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# New chiral phosphoramidite allenylidene complexes of ruthenium obtained with chirality transfer

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ABSTRACT

The synthesis and structural characterization of the first ruthenium phosphoramidite allenylidene complexes that are chiral at the metal are described. The precursor complex [RuCl(Ind)(PPh$_3$)$_2$] (Ind = indenyl anion) was reacted with 1 equiv of different chiral phosphoramidite ligands L to give complexes of the general formula [RuCl(Ind)(PPh$_3$)L]. These complexes are stereogenic at the metal and at the ligand L. One of these complexes was obtained in diastereomeric purity, and was subsequently converted to allenylidene complexes of the general formula [Ru=C=C=CR′R(Ind)(PPh$_3$)L]$^+$PF$_6$ (R = R′ = Ph; R = Ph, R′ = Me) in diastereomeric purity. As shown by X-ray, the chiral information is completely transferred from the precursor complex to the allenylidenes, which is of importance for potential catalytic applications.

Allenylidene complexes are carbon-rich metal cumulenylidenes of the general formula [M]=C=C=CRR′ (**1**, Fig. 1).[1] Albeit known since the 1970s,[2] the investigation of allenylidenes was advanced when Selegue reported in 1982 that they were easily accessible from an appropriate precursor metal complex and propargylic alcohols (**2**, Fig. 1).[3] They have recently attracted considerable interest both as catalysts for the metathesis reaction[4] and as potential intermediates in a variety of transition metal-catalyzed transformations of propargylic alcohols,[5] such as cyclizations[6] or nucleophilic substitution reactions of the propargylic OH group.[7] Chiral allenylidene complexes are much less explored than their achiral counterparts,[8] and only a few examples of allenylidene complexes exist that are chiral at the metal.[9]

We are currently investigating chiral ruthenium phosphoramidite complexes for activation and catalytic transformations of propargylic alcohols.[10] Phosphoramidites (**3**, representative examples shown in Fig. 1) are a versatile monodentate ligand class,[11] which have recently been employed in a variety of transition metal-catalyzed reactions.[12] To the best of our knowledge, allenylidene complexes containing phosphoramidite ligands have not been reported thus far. We are interested in such structures, as the properties of phosphoramidite allenylidene complexes can be sterically and electronically tuned via the ligand, which could eventually lead to catalytic applications.

Herein, we describe the synthesis and characterization of the first ruthenium indenyl phosphoramidite complexes that are chiral at the metal. One of these phosphoramidite complexes was converted successfully to the first phosphoramidite allenylidene complexes, which are also chiral at the metal.

For this initial study, chiral ruthenium phosphoramidite complexes were targeted. We have previously synthesized diastereomeric ruthenium complexes of the general formula [RuCl(Cp)(PPh$_3$)(**3a**,**b**)] by thermal ligand exchange from [RuCl(Cp)(PPh$_3$)$_2$] employing chiral phosphoramidites **3a**,**b**.[10a] These complexes are stereogenic both at the metal and at the ligand and they could be converted to allenylidenes. Due to side product formation, the purification of the allenylidene complexes remains a challenge. Thus, we were seeking alternative architectures for phosphoramidite allenylidene synthesis. We were also interested in determining whether simpler phosphoramidites that are not derived from BINOL could be employed in the synthesis of corresponding chiral ruthenium complexes.

Accordingly, phosphoramidite **4** derived from catechol and (*R*)-2-methylpyrrolidine was first synthesized in 78% yield following

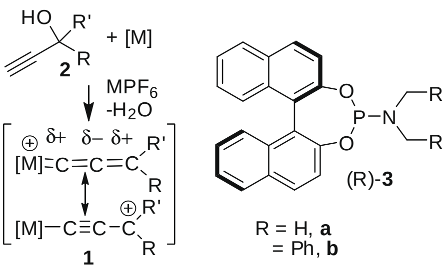

**Figure 1.** Allenylidene complexes and phosphoramidite ligands.

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procedures successfully employed for other phosphoramidites by us[10b] and others[11a] (Scheme 1).[13]

By analogy to the formation of [RuCl(Cp)(PPh$_3$)(**3a**,**b**)] described above,[10a] the precursor complex [RuCl(Ind)(PPh$_3$)$_2$] (**5**, Ind = indenyl anion)[14] was treated with 1 equiv of the phosphoramidite ligands **3a**,**b** and **4** (Scheme 2). The corresponding substitution products **6**, **7**, and **8** were isolated as orange powders in 67–87% yields.[13] The coordination of the phosphoramidite ligands to the metal complexes was best observed by the presence of a downfield shift of the $^{31}$P NMR signals. Coupling of the chemically non-equivalent phosphorus atoms of the phosphoramidite and PPh$_3$ ligands was observed ($J_{PP}$ = 58–77 Hz), demonstrating that both ligands are coordinated to the metal center. The FAB mass spectra also are in accordance with the proposed structures.

