Chemistry of Ruthenium(II) Alkyl Binap Complexes: Novel Bonding, Cyclometalation, and P−C Bond Splitting

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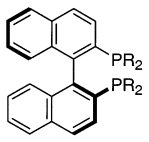
Reactions of the bis-isopropyl and bis-cyclohexyl alkyl Binap ligands, **8** and **9**, respectively, with $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ afford new dinuclear chloro-bridged Ru compounds which contain the Binap ligands as six- rather than four-electron donors. A backbone double bond proximate to one of the P-donors complexes the metal atom. NMR details of the olefin bonding plus isomerization reactions involving loss of the olefin complexation are reported. Reactions of **8** or **9** with $[Ru(OAc)_2(\eta^6\text{-}p\text{-cymene})]$ result in slow P−C bond cleavage and cyclometalation, instead of affording the anticipated $[Ru(OAc)_2(Binap)]$ complex. The new cyclometalated complexes, **15** and **16**, contain the complexed $R_2P-O(C{=}O)CH_3$ ligand and arise (presumably) via acetate attack at phosphorus with the electrons in the P−C bond moving to the ruthenium atom. The solid-state structure of one of these, the cyclohexyl analogue, **16**, is reported and represents a rare structural example of a molecule with three different chelate ligands. The complexed $R_2P-O(C{=}O)CH_3$ ligand is readily hydrolyzed in wet triflic acid to afford the $R_2P(OH)$ donor and an η^6-arene ligand (via Ru−C protonation).

Introduction

Interest in homogeneous catalysis using Binap, **1**, and related auxiliaries continues unabated.[1−8] Specifically, chiral Binap complexes of Ru(II) are now accepted as excellent hydrogenation catalysts.[9−12] Interestingly, details on the organometallic chemistry of Ru−Binap compounds are still scarce.



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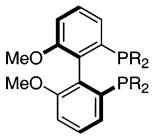

2

We have begun to follow the reactions of Ru−Binap (and the related MeO−Biphep, **2**) complexes when (a) weakly bound ligands (such as acetate) are removed from the coordination sphere and (b) at the same time no suitable strong donors are available. Interestingly, both the complexed Binap and MeO−Biphep find a way to donate additional electrons in that a double bond proximate to one of the P-donors complexes the metal, e.g., **3**;[13] see Scheme 1. Recently, more than a dozen complexes of type **4**[14] have been reported. As indicated in the scheme, there are additional examples of this bonding mode.[15−17] The last examples in the scheme are illustrative in that they involve the ubiquitous triphen-

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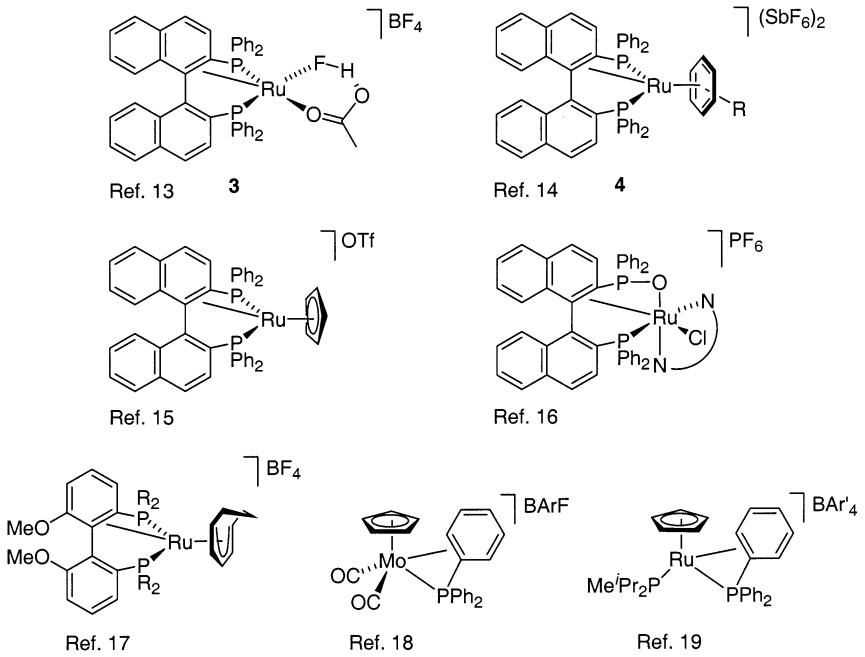
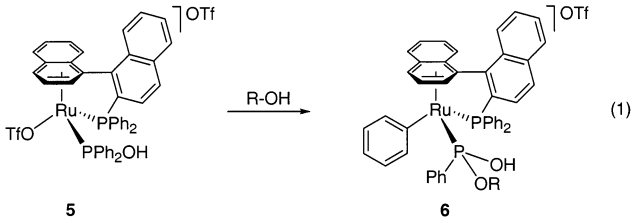
Scheme 1



ylphosphine,[18,19] thereby indicating that this type of bonding is not limited to biaryl bis-phosphines such as Binap.

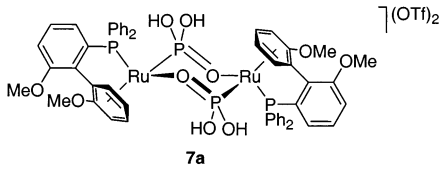
This six-electron bonding mode for Binap induces considerable strain in the naphthyl backbone[17] with the result that P−C bond cleavage becomes facile.[13] Reaction of [Ru(OAc)$_2$(Binap)] with slightly more than 2 equiv of wet triflic acid in 1,2-dichloroethane at 363 K gave the product **5** in good yield.[13]

Formally, the H^+ protonates the complexed acetate ligands and the water adds across the P−C bond. The metal, which is already complexed to the Binap π-system via the proximate double bond, need only slide across the face of the complexed olefin to reach a distorted η^6 mode. Attempts to generate an open coordination position in **5** by solvolyzing the weakly bound triflate ligand in simple alcohols resulted in the unusual compounds **6** (see eq 1).[20]



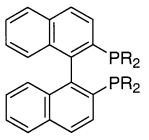
5 **6** (1)

The complexes **6** arise from migration of a P-phenyl fragment[21] and subsequent (or concomitant) attack of the alcohol on the P-center. In protic solvents containing water this type of reaction leads to complete stripping of the P-phenyl groups, i.e., the MeO−Biphep complex **7a** and its Binap analogue, **7b**.[22] Aspects of this chemistry have been summarized.[23]



7a

While this represents interesting chemistry, it stymies all attempts to generate potential solvent-stabilized cationic catalysts. With a view to further understanding this P−C bond splitting chemistry and possibly circumventing unwanted P-phenyl migration reactions, we synthesized the alkyl Binap ligands **8** and **9** and report on some of their Ru(II) complexes as well as one or two unusual aspects of this new chemistry.



8: R = *i*-Pr
9: R = Cy

Results and Discussion

6e Donor Complexes. The new alkyl-substituted Binap ligands were prepared as shown in eq 2. The ligand **9** has been prepared previously, though in a different manner,[24] whereas **8** represents a new derivative.

In contrast to the reaction with the classical phenyl-substituted Binap, which affords [RuCl(Binap)(η^6-*p*-cymene)]Cl, reaction of 1 equiv of the cymene complex

