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[CpRu(η^6-naphthalene)]PF_6 as Precursor in Complex Synthesis and Catalysis with the Cyclopentadienyl-Ruthenium(II) Cation

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The complex [CpRu(η^6-naphthalene)]PF_6 (**2**) is a readily accessible and air-stable source of the $CpRu^+$ fragment (Cp = η^5-C_5H_5) for applications in complex synthesis and catalysis. The utility of this precursor complex is demonstrated in a number of experiments: The counterion of **2** is exchanged by reaction with cinchonidinium Δ-TRISPHAT to give [CpRu(η^6-naphthalene)]Δ-TRISPHAT (**4**; with X-ray crystal structure). Ligand exchange of **2** in acetonitrile with (*Z*,*Z*)-1,5-cyclooctadiene (COD) produces [CpRu(η^2:η^2-COD)(MeCN)]PF_6 (**5**; with X-ray crystal structure); with chelating phosphanes (P−P), complexes [CpRu(P−P)(MeCN)]PF_6 are selectively generated, and starting with a 1,4-diazadiene, a solvento complex [CpRu(diazadiene-*N*,*N*′)(MeCN)]PF_6 is obtained. Stepwise reaction of **2** (or **4**) in acetonitrile with different monodentate phosphanes PR_3 and PR'_3 first gives [CpRu(PR_3)$(MeCN)_2$]$^+$ (**I**), then the chiral-at-metal cation [CpRu(PR_3)(PR'_3)(MeCN)]$^+$ (**II**), which was resolved spectroscopically (^{31}P NMR) when combined with the enantiopure Δ-TRISPHAT counterion. Complex cations of type **I** or **II** incorporating 2-diphenylphosphinopyridines as ligands display either the η^1-*P* or the chelating η^2-*P*,*N* coordination mode, depending on the size of the ligand and, in solution, the solvent. Reaction of **2** with 3 equiv of triarylphosphanes (PR_3) in hot acetone gives rise to [CpRu(PR_3)$_3$]$^+$, including the previously unknown cation [CpRu(PPh_3)$_3$]$^+$. The in situ combination of **2** and 2 equiv of bulky 6-substituted 2-pyridylphosphanes catalyzes the anti-Markovnikov hydration of terminal alkynes to aldehydes. Either complex **2** or **5** catalyzes the [2+2+2]-cycloaddition of COD with alkynes. Complex **5** is a catalyst for the coupling of allyl alcohols with terminal alkynes to give 4-alkenones.

Introduction

The η^5-cyclopentadienylruthenium(II) cation ($CpRu^+$; Cp is η^5-C_5H_5 throughout this work) displays a rich chemistry of pseudotetrahedral [CpRu(L^1)(L^2)(L^3)]$^+$ cations or neutral [CpRu(L^1)(L^2)X] complexes (L^n = neutral two-electron donor; X = monoanionic group), which has been the source of countless mechanistic and stereochemical studies or applications in organometallic catalysis.[1,2] A popular synthetic precursor in this chemistry is [CpRu$(MeCN)_3$]PF_6 (**1**),[1,3−6] because two of its acetonitrile ligands are displaced under mild conditions, often in a stepwise manner. Recently, **1** has been applied in the selective synthesis of monophosphane complexes [CpRu(PR_3)$(MeCN)_2$]X,[3,4,7−12] nonsymmetrical complexes [CpRu($PR^1{}_3$)(L)(MeCN)]X (L = $PR^2{}_3$ or NR_3),[3,7,10,13,14] and symmetrical bis-phosphane complexes [CpRu$(PR_3)_2$(MeCN)]X.[15−17] Furthermore, monoisonitrile[18]

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or -carbene[19] complexes $[CpRu(L)(MeCN)_2]X$ have been prepared. The high reactivity of **1** has also provided easy access to cations $[CpRu(N-N)(MeCN)]^+$ with N−N = diamines,[4] diimines,[9,20,21] or bipyridines,[21] which are not readily prepared from $CpRu(PPh_3)_2Cl$. For a long time, the preparation of **1** itself has been relatively involved and has relied on the use of toxic reagents (TlC_5H_4) and photochemical equipment.[4,5] Improved syntheses of **1** have recently been reported.[5,6] The Kündig route is a particular improvement:[6] it starts from $RuCl_3$ and leads, via $RuCp_2$ and $[CpRu(\eta^6\text{-naphthalene})]PF_6$ (**2**), to **1**.[6,22] In recent work on ruthenium-catalyzed anti-Markovnikov hydration of terminal alkynes, we have used complex **2**, rather than **1**, to prepare the catalysts $[CpRu(PR_3)_2(MeCN)]PF_6$ in situ by ligand exchange with several pyridyl-phosphanes.[23−25] We proposed that the air- and moisture-tolerant complex $[CpRu(naphthalene)]PF_6$ (**2**) can be an advantageous starting material for complex synthesis and catalysis with $CpRu^+$, which may replace **1** (which is moisture-sensitive and has a limited shelf life) in many applications.[23] Now, we support this proposal by reporting on uses of **2** in the synthesis of cationic ruthenium complexes with olefin, diazadiene, and phosphane ligands and as a catalyst precursor in alkyne hydration, [2+2+2]-cycloaddition, or alkene/alkyne coupling reactions.[26] Several advantages of the use of **2** have been identified, namely, (i) its availability and air-stability, (ii) its ready exchange of the counterion in aqueous biphasic reaction media, allowing for a simple entry into chiral enantiopure counterion chemistry, and (iii) the option to perform ligand exchanges at the $CpRu^+$ fragment in the absence of acetonitrile. These advantages outweigh the necessity for longer reaction times or higher temperatures relative to reactions with **1** that are sometimes needed.

Results and Discussion

Counterion Exchange. The complex cation $[CpRu(\eta^6\text{-naphthalene})]^+$ is already available with a range of counterions.[6] We have extended this range to include a chiral enantiopure counterion: reaction of **2** with cinchonidinium

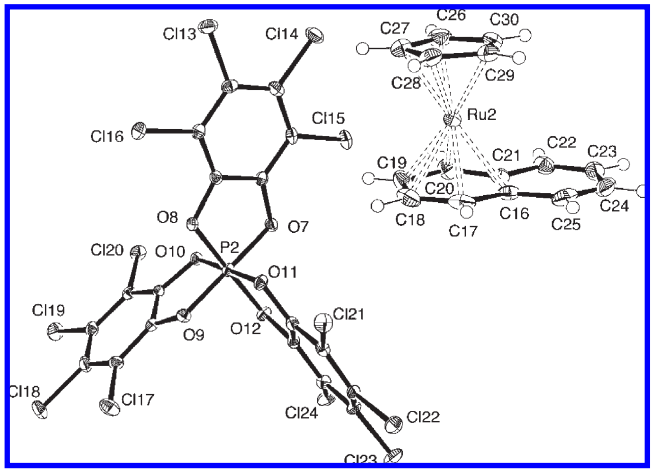
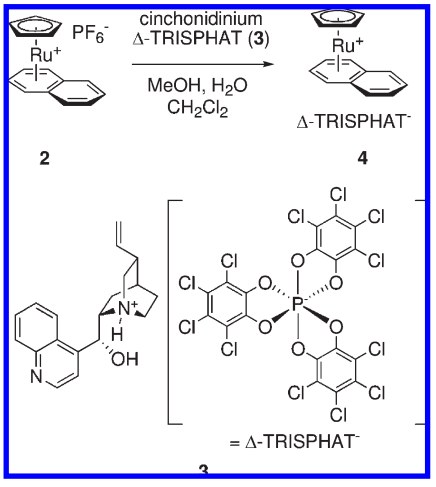


Figure 1. X-ray crystal structure of $[CpRu(\eta^6\text{-naphthalene})]\Delta\text{-TRISPHAT}\cdot CH_2Cl_2$ (**4**·CH_2Cl_2). Ellipsoid plots are drawn at the 50% probability level. The molecular structure of one independent cation and anion each is shown, but the solvent of crystallization is omitted. Hydrogen atoms are shown with arbitrary radius. Selected interatomic distances (Å) and angles (deg): Ru2−C20 2.199(3), Ru2−C17 2.210(3), Ru2−C19 2.211(3), Ru2−C18 2.216(3), Ru2−C21 2.273(3), Ru2−C16 2.281(3), P2−O7 1.7081(17), P2−O12 1.7099(17), P2−O11 1.7112(16), P2−O9, 1.7135(17), P2−O8 1.7157(16), P2−O10 1.7202(16), O7−P2−O9 179.14(9), O12−P2−O8 179.23(9), O11−P2−O10 179.01(9), C20−Ru2−C17 79.10(10).

Scheme 1. Ion Exchange Reaction of 2 with Cinchonidinium Δ-TRISPHAT (3)



Δ-TRISPHAT (**3**)[27] proceeds in a two-phase aqueous/organic solvent system, where the oganometallic ion-pair remains in the organic phase. After a filtration through aluminum oxide, $[CpRu(\eta^6\text{-naphthalene})]\Delta\text{-TRISPHAT}$ (**4**) is obtained in high yield (Scheme 1).

Compound **4** crystallized as a solvate with dichloromethane. The X-ray crystal structure is the first including a $[CpRu(naphthalene)]^+$ cation (Figure 1, Table 1). The unit cell contains two symmetrically independent cations and

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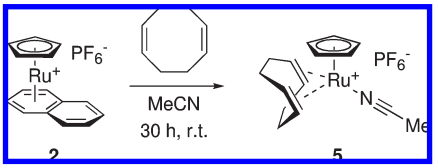
Table 1. Crystallographic Data for $4\cdot CH_2Cl_2$ and 5

	$4\cdot CH_2Cl_2$	5
empirical formula	$C_{34}H_{15}Cl_{14}O_6PRu$	$C_{15}H_{20}F_6NPRu$
fw	1147.80	460.36
cryst size (mm)	0.45 × 0.40 × 0.16	0.44 × 0.21 × 0.19
cryst habit	plate, yellow	rod, orange
cryst syst	monoclinic	orthorhombic
space group	$P2_1$	$Pna2_1$
a (Å)	10.1227(10)	15.4248(14)
b (Å)	20.0704(19)	14.9326(14)
c (Å)	20.0116(19)	7.1632(7)
β (deg)	99.168(2)	90
V (Å^3)	4013.8(7)	1649.9(3)
ρ_{calc} (g cm^{-3})	1.899	1.853
Z	4	4
T (K)	130(2)	130(2)
F(000)	2256	920
min./max. transmn	0.570−0.806	0.642−0.817
θ range (deg)	2.04−31.24	2.64−32.17
index ranges	$-14 \le h \le 14$	$-22 \le h \le 21$
	$-28 \le k \le 29$	$-20 \le k \le 20$
	$-28 \le l \le 28$	$-10 \le l \le 10$
no. of rflns measd	58 992	24 054
no. of unique rflns	23 197	5065
R_{int}	0.0273	0.0301
no. of params	1009	219
R_1 ($2\sigma(I)$)	0.0286	0.0242
R_1 (all data)	0.0316	0.0259
wR_2 (all data)	0.0662	0.0582
Flack param	−0.023(12)	0.46(3)
goodness of fit	1.030	1.075
diff peak/hole (e/Å^3)	1.136/−0.551	1.210/−0.367

Scheme 2. Ligand Exchange of 2 with COD



anions with largely identical geometrical parameters. The η^6-bonding of ruthenium to naphthalene is slightly asymmetric, with Ru−C bond lengths of 2.20−2.21 Å to the naphthalene α-carbons, 2.21−2.22 Å to the β-carbons, but 2.27−2.28 Å to the quaternary carbons.

