

Chiral Half-Sandwich Ruthenium(II) Complexes as Catalysts in 1,3-Dipolar Cycloaddition Reactions of Nitrones with Methacrolein

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Dedicated to Prof. Dr. Victor Riera on the occasion of his 70th birthday

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Ruthenium complexes of formula $[(\eta^6\text{-arene})\text{Ru}(\text{LL}^*)(\text{H}_2\text{O})][\text{SbF}_6]_2$ (arene = C_6H_6 , $p\text{-MeC}_6\text{H}_4\text{iPr}$, C_6Me_6 ; LL^* = bidentate chelate chiral ligand with PN, PP or NN donor atoms) have been tested as catalyst precursors for the asymmetric 1,3-dipolar cycloaddition of nitrones to methacrolein. The reaction occurs quantitatively with perfect *endo* selectivity and moderate enantioselectivity (up to 74 % ee). The ruthenium aqua complexes can be prepared from the corresponding chlorides, $[(\eta^6\text{-arene})\text{RuCl}(\text{LL}^*)][\text{SbF}_6]$. Dipolarophile intermediates $[(\eta^6\text{-arene})\text{Ru}(\text{PNiPr})(\text{methacrolein})][\text{SbF}_6]_2$ {PNiPr = (4*S*)-2-(2-diphenylphosphanylphenyl)-4-isopropyl-1,3-oxazoline} as well as nitrone-containing complexes $[(p\text{-Me-}$

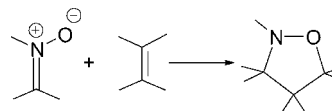
$\text{C}_6\text{H}_4\text{iPr})\text{Ru}(\text{PNiPr})(\text{nitrone})][\text{SbF}_6]_2$ (nitrone = *N*-benzylidenephénylamine *N*-oxide, *N*-benzylidenemethylamine *N*-oxide, 3,4-dihydroisoquinoline *N*-oxide) have been also isolated and characterised. The crystal structures of the chlorides $(R_{\text{Ru}})-[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}(\text{PNiPr})][\text{SbF}_6]$, $(R_{\text{Ru}})-[(\eta^6\text{-C}_6\text{H}_6)\text{RuCl}(\text{PNInd})][\text{SbF}_6]$ {PNInd = (3*aR*,8*aS*)-2-[2-(diphenylphosphanyl)phenyl]-3*a*,8*a*-dihydroindane[1,2-*d*]oxazole} and those of the aqua solvates $(R_{\text{Ru}})-[(\eta^6\text{-arene})\text{Ru}(\text{PNiPr})(\text{H}_2\text{O})][\text{SbF}_6]_2$ (arene = C_6H_6 , C_6Me_6) were determined by X-ray diffraction methods.

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Introduction

Asymmetric catalysis has achieved a position as one of the most important areas of modern organic chemistry.^[1] Among the wide variety of organic reactions that are used in asymmetric synthesis, cycloaddition processes are one of the most attractive synthetic methodologies because they allow the construction of new molecular skeletons with several stereogenic centres in a single step.^[2] 1,3-Dipolar cycloaddition reactions represent a highly atom-efficient and elegant method for the synthesis of five-membered ring systems and, depending on the choice of dipolar reagent and dipolarophile, a large variety of heterocycles can be prepared.^[3] Nitrones, in particular, have attracted much attention since they are readily available and easy to handle and

their reactions with olefins give convenient access to isoxazolidine derivatives (Scheme 1).^[4] Because its N–O bond is readily cleaved to form 3-amino alcohol equivalents under mild reducing conditions, these cyclic compounds have been applied as synthetic intermediates for the synthesis of useful compounds such as alkaloids, β -lactams, amino acids or amino sugars.^[3a,5] However, asymmetric versions of this reaction are scarce. Furthermore, alkenoyloxazolidinones are usually employed as bidentate dipolarophiles^[3b,4a] and only a few studies on monodentate α,β -unsaturated aldehydes have been reported so far.^[6]

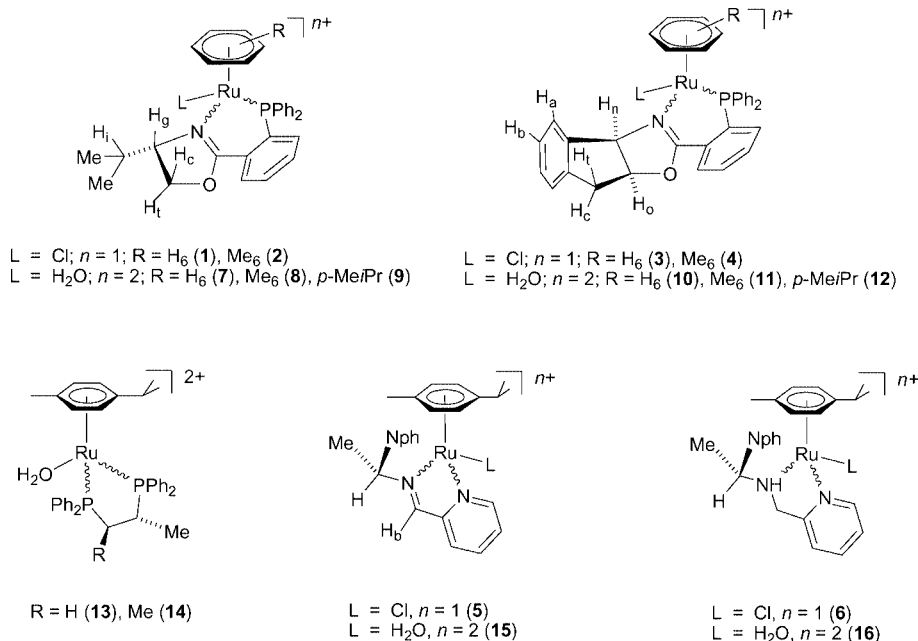


Scheme 1. Reaction of nitrones with alkenes.

On the other hand, it has been shown that chiral pseudo-tetrahedral metal half-sandwich complexes^[7] are efficient catalysts for the asymmetric Diels–Alder^[8] and hydrogen-transfer reactions.^[9] In this context, we have reported that the single-coordination-site transition-metal chiral Lewis acids $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\text{R-Phosphos})(\text{H}_2\text{O})][\text{SbF}_6]_2$ [M = Rh, Ir;

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Scheme 2. Half-sandwich hexafluoroantimonate complexes.

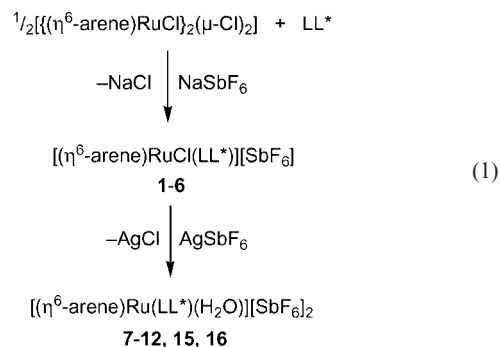
R-Prophos = 1,2-bis(diphenylphosphanyl)propane] efficiently promote enantioselective 1,3-dipolar cycloaddition reactions (DCR) of nitrones with methacrolein.^[10]

Taking into consideration all these data, we planned to test chiral half-sandwich ruthenium complexes of the general formula $[(\eta^6\text{-arene})Ru(LL^*)(H_2O)]^{2+}$ (LL^* = bidentate chelate chiral ligand) as catalysts in enantioselective 1,3-dipolar cycloadditions of nitrones with methacrolein. In this paper we report the preparation of new chloride complexes of general formula $[(\eta^6\text{-arene})RuCl(LL^*)][SbF_6]$ (**1–4**) which are precursors of aqua solvates (**7–16**, Scheme 2) and the use of the latter as catalysts in the above-mentioned process. The molecular structural details of four representative complexes, determined by X-ray diffraction methods, are also included.

Results and Discussion

Preparation and Characterisation of the Diastereomeric Complexes 1–16

The aqua complexes **7**, **8**, **10** and **11** were prepared by treating the corresponding chloride complexes **1–4** with equimolar amounts of $AgSbF_6$. The latter, in turn, were prepared from the dimers^[11] $[(\eta^6\text{-arene})RuCl]_2(\mu\text{-Cl})_2$ [Equation (1)]. The previously reported chloride **5** and solvates **9**, **12** and **15** were similarly prepared.^[8u,8x] The pyridylamino derivatives **6** and **16**, also prepared according to Equation (1), will be reported elsewhere.^[12] The diphosphanyl complexes **13** and **14** were prepared by treatment of the dimer $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})RuCl]_2(\mu\text{-Cl})_2$ with $AgSbF_6$, filtration of the $AgCl$ formed and subsequent addition of the corresponding diphosphane.



The new complexes were characterised by IR and NMR spectroscopy, circular dichroism (CD), elemental analysis (see Exp. Sect.) and by the X-ray crystal structure determination of one of the epimers at the metal atom of complexes **2**, **3**, **7** and **8**.

During the formation of the chloride complexes, the ruthenium atom becomes a chiral centre and, as the chiral LL^* ligand used is enantiopure, the new compounds are prepared as diastereomeric mixtures of both epimers at the metal atom. Variable degrees of diastereoselectivity are achieved, ranging from 10 to 96% *de* (see Exp. Sect.). Concerning the stereochemistry of the metal centres, it should be noted that due to the ligand priority rules,^[13] different descriptors are assigned to the chlorides and to their derived aqua complexes, although both display identical spatial disposition of the ligands around the metal atom.

The absolute configurations of the new complexes were assigned through NMR spectroscopic and CD measurements. Thus, for example, irradiation of the arene protons in the R_{Ru} chloride complexes (or in the S_{Ru} aqua solvates) induces NOE enhancements of the H_g or H_a protons for

PN*i*Pr- or PNInd-containing complexes, respectively (see Scheme 2). Similarly, this irradiation induces, in the S_{Ru} chlorides (or in the R_{Ru} aqua solvates), NOE enhancements of the H_i or H_n protons for PN*i*Pr- or PNInd-containing complexes, respectively.

Proton shielding by aromatic ring currents can also be used to distinguish between the two epimers at the metal atom of these chiral complexes. For example, the chemical shift of the C_6Me_6 protons differs by 0.43 ppm for the two epimers of the PNInd-containing complex **4**. Inspection of molecular models indicates that these protons can only be efficiently shielded by the aromatic indane ring current in the R_{Ru} epimers. Therefore, we assign the high-field resonance to the *R* epimer.

On the other hand, the difference in the chemical shift (ca. 1 ppm) between the signals of the two methyl protons of the PN*i*Pr ligand in complexes **1**, **2**, **7** and **8** could be explained by assuming that in these complexes the six-membered metallacycle adopts an 1S_2 screw boat conformation.^[8v,8x,14] Such a conformation has been found in the solid state for complexes **7** and **8** (see below). In this confor-

mation, one methyl group of the *i*Pr group lies over the *pro-R*-phenyl group of the PPh_2 group, becoming shielded by its aromatic ring current.

The aqua solvates **8**, **10** and **11** are fluxional. Although we have not measured the kinetic parameters for the dynamic process, the spectroscopic features encountered in the ^{31}P and 1H NMR spectra strongly indicate that it likely consists of a flip of the phosphanyloxazoline metallacycle between the 1S_2 and 2S_1 screw boat conformations as has been previously found in the related phosphanyloxazoline aqua solvates of ruthenium, **9** and **12**.^[8x]

The CD spectra of these complexes corroborate the above-assigned configurations. The main feature of the CD spectra of the S_{Ru} chlorides (R_{Ru} aqua complexes) is a maximum with a positive Cotton effect centred in the 360–390 nm range. The CD spectra of corresponding diastereomers with opposite configuration at the metal atom display a pseudo-enantiomorphous relationship, showing that the major contribution to the spectra corresponds to the metal atom. This transition thus gives direct insight into differences in the configurations at the metal atoms.

