Chloro(η^6-*p*-cymene)(phosphoramidite)ruthenium(II), a 16-Electron Fragment Stabilized by an η^2-Aryl–Metal Interaction, and Its Use in Asymmetric Cyclopropanation

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Dedicated to Professor *Giambattista Consiglio* on the occasion of his 65th birthday

Chloride abstraction from the half-sandwich complexes [$RuCl_2$(η^6-*p*-cymene)(P*-κP)] (**2a**: P* = (S_a,*R*,*R*)-**1a** = (1S_a)-[1,1′-binaphthalene]-2,2′-diyl bis[(1*R*)-1-phenylethyl)]phosphoramidite; **2b**: P* = (S_a,*R*,*R*)-**1b** = (1S_a)-[1,1′-binaphthalene]-2,2′-diyl bis[(1*R*)-(1-(1-naphthalen-1-yl)ethyl]phosphoramidite) with (Et_3O)[PF_6] or Tl[PF_6] gives the cationic, 18-electron complexes dichloro(η^6-*p*-cymene){(1S_a)-[1,1′-binaphthalene]-2,2′-diyl {(1*R*)-1-[(1,2-η)-phenyl]ethyl}[(1*R*)-1-phenylethyl]phosphoramidite-κP}ruthenium(II) hexafluorophosphate (**3a**) and [*Ru*(*S*)]-dichloro(η^6-*p*-cymene){(1S_a)-[1,1′-binaphthalene]-2,2′-diyl {(1*R*)-1-[(1,2-η)-naphthalen-1-yl]ethyl}[(1*R*)-1-(naphthalen-1-yl)ethyl]-phosphoramidite-κP)ruthenium(II) hexafluorophosphate (**3b**), which feature the η^2-coordination of one aryl substituent of the phosphoramidite ligand, as indicated by ^{1}H-, ^{13}C-, and ^{31}P-NMR spectroscopy and confirmed by an X-ray study of **3b**. Additionally, the dissociation of *p*-cymene from **2a** and **3a** gives dichloro{(1S_a)-[1,1′-binaphthalene]-2,2′-diyl [(1*R*)-(1-(η^6-phenyl)ethyl][(1*R*)-1-phenylethyl]phosphoramidite-κP)ruthenium(II) (**4a**) and di-μ-chlorobis{(1S_a)-[1,1′-binaphthalene]-2,2′-diyl [(1*R*)-1-(η^6-phenyl)ethyl][(1*R*)-1-phenylethyl]phosphoramidite-κP}diruthenium(II) bis(hexafluorophosphate) (**5a**), respectively, in which one phenyl group of the *N*-substituents is η^6-coordinated to the Ru-center. Complexes **3a** and **3b** catalyze the asymmetric cyclopropanation of α-methylstyrene with ethyl diazoacetate with up to 86 and 87% ee for the *cis*- and the *trans*-isomers, respectively.

Introduction. – After *Henri Brunner*'s seminal studies of [Mn(Cp)(CO)(PPh_3)-(NO)] (Cp = cyclopenta-2,4-dien-1-yl) [1], pseudotetrahedral complexes containing chirotopic metal atoms have been extensively investigated over the last 35 years, with particular emphasis on stereochemical aspects. As configurational stability is required for these studies, octahedral complexes of d^6 ions – mainly Mn^I [1], Re^I [2], Ru^{II} [3a,b] (for seminal papers concerning [RuCl(Cp)(P–P*)] complexes, see also [3c,d], [4a], for application as stoichiometric reagents in organic chemistry, see [4b,c]), Rh^{III} [5], and Ir^{III} [5] – have been used for the synthesis of substitutionally inert 18-electron species with stereogenic metal atoms (for the extension of this concept to formally seven-coordinate d^4 metal ions, see [6]). With Ru^I ions, two major classes of compounds have been studied: [RuCl(Cp)(P–P*)] (P–P* = chiral diphosphine) [3] and [RuX(η^6-arene)(L–L)]$^+$ [4].

Despite their long history, the application of chiral half-sandwich ruthenium complexes in asymmetric catalysis has been mainly restricted to hydrogenation [7][8] and *Diels–Alder* reactions [4c]. For the latter, *Kündig* and co-workers have developed com-

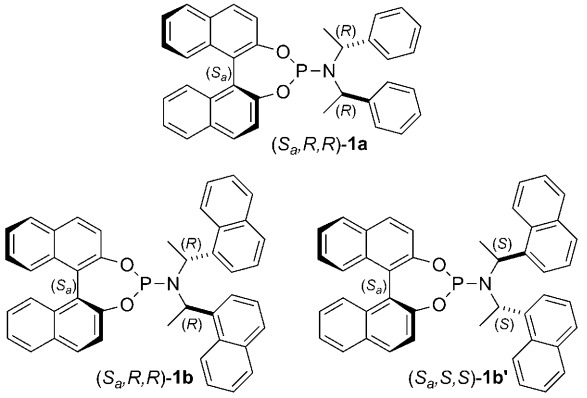
plexes based on the 16-electron fragment $[M(Cp)(P{-}P^*)]^+$ that contain an electron-poor chiral diphosphine P–P* and act as mild and highly selective *Lewis* acids [9]. On the same lines, *Davies* and co-workers (selected examples in [10]), *Oro* and co-workers (for selected references, see [11]), and *Faller* and co-workers (selected examples in [12]) have independently studied complexes of the type $[RuCl(\eta^6\text{-}p\text{-cymene})(L{-}L)]^+$ (L–L = P–O-, P–N-, N–N-, and P,S-hybrid ligands), mainly as *Diels–Alder* catalysts. A general structural feature of these complexes is the use of a chiral bidentate ligand (L–L*) to control the stereochemistry at the metal during the synthesis (or resolution of diastereoisomeric products), upon ligand substitution, and in catalysis.

We have been investigating the possibility of controlling the absolute configuration at the metal center by means of a *monodentate* chiral ligand. Although a few (arene)-ruthenium complexes containing chiral, monodentate P-donor ligands have been reported [13], monodentate stereogenic ligands have not been used in ruthenium half-sandwich precatalysts yet. Conceptually related approaches are the use of hemilabile bidentate ligands (*e.g.*, diphosphine monooxides) [12c] or of P-donors that are tethered to the arene or cyclopentadienyl ligand [14] [12e,f]. It should be noted that the use of a monodentate chiral ligand in pseudotetrahedral half-sandwich complexes opens new potential applications for the large number of recently developed, chiral monodentate phosphoramidite ligands [15a] (for recent applications in asymmetric catalysis, see, *e.g.*, [15b–j]).

As a model reaction, we chose the asymmetric cyclopropanation of olefins, which requires the formation of a diastereoisomerically enriched carbene intermediate, *e.g.*, $[RuCl(=CHR)(\eta^6\text{-}p\text{-cymene})(P^*)]^+$ (P* = chiral phosphoramidite). This species has a precedent in diastereoisomerically pure $[Fe(Cp)(=CHMe)(CO)(P^*)]^+$ reported by *Brookhart* and co-workers, where P* is a chiral monodentate phosphine [16]. Moreover, *Hossain* and co-workers have recently reported a diastereo- and enantioselective *stoichiometric* carbene transfer from analogous complexes to olefins [17]. In contrast, examples of *catalytic* cyclopropanation of olefins catalyzed by iron and ruthenium half-sandwich complexes are restricted to achiral systems. Examples thereof are $[Fe(Cp)(CO)_2(THF)]^+$ [18], $[RuCl(CO)_2(C_5Me_5)]$, $[RuCl_2(\eta^3\text{-allyl})(C_5Me_5)]$, and $[RuCl_2(\eta^6\text{-}p\text{-cymene})(P)]$ (P = monodentate phosphine with a pendant aryl group) [19], $[Ru(Cp)(MeCN)_3]^+$ [20], and/or $[RuCl(Cp)(PPh_3)_2]$ [21].

In preliminary reports, we have shown that $[RuCl_2(\eta^6\text{-}p\text{-cymene})(P^*)]$ (**2**; *p*-cymene = 1-methyl-4-(1-methylethyl)benzene; P* = (S_a,*R*,*R*)-**1a** = (1S_a)-[1,1′-binaphthalene]-2,2′-diyl bis[(1*R*)-1-phenylethyl]phosphoramidite; P* = (S_a,*R*,*R*)-**1b** = (1S_a)-[1,1′-binaphthalene]-2,2′-diyl bis[(1*R*)-1-(naphthalen-1-yl)ethyl]phosphoramidite[1]) catalyze the cyclopropanation of α-methylstyrene (= (1-methylethenyl)benzene) with ethyl diazoacetate after chloride abstraction by $(Et_3O)[PF_6]$ or $Tl[PF_6]$ with an enantioselectivity of up to 86 and 87% ee for the *cis*- and *trans*-cyclopropane derivatives, respectively [22]. The complex formed upon chloride abstraction from **2b** shows an unexpected (η^2-arene)–metal interaction [23]. In the present paper, besides a full account of the products of chloride abstraction from $[RuCl_2(\eta^6\text{-}p\text{-cymene})(P^*)]$, we

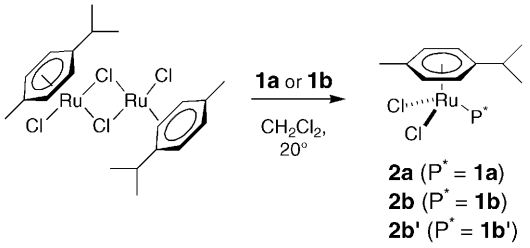
[1]) For systematic names, see *Exper. Part.*



describe the products of the dissociation of *p*-cymene from **2a** and **3a**, in which the coordination of the dangling aryl moiety of the P* ligand is turned from η^2 to η^6, as well as additional catalytic experiments.

Results and Discussion. – *[$RuCl_2(\eta^6$-p-cymene)(P*-κP)]*. Ligand **1a** readily reacts with [{$RuCl_2(\eta^6$-*p*-cymene)}$_2$] in CH_2Cl_2 at room temperature to give [$RuCl_2(\eta^6$-*p*-cymene)(**1a**-κ*P*)] (**2a**) in 93% yield (*Scheme*). The X-ray structure determination [22] of **2a** shows a relatively undistorted coordination geometry at the Ru center (*Table 1*, *Fig. 1*). Although the interpretation of such a half-sandwich complex as pseudotetrahedral is practical in terms of stereochemical understanding, the angles at Ru show that the coordination is more accurately described as octahedral. The Ru–P distance of 2.317(3) Å falls at the upper end of the range found for similar complexes. Thus, it is longer than in the cationic phosphoramidite (P) complex $[Ru(Cp)(CO)_2(P)]^+$ (2.265(4) Å) [24] or in the neutral [RuCl(Cp)($(PhO)_2PN(Me)N(Me)P(OPh)_2$)], which contains a bidentate phosphoramidite ligand (2.2129(6) and 2.1905(6) Å) [25], probably because of the chelate effect.