Ligand Exchange Reactions. An acetonitrile solution of [CpRu(η^6-naphthalene)]PF_6 (**2**) containing a small excess of (*Z*,*Z*)-1,5-cyclooctadiene (COD) was stirred overnight to give the complex [CpRu(η^2:η^2-COD)(MeCN)]PF_6 (**5**)[28] as a crystalline and air-stable material in high yield, after evaporation and recrystallization (Scheme 2). The monitoring of the ligand exchange at room temperature by ^{1}H NMR showed that the conversion reached 50% after 3 h and was essentially completed after 30 h. In acetone, less than 5% conversion occurred after 2 days at room temperature, pointing to the important role of the acetonitrile solvent to accelerate the ligand exchange reaction. The crystal structure analysis of **5** shows that the coordination around ruthenium can be interpreted as tetrahedral if Cp is considered a univalent ligand, thus resulting in a three-legged piano stool geometry.

Attempts to prepare the neutral complex CpRuCl(η^2:η^2-COD) (**6**)[29] by reaction of **5** with LiCl in MeOH at reflux or directly by stirring of **2** with COD and LiCl in acetonitrile were not successful. After addition of an excess of trimethylchlorosilane to a solution of **5** in acetone-d_6, ^{1}H NMR signals of the desired chloro complex **6** were detected,[29] but the reaction was incomplete and no satisfactory preparative procedure could be devised. Ligand exchange reactions of **2** with several chelating diphosphine ligands including 1,2-bis-diphenylphosphinoethane (dppe), (*R*)-(+)-BINAP, or (1*R*,S_P)-Josiphos[30] gave the cationic solvento complexes **7a**,[31] **7b**,[32] and **7c** (the latter as a mixture of diastereomers) in high yields (Scheme 3). An earlier synthesis of **7a** (56% yield) from [CpRu(MeCN)$_3$]PF_6 (**1**) and dppe suffered from side-reactions giving dinuclear products,[31] and a previous synthesis of **7b** from CpRuCl(BINAP) and $AgPF_6$ gave the product in 44% yield.[32] As reported, **7b** equilibrates with desolvated [CpRu(η^1:η^3-BINAP)]PF_6.[32] The complex syntheses starting from **2** and chelating ligands offer advantages in view of the high yields and the simple purification procedure, which simply consists in washing away of the naphthalene side-product with hexanes. This protocol was further extended to obtain the new diazadiene-*N*,*N*′ complex **8** in high yield from **2** and 1,4-bis(2,6-diisopropylphenyl)-1,4-diazabutadiene[33] (Scheme 3).

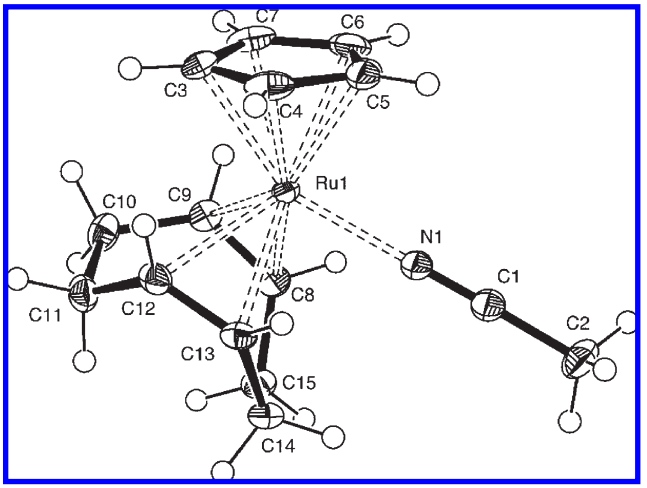


Figure 2. X-ray crystal structure of **5** (counterion omitted). ORTEP plot with 50% probability ellipsoids. Hydrogen atoms are shown with arbitrary radius. Selected interatomic distances (Å) and angles (deg): Ru1−N1 2.0792(18), Ru1−C13 2.2508(19), Ru1−C9 2.255(2), Ru1−C12 2.2609(19), Ru1−C8 2.274(2), N1−C1 1.131(3), C1−C2 1.463(3), C8−C9 1.378(3), C12−C13 1.382(3), C13−Ru1−C9 93.02(8), C12−Ru1−C8 84.66(7).

Coordination Chemistry of the CpRu$^+$ Fragment with Pyridylphosphanes. The stirring of **2** with 1 equiv of 6-(2,4,6-triphenylphenyl)-2-diphenylphospinopyridine ($^{2,4,6}Ph_3C_6H_2$-$PyPPh_2$) (**9**)[23,34] in acetonitrile at room temperature overnight forms [CpRu(η^1-**9**)(MeCN)$_2$]PF_6 (**10**) as the sole detectable

(28) Complex **5** has previously been obtained from **1** and COD: see ref 7.

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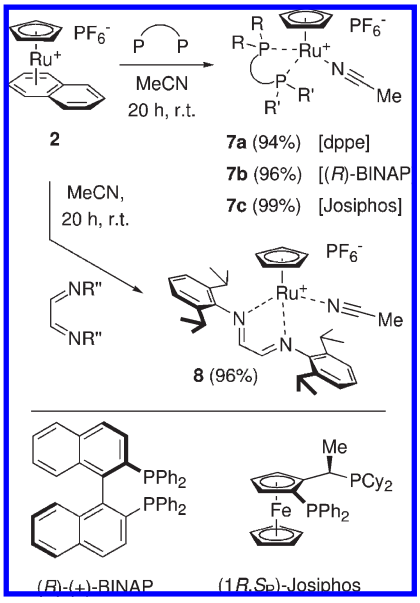
Scheme 3. Reactions of 2 with Chelating Ligands



species in solution (Scheme 4). The ^{31}P NMR spectrum shows that the pyridylphosphane binds in a η^1-fashion at phosphorus. After evaporation and redissolution in acetone-d_6, **10** (δ = 51.1 ppm, 65% abundance)[35] equilibrates with the chelated species [CpRu(η^2-**9**)(MeCN)]PF_6 (**11**; δ = 0.1 ppm, 35%) and uncomplexed acetonitrile. The latter complex displays the characteristic low-frequency ^{31}P NMR shift of phosphorus donors in four-membered chelate rings.[36] It is remarkable that phosphinopyridine **9** forms a chelate, because this type of ligand with a bulky group at pyridine-C6 has been designed to favor the η^1-binding mode of phosphorus,[37] where the noncomplexed nitrogen donor may undergo secondary interactions. However, a comparable observation has been reported by Grotjahn and co-workers, who found an equilibrium between [CpRu(η^1-^{t}BuPyPMe$_2$)$_2$(H_2O)]$^+$ and [CpRu(η^1-^{t}BuPyPMe$_2$)(η^2-^{t}BuPyPMe$_2$)]$^+$ (^{t}BuPyPMe$_2$ = 6-*tert*-butyl-2-dimethylphosphinopyridine) in CD_2Cl_2 solution.[38]

In the reaction of **2** with 2 equiv of **9** (cf. Scheme 5), complex [CpRu(η^1-**9**)$_2$(MeCN)]PF_6 (**12**) eventually forms, but substitution of the second acetonitrile ligand from intermediate **10** requires over a day at ambient temperature. This step was accelerated by heating to 60 °C overnight. Alternatively, the solution of **10** in acetonitrile was evaporated, and the resulting monophosphine complex mixture **10**/**11** was combined with an equivalent of **9** in acetone as a less coordinating solvent to bring about a fast second substitution. The counterion of **12** could be exchanged with $HNBu_3$-(±)-TRISPHAT[27] to give [CpRu(η^1-**9**)$_2$(MeCN)]-(±)-TRISPHAT (**13**), whose spectral characteristics were similar to **12**, showing a single ^{31}P NMR signal for the cation (**12**: δ = 43.2 ppm in acetonitrile-d_3 or δ = 44.1 ppm in $CDCl_3$; **13**: δ = 44.2 ppm in benzene-d_6) in several solvents, with no sign of chelation. The sterically less demanding ligand 2-diphenylphosphinopyridine (**14**) can be expected to show a higher tendency toward chelation. Nevertheless, exchange of [CpRu(η^6-naphthalene)]PF_6 (**2**) with a single equivalent of 2-diphenylphosphinopyridine (**14**; $\delta\{^{31}P\}$ = −4.3 ppm in acetonitrile-d_3, δ = −3.9 ppm in $CDCl_3$) in acetonitrile solution produced a single dissolved species, [CpRu(η^1-**14**)(MeCN)$_2$]PF_6 (**15**) (>95% abundance; cf. Table 2). After evaporation and dissolution of the sample in acetone-d_6, this had rearranged to the chelate [CpRu-(η^2-**14**)(MeCN)]PF_6 (**16**) (>95% abundance) with a characteristic low-frequency shift of the ^{31}P NMR signal (Table 2). The reaction of **2** with 2 equiv of **14** in acetonitrile directly produced an equilibrium mixture of [CpRu(η^1-**14**)$_2$-(MeCN)]PF_6 (**17**; 44% abundance)[35] and [CpRu(η^1-**14**)-(η^2-**14**)]PF_6 (**18**; 56% abundance).[35] After evaporation and redissolution in $CDCl_3$, **18** remained as the only detected species (>95% abundance).

