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Chiral monodentate phosphoramidite ligands control the absolute configuration at pseudotetrahedral ruthenium: asymmetric catalytic cyclopropanation of olefins

Dominik Huber and Antonio Mezzetti*

Department of Chemistry and Applied Biosciences, Swiss Federal Institute of Technology, ETH Hönggerberg, CH-8093 Zürich, Switzerland

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Abstract—Piano-stool ruthenium complexes of the type $[RuCl_2(p\text{-cymene})(L)]$ (L = chiral phosphoramidite ligand) catalyse the asymmetric cyclopropanation of styrene and α-methylstyrene with ethyl diazoacetate after activation with $TlPF_6$ or $(Et_3O)PF_6$ as halide scavengers. With α-methylstyrene, good enantioselectivities were observed (up to 86% and 87% ee for the *cis*- and *trans*-cyclopropane derivative, respectively). However, total yields and diastereoselectivities were generally low.

1. Introduction

Pseudotetrahedral complexes containing stereogenic metal atoms have been the object of extensive stereochemical investigations over the last 30 years starting with Brunner's pioneering investigations of $[Mn(Cp)(CO)(PPh_3)(NO)]$.[1] Chiral bidentate ligands have been extensively used to control the stereochemistry at the metal in complexes of the type [RuCl(Cp)(P–P*)] (P–P* = chiral diphosphine)[2] or $[RuX(\eta^6\text{-arene})(L–L)]^+$.[3] As substitutions at 18-electron complexes are generally assumed to occur dissociatively, the selectivity observed implies that the chiral diphosphine controls the geometry of the putative 16-electron intermediate and the direction of attack of the incoming ligand.

Despite their potential, the application of chiral half-sandwich ruthenium complexes in asymmetric catalysis has been mainly restricted to hydrogenation and Diels-Alder reactions.[3c] For the latter, Kündig has developed complexes of the type $[Ru(Cp)(OCMe_2)(P–P)]^+$ containing electron-poor chiral diphosphines (P–P).[4] Davies, Oro, and Faller have independently studied catalysts of the type $[RuCl(p\text{-cymene})(L–L)]^+$ (L–L = P–O-, P–N-, N–N- and P,S-hybrid ligands).[5] Noyori et al. and Ito et al. used half-sandwich ruthenium complexes containing bidentate N-donors as catalysts for ketone hydrogenation.[6] The common feature of these systems is the use of a *bidentate* chiral ligand. Our present approach investigates the possibility of controlling the absolute configuration at the metal by means of a *monodentate* chiral ligand. To the best of our knowledge, monodentate stereogenic ligands have not been used yet—unless bound to the arene or cyclopentadienyl ligand by a tether.[7,8] The advantage of our approach is that it allows us to vary freely two ligands of the pseudotetrahedral coordination sphere. It also opens up new potential applications for recently developed, bulky chiral monodentate ligands.[9]

2. Results and discussion

As a model reaction, we chose the asymmetric cyclopropanation of olefins, which requires the formation of a diastereomerically enriched carbene intermediate, for example, $[RuCl(=CHR)(p\text{-cymene})(P^*)]^+$ (P^* = chiral phosphoramidite). Brookhart has prepared the diastereomerically pure iron analogues of the type $[Fe(Cp)(=C(H)CH_3)(CO)(P^*)]^+$ **5** containing a chiral monodentate phosphine.[10] Diastereo- and enantioselective *stoichiometric* carbene transfer reactions to olefins have recently been reported by Hossain and co-workers,[11] whereas *catalytic* cyclopropanation of olefins catalysed by iron and ruthenium half-sandwich complexes is restricted to achiral systems, such as [RuCl

* Corresponding author. Tel.: +41-44-632-61-21; fax: +41-44-632-13-10; e-mail: mezzetti@inorg.chem.ethz.ch

