Pendant−Bridging−Chelating−Cleavage: A Series of Bonding Modes in Ruthenium(II)-BINAPO Complexes

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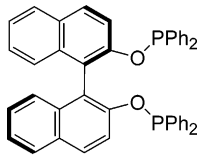
Reaction of 1,1′-bis(diphenylphosphino)binaphthol (BINAPO, **1**) with $[RuCl_2(\eta^6\text{-arene})]_2$ in methanol leads to dinuclear BINAPO-bridged Ru compounds $[\{RuCl_2(\eta^6\text{-}p\text{-cymene})\}_2(\mu\text{-BINAPO})]$, **2a**, in near quantitative yield. In dichloromethane or acetonitrile, **1** preferably affords mononuclear species in which one of the phosphine centers remains uncoordinated. These complexes can be further stabilized by reaction with BH_3 to afford, for example, $[RuCl_2(\eta^6\text{-}p\text{-cymene})(\eta^1\text{-BINAPO-}BH_3)]$, **4a**. Upon heating a mixture of **1** and $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ in DMF, P−O bond cleavage occurs to afford $[RuCl(\eta^2\text{-}PPh_2\text{-BINOL})(\eta^6\text{-}p\text{-cymene})]$, **5a**, bearing an anionic PO-chelating ligand. Ligand **1** acts as an intact chelate when reacted with $[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}p\text{-cymene})_2][PF_6]$ to yield $[RuCl(\eta^6\text{-}p\text{-cymene})(\eta^2\text{-BINAPO})][PF_6]$, **7**. Reaction of **1** with $[RuCp(CH_3CN)_3][PF_6]$ in acetonitrile or chloroform affords $[\{RuCp(CH_3CN)_2\}_2(\mu\text{-BINAPO})][PF_6]_2$, **8**, and $[RuCp(CH_3CN)(\eta^2\text{-BINAPO})][PF_6]$, **9**, respectively. The solid-state structures of **1**, **2a**, **4a**, and **7** are reported, that of **2a** representing a rare structural example of a molecule with a bridging binaphthyl-type ligand.

1. Introduction

In recent years a plethora of complexes containing C_2-symmetric bisphosphine ligands have been synthesized and successfully used for a large range of asymmetric transformations. In particular, ruthenium(II) complexes with chiral BINAP ligands are excellent hydrogenation catalysts.[1−3] Given this background, it is interesting to note that only very few metal complexes containing the related phosphinite BINAPO ligand, **1**, have been reported, namely, of palladium,[4,5] rhodium,[6,7] and ruthenium.[8,9] This is even more surprising, as enantiopure BINAPO is accessible in a facile manner from the relatively inexpensive chiral precursor 1,1′-dinaphthol.[10]



(*R*)-**1**

It has been demonstrated that with BINAPO ligands bearing substituents in the 3,3′-position of the binaphthyl backbone, good to excellent ee can be achieved in, for example, the rhodium-catalyzed hydrogenation of enamides[11] and the ruthenium-catalyzed hydrogenation of β-keto esters.[12] Yet, in both cases the catalysts were generated in situ and the nature of the active species was not determined. At present, well-defined ruthenium-BINAPO complexes are, to the best of our knowledge, restricted to the cationic $[RuXCp(BINAPO\text{-}F)]^+$ complexes prepared by Kündig and co-workers (bearing perfluorinated P-phenyl groups), which have been employed in asymmetric Diels−Alder reactions.[8] Herein, we report on the coordination chemistry of **1** with the widely used ruthenium complexes $[RuCp(CH_3CN)_3][PF_6]$, $[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}p\text{-cymene})_2][PF_6]$, and $[RuCl_2(\eta^6\text{-arene})]_2$, of which the latter has been previously used for the in situ generation of a ruthenium-BINAPO hydrogenation catalyst.[12]

2. Results and Discussion

The reaction between the dimeric ruthenium-arene halide, $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$, and **1** in methanol af-

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Scheme 1

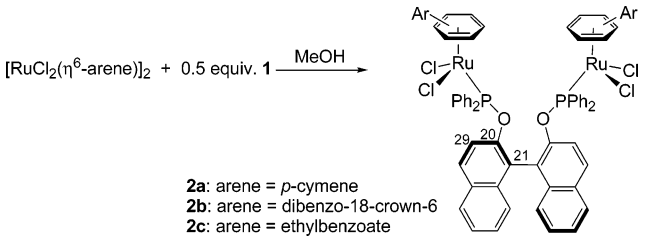


Table 1. Selected ^{13}C and ^{31}P NMR Chemical Shifts of Compounds 2a−5a and 7−9 (CD_2Cl_2 at 293 K)

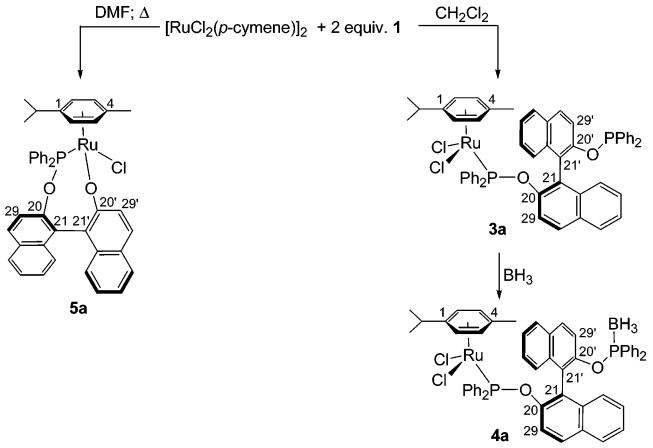
	2a	3a	4a	5a	7	8	9
C1	106.9	108.9	109.3	109.7	132.8	77.7	84.7
C4	101.1	98.8	98.7	98.2	100.0		
C20	149.9	148.4	148.5	148.2	148.1	150.2	150.1
C21	121.3	121.2	120.6	119.2	124.1	122.6	124.3
C29	122.5	120.9	121.0	121.3	118.5	120.0	121.6
C20′		153.3	149.1	151.9	150.0		149.1
C21′		121.5	123.3	115.2	121.6		124.8
C29′		119.5	120.4	118.2	120.3		120.4
P1	117.8	115.1	114.3	114.1	129.5	146.7	155.9
P2	117.8	114.1	110.2		129.5	146.7	153.7

forded the phosphinite-bridged ruthenium dimer complex **2a** in near quantitative yield, as shown in Scheme 1. Irrespective of the stoichiometry, i.e., even in the presence of 2 equiv of BINAPO, **2a** was formed exclusively and no mononuclear product with a chelating ligand was observed. Neither electronic nor steric factors of the complexed arene appear to influence the course of the reaction, exemplified by the reactions with electron-rich, bulky $[RuCl_2(\eta^6\text{-dibenzo-18-6-crown})]_2$ and electron-poor $[RuCl_2(\eta^6\text{-ethylbenzoate})]_2$, respectively, which readily afford the corresponding dinuclear products **2b** and **2c**, respectively, in high yield. The solubility of these dinuclear products is very poor in methanol, allowing facile isolation and purification. Selected NMR data for **2a** (and other compounds described below) are listed in Table 1.

