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Synthetic studies of permethylcyclopentadienyl ruthenium(II) complexes involving dppf, (±)-BINAP and (±)-DIOP ligands

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Abstract

1,1′-Bis(diphenylphosphino)ferrocene (dppf) reacted with $RuCl(Ph_3P)_2Cp^*$ to give $RuCl(dppf)Cp^*$ in good yield. The complex reacted with $AgBF_4$ in acetonitrile to give $[Ru(CH_3CN)(dppf)Cp^*]BF_4$ quantitatively and in acetone to give $[Ru(\eta^2\text{-}O_2)(dppf)Cp^*]BF_4$ in good yield. The structure of the latter was determined by X-ray analysis. (±)-BINAP and (±)-DIOP were reacted with $[RuCl_2Cp^*]_n/Zn$ to give RuCl[(±)-BINAP]Cp* and RuCl[(±)-DIOP]Cp*, respectively, in moderate yields. They reacted with phenylacetylene in the presence of NH_4PF_6 to afford the corresponding Ru^{II} phenylacetylide complexes. The asymmetric condensation of phenylacetylene with allyl alcohol in the presence of these diphosphine complexes was unsuccessful.

Keywords: Iron; Ruthenium

1. Introduction

Ruthenium complexes are versatile and capable of catalyzing a variety of organic reactions, and for this reason have been investigated from many viewpoints [1,2]. Ruthenium complexes of the half-sandwich type having a cyclopentadienyl (Cp) ligand are stable and their structure and reactivity have been fully investigated [3]. Recently, various types of ruthenium complexes containing a permethylcyclopentadienyl (Cp^*) ligand, which can stabilize metal complexes by its steric and electronic effect [4], have been reported [5–12]. In addition, quite a number of ruthenium complexes containing phosphines as an additional ligand have been prepared [13–20]. Of these complexes, a considerable number are stable despite containing a coordinatively unsaturated Ru atom as a result of the steric effect of the bulky ligand [17a]. The possibility that the arrangement of coordinatively unsaturated Ru atom in the proximity of ferrocene may result in a dative Fe—Ru bond is interesting because such a dative bond has been recently reported in Ru cluster complexes [21]. Also, it is known that the optically active Ru–phosphine complex is an effective asymmetric catalyst [22]. We report here the synthesis and some properties of Cp^*Ru complexes involving dppf, (±)-BINAP and (±)-DIOP ligands.

2. Results and discussion

The reaction of $RuCl(PPh_3)_2Cp^*$ (**1**) [13,16,23] with 1,1′-bis(diphenylphosphino)ferrocene (dppf) in refluxing benzene gave RuCl(dppf)Cp* (**2**) in excellent yield. The ^1H NMR spectrum of **2** showed the proton signal of the Cp^* ligand at δ 1.02 ppm and those of the ferrocene rings at δ 3.87, 4.06, 4.16 and 5.14 ppm, respectively. Such an asymmetric pattern for the proton signals of the ferrocenyl ring seems to indicate a stepped conformation [24] for **2**.

Reaction of **1** with (+)- and (−)-2,2′-bis(diphenylphosphino)binaphthalenyl [(+)- and (−)-BINAP] or (+)- and (−)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [(+)- and (−)-DIOP] in refluxing benzene was unsuccessful. Hence, the method using a coordinatively unsaturated complex $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ [10a,25] was employed. (+)- and (−)-BINAP were reacted with $[Cp^*RuCl_2]_n$ in the presence of zinc powder to give Cp*[(+)-BINAP]RuCl and Cp*[(−)-BINAP]RuCl (**3** and **4**), respectively, in moderate yields. Similarly, the reaction of $[Cp^*RuCl_2]_2$