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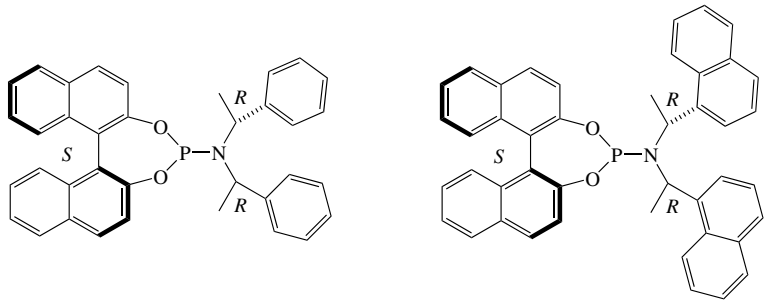
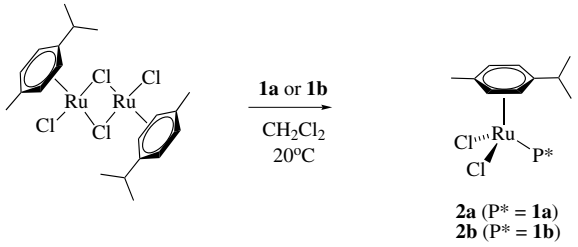


1a **1b**

Chart 1.

$(CO)_2(C_5Me_5)]$ and $[RuCl_2(\eta^3\text{-allyl})(C_5Me_5)]$,[12] $[RuCl_2(\eta^6\text{-}p\text{-cymene})(P)]$ (P = monodentate phosphine with a pendant aryl group),[13] $[Ru(Cp)(MeCN)_3]^+$[14] and $[RuCl(Cp)(PPh_3)_2]$.[15] The latter catalyst, similar to $[Fe(Cp)(CO)_2(THF)]^+$,[16] cyclopropanates styrene with moderate to good *cis*-selectivity. As *cis*-selective catalysts for asymmetric cyclopropanation are rare,[17–20] we decided to scrutinise the potential of half-sandwich complexes of ruthenium of the type $[RuCl_2(p\text{-cymene})(P^*)]$ (P^* = chiral monodentate P-containing ligand). Thus, we tested *O*,*O*′-(*S*)-(1,1′-dinaphthyl-2,2′-diyl)-*N*,*N*′-bis[(*R*)-1-phenylethyl]phosphoramidite **1a** and *O*,*O*′-(*S*)-(1,1′-dinaphthyl-2,2′-diyl-*N*,*N*′-bis[(*R*)-1-naphthylethyl]phosphoramidite **1b** (Chart 1).[21]



Scheme 1.

Ligand **1a** reacts readily with $[RuCl_2(p\text{-cymene})]_2$[22] (1.1 equiv, CH_2Cl_2, room temperature, 1 h) to give $[RuCl_2(p\text{-cymene})(\mathbf{1a})]$ **2a** (93% yield) (Scheme 1).[23] X-ray structure determination of **2a**[24] showed that the bulky phosphoramidite ligand effectively shields the ruthenium atom (Figs. 1 and 2). Ruthenium arene complexes containing chiral, monodentate P-donor ligands are rare[25] and, to the best of our knowledge, have never been used for asymmetric catalytic reactions.

Complex **2a** was activated by chloride abstraction with the aim of obtaining the coordinatively unsaturated 16-electron species $[RuCl(p\text{-cymene})(\mathbf{1a})]^+$. Both $(Et_3O)PF_6$ and $TlPF_6$ (1.1 equiv) react with **2a** in CH_2Cl_2 within 0.5 and 2 h, respectively, to give the same orange complex **3a** featuring a singlet at δ 153.0 in the ^{31}P NMR spectrum. Preliminary pulse gradient spin-echo (PGSE) measurements[26] suggest that **3a** is a monomeric complex based on the $[RuCl(p\text{-cymene})(\mathbf{1a})]^+$ fragment. Its structure is currently under investigation.