When the reaction between $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ and 2 equiv of **1** was performed in dichloromethane, four signals are observed in the ^{31}P NMR spectrum corresponding to the uncoordinated ligand ($\delta = 110.1$ ppm), complex **2a** ($\delta = 117.7$ ppm), and a new species, **3a**, with two singlets of equal intensity at $\delta = 114.1$ and 115.5 ppm, matching a ruthenium complex bearing a pendant bisphosphinite ligand. Similar spectra were also observed if the reaction was conducted in, for example, acetonitrile or DMSO. Compound **3a** is surprisingly stable with respect to coordination of the free phosphinite to a metal center, although to obtain the complex in an analytically pure form and to prevent oxidation of the pendant phosphinite moiety, **3a** was reacted with BH_3·THF to afford the borane adduct **4a** (Scheme 2). This is a common method for protecting valuable (usually chiral) phosphines from oxidation, during either storage or synthetic transformations.[13] Regeneration of the free phosphine is typically accomplished by, for example, addition of an amine base.

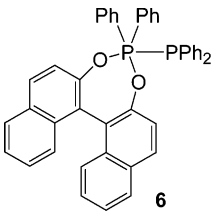
Attempts to introduce an additional donor ligand such as triphenylphosphine to either **2** or **4** resulted in complex mixtures, presumably due to abstraction and subsequent decomposition (see below) of the BINAPO ligand.

Scheme 2



A different product was obtained when a mixture of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ and 2 equiv of **1** was heated at 100 °C in DMF, in accordance with the procedure described previously by Zhang et al. for the in situ generation of a hydrogenation catalyst.[12] Under such conditions P−O bond cleavage occurred, resulting in the mononuclear complex **5a** as the predominant species. Compound **5a** is highly soluble in organic solvents, even dissolving to some extent in diethyl ether. The structure was unambiguously assigned by NMR spectroscopy, notably from the absence of any phosphorus coupling to carbon atoms C20′, C21′, and C29′ (see Scheme 2 for numbering). This complex is likely to be the precursor to the catalytically active species in the asymmetric hydrogenation of β-keto esters. In that an eight-membered ring is formed, the chiral center is in closer proximity to the metal, providing a plausible explanation for the observed high ee when alkyl substituents on the binaphthyl moiety are present.[12]

The facile loss of a PPh_2 fragment from **1** indicates that this ligand has only limited thermal stability. Indeed, when a solution of BINAPO was heated in DMF, two new doublets were observed in the ^{31}P NMR spectrum at $\delta = 34.2$ and -24.4 ppm with a coupling constant of $J_{PP} = 222$ Hz. On the basis of these data, we tentatively suggest a product arising from P−O bond rupture and subsequent P−P bond formation, as exemplified in compound **6**. Related compounds have been synthesized previously, and their NMR data agree well with that of **6**.[14]



To prepare a ruthenium-arene complex where **1** acts as a chelating ligand, viz., $[RuCl(\eta^6\text{-}p\text{-cymene})(\eta^2\text{-BINAPO})]^+$, it was necessary to use an activated

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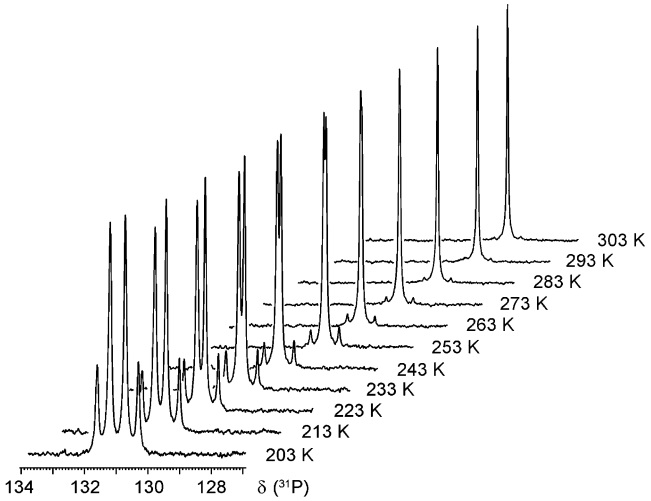
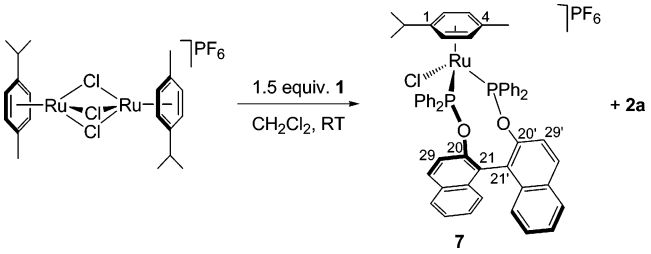


Figure 1. Variable-temperature ^{31}P NMR spectra of complex **7** between 203 and 303 K (CD_2Cl_2, 162 MHz).

Scheme 3



ruthenium arene precursor such as $[Ru_2(\mu\text{-}Cl)_3(\eta^6\text{-}p\text{-cymene})_2][PF_6]$. This species acts as the source for the coordinatively unsaturated, cationic synthon "$[RuCl(\eta^6\text{-}p\text{-cymene})]^+$" and readily reacts with **1** to afford complex **7**, as shown in Scheme 3. Attempts to synthesize **7** directly from **1** and $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ in the presence of $[NH_4][PF_6]$, $Ag[PF_6]$, or comparable chloride-abstracting agents were less successful, resulting in the formation of complex mixtures and low conversion toward the envisaged product, as evidenced by ^{31}P NMR.

With 1.5 equiv of ligand compound **2a** is formed as byproduct, facilitating the isolation of complex **7** from the reaction mixture by simple extraction with methanol. The ^{31}P NMR spectrum of **7** in CD_2Cl_2 at room temperature displays a broad singlet at $\delta = 129.5$ ppm, which upon cooling is resolved into an AB quartet with $^2J_{PP} = 67$ Hz at 203 K (see Figure 1), corroborating the proposed coordination mode. Such temperature-dependent characteristics are also known from ruthenium complexes with other chelating phosphines such as BINAP.[15] The ESI-MS of **7** exhibits a strong molecular ion peak at $[M]^+ = 925$, which upon selective fragmentation (MS/MS)[16] gives rise to a peak at $m/z = +791$ due to loss of the coordinated arene ligand.

Relative to complexes **2**−**5**, the C^1 carbon atom of the *p*-cymene ligand in **7** is shifted by more than 20 ppm to higher frequency, $\delta = 132.8$ ppm, as is readily established via C,H long-range correlation NMR, shown in Figure 2. These data suggest that in solution the interaction between C^1 and the metal is fairly weak. Accordingly, the bonding of the arene to the ruthenium is tending toward η^5-coordintaion rather than η^6, reflecting both a higher electron density at the metal due to the presence of two donor P atoms and increased steric bulk, pushing the isopropyl moiety away from the ruthenium. These effects are, though less pronounced, also present in the solid-state structure of **7** (vide infra).

