Synthesis, Characterization, Properties, and Asymmetric Catalytic Diels−Alder Reactions of Chiral-at-Metal Phosphinooxazoline-Rhodium(III) and −Iridium(III) Complexes§

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The synthesis and characterization of optically active phosphinooxazoline complexes (R_{Rh} and S_{Rh})-[(η^5-C_5Me_5)RhCl(PN)][A] (PN = (4*S*)-2-(2-diphenylphosphino)phenyl)-4-isopropyl-1,3-oxazoline (PN(^{i}Pr)), A = SbF_6 (**1a**,**1a′**), A = BF_4 (**1b**,**1b′**); PN = (4*S*)-2-(2-diphenylphosphino)phenyl)-4-methyl-1,3-oxazoline (PN(Me)), A = SbF_6 (**2a**,**2a′**), A = BF_4 (**2b**,**2b′**); PN = (3a*S*,8a*R*)-2-(2-diphenylphosphino)phenyl)-3a,8a-dihydroindane[1,2-d]oxazole] (PN(Ind)), A = SbF_6 (**3a**,**3a′**)), (S_{Rh} and R_{Rh})-[(η^5-C_5Me_5)RhI(PN(Me))][SbF_6] (**4a**,**4a′**) and (R_{Ir} and S_{Ir})-[(η^5-C_5Me_5)IrCl(PN)][A] (PN = PN(^{i}Pr), A = SbF_6 (**5a**,**5a′**), A = BF_4 (**5b**,**5b′**); PN = PN(Me), A = SbF_6 (**6a**,**6a′**), A = BF_4 (**6b**,**6b′**); PN = PN(Ind), A = SbF_6 (**7a**,**7a′**)), and the solvate complexes (S_{Rh} and R_{Rh})-[(η^5-C_5Me_5)Rh(PN)S][SbF_6]$_2$ (PN = PN(^{i}Pr) (**8a**,**8a′**), PN(Me) (**9a**,**9a′**), PN(Ind) (**10a**,**10a′**); S = H_2O, Me_2CO) and (S_{Ir} and R_{Ir})-[(η^5-C_5Me_5)Ir(PN)S][A]$_2$ (PN = PN(^{i}Pr), A = SbF_6 (**11a′**), A = BF_4 (**11b′**); PN = PN(Me), A = SbF_6 (**12a′**), A = BF_4 (**12b′**); PN = PN(Ind), A = SbF_6 (**13a**,**13a′**)) are reported. The crystal structures of the (R_{Rh})-**1a**, (S_{Rh})-**1a′**, (R_{Rh})-**2a**, (S_{Rh})-**2a′**, (R_{Rh})-**2b**, (R_{Rh})-**3a**, (S_{Rh})-**4a**, (R_{Ir})-**5b**, (R_{Ir})-**6a**, (S_{Ir})-**6a′,** and (R_{Rh})-**9a′** epimers were determined by X-ray diffractometric methods. All the complexes show the chiral metal center in a pseudo-octahedral environment, being bonded to an η^5-C_5Me_5 ring, to the nitrogen and phosphorus atoms of the phosphinooxazoline ligand in a chelate fashion, and to a terminal chlorine (**1a**, **1a′**, **2a**, **2a′**, **2b**, **3a**, **5b**, **6a**, **6a′**) or iodine (**4a**), or to the oxygen of an acetone molecule (**9a′**). Two conformations of the M−P−C−C−N metallacycle have been found in the crystals: the $^5S_4$ (unprimed complexes and **2a′**) and the $^1S_2$ (primed complexes and **2a**) screw-boat conformations. In solution, complexes **2**, **4**, **6**, **8a′**, **9**, **10**, **12**, and **13** exist as a mixture of conformers, most probably arising from the interconversion of the $^1S_2$ and $^5S_4$ conformations. This process was studied by ^{1}H and ^{31}P NMR spectroscopy. Dichloromethane solutions of the solvate complexes [(η^5-C_5Me_5)M(PN)S][SbF_6]$_2$ are active catalysts for the Diels−Alder reaction between methacrolein and cyclopentadiene. The reaction occurs rapidly at room temperature with good *exo:endo* ratio (from 81:19 to 95:5) and moderate enantioselectivity (up to 67% (Rh compounds), 65% (Ir compounds)).

Introduction

Due to the recent advances in asymmetric catalysis, catalytic enantioselective synthesis has become one of the most efficient methods for the preparation of enantiomerically enriched compounds.[1] The most successful examples of such reactions include those involving transition metal catalysts bound to chiral chelating ligands. In particular, organometallic complexes with

§ Dedicated to Prof. Domingo González, from the University of Zaragoza, on the occasion of his retirement.

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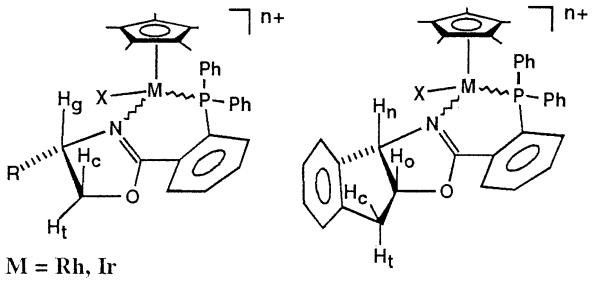
stereogenic metal centers are especially useful for stereochemical studies which can allow obtaining a better understanding of the stereocontrol of the enantioselectivity.[2] Most of these complexes possess half-sandwich geometries and chiral chelating ligands such as α-amino acids,[3] imines,[4] carbenes,[5]or diphosphines.[2f,6]

On the other hand, the Diels−Alder reaction is one of the most versatile and powerful synthetic transformations in organic chemistry. In this context, very impressive results have recently been reported for enantioselective Diels−Alder reactions catalyzed by chiral Lewis acids.[1a,b,7] Although, at a first stage, aluminum- and boron-based catalysts with chiral ligands dominate in this chemistry, recent focus in this area has been on the use of chiral transition-metal-based Lewis acid catalysts.[8] In particular, we have recently shown the ability of imino-iridium(III),[4g] -rhodium(III), and -ruthenium(II)[4h] complexes of formula [(ring)MCl(imine)][SbF_6] ((ring)M = (η^5-C_5Me_5)Rh, (η^5-C_5Me_5)Ir, (η^6-*p*-$MeC_6H_4{}^iPr$)Ru) and the diphosphine-rhodium compound[6b] [(η^5-C_5Me_5)Rh(*R*-Prophos)(H_2O)][SbF_6]$_2$ (*R*-Prophos = (*R*)-1,2-bis(diphenylphosphino)propane) to act as catalysts for the Diels−Alder reaction between methacrolein or acrolein and cyclopentadiene.

Scheme 1



M = Rh, Ir
X = Cl, I, S (S = H_2O, Me_2CO)
R = ^{i}Pr, Me
n = 1, 2

Recently, chiral phosphinooxazoline ligands, developed by the groups of Helmchen, Pfaltz, and Williams, have been successfully employed for enantiocontrol in a variety of metal-catalyzed reactions: Pd-, W-, and Pt-catalyzed allylic substitutions,[9] Heck reactions,[10] Ru-catalyzed transfer hydrogenations,[11] Rh-catalyzed transfer hydrosilylations,[12] Ir-catalyzed hydrogenation of imines[13] or olefins,[14] and Pd-catalyzed copolymerization of styrene and carbon monoxide.[15] We reported, for the first time, the application of phosphinooxazoline ligands as chiral auxiliaries in Diels−Alder reactions.[16] Moreover, Helmchen et al. have reported the Diels−Alder reaction of substituted *N*-acylamide dienophiles with cyclopentadiene catalyzed by phosphinooxazoline copper(II) compounds.[17] Encouraged by these results, we have followed our studies on transition metal complexes with chiral metal centers[3e−i,4g,h,6,18] by using phosphinooxazoline rhodium and iridium compounds as catalysts in enantioselective Diels−Alder reactions.

In this paper, we report the synthesis and characterization of complexes of general formula [(η^5-C_5Me_5)MX(PN)][A]$_n$ with enantiopure chiral phosphinooxazoline ligands (M = Rh, Ir; PN = (4*S*)-2-(2-diphenylphosphino)-phenyl)-4-isopropyl-1,3-oxazoline (PN(^{i}Pr)), (4*S*)-2-(2-diphenylphosphino)phenyl)-4-methyl-1,3-oxazoline (PN(Me)), (3a*S*,8a*R*)-2-(2-diphenylphosphino)phenyl)-3a,8a-dihydroindane[1,2-*d*]oxazole (PN(Ind)); X = Cl, I, H_2O, Me_2CO; A = SbF_6, BF_4; *n* = 1, 2, Scheme 1). The absolute configuration at the metal has been ascertained by a combination of X-ray diffraction, circular dichroism, and NMR measurements. We have also studied the conformational and configurational stability of the new compounds and the use of the solvated complexes [(η^5-

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$C_5Me_5)M(PN)S][A]_2$ (S = H_2O, Me_2CO) as enantioselective catalysts for the Diels−Alder reaction between methacrolein and cyclopentadiene.

Results and Discussion

Preparation of the Diastereomeric Complexes 1−7. At room temperature, the dimers[19] [{(η^5-C_5Me_5)-$MX\}_2(\mu$-$X)_2$] (M = Rh or Ir, X = Cl or I) react, in methanol, with stoichiometric amounts of the corresponding phosphinooxazoline, PN(^{i}Pr), PN(Me), or PN(Ind), and NaA (A = SbF_6 or BF_4) to give, in 69−98% chemical yield, diastereomeric mixtures of both epimers at the metal of the new compounds [(η^5-C_5Me_5)MX(PN)]-[A] with moderate stereoselectivity (eq 1).[20]

$$1/2\ [\{(\eta^5\text{-}C_5Me_5)MX\}_2(\mu\text{-}X)_2] + PN + NaA \rightarrow [(\eta^5\text{-}C_5Me_5)MX(PN)][A] + NaX \quad (1)$$

complex	M	X	PN	A	**a**/**a**′ or **b**/**b**′ molar ratio
1a,**1a**′	Rh	Cl	PN(^{i}Pr)	SbF_6	55:45
1b,**1b**′	Rh	Cl	PN(^{i}Pr)	BF_4	60:40
2a,**2a**′	Rh	Cl	PN(Me)	SbF_6	44:56
2b,**2b**′	Rh	Cl	PN(Me)	BF_4	45:55
3a,**3a**′	Rh	Cl	PN(Ind)	SbF_6	54:46
4a,**4a**′	Rh	I	PN(Me)	SbF_6	50:50
5a,**5a**′	Ir	Cl	PN(^{i}Pr)	SbF_6	79:21
5b,**5b**′	Ir	Cl	PN(^{i}Pr)	BF_4	59:41
6a,**6a**′	Ir	Cl	PN(Me)	SbF_6	57:43
6b,**6b**′	Ir	Cl	PN(Me)	BF_4	45:55
7a,**7a**′	Ir	Cl	PN(Ind)	SbF_6	40:60

Due to the different solubility in methanol, it has been proved possible to obtain, by fractional crystallization from this solvent, diastereomers **1a**, **2b**, **3a**, **4a**, **5a**, **6a**, and **7a**, in essentially complete optical purity (>98% by ^{1}H NMR), as well as mixtures enriched in one of the isomers for the following compounds: **1** (**1b**:**1b**′, 95:5), **2** (**2a**:**2a**′, 27:73, **2b**:**2b**′, 40:60), **3** (**3a**:**3a**′, 16:84), **4** (**4a**:**4a**′, 23:77), and **7** (**7a**:**7a**′, 15:85). Moreover, recrystallization from chloroform/diethyl ether afforded pure **1a**′ and from dichloromethane/diethyl ether led to diastereopure **5a**′, **5b**, **5b**′, **6a**′, and **6b**. All the new complexes were characterized by IR and NMR spectroscopy and elemental analysis (see Experimental Section) and from the crystal structure determination, by X-ray diffractometric methods, for compounds **1a**, **1a**′, **2a** + **2a**′, **2b**, **3a**, **4a**, **5b**, **6a**, and **6a**′.

Molecular Structure of the Diastereomers 1a, 1a′, 2a+2a′, 2b, 3a, 4a, 5b, 6a, and 6a′. Single crystals of the complexes were grown by slow diffusion of diethyl ether into $CDCl_3$ (**1a**, **1a**′, **2b**, **4a**), dichloromethane (**3a**, **5b**, **6a**, **6a**′), or acetone (**2a**:**2a**′, 50:50 mixture) solutions. It is noteworthy to point out that crystallization from **2a**:**2a**′ mixtures of 27:73 or 50:50 molar ratio composition afforded identical single crystals. In both cases, they contain two molecules, one of each epimer, in the unit cell. Although there are some examples in which both epimers at the metal are present in the same crystal unit cell,[3a,e,21] usually, single crystals formed from mixtures of diastereomers consist of only one diastereomer. To assign the configuration at the metal for complex **2**, single crystals of the tetrafluoroborate analogue **2b** were analyzed. Molecular representations of the cations of **1a**, **1a**′, **2a**+**2a**′, **3a**, and **4a** are depicted in Figures 1−4, and selected structural parameters of all these complexes are listed in Table 1. All cations exhibit "three-legged piano stool" geometries. An η^5-C_5Me_5 group occupies three *fac* positions, and the chelating *P*,*N*-phosphinooxazoline ligand and one chlorine atom (iodine in complex **4a**) complete the coordination sphere of the metal. The absolute configuration of the metal in unprimed complexes **1a**, **2a**, **2b**, **3a**, **5b**, and **6a** is *R* (*S* in the iodide complex **4a**) according to the ligand priority sequence[22] η^5-C_5Me_5 > Cl > P > N (I > η^5-C_5Me_5 > P > N in the iodide complex **4a**[23]) and the opposite one, *S*,

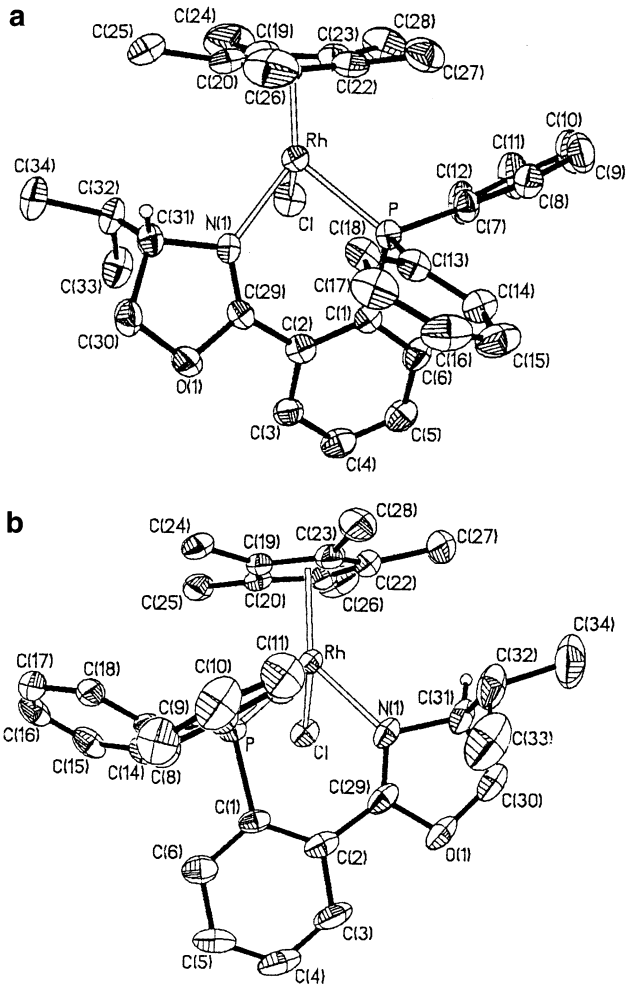

Figure 1. Molecular structure of the cationic complexes (a) (R_{Rh})-[(η^5-C_5Me_5)RhCl(PN(^{i}Pr))]$^+$ (**1a**) and (b) (S_{Rh})-[(η^5-C_5Me_5)RhCl(PN(^{i}Pr))]$^+$ (**1a**′) showing the structural relationship between the two diastereomers. Labeling scheme used for all structures is analogous with the only difference being the oxazoline substituent.

