An η^2-Aryl−Metal Interaction Turns a Chiral Monodentate Phosphoramidite into a Chelating Ligand in (S_a,S_{Ru},R_C,R_C)-[RuCl(η^6-*p*-cymene)(*O*,*O*′-(1,1′-dinaphthyl-2,2′-diyl)-*N*-(1-(1,2-η-1-naphthyl)ethyl)-*N*-(1-(1-naphthyl)ethyl)phosphoramidite-κP)]PF_6

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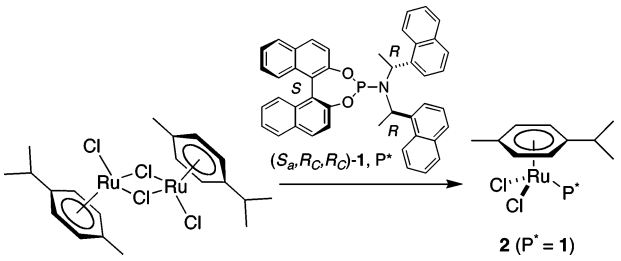
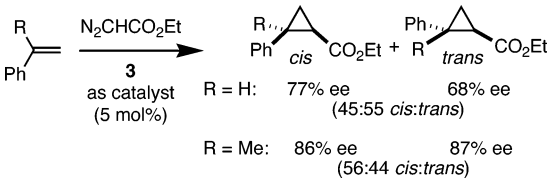
*Summary: Chloride abstraction from the half-sandwich complex [RuCl$_2$(η^6-p-cymene)(**1**-κP)] (**2**; **1** = (S_a,R_C,R_C)-O,O′-(1,1′-dinaphthyl-2,2′-diyl)-N,N-bis(1-(1-naphthyl)-ethyl)phosphoramidite) with TlPF$_6$ or (Et$_3$O)PF$_6$ gives the cationic, 18-electron complex (S_a,S_{Ru},R_C,R_C)-[RuCl-(η^6-p-cymene)(O,O′-(1,1′-dinaphthyl-2,2′-diyl)-N-(1-(1,2-η-1-naphthyl)ethyl)-N-(1-(1-naphthyl)ethyl)phosphoramidite-κP)]PF$_6$, (S_a,S_{Ru},R_C,R_C)-**3**, which features the η^2-coordination of a naphthyl substituent of the phosphoramidite ligand, as indicated by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy and by X-ray studies. Complex (S_a,S_{Ru},R_C,R_C)-**3** catalyzes the asymmetric cyclopropanation of styrene and α-methylstyrene with ethyl diazoacetate, giving good enantioselectivities for the latter olefin (up to 86% and 87% ee for the cis- and the trans-cyclopropane, respectively) when formed in situ in the presence of an excess of **1** to suppress ligand dissociation.*

Monodentate chiral phosphoramidite ligands[1] have found increasing application in asymmetric catalytic reactions such as C−C bond formation[1,2] and hydrogenation.[3] In some cases, the success of these ligands has been tentatively explained with their supposed ability to stabilize coordinatively unsaturated metal complexes in low oxidation state.[2a] However, there is no experimental evidence supporting this assumption. As recently reported from our laboratory,[4] [RuCl$_2$(η^6-*p*-cymene)(**1**-κP)] (**2**), prepared by reacting [RuCl$_2$(η^6-*p*-cymene)]$_2$ with (S_a,R_C,R_C)-*O*,*O*′-(1,1′-dinaphthyl-2,2′-diyl)-*N*,*N*-bis(1-(1-naphthyl)ethyl)phosphoramidite[5] (**1**) (Scheme 1), reacts with a chloride scavenger (TlPF$_6$ or (Et$_3$O)PF$_6$, 1.1 equiv) to give a hitherto unidentified species, **3**. Complex **3** catalyzes the cyclopropanation of styrene and α-methylstyrene with ethyl diazoacetate