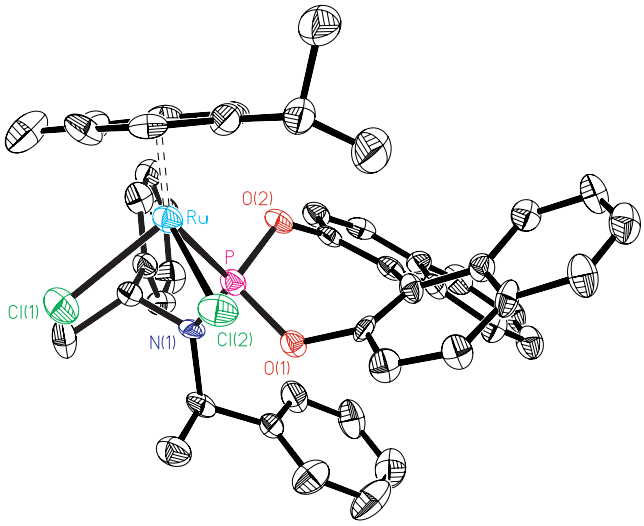


Figure 1. X-ray structure of **2a**. Distances (Å) and angles (deg): Ru–C(1), 2.201(12); Ru–C(2), 2.218(9); Ru–C(3), 2.213(11); Ru–C(4), 2.197(11); Ru–C(5), 2.170(10); Ru–C(6), 2.206(10); Ru–Cl(1), 2.405(3); Ru–Cl(2), 2.387(3); Ru–P, 2.317(3); P–Ru–Cl(1), 91.84(10); P–Ru–Cl(2), 89.06(9); Cl(2)–Ru–Cl(1), 85.50(10).

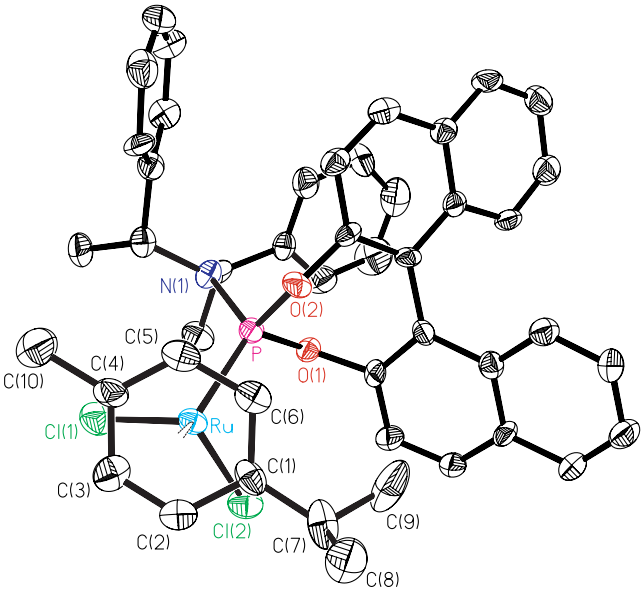
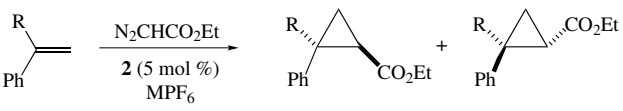


Figure 2. Top view of complex **2a**.

Table 1. Catalytic cyclopropanation[a]



R = H, Me *cis* *trans*

Run	Ligand	R	MPF_6 M^+	Conv. (%)	Yield (%)	*cis*/*trans*	Ee (%)[b]	
							cis	*trans*
1	**1a**	H	Et_3O^+	37	25	42:58	8 (1*R*,2*S*)	3 (1*R*,2*R*)
2	**1a**	H	Tl^+	30	15	40:60	2 (1*R*,2*S*)	5 (1*R*,2*R*)
3	**1a**	Me	Et_3O^+	31	31	60:40	*rac*	*rac*
4	**1a**	Me	Tl^+	31	29	61:39	8	*rac*
5	**1b**	H	Et_3O^+	6	5	45:55	77 (1*S*,2*R*)	68 (1*R*,2*R*)
6	**1b**	H	Tl^+	9	5	46:54	74 (1*S*,2*R*)	59 (1*R*,2*R*)
7	**1b**	Me	Et_3O^+	19	19	57:43	−86	87
8	**1b**	Me	Tl^+	19	19	57:43	−83	84
9	**1b**	Me	Et_3O^{+c}	13	9	60:40	−28	24