Scheme. *Synthesis of* **2a** *and* **2b**



Ligand **1b** reacts with [$RuCl_2(\eta^6$-*p*-cymene)]$_2$ to give [$RuCl_2(\eta^6$-*p*-cymene)(**1b**-κ*P*)] (**2b**) in 49% yield. A small amount of free ligand **1b** (*ca.* 4% of total) was present in the CD_2Cl_2 solutions of isolated **2b**, as indicated by the ^{31}P-NMR signal at δ 150.0. The ^{1}H-NMR spectrum indicated that an equivalent amount of [{$RuCl_2(\eta^6$-*p*-cymene)}$_2$] was present as impurity, suggesting that the bulky phosphoramidite **1b** dissociates from

Table 1. *Bond Distances* [Å] *and Angles* [°] *in* **2a**

Ru–Cl(1)	2.405(3)	Ru–Cl(2)	2.387(3)
Ru–P	2.317(3)	P–N(1)	1.681(7)
Ru–C(1)	2.201(12)	Ru–C(2)	2.218(9)
Ru–C(3)	2.213(11)	Ru–C(4)	2.197(11)
Ru–C(5)	2.170(10)	Ru–C(6)	2.206(10)
Cl(1)–Ru–Cl(2)	85.50(10)	Cl(2)–Ru–P	89.06(9)
Cl(1)–Ru–C(3)	87.8(3)	Cl(2)–Ru–C(1)	90.5(3)
Cl(1)–Ru–C(4)	89.0(3)	Cl(2)–Ru–C(2)	89.8(3)
P–Ru–C(5)	93.5(3)	P–Ru–C(6)	92.7(3)
Cl(1)–Ru–P	91.84(10)		

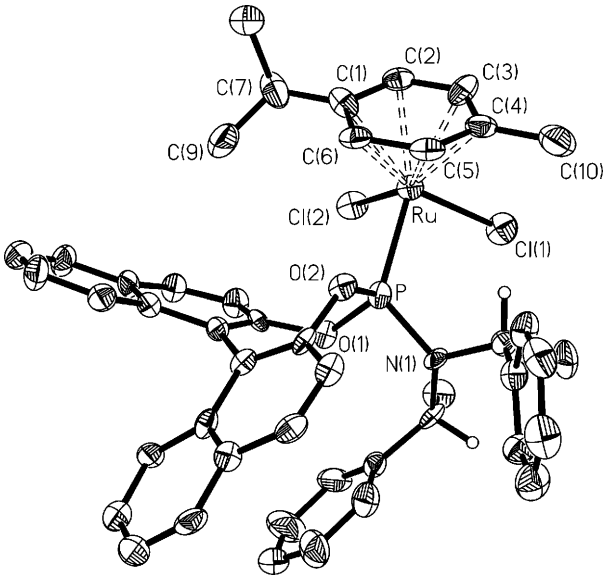


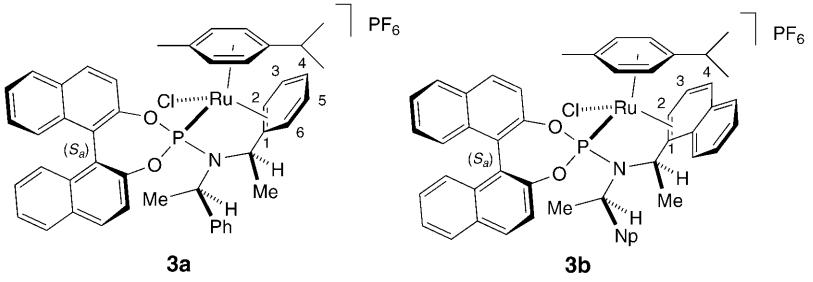
Fig. 1. *ORTEP plot of* (S_a,R,R)-**2a**. 30%-Probability ellipsoids. Arbitrary atom numbering.

2b in solution. Indeed, the amount of free ligand **1b** increased with time and reached 19% of the total integrated intensity after 7 h in solution. As additional, unidentified products were formed, whose ^{31}P-NMR signals accounted for 14% of the total integrated intensity, the dissociation reaction was not investigated further.

The above observations indicate that complexes [$RuCl_2$(η^6-*p*-cymene)(P*-κP)] are relatively unstable, following different decomposition pathways depending on the nature of the phosphoramidite ligand. Complex **2a** preferentially dissociates *p*-cymene (see below), whereas **2b** loses the phosphoramidite ligand. As the dichloro complexes **2a** and **2b** are catalytically inactive, we concentrated our efforts on the products of chloride abstraction, though.

[RuCl(η^6-p*-cymene)(1,2-η-P*-κP)]PF_6.* Complex **2a** reacted with (Et_3O)[PF_6] (or with Tl[PF_6]) in CH_2Cl_2 to give the yellow complex [RuCl(η^6-*p*-cymene)(1,2-η-**1a**-

κP)][PF_6] (**3a**) featuring a *s* at δ 154.6 in the ^{31}P-NMR spectrum, based on the NMR spectroscopic studies described below. Complex **3a** slowly converts to a new species both in the solid state and in solution (see below), which precluded X-ray analysis. The reaction of **2b** either with (Et_3O)[PF_6] or with Tl[PF_6] (1.1 equiv.) gave a yellow complex **3b** that showed a broadened *s* at δ 168.0 in the ^{31}P-NMR spectrum. Complex **3b** analyzes as [RuCl(η^6-*p*-cymene)(**1b**)][PF_6] and is stable in solution for (at least) 3 d and in the solid state for (at least) 7 weeks. Assuming that the phosphoramidite ligand acts as a two-electron donor, the formulation of **3a** and **3b** as [RuCl(η^6-*p*-cymene)-(P*-κP)][PF_6] would imply a 16-electron count and coordinative unsaturation at Ru^{II}. However, five-coordinate, 16-electron Ru^{II} complexes of the type [RuX(Cp*)(P^iPr_2-Ph)] (X = Cl, Br, I) are habitually dark blue or violet in color, whereas their 18-electron adducts [RuX(Cp*)(CO)(P^iPr_2Ph)] are orange/yellow [26]. A combination of multinuclear 2D-NMR measurements indicated that **3a** and **3b** are mononuclear six-coordinate complexes in which the coordination sphere of the 16-electron fragment [RuCl(η^6-*p*-cymene)(P*-κP)]$^+$ is saturated by means of an η^2 interaction between the Ru^{II} atom and the phenyl or naphthalenyl ring of one of the ArCH(Me) substituents at the N-atom (Ar = Ph or Np), which was confirmed by an X-ray study in the case of **3b**.



3a **3b**

The line widths for several proton resonances in the aromatic region of the room-temperature ^{1}H- and ^{13}C-NMR spectra of both **3a** and **3b** indicated a dynamic behavior on the NMR time scale. Upon cooling the samples to $-20°$, the signals sharpened sufficiently to measure one-bond and long-range ^{13}C,^{1}H correlations. Under these conditions, six resolved signals were observed for the phenyl C-atoms of one of the PhCH(Me)N groups of **3a**, indicating restricted rotation, whereas the phenyl group of the other PhCH(Me)N group is freely rotating. An HMBC experiment allowed us to attribute the ^{13}C-NMR signal of C(1) at δ 120.0 in **3a** (101.1 in **3b**) based on the three-bond interactions to H–C(3) and H–C(5), respectively (*Fig. 2*). Analogously, H–C(4) and H–C(6) correlate to C(2) at δ 105.8 for **3a** (δ 96.7 for **3b**) (*Table 2*). The low-frequency shifts $\Delta\delta$ of the C(1) and C(2) signals of **3a** indicate that one of the diastereotopic phenyl rings is η^2-bonded to Ru. The magnitudes of the coordination chemical shifts $\Delta\delta$ (24.3 and 22.4 ppm for C(1) and C(2), resp.) of **3a** indicate a modest-to-weak π-olefin-type complex [27]. The second, noncomplexed phenyl ring has ^{13}C-NMR chemical shifts in the normal aromatic region and shows two equivalent *ortho* (and *meta*) H- and C-atoms, which is indicative of free rotation at this temperature. The naphthalenyl derivative **3b** exhibits analogous features, with the C(1) and C(2) atoms of the naphthalenyl group resonating at δ 101.1 and 96.7, respectively.

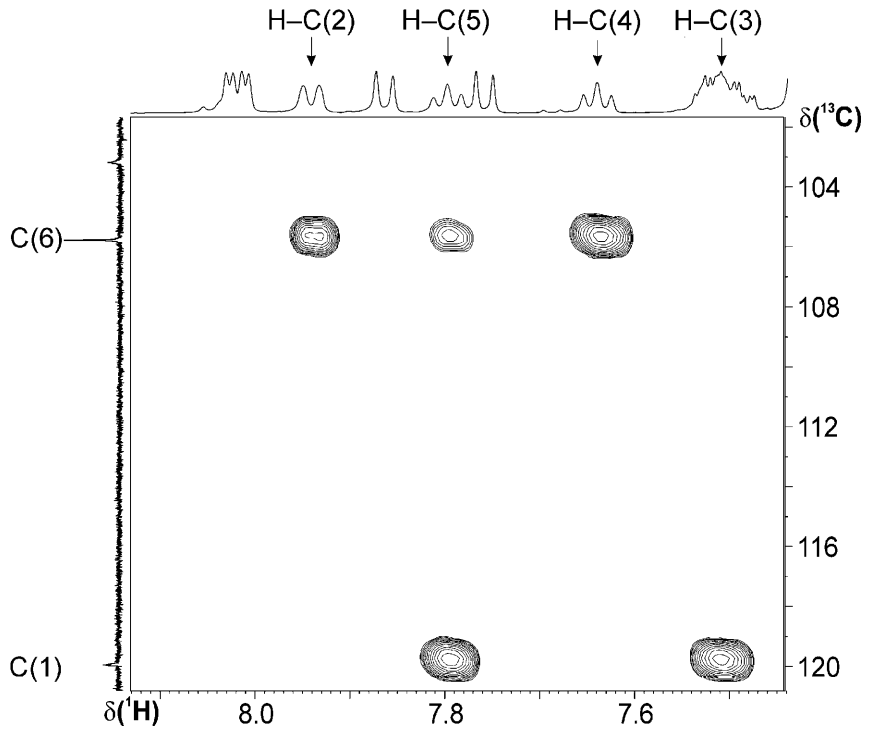


Fig. 2. *$^{13}C,^{1}H$ Long-range correlation from a heteronuclear multibond correlation* (HMBC) *spectrum of* **3a**. For atom numbering, see formula.

