Chiral Phosphinooxazoline−Ruthenium(II) and −Osmium(II) Complexes as Catalysts in Diels−Alder Reactions

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The synthesis and characterization of optically active phosphinooxazoline chloride complexes (S_M and R_M)-[(η^6-*p*-MeC_6H_4*i*Pr)MCl(PN)]A (M = Ru, Os; PN = phosphinooxazoline ligand; A = counteranion) and the derived aqua complexes (R_M and S_M)-[(η^6-*p*-MeC_6H_4*i*Pr)M(PN)(H_2O)]($A)_2$ are reported. The $OPOF_2$-containing compounds (R_M and S_M)-[(η^6-*p*-MeC_6H_4*i*Pr)M($OPOF_2$)(PN*i*Pr)][PF_6] (M = Ru, Os; PN*i*Pr = (4*S*)-2-(2-diphenylphosphinophenyl)-4-isopropyl-1,3-oxazoline) have been also prepared and characterized. The molecular structures of (S_M)-[(η^6-*p*-MeC_6H_4*i*Pr)MCl(PN*i*Pr)][SbF_6] (M = Ru, Os), (S_{Ru})-[(η^6-*p*-MeC_6H_4*i*Pr)RuCl(PNInd)][SbF_6] (PNInd = (3a*S*,8a*R*)-2-(2-diphenylphosphinophenyl)-3a,-8a-dihydroindane [1,2-*d*]oxazole), and (R_{Ru})-[(η^6-*p*-MeC_6H_4*i*Pr)Ru(PN*i*Pr)(H_2O)][SbF_6] and that of the $OPOF_2$-containing compounds (R_{Ru} and S_{Ru})-[(η^6-*p*-MeC_6H_4*i*Pr)Ru($OPOF_2$)(PN*i*Pr)][PF_6] have been determined by X-ray diffractometric methods. Dichloromethane solutions of the aqua complexes [(η^6-*p*-MeC_6H_4*i*Pr)M(PN)(H_2O)][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* selectivity (from 85:15 to 96:4) and moderate enantioselectivity (up to 47%). The intermediate Lewis acid−dienophile compound (R_{Ru} and S_{Ru})-[(η^6-*p*-MeC_6H_4*i*Pr)Ru(PNInd)(methacrolein)][SbF_6]$_2$ was isolated, and the molecular structure of the *S* epimer was determined by diffractometric means. The osmium complexes (S_{Os} and R_{Os})- [(η^6-*p*-MeC_6H_4*i*Pr)Os(PN)(H_2O)][A]$_2$ (PN = PN*i*Pr, A = SbF_6, BF_4; PN = PNInd, A = SbF_6) evolve to the phenyl-containing compounds (S_{Os} and R_{Os})-[(η^6-*p*-MeC_6H_4*i*Pr)OsPh(PN′)][SbF_6] (PN′ = (4*S*)-2-(2-hydroxyphenylphosphinophenyl)-4-isopropyl-1,3-oxazoline (PNOH*i*Pr), PN′ = (3a*S*,8a*R*)-2-(2-hydroxyphenylphosphinophenyl)-3a,8a-dihydroindane[1,2*d*]oxazole] (PNOHInd)) and (S_{Os} and R_{Os})-[(η^6-*p*-MeC_6H_4*i*Pr)OsPh(PNF*i*Pr)][BF_4] (PNF*i*Pr = (4*S*)-2-(2-fluorophenylphosphinophenyl)-4-isopropyl-1,3-oxazoline), respectively, in which the phosphinooxazoline ligand incorporates a hydroxy or fluoro functionality. On the basis of spectroscopic and crystallographic observations, a common pathway for these reactions is proposed.

Introduction

Enantioselective Diels−Alder (DA) reactions are classical pattern reactions that play an important role in the construction of complicated molecules with stereochemical control.[1] 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.[2] Among them, some ruthenium[3] and, to a lesser extent, osmium[4] complexes have proved to be very promising. However, attempts to elucidate the mechanism of catalysis and selectivity are hampered by the complexity of the chemical behavior of the catalytic systems. It is commonly assumed that for activated alkenes, such as acroleins, the catalytic activity implies an η^1-coordination mode through the oxygen atom followed by subsequent attack of the diene, but experimental results supporting this assumption are scarce.[3a,f,5]

On the other hand, chiral chelate phosphinooxazoline ligands have recently proven to be useful in the control of enantioselectivity of various metal-catalyzed asymmetric reactions.[6] The pronounced difference in electronic as well as steric properties between the two chelating arms has been proposed as the key factor for the efficiency of these reactions. In particular,

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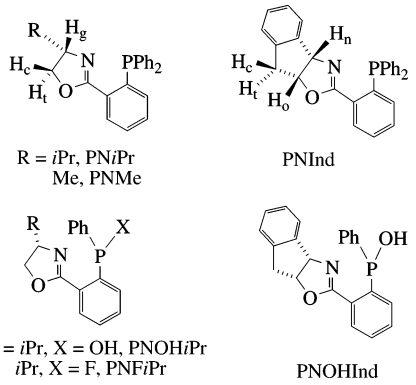
Chart 1. PN and PN′ Ligands Including NMR Proton Labeling



Helmchen et al. have reported the DA reaction of substituted *N*-acylamide dienophiles with cyclopentadiene catalyzed by phosphinooxazoline copper(II) compounds,[7] and we have shown the ability of phosphinooxazoline−rhodium(III) and −iridium(III) complexes to act as catalysts for the DA reaction between methacrolein and cyclopentadiene.[8] With these concerns in mind, it seemed reasonable to us to investigate the potential of phosphinooxazoline−ruthenium and −osmium complexes as catalysts for the DA reaction.

Some years ago, we communicated the crystallographic characterization of the Lewis acid−dienophile adduct involved in the DA reaction between methacrolein and cyclopentadiene, catalyzed by a PNInd-containing ruthenium complex.[9] Following our studies on transition-metal complexes with chiral metal centers,[2a,8,10] we report here on the synthesis and characterization of new complexes containing chiral enantiopure phosphinooxazoline ligands of general formula $[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)MX(PN)](A)_n$ (M = Ru, Os; PN = PN*i*Pr, PNMe, PNInd; X = Cl, H_2O; A = SbF_6, BF_4, CF_3SO_3, PF_6 (not all possible combinations)) and the use of the derived aqua complexes $[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)M(PN)(H_2O)](A)_2$ as enantioselective catalysts for the DA reaction between methacrolein and cyclopentadiene. These aqua complexes are fluxional. From NMR and crystallographic data, we propose that this fluxionality is associated with conformational changes of the metallacycle M−P−C−C−C−N formed by coordination of the PN ligands. Furthermore, the Lewis acid−dienophile compound $[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Ru(PNInd)(methacrolein)][SbF_6]_2$ is isolated and spectroscopically characterized as a diastereomeric mixture of the *R* and *S* at metal epimers. Finally, we show the diverse reactivity of the osmium aqua cations $[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Os(PN)(H_2O)](A)_2$, which is strongly influenced by the nature of the employed counteranion. Thus, we described the preparation and characterization of the unexpected phenyl complexes $[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)OsPh(PN')][SbF_6]$ (PN′ = PNOH*i*Pr, PNOHInd) and $[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)OsPh(PNFiPr)][BF_4]$ formed from the corresponding aqua complexes with SbF_6 or BF_4 anions, respectively.

Results and Discussion

Preparation of the Diastereomeric Complexes 1−6. At room temperature, the dimers $[\{(\eta^6\text{-}p\text{-}MeC_6H_4iPr)MCl\}_2(\mu\text{-}Cl)_2]$ (M = Ru[11a] or Os[11b]) react, in methanol, with stoichiometric amounts of the corresponding phosphinooxazoline PN*i*Pr, PNMe or PNInd, and NaA (A = SbF_6, BF_4, CF_3SO_3, or PF_6) to give, in 51−97% chemical yield, diastereomeric mixtures of both epimers at the metal of the new compounds $[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)MCl(PN)]A$ with moderate diastereoselectivity (eq 1).[12] Pure

$$1/2\,[\{(\eta^6\text{-}p\text{-}MeC_6H_4iPr)MCl\}_2(\mu\text{-}Cl)_2] + PN + NaA \longrightarrow [(\eta^6\text{-}p\text{-}MeC_6H_4iPr)MCl(PN)]A + NaCl \quad (1)$$

complex	M	PN	A	molar ratio
1a, **1a'**	Ru	PN*i*Pr	SbF_6	77:23
1b, **1b'**	Ru	PN*i*Pr	BF_4	60:40
1c, **1c'**	Ru	PN*i*Pr	CF_3SO_3	78:22
1d, **1d'**	Ru	PN*i*Pr	PF_6	73:27
2a, **2a'**	Ru	PNMe	SbF_6	67:33
3a, **3a'**	Ru	PNInd	SbF_6	71:29
3b, **3b'**	Ru	PNInd	BF_4	79:21
4a, **4a'**	Os	PN*i*Pr	SbF_6	51:49
5a, **5a'**	Os	PNMe	SbF_6	44:56
6a, **6a'**	Os	PNInd	SbF_6	41:59

samples of the epimers **1a**, **3a**, **3a′**, **3b**, **4a**, and **6a′** and diastereomeric mixtures, enriched in one of the isomers, for most of the remaining compounds have been isolated from appropriate fractional crystallization. All complexes are configurationally stable. Thus, for example, diastereomeric mixtures of **4**−**6** remained unchanged after 24 h of treatment in refluxing methanol, and the compositions of the ruthenium compounds **1**−**3** in acetone, at room temperature, do not change for hours. The new complexes were characterized by IR and NMR spectroscopy, by elemental analysis (see Experimental Section), and from the crystal structure determination, by X-ray diffractometric methods, for compounds **1a**, **3a**, and **4a**.

Molecular Structure of the Diastereomers 1a, 3a, and 4a. To determine the absolute stereochemistry of the chloro-

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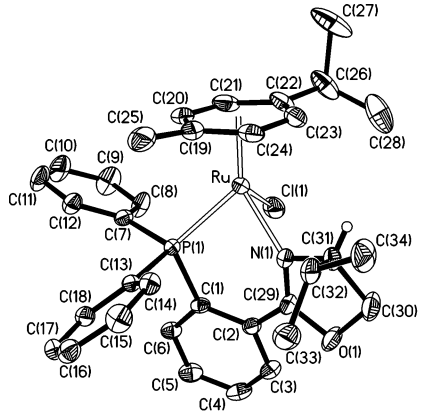
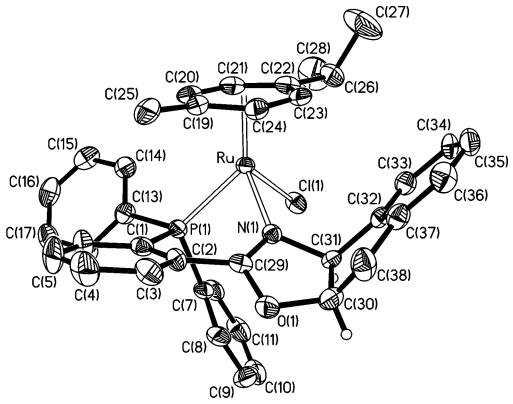
(12) Ratios were determined from ^{1}H NMR measurements. Error limits on each integer are estimated as ±2.



1a



3a

Figure 1. ORTEP views of the cation of the complexes (S_{Ru})-[(η^6-*p*-MeC$_6$H$_4$*i*Pr)RuCl(PN*i*Pr)][SbF$_6$] (**1a**) and (S_{Ru})-[(η^6-*p*-MeC$_6$H$_4$*i*Pr)-RuCl(PNInd)][SbF$_6$] (**3a**).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1a, 3a, and 4a

	1a (M = Ru)	**3a** (M = Ru)	**4a** (M = Os)
M−P(1)	2.2998(10)	2.3508(16)	2.313(2)
M−Cl(1)	2.4129(12)	2.3849(14)	2.419(3)
M−N(1)	2.113(3)	2.112(5)	2.114(7)
M−C(19)	2.251(5)	2.260(7)	2.275(11)
M−C(20)	2.186(5)	2.197(6)	2.203(10)
M−C(21)	2.175(5)	2.213(6)	2.163(10)
M−C(22)	2.282(4)	2.292(6)	2.265(9)
M−C(23)	2.273(4)	2.255(6)	2.282(8)
M−C(24)	2.220(5)	2.192(6)	2.205(10)
M−G[a]	1.731(2)	1.728(3)	1.724(4)
P(1)−C(1)	1.820(4)	1.841(6)	1.830(9)
N(1)−C(29)	1.281(6)	1.280(8)	1.293(11)
N(1)−C(31)	1.509(6)	1.517(7)	1.507(11)
C(1)−C(2)	1.409(6)	1.406(9)	1.414(12)
C(2)−C(29)	1.478(6)	1.476(9)	1.483(12)
C(2)−C(3)	1.397(6)	1.405(8)	1.366(12)
P(1)−M−Cl(1)	85.39(4)	87.48(5)	85.54(8)
P(1)−M−N(1)	84.08(10)	79.37(13)	84.48(19)
P(1)−M−G[a]	131.09(7)	133.69(10)	131.32(14)
Cl(1)−M−N(1)	85.19(11)	86.97(13)	84.0(2)
Cl(1)−M−G[a]	122.22(8)	126.01(10)	122.78(16)
N(1)−M−G[a]	132.78(12)	127.16(15)	132.4(3)
M−P(1)−C(1)	110.83(14)	103.1(2)	111.0(3)
M−N(1)−C(29)	128.0(3)	125.8(4)	126.3(6)
P(1)−C(1)−C(2)	121.0(3)	117.8(5)	121.2(7)
C(1)−C(2)−C(29)	123.3(4)	121.3(5)	122.2(7)
N(1)−C(29)−C(2)	130.2(4)	127.8(6)	132.5(7)

[a] G represents the centroid of the C(19)−C(24) *p*-cymene rings.

phosphinooxazoline compounds **1**−**6**, the molecular structures of **1a**, **3a**, and **4a** were elucidated by diffractometric means. Single crystals of the complexes were grown by slow diffusion of diethyl ether into acetone (**1a**, **3a**) or dichloromethane (**4a**) solutions. Molecular representations of the cations of these complexes are depicted in Figure 1 (that for **4a** is included in the Supporting Information), and selected structural parameters are listed in Table 1. Complex **4a** is isostructural to **1a**, showing nonsignificant differences in the geometric parameters. All cations exhibit "three-legged piano stool" geometries. An η^6-*p*-MeC$_6$H$_4$*i*Pr group occupies three *fac* positions, and the chelating phosphinooxazoline ligand and one chlorine atom complete the coordination sphere of the metal.

The M−C bond distances for the *p*-cymene carbon atoms display significant differences, most likely reflecting the greater structural *trans* effect of the phosphorus compared to those of chlorine or nitrogen atoms. The absolute configuration of the ruthenium or osmium center in the three complexes is *S*, in accord with the ligand priority sequence[13] η^6-*p*-MeC$_6$H$_4$*i*Pr > Cl > P > N. The six-membered M−P(1)−C(1)−C(2)−C(29)−N(1) chelate ring of complexes **1a** and **4a** adopts a $^1S_2$ screw-boat conformation[14] with the metal and phosphorus atoms above and below the best plane of the metallacycle, respectively. This conformation forces the *pro-R* and *pro-S* phenyls of the PPh$_2$ group to adopt pseudoaxial and pseudoequatorial arrays, respectively. However, in **3a**, the metallacycle adopts the enantiomeric conformation $^2S_1$,[14] with the relative positions of the metal and phosphorus atoms interchanged with respect to the mean plane of the ring. The rigidity and steric requirements of the indane moiety originate this flipping of the Ru−P vector, together with a notorious increase of the total puckering of the metallacycle. In this situation, the *pro-R* and *pro-S* phenyl groups occupy pseudoequatorial and pseudoaxial positions, respectively. Figure 2 shows the solid-state conformation of the metallacycle in the ruthenium complexes **1a** and **3a**, as well as values of the puckering coordinates.

NMR Spectroscopy. The ^{1}H NMR data of complexes **1**−**6** (see Experimental Section) were consistent with the presence of the *p*-cymene group and phosphinooxazoline ligand in an 1:1 ratio. Stereochemical assignments were accomplished through NOE experiments. Thus, for example, while irradiation of the methyl protons of the *p*-cymene ligand induces enhancement of the H$_g$ proton for complexes **1a′** and **4a′** and of the H$_n$ proton for **3a′** and **6a′** (Figure 3), no NOE enhancements were encountered for these protons when the methyl protons of the *p*-cymene ligand of the unprimed complexes **1a**, **3a**, **4a**, and **6a** were irradiated (see position of H(31) ≡ H$_n$ relative to Me group in Figure 2b). These NOE data are consistent with an *R* configuration at metal for the primed complexes and an *S* configuration for those unprimed, and they show that the metal configuration is retained on going from the crystal to solution.

Moreover, the configuration in solution for the PNInd-containing complexes **3** and **6** can be inferred from the chemical shift values of the methyl protons of the *p*-cymene ligand. A

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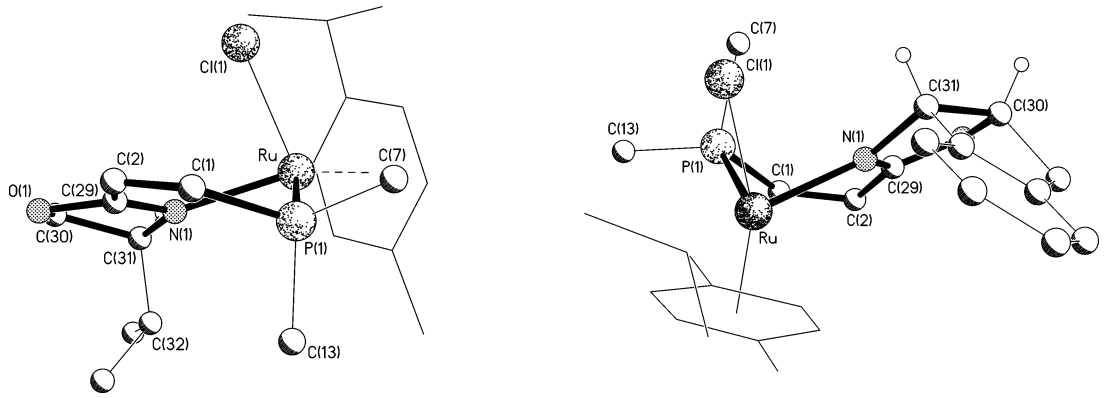


Figure 2. Solid-state conformation of the six-membered metallacycle rings (a) in **1a** ($^1S_2$ conformation: $Q = 0.672(3)$ Å, $\theta = 58.1(4)°$, $\phi = 15.8(4)°$) and (b) in **3a** ($^2S_1$ conformation: $Q = 0.973(3)$ Å, $\theta = 117.6(3)°$, $\phi = -157.6(3)°$).