[a] Catalyst preparation: **2a** (24 μmol) and $TlPF_6$ or $(Et_3O)PF_6$ (26 μmol, 1.1 equiv) were dissolved in CH_2Cl_2 (1 mL) and stirred at room temperature for 17 h. TlCl was filtered off with a syringe filter. With ligand **1b**, the catalyst was prepared in situ from $[RuCl_2(p\text{-cymene})]_2$ (12 μmol), **1b** (48 μmol) and the halide scavenger (26 μmol). Standard catalytic run: An internal standard and the olefin (0.48 mmol) were added to the solution 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 total reaction time was 20 h at room temperature in the dark. Results are the average of at least two experiments.

[b] The absolute configuration was determined for ethyl *cis*- and *trans*-phenylcyclopropane-1-carboxylate (as previously described)[20a,28] but not for ethyl *cis*- and *trans*-3-methyl-2-phenylcyclopropane-1-carboxylate.[20b,29]

[c] Two equivalents.

The **2a**/MPF_6 system (M = Et_3O or Tl) catalysed the cyclopropanation of styrene by decomposition of ethyl diazoacetate with low enantio- and diastereoselectivity (8% ee and 42:58 *cis*/*trans* ratio) (Table 1, run 1). Similar results were obtained with α-methylstyrene as the substrate (8% ee and 61:39 *cis*/*trans* ratio) (run 4). In the case of styrene, the formation of the *trans*-isomer was slightly favoured, whereas with α-methylstyrene the *cis*-isomer was predominant. This could be explained by the sterically more demanding methyl group. The yields were from low to moderate (15–31%), but increased when going from styrene to α-methylstyrene.

The enantioselectivity could be dramatically improved upon increasing the steric bulk of the phosphoramidite. Ligand **1b** reacts with $[RuCl_2(p\text{-cymene})]_2$ (1.1 equiv, CH_2Cl_2, room temperature, 1 h) to give $[RuCl_2(p\text{-cymene})(\mathbf{1b})]$ **2b** in 49% yield. We have not yet been able to isolate pure **2b**, which we attribute to the facile dissociation of the bulky phosphoramidite. Indeed, the ^{31}P spectrum of isolated **2b** exhibited a singlet at δ 145.0 for **2b** along with the signal of the free ligand **1b** (δ 148.3, 10%).[27] Either $TlPF_6$ or $(Et_3O)PF_6$ (1.1 equiv) abstract chloride from **2b** to give a new complex **3b** that shows a broadened singlet at δ 166.5 in the ^{31}P NMR spectrum and is presently being characterised.