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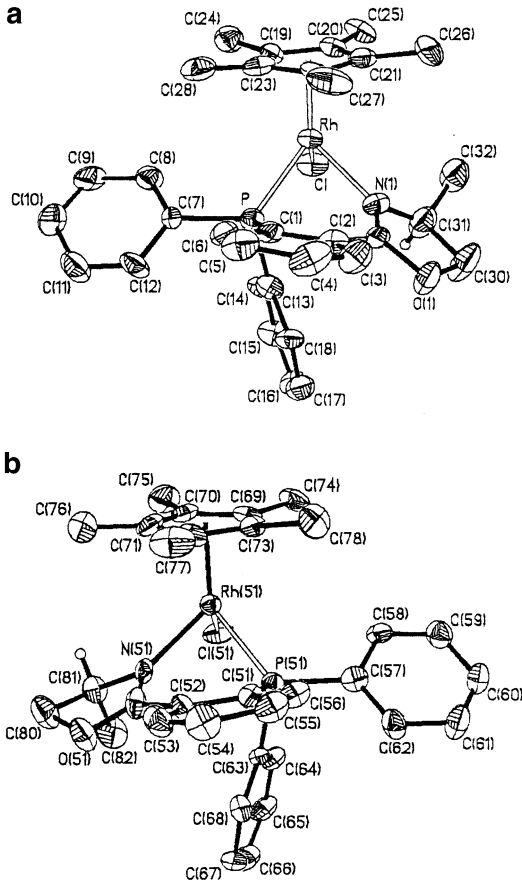


Figure 2. Molecular representation of the cations of the compounds (R_{Rh} and S_{Rh})-[(η^5-C_5Me_5)RhCl(PN(Me))][SbF_6] (**2a**+**2a′**).

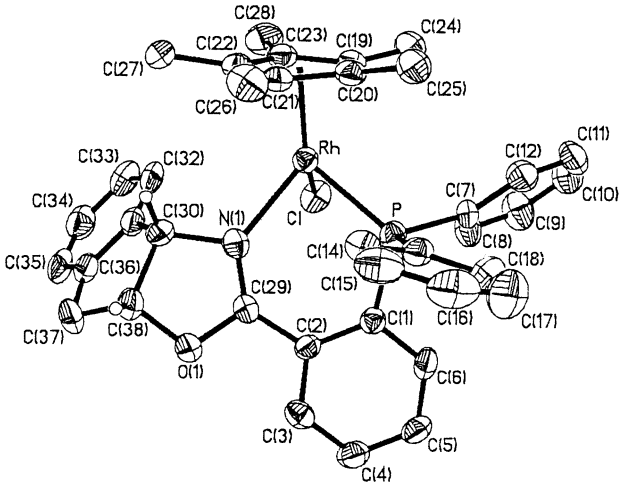


Figure 3. Molecular drawing of the cationic complex (R_{Rh})-[(η^5-C_5Me_5)RhCl(PN(Ind))]$^+$ (**3a**).

in the primed complexes **1a′**, **2a′**, and **6a′**. The six-membered M−P−C(1)−C(2)−C(29)−N(1) chelate ring in unprimed complexes **1a**, **2b**, **3a**, **4a**, **5b**, and **6a** and also in the S_{Rh} complex **2a′** adopts a $^5S_4$ screw-boat conformation,[24] with the ortho carbon atom of the phenyl

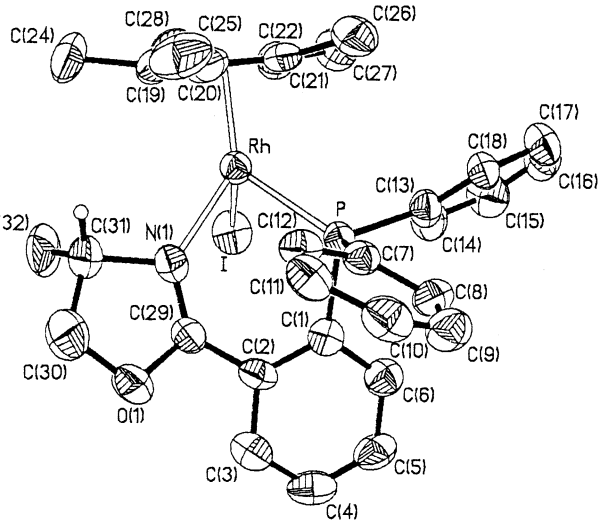


Figure 4. Molecular view of the cation of the compound (S_{Rh})-[(η^5-C_5Me_5)RhI(PN(Me))][SbF_6] (**4a**).

group (C(2)) and the carbon atom of the oxazoline ring (C(29)) below and above the plane of the chelate metallacycle, respectively. This conformation forces the *pro-R* and *pro-S* phenyl groups to adopt pseudoequatorial and pseudoaxial arrays, respectively. However, in primed compounds **1a′** and **6a′** as well as in complex **2a**, the metallacycle chelate ring adopts a $^1S_2$ screw-boat conformation[24] with the metal and phosphorus atoms above and below the best plane, respectively. Furthermore, the *pro-R* and *pro-S* phenyl groups occupy pseudoaxial and pseudoequatorial positions, respectively. As a representative example, Figure 5 shows the solid-state conformation of the phosphinooxazoline ligand in complexes **1a** and **1a′**, as well as the three puckering coordinates that define the out-of-plane deformation of the chelate ring. Moreover, in all complexes the five-membered oxazoline ring (O−C−N−C−C) adopts a $^4T_5$ conformation ($^5T_4$ in the chloride complex **2a′**)[24] with the CH_2 (CH_OR in complex **3a**) group and the asymmetric carbon atom above and below the plane of the oxazoline ring, respectively (the opposite is true for complex **2a′**).

NMR Spectroscopy and Solution Studies of the Complexes 1−7. In all cases, the ^1H NMR spectroscopic data (see Experimental Section) of complexes **1**−**7** were consistent with the presence of the η^5-C_5Me_5 group and phosphinooxazoline ligands in a 1:1 ratio (for phosphinooxazoline proton labeling, see Scheme 1). Stereochemical assignments were accomplished through NOE experiments (Figure 6). Thus, for example, the irradiation of the C_5Me_5 protons induces enhancement of the H_g proton for **1b**, **5a**, and **6b** and of the H_n proton for **3a** and **7a** compounds. Significantly smaller NOE signals were encountered for these protons when the C_5Me_5 protons of the primed complexes **1a′**, **3a′**, **5b′**, **6a′**, or **7a′** were irradiated. These NOE are consistent with an *R* configuration at the metal for the unprimed complexes and an *S* for those primed, indicating that the metal configuration is retained on going from the crystal to solution.

It is noteworthy to point out the significant difference in the chemical shift between the two ^{i}Pr methyl protons of the *S* at metal chloride complexes **1a′** ($\Delta\delta$ = 0.90), **1b′** ($\Delta\delta$ = 0.91), **5a′** ($\Delta\delta$ = 0.90), and **5b′** ($\Delta\delta$ = 0.91

(23) In the iodide compound **4**, the priority order is I > η^5-C_5Me_5 > P > N[22] and, consequently, a stereochemical disposition such as those found in **2** or **6** is denoted with the opposite descriptor.

(24) (a) Giacovazzo, C.; Monaco, H. L.; Viterbo, D.; Scordari, F.; Gilli, G.; Zanotti, G.; Catti, M. *Fundamentals of Crystallography*; Oxford University Press: Oxford, 1998. (b) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354.

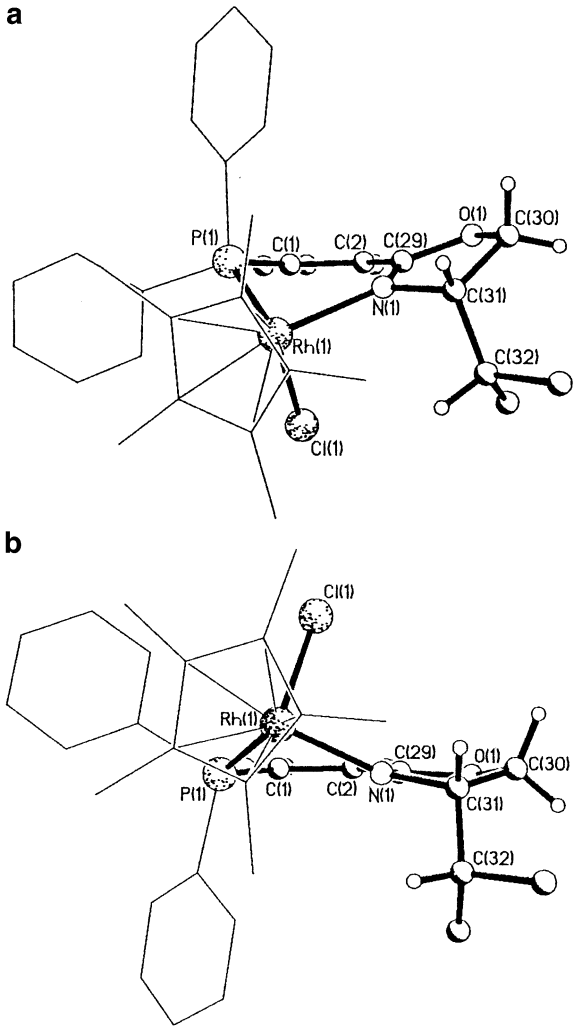
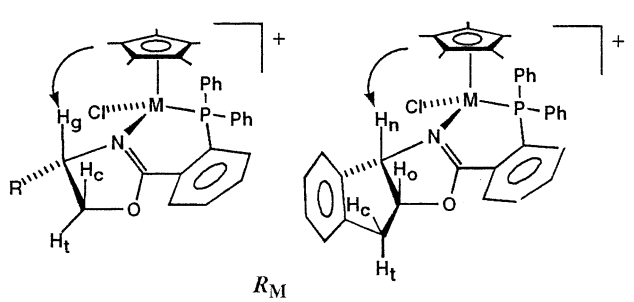


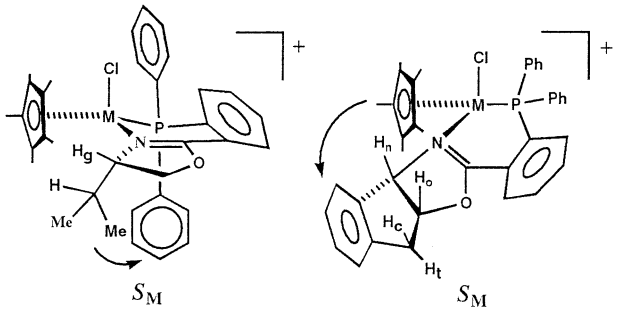
Figure 5. Solid-state conformation of the phosphinooxazoline ligand (a) in **1a** ($^5S_4$; $Q = 0.636(2)$ Å, $\varphi = -146.1(4)°$, $\theta = 116.6(4)°$) and (b) in **1a′** ($^1S_2$; $Q = 0.557(3)$ Å, $\varphi = 9.5(5)°$, $\theta = 55.2(5)°$). Representations of the M−P−C−C−C−N ring conformation have been performed with a similar orientation along the best plane through the ring.



M = Rh, R = ^{i}Pr (1b)
M = Ir; R = ^{i}Pr (5a), Me (6b)
M = Rh (3a)
M = Ir (7a)

Figure 6. Selected NOE effect for unprimed (*R* epimers) chloride complexes.

ppm) (Figure 7a). The observed values could be explained by assuming that in S_M complexes the six-membered ring of the phosphinooxazoline ligand adopts an $^1S_2$ screw-boat conformation similar to that found for complex **1a′** in the solid state. In this conformation, one methyl of the isopropyl group lies over the *pro-R* phenyl of the PPh_2 group, which becomes shielded by its aromatic ring current.



	δ_{CHMe_2} (^{1}H, ppm)
1a (1a')	0.74, 1.12 (0.17, 1.07)
1b (1b')	0.73, 1.11 (0.15, 1.06)
5a (5a')	0.88, 1.14 (0.17, 1.07)
5b (5b')	0.83, 1.13 (0.17, 1.08)

(a)

	$\delta_{C_5Me_5}$ (^{1}H, ppm)
3a (3a')	1.59 (1.14)
7a (7a')	1.64 (1.15)

(b)

Figure 7. (a) Schematic view of the proposed conformation in S_{Rh}-**1**(**a′**,**b′**) and S_{Rh}-**5**(**a′**,**b′**) showing the chemical shift of the ^{i}Pr methyl protons of **1** and **5**. (b) Schematic view of S_{Rh}-**3a′** and S_{Ir}-**7a′** and chemical shift of the C_5Me_5 protons of **3** and **7**.

