–Alder cycloadducts, and NMR spectra of **12a**,**a′**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dcarmona@unizar.es (D.C.); jfecer@unizar.es (J.F.) Tel: 34-976-762027. Fax: 34-976-761187.

Notes

The authors declare no competing financial interest.

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