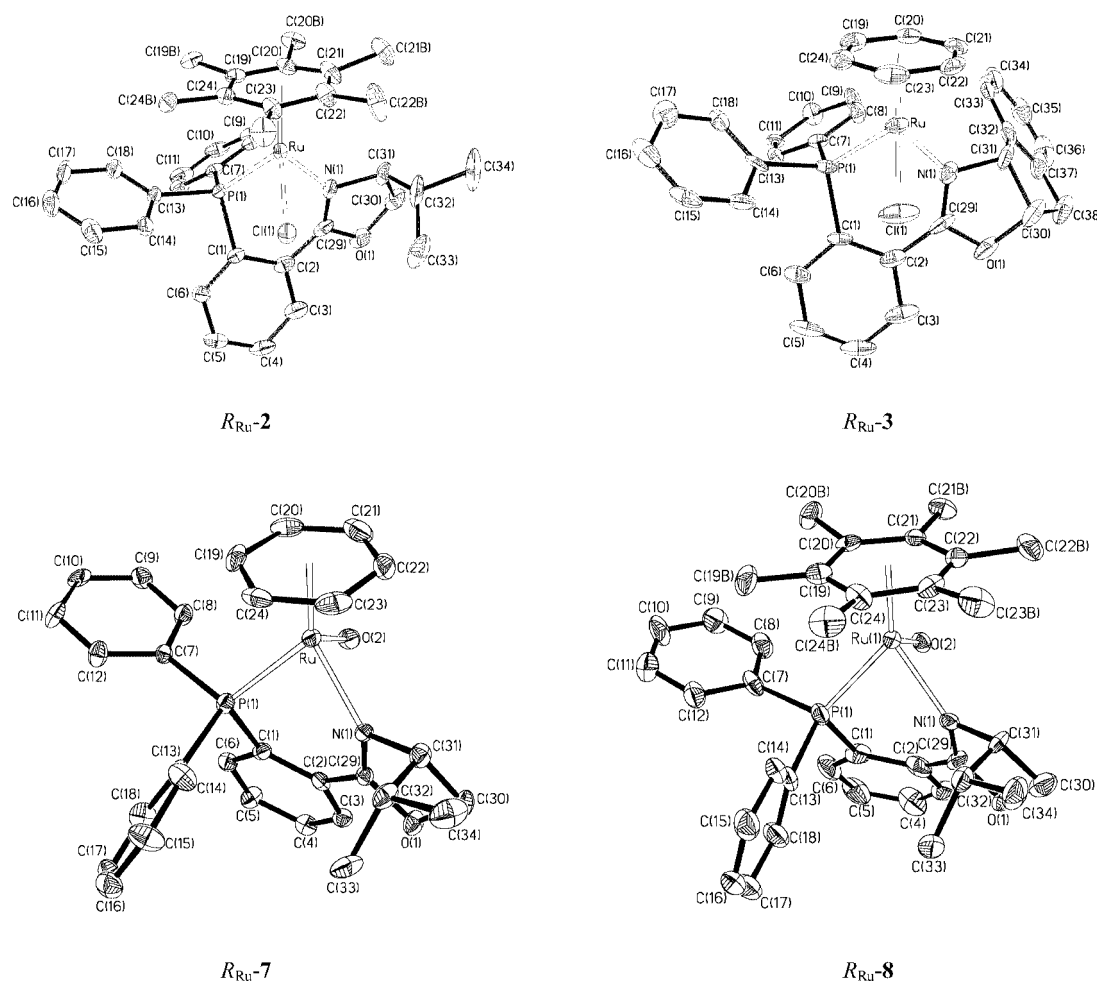


Figure 1. Molecular views of the cations of the complexes $R_{Ru}-[(\eta^6-C_6Me_6)RuCl(PN*i*Pr)][SbF_6]$ (R_{Ru} -**2**), $R_{Ru}-[(\eta^6-C_6H_6)RuCl(PNInd)][SbF_6]$ (R_{Ru} -**3**), $R_{Ru}-[(\eta^6-C_6H_6)Ru(PN*i*Pr)(H_2O)][SbF_6]_2$ (R_{Ru} -**7**) and $R_{Ru}-[(\eta^6-C_6Me_6)Ru(PN*i*Pr)(H_2O)][SbF_6]_2$ (R_{Ru} -**8**).

Table 1. Selected bond lengths [Å] and angles [°] for R_{Ru-2} , R_{Ru-3} , R_{Ru-7} and R_{Ru-8} .

	R_{Ru-2}	R_{Ru-3}	R_{Ru-7}	$R_{Ru-8}^{[a]}$	
Ru–P(1)	2.2920(10)	2.3011(18)	2.3235(15)	2.357(2)	2.363(2)
Ru–O(2)/Cl(1) ^[b]	2.3973(10)	2.3993(16)	2.156(4)	2.182(5)	2.164(5)
Ru–N(1)	2.133(3)	2.125(5)	2.095(4)	2.115(6)	2.138(6)
Ru–C(19)	2.238(4)	2.183(7)	2.195(5)	2.230(8)	2.222(7)
Ru–C(20)	2.267(4)	2.217(6)	2.186(6)	2.244(7)	2.251(8)
Ru–C(21)	2.372(4)	2.260(6)	2.236(6)	2.230(7)	2.236(8)
Ru–C(22)	2.338(4)	2.269(7)	2.271(6)	2.288(8)	2.278(8)
Ru–C(23)	2.238(4)	2.211(6)	2.229(6)	2.324(7)	2.305(8)
Ru–C(24)	2.253(4)	2.211(6)	2.208(6)	2.280(8)	2.280(8)
Ru–G ^[c]	1.7897(17)	1.727(3)	1.723(2)	1.766(3)	1.765(3)
P(1)–C(1)	1.824(4)	1.816(6)	1.825(6)	1.837(8)	1.843(8)
N(1)–C(29)	1.297(6)	1.301(8)	1.284(7)	1.292(10)	1.289(10)
N(1)–C(31)	1.499(5)	1.502(9)	1.508(7)	1.522(11)	1.488(9)
C(1)–C(2)	1.405(5)	1.397(10)	1.384(7)	1.406(12)	1.403(11)
C(2)–C(29)	1.460(6)	1.465(10)	1.484(8)	1.469(12)	1.467(11)
C(2)–C(3)	1.391(6)	1.414(9)	1.395(8)	1.393(11)	1.384(10)
P(1)–Ru–O(2)/Cl(1) ^[b]	87.00(3)	87.06(6)	85.43(13)	84.50(14)	85.79(17)
P(1)–Ru–N(1)	83.73(9)	84.12(15)	83.03(12)	80.47(19)	81.17(18)
P(1)–Ru–G ^[b]	129.21(6)	128.69(11)	130.68(9)	135.27(12)	134.54(14)
O(2)/Cl(1)–Ru–N(1) ^[b]	84.06(8)	83.89(16)	80.88(16)	81.9(2)	80.0(2)
O(2)/Cl(1)–Ru–G ^[b,c]	123.38(6)	123.32(10)	124.79(16)	121.49(18)	122.2(2)
N(1)–Ru–G ^[c]	133.62(11)	133.96(17)	134.31(14)	134.4(2)	134.2(2)
Ru–P(1)–C(1)	111.76(12)	111.5(2)	108.26(19)	106.7(3)	106.8(3)
Ru–N(1)–C(29)	131.5(3)	125.4(5)	128.8(4)	127.9(6)	125.4(5)
P(1)–C(1)–C(2)	117.8(3)	121.1(5)	121.0(4)	120.1(7)	120.1(6)
C(1)–C(2)–C(29)	123.9(4)	123.9(6)	122.5(5)	122.4(7)	121.9(7)
N(1)–C(29)–C(2)	129.2(4)	130.9(7)	130.1(5)	127.1(7)	131.3(7)

[a] There were two independent molecules in the crystal. [b] Data are included for the Ru–Cl (**2** and **3**) and the Ru–O(2) (**7** and **8**) bond lengths. [c] G represents the centroid of the arene ligand C(19)–C(24).

Molecular Structures of R_{Ru-2} , R_{Ru-3} , R_{Ru-7} , and R_{Ru-8}

Single crystals of the chlorides **2** and **3** and of the aqua complexes **7** and **8** were grown by slow diffusion of diethyl ether into dichloromethane solutions of the complexes. Their structures were determined by diffraction methods. Molecular representations of the cations of the four complexes are depicted in Figure 1 and selected structural parameters are listed in Table 1. The coordination around the ruthenium atom is pseudo-octahedral. The η^6 -arene ligand ideally occupies three *fac*-coordination positions. The phosphanyloxazoline ligand, coordinated through the phosphorus and the nitrogen atoms and one chlorine atom (**2**, **3**) or one water molecule (**7**, **8**) complete the coordination sphere of the metal atom. The absolute configuration of the ruthenium centre in the four complexes is *R*, in accordance with the ligand priority sequence^[13] η^6 -arene > Cl > P > N (chlorides) or η^6 -arene > P > O > N (aqua solvates).

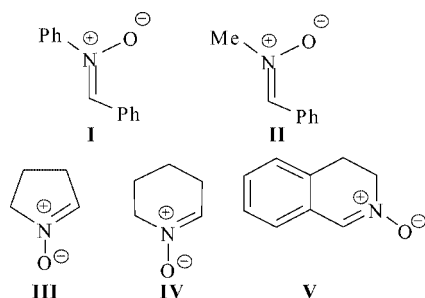
The six-membered Ru–P(1)–C(1)–C(2)–C(29)–N(1) metallacycle of complexes **3**, **7** and **8** adopts a 1S_2 screw-boat conformation^[14] with the metal and phosphorus atoms above and below the best plane, respectively. This conformation forces the *pro-R*- and *pro-S*-phenyl groups to adopt pseudo-axial and pseudo-equatorial arrays, respectively. In particular, in the solvate complexes **7** and **8**, the C(33) carbon atom of the isopropyl group lies over the *pro-R*-phenyl group of the PPh₂ group at 3.260(6) (**7**) and 3.405(9) Å (**8**) from the plane of the pseudo-axial phenyl group. In compound **2**, the metallacycle adopts a 2S_1 screw-boat confor-

mation,^[14] with the metal and phosphorus atoms below and above the best plane, respectively.

Catalytic Reactions

Firstly, we tried the (*p*-methylisopropylbenzene)ruthenium complexes **9** and **13–16**, which differ in the LL* bidentate chelate chiral ligand, as catalyst precursors for the cycloaddition reaction between methacrolein and the nitron *N*-benzylidenephénylamine *N*-oxide (nitron **1**, Scheme 3) (Table 2). These aqua complexes efficiently catalyse the proposed cycloaddition. The catalyst precursors were treated with methacrolein in the presence of molecular sieves (4 Å) before the addition of the nitron (see Exp. Sect.). Under these conditions, the formation of active methacrolein complexes of formula $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})\text{-Ru}(\text{LL}^*)(\text{methacrolein})]^{2+}$ is strongly favoured at the expense of the initial aqua complexes (see below) which prevents hydrolysis of the nitron catalysed by trace amounts of the latter.^[10b] Quantitative conversions with moderate *ee* values were achieved at –25 °C after a few hours. The best results in this series were obtained when the hybrid P,N-donor phosphanyloxazoline ligand (PNI*Pr*, complex **9**) was employed as chiral source (Entry 1, Table 2). Therefore, we focused on complex **9** in subsequent catalytic experiments (Table 3). Temperature variations slightly affected both product distribution and enantioselectivity, the latter smoothly increasing as temperature decreases. The pre-

viously reported^[8x] tetrafluoroborate and triflate complexes $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})\text{Ru}(\text{PNiPr})(\text{H}_2\text{O})][\text{BF}_4]_2$ (**9-BF₄**) and $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})\text{Ru}(\text{PNiPr})(\text{H}_2\text{O})][\text{CF}_3\text{SO}_3]_2$ (**9-CF₃SO₃**) were also tested as catalysts. As shown in Entries 5 and 6, the use of more coordinating anions decreased the yield, probably due to competition of the anion and the substrate for the Lewis acid site.^[8o,15] The catalyst can be easily recovered and reused.



Scheme 3. Nitrones employed in the catalytic experiments.