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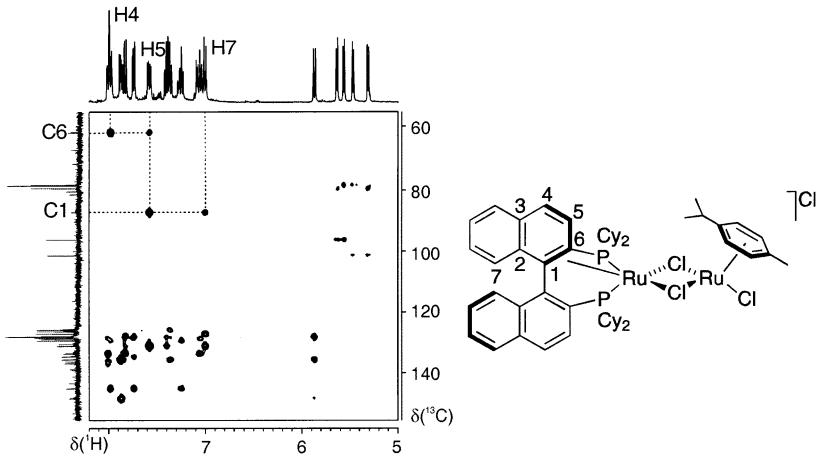
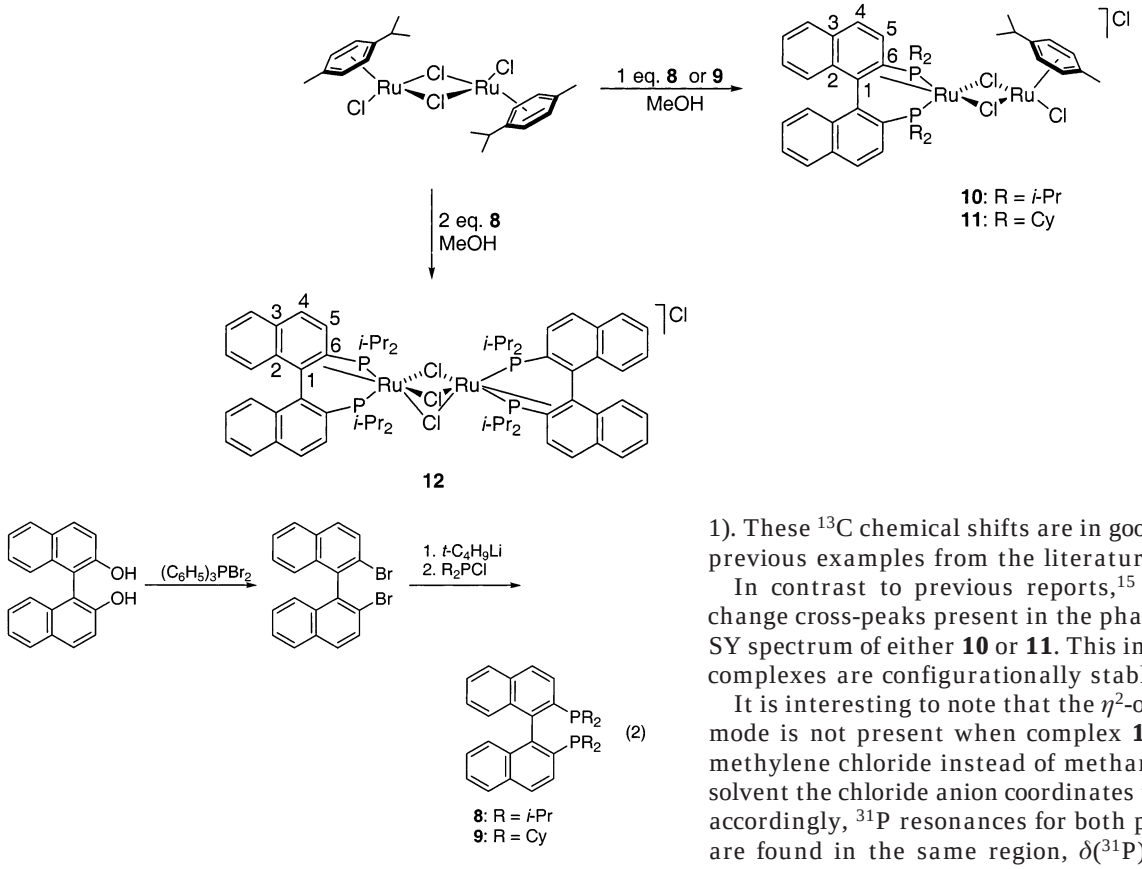


Figure 1. $^{13}C,^{1}H$ long-range spectrum of **11**, revealing the η^2-coordination from the backbone (d_4-methanol, 400 MHz).

Scheme 2

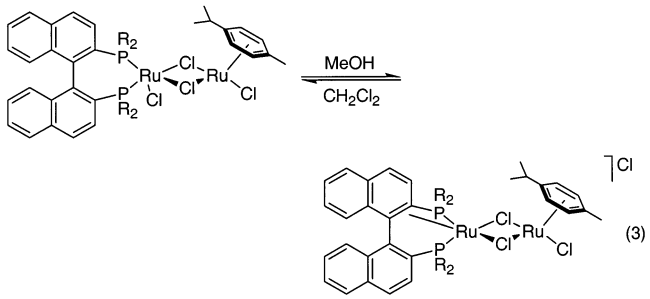


$[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ with 1 equiv of either racemic **8** or **9** afforded the new dinuclear products, **10** and **11**; see Scheme 2. Complexes **10** and **11** can be isolated in good yield as red solids and were fully characterized via NMR and microanalytical data.

The ^{31}P NMR spectra in methanol show the anticipated AX spin systems; however, the chemical shifts, δ 86.3 and 25.0 for **10** and δ 83.5 and 15.8 for **11**, were somewhat unexpected. The low-frequency shift of one of the two phosphorus nuclei provides an indication of the presence of a metal−olefin bond. The ^{13}C NMR data, obtained from long-range $^{13}C,^{1}H$ 2D spectra, reveal peaks at δ 87.4 and 62.3 for **10** and δ 87.4 and 61.7 for **11**, which stem from the carbon atoms C1 and C6 of the binaphthyl backbone, respectively, and thus strongly support the η^2-bonding mode (see Figure 1 and Table 1). These ^{13}C chemical shifts are in good agreement with previous examples from the literature.[13−19]

In contrast to previous reports,[15] there are no exchange cross-peaks present in the phase-sensitive NOESY spectrum of either **10** or **11**. This indicates that these complexes are configurationally stable.

It is interesting to note that the η^2-olefin coordination mode is not present when complex **10** is measured in methylene chloride instead of methanol. In the former solvent the chloride anion coordinates to ruthenium and, accordingly, ^{31}P resonances for both phosphorus atoms are found in the same region, $\delta(^{31}P) \approx 73$ ppm. This chloride exchange reaction is reversible, as indicated in eq 3.



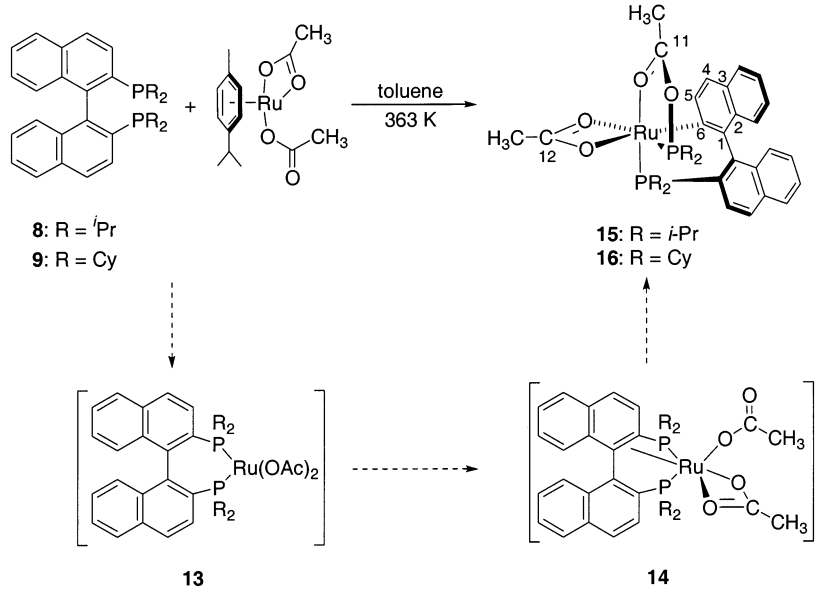
On the basis of ^{13}C and ^{31}P NMR data, loss of olefin coordination is also observed for solutions of **10** and **11**

Table 1. Selected ^{13}C NMR Data for Complexes 10−12

	C1	C2	C3	C4	C5	C6	P1	P2
10 (d_4-MeOH)[a]	87.4	145.0	130.9	134.9	124.9	62.3	86.3	25.0
10 (CD_2Cl_2)[b]	87.9	145.1	130.8	134.0	128.0	63.1	86.7	24.8
10 (CD_2Cl_2)[c]	139.3	133.6	133.6	126.8	130.7	144.5	73.8	72.5
10 (CD_3CN)[c]	139.0	133.3	134.0	128.6	128.5	132.4	67.3	63.5
11 (d_4-MeOH)[d]	87.4	144.7	130.9	134.3	128.3	61.7	83.5	15.8
12 (d_4-MeOH)[d,e]	87.0	144.8	131.0	133.6	125.2	65.9	86.1	19.1

[a] Anion: Cl^-, 500 MHz. [b] Anion: PF_6^-, 500 MHz. [c] Anion: Cl^-, 500 MHz. [d] 400 MHz. [e] Two isomers; data given for main isomer (>60%).

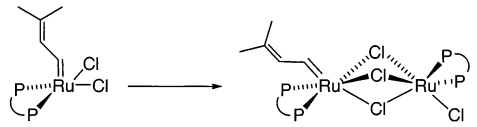
Scheme 3



in acetonitrile. If the chloride anion in these species is exchanged for a noncoordinating PF_6^- anion, the η^2-olefin coordination is maintained in methylene chloride. To some degree, it is surprising that in methanol the η^2-olefin coordination is present, since related complexes react quickly at ambient temperature with the alcohol to afford the corresponding ruthenium hydride.[14,25] However, even after 24 h in methanol at 80 °C, no change in the ^{31}P NMR spectrum for **10** or **11** was observed. Further, the reactions with terminal alkynes do not afford carbene complexes as expected from comparable reactions reported in the literature.[26−28]

The dinuclear complex **12**, formed when a second equivalent of **8** complexes to ruthenium, has NMR characteristics similar to those of **10**; that is, the Binap chelate functions as a six-electron donor. However, we note that this reaction (see bottom of Scheme 2) leads to two isomers, which reveal identical mass spectroscopic and similar NMR spectroscopic properties. Possibly, these isomers arise from pseudo-cis/trans configurations with respect to the complexed olefin double bond, and/or from the diastereomers (*R*,*R*/*S*,*S* and *R*,*S*/*S*,*R*) which are most likely present.