Table 2. *Selected ^{13}C-NMR Chemical Shift Values* δ [ppm] *for* **2a**, **3a**, **3b**, **4a**, *and* **5a**[a])

	2a	**3a**	**3b**	**4a**	**5a**
C(1)	144.3	120.0	101.1	106.6	106.0
C(2)	128.2	105.8	96.7	80.6	81.6
C(3)	127.7	136.4	131.8	104.9	105.5
C(4)	126.4	131.3	132.6	95.0	99.0
C(5)	*ca.* 127.7	130.7	[b])	97.8	90.8
C(6)	*ca.* 128.2	134.4	[b])	81.0	82.1

[a]) The numbering scheme is given in the formulae. The corresponding signals of **2b** were not attributed because they overlap with those of the ligand naphthalenyl groups. [b]) The ^{13}C-NMR chemical shift values are in the region δ 128–132.

Molecular-volume data obtained by NMR spectroscopy (pulse-gradient spin-echo (PGSE) diffusion measurements) (selected examples in [28]) confirm that the cationic complexes **3a** and **3b** are mononuclear, as their diffusion coefficients are similar to those of the neutral dichloro complexes **2a** and **2b** (*Table 3*). Additionally, the comparison of the hydrodynamic radii of the anion and cation gives information concerning the extent of ion pairing in solution. Thus, for 100% ion-pair formation, the r_h values for the cation and anion would be identical [28h]. Considerable ion pairing (>50%) occurs

Table 3. *Diffusion Coefficients* [$\cdot 10^{-10}$ m^2 s^{-1}] *and Hydrodynamic Radii* [Å] *in* CD_2Cl_2[a])

		D	r_h
1a		10.06	5.3
[$RuCl_2$(L)(**1a**-κP)] (**2a**)		8.66	6.2
[RuCl(L)((1,2-η)-**1a**-κP)][PF_6] (**3a**)	cation	8.12	6.6
	anion	9.83	5.4
[Ru_2Cl_2(η^6-**1a**-κP)$_2$][PF_6]$_2$ (**5a**)	cation	6.55	8.2
	anion	8.45	6.3
1b		9.44	5.7
[$RuCl_2$(L)(**1b**-κP)] (**2b**)		8.21	6.5
[RuCl(L)((1,2-η)-**1b**-κP)][PF_6] (**3b**)	cation	8.18	6.6
	anion	11.80	4.5

[a]) L is η^6-*p*-cymene.

between the complex cation **3a** and $[PF_6]^-$ (at 2 mM concentration in CD_2Cl_2), as indicated by the hydrodynamic radius r_h of 5.4 Å observed for the $[PF_6]^-$ counterion, which is much larger than for freely diffusing hexafluorophosphate (2.6 Å) [28d]. The ion pairing in the naphthalenyl analog **3b** is less pronounced ($r_h(PF_6) = 4.5$ Å).

Finally, it should be noted that the pseudotetrahedral Ru-atom of **3a** and **3b** is stereogenic, whereas this is not the case in **2a** and **2b**. The ^{31}P-, ^1H-, and ^{13}C-NMR spectra indicated that **3a** and **3b** are formed as a single diastereoisomer. The absolute configuration at the Ru center of **3b** was unambiguously determined by an X-ray study.

X-Ray Structure of rac-**3b**. After several unsuccessful attempts to crystallize **3b** containing enantiomerically pure (S_a,*R*,*R*)-**1b**, high-quality crystals were obtained with the racemic complex *rac*-**3b**, obtained by mixing (S_a,*R*,*R*)-**3b** and (R_a,*S*,*S*)-**3b** in a 1:1 ratio. The crystal was made up of pairs of discrete cations (S_{Ru},S_a,*R*,*R*)-**3b** and (R_{Ru},R_a,*S*,*S*)-**3b** (related by an inversion center), and of $[PF_6]^-$ anions with normal nonbonded distances. With ligand (S_a,*R*,*R*)-**1b**, the configuration at the Ru center is (*S*) (*Fig. 3*) [29]. Besides the chloro ligand and the P-atom of **1b**, the Ru center is coordinated in a η^6 fashion to *p*-cymene and in a η^2 fashion to the naphthalenyl group of one ArCH(Me)N moiety of the phosphoramidite to give an 18-electron complex.

The most interesting structural feature is obviously the η^2 coordination of the naphthalenyl moiety to the Ru center, as indicated by the Ru–C(1) and Ru–C(2) distances of 2.379(2) and 2.386(2) Å, respectively (*Table 4*). As an effect of coordination to Ru, the C(1)–C(2) distance of 1.407(3) Å is longer than the corresponding separation in the noncoordinated naphthalenyl moiety (C(15)–C(16), 1.375(3) Å). Additionally, the pattern of the alternating C–C bond distances suggests extensive loss of aromaticity of the η^2-coordinated ring as compared to the noncoordinated one. The distal ring is nearly not affected, most distances being the same within experimental error. As a consequence of the Ru–η^2-aryl bond, the C(1) atom is pyramidalized to some extent, as indicated by the sum of the C(2)–C(1)–C(10), C(2)–C(1)–C(11), and C(10)–C(1)–C(11) angles of 353.6°. However, nonbonded interactions between the naphthalenyl ring and the cymene ligand probably contribute to this disortion, as suggested by the shortest contact of 3.114(4) Å between C(3) and C(53).

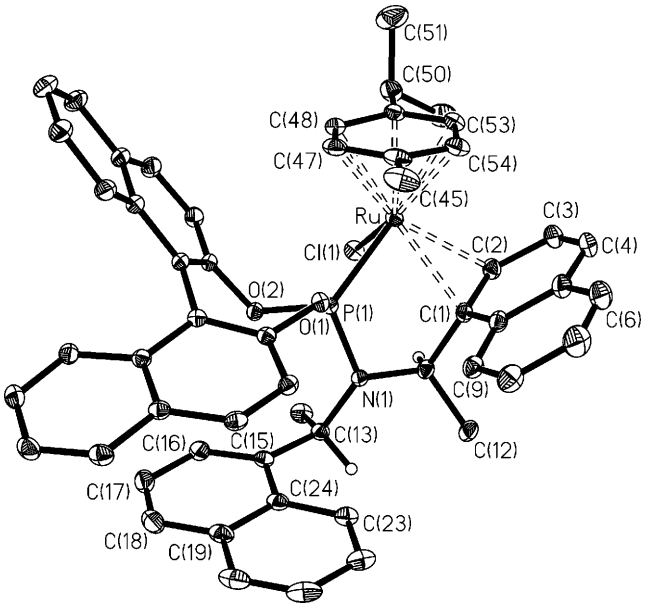


Fig. 3. *ORTEP plot of* (S_{Ru},S_a,R,R)-**3b**. 30%-Probability ellipsoids. Arbitrary atom numbering.

Table 4. *Bond Distances* [Å] *and Angles* [°] *in* **3b**

Ru–Cl(1)	2.3926(6)	Ru–P(1)	2.2783(5)
Ru–C(1)	2.379(2)	Ru–C(2)	2.386(2)
Ru–C(46)	2.258(2)	Ru–C(47)	2.216(2)
Ru–C(48)	2.208(2)	Ru–C(49)	2.306(2)
Ru–C(54)	2.221(2)	Ru–C(53)	2.298(2)
C(1)–C(2)	1.407(3)	C(15)–C(16)	1.375(3)
C(2)–C(3)	1.442(3)	C(16)–C(17)	1.409(4)
C(1)–C(10)	1.472(3)	C(15)–C(24)	1.432(2)
C(3)–C(4)	1.334(4)	C(17)–C(18)	1.355(4)
C(4)–C(5)	1.433(4)	C(18)–C(19)	1.419(4)
C(5)–C(10)	1.417(3)	C(19)–C(24)	1.421(3)
C(9)–C(10)	1.401(3)	C(23)–C(24)	1.418(3)
Cl(1)–Ru–C(1)	93.11(5)	Cl(1)–Ru–C(2)	84.04(6)
Cl(1)–Ru–P(1)	81.066(19)	Cl(1)–Ru–C(49)	88.88(6)
P(1)–Ru–C(1)	72.05(5)	P(1)–Ru–C(2)	103.25(6)
P(1)–Ru–C(47)	90.82(6)	C(53)–Ru-Cl(1)	113.11(6)
C(1)–Ru–C(54)	97.44(8)	C(2)–Ru–C(53)	85.14(8)

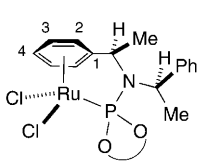
At difference with other η^2 interactions in Ru complexes reported so far [30–32], the bonding in **3b** involves a 'dangling' aryl group and not the chelate ring of a diphosphine. To the best of our knowledge, the only other example of η^2 interaction between a Ru-atom and a dangling aryl, besides **3b**, has been found in a heptanuclear Ru cluster in which a phenyl group at a μ_5-bridging alkyne loosely coordinates to a Ru-atom (2.42(1)

and 2.48(1) Å) [33]. Compared to these values, the Ru–C(1) and Ru–C(2) distances of 2.379(2) and 2.386(2) Å in **3b** are considerably shorter, but longer than in (olefin)ruthenium(II) complexes (average below 2.2 Å) [34] or in ruthenium(II) complexes containing the atropisomeric biarene diphosphines [2′-(diphenylphosphino)[1,1′-binaphthalen]-2-yl]diphenylphosphine oxide (2.255(4) and 2.346(4) Å) [31] and (6,6′-dimethoxy[1,1′-biphenyl]-2,2′-diyl)bis[diisopropylphosphine] (2.299(5) and 2.366(5) Å) [30b]. However, the latter Ru–aryl interactions are enhanced by the chelate effect as they involve a biaryl diphosphine bridge.

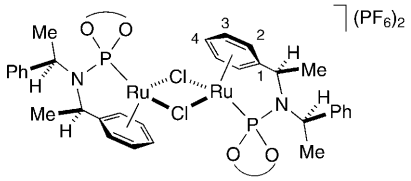
Although there is increasing circumstantial evidence that the coordination of pendant aromatic rings may play an important role in transition-metal catalysts by stabilizing metal complexes with a low electron count, thoroughly documented examples are still rare. Interestingly, an η^2 interaction between ligand **1a** and the metal has been predicted by calculation for nickel hydrovinylation catalysts, in which it stabilizes the hydride alkene intermediate [NiH(styrene)(1,2-η-**1a**-κP)] [35]. Our results may help explain the remarkable influence of the formal secondary-amine appendage (*N*-substituent) observed in the same reaction [36]. An analogous interaction involving a binaphthalene group has been claimed for cationic (monophosphine)palladium(II) complexes [37][38], but it is still controversial whether the coordination mode is η^2 or η^1 [39]. On similar lines, the cyclometalation of the phosphoramidite at the phenethyl Me group has been observed in iridium(I) complexes [40][41], which offers an alternative possibility of turning a 'monodentate' phosphoramidite into a chelating ligand.