Preliminary cyclopropanation tests with the catalysts prepared by reacting **2b** (either prepared in situ or isolated) with $TlPF_6$ or $(Et_3O)PF_6$ (1.1 equiv), indicated that ligand **1b** gave higher enantioselectivities than **1a**. The results were not reproducible though, probably due to the low stability of the catalyst. To suppress ligand dissociation, $[RuCl_2(p\text{-cymene})]$ was treated with 2 equiv of **1b** (vs Ru) and the halide scavenger. The ^{31}P NMR spectrum of this reaction solution displayed the signal of **3b** and that of the free ligand **1b**, indicating that only one ligand molecule bound to ruthenium. With this procedure, the performance of the catalytic system is stable at high enantioselectivity and is perfectly reproducible. Thus, styrene can be cyclopropanated with moderate enantioselectivity for both diastereoisomers (*cis*: 77%; *trans*: 68% ee) with $(Et_3O)PF_6$ as the chloride scavenger (Table 1, run 5). With α-methylstyrene, both diastereoisomers were formed with good enantioselectivity (*cis*: 86%; *trans*: 87% ee) with $(Et_3O)PF_6$ as the chloride scavenger (Table 1, run 7). Comparable results were obtained with $TlPF_6$ as chloride scavenger (runs 6 and 8). Although yields were lower than with **1a**, a significant, similar increase was observed upon increasing the substitution (styrene, 5%; α-methylstyrene, 19% yield), which points to the predominance of electronic factors over steric ones. The activation of **2b** with 2 equiv of $(Et_3O)PF_6$, which probably caused the abstraction of both chlorides, decreased both the yield and enantioselectivity (run 9).

Overall, some general trends can be recognised. Increasing the steric bulk of either the monodentate chiral ligand or of the substrate is beneficial to the enantioselectivity of the reaction, but not to the activity of the catalyst. The results with the naphthyl-substituted ligand **1b** and α-methylstyrene indicate that the system is promising for 1,1-disubstituted olefins, which are more difficult to cyclopropanate than styrene. A general drawback of these catalysts is the low cyclopropane yield (up to 37% for both diastereoisomers), which can be partially explained by the competitive homocoupling of the carbene. Indeed, after 20 h of reaction time, the

^{1}H NMR spectrum of the reaction solution (run 9) showed that, besides the cyclopropanation products (9%), maleate and fumarate also formed (ca. 46% and 8% yield, respectively). However, as unreacted ethyl diazoacetate is still present in the reaction solution (ca. 27% of starting amount), the homocoupling alone does not account for the low yield (at least in this case). Preliminary monitoring of the reaction course by gas chromatography suggests that the catalyst stays active during the whole reaction time. Thus, the most probable explanation of the low cyclopropane yield is the intrinsic low activity of the catalyst. Finally, the system did not show the expected *cis*-selectivity so far. Present efforts are being directed to improve the activity and stereoselectivity of the catalyst.

Acknowledgements

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23. $RuCl_2$(*p*-cymene)]$_2$ (387 mg, 0.632 mmol) and **1a** (750 mg, 1.39 mmol, 1.1 equiv) were dissolved in dry CH_2Cl_2 (20 mL) under an Ar atmosphere, with the resulting solution stirred at room temperature for 1 h. 2-Propanol (15 mL) was added and CH_2Cl_2 evaporated. The precipitate was filtered off and dried in vacuum to give **2a** as an orange solid. Yield: 992 mg (93%). $[\alpha]_D^{23} = +65$ (*c* 0.125, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.19 (d, $J = 6.9$ Hz, 3H, cymene-CH(CH_3)$_2$); 1.30 (d, $J = 6.9$ Hz, 3H, cymene-CH(CH_3)$_2$); 1.71 (d, $J = 6.9$ Hz, 6H, CH(Ph)(CH_3); 2.11 (s, 3H, cymene-CH_3); 2.85 (hept, $J = 6.9$ Hz, 1H, cymene-C*H*(CH_3)$_2$); 4.38 (d, $J = 4.8$ Hz, 1H, cymene-H_{arom}); 4.99 (d, $J = 6.0$ Hz, 1H, cymene-H_{arom}); 5.10–5.16 (m, 2H, NC*H*); 5.19 (d, $J = 6.0$ Hz, 1H, cymene-H_{arom}); 5.24 (d, $J = 6.0$ Hz, 1H, cymene-H_{arom}); 6.66–8.02 (m, 22H, H_{arom}). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 141.0 (s). MS (HiRes MALDI): *m*/*z* 676 ([M−(*p*-cymene)−Cl]$^+$, 100). Anal. Calcd for $C_{46}H_{44}Cl_2NO_2PRu$: C, 65.32; H, 5.24; N, 1.67. Found: C, 65.44; H, 5.40; N, 1.67.
24. Orange crystals of **2a** were grown from 2-propanol. Crystal data: monoclinic, $P2_1$, $0.30\times0.06\times0.03$ mm, $a = 12.3128(11)$, $b = 13.9824(12)$, $c = 12.3910(11)$ Å, $\beta = 112.163(2)°$, $V = 1975.6(3)$ Å^3, $Z = 2$, $F(000) = 872$, $D_{calcd} = 1.422$ Mg cm^{-3}, $\mu = 0.612$ mm^{-1}. Data were collected at room temperature on a Bruker AXS SMART APEX platform in the θ range 2.30–20.81°. The structure was solved with SHELXTL using direct methods. Of the 7619 measured ($-11 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 13$, $-12 \leqslant l \leqslant 12$), 4121 unique reflections were used in the refinement (full-matrix least squares on F^2 with anisotropic displacement