Complexes related to **12** were recently synthesized in connection with the catalytic oxidation of secondary alcohols.[29] Further, formation of such face-bridged dinuclear compounds is facile; see eq 4.[30]



Cyclometalation and P−C Bond Cleavage Reactions. The different steric and electronic properties of the new aliphatic Binap ligands relative to their phenyl analogues become obvious during the reactions of **8** and **9** with [Ru(OAc)$_2$(η^6-*p*-cymene)] (see Scheme 3). Instead of affording the anticipated Binap bis-acetate complex, e.g., **13**, slow P−C bond cleavage and cyclometalation occur after several days in toluene solution at 90 °C to give complexes **15** and **16**, respectively. Conceivably, these products arise via the two complexes **13** and **14** as outlined in Scheme 3. The ^{31}P NMR spectrum of the reaction solution for the cyclohexyl compound revealed resonances at δ 83.7 and 19.1, which are indicative of a complexation mode similar to intermediate **14**. Attempts to synthesize the initially envisaged bis-acetate complex **13** were not successful with these new ligands.

The ^{31}P NMR spectra of cyclometalated complexes **15** and **16** show AX spin systems, with the resonances for the phosphorus-acetate chelate found at unexpectedly high frequency, δ 240.0 and 237.7 for the isopropyl and

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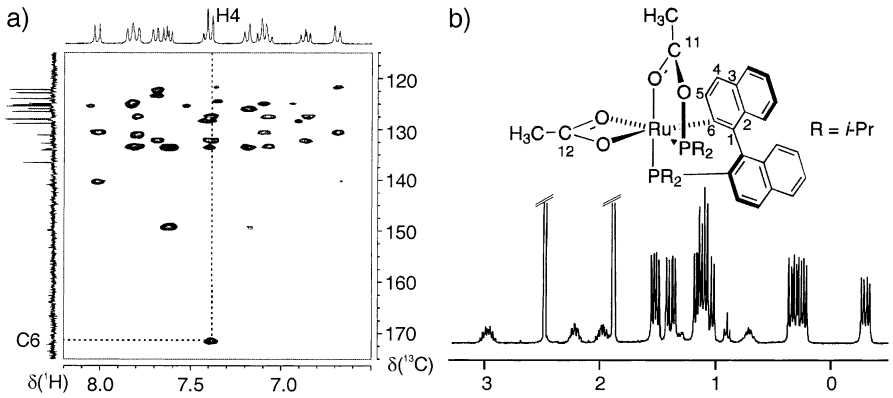
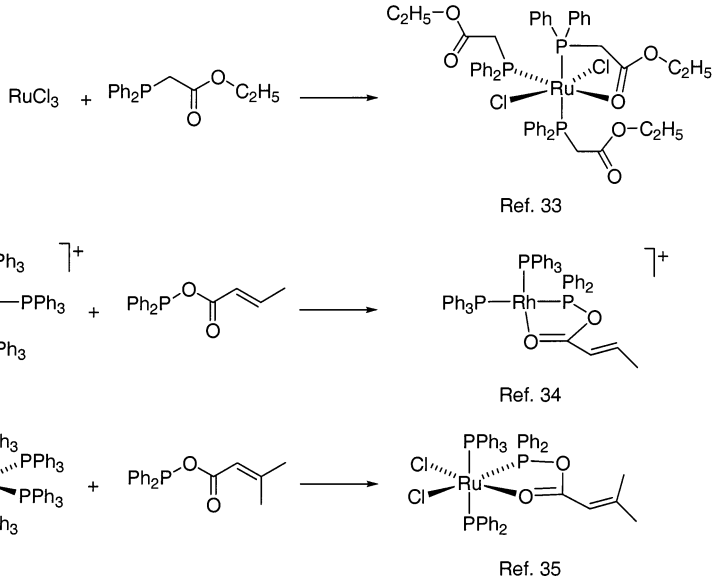


Figure 2. $^{13}C,^{1}H$ long-range correlation spectrum of **15**, revealing the high-frequency resonance of the σ-bound carbon atom, C6 (left), and aliphatic region of the ^{1}H NMR spectrum, showing the well-dispersed diastereotopic CH_3 groups (right); CD_2Cl_2, 300 MHz.

Scheme 4



cyclohexyl derivatives, respectively. It is known that P atoms included in a five-membered chelate ring reveal signals that are shifted to higher frequency.[31] However, the observed chemical shifts in **15** and **16** are certainly unusually high and may also develop to some extent from the better donor capabilities of the more electron-rich alkyl groups on the phosphorus donors.

The P−P coupling constant $^{2}J_{PP} \approx 31$ Hz is modest and indicates a cis arrangement (of the two spins). The σ-coordination of the naphthyl moiety is established from the typical high-frequency ^{13}C position[32] of C6, δ 171.4 and 174.1 for **15** and **16**, respectively (see Figure 2a). The proton NMR is straightforward, except for the diastereotopic alkyl substituents, which display well-separated resonances due to strong local anisotropic effects (e.g., one methyl in **15** is observed at −0.30 ppm, see Figure 2b).

Scheme 4 shows several structurally related complexes from the literature;[33−35] however, compounds **15** and **16** represent rare examples for a P−O−C=O chelate. Further, as can be seen from the scheme, the complexes presented were prepared by adding a preformed P−O chelate to a suitable ruthenium or rhodium precursor, whereas **15** and **16** arise (presumably) via intramolecular acetate attack at phosphorus with the electrons in the P−C bond moving to the ruthenium atom.

Solid-State Structure of 16, a Molecule with Three Different Chelate Ligands. Crystals of **16** suitable for X-ray diffraction studies were obtained upon slow evaporation of a methylene chloride solution, and a view of the molecule is shown in Figure 3. Selected bond lengths and bond angles are given in Table 2. The immediate coordination sphere around the ruthenium is best described as distorted octahedral. The phosphorus atom P1 of the dicyclohexyl−binaphthyl phosphine and the σ-bound arene, C6, make up one chelate ring. The phosphorus atom P2 of the $Cy_2P-O-C=O(22)CH_3$ chelate and its oxygen atom, O22, make up a second chelate, and the remaining two coordination positions are filled by the two oxygen atoms of the acetate. The

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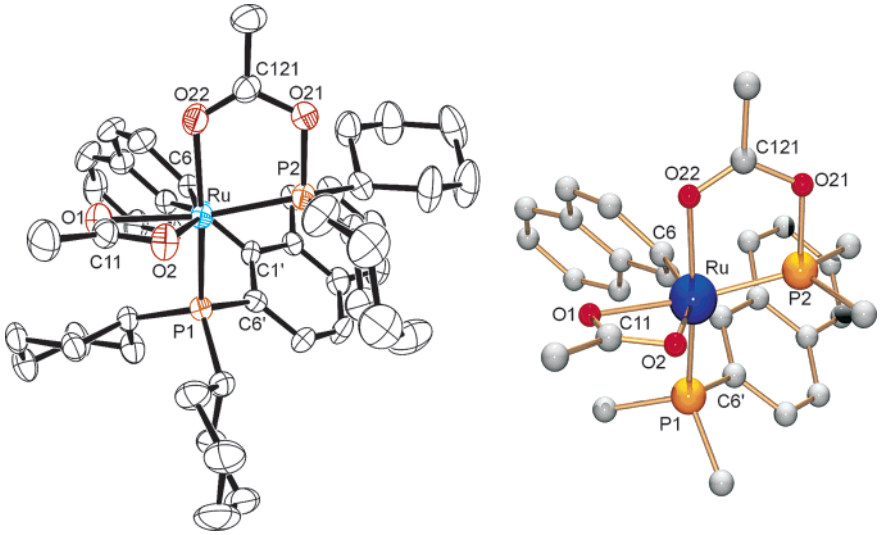


Figure 3. ORTEP view of **16**, together with a ball-and-stick representation of the immediate coordination environment around the metal center.

Table 2. Selected Distances (Å) and Angles (deg) for 16

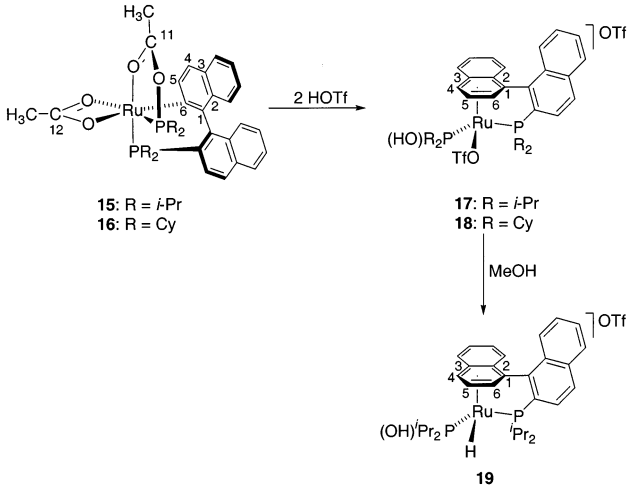
Ru−P1	2.262 (1)	C6−Ru−O22	93.21 (13)
Ru−P2	2.187 (1)	C6−Ru−O2	94.31 (12)
Ru−C6	2.051 (4)	C6−Ru−P2	100.65 (10)
Ru−O1	2.255 (3)	O22−Ru−P2	80.54 (8)
Ru−O2	2.180 (2)	O22−Ru−O2	83.90 (10)
Ru−O22	2.164 (3)	O1−Ru−O2	58.55 (9)
C11−O1	1.267 (4)	O1−Ru−O22	80.05 (10)
C11−O2	1.252 (4)	P1−Ru−P2	103.26 (4)
C121−O21	1.332 (4)	P1−Ru−O22	174.30 (8)
C121−O22	1.236 (4)		

three relatively strong donors, P1, P2, and C6, are all trans to oxygen donors, with P1 trans to O22.