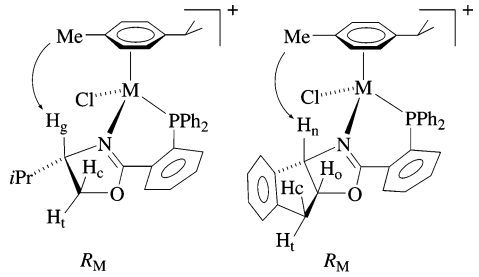
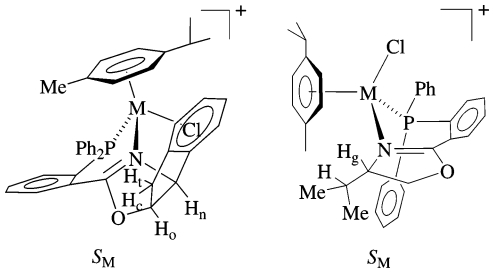


Figure 3. Selected NOE effects for chloride complexes (primed labeled, *R* epimers).



	δ (*Me*C$_6$H$_4$*i*Pr), ppm		δ (CH*Me*$_2$), ppm
3a	1.76	**1a**	0.47, 1.11
6a	1.50	**4a**	0.48, 1.14
3a'	2.19	**1a'**	0.84, 0.87
6a'	2.51	**4a'**	0.87, 1.16
	a		b

Figure 4. Schematic view of the proposed conformations in (a) S_{Ru}-**3a** and S_{Os}-**6a**; (b) S_{Ru}-**1a** and S_{Os}-**4a**.

strong shielding is observed for these protons in one of the epimers. Most probably, this shielding is produced by the electronic ring current of the aromatic bridging phenyl ring (Figure 4a) and is only compatible with an *S* at metal configuration, along with a $^2S_1$ screw-boat conformation for the six-membered chelate ring. Complex **3a** presents this structural disposition in the crystal (see above). Similarly, ^{1}H NMR data also indicate that the $^1S_2$ screw-boat conformation encountered for the *S* at metal **1a** and **4a** epimers in the solid state should be retained in solution. Thus, the chemical shift of the two isopropyl methyl protons of the PN*i*Pr ligand differs by 0.64 (**1a**) and 0.66 (**4a**) ppm. In the $^1S_2$ conformation, one methyl of the isopropyl group lies over the *pro-R* phenyl of the PPh_2 group (see Figure 4b), and therefore, it may be shielded by its aromatic ring current, accounting for the large difference observed in the chemical shift values.

The configuration at metal in the related tetrafluoroborate, triflate, and hexafluorophosphate complexes was established as S_{Ru} for the unprimed and R_{Ru} for the primed complexes, by comparison of the NMR spectral data with those of the corresponding hexafluoroantimonate complexes.

Circular Dichroism Spectra. The CD spectra of pure or enriched mixtures in the *R* epimers at metal **4a′**−**6a′** essentially consisted of two maxima centered within the ranges 330−335 and 400−435 nm, displaying negative and positive Cotton effects, respectively (see Figure 5a). The CD spectra of **1a** and **4a** (*S* epimers) are roughly enantiomorphic to those of **1a′** and **4a′**, respectively. Figure 5b shows the spectra of **4a** and **4a′**. Most probably, the major contribution to the spectra corresponds to the metal chromophore and its interaction with the ligand. However, the CD spectrum of a 95:5 molar ratio **3a**:**3a′** mixture is comparable to that of pure **3a′**, despite the change in the configuration at metal. As the conformation of the metallacycle M−P−C−C−C−N is $^1S_2$ in compounds **1a** and **4a** but $^2S_1$ in compound **3a** (see above), it seems that not only the configuration at metal but also the conformation of the matallacycle contributes to the CD spectra for this type of complex. In conclusion, this technique has to be carefully employed to make configurational assignments.[15]

Preparation of the Solvate Complexes 7−12. The chloride compounds **1**−**6** were not active as catalysts for the DA reaction between methacrolein and cyclopentadiene. To get more active catalysts, we prepared the aqua complexes [(η^6-*p*-MeC$_6$H$_4$*i*Pr)-Ru(PN)(H$_2$O)](A)$_2$ by treating the ruthenium complexes **1**−**3** with equimolar amounts of silver salts AgA (A = SbF_6, BF_4, CF_3SO_3), in acetone (eq 2). The osmium homologues were obtained by reacting the dimer [{(η^6-*p*-MeC$_6$H$_4$*i*Pr)OsCl}$_2$(μ-Cl)$_2$] with AgA and subsequent addition of 1 equiv of the corresponding PN ligand (eq 3).[16]

The diastereomeric composition measured is independent of the diastereomeric composition of the parent chlorides. However, it depends on the solvent. Thus, for example, the molar ratio of complexes **7a**:**7a′**, **8a**:**8a′**, and **9a**:**9a′** in CD_2Cl_2 is 69:31, 65:35, and 18:82, respectively.

The new complexes were characterized by IR and NMR[17] spectroscopy, elemental analysis (see Experimental Section), and

(15) (a) Consiglio, G.; Morandini, F. *Chem. Rev.* **1987**, *87*, 761. (b) Carmona, D.; Lahoz, F. J.; Oro, L. A.; Lamata, M. P.; Viguri, F.; San José, E. *Organometallics* **1996**, *15*, 2961.

(16) The water molecule may come from traces of water of the acetone solvent: see refs 3f, 8, 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.

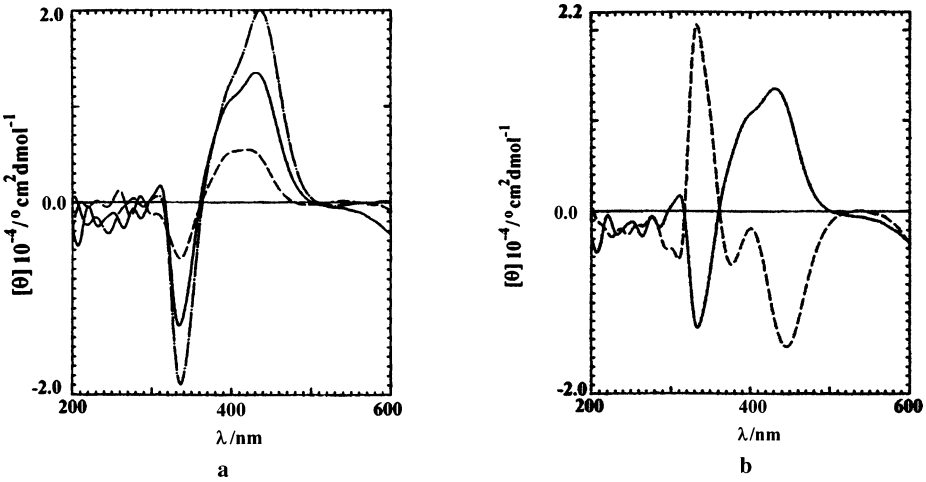


Figure 5. CD spectra in the 200−600 nm wavelength range: (a) (—) a 21:79 molar ratio **4a**:**4a′** mixture; (− − −) a 44:56 molar ratio **5a**:**5a′** mixture; (− · −) complex **6a′**; (b) (—) a 21:79 molar ratio **4a**:**4a′** mixture and (− − −) a 93:7 **4a**:**4a′** mixture.

from the crystal structure determination, X-ray diffractometric methods, for compound **7c** (see below). The aqua-solvated

$$[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4i\text{Pr})\text{RuCl(PN)}]\text{A} + \text{AgA} \longrightarrow [(\eta^6\text{-}p\text{-MeC}_6\text{H}_4i\text{Pr})\text{Ru(PN)(H}_2\text{O)}](\text{A})_2 + \text{AgCl} \quad (2)$$

$$1/2\ [(\eta^6\text{-}p\text{-MeC}_6\text{H}_4i\text{Pr})\text{OsCl}]_2(\mu\text{-Cl})_2] + 2\ \text{AgA} + \text{PN} \longrightarrow [(\eta^6\text{-}p\text{-MeC}_6\text{H}_4i\text{Pr})\text{Os(PN)(H}_2\text{O)}](\text{A})_2 + 2\ \text{AgCl} \quad (3)$$

Complex	M	PN	A	molar ratio[a]
7a, **7a'**	Ru	PN*i*Pr	SbF_6	80:20
7b, **7b'**	Ru	PN*i*Pr	BF_4	81:19
7c, **7c'**	Ru	PN*i*Pr	CF_3SO_3	83:17
8a, **8a'**	Ru	PNMe	SbF_6	50:50
9a, **9a'**	Ru	PNInd	SbF_6	35:65
10a, **10a'**	Os	PN*i*Pr	SbF_6	80:20
10b, **10b'**	Os	PN*i*Pr	BF_4	80:20
10c, **10c'**	Os	PN*i*Pr	CF_3SO_3	80:20
11a, **11a'**	Os	PNMe	SbF_6	53:47
12a, **12a'**	Os	PNInd	SbF_6	54:46

[a] In $(CD_3)_2CO$

nature of the complexes was inferred from IR and NMR measurements. The IR spectra of solid samples showed absorptions in the 3300−3700 and 1610−1625 cm^{-1} regions, attributable to coordinated water. The ^1H NMR spectrum of the major isomer of complexes **7**, in $(CD_3)_2CO$, showed peaks of coordinated and free water around 6.49 and 2.90 ppm, respectively. ROESY experiments indicated that slow exchange processes were occurring between free and coordinated water. On the other hand, the $^{31}P\{^1H\}$ NMR spectra of complexes **7b**,**7b′**, **7c**,**7c′**, and **10a**,**10a′**, in $(CD_3)_2CO$, showed the presence of a new compound. Addition of small amounts (15 μL) of water to the NMR sample led to disappearance of the new peaks, which are assigned to the acetone-coordinated complexes $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4i\text{Pr})\text{M(PN}i\text{Pr})((\text{CD}_3)_2\text{CO})](\text{A})_2$. Therefore, we conclude that the equilibrium between the acetone and the aqua solvates, depicted in eq 4, is operating and that the presence of water in trace amounts is enough to shift this equilibrium to the right.

$$[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4i\text{Pr})\text{M(PN}i\text{Pr})((\text{CD}_3)_2\text{CO})]^{2+} \underset{(\text{CD}_3)_2\text{CO}}{\overset{\text{H}_2\text{O}}{\rightleftharpoons}} [(\eta^6\text{-}p\text{-MeC}_6\text{H}_4i\text{Pr})\text{M(PN}i\text{Pr})(\text{H}_2\text{O})]^{2+} \quad (4)$$

On the other hand, when the preparation of the aqua-hexafluorophosphates $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4i\text{Pr})\text{M(PN}i\text{Pr})(\text{H}_2\text{O})][\text{PF}_6]_2$ (M = Ru, Os) was attempted according to eqs 2 and 3, the difluorophosphate anion-containing complexes $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{-}i\text{Pr})\text{M(PN}i\text{Pr})(\text{OPOF}_2)][\text{PF}_6]$ (M = Ru (**13d**, **13d′**), Os (**14d**, **14d′**)) were obtained instead. Probably, the aqua cations are intermediates in this reaction: one of the two hexafluorophosphates partially hydrolyzed to a difluorophosphate anion[18] and displaces the coordinated water, rendering the monocationic complexes **13** and **14**. The determination of the molecular structure by X-ray diffraction methods of **13d** and **13d′** confirmed this proposal.

Molecular Structure of 7c and 13d,13d′. Single crystals of the complexes were grown by slow diffusion of hexane into acetone solutions of 83:17 (**7c**:**7c′**) or 65:35 (**13d**:**13d′**) molar ratio mixtures. Notably, compound **13** crystallizes as a 1:1 mixture of the two diastereomers with opposite configuration at the metal. There are only a few examples known with two epimers at metal present in the same single crystal.[8,19,20]

Brunner has recently discussed this peculiar type of crystallization for diastereomeric half-sandwich complexes.[20] Table 2 collects the most relevant structural parameters of the complexes, and Figures 6 and 7 show molecular representations of the cations of **7c** and **13d′** (that for **13d** is included in the Supporting Information). All three cations exhibit "three-legged piano-stool" geometries. An $\eta^6\text{-}p\text{-MeC}_6\text{H}_4i\text{Pr}$ group occupies three *fac* positions of an ideal metal-octahedral environment, and the chelate phosphinooxazoline ligand and one molecule of water (**7c**) or one $PO_2F_2^-$ group bonded through an oxygen atom (**13d** and **13d′**) complete the coordination sphere of the metal. In accord with the ligand priority sequence[13] $\eta^6\text{-}p\text{-MeC}_6\text{H}_4i\text{Pr}$ > P > O > N, the absolute configuration at the ruthenium center is *R* in **7c** and **13d** and the opposite one, *S*, in **13d′**.[21] The phosphinooxazoline metallacycle Ru−P(1)−C(1)−C(2)−C(29)−N(1) adopts a $^1S_2$ screw-boat conformation in unprimed complexes **7c** and **13d** (Q = 0.7521(16) Å, θ = 59.2(2)°, ϕ =

(17) When the ^1H and $^{31}P\{^1H\}$ NMR spectra of the solvated osmium complexes (**10**−**12**) were recorded, in acetone, variable amounts (0−4%) of the parent chloride complexes **4**−**6**, respectively, were detected.

(18) The partial hydrolysis of PF_6^- to $PO_2F_2^-$ has been previously reported. (a) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Organomet. Chem.* **1977**, *134*, 319−325. (b) Connelly, N. G.; Einig, T.; García Herbosa, G.; Hopkins, P. M.; Mealli, C.; Guy Orpen, A.; Rosair, G. M.; Viguri, F. *J. Chem. Soc., Dalton Trans*. **1994**, 2025.

(19) Carmona, D.; Mendoza, A.; Lahoz, F. J.; Oro, L. A.; Lamata, M. P.; San José, E. *J. Organomet. Chem*. **1990**, *396*, C17.

(20) (a) Brunner, H.; Weber, M.; Zabel, M.; Zwack, T. *Angew. Chem., Int. Ed*. **2003**, *42*, 1859. (b) Brunner, H.; Zwack, T.; Zabel, M.; Beck, W.; Böhm, A. *Organometallics* **2003**, *22*, 1741.

(21) Note that the priority order is $\eta^6\text{-MeC}_6\text{Me}_4i\text{Pr}$ > P > O >N,[13] and consequently, a stereochemical disposition such as that found in the related chlorides is denoted with the opposite descriptor.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 7c, 13,[a] and 15a′

	7c	13d(R_{Ru})	13d′(S_{Ru}) [a]	15a′
Ru−P(1)	2.3460(7)	2.3132(11)	2.3122(11)	2.327(2)
Ru−O(2)	2.150(2)	2.143(3)	2.117(3)	2.110(5)
Ru−N(1)	2.110(2)	2.114(3)	2.124(3)	2.106(6)
Ru−C(19)	2.255(3)	2.240(4)	2.223(4)	2.235(7)
Ru−C(20)	2.203(3)	2.208(4)	2.172(4)	2.188(8)
Ru−C(21)	2.219(3)	2.189(4)	2.276(4)	2.183(7)
Ru−C(22)	2.272(3)	2.333(4)	2.293(4)	2.206(8)
Ru−C(23)	2.209(3)	2.293(4)	2.182(4)	2.274(7)
Ru−C(24)	2.222(3)	2.206(4)	2.211(4)	2.288(8)
Ru−G[b]	1.7264(13)	1.7477(17)	1.7211(17)	1.728(3)
P(1)−C(1)	1.821(3)	1.825(4)	1.825(4)	1.819(8)
N(1)−C(29)	1.292(3)	1.297(5)	1.287(5)	1.295(9)
N(1)−C(31)	1.498(3)	1.503(5)	1.512(5)	1.516(9)
C(1)−C(2)	1.407(4)	1.393(6)	1.401(6)	1.392(11)
C(2)−C(29)	1.460(4)	1.470(6)	1.479(6)	1.483(10)
C(2)−C(3)	1.404(4)	1.417(6)	1.395(6)	1.403(11)
P(1)−Ru−O(2)	84.24(6)	84.32(8)	90.19(9)	89.65(15)
P(1)−Ru−N(1)	82.64(7)	84.08(9)	81.55(10)	89.0(2)
P(1)−Ru−G[b]	131.20(5)	129.16(6)	128.22(7)	127.19(12)
O(2)−Ru−N(1)	82.74(8)	82.37(12)	79.48(12)	85.7(2)
O(2)−Ru−G[b]	124.99(7)	124.89(9)	125.77(10)	123.18(19)
N(1)−Ru−G[b]	133.45(7)	134.65(12)	134.94(10)	129.18(19)
Ru−P(1)−C(1)	107.87(11)	109.98(13)	106.88(14)	113.6(3)
Ru−N(1)−C(29)	128.90(18)	128.0(3)	126.5(3)	131.6(5)
P(1)−C(1)−C(2)	120.6(2)	121.1(3)	115.7(3)	124.5(6)
C(1)−C(2)−C(29)	123.2(2)	124.2(4)	122.2(4)	124.8(7)
N(1)−C(29)−C(2)	129.5(2)	129.9(4)	128.8(4)	130.7(7)

[a] Complex **13** crystallizes as a 1:1 diastereomeric mixture differing in the configuration at the metal center: R_{Ru} **13d** and S_{Ru} **13d′**. [b] G represents the centroid of the C(19)−C(24) *p*-cymene rings.

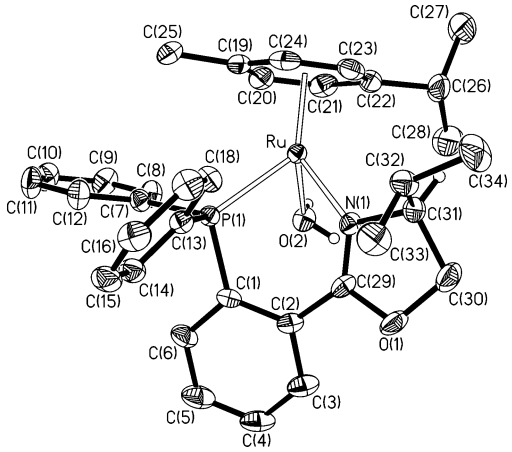


Figure 6. ORTEP view of the cation of the complex (R_{Ru})-[(η^6-*p*-MeC_6H_4*i*Pr)Ru(PN*i*Pr)(H_2O)][CF_3SO_3]$_2$ (**7c**).

22.1(3)° for **7c**, $Q = 0.673(2)$ Å, $\theta = 56.6(3)°$, $\phi = 18.4(3)°$ for **13d**) and a $^2S_1$ conformation[14] in the primed complex **13d′** ($Q = 0.881(2)$ Å, $\theta = 115.3(3)°$, $\phi = -150.4(3)°$).