On the other hand, the C_5Me_5 protons of the PN(Ind) containing compounds **3** and **7** present important chemical shift differences between the S_M and R_M epimers (see Figure 7b). When the metal adopts an *S* configuration (**3a′** and **7a′** epimers), the C_5Me_5 protons are forced to be near the C_6H_4 aromatic ring of the indane group and, therefore, could be affected by its shielding effect. Consequently, the resonances at higher field are attributed to the S_M epimers.

The ^{1}H and $^{31}P\{^1H\}$ spectra of complexes **1**, **3**, **5**, and **7** were essentially invariant over the −90 to +20 °C range, whereas the modifications of the spectra of the PN(Me)-containing complexes **2**, **4**, and **6** on changing temperature strongly indicated fluxionality. As a representative example, Figure 8 shows the $^{31}P\{^1H\}$ NMR spectrum of complexes **2a** and **2a′**, in acetone, at selected temperatures. At −100 °C the $^{31}P\{^1H\}$ spectra of **2a** (R_{Rh}) and **2a′** (S_{Rh}) consisted of two doublets centered at 41.6 and 29.3 (**2a**, 77:23 ratio) and 39.9 and 29.9 (**2a′** 27:73 ratio). On raising the temperature, the signals broaden and coalesce at −71 °C (**2a**) and −8 °C (**2a′**). At +20 °C, complex **2a** showed a sharp doublet, centered at 36.5 ppm, and the spectra of **2a′** consisted of one broad signal at 33.6 ppm.

Similar trends present the spectra of the related compounds **4a**, **4a′**, **6a**, and **6a′**, and from the equilibration of the phosphorus nuclei, the free energy of activation, $\Delta G^‡$, at the coalescence temperature,[25] for the fluxional process has been calculated: $\Delta G^‡ = 33.4 \pm 0.5$ kJ mol^{-1} (**2a**), 44.9 ± 0.5 kJ mol^{-1} (**2a′**), 44.7 ± 0.5 kJ mol^{-1} (**4a**), 49.7 ± 0.5 kJ mol^{-1} (**4a′**), 40.2 ± 0.5 kJ mol^{-1} (**6a′**).

Parallel observations can be made in the corresponding ^{1}H NMR spectra. The most valuable information comes from the spectra of the **4a** and **2a′** isomers. Thus, at −84 °C, in acetone, the spectrum of the iodide complex **4a** (*S* epimer)[23] shows two broad singlets at 1.30 and 0.38 ppm (90:10 ratio) that can be assigned to the methyl group of the phosphinooxazoline ligand. On

(25) (a) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: London, 1982. (b) Green, M. L. H.; Wong, L. *Organometallics* **1992**, *11*, 2660.

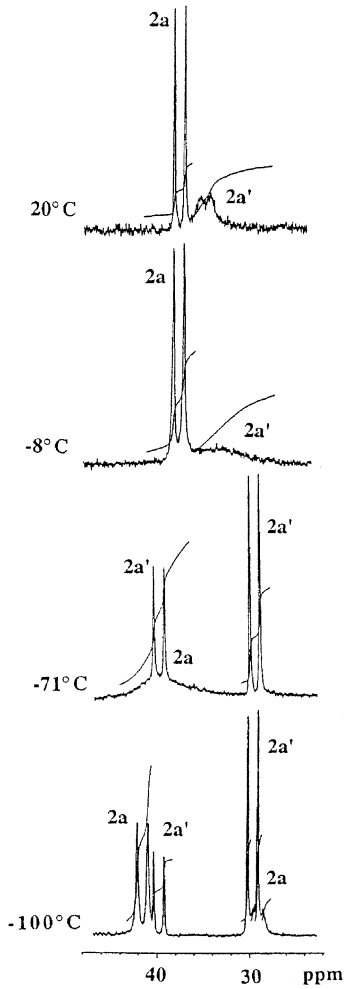


Figure 8. $^{31}P\{^1H\}$ spectra of **2a** and **2a′** in $(CD_3)_2CO$ at different temperatures.

raising the temperature, they coalesce, and the resulting averaged signal sharpens to give, at room temperature, a sole doublet centered at 1.25 ppm (J_{HgMe} = 6.5 Hz). These ^1H NMR data as well as the ^{31}P NMR variable-temperature behavior can be understood as the result of an equilibrium between two conformational isomers present in a 90:10 ratio. In particular, the conformation of the metallacycle of the minor isomer was derived from the high-field shift of the resonance of its methyl group at low temperature (0.38 ppm): a $^1S_2$ screw-boat conformation forces the *pro-R* phenyl group of the oxazoline ligand to adopt a pseudoaxial disposition, lying above the oxazoline methyl. Then, most probably, it shields the methyl and, therefore, causes the observed upfield shift of its resonance.[26]

Similar behavior has been found in the ^1H NMR spectra of **2a′**. The methyl group of the oxazoline ligand appears as a doublet centered at 1.25 ppm at +20 °C (J_{HgMe} = 6.3 Hz) and as a broad singlet, at a very low frequency, 0.30 ppm, at −100 °C. Again, these data can be accounted for by assuming a flip of the metallacycle between the $^1S_2$ and $^5S_4$ conformations, the methyl group still being subject to rapid movement and time averaging on the ^1H NMR time scale at −100 °C. Furthermore, the major isomer has to be the $^1S_2$ conformer because, in such a conformation, the shielding of the methyl group of the oxazoline by the axial phenyl substituent of the same ligand can take place, thus accounting for the observed high-field shift of the methyl resonance of the major component of the mixture.[27]

In summary, in the PN(Me)-containing compounds **2**, **4**, and **6**, a fluxional process that implies the exchange between the $^1S_2$ and $^5S_4$ conformers of the chelate metallacycle occurs. From the calculated data, it seems that this process is slightly more demanding in energy for the S_{Rh} than for the R_{Rh} epimers, probably due to steric hindrance between the methyl oxazoline group and C_5Me_5 ligand of the S_{Rh} isomers. The activation energy is also greater for the iodides **4** than for the corresponding chlorides **2**. Again, steric hindrance associated with the greater size of the iodide ligand can be argued to account for the measured increment. The X-ray diffraction studies also revealed two different conformations, $^4T_5$ and $^5T_4$, for the five-membered O−C−N−C−C oxazoline ring. The exchange between these two conformations should be fast even at −100 °C because we have not observed any spectroscopic indication about them.

Circular Dichroism Spectra. In general, rhodium and iridium epimers differing in the metal configuration exhibit circular dichroism (CD) spectra that are roughly mirror images of each other, showing that the major contribution to the spectra corresponds to the metal chromophore and its interaction with the ligands. Thus, the CD spectra of complex **2b** and that of a 27:73 **2a**:**2a′** mixture are roughly enantiomorphic (Figure 9a), the CD spectra of **6a** almost matches that of **7a** (Figure 9b), and the CD spectra of **1a**, **2b**, and that of a 95:5 **3a**:**3a′** mixture show very similar trends (Figure 9c), as expected for epimers with equal configuration at the metal. However, it should be pointed out that there are exceptions to this behavior, and in fact, we have found some of them among the new complexes **1**−**7**. Thus, both the CD spectra of the R_{Ir} epimer **7a** and that of a 15:85 **7a**:**7a′** mixture present a positive maximun at ca. 410 nm, despite the change in the configuration at the metal of the major component (Figure 9d), and the spectrum of a 5:95 **3a**:**3a′** mixture clearly differs from those of **1a**:**1a′** or **2a**:**2a′** mixtures also enriched in the primed isomers (Figure 9e). Therefore, no safe conclusions on the stereochemistry of epimers differing in the metal configuration can be drawn on the sole basis of CD curves.

Epimerization of the Complexes 1−7. At room temperature, in acetone or chloroform, the metal center in complexes **1**−**7** is configurationally stable; the composition of mixtures of epimers remains unchanged for days. This configurational stability is comparable to that found in the related half-sandwich rhodium, iridium, or ruthenium systems with imino N,N′ ligands,[4g,h,28] pyridyloxazoline-ruthenium complexes,[29] or diphos-

(26) In the solid state, complex **4a** adopts a $^5S_4$ screw-boat conformation. It seems likely that the preferred conformation in solution (90% abundance) was the same as in the crystal.

(27) However, in chloroform, at −60 °C, according to NMR data, the more abundant component should be the $^5S_4$ conformer of **2a′**. ^1H NMR: δ 0.98 ppm (bs). ^{31}P NMR: δ 39.2 (d, J_{RhP} = 137.5 Hz), 29.2 (d, J_{RhP} = 131.0 Hz) in a 63:37 intensity ratio.

(28) Davies, D. L.; Fawcett, J.; Krafczyk, R.; Russell, D. R. *J. Organomet. Chem.* **1997**, *545*−*546*, 581.

(29) Davenport, A.; Davies, D. L.; Fawcett, J.; Garratt S. A.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **2000**, 4432.

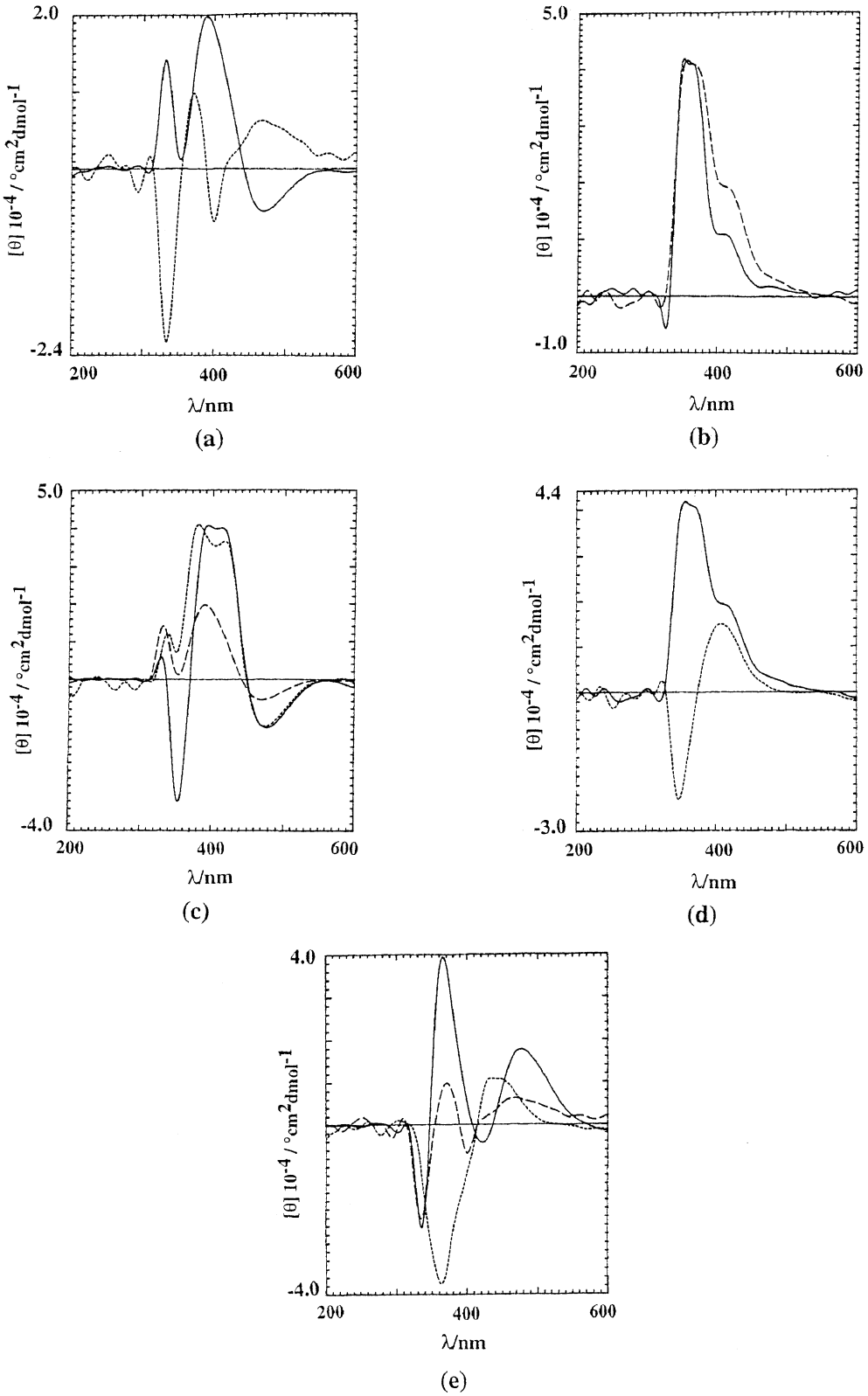


Figure 9. CD spectra (Me_2CO, 5×10^{-4} mol L^{-1}) in the 200−600 nm wavelength range: (a) (—) complex **2b** and (- - -) a 27:73 **2a**:**2a′** mixture; (b) (—) complex **6a** and (— —) complex **7a**; (c) (—) complex **1a**, (— —) complex **2b**, and (- - -) a 95:5 **3a**:**3a′** mixture; (d) (—) complex **7a** and (- - -) a 15:85 **7a**:**7a′** mixture; (e) (—) a 20:80 **1a**:**1a′** mixture, (— —) a 27:73 **2a**:**2a′** mixture, and (- - -) a 5:95 **3a**:**3a′** mixture.

phino-rhodium compounds[6a] and strongly contrasts with the high lability found for the same type of systems with imino[4a,b,e] or amino acidato[3a,e−g] N,O ligands.