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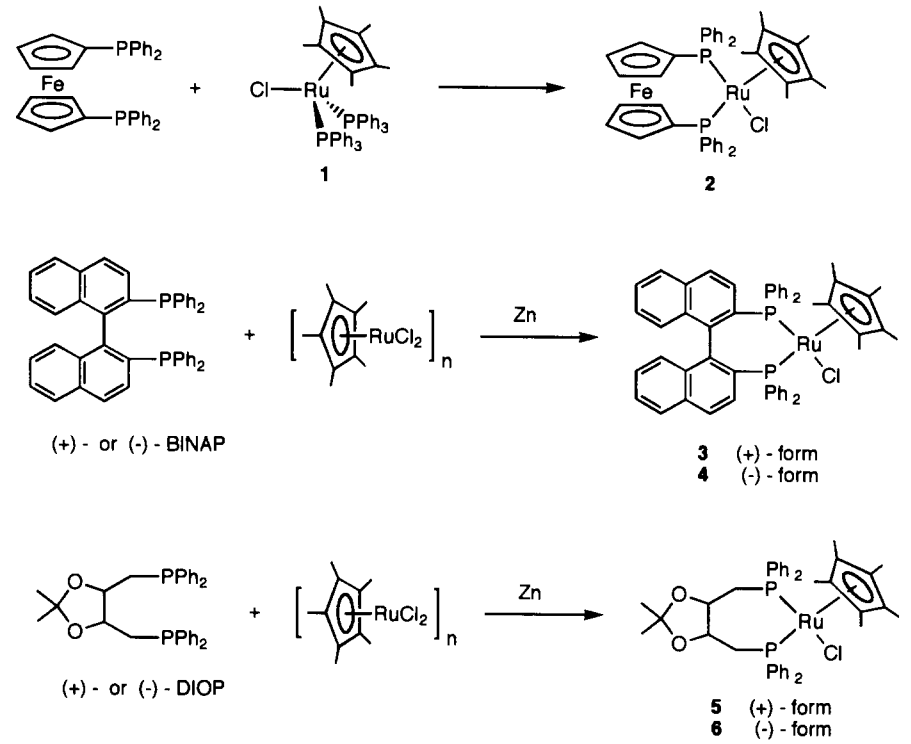


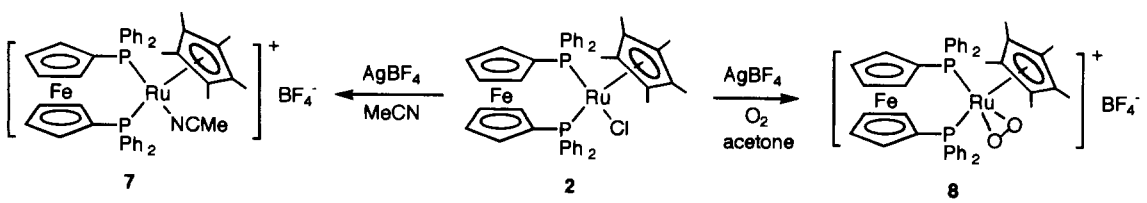
Scheme 1.

with (+)- and (−)-DIOP in the presence of zinc afforded Cp*[(+)-DIOP]RuCl or Cp*[(−)-DIOP]RuCl (**5** and **6**), respectively, in good yield (see Scheme 1).

The structures of **3–6** were confirmed from their ^{1}H NMR spectra and by elemental analyses. The ^{1}H NMR spectrum of **3** showed the methyl protons of the Cp* ligand at δ 1.10 ppm and the aromatic protons at δ 6.06–7.70 ppm in a pattern which was similar to that of the starting (+)-BINAP. In the ^{1}H NMR spectrum of **5**, the protons of the Cp* ligand resonated at δ 1.08 ppm, the unequivalent methyl protons at δ 1.19 and 1.22 ppm, the methyne protons at δ 3.49 and 4.09 ppm, and the methylene protons at δ 2.04, 2.68, 3.10 and 3.70 ppm, respectively. The assignment of the methyne and methylene signals was accomplished by 2D H,H- and C,H-COSY experiments. The optical rotation of **3** and **4** indicates that the optical activity of the ligand is maintained in these complexes.

Reaction of **1** with $AgBF_4$ in acetonitrile gave the cation complex **7**, in which acetonitrile coordinated to the metal as yellow crystals in good yield. Its structure was determined on the basis of the IR and ^{1}H NMR spectra, and from elemental analysis. The IR spectrum of **7** showed the C≡N stretching vibration of the coordinating acetonitrile at 2260 cm^{-1} and the absorption band characteristic of a BF_4 anion at 1134 cm^{-1}. In the ^{1}H NMR spectrum of **7** the proton signal of the coordinating acetonitrile was observed at δ 2.94 ppm and that of the Cp* ligand at δ 1.06 ppm. The ring protons of the ferrocene moiety resonated at δ 4.04, 4.19, 4.33 and 4.34 ppm, respectively. The unusual deshielding ($\Delta \sim$ 1.0 ppm) of the methyl protons of the coordinating acetonitrile may be caused by steric forcing of these protons into the deshielding zone of the ferrocene molecule.