A conflicting literature report concerning the coordination chemistry of phosphinopyridine **14** with the $CpRu^+$ fragment is available, based on NMR observation of ligand exchange experiments:[39] the reaction mixture of [CpRu(MeCN)$_3$]PF_6 (**1**) and 2 equiv of **14** in $CDCl_3$ was reported to display signals at $\delta(^{31}P)$ = 51.5 ppm (>90% abundance), assigned to [CpRu(η^1-**14**-κP)$_2$(MeCN)]PF_6 (i.e., our species **17**) and a minor signal at $\delta(^{31}P)$ = 0.35 ppm (<10%), speculatively assigned to the unusual[40] nitrogen-coordinated [CpRu(η^1-**14**-κN)$_2$(MeCN)]PF_6. These data are at variance with ours (Table 2) and do not fit the chemical shift value found for [CpRu(L)$_2$(MeCN)]PF_6 (L = various 6-substituted 2-diphenylphosphinopyridines), which is typically around δ = 43 ppm.[23,41] Moreover, comparison with Table 2 implies that the reported[39] values of δ = 51.5 and 0.35 ppm correspond to the monophosphane complexes **15** and **16**. To clarify the issue, we have repeated the NMR experiment and find that stirring of **1** with 2 equiv of **14** in $CDCl_3$ for 12 h gives clean ^{31}P NMR signals for **18** as major species (≥95% abundance) and **17** as a minor component (≤5%; see Table 2 for δ-values). Apparently, the mixing ratios used in the NMR experiment of ref 39 have been mistaken, leading to incorrect assignments.

Synthesis of Heteroleptic Complexes. The kinetic differentiation of the first and second substitution step at [CpRu(η^6-naphthalene)]PF_6 (**2**) with phosphanes in acetonitrile solution implied that nonsymmetrical complex cations of the type [CpRu(L^1)(L^2)(MeCN)]$^+$ should result from sequential substitution. Indeed, addition of ^{t}BuPyPPh$_2$ (**19**)[37] to a solution of **10**/**11** in acetone gave rise to the mixed complex [CpRu(η^1-**9**)(η^1-**19**)(MeCN)]PF_6 (**20**; Scheme 5) with signals at $\delta(^{31}P)$ = 42.6 and 44.4 ppm and a $^2J_{P,P}$ coupling constant of 34.9 Hz (Figure 3a). On the basis of the established pseudotetrahedral coordination geometry of [CpRu(L)$_3$]$^+$, heteroleptic cations [CpRu(L^1)(L^2)(L^3)]$^+$ must display metal-centered chirality[42] and occur in enantiomeric forms. This was proven by performing a sequential substitution starting from [CpRu(η^6-naphthalene)]Δ-TRISPHAT (**4**) in

(35) Abundances of equilibrating species can be concentration dependent. The data given are representative for NMR sample concentrations of 30−50 mg/mL.

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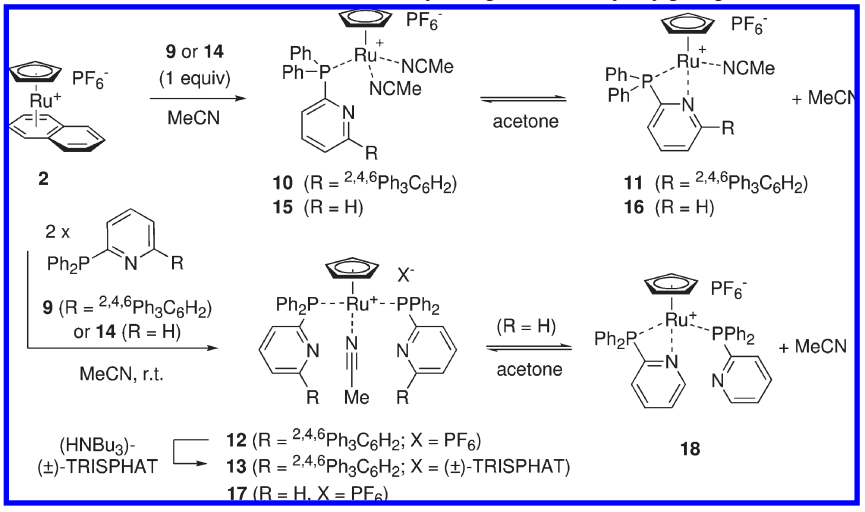
(42) Brunner, H. *Angew. Chem.* **1999**, *111*, 1248. *Angew. Chem., Int. Ed.* **1999**, *38*, 1194.

Scheme 4. Coordination Chemistry of $CpRu^+$ with Pyridylphosphanes



Scheme 5. Synthesis of Chiral-at-Metal Complexes

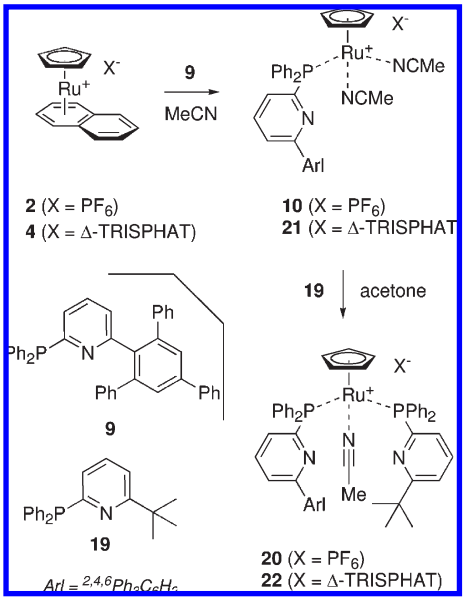


Table 2. ^{31}P NMR Parameters of $[CpRu(14)_n(MeCN)_m]^+$ Cations

compound[a]	$\delta(^{31}P)$, ppm	$J_{P,P}$, Hz	solvent
$[CpRu(\eta^1\text{-}14)(MeCN)_2]PF_6$ (**15**)	50.4		MeCN-d_3
$[CpRu(\eta^2\text{-}14)(MeCN)]PF_6$ (**16**)	−0.5		Me_2CO-d_6
$[CpRu(\eta^1\text{-}14)_2(MeCN)]PF_6$ (**17**)	44.0		MeCN-d_3
$[CpRu(\eta^1\text{-}14)_2(MeCN)]PF_6$ (**17**)	44.4		$CDCl_3$
$[CpRu(\eta^1\text{-}14)(\eta^2\text{-}14)]PF_6$ (**18**)	50.6/−8.4	38.3	MeCN-d_3
$[CpRu(\eta^1\text{-}14)(\eta^2\text{-}14)]PF_6$ (**18**)	51.2/−8.2	38.2	$CDCl_3$

[a] In the case of measurements performed in MeCN-d_3, the values refer to the MeCN-d_3 solvate analogues.

acetonitrile with ligands **9** and **19**, giving, via **21**, the mixed complex $[CpRu(\eta^1\text{-}9)(\eta^1\text{-}19)(MeCN)]\Delta$-TRISPHAT (**22**) (Scheme 5). Under the influence of the enantiopure counterion, two sets of signals are observed by ^{31}P NMR spectroscopy, revealing the presence of enantiomeric cations in a 50:50 ratio (Figure 3b); solvents such as $CDCl_3$ (Figure 3b) or benzene-d_6 achieve complete separation of signals for the diastereomeric ion-pairs (Figure 3c).

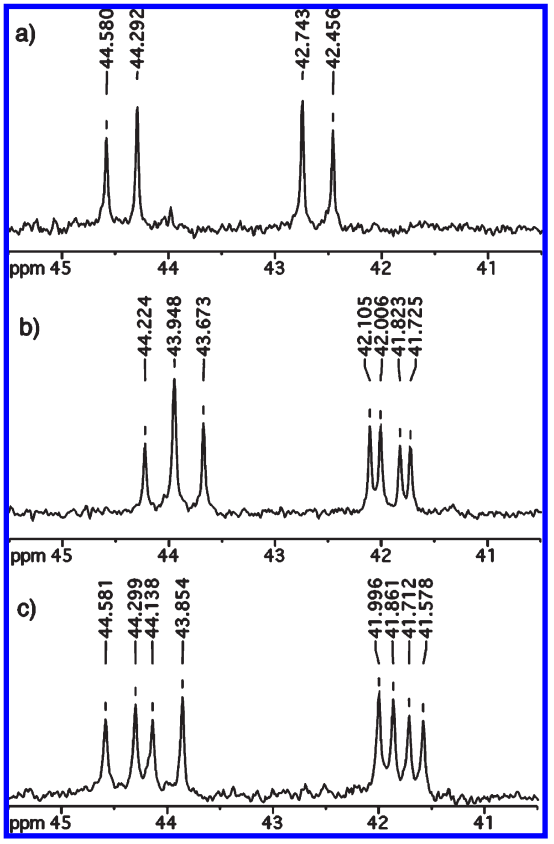


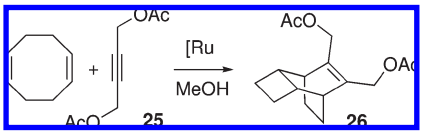
Figure 3. ^{31}P NMR spectra at 121 MHz of (a) **20** in $CDCl_3$; (b) **22** in $CDCl_3$; (c) **22** in C_6D_6.

Characterization of $[CpRu(P\{aryl\}_3)_3]^+$ Cations. The ligand exchange reactions on **2** have so far been carried out in acetonitrile solution. Acetonitrile is a relatively strong donor, and because it is desirable to have access to $[CpRu(L)_2(solvento)]^+$ complexes with weakly coordinating solvents, we also tried to perform ligand exchange reactions of **2** in less coordinating solvents, but under thermally more forcing conditions. In an attempt to synthesize $[CpRu(\eta^1\text{-}19)_2(H_2O)]PF_6$, **2** was heated to 60 °C in the presence of 2 equiv of ^{t}BuPyPPh$_2$ (**19**) in acetone and a little water for 3 days. However, crystals of the tris-phosphine complex $[CpRu(\eta^1\text{-}19)_3]PF_6$ (**23**) separated from the reaction solution

