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Half-Sandwich η^5-Indenyl- and η^6-Areneruthenium(II) Complexes Bearing the Chiral Ligand (4*S*)-2-[(S_p)-2-(Diphenylphosphanyl)ferrocenyl]-4-(methylethyl)-oxazoline (FcPN)

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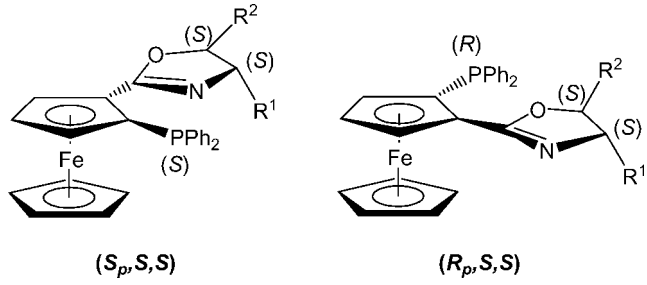
Keywords: N,P ligands / Phosphanes / Indenyl complexes / Arene complexes / Ruthenium

Chiral indenylruthenium(II) [Ru(η^5-C_9H_7){κ^2(*P*,*N*)-FcPN}(PPh$_3$)][PF$_6$] (**1**), [Ru(η^5-C_9H_7)Cl{κ^2(*P*,*N*)-FcPN}] (**2**) and areneruthenium(II) [RuX(η^6-arene){κ^2(*P*,*N*)-FcPN}][PF$_6$] [η^6-arene = *p*-cymene, X = Cl (**6a**), H (**7**), N$_3$ (**8**); η^6-arene = 1,2,3,4-tetramethylbenzene, X = Cl (**6b**)] complexes containing the chiral ligand (4*S*)-2-[(S_P)-2-(diphenylphosphanyl)ferrocenyl]-4-(methylethyl)oxazoline (FcPN) have been synthesised diastereoselectively. Reaction of **2** with terminal alkynes allows the synthesis of alkynyl [Ru(η^5-C_9H_7)(C≡CR){κ^2(*P*,*N*)-FcPN}] [R = Ph (**3a**), *p*-$CH_3C_6H_4$ (**3b**)], allenylidene [Ru(η^5-C_9H_7)-{κ^2(*P*,*N*)-FcPN}(=C=C=CPh$_2$)][PF$_6$] (**4**) and Fischer-type carbene [Ru(η^5-C_9H_7){κ^2(*P*,*N*)-FcPN}{=C(OMe)CH=CHPh}][PF$_6$] (**5**) complexes. The structures of complexes **2**, **3a** and **6a** have been determined by X-ray diffraction methods.

Introduction

Metal-mediated asymmetric catalysis has emerged as a very valuable synthetic tool to obtain enantiomerically pure substances.[1] Chiral ferrocene-based ligands incorporating both planar and central chirality are especially attractive due to their potential use in asymmetric induction.[2] Phosphanylferrocenyloxazoline derivatives[3,4] (Scheme 1) belong to this class of ligands and show a remarkable versatility since the substituents in the oxazoline group allow the modulation of the stereogenic centre located close to the N donor atom. Hybrid hemilabile phosphorus–nitrogen ligands are also gaining increasing relevance in coordination and organometallic chemistry since they can reversibly create and/or occupy a vacant coordination site at the metal.[5] In particular, ruthenium complexes containing chiral phosphanylferrocenyloxazoline ligands have proven to be good catalysts in hydrogenation,[6] hydrosilylation,[7] and transfer hydrogenation[8,9] of ketones, imines and ketoximes. However, most of the active species are formed in situ and therefore their coordination chemistry has been scarcely studied.



(S_p,*S*,*S*) (R_p,*S*,*S*)

Scheme 1.

The only isolated ruthenium(II) derivatives with FcPN ligands are either five-coordinate, such as [RuCl$_2${κ^2(*P*,*N*)-FcPN}(PPh$_3$)],[9] or octahedral complexes, such as [RuX$_2${κ^2(*P*,*N*)-FcPN}(PR$_3$)$_2$], [RuCl$_2${κ^2(*P*,*N*)-FcPN}-(dppm)], [RuCl$_2$(CO){κ^2(*P*,*N*)-FcPN}(L)] and [RuCl(CO)-{κ^2(*P*,*N*)-FcPN}(dppm)][PF$_6$] [dppm = bis(diphenylphosphanyl)methane].[10,11] It is interesting to note that no half-sandwich species have been described to date.

Following our interest in the chemistry of half-sandwich ruthenium(II) fragments and their use as promoters of catalytic[12] and stoichiometric C–C coupling reactions,[13] we report herein the diastereoselective synthesis of the first half-sandwich η^5-indenyl- and η^6-areneruthenium(II) complexes containing the chiral ligand FcPN (Scheme 2).

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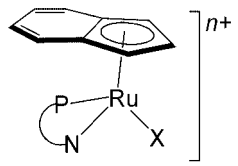
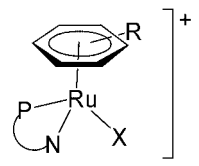
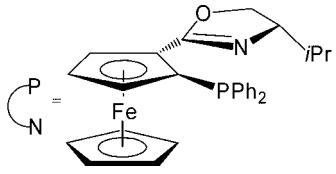


X = Cl, C≡CR, n = 0;
X = PPh_3, =C=C=CPh_2,
=C(OMe)CH=CHPh, n = 1



η^6-arene = *p*-cymene,
X = Cl, H, N_3; arene =
1,2,3,4-tetramethylbenzene;
X = Cl



Scheme 2.

Results and Discussion

Synthesis of Indenyl Complexes

Synthesis of [Ru(η^5-C_9H_7){κ^2(P,N)-FcPN}(PPh_3)][PF_6] (1)

The lability of the triphenylphosphane ligands in the complex [Ru(η^5-C_9H_7)Cl(PPh_3)$_2$] allows their ready exchange and the synthesis of a large series of mixed and chelating diphosphane complexes such as [Ru(η^5-C_9H_7)-Cl(PPh_3)L] and [Ru(η^5-C_9H_7)Cl(L–L)].[14] Following this methodology, the reaction of [Ru(η^5-C_9H_7)Cl(PPh_3)$_2$] with FcPN in refluxing toluene does not lead, however, to the expected phosphane exchange. Rather, the cationic complex [Ru(η^5-C_9H_7){κ^2(*P*,*N*)-FcPN}(PPh_3)][Cl] is formed. Subsequent treatment with $NaPF_6$ in methanol leads to the hexafluorophosphate salt [Ru(η^5-C_9H_7){κ^2(*P*,*N*)-FcPN}(PPh_3)]-[PF_6] (**1**) in 81% yield, which was isolated as a red, air-stable solid (Scheme 3).

[Ru(η^5-C_9H_7)Cl(PPh_3)$_2$] —(i) FcPN, toluene, Δ; (ii) $NaPF_6$, MeOH→ [Ru(η^5-C_9H_7){κ^2(*P*,*N*)-FcPN}(PPh_3)][PF_6]

1

Scheme 3.

Complex **1** is soluble in dichloromethane and thf and insoluble in diethyl ether and hexane. It was characterised by analytical and spectroscopic methods (see Experimental Section for details). The most remarkable spectroscopic features are: i) the IR spectrum (KBr) shows a strong absorption at 841 cm^{-1} due to the PF_6^- group, and ii) the $^{31}P\{^1H\}$ NMR spectrum displays two doublet resonances at δ = 34.7 and 58.8 ppm ($^2J_{P,P}$ = 36.5 Hz), as expected for an AB system arising from the presence of the inequivalent phosphorus nuclei.

Synthesis of [Ru(η^5-C_9H_7)Cl{κ^2(P,N)-FcPN}] (2)

The neutral, chelating FcPN complex [Ru(η^5-C_9H_7)-Cl{κ^2(*P*,*N*)-FcPN}] (**2**) was readily obtained by displacement of the labile COD ligand in [Ru(η^5-C_9H_7)Cl-(COD)][12e] (COD = 1,5-cyclooctadiene) by treatment with one equivalent of FcPN in refluxing thf (Scheme 4). Complex **2** was isolated (95% yield) as an air-stable, red solid that is soluble in dichloromethane, thf and diethyl ether and insoluble in hexane. It was fully characterised by analytical and spectroscopic methods and X-ray crystallography, which confirmed the chelating coordination mode of FcPN. Slow diffusion of hexane into a solution of **2** in dichloromethane resulted in crystals suitable for X-ray diffraction studies. An ORTEP view of the molecule is shown in Figure 1; selected bond lengths are listed in the caption.

[Ru(η^5-C_9H_7)Cl(COD)] —FcPN, THF, Δ→ [Ru(η^5-C_9H_7)Cl{κ^2(*P*,*N*)-FcPN}]

2

Scheme 4.