The μ^2-acetate ligand is rotated with respect to the coordination plane (defined by atoms Ru,C6,P2,O1,O2); the O1 atom lies ca. −0.02 Å below this plane, while O2 lies ca. 0.1 Å above it. The ruthenium atom is situated ca. 0.2 Å below this plane. There is almost perfect delocalization of the negative charge in the acetate ligand, in that the C11−O1 and C11−O2 bond lengths, 1.267(4) and 1.252(4) Å, respectively, are not significantly different. Within the P,O chelate, the bond from the carbonyl carbon C121 to the P-bound oxygen, C121−O21 = 1.332(4) Å, is relatively long, whereas the C121−O22 bond is significantly shorter, 1.236(4) Å, and better described as a double bond. The ruthenium−carbon bond distance, Ru−C6, 2.051(4) Å, is in the expected range,[36] as is the Ru−P1 bond, 2.262(1) Å. However, the Ru−P2 distance is rather short, 2.187(1) Å. The Ru−P separation in the related structure from Braunstein et al. (see Scheme 4) at 2.363(1) Å is markedly longer.[33] The coordination angles all vary significantly from 90°, with P1−Ru1−P2, ca. 103°, the largest, and the acetate O1−Ru1−O2, ca. 59°, the smallest. Interestingly, the two rings of the cyclometalated binaphthyl moiety are no longer coplanar: the angle between the two fused rings is ca. 8°. Moreover, while the C1′−C6′ ring is still approximately planar (the only significant deviation is for C1′, ca. 0.02 Å), for the C1−C6 ring the deviations are more pronounced with atomsC1 and C6 at ca. 0.07 and −0.06 Å away, respectively, from the best plane for these six atoms.

(36) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton* **1989**, S1.

Scheme 5



Ru{PR$_2$(OH)} Complexes. The complexes **15** and **16** react with 2 equiv of wet triflic acid to afford the new hydroxydiphenylphosphino derivatives **17** and **18** (see Scheme 5). These are alkyl analogues of **3**, and as we have already reported[13] the characterization of **3** and related derivatives (including two solid-state structures), there is no need for a lengthy description of their NMR properties (see Experimental Part). We do note that there is a marked high-frequency shift in the ^{31}P frequency of the PR$_2$(OH) moiety (146.3 and 138.9 ppm for **17** and **18**, respectively) relative to the phenyl derivative, 114.5 ppm. Obviously, after protonation of the chelating acetate opens one or more coordination positions, the complexed P−O(C=O)CH$_3$ ligand is susceptible to acid-assisted hydrolysis to afford the PR$_2$-(OH) donor.

Primarily, compounds **17** and **18** were synthesized to test whether the observed P-phenyl migration leading to **6** and **7** could be suppressed. Consequently, complex **17** was dissolved in methanol, which presumably solvolyzes the triflate anion.[21,37] Indeed, no P-alkyl migration takes place; however, the presumed 16e complex formed slowly reacts with methanol at room tempera-

ture to form the hydride complex **19**. This was unambiguously identified via the typical low-frequency hydride ^{1}H NMR resonance at δ −13.45 as a doublet of doublets due to the two phosphorus nuclei. The ^{31}P spectrum reveals two resonances, δ 157.7 and 83.5 with $^2J_{PP} = 30$ Hz. The η^6-arene is still present, as indicated by its ^{13}C NMR characteristics (see Experimental Part). Clearly, although the tendency to split the remaining P−C bonds of the $PR_2(OH)$ moiety has been reduced, the distorted η^6-arene bonding in this type of complex[23] readily opens a coordination position thereby facilitating β-H elimination.

Conclusions. Compared to their phenyl counterparts, the ruthenium isopropyl and cyclohexyl Binap analogues show some similar bonding properties, e.g., the η^2-olefin 6e coordination mode; however, these are housed in rather different molecular structures. It is tempting to believe that the observed slower reactions with the alkyl compounds allow the isolation of intermediates such as **10** and **11**, or **15** and **16**, which were only fleeting for the phenyl-substituted complexes. The Ru complexes of ligands **8** and **9** do not undergo multiple P−C bond breaking; nevertheless, the strain introduced as a consequence of the η^2-olefin 6e coordination mode still facilitates the first P−C bond scission. As might be expected, the η^2-olefin bond from the Binap is not very strong and can be substituted by either a coordinating anion, such as chloride, or acetonitrile. The cyclometalated compounds **15** and **16** should be a possible source of new "MOP" type ligands,[38] and studies in this direction are under consideration.

Experimental Part

Crystallography. Light yellow crystals of **16**, suitable for X-ray diffraction, were obtained by crystallization from CH_2Cl_2 and are air stable. A platelike single crystal was mounted for the data collection on a glass fiber at a random orientation on a Bruker SMART CCD diffractometer at room temperature. The crystal symmetry was found to be triclinic, and the space group, assumed to be $P\bar{1}$, was unambiguously confirmed by the structure solution and refinement. Data were collected by using ω scans, in steps of 0.3 deg, and counting time of 20 s per frame. The collected intensities[39] were corrected for Lorentz and polarization factors and empirically for absorption.[40]

Selected crystallographic and other relevant data are listed in Table 3 and in Table S1. The standard deviations on intensities were calculated in term of statistics alone, while those on F_o^2 were calculated as shown in Table S1. The structure was solved by Patterson and Fourier methods and refined by full matrix least squares,[41] minimizing the function $[\sum w(F_o^2 - (1/k)F_c^2)^2]$. Anisotropic displacement parameters were used for all atoms. The contribution of the hydrogen atoms, in their calculated position, was included in the refinement using a riding model. No extinction correction was found to be necessary. Upon convergence, the final Fourier difference map showed no significant peaks. The scattering factors used, corrected for the real and imaginary parts of the anomalous dispersion, were taken from the literature.[42] All calculations were carried out by using the PC version of the SHELX-97 programs.[41]

Table 3. Crystal and Structure Refinement Data for 16

chemical formula	$C_{48}H_{62}O_4P_2Ru$
fw	865.99
data coll T, K	293(2)
diffractometer	Bruker SMART CCD
cryst syst	triclinic
space group	$P\bar{1}$
a, Å	11.7221(8)
b, Å	13.1315(9)
c, Å	15.3555(10)
α, deg	89.318(2)
β, deg	75.723(2)
γ, deg	66.728(2)
V, Å^3	2.094(5)
Z	2
ρ_{calcd}, g cm^{-3}	1.373
μ, cm^{-1}	4.95
radiation	Mo Kα (graphite monochromated $\lambda = 0.71079$ Å)
measured reflns	$\pm h, \pm k, \pm l$
θ range, deg	$1.37 < \theta < 28.08$
transmn coeff	1.0000−0.8754
no. of data coll	21 971
no. of ind data	9687
no. of obsd reflns (n_o)	4573 [$\|I_o\| > 2.0\sigma(\|I\|)$]
no. of params refined (n_v)	496
R_{av}[a]	0.0392
R, R_w^2 (obsd reflns)[b]	0.0466, 0.0796
R, R_w^2 (all data)[b]	0.1223, 0.0943
GOF	0.723

[a] $R_{av} = \sum|F_o^2 - F_{o,av}^2|/\sum|F_o^2|$; $R = \sum(|F_o - (1/k)F_c|)/\sum|F_o|$. [b] $R_w^2 = [\sum w(F_o^2 - (1/k)F_c^2)^2/\sum w|F_o^2|^2]$; GOF $= [\sum_w(F_o^2 - (1/k)F_c^2)^2/(n_o - n_v)]^{1/2}$.

Synthesis. All organometallic manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Pentane and diethyl ether were distilled from sodium−potassium alloy, dichloromethane and 1,2-dichloroethane from CaH_2, methanol from magnesium, and toluene from potassium. 2,2′-Dibromo-1,1′-binaphthyl[43] and $[Ru(OAc)_2(\eta^6\text{-}p\text{-cymeme})]$[44] were prepared according to literature methods. All other chemicals were commercial products and were used as received. Spectra were recorded with Bruker DPX-300 and Avance 400 and 500 spectrometers. Chemical shifts are given in ppm and coupling constants (J) in Hz. Elemental analyses and mass spectroscopic studies were performed at the ETHZ.