instead. The same complex was also obtained by heating **2** with 4 equiv of **19** in acetone to 90 °C in a pressure tube overnight. The ^{31}P NMR signal of this complex, at $\delta(^{31}P)$ = 38.4 ppm, is at lower frequency than the corresponding mono- (δ = 50.0 ppm) or diphosphine (δ = 43.6 ppm) solvato complexes,[41] and the Cp signal is characteristically high at $\delta(^{1}H)$ = 5.09 ppm (all data in $CDCl_3$). Interestingly, recrystallization attempts of [CpRu(η^1-**19**)$_2$(MeCN)]OTf under a variety of conditions had earlier been noted to give crystals of [CpRu(η^1-**19**)$_3$]OTf.[43,44] We still found it noteworthy that [CpRu(P{aryl}$_3$)$_3$]X complexes with monodentate triarylphosphanes are stable at all. Bruce and coworkers, in their fundamental paper on the substitution chemistry of $CpRuCl(PPh_3)_2$, had written, "Interestingly we have been unable to isolate the cation [Ru(PPh_3)$_3$(η^5-C_5H_5)]$^+$ from any reactions involving excess PPh_3, and we ascribe this to the difficulty of fitting three bulky PPh_3 molecules [...] around the central atom."[45] The [CpRu(PPh_3)$_3$]$^+$ cation has not yet been reported in the literature. By heating [CpRu(η^6-naphthalene)]Δ-TRISPHAT (**4**) with a slight excess of triphenylphosphine in acetone at 90 °C, we obtained the tris-substituted species [CpRu(PPh_3)$_3$]Δ-TRISPHAT (**24**) with a phosphorus NMR signal at δ = 32.4 ppm (in CD_2Cl_2) for the complex cation. The compound decomposes in $CDCl_3$ and partially dissociates in coordinating solvents to give [CpRu(PPh_3)$_2$(solvento)]$^+$ species, e.g., with δ = 40.5 ppm (in acetone-d_6). The hexafluorophosphate salt [CpRu(PPh_3)$_3$]PF_6, δ = 32.6 ppm (acetone-d_6), is prepared similarly, but could not be readily purified due to its sensitivity and amorphous nature. There is a gradual decrease of the phosphorus NMR chemical shift on going from [CpRu(PPh_3)(MeCN)$_2$]PF_6, δ = 51.7 ppm in $CDCl_3$,[7] or δ = 50.8 ppm in acetone-d_6,[12c,46] to [CpRu(PPh_3)$_2$(MeCN)]PF_6 with δ = 42.5 ppm in $CDCl_3$,[12b] or 41.9 ppm in acetone-d_6,[47] to the tris-phosphane cation with δ = 32.6 ppm in acetone-d_6.

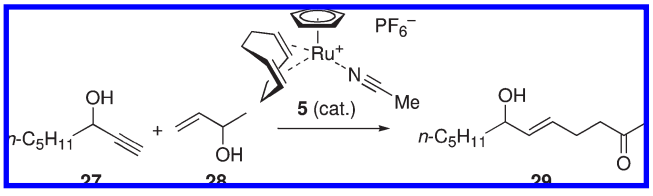
Catalysis with [CpRu(η^6-naphthalene)]PF_6 (2) and [CpRu(η^2:η^2-COD)(MeCN)]PF_6 (5) as Precursor Complexes. Trost and co-workers have catalyzed a range of C−C bond forming reactions with complex $CpRuCl(PPh_3)_2$ or CpRuCl(COD), often in the presence cocatalytic amounts of NH_4PF_6 or Lewis acids.[2] Assuming that the co-catalysts assist in the ionization of the neutral precursor complexes to give cationic species, we expected that the complex [CpRu(η^2:η^2-COD)(MeCN)]PF_6 (**5**) should be an activated catalyst with no need for co-catalytic additives. To test this hypothesis, we have investigated the ruthenium-catalyzed [2+2+2]-cycloaddition of (*Z*,*Z*)-1,5-cyclooctadiene with alkynes (1,4-diacetoxy-2-butyne **25**, in this instance) to give

Table 4. Ruthenium-Catalyzed [2+2+2]-Cycloaddition



entry	catalyst	mol %	*T*, °C	time, h	yield, %
1	**5**	5	70	2	90
2	**5**	1	70	10	68
3	**5**	2	70	1	93
4	**5**	5	rt	10	89
5	**2**	5	70	36	90

Table 5. Ruthenium-Catalyzed Alkyne/Allyl Alcohol Coupling



entry	loading, mol %	ratio **28**/**27**	solvent	*T*, °C	time, h	yield, %
1	5	3	DMF/H_2O	90	1	59
2	5	3	DMF/H_2O	rt	19	59
3	5	3	THF/H_2O	70	6	39
4	5	2	THF	rt	19	10
5	5	2	acetone	rt	19	0

fascinating tricyclic products such as **26**.[48] The original reaction conditions asked for heating of the reactants with 5 mol % of CpRuCl(COD) in methanol for unspecified reaction times.[48] The results in Table 4 show that complex **5** performs favorably under these conditions (entries 1−3); the catalyst loading can be reduced to 2 mol %, still getting a near-optimal performance (entry 3).

The reaction even proceeded at room temperature (entry 4), reinforcing the assumption that **5** is an activated catalyst precursor superior to CpRuCl(COD). Interestingly, [CpRu(η^6-naphthalene)]PF_6 (**2**) was also a catalyst precursor, but it requires prolonged reaction times, presumably as a consequence of the slow release of naphthalene from **2** in methanol. Complex **5** was used in another reaction that the Trost group had originally catalyzed with CpRuCl(COD):[49] the coupling of propargyl alcohol **27** with 3-buten-2-ol (**28**) in water/*N*,*N*-dimethyl formamide solution at 90 °C with 5 mol % of catalyst gave a 60% yield of keto alcohol **29** after 2.5 h. The results in Table 5 show that cationic complex **5** is again a valid replacement for CpRuCl(COD) (entries 1, 2), although the coupling remains a difficult one in terms of the yield and choice of solvent (entries 3−5). Notably, the high reactivity of **5** allowed us to perform the reaction at room temperature with no reduction in yield (entry 2).

We have earlier reported on the catalytic anti-Markovnikov hydration of terminal alkynes by means of [CpRu(L)$_2$(MeCN)]PF_6 complexes, which had been obtained from [CpRu(η^6-naphthalene)]PF_6 (**2**) and 2 equiv of azaarylphosphanes[34] L (typically **19** or **9**) in hot acetonitrile.[23] Since

(43) Grotjahn, D. B.; Lev, D. A. *J. Am. Chem. Soc.* **2004**, *126*, 12232, and Supporting Information.

(44) The Supporting Information of ref 43 gives $\delta(^{31}P)$ = 56.2 ppm ($CDCl_3$) for [CpRu(^{t}BuPyPPh$_2$)$_3$]OTf, but this is presumably a clerical error.

(45) Ashby, G. S.; Bruce, M. I.; Tomkins, I. B.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1003.

(46) Ref 39 reports $\delta(^{31}P)$ = 51.5 ppm for what was presumed to be [CpRu(PPh_3)$_2$(MeCN)]PF_6, which was prepared in situ from **1** and 2 equiv of PPh_3 in $CDCl_3$. As the measured value perfectly fits the monophosphino complex, this reinforces our assumption that a systematic weighing error has occurred in that work.

(47) We prepared a reference sample of [CpRu(PPh_3)$_2$(MeCN)]PF_6 by stirring **2** with 2 equiv of PPh_3 in MeCN at 50 °C overnight, followed by evaporation and washing of the residue with hexanes.

(48) Trost, B. M.; Imi, K.; Indolese, A. F. *J. Am. Chem. Soc.* **1993**, *115*, 8831.

(49) Trost, B. M.; Martinez, J. A.; Kulawiec, R. J.; Indolese, A. F. *J. Am. Chem. Soc.* **1993**, *115*, 10402.

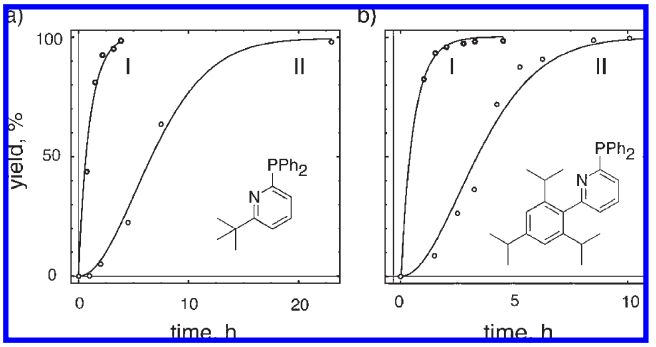
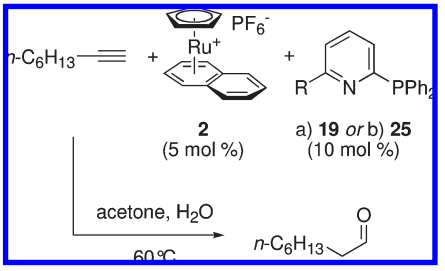


Figure 4. Kinetics of catalytic hydration of 1-octyne to octanal (cf. Scheme 6). Yields of octanal were measured by GC with tetradecane as internal standard. (a) Experiments with ligand **19**: curve I, catalytic hydration with preformed complex $[CpRu(\mathbf{19})_2(MeCN)]PF_6$; curve II, catalytic hydration with a mixture of **2** and **19**. (b) Experiments with ligand **25**: curve I, catalytic hydration with preformed complex $[CpRu(\mathbf{25})_2(MeCN)]PF_6$; curve II, catalytic hydration with a mixture of **2** and **25**.

Scheme 6. Catalytic Anti-Markovnikov Hydration of 1-Octyne



the acetonitrile used for the ligand exchange inhibits the catalytic hydration reaction, a change of solvent by evaporation/redissolution of the in situ catalyst was necessary in the earlier work. We hoped to spare this solvent change by using acetone as solvent for both the ligand exchange and the catalysis. ^{31}P NMR spectroscopy of a solution of **2** and 2 equiv of $^{t}BuPyPPh_2$ (**19**) in acetone-d_6 showed that about 10% of the phosphane ligand **19** ($\delta = -4.2$ ppm) had reacted after 24 h at room temperature, generating a new species with $\delta = 37.9$ ppm, which is characteristic of the tris-phosphane complex $[CpRu(\eta^1\text{-}\mathbf{19})_3]PF_6$ (see above). As expected, decomplexation of naphthalene is slow in acetone at room temperature, but can be expected to be faster at the temperature of the actual catalysis, allowing for an in situ catalyst generation/hydration. We thus hydrated the test substrate 1-octyne in hot acetone with some water by adding either (i) 5 mol % of preformed complex $[CpRu(L)_2(MeCN)]PF_6$, or (ii) a mixture of **2** and 10 mol % of ligand **19** or 6-(2,4,6-triisopropylphenyl)-2-diphenylphosphinopyridine (**25**)[23,24] (Scheme 6). Figure 4 shows the corresponding reaction progress curves of the 1-octyne hydrations. As expected from previous work,[23,43] the preformed complexes induce a fast catalytic hydration with complete conversion within 2−3 h. However, the in situ catalysis is also successful (curves II): it is characterized by an induction period of ca. 2 h, followed by a steadily increasing catalytic conversion that eventually reaches completion. For synthetic applications, the prolonged reaction times of curves II are still attractive, considering the very simple catalysis setup.[50]

Conclusion

The air-stable and readily available complex $[CpRu(\eta^6\text{-naphthalene})]PF_6$ (**2**) is a highly useful precursor material for the $CpRu^+$ cation in complex chemistry and catalysis. It may supplement, and in part replace, the more reactive precursors $[CpRu(MeCN)_3]PF_6$ (**1**) and CpRuCl(COD) (**6**), which are now commonly used for these purposes. The application examples presented here show the utility of **2** in a range of experiments, including the synthesis of chiral-at-metal complexes and the study of their interaction with enantiopure counterions. The synthesis of salt **4** by anion exchange in aqueous medium is notable, because a similar reaction would be out of reach for the moisture-sensitive precursor $[CpRu(MeCN)_3]PF_6$ (**1**). The option of releasing the $CpRu^+$ cation in the absence of strongly coordinating solvents has allowed us to prepare the sterically encumbered $[CpRu(PPh_3)_3]^+$ complex cation, which is not available from $[CpRu(MeCN)_3]PF_6$, because of the strong donor properties of acetonitrile. The substitution reactions of **2** in acetonitrile solution with phosphanes or other donors are very selective; for example, the synthesis of $[CpRu(dppe)(MeCN)]PF_6$ (**7a**) by our method gives improved yields and does not suffer from generation of bridging side-products as observed when starting from **1** and dppe.[31] The simplicity of generating solvento complexes by stepwise substitution enabled us to study the intricate complex chemistry of the $CpRu^+$ fragment with 2-diphenylphosphinopyridine (**14**). Overall, the thematically widespread application examples presented herein should serve to promote further applications of **2** as a useful precursor in $CpRu^+$ complex chemistry and catalysis.