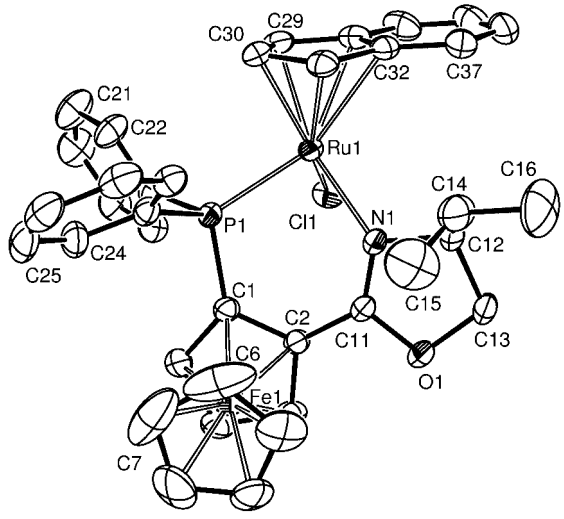


Figure 1. Molecular structure and atom-labelling scheme for complex **2**. Non-hydrogen atoms are represented by their 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: Ru(1)–C* 1.884(4), Ru(1)–N(1) 2.137(2), Ru(1)–P(1) 2.228(1), Ru(1)–Cl(1) 2.434(1), N(1)–C(11) 1.284(3), P(1)–C(1) 1.813(3), C(1)–C(2) 1.444(4), C(2)–C(11) 1.444(4). Selected bond angles [°]: C*–Ru(1)–P(1) 126.27(6), C*–Ru(1)–N(1) 132.78(8), C*–Ru(1)–Cl(1) 120.73(6), N(1)–Ru(1)–P(1) 90.65(6), N(1)–Ru(1)–Cl(1) 83.56(6), P(1)–Ru(1)–Cl(1) 88.60(3), C(1)–P(1)–Ru(1) 112.94(9), N(1)–C(11)–C(2) 128.8(2), C(1)–C(2)–C(11) 125.8(2), C(2)–C(1)–P(1) 123.6(2). C* means the centroid of atoms C(29), C(30), C(31), C(32) and C(33).

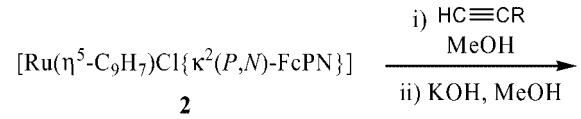
The complex adopts a three-legged piano-stool structure with P and N atoms from the bidentate chelating FcPN ligand and the Cl atom as the legs. The Ru–N, Ru–P and

Ru–Cl bond lengths are 2.137(2), 2.227(1) and 2.434(1) Å respectively. The ruthenium atom interacts in an η^5 fashion with the five-membered C29–C33 ring of the indenyl ligand, although in an asymmetric way as the Ru–C bond lengths range from 2.134(3) to 2.382(3) Å. The chelating six-membered ring shows an envelope conformation. The crystal structure of **2** indicates that only one diastereoisomer (S_{Ru},*S*,S_P) is present in the crystal.

Although the crystallisation of complex **2** gives rise to the isolation of only one diastereoisomer, the ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra in CD_2Cl_2 (see Experimental Section) indicate the presence of two isomers. In particular, the $^{31}P\{^1H\}$ NMR spectrum shows two signals at δ = 63.8 and 60.7 ppm whose ratio is dependent on the solvent, thereby suggesting a potential epimerisation of the S_{Ru},*S*,S_P into the R_{Ru},*S*,S_P diastereoisomer, a behaviour that is typical for configurationally unstable chiral-at-metal complexes.[15] Chloride dissociation as well as the opening of the Ru–P–N chelate ring could promote this isomerisation. However, complex **2** behaves as a neutral species since its conductivity values in dichloromethane (4.2 $\Omega^{-1}cm^2mol^{-1}$) and acetone (1.5 $\Omega^{-1}cm^2mol^{-1}$) are rather low. Provided that no ring opening is observed for ruthenium complexes with the FcPN ligand,[10,11] we assume that two rotamers[16] arising from different favoured conformations of the indenyl ring[14] are formed in solution.

Synthesis of the Alkynyl Derivatives [Ru(η⁵-C₉H₇)-(C≡CR){κ²(P,N)-FcPN}] [R = Ph (3a), p-CH₃C₆H₄ (3b)]

Reaction of complex **2** with HC≡CR and KOH in methanol affords the alkynyl complexes [Ru(η^5-C_9H_7)-(C≡CR){κ^2(*P*,*N*)-FcPN}] [R = Ph (**3a**), *p*-$CH_3C_6H_4$ (**3b**)], which were isolated as air-stable brown solids [Yields: 79% (**3a**) and 69% (**3b**); Scheme 5].



[Ru(η^5-C_9H_7)(C≡CR){κ^2(*P*,*N*)-FcPN}]

R = Ph (**3a**), *p*-$CH_3C_6H_4$ (**3b**)

Scheme 5.

Complexes **3a**,**b** are soluble in dichloromethane, thf and diethyl ether and insoluble in hexane. Both complexes were characterised analytically and spectroscopically (see the Experimental Section for details). In contrast to its chloride precursor **2**, all spectroscopic data are consistent with the presence of only one diastereoisomer. The following observations are of particular interest: i) the singlet resonances observed at δ = 69.3 (**3a**) and 68.4 ppm (**3b**) in the $^{31}P\{^1H\}$ NMR spectra remain unchanged within the range –90 to 20 °C, thus obviating the possibility of a dynamic process in solution; ii) the $^{13}C\{^1H\}$ NMR spectrum shows the expected resonances of the alkynyl groups (doublet signals for C_α [δ = 82.8 ppm ($J_{C,P}$ = 44.0 Hz) for **3a**; δ = 82.1 ppm ($J_{C,P}$ = 44.7 Hz) for **3b**] and singlets for C_β [δ = 110.7 (**3a**) and 109.9 ppm (**3b**)]). In addition, the IR spectra (KBr) show the characteristic ν(C≡C) absorption at 2073 (**3a**) and 2074 cm^{-1} (**3b**).

The absolute configuration of the ruthenium atom in these complexes was determined from an X-ray diffraction study of complex **3a**. Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a solution of complex **3a** in dichloromethane. An ORTEP-type view of the complex is shown in Figure 2; selected bonding data are listed in the caption.

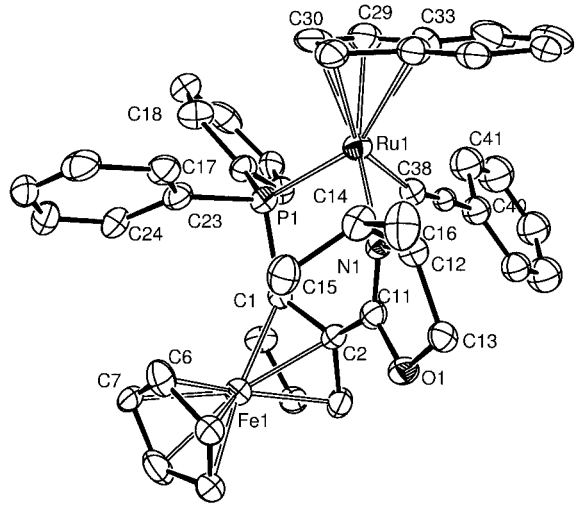
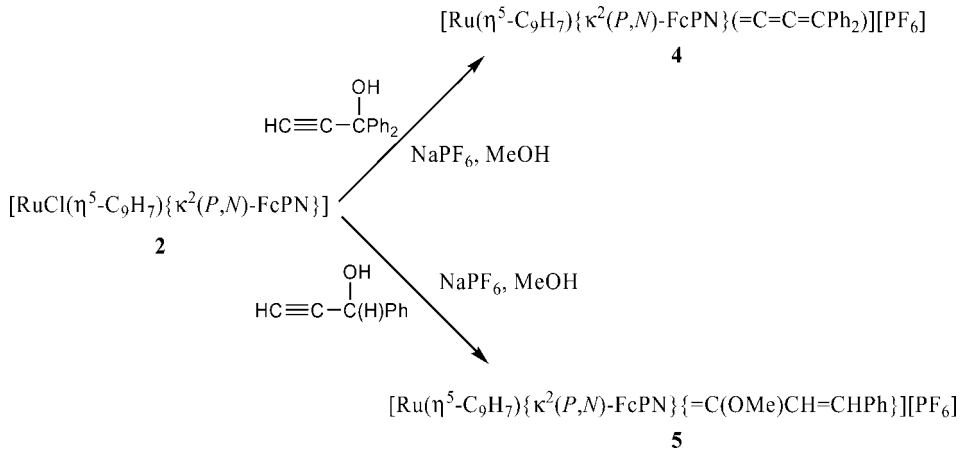


Figure 2. Molecular structure and atom-labelling scheme for complex **3a**. Non-hydrogen atoms are represented by their 10% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: Ru(1)–C* 1.894(4), Ru(1)–N(1) 2.098(11), Ru(1)–P(1) 2.207(4), Ru(1)–C(38) 2.042(14), C(38)–C(39) 1.11(2) [1.27(3)], N(1)–C(11) 1.438(16), P(1)–C(1) 1.867(14), C(1)–C(2) 1.446(17), C(2)–C(11) 1.462(18). Selected bond angles [°]: C*–Ru(1)–P(1) 127.77(7), C*–Ru(1)–N(1) 132.33(5), C*–Ru(1)–C(38) 119.27(7), N(1)–Ru(1)–P(1) 89.6(3), N(1)–Ru(1)–C(38) 88.0(4), P(1)–Ru(1)–C(38) 84.6(4), C(1)–P(1)–Ru(1) 111.5(4), N(1)–C(11)–C(2) 124.8(14), C(1)–C(2)–C(11) 127.4(13), C(2)–C(1)–P(1) 120.5(11). C* means the centroid of atoms C(29), C(30), C(31), C(32) and C(33).