Solution Studies of the Solvated Complexes 7−12. Stereochemical assignments of complexes **7**, **9**, and **10** were accomplished through NOE experiments. NOE difference spectra for the ruthenium complex **9a′** showed enhancement of the methyl and one of the isopropyl methyl cymene protons when the H_n proton was irradiated. However, no NOE effect was observed for the cymene protons when the H_g proton of compound **7a** or **10a** was irradiated. These NOE data are consistent with an *S* configuration at the metal for complex **9a′** and an *R* configuration for compounds **7a** and **10a**.[21] Moreover, as stated before for the chloride compounds, the difference in the chemical shift between the two isopropyl methyl protons of phosphinooxazoline ligand of the *R* at metal complexes **7a** ($\Delta\delta = 0.87$ ppm) and **10a** ($\Delta\delta = 0.88$ ppm) can be accounted for by assuming that the phosphinooxazoline ligand adopts an $^1S_2$ screw-boat conformation.

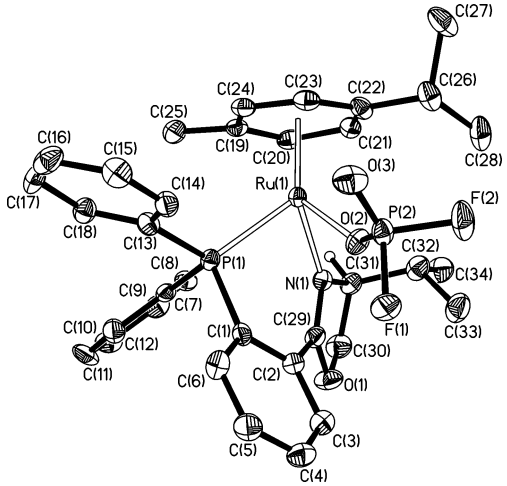


Figure 7. Molecular diagram of the cation of the complex (S_{Ru})-[(η^6-*p*-MeC_6H_4*i*Pr)Ru(OPF_2O)(PN*i*Pr)][PF_6] (**13d′**).

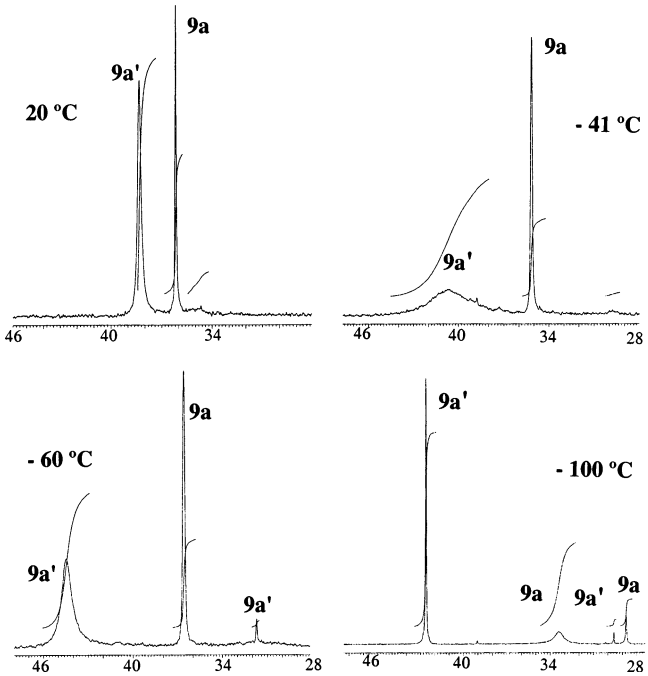
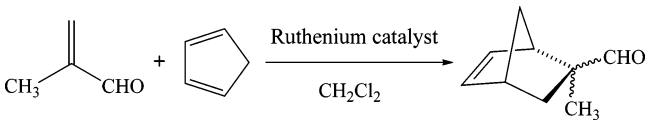


Figure 8. $^{31}P\{^1H\}$ spectra of **9a** and **9a′** in $(CD_3)_2CO$ at different temperatures.

On the other hand, variable-temperature NMR experiments show that the solvate complexes **7**−**12** are fluxional. As an example, Figure 8 collects the ^{31}P NMR spectra of complex **9**, in d_6-acetone, at selected temperatures. At +20 °C, the spectrum consists of two resonances, centered at 37.5 and 35.5 ppm, attributed to the **9a′** (S_{Ru}) and **9a** (R_{Ru}) isomers, respectively. When the temperature decreases, the **9a′** signal broadens, and after its coalescence at about −41 °C, it splits into two peaks. At −100 °C, the low-limiting temperature spectrum is achieved. From this equilibration, a free energy of activation, at the coalescence temperature, $\Delta G^{\ddagger}$, of 38.5 ± 0.5 kJ mol^{-1} has been calculated for the process.[22] The signal attributed to the **9a** isomer does not show any significant change from +20 to −90 °C, but at −100 °C it also splits into two peaks at 33.4 (broad)

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

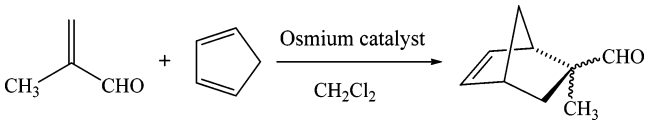
Table 3. Enantioselective DA Reactions of Methacrolein with Cyclopentadiene Catalyzed by the Ruthenium Complexes 1−3



entry	precatalyst (S_{Ru}:R_{Ru} ratio)	temp (°C)	time (h)	yield (%)	isomer ratio (*exo*:*endo*)	ee (%)
1		RT	1	0.5		
2[a]		RT	1	1		
3	**1a**, **1a′** (95:5)	RT	0.7	95	91:9	7
4	**1a**, **1a′** (20:80)	RT	0.6	72	91:9	11
5	**1a**, **1a′** (95:5)	−20	173	85	92:8	13
6[a]	**1a**, **1a′** (95:5)	RT	49	22	88:12	0
7	**2a**, **2a′** (67:33)	RT	1	85	85:15	28
8	**3a**, **3a′** (95:5)	RT	0.3	91	92:8	46
9	**3a**, **3a′** (95:5)	−20	96	72	93:7	47
10[a]	**3a**, **3a′** (95:5)	RT	22	93	96:4	20
11	**1b**, **1b′** (60:40)	RT	2.2	90	91:9	0
12	**3b′**	RT	1.3	81	94:6	46

[a] In acetone.

Table 4. Enantioselective DA Reactions of Methacrolein with Cyclopentadiene Catalyzed by Osmium Complexes 10−12



entry	catalyst	temp (°C)	time (h)	yield (%)	isomer ratio (*exo*:*endo*)	ee (%)
1	**10a**, **10a′** (75:25)	RT	0.25	86	90:10	17
2	**10a**, **10a′** (75:25)	−20	6	90	90:10	27
3	**10a**, **10a′** (75:25)	−40	48	92	92:8	34
4[a]	**10a**, **10a′** (75:25)	RT	3	84	91:9	10
5	**11a**, **11a′** (53:47)	RT	0.8	78	92:8	29
6	**11a**, **11a′** (53:47)	−20	24	83	92:8	35
7	**11a**, **11a′** (53:47)	−40	192	83	94:6	36
8[a]	**11a**, **11a′** (53:47)	RT	72	90	94:6	12
9	**12a**, **12a′** (54:46)	−20	72	93	87:13	31
10	**12a**, **12a′** (54:46)	−40	192	73	88:12	39
11[a]	**12a**, **12a′** (54:46)	RT	24	90	90:10	15

[a] In acetone.

and 28.7 ppm (Figure 8). From the NMR and crystallographic data, we propose that this fluxional behavior consists of a flip of the phosphinooxazoline metallacycle, M−P−C−C−C−N, between the two crystallographically observed $^1S_2$ and $^2S_1$ screw-boat conformations (see Figure 2).

Catalytic Diels−Alder Reactions. The solvate complexes $[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)M(PN)(H_2O)]^{2+}$ are active catalysts for the DA reaction between methacrolein and cyclopentadiene. Tables 3 and 4 summarize the most representative results for the ruthenium (Table 3) or osmium (Table 4) catalysts. The ruthenium solvates were prepared in situ from the corresponding chloride and AgA; the osmium ones were previously isolated. A low catalyst loading (5% mol) and 6:1 cyclopentadiene: methacrolein molar ratio were used in all cases. Good *exo*/*endo* selectivities and enantioselectivities up to 47% were achieved, and the preferential adduct obtained was, in all cases, (1*S*,2*R*,4*S*)-2-methylbicyclo[2.2.1]hept-5-ene-2-carbaldehyde.[23] No reaction occurs in the absence of catalyst (Table 3, entries 1 and 2). As the diastereomeric composition of the aqua complexes is independent of the diastereomeric composition of the starting

(23) In our previous communication,[9] we erroneously assigned to the major *exo* product the stereochemistry (1*R*,2*S*,4*R*).

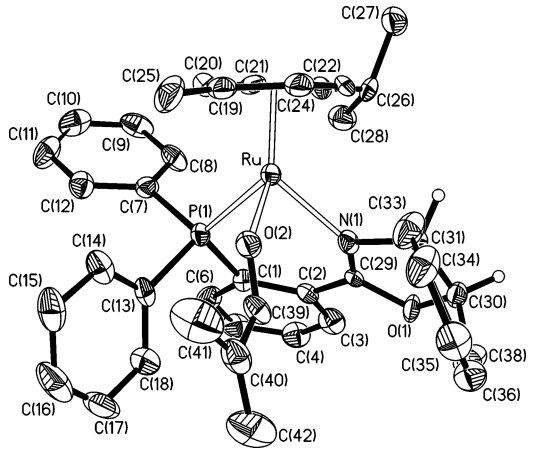


Figure 9. ORTEP view of the cation of the complex (S_{Ru})-$[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Ru(PNInd)(methacrolein)][SbF_6]_2$ (**15a′**). Selected bond distances for methacrolein moiety (Å): O(2)−C(39) 1.218(9), C(39)−C(40) 1.448(11), C(40)−C(41) 1.475(14), and C(40)−C(42) 1.326(14).

chlorides (see above), similar results have been obtained using precatalysts differing in their epimeric composition at metal (Table 3, entries 3 and 4). When acetone was used as solvent, selectivities decreased with respect to those obtained in dichloromethane (Table 3, entries 6 and 10; Table 4, entries 4, 8, and 11). Lowering the reaction temperature has very little effect on the *exo*:*endo* ratio or on the enantioselectivity for the rhutenium complexes (Table 3, entries 5 and 9), but significant improvements in the enantioselectivity are achieved for osmium complexes (Table 4, entries 2, 3; 6, 7; and 9, 10). Ruthenium tetrafluoroborates exhibit enantioselectivity lower than or similar to the corresponding SbF_6^- salts (Table 3, entries 11 and 12).

To obtain information about the mechanism of the DA catalysis, the aqua complex $[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Ru(PNInd)(H_2O)][SbF_6]_2$ (18:82, **9a**:**9a′** mixture) was combined separately with HCp and methacrolein in CD_2Cl_2 (**9**:methacrolein or HCp, 1:20 molar ratio), and the solutions were monitored by NMR spectroscopy. While no interaction with HCp was detected, immediate adduct formation with methacrolein occurred to give the complex $[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Ru(PNInd)(methacrolein)][SbF_6]_2$ (**15a**, **15a′**) as a 90:10 mixture of epimers at metal. From the NMR solution single crystals of **15** were obtained and the crystal structure was determined by X-ray methods. A molecular representation of the cation is depicted in Figure 9, and selected structural parameters are listed in Table 2. The ruthenium atom has a piano-stool geometry coordinated by a $\eta^6\text{-}p\text{-}MeC_6H_4iPr$ group, the P,N-chelate ligand, and a molecule of methacrolein, η^1-coordinated through the oxygen atom. The methacrolein fragment adopts an *s-trans* conformation, lies in a plane roughly perpendicular to the metallacycle Ru−P(1)−C(1)−C(2)−C(29)−N(1) (87.8(2)°), and maintains its planar structure upon coordination [O(2)−C(39)−C(40)−C(42) torsion angle, −178.5(8)°], with the metal atom slightly out of this plane by 0.024(6) Å. The methacrolein coordinates through the oxygen lone pair *syn* to the aldehyde proton. The absolute configuration at the metal center is *S*, and the phosphinooxazoline metallacycle Ru−P−C(1)−C(2)−C(29)−N(1) adopts an $^1S_2$ screw-boat conformation (Q = 0.345(4) Å, θ = 61.5(12)°, ϕ = 11.4(12)°).

Subsequent addition at 183 K of HCp to CD_2Cl_2 solutions of **15**, prepared as above (complex:methacrolein:HCp, 1:20:40 molar ratio), produced the appearance of a new resonance most probably due to one of the several possible metal−complex diastereoisomers in which the DA adduct is coordinated to the metal. On warming to 253 K, catalysis starts and the sole species

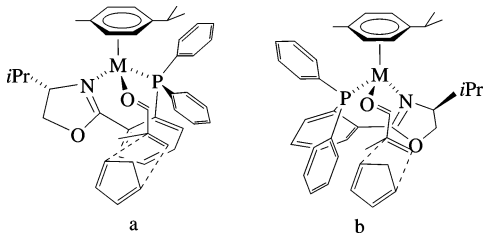
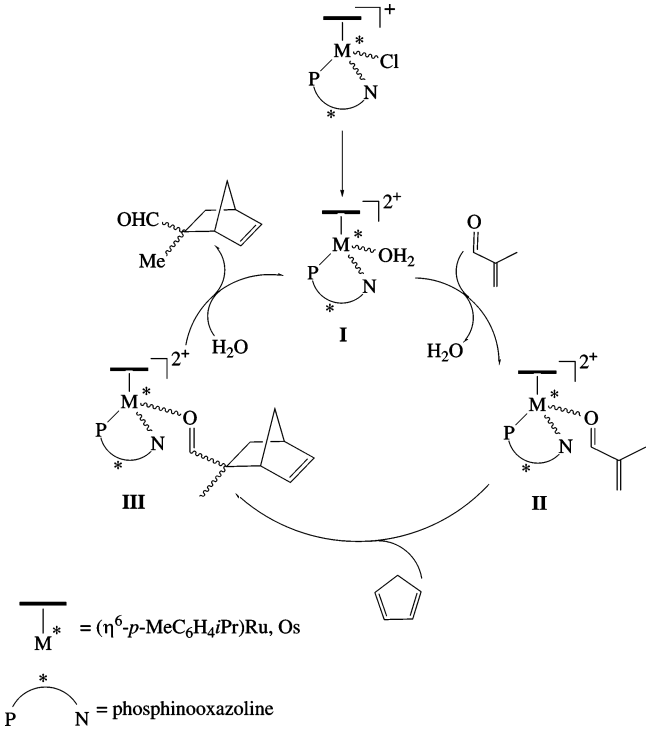


Figure 10. Proposed transition states.

Scheme 1. Proposed Catalytic Cycle



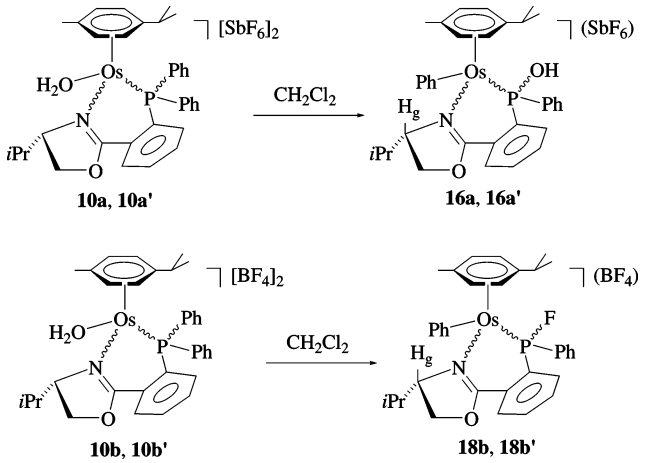
observed during the process are the aqua complexes **9**. When the catalysis has been completed, compounds **9** remain and, as expected, addition of methacrolein regenerates compounds **15** and restarts the catalytic process.

Taking into account the crystallographic and NMR data, the catalytic cycle depicted in Scheme 1 is proposed. Methacrolein displaces water from the aqua complex **I** and generates the methacrolein compound **II**. Cyclopentadiene attack to coordinated methacrolein renders the adduct complex **III**. The adduct is displaced from **III** by a water molecule, affording the aqua complex, which is the actual catalyst that restarts the cycle.

The absolute configuration of the major *exo* product (1*S*,2*R*,4*S*) suggests that the reaction proceeds through the transition states depicted in Figure 10, for PN*i*Pr-containing catalysts. The *Re*-face of the dienophile is shielded by the *pro-S* phenyl ring of the PPh_2 group, in the *R* at metal isomers (Figure 10a), or by the methyl groups of the isopropyl substituent of the oxazoline fragment, in the *S* at metal isomers (Figure 10b). In both cases, the attack of the cyclopentadiene takes place preferentially through the *Si*-face of the dienophile, in good agreement with the measured enantioselectivities.

P−C Bond Splitting Reactions of the Osmium Aqua Complexes. When the aqua solvates **10**−**12** were used as catalyst precursors for the DA reaction between methacrolein and cyclopentadiene and the room-temperature catalytic reaction required long reaction times to go to completion, the rate and selectivities are not reproducible. Furthermore, the results are strongly dependent on the anion employed. To obtain a deeper

Scheme 2. Reactivity of the Osmium Aqua Complexes



insight into the catalytic system, we studied the behavior in solution of the SbF_6^-, BF_4^-, and $CF_3SO_3^-$ salts[24] of the cations $[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Os(PN)(H_2O)]^{2+}$ (PN = PN*i*Pr, PNInd). At room temperature, dichloromethane solutions of $[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)Os(PNiPr)(H_2O)](SbF_6)_2$ (**10a**, **10a′**) evolve with P−C bond cleavage and formation of the new phenyl derivatives **16a** and **16a′**, in which a P−OH group replaces the phenyl group transferred to the metal (Scheme 2). For preparative purposes, the reaction was conducted at higher temperatures, rendering the products in 82% yield, after 2 h of treatment in refluxing dichloromethane. The formation of **16a** and **16a′** was monitored by ^{31}P NMR spectroscopy: two new singlets emerged at 70.6 and 66.5 ppm at the expense of the two singlets of the starting material at 8.1 and 0.1 ppm. Although at a slower rate, the process also takes place in acetone, but it is inhibited in more coordinating solvents such as acetonitrile or methanol. It is also inhibited at −20 °C. The related PNInd-containing complexes **12a** and **12a′** behave similarly. They afford the corresponding phenyl derivative **17a′**, the rate of formation of the latter being significantly higher: it was isolated in 78% yield after 30 min of reaction, in dichloromethane, at room temperature. Notably, the tetrafluoroborate complexes **10b** and **10b′** also yield the phenyl derivatives **18b** and **18b′**, but they present a P−F functionality instead of the P−OH group of compounds **16** and **17** (Scheme 2). However, the triflate salt is stable in dichloromethane solution and can be recovered unchanged from it.