Table 2. Enantioselective 1,3-dipolar cycloadditions of methacrolein with nitrone **I** catalysed by $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})\text{Ru}(\text{LL}^*)(\text{H}_2\text{O})][\text{SbF}_6]_2$ complexes.^[a]

Entry	Complex	<i>t</i> [h]	Yield [%] ^[b,c]	3,4- <i>endo</i> ^[c]	3,5- <i>endo</i> ^[c]	<i>ee</i> [%] ^[d]
1	9	15	100	69	31	54:40
2	13	48	40	40	60	43/–42
3	14	15	90	32	68	6:3
4 ^[e]	15	48	98	36	64	–18/–31
5 ^[e]	16	48	100	91	9	–6/–4

[a] Reaction conditions: catalyst (0.06 mmol, 5.0 mol-%), methacrolein (1.68 mmol), molecular sieves (4 Å) (100 mg) and nitrone (1.2 mmol) in CH_2Cl_2 (5 mL). [b] Based on nitrone. [c] Determined by ^1H NMR spectroscopy. [d] Determined by integration of the ^1H NMR signals of the 3-H proton of the diastereomeric *R*-methylbenzylamine derivatives. Positive *ee* values correspond to the *endo*-3*R*,4*R* adduct. For the 3,5-*endo* adduct, positive values are arbitrarily assigned to the *ee* in the lower-field ^1H NMR signal diastereomer. [e] Methacrolein (8.4 mmol) was used.

Consecutive runs of up to three more times were performed, producing a smooth decrease in the conversion rate. However, neither the 3,4-*endo*/3,5-*endo* ratio nor the *ee* were significantly affected (Entries 7.1–7.4).

To investigate the stereoelectronic influence of the η^6 -coordinated arene ligand, we used the new benzene (**7**, **10**) and hexamethylbenzene (**8**, **11**) derivatives with PNiPr or PNInd ligands as catalyst precursors for the cycloaddition of methacrolein with nitrone **I** (Table 4). Reactions carried out at -25°C gave nearly quantitative conversions after

Table 3. Enantioselective 1,3-dipolar cycloadditions between methacrolein and nitrone **I** catalysed by $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})\text{Ru}(\text{PNiPr})(\text{H}_2\text{O})]^{2+}$.^[a]

Entry	Complex	<i>T</i> [°C]	<i>t</i> [h]	Yield [%]	3,4- <i>endo</i>	3,5- <i>endo</i>	<i>ee</i> [%]
1	9	0	15	100	57	43	40:30
2	9	–10	24	100	62	38	46:31
3	9	–25	15	100	69	31	54:40
4	9	–45	48	93	74	26	56:49
5	9-BF₄	–25	15	79	73	27	29:30
6	9-CF₃SO₃	–25	15	5	72	28	–
7.1	9	–25	15	100	69	31	54:40
7.2	9	–25	15	92	70	30	56:38
7.3	9	–25	15	75	70	30	56:39
7.4	9	–25	15	62	68	32	56:39

[a] For conditions see footnote of Table 2.

15 h. It seems that the PNiPr ligand performs better than its PNInd congener with *ee* values of up to 74% being achieved with the former. On the other hand, no obvious trends were observed within the arene series.

Table 4. Enantioselective 1,3-dipolar cycloadditions of methacrolein with nitrone **I** catalysed by complexes **7**–**12**.^[a]

Entry	Complex	Arene	LL*	Yield [%]	3,4- <i>endo</i>	3,5- <i>endo</i>	<i>ee</i> [%]
1 ^[b]	7	C_6H_6	PNiPr	93	48	52	20:52
2	9	<i>p</i> -MeC ₆ H ₄ iPr		100	69	31	54:40
3	8	C_6Me_6		94	67	33	74:45
4 ^[b]	10	C_6H_6	PNInd	98	38	62	–22/–56
5	12	<i>p</i> -MeC ₆ H ₄ iPr		98	62	38	25/–20
6	11	C_6Me_6		95	66	34	–32/–34

[a] For conditions see footnote of Table 2. [b] Methacrolein (8.4 mmol) was used.

Finally, we examined the reaction of other acyclic as well as cyclic nitrones in the catalytic process (Scheme 3, Table 5). In general, good conversions were achieved, with

Table 5. Enantioselective 1,3-dipolar cycloadditions of methacrolein with nitrones **II**–**V**.^[a]

Entry	Complex	Nitron	<i>T</i> [°C]	<i>t</i> [h] ^[b]	Yield [%]	3,5- <i>endo</i>	<i>ee</i> [%] ^[c]
1	9	II	0	48	99	98 ^[d]	27
2	9	III	–25	16	92	100	39
3	9	IV	–25	16	100	100	7
4	9	V	–25	48	98	100	16
5	7	II	0	48	5	100	6
6	7	V	–25	48	86	100	6
7	8	II	0	24	17	100	–36
8	8	V	–25	24	51	100	–61
9	12	II	0	48	100	96 ^[e]	27
10	12	V	–25	48	100	100	12

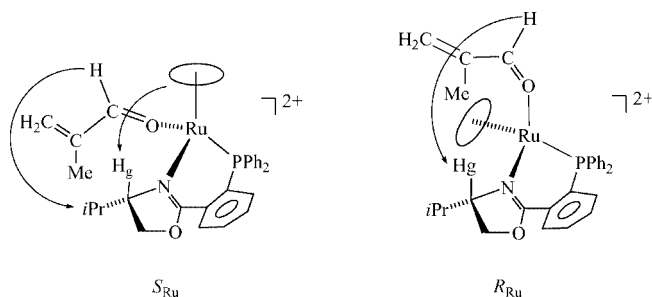
[a] Conditions were those indicated in footnote of Table 2 but using methacrolein (8.4 mmol). [b] Total reaction time; addition of nitrones was accomplished over 15 h. [c] Determined by integration of the ^1H NMR signals of the 3-H proton of the diastereomeric *R*-methylbenzylamine (nitrone **II**) derivative, the CHO proton of the (+)-*S*-mandelic acid (nitrone **IV**) derivative or the CHO proton observed after addition of the chiral shift reagent $\text{Eu}(\text{hfc})_3$ (nitrones **III** and **V**). Positive *ee* values correspond to the (+)-*endo*-3*R*,5*R* (nitrone **III**), (–)-*endo*-3*R*,5*R* (nitrone **IV**) and (–)-*endo*-3*S*,5*R* (nitrone **V**) adducts. For the adducts of nitrone **II**, positive values are arbitrarily assigned to the *ee* in the lower-field ^1H NMR signal diastereomer. [d] 2% of the 3,5-*exo* isomer was also obtained. [e] 4% of the 3,4-*endo* isomer was also obtained.

perfect regio- and diastereoselectivity for the 3,5-*endo* isomer. In all cases, low to moderate *ee* values were achieved. The hexamethylbenzene complex $[(\eta^6\text{-C}_6\text{Me}_6)\text{Ru}(\text{PNiPr})(\text{H}_2\text{O})][\text{SbF}_6]_2$ (**8**) is the least active catalyst precursor tried but the most enantioselective (61% *ee*) and the acyclic nitron **II** generates the least active system even at higher temperature (0 °C).

The Methacrolein Complexes $[(\eta^6\text{-arene})\text{Ru}(\text{PNiPr})\text{-(methacrolein)}][\text{SbF}_6]_2$ [arene = C₆H₆ (17**), *p*-MeC₆H₄*i*Pr (**18**), C₆Me₆ (**19**)]**

To obtain a deeper insight into the catalytic systems, we studied the solution behaviour of mixtures of aqua complexes $[(\eta^6\text{-arene})\text{Ru}(\text{PNiPr})(\text{H}_2\text{O})]^{2+}$ with methacrolein by NMR spectroscopy. When 4 equiv. of methacrolein were added to solutions of complexes **7–9** at 0 °C, the new complexes $[(\eta^6\text{-arene})\text{Ru}(\text{PNiPr})(\text{methacrolein})]^{2+}$ were formed according to ³¹P NMR spectroscopic measurements. Both complexes are in equilibrium, but in the presence of molecular sieves (4 Å) the position of equilibrium is completely shifted towards the formation of the methacrolein complex. In fact, pure complexes **17–19** were isolated from these solutions in about 40% *de*. The new complexes were characterised by analytical and spectroscopic means. An IR band at ca. 1650 cm⁻¹ along with ¹H NMR peaks at $\delta \approx 9.50$ (CHO) and 6.60 (=CH₂) ppm and a ¹³C NMR resonance at $\delta \approx 213$ ppm are diagnostic of coordinated methacrolein. NOE measurements allowed us to assign the absolute configuration at the metal atom in these complexes. Thus, irradiation of the arene or the CHO protons in the *S*_{Ru} epimers produced NOE enhancement in the H_g or the isopropyl methyl protons of the PNiPr ligand, respectively. On the other hand, irradiation of the CHO proton in the *R*_{Ru} epimers gave enhancement in the H_g proton (Scheme 4). From these data we propose that the major epimer is the *R*_{Ru} isomer for the benzene and hexamethylbenzene complexes **17** and **19** and the *S*_{Ru} isomer for the *p*-MeC₆H₄*i*Pr complex **18**.

On the other hand, the considerable difference in the chemical shift between the two *i*Pr methyl protons of the phosphanyloxazoline ligand of the complexes ($\Delta\delta \approx 1.0$ ppm) at low temperature, could be explained by assuming that the six-membered chelate ring of the phosphanyloxazoline ligand adopts a ¹S₂ screw-boat conforma-

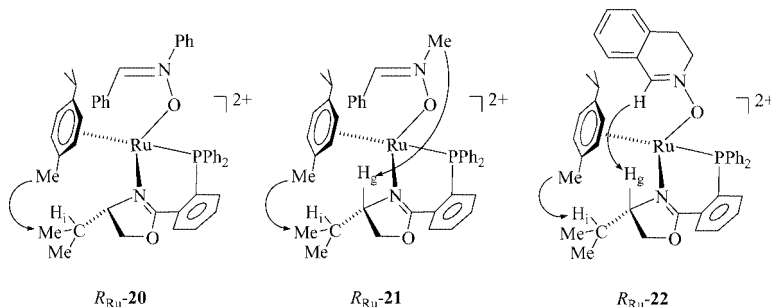


Scheme 4. NOEs observed in complexes **17–19**.

tion^[14] in the ground state. At higher temperature, the NMR spectroscopic data again indicate a fluxional process, most probably involving a flip of the phosphanyloxazoline metallacycle between the ¹S₂ and ²S₁ screw boat conformations.

