Chiral Arene Ruthenium Complexes. 6.† Diastereoselective Formation of Chiral-At-Metal P-Tethered Arene Ruthenium(II) Complexes

Patrícia Pinto, Guido Marconi, Frank W. Heinemann, and Ulrich Zenneck*

Institut für Anorganische Chemie, Universität Erlangen-Nürnberg, Egerlandstrasse 1, D-91058 Erlangen, Germany

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The easily accessible (*R*)-3-phenylbutanol (**1**) can be transformed into the novel enantiopure ligand diphenyl((*R*)-3-phenylbutyl)phosphane (**3**). **3** splits the complex dimer [{$RuCl_2(\eta^6$-$C_6H_5CO_2Me)\}_2$] (**6**) by adding as a σ-ligand to form mononuclear [$RuCl_2(\eta^6$-$C_6H_5COOMe)$-$((R)$-η^1-$PPh_2(CH_2)_2CH(CH_3)Ph)$] (**7**). An intramolecular arene ligand displacement reaction leads to [$RuCl_2((R)$-η^1-$PPh_2(CH_2)_2CH(CH_3)$-η^6-$C_6H_5)$] (**8**) with a tethered side chain of the arene ligand. Nucleophilic substitution of a chloride ligand by primary or secondary amines with the assistance of $NaBF_4$ gives access to the diastereomeric complex salts [RuCl(amine)-$((R)$-η^1-$PPh_2(CH_2)_2CH(CH_3)$-η^6-$C_6H_5)]BF_4$. Good diastereoselectivities were obtained for aniline, piperidine, benzylamine, and butylamine complex salts **9**−**12** (de = 82−90%). The absolute structures of **8**−**10** have been determined by X-ray structure analysis. S_{Ru},R_C configurations were found for the major diastereomers of aniline and piperidine complex salts **9** and **10**. Not only the side chain stereogenic center but also the metal configuration of the cation of salt **9** is stable for longer periods at low and at elevated temperatures in different solutions.

Introduction

After the first examples of configurationally stable chiral-at-metal half-sandwich complexes had been synthesized by Brunner et al. in 1978,[2,3] several studies on the stereochemistry of such complexes followed.[4−7] One reason for a still-increasing interest in this class of compounds is their importance in catalysis. Asymmetric arene ruthenium complexes can be used in catalytic Diels−Alder reactions,[8] in alkene metathesis,[9] and as enantioselective hydrogen transfer catalysts for carbonyl or imine group reduction,[10,11] for example. A current aspect of arene ruthenium complex chemistry deals with tethered (η^6:η^1-arene∩donor)ruthenium(II) species (∩ = link between arene ring and donor center), in which one or more hydrogen atoms of the arene ring are replaced by a side chain, which contains a suitable end group for interactions with the central metal. Tethering the side chain to the metal atom has two consequences.

(i) The chelate effect stabilizes such complexes toward arene substitution,[12] and this should be true for catalytically active species as well.

(ii) In the case of chiral side chains it connects the η^6-arene moiety, the stereogenic center, and the metal by σ bonds and thus causes a restricted stereochemical situation within the coordination sphere of the ruthenium atom.

Examples of tethered η^6-arene ruthenium(II) complexes have been reported with nitrogen, oxygen,[1,13] and phosphorus[12−18] donor atoms.

In previous studies we investigated the arene ruthenium(II) complex chemistry of an enantiopure arene ligand with an OH donor group in the side chain[1] and a series of arene ruthenium(0) complexes with dangling N or O donors.[19] This paper deals with the ruthenium-

* To whom correspondence should be addressed: Fax: int. + 49 9131 852 7464. E-mail: zenneck@chemie.uni-erlangen.de.

† Dedicated in honor of Professor Dr. E. O. Fischer on the occasion of his 85th birthday. For part 5, see ref 1.

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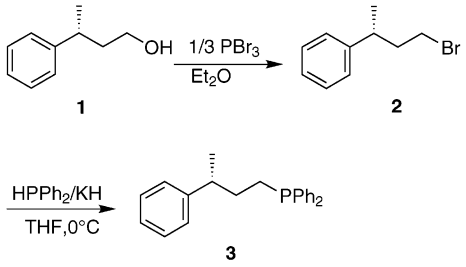
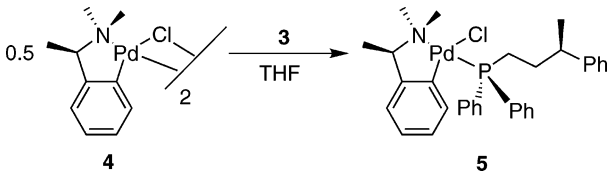
Scheme 1



Scheme 2



(II) complex chemistry of enantiopure diphenyl((*R*)-3-phenylbutyl)phosphane. Some ruthenium(II) complexes of the achiral analogue diphenyl(3-phenylpropyl)phosphane have been reported by Smith and co-workers.[12]

Results and Discussion

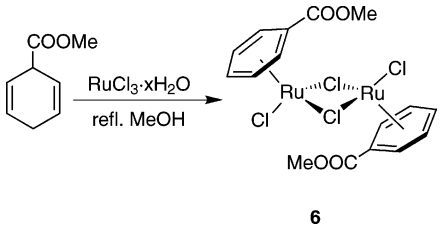
The preparation of the enantiopure ligand diphenyl((*R*)-3-phenylbutyl)phosphane (**3**) is based on the nucleophilic substitution of the OH group of (*R*)-3-phenylbutanol (**1**), which we already used as a chiral arene ligand of ruthenium(II) earlier.[1] The reaction leads to 1-bromo-(*R*)-3-phenylbutane (**2**),[20] which can be reacted with 1 equiv of $KPPh_2$ in THF to form the chiral target molecule **3** (Scheme 1). **3** was isolated as a viscous colorless oil.

The optical purity of **3** was determined by diastereomeric derivatization.[21] **3** can be reacted with the commercially available, optically pure binuclear Pd complex **4**. The chiral phosphane **3** splits dimer **4** by addition to the metal and forms the monomeric complex **5**, which combines the stereogenic centers of both components (Scheme 2). As **5** exhibits a one-line absorption of a single diastereomer in ^{31}P NMR spectroscopy, the finding confirms an optical purity of **3** of better than 98% ee. A rapid exchange process of ligand **3**, which could lead to erroneous interpretations of the optical purity,[22] is unlikely for the square-planar coordination sphere of the Pd(II) ion of **5**.