On the other hand, reaction of **1** with 1 equiv. of $AgBF_4$ in acetone gave the oxidized complex **8** as dark brown crystals (see Scheme 2). Complex **8** exhibited the BF_4 group absorption at 1154 cm^{-1} but no carbonyl absorption. In the ^{1}H NMR spectrum of **8**, the proton signals of the ferrocenyl ring resonated at δ 4.28, 4.51, 4.59 and 5.15 ppm, and the methyl proton of the Cp*



Scheme 2.

ligand at δ 1.25 ppm. No signal was observed for the coordinating acetone. Hence, because of its similarity with the reaction product of RuCl(dppe)Cp* and $AgBF_4$ [26], complex **8** is assigned as [Ru(η^2-O_2)(dppf)Cp*]-BF_4. The observation of the O–O stretching vibration at 840 cm^{-1} supports this assignment (the O–O stretching vibration is normally observed at 800–900 cm^{-1}) [27].

An X-ray single-crystal analysis has established the structure of **8**. The corresponding crystallographic parameters are collected in Table 1, the ORTEP view of **8** is shown in Fig. 1 and selected bond distances and bond angles are given in Table 2. The O(1)—O(2) distance is 1.381(11) Å which is similar to that in [Ru(η^2-O_2)(dppe)Cp*]BF_4 [1.398(5) Å] [26] and [RuH(η^2-O_2)(dippe)$_2$]BPh_4 [1.360(10) Å] [28] and [Ru(η^2-O_2)(P ~ O)Cp*]BPh_4 [1.394(9) Å] [29]. The O—O distance is approximately intermediate between the reported peroxide (1.49 Å in H_2O_2) [30] and superoxide distances (1.28 Å in KO_2) [27], suggesting that complex **8** should formally be considered as an Ru^{IV} complex. This suggestion is supported by the observation that the ring-carbon resonance of the Cp* ligand in the ^{13}C NMR spectrum (δ 108.71 ppm) appeared in the down-field region similar to that in the Ru^{IV} complex, [RuBr(Cp)Cp*]$^+$ (δ 112.4 ppm), in contrast to the corresponding carbon resonance of the Ru^{II} complex, RuCl(dppf)Cp* (δ 88.57 ppm). The Ru—O distances, 2.035(8) and 2.029(8) Å, are similar to those in [Ru(η^2-O_2)(dppe)Cp*]BF_4 [2.040(3) and 2.023(3) Å] [26] and [RuH(η^2-O_2)(dippe)$_2$]BPh_4 [2.04(1) and 2.00(1) Å] [28].

Table 1
Crystal and intensity collection data for **8**

Molecular formula	$C_{44}H_{43}BF_4O_2P_2FeRu$
Molecular weight	909.50
Crystal system	monoclinic
Space group	$P21/a$ (No. 14)
a (Å)	15.193(6)
b (Å)	25.08(1)
c (Å)	11.010(6)
β (°)	109.69(4)
V (Å^3)	3951(3)
Z	4
D_{cal} (g cm^{-3})	1.53
Crystal dimensions (mm)	0.22 × 0.24 × 0.12
Linear absorption coefficient (cm^{-1})	8.761
Radiation (λ, Å)	Mo Kα (0.71073)
Reflection limits (hkl)	$19 < h < 18$, $-7 < k < 32$, $0 < l < 13$
Total no. of reflections measured	8965
No. of unique reflections	8029
No. of reflections used in least squares	4821
Least-squares parameters	600
R	0.075
R_w	0.078
Max. peak in final Fourier map, e Å^{-3}	1.21
Min. peak in final Fourier map, e Å^{-3}	−1.23