The complex is very similar to complex **2**. The Ru–N and Ru–P bond lengths are 2.098(11) and 2.207(4) Å, respectively, very similar to those found in **2**. The alkynyl ligand is disordered and is distributed over two positions with an equal occupancy factor. The two images have C38 as common atom [the Ru–C(38) bond length is 2.042(14) Å]. The Ru–C bond lengths involving the asymmetric η^5 interaction of the Ru atom with the five-membered ring of the indenyl ligand span from 2.10(2) to 2.34(2) Å. The stereochemistry around the ruthenium atom is S_{Ru},*S*,S_P and therefore no change occurs with respect to the precursor complex **2**.



Scheme 6.

Synthesis of Allenylidene [Ru(η⁵-C₉H₇)[κ²(P,N)-FcPN](=C=C=CPh₂)][PF₆] (4) and Methoxycarbene [Ru(η⁵-C₉H₇){κ²(P,N)-FcPN}{=C(OMe)CH=CHPh}][PF₆] (5) Complexes

The activation of terminal alkynes with ruthenium(II) complexes is the most direct route to cumulenylidene and related carbene complexes.[17] Following this methodology we explored the reactivity of [Ru(η^5-C_9H_7)Cl{κ^2(*P*,*N*)-FcPN}] (**2**) towards propargylic alcohols. As expected, the reaction of equimolecular amounts of complex **2** and 1,1-diphenyl-2-propyn-1-ol in methanol in the presence of $NaPF_6$ yields the allenylidene derivative [Ru(η^5-C_9H_7){κ^2(*P*,*N*)-FcPN}(=C=C=CPh_2)][PF_6] (**4**), which was isolated as a purple-red solid in 65% yield after work-up (Scheme 6). However, the reaction with 1-phenyl-2-propyn-1-ol gives the alkenyl carbene [Ru(η^5-C_9H_7){κ^2(*P*,*N*)-FcPN}{=C(OMe)CH=CHPh}][PF_6] (**5**), which was isolated as a yellow solid in 73% yield after work-up (Scheme 6).

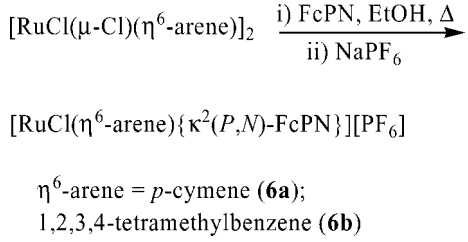
Complexes **4** and **5** are soluble in dichloromethane and thf and insoluble in diethyl ether and hexane. The elemental analysis and IR and NMR spectroscopic data are in accordance with the proposed formulations (see Experimental Section for details). The most representative spectroscopic data are as follows. The IR spectrum of complex **4** shows the ν(C=C=C) absorption at 1926 cm^{-1} and the absorption corresponding to the PF_6^- group at 841 cm^{-1}. Its $^{31}P\{^1H\}$ spectrum displays a singlet resonance at δ = 50.7 ppm and its $^{13}C\{^1H\}$ NMR spectrum shows a low-field signal for C_α [doublet at δ = 286.9 ppm ($J_{C,P}$ = 21.0 Hz)] and two broad singlet resonances at δ = 215.9 and 154.5 ppm for C_β and C_γ, respectively. The IR spectrum of complex **5** shows the ν(Ru=C) absorption at 1955 cm^{-1} and the ν(P–F) absorption at 841 cm^{-1}. The expected singlet in the $^{31}P\{^1H\}$ NMR spectra appears at δ = 57.4 ppm, and the ^1H NMR spectrum shows a singlet at δ = 3.75 ppm due to the methoxy group and two doublets at δ = 5.09 and 5.97 ppm ($J_{H,H}$ = 16.0 Hz) for the hydrogen atoms of the alkenyl group. The coupling constant for these doublets indicates a *trans* disposition. The $^{13}C\{^1H\}$NMR spectrum shows a low-field doublet at δ = 305.9 ppm ($J_{C,P}$ = 16.4 Hz) due to the C_α resonance.

The formation of **5** probably proceeds through the nucleophilic addition of one methanol molecule to the intermediate cationic allenylidene complex [Ru(η^5-C_9H_7){κ^2(*P*,*N*)-FcPN}(=C=C=CHPh)]$^+$.[17]

Synthesis of η^6-Arene Complexes

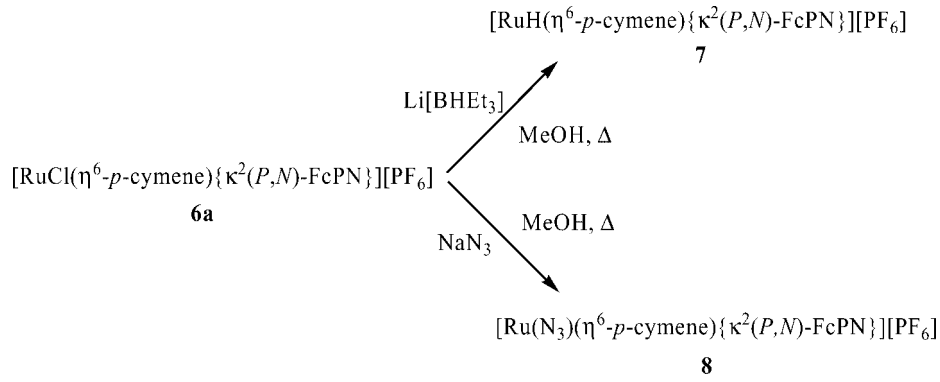
Synthesis of [RuX(η⁶-arene){κ²(P,N)-FcPN}][PF₆] [arene = p-cymene, X = Cl (6a), H (7), N₃ (8); arene = 1,2,3,4-tetramethylbenzene, X = Cl (6b)]

The reaction of two equivalents of FcPN with [RuCl(μ-Cl)(η^6-arene)]$_2$ (η^6-arene = *p*-cymene, 1,2,3,4-tetramethylbenzene) in refluxing ethanol leads to the complexes [RuCl(η^6-arene){κ^2(*P*,*N*)-FcPN}][Cl]. Subsequent chloride exchange with $NaPF_6$ gives the hexafluorophosphate salts [RuCl(η^6-arene){κ^2(*P*,*N*)-FcPN}][PF_6] [η^6-arene = *p*-cymene (**6a**), 1,2,3,4-tetramethylbenzene (**6b**)], which were isolated as air-stable orange solids in yields of 89% (**6a**) and 86% (**6b**; Scheme 7).



Scheme 7.

Complex **6a** has been shown to be a good precursor of analogous derivatives by metathesis of the chloride ligand. Thus, the reaction with an excess of Li[$BHEt_3$] leads to the hydride derivative [RuH(η^6-*p*-cymene){κ^2(*P*,*N*)-FcPN}][PF_6] (**7**), which was isolated as an air-stable green solid in 75% yield. Likewise, the treatment of **6a** with sodium azide in refluxing methanol gives [Ru(N_3)(η^6-*p*-cymene){κ^2(*P*,*N*)-

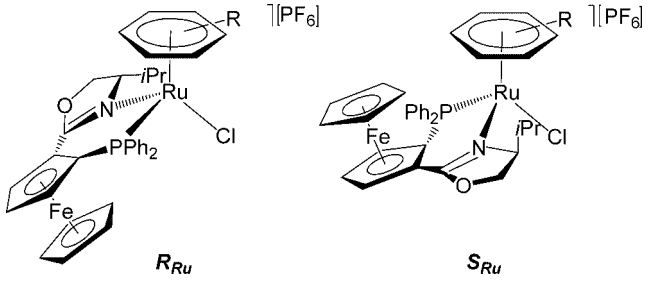


Scheme 8.

FcPN}][PF_6] (**8**), which was isolated as a brown solid in 71% yield (Scheme 8).