The new complexes were characterized by analytical and spectroscopic means including ^1H, ^{31}P, ^{13}C, and ^{19}F NMR, circular dichroism, and mass spectrometry (see Experimental Section). The large shift of the ^{31}P resonance toward lower field, produced for the substitution of the P−Ph bond by P−OH (around 70 ppm) or by P−F (around 125 ppm) bonds, is strongly indicative of the presence of the electronegative atoms bonded to the phosphorus. A new low-field resonance attributable to the *ipso*-carbon of a phenyl group σ-bonded to osmium[25] indicates the formation of a new osmium−carbon bond. In complexes **18**, $^{31}P-^{19}F$ couplings (893 (**18a**), 904 (**18a′**) Hz)[26] establish the presence of a P−F bond.

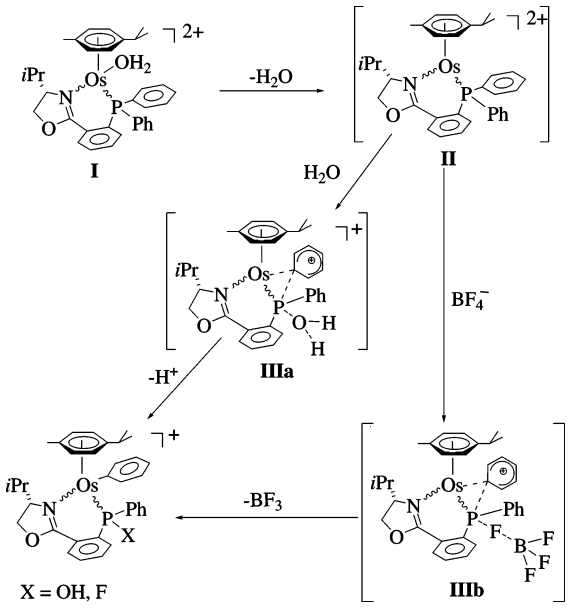
Stereochemical assigments were accomplished through NOE experiments. While irradiation of the H_g or H_n protons produces

(24) Note that one of the PF_6 anions of the related hexafluorophosphate complexes $[(\eta^6\text{-}p\text{-}MeC_6H_4iPr)M(PNiPr)(H_2O)](PF_6)_2$ (M = Ru, Os) hydrolyzed to a difluorophosphate anion, rendering complexes **13** and **14** (see text).

(25) Baya, M.; Esteruelas, M. A.; Oñate, E.*Organometallics* **2001**, *20*, 4875.

(26) *NMR and the Periodic Table*; Harris, R. K., Mann, B. E., Eds.; Academic Press: New York, 1978.

Scheme 3. Proposed Path for the Formation of 16−18



enhancement of the *ortho* hydrogen atoms of the phenyl ligand, in the unprimed complexes, it does not produce an NOE effect in the primed ones. These NOE data are consistent with an *S* configuration at metal for the former and an *R* configuration for the latter.

In the new compounds, the phosphorus atom become a stereogenic center. Notably, spectroscopic data support that it adopts the same configuration that the metal presents, the formation process being, therefore, stereospecific. Thus, for example, the relatively small difference between the chemical shift of the isopropyl methyl protons of the *S* at metal complexes ($\Delta\delta = 0.31$ ppm, **16a**, 0.30, **18b**) is only compatible with an *S* configuration at phosphorus. On the other hand, the shielding of the *ortho* and *meta* hydrogen atoms of the phenyl ring bonded to phosphorus by the phenyl-osmium ring, in complex **17a′**, is compatible only with an *R* configuration at phosphorus.

Complexes **16**−**18** are fluxional. Analysis of the ^{31}P NMR spectra at different temperatures gives $\Delta G^{\ddagger}$ values of 39.6 ± 0.5 kJ mol^{-1} (**17a′**) and 37.1 ± 0.5 (**18b**) kJ mol^{-1} for the process, at the coalescence temperature. These values are similar to those obtained for the parent aqua complexes (see above), and therefore, we propose that, again, the observed phosphorus equilibration corresponds to a flip between $^{1}S_2$ and $^{2}S_1$ metallacycle conformers.

A possible reaction pathway that rationalizes the stereospecific formation of compounds **16**−**18** is outlined in Scheme 3 for the PN*i*Pr-containing complexes.[27] The loss of the coordinated water from **I** would generate the cationic [(η^6-*p*-MeC$_6$H$_4$*i*Pr)Os(PN*i*Pr)]$^{2+}$ 16-electron species **II**. This intermediate undergoes a [1,2]-shift of a phenyl group from phosphorus to osmium, promoted by the nucleophilic attack of H_2O or BF_4^- on the phosphorus, to give **IIIa** or **IIIb**. The nucleophilic attack has to occur from the side opposite that of the osmium−phosphorus phenyl bridge, accounting for the observed stereospecificity. Dissociation of H^+ or BF_3 from **IIIa** or **IIIb** generates the final adducts. More coordinating counterions or solvents avoid the process by coordination to the unsaturated 16 e$^-$ species **II**. The reactivity collected in Scheme 2 along with the path proposed in Scheme 3 account for the erratic catalytic results. Obviously, the concentration of the active catalytic species is anion-dependent and the achiral H^+ or BF_3 Lewis acids produced may contribute to the catalytic outcome, diminishing the enantioselectivity and making it difficult to reproduce the results.

(27) For P−C bond cleavage in (arene)Ru complexes: (a) Crochet, P.; Demerseman, B.; Rocaboy, C.; Schleyer, D. *Organometallics* **1996**, *15*, 3048. (b) Geldbach, T. J.; Pregosin P. S. *Eur. J. Inorg. Chem.* **2002**, 1907.

Concluding Remarks

The solvate complexes [(η^6-*p*-MeC$_6$H$_4$*i*Pr)M(PN)(H$_2$O)][SbF$_6$]$_2$ (M = Ru, Os) are active catalysts for the DA reaction between methacrolein and cyclopentadiene with good *exo*:*endo* diasteroselectivity and up to 47% ee. Spectroscopic and crystallographic evidence for the Lewis acid−dienophile intermediate (S_{Ru})-[(η^6-*p*-MeC$_6$H$_4$*i*Pr)Ru(PNInd)(methacrolein)][SbF$_6$]$_2$ are reported. The reactivity of the osmium cations [(η^6-*p*-MeC$_6$H$_4$*i*Pr)Os(PN)(H$_2$O)](A)$_2$ (A = SbF$_6$, BF$_4$) in catalytic conditions strongly depends on the nature of the weakly coordinating anion employed. A P−C bond splitting reaction along with a nucleophilic attack to the phosphorus of water or tetrafluoroborate account for the observed results and represent a new type of noninnocent counteranion behavior.

Experimental Section

General Comments. All solvents were dried over appropriate drying agents, distilled under nitrogen, and degassed prior to use. All preparations have been carried out under nitrogen. Infrared spectra were obtained as Nujol mulls with a Perkin-Elmer 1330 spectrophotometer. Carbon, hydrogen, and nitrogen analyses were performed using a Perkin-Elmer 240 B microanalyzer. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on a Varian Unity 300 spectrometer (299.95 MHz) or a Bruker 300 ARX (300.10 MHz). Chemical shifts are expressed in ppm upfield from SiMe$_4$ or 85% H$_3$PO$_4$ (^{31}P). CD spectra were determined in ca. 5×10^{-4} mol L^{-1} acetone solutions, in a 1 cm path length cell by using a Jasco-710 apparatus. NOEDIFF and ROESY spectra were obtained using standard procedures.

Preparation of [(η^6-*p*-MeC$_6$H$_4$*i*Pr)RuCl(PN)]A (1−3). At room temperature, a mixture of [{(η^6-*p*-MeC$_6$H$_4$*i*Pr)RuCl}$_2$(μ-Cl)$_2$] (151.8 mg, 0.25 mmol), the appropriate NaA salt (A = SbF$_6$, BF$_4$, CF$_3$SO$_3$ or PF$_6$) (0.50 mmol), and phosphinooxazoline (PN*i*Pr, PNMe, or PNInd) (0.50 mmol), in methanol (10 mL), was stirred for 1 h. During this time the precipitation of an orange solid was observed for **1a**, **1a′**; **3a**, **3a′**; and **3b**, **3b′**. The solid was filtered off, washed with cold methanol, and air-dried (first fraction). The filtrate, or the original solution for the other compounds, was vacuum-evaporated to dryness. The resulting solid was extracted with dichloromethane (3 × 5 mL) and the solution partially concentrated under reduced pressure. Slow addition of diethyl ether gave orange solids, which were filtered off, washed with diethyl ether, and air-dried (second fraction for compounds **1a**, **1a′**; **3a**, **3a′**; and **3b**, **3b′**).

1a, **1a′:** first fraction, 95:5 molar ratio, 73% yield; second fraction, 20:80 molar ratio, 23% yield. Anal. Calcd for C$_{34}$H$_{38}$NClF$_6$RuOPSb: C, 46.4; H, 4.3; N, 1.6. Found: C, 46.7; H 4.2; N, 1.5. IR (Nujol, cm^{-1}): ν(CN) 1595 (s), ν(SbF$_6$) 285 (m). CD (Me$_2$CO, [Θ] (λ, nm) maxima, minima and nodes): **1a**:**1a′**, 95:5 molar ratio: +8000 (380), +8000 (400), 0 (420), −3000 (440), 0 (460), +2020 (500); **1a**:**1a′**, 20:80 molar ratio: −8000 (380), 0 (400), +8000 (420), +7700 (470). **1a**: ^{1}H NMR ((CD$_3$)$_2$CO) δ 0.47 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH), 1.11 (d, J_{HH} = 6.6 Hz, 3H, Me*Me*CH), 1.25 (d, J_{HH} = 7.1 Hz, 3H, *Me*MeCH of *p*-cymene), 1.35 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH of *p*-cymene), 1.90 (s, 3H, Me of *p*-cymene), 2.40 (psp, 1H, MeMeC*H*), 2.94 (psp, 1H, MeMeC*H* of *p*-cymene), 4.53 (pt, 1H, H$_c$), 4.61 (dpt, J_{HcHg} = 9.0 Hz, $J_{HiHg} \approx J_{HtHg}$ = 2.4 Hz, 1H, H$_g$), 4.76 (dd, J_{HcHt} = 9.0 Hz, 1H, H$_t$), 4.90 (d, J_{AB} = 6.5 Hz, 1H, H$_A$H$_B$), 5.45 (d, 1H, H$_A$H$_B$), 6.19

(d, $J_{A'B'}$ = 5.6 Hz, 1H, $H_{A'}H_{B'}$), 6.44 (d, 1H, $H_{A'}H_{B'}$), 7.3−8.0 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 40.6 s. **1a′**: ^1H NMR ($(CD_3)_2CO$) δ 0.84 (d, J_{HH} = 6.8 Hz, 3H, *Me*MeCH), 0.88 (d, J_{HH} = 6.6 Hz, 3H, Me*Me*CH of *p*-cymene), 0.91 (d, J_{HH} = 7.1 Hz, 3H, *Me*MeCH of *p*-cymene), 1.18 (d, J_{HH} = 7.1 Hz, 3H, Me*Me*CH), 2.20 (s, 3H, Me of *p*-cymene), 2.66 (psp, 1H, MeMeC*H*), 2.94 (psp, 1H, MeMeC*H* of *p*-cymene), 4.59 (pt, 1H, H_c), 4.72 (d, J_{HcHg} = 9.0 Hz, 1H, H_g), 4.94 (dd, J_{HcHt} = 9.0 Hz, J_{HgHt} = 2.4 Hz, 1H, H_t), 5.39 (d, J_{AB} = 6.0 Hz, 1H, H_AH_B), 5.98 (d, 1H, H_AH_B), 5.98 (d, $J_{A'B'}$ = 6.0 Hz, 1H, $H_{A'}H_{B'}$), 6.15 (d, 1H, $H_{A'}H_{B'}$), 7.2−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 38.3 s.

1b:1b′: 60:40 molar ratio, 74% yield. Anal. Calcd for $C_{34}H_{38}NClF_4RuOPB$: C, 55.9; H, 5.2; N, 1.9. Found: C, 56.2; H 5.3; N, 1.7. IR (Nujol, cm^{-1}): ν(CN) 1600 (s), $\nu(BF_4)$ 1070(s), ν(RuCl) 290 (m). CD (Me_2CO, [Θ] (λ, nm) maxima, minima and nodes): **1b**:**1b′**, 75:25 molar ratio: −3000 (340), 0 (350), +12500 (380), +1000 (430), +3000 (480). **1b**: ^1H NMR ($(CD_3)_2CO$) δ 0.47 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH), 1.08 (d, J_{HH} = 6.6 Hz, 3H, Me*Me*CH), 1.26 (d, J_{HH} = 7.0 Hz, 3H, *Me*MeCH of *p*-cymene), 1.36 (d, J_{HH} = 7.0 Hz, 3H, Me*Me*CH of *p*-cymene), 1.91 (s, 3H, Me of *p*-cymene), 2.40 (psp, 1H, MeMeC*H*), 2.99 (psp, 1H, MeMeC*H* of *p*-cymene), 4.55 (pt, 1H, H_c), 4.65 (pdt, J_{HcHg} = 9.0 Hz, $J_{HiHg} \approx J_{HtHg}$ = 2.4 Hz, 1 H, H_g), 4.80 (dd, J_{HcHt} = 9.0 Hz, 1H, H_t), 4.94 (d, J_{AB} = 6.5 Hz, 1H, H_AH_B), 5.50 (d, 1H, H_AH_B), 6.19 (d, $J_{A'B'}$ = 5.9 Hz, 1H, $H_{A'}H_{B'}$), 6.36 (d, 1H, $H_{A'}H_{B'}$), 7.3−8.0 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 40.7 s. **1b′**: ^1H NMR ($(CD_3)_2CO$) δ 0.87 (d, J_{HH} = 7.0 Hz, 3H, *Me*MeCH), 0.95 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH of *p*-cymene), 0.95 (d, J_{HH} = 7.1 Hz, 3H, *Me*MeCH of *p*-cymene), 1.17 (d, J_{HH} = 7.1 Hz, 3H, Me*Me*CH), 2.16 (s, 3H, Me of *p*-cymene), 2.29 (psp, ^1H, MeMeC*H*), 2.69 (psp, ^1H, MeMeC*H* of *p*-cymene), 4.58 (pt, 1H, H_c), 4.71 (d, J_{HcHg} = 9.0 Hz, 1 H, H_g), 4.90 (dd, J_{HcHt} = 9.0 Hz, J_{HgHt} = 2.1 Hz, 1H, H_t), 5.32 (d, J_{AB} = 6.0 Hz, 1H, H_AH_B), 5.98 (d, $J_{A'B'}$ = 6.0 Hz, 1H, $H_{A'}H_{B'}$), 6.08 (d, 1H, H_AH_B), 6.15 (d, 1H, $H_{A'}H_{B'}$), 7.2−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 38.9 s.

1c:1c′: 78:22 molar ratio, 94% yield. Anal. Calcd for $C_{35}H_{38}NClF_3RuO_4PS$: C, 51.5; H, 4.7; N, 1.8. Found: C, 51.8; H 4.8; N, 1.7. IR (Nujol, cm^{-1}): ν(CN) 1600 (s). CD (Me_2CO, [Θ] (λ, nm) maxima, minima and nodes): **1c**:**1c′**, 78:22 molar ratio: −10000 (330), 0 (340), +17000 (370), +1000 (430), +3000 (480). **1c**: ^1H NMR ($(CD_3)_2CO$) δ 0.49 (d, J_{HH} = 6.8 Hz, 3H, *Me*MeCH), 1.15 (d, J_{HH} = 7.1 Hz, 3H, Me*Me*CH), 1.28 (d, J_{HH} = 7.0 Hz, 3H, *Me*MeCH of *p*-cymene), 1.39 (d, J_{HH} = 7.1 Hz, 3H, Me*Me*CH of *p*-cymene), 1.94 (s, 3H, Me of *p*-cymene), 2.43 (psp, 1H, MeMeC*H*), 3.02 (psp, 1H, MeMeC*H* of *p*-cymene), 4.57 (pt, 1H, H_c), 4.70 (dpt, J_{HcHg} = 9.1 Hz, $J_{HiHg} \approx J_{HtHg}$ = 2.3 Hz, 1H, H_g), 4.83 (dd, J_{HcHt} = 9.6 Hz, 1H, H_t), 4.95 (d, J_{AB} = 6.4 Hz, 1H, H_AH_B), 5.53 (d, 1H, H_AH_B), 6.33 (d, $J_{A'B'}$ = 6.3 Hz, 1H, $H_{A'}H_{B'}$), 6.55 (d, 1H, $H_{A'}H_{B'}$), 7.4−8.1 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 41.2 s. **1c′**: ^1H NMR ($(CD_3)_2CO$) δ 0.88 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH), 0.89 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH of *p*-cymene), 0.97 (d, J_{HH} = 7.1 Hz, 3H, *Me*MeCH of *p*-cymene), 1.20 (d, J_{HH} = 7.1 Hz, 3H, Me*Me*CH), 2.19 (s, 3H, Me of *p*-cymene), 2.70 (psp, 1H, MeMeC*H*), 2.94 (psp, 1H, MeMeC*H* of *p*-cymene), 4.61 (pt, 1H, H_c), 4.78 (bd, J_{HcHg} = 8.8 Hz, 1 H, H_g), 4.92 (dd, J_{HcHt} = 9.0 Hz, J_{HgHt} = 2.5 Hz, 1H, H_t), 5.36 (d, J_{AB} = 6.3 Hz, 1H, H_AH_B), 5.85 (d, 1H, H_AH_B), 6.07 (d, $J_{A'B'}$ = 6.1 Hz, 1H, $H_{A'}H_{B'}$), 6.18 (d, 1H, $H_{A'}H_{B'}$), 7.3−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 39.3 s.