The results described above seem to suggest that the

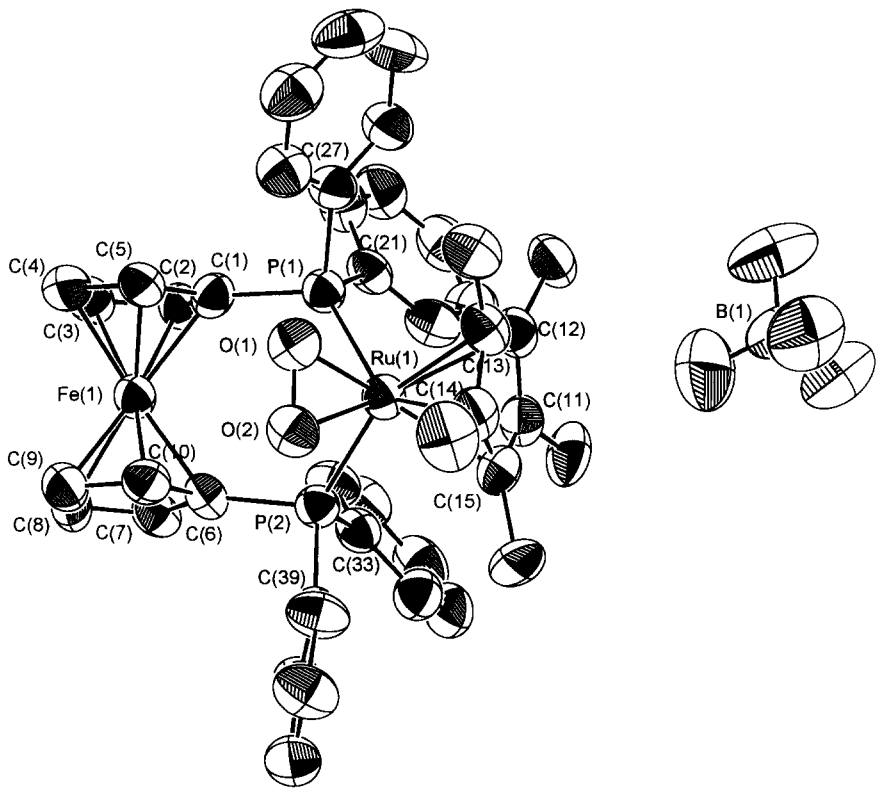


Fig. 1. ORTEP view of complex **8**.

Table 2
Selected bond distances (Å) and bond angles (°) for **8**

Bond distances			
Ru–P(1)	2.408(3)	Ru–P(2)	2.390(3)
Ru–O(1)	2.036(8)	Ru–O(2)	2.029(8)
Ru–C(11)	2.289(11)	Ru–C(12)	2.339(11)
Ru–C(13)	2.301(10)	Ru–C(14)	2.234(12)
Ru–C(15)	2.266(11)	P(1)–C(1)	1.812(11)
P(2)–C(6)	1.790(11)	O(1)–O(2)	1.381(11)
Bond angles			
P(1)–Ru–P(2)	91.6(1)	P(1)–Ru–O(1)	77.6(3)
P(1)–Ru–O(2)	106.9(3)	P(2)–Ru–O(1)	107.1(3)
P(2)–Ru–O(2)	80.0(3)	O(1)–Ru–O(2)	39.7(4)
Ru–P(1)–C(1)	119.8(4)	Ru–P(1)–C(21)	119.2(4)
Ru–P(1)–C(27)	109.0(4)	Ru–P(2)–C(6)	116.5(4)
Ru–P(2)–C(33)	117.8(4)	Ru–P(2)–C(39)	114.4(4)

reaction between **1** and an Ag^+ ion in acetone initially yields a coordinatively unsaturated Ru complex, which may be weakly coordinated by acetone. The complex then absorbs oxygen from the atmosphere to give the dioxygen complex **8**. A partial electronic interaction between the Fe atom of the ferrocene moiety and the Ru site may be anticipated in **8**, because ferrocene is an electron-rich system and the Ru atom is in the electron-deficient Ru^{IV} state. However, upon refluxing a solution of **8** in acetonitrile, no removal of the η-O_2 ligand was observed as in the similar reaction of Ru(η-O_2)(dppe)Cp* [26]. Hence, there is little, if any, electron donation from the Fe atom to Ru atom in complex **8**.