Complexes $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})\text{Ru}(\text{PNiPr})(\text{nitron})][\text{SbF}_6]_2$ [nitron = **I (**20**), **II** (**21**) and **V** (**22**)]**

The reaction of the nitron with the coordinated alkene is usually the rate- and enantio-determining step for the DCR between nitrones and enals.^[7b] We therefore studied, by NMR spectroscopy, the system generated after addition of a nitron to the methacrolein-containing complex $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})\text{Ru}(\text{PNiPr})(\text{methacrolein})]^{2+}$. While a partial displacement of coordinated methacrolein was observed when nitron **I** was added to complex **18**, nitron **II** readily substituted the coordinated enal, affording the new nitron-containing complex $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4\text{iPr})\text{Ru}(\text{PNiPr})(\text{II})]^{2+}$. It is important to note that in normal-electron-demand DCR, the reaction must occur by dipole attack at the coordinated dipolarophile. To circumvent this problem, we have carried out the catalysis with slow addition of nitrones **II–V** (see Exp. Sect.). From the solution, we have isolated and characterised the nitron complexes **20–22**. One singlet in the $\delta = 8\text{--}8.5$ ppm region of the ¹H NMR spectrum, along with a peak at $\delta \approx 150$ ppm in the ¹³C NMR spectrum (attributed to the N=CH proton and C atom, respectively) strongly support the coordination of the nitron ligand. Only one epimer at metal atom has been detected for these complexes from –90 °C to room temperature. NOE experiments (see Scheme 5) allow us to propose that the solely detected isomer is the *R*_{Ru} epimer. According to the observed $\Delta\delta$ value



Scheme 5. NOEs observed in complexes **20–22**.

in the chemical shift of the isopropyl methyl protons of the phosphanyloxazoline ligand (see above) the metallacycle Ru–P–C–C–N should adopt a 1S_2 screw-boat conformation.^[14]

Conclusions

The half-sandwich ruthenium complexes $[(\eta^6\text{-arene})\text{-Ru}(\text{LL}^*)(\text{H}_2\text{O})]^{2+}$ are efficient catalyst precursors for the DCR of methacrolein with a series of nitrones. Typically, quantitative conversions are achieved at -25°C in a few hours. Perfect diastereoselectivity for the *endo* adducts can be observed but only low to moderate enantioselectivity is obtained. Some structural features of the complexes involved in catalysis are illustrative. Firstly, the methacrolein complexes, presumably the active catalysts, are formed as mixtures of both epimers at the metal atom. Secondly, the metallacycle formed by coordination of the LL^* ligand is conformationally labile. Thirdly, the methacrolein rotamer around the Ru–O bond is not fixed. In the related $[(\eta^5\text{-C}_5\text{Me}_5)\text{M}(\text{R-Prophos})(\text{methacrolein})]^{2+}$ ($\text{M} = \text{Rh}, \text{Ir}$) system, (i) only S_M epimers can be detected, (ii) the metallacycle coordination only presents the λ conformation and is not labile, (iii) $\text{O}=\text{CH}\cdots\pi$ attractive interactions set the conformation around the M–O bond in both the solid state and solution. In particular, a very strong shielding of the $\text{O}=\text{CH}$ proton (about 2.5 ppm) indicates that this rotamer is fixed in solution. However, no significant shielding has been observed for the CHO proton of coordinated methacrolein in the ruthenium complexes reported in this work. In summary, all these structural differences could explain the distinct enantioselective behaviour encountered for these otherwise closely related half-sandwich complexes. The structural analysis carried out in this work provides a useful guide for the a priori selection of new enantioselective catalytic systems. In this context, the isolation of pure R_{Ru} epimers for the nitrone complexes $[(\eta^6\text{-}p\text{-MeC}_6\text{H}_4i\text{Pr})\text{Ru}(\text{PNiPr})(\text{nitrone})]^{2+}$ opens the door to new enantioselective processes that will be investigated in our laboratory in due course.

Experimental Section

General Comments: All solvents were dried with appropriate drying agents, distilled under argon and degassed prior to use. All preparations were carried out under argon. Infrared spectra were obtained as Nujol mulls with a Perkin–Elmer 1330 spectrophotometer. Carbon, hydrogen and nitrogen analyses were performed using a Perkin–Elmer 240C microanalyser. NMR spectra were recorded with a Bruker AV-400 (400.16 MHz) or 300-ARX (300.10 MHz) instrument. Chemical shifts are expressed in ppm upfield from SiMe_4 or 85% H_3PO_4 (^{31}P). NOEDIFF, ^{13}C , ^{31}P and ^1H correlation spectra were obtained using standard procedures. CD spectra were determined in acetone or dichloromethane (ca. $5 \times 10^{-4} \text{ mol L}^{-1}$ solutions) in a cell with 1 cm path length using a Jasco-710 apparatus. The nitrones were prepared according to literature procedures.^[16]

Preparation of the Complexes $[(\eta^6\text{-arene})\text{RuCl}(\text{LL}^*)][\text{SbF}_6]$ (1–4): A mixture of the appropriate $[(\eta^6\text{-arene})\text{RuCl}]_2(\mu\text{-Cl})_2$ (0.25 mmol),

NaSbF_6 (129.4 mg, 0.50 mmol) and the corresponding LL^* ligand (0.50 mmol) in methanol (10 mL) was stirred for 5 h. During this time, the precipitation of an orange solid was observed. The resultant suspension was vacuum-concentrated to dryness. The residue was extracted with dichloromethane ($3 \times 5 \text{ mL}$) and the solution 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. By recrystallisation from methanol/diethyl ether, pure R_{Ru} -4 and mixtures of molar compositions S_{Ru} -1/ R_{Ru} -1 (95:5) and S_{Ru} -4/ R_{Ru} -4 (95:5) were obtained.

Complex 1: Yield 313 mg (76%), 50% *de* in S_{Ru} -1. $\text{C}_{30}\text{H}_{30}\text{ClF}_6\text{NO-PRuSb}$ (823.81): calcd. C 43.74, H 3.67, N 1.70; found C 43.55, H 3.91, N 1.68. IR (Nujol): $\tilde{\nu} = 1603$ (m, CN), 658 (s, SbF_6) cm^{-1} . CD [Me_2CO ; S_{Ru} -1/ R_{Ru} -1 (95:5) mixture; maxima, minima, and nodes]: $\Theta(\lambda) = -10000$ (330), 0 (340), +34000 (365), 0 (410), -4000 (430 nm). S_{Ru} -1: ^1H NMR (CDCl_3): $\delta = 0.12$ (d, $J_{\text{H,H}} = 6.7 \text{ Hz}$, 3 H, *MeMeCH*), 1.04 (d, $J_{\text{H,H}} = 7.2 \text{ Hz}$, 3 H, *MeMeCH*), 1.90 (pseudo-sept, 1 H, *MeMeCH*), 4.53 (m, 3 H, H_g , H_c , H_l), 5.89 (s, 6 H, C_6H_6), 7.1–8.1 (m, 14 H, Ph) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 39.7$ (s) ppm. ^{13}C NMR (CDCl_3): $\delta = 13.44$ (*MeMeCH*), 18.76 (*MeMeCH*), 29.87 (*MeMeCH*), 68.37 (CH_cH_l), 80.93 (CH_g), 92.02 (d, $J_{\text{P,C}} = 3.2 \text{ Hz}$, C_6H_6), 128–134 (Ph), 167.1 (d, $J_{\text{P,C}} = 4.75 \text{ Hz}$, C=N) ppm. R_{Ru} -1: ^1H NMR (CDCl_3): $\delta = 0.90$ (d, $J_{\text{H,H}} = 6.7 \text{ Hz}$, 3 H, *MeMeCH*), 1.19 (d, $J_{\text{H,H}} = 7.2 \text{ Hz}$, 3 H, *MeMeCH*), 2.74 (pseudo-sept, 1 H, *MeMeCH*), 4.58 (m, 2 H, H_c , H_l), 4.76 (m, 1 H, H_g), 5.74 (s, 6 H, C_6H_6), 7.1–8.1 (m, 14 H, Ph) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): $\delta = 41.1$ (s) ppm. ^{13}C NMR (CDCl_3): $\delta = 14.74$ (*MeMeCH*), 18.38 (*MeMeCH*), 29.32 (*MeMeCH*), 69.16 (CH_cH_l), 78.48 (CH_g), 91.51 (d, $J_{\text{P,C}} = 2.4 \text{ Hz}$, C_6H_6), 128–134 (Ph) ppm.

Complex 2: Yield: 427 mg (94%), 12% *de* in R_{Ru} -2. $\text{C}_{36}\text{H}_{42}\text{ClF}_6\text{NOPRuSb}$ (907.97): calcd. C 47.60, H 4.66, N 1.54; found C 47.74, H 4.30, N 1.38. IR (Nujol): $\tilde{\nu} = 1591$ (m, CN), 657 (s, SbF_6) cm^{-1} . S_{Ru} -2: ^1H NMR (CD_2Cl_2): $\delta = 0.28$ (d, $J_{\text{H,H}} = 6.8 \text{ Hz}$, 3 H, *MeMeCH*), 1.12 (d, $J_{\text{H,H}} = 7.2 \text{ Hz}$, 3 H, *MeMeCH*), 1.92 (s, 18 H, C_6Me_6), 2.01 (m, 1 H, *MeMeCH*), 4.20 (dpt, $J_{\text{Ht,Hg}} = 8.4 \text{ Hz}$, $J_{\text{Hc,Hg}} \approx J_{\text{Hi,Hg}} = 2.7 \text{ Hz}$, 1 H, H_g), 4.30 (pt, $J_{\text{Hc,Ht}} = 8.6 \text{ Hz}$, 1 H, H_l), 4.53 (dd, 1 H, H_c), 7.3–7.8 (m, 14 H, Ph) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 42.9$ (br. s) ppm. ^{13}C NMR (CD_2Cl_2): $\delta = 14.41$ (*MeMeCH*), 15.94 (C_6Me_6), 18.31 (*MeMeCH*), 29.77 (*MeMeCH*), 67.57 (CH_cH_l), 76.30 (CH_g), 101.84 (d, $J_{\text{P,C}} = 2.8 \text{ Hz}$, C_6Me_6), 129–135 (Ph) ppm. R_{Ru} -2: ^1H NMR (CD_2Cl_2): $\delta = 0.67$ (d, $J_{\text{H,H}} = 6.7 \text{ Hz}$, 3 H, *MeMeCH*), 1.14 (d, $J_{\text{H,H}} = 7.2 \text{ Hz}$, 3 H, *MeMeCH*), 1.87 (s, 18, C_6Me_6), 2.20 (m, 1 H, *MeMeCH*), 4.25 (dpt, $J_{\text{Ht,Hg}} = 8.4 \text{ Hz}$, $J_{\text{Hc,Hg}} \approx J_{\text{Hi,Hg}} = 2.7 \text{ Hz}$, 1 H, H_g), 4.37 (pt, $J_{\text{Hc,Ht}} = 8.4 \text{ Hz}$, 1 H, H_l), 4.63 (dd, 1 H, H_c), 7.3–7.8 (m, 14 H, Ph) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): $\delta = 44.5$ (s) ppm. ^{13}C NMR (CD_2Cl_2): $\delta = 14.66$ (*MeMeCH*), 16.44 (C_6Me_6), 18.44 (*MeMeCH*), 28.96 (*MeMeCH*), 68.56 (CH_cH_l), 76.02 (CH_g), 101.65 (d, $J_{\text{P,C}} = 2.8 \text{ Hz}$, C_6Me_6), 129–135 (Ph) ppm.

Complex 3: Yield: 370 mg (85%), 96% *de* in R_{Ru} -3. $\text{C}_{34}\text{H}_{28}\text{ClF}_6\text{NOPRuSb}$ (869.84): calcd. C 46.95, H 3.24, N 1.61; found C 46.71, H 2.94, N 1.60. IR (Nujol): $\tilde{\nu} = 1588$ (m, CN), 659 (s, SbF_6) cm^{-1} . CD [Me_2CO ; S_{Ru} -3/ R_{Ru} -3 (2:98) mixture; maxima, minima and nodes]: $\Theta(\lambda) = +16000$ (330), 0 (340), -42000 (370 nm). S_{Ru} -3: $^{31}\text{P}\{^1\text{H}\}$ NMR [$(\text{CD}_3)_2\text{CO}$]: $\delta = 39.7$ (s) ppm. ^{13}C NMR [$(\text{CD}_3)_2\text{CO}$]: $\delta = 92.67$ (d, $J_{\text{P,C}} = 2.8$, C_6H_6) ppm. R_{Ru} -3: ^1H NMR [$(\text{CD}_3)_2\text{CO}$]: $\delta = 3.55$, 3.62 (AB part of an ABX system, $J_{\text{A,B}} = 18.0 \text{ Hz}$, $J_{\text{A,X}} = 4.0 \text{ Hz}$, $J_{\text{B,X}} \approx 0 \text{ Hz}$, 2 H, H_c , H_l), 5.84 (pt, $J_{\text{Ht,Ho}} = J_{\text{Hn,Ho}} = 5.0 \text{ Hz}$, H_o), 6.10 (d, 1 H, H_n), 6.24 (s, 6 H, C_6H_6), 6.53 (br. d, $J_{\text{Ha,Hb}} = 6.2$, 1 H, H_a), 6.83 (pt, 1 H, H_b), 6.9–8.1 (m, 16 H, Ph) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR [$(\text{CD}_3)_2\text{CO}$]: $\delta = 37.39$ (br. s) ppm. ^{13}C NMR [$(\text{CD}_3)_2\text{CO}$]: $\delta = 36.54$ (CH_cH_l), 83.03 (CH_n),

87.07 (CH₃); 91.90 (d, $J_{\text{PC}} = 2.8$, C₆H₆), 124–140 (Ph), 168.79 (d, $J_{\text{PC}} = 4.18$, C=N) ppm.