$[\{RuCl_2(\eta^6\text{-}C_6H_5CO_2Me)\}_2]$ (**6**) was chosen as the organometallic precursor for the investigations. It forms a poorly soluble orange solid by treatment of $RuCl_3$ with 3-(methoxycarbonyl)cyclohexa-1,4-diene (3 equiv) in refluxing methanol (Scheme 3).

Like other P-donor ligands,[12,14,15,18] phosphane **3** splits the arene ruthenium dichloride dimer **6** at room temperature effectively to form the mononuclear complex $[RuCl_2(\eta^6\text{-}C_6H_5COOMe)((R)\text{-}\eta^1\text{-}PPh_2(CH_2)_2CH(CH_3)Ph)]$

Scheme 3



(**7**). **7** can be precipitated from the reaction mixture by the addition of *n*-hexane and forms a deep orange powder. The ^{31}P NMR spectrum of **7** provides clear evidence of the coordination of the phosphane ligand by showing a single peak at 24.7 ppm. Due to the chirality of the incoming P-ligand, all five arene ring protons of the η^6-methyl benzoate become inequivalent. They form five well-separated peaks in the ^1H NMR spectrum with identical integrated intensities in the spectroscopic range between 6.31 and 4.98 ppm.

As observed earlier, the η^6-arene ligand methyl benzoate is labile at Ru(II) centers at elevated temperatures;[14] thus, complex **7** is prone to an intramolecular arene exchange reaction, which leads to the targeted formation of the P-tethered complex $[RuCl_2((R)\text{-}\eta^1\text{-}PPh_2(CH_2)_2CH(CH_3)\text{-}\eta^6\text{-}C_6H_5)]$ (**8**) at 120 °C in dichloromethane solution in a sealed tube.[14,15] Slow addition of *n*-hexane to the CH_2Cl_2 solution of the raw product leads to the formation of orange needles of pure **8** at room temperature in good yield.

^1H, ^{13}C, and ^{31}P NMR investigation of solutions of **8** provided clear evidence for the η^6:η^1 coordination of the designed ligand functions of **3**: namely, the carbon-bound phenyl group and the phosphorus atom. As for its precursor **7**, the C_1 symmetry of **8** is documented by the inequivalence of all ring proton and carbon atoms of the η^6-bound phenyl group, whereas the coordinated arene part of the achiral analogue [(η^6:η^1-diphenyl(3-phenylpropyl)phosphane)RuL_2] complexes exhibit only four resonances in the characteristic spectroscopic region between 79 and 102 ppm in ^{13}C NMR.[12] The alkyl chain forms an $ABCDEX_3$ spin system in ^1H NMR, but the signals overlap partially, even at 400 MHz. Despite that, the doublet at 1.27 ppm can be assigned unambiguously to the methyl protons of the tethered side chain. A $^1H-^1H$ COSY experiment leads to the identification of the two spectroscopically inequivalent phenyl substituents of the phosphorus atom.

The molecular structure of **8** was determined by single-crystal X-ray analysis. **8** crystallizes in the chiral space group $P2_1$ with two symmetry-related molecules of only one enantiomer of complex **8** and two CH_2Cl_2 solvent molecules in the unit cell. The crystal structure of **8** was determined twice with different crystals. The results of both analyses are identical, including stereochemistry, within the margin of the experimental errors. The absolute structure of the complex has been determined. The *R* configuration of the benzylic carbon atom stereogenic center is identical with that of the starting material of the chiral ligand **3**. Figure 1 gives a side and a top view of **8** in the solid state. Selected bond distances and angles are given in Table 1; details of the crystal structure determination are summarized in Table 2.

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Table 1. Selected Bond Distances (Å) and Angles (deg) for 8·2CH_2Cl_2, 9, and 10

8·2CH_2Cl_2		**9**		**10**	
		Distances			
Ru(1)−C(1)	2.194(3)	Ru(1)−C(1)	2.173(3)	Ru(1)−C(1)	2.216(4)
Ru(1)−C(2)	2.253(2)	Ru(1)−C(2)	2.288(3)	Ru(1)−C(2)	2.242(5)
Ru(1)−C(3)	2.262(3)	Ru(1)−C(3)	2.295(3)	Ru(1)−C(3)	2.249(5)
Ru(1)−C(4)	2.175(3)	Ru(1)−C(4)	2.197(3)	Ru(1)−C(4)	2.184(4)
Ru(1)−C(5)	2.183(3)	Ru(1)−C(5)	2.202(3)	Ru(1)−C(5)	2.216(4)
Ru(1)−C(6)	2.212(3)	Ru(1)−C(6)	2.209(3)	Ru(1)−C(6)	2.226(5)
Ru(1)−Cl(1)	2.4037(7)	Ru(1)−Cl(1)	2.4031(7)	Ru(1)−Cl(1)	2.408(2)
Ru(1)−Cl(2)	2.4271(6)	Ru(1)−N(1)	2.177(2)	Ru(1)−N(31)	2.153(4)
Ru(1)−P(1)	2.3199(6)	Ru(1)−P(1)	2.3177(7)	Ru(1)−P(1)	2.343(2)
		Angles			
P(1)−Ru(1)−Cl(1)	88.97(2)	P(1)−Ru(1)−Cl(1)	85.99(2)	P(1)−Ru(1)−Cl(1)	88.15(4)
P(1)−Ru(1)−Cl(2)	86.85(2)	P(1)−Ru(1)−N(1)	86.95(7)	P(1)−Ru(1)−N(31)	88.8(1)
Cl(1)−Ru(1)−Cl(2)	86.98(2)	Cl(1)−Ru(1)−N(1)	83.84(8)	Cl(1)−Ru(1)−N(31)	83.4(1)

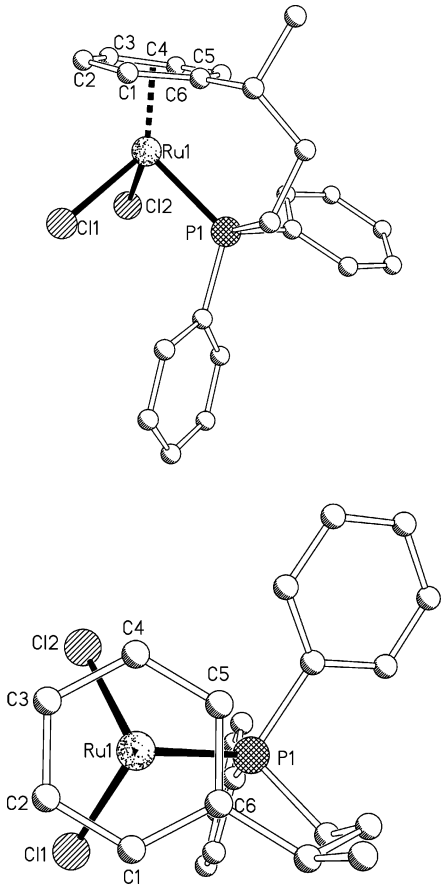


Figure 1. Molecular structure of **8** in the solid state: (A, top) side view; (B, bottom) top view. The solvent molecule CH_2Cl_2 and hydrogen atoms have been omitted for clarity.