The analytical and spectroscopic data support these formulations (see Experimental Section for details). The syntheses are diastereoselective, as determined from the NMR spectra (^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$). In particular, the $^{31}P\{^1H\}$ NMR spectra display only a singlet resonance at δ = 24.9 (**6a**) 26.5 (**6b**) 50.7 (**7**) and 23.1 ppm (**8**) at room temperature. The spectra of the complexes remain unchanged in the range –90 to 20 °C, thus indicating that, as for the analogous indenyl complex **1**, no dynamic processes take place in this temperature range. The most characteristic spectroscopic features are the ν(Ru–H) absorption at 1967 cm^{-1} in the IR spectrum (KBr) and a high-field doublet for the hydride resonance at δ = –8.66 ($^2J_{H,P}$ = 43.7 Hz) in the ^1H NMR spectrum of complex **7**, and the ν(N=N=N) absorption at 2035 cm^{-1}in the IR spectrum (KBr) of complex **8**.

NOESY experiments performed on complex **6a** show cross-peaks between the OCH_2 and CHN protons of the oxazoline and the isopropyl group of the *p*-cymene ligand, thus indicating thier spatial proximity and suggesting that the stereochemistry around the metal is R_{Ru} (see Scheme 9).



Scheme 9.

This stereochemistry was confirmed by an X-ray crystal diffraction study. Single crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a solution of complex **6a** in dichloromethane. Two crystallographically independent cations (A and B) and two PF_6^- anions are present in the crystals of **6a**. The two independent complexes are very similar but differ in the coordination of the *p*-cymene: in the former the isopropyl substituent is almost eclipsed with respect to the Cl atom whereas in the latter the methyl substituent is almost eclipsed with the Cl atom. Practically, the *p*-cymene ligand is rotated by 180° in the two complexes. An ORTEP view of one of the two independent cationic complexes (B) is shown in Figure 3; selected bonding data for both complexes are listed in the caption.

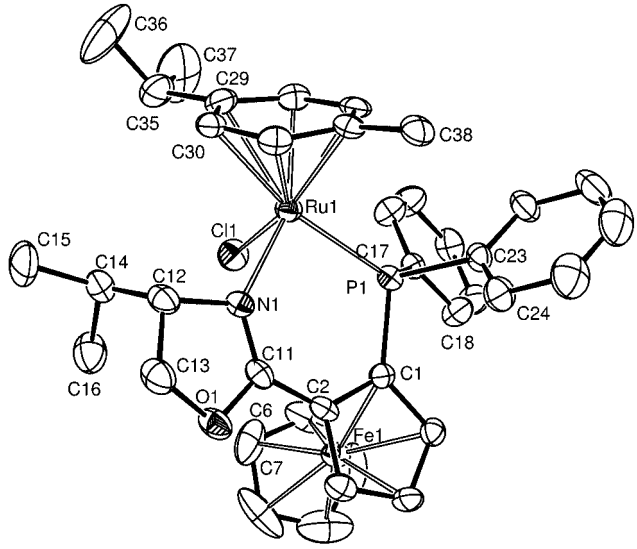


Figure 3. Molecular structure and atom-labelling scheme for complex **6a**. Non-hydrogen atoms are represented by their 30% probability ellipsoids. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: Ru(1)–C* 1.749(4) [1.744(5)], Ru(1)–N(1) 2.150(4) [2.122(3)], Ru(1)–P(1) 2.349(1) [2.347(1)], Ru(1)–Cl(1) 2.374(1) [2.390(1)], N(1)–C(11) 1.270(5) [1.283(5)], P(1)–C(1) 1.806(4) [1.824(5)], C(1)–C(2) 1.433(6) [1.427(6)], C(2)–C(11) 1.445(6) [1.443(6)]. Selected bond angles [°]: C*–Ru(1)–P(1) 127.66(6) [129.30(5)], C*–Ru(1)–N(1) 129.99(4) [126.22(4)], C*–Ru(1)–Cl(1) 122.58(8) [125.27(5)], N(1)–Ru(1)–P(1) 89.41(10) [91.54(11)], N(1)–Ru(1)–Cl(1) 84.23(10) [84.99(10)], P(1)–Ru(1)–Cl(1) 89.35(5) [85.68(4)], C(1)–P(1)–Ru(1) 114.27(15) [113.32(15)], N(1)–C(11)–C(2) 131.5(5) [129.0(5)], C(1)–C(2)–C(11) 127.3(4) [129.8(4)], C(2)–C(1)–P(1) 122.6(4) [122.9(4)]. C* means the centroid of atoms C(29), C(30), C(31), C(32), C(33), C(34). Data in square brackets refer to complex B.

As shown in Figure 3, the absolute configuration at the ruthenium atom (R_{Ru}) is the opposite to that found for the indenyl complexes **2** and **3a**. The Ru–N bond lengths [2.150(4) and 2.122(3) Å for cation B] do not differ significantly from those observed in **2** and **3a**, while the Ru–P

ones are longer [2.349(1) and 2.347(1) Å]. The Ru–Cl bond lengths [2.374(1) and 2.390(1) Å] are slightly shorter than that found in **2** [2.434(1) Å]. The Ru–C bond lengths of the *p*-cymene ligand span from 2.180(5) to 2.321(4) Å.

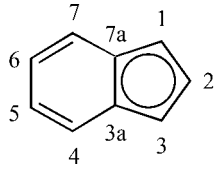
The stereochemistry R_{Ru} found for complex **6a** can also be tentatively assigned to be the same for the chloride (**6b**), hydride (**7**) and azide (**8**) complexes.

Conclusions

In summary, we have described the diastereoselective synthesis of new chiral-at-metal η^5 and η^6 half-sandwich ruthenium(II) complexes containing the chiral ligand (4*S*)-2-[(S_p)-2-(diphenylphosphanyl)ferrocenyl]-4-(methylethyl)-oxazoline (FcPN). The absolute configuration of the ruthenium atoms has been determined by X-ray analyses of complexes **2**, **3a** and **6a**.

Experimental Section

General Procedures: All manipulations were performed under an atmosphere of dry nitrogen using standard vacuum-line and Schlenk techniques. All reagents were obtained from commercial suppliers and used without further purification. Solvents were dried by standard methods and distilled under nitrogen before use. The compounds [Ru(η^5-C_9H_7)Cl(COD)],[12e] [Ru(η^5-C_9H_7)Cl(PPh_3)],[18] [RuCl(μ-Cl)(η^6-$C_{10}H_{14}$)]$_2$ [19] and (4*S*)-2-[(S_p)-2-(diphenylphosphanyl)ferrocenyl]-4-(methylethyl)oxazoline (FcPN).[4] were prepared by previously reported methods. IR spectra were recorded with a Perkin–Elmer FT-IR Paragon 1000 spectrometer. The conductivities were measured at room temperature, for approximately 5×10^{-4} M water solutions, with a Jenway PCM3 conductimeter. The C, H and N analyses were carried out with a Perkin–Elmer 240-B microanalyzer. NMR spectra were recorded with a Bruker AC300 or 300DPX instrument at 300 (^{1}H), 121.5 (^{31}P) or 75.4 MHz (^{13}C) using $SiMe_4$ or 85% H_3PO_4 as standards. DEPT experiments were carried out for all compounds. The following atom labels are used for the indenyl ^{1}H and ^{13}C{^{1}H} spectroscopic data. The label Ind-6 is used for the benzo ring.



Synthesis of [Ru(η^5-C_9H_7){κ^2(*P*,*N*)-FcPN}(PPh_3)][PF_6] (1): FcPN (859 mg, 1.8 mmol) was added to a solution of [Ru (η^5-C_9H_7)-Cl(PPh_3)$_2$] (1320 mg, 1.7 mmol) in toluene (80 mL) and the reaction mixture was refluxed for 2.5 h. The solvents were removed under vacuum and the resulting solid was dissolved in methanol (65 mL). $NaPF_6$ (857 mg, 5.1 mmol) was added and the solution was stirred for 1 h at room temperature. The solvents were then removed under vacuum and the solid residue extracted with CH_2Cl_2. The solution was filtered through kieselguhr, concentrated under vacuum to a volume of about 5 mL, and diethyl ether (80 mL) was added. The solid was washed with diethyl ether (2×80 mL) and dried under vacuum to afford complex **1** as an orange-red solid. Yield: 1.521 g (81%). Conductivity [$(CH_3)_2CO$, 20 °C]: 123 Ω^{-1} cm^2 mol^{-1}. FTIR (KBr): $\tilde{\nu}$ = 841 cm^{-1} (PF_6^-). ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C): δ = 7.77–7.05 (m, 28 H, Ph, Ind-6), 5.91 (m, 1 H, H-1 or H-3), 5.65 (d, $^3J_{H,H}$ = 8.3 Hz, 1 H, Ind-6), 5.32 (m, 1 H, H-1 or H-3), 4.94 (m, 1 H, C_5H_3), 4.68 (t, $^3J_{H,H}$ = 5.0 Hz, 1 H, C_5H_3), 4.66 (m, 1 H, C_5H_3), 4.34 (dd, $^2J_{H,H}$ = 1.9, $^3J_{H,H}$ = 8.7 Hz, 1 H, OCH_2), 3.64 (s, 5 H, C_5H_5), 3.60 (d, $^3J_{H,H}$ = 8.7 Hz, 1 H, OCH_2), 3.18 (m, 1 H, H-2), 3.03 (t, $^3J_{H,H}$ = 8.7 Hz, 1 H, CHN), 2.89 [sept d, $^3J_{H,H}$ = 2.6, $^3J_{H,H}$ = 7.0 Hz, 1 H, C*H*(CH_3)$_2$], 1.28 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 1.26 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, CD_2Cl_2, 20 °C): δ = 170.8 (s, *C*OCH_2), 143.6–128.0 (Ph, Ind-6), 124.6 (s, Ind-6), 124.4 (s, Ind), 116.8 (d, $^2J_{C,P}$ = 3.8 Hz, C-3a or C-7a), 112.3 (m, C-3a or C-7a), 93.7 (s, C-2), 79.0 (d, $J_{C,P}$ = 39.4 Hz, $CPPh_2$), 75.7 (s, C_5H_3), 75.3 (s, C_5H_3), 74.5 (d, $^2J_{C,P}$ = 19.1 Hz, *C*$CPPh_2$), 73.2 (d, $^3J_{C,P}$ = 6.4 Hz, CHN), 72.9 (d, $^2J_{C,P}$ = 7.0 Hz, C_5H_3), 72.3 (s, C_5H_5), 68.4 (d, $^2J_{C,P}$ = 12.7 Hz, C-1 or C-3), 67.7 (s, OCH_2), 63.6 (s, C-1 or C-3), 29.2 [s, *C*H(CH_3)$_2$], 19.5 (s, CH_3), 15.2 (s, CH_3) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 20 °C): δ = 58.8 (d, $^2J_{P,P}$ = 36.5 Hz), 34.7 (d, $^2J_{P,P}$ = 36.5 Hz) ppm. $C_{55}H_{50}F_6FeNOP_3Ru$ (1104.82): calcd. C 59.79, H 4.56, N 1.27; found C 59.42, H 4.48, N 1.27.