Loss of p-*Cymene.* As mentioned above, the derivatives containing ligand **1a** (**2a**, and **3a**), are prone to lose *p*-cymene both in solution and in the solid state. Complex **2a** slowly dissociates *p*-cymene upon standing for several days in CD_2Cl_2. The ^{31}P-NMR spectra of the reaction solution indicate that dichloro{(1S_a)-[1,1′-binaphthalene]-2,2′-diyl [(1*R*)-1-(η^6-phenyl)ethyl][(1*R*)-1-phenylethyl]phosphoramidite-κP}ruthenium(II)[1] (**4a**), featuring a *s* at δ 150.9, is slowly formed. At room temperature, quantitative conversion of **2a** to **4a** required about one month, after which pure **4a** was isolated by evaporation of the solvent under reduced pressure. Besides MALDI mass spectrometry and elemental analysis, ^{31}P-, ^{1}H-, ^{13}C-NMR spectroscopy, ^{31}P,^{1}H-HMQC, ^{13}C,^{1}H-HMQC, ^{1}H,^{1}H-COSY, and ^{1}H,^{1}H-NOESY 2D-NMR measurements (*Exper. Part* and *Table 2*) were used to characterize **4a** with a procedure analogous to that described for **5a** (see below).

Similarly, on standing in CD_2Cl_2 solution, **3a** is converted to **5a**, which features a *s* at δ 150.4 in the ^{31}P-NMR spectrum. The reaction is quantitative after 16 d at room temperature or within 17 h at 40°. The process also takes place in the solid state, albeit on a



4a



5a

longer time scale (2–3 months, room temperature, under Ar). Attempts to obtain pure **5a** by repeated recrystallizations of **3a** gave samples that were spectroscopically but not analytically pure. Finally, **3a** was heated in the solid state under high vacuum ($< 5 \cdot 10^{-3}$ mbar) at 150° for 77 h. Mass spectroscopy and elemental analysis indicate the empirical formula [RuCl(**1a**)][PF_6] for **5a**. The same combination of NMR multinuclear and PGSE methods used for **3a** and **3b** indicated that **5a** is the binuclear species [$Ru_2Cl_2(\eta^6$-**1a**-$\kappa P)_2]^{2+}$, in which the phenyl ring of one PhCH(Me)N moiety binds the Ru-atom in an η^6 fashion. ^{1}H- and ^{13}C-NMR Data confirmed the absence of the η^6-*p*-cymene and that only one phenyl ring is freely rotating.

The ^{31}P,^{1}H-HMQC correlation allowed the assignement of the different PhCH(Me)N methine H- and C-atoms of **5a** and, thus, with the help of NOEs, to connect these to the corresponding coordinated and free phenyl rings. As expected, a set of six ^{13}C-NMR signals from one of the PhCH(Me)N phenyl rings is displaced to lower frequency (*Table 2*, *Fig. 4*), thus confirming an η^6 complexation to Ru. Distinct patterns are observed for the two PhCH(Me)N methine H-atoms. The one belonging to the η^6-complexed moiety appears as a *dq* (δ 4.14, ^3J(P,H) = 42.7 Hz), whereas that of the dangling PhCH(Me)N group is observed as a *m* (δ 4.70, ^3J(P,H) = 7.0 Hz). These very different ^3J(P,H) values reflect the different conformations of the PhCH(Me)N groups. The PGSE measurements for the cation **5a** in CD_2Cl_2 show a large hydrodynamic radius r_h of 8.2 Å, which is consistent with a binuclear structure [28a,b] (*Table 3*). Again, we note very substantial ion pairing between cation **5a** and $[PF_6]^-$ in that the r_h value 6.3 Å is much larger than the hydrodynamic radius of $[PF_6]^-$ in MeOH (2.6 Å) [28d].

In contrast to **3a**, **3b** remained substantially unchanged for 3 d in CD_2Cl_2 at room temperature. After 12 days in solution, a new *s* at δ 153.1 in the ^{31}P-NMR spectrum of the solution indicated a small amount (7% of total intensity) of an unidentified product, which was not further investigated. The fact that *p*-cymene is less susceptible of dissociation in **3b** than in **3a** may indicate that the η^6 coordination is less favorable for naphthalenyl than for phenyl. This would explain why **2b** dissociates the phosphoramidite ligand rather than *p*-cymene, as well as the fact that an excess of **1b** is required in catalytic cyclopropanation, as discussed below.

Asymmetric Cyclopropanation. Complex **3a**, formed *in situ* by treating **2a** with a chloride scavenger ($(Et_3O)[PF_6]$ or $Tl[PF_6]$), cyclopropanates styrene in the presence of ethyl diazoacetate as carbene source to give a nearly 1:1 racemic mixture of *cis*- and *trans*-cyclopropanes (*Table 5*, *Run 1*) [22]. Racemic cyclopropanes are formed from α-methylstyrene, too, with low *cis* selectivity (*Run 4*). The low level of asymmetric induction is probably not an effect of *p*-cymene dissociation from **3a** to give **5a**, as **5a** cyclopropanates α-methylstyrene with a low but significant level of enantioselectivity (26 and 21% ee for the *cis* (1*R*,2*S*) and *trans* (1*R*,2*R*) isomers, resp.; *Run 5*).

Preliminary tests indicated substantial asymmetric induction with the more encumbered naphthalenyl-containing ligand **1b**, but a number of parameters had to be optimized. Eventually, an *in situ* preparation of **3b** was developed, in which [{$RuCl_2(\eta^6$-*p*-cymene)}$_2$] was treated with an excess of **1b** (2 equiv. *vs.* Ru) to suppress ligand dissociation, followed by addition of the chloride scavenger (either $(Et_3O)[PF_6]$ or $Tl[PF_6]$, 1 equiv. *vs.* Ru). With this protocol, styrene is reproducibly cyclopropanated

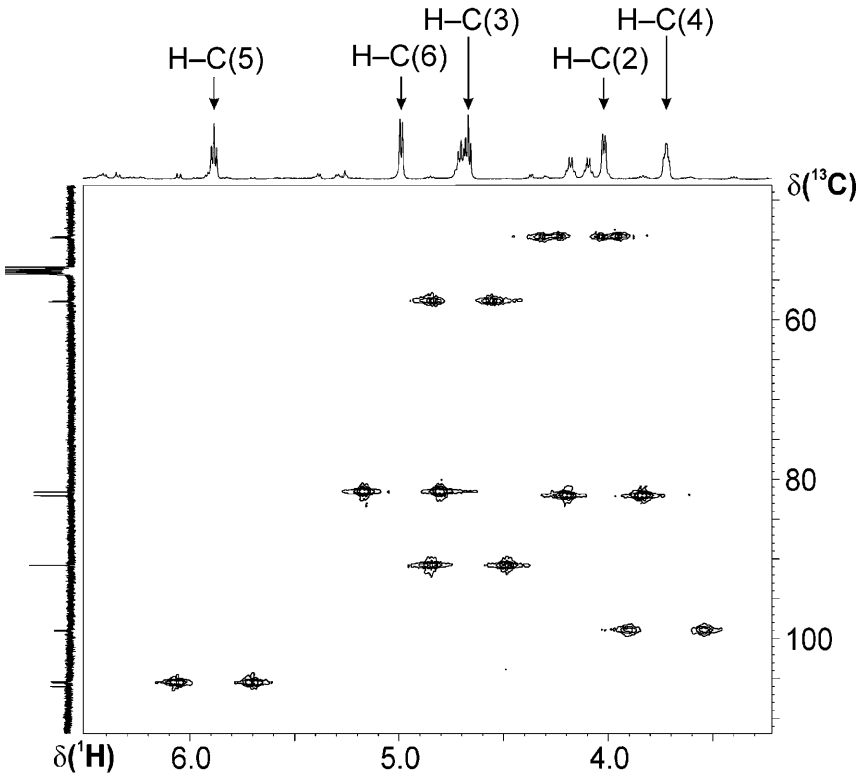


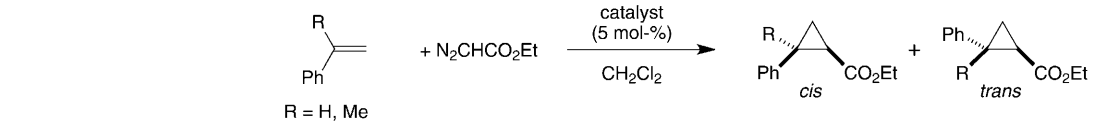
Fig. 4. *One bond $^{13}C,^{1}H$ correlation showing the five aromatic protons of the η^6-bound phenyl ring plus the two CH(Me)N protons in* **5a**. For atom numbering, see formula.

with an enantioselectivity as high as 77 and 68% ee for the *cis* and *trans* isomers, respectively, with ligand **1b**, albeit with no diastereoselectivity (*Run 2*).

The best results were obtained with **3b** and α-methylstyrene, a 1,1-disubstituted olefin, which is cyclopropanated with 86 and 87% ee for the *cis* and *trans* isomers, respectively (*Run 6*). As catalyst **3a** gives racemic products (*Run 4*), enantioselection requires bulky residues at the *N*-substituent of the ligand (the naphthalenyl group of **1b**). This effect is reinforced with an α-substituted styrene such as α-methylstyrene, which was chosen, therefore, as substrate for further studies. As the catalyst performance is independent of the chloride scavenger used, only runs obtained with $(Et_3O)[PF_6]$ are reported in *Table 5*. However, the presence of one chloro ligand is required to achieve high enantioselectivity, as activation of **2b** with 2 equiv. of $(Et_3O)[PF_6]$, which probably causes abstraction of both chlorides, decreases both the yield and the enantioselectivity (*Run 8*).