Experimental Section

General Comments. All reactions were performed in degassed solvents under argon. Acetonitrile (MeCN) was stored over 3 Å molecular sieves. "Hexanes" denotes a petroleum ether fraction (40−60 °C). $[CpRu(\eta^6\text{-naphthalene})]PF_6$ (**2**),[6] $NBu_3H\text{-}(\pm)\text{-TRISPHAT}$[27] (TRISPHAT is tris(tetrachlorocatecholato)-phosphate(V)), cinchonidinium Δ-TRISPHAT,[27] diazadiene **8**,[33] 6-(2,4,6-triphenylphenyl)-2-diphenylphosphinopyridine ($^{2,4,6}Ph_3\text{-}C_6H_2PyPPh_2$; **9**),[23,34] and 6-*tert*-butyl-2-diphenylphosphinopyridine ($^{t}BuPyPPh_2$; **19**)[37,43,51] were obtained according to literature procedures. 1,4-Diacetoxy-2-butyne (**25**) was prepared by acetylation of 2-butyne-1,4-diol (Ac_2O/NEt_3/DMAP; CH_2Cl_2). Other materials, including (*R*)-(+)-BINAP ({*R*}-2,2′-bis-diphenylphosphino-1,1′-binaphthyl) and (1*R*,S_P)-Josiphos,[30] were obtained from commercial suppliers. NMR spectra were measured at ambient temperature (295 K), and chemical shifts δ are given in ppm and were referenced to internal TMS (^1H) or to external TMS via the solvent signal (^{13}C, measured with ^1H decoupling) or externally to 85% H_3PO_4 (^{31}P, measured with ^1H decoupling).

Single-Crystal X-ray Diffraction. Crystal data, parameters for intensity data collection, and convergence results are compiled in Table 1. Data were collected with Mo Kα radiation (graphite monochromator, $\lambda = 0.71073$ Å) on a Bruker D8 goniometer with a SMART APEX CCD area detector. Absorption correction was performed by SADABS.[52] Unit-cell parameters were obtained by least-squares refinement of up to 9999 reflections.

(50) For a first application of this protocol, see: Kribber, T.; Labonne, A.; Hintermann, L. *Synthesis* **2007**, 2809.

(51) Hintermann, L.; Xiao, L.; Labonne, A. *Angew. Chem.* **2008**, *120*, 8370. *Angew. Chem., Int. Ed.* **2008**, *47*, 8246.

(52) Sheldrick, G. M. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen, **1996**.

The structures were solved by direct methods (SHELXS97) and refined by full matrix least-squares procedures based on F^2 with all measured reflections (SHELXL97).[53] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in calculated positions and were refined using a riding model. The absolute configuration of compound **4** was also confirmed by evaluation of the Flack parameter.[54] The crystal of **5** used for intensity data collection proved to be a twin with respect to the polarity of the *c*-axis in space group $Pna2_1$. The Flack parameter quoted in Table 1 results from refinement as an inversion twin. Crystallographic data for all structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary data: CCDC 725213 (for **4**·CH_2Cl_2) and 725214 (for **5**).

[CpRu(η^6-naphthalene)]Δ-TRISPHAT (4). Cinchonidinium Δ-TRISPHAT (274 mg, 0.258 mmol) and **2** (109 mg, 0.248 mmol) were stirred in a mixture of CH_2Cl_2 (12 mL), MeOH (5 mL), and acetone (10 mL) until the solids had completely dissolved (ca. 30 min). Using more CH_2Cl_2 (ca. 8 mL), the solution was transferred to a separatory funnel containing water (50 mL). After thorough shaking, the organic phase was collected and the water phase extracted twice with CH_2Cl_2 (5 mL). The combined organic phases were filtered over a column of neutral Al_2O_3 (40 × 15 mm), and the column was eluted with more CH_2Cl_2 (25 mL, then 50 mL). The yellow filtrate was evaporated to dryness to leave 288.6 mg (first fraction) and 5.6 mg (second fraction) of solids. The solids were dissolved in CH_2Cl_2 (3 mL) and overlayed with ^{t}BuOMe (5 mL) and hexanes (15 mL). After standing overnight at 4 °C, the crystalline solid was washed with hexanes, ground, and dried under high vacuum at 50 °C. Yield: 249 mg (94%) of solvent-free beige powder. Mp > 260 °C (dec). ^{1}H NMR (400 MHz, acetone-d_6): 5.14 (s, 5 H, Cp), 6.46−6.50 (m, 2 H), 7.22−7.27 (m, 2 H), 7.69−7.75 (m, 2 H), 7.86−7.92 (m, 2 H). ^{13}C NMR (100 MHz, acetone-d_6): 80.4 (CH), 84.5/84.5 (Δδ = 1.2 Hz, CH), 86.5/86.5 (Δδ = 1.0 Hz, CH), 97.9 (C), 114.2 (d, J_{PC} = 19.9 Hz, $C_{TRISPHAT}$), 122.9 ($C_{TRISPHAT}$), 129.8/129.8 (Δδ = 2.9 Hz, CH), 132.1/132.1 (Δδ = 0.7 Hz, CH), 142.7 (d, J_{PC} = 6.6 Hz, $C_{TRISPHAT}$); the splitting of signals for several enantiotopic carbons is due to the chiral environment generated by the enantiopure counterion. ^{31}P NMR (162 MHz, acetone-d_6): −80.7 (s). ESI-MS ($CHCl_3$): 295 $[CpRu(C_{10}H_8)]^+$; 768.5 $TRISPHAT^-$ (negative mode). Anal. Calcd for $C_{33}H_{13}Cl_{12}O_6PRu$: C 37.29, H 1.23. Found: C 37.48, H 1.53.

[CpRu(η^2:η^2-COD)(MeCN)]PF_6 (5). A solution of (*Z,Z*)-1,5-cyclooctadiene (0.10 mL, 0.81 mmol) and **2** (200 mg, 0.45 mmol) in MeCN (7 mL) was stirred at room temperature for 45 h. After evaporation, the residue was dissolved in CH_2Cl_2 (2 mL) and overlayed with ^{t}BuOMe (3 mL) and hexanes (10 mL). After standing overnight at 4 °C, liquids were decanted, and the precipitate was washed with ^{t}BuOMe (2 × 3 mL) and dried under high vacuum: yellow solid (196 mg, 94%). Crystals for the X-ray structure analysis were obtained by diffusion of hexanes into an acetone solution of the complex. ^{1}H NMR (400 MHz, acetone-d_6): 2.13−2.23 (m, 4 H, CH_2), 2.24−2.35 (m, 2 H, CH_2), 2.40−2.51 (m, 2 H, CH_2), 2.71 (s, 3 H, *Me*CN), 4.36−4.46 (m, 2 H, C=C*H*), 5.32 (s, 5 H, Cp), 5.66−5.75 (m, 2 H, C=C*H*). ^{13}C NMR (100 MHz, acetone-d_6): 4.4 (CH_3), 28.0 (CH_2), 32.4 (CH_2), 85.3 (Cp), 85.4 (CH), 86.8 (CH), 130.5 (Me*C*N); the weak signal of Me*C*N is insecure. ^{13}P NMR (162 MHz, acetone-d_6): −144.4 (sept, J_{PF} = 710 Hz, PF_6^-). ESI-MS: *m*/*z* = 734.5 [2 M − MeCN − PF_6]$^+$, 274 $[CpRu(COD)]^+$. IR (KBr, cm^{-1}): 2846 (m), 2282 (w), 841 (s). Anal. Calcd for $C_{15}H_{20}F_6NPRu$: C 39.13, H 4.38, N 3.04. Found: C 39.56, H 4.34, N 2.87.

[CpRu(dppe)(MeCN)]PF_6 (7a). A solution of **2** (150 mg, 0.34 mmol) and 1,2-bis(diphenylphosphino)ethane (144 mg, 0.36 mmol) in MeCN (4 mL) was stirred at room temperature for 24 h. After evaporation, the residue was dissolved in CH_2Cl_2 (2 mL) and overlayed with ^{t}BuOMe (3 mL) and hexanes (10 mL). Standing overnight at 4 °C precipitated a solid, which was washed with ^{t}BuOMe (2 × 3 mL) and dried under high vacuum. Yellow powder (241 mg, 94%). ^{1}H NMR (400 MHz, acetone-d_6): 1.61 (s, 3 H, *Me*CN), 2.67−2.83 (m, 4 H, CH_2CH_2), 4.86 (s, 5 H, Cp), 7.42−7.49 (m, 8 H_{Arl}), 7.53−7.60 (m, 6 H_{Arl}), 7.89−7.94 (m, 6 H_{Arl}). ^{31}P NMR (161 MHz, acetone-d_6): −144.4 (sept, J_{PF} = 710 Hz, PF_6^-), 79.3 (s). MS (ESI): *m*/*z* = 565 $[CpRu(dppe)]^+$. Anal. Calcd for $C_{33}H_{32}F_6NP_3Ru$ (750.60): C 52.81, H 4.30, N 1.87. Found: C 52.43, H 4.27, N 2.22.