The molecular structure of **8** in the solid state corresponds fully to the spectroscopic results in solution. As designed, the alkyl chain forms a tether, which links the two coordinated moieties of the ligand: the C-bound phenyl group and the phosphorus atom. The top view (Figure 1B) reveals some details of the chelate ring. It forms a chairlike conformation, if one includes the connection between the ipso carbon atom C(6) and the ruthenium atom into consideration. The two phenyl substituents occupy axial and equatorial positions, with respect to the chelate six-membered ring.

An interesting feature of the molecular structure of **8** is the position adopted by the benzyl methyl group, which causes the asymmetry of the ligand. It is located considerably above the plane of the π-coordinated arene ring, which can be attributed to a repulsive interaction with the ortho hydrogen atom of C(5). As a consequence, the chelate ring is tilted and P(1) occupies a position below the middle of the bond C(5)−C(6).

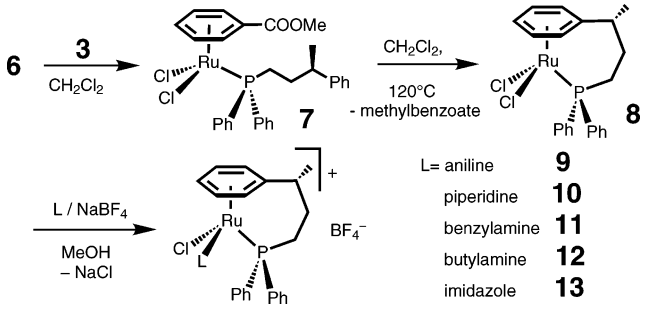
Table 2. Crystallographic Data for 8·CH_2Cl_2, 9, and 10

	8·CH_2Cl_2	**9**	**10**
empirical formula	$C_{23}H_{25}Cl_4PRu$	$C_{28}H_{30}BClF_4NPRu$	$C_{27}H_{34}BClF_4NPRu$
formula wt	575.27	634.83	626.85
color, form	orange, needle	orange, plate	orange, block
size, mm	0.36 × 0.11 × 0.07	0.32 × 0.19 × 0.07	0.52 × 0.26 × 0.24
cryst syst	monoclinic	orthorhombic	orthorhombic
space group	$P2_1$	$P2_12_12_1$	$P2_12_12_1$
a, Å	10.3565(1)	9.1046(2)	10.6195(2)
b, Å	8.3648(1)	14.5909(3)	14.7711(3)
c, Å	14.5157(2)	20.4658(5)	17.2983(3)
β, deg	105.689(1)	90	90
V, Å^3	1210.65(2)	2718.8(1)	2713.4(1)
Z	2	4	4
ρ_{calcd}, g cm^{-3}	1.578	1.551	1.534
μ, mm^{-1}	1.163	0.780	0.780
T_{min}, T_{max}	0.734, 0.925	0.777, 0.909	0.765, 0.908
no. of refined params	337	461	427
F(000)	580	1288	1280
no. of rflns measd	20 898	22 795	36 865
no. of indep rflns	7040	6539	5915
no. of obsd rflns ($I \geq 2\sigma(I)$)	6384	6009	5267
goodness of fit on F^2	1.023	1.039	1.148
R1 ($I \geq 2\sigma(I)$)	0.0309	0.0306	0.0429
wR2 (all data)	0.0610	0.0663	0.0870
abs structure param[26]	−0.03(2)	−0.03(2)	−0.03(3)
max, min resid density, e Å^{-3}	0.694, −0.517	0.976, −0.461	1.593, −0.729

Treatment of **8** with 1 equiv of N-donor ligands at room temperature in the presence of $NaBF_4$ leads to the elimination of sodium chloride, and the amine enters the coordination sphere of the metal to form the complex salts [RuCl((*R*)-η^1-$PPh_2(CH_2)_2CH(CH_3)$-η^6-C_6H_5)](L)]BF_4 (**9**, L = aniline; **10,** L = piperidine; **11**, L = benzylamine; **12**, L = butylamine; **13**, L = imidazole) (Scheme 4). Salts **9**−**13** can be isolated as yellow-orange air-stable solids.

The substitution of one of the two diastereotopic chlorides by another ligand creates the desired chiral-at-metal situation. In combination with the side chain stereogenic center, diastereomers are formed if the reaction is not completely diastereoselective. Due to the single-line absorption of the diastereomers, $^{31}P\{^1H\}$ NMR is the method of choice to determine the diastereoselectivity of the substitution reaction. Good diastereoselectivities were obtained for aniline, piperidine, benzylamine, and butylamine complex salts **9**−**12** (de =

Scheme 4



82−90%). In the case of complex salts **9** and **10** it was possible to isolate the major diastereomer upon crystallization. Only the imidazole complex salt **13** drops out of the series with a low de of 14%. An explanation for the stereochemical diversity of the salts **9**−**13** has not been found yet; however, the good diastereoselectivities for the primary and secondary amine complexes point to an interesting potential of the tethered $[(\eta^6{:}\eta^1\text{-arene}\cap PPh_2)(\text{amine})RuCl]^+$ complex salts for stereoselective interactions with prochiral substrates of different kinds.

The stereochemical stability of salt **9** was carefully investigated to prevent erroneous interpretations.[22] The $^{31}P\{^1H\}$ NMR spectrum of the diastereomeric mixture of **9** consists of two singlets only. Their ratio is 95:5, which represents a de of 90%. The spectrum in dichloromethane-d_2 solution was recorded at various temperatures between 25 and −70 °C. Neither a change of the integration ratio nor a significant signal broadening which could be related to exchange processes was observable. Below −70 °C the solubility of **9** was too poor to allow further investigations of this kind. To check for long time effects, the NMR samples were controlled after storage for 1 week at room temperature. Another sample was heated in toluene-d_8 at 80 °C for 22 h. As for the low-temperature experiment, ^{31}P NMR of this sample gives no hint on a change of the excess of the major diastereomer; thus, no significant epimerization takes place under these conditions.