However, at higher temperatures, in more polar solvents such as methanol, the complex cations slowly epimerize at the metal, with no apparent decomposition. Table 2 collects the initial diastereomeric compositions[20] and those at the equilibrium reached, in most cases from both sides, after about 24 h (48 h for complexes **6** and **7**) of treatment in refluxing methanol. The 39:61 **a**:**a′**

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Cationic Complexes 1a, 1a′, 2a+2a′, and 2b and Complexes 3a, 4a, 5b, 6a, and 6a′ (M = Rh 3a, 4a; M = Ir 5b, 6a, 6a′; X = Cl, except X = I in 4a)[a]

	1a	1a′	2a	2a′	2b
Rh−Cl	2.3992(12)	2.4033(12)	2.4023(19)	2.405(2)	2.407(3)
Rh−P	2.2893(12)	2.2794(13)	2.3106(19)	2.312(2)	2.299(3)
Rh−N(1)	2.140(4)	2.145(4)	2.125(7)	2.157(8)	2.122(9)
Rh−C(19)	2.238(5)	2.192(4)	2.180(9)	2.180(10)	2.256(11)
Rh−C(20)	2.288(5)	2.151(4)	2.233(8)	2.229(8)	2.309(10)
Rh−C(21)	2.209(5)	2.251(5)	2.228(8)	2.228(8)	2.223(11)
Rh−C(22)	2.186(5)	2.265(5)	2.171(8)	2.161(8)	2.204(10)
Rh−C(23)	2.153(5)	2.208(5)	2.177(9)	2.222(9)	2.155(11)
Rh−G	1.852(3)	1.854(2)	1.832(4)	1.834(4)	1.865(5)
P−C(1)	1.823(5)	1.823(5)	1.806(6)	1.845(7)	1.818(10)
C(1)−C(2)	1.410(7)	1.394(7)	1.440(10)	1.390(11)	1.390(13)
C(2)−C(29)	1.467(7)	1.494(8)	1.491(9)	1.439(11)	1.493(14)
N(1)−C(29)	1.270(6)	1.282(7)	1.313(10)	1.277(9)	1.272(12)
Cl−Rh−P	88.47(4)	89.91(4)	93.82(7)	94.01(8)	89.28(10)
Cl−Rh−N(1)	86.05(11)	82.96(11)	96.02(18)	91.90(19)	86.4(3)
Cl−Rh-G	120.43(9)	120.05(8)	119.95(14)	120.63(14)	119.8(2)
P−Rh−N(1)	86.65(10)	86.17(13)	79.39(16)	77.68(19)	85.6(2)
P−Rh−G	127.94(9)	127.69(8)	132.47(13)	131.69(14)	128.71(18)
N(1)−Rh−G	133.97(13)	135.19(15)	124.0(2)	128.1(2)	133.2(3)
Rh−P−C(1)	110.69(15)	112.31(18)	103.0(2)	101.5(2)	111.1(3)
P−C(1)−C(2)	119.8(3)	123.4(4)	118.3(5)	115.7(6)	120.9(7)
C(1)−C(2)-C(29)	123.4(4)	124.0(5)	121.7(6)	121.0(7)	123.3(9)
C(2)−C(29)-N(1)	130.3(4)	129.5(5)	125.0(8)	130.2(9)	130.8(10)
Rh−N(1)−C(29)	129.9(3)	128.1(4)	127.8(5)	123.7(6)	130.7(7)

	3a	4a	5b	6a	6a′
M−X	2.3781(15)	2.6863(7)	2.4013(13)	2.4020(15)	2.407 (2)
M−P	2.2961(17)	2.2744(16)	2.2772(12)	2.2710(13)	2.289(2)
M−N(1)	2.151(5)	2.131(5)	2.110(4)	2.102(5)	2.107(7)
M−C(19)	2.147(6)	2.289(7)	2.178(5)	2.200(8)	2.212(8)
M−C(20)	2.190(6)	2.284(7)	2.161(5)	2.166(6)	2.187(9)
M−C(21)	2.210(6)	2.162(7)	2.264(5)	2.268(6)	2.171(9)
M−C(22)	2.304(6)	2.202(7)	2.289(5)	2.295(6)	2.216(11)
M−C(23)	2.260(6)	2.225(7)	2.186(5)	2.193(6)	2.326(10)
M−G[a]	1.859(3)	1.872(3)	1.851(2)	1.860(3)	1.862(5)
P−C(1)	1.821(6)	1.830(7)	1.820(4)	1.825(6)	1.816(9)
C(1)−C(2)	1.393(8)	1.394(9)	1.416(6)	1.397(8)	1.401(13)
C(2)−C(29)	1.454(8)	1.466(9)	1.471(6)	1.491(9)	1.467(13)
N(1)−C(29)	1.300(7)	1.282(9)	1.276(6)	1.282(9)	1.295(12)
X−M−P	85.28(6)	90.46(5)	88.51(4)	88.54(5)	89.96(9)
X−M−N(1)	86.09(13)	86.59(15)	85.48(11)	83.98(15)	82.7(2)
X−M−G[a]	122.14(11)	120.34(12)	121.80(8)	121.42(11)	118.50(17)
P−M−N(1)	87.65(15)	84.44(16)	85.69(11)	84.90(15)	83.6(2)
P−M−G[#]	128.39(10)	127.81(12)	129.01(7)	129.04(10)	131.26(15)
N(1)−M−G[#]	132.26(16)	133.60(19)	131.96(12)	133.81(18)	135.0(2)
M−P−C(1)	113.7(2)	111.8(2)	111.87(15)	111.80(19)	109.3(3)
P−C(1)−C(2)	123.0(5)	118.5(5)	118.4(3)	118.5(4)	119.8(7)
C(1)−C(2)−C(29)	124.6(5)	123.9(6)	123.2(4)	123.6(5)	124.3(8)
C(2)−C(29)−N(1)	131.5(6)	129.7(6)	130.3(4)	129.2(6)	128.4(8)
M−N(1)−C(29)	130.8(4)	131.8(5)	130.8(3)	132.0(4)	129.8(6)

[a] G represents the centroid of the cyclopentadiene ring (C(19), C(20), C(21), C(22) and C(23) atoms).

Table 2. Diastereomeric Composition of Complexes 1−7

complex	initial **a**:**a′** molar ratio	equilibrium **a**:**a′** molar ratio
1	71:29, 18:82	50:50
2	49:51, 27:73	40:60
3	96:4, 10:90	15:85
4	77:23	39:61
5	100:0, 34:66	50:50
6	100:0, 37:63	60:40
7	100:0, 15:85	45:55

molar ratio, obtained for **4**, remained unchanged after refluxing it for 8 additional hours.

Preparation of the Solvate Complexes 8−13. Preliminary studies showed that the chloride compounds **1**−**7** were not active catalysts for the Diels−Alder reaction between methacrolein and cyclopentadiene. Most probably, the coordinative saturation of the metallic center avoids catalysis. To solve this problem, we tried to prepare solvate complexes of general formula $[(\eta^5\text{-}C_5Me_5)M(PN)S][A]_2$. Thus, treatment of dichloromethane solutions of the chloride rhodium compounds $[(\eta^5\text{-}C_5Me_5)RhCl(PN)][SbF_6]$ (**1**−**3**) with equimolar amounts of $AgSbF_6$ in acetone[30] afforded $[(\eta^5\text{-}C_5Me_5)Rh(PN)S][SbF_6]_2$ complexes (PN = PN(^{i}Pr) (**8a**,**8a′**), PN(Me) (**9a**,**9a′**), and PN(Ind) (**10a**,**10a′**)) (eq 2). An alternative route is the reaction of the in situ prepared trissolvate species[31] $[(\eta^5\text{-}C_5Me_5)MS_3]^{2+}$ with 1 equiv of the corresponding PN ligand (eq 3). The iridium compounds $[(\eta^5\text{-}C_5Me_5)Ir(PN)S][A]_2$ (PN = PN(^{i}Pr), A = SbF_6 (**11a′**), BF_4 (**11b′**); PN = PN(Me), A = SbF_6 (**12a′**), BF_4 (**12b′**); PN = PN(Ind) A = SbF_6 (**13a**,**13a′**)) were prepared by the latter route.

(30) The $AgSbF_6$ salt is not soluble enough in dichloromethane to cause precipitation of silver chloride from compounds **1**−**3**.

(31) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1654.

$$[(\eta^5\text{-}C_5Me_5)RhCl(PN)][SbF_6] + AgSbF_6 \rightarrow [(\eta^5\text{-}C_5Me_5)Rh(PN)S][SbF_6]_2 + AgCl$$

$$S = Me_2CO \text{ or } H_2O^{32} \quad (2)$$

$$1/2\ [\{(\eta^5\text{-}C_5Me_5)IrCl\}_2(\mu\text{-}Cl)_2] + 2\ AgA + PN \rightarrow [(\eta^5\text{-}C_5Me_5)Ir(PN)S][A]_2 + 2\ AgCl$$

$$S = Me_2CO \text{ or } H_2O^{32} \quad (3)$$

complex	M	PN	A	**a**:**a′** or **b**:**b′** molar ratio
8a,**8a′**	Rh	PN(^{i}Pr)	SbF_6	0−15:100−85[a]
9a,**9a′**	Rh	PN(Me)	SbF_6	16:84[b]
10a,**10a′**	Rh	PN(Ind)	SbF_6	48:52[c]
11a′	Ir	PN(^{i}Pr)	SbF_6	0:100
11b′	Ir	PN(^{i}Pr)	BF_4	0:100
12a′	Ir	PN(Me)	SbF_6	0:100
12b′	Ir	PN(Me)	BF_4	0:100
13a,**13a′**	Ir	PN(Ind)	SbF_6	53:47[d]

[a] The diastereomeric composition changes from one preparation to another. [b] Diastereomeric compositon in acetone at −90 °C. [c] Diastereomeric compositon in acetone at −95 °C. [d] Diastereomeric compositon in acetone at −90 °C of the in situ generated complexes.

The formation of compounds **8** and **11b′**, from the corresponding solvates $[(\eta^5\text{-}C_5Me_5)M((CD_3)_2CO)_3]^{2+}$, was monitored by ^1H and ^{31}P NMR spectroscopy, at −78 °C. This technique showed that the formation of **8** (7:93 **8a**:**8a′** ratio) was complete after 5 min of reaction. In the case of the iridium compound **11b′**, two not identified intermediates were detected at −78 °C, **11b′** being the only detected product at room temperature.

We have also checked that the composition obtained is independent of the diastereomeric composition of the starting chlorides for compounds **8** and **10**.

The new complexes were characterized by IR and NMR[33] spectroscopy and elemental analysis (see Experimental Section), and by the crystal structure determination by X-ray diffractometric methods for compound **9a′**. The actual nature of the solvent molecule S in these solvate complexes merits some comments. The IR spectra of solid samples of all of them showed absorptions in the 3550−3600 and 1610−1650 cm^{-1} regions attributable to coordinated water, and all the hexafluoroantimoniates presented, additionally, a band at ca. 1690 cm^{-1}, which can be assigned to the ν(CO) vibration of coordinated acetone. Therefore, in the solid state, the compounds are aquo solvates or mixtures of aquo and acetone solvates. ^1H NMR measurements give us interesting information about the nature of the solvates in solution. Three solvents have been considered: dichloromethane, acetone, and water. The addition of small amounts of H_2O or $(CH_3)_2CO$ (10−50 μL) to solutions of the complexes in CD_2Cl_2 or $(CD_3)_2CO$ permits us to establish that the equilibrium between the acetone and the aquo solvates, depicted in eq 4, is

$$[(\eta^5\text{-}C_5Me_5)M(PN)(acetone)]^{2+} \underset{\text{acetone}}{\overset{\text{water}}{\rightleftharpoons}} [(\eta^5\text{-}C_5Me_5)M(PN)(water)]^{2+} \quad (4)$$

operating and that the presence of water in trace amounts is enough to shift this equilibrium to the right. Resonances assignable to dichloromethane solvates $[(\eta^5\text{-}C_5Me_5)M(PN)(dichloromethane)]^{2+}$ have not been detected. Therefore, if this type of solvates are eventually formed, dichloromethane is easily displaced from the coordination sphere of the metal for the more coordinating solvents, acetone or water. Resonances attributable to coordinated water were absent at room temperature, but the aquo-solvated nature of the complexes was inferred from ^1H NMR measurements at low temperature. Thus, for example, at −90 °C, the spectrum of **8a′** in $(CD_3)_2CO$ showed the presence of two peaks at δ 6.30 and 4.30 ppm assigned to coordinated and free water, respectively.[4g,34] ROESY experiments indicated that a slow exchange process between free and coordinated water was occurring at the aforementioned temperature.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for the Cationic Complex of 9a′

Rh−P	2.330(2)	Rh−O(2)	2.204(6)
Rh−N(1)	2.112(6)	Rh−G[a]	1.836(4)
Rh−C(19)	2.174(8)	P−C(1)	1.816(8)
Rh−C(20)	2.126(7)	C(1)−C(2)	1.408(11)
Rh−C(21)	2.251(8)	C(2)−C(29)	1.499(11)
Rh−C(22)	2.286(8)	N(1)−C(29)	1.287(10)
Rh−C(23)	2.181(8)		
P−Rh−O(2)	82.20(15)	Rh−P−C(1)	108.0(3)
P−Rh−N(1)	82.90(19)	P−C(1)−C(2)	121.4(6)
P−Rh−G[a]	131.03(12)	C(1)−C(2)−C(29)	122.1(7)
O(2)−Rh−N(1)	87.6(2)	C(2)−C(29)−N(1)	128.5(8)
O(2)−Rh−G[a]	120.94(17)	Rh−N(1)−C(29)	129.8(6)
N(1)−Rh−G[a]	135.0(2)		

[a] G represents the centroid of the cyclopentadiene ring (C(19), C(20), C(21), C(22) and C(23) atoms).

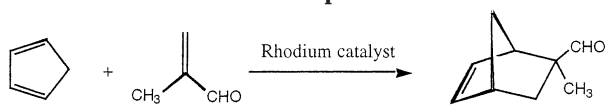
Molecular Structure of the Diastereomer 9a′. To obtain more information about the nature of the solvate compounds, the X-ray crystal structure of complex **9a′** has been determined. Single crystals of the complex were grown by slow diffusion of diethyl ether into an acetone solution of the compound. A molecular representation of the cation of this complex is depicted in Figure 10, and selected structural parameters are listed in Table 3. A similar metal coordination to that of the previously described halogen complexes has been found. The cation exhibit a "three-legged piano stool" geometry. An η^5-C_5Me_5 group occupies three *fac* positions, and the chelating phosphinooxazoline ligand and one molecule of acetone complete the coordination sphere of the metal. The absolute configuration at the rhodium center is *R*, in accord with the ligand priority sequence[22] η^5-C_5Me_5 > P > O > N. The phosphinooxazoline metallacycle Rh−P−C(1)−C(2)−C(29)−N(1) and the five-membered

(32) The water molecule may come from traces of water of the acetone solvent: see for example refs 4h and 29, and: (a) Faller, J. W.; Grimmond, B. J.; D'Alliessi, D. G. *J. Am. Chem. Soc.* **2001**, *123*, 2525. (b) Takahashi, Y.; Hikichi, S.; Akita, M.; Morooka, Y. *Chem. Commun.* **1999**, 1491. (c) Therrien, B.; Ward, T. R. *Angew. Chem., Int. Ed.* **1999**, *38*, 405.

(33) When the ^1H and $^{31}P\{^1H\}$ NMR spectra of the solvated iridium complexes **11** and **12** were recorded, in acetone or dichloromethane, variable amounts (0−20%) of the chloride complexes $[(\eta^5\text{-}C_5Me_5)IrCl(PN)][A]$ (**5** and **6**, respectively) have been detected. The $^{31}P\{^1H\}$NMR spectrum of complex **13** showed the presence of ca. 13% of a new compound (δ 53.0, $(CD_3)_2CO$) whose structure has not been further investigated.