Complex 4: Yield: 425 mg (89%), 10% *de* in $S_{\text{Ru-4}}$. C₄₀H₄₀ClF₆NOPRuSb (954.00): calcd. C 50.36, H 4.23, N 1.47; found C 50.42, H 4.10, N 1.38. IR (Nujol): $\tilde{\nu} = 1595$ (m, CN), 654 (s, SbF₆) cm⁻¹. $S_{\text{Ru-4}}$: ¹H NMR [(CD₃)₂CO]: $\delta = 1.99$ (s, 18 H, C₆Me₆), 3.52 (m, 2 H, H_c, H_t), 5.81 (d, 1 H, $J_{\text{Hn,Ho}} = 5.7$ Hz, H_n), 5.85 (m, 1 H, H_o), 6.9–8.1 (m, Ph) ppm. ³¹P{¹H} NMR [(CD₃)₂CO]: $\delta = 37.4$ (br. s) ppm. ¹³C NMR [(CD₃)₂CO]: $\delta = 15.26$ (C₆Me₆), 36.30 (CH₂H_i), 79.31 (CH_n), 89.00 (CH_o), 101.02 (d, $J_{\text{PC}} = 3.0$ Hz, C₆Me₆), 124–139 (Ph), 168.24 (d, $J_{\text{PC}} = 7.2$ Hz, C=N) ppm. $R_{\text{Ru-4}}$: ¹H NMR [(CD₃)₂CO]: $\delta = 1.56$ (s, 18 H, C₆Me₆), 3.61 (m, 2 H, H_c, H_i), 4.55 (d, 1 H, $J_{\text{Ho,Hn}} = 9.0$ Hz, H_n), 5.49 (m, $J_{\text{Ht,Ho}} = J_{\text{Hc,Ho}} = 6.8$ Hz, H_o), 7.1–8.5 (m, Ph) ppm. ³¹P{¹H} NMR [(CD₃)₂CO]: $\delta = 28.66$ (s) ppm. ¹³C NMR [(CD₃)₂CO]: $\delta = 14.93$ (C₆Me₆), 39.59 (CH₂H_i), 77.90 (CH_n), 85.61 (CH_o), 91.90 (d, $J_{\text{PC}} = 2.8$ Hz), 100.79 (d, $J_{\text{PC}} = 2.9$ Hz, C₆Me₆), 125–142 (Ph), 167.54 (d, $J_{\text{PC}} = 8.8$ Hz, C=N) ppm.

Preparation of the Complexes [(η⁶-arene)Ru(LL*)(H₂O)][SbF₆]₂ (7, 8, 10, 11): To a solution of the corresponding chloro compounds 1–4 (0.20 mmol) in dichloromethane (25 mL) was added AgSbF₆ (68.7 mg, 0.20 mmol) in acetone (2 mL). 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 hexane (20 mL) afforded an orange oil that was converted into a solid powder after vigorous stirring. The solid was filtered, washed with hexane and dried under vacuum.

Complex 7: Yield: 150 mg (84%), 72% *de* in $R_{\text{Ru-7}}$. C₃₀H₃₂F₁₂NO₂-PRuSb₂ (1042.11): calcd. C 34.58, H 3.09, N 1.34; found C 34.71, H 3.26, N 1.30. IR (Nujol): $\tilde{\nu} = 3427$ (m, H₂O), 1598 (s, CN), 658 (vs, SbF₆) cm⁻¹. CD [Me₂CO, $R_{\text{Ru-7}}$ / $S_{\text{Ru-7}}$ (90:10) mixture, maxima, minima, and nodes]: $\theta(\lambda) = +46000$ (360), 0 (400), -6000 (425 nm). $R_{\text{Ru-7}}$: ¹H NMR (CD₂Cl₂): $\delta = 0.01$ (d, $J_{\text{H,H}} = 6.5$ Hz, 3 H, MeMeCH), 1.03 (d, $J_{\text{H,H}} = 6.9$ Hz, 3 H, MeMeCH), 1.66 (m, 1 H, MeMeCH), 4.64, 4.79 (m, 3 H, H_g, H_c, H_i), 6.13 (s, 6 H, C₆H₆), 7.1–8.2 (m, Ph) ppm. ³¹P{¹H} NMR (CD₂Cl₂): $\delta = 39.05$ (s) ppm. ¹³C NMR [(CD₃)₂CO]: $\delta = 12.79$ (MeMeCH), 18.07 (MeMeCH), 29.0 (MeMeCH), 69.21 (CH₂H_i), 80.64 (CH₂), 90.61 (d, $J_{\text{PC}} = 2.4$ Hz, C₆H₆), 126–135 (Ph), 167.41 (d, $J_{\text{PC}} = 6.7$ Hz, C=N) ppm. $S_{\text{Ru-7}}$: ¹H NMR (CD₂Cl₂): $\delta = 0.86$ (d, $J_{\text{H,H}} = 6.6$ Hz, 3 H, MeMeCH), 1.25 (d, $J_{\text{H,H}} = 6.9$ Hz, 3 H, MeMeCH), 6.00 (s, 6 H, C₆H₆), 7.1–8.2 (m, Ph) ppm. ³¹P{¹H} NMR (CD₂Cl₂): $\delta = 40.2$ (s) ppm. ¹³C NMR [(CD₃)₂CO]: $\delta = 91.24$ (d, $J_{\text{PC}} = 2.4$ Hz, C₆H₆) ppm.

Complex 8: Yield: 221 mg (98%), 94% *de* in $R_{\text{Ru-8}}$. C₃₆H₄₄F₁₂NO₂-PRuSb₂ (1126.27): calcd. C 38.39, H 3.94, N 1.24; found C 38.27, H 3.76, N 1.13. IR (Nujol): $\tilde{\nu} = 3370$ (w, H₂O), 1645 (m), 1591 (m, CN), 657 (s, SbF₆) cm⁻¹. CD [Me₂CO, $R_{\text{Ru-8}}$ / $S_{\text{Ru-8}}$ (97:3) mixture; maxima, minima and nodes]: $\theta(\lambda) = -12000$ (330), 0 (360), +18500 (390 nm). $R_{\text{Ru-8}}$: ¹H NMR (CD₂Cl₂): $\delta = 0.00$ (br. d), 0.50 (br. d), 1.15 (br. d, Me₂CH), 1.97 (br. s), 2.12 (br. s, C₆Me₆), 4.55 (br. m), 4.64 (br. m, H_c, H_t, H_g). ¹H NMR [(CD₃)₂CO, -30 °C]: $\delta = -0.05$ (d, $J_{\text{H,H}} = 6.5$ Hz, 3 H, MeMeCH), 1.12 (d, $J_{\text{H,H}} = 6.8$ Hz, 3 H, MeMeCH), 2.10 (m, 1 H, MeMeCH), 2.15 (s, 18 H, C₆Me₆), 4.66 (pt, $J_{\text{Ht,Hc}} = J_{\text{Ht,Hg}} = 9.2$ Hz, 1 H, H_i), 4.92 (m, 2 H, H_c, H_g), 5.20 (s, 2 H, H₂O), 7.4–8.2 (m, Ph) ppm. ³¹P{¹H} NMR (CD₂Cl₂, -90 °C): $\delta = 45.0$ (br. s) ppm. ³¹P{¹H} NMR [(CD₃)₂CO, -30 °C]: $\delta = 44.73$ (s) ppm. ¹³C NMR [(CD₃)₂CO, -30 °C]: $\delta = 13.34$ (MeMeCH), 16.17 (C₆Me₆), 17.72 (MeMeCH), 23–30 (MeMeCH), 68.55 (CH₂H_i), 76.25 (CH₂), 101.35 (d, $J_{\text{PC}} = 2.3$ Hz, C₆Me₆), 125–136 (Ph), 167.91 (d, $J_{\text{PC}} = 4.6$ Hz, C=N). $S_{\text{Ru-8}}$: ³¹P{¹H} NMR (CD₂Cl₂, -90 °C): $\delta = 42.7$ (br. s) ppm.

Complex 10: Yield: 168 mg (77%), 86% *de* in $S_{\text{Ru-10}}$. C₃₄H₃₀F₁₂NO₂PRuSb₂ (1088.14): calcd. C 37.53, H 2.78, N 1.29; found C 37.04, H 2.80, N 1.20. IR (Nujol): $\tilde{\nu} = 3442$ (m, H₂O), 1644(m), 1595 (m, CN), 660 (s, SbF₆) cm⁻¹. CD [CH₂Cl₂; $R_{\text{Ru-10}}$ / $S_{\text{Ru-10}}$ (7:93) mixture; maxima, minima and nodes]: $\theta(\lambda) = +16000$ (300), 0 (320), -62000 (360), 0 (420), +2000 (430 nm). $R_{\text{Ru-10}}$: ¹H NMR (CD₂Cl₂): $\delta = 4.56$ (s, 2 H, H₂O), 6.13 (s, 6 H, C₆H₆) ppm. ³¹P{¹H} NMR (CD₂Cl₂): $\delta = 39.4$ (s) ppm. ¹³C NMR (CD₂Cl₂): $\delta = 91.13$ (d, $J_{\text{PC}} = 2.3$ Hz, C₆H₆) ppm. $S_{\text{Ru-10}}$: ¹H NMR (CD₂Cl₂): $\delta = 3.62$ (m, 2 H, H_c, H_i), 4.90 (s, 2 H, H₂O), 5.94 (m, 2 H, H_o, H_a), 6.04 (d, $J_{\text{Hn,Ho}} = 6.04$ Hz, 1 H, H_n), 6.24 (s, 6 H, C₆H₆), 6.69 (m, 1 H, H_b), 6.6–8.2 (m, Ph) ppm. ³¹P{¹H} NMR (CD₂Cl₂): $\delta = 36.6$ (br. s), 38.13 (s) ppm. ¹³C NMR (CD₂Cl₂): $\delta = 36.53$ (CH₂H_i), 83.51 (CH_n), 88.33 (CH_o), 90.28 (d, $J_{\text{PC}} = 2.3$ Hz, C₆H₆), 90.47 (d, $J_{\text{PC}} = 3.1$ Hz, C₆H₆), 122.65 (CH_a), 124–140 (Ph), 168.79 (d, $J_{\text{PC}} = 4.7$, C=N) ppm.

Complex 11: Yield: 174 mg (73%), 40% *de* in $S_{\text{Ru-11}}$. C₄₀H₄₃F₁₂NO₃PRuSb₂ (1190.32): calcd. C 40.36, H 3.55, N 1.17; found C 39.73, H 3.75, N 1.15. IR (Nujol): $\tilde{\nu} = 3370$ (w, H₂O), 1624 (s), 1596 (m, CN), 660 (m, SbF₆) cm⁻¹. CD [Me₂CO; $R_{\text{Ru-11}}$ / $S_{\text{Ru-11}}$ (30:70) mixture; maxima, minima and nodes]: $\theta(\lambda) = +8500$ (330), 0 (340), -17500 (390 nm). $R_{\text{Ru-11}}$: ¹H NMR [(CD₃)₂CO]: $\delta = 2.27$ (s, 18 H, C₆Me₆) ppm. ³¹P{¹H} NMR [(CD₃)₂CO]: $\delta = 41.0$ (br. s) ppm. ¹³C NMR [(CD₃)₂CO]: $\delta = 17.34$ (C₆Me₆), 102.32 (d, $J_{\text{PC}} = 2.4$ Hz, C₆Me₆), 171.0 (d, $J_{\text{PC}} = 4.0$ Hz, C=N) ppm. $S_{\text{Ru-11}}$: ¹H NMR [(CD₃)₂CO]: $\delta = 2.12$ (s, 18 H, C₆Me₆), 3.55, 3.63 (AB part of an ABX system, $J_{\text{A,B}} = 18.0$ Hz, $J_{\text{A,X}} = 4.3$ Hz, $J_{\text{B,X}} \approx 0$ Hz, 2 H, H_c, H_i), 6.05 (d, 1 H, $J_{\text{Hn,Ho}} = 5.7$ Hz, H_n), 6.12 (m, 1 H, H_o), 6.6–8.4 (m, Ph) ppm. ³¹P{¹H} NMR [(CD₃)₂CO]: $\delta = 37.3$ (br. s) ppm. ¹³C NMR [(CD₃)₂CO]: $\delta = 10.61$ (C₆Me₆), 37.18 (CH₂H_i), 80.30 (CH_n), 91.77 (CH_o), 101.77 (d, $J_{\text{PC}} = 1.6$ Hz, C₆Me₆), 126–141 (Ph), 170.73 (d, $J_{\text{PC}} = 7.2$ Hz, C=N) ppm.