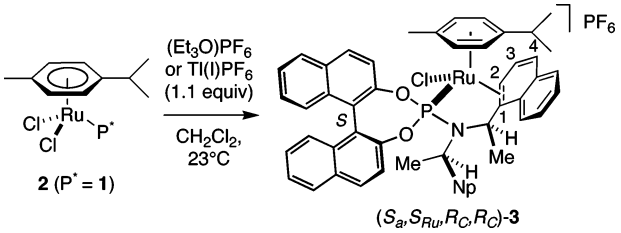
Scheme 1



Scheme 2



Scheme 3



with up to 86% and 87% ee for the *cis*- and the *trans*-cyclopropane, respectively (Scheme 2).[4] We report here the characterization of **3** as the cationic, 18-electron complex (S_a,S_{Ru},R_C,R_C)-[RuCl(η^6-*p*-cymene)(*O*,*O*′-(1,1′-dinaphthyl-2,2′-diyl)-*N*-(1-(1,2-η-1-naphthyl)ethyl)-*N*-(1-(1-naphthyl)ethyl)phosphoramidite-κP)]PF$_6$, (S_a,S_{Ru},R_C,R_C)-**3**, which features the η^2-coordination of one naphthyl group of the phosphoramidite ligand. Complex (S_a,S_{Ru},R_C,R_C)-**3** was prepared as shown in Scheme 3 and fully characterized, including multinuclear NMR and X-ray studies.

Complex (S_a,S_{Ru},R_C,R_C)-**3** shows a broadened singlet at δ 168.0 in the ^{31}P NMR spectrum, is stable in solution for (at least) 3 days and in the solid state for (at least) 7 weeks, and analyzes as [RuCl(*p*-cymene)(**1**)]PF$_6$,[6] which would imply a 16-electron count. However, five-coordinate, 16-electron ruthenium(II) complexes of the type [RuX(Cp*)(P^{i}Pr$_2$Ph)] (X = Cl, Br, I) are usually

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dark blue or violet in color, whereas their 18-electron adducts [RuX(Cp*)(CO)(P^{i}Pr$_2$Ph)] are orange-yellow.[7] Molecular volume data obtained by NMR spectroscopy (PGSE diffusion measurements)[8] ruled out the binuclear formulation [Ru(μ-Cl)(*p*-cymene)(**1**)]$_2$. Eventually, a combination of multinuclear 2D NMR measurements indicated that **3** is a mononuclear six-coordinate complex in which the coordination sphere of ruthenium is saturated by means of an η^2-interaction with the naphthyl ring of one of the CH(Me)(1-Np) groups.

The line widths for several proton resonances in the aromatic region of the room-temperature ^{1}H and ^{13}C NMR spectra of **3** indicated a dynamic behavior on the NMR time scale. Upon cooling to −20 °C, the signals sharpened sufficiently to measure both one-bond and long-range ^{13}C−^{1}H correlations, which revealed the ^{13}C NMR signals of C(1) and C(2) of one of the diastereotopic naphthyl rings at δ 100.9 and 96.8, respectively.[9] The low-frequency shifts of these signals (the coordination chemical shifts $\Delta\delta$ are 44.5 and 31.4 ppm for C(1) and C(2), respectively) indicate that one of the diastereotopic naphthyl rings is bonded to ruthenium in an η^2-fashion.[10] The second, noncomplexed naphthyl ring reveals carbon chemical shifts in the normal aromatic region.

It should be noted that the pseudotetrahedral ruthenium atom of **3** is stereogenic, whereas this is not the case in **2**. The ^{31}P, ^{1}H, and ^{13}C NMR spectra indicated that **3** is formed as a single diastereomer. Molecular modeling calculations indicated that, with ligand (S_a,R_C,R_C)-**1**, the *S* configuration[11] at ruthenium is preferred over the *R* isomer by 8.5 kcal/mol (Figure 1),[12] and an X-ray study confirmed the accuracy of the MM prediction.