To analyze the effect of the relative configuration at the atropisomeric 1,1′-binaphthalene moiety and at the *N*-substituents, the diastereoisomeric ligand (S_a,*S*,*S*)-**1b**′ was used instead of (S_a,*R*,*R*)-**1b** in selected catalytic reactions. The spectroscopic data (including a complete NMR structural analysis as for **3b**) indicate that the diastereoisomer pairs of complexes **2b**/**2b**′ and **3b**/**3b**′ have a similar structure (see *Exper.*

Table 5. *Catalytic Cyclopropanation*[a])



Run	Catalyst	R	Conv. [%]	Yield [%]	*cis*/*trans*	ee [%] (abs. config.)	
						cis	*trans*
1	**3a**	H	38	26	41:59	8 (1*S*,2*R*)	3 (1*R*,2*R*)
2	**3b**	H	6	5	45:55	77 (1*R*,2*S*)	68 (1*R*,2*R*)
3	**3b′**	H	28	20	47:53	5 (1*S*,2*R*)	13 (1*S*,2*S*)
4	**3a**	Me	31	31	60:40	*rac*	*rac*
5	**5a**	Me	19	17	59:41	26 (1*R*,2*S*)	21 (1*R*,2*R*)
6	**3b**	Me	20	19	56:44	86 (1*R*,2*S*)	87 (1*R*,2*R*)
7	**3b′**	Me	47	47	66:34	9 (1*S*,2*R*)	7 (1*S*,2*S*)
8	**2b**[b])	Me	12	7	61:39	19 (1*R*,2*S*)	19 (1*R*,2*R*)
9	**3b**[c])	Me	25	23	57:43	82 (1*R*,2*S*)	83 (1*R*,2*R*)
10	**3b**[d])	Me	23	21	56:44	83 (1*R*,2*S*)	84 (1*R*,2*R*)
11	**3b**[e])	Me	20	14	57:43	48 (1*R*,2*S*)	46 (1*R*,2*R*)
12	**3b**[f])	Me	17	13	59:41	73 (1*R*,2*S*)	73 (1*R*,2*R*)
13	**3b″**	Me	24	23	57:43	86 (1*S*,2*R*)	87 (1*S*,2*S*)

[a]) See *Exper. Part* for catalyst preparation. 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 soln. of the olefin (0.48 mmol) and the catalyst (24 μmol, 5 mol-%). The total reaction time was 20 h, unless otherwise stated. [b]) 2.1 equiv. of $(Et_3O)[PF_6]$ were added. [c]) The total reaction time was 44 h. [d]) Ethyl diazoacetate was added in one portion. [e]) Isolated complex **3b** was used. [f]) Isolated complex **3b** plus 1 equiv. of **1b** were used.

Part). With both substrates tested in asymmetric cyclopropanation, the (S_a,*R*,*R*)-diastereoisomer **1b** is the matched one, and the (S_a,*S*,*S*)-diastereoisomer **1b′** the mismatched one, as the enantioselectivity for the *cis* isomer collapses from 77% ee (styrene) and 86% ee (α-methylstyrene) to nearly racemic on changing from **1b** to **1b′** (*Runs 2 vs. 3* and *6 vs. 7*). With α-methylstyrene, the change is larger than with styrene, and the sense of induction is reversed. The same trend is observed for the enantiomeric excess of the *trans* isomer, whereas the diastereoselectivity changes to a low extent. The sharp decrease of the enantioselectivity to nearly racemic on inversion of the relative configuration indicates that both types of stereogenic units, *i.e.*, that of the *N*,*N*-bis(1-arylethyl) moiety and that of the 1,1′-binaphthalene framework, contribute to enantioselection to a similar extent, with minor variations depending on the substrate. In contrast, the chiral *N*,*N*-bis(1-phenylethyl) moiety dominates stereoselection in the copper-catalyzed conjugate addition of diethylzinc to cyclohexenone, in which the matched (S_a,*R*,*R*)-**1a** and mismatched (S_a,*S*,*S*)-**1a** ligands give >98 and 75% ee, respectively [42], and in the enantioselective allylic amination of achiral allylic esters with an iridium–**1a** complex, where (R_a,*R*,*R*)-**1a** and (S_a,*R*,*R*)-**1a** gave up to 97 and 75% ee, respectively [43].

The issue of the stability of catalyst **3b** was briefly studied with respect to the dissociation of the phosphoramidite. When isolated **3b** is used, lower yield and reduced

enantioselectivity (48 and 46%) are observed (*Run 11*). The enantioselectivity is partially restored (73% for both isomers, *Run 12*) upon addition of 1 equiv. of ligand **1b** to isolated **3b**. The ^{31}P-NMR spectra of the resulting solutions display the signal of **3b** and that of the free ligand **1b** in a *ca.* 1:1 intensity ratio, indicating that only one ligand molecule binds to the Ru center. These observations suggest dissociation of **1b** from **3b** in solution, a reaction that has been observed by NMR spectroscopy for CD_2Cl_2 solutions of **2b**, but has not been clearly established with cationic **3b** (see above).

The good *cis* selectivity observed with the achiral half-sandwich complexes $[Fe(Cp)(CO)_2(THF)]^+$ [18] and $[RuCl(Cp)(PPh_3)2]$ [21] was the rationale for the choice of chiral analogues as enantioselective, highly *cis*-diastereoselective cyclopropanation catalysts, which are still rare [44–46] as compared to *trans*-selective ones (for a recent comprehensive review, see [47a]; see also [47b]). The results with [RuCl(η^6-*p*-cymene)(1,2-η-P*-κP)] do not match this expectation, though, as the diastereoselectivity is very modest. The best ligand/substrate combination is **1b**/α-methylstyrene, which combines the highest enantioselectivity for both diastereoisomers with one of the highest *cis*/*trans* ratios (56:44; *Run 6*). With both ligands, the formation of the *trans* isomer is slightly favored in the case of styrene, but the *cis* isomer prevails with α-methylstyrene (*Runs 1 vs. 4*, *2 vs. 6*, and *3 vs. 7*). This diastereoselectivity trend is opposite to that observed for $[Fe(Cp)(CO)_2(THF)]^+$, which shows decreasing selectivity on going from styrene (*cis*/*trans* ratio of 85:15) to α- and *p*-methylstyrene (both 60:40), 2-methoxypropene (55:45), and ethyl vinyl ether (45:55) [18]. The explanation was that electron-releasing substituents on the olefin slow down the collapse of the short-lived γ-carbocationic intermediate, giving time for a conformational rearrangement, as originally proposed by *Brookhart* and *Liu* for the analogous stoichiometric reaction [48]. The fact that we observed the opposite trend hints to substantial mechanistic differences between $[Fe(Cp)(CO)_2(THF)]^+$ and [RuCl(η^6-*p*-cymene)(1,2η-P*-κP)]$^+$. Finally, it should be noted that the related half-sandwich complex [Ru(η^5-Me_5C_5)(MeCN)(P–N)]$^+$ (P–N = 2-[2-(diphenylphosphino)phenyl]-4,5-dihydro-4-isopropyloxazole) is neither diastereoselective (*cis*/*trans* ratio 46:54) nor enantioselective [11c].

The catalytic activity of [RuCl(η^6-*p*-cymene)(1,2η-P*-κP)]$^+$ is generally low. Longer reaction times (44 instead of 24 h) marginally increased the overall cyclopropane yield from 19 to 23% (*Run 9*). Monitoring the reaction course by gas chromatography showed a small but steady increase of the product concentration, which suggests that the catalyst stays active during the entire reaction time. After 20 h, the ^{1}H-NMR spectrum of a reaction solution with ligand **1b** and α-methylstyrene shows that, in addition to the cyclopropanation products (9%), maleate and fumarate were formed (*ca.* 46 and 8% yield, resp.). However, as unreacted ethyl diazoacetate was still present in the reaction solution (*ca.* 27% of starting amount), the most probable explanation of the low cyclopropane yield is the intrinsic low activity of the catalyst and not the competing homocoupling reaction of carbene to maleate and fumarate. This conclusion is also supported by the observation that the addition of ethyl diazoacetate in one portion does not affect significantly the reaction yield (*Run 10*).

Although no clear trend can be distinguished, the increased productivity of both catalysts with α-methylstyrene as compared to styrene (*Runs 1 vs. 4* and *2 vs. 6*) is probably an electronic effect. In fact, as (carbene)ruthenium complexes are relatively weak electrophiles [49], an electron-rich olefin such as α-methylstyrene is expected to react

faster than styrene with the putative (carbene)ruthenium. We have previously noted that electron-rich olefins are more prone to carbene transfer from $[RuCl(PNNP)]^+$ catalysts (PNNP = chiral tetradentate ligand with a P_2N_2 donor set) [46b]. Furthermore, for each substrate, yields decrease with increasing steric bulk of the ligand, that is, on going from **1a** to **1b**.

Conclusion. – The coordination chemistry described above clearly shows that phosphoramidite ligands can behave as two-, four-, or eight-electron donors. Thus, it cannot be considered a general fact that they are 'monodentate chiral ligands', and care should be taken when this assumption is made without supporting evidence. The application to catalytic cyclopropanation indicates that the η^2-aryl interaction offers an additional possibility to stabilize catalytically active 16-electron fragments. Provided that a bulky phosphoramidite ligand is used, highly enantioselective carbene transfer is achieved with α-methylstyrene, an example of 1,1-disubstituted olefins, which are more difficult to cyclopropanate than styrene. However, despite the secondary η^2- and η^6-aryl interactions, bulky phosphoramidites tend to dissociate from the metal, which suggests that the thermodynamic chelate effect is less efficient than with diphosphines.