Single crystals suitable for X-ray structure analysis of the major diastereomer of the tethered arene ruthenium(II) complex salts **9** and **10** have been obtained from CH_2Cl_2/*n*-hexane solutions. Both crystallize in the chiral space group $P2_12_12_1$ with four symmetry-related molecules of always the same enantiomer in the unit cell. The BF_4^- ions are disordered in the case of **9**. As for **8**, the absolute structures have been determined for the complex cations, and the results for the side chain stereogenic centers are identical in all three cases. The molecular structures of the complex cations of **9** and **10** are presented in Figures 2 and 3, respectively. Selected bond distances and angles are reported in Table 1, and the crystallographic data are given in Table 2.

As usual for (π-arene)RuL_3 derivatives, the coordination spheres of the metal atoms of **8**−**10** represent a piano stool geometry. All nine bond angles P(1)−Ru(1)−Cl(1), P(1)−Ru(1)−X and X−Ru(1)−Cl(1) (X = Cl(2) (**8**), N (**9**, **10**)) fall in the relatively small range of 83.4−89°. This indicates only slight strain for the P-tethered arene ruthenium(II) complex units with their C_3 bridge between the ligand functions. The angles Cl(1)−Ru(1)−N of **9** and **10** (83.8 and 83.4°) represent the

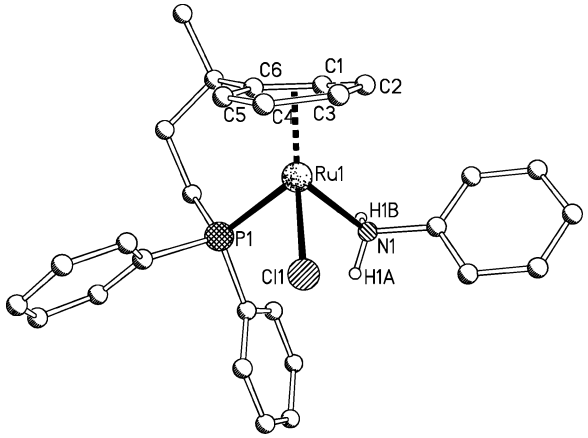


Figure 2. Molecular structure of the cation of complex salt **9** in the solid state. The counterion BF_4 and the carbon-bound hydrogen atoms have been omitted for clarity.

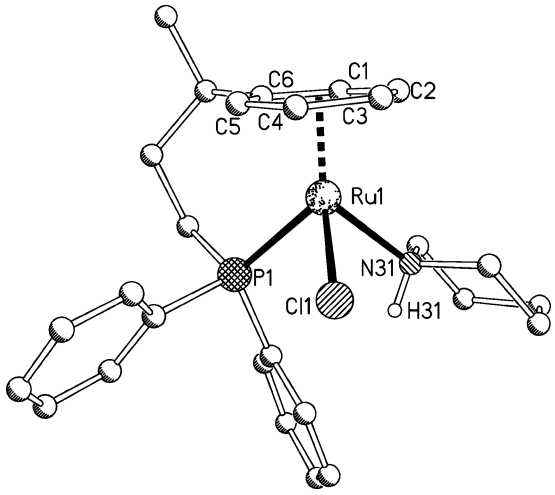


Figure 3. Molecular structure of the cation of complex salt **10** in the solid state. The counterion BF_4 and the carbon-bound hydrogen atoms have been omitted for clarity.

maximum deviation from the ideal rectangular arrangement. This points to a significant, but not very strong, repulsive interaction between the two phenyl substituents of the phosphorus atom and chloride and amino σ-ligands of the metal. The carbon atoms of the π-coordinated arene rings and the benzylic stereogenic centers are always located very close to a common plane, another hint of a virtually unstrained chelate ring. It is noticeable that the Ru−C distances of the carbon atoms trans to the P-donor (2.242−2.295 Å) are substantially longer than the other Ru−C distances (2.173−2.226 Å). This finding reflects the trans influence of the phosphorus ligand, which has been previously reported for related tethered or nontethered $[(\text{arene})(PR_3)Ru^{II}L_2]$ complexes.[1,12,16]

The stereogenic centers of **8**−**10** share the *R* configuration of the benzyl carbon atom with the organic starting material, and all three tethers form almost identical six-membered chelate rings in chair conformations. Consequently, the equatorial and axial orientations of the phenyl substituents of the phosphorus atoms remain almost untouched by the coligands, even after substitution of one of the chloride ligands of **8** by amines. As one would suppose, the amines of the major diastereomers occupy positions which minimize the interac-

tions with the phosphorus phenyl substituents. According to the Cahn−Ingold−Prelog rules, both represent S_{Ru},R_C configurations.

Conclusions

A high-yield enantioselective preparative route to the chiral complex [$RuCl_2$((*R*)-η^1-$PPh_2(CH_2)_2CH(CH_3)$-η^6-C_6H_5)] (**8**) with a tethered side chain of the arene ligand is reported. Nucleophilic substitution of one of the two diastereotopic chloride ligands by primary or secondary amines in the presence of $NaBF_4$ is highly diastereoselective (de = 82−90%) and leads to the salts [(*S*)-RuCl(amine)((*R*)-η^1-$PPh_2(CH_2)_2CH(CH_3)$-η^6-C_6H_5)]BF_4 (**9**−**12**). Both the side chain and the metal stereogenic center of aniline complex salt **9** are stable in their configuration for 1 week at the minimum at room temperature and for 22 h at 80 °C. To sum up, we hereby present an effective pathway to combine high diastereoselectivity and robustness of the metal configuration for diastereomeric arene ruthenium complexes. Related tethered (η^6:η^1-arene∩donor)ruthenium(II) complexes with a side chain stereogenic center closer to the metal atom and experiments to utilize the novel chiral complexes in enantioselective catalysis are under current investigation.

Experimental Section

All reactions involving organometallic compounds were carried out under a dry nitrogen or argon atmosphere, using conventional Schlenk-tube techniques. The arene ruthenium(II) complexes are fully air-stable in the solid state and only slightly air-sensitive in solution. Solvents were dried and degassed before use. NMR spectra were recorded at room temperature on JEOL FT-JNM-EX 270, JEOL FT-JNM-LA 400, and Bruker Advance DPX 300 spectrometers, using dimethylpolysiloxane and solvent signals as internal standards. NMR spectra at low temperatures were recorded on JEOL FT-JNM-LA 400 spectrometers, using dimethylpolysiloxane and solvent signals as internal standards. Mass spectra were recorded on a Varian MAT 212 spectrometer, microanalyses were performed using a Carlo Erba Model 1106 elemental analyzer, and polarimetric measurements were performed on a Perkin-Elmer polarimeter. The compounds (*R*)-3-phenylbutanol (**1**),[1] (*R*)-3-phenylbutyl bromide (**2**),[20] and 3-(methoxycarbonyl)cyclohexa-1,4-diene[23] were prepared as reported in the literature.