(34) Asano, H.; Katayama, K.; Kurosawa, H. *Inorg. Chem.* **1996**, *35*, 5760.

Table 4. Enantioselective Diels−Alder Reactions of Methacrolein with Cyclopentadiene Catalyzed by the Rhodium Complexes 8−10



entry	catalyst (S_{Rh}:R_{Rh} ratio)	solvent	temp (C)	time (h)	yield (%)	isomer ratio (*exo*:*endo*)	ee (%)
1		CH_2Cl_2	RT	1	0.5		
2	**8a**, **a′** (0−15:100−85)[a]	CH_2Cl_2	RT	0.1	92	83:17	22
3	**9a**, **a′** (16:84)[b]	CH_2Cl_2	RT	0.1	94	81:19	16
4	**10a**, **a′** (48:52)[c]	CH_2Cl_2	RT	0.1	94	81:19	16
5	**8a**, **a′** (0−15:100−85)[a]	CH_2Cl_2	−20	7.5	95	92:8	53
6	**9a**, **a′** (16:84)[b]	CH_2Cl_2	−20	8.0	95	94:6	57
7	**10a**, **a′** (48:52)[c]	CH_2Cl_2	−20	12	95	94:6	39
8	**8a**, **a′** (0−15:100−85)[a]	CH_2Cl_2	−50	48	92	93:7	66
9	**9a**, **a′** (16:84)[b]	CH_2Cl_2	−50	23	94	95:5	67
10	**8a**, **a′** (0−15:100−85)[a]	$(CH_3)_2CO$	RT	46	84	90:10	23
11	**9a**, **a′** (16:84)[b]	$(CH_3)_2CO$	RT	27	64	91:9	29
12	**10a**, **a′** (48:52)[c]	$(CH_3)_2CO$	RT	28	75	92:8	19

[a−c] See the corresponding footnotes *a*, *b*, and *c* in eqs 2 and 3.

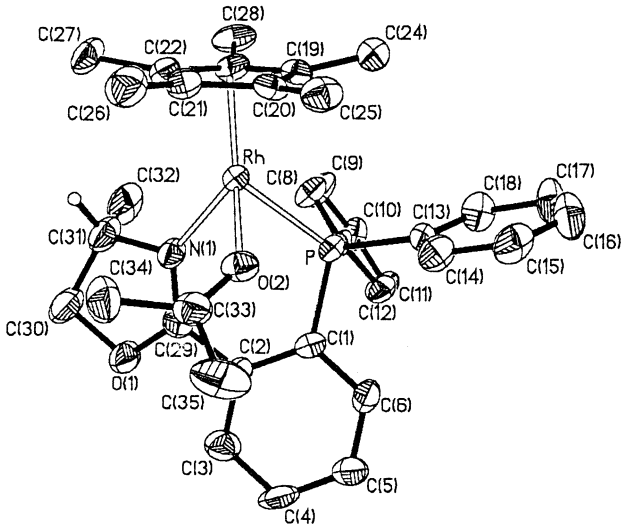


Figure 10. Molecular view of the cation of the complex (R_{Rh})-[(η^5-C_5Me_5)Rh(PN(Me))(Me_2CO)][BF_4]$_2$ (**9a′**).

oxazoline rings adopt $^1S_2$ screw-boat and $^4T_5$ conformations, respectively.

Solution Studies of the Solvate Complexes 8−13. The ^{1}H and ^{31}P{^{1}H} NMR spectra of the PN(^{i}Pr)-containing iridium complex **11a′** do not show any significant change from −90 to +20 °C. However, modifications of the spectra of all the remaining solvates indicate that they are fluxional in the NMR time scale. Again, these variable-temperature spectra could be explained assuming that an equilibrium between the two conformations, $^1S_2$ and $^5S_4$, of the corresponding phosphinooxazoline chelate ring is operating. From the ^{31}P NMR data, we have calculated that, for complex **10a**, the $\Delta G^{\ddagger}$ for this equilibrium is 37.6 ± 0.5 kJ mol^{-1}.

As stated before for the chloride compounds, the shielding produced by aromatic ring currents give us important stereochemical information. For example, the C_5Me_5 group of one of the conformers of the epimer **10a′** resonates at 1.13 ppm. This resonance is shifted about 0.5 ppm to higher frequencies, with respect to the C_5Me_5 resonances of complexes **10**. From the inspection of molecular models we assign this resonance to the *R* at the rhodium epimer in a $^5S_4$ screw-boat conformation because only in this conformer can the C_5Me_5 protons be effectively shielded by the ring current of the aromatic indane ring.

Some stereochemical assignments have been accomplished through NOE experiments. Thus, by way of example, irradiation of the C_5Me_5 protons of complexes **11b′** and **12b′** induces 0.7 and 0.5% NOE to one of the ^{i}Pr methyls and to the methyl protons of the phosphinooxazoline ligand, respectively. These NOE are consistent with an *R*[35] configuration at the metal in both compounds.

Finally, the molecular structure of complex **9** (diastereomeric composition at −90 °C, in acetone, 16:84 **9a**/**9a′**) was elucidated by diffractometric means (see above). Because the NMR spectrum of complex **9a′** compares well with that of the R_{Ir} analogue **12a′**, the measured X-ray structure, with *R* configuration at the metal, would correspond to the major isomer **9a′**.

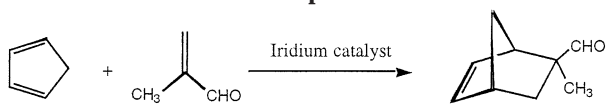
In summary, complexes **8**−**13** are isolated as mixtures of aquo and acetone solvates. In solution, exchange between free and coordinated solvent has been observed. In general, the solvates exist as mixtures of epimers at metal that at low temperature can be resolved into the $^1S_2$ and $^5S_4$ metallacycle conformers.

Catalytic Diels−Alder Reactions. Solvate complexes [(η^5-C_5Me_5)M(PN)S]$^{2+}$ (M = Rh, Ir) are active catalysts for the Diels−Alder reaction between methacrolein and cyclopentadiene. Tables 4 and 5 collect the most representative results. A low catalyst loading (5 mol %) and a 6:1 cyclopentadiene/methacrolein molar ratio were used in all cases. Enantioselectivities up to 67% were achieved, and the preferential adduct obtained with all the catalysts was (1*R*,2*S*,4*R*)-2-methylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde.

When the iridium derivatives **11**−**13** were used as catalysts (Table 5), reactions were faster than the corresponding rhodium-catalyzed reactions (Table 4). The different behavior of the rhodium with respect to the iridium complexes was also manifested in the stereoselectivity: working at room temperature, cata-

(35) Note that the priority order is η^5-C_5Me_5 > P > O > N[22] and, consequently, a stereochemical disposition such as those found in related chloride complexes is denoted with the opposite descriptor.

Table 5. Enantioselective Diels−Alder Reactions of Methacrolein with Cyclopentadiene Catalyzed by the Iridium Complexes 11−13



entry	catalyst (S_{Ir}:R_{Ir} ratio)	solvent	temp (C)	time (h)	yield (%)	isomer ratio (*exo*:*endo*)	ee (%)
1		CH_2Cl_2	RT	1	0.5		
2	**11a**, **a′** (0:100)	CH_2Cl_2	RT	0.1	95	91:9	58
3	**12a**, **a′** (0:100)	CH_2Cl_2	RT	0.1	96	91:9	51
4	**13a**, **a′** (53:47)[a]	CH_2Cl_2	RT	0.3	96	90:10	24
5	**11a**, **a′** (0:100)	CH_2Cl_2	−20	1.7	93	92:8	65
6	**12a**, **a′** (0:100)	CH_2Cl_2	−20	2.9	100	93:7	55
7	**13a**, **a′** (53:47)[a]	CH_2Cl_2	−20	0.3	96	92:8	36
8	**11a**, **a′** (0:100)	CH_2Cl_2	−50	2.1	95	93:7	63
9	**12a**, **a′** (0:100)	CH_2Cl_2	−45	2.7	91	93:7	57
10	**13a**, **a′** (53:47)[a]	CH_2Cl_2	−50	1.7	82	95:5	60
11	**11a**, **a′** (0:100)	$(CH_3)_2CO$	RT	118	77	91:9	24
12	**12a**, **a′** (0:100)	$(CH_3)_2CO$	RT	24	90	91:9	10
13	**13a**, **a′** (53:47)[a]	$(CH_3)_2CO$	RT	22	91	92:8	7
14	**11b**, **b′** (0:100)	CH_2Cl_2	RT	1.3	97	88:12	35
15	**12b**, **b′** (0:100)	CH_2Cl_2	RT	0.2	95	84:16	4

[a] See footnote *d* in eqs 2 and 3.

lysts **11** and **12** were much more enantioselective than the rhodium analogues **8** and **9** (Tables 4 and 5, entries 2 and 3). The use of acetone as solvent reduced both reaction rate and enantioselectivity for the iridium catalysts (Table 5, entries 11−13). In the case of the rhodium complexes, acetone also gave a reduction in the reaction rate but with a little enhancement in the enantioselectivity (Table 4, entries 10−12). BF_4^- iridium salts (Table 5, entries 14 and 15) exhibited lower *exo*/*endo* stereoselectivity and enantioselectivity than the corresponding SbF_6^- salts.

Lowering the reaction temperature gave the expected reduction in the reaction rate and increased the enantioselectivity, both effects being more pronounced in the rhodium-catalyzed reactions (Table 4, entries 5, 6, 8, and 9). However, with the iridium catalysts **11** and **12** enantioselectivity increased only ca. 6% when the temperature decreased about 75 °C (compare entries 2 with 8 or 3 with 9, Table 5). Only for the iridium complex **13** did temperature changes have as much effect as in the rhodium cases (Table 5, entries 4, 7, and 10).

The different diastereomeric composition of the catalysts together with the existence of two conformers are complicating factors that make it difficult to reasonably explain the observed enantioselectivity sense. However, it is possible to account for the preferential S configuration at C_2 in the *exo* Diels−Alder adduct, assuming that the most active species are the *R* at metal isomers, in the $^1S_2$ conformation, with the methacrolein adopting its *s-trans* preferred disposition.[16,36] In this conformation the *Si*-face of the dienophile is shielded by the aromatic ring that bears the oxazoline moiety. Therefore, the attack of the diene would take place preferentially on the *Re*-face and ee would be achieved in the 1*R*,2*S*,4*R*-configurated adduct, in good agreement with the measured enantioselectivity (Figure 11). Support for this suggestion stems from the molecular structure of the acetone solvate $[(\eta^5\text{-}C_5Me_5)Rh(PN(Me))(Me_2CO)][SbF_6]_2$ (**9a′**), in which, as stated above, the configuration at the metal is *R* and the conformation of the M−P−C−C−C−N metallacycle is $^1S_2$. The molecular structure also reveals that one of the faces of the acetone ligand is shielded by the aromatic ring of the PN ligand that bears the oxazoline moiety.

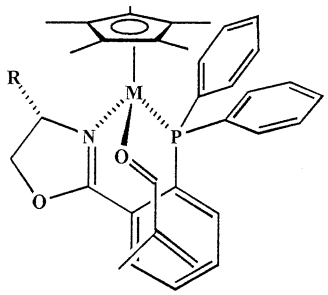


Figure 11. Proposed methacrolein complex (R_M)-$[(\eta^5\text{-}C_5Me_5)M(PN)(methacrolein)]^{2+}$ showing the shielding of the *Si*-face of the methacrolein.

Concluding Remarks

Cationic half-sandwich complexes of the type $[(\eta^5\text{-}C_5Me_5)MCl(PN)]^+$ (M = Rh, Ir) that incorporate chiral phosphinooxazoline ligands are easily prepared from the corresponding dimer $[\{(\eta^5\text{-}C_5Me_5)MCl\}_2(\mu\text{-}Cl)_2]$ as a mixture of epimers at the metal. Abstraction of the chloride affords the new solvato complexes $[(\eta^5\text{-}C_5Me_5)M(PN)S]^{2+}$. The six-membered M−P−C−C−C−N metallacycle of the solvates and of the PN(Me)-containing chlorides adopts two different conformations that, from the crystal structure determinations, have been established as screw-boat $^1S_2$ and $^5S_4$. The interconversion between them has been studied by NMR spectroscopy, and an activation energy of about 40 kJ mol^{-1} has been measured for the process. All the new solvates are active catalysts for the Diels−Alder reaction between methacrolein and cyclopentadiene with good *exo*:*endo* diasteroselectivity and up to 67% of *ee*. The sense of enantioselectivity could be explained by assuming that the most active species are *R* at metal complexes with the M−P−C−C−C−N metallacycle in an $^1S_2$ conformation.

(36) Kündig, E. P.; Saudan, C. M.; Bernardinelli, G. *Angew. Chem., Int. Ed.* **1999**, *38*, 1219.