Complexes **3–6** reacted with phenylacetylene in the presence of NH_4PF_6, and following treatment with base gave the Ru^{II} phenylacetylide complexes **9–12**, respectively, in moderate yield (see Scheme 3). The structures of complexes **9–12** have been confirmed by elemental analysis, and by IR and ^1H NMR spectroscopy. Thus, for example, the C≡C stretching vibration appeared at 2072 cm^{-1} in the IR spectrum of **11**, while in the ^1H NMR spectrum this complex the isopropyl protons resonated at δ 1.02 and 1.20 ppm, the methyl proton of the Cp* ligand at δ 1.21 ppm, the methyne protons at δ 3.47 and 4.38 ppm, and the methylene protons at δ 1.96, 2.79, 3.04 and 4.03 ppm, respectively. Signal assignment has been based on the similarity to the spectrum of the starting complex **5**. It has been reported recently that the reaction of phenylacetylene with allyl alcohols proceeds catalytically in the presence of $Cp(Ph_3P)_2RuCl$ and NH_4PF_6 [31]. For this reason, a similar catalytic reaction of phenylacetylene with allyl alcohol in the presence of complexes **3–6** and NH_4PF_6 was attempted. However, the desired reaction was not observed. This lack of success may probably be attributed to steric hindrance caused by the bulky Cp* ligand in complexes **3–6**.

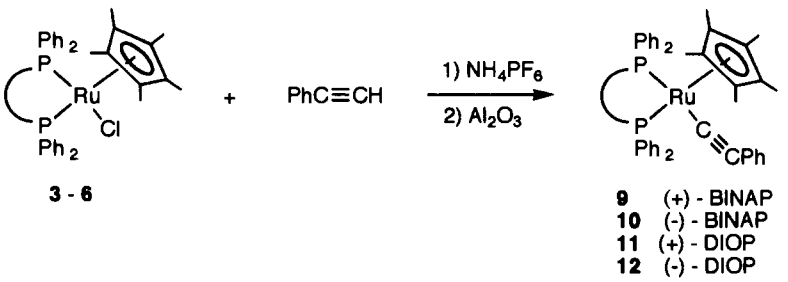
3. Experimental details

3.1. General

$[Cp^*RuCl_2]_n$ [10a] and $Cp^*(Ph_3P)_2RuCl$ (**1**) [23] were prepared by literature methods. All the other chemicals were reagent grade and were used as received from common commercial sources. Solvents were dried by standard procedures. IR spectra were recorded as KBr pellets on a Hitachi 270-50 spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-400 instrument using TMS as internal standard. ^{31}P NMR signals were referred to external 85% H_3PO_4 as standard.

3.2. Preparation of Cp*(dppf)RuCl (2)

A suspension of **1** (0.41 g, 0.52 mmol) and dppf (0.29 g, 0.52 mmol) in benzene (25 ml) was heated at reflux for 2 h under dinitrogen. The resulting yellow powder was filtered and dried. Yield, 0.39 g (90%). Recrystallization from toluene gave an analytical sample. M.p. 205°C. Analysis: found: C, 65.70; H, 5.44%. $C_{44}H_{43}ClPFeRu \cdot 1/2C_6H_5CH_3$ requires: C, 65.41; H, 5.43%. ^1H NMR ($CDCl_3$) δ: 1.02 (s, 15H); 3.87, 4.06, 4.16, 5.14 (s × 4, 8H); 7.31–7.67 (m, 20H) ppm. ^{13}C NMR ($CDCl_3$) δ: 8.79 (C_5Me_5); 88.57 (C_5Me_5); 126.3–134.7 (m, Ph) ppm.



Scheme 3.

3.3. Preparation of Cp*[(+)-BINAP]RuCl (3)

A mixture of $[Cp^*RuCl_2]_n$ (92 mg, 0.3 mmol), (+)-BINAP (187 mg, 0.3 mmol) and Zn powder (92 mg, 1.4 mmol) in benzene (10 ml) was stirred under dinitrogen bubbling for 6 h at room temperature. After addition of hexane (10 ml), the reaction mixture was filtered. On cooling the filtrate, orange crystals of **3** precipitated. Yield, 80 mg (30%). M.p. 287°C. Analysis: Found: C, 72.31; H, 5.41%. $C_{54}H_{47}P_2ClRu$ requires: C, 72.51; H, 5.30%. ^1H NMR ($CDCl_3$) δ: 1.10 (s, 15H, Me—Cp); 6.04–7.70 (m, 32H, Ph) ppm. ^{31}P NMR ($CDCl_3$) δ: 40.76 (d, $J = 51$ Hz); 49.34 (d, $J = 51$ Hz) ppm. $[\alpha]_D = 1091°$.