Preparation of (*R*)-$PPh_2(CH_2)_2CH(CH_3)Ph$ (3). Potassium hydride (0.445 g, 11,40 mmol) was added to a solution of diphenylphosphane (1.71 g, 9.2 mmol) in THF (30 mL), and the resulting deep orange mixture was stirred for 20 min. Then, a solution of bromide **2** (1.96 g, 9.2 mmol) in THF (15 mL) was added over 45 min. After a further 30 min of stirring, the reaction was quenched with 5 mL of degassed water, the volatiles were removed under high vacuum, and the crude product was extracted with diethyl ether and dried over sodium sulfate. On removal of the solvent a pale yellow oil was obtained, which furnished 2.08 g of **3** by crystallization from ethanol at −30 °C. **3** is a liquid at room temperature.

^{1}H NMR (269.7 MHz, $CDCl_3$, δ): 7.36−7.11 (m, 15 H, Ph); 2.83−2.72 (sext, 1H, CH_γ); 1.97−1.88 (m, 2H, CH_β); 1.75−1.64 (m, 2H, CH_α); 1.22 (d, 3H, CH_δ). ^{13}C{^{1}H} NMR (67.8 MHz, $CDCl_3$, δ): 146.66 (C_{ipso}, Ph); 132.80 (d, J_{PC} = 18.7 Hz, PPh); 132.53 (d, J_{PC} =18.1 Hz, PPh); 128.51 (aryl); 128.36 (aryl, partially superposed); 128.29 (aryl); 127.11 (aryl); 126.01 (aryl); 41.14 (d, J_{PC} = 13.5 Hz, tether); 34.22 (d, J_{PC} = 16.6 Hz, PCH_2 tether); 25.84 (d, J_{PC} = 11.4 Hz, tether); 22.29 (tether). ^{31}P-{^{1}H} NMR (161.7 MHz, $CDCl_3$, δ): −16.05. $[\alpha]_D^{RT}$ = −122.5° (CH_2Cl_2, c = 0.16). MS (FD, 2kV, m/z): 318 [M^+].

Preparation of [{$RuCl_2(\eta^6$-$C_6H_5CO_2Me)$}$_2$] (6). $RuCl_3$·$3H_2O$ (1.8 g, ca. 8.68 mmol of Ru) and 3-(methoxycarbonyl)-cyclohexa-1,4-diene (4.0 g, 28.9 mmol) were dissolved in methanol (40 mL), and the mixture was heated under reflux with magnetic stirring for 8 h. On standing overnight at room temperature, a red-brown powder of **6** settled down. The powder was collected, washed several times with methanol and diethyl ether, and dried in vacuo (2.41 g, 76%).

^{1}H NMR (269.7 MHz, CD_3CN, δ): 6.45 (d, $2H_{ortho}$, η^6-C_6H_5); 6.03 (t, $1H_{para}$, η^6-C_6H_5); 5.80 (t, $2H_{meta}$, η^6-C_6H_5); 3.92 (s, 3H, OCH_3). ^{13}C{^{1}H} NMR (67.8 MHz, CD_3CN, δ): 165.36 ($COOCH_3$); 89.74 (η^6-C_6H_5); 88.45 (η^6-C_6H_5); 81.89 (η^6-C_6H_5); 80.42 (η^6-C_6H_5, C_{ipso}); 52.91 (OCH_3). Anal. Found (calcd) for $C_{10}H_{14}Cl_2ORu$: C, 31.17 (30.93); H, 2.48 (2.60).

Preparation of [$RuCl_2(\eta^6$-$C_6H_5COOMe)$((*R*)-η^1-PPh_2-$(CH_2)_2CH(CH_3)Ph$)] (7). (*R*)-$PPh_2(CH_2)_2CH(CH_3)Ph$ (0.56 g, 1.84 mmol) was added to a suspension of Ru complex dimer **6** (0.57 g, 0.92 mmol) in CH_2Cl_2 (20 mL). After 2 h of stirring at room temperature, the solvent was removed from the reaction mixture. The red residue was washed several times with diethyl ether, crystallized from dichloromethane−hexane, and dried in vacuo to result in the formation of 0.949 g (84%) of complex **7**.

^{1}H NMR (399.7 MHz, CD_2Cl_2, δ): 7.80−7.45 (m, 10H, PPh_2); 7.26−7.15 (m, 3H, Ph); 6.70−6.98 (m, 2H, Ph); 6.31 (d, $1H_{ortho}$, η^6-C_6H_5); 6.22 (d, $1H_{ortho}$, η^6-C_6H_5); 5.42−5.39 (m, $1H_{para}$, η^6-C_6H_5); 5.09 (t, $1H_{meta}$, η^6-C_6H_5); 4.98 (t, $1H_{meta}$, η^6-C_6H_5); 3.82 (s, 3H, OCH_3); 2.65−2.51 (m, 2H, CH_γ + CH_β); 2.40−2.30 (m, 1H, CH_β); 1.43−1.36 (m, 2H, CH_α), 1.07 (d, 3H, CH_3). ^{13}C{^{1}H} NMR (100.4 MHz, CD_2Cl_2, δ): 164.84 ($COOCH_3$); 146.78 (C_{ipso}, Ph); 133.81 (aryl); 133.35 (aryl); 133.00 (aryl); 132.14 (aryl); 131.68 (aryl); 131.11 (aryl); 128.61 (aryl, partially superposed); 127.33 (aryl); 126.33 (aryl); 95.42 (η^6-C_6H_5); 95.04 (η^6-C_6H_5); 89.34 (η^6-C_6H_5); 86.22 (η^6-C_6H_5); 86.15 (η^6-C_6H_5); 85.00 (η^6-C_6H_5); 53.36 (OCH_3); 41.03 (d, J_{PC} = 11.0 Hz, C_γ); 31.91 (d, J_{PC} = 16.0 Hz, C_β); 22.99 (d, J_{PC} = 30.0 Hz, C_α); 22.01 (d, J_{PC} = 9.1 Hz, C_δ). ^{31}P{^{1}H} NMR (161.7 MHz, CD_2Cl_2, δ): 24.72. Anal. Found (calcd) for $C_{30}H_{31}Cl_2O_2PRu$: C, 57.80 (57.51); H, 4.94 (4.99). MS (FD, 2kV, m/z): 627 [M^+].