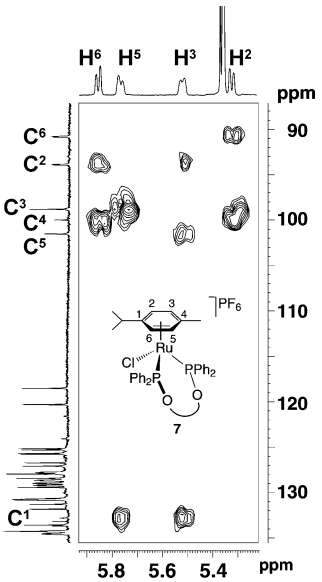


Figure 2. Section of the C,H long-range correlation spectrum of **7** showing the cross-peaks within the coordinated arene moiety arising predominantly from $^3J_{CH}$ couplings (CD_2Cl_2, 400 MHz).

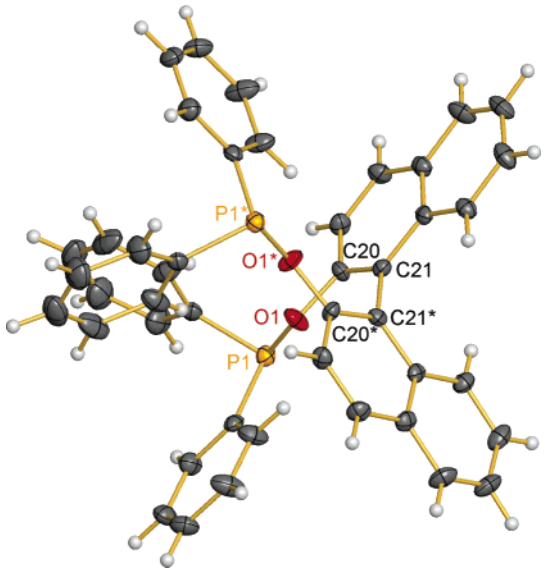


Figure 3. ORTEP plot of **1**; ellipsoids are drawn at the 40% probability level. The starred atoms are obtained by the symmetry operation $-x, y, -z$.

Crystals suitable for X-ray diffraction studies could be obtained of the free ligand **1** as well of those complexes where BINAPO acts as either bridging (**2a**), pendant (**4a**), or chelating (**7**) ligand, and representations of the structures are shown in Figures 3−6. In all crystals the binaphthyl ligand displays an *R*-configuration. Selected bond lengths and angles are given in Table 2, and relevant crystallographic data are listed in Table 3. Crystals of **2a** and **7** were of only poor quality, resulting in weak scattering and rather large thermal ellipsoids.

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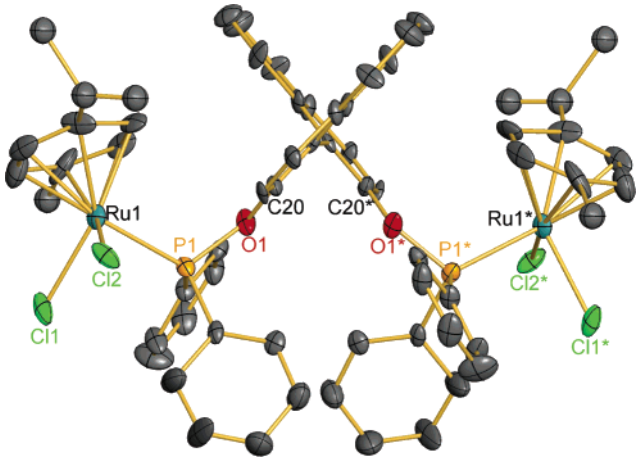


Figure 4. ORTEP plot of **2a**; ellipsoids are drawn at the 40% probability level; hydrogen atoms and solvent THF have been omitted for clarity. The starred atoms are obtained by the symmetry operation $-x$, $2-y$, z.

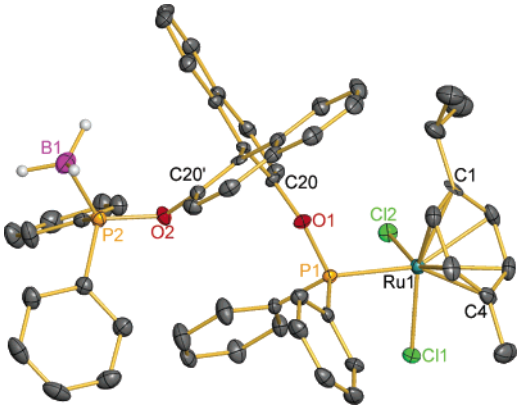


Figure 5. ORTEP plot of **4a**; ellipsoids are drawn at the 40% probability level; hydrogen atoms (except those of the BH_3) and solvent $CHCl_3$ have been omitted for clarity.

Table 2. Comparison of Selected Bond Lengths (Å) and Angles (deg) of 1, 2a, 4a, and 7

	1	2a	4a	7
Ru1−Cl1		2.365(4)	2.413(1)	2.390(2)
Ru1−Cl2		2.378(4)	2.414(1)	
Ru1−P1		2.299(4)	2.317(1)	2.323(2)
Ru1−P2				2.322(2)
P1−O1	1.659(2)	1.633(9)	1.637(3)	1.639(4)
P1−O2			1.616(3)	1.624(5)
O1−C20	1.377(2)	1.39(1)	1.403(4)	1.389(8)
O2−C20′			1.404(5)	1.383(8)
Cl1−Ru1−Cl2		87.3(1)	86.52(4)	
P1−Ru1−P2				95.65(8)
P1−Ru1−Cl1		87.6(1)	88.94(4)	85.77(7)
P2−Ru1−Cl1				82.46(7)
Cl2−Ru1−P1		90.1(1)	92.58(3)	
Ru1−P1−O1		114.1(4)	115.55(9)	121.5(2)
Ru1−P2−O2				115.0(2)

Coordination of the free ligand to the ruthenium leads to a moderate contraction of the P−O bond [1.659(2) Å in **1** versus 1.624(5)−1.640(9) Å], while interaction of the phosphinite with the Lewis acid BH_3 in **4a** has a more profound effect with an observed P(1)−O(1) bond of 1.616(3) Å. The P(2)−B(1) distance in **4a**, 1.894(6) Å,

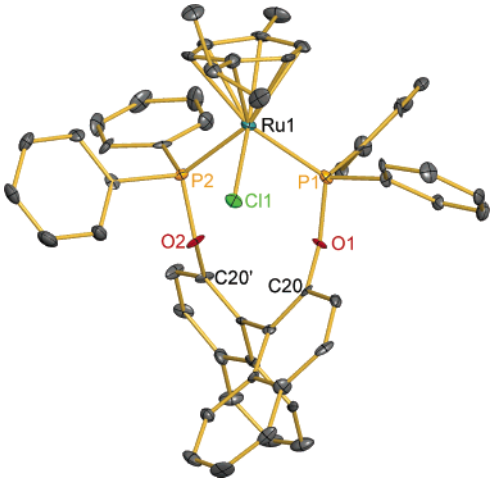
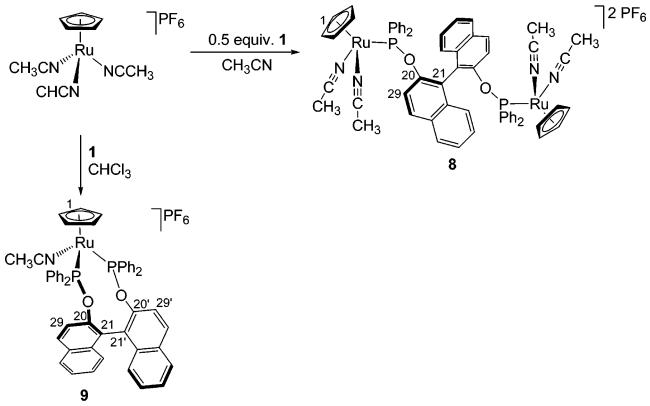


Figure 6. ORTEP plot of the cation of **7**; ellipsoids are drawn at the 40% probability level; hydrogen atoms and solvent CH_2Cl_2 have been omitted for clarity.