1d:1d′: 73:27 molar ratio, 94% yield. Anal. Calcd for $C_{34}H_{38}NClF_6RuOP_2$: C, 51.8; H, 4.7; N, 1.8. Found: C, 51.8; H 4.8; N, 1.8. IR (Nujol, cm^{-1}): ν(CN) 1600 (s). CD (Me_2CO, [Θ] (λ, nm) maxima, minima and nodes): **1d**:**1d′**, 73:27 molar ratio: +16500 (370), +2000 (440), +2500 (470). **1d**: ^1H NMR ($(CD_3)_2CO$) δ 0.54 (d, J_{HH} = 6.7 Hz, 3H, *Me*MeCH), 1.17 (d, J_{HH} = 7.1 Hz, 3H, Me*Me*CH), 1.30 (d, J_{HH} = 6.9 Hz, 3H, *Me*MeCH of *p*-cymene), 1.40 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH of *p*-cymene), 1.96 (s, 3H, Me of *p*-cymene), 2.44 (psp, 1H, MeMeC*H*), 3.06 (psp, 1H, MeMeC*H* of *p*-cymene), 4.60 (pt, 1H, H_c), 4.72 (dpt, J_{HcHg} = 9.2 Hz, $J_{HiHg} \approx J_{HtHg}$ = 2.6 Hz, 1H, H_g), 4.86 (dd, J_{HcHt} = 9.2 Hz, 1H, H_t), 5.04 (m, 1H, H_AH_B), 5.55 (d, J_{HcHt} = 9.2 Hz, 1H, H_AH_B), 6.28 (d, $J_{A'B'}$ = 6.2 Hz, 1H, $H_{A'}H_{B'}$), 6.54 (d, 1H, $H_{A'}H_{B'}$), 7.4−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 41.0 s. **1d′**: ^1H NMR ($(CD_3)_2CO$) δ 0.91 (d, J_{HH} = 6.8 Hz, 3H, *Me*MeCH), 0.92 (d, J_{HH} = 6.7 Hz, 3H, Me*Me*CH of *p*-cymene), 0.98 (d, J_{HH} = 7.1 Hz, 3H, *Me*MeCH of *p*-cymene), 1.22 (d, J_{HH} = 7.1 Hz, 3H, Me*Me*CH), 2.21(s, 3H, Me of *p*-cymene), 2.71 (psp, 1H, MeMeC*H*), 2.96 (psp, 1H, MeMeC*H* of *p*-cymene), 4.63 (pt, $J_{HgHc} \approx J_{HtHc}$ = 9.2 Hz, 1H, H_c), 4.91 (m, 2H, H_g and H_t), 5.35 (d, J_{AB} = 6.1 Hz, 1H, H_AH_B), 5.75 (m, 1H, H_AH_B), 6.22 (bs, 2H, H_AH_B), 7.2−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 39.2 s.

2a:2a′: 67:33 molar ratio, 93% yield. Anal. Calcd for $C_{32}H_{34}NClF_6RuOPSb$: C, 51.9 H, 4.6; N, 1.9. Found: C, 52.1; H 4.4; N, 1.8. IR (Nujol, cm^{-1}): ν(CN) 1600 (s), $\nu(SbF_6)$ 285 (m). CD (Me_2CO, [Θ] (λ, nm) maxima, minima and nodes): **2a**:**2a′**, 67:33 molar ratio: +2600 (390), +1200 (430), +2700 (470). **2a**: ^1H NMR ($(CD_3)_2CO$) δ 1.15 (d, J_{HH} = 6.9 Hz, 3H, *Me*MeCH), 1.29 (d, J_{HH} = 6.9 Hz, 3H, Me*Me*CH), 1.47 (d, J_{HgH} = 6.3 Hz, 3H, Me), 1.76 (s, 3H, Me of *p*-cymene), 2.89 (psp, 1H, MeMeC*H*), 4.7−4.9 (m, H_g, H_c, H_t overlapped with the corresponding **2a′** resonances), 5.25 (d, J_{AB} = 6.2 Hz, 1H, H_AH_B), 5.46 (d, 1H, H_AH_B), 6.20 (d, $J_{A'B'}$ = 6.5 Hz, 1H, $H_{A'}H_{B'}$), 6.47 (d, 1H, $H_{A'}H_{B'}$), 7.5−8.1 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 37.8 s. **2a′**: ^1H NMR ($(CD_3)_2CO$) δ 0.79 (d, J_{HH} = 6.9 Hz, 3H, *Me*MeCH), 0.86 (d, J_{HH} = 6.9 Hz, 3H, Me*Me*CH), 1.65 (d, 3H, Me J_{HgH} = 6.6), 2.61 (psp, 1H, MeMeC*H*), 4.7−4.9 (m, H_g, H_c, H_t overlapped with the corresponding **2a** resonances), 5.54 (d, J_{AB} = 6.3 Hz, 1H, H_AH_B), 6.1 (m, 1H, $H_{A'}H_{B'}$), 7.3−8.1 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 38.9 s.

3a, **3a′:** first fraction, 95:5 molar ratio, 73% yield; second fraction, 0:100 molar ratio, 24% yield. Anal. Calcd for $C_{38}H_{36}NClF_6RuOPSb$: C, 49.3; H, 3.9; N, 1.5. Found: C, 49.1; H, 4.0; N, 1.5. IR (Nujol, cm^{-1}): ν(CN) 1610 (s), $\nu(SbF_6)$ 285 (m). CD (Me_2CO, [Θ] (λ, nm) maxima, minima and nodes): **3a**:**3a′**, 95:5 molar ratio: +8000 (380), +8000 (400), 0 (420), −3000 (440), 0 (460), +2020 (500); **3a′**: −8200 (380), 0 (400), +7800 (440). **3a**: ^1H NMR ($(CD_3)_2CO$) δ 0.67 (d, J_{HH} = 6.9 Hz, 3H, *Me*MeCH), 1.07 (d, J_{HH} = 6.9 Hz, 3H, Me*Me*CH), 1.31 (s, 3H, Me), 2.59 (psp, 1H, MeMeC*H*), 3.58, 3.78 (2H, AB part of an ABX system, J_{AB} = 18.1 Hz, J_{AX} = 6.9 Hz, J_{BX} = 3.6 Hz, H_c, H_t), 4.56 (d, J_{AB} = 6.6 Hz, 1H, H_AH_B), 4.79 (d, $J_{A'B'}$ = 5.7 Hz, 1H, $H_{A'}H_{B'}$), 5.50 (d, 1H, $H_{A'}H_{B'}$), 5.95 (m, 1H, H_AH_B), 5.95 (m, 2H, H_o, H_N, overlapped with AB system), 7.9−8.3 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 27.5 s. **3a′**: 1H NMR ($(CD_3)_2CO$) δ 0.78 (d, J_{HH} = 6.9 Hz, 3H, *Me*MeCH), 0.84 (d, *J*HH = 6.9 Hz, 3H, Me*Me*CH), 2.36 (s, 3H, Me), 2.81 (psp, 1H, MeMeC*H*), 3.54, 3.67 (2H, AB part of an ABX system, J_{AB} =18.1 Hz, J_{AX} = 4.5 Hz, $J_{BX} \approx$ 0 Hz, H_c, H_t), 5.76 (dd, J_{HcHo} = 6.1 Hz, J_{HnHo} = 4.5 Hz, H_o) 5.82 (d, J_{AB} = 6.0 Hz, 1H, H_AH_B), 6.08 (d, $J_{A'B'}$ = 6.3 Hz, 1H, $H_{A'}H_{B'}$), 6.14 (d, 1H, H_AH_B), 6.19 (d, 1H, J_{HoHn} = 6.0 Hz, H_n) 6.42 (m, 1H, $H_{A'}H_{B'}$), 7.2−8.3 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 37.3 s.

3b, **3b′:** first fraction, 100:0 molar ratio, 60% yield; second fraction, 30:70 molar ratio, 26% yield. Anal. Calcd for $C_{38}H_{36}NClF_4RuOPB$: C, 58.7; H, 4.7; N, 1.8. Found: C, 59.0; H 4.7; N, 1.8. IR (Nujol, cm^{-1}): ν(CN) 1610 (s), $\nu(BF_4)$ 1060 (s), ν(RuCl) 275 (m). CD (Me_2CO, [Θ] (λ, nm) maxima, minima and nodes): **3b**: −5700 (390), 0 (430), +7600 (465). **3b**: ^1H NMR ($(CD_3)_2CO$) δ 0.68 (d, J_{HH} = 6.8 Hz, 3H, *Me*MeCH), 1.08 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH), 1.31 (s, 3H, Me), 2.59 (psp, 1H, MeMeC*H*), 3.58, 3.81 (2H, AB part of an ABX system, J_{AB} = 18.3 Hz, J_{AX} = 6.3 Hz, J_{BX} = 3.2 Hz, H_c, H_t), 4.58 (d, J_{AB} = 6.6 Hz, 1H, H_AH_B), 4.81 (d, $J_{A'B'}$ = 5.9 Hz, 1H, $H_{A'}H_{B'}$), 5.50 (d, 1H, $H_{A'}H_{B'}$), 5.95 (m, 1H, H_AH_B), 5.95 (m, 2H, H_o, H_n, overlapped with AB system), 7.4−8.3 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 26.6 s. **3b′**:

^{1}H NMR ($(CD_3)_2CO$) δ 0.81 (d, J_{HH} = 6.8 Hz, 3H, *Me*MeCH), 0.84 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH), 2.34 (s, 3H, Me), 2.82 (psp, 1H, MeMeC*H*), 3.57, 3.68 (2H, AB part of an ABX system, J_{AB} = 17.8 Hz, J_{AX} = 4.4 Hz, $J_{BX} \approx 0$ Hz, H_c, H_t), 5.77 (dd, J_{HcHo} = 6.1 Hz, J_{HnHo} = 4.5 Hz, H_o), 5.76 (d, J_{AB} = 6.1 Hz, 1H, H_AH_B), 5.93 (d, J_{HoHn} = 6.1 Hz, 1H, H_n), 6.08 (d, $J_{A'B'}$ = 6.0 Hz, 1H, $H_{A'}H_{B'}$), 6.14 (d, 1H, H_AH_B), 6.36 (m, 1H, $H_{A'}H_{B'}$), 7.2−8.3 (m, 14H, Ph). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$): δ 36.3 s.

Preparation of [(η^6-*p*-MeC$_6$H$_4$*i*Pr)OsCl(PN)][SbF$_6$] (4−6). A mixture of [(η^6-*p*-MeC$_6$H$_4$*i*Pr)OsCl}$_2$(μ-Cl)$_2$] (200.0 mg, 0.25 mmol), $NaSbF_6$ (0.5 mmol), and the corresponding phosphinooxazoline ligand (0.50 mmol) was stirred, in methanol (10 mL), for 3 h. During this time the precipitation of a yellow solid was observed for **4a**, **4a′** and **6a**, **6a′**. The yellow solid was filtered off, washed with cold methanol, and air-dried (first fraction). The filtrate (or the original solution for complexes **5**) was vacuum-evaporated to dryness, the resulting solid was extracted with dichloromethane (3 × 5 mL), and the solution was partially concentrated under reduced pressure. Slow addition of diethyl ether gave a yellow solid, which was filtered off, washed with diethyl ether, and air-dried (second fraction for complexes **4** and **6**).

4a:**4a′:** first fraction, 93:7 molar ratio, 34% yield; second fraction, 21:79 molar ratio, 48% yield. Anal. Calcd for $C_{34}H_{38}NClF_6OsOPSb$: C, 42.1; H, 3.95; N, 1.45. Found: C, 41.9; H 4.1; N, 1.6. IR (Nujol, cm^{-1}): ν(CN) 1595 (s), $\nu(SbF_6)$ 292 (m). CD (Me_2CO, [Θ] (λ, nm) maxima, minima and nodes): **4a**:**4a′**, 95:5 molar ratio: +21000 (330), 0 (360), −6000 (380), −1500 (400), −15000 (450); **4a**:**4a′**, 21:79 molar ratio: −13000 (330), 0 (360), +11000 (400), 14000 (430). **4a**: ^{1}H NMR ($(CD_3)_2CO$) δ 0.48 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH), 1.14 (d, J_{HH} = 7.1 Hz, 3H, Me*Me*CH), 1.29 (d, J_{HH} = 7.4 Hz, 3H, *Me*MeCH of *p*-cymene), 1.31 (d, J_{HH} = 7.4 Hz, 3H, Me*Me*CH of *p*-cymene), 2.11 (s, 3H, Me of *p*-cymene), 2.35 (psp, 1H, MeMeC*H*), 2.89 (psp, 1H, MeMeC*H* of *p*-cymene), 4.58 (pt, 1H, H_c), 4.66 (dpt, J_{HcHg} = 8.9 Hz, $J_{HiHg} \approx J_{HtHg}$ = 1.9 Hz, 1 H, H_g), 4.89 (dd, J_{HcHt} = 9.1 Hz, 1H, H_t), 5.12 (d, J_{AB} = 5.9 Hz, 1H, H_AH_B), 5.66 (d, 1H, H_AH_B), 6.49 (d, $J_{A'B'}$ = 6.1 Hz, 1H, $H_{A'}H_{B'}$), 6.52 (d, 1H, $H_{A'}H_{B'}$), 7.3−8.1 (m, 14H, Ph). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$): δ 0.7 s. **4a′**: ^{1}H NMR ($(CD_3)_2CO$) δ 0.87 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH), 0.91 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH of *p*-cymene), 0.96 (d, J_{HH} = 6.9 Hz, 3H, Me*Me*CH of *p*-cymene), 1.16 (d, J_{HH} = 7.1 Hz, 3H, Me*Me*CH), 2.33 (s, 3H, Me of *p*-cymene), 2.58 (psp, 1H, MeMeC*H* of *p*-cymene), 2.68 (psp, 1H, MeMeC*H*), 4.62 (pt, 1H, H_c), 4.78 (d, 1H, J_{HcHg} = 8.5 Hz, 1 H, H_g), 4.97 (d, J_{HcHt} = 9.6 Hz, 1H, H_t), 5.51 (d, J_{AB} = 5.6 Hz, 1H, H_AH_B), 5.94 (d, 1H, H_AH_B), 6.06 (d, 1H, $J_{A'B'}$ = 5.9 Hz, $H_{A'}H_{B'}$), 6.13 (d, 1H, $H_{A'}H_{B'}$), 7.3−8.1 (m, 14H, Ph). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$): δ −3.4 s.

5a, **5a′:** 44:56 molar ratio, 51% yield. Anal. Calcd for $C_{32}H_{34}NClF_6OsOPSb$: C, 40.8 H, 3.4; N, 1.5. Found: C, 41.1; H, 3.4; N, 1.5. IR (Nujol, cm^{-1}): ν(CN) 1602 (s), $\nu(SbF_6)$ 295 (m). CD (Me_2CO, [Θ] (λ, nm) maxima, minima and nodes): **5a**:**5a′**, 44:56 molar ratio: −6000 (335), 0 (360), +6000 (420). **5a**: ^{1}H NMR ($(CD_3)_2CO$) δ 1.25 (d, J_{HH} = 6.9 Hz, 3H, *Me*MeCH), 1.29 (d, J_{HH} = 6.9 Hz, 3H, Me*Me*CH), 1.41 (d, J_{HgH} = 6.3 Hz, 3H, Me), 1.97 (s, 3H, Me of *p*-cymene), 2.84 (psp, 1H, MeMeC*H*), 4.6−4.8 (m, H_g, H_c, H_t, overlapped with the corresponding **5a′** resonances), 5.32, 5.64 (m, system AB overlapped with the corresponding **5a′** resonances), 6.43 (d, $J_{A'B'}$ = 5.7 Hz, 1H, $H_{A'}H_{B'}$), 6.50 (d, 1H, $H_{A'}H_{B'}$) 7.3−8.2 (m, 14H, Ph). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$): δ −1.32 s. **5a′**: ^{1}H NMR ($(CD_3)_2CO$) δ 0.82 (d, J_{HH} = 6.9 Hz, 3H, *Me*MeCH), 0.92 (d, J_{HH} = 6.9 Hz, 3H, Me*Me*CH), 1.55 (d, J_{HgH} = 6.4, 3H, Me), 2.34 (s, 3H, Me of *p*-cymene), 2.54 (psp, 1H, MeMeC*H*), 4.6−4.8 (m, 3H, H_g, H_c, H_t, overlapped with the corresponding **5a** resonances); 5.64 m, 6.00 (bd, J_{AB} = 5.8 Hz), 6.08 m, (4H, two systems AB overlapped with the corresponding **5a** resonances), 7.3−8.1 (m, 14H, Ph). ^{31}P{1H} NMR ($(CD_3)_2CO$): δ −3.63 s.

6a, **6a′:** first fraction, 94:6 molar ratio, 30% yield; second fraction, 0:100, molar ratio, 39% yield. Anal. Calcd for $C_{38}H_{36}NClF_6OsOPSb$: C, 44.9; H, 3.6; N, 1.4. Found: C, 44.9; H, 3.7; N, 1.7. IR (Nujol, cm^{-1}): ν(CN) 1615 (s), $\nu(SbF_6)$ 295 (m). CD (Me_2CO, [Θ] (λ, nm) maxima, minima and nodes): **6a**:**6a′**, 94:6 molar ratio: +12000 (330), +2500 (370), +7000 (410); **6a′**: −19000 (335), 0 (360), +20000 (435). **6a**: ^{1}H NMR ($(CD_3)_2CO$) δ 0.82 (d, J_{HH} = 7.6 Hz, 3H, *Me*MeCH), 1.18 (d, J_{HH} = 7.1 Hz, 3H, Me*Me*CH), 1.50 (s, 3H, Me), 2.60 (psp, 1H, MeMeC*H*), 3.60, 3.76 (2H, AB part of an ABX system, J_{AB} =18.2 Hz, J_{AX} =7.45 Hz, J_{BX} = 3.7 Hz, H_c, H_t), 4.80 (d, J_{AB} = 6.6 Hz, 1H, H_AH_B), 5.02 (d, $J_{A'B'}$ = 4.4 Hz, 1H, $H_{A'}H_{B'}$), 5.70 (d, 1H, $H_{A'}H_{B'}$), 5.96 (d, 1H, H_AH_B), 6.00 (m, 1H, H_o, overlapped with AB system), 6.08 (d, J_{HoHn} = 8.2 Hz, 1H, H_n), 7.4−8.3 (m, 14H, Ph). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$): δ −12.6 s. **6a′**: ^{1}H NMR ($(CD_3)_2CO$) δ 0.81 (d, J_{HH} = 7.1 Hz, 3H, *Me*MeCH), 0.87 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH), 2.51 (s, 3H, Me), 2.76 (psp, 1H, MeMeC*H*), 3.54, 3.71 (2H, AB part of an ABX system, J_{AB} = 18.1 Hz, J_{AX} = 5.1 Hz, $J_{BX} \approx 0$ Hz, H_c, H_t), 5.77 (pt, H_o), 5.90 (d, J_{AB} = 6.0 Hz, 1H, H_AH_B), 6.10 (d, $J_{A'B'}$ = 6.1 Hz, 1H, $H_{A'}H_{B'}$), 6.15 (d, 1H, $H_{A'}H_{B'}$), 6.27 (d, 1H, J_{HoHn} = 5.9 Hz, H_n), 6.37 (d, 1H, H_AH_B), 7.2−8.1 (m, 14H, Ph). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$): δ −5.3 s.