Synthesis of 8. A solution of 2,2′-dibromo-1,1′-binaphthyl (1.015 g, 2.46 mmol) in toluene (50 mL) was cooled to −75 °C and *tert*-butyllithium (5.9 mL, 10.0 mmol) added dropwise from a syringe. The resulting pale yellow solution was kept at −75 °C for 45 min. Slow warming to −30 °C was accompanied by formation of a white precipitate. To this mixture was added a solution of chlorodiisopropylphosphine (990 μL, 6.16 mmol) in diethyl ether (5 mL) in a dropwise fashion. The clear solution was stirred at −35 °C for 20 min and then allowed to warm to RT, leading to precipitation of a white solid. After stirring at RT for 1 h, the mixture was hydrolyzed and washed with brine, and the organic phase was dried with sodium sulfate and then evaporated to dryness. The remaining yellow crude product was dissolved in 1:1 ethyl acetate/hexane and filtered through

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(40) Sheldrick, G. M. *SADABS*, Universität Göttingen.
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(42) *International Tables for X-ray Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publisher: Dordrecht, The Netherlands, 1992; Vol. C.
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a layer of silica gel. The white residue was recrystallized from hot hexane to afford **8** as white microcrystals. Yield: 805 mg (68%). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.96 (d, $^3J_{HH}$ = 8.5, 2H, H^4), 7.89 (d, $^3J_{HH}$ = 8.3, 2H, H^{10}), 7.77 (dd, $^3J_{HH}$ = 8.4, $^3J_{PH}$ = 1, 2H, H^5), 7.41 (m, 2H, H^9), 7.15 (m, 2H, H^8), 6.97 (d, $^3J_{HH}$ = 8.6, 2H, H^7), 2.37 (m, 2H, C*H*), 1.70 (m, 2H, C*H*), 1.15 (m, 12H, C*H*$_3$), 0.82 (dd, $^3J_{HH}$ = 7.1, $^3J_{PH}$ = 11, 6H, C*H*$_3$), 0.70 (dd, $^3J_{HH}$ = 7.4, $^3J_{PH}$ = 13, 6H, C*H*$_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): 145.4 (br, C^1), 136.2 (br, C^6), 134.2 (d, $^3J_{CP}$ = 4, C^2), 133.4 (C^3), 129.1 (br, C^5), 128.5 (C^7), 128.2 (C^{10}), 127.4 (C^4), 126.4 (C^9), 125.8 (C^8), 25.9 (d, $^1J_{CP}$ = 16), 23.2 (d, $^1J_{CP}$ = 12), 22.6, 21.5 (d, $^2J_{CP}$ = 16), 20.4 (d, $^2J_{CP}$ = 18), 19.5 (d, $^2J_{CP}$ = 10). ^{31}P NMR ($CDCl_3$ 162 MHz): −1.8 (s). MS (MALDI): 487.3 (M$^+$, 100%), 444.2 (M$^+$ − *i*-Pr). Anal. Calcd for $C_{32}H_{40}P_2$: C, 78.98; H, 8.28. Found: C, 79.05; H, 8.37.

Synthesis of 9. A solution of 2,2′-dibromo-1,1′-binaphthyl (1.00 g, 2.43 mmol) in toluene (50 mL) was cooled to −75 °C and *tert*-butyllithium (5.9 mL, 10.0 mmol) added dropwise from a syringe. The resulting pale orange solution was kept at −75 °C for 45 min. Slow warming to RT was accompanied by formation of a white precipitate. To this mixture was added dropwise chlorodicyclohexylphosphine (1.41 mL, 6.07 mmol). The gray mixture was stirred at 60 °C overnight, hydrolyzed, and washed with brine. The organic phase was dried with sodium sulfate and then evaporated to dryness. The yellow residue was washed with 10:1 hexane/ethyl acetate, the residue was dissolved in toluene and filtered through a short layer of silica, and the remaining colorless solution was evaporated to dryness. Yield: 974 mg (62%). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.94 (d, $^3J_{HH}$ = 8.5, H^4), 7.89 (d,$^3J_{HH}$ = 8.1, H^{10}), 7.75 (d, $^3J_{HH}$ = 8.5, H^5), 7.41 (m, H^9), 7.17 (m, H^8), 7.01 (d, $^3J_{HH}$ = 8.7, H^7), 2.19 (br, 2H), 1.89 (br, d, $^2J_{PH}$ = 12.0, 2H), 1.77 (m, 8H), 1.55−1.18 (m, 22H), 1.02−0.73 (m, 10H). ^{13}C NMR ($CDCl_3$, 100 MHz): 145.6 (m, C1, C6), 134.5 (dd, $^3J_{CP}$ = 5, $^4J_{CP}$ = 5, C^2), 133.4 (C^3), 129.5 (C^5), 128.7 (C^7), 128.1 (C^{10}), 127.0 (C^4), 126.2 (C^9), 125.6 (C^8), 36.7 (m), 33.6 (m), 32.1 (m), 31.8 (m), 31.0 (m), 29.8 (m), 28.1 (m), 27.7 (m), 27.2 (m), 26.7. ^{31}P NMR ($CDCl_3$ 162 MHz): −8.4 (s). MS (EI): 647.4 (M$^+$, 100%), 563.5 (M$^+$ − Cy). Anal. Calcd for $C_{44}H_{56}P_2$: C, 81.70; H, 8.73. Found: C, 81.67; H, 8.51.

Synthesis of 10. A suspension of [$RuCl_2$(η^6-*p*-cymene)]$_2$ (25 mg, 0.041 mmol) and ligand **8** (20 mg, 0.041 mmol) in methanol (8 mL) was stirred overnight at room temperature, resulting in a clear red solution. The solvent was evaporated and the residue washed twice with diethyl ether to afford **10** as a red solid. Yield: 37 mg (94%). ^{1}H NMR (d_4-MeOH, 400 MHz): 8.04 (dd, $^4J_{PH}$ = 1.9, $^3J_{HH}$ = 8.9, H^4), 7.98 (dd, $^3J_{PH}$ = 1.9, $^4J_{HH}$ = 8.6, H$^{4'}$), 7.82 (m, H$^{5'}$, H$^{10'}$), 7.74 (dd, $^4J_{HH}$ = 1.0, $^3J_{HH}$ = 8.0, H^{10}), 7.65 (dd, $^3J_{PH}$ = 4.7, $^3J_{HH}$ = 9.0, H^5), 7.38 (m, H,^{9} H$^{9'}$), 7.24 (m, H^8), 7.07 (m, H,^{7} H$^{8'}$), 5.92 (d, $^3J_{HH}$ = 8.6, H$^{7'}$), 5.63 (d, $^3J_{HH}$ = 5.9, H^{12}), 5.56 (d, $^3J_{HH}$ = 5.9, H^{16}), 5.45 (d, $^3J_{HH}$ = 5.9, H^{13}), 5.37 (d, $^3J_{HH}$ = 5.9, H^{15}), 4.05 (m, 1H, C*H*), 3.58 (m, 1H, C*H*), 2.69 (septet, $^3J_{HH}$ = 6.8, 1H, C*H*), 2.49 (m, 1H, C*H*), 2.10 (s, 3H, C*H*$_3$), 1.86−1.72 (m, 9H), 1.68−1.58 (m, 9H), 1.24 (d, $^3J_{HH}$ = 6.9, 3H, C*H*$_3$), 1.22 (d, $^3J_{HH}$ = 6.9, 3H, C*H*$_3$), 1.04 (dd, $^3J_{PH}$ = 18.7, $^3J_{HH}$ = 7.5, 3H, C*H*$_3$), 0.15 (dd, $^3J_{PH}$ = 23.0, $^3J_{HH}$ = 7.4, 3H, C*H*$_3$), −0.33 (m, 1H, C*H*). ^{13}C NMR (d_4-MeOH, 100 MHz): 147.9 (C$^{1'}$), 145.0 (d, $^3J_{PC}$ = 7, C^2), 137.1 (C$^{6'}$), 135.1 (C$^{3'}$), 134.9 (C^4), 133.4 (C$^{2'}$), 130.9 (C^3), 130.5 (d, $^3J_{PC}$ = 6, C$^{4'}$), 129.2 (C^{10}), 128.3 (C$^{10'}$), 127.9 (C,^{7} C$^{8'}$), 127.8 (C^8), 127.7 (C$^{5'}$, C$^{9'}$), 126.9 (C^9), 125.7 (C$^{7'}$), 124.9 (C^5), 101.2 (C^{11}), 96.4 (C^{14}), 87.4 (br, C^1), 79.7 (C^{16}), 79.3 (C^{12}), 78.7 (C^{13}), 62.3 (C^6), 32.4 (d, $^1J_{PC}$ = 25, *C*H), 31.4 (*C*H cymene), 30.1 (d, $^1J_{PC}$ = 22, *C*H), 29.9 (d, $^1J_{PC}$ = 30, *C*H), 24.3 (d, $^1J_{PC}$ = 15, *C*H), 23.1 (d, $^2J_{PC}$ = 9, *C*H$_3$), 21.4 (*C*H$_3$ cymene), 21.2 (*C*H$_3$ cymene), 20.7 (*C*H$_3$), 20.0 (d, $^2J_{PC}$ = 8, *C*H$_3$), 19.7 (d, $^2J_{PC}$ = 4, *C*H$_3$), 19.0 (d, $^2J_{PC}$ = 6, *C*H$_3$), 18.5 (*C*H$_3$), 17.6 (*C*H$_3$ cymene), 17.6 (d, $^2J_{PC}$ = 2, *C*H$_3$). ^{31}P NMR (d_4-MeOH, 162 MHz): 86.3 (d, $^2J_{PP}$ = 36), 25.0 (d, $^2J_{PP}$ = 36). MS (ESI): 928.9 (M$^+$), 622.8 (RuCl−Binap). Anal. Calcd for $C_{42}H_{54}Cl_4P_2Ru_2$: C, 52.29; H, 5.64. Found: C, 52.47; H, 5.87.