Scheme 4



is comparable to other phosphine-BH_3 adducts.[17] The dihedral angle between the planes of the naphthyl rings in **1** is almost perpendicular, 87.75(4)°, and changes only moderately in complexes **2a** and **4a**, with values of 82.5(2)° and 89.91(5)°, respectively. However, in **7**, where **1** binds to the ruthenium in a chelating mode, a considerably smaller dihedral angle of 69.39(8)° is observed, differing from previously reported RuCp-(η^2-BINAPO-F) complexes, where the angle is close to 90°.[8]

Structural parameters around the metal center in **2a**, **4a**, and **7** are of routine nature, exhibiting the typical "piano-stool" geometry around the ruthenium. Ru−P distances are found in a range from 2.298(4) to 2.323(2) Å, Ru−Cl distances vary between 2.365(4) and 2.414(1) Å, and these data are in good agreement with those of related Ru(II) arene complexes.[18] Bond lengths

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Table 3. Crystallographic Data for 1, 2a, 4a, and 7

formula	$C_{44}H_{32}O_2P_2$	$C_{64}H_{60}Cl_4O_2P_2Ru_2\cdot 2THF$	$C_{54}H_{49}BCl_2O_2P_2Ru\cdot CHCl_3$	$C_{54}H_{46}ClF_6O_2P_3Ru\cdot CH_2Cl_2$
M	654.64	1411.21	1094.02	1155.26
T [K]	140(2)	140(2)	140(2)	140(2)
cryst syst	monoclinic	orthorhombic	triclinic	orthorhombic
space group	$I2$	$P2_12_12$	$P1$	$P2_12_12_1$
a [Å]	12.3895(10)	13.776(2)	9.9885(9)	13.4669(15)
b [Å]	10.1181(6)	21.201(2)	10.8157(13)	14.7201(17)
c [Å]	13.7513(12)	10.796(2)	13.5361(10)	25.264(2)
α [deg]	90.0	90.0	99.160(10)	90.0
β [deg]	90.954(7)	90.0	99.000(7)	90.0
γ [deg]	90.0	90.0	117.294(9)	90.0
V [Å^3]	1723.6(2)	3153.0(8)	1238.3(2)	5008.2(9)
Z	2	2	1	4
density [Mg/m^3]	1.261	1.469	1.467	1.532
μ [mm^{-1}]	0.164	0.749	0.693	0.634
2θ range [deg]	$3.29 \le 2\theta \le 25.02$	$3.07 \le 2\theta \le 25.02$	$3.34 \le 2\theta \le 25.03$	$2.85 \le 2\theta \le 25.03$
no. of reflns collected	5151	19 418	7295	30 890
independent reflns	2715 [$R_{int} = 0.0239$]	5548 [$R_{int} = 0.1697$]	6434 [$R_{int} = 0.0301$]	8332 [$R_{int} = 0.1332$]
GooF on F^2	0.950	0.860	1.001	0.645
final R1, wR2 [$I > 2\sigma(I)$]	0.0314, 0.0669	0.0703, 0.1283	0.0277, 0.0639	0.0450, 0.0558
Flack x (esd)	−0.04(8)	0.20(10)	−0.02(2)	0.01(4)

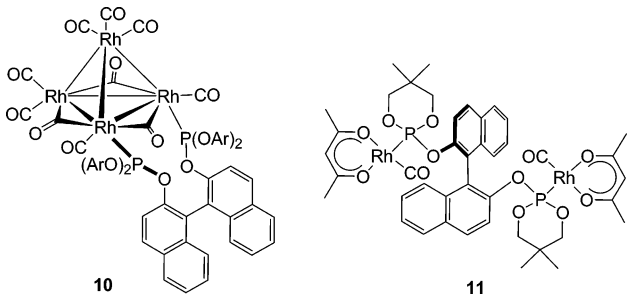

Figure 7.

between the metal and the carbon atoms of the coordinated arene are of comparable length in **2a** and **4a** [2.12(2)−2.255(4) Å] and somewhat longer in **7** [2.219(8)−2.345(8) Å], reflecting both higher electron density at the metal as well as increased steric bulk in the latter complex. In **7** the distance between the ruthenium and C(1), 2.345(8) Å, is relatively long, in agreement with the solution ^{13}C NMR data, but still sufficiently short to consider the coordination of the arene in the solid state as η^6. The bite angle of the bisphosphinite in complex **7** is 95.65(8)°, comparable to that of bisdiphenylphosphino ferrocene (dppf).[19]

A diverse coordination chemistry of ligand **1** also emerges when $[RuCp(CH_3CN)_3][PF_6]$ is employed as precursor instead of dimeric ruthenium-arene complexes; see Scheme 4. In acetonitrile, the ruthenium complex reacts with **1** to afford the dicationic complex **8** as the only product, as is evident from a singlet in the ^{31}P NMR spectrum, $\delta = 146.7$ ppm, as well as from ESI-MS, $[M]^{2+} = 575.3$. However, in noncoordinating solvents such as chloroform, **1** binds preferably in a chelating mode, affording the cationic complex **9**. This compound is readily identified from the appearance of two doublets in the ^{31}P NMR at $\delta = 155.9$ and 153.7 with a coupling constant $^2J_{PP} = 50$ Hz, as well as from the mass of the molecular ion, $[M]^+ = 861.7$.

While there are few examples for complexes bearing **1** as ligand, compounds with binaphthyl-based ligands bridging two metal centers are very rare. We are aware of only two examples where this is the case, both involving rhodium carbonyl complexes; see Figure 7. These examples differ in some respect from the compounds described herein in that they deal with phosphite ($P(OR)_3$) rather than phosphinite ($P(OR)R_2$) ligands. In **10**, a diphosphite-binaphthyl ligand coordinates to two rhodium centers in a tetranuclear Rh-carbonyl cluster,[20] whereas in the other example, assigned on the basis of its IR and ^{31}P NMR spectra, a similar ligand bridges between two rhodium centers, affording the dinuclear complex **11**.[21]

In conclusion a series of ruthenium(II) complexes bearing BINAPO ligands have been prepared, demonstrating that rather subtle changes in the reaction conditions can induce very different coordination modes of the ligand. Relative to other binaphthyl-based bisphosphines such as the widely used BINAP, ligand **1** is less likely to coordinate in a chelating manner and activated precursors are required to afford complexes of the type $[RuX(\eta^2\text{-BINAPO})(\eta^6\text{-arene})]^+$. Otherwise complexes where **1** acts as either bridging or pendant ligand predominate. These observations may have implications for the use of **1** as ligand in catalysis in that a change of solvent and/or reaction temperature may afford markedly different species, thereby potentially deciding over success or failure of a given transformation.