Preparation of [(η^6-*p*-MeC$_6$H$_4$*i*Pr)Ru(PN)(H$_2$O)](A)$_2$ (7−9). To a diastereomeric mixture of the chloro compounds **1**−**3** (0.20 mmol; **1a**:**1a′**, 95:5 or 20:80; **1b**:**1b′**, 60:40; **1c**:**1c′**, 73:27; **2a**:**2a′**, 67:33; **3a**:**3a′**, 95:5 or 0:100 molar ratio) in 25 mL of dichloromethane was added 70.2 mg (0.20 mmol) of the appropriate AgA salt (A = SbF_6, BF_4, or CF_3SO_3) in 2 mL of acetone. The suspension was stirred for 30 min. The AgCl formed was separated by filtration, and the filtrate was partially concentrated under reduced pressure. Slow addition of diethyl ether gave an orange solid, which was filtered off, washed with diethyl ether, and air-dried.

7a, **7a′:** 80:20 molar ratio, 84% yield. Anal. Calcd for $C_{34}H_{44}NF_{12}RuO_4PSb_2$: C, 36.0; H, 3.9; N, 1.2. Found: C, 36.1; H, 3.7; N, 1.2. IR (Nujol, cm^{-1}): $\nu(H_2O)$ 3510 (m), 1620 (m), ν(CN) 1585 (s), $\nu(SbF_6)$ 285 (m). CD (Me_2CO, [Θ] (λ, nm) maxima, minima and nodes): **7a**:**7a′**, 80:20 molar ratio: +7900 (365), +7900 (400), 0 (430), −1000 (445), 0 (460), +900 (500). **7a**: ^{1}H NMR ($(CD_3)_2CO$) δ 0.29 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH), 1.16 (d, J_{HH} = 7.1 Hz, 3H, Me*Me*CH), 1.40 (d, J_{HH} = 7.0 Hz, 3H, *Me*MeCH of *p*-cymene), 1.44 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH of *p*-cymene), 2.07 (s, 3H, Me of *p*-cymene), 2.34 (psp, 1H, MeMeC*H*), 3.15 (psp, 1H, MeMeC*H* of *p*-cymene), 4.78 (pt, 1H, H_c), 4.95 (dd, J_{HcHt} = 9.2 Hz, J_{HgHt} = 2.2 Hz, 1 H, H_t), 5.01 (dpt, J_{HcHg} = 8.9 Hz, $J_{HtHg} \approx J_{HiHg}$ = 2.3 Hz, 1H, H_g), 5.31 (d, J_{AB} = 6.2 Hz, 1H, H_AH_B), 6.27 (d, 1H, H_AH_B), 6.44 (d, $J_{A'B'}$ = 6.3 Hz, 1H, $H_{A'}H_{B'}$), 6.49 (bs, 2H, H_2O), 6.84 (d, 1H, $H_{A'}H_{B'}$), 7.4−8.1 (m, 14H, Ph). ^{1}H NMR (CD_2Cl_2) δ 0.15 (d, J_{HH} = 6.5 Hz, 3H, *Me*MeCH), 1.11 (d, J_{HH} = 6.7 Hz, 3H, Me*Me*CH), 1.38 (d, J_{HH} = 6.6 Hz, 6H, MeMeCH of *p*-cymene), 1.86 (s, 3H, Me of *p*-cymene), 1.95 (m, 1H, MeMeC*H*), 2.95 (psp, 1H, MeMeC*H* of *p*-cymene), 4.30 (bs, 2H, H_2O), 4.50−4.8 (m, 3H, H_c, H_t, H_g), 5.13 (d, J_{AB} = 6.0 Hz, 1H, H_AH_B), 5.71 (d, 1H, H_AH_B), 6.17 (d, $J_{A'B'}$ = 6.0 Hz, 1H, $H_{A'}H_{B'}$), 6.23 (d, 1H, $H_{A'}H_{B'}$), 7.1−8.1 (m, 14H, Ph). ^{31}P{^{1}H} NMR ($(CD_3)_2CO$): δ 43.1 s. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 42.3 s. **7a′**: ^{1}H NMR ($(CD_3)_2CO$) δ 0.87 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH of *p*-cymene), 0.91 (d, J_{HH} = 7.3 Hz, 3H, Me*Me*CH of *p*-cymene), 1.07 (d, J_{HH} = 6.8 Hz, 3H, *Me*MeCH), 1.25 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH), 2.15 (s, 3H, Me of *p*-cymene), 2.51 (psp, 1H, MeMeC*H*), 2.76 (psp, 1H, MeMeC*H* of *p*-cymene), 4.74 (pt, 1H, H_c), 5.02 (m, 1H, H_g), 5.12 (dd, J_{HcHt} = 9.2 Hz, J_{HgHt} = 2.3 Hz, 1H, H_t), 6.1−6.6 (m, 4H, systems AB overlapped with the corresponding **7a** resonances), 7.4−81 (m, 14H, Ph). ^{1}H NMR (CD_2Cl_2): δ 0.71 (d, J_{HH} = 6.5 Hz, 3H, *Me*MeCH), 1.0−1.3 (9H, overlapped with **7a** resonance, *MeMe*CH), 1.96 (s, 3H, Me of *p*-cymene), 2.57 (m, 1H, MeMeC*H*), 2.72 (psp, 1H, MeMeC*H*), 3.78 (bs, 2H, H_2O), 4.50−4.80 (3H,

overlapped with the corresponding **7a** resonances, H_c, H_t, H_g,), 4.79 (d, J_{AB} = 6.5 Hz, 1H, H_AH_B), 5.76 (d, 1H, H_AH_B), 5.90 (d, $J_{A'B'}$ = 6.0 Hz, 1H, $H_{A'}H_{B'}$), 6.12 (d, 1H, $H_{A'}H_{B'}$), 7.1−8.1 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 36.5 s. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 40.8 s.

7b, **7b′:** 81:19 molar ratio, 98% yield. Anal. Calcd for $C_{34}H_{40}NB_2F_8O_2PRu$: C, 51.1; H, 4.9; N, 1.75. Found: C, 51.0; H, 5.0; N, 1.8. IR (Nujol, cm^{-1}): $\nu(H_2O)$ 3550 (m), 1620 (m), ν(CN) 1590 (s), $\nu(BF_4)$ 1100 (s). CD (Me_2CO, [Θ] (λ, nm) maxima, minima and nodes): **7b**:**7b′**, 81:19 molar ratio: −1000 (315), 0 (325), +19500 (370), +1000 (450), +2000 (480). **7b**: ^1H NMR ($(CD_3)_2CO$) δ 0.19 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH), 1.12 (d, J_{HH} = 7.1 Hz, 3H, Me*Me*CH), 1.37 (d, J_{HH} = 7.1 Hz, 3H, *Me*MeCH of *p*-cymene), 1.40 (d, J_{HH} = 7.1 Hz, 3H, Me*Me*CH of *p*-cymene), 1.95 (s, 3H, Me of *p*-cymene), 2.28 (psp, 1H, MeMeC*H*), 2.82 (psp, 1H, MeMeC*H* of *p*-cymene), 4.7−5.0 (m, 3H, H_c, H_t, H_g), 5.19 (d, J_{AB} = 6.6 Hz, 1H, H_AH_B), 6.01 (s, 2H, H_2O), 6.24 (d, 1H, H_AH_B), 6.46 (d, $J_{A'B'}$ = 6.6 Hz, 1H, $H_{A'}H_{B'}$), 6.73 (d, 1H, $H_{A'}H_{B'}$), 7.2−8.0 (m, 14H, Ph). ^1H NMR (CD_2Cl_2): δ 0.05 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH), 1.04 (d, J_{HH} = 7.1 Hz, 3H, Me*Me*CH), 1.28 (d, J_{HH} = 6.9 Hz, 3H, *Me*MeCH of *p*-cymene), 1.30 (d, J_{HH} = 7.0 Hz, 3H, Me*Me*CH of *p*-cymene), 1.82 (s, 3H, Me of *p*-cymene), 1.91 (psp, 1H, MeMeC*H*), 2.96 (psp, 1H, MeMeC*H* of *p*-cymene); 4.53 (d, J_{HH} = 9.2, 1H), 4.60 (d, J_{HH} = 9.0, 1H), 4.77 (m, 1H) (H_c, H_t, H_g); 5.16 (d, J_{AB} = 6.6 Hz, 1H, H_AH_B), 5.76 (d, 1H, H_AH_B), 6.16 (d, $J_{A'B'}$ = 5.9 Hz, 1H, $H_{A'}H_{B'}$), 6.34 (d, 1H, $H_{A'}H_{B'}$), 7.0−8.1 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 43.5 s. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 42.4 s. **7b′**: ^1H NMR (CD_2Cl_2) δ 0.62 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH), 1.05 (d, J_{HH} = 6.8, 3H), 1.08 (d, J_{HH} = 6.8, 3H), 1.12 (d, J_{HH} = 6.8, 3H) (*MeMe*CH); 1.88 (s, 3H, Me of *p*-cymene), 2.53 (m, 1H, MeMeC*H*), 2.68 (psp, 1H, MeMeC*H*) 4.50−4.80 (3H, overlapped with the corresponding **7b** resonances, H_c, H_t, H_g,), 4.72 (bd, 1H, H_AH_B), 5.25 (bd, 1H, H_AH_B), 5.80 (d, $J_{A'B'}$ = 6.1 Hz, 1H, $H_{A'}H_{B'}$), 6.02 (d, 1H, $H_{A'}H_{B'}$), 7.0−8.1 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 38.8 s. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 39.5 s.

7c, 7c′: 83:17 molar ratio, 87% yield. Anal. Calcd for $C_{36}H_{40}NF_6O_8PRuS_2$: C, 45.5; H, 4.25; N, 1.5. Found: C, 45.5; H, 4.4; N, 1.5. IR (Nujol, cm^{-1}): $\nu(H_2O)$ 3600 (m), ν(CN) 1596 (s). CD (Me_2CO, [Θ] (λ, nm) maxima, minima and nodes): **7c**:**7c′**, 83:17 molar ratio: −1200 (310), 0 (320), +27500 (365), 0 (420), −3000 (440). **7c**: ^1H NMR ($(CD_3)_2CO$) δ 0.24 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH), 1.16 (d, J_{HH} = 7.1 Hz, 3H, Me*Me*CH), 1.41 (d, J_{HH} = 7.1 Hz, 3H, *Me*MeCH of *p*-cymene), 1.44 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH of *p*-cymene), 2.00 (s, 3H, Me of *p*-cymene), 2.36 (psp, 1H, MeMeC*H*), 3.20 (psp, 1H, MeMeC*H* of *p*-cymene), 4.88 (m, 1H, H_c), 4.88 (m, 1H, H_t), 4.95 (dpt, J_{HcHg} = 8.6 Hz, $J_{HtHg} \approx J_{HiHg}$ = 2.3 Hz, 1H, H_g), 5.12 (d, J_{AB} = 6.6 Hz, 1H, H_AH_B), 6.29 (s, 2H, H_2O), 6.31 (d, 1H, H_AH_B), 6.58 (d, $J_{A'B'}$ = 6.6 Hz, 1H, $H_{A'}H_{B'}$), 6.79 (d, 1H, $H_{A'}H_{B'}$), 7.3−8.1 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 43.8 s. **7c′**: $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$) δ 39.2 s.

8a, **8a′:** 50:50 molar ratio, 76% yield. Anal. Calcd for $C_{32}H_{40}NF_{12}RuO_4PSb_2$: C, 35.0; H, 3.4; N, 1.2. Found: C, 34.7; H 3.6; N, 1.3. IR (Nujol, cm^{-1}): $\nu(H_2O)$ 3510 (m), 1620 (m), ν(CN) 1590 (s), $\nu(SbF_6)$ 290 (m). **8a**: ^1H NMR ($(CD_3)_2CO$) δ 1.01 (d, J_{HgH} = 6.9 Hz, 3H, Me), 1.34 (d, J_{HH} = 6.9 Hz, 3H, *Me*MeCH), 1.37 (d, J_{HH} = 6.9 Hz, 3H, Me*Me*CH), 2.20 (s, 3H, Me of *p*-cymene), 2.79 (psp, 1H, MeMeC*H*), 4.66 (dd, J_{HcHt} = 8.9 Hz, J_{HgHt} = 3.7 Hz 1H, H_t), 4.85 (t, J_{HgHc} = 8.9 Hz, overlapped with the corresponding **8a′** resonance, 1H, H_c), 5.15 (m, 1H, H_g), 5.5−6.9 (m, 4H, systems AB overlapped with the corresponding **8a′** resonances), 6.46 (bs, 2H, H_2O), 7.5−8.1 (m, 14H, Ph). ^1H NMR (CD_2Cl_2): δ 1.17 (d, J_{HgH} = 6.8 Hz, 3H, Me), 1.34 (d, J_{HH} = 6.4 Hz, 3H, *Me*MeCH), 1.36 (d, J_{HH} = 6.4 Hz, 3H, Me*Me*CH), 1.85 (s, 3H, Me of *p*-cymene), 2.55 (psp, 1H, MeMeC*H*), 4.15 (bs, 2H, H_2O), 4.45 (dd, J_{HcHt} = 8.4 Hz, J_{HgHt} = 2.9 Hz 1H, H_t), 4.71 (t, J_{HgHc} = 8.4 Hz, 1H, H_c), 5.22 (d, J_{AB} = 6.1 Hz, 1H, H_AH_B), 5.61 (d, $J_A'B'$ = 6.5 Hz, 1H, $H_A'H_B'$), 5.93 (m, 1H, H_g), 6.16 (d, 1H, H_AH_B), 6.38 (d, 1H, $H_A'H_B'$), 6.46 (bs, 2H, H_2O), 7.1−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 42.8 s. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 41.7 s. **8a′**: ^1H NMR ($(CD_3)_2CO$) δ 1.10 (d, J_{HH} = 7.0 Hz, 3H, *Me*MeCH), 1.11 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH), 1.77 (d, J_{HgH} = 6.9 Hz, 3H, Me), 1.96 (s, 3H, Me of *p*-cymene), 2.65 (psp, 1H, MeMeC*H*), 4.72 (dd, J_{HcHt} = 8.9 Hz, J_{HgHt} = 4.6 Hz 1H, H_t), 4.91 (pt, J_{HgHc} = 8.9 Hz, overlapped with the corresponding **8a** resonance, 1H, H_c), 5.22 (m, 1H, H_g), 5.5−6.9 (m, 4H, systems AB overlapped with the corresponding **8a** resonances), 6.28 (bs, 2H, H_2O), 7.3−8.3 (m, 14H, Ph). ^1H NMR (CD_2Cl_2) δ 1.08 (d, J_{HH} = 6.8 Hz, 3H, *Me*MeCH), 1.21 (d, J_{HH} = 7.0 Hz, 3H, Me*Me*CH), 1.63 (d, J_{HgH} = 6.4 Hz, 3H, Me), 2.00 (s, 3H, Me of *p*-cymene), 2.64 (psp, 1H, MeMeC*H*), 3.98 (bs, 2H, H_2O), 4.58 (dd, J_{HcHt} = 9.3 Hz, J_{HgHt} = 4.1 Hz 1H, H_t), 4.7−4.8 (m, overlapped with the corresponding **8a** resonances, 2H, H_c, H_g), 5.5−6.0 (m, 4H, systems AB overlapped with the corresponding **8a** resonances), 7.3−8.3 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 39.8 s. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 40.2 s.

9a, **9a′:** 35:65 molar ratio, 85% yield. Anal. Calcd for $C_{38}H_{42}NF_{12}RuO_4PSb_2$: C, 38,7; H, 3.6; N, 1.2. Found: C, 38.6; H, 3.6; N, 1.2. IR (Nujol, cm^{-1}): $\nu(H_2O)$ 3510 (m), 1615 (m), ν(CN) 1590 (s), $\nu(SbF_6)$ 285 (m). CD (Me_2CO, [Θ] (λ, nm) maxima, minima and nodes): **9a**:**9a′**, 35:65 molar ratio: +8000 (370), +7900 (420). **9a**: ^1H NMR ($(CD_3)_2CO$) δ 0.95 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH), 1.11 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH), 2.32 (s, 3H, Me), 2.67 (psp, 1H, MeMeC*H*), 3.67 (m, 2H, H_c, H_t), 5.7−6.8 (m, 4H, systems AB overlapped with the corresponding **9a′** resonances), 5.96 (m, 2H, H_o, H_n, overlapped with AB system), 6.21 (bs, 2H, H_2O), 7.1−8.3 (m, 14H, Ph). ^1H NMR (CD_2Cl_2): δ 0.98 (d, J_{HH} = 7.1 Hz, 3H, *Me*MeCH), 1.09 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH), 2.10 (s, 3H, Me), 2.66 (psp, 1H, MeMeC*H*), 4.26 (bs, 2H, H_2O), 5.0−6.4 (m, 4H, systems AB overlapped with the corresponding **9a** resonances). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 35.5 s. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 34.9 s. **9a′**: ^1H NMR ($(CD_3)_2CO$) δ 1.31 (d, J_{HH} = 6.8 Hz, 3H, *Me*MeCH), 1.36 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH), 1.86 (s, 3H, Me), 3.20 (psp, 1H, MeMeC*H*), 3.64 (m, 2H, H_c, H_t), 5.7−6.8 (m, 4H, systems AB overlapped with the corresponding **9a** resonances), 6.08 (m, 2H, H_o, H_n, overlapped with AB system), 6.73 (bs, 2H, H_2O), 7.1−8.3 (m, 14H, Ph). ^1H NMR (CD_2Cl_2): δ 1.24 (d, J_{HH} = 6.7 Hz, 3H, *Me*MeCH), 1.25 (d, J_{HH} = 6.7 Hz, 3H, Me*Me*CH), 1.69 (s, 3H, Me), 2.88 (psp, 1H, MeMeC*H*), 3.54, 3.68, (2H, AB part of an ABX system, J_{AB} =18.2 Hz, J_{AX} = 5.9 Hz, $J_{BX} \approx$ 0 Hz, H_c, H_t), 4.44 (bs, 2H, H_2O), 5.08 (d, J_{AB} = 6.3 Hz, 1H, H_{AB}), 5.40 (d, $J_A'B'$ = 6.2 Hz, 1H, H_{AB}), 5.74 (d, 1H, H_{AB}), 6.04 (d, 1H, $H_A'B'$), 7.1−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 37.5 s. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 36.1 s.

Preparation of [(η^6-*p*-MeC_6H_4*i*Pr)Os(PN)(H_2O)](A)$_2$ (10−12). A mixture of [{(η^6-*p*-MeC_6H_4*i*Pr)OsCl}$_2$(μ-Cl)$_2$] (150.0 mg, 0.19 mmol) and the appropriate AgA salt (A = SbF_6, BF_4, or CF_3SO_3) (0.8 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 (0.39 mmol) in 5 mL of acetone. After stirring for 20 min, the solution was vacuum evaporated to dryness. The addition of *n*-hexane gave a yellow solid, which was filtered off, washed with *n*-hexane, and air-dried.