Table 6. Crystallographic Data for the Structural Analysis of Complexes 1a, 1a′, 2a+2a′, 2b, 3a, 4a, 5b, 6a, 6a′, and 9a′

	1a	1a′	2a+2a′	2b	3a
formula	$C_{34}H_{39}ClF_6NOPRhSb$	$C_{34}H_{39}ClF_6NOPRhSb$	$C_{32}H_{35}ClF_6NOPRhSb$	$C_{32}H_{35}BClF_4NOPRh\cdot 0.25C_4H_{10}O$	$C_{38}H_{37}ClF_6NOPRhSb$
fw	882.74	882.74	854.69	724.28	928.77
cryst syst	monoclinic	orthorhombic	monoclinic	orthorhombic	orthorhombic
space group	$P2_1$ (no. 4)	$P2_12_12_1$ (no. 19)	$P2_1$ (no. 4)	$P2_12_12_1$ (no. 19)	$P2_12_12_1$ (no. 19)
a, Å	10.5421(9)	10.7042(5)	16.770(2)	10.992(2)	11.8950(8)
b, Å	14.1772(14)	11.9454(7)	10.3402(14)	14.157(3)	12.7601(8)
c, Å	11.9537(13)	27.896(2)	19.6038(19)	22.863(4)	23.865(2)
β, deg	90.278(9)	90.0	99.276(9)	90.0	90.0
Z; V, Å^3	2; 1786.5(3)	4; 3567.0(4)	4; 3355.0(7)	4; 3557.6(13)	4; 3622.3(5)
ρ(calcd), g cm^{-3}	1.641	1.644	1.692	1.352	1.703
μ(Mo Kα), mm^{-1}	1.396	1.399	1.484	0.647	1.382
θ range data, deg	1.70−27.49	2.04−27.26	1.74−24.99	2.06−23.01	1.71−25.02
no. collect reflns	8822	8970	12 881	5527	11 124
no. unique reflns	8185 (R_{int} = 0.0203)	8016 (R_{int} = 0.0131)	11770 (R_{int} = 0.0367)	4878 (R_{int} = 0.0391)	6388 (R_{int} = 0.0488)
no. obsd reflns	7721	6416	10 299	3177	5092
min., max. transmn fact	0.592, 0.736	0.577, 0.715	0.490, 0.602	0.846, 0.930	0.618, 0.769
no. data/restrns/params	8185/37/434	8016/36/435	11770/77/817	4878/30/388	6388/0/460
Flack param	0.00(2)	−0.06(2)	−0.01(3)	−0.03(7)	−0.02(3)
GOF[a]	1.102	0.958	1.097	0.948	1.028
$R_1(F)$, w$R_2(F^2)$ [obsd][b]	0.0399, 0.1011	0.0380, 0.0824	0.0372, 0.0951	0.0614, 0.1119	0.0418, 0.0729
$R_1(F)$, w$R_2(F^2)$ [all]	0.0432, 0.1035	0.0508, 0.0856	0.0434, 0.0977	0.1151, 0.1275	0.0632, 0.0815

	4a	5b	6a	6a′	9a′
formula	$C_{32}H_{35}F_6INOPRhSb$	$C_{34}H_{39}BClF_4IrNOP$	$C_{32}H_{35}ClF_6IrNOPSb$	$C_{32}H_{35}ClF_6IrNOPSb\cdot 0.5\ CH_2Cl_2$	$C_{35}H_{41}F_6NO_2PRhSb\cdot C_3H_6O$
fw	946.14	823.09	943.98	986.44	1171.15
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic	orthorhombic
space group	$P2_1$ (no. 4)	$P2_12_12_1$ (no. 19)	$P2_1$ (no. 4)	$P2_1$ (no. 4)	$P2_12_12_1$ (no. 19)
a, Å	10.9800(11)	11.7815(7)	10.6110(10)	8.8103(18)	11.1225(13)
b, Å	14.3400(17)	16.1335(10)	14.2880(10)	15.798(3)	15.7307 (15)
c, Å	11.0300(15)	17.2609(13)	11.0420(10)	13.853(3)	25.126(3)
β, deg	100.600(16)	90.0	101.129(4)	91.39(3)	90.0
Z; V, Å^3	2; 1707.1(4)	4; 3280(4)	2; 1642.6(2)	2; 1927.5(7)	4; 4396.3(8)
ρ(calcd), g cm^{-3}	1.841	1.666	1.909	1.700	1.769
μ(Mo Kα), mm^{-1}	2.285	4.251	5.060	4.383	1.714
θ range data, deg	1.88−26.02	2.09−28.99	2.36−27.47	1.96−25.00	2.00−25.00
no. collect reflns	7870	9636	8207	8060	8569
no. unique reflns	6711 (R_{int} = 0.0221)	8689 (R_{int} = 0.0183)	7515 (R_{int} = 0.0330)	6791 (R_{int} = 0.0565)	7675 (R_{int} = 0.0326)
no. obsd reflns	5950	7531	7235	6368	5667
min., max. transmn fact	0.591, 0.711	0.188, 0.427	0.131, 0.208	0.254, 0.490	0.493, 0.659
no. data/restrns/params	6711/37/412	8689/20/413	7515/37/413	6791/307/467	7675/54/522
Flack param	-0.02(2)	-0.020(6)	0.004(6)	-0.018(9)	-0.03(3)
GOF[a]	1.112	0.951	1.038	1.056	0.927
$R_1(F)$, w$R_2(F^2)$ [obsd][b]	0.0378, 0.0785	0.0313, 0.0651	0.0352, 0.0891	0.0478, 0.1207	0.0431, 0.0850
$R_1(F)$, w$R_2(F^2)$ [all]	0.0483, 0.0858	0.0393, 0.0667	0.0363, 0.0896	0.0513, 0.1255	0.0638, 0.0894

[a] GOF = $(\sum[w(F_o^2 - F_c^2)^2]/(n-p))^{1/2}$, where n and p are the number of data and parameters. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR_2 = (\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2])^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ and $P = [\mathrm{Max}(0, F_o^2) + 2F_c^2]/3$.

Experimental Section

General Comments. All solvents were dried over appropriate drying agents, distilled under nitrogen, and degassed prior to being used. All preparations have been carried out under a nitrogen atmosphere. Infrared spectra were recorded on a Perkin-Elmer 1330 spectrophotometer. Carbon, hydrogen, and nitrogen analyses were performed using a Perkin-Elmer 240C microanalyzer. ^{1}H and ^{31}P{^{1}H} spectra were recorded on a Varian UNITY 300 (299.95 MHz) or a Bruker 300 ARX (300.10 MHz). Chemical shifts are expressed in ppm upfield from $SiMe_4$ and 85% H_3PO_4 (^{31}P). CD spectra were determined in acetone or dichloromethane (ca. 5×10^{-4} mol L^{-1} solutions) in a 1 cm path length cell by using a Jasco-710 apparatus. NOEDIFF and ^{31}P, ^{1}H correlation spectra were obtained using standard procedures. The ROESY spectrum was obtained for a spin-locking (mixing) time of 400 ms.

Preparation of [(η^5-C_5Me_5)RhCl(PN)][A] (1−3). A mixture of [{(η^5-C_5Me_5)RhCl}$_2$(μ-Cl)$_2$] (200.0 mg, 0.324 mmol), the appropriate salt $NaSbF_6$ or $NaBF_4$ (0.647 mmol), and the phosphinooxazoline ligand PN(^{i}Pr), PN(Me), or PN(Ind) (0.647 mmol) in methanol (25 mL) was stirred for 5 h. During this time the precipitation of an orange solid was observed. The resulting suspension was vacuum-evaporated to dryness. The residue was extracted with dichloromethane (15 mL), and the solution partially concentrated under reduced pressure. Slow addition of diethyl ether gave an orange microcrystalline solid, which was filtered off, washed with diethyl ether, and air-dried. Complex **4** was also prepared according to this procedure from [{(η^5-C_5Me_5)RhI}$_2$(μ-I)$_2$]. By recrystallization from methanol/diethyl ether and chloroform/diethyl ether, pure **1a**, **2b**, **3a**, and **4a**, mixtures of molar compositions 27:73 **2a**:**2a′**, 16:84 **3a**:**3a′**, 23:77 **4a**:**4a′**, 95:5 **1b**:**1b′**, and 40:60 **2b**:**2b′**, and pure **1a′** were obtained, respectively. Complex **1**: Yield: 98%, **1a**:

1a′ molar ratio 55:45. Anal. Calcd for $C_{34}H_{39}NClF_6OPRhSb$: C, 46.27; H, 4.45; N, 1.59. Found: C, 45.79; H, 3.86; N, 1.62. IR (Nujol, cm^{-1}): ν(CN) 1605 (s), $\nu(SbF_6)$ 280 (s). Yield: 69%, **1b**:**1b′** molar ratio 60:40. Anal. Calcd for $C_{34}H_{39}NBClF_4OPRh$: C, 55.65; H, 5.57; N, 1.91. Found: C, 55.32; H, 4.58; N, 1.99. IR (Nujol, cm^{-1}): ν(CN) 1600 (s), $\nu(BF_4)$ 1050 (s), ν(RhCl) 280 (s). **1a**: ^{1}H NMR ($(CD_3)_2CO$): δ 0.74 (d, $J_{HH} = 6.6$ Hz, 3H, *Me*MeCH$_i$), 1.12 (d, $J_{HH} = 7.1$ Hz, 3H, Me*Me*CH$_i$), 1.55 (d, $J_{PH} = 4.5$ Hz, 15H, C_5Me_5), 1.94 (m, 1H, MeMeC*H$_i$*), 4.49 (m, 1H, H$_c$), 4.62 (pdt, $J_{HcHg} = 8.5$ Hz, $J_{HiHg} \approx J_{HtHg} = 2.3$ Hz, 1H, H$_g$), 4.85 (dd, $J_{HcHt} = 9.3$ Hz, 1H, H$_t$), 7.3−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$): δ 39.4 (d, $J_{RhP} = 139.8$ Hz). **1a′**: ^{1}H NMR ($(CD_3)_2CO$): δ 0.17 (d, $J_{HH} = 6.8$ Hz, 3H, *Me*MeCH$_i$), 1.07 (d, $J_{HH} = 7.1$ Hz, 3H, Me*Me*CH$_i$), 1.60 (d, $J_{PH} = 3.9$ Hz, 15H, C_5Me_5), 2.24 (m, 1H, MeMeC*H$_i$*), 4.50 (m, 1H, H$_c$), 4.53 (m, 1H, H$_g$), 4.73 (dd, $J_{HcHt} = 7.8$ Hz, $J_{HgHt} = 1.5$ Hz, 1H, H$_t$), 7.3−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$): δ 39.6 (d, $J_{RhP} = 138.9$ Hz). **1b**: ^{1}H NMR ($(CD_3)_2CO$): δ 0.73 (d, $J_{HH} = 6.7$ Hz, 3H, *Me*MeCH$_i$), 1.11 (d, $J_{HH} = 7.0$ Hz, 3H, Me*Me*CH$_i$), 1.53 (d, $J_{PH} = 4.0$ Hz, 15H, C_5Me_5), 1.95 (m, 1H, MeMeC*H$_i$*), 4.53 (pt, 1H, H$_c$), 4.68 (pdt, $J_{HcHg} = 8.5$ Hz, $J_{HiHg} \approx J_{HtHg} = 2.3$ Hz, 1H, H$_g$), 4.80 (dd, $J_{HcHt} = 9.2$ Hz, 1H, H$_t$), 7.4−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$): δ 40.4 (d, $J_{RhP} = 140.5$ Hz). **1b′**: ^{1}H NMR ($(CD_3)_2CO$): δ 0.15 (d, $J_{HH} = 6.7$ Hz, 3H, *Me*MeCH$_i$), 1.06 (d, $J_{HH} = 7.1$ Hz, 3H, Me*Me*CH$_i$), 1.59 (d, $J_{PH} = 3.9$ Hz, 15H, C_5Me_5), 2.27 (m, 1H, MeMeC*H$_i$*), 4.50−4.60 (m, H$_c$, H$_g$, overlapped with the corresponding **1b** resonances), 4.72 (dd, $J_{HcHt} = 6.3$ Hz, $J_{HgHt} = 1.8$ Hz, 1H, H$_t$), 7.3−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$): δ 40.3 (d, $J_{RhP} = 139.9$ Hz). Complex **2**: Yield: 93%, **2a**:**2a′** molar ratio 44:56. Anal. Calcd for $C_{32}H_{35}NClF_6OPRhSb$: C, 44.97; H, 4.13; N, 1.64. Found: C, 44.95; H, 4.00; N, 1.64. IR (Nujol, cm^{-1}): ν(CN) 1600 (s), $\nu(SbF_6)$ 280 (s). Yield: 79%, **2b**:**2b′** molar ratio 45:55. Anal. Calcd for $C_{32}H_{35}NBClF_4OPRh$: C, 54.46; H, 5.00; N, 1.98. Found: C, 53.51; H, 4.72; N, 2.15. IR (Nujol, cm^{-1}): ν(CN) 1600 (s), $\nu(BF_4)$ 1050 (s), ν(RhCl) 280 (s). **2a**: ^{1}H NMR ($(CD_3)_2CO$): δ 1.02 (d, $J_{HgH} = 6.3$ Hz, 3H, Me), 1.50 (d, $J_{PH} = 3.9$ Hz, 15H, C_5Me_5), 4.60 (m, 3H, H$_c$, H$_g$, H$_t$), 7.4−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$), −100 °C): δ 29.3 (bd, $J_{RhP} = 121.7$ Hz), 41.6 (d, $J_{RhP} = 139.9$ Hz). **2a′**: ^{1}H NMR ($(CD_3)_2CO$): δ 1.25 (d, $J_{HgH} = 6.5$ Hz, 3H, Me), 1.50 (d, $J_{PH} = 3.9$ Hz, 15H, C_5Me_5), 4.02 (m, 1H, H$_g$), 4.36 (pt, $J_{HgHt} \approx J_{HcHt} = 8.3$ Hz, 1H, H$_t$), 4.54 (pt, J_{HgHc}= 9.0 Hz, 1H, H$_c$), 7.4−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$, −100 °C): δ 29.9 (d, $J_{RhP} = 131.5$ Hz), 39.9 (d, $J_{RhP} = 137.1$ Hz). **2b**: ^{1}H NMR ($(CD_3)_2CO$): δ 1.04 (d, $J_{HgH} = 6.3$ Hz, 3H, Me), 1.51 (d, $J_{PH} = 4.0$ Hz, 15H, C_5Me_5), 4.60 (m, 3H, H$_c$, H$_g$, H$_t$), 7.5−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$)): δ, 36.6 (d, $J_{RhP} = 136.5$ Hz). **2b′**: ^{1}H NMR ($(CD_3)_2CO$): δ 1.25 (d, $J_{HgH} = 6.5$ Hz, 3H, Me), 1.50 (d, $J_{PH} = 3.9$ Hz, 15H, C_5Me_5), 4.00 (m, 1H, H$_g$), 4.37 (pt, $J_{HgHt} \approx J_{HcHt} = 8.3$ Hz, 1H, H$_t$), 4.54 (pt, J_{HgHc}= 9.0 Hz, 1H, H$_c$), 7.4−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$): δ 32−36 bm. Complex **3**. Yield: 98%, **3a**:**3a′** molar ratio 54:46. Anal. Calcd for $C_{38}H_{37}NClF_6OPRhSb$: C, 49.03; H, 4.22; N, 1.50. Found: C, 48.76; H, 3.80; N, 1.49. IR (Nujol, cm^{-1}): ν(CN) 1605 (s), $\nu(SbF_6)$ 290 (s). **3a**: ^{1}H NMR ($(CD_3)_2CO$): δ 1.59 (d, $J_{PH} = 3.9$ Hz, 15H, C_5Me_5), 3.50, 3.55 (2H, AB part of an ABX system, $J_{AB} = 17.8$, $J_{AX} = 3.7$, $J_{BX} \approx 0$ Hz, H$_t$, H$_c$), 5.79 (m, 1H, H$_O$), 5.89 (d, $J_{H_OH_n} = 5.9$ Hz, 1H, H$_n$), 7.0−8.0 (m, 18H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$): δ 38.1 (d, $J_{RhP} = 135.9$ Hz). **3a′**: ^{1}H NMR ($(CD_3)_2CO$): δ 1.14 (d, $J_{PH} = 3.9$ Hz, 15H, C_5Me_5), 3.62 (m, 2H, H$_c$, H$_t$), 4.90 (d, $J_{H_OH_n} = 8.8$ Hz, 1H, H$_n$), 5.54 (m, 1H, H$_O$), 7.3−8.4 (m, 18H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$): δ 28.0 (d, $J_{RhP} = 131.5$ Hz). Complex **4**: Yield: 78%, **4a**:**4a′** molar ratio 50:50. Anal. Calcd for $C_{32}H_{35}NF_6IOPRhSb$: C, 40.62; H, 3.73; N, 1.48. Found: C, 40.71; H, 3.80; N, 1.53. IR (Nujol, cm^{-1}): ν(CN) 1595 (s), $\nu(SbF_6)$ 280 (s). CD spectrum (5×10^{-4} mol L^{-1}, Me_2CO) of a 95:5 **4a**:**4a′** mixture, [θ] values of maxima, minima, and nodes (λ, nm): −45 (370), −50 (390), 0 (400), +190 (440), 0 (500), −30 (520). CD spectrum (5×10^{-4} mol L^{-1}, Me_2CO) of a 23:77 **4a**:**4a′** mixture, [θ] values of maxima, minima, and nodes (λ, nm): −20 (340), −10 (360), 0 (370), +40 (380), +60 (400), 0 (420), −40 (445) 0 (475), +20 (505). **4a**: ^{1}H NMR ($(CD_3)_2CO$): δ 1.25 (d, $J_{PH} = 6.5$ Hz, 3H, Me), 1.75 (d, $J_{PH} = 3.85$ Hz, 15H, C_5Me_5), 4.60 (m, H$_g$), 4.59 (d, $J_{HcHt} = 5.6$ Hz, 1H, H$_t$), 4.67 (pt, $J_{HgHc} = 6.5$ Hz, 1H, H$_c$), 7.4−8.3 (m, 14H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$), −84 °C): δ, 28.4 (d, $J_{RhP} = 129.7$ Hz), 38.9 (d, $J_{RhP} = 141.7$ Hz). **4a′**: ^{1}H NMR ($(CD_3)_2CO$): δ 1.26 (bs,3H, Me), 1.70 (d, $J_{PH} = 3.70$ Hz, 15H, C_5Me_5), 4.00 (m, H$_g$), 4.44 (pt, $J_{HgHt} \approx J_{HcHt} = 8.45$ Hz, 1H, H$_t$), 4.59 (pt, $J_{HgHc} = 9.1$ Hz, 1H, H$_c$), 7.5−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$), −94 °C): δ 29.6 (d, $J_{RhP} = 130.6$ Hz), 37.3 (d, $J_{RhP} = 139.9$ Hz).