Preparation of the Complexes [(η⁶-p-MeC₆H₄iPr)Ru(LL*)(H₂O)][SbF₆]₂ [LL* = *R*-Prophos (13); 2,3-Bis(diphenylphosphanyl)-butane, *R,R*-Chiraphos (14)]: To a suspension of [(η⁶-p-MeC₆H₄iPr)Ru]₂(μ-Cl)₂ (102.3 mg, 0.17 mmol) in acetone (7 mL) was added AgSbF₆ (229.6 mg, 0.68 mmol). The resultant suspension was stirred for 30 min and the AgCl formed was filtered off. Solid LL* (0.34 mmol) was added to the filtrate and the resultant solution was stirred for 30 min. Slow addition of hexane (20 mL) afforded an orange oil which could be converted into a solid powder after vigorous stirring. The solid was filtered, washed with hexane and dried under vacuum.

Complex 13: Yield: 290 mg (75%), pure $S_{\text{Ru-13}}$. C₃₇H₄₂F₁₂OP₂-RuSb₂ (1136.91): calcd. C 39.07, H 3.72; found C 38.94, H 3.44. IR (Nujol): $\tilde{\nu} = 3603$ (br., H₂O), 1643 (m), 658 (s, SbF₆) cm⁻¹. ¹H NMR (CD₂Cl₂): $\delta = 0.93$ (d, $J_{\text{H,H}} = 6.6$ Hz, 3 H, MeMeCH), 0.95 (d, $J_{\text{H,H}} = 6.6$ Hz, 3 H, MeMeCH), 1.16 (dd, $J_{\text{PH}} = 12.9$, $J_{\text{H,H}} = 6.6$ Hz, 3 H, Me), 1.65 (s, 3 H, Me of *p*-MeC₆H₄iPr), 1.95 (m, 1 H, H_i), 2.45 (pseudo-sept, 1 H, MeMeCH), 2.45(m, 1 H, H_g), 2.88 (br. s, 2 H, H₂O), 3.05 (m, 1 H, H_c), 5.39 (d, $J_{\text{A,B}} = 6.2$ Hz, 1 H, H_AH_B), 5.97 (d, $J_{\text{A',B'}} = 6.6$ Hz, 1 H, H_{A'}H_{B'}), 6.02 (d, 1 H, H_AH_B), 6.06 (d, 1 H, H_{A'}H_{B'}), 7.1–7.9 (m, Ph) ppm. ³¹P{¹H} NMR (CD₂Cl₂): $\delta = 54.1$ (d, $J_{\text{P1,P2}} = 42.1$ Hz, P¹), 76.45 (d, P²) ppm. ¹³C NMR (CD₂Cl₂): $\delta = 15.08$ (dd, $J = 18.3$, 5.1 Hz, Me), 17.63 (Me of *p*-MeC₆H₄iPr), 21.55, 22.45 (MeMeCH), 30.46 (dd, $J_{\text{PC}} = 30.7$, 9.5 Hz, CMe), 30.96 (MeMeCH), 31.95 (dd, $J_{\text{PC}} = 34.4$, 15.4 Hz, CH₂H_i), 87.22, 91.95, 93.05 (d, $J_{\text{PC}} = 4.4$ Hz), 93.46 (C of *p*-MeC₆H₄iPr), 109.54 (CMe of *p*-MeC₆H₄iPr), 124.39 (dd, $J_{\text{PC}} = 4.4$, $J = 2.2$ Hz, CCMe₂H), 121–136 (Ph) ppm.

Complex 14: Yield: 317 mg (81%). C₃₈H₃₄F₁₂OP₂RuSb₂ (1151.26): calcd. C 39.64, H 3.67; found C 40.01, H 3.39. IR (Nujol): $\tilde{\nu} =$

3524 (br., H₂O), 1644 (s), 660 (s, SbF₆) cm⁻¹. ¹H NMR (CD₂Cl₂): δ = 0.83 (d, $J_{\text{H,H}}$ = 7.3 Hz, 3 H, *MeMeCH*), 0.88 (d, $J_{\text{H,H}}$ = 7.3 Hz, 3 H, *MeMeCH*), 0.95 (dd, $J_{\text{P,H}}$ = 13.9, $J_{\text{H,H}}$ = 6.6 Hz, 3 H, Me), 1.10 (dd, $J_{\text{P,H}}$ = 13.9, $J_{\text{H,H}}$ = 6.6 Hz, 3 H, Me), 1.62 (s, 3 H, Me of *p*-MeC₆H₄iPr), 2.16 (pseudo-sept, 1 H, *MeMeCH*), 2.30, 2.53 (m, 2 H, *CHMe*), 5.45 (d, $J_{\text{A,B}}$ = 6.3 Hz, 1 H, H_AH_B), 5.58 (d, $J_{\text{A',B'}}$ = 6.3 Hz, 1 H, H_{A'}H_{B'}), 5.80 (d, 2 H, H_AH_B, H_{A'}H_{B'}), 7.0–7.8 (m, Ph) ppm. ³¹P{¹H} NMR (CD₂Cl₂): δ = 74.9, 68.3 (d, $J_{\text{P1,P2}}$ = 48.4 Hz) ppm. ¹³C NMR (CD₂Cl₂): δ = 13.17 (dd, J = 17.6, 5.9 Hz, Me), 15.14 (dd, J = 16.8, 4.4 Hz, Me), 18.13 (Me of *p*-MeC₆H₄iPr), 21.94, 22.69 (*MeMeCH*), 30.58 (*MeMeCH*), 34.03 (dd, $J_{\text{P,C}}$ = 32.2, 11.0 Hz, CMe), 43.45 (dd, $J_{\text{P,C}}$ = 32.9, 15.4 Hz, CMe), 89.82 (d, $J_{\text{P,C}}$ = 2.2 Hz), 90.11 (d, $J_{\text{P,C}}$ = 2.9 Hz), 93.08, 93.21 (C of *p*-MeC₆H₄iPr), 105.25 (CMe of *p*-MeC₆H₄iPr), 114.23 (CCMe₂H), 121–135 (Ph) ppm.

Catalytic Procedure: The complexes [(η⁶-arene)Ru(LL*)(H₂O)](A)₂ (0.06 mmol, 5 mol-%) were dissolved in CH₂Cl₂ (3 mL) at 0 °C. Freshly distilled methacrolein [0.14 mL (1.68 mmol) or 0.70 mL (8.40 mmol)] and activated molecular sieves (4 Å) (100.0 mg) were added and the suspension was stirred for 30 min. A solution of the corresponding nitron (1.20 mmol) in CH₂Cl₂ (2 mL) was added. For nitrones II–V, the nitron solution was added dropwise with a syringe pump over 15 h. After stirring at the appropriate temperature for the reaction time indicated in the tables, hexanes (20 mL) were added. After filtration through diatomaceous earth, the solution was concentrated to dryness. The residue was purified by chromatography (SiO₂) to provide a mixture of the corresponding isomers. Regioselectivity was determined on the crude mixture by ¹H NMR spectroscopic analysis in C₆D₆ (nitrones I, II, and V) or CDCl₃ (nitrones III and IV). Enantioselectivity was determined as indicated in the footnote of Tables 2 and 5.

Preparation of the Complexes [(η⁶-arene)Ru(PNiPr)(methacrolein)]-[SbF₆]₂ [arene = C₆H₆ (17), *p*-MeC₆H₄iPr (18), C₆Me₆ (19)]: To a solution of the corresponding aqua complex [(η⁶-arene)Ru(PNiPr)(H₂O)](SbF₆)₂ (0.10 mmol) in CH₂Cl₂ (5 mL) at 0 °C under argon, methacrolein (33.0 μL, 0.395 mmol) and molecular sieves (4 Å) (200.0 mg) were added. The solutions were stirred for 20 min and the solvent was then vacuum-evaporated. The residues were extracted with CH₂Cl₂ (3 × 2 mL). Addition of dry hexane (20 mL) to the yellow filtrate afforded yellow solids which were washed with hexane and vacuum-dried.

Complex 17: Yield: 61 mg, (63%), 40% *de* in *R*_{Ru}-17. C₃₃H₃₅F₁₂NO₂PRuSb₂ (1093.77): calcd. C 36.23, H 3.22, N 1.28; found C 36.39, H 3.57, N 1.38. IR (Nujol): $\tilde{\nu}$ = 1687 (m, CO), 1599 (s, CN), 660 (s, SbF₆) cm⁻¹. *R*_{Ru}-17: ¹H NMR (CD₂Cl₂, 0 °C): δ = -0.05 (d, $J_{\text{H,H}}$ = 6.6 Hz, 3 H, *MeMeCH*), 1.01 (d, $J_{\text{H,H}}$ = 7.3 Hz, 3 H, *MeMeCH*), 1.03 [s, 3 H, CHO(CH₃)CHH], 1.63 (pseudo-sept, 1 H, *MeMeCH*), 4.63, 4.80 (m, 2 H, H_C, H_I), 4.81 (m, 1 H, H_G), 6.17 (s, C₆H₆), 6.66 [s, 2 H, CHOC(CH₃)CHH], 7.1–8.0 (m, 14 H, Ph), 9.80 (s, 1 H, COH) ppm. ³¹P{¹H} NMR (CD₂Cl₂, 0 °C): δ = 39.6 (s) ppm. ¹³C NMR (CD₂Cl₂, 0 °C): δ = 12.5 [CHOC(CH₃)CHH], 12.59 (*MeMeCH*), 18.66 (*MeMeCH*), 30.24 (*MeMeCH*), 69.51 (CH_CH_I), 80.29 (CH_G), 90.58 (C₆H₆), 124–135 (Ph), 145.62 [CHOC(CH₃)CHH], 149.07 [CHOC(CH₃)CHH], 166.82 (d, $J_{\text{P,C}}$ = 4.6 Hz, C=N), 214.81 (CHO) ppm. *S*_{Ru}-17: ¹H NMR (CD₂Cl₂, 0 °C): δ = 0.73 (d, $J_{\text{H,H}}$ = 6.6 Hz, 3 H, *MeMeCH*), 1.24 (d, $J_{\text{H,H}}$ = 6.5 Hz, 3 H, *MeMeCH*), 1.01 [s, 3 H, CHO(CH₃)CHH], 2.70 (pseudo-sept, 1 H, *MeMeCH*), 4.77 (m, 1 H, H_G), 6.05 (s, C₆H₆), 6.60, 6.63 [s, 2 H, CHOC(CH₃)CHH], 7.1–8.0 (m, 14 H, Ph), 9.51 (s, 1 H, COH) ppm. ³¹P{¹H} NMR (CD₂Cl₂, 0 °C): δ = 40.75 (s) ppm. ¹³C NMR (CD₂Cl₂, 0 °C): δ = 12.75 [CHOC(CH₃)CHH], 14.23 (*MeMeCH*), 18.08 (*MeMeCH*), 29.57 (*MeMeCH*), 70.02

(CH_CH_I), 78.11 (CH_G), 91.30 (C₆H₆), 124–135 (Ph), 144.73 [CHOC(CH₃)CHH], 149.02 [CHOC(CH₃)CHH], 166.45 (d, $J_{\text{P,C}}$ = 9.1 Hz, C=N), 214.27 (CHO) ppm.