3. Experimental Section

General Techniques. All manipulations were performed under an atmosphere of nitrogen, using standard Schlenk techniques. Solvents were dried catalytically (Et_2O, CH_2Cl_2), distilled from calcium hydride (acetonitrile, DMF), or used as received following saturation with nitrogen (MeOH, chloroform). Chromatographic separations where carried out in air using 1.0 × 20 × 20 mm silica gel 60 F254 plates (Merck). $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$,[22] $[RuCl_2(\eta^6\text{-dibenzo-18-crown-6})]_2$,[23] $[RuCl_2(\eta^6\text{-ethylbenzoate})]_2$,[24] $[Ru_2(\mu\text{-Cl})_3(\eta^6\text{-}p\text{-cymene})_2][PF_6]$,[25]

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$[RuCp(CH_3CN)_3][PF_6]$,[26] and (*R*)-**1**[27] were prepared according to methods described previously; all other compounds were commercially available and used as received. NMR spectra were recorded on a Bruker Avance 400 with chemical shifts δ given in ppm (internal lock as reference) and coupling constants *J* given in Hz as positive values regardless of their real individual signs. Electrospray ionization mass spectra (ESI-MS) were recorded on a ThermoFinnigan LCQ Deca XP Plus quadrupole ion trap instrument, and elementary analyses were carried out at the EPFL.

Synthesis of 2a. A suspension of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (100 mg, 0.16 mmol) and **1** (110 mg, 0.17 mmol) in methanol (10 mL) was heated to reflux for 5 min, and then stirring continued at room temperature for another 30 min, during which time a salmon-colored precipitate forms. The solvent was removed by filtration and the residue washed twice with methanol. Yield: 194 mg (94%). ^{1}H NMR (CD_2Cl_2, 400 MHz): 8.24 (d, $^3J_{HH}$ = 7.9, 2H, H^{26}), 8.23 (d, $^3J_{HH}$ = 9.1, 2H, H^{28}), 8.04 (d, $^3J_{HH}$ = 9.1, 2H, H^{29}), 7.76 (m, 6H), 7.61 (dd, 2H, H^{25}), 7.50 (dd, 2H, H^{24}), 7.21 (m, 2H), 7.00 (m, 4H), 6.92 (m, 4H), 6.22 (m, 4H), 5.52 (d, $^3J_{HH}$ = 6.7, 2H, H^3), 5.37 (br, 2H, H^2), 5.00 (br, 2H, H^6), 4.75 (d, $^3J_{HH}$ = 5.9, 2H, H^5), 1.83 (dq, 2H, H^7), 1.53 (s, 6H, H^{10}), 0.74 (d, $^3J_{HH}$ = 7.0, 6H, H$^{8/9}$), 0.47 (d, $^3J_{HH}$ = 6.7, 6H, H$^{8/9}$). ^{13}C NMR (CD_2Cl_2, 100 MHz): 149.9 (d, $^2J_{PC}$ = 3, C^{20}), 133.5 (C^{22}), 132.7 (d, $^2J_{PC}$ = 11), 130.5 (d, $^4J_{PC}$ = 3), 130.5 (C^{27}), 130.1 (d, $^4J_{PC}$ = 2), 130.0 (C^{28}), 129.5 (d, $^2J_{PC}$ = 9), 129.3 (C^{26}), 127.8 (d, $^3J_{PC}$ = 11), 127.6 (C^{24}), 127.0 (d, $^3J_{PC}$ = 11), 125.4 (C^{25}), 124.9 (C^{23}), 122.5 (d, $^3J_{PC}$ = 6, C^{29}), 121.3 (d, $^3J_{PC}$ = 6, C^{21}), 106.9 (C^1), 101.1 (C^4), 92.2 (d, $^2J_{PC}$ = 10, C^3), 91.6 (br, C^2), 85.5 (br, C^5), 85.1 (d, $^2J_{PC}$ = 3, C^6), 29.8 (C^7), 21.6 (C^9), 20.7 (C^8), 17.4 (C^{10}). ^{31}P NMR (CD_2Cl_2, 162 MHz): 117.8 (s). Anal. Calcd for $C_{64}H_{60}Cl_4O_2P_2Ru_2$: C, 60.67; H, 4.77. Found: C, 60.52; H, 5.03.

Synthesis of 2b. As described for **2a** but with $[RuCl_2(\eta^6\text{-dibenzo-18-crown-6})]_2$ as substrate. Yield: 92%. ^{1}H NMR (CD_2Cl_2, 400 MHz): 8.21 (d, $^3J_{HH}$ = 8.1, 2H, H^{26}), 8.20 (d, $^3J_{HH}$ = 9.2, 2H, H^{28}), 8.15 (d, $^3J_{HH}$ = 9.2, 2H, H^{29}), 7.78 (dd, br, 4H), 7.65 (d, $^3J_{HH}$ = 8.3, 2H, H^{23}), 7.61 (m, 2H, H^{25}), 7.49 (m, 2H, H^{24}), 7.21 (m, 2H), 7.03−6.97 (m, 10H), 6.90−6.81 (m, 8H), 6.36 (br, 4H), 5.29 (br, 2H, H^2), 4.76 (br, 2H, H^3), 4.55 (br, 2H, H^4), 4.32 (br, 2H, H^5), 4.24−3.72 (m, 24H), 3.61 (br, 2H), 3.24 (br, 4H), 2.67 (br, 2H). ^{13}C NMR (CD_2Cl_2, 100 MHz): 149.6 (d, $^2J_{PC}$ = 3, C^{20}), 148.6, 148.5, 133.6 (C^{22}), 132.6 (d, $^2J_{PC}$ = 11), 130.6 (d, $^4J_{PC}$ = 3), 130.5 (C^{27}), 130.2 (br), 129.9 (C^{28}), 129.4 (d, $^2J_{PC}$ = 10), 129.1 (C^{26}), 128.0 (d, $^3J_{PC}$ = 11), 127.7 (C^{24}), 127.2 (d, $^3J_{PC}$ = 10), 125.5 (C^{25}), 124.7 (C^{23}), 122.3 (br, C^6), 121.9 (d, $^3J_{PC}$ = 6, C^{29}), 121.2 (d, $^3J_{PC}$ = 6, C^{21}), 120.8, 120.7, 112.6, 112.5, 81.7 (br, C^3), 76.0 (br, C^2), 75.5 (br, C^4), 72.3 (br, C^5), 70.2, 70.0, 69.8, 69.1, 69.0, 68.9, 67.8, 67.7. ^{31}P NMR (CD_2Cl_2, 162 MHz): 124.1 (s). Anal. Calcd for $C_{84}H_{80}Cl_4O_{14}P_2Ru_2 \cdot 2H_2O$: C, 57.47; H, 4.82. Found: C, 57.38; H, 4.02.