The complexes **6**–**8** are stereogenic both at the metal and at the ligand. Enantiopure ligands were employed in the synthesis of the complexes **6** and **7**, which were obtained as a mixture of diastereomers that differ in the absolute configuration at the metal. The diastereomeric ratios were determined by $^1$H and $^{31}$P NMR to be 1:1 for **6** and 2:1 for **7**, and all efforts to isolate one of the complexes as diastereopure material have failed to date. However, complex **8** was formed in diastereomeric purity, and no spectroscopic signals for a second diastereomer were observed in the crude product or after purification.

In order to unequivocally establish the structures of the new phosphoramidite complexes, an X-ray structure of complex **8** was determined (Fig. 2 and Supplementary data).[15] Bond lengths and angles are as expected, and match those of the structurally related complexes [RuCl(Cp)(PPh$_3$)(**3a**,**b**)].[10a] The aryl ring of the indenyl ligand points away from the bulky phosphoramidite ligand **3b**, possibly due to steric constraints.

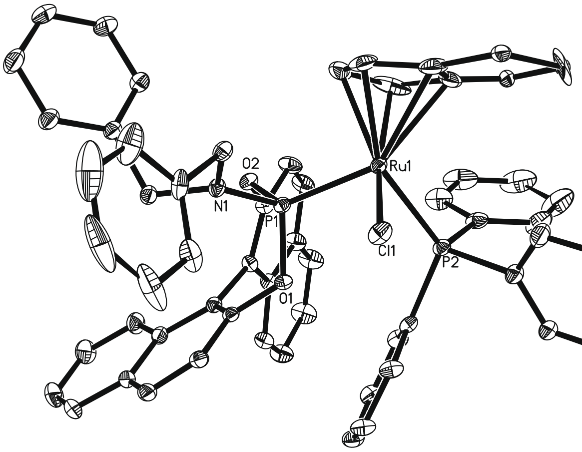
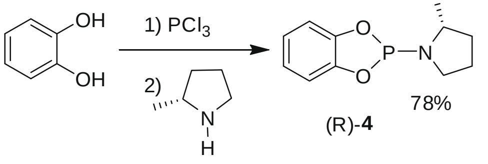
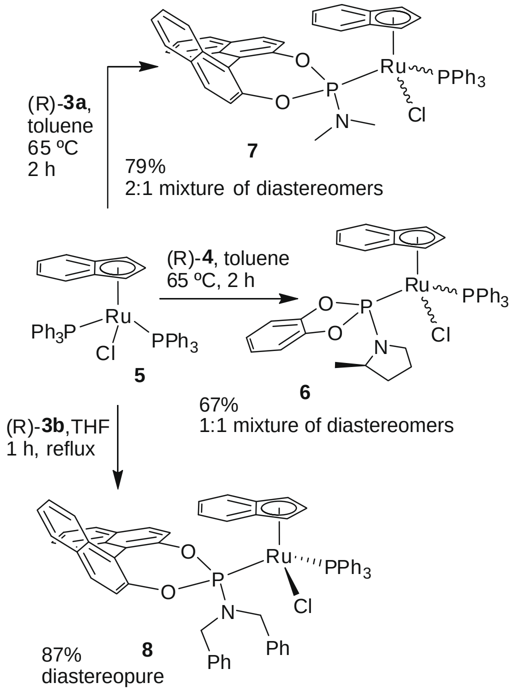


**Figure 2.** Molecular structure of **8** (depicted with 30% probability ellipsoids; H atoms and solvents are omitted for clarity). Key bond lengths (Å) and bond angles (°): Ru1–P1, 2.1961(7); Ru1–P2, 2.3504(8); Ru1–Cl1, 2.4439(7); Cl1–Ru1–P1, 89.28(3); Cl1–Ru1–P2, 86.99(3); P1–Ru1–P2, 98.87(3); O1–P1–O2, 99.58(10); O1–P1–N1, 108.61(12); O2–P1–N1, 95.13(12).