Preparation of [$RuCl_2$((*R*)-η^1-$PPh_2(CH_2)_2CH(CH_3)$-η^6-C_6H_5)] (8). A solution of arene complex **7** (0.665 g, 1.06 mmol) in dichloromethane (20 mL) was heated in a Schlenk pressure glass tube to 120 °C for 24 h. The solvent was removed in vacuo from the reaction mixture, the brown-red residue was washed several times with hexane and extracted with dichloromethane, and the extract was filtered. The extract was layered with hexane and left for crystallization to yield orange needles of the tethered complex **8**. These were washed with hexane and dried in vacuo (0.44 g, 85%).

^{1}H NMR (399.7 MHz, $CDCl_3$, δ): 7.89−7.85 (m, 2H, PPh^1); 7.56−7.49 (m, 3H, PPh^1); 7.36−7.31 (m, 3H, PPh^2); 7.26−7.21 (m, 2H, PPh^2); 6.39 (t, 1H, η^6-C_6H_5); 6.27 (t, 1H, η^6-C_6H_5); 5.23 (t, 1H, η^6-C_6H_5); 5.11 (d, 1H, η^6-C_6H_5); 5.05 (t, 1H, η^6-C_6H_5); 2.93−2.84 (m, 1H, tether); 2.49−2.15 (m, 3H, tether); 1.81−1.68 (quintet, 1H, tether), 1.27 (d, 3H, CH_3). ^{13}C{^{1}H} NMR (100.4 MHz, CD_2Cl_2, δ): 134.45 (PPh); 133.99 (PPh); 133.09 (d, $^1J_{PC}$ = 46.7 Hz, C_{ipso} PPh); 131.51 (d, $^1J_{PC}$ = 43.8 Hz, C_{ipso} PPh); 131.30 (PPh); 129.88 (PPh); 128.94 (PPh); 127.23 (PPh); 101.34 (d, J_{CP} = 10.0 Hz, η^6-C_6H_5); 98.09 (d, J_{CP} = 10.0 Hz, η^6-C_6H_5); 93.83 (η^6-C_6H_5); 87.27 (d, J_{CP} = 7.0 Hz, η^6-C_6H_5); 82.23 (η^6-C_6H_5); 79.91 (d, J_{CP} = 6.0 Hz, η^6-C_6H_5); 37.42 (tether); 28.64 (tether); 24.68 (d, J_{CP} = 32.1 Hz, C_α tether); 24.17 (d, J_{CP} = 8 Hz, tether). ^{31}P{^{1}H} NMR (161.7 MHz, CD_2Cl_2, δ): 24.82. Anal. Found (calcd) for $C_{22}H_{23}Cl_2PRu$: C, 53.83 (54.04); H, 4.60 (4.74). MS (FD, 2kV, m/z): 490 (100%, [M^+]). Mp: 220 °C dec.

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Preparation of [RuCl($C_6H_5NH_2$)((*R*)-η^1-$PPh_2(CH_2)_2CH(CH_3)$-η^6-C_6H_5)]BF_4 (9). A mixture of tethered complex **8** (0.1 g, 0.2 mmol), aniline (25 μL, 0.2 mmol), and $NaBF_4$ (0.022 g, 0.2 mmol) in methanol (20 mL) was stirred overnight at room temperature. The solvent was then removed in vacuo from the reaction mixture. The yellow residue was dissolved in dichloromethane (10 mL). After filtration the yellow solution was concentrated in vacuo again. Yellow crystals of the complex salt **9** were obtained by slow addition of *n*-hexane (0.056 g, 43%). **9** forms two diastereomers with a diastereomeric excess of 90% (^{31}P NMR). With the exception of ^{31}P NMR, the spectroscopic data are given for the major diastereomer; those of the second diastereomer fit to this interpretation.

^{1}H NMR (399.7 MHz, CD_2Cl_2, δ): 7.78−7.73 (m, 2H, PPh); 7.60−7.51 (m, 8H, PPh); 7.44−7.32 (m, 4H, NPh); 7.20 (t, 1H, NPh); 6.02 (t, 1H, η^6-C_6H_5); 5.67 (d, 1H, η^6-C_6H_5); 5.60 (t, 1H, η^6-C_6H_5); 5.15−5.14 (m, 1H, η^6-C_6H_5); 4.74 (t, 1H, η^6-C_6H_5); 3.16−3.12 (m, 1H, tether), 2.87−2.79 (m, 2H, tether); 2.40−2.31 (m, 1H, tether); 1.56−1.46 (quintet, 1H, tether); 1.28 (d, 3H, CH_3). ^{13}C{^{1}H} NMR (100.4 MHz, CD_2Cl_2, δ): 148.69 (C_{ipso}, NPh); 135.12 (d, J_{CP} = 10.4 Hz, PPh); 133.38 (d, J_{CP} = 8.2 Hz, PPh); 132.04 (d, J_{CP} = 3.0 Hz, PPh); 131.62 (d, J_{CP} = 3.0 Hz, PPh); 131.29 (d, $^1J_{CP}$ = 55.5 Hz, PPh); 129.76 (aryl); 129.16 (aryl, partially superposed); 128.03 (d, $^1J_{CP}$ = 48.4 Hz, PPh); 126.36 (aryl) 108.99 (η^6-C_6H_5); 100.50 (C_{ipso}, η^6-C_6H_5); 97.67 (d, $^1J_{CP}$ = 16.7 Hz, η^6-C_6H_5); 85.93 (η^6-C_6H_5); 81.79 (η^6-C_6H_5); 76.53 (η^6-C_6H_5); 35.60 (tether); 28.28 (tether); 24.66 (d, J_{CP} = 32.0 Hz, C_α tether); 24.45 (tether). ^{31}P{^{1}H} NMR (161.7 MHz, CD_2Cl_2, δ; br indicates broadening due to partial precipitation of the compound):

	δ (ppm)	
temp (°C)	major diastereomer	minor diastereomer
25	30.30 (95%)	30.82 (5%)
−20	30.80	30.80
−50	31.25 (95%)	30.78 (5%)
−70	31.62 (br)	30.72 (br)

Anal. Found (calcd) for $C_{28}H_{30}ClBF_4NPRu$: C, 53.16 (52.98); H, 5.03 (4.76); N, 2.11 (2.20). MS (FD, 2kV, *m*/*z*): 548 [M^+]. Mp: 198 °C dec.