After several attempts to crystallize enantiomerically pure **3**, suitable crystals were obtained with the racemic

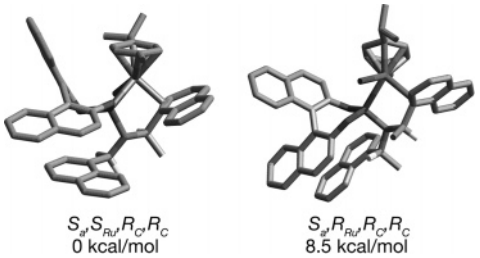

Figure 1. Energy-minimized MM structures (Cerius^2) of (S_a,S_{Ru},R_C,R_C)-**3** and (R_a,R_{Ru},S_C,S_C)-**3**.

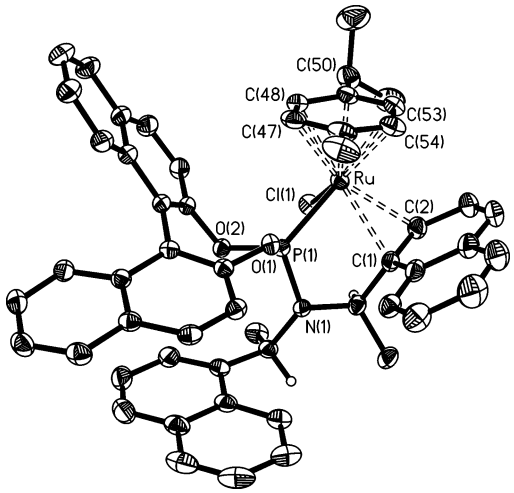

Figure 2. ORTEP drawing of (S_a,S_{Ru},R_C,R_C)-**3** (50% probability ellipsoids). Selected bond distances (Å) and angles (deg): Ru(1)−Cl(1), 2.3926(6); Ru(1)−P(1), 2.2783(5); Ru(1)−C(1), 2.379(2); Ru(1)−C(2), 2.386(2); Ru(1)−C(46), 2.258-(2); Ru(1)−C(47), 2.216(2); Ru(1)−C(48), 2.208(2); Ru(1)−C(49), 2.306(2); Ru(1)−C(54), 2.221(2); Ru(1)−C(53), 2.298(2); Cl(1)−Ru−P(1), 81.07(2); Cl(1)−Ru−C(2), 84.04(6); Cl(1)−Ru(1)−C(48), 91.47(7); P(1)−Ru−C(1), 72.05(5); P(1)−Ru(1)−C(47), 90.82(6); C(2)−Ru(1)−C(53), 85.14(8).

complex (*rac*)-**3**, obtained by mixing (S_a,R_C,R_C)-**1** and (R_a,S_C,S_C)-**1** in 1:1 ratio.[13] The crystal is made up of pairs of discrete cations (S_a,S_{Ru},R_C,R_C)-**3** and (R_a,R_{Ru}, S_C,S_C)-**3** (related by an inversion center) and of [PF$_6$]$^-$ anions with normal nonbonded distances. Figure 2 depicts the structure of (S_a,S_{Ru},R_C,R_C)-**3**. Besides the chloro ligand and the P atom of **1**, the ruthenium is coordinated in a η^6-fashion to *p*-cymene and in a η^2-fashion to a naphthyl group of one amine moiety of the phosphoramidite to give an 18-electron complex. The η^2-coordination of the aromatic C−C bond is supported by the Ru−C(1) and Ru−C(2) distances of 2.379(2) and 2.386(2) Å, respectively, and by the fact that the C(1)−C(2) distance of 1.407(3) Å is longer than the corresponding separation in the noncoordinated naphthyl (C(15)−C(16), 1.375(3) Å), which indicates significant back-bonding from ruthenium. The C(1) carbon atom is pyramidalized to some extent, as indicated by the sum of the C(2)−C(10), C(2)−C(1)−C(11), and C(10)−C(1)−C(2) angles of 353.6°, as a consequence of the Ru−η^2-aryl bond and of the nonbonded interactions between the naphthyl ring and the *p*-cymene ligand.