10a, **10a′:** 80:20 molar ratio, 81% yield. Anal. Calcd for $C_{34}H_{40}NF_{12}OsO_2PSb_2$: C, 34.4; H, 3.4; N, 1.2. Found: C, 34.5; H, 3.7; N, 1.2. IR (Nujol, cm^{-1}): $\nu(H_2O)$ 3610 (m) 3400 (m), 1625 (m), ν(CN) 1590 (s), $\nu(SbF_6)$ 290 (m). CD (Me_2CO, [Θ] (λ, nm) maxima, minima and nodes): **10a**:**10a′**, 80:20 molar ratio: +12500 (335), 0 (390), −6000 (440). **10a**: ^1H NMR ($(CD_3)_2CO$) δ 0.28 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH), 1.16 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH), 1.40 (d, J_{HH} = 6.8 Hz, 6H, *MeMe*CH of *p*-cymene), 2.19 (s, 3H, Me of *p*-cymene), 2.35 (psp, 1H, MeMeC*H*), 3.06 (m, 1H, MeMeC*H* of *p*-cymene), 4.80 (pt, 1H, H_c), 4.92 (d, J_{HcHg} = 8.8 Hz, 1H, H_g), 5.00 (dd, J_{HcHt} = 9.4 Hz, J_{HgHt} = 2.3 Hz, 1H, H_t),

5.50 (d, J_{AB} = 6.3 Hz, 1H, H_AH_B), 6.65 (d, 1H, H_AH_B), 6.76 (d, $J_{A'B'}$ = 5.6 Hz, 1H, $H_{A'}H_{B'}$), 6.96 (d, 1H, $H_{A'}H_{B'}$), 7.2−8.1 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 8.1 s. **10a′**: ^1H NMR ($(CD_3)_2CO$) δ 0.89 (d, J_{HH} = 7.8 Hz, 3H, *Me*MeCH), 0.91 (d, J_{HH} = 6.8 Hz, 3H, *Me*MeCH of *p*-cymene), 1.12 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH of *p*-cymene), 1.22 (d, J_{HH} = 7.1 Hz, 3H, Me*Me*CH), 2.38 (s, 3H, Me of *p*-cymene), 5.14 (dd, J_{HcHt} = 9.9 Hz, J_{HgHt} = 2.6, 1H, H_t), 6.19 (d, J_{AB} = 5.6 Hz, 1H, H_AH_B), 6.33 (d, $J_{A'B'}$ = 6.2 Hz, 1H, $H_{A'}H_{B'}$), 6.40 (d, 1H, $H_{A'}H_{B'}$), 6.46 (d, 1H, H_AH_B), 7.3−8.4 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 0.1s.

10b, **10b′:** 80:20 molar ratio, 82% yield. Anal. Calcd for $C_{34}H_{40}NB_2F_8O_2OsP$: C, 45.9; H, 4.5; N, 1.6. Found: C, 45.7; H, 5.4; N, 1.7. IR (Nujol, cm^{-1}): $\nu(H_2O)$ 3600 (m), 1625 (m), ν(CN) 1580 (s), $\nu(BF_4)$ 1100 (s), 540 (m). CD (Me_2CO, [Θ] (λ, nm) maxima, minima and nodes): **10b**:**10b′**, 80:20 molar ratio: +18000 (340), 0 (390), −7000 (440). **10b**: ^1H NMR ($(CD_3)_2CO$) δ 0.23 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH), 1.13 (d, J_{HH} = 7.1 Hz, 3H, Me*Me*CH), 1.36 (d, J_{HH} = 6.8 Hz, 6H, *MeMe*CH of *p*-cymene), 2.15 (s, 3H, Me of *p*-cymene), 2.30 (psp, 1H, MeMeC*H*), 3.04 (m, 1H, MeMeC*H* of *p*-cymene), 4.76 (pt, 1H, H_c), 4.86 (d, J_{HcHg} = 8.8 Hz, 1H, H_g), 4.94 (d, J_{HcHt} = 10.1 Hz, 1H, H_t), 5.44 (d, J_{AB} = 6.2 Hz, 1H, H_AH_B), 6.67 (d, 1H, H_AH_B), 6.74 (d, $J_{A'B'}$ = 6.0 Hz, 1H, $H_{A'}H_{B'}$), 6.89 (d, 1H, $H_{A'}H_{B'}$), 7.2−8.3 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 8.2 s. **10b′**: ^1H NMR ($(CD_3)_2CO$) δ 0.88 (d, J_{HH} = 6.8 Hz, 3H, *Me*MeCH), 0.97 (d, J_{HH} = 7.1 Hz, 3H, *Me*MeCH), 1.05 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH), 1.19 (d, J_{HH} = 6.6 Hz, 3H, Me*Me*CH), 2.31 (s, 3H, Me of *p*-cymene). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 2.3s.

10c, **10c′:** 80:20 molar ratio, 77% yield. Anal. Calcd for $C_{36}H_{40}NF_6OsO_8PS_2$: C, 41.5; H, 4.0; N, 1.4. Found: C, 43.3; H, 4.2; N, 1.1.[28] IR (Nujol, cm^{-1}): $\nu(H_2O)$ 3610 (m), 1625 (m), ν(CN) 1590 (s). CD (Me_2CO, [Θ] (λ, nm) maxima, minima and nodes): **10c**:**10c′**, 80:20 molar ratio: +17000 (335), 0 (380), −10000 (430). **10c**: ^1H NMR ($(CD_3)_2CO$) δ 0.25 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH), 1.16 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH), 1.38 (d, J_{HH} = 6.8 Hz, 6H, *MeMe*CH of *p*-cymene), 2.17 (s, 3H, Me of *p*-cymene), 2.35 (psp, 1H, MeMeC*H*), 3.09 (m, 1H, MeMeC*H* of *p*-cymene), 4.82 (m, 2H, H_c, H_g), 4.93 (d, J = 6.1 Hz, H_t), 5.33 (d, J_{AB} = 6.1 Hz, 1H, H_AH_B), 6.76 (d, 1H, H_AH_B), 6.78 (d, $J_{A'B'}$ = 5.6 Hz, 1H, $H_{A'}H_{B'}$), 6.89 (d, 1H, $H_{A'}H_{B'}$), 7.2−8.2 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 8.3 s. **10c′**: ^1H NMR ($(CD_3)_2CO$) δ 0.86 (d, J_{HH} = 7.1 Hz, 3H, *Me*MeCH), 0.91 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH), 1.01 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH), 1.21 (d, J_{HH} = 7.1 Hz, 3H, Me*Me*CH), 2.33 (s, 3H, Me of *p*-cymene), 6.00 (d, J = 6.1 Hz, 1H,), 6.26 (d, J = 5.4 Hz, 1H), 6.30 (d, J = 5.6, 1H), 6.55 (d, J = 5.9 Hz, 1H). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 2.4s.

11a, 11a′: 53:47 molar ratio, 84% yield. Anal. Calcd for $C_{32}H_{36}NF_{12}OsO_2PSb_2$: C, 33.2; H, 3.1; N, 1.2. Found: C, 33.2; H 3.1; N, 1.2. IR (Nujol, cm^{-1}): $\nu(H_2O)$ 3600 (m), 3420 (m), 1625 (m), ν(CN) 1590 (s), $\nu(SbF_6)$ 285 (m). ^1H NMR ($(CD_3)_2CO$): δ 1.01 (d, J_{HH} = 6.9 Hz, 3H), 1.21 (d, J_{HH} = 6.8 Hz, 3H), 1.35 (m, 9H), 1.64 (d, J_{HH} = 6.5 Hz, 3H) (Me, *MeMe*CH of *p*-cymene), 2.15 (s, 3H, Me of *p*-cymene of major diastereomer), 2.45 (s, 3H, Me of *p*-cymene of minor diastereomer), 2.80 (psp, 1H, MeMeC*H*), 3.05 (m, 1H, MeMeC*H*), 4.64 (dd, J_{HcHt} = 9.0 Hz, J_{HgHt} = 5.8 Hz, 1H, H_t), 4.70 (dd, J_{HcHt} = 9.0 Hz, J_{HgHt} = 3.3 Hz, 1H, H_t), 4.81 (pt, J_{HgHc} = 8.7, 1H, H_c), 4.97 (pt, J_{HgHc} = 9.1, 1H, H_c), 5.10 (m, 1H, H_g), 5.24 (m, 1H, H_g), 5.62 (d, J_{AB} = 5.9 Hz, 1H), 5.77 (d, J_{AB} = 5.0 Hz, 1H), 6.18 (d, J_{AB} = 5.7 Hz, 1H), 6.51 (d, J_{AB} = 6.6 Hz, 1H), 6.58 (d, J_{AB} = 6.1 Hz, 1H), 6.65 (d, J_{AB} = 6.9 Hz, 1H), 6.69 (d, J_{AB} = 6.9 Hz, 1H), 7.06 (d, J_{AB} = 5.6 Hz, 1H) (H_AH_B), 7.2−8.5 (Ph). $^{31}P\{^1H\}$ NMR ($CD_3)_2CO$): δ 7.8 s (major diastereomer), 3.3 s (minor diastereomer).

(28) Variable amounts of the acetone solvate [(η^6-*p*-MeC_6H_4*i*Pr)Os(PN*i*Pr)($(CH_3)_2CO$)]($CF_3SO_3)_2$, detected by NMR spectroscopy, account for the value obtained in the carbon microanalysis (calc for [(η^6-*p*-MeC_6H_4*i*Pr)Os(PN*i*Pr)($(CH_3)_2CO$)]($CF_3SO_3)_2$: C, 44.4; H, 4.2; N, 1.3).

12a, **12a′:** 54:46 molar ratio, 73% yield. Anal. Calcd for $C_{38}H_{38}NF_{12}OsO_2PSb_2$: C, 37,0; H, 3.1; N, 1.1. Found: C, 36.7; H, 3.1; N, 1.1. IR (Nujol, cm^{-1}): $\nu(H_2O)$ 3300−3700 (m), 1620 (m), ν(CN) 1610 (s), $\nu(SbF_6)$ 285 (m). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 4.4 s (major diastereomer), 0.7 s (minor diastereomer).

Preparation of [(η^6-*p*-MeC_6H_4*i*Pr)Ru(PN*i*Pr)($OPOF_2$)][PF_6] (13d, 13d′). To a 78:22 diastereomeric mixture of the chloro compounds **1d**:**1d′** (157.7 mg, 0.20 mmol) in 25 mL of dichloromethane was added 70.2 mg (0.20 mmol) of $AgPF_6$ in 2 mL of acetone. The suspension was stirred for 30 min. The AgCl formed was separated by filtration, and the filtrate was partially concentrated under reduced pressure. Slow addition of diethyl ether gave an orange solid, which was filtered off, washed with diethyl ether, and air-dried.

13d, **13d′:** 65:35 molar ratio, 90% yield. Anal. Calcd for $C_{34}H_{38}NF_8O_3P_3Ru$: C, 47.8; H, 4.4; N, 1.6. Found: C, 47.6; H, 4.4; N, 1.6. IR (Nujol, cm^{-1}): ν(CN) 1591 (s). **13d**: ^1H NMR ($(CD_3)_2CO$) δ 0.28 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH), 1.13 (d, J_{HH} = 7.0 Hz, 3H, Me*Me*CH), 1.32 (d, J_{HH} = 6.8 Hz, 3H, *Me*MeCH of *p*-cymene), 1.40 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH of *p*-cymene), 1.89 (s, 3H, Me of *p*-cymene), 2.20 (psp, 1H, MeMeC*H*), 3.08 (psp, 1H, MeMeC*H* of *p*-cymene), 4.72 (pt, 1H, $J_{HtHc} \approx J_{HgHc}$ = 9.4 Hz, H_c), 4.88 (m, 2H, H_t, H_g), 5.41 (d, J_{AB} = 6.3 Hz, 1H, H_AH_B), 6.15 (d, 1H, H_AH_B), 6.20 (d, $J_{A'B'}$ = 6.6 Hz, 1H, $H_{A'}H_{B'}$), 6.60 (d, 1H, $H_{A'}H_{B'}$), 7.2−8.1 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 41.4 s, −11.6 (t, J_{FP} = 957.3 Hz). **13d′**: ^1H NMR ($(CD_3)_2CO$) δ 0.82 (d, J_{HH} = 6.7 Hz, 3H, *Me*MeCH of *p*-cymene), 1.00 (d, J_{HH} = 6.9 Hz, 6H, Me*Me*CH of *p*-cymene), 1.22 (d, J_{HH} = 7.1 Hz, 3H, Me*Me*CH), 2.10 (s, 3H, Me of *p*-cymene), 2.85 (psp, 1H, MeMeC*H*), 4.60 (pt, 1H, $J_{HtHc} \approx J_{HgHc}$ = 9.1 Hz, H_c), 4.85 (m, 1H, H_g), 5.02 (bd, J_{HcHt} = 9.3 Hz, 1H, H_t); 5.79 (d, J_{AB} = 6.7 Hz, 1H, H_AH_B), 5.86 (m, 1H, H_AH_B), 6.20 (1H, overlapped with the corresponding **13d** resonances, H_AH_B), 6.42 (d, J_{AB} = 6.0 Hz, 1H, H_AH_B), 7.2−8.1 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 38.7 s, −10.7 (t, J_{FP} = 953.3 Hz).

Preparation of [(η^6-*p*-MeC_6H_4*i*Pr)Os(PN*i*Pr)($OPOF_2$)][PF_6] (14d, 14d′). A mixture of [{(η^6-*p*-MeC_6H_4*i*Pr)$OsCl\}_2(\mu$-$Cl)_2$] (150.0 mg, 0.19 mmol) and $AgPF_6$ (211.0 mg, 0.83 mmol) in acetone (25 mL) was stirred for 15 min. The AgCl formed was separated by filtration. To the resulting solution was added PN*i*Pr (148.0 mg, 0.39 mmol) in 5 mL of acetone. After stirring for 20 min, the solution was vacuum evaporated to dryness. The addition of *n*-hexane gave a yellow solid, which was filtered off, washed with *n*-hexane, and air-dried.

14d, **14d′:** 56:44 molar ratio, 90% yield. Anal. Calcd for $C_{34}H_{38}NF_8O_3OsP_3$: C, 43.3; H, 4.1; N, 1.5. Found: C, 43.2; H, 4.3; N, 1.5. IR (Nujol, cm^{-1}): ν(CN) 1590 (s). **14d**: ^1H NMR (CD_2Cl_2) δ −0.01 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH), 1.02 (d, J_{HH} = 7.3 Hz, 3H, Me*Me*CH), 1.10 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH of *p*-cymene), 1.16 (d, J_{HH} = 7.3 Hz, 3H, Me*Me*CH of *p*-cymene), 1.74 (s, 3H, Me of *p*-cymene), 2.66 (psp, 1H, MeMeC*H*), 4.33 (bd, J = 8.8 Hz, 1H), 4.38 (pt, J = 8.8 Hz, 1H), 4.47 (dd, J = 8.8 Hz, J = 1.5 Hz, 1H), 5.18 (d, J_{AB} = 5.9 Hz, 1H, H_AH_B), 5.98 (d, J_{AB} = 6.9 Hz, 1H, H_AH_B), 6.04 (d, J_{AB}= 5.1 Hz, 1H, H_AH_B), 6.15 (d, J_{AB} = 5.9 Hz, 1H, H_AH_B), 6.8−8.0 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 5.3 s, −15.5 (t, J_{FP} = 961.4 Hz). **14d′**: ^1H NMR (CD_2Cl_2) δ 0.63 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH), 0.90 (d, J_{HH} = 7.3 Hz, 6H, *Me*MeCH, Me*Me*CH), 1.01 (d, J_{HH} = 7.3 Hz, 3H, Me*Me*CH), 1.96 (s, 3H, Me of *p*-cymene), 2.35 (psp, 1H, MeMeC*H*), 2.58 (psp, 1H, MeMeC*H*), 4.18 (st, J = 9.2 Hz, 1H), 4.55 (dd, J = 9.5 Hz, J = 2.2 Hz, 1H), 4.61 (bd, J = 8.8 Hz, 1H), 5.76 (d, J_{AB} = 5.9 Hz, 1H, H_AH_B), 5.98 (d, J_{AB} = 6.9 Hz, 1H, H_AH_B), 6.05 (bd, 1H, H_AH_B), 6.12 (d, J_{AB} = 5.9 Hz, 1H, H_AH_B), 6.8−8.0 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 7.2 s, −14.8 (t, J_{FP} = 958.0 Hz).

Preparation of [(η^6-*p*-MeC_6H_4*i*Pr)Ru(PNInd)(methacrolein)][$SbF_6]_2$ (15a, 15a′). To a solution of **9** (150.2 mg, 0.13 mmol) in 5 mL of dichloromethane was added methacrolein (184.0 mg, 2.6

mmol) under nitrogen. The resulting suspension was stirred for 15 min and then partially concentrated under reduced pressure. A brown solid was filtered off, washed with diethyl ether, and air-dried.

15a, **15a′:** 70:30 molar ratio, 70% yield. Anal. Calcd for $C_{42}H_{42}NF_{12}RuO_2PSb_2$: C, 42.2; H, 3.4; N, 1.2. Found: C, 42.1; H, 3.2; N, 1.2. IR (Nujol, cm^{-1}): ν(CN) 1610 (s), $\nu(SbF_6)$ 285 (m). **15a**: ^{1}H NMR (CD_2Cl_2) δ 0.92−1.32 (m, 6H, *MeMe*CH, overlapped with the corresponding **15a′** resonances), 1.77 (s, 3H, $CH_2C(CH_3)CHO$), 2.26 (s, 3H, Me), 2.64 (psp, 1H, MeMeC*H*), 5.97 (s, 2H, $CH_2C(CH_3)CHO$), 9.64 (s, 1H, $CH_2C(CH_3)CHO$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 41.1 s. **15a′**: ^{1}H NMR (CD_2Cl_2) δ 0.92−1.32 (m, 6H, *MeMe*CH, overlapped with the corresponding **15a** resonances), 1.62 (s, 3H, $CH_2C(CH_3)CHO$), 2.12 (s, 3H, Me), 2.84 (psp, 1H, MeMeC*H*), 6.28 (s, 2H, $CH_2C(CH_3)CHO$), 9.41 (s, 1H, $CH_2C(CH_3)CHO$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 36.7 s.

Preparation of [(η^6-*p*-MeC$_6$H$_4$*i*Pr)OsPh(PNOH)][SbF$_6$] (16, 17). A solution of 0.025 mmol of the complex **10** or **12** was stirred, in 25 mL of dichloromethane, for 2 h under reflux (**10**) or 0.5 h at room temperature (**12**). The resulting brown solution was evaporated to dryness and the residue extracted with dichloromethane (3 × 5 mL). The solution was concentrated under reduced pressure. Addition of *n*-hexane gave a brown-yellow solid, which was filtered off, washed with *n*-hexane, and air-dried.