Synthesis of 2c. As described for **2a** but with $[RuCl_2(\eta^6\text{-ethylbenzoate})]_2$ as substrate. Yield: 85%. ^{1}H NMR (CD_2Cl_2, 400 MHz): 8.23 (m, 2H, H^{26,28}), 8.11 (d, $^3J_{HH}$ = 9.1, 2H, H^{29}), 7.71 (dd, 4H), 7.66−7.62 (m, 4H, H^{25,23}), 7.49 (dd, 2H, H^{24}), 7.27 (dt, 2H), 7.12−6.97 (m, 10H), 6.50 (m, 4H), 6.45 (d, $^3J_{HH}$ = 6.2, 2H, H^2), 6.27 (d, $^3J_{HH}$ = 5.9, 2H, H^6), 5.32 (dd, 2H, H^4), 5.02 (dd, 2H, H^3), 4.60 (dd, 2H, H^5), 4.22 (m, 4H, H^8), 1.29 (t, $^3J_{HH}$ = 7.1, H^9). ^{13}C NMR (CD_2Cl_2, 100 MHz): 162.9 (C^7), 149.6 (d, $^2J_{PC}$ = 4, C^{20}), 133.5 (C^{22}), 132.6 (d, $^2J_{PC}$ = 11), 131.2 (d, $^4J_{PC}$ = 3), 130.8 (d, $^4J_{PC}$ = 2), 130.6 (C^{27}), 130.2 (C^{28}), 130.0 (d, $^2J_{PC}$ = 11), 129.2 (C^{26}), 127.9 (d, $^3J_{PC}$ = 11), 127.8 (C^{24}), 127.5 (d, $^3J_{PC}$ = 11), 125.7 (C^{25}), 124.9 (C^{23}), 121.7 (d, $^3J_{PC}$ = 6, C^{29}), 121.3 (d, $^3J_{PC}$ = 6, C^{21}), 98.6 (C^2), 97.3 (d, $^2J_{PC}$ = 3, C^6), 89.0 (d, $^3J_{PC}$ = 10, C^7), 88.6 (C^4), 83.6 (d, $^2J_{PC}$ = 3, C^3), 82.8 (C^5), 62.5 (C^8), 14.2 (C^9). ^{31}P NMR (CD_2Cl_2, 162 MHz): 117.2 (s). Anal. Calcd for $C_{62}H_{52}Cl_4O_6P_2Ru_2 \cdot 2H_2O$: C, 55.78; H, 4.23. Found: C, 56.07; H, 4.39.

Synthesis of 4a. A solution of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (468 mg, 0.076 mmol) and **1** (100 mg, 0.15 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 5 min, then cooled to 0 °C, and a solution of BH_3 in THF (∼1.2 M, 0.26 mL, 0.31 mmol) was added. Following stirring a further 30 min at room temperature, the solution was concentrated to ca. 2 mL in vacuo and subjected to preparative TLC (1:10 acetone−CH_2Cl_2). The product was isolated by extraction of the first orange band (R_f = 0.68) with THF. Yield: 66 mg (44%). ^{1}H NMR (CD_2Cl_2, 400 MHz): 8.16 (d, $^3J_{HH}$ = 9.1, 1H, H$^{28'}$), 8.10 (d, $^3J_{HH}$ = 8.2, 1H, H$^{26'}$), 8.00 (d, $^3J_{HH}$ = 7.9, 1H, H^{26}), 7.98 (d, $^3J_{HH}$ = 9.0, 1H, H^{29}), 7.91 (d, $^3J_{HH}$ = 9.0, 1H, H^{28}), 7.76 (d, $^3J_{HH}$ = 9.0, 1H, H$^{29'}$), 6.9−7.6 (m, 24H), 6.7−6.8 (m, 2H), 5.19 (d, $^3J_{HH}$ = 5.9, 1H, H^6), 5.15 (d, $^3J_{HH}$ = 5.8, 1H, H^3), 5.12 (d, $^3J_{HH}$ = 5.9, 1H, H^2), 5.03 (d, $^3J_{HH}$ = 6.0, 1H, H^5), 2.17 (septet, $^3J_{HH}$ = 6.9, 1H, H^7), 1.30 (s, 1H, H^{10}), 1.0 (br, 3H, BH_3), 0.75 (d, $^3J_{HH}$ = 6.7, 6H, H^{8,9}). ^{13}C NMR (CD_2Cl_2, 100 MHz): 149.1 (d, $^2J_{PC}$ = 5, C$^{20'}$), 148.5 (d, $^2J_{PC}$ = 5, C^{20}), 133.7 (C$^{22,22'}$), 132.2 (d, $^4J_{PC}$ = 2), 132.1 (d, $^4J_{PC}$ = 2), 131.5 (br), 131.3(br), 131.2 (d, J_{PC} = 12), 131.1 (d, J_{PC} = 11), 130.5 (C$^{27'}$), 130.5 (d, $^4J_{PC}$ = 2), 130.4 (d, $^4J_{PC}$ = 2), 130.0 (C^{27}), 129.6 (C$^{28,28'}$), 128.9 (d, J_{PC} = 11), 128.6 (C$^{26'}$), 128.4 (d, J_{PC} = 11), 128.2 (C^{26}), 127.6 (d, J_{PC} = 10), 127.4 (d, J_{PC} = 11), 127.3 (C^{24}), 127.1 (C$^{24'}$), 125.8, 125.6, 125.4, 125.1, 123.3 (d, $^3J_{PC}$ = 5, C$^{21'}$), 121.0 (d, $^3J_{PC}$ = 6, C^{29}), 120.6 (d, $^3J_{PC}$ = 6, C^{21}), 120.4 (d, $^3J_{PC}$ = 5, C$^{29'}$), 109.3 (C^1), 98.7 (C^4), 90.4 (br, C^3), 89.7 (br, C^5), 89.0 (d, $^2J_{PC}$ = 5, C^2), 87.6 (d, $^2J_{PC}$ = 4, C^6), 29.9 (C^7), 21.2 (C^{8,9}), 17.2 (C^{10}). ^{31}P NMR (CD_2Cl_2, 162 MHz): 114.3 (s, RuP), 110.2 (br, PBH_3). ^{11}B NMR (CD_2Cl_2, 128 MHz): −38.8 (br). Anal. Calcd for $C_{54}H_{49}BCl_2O_2P_2Ru \cdot 1^1/_3CH_2Cl_2$: C, 61.09; H, 4.79. Found: C, 61.17; H, 4.49.