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Experimental Part

General. Reactions with air- or moisture-sensitive materials were carried out under Ar by using *Schlenk* techniques, or in a glove box under purified N_2. (−)-Bis[(1*R*)-1-phenylethyl]amine hydrochloride, (−)-bis[(1*R*)-1-(naphthalen-1-yl)ethyl]amine hydrochloride, (−)-bis[(1*S*)-1-(naphthalen-1-yl)-ethyl]amine hydrochloride, ethyl diazoacetate, α-methylstyrene, and decane were obtained from *Aldrich*. (−)-(1*S*)-[1,1′-Binaphthalene]-2,2′-diol, styrene, dodecane, triethyloxonium hexafluorophosphate, (−)-(*R*)-α-phellandrene, and phosphorus trichloride were purchased from *Fluka*, thallium hexafluorophosphate from *Strem* or *Alfa Aesar*, and ruthenium(III) chloride trihydrate from *Pressure Chemicals*. Ethyl diazoacetate was distilled and stored over 4-Å molecular sieves. All other commercially available reagents were used without further purification. Solvents were purified by standard procedures: CH_2Cl_2 was distilled from CaH_2. $[RuCl_2(\eta^6\text{-}p\text{-cymene})]_2$ [50], (1S_a)-[1,1′-binaphthalene]-2,2′-diyl bis[(1*R*)-1-phenylethyl]phosphoramidite (= *(11b*S$_a$*)*-N,N-*Bis-[(1*R*)-1-phenylethyl]dinaphthol[2,1-*d*:1′,2′-f][1,3,2]dioxaphosphepin-4-amine*; **1a**), (1S_a)-[1,1′-binaphthalene]-2,2′-diyl bis[(1*R*)-1-(naphthalen-1-yl)ethyl]phosphoramidite (= *(11b*S$_a$*)*-N,N-*Bis[(1*R*)-1-(naphthalen-1-yl)ethyl]dinaphtho[2,1-*d*:1′,2′-f][1,3,2]dioxaphosphepin-4-amine*; **1b**) and (1S_a)-[1,1′-binaphthalene]-2,2′-diyl bis[(1*S*)-1-(naphthalen-1-yl)ethyl]phosphoramidite (= *(11b*S$_a$*)*-N,N-*Bis[(1*S*)-1-(naphthalen-1-yl)ethyl]dinaphtho[2,1-*d*:1′,2′-f][1,3,2]dioxaphosphepin-4-amine*; **1b**′), were prepared according to literature procedures [42][51]. $[\alpha]_D$: *Perkin-Elmer-341* polarimeter; 1-dm cell; in $CHCl_3$, unless otherwise stated. ^{1}H- (500 MHz), ^{31}P- (202.5 MHz), and ^{13}C-NMR (125.8 MHz) Spectra: *Bruker-Avance* spectrometer; CD_2Cl_2 solns., unless otherwise stated; chemical shifts δ in ppm downfield of $SiMe_4$; δ(P) referenced externally to 85% H_3PO_4 (δ 0.0); coupling constants *J* in Hz. Mass spectra were measured by the MS service (Laboratorium für Organische Chemie, ETH Zürich). ESI-MS: *Micromass-Auto-SpecUltima* mass spectrometer, at 70 eV. HR-MALDI-MS: *IonSpec-Ultima-HR-MALDI-FT-ICR* mass spectrometer, at 4.7 Tesla; DCTB (*trans*-2-{3-[4-(*tert*-butyl)phenyl]-2-methylprop-2-enylidene}malononitrile) matrix. Elemental analyses were carried out by the Laboratory of Microelemental Analysis (Laboratorium für Organische Chemie, ETH Zürich).

*{(11b*S$_a$*)*-N,N-*Bis[(1*R*)-1-phenylethyl]dinaphtho[2,1-*d*:1′,2′-f][1,3,2]dioxaphosphepin-4-amine-*κP^4*}-dichloro[η^6-1-methyl-4-(1-methylethyl)benzene]ruthenium* (**2a**). $[\{RuCl_2(\eta^6\text{-}p\text{-cymene})\}_2]$ (387 mg, 0.632

mmol) and **1a** (750 mg, 1.39 mmol, 1.1 equiv.) were dissolved in CH_2Cl_2 (20 ml). The resulting soln. was stirred at r.t. for 1 h. ^{i}PrOH (15 ml) was added, and CH_2Cl_2 was evaporated. The precipitate was filtered off and dried *in vacuo*: **2a** (992 mg, 93%). Orange solid. $[\alpha]_D^{20} = +65$ ($c = 0.125$). ^{1}H-NMR: 1.09 (*d*, *J* = 7.0, 3 H, *Me*$_2$CH (cym)); 1.21 (*d*, *J* = 7.0, 3 H, *Me*$_2$CH (cym)); 1.53 (*d*, *J* = 6.8, 6 H, PhCH(*Me*)); 2.00 (*s*, Me (cym)); 2.74 (*sept.*, *J* = 7.0, Me$_2$C*H* (cym)); 4.21 (*d*, *J* = 5.9, 1 arom. H (cym)); 4.93 (*d*, *J* = 5.9, 1 arom. H (cym)); 4.98–5.11 (*m*, 2 CHN); 5.16 (*d*, *J* = 6.1, 1 arom. H (cym)); 5.22 (*d*, *J* = 6.1, 1 arom. H (cym)); 6.59–7.96 (*m*, 22 arom. H). ^{31}P-NMR: 142.3 (*s*). MALDI-MS: 846 (8, $[RuCl_2(\eta^6$-*p*-cymene)(**1a**)$]^+$), 810 (2, $[RuCl(\eta^6$-*p*-cymene)(**1a**)$]^+$), 712 (3, $[RuCl_2($**1a**$)]^+$), 676 (100, $[RuCl($**1a**$)]^+$), 641 (5, $[Ru($**1a**$)]^+$). Anal. calc. for $C_{46}H_{44}Cl_2NO_2PRu$ (845.80): C 65.32, H 5.24, N 1.66; found: C 65.44, H 5.40, N 1.67.

*{(11b*S$_a$*)*-N,N-*Bis[(1*R*)-1-(naphthalen-1-yl)ethyl]dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-4-amine-*κP^4*}dichloro[η^6-1-methyl-4-(1-methylethyl)benzene]ruthenium* (**2b**). As described for **2a**, from $[\{RuCl_2(\eta^6$-*p*-cymene)$\}_2]$ (196 mg, 0.320 mmol) and **1b** (451 mg, 0.705 mmol, 1.1 equiv.) in CH_2Cl_2 (10 ml): **2b** (260 mg, 49%). Orange solid. $[\alpha]_D^{20} = +155$ ($c = 0.125$). ^{1}H-NMR ($-40°$): 1.13 (*d*, *J* = 6.9, 3 H, *Me*$_2$-CH (cym)); 1.21 (*d*, *J* = 6.9, 3 H *Me*$_2$CH (cym)); 1.90 (br. *s*, 3 H, ArCH(*Me*)); 1.96 (*s*, Me (cym)); 2.00 (*d*, *J* = 6.5, 3 H, ArCH(*Me*)); 2.83 (*sept.*, *J* = 6.9, Me$_2$C*H* (cym)); 4.77 (*d*, *J* = 4.9, 1 arom. H (cym)); 4.88 (*d*, *J* = 5.5, 1 arom. H (cym)); 4.93 (*d*, *J* = 5.7, 1 arom. H (cym)); 4.93–5.01 (*m*, 1 arom. H); 5.40 (*d*, *J* = 5.5, 1 arom. H (cym)); 5.53 (*dq*, ^3J(H,H) = 7.0, ^3J(H,P) = 19.4, 1 CHN); 6.47–6.65 (*m*, 1 CHN); 6.81–8.16 (*m*, 24 arom. H); 8.41–8.55 (*m*, 1 arom. H). ^{31}P-NMR: 146.6 (*s*, 96%, complex **2b**); 150.0 (*s*, 4%, free ligand **1b**). MALDI-MS: 910 (7, $[RuCl(\eta^6$-*p*-cymene)(**1b**)$]^+$), 776 (100, $[RuCl($**1b**$)]^+$), 741 (11, $[Ru($**1b**$)]^+$), 640 (64, $[$**1b**$]^+$). Anal. calc. for $C_{54}H_{48}Cl_2NO_2PRu$ (945.91): C 68.57, H 5.11, N 1.48; found: C 68.62, H 5.27, N 1.51.

*{(11b*S$_a$*)*-N,N-*Bis[(1*S*)-1-(naphthalen-1-yl)ethyl]dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-4-amine-*κP^4*}dichloro[η^6-1-methyl-4-(1-methylethyl)benzene]ruthenium* (**2b′**). As described for **2b**, from $[RuCl_2(\eta^6$-*p*-cymene)$]_2$ (65 mg, 0.107 mmol) and **1b′** (150 mg, 0.234 mmol, 1.1 equiv.) in CH_2Cl_2 (10 ml): **2b′** (165 mg, 82%). Orange solid. ^{1}H-NMR ($-40°$): 1.13 (*d*, *J* = 7.0, 3 H, *Me*$_2$CH (cym)); 1.19 (*d*, *J* = 7.0, 3 H, *Me*$_2$CH (cym)); 1.86 (*s*, 3 H, Me (cym)); 1.89 (*d*, *J* = 7.0, 3 H, ArCH(*Me*)); 2.14 (*d*, *J* = 6.0, 3 H, ArCH(*Me*)); 2.83 (*sept.*, *J* = 6.8, Me$_2$C*H* (cym)); 4.58 (*d*, *J* = 5.9, 1 arom. H (cym)); 4.61 (*d*, *J* = 5.9, 1 arom. H (cym)); 4.93 (*d*, *J* = 5.7, 1 arom. H (cym)); 4.98 (*t*, *J* = 7.5, 1 arom. H (naph)); 5.59 (*d*, *J* = 5.9, 1 arom. H (cym)); 5.85 (*t*, *J* = 7.5, 1 arom. H (naph)); 5.89–5.96 (*m*, 1 CHN); 5.95 (*t*, *J* = 7.5, 1 arom. H (naph)); 6.13–6.21 (*m*, 1 CHN); 6.27 (*d*, *J* = 6.5, 1 arom. H (naph)); 6.37 (*d*, *J* = 7.0, 1 arom. H (naph)); 6.61 (*t*, *J* = 7.5, 1 arom. H (naph)); 6.83 (*d*, *J* = 8.0, 1 arom. H (naph)); 6.97 (*d*, *J* = 8.0, 1 arom. H (naph)); 7.23 (*d*, *J* = 8.0, 1 arom. H (naph)); 7.29–7.62 (*m*, 11 arom. H (incl. naph)); 7.76 (*d*, *J* = 8.5, 1 arom. H); 7.80 (*d*, *J* = 9.0, 1 arom. H); 7.98 (*d*, *J* = 8.0, 1 arom. H); 8.03 (*t*, *J* = 9.0, 1 arom. H (naph)); 8.11 (*d*, *J* = 9.0, 1 arom. H); 8.41 (*d*, *J* = 9.0, 1 arom. H); ^{31}P-NMR: 162.6 (*s*).