Synthesis of [Ru(η^5-C_9H_7)Cl{κ^2(*P*,*N*)-FcPN}] (2): FcPN (1203 mg, 2.5 mmol) was added to a solution of [RuCl(η^5-C_9H_7)(COD)] (900 mg, 2.5 mmol) in thf (90 mL) and the reaction mixture was refluxed for 7 h. The solvents were removed under vacuum to a volume of about 5 mL, and hexane (50 mL) was added. The solid was washed with hexane (2×50 mL) and dried under vacuum to afford complex **2** as a red solid. Yield: 1.741 g (95%). $C_{37}H_{35}ClFeNOPRu$ (733.02): calcd. C 60.63, H 4.81, N 1.91; found C 60.47, H 4.72, N 1.83.

Rotamer 2a: ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 8.67–7.01 (m, 14 H, Ph, Ind-6), 5.07 (m, 1 H, H-1 or H-3), 4.87 (m, 1 H, H-1 or H-3), 4.49–4.38 (m, 3 H, CHN, C_5H_3), 4.32 (dd, $^2J_{H,H}$ = 4.1, $^3J_{H,H}$ = 8.7 Hz, 1 H, OCH_2), 4.10 (br. s, 1 H, C_5H_3), 4.04 (s, 5 H, C_5H_5), 3.74 (m, 1 H, OCH_2), 3.05 (m, 1 H, H-2), 2.37 [m, 1 H, C*H*(CH_3)$_2$], 0.76 (d, $^3J_{H,H}$ = 6.4 Hz, 3 H, CH_3), 0.69 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, CD_2Cl_2, 20 °C): δ = 166.4 (s, *C*OCH_2), 145.6–124.6 (Ph, Ind-6), 121.1 (s, Ind-6), 117.4 (d, $^2J_{C,P}$ = 6.0 Hz, C-3a or C-7a), 111.6 4 (m, C-3a or C-7a), 85.7 (s, C-6), 77.7 (br. s, C_5H_3), 75.8 (d, $J_{C,P}$ = 37.0 Hz, $CPPh_2$), 75.0 (d, $^2J_{C,P}$ = 18.1 Hz, *C*$CPPh_2$), 73.8 (d, $^2J_{C,P}$ = 3.8 Hz, C_5H_3), 71.8 (s, C_5H_5), 71.6 (m, CHN), 71.0 (s, C_5H_3), 68.0 (s, OCH_2), 63.6 (s, C-1 or C-3), 50.8 (s, C-1 or C-3), 28.0 [s, *C*H(CH_3)$_2$], 19.4 (s, CH_3), 15.8 (s, CH_3) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 20 °C): δ = 60.7 (s) ppm.

Rotamer 2b: ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 8.67–7.01 (m, 14 H, Ph, Ind-6), 4.82 (m, 1 H, H-1 or H-3), 4.72 (m, 1 H, H-1 or H-3), 4.56 (m, 2 H, CHN, C_5H_3), 4.53 (t, $^3J_{H,H}$ = 2.7 Hz, 1 H, C_5H_3), 4.24 (m, 1 H, OCH_2), 4.14 (br. s, 1 H, C_5H_3), 3.61 (m, 1 H, OCH_2), 3.56 (m, 1 H, H-2), 3.52 (s, 5 H, C_5H_5), 2.73 [m, 1 H, C*H*(CH_3)$_2$], 1.13 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3), 1.03 (d, $^3J_{H,H}$ = 6.9 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, CD_2Cl_2, 20 °C): δ = 168.0 (s, *C*OCH_2), 140.1–124.6 (Ph, Ind-6), 122.5 (s, Ind-6), 114.3 (d, $^2J_{C,P}$ = 5.3 Hz, C-3a or C-7a), 111.6 (d, $^2J_{C,P}$ = 7.6 Hz, C-3a or C-7a), 82.3 (s, C-2), 80.7 (d, $J_{C,P}$ = 37.8 Hz, $CPPh_2$), 75.3 (br. s, C_5H_3), 74.4 (d, $^2J_{C,P}$ = 18.9 Hz, *C*$CPPh_2$), 73.3 (br. s, C_5H_3), 73.2 (m, CHN), 71.3 (s, C_5H_5), 71.1 (s, C_5H_3), 67.7 (s, OCH_2), 57.8 (s, C-1 or C-3), 55.2 (s, C-1 or C-3), 29.4 [s, *C*H(CH_3)$_2$], 19.1 (s, CH_3), 14.3 (s, CH_3) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 20 °C): δ = 63.8 (s) ppm.

Synthesis of [Ru(η^5-C_9H_7)(C≡CR){κ^2(*P*,*N*)-FcPN}] [R = Ph (3a), *p*-$CH_3C_6H_4$ (3b)]: HC≡CR (0.55 mmol) was added to a solution of complex **2** (367 mg, 0.5 mmol) in MeOH (35 mL), and the reaction mixture was stirred at room temperature for 10 min. A solution of

KOH in MeOH (5 mL, 0.11 M) was then added and the resulting solution stirred at room temperature for 5 h (**3a**) or 1.5 h (**3b**). The solvents were removed under vacuum and the resulting solid extracted with CH_2Cl_2. The solution was filtered through kieselguhr, concentrated under vacuum to a volume of about 2 mL, and hexane (20 mL) was added. The solid was washed with hexane (20 mL) and dried under vacuum to afford complexes **3a**,**b** as brown solids.

3a: Yield: 0.315 g (79%). FTIR (KBr): $\tilde{\nu}$ = 2073 cm^{-1} (C≡C). ^1H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 8.08–6.99 (m, 16 H, Ph, Ind-6), 6.88 (d, $^3J_{H,H}$ = 7.4 Hz, 1 H, Ind-6), 6.75 (d, $^3J_{H,H}$ = 7.4 Hz, 2 H, Ind-6), 5.34 (br. s, 1 H, H-1 or H-3), 4.73 (m, 2 H, C_5H_3 and H-1 or H-3), 4.62 (br. s, 1 H, C_5H_3), 4.56 (m, 1 H, C_5H_3), 4.22 (dd, $^2J_{H,H}$ = 4.2, $^3J_{H,H}$ = 8.9 Hz, 1 H, OCH_2), 4.06 (t, $^3J_{H,H}$ = 8.9 Hz, 1 H, CHN), 3.49 (s, 5 H, C_5H_5), 3.28 (br. s, 1 H, H-2), 3.22 (m, 1 H, OCH_2), 2.78 [m, 1 H, C*H*$(CH_3)_2$], 1.08 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 0.93 (d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, CD_2Cl_2, 20 °C): δ = 165.9 (s, *C*OCH_2), 141.3–125.1 (Ph), 124.9 (s, Ind), 123.2 (s, Ind), 123.0 (s, Ind), 120.7 (s, Ind), 113.9 (d, $^2J_{C,P}$ = 6.1 Hz, C-3a or C-7a), 112.0 (d, $^2J_{C,P}$ = 4.6 Hz, C-3a or C-7a), 110.7 (br. s, C_β) 87.4 (s, C-2), 82.8 (d, $^2J_{C,P}$ = 44.0 Hz, C_α), 74.9 (br. s, C_5H_3), 74.7 (m, *C*$CPPh_2$), 73.4 (br. s, C_5H_3), 73.2 (m, $CPPh_2$), 71.0 (s, C_5H_5), 70.5 (m, CHN, C_5H_3), 66.6 (s, OCH_2), 63.6 (s, C-1 or C-3), 58.4 (s, C-1 or C-3), 28.8 [s, *C*$H(CH_3)_2$], 18.9 (s, CH_3), 14.5 (s, CH_3) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 20 °C): δ = 69.3 (s) ppm. $C_{45}H_{40}FeNOPRu{\cdot}CH_2Cl_2$ (883.63): calcd. C 62.53, H 4.79, N 1.59; found C 62.39, H 4.63, N 1.50.