[CpRu({*R*}-BINAP)(MeCN)]PF_6 (7b). This complex was prepared as described for **7a** from **2** (70.6 mg, 0.161 mmol) and (*R*)-(+)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (100 mg, 0.161 mmol) in MeCN (4 mL). Yellow solid: 150 mg (96%). ^{1}H NMR (300 MHz, MeCN-d_3): 2.14 (s, 3 H, noncomplexed MeCN), 4.50 (s, 5 H, Cp), 6.30 (br d, *J* = 8.6 Hz, 1 H), 6.65 (br d, *J* = 8.7 Hz, 1 H), 6.73−6.84 (m, 2 H), 6.94−7.13 (m, 6 H), 7.19−7.27 (m, 3 H), 7.28−7.58 (m, 16 H), 7.68 (br d, *J* = 8.2, 1 H), 7.74 (br d, *J* = 8.2 Hz, 1 H), 7.82 (br d, *J* = 8.9 Hz, 1 H). ^{1}H NMR (400 MHz, $CDCl_3$): 1.18 (t, J_{PH} = 1.2 Hz, 3 H, *Me*CN), 4.48 (s, Cp, 5 H), 6.28 (d, *J* = 8.7 Hz, 1 H), 6.62 (d, *J* ≈ 9 Hz, 1 H), 6.71−6.79 (m, 2 H), 6.95−7.15 (m, 6 H_{Arl}), 7.19−7.56 (m, 19 H), 7.59−7.77 (m, 3 H); selected signals for [CpRu(κ^1*P*:κ^3*P*,*C*,*C*-BINAP)]PF_6 (ca. 14% abundance): 4.41 (s, Cp). ^{31}P NMR (121 MHz, MeCN-d_3): −144.7 (sept, J_{PF} = 704 Hz, PF_6^-), 45.9 (d, J_{PP} = 45.8 Hz), 54.5 (d, J_{PP} = 45.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): −144.3 (sept, J_{PF} = 713 Hz, PF_6^-), 47.1 (d, J_{PP} = 45.9 Hz), 55.3 (d, J_{PP} = 45.9 Hz); signals for [CpRu(κ^1*P*:κ^3*P*,*C*,*C*-BINAP)]PF_6: 14.6 (d, J_{PP} = 44.4 Hz), 73.8 (d, J_{PP} = 44.4 Hz). ESI-MS: *m*/*z* = 789 $[CpRu(BINAP)]^+$. Anal. Calcd for $C_{51}H_{40}F_6NP_3Ru$: C 62.83, H 4.14, N 1.44. Found: C 62.51, H 4.51, N 1.17.

[CpRu({1*R*,*S*$_P$}-Josiphos)(MeCN)]PF_6 (7c). This complex was prepared as described for **7a** from **2** (73.9 mg, 0.168 mmol) and (1*R*,*S*$_p$)-Josiphos (100 mg, 0.168 mmol) in MeCN (4 mL). Orange foam (158 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$), signals for the main diastereomer (76% abundance): 0.67−2.13 (m, 21 H_{Cy}), 1.67 (dd, *J* = 10.0, 7.5 Hz, 3 H, *Me*CH), 2.38−2.51 (m, 1 H_{Cy}), 2.43 (t, J_{PH} = 1.0 Hz, 3 H, MeCN), 3.51 (quint, *J* = 7.4 Hz, 1 H, MeC*H*), 3.57 (s, 5 H, Cp'Fe), 4.41−4.44 (m, 1 H, FeC_5H_3), 4.47 (t, *J* = 2.5 Hz, 1 H, FeC_5H_3), 4.58 (s, 5 H, CpRu), 4.61−4.64 (m, 1 H, FeC_5H_3), 6.76−6.86 (m, 2 H_{Ph}), 7.18−7.23 (m, 3 H_{Ph}), 7.55−7.73 (m, 3 H_{Ph}), 7.99−8.09 (m, 2 H_{Ph}); selected signals for the minor isomer (24% abundance): 1.78 (dd, *J* = 9.7, 7.1 Hz, 3 H, *Me*CH), 1.88 (t, J_{PH} = 1.0 Hz, 3 H, MeCN), 4.29 (s, 5 H, Cp'Fe), 4.75 (s, 5 H, CpRu). ^{31}P NMR (162 MHz, $CDCl_3$): −144.4 (sept, J_{PF} = 713 Hz, PF_6^-), 38.5 (d, J_{PP} = 46.0 Hz, major diastereomer), 47.8 (d, J_{PP} = 43.8 Hz, minor), 69.3 (d, J_{PP} = 46.0 Hz, major), 70.3 (d, J_{PP} = 43.9 Hz, minor). ESI-MS: *m*/*z* = 761 $[CpRu(Josiphos)]^+$. Anal. Calcd for $C_{43}H_{52}F_6FeNP_3Ru$: C 54.55, H 5.54, N 1.48. Found: C 54.91, H 5.83, N 1.34.

[CpRu{1,4-bis(2,6-diisopropylphenyl)-1,4-diaza-1,3-butadiene-*N*,*N*′}(MeCN)]PF_6 (8). A solution of **2** (150 mg, 0.341 mmol) and 1,4-bis(2,6-diisopropyl)phenyl-1,4-diaza-1,3-butadiene (135 mg, 0.358 mmol) in MeCN (4 mL) was stirred at room temperature for 24 h. The residue of evaporation was dissolved in CH_2Cl_2 (2 mL) and overlayed with ^{t}BuOMe (3 mL) and hexanes (10 mL). After standing overnight at 4 °C, liquids were decanted and the residual solid was washed with ^{t}BuOMe (2 × 3 mL) and dried under high vacuum. Brown-violet powder, 239 mg (96%). ^{1}H NMR (400 MHz, $CDCl_3$): 1.16 (d, *J* = 6.8 Hz, 6 H, 2 × Me), 1.23 (d, *J* = 6.8 Hz, 12 H, 4 × Me), 1.23 (d, *J* = 6.8 Hz, 6 H, 2 × Me), 2.52 (s, 3 H, *Me*CN), 2.57 (sept, *J* = 6.8 Hz, 2 H, C*H*Me$_2$), 3.06 (sept, *J* = 6.8 Hz, 2 H, 2 × C*H*Me$_2$), 4.28 (s, 5 H, Cp), 7.19 (dd, *J* = 7.5, 1.5 Hz, 2 H_{Arl}), 7.28 (dd, *J* = 7.8, 1.5 Hz, 2 H_{Arl}), 7.34 (t, *J* = 7.7 Hz, 2 H_{Arl}), 8.52 (s, 2 H, N=C*H*). ^{13}C NMR (100 MHz, $CDCl_3$): 4.1 (CH_3), 22.8 (CH_3), 24.2 (CH_3), 24.5 (CH_3), 26.7 (CH_3), 27.7 (CH), 28.1 (CH), 79.8 (CH), 123.2 (CH), 124.5 (CH), 127.9 (CH), 130.5 (C, Me*C*N), 138.2 (C), 139.2 (C), 150.0 (C), 166.0 (CH). ^{31}P NMR

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(162 MHz, $CDCl_3$): −144.7 (sept, J_{PF} = 713 Hz, PF_6^-). ESI-MS: m/z = 543 [CpRu(diazadiene)]$^+$. Anal. Calcd for $C_{33}H_{44}F_6N_3PRu$ + 0.5 H_2O: C 53.72, H 6.15, N 5.70. Found: C 53.58, H 5.99, N 5.53.

[CpRu(2,4,6-$Ph_3C_6H_2PyPPh_2$-κP)(MeCN)$_2$]PF_6 (10) and [CpRu(2,4,6-$Ph_3C_6H_2PyPPh_2$-κP,κN)(MeCN)]PF_6 (11). Pyridylphosphane **9** (646 mg, 1.138 mmol) was suspended in a solution of **2** (500 mg, 1.138 mmol) in MeCN (20 mL) and stirred at room temperature for 20 h. The resulting yellow solution was evaporated and the residue washed with hexanes. Bright yellow powder: 1.09 g (quant). The solid has a variable composition, losing coordinated MeCN with formation of **11**. ^{1}H NMR (400 MHz, acetone-d_6), data for **10** (65% abundance): 2.05 (s, free MeCN), 2.23 (d, J_{PH} = 1.4 Hz, 6 H, 2 × MeCN), 4.43 (s, 5 H, Cp), 7.15−7.99 (m, 27 H_{Arl}), 7.70 (s, 2 H_{Arl}), 7.97 (t, J = 1.8 Hz, 1 H_{Arl}); data for **11** (35% abundance): 1.66 (d, J_{PH} = 2.0, 3 H, MeCN), 4.32 (s, 5 H, Cp), 7.09−7.99 (m, 30 H_{Arl}). ^{31}P NMR (162 MHz, acetone-d_6): −144.4 (sept, J_{PF} = 709 Hz, PF_6^-), 0.1 (s, **11**), 51.1 (s, **10**). ESI-MS: m/z = 734.3 [CpRu(**9**)]$^+$.

[CpRu($Ph_3C_6H_2PyPPh_2$-κP)$_2$(MeCN)]PF_6 (12). A mixture of **9** (1.14 g, 2.0 mmol) and **2** (440 mg, 1.0 mmol) in MeCN (25 mL) was stirred for 10 h at 60−65 °C. The suspension turned into a yellow solution. After evaporation and drying under high vacuum, hexanes (10 mL) were added to the yellow resinous residue and the mixture was kept at 45 °C for 1 h. The solid was ground to a powder by means of a spatula and the suspension filtered. The solid was washed with hexanes (2 × 10 mL) and dried under high vacuum. Yellow powder: 1.29 g (99%). ^{1}H NMR (400 MHz, $CDCl_3$): 2.01 (br t, J_{PH} ≈ 1.2 Hz, 3 H, MeCN), 4.00 (s, 5 H, Cp), 6.73−6.79 (m, 3 H_{Arl}), 6.82−6.95 (m, 9 H_{Arl}), 6.97−7.13 (m, 23 H_{Arl}), 7.16−7.22 (m, 3 H_{Arl}), 7.25−7.34 (m, 4 H_{Arl}), 7.36−7.42 (m, 2 H_{Arl}), 7.44−7.50 (m, 6 H_{Arl}), 7.66 (s, 4 H_{Arl}), 7.68−7.73 (m, 4 H_{Arl}), 7.82−7.87 (m, 2 H_{Arl}). ^{31}P NMR (162 MHz, $CDCl_3$): −144.4 (sept, J_{PF} = 713 Hz, PF_6^-), 44.1 (s). ^{31}P NMR (121 MHz, MeCN-d_3): −144.6 (sept, J_{PF} = 706 Hz, PF_6^-), 43.2 (s). ESI-MS: m/z = 1301 [CpRu(**9**)$_2$]$^+$, 734 [CpRu(**9**)]$^+$. Anal. Calcd for $C_{89}H_{68}F_6N_3P_3Ru$: C 71.86, H 4.61, N 2.82. Found: C 72.02, H 4.84, N 2.71.