*Chloro[η^6-1-methyl-4-(1-methylethyl)benzene]{(11b*S$_a$*)*-N-*{(1*R*)-1-[(1,2-η)-phenyl]ethyl}*-N-*[(1*R*)-1-dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-4-amine-*κP^4*}ruthenium(1+) Hexafluorophosphate(1−)* (**3a**). Complex **2a** (200 mg, 0.236 mmol) was treated with $Tl[PF_6]$ (87 mg, 0.248 mmol, 1.05 equiv.) in CH_2Cl_2 (12 ml). After stirring at r.t. for 21 h, TlCl was filtered off, ^{i}PrOH (17 ml) was added, and CH_2Cl_2 was evaporated. The precipitate was filtered off and dried *in vacuo*: **3a** (201 mg, 89%). Orange solid. The integration of the ^{1}H- and ^{31}P-NMR spectra (**3a**, 87%; **5a**, 13%) indicated that the sample contained some **5a** as impurity. $[\alpha]_D^{20} = +99$ ($c = 0.105$). ^{1}H-NMR ($-20°$): 0.90 (*d*, *J* = 7.0, 3 H, Ph$_{coord}$CH(*Me*)); 1.15 (*d*, *J* = 7.0, 3 H, *Me*$_2$CH (cym)); 1.32 (*d*, *J* = 6.5, 3 H, *Me*$_2$CH (cym)); 1.48 (*d*, *J* = 7.5, 3 H, Ph$_{free}$CH(*Me*)); 1.57 (*s*, Me (cym)); 2.87 (*sept.*, *J* = 7.0, Me$_2$C*H* (cym)); 2.96 (*d*, *J* = 5.9, 1 arom. H (cym)); 3.27–3.35 (*m*, Ph$_{coord}$C*H*N); 4.15 (br. *s*, 1 arom. H (cym)); 4.44 (*d*, *J* = 5.9, 1 arom. H (cym)); 4.78 (*quint.*, ^3J(H,H) = 7.2, ^3J(H,P) = 7.2, Ph$_{free}$C*H*N); 5.36 (*d*, *J* = 6.1, 1 arom. H (cym)); 6.41 (*d*, *J* = 6.5, 1 arom. H of (C=C)$_{coord}$); 7.03–8.23 (*m*, 21 arom. H). ^{31}P-NMR: 154.6 (*s*, 93%, complex **3a**); 150.4 (*s*, 7%, complex **5a**). ESI-MS: 774 (100, $[M - HCl]^+$), 676 (20, $[RuCl($**1a**$)]^+$). The elemental analysis of a sample containing **3a** (87%) and **5a** (13%, as determined by integration of the ^{31}P-NMR spectrum) gave: Anal. calc. for $C_{46}H_{44}ClF_6NO_2P_2Ru$ (955.31; 87%)/$C_{72}H_{60}Cl_2F_{12}N_2O_4P_4Ru_2$ (1642.18; 13%): C 57.16, H 4.51, N 1.50; found: C 57.19, H 4.54, N 1.50.

*[*Ru*(*S*)]-Chloro[η^6-1-methyl-4-(1-methylethyl)benzene]{(11b*S$_a$*)*-N-*{(1*R*)-1-[(1,2-η)-naphthalen-1-yl]ethyl}*-N-*[(1*R*)-1-(naphtalen-1-yl)ethyl]dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-4-amine-*κP^4*}-ruthenium(1+) Hexafluorophosphate(1−)* (**3b**). $[\{RuCl_2(\eta^6$-*p*-cymene)$\}_2]$ (65 mg, 0.107 mmol) and **1b**

(150 mg, 0.234 mmol, 1.1 equiv.) were dissolved in CH_2Cl_2 (12 ml). After stirring at r.t. for 1 h, Tl[PF_6] was added, and the resulting soln. was stirred at r.t. for 21 h. Then, TlCl was filtered off, ^{i}PrOH (18 ml) was added, and CH_2Cl_2 was evaporated. The precipitate was filtered off and dried *in vacuo*: **3b** (203 mg, 89%). Red solid. $[\alpha]_D^{20} = +381$ ($c = 0.125$). ^{1}H-NMR ($-20°$): 0.08 (*s*, Me (cym)); 1.18 (*d*, $J = 7.0$, 3 H, Me_2CH(cym)); 1.47 (*d*, $J = 7.0$, 3 H, Me_2CH(cym)); 1.54 (*d*, $J = 7.0$, 3 H, $naph_{coord}$CH(*Me*)); 1.73 (*d*, $J = 6.7$, 3 H, $naph_{free}$CH(*Me*)); 2.62 (*d*, $J = 5.5$, 1 arom. H (cym)); 2.90 (*sept.*, $J = 7.0$, Me_2C*H* (cym)); 3.52–3.58 (*m*, $naph_{coord}$C*H*N); 3.81 (*d*, $J = 5.5$, 1 arom. H (cym)); 4.62 (*d*, $J = 6.1$, 1 arom. H (cym)); 5.05 (*dq*, ^3J(H,P) = 25.3, ^3J(H,H) = 6.7, $naph_{free}$C*H*N); 5.71 (*d*, $J = 6.1$, 1 arom. H (cym)); 6.75–8.20 (*m*, 25 arom. H); 9.24 (*d*, $J = 8.5$, 1 arom. H). ^{31}P-NMR: 168.0 (*s*). ESI-MS: 910 (100, [RuCl(η^6-*p*-cymene)(**1b**)]$^+$), 875 (3, [Ru(η^6-*p*-cymene)(**1b**)]$^+$). Anal. calc. for $C_{54}H_{48}ClF_6NO_2P_2Ru$ (1055.43): C 61.45, H 4.58, N 1.33; found: C 61.31, H 4.66, N 1.35.

*Chloro[η^6-1-methyl-4-(1-methylethyl)benzene]{(11b*S*$_a$)-*N*-{(1*S*)-1-[(1,2-η)-naphthalen-1-yl]ethyl}-*N*-[(1*S*)-1-(naphthalen-1-yl)ethyl]dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepin-4-amine-κP^4}ruthenium(1+) Hexafluorophosphate (1−)* (**3b′**). Complex **2b′** (30 mg, 0.032 mmol) was treated with Tl[PF_6] (12 mg, 0.035 mmol, 1.1 equiv.) in CD_2Cl_2 (1 ml). After stirring at r.t. for 19 h, TlCl was filtered off. The resulting soln. of **3b′** was characterized spectroscopically. ^{1}H-NMR ($-60°$): 0.30 (*s*, Me (cym)); 0.82 (br. *s*, $naph_{coord}$-CH(*Me*)); 1.13 (*d*, $J = 7.0$, 3 H, Me_2CH (cym)); 1.44 (br. *s*, $naph_{free}$CH(*Me*)); 1.45 (br. *s*, 3 H, Me_2CH (cym)); 2.58 (*d*, $J = 5.9$, 1 arom. H (cym)); 2.90 (*sept.*, $J = 7.0$, Me_2C*H* (cym)); 4.05 (*d*, $J = 5.3$, 1 arom. H (cym)); 4.53 (*d*, $J = 6.0$, 1 arom. H (cym)); 4.58 (*dq*, ^3J(H,H) = 6.4, ^3J(H,P) = 20.8, $naph_{coord}$C*H*N); 5.30–5.40 (*m*, $naph_{free}$C*H*N); 5.65 (*d*, $J = 5.7$, 1 arom. H (cym)); 6.51 (*d*, $J = 5.5$, 1 arom. H (naph)); 6.73–8.31 (*m*, 24 arom. H (incl. naph)); 8.72 (*d*, $J = 8.0$, 1 arom. H (naph)). ^{31}P-NMR: 151.2 (*s*).

*Dichloro{(11b*S*$_a$)-*N*-[(1*R*)-1-(η_6-phenyl)ethyl]-*N*-[(1*R*)-1-phenylethyl]dinaphtho[2,1-*d*:1′,2′-*f*][1,3,2]-dioxaphosphepin-4-amine-κP^4}ruthenium* (**4a**). Complex **4a** was prepared by two different procedures: *a*) A soln. of [{Ru(*p*-cymene)Cl_2}$_2$] (61.2 mg, 0.1 mmol) and ligand **1a** (107.9 mg, 0.2 mmol) in CH_2Cl_2 (5 ml) was stored for 30 d. Then the solvent was evaporated up to *ca.* 1 ml, and the complex **4a** was precipitated with Et_2O. The product thus obtained was washed twice with a small amount of Et_2O and pentane and dried in air and then *in vacuo*: **4a** (133 mg, 93%). *b*) A soln. of [{Ru(*p*-cymene)Cl_2}$_2$] (122.4 mg, 0.2 mmol) and the ligand **1a** (215.8 mg, 0.4 mmol) in $CHCl_3$ (30 ml) was stirred under reflux for 7 d. Then, the solvent was evaporated up to *ca.* 2 ml, and the complex **4a** was precipitated with Et_2O. The crude product thus obtained was washed twice with Et_2O and purified by flash chromatography (SiO_2; CH_2Cl_2/MeOH 98:2; R_f 0.15): **4a** (125 mg, 44%). $[\alpha]_D^{20} = +267$ ($c = 0.4$, CH_2Cl_2). ^{1}H-NMR: 1.10 (*d*, $J = 7.3$, Ph_{free}-CH(*Me*)); 1.87 (*d*, $J = 6.5$, Ph_{coord}CH(*Me*)); 4.23 (*d*, $J = 6.0$, 1 H_o (Ph_{coord})); 4.24 (*dq*, ^3J(H,H) = 6.5, ^3J(H,P) = 35.8, Ph_{coord}C*H*N); 4.83 (*quint.*, ^3J(H,H) = 6.8, ^3J(H,P) = 6.8, Ph_{free}C*H*N); 5.52 (*d*, $J = 4.9$, 1 H_o (Ph_{coord})); 5.76–5.80 (*m*, 1 H_m (Ph_{coord})); 6.22–6.26 (*m*, 1 H_m (Ph_{coord})); 6.24–6.29 (*m*, 1 H_p (Ph_{coord})); 7.16–7.57 (*m*, 11 arom. H); 7.70 (*d*, $J = 8.9$, 1 arom. H); 7.97 (*d*, $J = 8.2$, 1 arom. H); 8.02 (*s*, 2 arom. H); 8.05 (*d*, $J = 8.4$, 1 arom. H); 8.18 (*d*, $J = 8.9$, 1 arom. H). ^{13}C-NMR: 19.5 (Ph_{free}CH(*Me*)); 21.7 (Ph_{coord}-CH(*Me*)); 49.8 (^2J(C,P) = 20.2, Ph_{coord}C*H*N); 56.2 (^2J(C,P) = 5.4, Ph_{free}C*H*N), 80.6 (C_o (Ph_{coord})); 81.0 (C_o (Ph_{coord})); 95.0 (^2J(C,P) = 21.2, C_p (Ph_{coord})); 97.8 (C_m (Ph_{coord})); 104.9 (^2J(C,P) = 8.3, C_m (Ph_{coord})); 106.6 (J(C,P) = 1.4, C_{ipso} (Ph_{coord})); 121.2 (Ar); 122.3 (J(C,P) = 1.7, Ar); 123.4 (J(C,P) = 2.9, Ar); 124.5 (J(C,P) = 4.0, Ar); 125.8, 126.0, 126.4, 126.9 (Ar); 127.5 (J(C,P) = 2.1, Ar); 128.4, 128.6, 128.7, 128.8, 129.2, 130.0 (Ar); 131.1 (J(C,P) = 1.4, Ar); 132.0, 132.1, 132.3 (Ar); 133.2 (J(C,P) = 1.7, Ar); 140.5 (^3J(C,P) = 2.3, C_{ipso} (Ph)); 148.5 (^2J(C,P) = 15.2, POC); 149.0 (^2J(C,P) = 7.3, POC). ^{31}P-NMR: 150.9 (*s*). MALDI-MS: 676 (81, [RuCl(**1a**)]$^+$), 641 (25, [Ru(**1a**)]$^+$). Anal. calc. for $C_{36}H_{30}Cl_2NO_2PRu$ (711.59): C 60.76, H 4.25, N 1.97; found: C 60.74, H 4.30, N 2.01.