3b: Yield: 0.280 g (69%). FTIR (KBr): $\tilde{\nu}$ = 2074 cm^{-1} (C≡C). ^1H NMR (300 MHz, CD_2Cl_2, 20 °C): δ = 8.07–7.01 (m, 14 H, Ph), 6.82 (m, 2 H, Ind-6), 6.64 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, Ind-6), 5.32 (br. s, 1 H, H-1 or H-3), 4.72 (m, 2 H, C_5H_3 and H-1 or H-3), 4.61 (br. s, 1 H, C_5H_3), 4.54 (m, 1 H, C_5H_3), 4.22 (dd, $^2J_{H,H}$ = 4.4, $^3J_{H,H}$ = 9.0 Hz, 1 H, OCH_2), 4.05 (t, $^3J_{H,H}$ = 9.0 Hz, 1 H, CHN), 3.48 (s, 5 H, C_5H_5), 3.27 (br. s, 1 H, H-2), 3.22 (dd, $^2J_{H,H}$ = 4.4, $^3J_{H,H}$ = 9.0 Hz, 1 H, OCH_2), 2.79 [sept d, $^3J_{H,H}$ = 2.8, $^3J_{H,H}$ = 7.0 Hz, 1 H, C*H*$(CH_3)_2$], 2.21 (s, 3 H, $C_6H_4CH_3$) 1.07 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 0.92 (d, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, CD_2Cl_2, 20 °C): δ = 166.1 (s, *C*OCH_2), 141.6–127.1 (Ph), 126.3 (s, Ind), 125.1 (s, Ind), 123.2 (s, Ind), 121.0 (s, Ind), 113.3 (d, $^2J_{C,P}$ = 6.5 Hz, C-3a or C-7a), 111.9 (d, $^2J_{C,P}$ = 4.4 Hz, C-3a or C-7a), 109.9 (br. s, C_β) 87.7 (s, C-2), 82.1 (d, $^2J_{C,P}$ = 44.7 Hz, C_α), 74.9 (br. s, C_5H_3), 74.5 (d, $^2J_{C,P}$ = 18.5 Hz, *C*$CPPh_2$), 73.6 (br. s, C_5H_3), 73.3 (m, $CPPh_2$), 71.2 (s, C_5H_5), 70.8 (m, CHN, C_5H_3), 67.3 (s, OCH_2), 66.6 (s, C-1 or C-3), 57.4 (s, C-1 or C-3), 29.1 [s, *C*$H(CH_3)_2$], 21.3 (s, $C_6H_4CH_3$), 19.2 (s, CH_3), 14.7 (s, CH_3) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 20 °C): δ = 68.4 (s) ppm. $C_{46}H_{42}FeNOPRu$ (812.72): calcd. C 67.98, H 5.21, N 1.72; found C 67.53, H 5.12, N 1.66.

Synthesis of [Ru(η⁵-C_9H_7){κ²(*P*,*N*)-FcPN}(=C=C=CPh_2)][PF_6] (4): A solution of complex **2** (220 mg, 0.3 mmol) and $NaPF_6$ (55 mg, 0.33 mmol) in methanol (25 mL) was stirred at room temperature for 10 min and 1,1-diphenyl-2-propyn-1-ol (69 mg, 0.33 mmol) was then added. The reaction mixture was stirred at room temperature for 1.5 h. The solvents were removed under vacuum and the resulting solid extracted with CH_2Cl_2. The solution was filtered through kieselguhr, concentrated under vacuum to a volume of about 2 mL, and diethyl ether (50 mL) was added. The solid was washed with diethyl ether (2 × 50 mL) and dried under vacuum to afford complex **4** as a purple solid. Yield: 0.201 g (65%). Conductivity [$(CH_3)_2CO$, 20 °C]: 103 $\Omega^{-1}cm^2mol^{-1}$. FTIR (KBr): $\tilde{\nu}$ = 1926 (C=C=C), 841 (PF_6^-) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 8.07–7.15 (m, 22 H, Ph, Ind-6), 5.76 (m, 2 H, Ind-6), 5.21 (br. s, 1 H, Ind), 5.16 (br. s, 1 H, Ind), 5.10 (m, 1 H, C_5H_3), 5.00 (br. s, 1 H, Ind), 4.65 (dd, $^2J_{H,H}$ = 3.6, $^3J_{H,H}$ = 9.1 Hz, 1 H, OCH_2), 4.38 (s, 5 H, C_5H_5), 4.33 (t, $^3J_{H,H}$ = 9.1 Hz, 1 H, CHN), 4.10 (br. s, 1 H, C_5H_3), 3.70 (s, 5 H, C_5H_5), 3.49 (m, 1 H, OCH_2), 2.57 [m, 1 H, C*H*$(CH_3)_2$], 1.18 (d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3), 1.00 (d, $^3J_{H,H}$ = 6.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, CD_2Cl_2, 20 °C): δ = 286.9 (d, $^2J_{C,P}$ = 21.0 Hz, C_α), 215.9 (s, C_β), 171.3 (s, *C*OCH_2), 154.5 (s, C_γ), 145.6–128.4 (Ph, Ind-6), 126.3 (s, Ind-6), 124.4 (s, Ind-6), 118.4 (br. s, C-3a or C-7a), 117.8 (br. s, C-3a or C-7a), 99.0 (s, C-2), 80.6 (d, $J_{C,P}$ = 50.7 Hz, $CPPh_2$), 77.1 (m, *C*$CPPh_2$, C-1, C-3), 76.0 (s, C_5H_3), 74.0 (m, CHN, C_5H_3), 72.8 (s, C_5H_5), 68.8 (s, OCH_2), 30.7 [s, *C*$H(CH_3)_2$], 18.9 (s, CH_3), 14.8 (s, CH_3) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 20 °C): δ = 50.7 (s) ppm. $C_{52}H_{45}F_6FeNOP_2Ru$ (1032.77): calcd. C 60.47, H 4.39, N 1.36; found C 61.02, H 4.61, N 1.32.

Synthesis of [Ru(η⁵-C_9H_7){κ²(*P*,*N*)-FcPN}{=C(OMe)CH=CHPh}][PF_6] (5): A solution of complex **2** (357 mg, 0.5 mmol) and $NaPF_6$ (92 mg, 0.55 mmol) in methanol (40 mL) was stirred at room temperature for 10 min. 1-Phenyl-2-propyn-1-ol (67 μL, 0.55 mmol) was then added and the reaction mixture stirred at room temperature for 3 h. The solvents were removed under vacuum and the resulting solid extracted with CH_2Cl_2. The solution was filtered through kieselguhr, concentrated under vacuum to a volume of about 2 mL, and diethyl ether (50 mL) was added. The solid was washed with diethyl ether (2 × 50 mL) and dried under vacuum to afford complex **5** as a yellow solid. Yield: 0.361 g (73%). Conductivity [$(CH_3)_2CO$, 20 °C]: 107 $\Omega^{-1}cm^2mol^{-1}$. FTIR (KBr): $\tilde{\nu}$ = 1955 (Ru=C), 841 (PF_6^-) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 7.87–7.03 (m, 19 H, Ph, Ind-6), 5.97 (d, $^3J_{H,H}$ = 16.0 Hz, 1 H, =CH), 5.39 (br. s, 1 H, Ind), 5.09 (d, $^3J_{H,H}$ = 16.0 Hz, 1 H, =CH), 4.88 (br. s, 2 H, Ind, C_5H_3), 4.81 (br. s, 2 H, Ind, C_5H_3), 4.73 (br. s, 2 H, Ind, C_5H_3), 4.28 (m, 2 H, C_5H_3, OCH_2), 4.09 (br. s, 1 H, C_5H_3), 3.82 (m, 1 H, OCH_2), 3.75 (s, 1 H, OCH_3), 3.73 (m, 1 H, CHN), 3.52 (s, 5 H, C_5H_5), 2.82 [m, 1 H, C*H*$(CH_3)_2$], 1.22 (d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH_3), 0.94 (d, $^3J_{H,H}$ = 6.7 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, CD_2Cl_2, 20 °C): δ = 305.9 (d, $^2J_{C,P}$ = 16.4 Hz, C_α), 170.3 (s, *C*OCH_2), 140.8 (s, =CH), 139.3–126.9 (Ph, Ind-6, =CH), 123.6 (s, Ind-6), 123.4 (s, Ind-6), 115.4 (br. s, C-3a or C-7a), 112.9 (d, $^2J_{C,P}$ = 4.6 Hz, C-3a or C-7a), 96.7 (s, C-2), 80.4 (d, $J_{C,P}$ = 44.6 Hz, $CPPh_2$), 76.4 (s, C_5H_3), 75.7 (s, C_5H_3), 73.5 (d, $^2J_{C,P}$ = 19.5 Hz, *C*$CPPh_2$), 72.5 (m, CHN, C_5H_3), 72.2 (s, C_5H_5), 70.0 (s, C-1 or C-3), 68.0 (s, OCH_2), 63.6 (s, OCH_3), 63.5 (s, C-1 or C-3), 29.3 [s, *C*$H(CH_3)_2$], 19.4 (s, CH_3), 15.0 (s, CH_3) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_2Cl_2, 20 °C): δ = 57.4 (s) ppm. $C_{47}H_{45}F_6FeNO_2P_2Ru{\cdot}CH_2Cl_2$ (1073.65): calcd. C 53.70, H 4.41, N 1.30; found C 54.18, H 4.53, N 1.33.