[CpRu(2,4,6-$Ph_3C_6H_2PyPPh_2$-κP)$_2$(MeCN)](±)-TRISPHAT (13). Tributylammonium (±)-TRISPHAT[27] (290 mg, 0.303 mmol) and **12** (444 mg, 0.2985 mmol) were stirred in CH_2Cl_2 (10 mL) for 30 min to give a clear yellow solution. After evaporation to 2−3 mL, the solution was placed on top of a chromatography column (SiO_2, wetted with CH_2Cl_2/hexanes, 1:1) and eluted with CH_2Cl_2/hexanes 60:40 → 70:30 → 100:0. The yellow, pure product fractions (TLC-control) were combined and evaporated. The solid residue was washed with hexanes and dried under vacuum. Bright yellow foam: 670 mg (90%), as clathrate with cyclohexane (derived from the "hexanes" fraction). ^{1}H NMR (400 MHz, C_6D_6): 1.40 (s, cyclohexane), 1.74 (br t, J ≈ 1.3 Hz, 3 H, MeCN), 3.97 (s, 5 H, Cp), 6.61 (br d, J = 7.6, 2 H), 6.72−6.83 (m, 8 H), 6.92−7.13 (m, 34 H), 7.17−7.21 (m, 2 H), 7.24−7.29 (m, 5 H), 7.50−7.55 (m, 4 H), 7.61−7.66 (m, 1 H), 7.72 (q, J ≈ 1.2 Hz, 4 H). ^{31}P NMR (161 MHz, C_6D_6): −79.9 (s, TRISPHAT), 44.2 (s). ESI-MS: m/z = 1301 [CpRu(**9**)$_2$]$^+$, 734 [CpRu(**9**)]$^+$. Anal. Calcd for $C_{107}H_{68}Cl_{12}N_3O_6P_3Ru$ + 1.5C_6H_{12}: C 62.27, H 3.87, N 1.88. Found: C 62.33, H 3.73, N 1.85.

[CpRu($PyPPh_2$-κP)(MeCN)$_2$]PF_6 (15) and [CpRu($PyPPh_2$-κP,κN)(MeCN)]PF_6 (16). A solution of **2** (66 mg, 0.15 mmol) and 2-diphenylphosphinopyridine (**14**; 39.9 mg, 0.15 mmol) in MeCN (3 mL) was stirred at room temperature for 20 h. The solution was evaporated under vacuum (10 mbar), and the residue was dissolved in CH_2Cl_2 (2 mL) and overlayed with ^{t}BuOMe (3 mL) and hexanes (10 mL). After standing at 4 °C overnight, filtration, washing with hexanes, and drying under vacuum gave **16** (90 mg, 97%) as a yellow foam. The NMR spectrum of **16** is observed in acetone-d_6 or $CDCl_3$ solution (>95% abundance), whereas the spectrum for **15** (>95% abundance) is observed when **16** is dissolved in MeCN-d_3. ^{1}H NMR (400 MHz, acetone-d_6), signals for **16**: 2.22 (d, J = 1.9 Hz, 3 H, MeCN), 4.68 (s, 5 H, Cp), 7.51−7.75 (m, 10 H), 7.83−7.90 (m, 2 H), 8.08 (tt, J = 7.9, 1.5 Hz, 1 H_{Py}), 8.90 (d × m, J = 5.3 Hz, 1 H_{Py}). ^{1}H NMR (300 MHz, MeCN-d_3), signals for **15**: 1.97 (s, 3 H, free MeCN), 4.46 (s, 5 H, Cp), 7.32 (ddt, J = 7.8, 4.5, 1.1 Hz, 1 H_{Py}), 7.38 (dddd, J = 7.7, 4.7, 2.5, 1.2 Hz, 1 H_{Py}), 7.43−7.55 (m, 10 H_{Ph}), 7.76 (tdd, J = 7.8, 3.4, 1.8 Hz, 1 H_{Py}), 8.73 (dddd, J = 4.7, 1.8, 1.0, 0.7 Hz, 1 H_{Py}). ^{31}P NMR (162 MHz, acetone-d_6), signals for **16**: −144.4 (sept, J_{PF} = 708 Hz, PF_6^-), −0.5 (s). ^{31}P NMR (121 MHz, MeCN-d_3), signals for **15**: −144.7 (sept, J_{PF} = 708 Hz, PF_6^-), 50.4 (s). ESI-MS: m/z = 430 [CpRu(**14**)]$^+$. Anal. Calcd for **16**, $C_{24}H_{22}F_6N_2P_2Ru$: C 46.84, H 3.60, N 4.55. Found: C 46.91, H 3.99, N 4.19.

[CpRu($PyPPh_2$-κP,κN)($PyPPh_2$-κP)]PF_6 (18). A solution of **2** (70 mg, 0.16 mmol) and **14** (83.9 mg, 0.32 mmol) in MeCN (4 mL) was stirred at 50 °C for 21 h. The reaction mixture was evaporated, the residue dissolved in CH_2Cl_2 (2 mL), and the solution overlayed with ^{t}BuOMe (3 mL) and hexanes (10 mL). After standing at 4 °C overnight, liquids were decanted and the solid was washed with hexanes. Drying under vacuum gave **18** as a yellow foam (131 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): 4.46 (s, 5 H, Cp), 6.70 (dd, J = 7.8, 2.8 Hz, 1 H_{Py}), 6.95−7.00 (m, 1 H_{Py}), 7.06−7.48 (m, 23 H_{Arl}), 7.76 (tt, J = 7.8, 1.4 Hz, 1 H_{Py}), 8.07 (br d, J = 4.1 Hz, 1 H_{Py}), 8.52 (d, J = 5.3 Hz, 1 H_{Py}). ^{31}P NMR (161 MHz, $CDCl_3$): −144.3 (sept, J_{PF} = 713 Hz, PF_6^-), −8.2 (d, J_{PP} = 38.2 Hz), 51.2 (d, J_{PP} = 38.2 Hz). ESI-MS: m/z = 692 [CpRu(**14**)$_2$]$^+$, 430 [CpRu(**14**)]$^+$. Anal. Calcd for $C_{39}H_{33}F_6N_2P_3Ru$: C 55.92, H 3.97, N 3.34. Found: C 56.26, H 4.35, N 3.00.

In Situ Ligand Exchange Experiments of 1 or 2 with 2-Diphenylphosphinopyridine (14): 15, 16, [CpRu($PyPPh_2$-κP)$_2$(MeCN)]PF_6 (17), and 18. (a) Reaction of **2** with **14** (1:1 ratio) in MeCN-d_3: In an NMR tube, **2** (10 mg, 0.023 mmol) and **14** (6.0 mg, 0.023 mmol) were dissolved in degassed MeCN-d_3 (0.7 mL) and kept at room temperature for 20 h. (b) Reaction of **2** with **14** (1:2 ratio) in MeCN-d_3: In an NMR tube, **2** (10 mg, 0.023 mmol) and **14** (12.0 mg, 0.046 mmol) were dissolved in degassed MeCN-d_3 (0.7 mL) and placed in an oil bath at 50 °C for 20 h. (c) Reaction of CpRu(MeCN)$_3$]PF_6 (**1**) with **14** (1:2 ratio) in $CDCl_3$: A mixture of **1** (10 mg, 0.023 mmol) and **14** (11.9 mg, 0.045 mmol) in degassed $CDCl_3$ (0.6 mL) was kept at room temperature for 24 h. See Table 2 and text for results.

[CpRu(2,4,6-$Ph_3C_6H_2PyPPh_2$-κP)(^{t}BuPyPPh$_2$-κP)(MeCN)]PF_6 (20). A suspension of **2** (100 mg, 0.228 mmol) and **9** (129 mg, 0.227 mmol) in MeCN (8 mL) was stirred at room temperature for 20 h. After evaporation under vacuum, the residue was dissolved in acetone (5 mL), **9** (72.7 mg, 0.228 mmol) was added at 0 °C, and the solution was stirred at room temperature for 3 h. After evaporation, the residue was dissolved in CH_2Cl_2 (2 mL) and overlayed with ^{t}BuOMe (3 mL) and hexanes (10 mL). After standing overnight at 4 °C, liquids were decanted and the solid was washed with ^{t}BuOMe (2 × 3 mL). Drying under high vacuum gave a bright yellow powder: 262 mg (93%). ^{1}H NMR (300 MHz, $CDCl_3$): 1.33 (s, 9 H, ^{t}Bu), 2.12 (t, J = 1.2 Hz, 3 H, MeCN), 4.14 (s, 5 H, Cp), 6.57 (dd, J = 7.6, 3.5 Hz, 1 H), 6.73−6.82 (m, 2 H), 6.90−7.54 (m, 33 H), 7.68−7.78 (m, 4 H), 7.82−7.88 (m, 3 H). ^{31}P NMR (121 MHz, $CDCl_3$): −144.3 (sept, J_{PF} = 709 Hz, PF_6^-), 42.6 (d, J_{PP} = 34.9 Hz), 44.4 (d, J_{PP} = 34.9 Hz). ESI-MS: m/z = 1053 [CpRu(**9**)(**19**)]$^+$, 734 [CpRu(**9**)]$^+$, 486 [CpRu(**19**)]$^+$. Anal. Calcd for $C_{69}H_{60}F_6N_3P_3Ru$ + 0.5H_2O: C 66.39, H 4.93, N 3.37. Found: C 66.62, H 5.45, N 3.04.

[CpRu(2,4,6-$Ph_3C_6H_2PyPPh_2$-κP)(^{t}BuPyPPh$_2$-κP)(MeCN)]-Δ-TRISPHAT (21). A solution of **4** (47 mg, 0.044 mmol) and **9** (24.9 mg, 0.044 mmol) in MeCN (3 mL) was stirred for 20 h at room temperature, followed by evaporation of the solvent under vacuum. To the residue were added **19** (14.0 mg, 0.044 mmol) and acetone (2 mL), and the solution was stirred at room temperature for 2 h. The solvent was evaporated and the residue dissolved in CH_2Cl_2 (0.5 mL). After overlaying with

hexanes (5 mL) and standing overnight at 4 °C, liquids were decanted and the solid was washed with hexanes (2 × 3 mL). Drying under high vacuum gave a bright yellow powder (76 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$), two shifts given in case of diastereomeric signals: 1.35 (s, 9 H, ^{t}Bu), 1.95/1.96 (t, J_{PH} = 1.4 Hz, 3 H, MeCN), 4.02/4.03 (s, 5 H, Cp), 6.42−6.49 (m, 1 H), 6.61−6.69 (m, 1 H), 6.74−6.84 (m, 2 H), 6.90−7.55 (m, 33 H), 7.71−7.79 (m, 4 H), 7.81−7.88 (m, 2 H). ^{31}P NMR (121 MHz, $CDCl_3$): −81.1 (s, TRISPHAT), 41.9 (d, J_{PP} = 34.2 Hz), 42.0 (d, J_{PP} = 34.2 Hz), 43.8 (d, J_{PP} = 33.5 Hz), 44.1 (d, J_{PP} = 33.5 Hz). ESI-MS: m/z = 1053 [CpRu(**9**)(**19**)]$^+$, 734 [CpRu(**9**)$^+$], 486 [CpRu(**19**)]$^+$; negative mode: 769 TRISPHAT$^-$. Anal. Calcd for $C_{87}H_{60}Cl_{12}N_3O_6P_3Ru$: C 56.09, H 3.25, N 2.26. Found: C 56.20, H 3.52, N 1.98.