Complex 18: Yield: 102 mg (88.5%), 36% *de* in *S*_{Ru}-18. C₃₈H₄₄F₁₂NO₂PRuSb₂ (1150.30): calcd. C 39.68, H 3.85, N 1.21; found C 39.44, H 4.01, N 1.14. IR (Nujol): $\tilde{\nu}$ = 1687 (m, CO), 1598 (m, CN), 659 (s, SbF₆) cm⁻¹. *R*_{Ru}-18: ¹H NMR (CD₂Cl₂, -50 °C): δ = 0.14 (d, $J_{\text{H,H}}$ = 6.3 Hz, 3 H, *MeMeCH*), 1.06 (d, $J_{\text{H,H}}$ = 6.7 Hz, 3 H, *MeMeCH*), 1.11 (d, $J_{\text{H,H}}$ = 7.2 Hz, 3 H, *MeMeCH*, MeC₆H₄iPr), 1.12 (s, 3 H, CHOC(CH₃)CHH), 1.26 (d, $J_{\text{H,H}}$ = 6.3 Hz, 3 H, *MeMeCH*, MeC₆H₄iPr), 1.73 (pseudo-sept, 1 H, *MeMeCH*), 1.92 (s, 3 H, Me, MeC₆H₄iPr), 2.41 (pseudo-sept, 1 H, *MeMeCH*, MeC₆H₄iPr), 4.70–4.76 (m, 3 H, H_G, H_C, H_I), 5.56 (d, $J_{\text{A,B}}$ = 6.1 Hz, 1 H, H_AH_B), 5.82 (d, 1 H, H_AH_B), 6.04 (d, $J_{\text{A',B'}}$ = 6.3 Hz, 1 H, H_{A'}H_{B'}), 6.39 (d, 1 H, H_{A'}H_{B'}), 6.66 (s, 2 H, CHOC(CH₃)CHH), 7.1–8.1 (m, 14 H, Ph), 9.64 (s, 1 H, CHO) ppm. ³¹P{¹H} NMR (CD₂Cl₂, -50 °C): δ = 39.0 (s) ppm. ¹³C NMR (CD₂Cl₂, -50 °C): δ = 13.5 [CHOC(CH₃)CHH], 13.4 (*MeMeCH*), 19.0 (Me, MeC₆H₄iPr), 18.9 (*MeMeCH*), 23.2 (*MeMeCH*, MeC₆H₄iPr), 30.3 (*MeMeCH*), 32.1 (*MeMeCH*, MeC₆H₄iPr), 69.6 (CH_CH_I), 79.8 (CH_G), 86.6, 87.4, 89.7, 92.2 (C, MeC₆H₄iPr), 101.7, 120.1 (d, $J_{\text{P,C}}$ = 4.3 Hz), (CMe and CCMe₂H, MeC₆H₄iPr), 124–136 (Ph), 145.9 [CHOC(CH₃)CHH], 150.1 [CHOC(CH₃)CHH], 167.6 (d, $J_{\text{P,C}}$ = 5.1 Hz, C=N), 214.1 (CHO) ppm. *S*_{Ru}-18: ¹H NMR (CD₂Cl₂, -50 °C): δ = 0.76 (d, $J_{\text{H,H}}$ = 6.3 Hz, 3 H, *MeMeCH*), 0.96 (d, $J_{\text{H,H}}$ = 7.2 Hz, 3 H, *MeMeCH*, MeC₆H₄iPr), 0.98 (d, $J_{\text{H,H}}$ = 7.4 Hz, 3 H, *MeMeCH*, MeC₆H₄iPr), 1.05 [s, 3 H, CHO(CH₃)CHH], 1.26 (d, $J_{\text{H,H}}$ = 6.3 Hz, 3 H, *MeMeCH*), 1.97 (s, 3 H, Me, MeC₆H₄iPr), 2.49 (pseudo-sept, 1 H, *MeMeCH*, MeC₆H₄iPr), 2.64 (pseudo-sept, 1 H, *MeMeCH*), 4.5, 4.82 (m, 2 H, H_C, H_I), 4.63 (m, 1 H, H_G), 5.69 (d, $J_{\text{A,B}}$ = 6.5 Hz, 1 H, H_AH_B), 5.75 (d, 1 H, H_AH_B), 5.93 (d, $J_{\text{A',B'}}$ = 6.0 Hz, 1 H, H_{A'}H_{B'}), 6.24 (d, 1 H, H_{A'}H_{B'}), 6.69 [s, 2 H, CHOC(CH₃)CHH], 7.1–8.1 (m, 14 H, Ph), 9.56 (s, 1 H, COH) ppm. ³¹P{¹H} NMR (CD₂Cl₂, -50 °C): δ = 40.4 (s) ppm. ¹³C NMR (CD₂Cl₂, -50 °C): δ = 13.6 [CHOC(CH₃)CHH], 14.6 (*MeMeCH*), 18.4 (*MeMeCH*), 18.5 (Me, MeC₆H₄iPr), 21.8, 22.0 (*MeMeCH*, MeC₆H₄iPr), 29.9 (*MeMeCH*), 32.3 (*MeMeCH*, MeC₆H₄iPr), 70.5 (CH_CH_I), 77.9 (CH_G), 87.9, 91.0, 91.9, 94.4 (C, MeC₆H₄iPr), 99.3 (d, $J_{\text{P,C}}$ = 3.3, CMe, MeC₆H₄iPr); 115.5 (d, $J_{\text{P,C}}$ = 3.3 Hz, CCMe₂H, MeC₆H₄iPr), 124–136 (Ph), 145.3 [CHOC(CH₃)CHH], 150.0 [CHOC(CH₃)CHH], 167.4 (d, $J_{\text{P,C}}$ = 8.4 Hz, C=N), 213.8 (CHO) ppm.

Complex 19: Yield: 111 mg, (94%), 40% *de* in *R*_{Ru}-19. C₃₉H₄₇F₁₂NO₂PRuSb₂ (1178.35): calcd. C 40.77, H 4.10, N 1.18; found C 40.44, H 4.01, N 1.12. IR (Nujol): $\tilde{\nu}$ = 1688 (m, CO), 1598 (s, CN), 660 (s, SbF₆) cm⁻¹. *R*_{Ru}-19: ¹H NMR (CD₂Cl₂, -30 °C): δ = 0.06 (d, $J_{\text{H,H}}$ = 6.2 Hz, 3 H, *MeMeCH*), 1.13 (m, 3 H, *MeMeCH*), 1.20 [s, 3 H, CHO(CH₃)CHH], 1.90 (pseudo-sept, 1 H, *MeMeCH*), 1.92 (C₆Me₆), 4.7 (m, 3 H, H_C, H_G, H_I), 6.71, 6.77 [s, 2 H, CHOC(CH₃)CHH], 7.3–7.9 (m, 14 H, Ph), 9.42 (s, 1 H, COH) ppm. ³¹P{¹H} NMR (CD₂Cl₂, -30 °C): δ = 43.3 (s) ppm. ¹³C NMR (CD₂Cl₂, -30 °C): δ = 13.60 [CHOC(CH₃)CHH], 13.99 (*MeMeCH*), 16.35 (C₆Me₆), 18.33 (*MeMeCH*), 30.03 (*MeMeCH*), 68.91 (CH_CH_I), 76.21 (CH_G), 101.81 (d, $J_{\text{P,C}}$ = 2.3 Hz, C₆Me₆), 123–135 (Ph), 145.76 [CHOC(CH₃)CHH], 149.84 [CHOC(CH₃)CHH], 167.36 (d, $J_{\text{P,C}}$ = 5.7 Hz, C=N), 212.65 (CHO) ppm. *S*_{Ru}-19: ¹H NMR (CD₂Cl₂, -30 °C): δ = 0.73 (d, $J_{\text{H,H}}$ = 6.7 Hz, 3 H, *MeMeCH*), 1.29 (d, $J_{\text{H,H}}$ = 6.7 Hz, 3 H, *MeMeCH*), 1.12 [s, 3 H, CHO(CH₃)CHH], 1.89 (C₆Me₆), 2.10 (pseudo-sept, 1 H, *MeMeCH*), 4.47 (m, 1 H, H_G), 4.62, 4.75 (m, 2 H, H_C, H_I), 6.58, 6.69 [s, 2 H, CHOC(CH₃)CHH], 7.3–7.9 (m, 14 H, Ph), 9.24 (s, 1 H, COH) ppm. ³¹P{¹H} NMR (CD₂Cl₂, -30 °C): δ = 45.57 (s) ppm. ¹³C NMR (CD₂Cl₂, -30 °C): δ = 13.42 [CHOC(CH₃)CHH], 14.97

(*MeMeCH*), 15.89 (*C₆Me₆*), 17.85 (*MeMeCH*), 30.22 (*MeMeCH*), 70.38 (*CH₂H₁*), 74.67 (*CH₂*), 100.90 (d, $J_{\text{PC}} = 2.3$ Hz, *C₆Me₆*), 123–135 (Ph), 144.77 [*CHOC(CH₃)CHH*], 149.58 [*CHOC(CH₃)CHH*], 167.83 (d, $J_{\text{PC}} = 9.1$ Hz, C=N), 210.68 (*CHO*) ppm.

Preparation of the Complexes [(η^6 -*p*-MeC₆H₄iPr)Ru(PNiPr)(nitro-*ne*)]SbF₆]₂ [nitro-*ne* = **I (**20**), **II** (**21**), **V** (**22**):** A solution of [(η^6 -*p*-MeC₆H₄iPr)Ru(PNiPr)(H₂O)]SbF₆]₂ (0.1 mmol) in CH₂Cl₂ (4 mL) was stirred in the presence of molecular sieves (4 Å) (200.0 mg) at 0 °C under argon for 20 min. The corresponding nitro-*ne* **I**, **II** or **V** (0.1 mmol) was then added and the suspension stirred for 20 min. Addition of hexanes (20 mL) caused the precipitation of a solid. The solvents were separated by decantation and the residue was washed with hexanes (3 × 20 mL). After washing, the residue was extracted with CH₂Cl₂ (5 mL). Addition of hexanes (20 mL) to the resultant solution gave an orange-red solid which was washed with hexanes and vacuum-dried.

Complex 20: Yield: 100 mg (78%) of pure *R_{Ru}* epimer. C₄₇H₄₉F₁₂N₂RuO₂PSb₂ (1277.44): calcd. C 44.19, H 3.86, N 2.19; found C 43.93, H 3.63, N 1.98. IR (Nujol): $\tilde{\nu} = 1595$ (s, CN), 659 (s, SbF₆) cm⁻¹. ¹H NMR (CD₂Cl₂, -25 °C): $\delta = -0.37$ (d, $J_{\text{H,H}} = 6.5$ Hz, 3 H, *MeMeCH*), 0.83 (d, $J_{\text{H,H}} = 7.2$ Hz, 3 H, *MeMeCH*, MeC₆H₄iPr), 0.92 (d, $J_{\text{H,H}} = 6.8$ Hz, 3 H, *MeMeCH*, MeC₆H₄iPr), 0.97 (d, $J_{\text{H,H}} = 6.8$ Hz, 3 H, *MeMeCH*), 1.37 (s, 3 H, Me, MeC₆H₄iPr), 1.72 (m, 1 H, *MeMeCH*), 1.83 (pseudo-sept, 1 H, *MeMeCH*, MeC₆H₄iPr), 4.44 (m, 1 H, H_g), 4.62, 4.74 (m, 2 H, H_c, H_t), 5.50 (m, 1 H, H_AH_B), 5.57 (d, $J_{\text{A,B}} = 6.3$ Hz, 1 H, H_AH_B), 5.57 (d, $J_{\text{A',B'}} = 6.3$ Hz, 1 H, H_{A'}H_{B'}), 5.67 (d, 1 H, H_{A'}H_{B'}), 6.9–8.3 (m, Ph), 8.63 (s, 1 H, NCH) ppm. ³¹P{¹H} NMR (CD₂Cl₂, -25 °C): $\delta = 43.8$ (br. s) ppm. ¹³C NMR (CD₂Cl₂, -25 °C): $\delta = 12.4$ (*MeMeCH*), 18.8 (*MeMeCH*), 21.4 (Me, MeC₆H₄iPr), 21.4, 23.3 (*MeMeCH*, MeC₆H₄iPr), 30.7 (*MeMeCH*), 30.8 (*MeMeCH*, MeC₆H₄iPr), 69.2 (*CH₂H₁*), 78.6 (*CH₂*), 78.8, 85.2, 85.2, 86.3 (C, MeC₆H₄iPr), 123–137 (Ph), 155.7 (NCH), 168.2 (d, $J_{\text{PC}} = 5.3$ Hz, C=N) ppm.