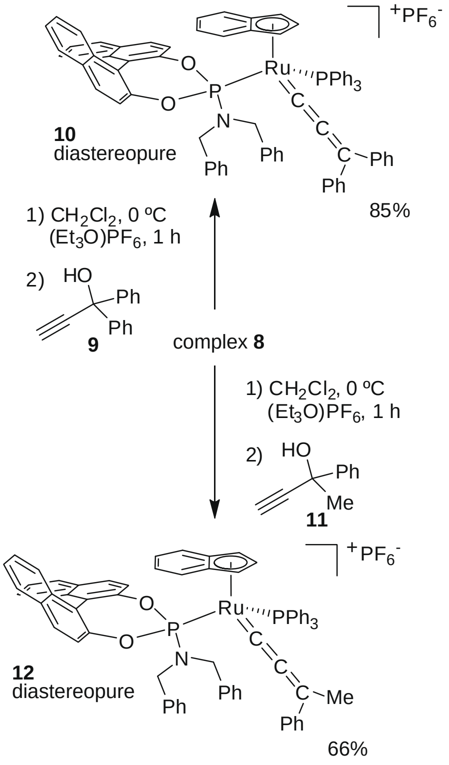
Next, we investigated the conversion of the complexes **6**–**8** to the corresponding allenylidene complexes, applying Selegue's protocol with slight modifications (Scheme 3). The formation of allenylidenes from complexes **6** and **7** was accompanied by side products, and purification of the crude material resulted in ongoing decomposition. However, upon reaction with 1,1-diphenyl-2-propyn-1-ol (**9**), complex **8** was successfully converted to the allenylidene complex [**10**]$^+$ as its PF$_6$ salt, which will subsequently be referred to without charge and counterion (Scheme 3).



**Scheme 1.** Phosphoramidite synthesis.



**Scheme 2.** Ruthenium phosphoramidite complex synthesis.



**Scheme 3.** Allenylidene complex syntheses.

Allenylidene **10** was isolated in diastereomeric purity by recrystallization as an intensely colored purple solid in 85% yield.[13] The chloride scavenger $(Et_3O)PF_6$ was employed to activate the precursor complex **8**, and the reaction proceeds within 1 h at 0 °C.

The $^{31}P$ NMR signals for complex **10** were slightly shifted compared to those for the starting material **8**. As in the $^1H$ and $^{13}C$ NMR spectra, only one set of signals was observed, confirming that complex **10** was isolated as a single diastereomer. No evidence of the formation of a second diastereomer was observed in the NMR spectra of the crude reaction mixture. Thus, the chiral information in **8** is completely transferred to complex **10**. The allenylidene chain in **10** exhibited resonances in the $^{13}C$ NMR spectrum at 293.8, 199.2, and 160.3 ppm, which are typical for structurally related allenylidene complexes of ruthenium.[1b] Also, a strong band at 1935 $cm^{-1}$ was observed in the IR spectrum, which is also characteristic of allenylidene complexes.[1]

In order to establish the structure and especially the chirality transfer from complex **8** to **10**, the X-ray structure of complex **10** was determined (Fig. 3 and Supplementary data).[15] Indeed, both complexes **8** and **10** have the same configuration about the metal center, and thus the chloro ligand in **8** is replaced by the allenylidene chain in **10** without overall isomerization. The bond angles about the ruthenium range from 85.82(7) to 100.13(2) Å, and the structure is thus best described as a slightly distorted octahedron. The C=C bond distances of the allenylidene chain in **10** are not equal. The internal C=C double bond is significantly shorter (C10–C11, 1.250(4) Å) than the terminal double bond (C11–C12, 1.357(4) Å). This might be a consequence of a second resonance contributor (see **1** in Fig. 1), which also explains why the γ carbon is electrophilic. As has been pointed out previously, the carbons α and γ to the metal center are electrophilic (**1** in Fig. 1).[1b] Nucleophilic attack of the allenylidene chain in related complexes has been described previously to take place preferentially at the carbon γ to the metal.[1b,d,9b]

Finally, we were interested in determining if the chirality transfer described above also works with chiral propargylic alcohols. An allenylidene complex formed from precursor **8** and a chiral propargylic alcohol has three stereogenic centers: one at the metal, one at the ligand, and one at the allenylidene chain. Accordingly, racemic propargylic alcohol **11** was reacted with complex **8** under conditions identical to those for the formation of **10** (Scheme 3). The new allenylidene complex **12** was obtained in 66% yield as a purple powder, and was analyzed as described above for complex **10**. The allenylidene chain in **12** exhibited resonances in the $^{13}C$ NMR spectrum at 297.5, 195.5, and 162.8 ppm and a strong band at 1942 $cm^{-1}$ in the IR spectrum. Most significantly, again only one diastereomer was formed, as shown by NMR ($^1H$, $^{13}C$, $^{31}P$). The $^{31}P$ NMR spectrum exhibited only two signals, as expected for a single diastereomer. Similarly, in the $^1H$ and $^{13}C$ NMR, only one signal for the methyl group on the allenylidene chain was observed. In order to establish the connectivity and absolute configuration about the ruthenium, the X-ray structure of complex **12** was also determined (Fig. 4 and Supplementary data).[15] It closely resembles that of complex **10**. The carbon–carbon bond lengths of the allenylidene chain are not equal (1.250(3) and 1.348(3) Å, respectively), as observed for complex **10**. Again, the stereochemistry about the ruthenium center is identical to that in the precursor complex **8**. Significantly, the formation of vinylvinylidenes was not observed for allenylidene complex **12**. It has previously been reported in the literature that aliphatic propargylic alcohols tend to form vinylvinylidenes, which can be in equilibrium with their respective allenylidenes.[16]