Synthesis of [RuCl(η⁶-arene){κ²(*P*,*N*)-FcPN}][PF_6] [arene = *p*-cymene (6a), 1,2,3,4-tetramethylbenzene (6b)]: FcPN (770 mg, 1.6 mmol) was added to a solution of [RuCl(μ-Cl)(η⁶-arene)]$_2$ (490 mg, 0.8 mmol) in ethanol (100 mL), and the reaction mixture was refluxed for 2 h. After cooling, $NaPF_6$ (269 mg, 1.6 mmol) was added and the solution was stirred for 1 h at room temperature. The solvents were removed under vacuum and the solid residue extracted with CH_2Cl_2. The solution was filtered through kieselguhr, concentrated under vacuum to a volume of about 5 mL, and diethyl ether (50 mL) was added. The solid residue was washed with diethyl ether (2 × 50 mL) and dried under vacuum to afford complexes **6a**,**b** as orange solids.

6a: Yield: 1.277 g (89%). Conductivity [$(CH_3)_2CO$, 20 °C]: 101 $\Omega^{-1}cm^2mol^{-1}$. FTIR (KBr): $\tilde{\nu}$ = 841 (PF_6^-) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 8.23 (m, 2 H, Ph), 7.62 (m, 3 H, Ph), 7.41 (m, 3 H, Ph), 6.92 (m, 2 H, Ph), 5.82 (d, $^3J_{H,H}$ = 6.3 Hz,

1 H, CH), 5.59 (d, $^3J_{H,H}$ = 6.3 Hz, 1 H, CH), 5.55 (d, $^3J_{H,H}$ = 6.0 Hz, 1 H, CH), 5.16 (br. s, 1 H, C_5H_3), 4.80 (t, $^3J_{H,H}$ = 2.6 Hz, 1 H, C_5H_3), 4.77 (m, 1 H, OCH_2), 4.55 (m, 4 H, C_5H_3, OCH_2, CHN, CH), 4.05 (s, 5 H, C_5H_5), 2.93 [m, 1 H, C*H*$(CH_3)_2$], 2.08 [m, 1 H, C*H*$(CH_3)_2$], 1.94 (s, 3 H, CH_3), 1.14 (d, $^3J_{H,H}$ = 7.1 Hz, 3 H, CH_3), 1.03 (d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3), 0.96 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H, CH_3), 0.85 (d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, CD_2Cl_2, 20 °C): δ = 171.0 (br. s, *C*OCH_2), 141.1–128.7 (Ph), 110.4 (s, *C*CH), 102.3 (s, *C*CH), 98.6 (d, $^2J_{C,P}$ = 7.6 Hz, CH), 92.5 (m, CH), 89.4 (br. s, CH), 85.1 (m, CH), 80.3 (br. s, C_5H_3), 76.0 (d, CHN, $^3J_{C,P}$ = 5.1 Hz), 75.2 (br. s, C_5H_3), 74.2 (d, $J_{C,P}$ = 7.6 Hz, C_5H_3), 73.4 (d, $J_{C,P}$ = 17.2 Hz, *C*$CPPh_2$), 72.8 (s, C_5H_5), 70.7 (d, $^2J_{C,P}$ = 47.7 Hz, $CPPh_2$), 68.6 (s, OCH_2), 30.8 [s, *C*H$(CH_3)_2$], 29.2 [s, *C*H$(CH_3)_2$], 23.8 (s, *C*CH_3), 21.6 (s, CH_3), 20.1 (s, CH_3), 18.1 (s, CH_3), 16.2 (s, CH_3) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 20 °C): δ = 24.9 (s) ppm. $C_{38}H_{42}ClF_6FeNOP_2Ru$ (897.05): calcd. C 50.88, H 4.72, N 1.56; found C 51.12, H 4.86, N 1.40.

6b: Yield: 1.234 g (86%. Conductivity [$(CH_3)_2CO$, 20 °C]: 115 Ω^{-1} cm^2 mol^{-1}. FTIR (KBr): $\tilde{\nu}$ = 846 (PF_6^-) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C): δ = 8.26 (m, 2 H, Ph), 7.70–7.61 (m, 3 H, Ph), 7.43 (m, 3 H, Ph), 7.04 (m, 2 H, Ph), 5.13 (br. s, 1 H, C_5H_3), 4.96 (m, 1 H, CH), 4.79 (br. s, 1 H, C_5H_3), 4.59 (m, 2 H, C_5H_3, CH), 4.40 (m, 1 H, OCH_2), 4.17 (m, 1 H, OCH_2), 4.01 (s, 5 H, C_5H_5), 3.03 (s, 1 H, CHN), 2.47 [m, 1 H, C*H*$(CH_3)_2$], 2.22 (s, 3 H, CH_3), 2.09 (br. s, 3 H, CH_3), 2.07 (br. s, 3 H, CH_3), 1.70 (br. s, 3 H, CH_3), 1.07 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H, CH_3), 0.97 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, CD_2Cl_2, 20 °C): δ = 171.3 (s, *C*OCH_2), 142.9–128.5 (Ph), 113.5 (d, $^2J_{C,P}$ = 8.3 Hz, *C*Me), 112.5 (d, $^2J_{C,P}$ = 7.4 Hz, *C*Me), 96.9 (d, $^2J_{C,P}$ = 8.3 Hz, 2 *C*Me), 90.8 (s, CH), 83.6 (s, CH), 77.8 (d, $J_{C,P}$ = 51.8 Hz, $CPPh_2$), 76.4 (br. s, C_5H_3), 76.0 (d, $^2J_{C,P}$ = 5.6 Hz, CHN), 74.3 (br. s, C_5H_3), 74.2 (d, $^2J_{C,P}$ = 8.3 Hz, C_5H_3), 73.3 (d, $^2J_{C,P}$ = 17.6 Hz, *C*$CPPh_2$), 72.6 (s, C_5H_5), 69.2 (br. s, OCH_2), 28.6 [s, *C*H$(CH_3)_2$], 19.5(s, CH_3), 19.0 (s, CH_3), 18.4 (s, CH_3), 16.6 (s, CH_3), 16.3 (s, CH_3), 14.6 (s, CH_3) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 20 °C): δ = 26.5 (s) ppm. $C_{38}H_{42}ClF_6FeNOP_2Ru$ (897.05): calcd. C 50.88, H 4.72. N 1.56; found C 50.18, H 4.40, N 1.34.