parameters). The absolute structure parameter 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 e Å^{-3}. Crystallographic data (excluding structure factors) for **2a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 234351. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

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27. Synthesis as for **2a** from $[RuCl_2(p\text{-cymene})]_2$ (196 mg, 0.320 mmol) and **1b** (451 mg, 0.705 mmol, 1.1 equiv). Yield: orange solid, 260 mg (49%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.17 (d, $J = 6.9$ Hz, 3H, cymene-CH(CH_3)$_2$); 1.21 (d, $J = 6.6$ Hz, 3H, cymene-CH(CH_3)$_2$); 2.00 (s, 3H, cymene-CH_3); 2.05 (d, $J = 5.7$ Hz, 6H, CH(Ph)(CH_3); 2.88 (hept, $J = 6.9$ Hz, 1H, cymene-CH(CH$_3$)$_2$); 4.89–5.93 (m, 4H, cymene-H_{arom} and NCH); 5.07 (d, $J = 8.7$ Hz, 1H, cymene-H_{arom} and NCH); 5.35 (d, $J = 6.0$ Hz, 1H, cymene-H_{arom} and NCH); 6.93–8.20 (m, 26H, H_{arom}). ^{31}P NMR (121.5 MHz, $CDCl_3$): δ 145.0 (s, 90%, complex **2b**); 148.3 (s, 10%, free ligand **1b**).
28. Achiral GC analysis: Optima, 25 m, He carrier (100 kPa). Temperature programme: 50 °C isotherm for 5 min, then to 200 °C at 5 °C min^{-1}. t_R (min): styrene, 8.5; decane (internal standard), 12.8; ethyl-*cis*-2-phenyl-cyclopropane carboxylate, 26.5; ethyl-*trans*-2-phenyl-cyclopropane carboxylate, 27.9. Chiral GC analysis: Supelco Beta Dex 120, 1.4 mL He min^{-1}; temperature programme: 120 °C isotherm. t_R (min): *cis*-(1*R*,2*S*), 52.8; *cis*-(1*S*,2*R*), 55.5; *trans*-(1*R*,2*R*), 62.7; *trans*-(1*S*,2*S*), 64.6.
29. Achiral GC analysis: as for styrene. t_R (min): α-methyl-styrene, 12.0; dodecane (internal standard) 19.6; ethyl (*cis*)-2-methyl-phenylcyclopropane-1-carboxylate, 26.3; ethyl (*trans*)-2-methyl-phenylcyclopropane-1-carboxylate, 27.6. Chiral GC analysis: Supelco Beta Dex 120, 1.4 mL He min^{-1}; temperature programme: 120 °C isotherm. t_R (min) (*cis*)-**I**, 39.3; (*cis*)-**II**, 41.3; (*trans*)-**I**, 49.7; (*trans*)-**II**, 50.9. Positive ee values mean that **II** is the major isomer.