*Di-μ-chlorobis{(11b*S*$_a$)-*N*-[(1*R*)-1-(η^6-phenyl)ethyl]-*N*-[(1*R*)-1-phenylethyl]dinaphtho[2,1-*d*:1′,2′-*f*]-[1,3,2]dioxaphosphepin-4-amine-κP^4)diruthenium(2+) Bis[hexafluorophosphate (1−)]* (**5a**). A *Young–Schlenk* vessel was charged with **3a** (62 mg, 0.065 mmol) under Ar. The vessel was evacuated (high vacuum, $< 5\times10^{-3}$ mbar), and the solid was heated in an oil bath at 150° for 77 h: **5a** (quant.). Orange solid. $[\alpha]_D^{20} = +189$ ($c = 0.125$). ^{1}H-NMR: 1.09 (*d*, $J = 7.2$, 6 H, Ph_{free}CH(*Me*)); 1.54 (*d*, $J = 6.4$, 6 H, Ph_{coord}-CH(*Me*)); 3.69–3.76 (*m*, 2 arom. H (Ph_{coord})); 4.02 (*d*, $J = 6.2$, 2 arom. H (Ph_{coord})); 4.14 (*dq*, ^3J(H,P) = 42.7, ^3J(H,H) = 6.4, 2 H, Ph_{coord}C*H*N); 4.67 (*t*, $J = 6.1$, 2 arom. H (Ph_{coord})); 4.70 (*quint.*, ^3J(H,H) = 7.0, ^3J(H,P) = 7.0, 2 H, Ph_{free}C*H*N); 4.99 (*d*, $J = 5.9$, 2 arom. H (Ph_{coord})); 5.90 (*t*, $J = 6.4$, 2 arom. H

(Ph_{coord})); 7.03–8.29 (*m*, 34 arom. H). ^{31}P-NMR: 150.4 (*s*). ESI-MS: 1352 (5, $[Ru_2Cl_2(\mathbf{1a})_2]^+$), 1317 (7, $[Ru_2Cl(\mathbf{1a})_2]^+$), 676 (31, $[RuCl(\mathbf{1a})]^+$), 641 (13, $[Ru(\mathbf{1a})]^+$). Anal. calc. for $C_{72}H_{60}Cl_2F_{12}N_2O_4P_4Ru_2$ (1642.18): C 52.66, H 3.68, N 1.71; found: C 52.87, H 3.87, N 1.78.

X-Ray Structure Determination of **2a**[2]). Orange crystals of **2a** were grown from ^{i}PrOH. Crystal data: $C_{46}H_{44}Cl_2NO_2PRu$, monoclinic, $P2_1$, $0.30\times0.06\times0.03$ mm, $a=12.3128(11)$, $b=13.9824(12)$, $c=12.3910(11)$ Å, $\beta=112.163(2)^\circ$, $V=1975.6(3)$ Å^3, $Z=2$, $F(000)=872$, $D_{calc}=1.422$ Mg cm^{-3}, $\mu=0.612$ mm^{-1}, MoK_α (λ 0.71073 Å). Data were collected at r.t. with a *Bruker-AXS-Smart-Apex* platform in the θ range 2.30–20.81°. The structure was solved with SHELXTL by direct methods. Of the 7619 measured reflections ($-11\le h\le 2$, $-13\le k\le 13$, $-12\le l\le 12$), 4121 unique reflections were used in the refinement (full-matrix least squares on F^2 with anisotropic displacement parameters). The absolute structure parameter was refined to $-0.03(5)$. $R_1=0.0557$ (3578 data with $F_o>2\sigma(F_o)$), $wR_2=0.1091$ (all 4121 data). Max. and min. difference peaks were $+0.417$ and -0.598 eÅ^{-3}.

X-Ray Structure Determination of **3b**[2]). Red crystals of **3b** were grown by layering hexane over a CH_2Cl_2 soln. of *rac*-**3b** (obtained by mixing (S_a,*R*,*R*)-**1b** and (R_a,*S*,*S*)-**1b** in a 1:1 ratio). Crystal data: $C_{55.5}H_{48}Cl_4F_6NO_2P_2Ru$, triclinic, $P-1$, $0.76\times0.49\times0.28$ mm, $a=13.3040(8)$, $b=13.7074(8)$, $c=15.1350(9)$ Å, $\alpha=98.822(1)$, $\beta=96.636(1)$, $\gamma=11.659(1)^\circ$, $V=2489.9(3)$ Å^3, $Z=2$, $F(000)=1200$, $D_{calc}=1.574$ g cm^{-3}, $\mu=0.661$ mm^{-1}. Data were collected at r.t. on a *Bruker-AXS-Smart-Apex* platform in the θ range 1.64–28.28°. The structure was solved with SHELXTL by direct methods. Of the 25914 measured reflections ($-17\le h\le 17$, $-18\le k\le 18$, $-20\le l\le 20$), 12262 unique reflections were used in the refinement (full-matrix least squares on F^2 with anisotropic displacement parameters). $R_1=0.0405$ (11071 data with $F_o>4\sigma(F_o)$), $wR_2=0.1112$ (all data). Max. and min. difference peaks were $+1.501$ and -0.865 eÅ^{-3}.

NMR PGSE Diffusion Measurements. Pulsed-gradient spin-echo (PGSE) diffusion measurements were carried out by using the stimulated spin-echo sequence [28]. The diffusion coefficient *D* was derived from *Eqn. 1* where *G* = gradient strength, Δ = delay between the midpoints of the gradients, and δ = gradient length.

$$\ln\left(\frac{I}{I_0}\right) = -(\gamma\delta)^2G^2\left(\Delta-\frac{\delta}{3}\right)D \qquad (1)$$

All diffusion measurements were performed on a *Bruker-Avance* 400-MHz spectrometer equipped with a microprocessor-controlled gradient unit and a multinuclear inverse probe with an actively shielded *Z*-gradient coil. The shape of the gradient pulse was rectangular, its length 1.75 ms, and its strength varied automatically in the course of the experiment. The time between midpoints of the gradients (Δ) was chosen as 167.75 ms. The measurements were carried out without sample spinning and in the absence of external airflow. The sample temp. (300 K for r.t. measurements) was controlled by a digital *BVT-3000* variable-temp. unit. The error coefficients for the *D* values based on our experience is ±0.06. The viscosity used in the *Stokes–Einstein* relation is that of pure CH_2Cl_2, 0.41 [28h]. The ^{1}H,^{19}F-HOESY-NMR measurements were carried out with a doubly tuned *TXI* probe. A mixing time of 800 ms was used, and 32 scans for each of the 1024 t_1 increments were recorded.

Standard Catalytic Run. Complex **2a** (24 μmol) and $(Et_3O)[PF_6]$ or $Tl[PF_6]$ (26 μmol, 1.1 equiv.) were dissolved in CH_2Cl_2 (1 ml) and stirred at r.t. for 17 h. TlCl was filtered off with a syringe filter. With ligand **1b**, the catalyst was prepared *in situ* from $[\{RuCl_2(\eta^6\text{-}p\text{-cymene})\}_2]$ (12 μmol), **1b** (48 μmol), and the halide scavenger (26 μmol, 1.1 equiv.). The internal standard and the olefin (0.48 mmol) were added to the soln. of the catalyst (24 μmol, 5 mol-%). Ethyl diazoacetate (0.48 mmol, 1 equiv. *vs.* olefin) in CH_2Cl_2 (1 ml) was added over 6 h by a syringe pump. The soln., which was protected from light, was stirred for additional 14 h at r.t. and then analyzed by GC. The total reaction time was 20 h at r.t. Each experiment was at

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[2]) CCDC-291266 and CCDC-29166 contain the supplementary crystallographic data for **2a** and **3b**, resp. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif from the *Cambridge Crystallographic Data Centre.*

least reproduced once, and deviations between two to five experiments were usually less than 2%. A control reaction without the catalyst indicated that there was no formation of the cyclopropane derivatives under the conditions used.

Styrene. Olefin conversion and yields of *cis* and *trans* products were determined by GC analysis with decane as internal standard. Samples for GC analyses were prepared by filtration over a plug of alumina to remove the catalyst. Achiral GC analysis: *Optima* column (25 m), He carrier (100 kPa); temp. program: 50° isotherm for 5 min, then to 200° at 5° min^{-1}. t_R [min]: styrene 8.5, decane (internal standard) 12.8, ethyl *cis*-2-phenylcyclopropanecarboxylate 26.5, and ethyl *trans*-2-phenylcyclopropanecarboxylate 27.9. Chiral GC analysis: the enantiomeric excesses (ee) of the *cis* and *trans* products were determined with a *Supelco-Beta-Dex-120* column, 1.4 ml He min^{-1}; temp. program: 120° isotherm; t_R [min]: *cis*-(1*S*,2*R*) 52.8, *cis*-(1*R*,2*S*) 55.5, *trans*-(1*R*,2*R*) 62.7, and *trans*-(1*S*,2*S*) 64.6. The abs. configuration was determined for *cis*- and *trans*-ethyl 2-phenylcyclopropanecarboxylate by comparison of the sign of the optical rotation with literature values [52].

α-Methylstyrene. As for styrene, with dodecane as internal standard. Achiral GC analysis: as for styrene; t_R [min]: α-methylstyrene 12.0, dodecane 19.6, ethyl *cis*-2-methyl-2-phenylcyclopropanecarboxylate 26.3, ethyl *trans*-2-methyl-2-phenylcyclopropanecarboxylate 27.6. Chiral GC analysis: as for styrene; t_R [min]: *cis*-(1*R*,2*S*) 40.6, *cis*-(1*S*,2*R*) 42.8, *trans*-(1*S*,2*S*) 51.5, and *trans*-(1*R*,2*R*) 52.7. The abs. configuration was determined for ethyl *cis*- and *trans*-2-methyl-2-phenylcyclopropanecarboxylate by comparison of the sign of the optical rotation with literature values [53].

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