Synthesis of [RuH(η^6-*p*-cymene){κ^2(*P*,*N*)-FcPN}][PF_6] (7): $Li[BHEt_3]$ (1.3 mL of a 1 M solution in thf, 1.3 mmol) was added to a solution of **6a** (897 mg, 1.0 mmol) in thf (100 mL) and the reaction mixture was stirred at room temp. for 14 h. The solvents were removed under vacuum and the solid residue extracted with CH_2Cl_2. The solution was filtered through kieselguhr, concentrated under vacuum to a volume of about 5 mL, and diethyl ether (50 mL) was added. The solid was washed with diethyl ether (2 × 50 mL) and dried under vacuum to afford complex **7** as a green solid. Yield: 0.647 g (75%). Conductivity [$(CH_3)_2CO$, 20 °C]: 96 Ω^{-1} cm^2 mol^{-1}. FTIR (KBr): $\tilde{\nu}$ = 1967 (RuH), 842 (PF_6^-) cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C): δ = 8.12 (m, 2 H, Ph), 7.64 (m, 3 H, Ph), 7.40 (m, 3 H, Ph), 7.06 (m, 2 H, Ph), 5.12 (m, 1 H, CH), 5.02 (br. s, 1 H, C_5H_3), 4.98 (m, 2 H, CH), 4.90 (m, 1 H, CH), 4.74 (t, $^3J_{H,H}$ = 2.4 Hz, 1 H, C_5H_3), 4.52 (br. s, 1 H, C_5H_3), 4.42 (dd, $^2J_{H,H}$ = 4.0, $^3J_{H,H}$ = 9.1 Hz, 1 H, OCH_2), 4.31 (t, $^3J_{H,H}$ = 9.1 Hz, 1 H, CHN), 3.73 (m, 6 H, C_5H_5, OCH_2), 2.55 [sept d, $^3J_{H,H}$ = 3.2, $^3J_{H,H}$ = 7.2 Hz, 1 H, C*H*$(CH_3)_2$], 2.30 [m, 1 H, C*H*-$(CH_3)_2$], 1.86 (br. s, 3 H, CH_3), 1.26 (d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3), 1.16 (d, $^3J_{H,H}$ = 6.8 Hz, 3 H, CH_3), 1.02 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), 0.84 (d, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3), –8.66 (d, $^2J_{H,P}$ = 43.7 Hz, 1 H, RuH) ppm. ^{13}C NMR (75.4 MHz, CD_2Cl_2, 20 °C): δ = 168.6 (br. s, *C*OCH_2), 141.9–128.7 (Ph), 119.7 (s, *C*CH), 106.3 (m, *C*CH), 93.4 (s, 2 C, CH), 92.3 (s, 2 C, CH), 78.3 (br. s, C_5H_3), 75.6 (d, $^3J_{C,P}$ = 4.5 Hz, CHN), 75.0 (br. s, C_5H_3), 74.2 (d, $J_{C,P}$ = 46.7 Hz, $CPPh_2$), 73.7 (m, *C*$CPPh_2$, C_5H_3), 71.8 (s, C_5H_5), 67.5 (s, OCH_2), 32.2 [s, *C*H$(CH_3)_2$], 24.5 [s, *C*H$(CH_3)_2$], 24.4 (s, CH_3), 23.6 (s, CH_3), 19.1 (s, CH_3), 18.8 (s, CH_3), 13.8 (s, CH_3) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 20 °C): δ = 50.7 (s) ppm. $C_{40}H_{47}F_6FeNOP_2Ru{\cdot}2CH_2Cl_2$ (1032.5): calcd. C 46.53, H 4.59, N 1.36; found C 46.05, H 4.29, N 1.61.

Synthesis of [Ru(N_3)(η^6-*p*-cymene){κ^2(*P*,*N*)-FcPN}][PF_6] (8): A solution of **6a** (449 mg, 0.5 mmol) and NaN_3 (49 mg, 0.75 mmol) in methanol (50 mL) was refluxed for 4 h. After cooling, the solvents were removed under vacuum and the solid residue extracted with CH_2Cl_2. The solution was filtered through kieselguhr, concentrated under vacuum to a volume of about 5 mL, and diethyl ether (70 mL) was added. The solid was washed with diethyl ether (2 × 70 mL) and dried under vacuum to afford complex **8** as a brown solid. Yield: 0.321 g (71%). Conductivity [$(CH_3)_2CO$, 20 °C]: 84 Ω^{-1} cm^2 mol^{-1}. FTIR (KBr): $\tilde{\nu}$ = 2035 (N_3), 841 (PF_6^-) cm^{-1}. ^{1}H NMR (300 MHz, CD_2Cl_2, 20 °C): δ = 8.10 (m, 2 H, Ph), 7.70 (m, 3 H, Ph), 7.45 (m, 3 H, Ph), 7.03 (m, 2 H, Ph), 5.89 (d, $^3J_{H,H}$ = 6.0 Hz, 1 H, 1 H, CH), 5.81 (d, $^3J_{H,H}$ = 6.0 Hz, 1 H, 1 H, CH), 5.39 (br. s, 1 H, CH), 5.17 (br. s, 1 H, C_5H_3), 4.84 (br. s, 1 H, C_5H_3), 4.64 (m, 1 H, OCH_2), 4.57 (br. s, 1 H, C_5H_3), 4.45 (t, $^3J_{H,H}$ = 9.0 Hz, 1 H, CHN), 4.33 (m, 1 H, OCH_2), 4.12 (br. s, 1 H, CH), 3.98 (s, 5 H, C_5H_5), 2.70 [m, 1 H, C*H*$(CH_3)_2$], 2.38 [m, 1 H, C*H*$(CH_3)_2$], 2.32 (s, 3 H, CH_3), 1.17 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H, CH_3), 1.11 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H, CH_3), 1.02 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H, CH_3), 0.67 (d, $^3J_{H,H}$ = 6.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75.4 MHz, CD_2Cl_2, 20 °C): δ = 171.3 (br. s, *C*OCH_2), 139.7–129.2 (Ph), 119.4 (s, *C*CH), 99.9 (m, CH), 99.2 (s, *C*CH), 94.3 (m, CH), 88.4 (br. s, CH), 85.4 (s, CH), 79.7 (s, C_5H_3), 76.4 (d, $^3J_{C,P}$ = 5.4 Hz, CHN), 75.2 (s, C_5H_3), 74.4 (d, $^2J_{C,P}$ = 7.2 Hz, C_5H_3), 72.5 (m, C_5H_5, *C*$CPPh_2$), 69.4 (d, $J_{C,P}$ = 33.2 Hz, $CPPh_2$), 68.4 (s, OCH_2), 31.0 [s, *C*H$(CH_3)_2$], 29.9 [s, *C*H$(CH_3)_2$], 24.4 (s, CH_3), 21.1 (s, CH_3), 19.9 (s, CH_3), 17.4 (s, CH_3), 14.0 (s, CH_3) ppm. ^{31}P{^{1}H} NMR (121.5 MHz, CD_2Cl_2, 20 °C): δ = 23.1 (s) ppm. $C_{38}H_{42}F_6FeN_4OP_2Ru$ (903.62): calcd. C 50.51, H 4.68, N 6.20; found C 49.9, H 4.75, N 6.24.

X-ray Crystal Structure Determination of Complexes 2·CH_2Cl_2, 3a and 6a: Data for **2**·CH_2Cl_2 and **6a** were collected at 293 K with a Bruker AXS SMART 1000 single-crystal diffractometer (Mo-K_α graphite-monochromated radiation, λ = 0.71073 Å) equipped with an area detector,[20] while data for compound **3a** were collected at 293 K with a Philips PW1100 single-crystal diffractometer (Mo-K_α graphite-monochromated radiation, λ = 0.71073 Å). Crystals of **3a** were of poor quality, so the collection of the reflections was limited to θ = 22°. Details of the X-ray data collections are reported in Table 1. The structures were solved by Patterson and direct methods with SHELXS-97 and refined against F^2 with SHELXL-97,[21] with anisotropic thermal parameters for all non-hydrogen atoms. The dichloromethane molecule in **2**·CH_2Cl_2 was found to be disordered over two positions with occupancy factors of 0.60 and 0.40 and refined isotropically. The C≡CPh moiety in **3a** was found to be disordered over two positions with occupancy factors of 0.5 and refined with geometrical restraints (idealised planar ring). Four fluorine atoms of the two independent PF_6^- anions in **6a** were found to be disordered and distributed over two positions (occupancy factors of 0.7 and 0.3). The absolute configuration of the three structures was confirmed by refining the Flack parameter, which showed the enantiopure character of the crystal.

CCDC-608692 (for **2**), -608693 (for **3a**) and -608694 (for **6a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic data for **2**, **3a** and **6a**.[a]

	2·CH_2Cl_2	**3a**	**6a**
Formula	$C_{37}H_{35}ClFeNOPRu{\cdot}CH_2Cl_2$	$C_{45}H_{40}FeNOPRu$	$C_{38}H_{42}ClFeNOPRu{\cdot}PF_6$
Formula weight	817.93	798.67	897.04
Crystal system	orthorhombic	tetragonal	orthorhombic
Space group	$P2_12_12_1$	$P4_32_12$	$P2_12_12_1$
a [Å]	11.399(3)	13.802(2)	10.778(3)
b [Å]	16.106(5)	13.802(2)	19.283(5)
c [Å]	19.434(5)	42.161(7)	36.654(9)
V [Å^3]	3568(2)	8031(2)	7618(3)
Z, D_{calcd} [g cm^{-3}]	4, 1.523	8, 1.321	4, 1.564
F(000)	1664	3280	3648
μ [cm^{-1}]	11.31	8.10	9.93
Reflections collected	54445	5424	72709
Reflections unique	10623 [R_{int} = 0.0365]	4862 [R_{int} = 0.0487]	13434 [R_{int} = 0.0852]
Observed reflections [$I > 2\sigma(I)$]	9535	2559	8666
Parameters	414	419	1001
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0329 wR_2 = 0.0909	R_1 = 0.0658 wR_2 = 0.1516	R_1 = 0.0366 wR_2 = 0.0480
Final R indices [all data]	R_1 = 0.0392 wR_2 = 0.0965	R_1 = 0.1292 wR_2 = 0.1936	R_1 = 0.0705 wR_2 = 0.0529
Flack parameter	–0.02	–0.03	–0.008

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma(F_o)$; $wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\}/\Sigma\{w(F_o^2)^2\}]^{1/2}$.

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