Preparation of [RuCl($C_5H_{10}NH$)(η^1-$PPh_2(CH_2)_2CH(CH_3)$-η^6-C_6H_5)]BF_4 (10). This compound was prepared analogously to **9** from the tethered complex **8** (0. 148 g, 0.3 mmol), piperidine (30 μL, 0.3 mmol), and $NaBF_4$ (0.033 g, 0.3 mmol) in methanol (20 mL). Yield of **10**: 0,101 g (53%). **10** forms two diastereomers with a diastereomeric excess of 86% (^{31}P NMR). With the exception of ^{31}P NMR, the spectroscopic data are given for the major diastereomer; those of the second diastereomer fit to this interpretation.

^{1}H NMR (399.7 MHz, $CDCl_3$, δ): 7.73 (t, 2H, Ph); 7.62−7.44 (m, 8H, Ph); 6.72 (t, 1H, η^6-C_6H_5); 6.21 (t, 1H, η^6-C_6H_5); 5.84 (t, 1H, η^6-C_6H_5); 5.65 (d, 1H, η^6-C_6H_5); 5.24 (d, 1H, η^6-C_6H_5); 3.89 (d, 1H, NH); 3.12−3.06 (m, 1H, tether); 2.96−2.93 (m, 1H, tether); 2.79−2.72 (m, 4H, aliphatic), 2.33−2.19 (m, 1H, tether), 1.61−1.37 (m, 8H, aliphatic); 1.28 (d, 3H, CH_3). ^{13}C{^{1}H} NMR (100.4 MHz, $CDCl_3$, δ): 134.63 (d, J = 9.8 Hz, PPh); 132.72 (d, J_{CP} = 7.4 Hz, PPh); 131.57 (d, $^1J_{CP}$ = 52.9 Hz, C_{ipso} PPh); 131.57 (PPh); 131.43 (PPh); 129.36 (d, J_{CP} = 9.1 Hz, PPh); 128.71 (d, J_{CP} = 10.7 Hz, PPh); 128.70 (d, $^1J_{CP}$ = 42.1, PPh C_{ipso}); 103.70 (d, J_{CP} = 5.0 Hz, η^6-C_6H_5); 103.53 (η^6-C_6H_5); 93.30 (d, J_{CP} = 11.1 Hz, η^6-C_6H_5); 90.91 (η^6-C_6H_5); 81.99 (η^6-C_6H_5); 74.41 (η^6-C_6H_5); 59.96 (C_α, piperidine); 58.45 (C_α, piperidine); 35.84 (aliphatic); 31.54 (aliphatic); 29.77 (aliphatic); 28.91(aliphatic); 27.88 (aliphatic); 25.47 (d, $^1J_{CP}$ = 31.4 Hz, C_α tether); 23.95(aliphatic); 22.64 (d, J = 6.5 Hz, tether). ^{31}P{^{1}H} NMR (161.7 MHz, CD_2Cl_2, δ): 28.19 (93%); 28.77 (7%). Anal. Found (calcd) for $C_{27}H_{34}ClBF_4NPRu$: C, 51.29 (51.76); H, 5.71 (5.47); N, 1.92 (2.24). MS (FD, 2kV, *m*/*z*): 541 (100%, [M^+]). Mp: 196 °C dec.

Preparation of [RuCl($C_6H_5CH_2NH_2$)((*R*)-η^1-$PPh_2(CH_2)_2CH(CH_3)$-η^6-C_6H_5)]BF_4 (11). This compound was prepared analogously to **9** from the tethered complex **8** (0. 100 g, 0.2 mmol), benzylamine (22 μL, 0.2 mmol), and $NaBF_4$ (0.022 g, 0.2 mmol) in methanol (20 mL). Yield of **11**: 0.080 g, 60%. **11** forms two diastereomers with a diastereomeric excess of 86% (^{31}P NMR). With the exception of ^{31}P NMR, the spectroscopic data are given for the major diastereomer; those of the second diastereomer fit to this interpretation.

^{1}H NMR (399.7 MHz, CD_2Cl_2, δ): 7.83−7.78 (m, 2H, PPh); 7.62−7.59 (m, 3H, PPh); 7.26−7.20 (m, 8H, aryl); 6.45−6.93 (m, 2H, H_o, NCH_2Ph); 6.46 (t, 1H, η^6-C_6H_5); 6.30 (t, 1H, η^6-C_6H_5); 5.86 (d, 1H, η^6-C_6H_5); 5.77 (t, 1H, η^6-C_6H_5); 5.33 (m, 1H, η^6-C_6H_5); 4.58 (br, 2H, NH_2); 4.11−3.99 (m, 2H, NCH_2); 2.81−2.66 (m, 3H, tether); 2.36−2.14 (m, 1H, tether); 1.56−1.43 (quintet, 1H, tether); 1.33 (d, 3H, CH_3). ^{13}C{^{1}H} NMR (100.4 MHz, CD_2Cl_2, δ): 139.50 (C_{ipso}, NCH_2Ph); 135.18 (d, J = 10.7 Hz, PPh); 132.97 (d, J_{CP} = 7.5 Hz, PPh); 132.10 (d, J_{CP} = 2.5 Hz, PPh); 131.47 (d, J_{CP} = 2.5 Hz, PPh); 130.85 (d, $^1J_{CP}$ = 52.1 Hz, C_{ipso} PPh); 129.22 (d, J_{CP} = 10.7 Hz, PPh); 128.98 (NCH_2Ph); 128.95 (d, J_{CP} = 9.5 Hz, PPh); 128.20 (NCH_2Ph); 127.96 (d, $^1J_{CP}$ = 47.5 Hz, C_{ipso} PPh); 127.84 (NCH_2Ph); 101.83 (d, J_{CP} = 6.6 Hz, η^6-C_6H_5); 100.40 (η^6-C_6H_5); 97.26 (d, J_{CP} = 10.7 Hz, η^6-C_6H_5); 87.82 (η^6-C_6H_5); 81.49 (η^6-C_6H_5); 78.75 (η^6-C_6H_5); 55.43 (d, J_{CP} = 3.2 Hz, CH_2N); 35.96 (tether); 28.21 (tether); 24.79 (d, $^1J_{CP}$ = 32.2 Hz, C_α tether); 24.35 (tether). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, δ): 34.98 (7%); 33.71 (93%). Anal. Found (calcd) for $C_{29}H_{32}ClBF_4NPRu$: C, 54.04 (53.68); H, 5.29 (4.97); N, 2.07 (2.16). MS (FD, 2kV, *m*/*z*): 562 (100%, [M^+]).