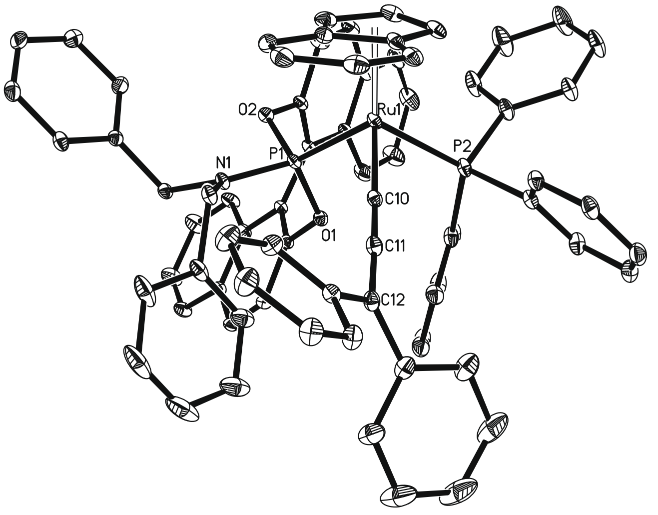


**Figure 3.** Molecular structure of **10** (depicted with 30% probability ellipsoids; H atoms, counterion, and solvents are omitted for clarity). Key bond lengths (Å) and bond angles (°): Ru1–P1, 2.2730(6); Ru1–P2, 2.3131(7); Ru1–C10, 1.887(2); C10–C11, 1.250(4); C11–C12, 1.357(4); C10–Ru1–P1, 92.73(7); C10–Ru1–P2, 85.82(7); P1–Ru1–P2, 100.13(2); O1–P1–O2, 100.12(9); O1–P1–N1, 110.33(11); O2–P1–N1, 95.56(10).

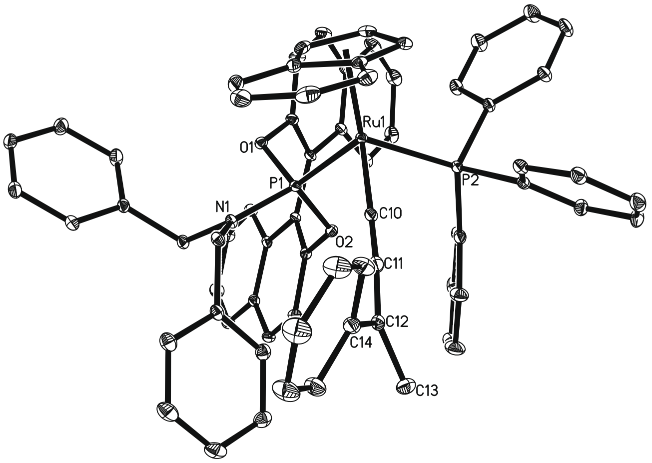


**Figure 4.** Molecular structure of **12** (depicted with 30% probability ellipsoids; H atoms, counterion, and solvents are omitted for clarity). Key bond lengths (Å) and bond angles (°): Ru1–P1, 2.2729(5); Ru1–P2, 2.3037(5); Ru1–C10, 1.8937(19); C10–C11, 1.250(3); C11–C12, 1.348(3); C10–Ru1–P1, 92.39(6); C10–Ru1–P2, 84.81(6); P1–Ru1–P2, 100.416(17); O1–P1–O2, 99.76(7); O1–P1–N1, 109.91(8); O2–P1–N1, 96.36(8).

In conclusion, we have synthesized and characterized the first phosphoramidite ruthenium indenyl complexes which are chiral at the metal. One of these complexes was obtained diastereomerically pure. It activates propargylic alcohols and was converted to the first phosphoramidite allenylidene complexes under mild reaction conditions. The new complexes are among the rare examples of allenylidene complexes chiral at the metal, and the chiral information has been completely transferred from the precursor to the products. Thus, the precursor phosphoramidite complex is a chiral organometallic platform for the formation of chiral at the metal allenylidene complexes in diastereomeric purity. These findings are of importance for potential catalytic applications of the systems described herein. Further investigations of the synthesis as well as the development of catalytic cycles involving these allenylidenes as intermediates are currently underway.

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## Supplementary data

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre: CCDC 726745 (**8**), CCDC 726746 ([**10**][$PF_6$]), and CCDC 730038 ([**12**][$PF_6$]). 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). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.07.069.

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