(6) Synthesis of **3**: [RuCl$_2$(η^6-*p*-cymene)]$_2$ (65 mg, 0.107 mmol) and **1**[5] (150 mg, 0.234 mmol, 1.1 equiv) were dissolved in dry CH_2Cl_2 (12 mL) under an Ar atmosphere. After stirring at 23 °C for 1 h, $TlPF_6$ (78 mg, 0.224 mmol, 1.05 equiv) was added and the resulting solution was stirred at 23 °C for 21 h. Then, TlCl was filtered off, 2-propanol (18 mL) was added, and CH_2Cl_2 was evaporated. The precipitate was filtered off and dried in a vacuum to give **3** as a red solid. Yield: 201 mg (89%). [α]$^{20}_D$: +381 (*c* 0.125, $CHCl_3$). ^{31}P NMR (202.5 MHz, CD_2Cl_2): δ 168.0 (s). MS (ESI): 910.1 ([**3**]$^+$, 100). Anal. Calcd for $C_{54}H_{48}ClF_6NO_2P_2Ru$: C, 61.45; H, 4.58; N, 1.33. Found: C, 61.31; H, 4.66; N, 1.35.

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(9) The signal of C(1) was attributed on the basis of the three-bond interactions to H(3) and H(5), respectively. Analogously, protons H(4) and H(6) correlate to C(2) (δ 96.8). Relevant ^{13}C NMR signals are C(1), 100.9; C(2), 96.8; C(3), 131.8; C(4), 132.6; C(5) and C(6) are not resolved in the region 128−132 ppm.

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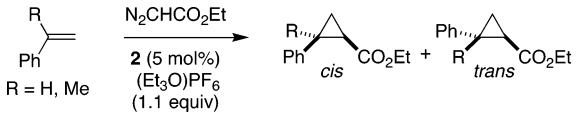
(13) X-ray study of **3**: chemical formula: $C_{55.5}H_{48}Cl_4F_6NO_2P_2Ru$, a = 13.3040(8) Å, b = 13.7074(8) Å, c = 15.1350(9) Å, α = 98.822(1)°, β = 96.636(1)°, γ = 11.659(1)°, V = 2489.9(3) Å^3, triclinic, $P\bar{1}$, Z = 2, ω-scans, T = 201 K, refinement on F^2 (SHELXTL-97), R_1 = 0.0405 for 11 071 $F_o > 4\ \sigma(F_o)$ and 0.0447 for all 12 262 data (715 parameters), wR_2 = 0.1112.

Table 1. Catalytic Cyclopropanation[a]



						ee (%)[b]	
run	catalyst	R	conv (%)	yield (%)	*cis*:*trans*	*cis* (1*R*,2*S*)	*trans* (1*R*,2*R*)
1[c]	(S_a,S_{Ru},R_C,R_C)-**3** (in situ)	H	6	5	45:55	77	68
2[c]	(S_a,S_{Ru},R_C,R_C)-**3** (in situ)	Me	20	19	56:44	86	87
3	(S_a,S_{Ru},R_C,R_C)-**3** (isolated)	Me	20	14	61:39	48	46
4	**3** (isolated) + **1**	Me	17	13	59:41	73	73
5	**2** + 2 $(Et_3O)PF_6$	Me	12	7	61:39	19	19

[a] Reaction conditions: ethyl diazoacetate (0.48 mmol, 1 equiv vs olefin) in CH_2Cl_2 (1 mL) was added over 6 h to a CH_2Cl_2 solution of the olefin (0.48 mmol) and the catalyst (24 μmol, 5 mol %, prepared in situ). The total reaction time was 20 h at 23 °C. Each experiment was reproduced at least once. [b] Determined by chiral GC analysis, see Supporting Information. [c] From ref 4.