Preparation of [RuCl(n-$BuNH_2$)((*R*)-η^1-$PPh_2(CH_2)_2CH(CH_3)$-η^6-C_6H_5)]BF_4 (12). This compound was prepared analogously to **9** from the tethered complex **8** (0. 046 g, 0.09 mmol), *n*-butylamine (9.3 μL, 0.09 mmol), and $NaBF_4$ (0.010 g, 0.09 mmol) in methanol (14 mL). Yield of **12**: 0.020 g, 34.6%. **12** forms two diastereomers with a diastereomeric excess of 82% (^{31}P NMR). With the exception of ^{31}P NMR, the spectroscopic data are given for the major diastereomer; those of the second diastereomer fit to this interpretation.

^{1}H NMR (399.7 MHz, $CDCl_3$, δ): 7.82−7.77 (m, 2H, PPh); 7.60−7.37 (m, 8H, PPh); 6.40 (t, 1H, η^6-C_6H_5); 6.23 (t, 1H, η^6-C_6H_5); 5.87 (d, 1H, η^6-C_6H_5); 5.65 (t, 1H, η^6-C_6H_5); 5.28−5.23 (m, 1H, η^6-C_6H_5); 4.22 (br, 2H, NH_2); 3.01−2.96 (m, 5H, aliphatic); 2.35−2.22 (m, 1H, tether); 1.53−1.41 (quintet, 1H, tether); 1.33−1.20 (m, 4H, CH_3 + 1H butylamine); 1.21−1.03 (m, 1H, butylamine); 0.91−0.79 (m, 2H, butylamine); 0.69 (t, 3H, butylamine). ^{13}C{^{1}H} NMR (100.4 MHz, $CDCl_3$, δ): 134.98 (d, J_{CP} = 11.0 Hz, PPh); 133.17 (d, J_{CP} = 8.3 Hz, PPh); 132.09 (d, J_{CP} = 2.4 Hz, PPh); 131.47 (d, J_{CP} = 2.5 Hz, PPh); 130.87 (d, $^1J_{CP}$ = 52.6 Hz, C_{ipso} PPh); 129.28 (d, J_{CP} = 10.7 Hz, PPh); 129.12 (d, J_{CP} = 9.9 Hz, PPh); 127.83 (d, $^1J_{CP}$ = 44.4 Hz, C_{ipso} PPh); 102.50 (d, J_{CP} = 6.6 Hz, η^6-C_6H_5); 99.68 (η^6-C_6H_5); 97.24 (d, J_{CP} = 10.7 Hz, η^6-C_6H_5); 86.78 (η^6-C_6H_5); 81.62 (η^6-C_6H_5); 79.11 (η^6-C_6H_5); 52.60 (d, J_{CP} = 3.3 Hz, aliphatic); 35.56 (d, J_{CP} = 1.6 Hz, tether); 34.89 (aliphatic**)** 28.24 (aliphatic); 24.69 (aliphatic); 24.57 (d, J_{CP} = 31.4 Hz, C_α tether); 19.02 (aliphatic); 13.65 (aliphatic). ^{31}P{^{1}H} NMR (109.4 MHz, $CDCl_3$, δ): 33.08 (9%); 32.77 (91%). MS (FD, 2kV, *m*/*z*): 528 (100%, [M^+]).

Preparation of [RuCl($C_3H_4N_2$)((*R*)-η^1-$PPh_2(CH_2)_2CH(CH_3)$-η^6-C_6H_5)]BF_4 (13). This compound was prepared analogously to **9** from the tethered complex **8** (0. 072 g, 0.15 mmol), imidazole (0.01 g, 0.15 mmol), and $NaBF_4$ (0.016 g, 0.15 mmol) in methanol (15 mL). Yield of **13**: 0.079 g, 88.1%. **13** forms two diastereomers with a diastereomeric excess of 14% (^{31}P NMR). Due to the small differences in the intensities of the NMR signals of both diastereomers, they cannot be assigned unambiguously to complete sets for the two individual species; however, all NMR spectroscopic observations fit to the given interpretation. The ^{13}C NMR spectra of **13** are characterized by numerous signal overlaps; thus, no clear assignments were possible.

^{1}H NMR (300.13 MHz, CD_2Cl_2, δ): 10.72 (br, 1H, NH); 10.46 (br, 1H, NH); 7.89−6.93 (m, 20H PPh + 6H CH imidazole + 2H η^6-C_6H_5); 6.51−6.41 (m, 2H, η^6-C_6H_5); 6.21−6.15 (m, 2H, η^6-C_6H_5); 5.98 (t, 1H, η^6-C_6H_5); 5.76 (t, 1H, η^6-C_6H_5); 5.57−5.55 (m, 2H, η^6-C_6H_5); 2.91−2.19 (m, 8H, tether); 2.06−1.91 (m, 1H, tether); 1.73−1.56 (quintet, 1H, tether); 1.43 (d, 6H, CH_3 tether). ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, δ): 32.16 (57%); 31.52 (43%). Anal. Found (calcd) for $C_{25}H_{27}ClBF_4N_2PRu$: C, 49.45 (49.24); H, 4.73 (4.46); N, 5.63 (4.59). MS (FD, 2kV, *m*/*z*): 522 (100%, [M^+]).

Crystal Structure Determination of 8·CH_2Cl_2, 9, and 10. Intensity data were collected at 100 K on a Nonius Kappa-CCD diffractometer using Mo Kα radiation (λ = 0.710 73 Å, graphite monochromator). Data were corrected for Lorentz and polarization effects. Absorption effects have been taken into account either using an empirical correction based on multiple scans (**9** and **10**[24]) or using a numerical correction from indexing of crystal faces (**8**·CH_2Cl_2). Structures were solved by direct methods and refined by full-matrix least-squares procedures against F^2 with all reflections (SHELXTL 5.10[25]). All non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were taken from difference Fourier syntheses. The positional parameters of the H atoms were refined while a common isotropic displacement parameter was kept fixed during the refinement. The BF_4^- anion in **9** is disordered; two alternative positions could be refined, giving site occupancies of 56(5) and 44(5)%, respectively.

Crystal data and experimental details are summarized in Table 2.

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Supporting Information Available: Tables giving X-ray crystallographic data for **8**·CH_2Cl_2, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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