Synthesis of 5a. A solution of $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (35 mg, 0.06 mmol) and **1** (80 mg, 0.12 mmol) in DMF (6 mL) was heated to 100 °C for 10 min, then the solvent was removed in vacuo. The crude product was washed with Et_2O−pentane (1:1, 5 mL) and then extracted with Et_2O−methanol (10:1) to afford the product as an orange-red solid. Yield: 57 mg (68%). ^{1}H NMR (CD_2Cl_2, 400 MHz): 8.20 (d, $^3J_{HH}$ = 8.9, 1H, H$^{28'}$), 8.10 (d, $^3J_{HH}$ = 7.8, 1H, H^{26}), 8.07 (d, $^3J_{HH}$ = 9.1, 1H, H^{29}), 7.93 (d, $^3J_{HH}$ = 8.0, 1H, H^{26}), 7.87 (d, $^3J_{HH}$ = 9.1, 1H, H^{28}), 7.56 (d, $^3J_{HH}$ = 8.9, 1H, H$^{29'}$), 7.54−7.23 (m, 13H), 7.16−7.08 (m, 4H), 5.28 (d, $^3J_{HH}$ = 5.9, 1H, H^2), 5.20 (d, $^3J_{HH}$ = 5.9, 1H, H^6), 5.18 (d, $^3J_{HH}$ = 5.9, 1H, H^3), 5.15 (d, $^3J_{HH}$ = 5.9, 1H, H^5), 2.34 (dq, 1H, H^7), 1.53 (s, 3H, H^{10}), 0.85 (d, $^3J_{HH}$ = 6.9, 3H, H$^{8/9}$), 0.79 (d, $^3J_{HH}$ = 6.9, 3H, H$^{8/9}$). ^{13}C NMR (CD_2Cl_2, 100 MHz): 151.9 (C$^{20'}$), 148.2 (d, $^2J_{PC}$ = 8, C^{20}), 134.0 (C^{22}), 133.8 (C$^{22'}$), 131.9 (d, $^2J_{PC}$ = 11), 131.3 (d, $^2J_{PC}$ = 11), 130.6 (d, $^4J_{PC}$ = 2), 130.5 (d, $^4J_{PC}$ = 2), 130.3 (C^{27}), 130.2 (C$^{28,28'}$), 129.6 (C$^{27'}$), 128.5 (C^{26}), 128.4 (C$^{26'}$), 127.6 (d, $^3J_{PC}$ = 11), 127.5 (d, $^3J_{PC}$ = 11), 127.3 (C^{24}), 127.0 (C$^{24'}$), 125.1 (C^{23}), 124.9 (C^{25}), 124.5 (C$^{23'}$), 123.8 (C$^{25'}$), 121.3 (d, $^3J_{PC}$ = 6, C^{29}), 119.2 (d, $^3J_{PC}$ = 5, C^{21}), 118.2 (C$^{29'}$), 115.2 (C$^{21'}$), 109.7 (C^1), 98.2 (C^4), 91.3 (d, $^2J_{PC}$ = 5, C^5), 90.9 (d, $^2J_{PC}$ = 5, C^3), 88.0 (d, $^2J_{PC}$ = 6, C^2), 87.8 (d, $^2J_{PC}$ = 6, C^6), 30.0 (C^7), 21.2 (C^{8,9}), 17.3 (C^{10}). ^{31}P NMR (CD_2Cl_2, 162 MHz): 114.1 (s).

Synthesis of 7. To a solution of $[Ru_2(\mu\text{-Cl})_3(\eta^6\text{-}p\text{-cymene}_2)][PF_6]$ (78 mg, 0.107 mmol) in CH_2Cl_2 (20 mL) was added **1** (105 mg, 0.161 mmol) and the solution stirred at RT for 4 h before the solvent was removed in vacuo. The residue was washed with MeOH (2 × 5 mL), leaving an orange solid, and the washings were subjected to preparative TLC (CH_2Cl_2) following concentration. The first (broad) yellow band (R_f = 0.27) was extracted with CH_2Cl_2−MeOH to give the product as a yellow powder (yield: 14 mg). Further extraction of the orange solid with MeOH (100 mL) gave additional product (70 mg, >92% purity by ^{31}P NMR). Total yield: 68% per Ru_2. Analytically pure samples can be obtained (in low yield) by preparative TLC as described above. ^{1}H NMR

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(CD_2Cl_2, 400 MHz): 7.98 (br, 2H), 7.90−7.80 (m, 4H), 7.69−7.53 (m, 9H), 7.47−7.29 (m, 9H), 7.26−7.18 (m, 2H, $H^{24,24'}$), 7.10 (br, 2H), 6.91 (d, $^3J_{HH}$ = 8.5, 1H, $H^{23'}$), 6.82 (d, $^3J_{HH}$ = 8.5, 1H, H^{23}), 6.40 (d, $^3J_{HH}$ = 9.4, 1H, $H^{29'}$), 6.11 (d, $^3J_{HH}$ = 9.4, 1H, H^{29}), 5.85 (m, 1H, H^2), 5.76 (m, 1H, H^3), 5.52 (m, 1H, H^5), 5.32 (m, 1H, H^6), 2.56 (dq, 1H, H^7), 1.29 (s, 3H, H^{10}), 1.24 (d, $^3J_{HH}$ = 7.0, 3H, $H^{8/9}$), 0.60 (d, $^3J_{HH}$ = 6.7, 3H, $H^{8/9}$). ^{13}C NMR (CD_2Cl_2, 100 MHz): 150.0 (br, $C^{20'}$), 148.1 (br, C^{20}), 134.5 (m), 134.3 (br), 133.7 (C^{22}), 133.6 (br), 133.1 ($C^{22'}$), 132.8 (C^1), 131.8 (br), 131.3 (br), 130.8 (br), 130.6 ($C^{27,27'}$), 129.4 (br), 129.2 (m), 129.0 (m), 128.7 (m), 128.1 (br), 128.0 (C^{26}), 127.9 ($C^{26'}$), 127.8 (m), 127.1 (C^{24}), 126.7 ($C^{24'}$), 125.8 (C^{23}), 125.7 ($C^{25'}$), 125.3 (C^{25}), 125.2 ($C^{23'}$), 124.1 (C^{21}), 121.6 ($C^{21'}$), 120.3 ($C^{29'}$), 118.5 (C^{29}), 101.5 (br, C^3), 100.0 (C^4), 98.8 (br, C^5), 93.8 (dd, $^2J_{PC}$ = 6, J_{PC} = 4, C^6), 90.8 (dd, $^2J_{PC}$ = 7, $^2J_{PC}$ = 4, C^2), 31.3 (C^7), 22.5 ($C^{8/9}$), 18.6 ($C^{8/9}$), 15.9 (C^{10}). ^{31}P NMR (CD_2Cl_2, 162 MHz): 129.5 (s). ESI-MS (CH_2Cl_2) positive ion: *m/z* +925 $[M]^+$. ESI-MS/MS(+925): *m/z* +791 $[M - C_{10}H_{14}]^+$. ESI-MS(CH_2Cl_2) negative ion: *m/z* −145 $[PF_6]^-$. Anal. Calcd for $C_{54}H_{46}ClF_6O_2P_3Ru$: C, 60.59; H, 4.33. Found: C, 60.22; H, 4.31.