Complex 21: Yield: 94 mg (77%) of pure *R_{Ru}* epimer. C₄₂H₄₇F₁₂N₂RuO₂PSb₂ (1216.27): calcd. C 41.47, H 3.89, N 2.30; found C 41.19, H 4.04, N 2.21. IR (Nujol): $\tilde{\nu} = 1595$ (s, CN), 658 (s, SbF₆) cm⁻¹. ¹H NMR (CD₂Cl₂, -60 °C): $\delta = 0.22$ (d, $J_{\text{H,H}} = 6.2$ Hz, 3 H, *MeMeCH*), 1.01 (d, $J_{\text{H,H}} = 6.6$ Hz, 3 H, *MeMeCH*, MeC₆H₄iPr), 1.09 (d, $J_{\text{H,H}} = 6.6$ Hz, 3 H, *MeMeCH*, MeC₆H₄iPr), 1.20 (m, 3 H, *MeMeCH*, MeC₆H₄iPr), 1.50 (m, 1 H, *MeMeCH*), 1.55 (s, 3 H, Me, MeC₆H₄iPr), 2.34 (pseudo-sept, 1 H, *MeMeCH*, MeC₆H₄iPr), 4.15 (s, 3 H, NMe), 4.75 (m, 2 H, H_c, H_t), 4.84 (m, 1 H, H_g), 5.52 (m, 1 H, H_AH_B), 6.10 (d, $J_{\text{A,B}} = 5.9$ Hz, 1 H, H_AH_B), 6.22 (d, $J_{\text{A',B'}} = 6.2$ Hz, 1 H, H_{A'}H_{B'}), 6.47 (d, 1 H, H_{A'}H_{B'}), 7.1–8.0 (m, Ph), 8.03 (s, 1 H, NCH) ppm. ³¹P{¹H} NMR (CD₂Cl₂, -60 °C): $\delta = 37.8$ (s) ppm. ¹³C NMR (CD₂Cl₂, -60 °C): $\delta = 13.70$ (*MeMeCH*), 17.33 (Me, MeC₆H₄iPr), 18.30 (*MeMeCH*), 19.76, 23.81 (*MeMeCH*, MeC₆H₄iPr); 29.65 (*MeMeCH*); 31.73 (*MeMeCH*, MeC₆H₄iPr), 51.03 (NMe), 68.67 (*CH₂H₁*), 79.67 (*CH₂*), 79.8, 88.0 (d, $J_{\text{PC}} = 7.9$ Hz), 88.7, 97.0 (d, $J_{\text{PC}} = 3.7$ Hz) (C, MeC₆H₄iPr), 122–136 (Ph), 154.19 (NCH), 167.68 (d, $J_{\text{PC}} = 4.9$ Hz, C=N) ppm.

Complex 22: Yield: 96 mg (78%) of pure *R_{Ru}* epimer. C₄₃H₄₇F₁₂N₂O₂PRuSb₂ (1227.28): calcd. C 42.08, H 3.85, N 2.28; found C 42.19, H 4.01, N 2.36. IR (Nujol): $\tilde{\nu} = 1598$ (s, CN), 659 (s, SbF₆) cm⁻¹. ¹H NMR (CD₂Cl₂, -30 °C): $\delta = 0.18$ (d, $J_{\text{H,H}} = 6.6$ Hz, 3 H, *MeMeCH*), 1.09 (d, $J_{\text{H,H}} = 6.9$ Hz, 3 H, *MeMeCH*), 1.11 (d, $J_{\text{H,H}} = 8.4$ Hz, 3 H, *MeMeCH*, MeC₆H₄iPr), 1.20 (d, $J_{\text{H,H}} = 6.6$ Hz, 3 H, *MeMeCH*, MeC₆H₄iPr), 1.65 (m, 1 H, *MeMeCH*), 2.01 (s, 3 H, Me, MeC₆H₄iPr), 2.41 (pseudo-sept, 1 H, *MeMeCH*, MeC₆H₄iPr), 2.67, 2.86, 3.10, 3.94 (m, 4 H, NCH₂CH₂), 4.40 (pt, 1 H, $J_{\text{Hc,Ht}} = 10.2$ Hz, $J_{\text{Hc,Hg}} = 1.8$ Hz, H_c), 4.68 (dd, 1 H, H_t), 4.96 (m, 1 H, H_g), 4.98 (m, 1 H, H_AH_B), 6.08 (m, 1 H, H_AH_B),

6.25 (d, $J_{\text{A',B'}} = 6.2$ Hz, 1 H, H_{A'}H_{B'}), 6.77 (d, 1 H, H_{A'}H_{B'}), 7.2–7.9 (m, Ph), 8.11 (s, 1 H, N=CH) ppm. ³¹P{¹H} NMR (CD₂Cl₂, -30 °C): $\delta = 39.35$ (s) ppm. ¹³C NMR (CD₂Cl₂, -30 °C): $\delta = 13.59$ (*MeMeCH*), 18.19 (Me, MeC₆H₄iPr), 20.43 (*MeMeCH*), 18.49, 23.11 (*MeMeCH*, MeC₆H₄iPr), 27.08 (NCH₂CH₂), 29.83 (*MeMeCH*), 31.73 (*MeMeCH*, MeC₆H₄iPr), 56.02 (NCH₂CH₂), 51.03 (NMe), 69.07 (*CH₂H₁*), 79.72 (*CH₂*), 81.39, 88.36 (d, $J_{\text{PC}} = 8.0$ Hz), 88.94, 95.74 (d, $J_{\text{PC}} = 2.3$ Hz) (C, MeC₆H₄iPr), 122–136 (Ph), 144.35 (NCH), 166.78 (d, $J_{\text{PC}} = 5.7$ Hz, C=N) ppm.

Crystal Structure Determination of Complexes *R_{Ru}*-2, *R_{Ru}*-3, *R_{Ru}*-7 and *R_{Ru}*-8: X-ray data were collected for all complexes at low temperature [100(2) K] with a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo-*K_α* radiation ($\lambda = 0.71073$ Å). Data were corrected for absorption using a multiscan method applied with the SADABS program.^[17] The structures were solved by direct methods with SHELXS-86.^[18] Refinement, by full-matrix least squares on F^2 with SHELXL97,^[18] 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 significance. In all structures, in addition to the internal configuration reference of the oxazoline ligand, the Flack parameter was refined as a check of the correct absolute configuration determination.^[19] CCDC-297912, -297913, -297914 and -297915 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_requested/cif.

Crystal Data for *R_{Ru}*-2: C₃₆H₄₂ClF₆NOPRuSb, $M = 907.95$; red prism, 0.10 × 0.09 × 0.08 mm; orthorhombic, $P2_12_12_1$; $a = 11.7929(9)$, $b = 14.0329(10)$, $c = 21.8518(16)$ Å; $Z = 4$; $V = 3616.2(5)$ Å³; $D_c = 1.668$ g cm⁻³; $\mu = 1.334$ mm⁻¹, min/max transmission factors 0.8762/0.9013; $2\theta_{\text{max}} = 57.74^\circ$; 43058 reflections collected, 8852 unique ($R_{\text{int}} = 0.0395$); number of data/restraints/parameters = 8852/0/510; final $GoF = 1.103$, $R_1 = 0.0360$ [8516 reflections, $I > 2\sigma(I)$], $wR_2 = 0.0807$ for all data; Flack parameter $x = -0.025(18)$; three electron residual peaks above 1 e Å⁻³ were located close to the fluorine atoms (distances shorter than 1 Å) and have no chemical significance. Most of the hydrogen atoms were observed in the difference Fourier maps and included in the model as free isotropic atoms; hydrogen atoms of the terminal methyl groups were included in calculated positions and refined with positional and thermal riding parameters.

Crystal Data for *R_{Ru}*-3: C₃₄H₂₈ClF₆NOPRuSb, $M = 869.81$; orange prism, 0.18 × 0.07 × 0.04 mm; orthorhombic, $P2_12_12_1$; $a = 11.1353(11)$, $b = 16.1491(16)$, $c = 17.6001(18)$ Å; $Z = 4$; $V = 3164.9(5)$ Å³; $D_c = 1.825$ g cm⁻³; $\mu = 1.531$ mm⁻¹, min/max transmission factors 0.7669/0.9357; $2\theta_{\text{max}} = 57.8^\circ$; 21412 reflections collected, 7573 unique ($R_{\text{int}} = 0.0648$); number of data/restraints/parameters = 7573/12/475; final $GoF = 1.059$, $R_1 = 0.0557$ [6161 reflections, $I > 2\sigma(I)$], $wR_2 = 0.0963$ for all data; Flack parameter $x = 0.00(3)$; largest difference peak 1.26 e Å⁻³ (close to Sb atom). Most of the hydrogen atoms were observed in the difference Fourier maps and included in the model as free isotropic atoms; the remaining hydrogen atoms were included in calculated positions and refined with positional and thermal riding parameters.

Crystal Data for *R_{Ru}*-7: C₃₀H₃₂F₁₂NO₂PRuSb₂, $M = 1042.11$; amber irregular block, 0.15 × 0.09 × 0.06 mm; orthorhombic, $P2_12_12_1$; $a = 10.1400(17)$, $b = 17.020(3)$, $c = 19.899(3)$ Å; $Z = 4$; $V = 3434.1(10)$ Å³; $D_c = 2.016$ g cm⁻³; $\mu = 2.138$ mm⁻¹, min/max trans-

mission factors 0.7398/0.8771; $2\theta_{\max} = 57.96^\circ$; 23407 reflections collected, 8218 unique ($R_{\text{int}} = 0.0570$); number of data/restraints/parameters = 8218/2/451; final $GoF = 1.052$, $R_1 = 0.0455$ [7064 reflections, $I > 2\sigma(I)$], $wR_2 = 0.0790$ for all data; Flack parameter $x = -0.02(2)$. Hydrogen atoms were included in calculated positions and refined with a positional and thermal riding model. The two hydrogen atoms of the coordinated water molecule were included from observed positions and refined as free isotropic atoms.

Crystal Data for $R_{\text{Ru}}\cdot 8\cdot \text{C}_4\text{H}_{10}\text{O}$: $\text{C}_{80}\text{H}_{84}\text{F}_{24}\text{N}_2\text{O}_6\text{P}_2\text{Ru}_2\text{Sb}_4$, $M = 2376.57$; red lamina, $0.23 \times 0.19 \times 0.01$ mm; monoclinic, $P2_1$; $a = 11.145(5)$, $b = 17.873(5)$, $c = 23.274(5)$ Å; $\beta = 103.139(5)^\circ$; $Z = 2$; $V = 4515(3)$ Å³; $D_c = 1.748$ g cm⁻³; $\mu = 1.640$ mm⁻¹, min/max transmission factors 0.7072/0.9774; $2\theta_{\max} = 57.7^\circ$; 30335 reflections collected, 19946 unique ($R_{\text{int}} = 0.0297$); number of data/restraints/parameters = 19946/3/1036; final $GoF = 1.076$, $R_1 = 0.0564$ [18151 reflections, $I > 2\sigma(I)$], $wR_2 = 0.1275$ for all data; Flack parameter $x = 0.03(2)$. Two independent molecules were observed in the crystal. Two of the SbF_6^- anions were observed disordered and a similar model was built for both anions using two F_6 moieties in each case; they were refined with complementary occupancy factors. Even with this model there was some residual electronic density left in the proximity of these groups. Hydrogen atoms were included in calculated positions and refined as free isotropic atoms. At this point, several residual peaks were still present in the difference Fourier maps, clearly separated from anions and cations. They were interpreted as originated from two heavily disordered diethyl ether solvent molecules. After several attempts to include these peaks in geometrically reasonable positions without success, the highest residuals were included to take account of solvent ($\text{C}_4\text{H}_{10}\text{O}$) presence.

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