16a, **16a′:** from 25:75 to 44:56 variable molar ratio, 82% yield. Anal. Calcd for $C_{34}H_{39}NF_6OsO_2PSb$: C, 42.9; H, 4.1; N, 1.5. Found: C, 43.2; H, 4.2; N, 1.4. IR (Nujol, cm^{-1}): ν(OH) 3300−3700 (m, br), ν(CN) 1615 (m), $\nu(SbF_6)$ 280 (s). FAB$^+$ MS *m*/*z* (*m*-nitrobenzyl alcohol) 716 (M$^+$, 100). **16a**: ^{1}H NMR ($(CD_3)_2CO$) δ 0.65 (d, J_{HH} = 6.9 Hz, 3H, *Me*MeCH of *p*-cymene), 0.74 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH), 1.05 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH), 1.19 (d, J_{HH} = 7.0 Hz, 3H, Me*Me*CH of *p*-cymene), 2.13 (s, 3H, Me of *p*-cymene), 2.50 (m, 2H, MeMeC*H*), 4.33 (m, 1H, H_g), 4.43 (pt, J_{HgHc} = 9.0 Hz, 1H, H_c), 4.66 (dd, J_{HcHt} = 9.0 Hz, J_{HgHt} = 4.6, 1H, H_t), 5.22 (d, J_{AB} = 5.3 Hz, 1H, H_AH_B), 5.58 (d, $J_{A'B'}$ = 5.8 Hz, 1H, $H_{A'}H_{B'}$), 6.16 (d, 1H, H_AH_B), 6.40 (d, 1H, $H_{A'}H_{B'}$), 6.8−8.2(m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 70.6 s. **16a′**: ^{1}H NMR ($(CD_3)_2CO$) δ 0.55 (d, J_{HH} = 6.8 Hz, 3H, *Me*MeCH), 0.97 (d, J_{HH} = 6.6 Hz, 3H, Me*Me*CH), 1.13 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH of *p*-cymene), 1.20 (d, J_{HH} = 6.8 Hz, 3H, *Me*MeCH of *p*-cymene), 1.97 (s, 3H, Me of *p*-cymene), 2.25 (m, 1H, MeMeC*H*), 2.50 (m, 1H, MeMeC*H* of *p*-cymene), 4.27 (m, 1H, H_g), 4.72 (pt, J_{HcHt} = 7.7 Hz, 1H, H_c or H_t), 4.81 (pt, J_{HcHt} = 9.4 Hz, 1H, H_c or H_t), 5.66 (d, J_{AB} = 4.8 Hz, 1H, H_AH_B), 5.68 (d, J_{AB} = 4.5 Hz, 1H, H_AH_B), 6.00 (d, $J_{A'B'}$ = 5.6 Hz, 1H, $H_{A'}H_{B'}$), 6.16 (d, $J_{A'B'}$ = 5.6 Hz, 1H, $H_{A'}H_{B'}$), 6.8−8.0 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 66.5 s. **16a**, **16a′**: ^{13}C NMR ($(CD_3)_2CO$) δ 13.5, 16.2, 17.3, 18.3, 18.4, 20.0, 20.2, 20.6, 22.9, 23.5 (*MeMe*CH and *MeMe*CH and Me of *p*-cymene); 28.8, 30.0, 30.3, 30.9 (MeMeCH); 71.2, 71.9, 73.5, 76.3, 78.8, 78.9, 79.3, 82.1, 85.0 (C of *p*-cymene ring, CH_g, CH_cH_t); 79.7 (d, J_{PC} = 6.6 Hz), 82.7 (d, J_{PC} = 6.3 Hz) (C of *p*-cymene ring); 111.5 (d, J_{PC} = 7.3 Hz), 115.2 (d, J_{PC} = 7.3 Hz), 106.5, 105.1 (*C*-Me, *C*-*i*Pr of *p*-cymene ring), 122−144 (Ph), 134.7 (d, J_{PC} = 59.4 Hz, C−P), 136.1 (d, J_{PC} = 59.4 Hz, C−P), 137.7 (d, J_{PC} = 64.6 Hz, C−P), 139.2 (d, J_{PC} = 58.3 Hz, C−P), 158.8 (d, J_{PC} = 15.7 Hz, C−Os), 158.3 (d, J_{PC} = 15.7 Hz, C−Os), 179.1 (C═N), 179.7 (C═N).

17a′: yield 78%. Anal. Calcd for $C_{38}H_{37}NF_6OsO_2PSb$: C, 45.8; H, 3.7; N, 1.4. Found: C, 45.3; H, 3.9; N, 1.5. IR (Nujol, cm^{-1}): ν(OH) 3300−3700 (m, br), ν(CN) 1614 (m), $\nu(SbF_6)$ 280 (s). FAB$^+$ MS *m*/*z* (*m*-nitrobenzyl alcohol) 762 (M$^+$, 100). CD (Me_2CO, [Θ] (λ, nm) maxima, minima and nodes): −14000 (360). ^{1}H NMR ($(CD_3)_2CO$): δ 0.63 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH), 1.13 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH), 2.37 (s, 3H, Me), 2.58 (psp, 1H, MeMeC*H*), 2.80 (dd, J_{HcHt} = 18.2, J_{HoHt} = 3.8 Hz, 1H, H_t), 3.56 (dd, J_{HoHc} = 8.3 Hz, 1H, H_c), 5.74 (d, J_{HoHn} = 8.8 Hz, 1H, H_n), 5.91 (ptd, 1H, H_o), 5.65 (m, 1H, H_AH_B), 6.06 (d, $J_{A'B'}$ = 6.1 Hz, 1H, $H_{A'}H_{B'}$), 6.15 (d, 1H, $J_{A'B'}$ = 5.6 Hz, H_AH_B), 6.58 (d, 1H, $H_A'H_B'$), 6.8−8.0 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 74.2 s. ^{13}C NMR (CD_2Cl_2): δ 18.8 (Me), 20.2 (*Me*MeCH), 23.9 (Me*Me*CH), 31.1 (d, J_{PC} = 25.7 MeMe*C*H), 40.0 (CH_cH_t), 77.6 (CH_n), 79.8 (CH_o), 77.8, 82.8 (d, J_{PC} = 6.6), 86.8, 87.3 (C of *p*-cymene ring), 103.7, 112.7 (d, J_{PC} = 8.1, *C*-Me, *C*-*i*Pr of *p*-cymene ring), 122−143 (Ph), 133.8 (d, J_{PC} = 60.4, C−P), 137.1-(d, J_{PC} = 66.5, C−P), 157.0 (d, J_{PC} = 15.1, C−Os), 178.6 (C═N).

Preparation of [(η^6-*p*-MeC$_6$H$_4$*i*Pr)OsPh(PNF*i*Pr)][BF$_4$] (18b, 18b′). A solution of **10b**:**10b′** (288.0 mg, 0.324 mmol) was stirred for 48 h, in 25 mL of dichloromethane. During this time, the color changed to green-yellow. The solution was filtered and concentrated under reduced pressure. The addition of *n*-hexane gave a green-yellow solid, which was filtered off, washed with *n*-hexane, and air-dried.

18b, **18b′:** 89:11 molar ratio, 86% yield. Anal. Cald for $C_{34}H_{38}NF_5OsOPB$: C, 50.8; H, 4.8; N, 1.7. Found: C, 50.6; H 4.8; N, 1.6. IR (Nujol, cm^{-1}): ν(CN) 1616 (m), $\nu(BF_4)$ 1050(s). FAB$^+$ MS *m*/*z* (*m*-nitrobenzyl alcohol) 719 (M$^+$, 100). CD (Me_2CO, [Θ] (λ, nm) maxima, minima and nodes): **18b**:**18b′**, 89:11 molar ratio: +25000 (340). **18b**: ^{1}H NMR ($(CD_3)_2CO$) δ 0.75 (d, J_{HH} = 6.8 Hz, 3H, *Me*MeCH of *p*-cymene), 0.76 (d, J_{HH} = 6.6 Hz, 3H, *Me*MeCH), 1.06 (d, J_{HH} = 6.8 Hz, 3H, Me*Me*CH), 1.29 (d, J_{HH} = 7.0 Hz, 3H, Me*Me*CH of *p*-cymene), 2.25 (s, 3H, Me of *p*-cymene), 2.43 (m, 1H, MeMeC*H*), 2.65 (psp, 1H, MeMeC*H* of *p*-cymene), 4.22 (m, 1H, H_g), 4.33 (pt, J_{HgHc} = 9.4 Hz, 1 H, H_c), 4.71 (dd, J_{HcHt} = 9.1 Hz, J_{HgHt} = 4.4 Hz, 1H, H_t), 5.59 (d, J_{AB} = 5.7 Hz, 1H, H_AH_B), 5.78 (d, $J_{A'B'}$ = 5.7 Hz, 1H, $H_A'H_B'$), 6.61 (d, 1H, H_AH_B), 6.67 (d, 1H, $H_{A'}H_{B'}$), 7.3−8.1 (m, 14H, Ph). $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$): δ 132.0 (d, J_{P-F} = 892.9 Hz). $^{19}F\{^1H\}$ NMR ((CD_3)-CO): δ −125.1. ^{13}C NMR ($(CD_3)_2CO$): δ 14.0, 18.7, 19.0, 21.5, 23.3 (*MeMe*CH and *MeMe*CH and Me of *p*-cymene), 31.8 (Me-Me*C*H), 72.2 (s), 72.8, 80.9, 82.6, 83.4, 84.5 (d, J_{PC} = 5.5) (C of *p*-cymene ring, CH_g, CH_cH_t), 109.7, 116.6 (d, J_{PC} = 6.0) (*C*-Me, *C*-*i*Pr of *p*-cymene ring); 123−143 (Ph), 137.1 (dd, J_{PC} = 63.0, J_{FC} = 16.1, C−P), 155.5 (d, J_{PC} = 17.1, C−Os), 179.7 (C═N). **18b′**: $^{31}P\{^1H\}$ NMR ($(CD_3)_2CO$) δ 125.2 (d, J_{P-F}= 904.9 Hz). $^{19}F\{^1H\}$ NMR ($(CD_3)CO$): δ −136.2 d.

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. The ruthenium aqua solvates were prepared in situ from the corresponding chloride, as reported above. 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, washed with CH_2Cl_2/hexane (1:1, catalysts of ruthenium, or 2:1, catalysts of osmium) before the determination of the enantiomeric purity. Enantiomeric excesses (ee) were determined by integration of the aldehyde proton of both enantiomers in ^{1}H 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 $[\alpha]^D$ with that in the literature.[29]

Crystal Structure Determination of Complexes 1a, 3a, 4a, 7c, 13, and 15a′. X-ray data were collected for all complexes at low temperature (200(1) K for **1a**, **3a**, **4a**, and **15a′**, 150(1) K for **7c**, and 100(1) K for **13**) on a Bruker SMART APEX CCD diffractometer (**13**) or on a Siemens P4 diffractometer (**1a**, **3a**, **4a**, and **15a′**), in both cases with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å); data for **7c** were measured on a Daresbury SRS Station 9.8 with silicon-monochromated synchrotron

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radiation ($\lambda = 0.69340$ Å). Data were corrected for absorption by using a psi-scan (**1a**, **3a**, **4a**, and **15a′**)[30] or a multiscan method (**7c** and **13**) applied with the SADABS program.[31] The structures were solved by direct methods with SHELXS-86.[32] Refinement, by full-matrix least squares on F^2 with SHELXL97,[32] was similar for all complexes, including isotropic and subsequently anisotropic displacement parameters for all non-hydrogen nondisordered atoms. Particular details concerning the existence of static disorder and hydrogen refinement are listed below. All the highest electronic residuals (smaller than 1.0 e/ Å^3) were observed in close proximity to the metal or Sb atoms and have no chemical sense. In all structures, additionally to the internal configuration reference of the oxazoline ligand, the Flack parameter was refined as a check of the correct absolute configuration determination.[33]

Crystal data for 1a: $C_{34}H_{38}ClF_6NOPRuSb$, $M = 879.89$; orange irregular block, 0.37 × 0.29 × 0.26 mm^3; orthorhombic, $P2_12_12_1$; $a = 8.8061(5)$ Å, $b = 14.6680(8)$ Å, $c = 27.1709(17)$ Å; $Z = 4$; $V = 3509.6(4)$ Å^3; $D_c = 1.665$ g/cm^3; $\mu = 1.382$ mm^{-1}, min. and max. transmission factors 0.542 and 0.700; $2\theta_{max} = 52.0°$; 7742 reflections collected, 6866 unique [R(int) = 0.0093]; number of data/restraints/parameters 6866/36/536; final GoF 1.043, R1 = 0.0321 [6456 reflections, $I > 2\sigma(I)$], wR2 = 0.0813 for all data; Flack parameter $x = -0.03(2)$. The SbF_6^- anion was observed disordered, and a model was built from two moieties refined with complementary occupancy factors. Hydrogen atoms were partially observed in the difference Fourier maps and included in the model as free isotropic atoms; hydrogens of the terminal methyl groups were included in calculated positions and refined with positional and thermal riding parameters.

Crystal data for 3a: $C_{38}H_{36}ClF_6NOPRuSb$, $M = 925.92$; orange prism, 0.34 × 0.26 × 0.12 mm^3; monoclinic, $P2_1$; $a = 10.3448(7)$ Å, $b = 15.1685(8)$ Å, $c = 11.5034(7)$ Å, $\beta = 95.782(5)°$; $Z = 2$; $V = 1795.87(19)$ Å^3; $D_c = 1.712$ g/cm^3; $\mu = 1.355$ mm^{-1}, min. and max. transmission factors 0.656 and 0.854; $2\theta_{max} = 55.0°$; 8954 reflections collected, 8219 unique [R(int) = 0.0378]; number of data/restraints/parameters 8219/37/463; final GoF 1.079, R1 = 0.0427 [7179 reflections, $I > 2\sigma(I)$], wR2 = 0.1112 for all data; Flack parameter $x = 0.01(3)$. Anion disorder observed and refined as described in **1a**. Hydrogen treatment as reported for **1a**.

Crystal data for 4a: $C_{34}H_{38}ClF_6NOOsPSb$, $M = 969.02$; yellow-orange prism, 0.44 × 0.42 × 0.24 mm^3; orthorhombic, $P2_12_12_1$; $a = 8.8403(9)$ Å, $b = 14.6825(16)$ Å, $c = 27.236(2)$ Å; $Z = 4$; $V = 3535.2(6)$ Å^3; $D_c = 1.821$ g/cm^3; $\mu = 4.535$ mm^{-1}, min. and max. transmission factors 0.197 and 0.336; $2\theta_{max} = 50.0°$; 7161 reflections collected, 6226 unique [R(int) = 0.0288]; number of data/restraints/parameters 6226/55/464; final GoF 1.032, R1 = 0.0394 [5441 reflections, $I > 2\sigma(I)$], wR2 = 0.0877 for all data; Flack parameter $x = -0.023(9)$; largest difference peak 1.194 e/Å^3 (close to Os atom). The SbF_6^- anion was observed disordered, and a model with three SbF_6 moieties was eventually refined. Hydrogens were included in the refinement from observed positions and were refined as constrained atoms with a positional riding model and four common thermal parameters.

Crystal data for 7c: $C_{36}H_{40}F_6NO_8PRuS_2$, $M = 924.85$; orange plate, 0.10 × 0.05 × 0.02 mm^3; monoclinic, $P2_1$; $a = 10.3493(15)$ Å, $b = 10.9548(16)$ Å, $c = 17.044(2)$ Å, $\beta = 94.730(3)°$; $Z = 2$; $V = 1925.8(5)$ Å^3; $D_c = 1.595$ g/cm^3; $\mu = 0.638$ mm^{-1}, min. and max. transmission factors 0.939 and 0.987; $2\theta_{max} = 61.14°$; 16 037 reflections collected, 10 002 unique [R(int) = 0.0261]; number of data/restraints/parameters 10002/58/582; final GoF 1.037, R1 = 0.0347 [9604 reflections, $I > 2\sigma(I)$], wR2 = 0.0909 for all data; Flack parameter $x = 0.017(19)$; largest difference peak 1.008 e/Å^3 (close to Ru atom). One of the triflate anions was observed disordered and was modeled with two separated CF_3SO_3 moieties of complementary occupancies; several attempts to improve the disorder model based upon isotropic atoms were carried out, but no geometric consistency was achieved. Eventually, dynamic disorder was assumed. Hydrogen atoms were included in calculated positions and refined with a positional and thermal riding model. The two hydrogens of the coordinated water molecule were included from observed positions and refined as free isotropic atoms.

Crystal data for 13: $C_{34}H_{38}F_8NO_3P_3Ru$, $M = 854.63$; red prism, 0.247 × 0.143 × 0.135 mm^3; monoclinic, $P2_1$; $a = 9.9134(6)$ Å, $b = 25.1523(15)$ Å, $c = 13.8912(8)$ Å, $\beta = 99.5550(10)°$; $Z = 4$; $V = 3415.6(4)$ Å^3; $D_c = 1.662$ g/cm^3; $\mu = 0.681$ mm^{-1}, min. and max. transmission factors 0.850 and 0.914; $2\theta_{max} = 56.64°$; 23 054 reflections collected, 14 908 unique [R(int) = 0.0330]; number of data/restraints/parameters 14 908/1/1013; final GoF 1.008, R1 = 0.0418 [13 421 reflections, $I > 2\sigma(I)$], wR2 = 0.0863 for all data; Flack parameter $x = -0.004(17)$. Two independent molecules, with different configuration at the metal center, were observed in the crystal structure. One of the two PF_6^- anions was observed disordered and refined with two complementary moieties. Hydrogens were included in observed or calculated positions and refined with riding parameters.

Crystal data for 15a′: $C_{42}H_{42}F_{12}NO_2PRuSb_2$, $M = 1196.32$; orange irregular block, 0.69 × 0.48 × 0.38 mm^3; orthorhombic, $P2_12_12_1$; $a = 11.3401(8)$ Å, $b = 18.2209(12)$ Å, $c = 20.7142(13)$ Å; $Z = 4$; $V = 4280.1(5)$ Å^3; $D_c = 1.857$ g/cm^3; $\mu = 1.729$ mm^{-1}, min. and max. transmission factors 0.530 and 0.977; $2\theta_{max} = 50.04°$; 8444 reflections collected, 7521 unique [R(int) = 0.0224]; number of data/restraints/parameters 7508/72/570; final GoF 1.058, R1 = 0.0431 [6232 reflections, $I > 2\sigma(I)$], wR2 = 0.0950 for all data; Flack parameter $x = -0.03(3)$. Both anions were observed disordered and were modeled based on two moieties SbF_6 with complementary occupancy factors. A partially restrained octahedral symmetry was assumed for these groups. Hydrogen atoms of the methyl groups were included in calculated positions; all the remaining were obtained from difference Fourier maps. All the hydrogens were refined riding on carbon atoms with four common thermal parameters.

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Supporting Information Available: ORTEP representations of the cations of **4a** and **13d**. X-ray crystallographic information files containing full details of the structural analysis of the six crystal structures (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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