[CpRu(^{t}BuPyPPh$_2$-κP)$_3$]PF$_6$ (23). A mixture of **2** (45.0 mg, 0.102 mmol) and **19** (130 mg, 0.41 mmol) in acetone (5 mL) and water (2 drops) was heated to 90 °C in a closed vessel for 35 h. The yellow solution was evaporated to a small volume and overlayed with hexanes (5 mL). After standing overnight at 4 °C, the solid was washed with ^{t}BuOMe and hexanes and dried under high vacuum. Crystalline yellow powder, 91 mg (70%). ^{1}H NMR (300 MHz, $CDCl_3$): 1.31 (s, 27 H, ^{t}Bu), 5.08 (s, 5 H, Cp), 6.45 (d, J = 6.7 Hz, 3 H), 6.90−7.07 (m, 23 H), 7.24−7.45 (m, 13 H). ^{31}P NMR (121 MHz, $CDCl_3$): −144.3 (sept, J_{PF} = 713, PF_6^-), 38.4 (s). ESI-MS: m/z = 805 [CpRu(**19**)$_2$]$^+$, 486 [CpRu(**19**)]$^+$. Anal. Calcd for $C_{68}H_{71}N_3F_6P_4Ru\cdot 2H_2O$: C 62.57, H 5.79, N 3.22. Found: C 62.37, H 5.53, N 3.00.

[CpRu(PPh$_3$)$_3$](Δ)-TRISPHAT (24).[55] A solution of **4** (70.2 mg, 0.066 mmol) and PPh_3 (74.2 mg, 0.28 mmol) in acetone (3 mL) was stirred at 90 °C for 32 h. The solvent was evaporated under vacuum, and the residue was dissolved in CH_2Cl_2 (1 mL) and overlayed with ^{t}BuOMe (2 mL) and hexanes (5 mL). After standing overnight at 4 °C, liquids were decanted and the precipitate was washed with ^{t}BuOMe (2 × 3 mL) and dried under high vacuum to give a yellow solid (108 mg, 95%). The product is light sensitive and unstable in acetone-d_6 (partial dissociation) or $CDCl_3$ (oxidation). ^{1}H NMR (400 MHz, CD_2Cl_2): 4.49 (s, 5 H, Cp), 6.88−6.96 (m, 18 H_{Ph}) 7.09−7.18 (m, 18 H_{Ph}), 7.34−7.40 (m, 9 H_{Ph}). ^{13}P NMR (121 MHz, CD_2Cl_2): −81.2 (s, TRISPHAT$^-$), 32.3 (s). ESI-MS: m/z = 691 [CpRu(PPh$_3$)$_2$]$^+$, 429 [CpRu(PPh$_3$)]$^+$. Anal. Calcd for $C_{77}H_{50}Cl_{12}O_6P_4Ru\cdot H_2O$: C 53.16, H 3.01. Found: C 53.32, H 3.27.

[CpRu(PPh$_3$)$_3$]PF$_6$. A solution of **2** (45 mg, 0.10 mmol) and PPh_3 (111 mg, 0.42 mmol) in acetone (3 mL) was heated to 90 °C in a pressure tube for 30 h. The dark yellow solution was evaporated to a small volume, overlayed with ^{t}BuOMe (6 mL), and kept at 4 °C overnight. After decantation, the residue was dissolved in CH_2Cl_2 (1 mL) and overlayed with hexanes (6 mL). After standing overnight at 4 °C, liquids were decanted and the semisolid was washed with hexanes and dried under high vacuum. Yellow resin, 70 mg (71%). No corresponding analysis was obtained. The compound easily dissociates PPh_3 to give solvated [CpRu(PPh$_3$)$_2$(S)]$^+$ complexes, where S is either a coordinating solvent or water. In $CDCl_3$, slow decomposition with partial generation of CpRu(PPh$_3$)$_2$Cl, $\delta(^{31}P)$ = 38.8 ppm, is observed. ^{1}H NMR (300 MHz, acetone-d_6), signals for [CpRu(PPh$_3$)$_3$]$^+$ (60% abundance): 4.61 (s, 5 H, Cp), 7.02−7.54 (m, 45 H, Ph); selected signals for [CpRu(PPh$_3$)$_2$(S)]$^+$ (40% abundance): 4.75 (s, 5 H, Cp). ^{31}P NMR (121 MHz, acetone-d_6): −144.3 (sept, J_{PF} = 709 Hz, PF_6^-), −5.7 (s, PPh_3), 32.6 (s, [CpRu(PPh$_3$)$_3$]$^+$), 40.5 (s, [CpRu(PPh$_3$)$_2$(S)]$^+$).

(55) A referee suspects that racemization of the Δ-TRISPHAT counterion may have occurred under the conditions of this ligand exchange reaction; this cannot currently be excluded.

Catalytic Reactions: 7,8-Diacetoxymethyltricyclo[4.2.2.0^{2,5}]-dec-7-ene (26).[48] The catalyst **5** (11.5 mg, 0.025 mmol, 5 mol %; or 4.6 mg, 0.01 mmol, 2 mol %) or **2** (11.0 mg, 0.025 mmol, 5 mol %) was added to a solution of (*Z*,*Z*)-1,5-cyclooctadiene (65 mg, 74 μL, 0.6 mmol) and 1,4-diacetoxy-2-butyne (85 mg, 0.50 mmol) in degassed methanol (5 mL) under argon. The reaction mixture was stirred at the indicated temperature (Table 4) until TLC indicated completion of the reaction. The solvent was removed under vacuum, and the residue purified by chromatography (SiO_2, ^{t}BuOMe/hexanes, 1:10) to give a colorless liquid that solidified on standing. See Table 4 for results. Mp: 53.5−55 °C. ^{1}H NMR (400 MHz, $CDCl_3$): 1.11−1.21 (m, 2 H), 1.85−1.95 (m, 2 H), 1.97−2.02 (m, 2 H), 2.05 (s, 6 H, 2 × $MeCO_2$), 2.09−2.21 (m, 4 H), 2.48−2.51 (m, 2 H), 4.73 (AB system, $J \approx$ 13 Hz, 4 H, 2 × CH_2OAc). ^{13}C NMR (100 MHz, $CDCl_3$): 18.0 (CH_2), 20.4 (CH_2), 21.1 (CH_3), 35.1 (CH), 36.6 (CH), 61.6 (CH_2), 138.3 (CH), 170.8 (C). EI-MS: m/z (%) = 278 (1) M$^+$, 218 (28), 176 (100). IR (KBr, cm^{-1}): 2943, 1732 (C=O), 1240. Anal. Calcd for $C_{16}H_{22}O_4$: C 69.04, H 7.97. Found: C 68.91, H 7.85.

7-Hydroxy-5-dodecen-2-one.[49] A solution of 3-buten-2-ol (**28**; 90 μL, 1.0 mmol), 1-octyn-3-ol (**27**; 75 μL, 0.50 mmol), and **5** (11.5 mg, 0.025 mmol, 5 mol %) in DMF/H_2O (1:1, 3 mL) was stirred at the specified temperature until completion of the reaction, as judged by TLC. After dilution with water and extraction with ^{t}BuOMe, the organic phase was evaporated and the residue purified by column chromatography (SiO_2, ^{t}BuOMe/hexanes, 1:3−1:1) to give a yellowish liquid. See Table 5 for results. Known compound.[49] ^{1}H NMR (400 MHz, $CDCl_3$): 0.88 (t, J = 7.1 Hz, 3 H, Me), 1.21−1.58 (m, 8 H, 4 × CH_2), 1.83 (br s, 1 H, OH), 2.14 (s, 3 H, Me), 2.31 (q, J = 7.2 Hz, 2 H, CH_2), 2.53 (t, J = 7.4 Hz, 2 H, CH_2), 4.02 (q, J = 6.7 Hz, 1 H), 5.49 (ddt, J = 15.4, 6.8, 1.3 Hz, 1 HC=C), 5.62 (dtd, J = 15.4, 6.4, 0.8 Hz, 1 HC=C). ^{13}C NMR (100 MHz, $CDCl_3$): 14.0 (CH_3), 22.6 (CH_2), 25.1 (CH_2), 26.2 (CH_2), 29.9 (CH_3) 31.7 (CH_2), 37.2 (CH_2), 43.0 (CH_2), 72.7 (CH), 129.4 (CH), 134.0 (CH), 207.8 (C=O).

Catalytic Anti-Markovnikov Hydration of 1-Octyne. (a) Preparation of catalyst complexes: A Schlenk flask was charged with **2** (22 mg, 0.05 mmol), ligand **19** or **25** (32 mg or 47 mg, 0.10 mmol), and MeCN (degassed, 3 mL). The mixture was stirred at 60 °C for 6 h or preferably overnight. The solvent was removed in vacuo to give a yellow powder or resin, which was used as the catalyst. (b) Catalytic reaction for kinetic measurements: A solution of 1-octyne (150 μL, 1 mmol, 1 equiv), H_2O (5 mmol, 5 equiv), and tetradecane (100 μL) in acetone (4 mL) was added either to the Schlenk flask containing the in situ catalyst (see above) or to a Schlenk flask containing a mixture of **2** (22 mg, 0.05 mmol) and ligand **19** or **25** (32 or 47 mg, 0.10 mmol). The solution was stirred at 60 °C. Aliquots were removed at regular intervals to monitor reaction progress by GC analysis with FID detection. Quantification was based on independently determined response factors of the tetradecane standard relative to 1-octyne and octanal. The results are displayed in Figure 4.

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Supporting Information Available: Crystallographic data for **4**·CH_2Cl_2 and **5** as CIF data files. This material is available free of charge via the Internet at http://pubs.acs.org.