To the best of our knowledge, this is the first well-documented η^2-coordination of the arylamine moiety of a phosphoramidite ligand, although such bonding has been predicted by calculation in a study on nickel-catalyzed hydrovinylation.[14] Our results may help explain the remarkable influence of the secondary amine appendage observed in the same reaction.[15] In contrast with other η^2-interactions in ruthenium complexes reported so far,[16] the bonding in **3** involves a "dangling" aryl group and not the chelate ring of a diphosphine. An analogous interaction involving a binaphthyl group has been claimed for cationic palladium(II) MOP[17] complexes,[18] but it is still controversial as to whether the coordination mode is η^2 or η^1.[19] On similar lines, the cyclometalation of the phosphoramidite at the phenethyl methyl group has been observed in iridium(I) complexes,[20] which offers an alternative possibility of turning a "monodentate" phosphoramidite into a chelating ligand.

As reported previously, **3** cyclopropanates styrene and α-methylstyrene with high enantioselectivity (Table 1, runs 1, 2) when prepared in situ from $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$, ligand **1**, and $(Et_3O)PF_6$ (1 equiv).[21] Surprisingly, isolated **3** gives lower enantioselectivity with α-methylstyrene (48 and 46% ee for the *cis* and *trans* isomers, respectively) (run 3) than the catalyst formed in situ (run 2). This may be related to an equilibrium involving dissociation of ligand **1** from complex **3** in solution. Accordingly, the addition of 1 equiv of **1** to the isolated complex **3** partially restores the enantioselectivity (73% ee for both isomers, run 4). Previous experiments show that only one P* ligand coordinates to ruthenium even in the presence of an excess of **1**.[4] Further, indirect evidence of the involvement of **3** in the catalytic cyclopropanation is the observation that double chloride abstraction from **2** decreases both the yield and the enantioselectivity (run 5).

Summarizing, the usually monodentate phosphoramidite **1** can assume a bidentate coordination (1,2-η-κP) mode in the presence of a 16-electron fragment. In the present case, the hapticity change is triggered by chloride abstraction from **2**. Albeit an 18-electron complex, **3** is catalytically active in asymmetric cyclopropanation, which suggests a hemilabile behavior of the 1,2-η-κP-coordinated phosphoramidite. Preliminary results with the bis(phenethyl)amine derivative of **1** indicate an analogous coordination and catalytic behavior, which points to a general ability of Feringa-type phosphoramidites to act as four-electron donors toward coordinatively unsaturated metals. This finding should be useful in the tailoring of catalytically active complexes containing "monodentate" P-donor ligands.

Acknowledgment. We thank Sebastian Gischig for the X-ray structure determination of **3** and the Swiss National Science Foundation for financial support to D.H. (grant 200020-101357).

Supporting Information Available: CIF file of the X-ray study of **3** and details of syntheses and catalytic reactions. This material is available free of charge at http://pubs.acs.org.

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(21) Catalyst preparation: $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ (7.3 mg, 12 μmol), **1** (30.7 mg, 48 μmol), and $(Et_3O)PF_6$ (6.6 mg, 26 μmol, 1.1 equiv) were dissolved in CH_2Cl_2 (1 mL) and stirred at 23 °C for 17 h. TlCl was filtered off with a syringe filter. Standard catalytic run: The internal standard and the olefin (0.48 mmol) were added to the solution of the catalyst (24 μmol, 5 mol %). Ethyl diazoacetate (50.5 μL, 0.48 mmol, 1 equiv vs olefin) in CH_2Cl_2 (1 mL) was added over 6 h by syringe pump. The solution, which was protected from light, was stirred for an additional 14 h at 23 °C and then analyzed by GC. The total reaction time was 20 h at 23 °C. Each experiment was at least reproduced once. A control reaction without the catalyst indicated that there is no formation of the cyclopropane derivatives under the conditions used.