Synthesis of 11. A suspension of [$RuCl_2$(η^6-*p*-cymene)]$_2$ (29 mg, 0.048 mmol) and ligand **9** (31 mg, 0.048 mmol) in methanol (8 mL) was stirred for 3 days at room temperature, resulting in a clear red solution. The solvent was evaporated and the residue washed twice with a 1:1 mixture of diethyl ether and pentane to afford **11** as a red solid. Yield: 50 mg (93%). ^{1}H NMR (d_4-MeOH, 400 MHz): 7.99 (m, H,^{5} H$^{5'}$), 7.87 (dd, $^3J_{PH}$ = 5.6, $^3J_{HH}$ = 8.6, H$^{4'}$), 7.83 (d, $^3J_{HH}$ = 8.2, H$^{10'}$), 7.74 (d, $^3J_{HH}$ = 7.9, H^{10}), 7.58 (dd, $^3J_{PH}$ = 4.5, $^3J_{HH}$ = 9.0, H^5), 7.42−7.35 (m, H,^{9} H$^{9'}$), 7.25 (dd, $^3J_{HH}$ = 8.2, $^3J_{HH}$ = 8.2, H^8) 7.06 (dd, $^3J_{HH}$ = 7.0, $^3J_{HH}$ = 7.1, H$^{8'}$), 7.00 (d, $^3J_{HH}$ = 8.1, H^7), 5.87 (d, $^3J_{HH}$ = 8.6, H$^{7'}$), 5.64 (d, $^3J_{HH}$ = 5.8, 1H), 5.56 (d, $^3J_{HH}$ = 5.9, 1H), 5.47 (d, $^3J_{HH}$ = 5.9, 1H), 5.31 (d, $^3J_{HH}$ = 5.8, 1H), 3.81 (m, 1H), 3.40 (m, 1H), 2.82−1.06 (m, 46H), 0.88 (m, 1H), 0.47 (m, 2H), 0.05 (m, 1H), −0.66 (m, 1H), −0.92 (m, 1H). ^{13}C NMR (d_4-MeOH, 100 MHz): 147.9 (dd, $^2J_{PC}$ = 24, $^3J_{PC}$ = 2, C$^{1'}$), 144.7 (d, $^3J_{PC}$ = 7, C^2), 136.3 (d, $^1J_{PC}$ = 42, C$^{6'}$), 135.2 (d, $^4J_{PC}$ = 2, C$^{3'}$), 134.3 (d, $^3J_{PC}$ = 6, C^4), 133.3 (d, $^3J_{PC}$ = 15, C$^{2'}$), 130.9 (C^3), 130.3 (d, $^3J_{PC}$ = 6, C$^{4'}$), 129.3 (C^{10}), 128.4 (C$^{10'}$), 128.3 (d, $^2J_{PC}$ = 7, C^5), 128.0 (C$^{9'}$), 127.9 (C^8), 127.7 (C^7, C$^{8'}$), 126.7 (C^9), 125.7 (C$^{7'}$), 125.6 (C$^{5'}$), 101.5 (q-cym), 96.3 (q-cym), 87.4 (br, C^1), 79.8 (cym), 78.9 (cym), 78.6 (cym), 61.7 (d, $^1J_{PC}$ = 28, C^6), 43.6 (d, $^1J_{PC}$ = 24, *C*H), 40.1 (d, $^1J_{PC}$ = 21, *C*H), 39.0 (d, $^1J_{PC}$ = 25, *C*H), 35.4 (d, J_{PC} = 13, *C*H$_2$), 34.8 (d, J_{PC} = 10, *C*H$_2$), 32.7 (d, J_{PC} = 5, *C*H$_2$), 31.8 (s, *C*H$_2$), 31.6 (d, J_{PC} = 8, *C*H$_2$), 31.4 (s, *C*H$_2$), 31.0 (d, J_{PC} = 6, *C*H$_2$), 29.2 (d, J_{PC} = 6, *C*H$_2$), 29.0 (s, *C*H$_2$), 28.2−27.6 (m), 27.5 (d, J_{PC} = 6, *C*H$_2$), 27.4 (s, *C*H$_2$), 27.2 (d, J_{PC} = 9, *C*H$_2$), 26.9 (d, J_{PC} =12, *C*H$_2$), 26.3 (s, *C*H$_2$), 26.0 (s, *C*H$_2$), 25.1 (s, *C*H$_2$), 23.5 (s, *C*H$_2$), 21.9 (s, *C*H$_2$), 20.8 (s, *C*H$_2$), 17.8 (s, *C*H$_2$). ^{31}P NMR (d_4-MeOH, 162 MHz): 83.5 (d, $^2J_{PP}$ = 34), 15.8 (d, $^2J_{PP}$ = 34). MS (ESI): 1089.1 (M$^+$, 100%), 783.1 (Ru−Binap). Anal. Calcd for $C_{54}H_{70}Cl_4P_2Ru_2$: C, 57.65; H, 6.27. Found: C, 57.08; H, 6.48.

Synthesis of 12. A mixture of [$RuCl_2$(η^6-*p*-cymene)]$_2$ (25 mg, 0.041 mmol) and ligand **8** (40 mg, 0.082 mmol) in methanol (5 mL) was stirred overnight at room temperature, resulting in a clear red solution. The solvent was removed in vacuo and the residue washed with pentane to afford **12** as a red-brown solid. Yield: 51 mg (95%). ^{1}H NMR (d_4-MeOH, 400 MHz): 8.02 (m, H^4), 7.87 (m, H$^{4'}$), 7.76 (m, H,^{10} H$^{10'}$), 7.67 (m, H,^{5} H$^{5'}$), 7.36 (m, H^9), 7.31 (m, H^9), 7.11 (m, H^8), 6.99 (m, H$^{8'}$), 6.92 (d, $^3J_{HH}$ = 8.0, H^7), 5.80 (d, $^3J_{HH}$ = 8.6, H$^{7'}$), 4.26 (m, C*H*), 2.98 (m, C*H*), 2.70 (m, C*H*), 1.90 (dd, $^3J_{PH}$ = 19.0, $^3J_{HH}$ = 7.6, C*H*$_3$), 1.75 (m, 6H), 1.46 (dd, $^3J_{PH}$ = 15.3, $^3J_{HH}$ = 7.3, C*H*$_3$), 1.16 (dd, $^3J_{PH}$ = 14.6, $^3J_{HH}$ = 7.4, C*H*$_3$), 1.00 (dd, $^3J_{PH}$ = 18.3, $^3J_{HH}$ = 7.4, C*H*$_3$), 0.87 (dd, $^3J_{PH}$ = 15.6, $^3J_{HH}$ = 7.0, C*H*$_3$), 0.02 (dd, $^3J_{PH}$ = 13.7, $^3J_{HH}$ = 7.3, C*H*$_3$), −0.52 (m, C*H*). ^{13}C NMR (d_4-MeOH, 100 MHz): 148.1 (dd, $^2J_{PC}$ = 22, C$^{1'}$), 144.8 (d, $^3J_{PC}$ = 7, C^2), 136.9 (d, $^1J_{PC}$ = 41, C$^{6'}$), 134.9 (d, $^4J_{PC}$ = 2, C$^{3'}$), 134.0 (d, $^3J_{PC}$ = 6, C$^{2'}$), 133.6 (d, $^3J_{PC}$ = 15, C^4), 131.0 (C^3), 129.9 (d, $^3J_{PC}$ = 6, C$^{4'}$), 129.8 (C$^{10'}$), 128.5 (C^7), 128.4 (C^5), 128.2 (C$^{10'}$), 127.9 (C^8), 127.6 (C$^{9'}$), 127.3 (C$^{8'}$), 126.4 (C^9), 125.8 (C$^{7'}$), 125.2 (C^5), 87.0 (d, $^2J_{PC}$ = 7, C^1), 65.9 (C^6), 31.3 (d, $^1J_{PH}$ = 26, *C*H), 29.7 (d, $^1J_{PH}$ = 21, *C*H), 27.9 (d, $^1J_{PH}$ = 27, *C*H), 23.5 (d, $^1J_{PH}$ = 13, *C*H), 23.2 (d, $^2J_{PH}$ = 9, *C*H$_3$), 21.3 (d, $^2J_{PH}$ = 3, *C*H$_3$), 21.0 (*C*H$_3$), 20.3 (*C*H$_3$), 20.2 (d, $^2J_{PH}$ = 5, *C*H$_3$), 19.8 (d, $^2J_{PH}$ = 6, *C*H$_3$), 19.0 (*C*H$_3$), 18.2 (d, $^2J_{PH}$ = 3, *C*H$_3$). ^{31}P NMR (d_4-MeOH, 202 MHz): 86.1 (d, $^2J_{PP}$ = 35), 19.1 (d, $^2J_{PP}$ = 35). MS (ESI): 1282.0 (M$^+$), 623.1 (RuCl−Binap). Anal. Calcd for $C_{64}H_{80}Cl_4P_4Ru_2$: C, 58.36; H, 6.12. Found: C, 58.51; H, 6.12.