Synthesis of 8. A solution of $[RuCp(NCCH_3)_3][PF_6]$ (50 mg, 0.12 mmol) and **1** (40 mg, 0.06 mmol) in acetonitrile (5 mL) was stirred at room temperature for 1 h, then concentrated, and diethyl ether was added, resulting in the precipitation of a yellow-brown solid, which was washed further with Et_2O to afford the product. Yield: 74 mg (89%). ^1H NMR (CD_2Cl_2, 400 MHz): 8.08 (d, $^3J_{HH}$ = 8.1, 2H, H^{26}), 8.04 (d, $^3J_{HH}$ = 9.1, 2H, H^{28}), 7.55 (m, 2H, H^{25}), 7.48−7.39 (m, 8H), 7.30 (d, $^3J_{HH}$ = 8.5, 2H, H^{23}), 7.30 (br, 2H), 7.25 (d, $^3J_{HH}$ = 9.1, 2H, H^{29}), 7.15−7.06 (m, 8H), 6.61 (m, 4H), 4.32 (s, 10H, H^1), 2.15 (s, 6H, CH_3), 1.95 (s, 6H, CH_3). ^{13}C NMR (CD_2Cl_2, 100 MHz): 150.2 (d, $^2J_{PC}$ = 4, C^{20}), 138.9 (d, $^1J_{PC}$ = 55), 136.7 (d, $^1J_{PC}$ = 38), 133.5 (C^{22}), 131.5 (d, $^3J_{PC}$ = 14), 131.5 (d, $^4J_{PC}$ = 2), 130.2 (C^{27}), 130.1 (d, $^4J_{PC}$ = 2), 129.3 (C^{28}), 129.0 (C^{26}), 128.8 (d, $^3J_{PC}$ = 10), 128.7 (d, $^2J_{PC}$ = 14), 128.1 (d, $^2J_{PC}$ = 10), 127.8 (*C*N), 127.7 (*C*N), 127.3 (C^{24}), 125.5 (C^{23}), 125.4 (C^{25}), 122.6 (d, $^3J_{PC}$ = 6, C^{21}), 120.0 (d, $^3J_{PC}$ = 8, C^{29}), 77.7 (d, $^2J_{PC}$ = 2, C^1), 3.9 (*C*H_3), 3.5 (*C*H_3). ^{31}P NMR (CD_2Cl_2, 162 MHz): 147.6 (s). ESI-MS (CH_2Cl_2): *m/z* +575.3 $[M]^{2+}$. Anal. Calcd for $C_{62}H_{54}F_{12}N_4O_2P_4Ru_2$: C, 51.67; H, 3.78; N, 3.89. Found: C, 52.04; H, 3.79; N, 3.94.

Synthesis of 9. A solution of $[RuCp(NCCH_3)_3][PF_6]$ (50 mg, 0.12 mmol) and **1** (80 mg, 0.12 mmol) in chloroform (25 mL) was heated to reflux for 1 h, then filtered through a glass fiber filter, and the solution was concentrated. Addition of diethyl ether led to the precipitation of the product as a pale yellow, almost white solid. Yield: 92 mg (79%). ^1H NMR (CD_2Cl_2, 400 MHz): 7.89 (d, $^3J_{HH}$ = 8.1, 1H, H^{26}), 7.79 (d, $^3J_{HH}$ = 9.1, 1H, H^{28}), 7.78 (d, $^3J_{HH}$ = 8.2, 1H, $H^{26'}$), 7.62 (d, $^3J_{HH}$ = 9.1, 1H, $H^{28'}$), 7.61 (m, 1H), 7.57−7.39 (m, 13H), 7.18 (d, $^3J_{HH}$ = 8.5, 1H, H^{23}), 7.14 (d, $^3J_{HH}$ = 9.1, 1H, H^{29}), 7.11 (m, 2H), 7.04 (d, $^3J_{HH}$ = 8.2, 1H, $H^{23'}$), 7.02 (m, 2H), 6.91 (m, 2H), 6.69 (m, 2H), 6.55 (d, $^3J_{HH}$ = 9.1, 1H, $H^{29'}$), 4.43 (s, 5H, H^1), 1.72 (s, 3H, CH_3). ^{13}C NMR (CD_2Cl_2, 100 MHz): 150.1 (d, $^2J_{PC}$ = 6, C^{20}), 149.1 (d, $^2J_{PC}$ = 6, $C^{20'}$), 143.3 (d, $^1J_{PC}$ = 48), 141.6 (d, $^1J_{PC}$ = 43), 139.6 (d, $^1J_{PC}$ = 60), 136.7 (d, $^1J_{PC}$ = 59), 133.8 (C^{22}), 133.6 ($C^{22'}$), 131.8 (d, $^4J_{PC}$ = 2), 131.5 (d, J_{PC} = 12), 131.4 (d, J_{PC} = 14), 131.3 (d, $^4J_{PC}$ = 2), 130.8 ($C^{27,27'}$), 130.5 ($C^{28'}$), 130.3 (d, $^4J_{PC}$ = 2), 130.0 (d, $^4J_{PC}$ = 2), 129.9 (d, J_{PC} = 12), 129.8 (d, J_{PC} = 13), 129.5 (C^{28}), 129.1 (*C*N), 128.7 (d, J_{PC} = 10), 128.6 (d, J_{PC} = 10), 128.2 ($C^{26'}$), 128.0 (C^{26}), 127.9 (d, J_{PC} = 11), 127.5 (d, J_{PC} = 14), 127.4 ($C^{24'}$), 127.3 (C^{24}), 125.8 (C^{25}), 125.6 ($C^{25'}$), 125.4 (C^{23}), 125.2 ($C^{23'}$), 124.8 (d, $^3J_{PC}$ = 5, $C^{21'}$), 124.3 (d, $^3J_{PC}$ = 4, $C^{21'}$), 121.6 (d, $^3J_{PC}$ = 3, C^{29}), 120.4 (d, $^3J_{PC}$ = 2, $C^{29'}$), 84.7 (d, $^2J_{PC}$ = 2, C^1), 4.3 (*C*H_3). ^{31}P NMR (CD_2Cl_2, 162 MHz): 155.9 (d, $^2J_{PP}$ = 50), 153.7 (d, $^2J_{PP}$ = 50). ESI-MS (CH_2Cl_2): *m/z* +861.7 $[M]^+$, +821.3 $[M - CH_3CN]^+$. Anal. Calcd for $C_{51}H_{40}F_6NO_2P_3Ru$: C, 60.84; H, 4.00; N, 1.39. Found: C, 61.06; H, 4.60; N, 1.81.

Crystallography. Data collection for the X-ray structure determinations were performed on a KUMA CCD diffractometer system using graphite-monochromated Mo Kα (0.71070 Å) radiation and a low-temperature device [*T* = 140(2) K]. Crystals suitable for X-ray diffraction studies of **1** were obtained by cooling a CH_2Cl_2−acetonitrile solution (1:1) to −25 °C for **1**, diffusion of diethyl ether into a THF solution for **2a**, diffusion of pentane into a $CHCl_3$ solution for **4a**, and diffusion of pentane into a CH_2Cl_2 solution for **7**. Data reductions were performed by CrysAlis RED.[28] The structures of **1**, **2a**, and **7** were solved with SHELX97,[29] and that of **4a** with SIR-97.[30] Refinement was performed on PCs using the SHELX97 software package. Graphical representations of the structures were made with DIAMOND 3.0. Structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by full matrix least-squares refinement (against F^2). An empirical absorption correction (DELABS)[31] was applied to **1** and **4a**. All non-hydrogen atoms were refined anisotropically except for those of the THF solvent molecule and carbon atoms C7−C10 in **2a**, which were kept isotropic. In **2a** and **7** the structure was restrained using the DELU command, and some atoms were further restrained using the ISOR command. The contribution of the hydrogen atoms, in their calculated positions, were included in the refinement using a riding model with the exception of the BH-hydrogen atoms, which were located on the Fourier difference map and then constrained to equal B−H bond lengths and H−B−H angles. Some of the fluorine atoms of the $[PF_6]^-$ anion in **7** were split over two positions. Relevant crystallographic data are compiled in Table 3.

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Supporting Information Available: Additional NMR spectra and crystallographic information files (CIF) of **1**, **2a**, **4a**, and **7** are available free of charge via the Internet at http://pubs.acs.org.

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