Preparation of [(η^5-C_5Me_5)IrCl(PN)][A] (5−7). A mixture of [{(η^5-C_5Me_5)IrCl}$_2$(μ-Cl)$_2$] (150.0 mg, 0.188 mmol), the appropriate salt $NaSbF_6$ or $NaBF_4$ (0.376 mmol), and the phosphinooxazoline ligand PN(^{i}Pr), PN(Me), or PN(Ind) (0.376 mmol) in methanol (25 mL) was stirred for 6 h. During this time the precipitation of a yellow solid was observed for the hexafluoroantimonate complexes. The resulting mixture was vacuum-evaporated to dryness. The residue was extracted with dichloromethane (15 mL), and the solution partially concentrated under reduced pressure. Slow addition of diethyl ether gave a yellow microcrystalline solid, which was filtered off, washed with diethyl ether, and air-dried. By recrystallization from methanol/diethyl ether pure **5a**, **6a**, and **7a**, as well as a 15:85 mixture of **7a**:**7a′**, were obtained. From dichloromethane/diethyl ether pure **5a′**, **6a′**, **5b**, **5b′**, and **6b** were obtained. Complex **5**: Yield: 91%, **5a**:**5a′** molar ratio 79:21. Anal. Calcd for $C_{34}H_{39}NClF_6IrOPSb$: C, 42.01; H, 4.35; N, 1.39. Found: C, 41.94; H, 4.24; N, 1.44. IR (Nujol, cm^{-1}): ν(CN) 1595 (s), $\nu(SbF_6)$ 285 (s). Yield: 86%, **5b**:**5b′** molar ratio 59:41. Anal. Calcd for $C_{34}H_{39}NBClF_4IrOP$: C, 49.61; H, 4.77; N, 1.70. Found: C, 49.59; H, 4.90; N, 1.80. IR (Nujol, cm^{-1}): ν(CN) 1600 (s), $\nu(BF_4)$ 1050 (s), ν(IrCl) 280 (s). **5a**: ^{1}H NMR ($(CD_3)_2CO$): δ 0.84 (d, $J_{HH} = 6.7$ Hz, 3H, *Me*MeCH$_i$), 1.14 (d, $J_{HH} = 7.1$ Hz, 3H, Me*Me*CH$_i$), 1.56 (d, $J_{PH} = 2.7$ Hz, 15H, C_5Me_5), 2.12 (m, 1H, MeMeC*H$_i$*), 4.50 (pt, 1H, H$_c$), 4.62 (pdt, $J_{HcHg} = 8.4$ Hz, $J_{HiHg} \approx J_{HtHg} = 2.1$ Hz, 1H, H$_g$), 4.86 (dd, $J_{HcHt} = 9.4$ Hz, 1H, H$_t$), 7.4−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$): δ 10.6 s. **5a′**: ^{1}H NMR ($(CD_3)_2CO$): δ 0.17 (d, $J_{HH} = 6.7$ Hz, 3H, *Me*MeCH$_i$), 1.07 (d, $J_{HH} = 7.0$ Hz, 3H, Me*Me*CH$_i$), 1.59 (d, $J_{PH} = 2.6$ Hz, 15H, C_5Me_5), 1.90 (m, 1H, MeMeC*H$_i$*), 4.54 (pt 1H, H$_c$), 4.48 (pdt, $J_{HcHg} = 9.0$ Hz, $J_{HiHg} \approx J_{HtHg} = 2.1$ Hz, 1H, H$_g$), 4.75 (dd, $J_{HcHt} = 8.7$ Hz, 1H, H$_t$), 7.2−8.4 (m, 14H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$): δ 9.9 s. **5b**: ^{1}H NMR ($(CD_3)_2CO$): δ 0.83 (d, $J_{HH} = 6.6$ Hz, 3H, *Me*MeCH$_i$), 1.13 (d, $J_{HH} = 7.0$ Hz, 3H, Me*Me*CH$_i$), 1.55 (d, $J_{PH} = 2.6$ Hz, 15H, C_5Me_5), 2.10 (m, 1H, MeMeC*H$_i$*), 4.50 (pt, 1H, H$_c$), 4.64 (pdt, $J_{HcHg} = 8.0$ Hz, $J_{HiHg} \approx J_{HtHg} = 2.0$ Hz, 1H, H$_g$), 4.88 (dd, $J_{HcHt} = 9.3$ Hz, 1H, H$_t$), 7.4−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$): δ 10.5 s. **5b′**: ^{1}H NMR ($(CD_3)_2CO$): δ 0.17 (d, $J_{HH} = 6.7$ Hz, 3H, *Me*MeCH$_i$), 1.08 (d, $J_{HH} = 7.1$ Hz, 3H, Me*Me*CH$_i$), 1.60 (d, $J_{PH} = 2.4$ Hz, 15H, C_5Me_5), 1.97 (m, 1H, MeMeC*H$_i$*), 4.50 (m, 1H, H$_g$), 4.55 (pt, $J_{HgHc} \approx J_{HtHc} = 8.8$ Hz, 1H, H$_c$), 4.76 (d, 1H, H$_t$), 7.2−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$): δ 9.95 s. Complex **6**. Yield: 80%, **6a**:**6a′** molar ratio 57:43. Anal. Calcd for $C_{32}H_{35}NClF_6IrOPSb$: C, 40.71; H, 3.73; N, 1.48. Found: C, 40.45; H, 3.48; N, 1.40. IR (Nujol, cm^{-1}): ν(CN) 1600 (s), $\nu(SbF_6)$ 290 (s). Yield: 74%, **6b**:**6b′** molar ratio 45:55. Anal. Calcd for $C_{32}H_{35}NBClF_4IrOP$: C, 48.34; H, 4.44; N, 1.76. Found: C, 47.87; H, 4.49; N, 1.75. IR (Nujol, cm^{-1}): ν(CN) 1600 (s), $\nu(BF_4)$ 1050 (s), ν(IrCl) 280 (s). **6a**: ^{1}H NMR ($(CD_3)_2CO$): δ 1.26 (d, $J_{HgH} = 6.3$ Hz, 3H, Me), 1.54 (d, $J_{PH} = 2.8$ Hz, 15H, C_5Me_5), 4.58 (pt, $J_{HgHc} = 7.4$ Hz, 1H, H$_c$), 4.70 (dd, $J_{HcHt} = 8.8$ Hz, $J_{HgHt} = 1.3$, H$_t$), 4.74 (m, 1H, H$_g$), 7.5−8.1 (m, 14H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$)): δ, 9.3 s. **6a′**: ^{1}H NMR ($(CD_3)_2CO$): δ 1.14 (d, $J_{HgH} = 6.4$ Hz, 3H, Me), 1.57 (d, $J_{PH} = 2.6$ Hz, 15H, C_5Me_5), 4.47 (m, 1H, H$_g$), 4.51 (m, 1H, H$_t$), 4.65 (pt, $J_{HgHc} \approx J_{HtHc} = 8.5$ Hz, 1H, H$_c$), 7.2−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$, −94 °C): δ −1.6 s, 8.3 s. **6b**: ^{1}H NMR ($(CD_3)_2CO$): δ 1.25 (d, $J_{HgH} = 6.4$ Hz, 3H, Me), 1.54 (d, $J_{PH} = 2.6$ Hz, 15H, C_5Me_5), 4.59 (pt, $J_{HgHc} = 7.3$ Hz, 1H, H$_c$), 4.70 (dd, $J_{HcHt} = 8.9$, $J_{HgHt} = 1.7$, 1H, H$_t$), 4.74 (m, 1H, H$_g$), 7.4−8.1 (m, 14H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$): δ, 9.35 s. **6b′**: ^{1}H NMR

($(CD_3)_2CO$): δ 1.13 (d, J_{HgH} = 6.6 Hz, 3H, Me), 1.57 (d, J_{PH} = 2.6 Hz, 15H, C_5Me_5), 4.4−4.8 (m, H_g, H_c, H_t, overlapped with the corresponding **6b** resonances), 7.3−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$): δ 7.5 bs. Complex **7**: Yield: 91%, **7a**:**7a′** molar ratio 40:60. Anal. Calcd for $C_{38}H_{37}NClF_6IrOPSb$: C, 42.21; H, 3.85; N, 1.37. Found: C, 42.70; H, 3.66; N, 1.40. IR (Nujol, cm^{-1}): ν(CN) 1600 (s), $\nu(SbF_6)$ 285 (s). **7a**: ^1H NMR ($(CD_3)_2CO$): δ 1.64 (d, J_{PH} = 2.7 Hz, 15H, C_5Me_5), 3.50, 3.62 (2H, AB part of an ABX system, J_{AB} = 18.1, J_{AX} = 4.15, $J_{BX} \approx$ 0 Hz, H_t, H_c), 5.73 (pt, $J_{H_cH_o}$ = 5.0 Hz, 1H, H_O), 6.04 (d, $J_{H_OH_n}$ = 5.9 Hz, 1H, H_n), 7.2−8.5 (m, 18H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$): δ 9.2 s. **7a′**: ^1H NMR ($(CD_3)_2CO$): δ 1.15 (d, J_{HH} = 2.2 Hz, 15H, C_5Me_5), 3.65 (m, 2H, H_c, H_t), 5.07 (d, $J_{H_OH_n}$ = 8.1 Hz, 1H, H_n), 5.64 (m, 1H, H_O), 7.2−8.5 (m, 18H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$): δ −2.3 s.