Synthesis of 15. A solution of [Ru(OAc)$_2$(η^6-*p*-cymene)] (110 mg, 0.31 mmol) and ligand **8** (150 mg, 0.31 mmol) in toluene (20 mL) was stirred in an ampule at 100 °C for 5 days. The solvent was evaporated and the residue washed twice with pentane (3 mL). **15** was obtained as a yellow solid. Yield: 156 mg (71%). ^{1}H NMR (CD_2Cl_2, 300 MHz): 8.02 (d, $^3J_{HH}$ = 8.8, H^5), 7.84 (d, $^3J_{HH}$ = 8.8, H$^{10'}$), 7.80 (d, $^3J_{HH}$ = 8.2, H$^{4'}$), 7.70 (d, $^3J_{HH}$ = 8.2, H^{10}), 7.63 (dd, $^3J_{HH}$ = 8.5, $^2J_{PH}$ = 5.8, H$^{5'}$), 7.41 (m, 2H, H$^{9'}$, H^4), 7.20 (d, $^3J_{HH}$ = 8.8, H$^{7'}$), 7.10 (m, 2H, H$^{8'}$, H^9), 6.87 (m, H^8), 6.69 (d, $^3J_{HH}$ = 8.8, H^7), 2.97 (m, 1H), 2.47 (s, 3H, OAc), 2.22 (m, 1H), 1.98 (m, 1H), 1.89 (s, 3H, OAc), 1.52

(dd, $^2J_{PH}$ = 12.1, $^3J_{HH}$ = 7.1, 3H), 1.39 (dd, $^2J_{PH}$ = 16.2, $^3J_{HH}$ = 7.1, 3H), 1.19−1.02 (m, 9H), 0.72 (m, 1H), 0.34 (dd, $^2J_{PH}$ = 13.5, $^3J_{HH}$ = 7.1, 3H), 0.25 (dd, $^2J_{PH}$ = 13.5, $^3J_{HH}$ = 7.1, 3H), −0.30 (dd, $^2J_{PH}$ = 14.6, $^3J_{HH}$ = 7.1, 3H). ^{13}C NMR (CD_2Cl_2, 75 MHz): 184.7 (d, $^2J_{PC}$ = 2, *C*O, C^{11}), 179.5 (d, $^2J_{PC}$ = 2, *C*O, C^{12}), 171.4 (m, C^6), 149.8 (d, $^2J_{PC}$ = 12, C$^{1'}$), 140.0 (d, $^3J_{PC}$ = 11, C^1), 136.5 (C^5), 134.1 (d, $^4J_{PC}$ = 2, C$^{3'}$), 133.9 (d, $^3J_{PC}$ = 9, C$^{2'}$), 132.7 (C^2), 131.1 (C^3), 128.8 (C$^{7'}$), 128.0 (C$^{10'}$), 127.9 (C^{10}), 126.5 (C$^{9'}$), 125.9 (d, $^3J_{PC}$ = 7, C$^{4'}$), 125.4 (C^7), 125.2 (C$^{8'}$), 124.9 (d, $^2J_{PC}$ = 4, C$^{5'}$), 123.9 (C^8), 122.8 (C^4), 122.2 (C^9), 33.5 (d, $^1J_{PC}$ = 19, *C*H), 29.7 (d, $^1J_{PC}$ = 16, *C*H), 27.6 (d, $^1J_{PC}$ = 23, *C*H), 27.3 (d, $^1J_{PC}$ = 24, *C*H), 24.2 (d, $^3J_{PC}$ = 2, OAc), 20.6 (d, $^2J_{PC}$ = 6, *C*H$_3$), 20.4 (d, $^3J_{PC}$ = 2, OAc), 19.9 (d, $^2J_{PC}$ = 2, *C*H$_3$), 18.9 (s, *C*H$_3$), 18.7 (d, $^2J_{PC}$ = 3, *C*H$_3$), 18.2 (d, $^2J_{PC}$ = 3, *C*H$_3$), 17.9 (d, $^2J_{PC}$ = 3, *C*H$_3$), 17.7 (d, $^2J_{PC}$ = 6, *C*H$_3$), 14.4 (s, *C*H$_3$). ^{31}P NMR (CD_2Cl_2, 121 MHz): 240.0 (d, $^2J_{PP}$ =32), 74.6 (d, $^2J_{PP}$ = 32). MS (ESI): 706.1 (M$^+$, 100%), 530.0 (M$^+$ − P-^{i}Pr$_2$, − OAc). Anal. Calcd for $C_{36}H_{46}O_4P_2Ru$: C, 61.27; H, 6.57. Found: C, 61.40; H, 6.78.

Synthesis of 16. A solution of [Ru(OAc)$_2$(η^6-*p*-cymene)] (33 mg, 0.093 mmol) and ligand **9** (60 mg, 0.093 mmol) in toluene (8 mL) was stirred in an ampule at 110 °C for 5 days. The solvent was evaporated and the residue washed twice with pentane (3 mL). **16** was obtained as a yellow solid. Yield: 54 mg (67%). ^{1}H NMR (CD_2Cl_2, 500 MHz): 8.11 (d, $^3J_{HH}$ = 8.6, H^5), 7.88 (m, H$^{10'}$), 7.82 (dd, $^3J_{HH}$ = 8.3, $^4J_{PH}$ = 1.5, H$^{4'}$), 7.75 (dd, $^3J_{HH}$ = 8.3, $^4J_{HH}$ = 1, H^{10}), 7.56 (dd, $^3J_{HH}$ = 8.6, $^3J_{PH}$ = 5.3, H$^{5'}$) 7.45 (d, $^3J_{HH}$ = 8.3, H^4), 7.42 (m, H$^{9'}$), 7.38 (d, $^3J_{HH}$ = 8.6, H$^{7'}$), 7.16 (m, H$^{8'}$), 7.14 (m, H^9), 6.91 (m, H^8), 6.79 (m, H^7). ^{13}C NMR (CD_2Cl_2, 125 MHz): 184.4 (d, $^2J_{PC}$ = 2, *C*O), 179.2 (d, $^2J_{PC}$ = 2, *C*O), 174.1 (m, C^6), 148.9 (d, $^2J_{PC}$ = 12, C$^{1'}$), 140.7 (d, $^3J_{PC}$ = 11, C^1), 136.5 (C^5), 134.0 (C$^{6'}$), 133.9 (C$^{3'}$), 133.1 (d, $^3J_{PC}$ = 8, C$^{2'}$), 132.2 (C^2), 131.1 (C^3), 129.7 (C$^{7'}$), 128.2 (C$^{10'}$), 127.9 (C^{10}), 126.4 (C$^{9'}$), 125.8 (d, $^3J_{PC}$ = 7, C$^{4'}$), 125.6 (C,^{7} C$^{8'}$), 124.3 (d, $^2J_{PC}$ = 4, C$^{5'}$), 123.7 (C^8), 122.6 (C^4), 122.0 (C^9), 43.2 (d, $^1J_{PC}$ = 20, *C*H), 40.0 (d, $^1J_{PC}$ = 15, *C*H), 39.0 (d, $^1J_{PC}$ = 22, *C*H), 34.5 (s, *C*H$_2$), 30.4−25.7 (m), 24.1 (s, *C*H$_2$), 22.7 (s, *C*H$_2$), 20.4 (s, *C*H$_2$), 14. (s, *C*H$_2$). ^{31}P NMR (CD_2Cl_2, 202 MHz): 237.7 (d, $^2J_{PP}$ = 31), 65.8 (d, $^2J_{PP}$ = 31). MS (ESI): 866.2 (M$^+$, 100%), 807.3 (M$^+$ − OAc). Anal. Calcd for $C_{48}H_{62}O_4P_2Ru$: C, 66.57; H, 7.22. Found: C, 66.59; H, 7.32.

Synthesis of 17. A solution of **15** (15 mg, 0.021 mmol) in 1,2-dichloroethane (2 mL) was treated with triflic acid (5 μL, 0.057 mmol) and heated to 80 °C for 5 min. The orange solution was pumped to dryness and washed with pentane to afford **17** as an orange solid. Yield: 12 mg (62%). ^{1}H NMR (CD_2Cl_2, 500 MHz): 8.59 (br, O*H*), 8.30 (dd, $^3J_{HH}$ = 8.7, $^4J_{PH}$ = 1.8, H$^{4'}$), 8.17 (d, $^3J_{HH}$ = 8.4, H$^{10'}$), 8.07 (m, H^9), 7.86 (m, H$^{5'}$, H^{10}), 7.78 (m, H$^{9'}$), 7.61 (m, H$^{7'}$, H$^{8'}$), 7.46 (m, H^5), 7.41 (m, H^8), 7.12 (d, $^3J_{HH}$ = 6.7, H^4), 6.65 (d, $^3J_{HH}$ = 8.5, H^7), 5.16 (m, H^6), 3.35 (m, C*H*), 3.15 (m, C*H*), 2.67 (m, C*H*, 2H), 1.72 (dd, $^3J_{HH}$ = 7.3, $^3J_{PH}$ = 18.3, C*H*$_3$), 1.64 (dd, $^3J_{HH}$ = 7.3, $^3J_{PH}$ = 14.2, C*H*$_3$), 1.59 (dd, $^3J_{HH}$ = 7.0, $^3J_{PH}$ = 13.3, C*H*$_3$), 1.44 (dd, $^3J_{HH}$ = 7.3, $^3J_{PH}$ = 13.6, C*H*$_3$), 1.39 (dd, $^3J_{HH}$ = 7.3, $^3J_{PH}$ = 18.0, C*H*$_3$), 1.23 (dd, $^3J_{HH}$ = 7.3, $^3J_{PH}$ = 16.8, C*H*$_3$), 0.94 (dd, $^3J_{HH}$ = 7.2, $^3J_{PH}$ = 18.2, C*H*$_3$), 0.57 (dd, $^3J_{HH}$ = 6.9, $^3J_{PH}$ = 16.5, C*H*$_3$). ^{13}C NMR (CD_2Cl_2, 125 MHz): 140.5 (C$^{1'}$), 139.2 (C$^{6'}$), 138.8 (C^9), 134.9 (C$^{3'}$), 132.1 (C^8, C^7), 132.0 (C$^{4'}$), 131.9 (C$^{2'}$), 129.6 (C$^{9'}$), 129.3 (C$^{8'}$), 128.9 (C,^{10} C$^{9'}$), 128.8 (C$^{10'}$), 125.4 (C$^{5'}$), 124.4 (C$^{7'}$), 119.3 (C^3), 113.7 (C^1), 106.9 (C^2), 98.2 (C^5), 89.4 (C^4), 68.7 (C^6), 41.9 (*C*H), 38.6 (*C*H), 29.3 (*C*H), 28.0 (*C*H), 20.3 (*C*H$_3$), 20.2 (*C*H$_3$), 19.2 (*C*H$_3$), 18.6 (*C*H$_3$), 18.4 (*C*H$_3$), 18.0 (*C*H$_3$), 17.4 (*C*H$_3$), 16.7 (*C*H$_3$). ^{19}F NMR (CD_2Cl_2, 282 MHz): −77.23 (s), −79.45 (s). ^{31}P NMR (CD_2Cl_2, 162 MHz): 146.3 (d, $^2J_{PP}$ = 42), 67.1 (d, $^2J_{PP}$ = 42). MS (ESI): 604.9 (M$^+$, −OTf, 100%). Anal. Calcd for $C_{34}H_{41}F_6O_7P_2RuS_2$: C, 45.23; H, 4.58. Found: C, 44.70; H, 5.07.