Preparation of [(η^5-C_5Me_5)Rh(PN)(S)][SbF_6]$_2$ (8−10). To a diastereomeric mixture of chloro compounds **1**−**3** (0.227 mmol; **1a**:**1a′** molar ratio 71:29 or 18:82; **2a**:**2a′** molar ratio 50:50; **3a**:**3a′** molar ratio 95:5 or 16:84) in 25 mL of dichlorometane was added 78.0 mg (0.227 mmol) of $AgSbF_6$ in 2 mL of acetone. The suspension was stirred for 30 min. The AgCl formed was separated by filtration. The solution was vacuum-evaporated to dryness, and the addition of diethyl ether gave an orange solid, which was filtered off, washed with diethyl ether, and air-dried. Complex **8**: Yield: 73%, **8a**:**8a′** molar ratio 0:100 when **1a**:**1a′** molar ratio was 71:29 or 8:92 when **1a**:**1a′** molar ratio was 18:82. Anal. Calcd for $C_{34}H_{41}NF_{12}O_2PRhSb_2$ (S = H_2O): C, 37.09; H, 3.75; N, 1.27. Anal. Calcd for $C_{37}H_{45}NF_{12}O_2PRhSb_2$ (S = $(CH_3)_2CO$): C, 38.94; H, 3.97; N, 1.23. Found: C, 37.40; H, 3.34; N, 1.16. IR (Nujol, cm^{-1}): $\nu(H_2O)$ 3600 (s), 1650 (w), ν(CO) 1700 (s), ν(CN) 1600 (s), $\nu(SbF_6)$ 290 (s). **8a**: ^1H NMR ($(CD_3)_2CO$): δ 0.73 (d, J_{HH} = 6.8 Hz, 3H, *Me*MeCH$_i$), 1.11 (d, J_{HH} = 7.0 Hz, 3H, Me*Me*CH$_i$), 1.53 (d, J_{PH} = 4.0 Hz, 15H, C_5Me_5), 7.4−8.4 (m, 14H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$): δ 40.3 (d, J_{RhP} = 139.2 Hz). **8a′**: ^1H NMR (CD_2Cl_2): δ 0.01 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH$_i$), 1.01 (d, J_{HH} = 7.1 Hz, 3H, Me*Me*CH$_i$), 1.50 (d, J_{PH} = 3.7 Hz, 15H, C_5Me_5), 1.68 (m, 1H, MeMeC*H$_i$*), 4.58 (m, 2H, H_g, H_t), 4.75 (m, 1H, H_c), 7.2−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ ($(CD_3)_2CO$, −90 °C): δ 36.6 (d, J_{RhP} = 138.9 Hz), 39.1 (d, J_{RhP} = 140.8), (11:89 ratio). Complex **9**: Yield: 86%, **9a**:**9a′** molar ratio 16:84. Anal. Calcd for $C_{32}H_{37}NF_{12}O_2PRhSb_2$ (S = H_2O): C, 35.82; H, 3.48; N, 1.31. Anal. Calcd for $C_{35}H_{41}NF_{12}O_2PRhSb_2$ (S = $(CH_3)_2CO$): C, 37.77; H, 3.71; N, 1.26. Found: C, 36.36; H, 3.34; N, 1.00. IR (Nujol, cm^{-1}): $\nu(H_2O)$ 3620 (s), 1650 (w), ν(CO) 1700 (s), ν(CN) 1600 (s), $\nu(SbF_6)$ 290 (s). **9a**,**a′**: ^1H NMR (CD_2Cl_2): δ 0.83 (d, J_{HgH} = 6.6 Hz, 3H, Me), 1.51 (d, J_{PH} = 3.7 Hz, 15H, C_5Me_5), 4.43 (dd, J_{HcHt} = 8.8, J_{HgHt} = 2.2, 1H, H_t), 4.65 (m, 1H, H_g), 4.84 (pt, J_{HgHc} = 8.8, 1H, H_c), 7.1−8.2 (m, 14H, Ph). ^1H NMR ($(CD_3)_2CO$, −90 °C): δ 0.76, 0.67, 0.07 (3 × bs PN(*Me*)). **9a**: $^{31}P\{^1H\}$ ($(CD_3)_2CO$, −90 °C) δ 36.1 (d, J_{RhP} = 137.1 Hz), 39.5 bs (44:56 ratio). **9a′**: $^{31}P\{^1H\}$ ($(CD_3)_2CO$, −90 °C): δ 31.6 bs, 38.5 (d, J_{RhP} = 139.9 Hz), (33:67 ratio). Complex **10**: Yield: 81%, **10a**:**10a′** molar ratio 48:52. Anal. Calcd for $C_{38}H_{39}NF_{12}O_2PRhSb_2$ (S = H_2O): C, 39.72; H, 3.60; N, 1.22. Anal. Calcd for $C_{41}H_{43}NF_{12}O_2PRhSb_2$ (S = $(CH_3)_2CO$): C, 41.41; H, 3.81; N, 1.18. Found: C, 40.73; H, 3.34; N, 1.15. IR (Nujol, cm^{-1}): $\nu(H_2O)$ 3600 (s), 1650 (w), ν(CO) 1690 (s), ν(CN) 1595 (s), $\nu(SbF_6)$ 290 (s). **10a,a′**: ^1H NMR ($(CD_3)_2CO$): δ 1.23, 1.70 (2 × bs, C_5Me_5), 3.5−4.0 (m, H_c, H_t), 4.80 (d, $J_{H_OH_n}$ = 8.5 Hz, H_n), 5.97 (m, 1H, H_O), 6.17 (bd, 1H, H_n), 6.5−8.6 (m, 18H, Ph). **10a**: ^1H NMR ($(CD_3)_2CO$, −95 °C): δ 1.60 (bs, C_5Me_5). $^{31}P\{^1H\}$ ($(CD_3)_2CO$), −95 °C): δ, 33.5 (d, J_{RhP} = 130.6 Hz), 39.8 (d, J_{RhP} = 140.8 Hz), (50:50 ratio). **10a′**: ^1H NMR ($(CD_3)_2CO$, −95 °C): δ 1.13, 1.70 (2 × bs, C_5Me_5). $^{31}P\{^1H\}$ ($(CD_3)_2CO$, −95 °C): δ, 34.4 (d, J_{RhP} = 131.5 Hz), 38.25 (d, J_{RhP} = 138.9 Hz) (69:31 ratio).

Preparation of [(<bold>η^5-C_5Me_5)Ir(PN)(S)][A]$_2$ (11−13). A mixture of [{(η^5-C_5Me_5)IrCl}$_2$(μ-Cl)$_2$] (150.0 mg, 0.188 mmol) and AgA (A = SbF_6 or BF_4, 0.828 mmol) in acetone (25 mL) was stirred for 15 min. The AgCl formed was separated by filtration. To the resulting solution was added the appropriate phosphinooxazoline ligand PN(^{i}Pr), PN(Me), or PN(Ind) (0.376 mmol) in 5 mL of acetone. After stirring for 20 min, the solution was vacuum-evaporated to dryness, and the addition of diethyl ether gave a yellow solid, which was filtered off, washed with diethyl ether, and air-dried. Complex **11a′**: Yield: 87%. Anal. Calcd for $C_{34}H_{41}NF_{12}IrO_2PSb_2$ (S = H_2O): C, 34.30; H, 3.47; N, 1.17. Anal. Calcd for $C_{37}H_{45}NF_{12}IrO_2PSb_2$ (S = $(CH_3)_2CO$): C, 36.12; H, 3.68; N, 1.14. Found: C, 34.99; H, 3.60; N, 1.15. IR (Nujol, cm^{-1}): $\nu(H_2O)$ 3550 (s), 1630 (w), ν(CO) 1690, ν(CN) 1590 (s), $\nu(SbF_6)$ 280 (s). ^1H NMR (CD_2Cl_2): δ 0.01 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH$_i$), 1.02 (d, J_{HH} = 7.0 Hz, 3H, Me*Me*CH$_i$), 1.51 (d, J_{PH} = 2.5 Hz, 15H, C_5Me_5), 1.70 (m, 1H, MeMeC*H$_i$*), 4.50 (dpt, J_{HcHg} = 8.9, $J_{HtHg} \approx J_{HiHg}$ = 2.4 Hz, 1H, H_g), 4.60 (dd, J_{HcHt} = 9.5, 1H, H_t), 4.72 (pt, 1H, H_c), 7.2−8.3 (m, 14H, Ph). $^{31}P\{^1H\}$ (CD_2Cl_2): δ 16.1 s. Complex **11b′**: Yield: 90%. Anal. Calcd for $C_{34}H_{41}NB_2F_8IrO_2P$ (S = H_2O): C, 47.75; H, 4.63; N, 1.57. Found: C, 47.38; H, 4.51; N, 1.45. IR (Nujol, cm^{-1}): $\nu(H_2O)$ 3600 (s), 1635 (w), ν(CN) 1600 (s), $\nu(BF_4)$ 1060 (s). ^1H NMR (CD_2Cl_2): δ −0.14 (d, J_{HH} = 6.7 Hz, 3H, *Me*MeCH$_i$), 0.93 (d, J_{HH} = 6.3 Hz, 3H, Me*Me*CH$_i$), 1.44 (d, J_{PH} = 2.6 Hz, 15H, C_5Me_5), 4.3−4.6 (m, 2H, H_g, Ht), 4.78 (pt, $J_{HtHc} \approx J_{HgHc}$ = 9.8 Hz, 1H, H_c), 7.0−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ (CD_2Cl_2): δ 16.3 s. Complex **12a′**: Yield: 90%. Anal. Calcd for $C_{32}H_{37}NF_{12}IrO_2PSb_2$ (S = H_2O): C, 33.07; H, 3.21; N, 1.12. Anal. Calcd for $C_{35}H_{41}NF_{12}IrO_2PSb_2$ (S = $(CH_3)_2CO$): C, 34.96; H, 3.44; N, 1.16. Found: C, 32.43; H, 3.09; N, 1.13. IR (Nujol, cm^{-1}): $\nu(H_2O)$ 3610 (s), 1610 (w), ν(CO) 1695 (s), ν(CN) 1600 (s), $\nu(SbF_6)$ 290 (s). ^1H NMR (CD_2Cl_2): δ 0.91 (d, J_{HH} = 6.6 Hz, 3H, Me), 1.52 (d, J_{PH} = 2.4 Hz, 15H, C_5Me_5), 4.45 (dd, J_{HcHt} = 8.9, J_{HgHt} = 2.6, 1H, H_t), 4.60 (m, 1H, H_g), 4.81 (pt, J_{HgHc} = 8.7, 1H, H_c), 7.1−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ (CD_2Cl_2, −80 °C): δ 14.0 s, 14.9 s, (14:86 ratio). Complex **12b′**: Yield: 98%. Anal. Calcd for $C_{32}H_{37}NB_2F_8IrO_2P$ (S = H_2O): C, 44.46; H, 4.31; N, 1.62. Found: C, 42.83; H, 3.34; N, 1.54. IR (Nujol, cm^{-1}): $\nu(H_2O)$ 3600 (s), 1635 (w), ν(CN) 1600 (s), $\nu(BF_4)$ 1085 (s). ^1H NMR (CD_2Cl_2): δ 0.75 (d, J_{HH} = 6.6 Hz, 3H, Me), 1.44 (d, J_{PH} = 2.45 Hz, 15H, C_5Me_5), 4.24 (d, J_{HcHt} = 8.5, 1H, H_t), 4.57 (m, 1H, H_g), 4.84 (pt, J_{HgHc} = 8.4, 1H, H_c), 7.0−8.1 (m, 14H, Ph). $^{31}P\{^1H\}$ (CD_2Cl_2): δ 15.8 s. Complex **13a**,**a′**: Yield: 94%, **13a**:**13a′** molar ratio 53:47. Anal. Calcd for $C_{38}H_{39}NF_{12}IrO_2PSb_2$ (S = H_2O): C, 36.85; H, 3.17; N, 1.13. Anal. Calcd for $C_{41}H_{43}NF_{12}IrO_2PSb_2$ (S = $(CH_3)_2CO$): C, 38.52; H, 3.40; N, 1.10. Found: C, 36.16; H, 3.20; N, 1.02. IR (Nujol, cm^{-1}): $\nu(H_2O)$ 3610 (s), 1610 (w), ν(CO) 1685 (s), ν(CN) 1590 (s), $\nu(SbF_6)$ 285 (s). **13a**,**a′**: ^1H NMR ($(CD_3)_2CO$): δ 1.69, 1.1−1.3 (bs, bm, C_5Me_5), 3.65 (m, 2H, H_c, H_t), 5.94 (m, 1H, H_O), 6.15 (m, 1H, H_n), 6.8−8.3 (m, 18H, Ph). **13a**: ^1H NMR ($(CD_3)_2CO$, −90 °C): δ 1.61 (bs, C_5Me_5). $^{31}P\{^1H\}$ ($(CD_3)_2CO$), −100 °C): δ 8.4 s, 14.6 s (34:66 ratio). **13a′**: ^1H NMR ($(CD_3)_2CO$, −90 °C): δ 1.11, 1.71 (2 × bs, C_5Me_5). $^{31}P\{^1H\}$ ($(CD_3)_2CO$), −100 °C): δ 9.6 s, 14.8 s, (13:87 ratio).

Catalytic Diels−Alder Reaction between Methacrolein and Cyclopentadiene. A solution of the corresponding catalyst (0.025 mmol) in 2 mL of dry CH_2Cl_2 was prepared under argon. Methacrolein (0.5 mmol in 2 mL of dry CH_2Cl_2) and freshly distilled cyclopentadiene (3 mmol in 2 mL of dry CH_2Cl_2) were added consecutively by syringe. The resulting reaction was monitored by gas chromatography (GC) until the dienophile was consumed or its concentration remained unchangeable. Yields and *exo*:*endo* ratios were determined by GC analysis. The reaction mixture was concentrated to ca. 0.3 mL and filtered through silica gel, washing with CH_2Cl_2/hexane (1:3) before the determination of the enantiomeric purity. Enantiomeric excesses (ee) were determined by integration of the aldehyde proton of both enantiomers in ^1H NMR spectra using Eu(hfc)$_3$ in a 0.3 ratio as a chiral shift reagent. The absolute configuration of the major adduct was assigned by comparing the sign of [α]^D with that of the literature.[37]

Crystal Structure Determination of Complexes 1a, 1a′, 2a+2a′, 2b, 3a, 4a, 5b, 6a, 6a′, and 9a′. X-ray data were

collected for all complexes at low temperature (200(1) K, except for **9a′**, measured at 173(1) K) in a four-circle Siemens P4 (**2a**+**2a′**, **2b**, **3a**, **5b**, **6a**, and **6a′**) or a Stoe-Siemens AED-2 diffractometer (**1a**, **1a′**, **4a**, and **9a′**) equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) using $\omega/2\theta$ scans (3 and 7). Data were corrected for absorption using a ψ-scan method.[38]

All the structures were solved by Patterson or direct methods using SHELXS-86.[39] Refinement, by full-matrix least squares on F^2 using SHELXL97,[39] was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters for all non-hydrogen nondisordered atoms. In most cases the counteranion (SbF_6 or BF_4) was observed disordered and modeled on the base or two (**1a**, **1a′**, **2a**+**2a′**, **2b**, **4a**, **5b**, **6a**, and **9a′**) or three (**6a′**) complementary moieties including geometric restraints. Hydrogens were included in the model in most cases from observed (phenyl and oxazoline hydrogens) and calculated (methyl groups) positions depending on the quality of data. Hydrogen refinement was usually carried out with the light atoms riding on their carbon atoms with three common thermal parameters (methyl, phenyl, and oxazoline hydrogens). The presence of crystallization solvent molecules was observed in some cases (diethyl ether in **2b**, dichloromethane in **6a′**, and acetone in **9a′**). In all cases these molecules were included with isotropic atoms and with no hydrogens. In complex **2b** the extremely disordered solvent molecule could not be modeled; the contribution of the electronic density of this spatial region to the structure factors was evaluated with the SQUEEZE program,[40] and the final refinement was carried out with a set of modified data. A diethyl ether molecule was included in the final calculation of crystal data for this complex. All the final highest electronic residuals were observed in close proximity of the metal centers or in the disordered regions (anion or solvent) and have no chemical sense. In all cases the absolute configuration was checked by the estimation of the Flack parameter x in the final cycles of refinement.[41]

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Supporting Information Available: Molecular drawings of the complexes not included as figures in the text (**2b**, **5**, **6a**, and **6a′**) and an X-ray crystallographic file containing full details of the structural analysis of the 10 structures (CIF file). This material is available free of charge via the Internet at http://pubs.acs.org.

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