Synthesis of 18. A solution of **16** (15 mg, 0.017 mmol) in 1,2-dichloroethane (2 mL) was treated with triflic acid (4 μL, 0.046 mmol) and heated to 80 °C for 5 min. The orange solution was pumped to dryness and washed with pentane to afford **18** as an orange solid. Yield: 11 mg (59%). ^{1}H NMR (CD_2Cl_2, 400 MHz): 8.56 (br, O*H*), 8.29 (dd, $^3J_{HH}$ = 8.6, $^4J_{PH}$ = 2.0, H$^{4'}$), 8.15 (d, $^3J_{HH}$ = 8.1, H$^{10'}$), 8.06 (m, H^9), 7.88 (dd, $^3J_{HH}$ = 8.6, $^3J_{PH}$ = 5.8, H$^{5'}$), 7.83 (d, $^3J_{HH}$ = 8.4, H^{10}), 7.76 (m, H$^{9'}$), 7.59 (m, H$^{7'}$, H$^{8'}$), 7.40 (m, H^5, H^8), 7.00 (d, $^3J_{HH}$ = 6.6, H^4), 6.64 (d, $^3J_{HH}$ = 8.9, H^7), 5.09 (dd, $^3J_{HH}$ = 5.3, J_{PH} = 2.0, H^6), 2.98 (br, 2H), 2.60−1.00 (m, *x*H), 0.18 (br, 1H). ^{13}C NMR (CD_2Cl_2, 100 MHz): 139.6 (C$^{1'}$), 139.2 (C$^{6'}$), 138.7 (C^9), 134.8 (C$^{3'}$), 134.0 (C$^{2'}$), 132.2 (C^7), 132.0 (C,^{7} C$^{4'}$), 129.5 (C$^{8'}$), 129.3 (C$^{9'}$), 128.8 (C$^{10'}$), 128.7 (C^{10}), 125.7 (C$^{5'}$), 124.8 (C$^{7'}$), 119.4 (C^3), 113.4 (C^1), 106.3 (C^2), 98.3 (C^5), 89.3 (C^4), 68.2 (C^6), 49.9 (d, $^1J_{PC}$ = 25, *C*H), 38.3 (d, $^1J_{PC}$ = 21, *C*H), 30.9 (s, *C*H$_2$), 30.2−26.5 (m), 26.1 (s, *C*H$_2$), 24.7 (s, *C*H$_2$). ^{19}F NMR (CD_2Cl_2, 282 MHz): −77.20 (s), −79.23 (s). ^{31}P NMR (CD_2Cl_2, 162 MHz): 138.9 (br), 58.7 (d, $^2J_{PP}$ = 42).

Synthesis of 19. A solution of **17** (15 mg, 0.017 mmol) in methanol (5 mL) was stirred at RT overnight, resulting in a pale yellow solution. The solvent was removed in vacuo and the yellow residue washed with pentane. Yield: 10 mg (81%). ^{1}H NMR (d_8-thf, 500 MHz): 8.19 (d, $^3J_{HH}$ = 8.6, H$^{4'}$), 8.15 (d, $^3J_{HH}$ = 8.3, H$^{10'}$), 7.98 (d, $^3J_{HH}$ = 8.6, H^{10}), 7.86 (d, $^3J_{HH}$ = 8.6, H^7), 7.82 (m, H$^{5'}$, H^9), 7.72 (dd, $^3J_{HH}$ = 7.0, $^3J_{HH}$ = 7.0, H^9), 7.59 (m, H$^{8'}$), 7.48 (m, H^8), 7.09 (d, $^3J_{HH}$ = 8.6, H^7), 6.63 (d, $^3J_{HH}$ = 6.2, H^4), 6.55 (m, H^5), 5.76 (d, $^3J_{HH}$ = 4.9, H^6), 2.79 (m, C*H*, 2H), 2.41 (m, C*H*), 1.75 (m, C*H*), 1.46 (dd, $^3J_{HH}$ = 6.8, $^3J_{PH}$ = 12.1, C*H*$_3$), 1.29 (dd, $^3J_{HH}$ = 6.6, $^3J_{PH}$ = 15.6, C*H*$_3$), 1.21 (dd, $^3J_{HH}$ = 6.8, $^3J_{PH}$ = 16.7, C*H*$_3$), 1.13 (dd, $^3J_{HH}$ = 6.8, $^3J_{PH}$ = 12.0, C*H*$_3$), 1.07 (dd, $^3J_{HH}$ = 7.0, $^3J_{PH}$ = 18.4, C*H*$_3$), 0.85 (dd, $^3J_{HH}$ = 6.4, $^3J_{PH}$ = 17.1, C*H*$_3$), 0.57 (dd, $^3J_{HH}$ = 6.8, $^3J_{PH}$ = 17.5, C*H*$_3$), 0.19 (dd, $^3J_{HH}$ = 7.3, $^3J_{PH}$ = 16.8, C*H*$_3$), −13.45 (dd, $^2J_{PH}$ = 34.5, $^2J_{PH}$ = 36.5). ^{13}C NMR (d_8-thf, 125 MHz): 143.9 (d, $^1J_{PC}$ = 36, C$^{6'}$), 142.5 (d, $^2J_{PC}$ = 18, C$^{1'}$), 134.7 (d, $^4J_{PC}$ = 2, C$^{3'}$), 132.3 (C$^{5'}$), 132.1 (d, $^3J_{PC}$ = 13, C$^{2'}$), 130.5 (d, $^3J_{PC}$ = 6, C$^{4'}$), 129.2 (C^8), 128.5 (C$^{10'}$), 128.4 (C$^{9'}$), 128.2 (C^7), 126.8 (C^9), 126.4 (C^{10}), 125.9 (C$^{7'}$), 113.7 (C^3), 112.7 (C^2), 110.2 (dd, $^2J_{PC}$ = 9, $^2J_{PC}$ = 3, C^1), 89.1 (d, $^2J_{PC}$ = 4, C^5), 85.2 (dd, $^2J_{PC}$ = 9, $^4J_{PH}$ = 1, C^6), 82.6 (d, $^2J_{PC}$ = 8, C^4), 35.6 (d, $^1J_{PC}$ = 21, *C*H), 31.2 (d, $^1J_{PC}$ = 32, *C*H), 29.5 (d, $^1J_{PC}$ = 19, *C*H), 26.0 (d, $^1J_{PC}$ = 321, *C*H), 19.8 (d, $^2J_{PC}$ = 3, *C*H$_3$), 19.2 (d, $^2J_{PC}$ = 1, *C*H$_3$), 19.1 (d, $^2J_{PC}$ = 3, *C*H$_3$), 18.0 (d, $^2J_{PC}$ = 4, *C*H$_3$), 17.9 (d, $^2J_{PC}$ = 3, *C*H$_3$), 17.7 (d, $^2J_{PC}$ = 8, *C*H$_3$), 17.0 (d, $^2J_{PC}$ = 7, *C*H$_3$), 15.7 (d, $^2J_{PC}$ = 6, *C*H$_3$). ^{19}F NMR (d_8-thf, 282 MHz): −79.45 (s). ^{31}P NMR (d_8-thf, 162 MHz): 157.7 (d, $^2J_{PP}$ = 30), 83.5 (d, $^2J_{PP}$ = 30). MS (ESI): 607.0 (M$^+$, 100%). Anal. Calcd for $C_{33}H_{43}F_3O_4P_2RuS\cdot{}^1/_2HOTf$: C, 48.46; H, 5.22. Found: C, 48.64; H, 5.87.

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Supporting Information Available: Text giving experimental details and a full listing of crystallographic data for compound **16** including tables of positional and isotropic equivalent displacement parameters, calculated positions of the hydrogen atoms, anisotropic displacement parameters, bond distances and angles and an ORTEP figure showing the full numbering scheme. This material is available free of charge via the Internet at http://pubs.acs.org.

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