Cp*[(−)-BINAP]RuCl (**4**) was prepared in a similar manner. Yield, 80 mg (30%). M.p. 285°C. Analysis: Found: C, 72.78; H, 5.44%. $C_{54}H_{47}P_2ClRu$ requires: C, 72.51; H, 5.30%. ^1H NMR ($CDCl_3$) δ: 1.10 (s, 15H, Me—Cp); 6.04–7.70 (m, 32H, Ph) ppm. $[\alpha]_D = -1026°$.

3.4. Preparation of Cp*[(+)-DIOP]RuCl (5)

A mixture of $[Cp^*RuCl_2]_n$ (92 mg, 0.3 mmol), (+)-DIOP (147 mg, 0.3 mmol) and Zn powder (92 mg, 1.4 mmol) in benzene (10 ml) was stirred under dinitrogen bubbling for 6 h at room temperature. After evaporation, the oily residue was dissolved in acetonitrile (1 ml) and the solution was then cooled on an ice bath to give **5** as orange crystals (120 mg, 52%). M.p. 264°C. Analysis: Found: C, 64.20; H, 6.15%. $C_{41}H_{47}ClO_2P_2Ru$ requires: C, 63.93; H, 6.15%. ^1H NMR ($CDCl_3$) δ: 1.08 (s, 15H; Me—Cp); 1.19, 1.22 (s, 3H, Me); 2.04, 2.68, 3.10, 3.70 (m, 1H, CH_2); 3.49, 4.09 (m, 1H, CH); 7.05–7.67 (m, 20H, Ph) ppm. ^{13}C NMR ($CDCl_3$) δ: 9.06 (s, C_5Me_5); 26.89, 27.18 (s, Me); 29.70 (d, $J =$ 21.3 Hz, CH_2); 36.48 (dd, $J = 24.0$, 5.6 Hz, CH_2); 74.68 (d, $J = 12.2$ Hz, CH); 80.12 (d, $J = 7.7$ Hz, CH); 107.95 (s, C); 127.3–142.2 (m, Ph) ppm. ^{31}P NMR ($CDCl_3$) δ: 30.79 (d, $J = 38$ Hz); 34.47 (d, $J = 38$ Hz) ppm. $[\alpha]_D = 65°$.

Cp*[(−)-DIOP]RuCl (**6**) was prepared in a similar manner. Yield, 120 mg (52%). M.p. 262°C. Analysis: Found: C, 64.03; H, 6.17; N, 0.88%. $C_{41}H_{47}ClO_2P_2Ru \cdot 1/2CH_3CN$ requires: C, 63.78; H, 6.18; N, 0.68%. ^1H NMR ($CDCl_3$) δ: 1.08 (s, 15H, Me—Cp); 1.19, 1.22 (s, 3H, Me); 2.04, 2.68, 3.10, 3.70 (m, 1H, CH_2); 3.49, 4.09 (m, 1H, CH); 7.05–7.67 (m, 20H, Ph) ppm. $[\alpha]_D = -62°$.

3.5. Preparation of [Ru(CH$_3$CN)(dppf)Cp*]BF$_4$ (7)

To a suspension of **2** (42 mg, 0.05 mmol) in anhydrous acetone (5 ml) was added $AgBF_4$ (10 mg, 0.05 mmol). The mixture was stirred for 2 h under a dinitrogen atmosphere. The reaction mixture was evaporated and the residue dissolved in CH_2Cl_2 (5 ml). After the mixture had been filtered and the solvent evaporated, the residue was dissolved in CH_3CN (2 ml) and the solution diluted with anhydrous ether (7 ml). On storing the solution in a refrigerator overnight, yellow crystals (36 mg, 76%) were obtained. M.p. 210°C. Analysis: Found: C, 60.33; H, 5.34; N, 2.65%. $C_{46}H_{46}BF_4NP_2FeRu \cdot CH_3CN$ requires: C, 60.07; H, 5.14; N, 2.91%. ^1H NMR ($CDCl_3$) δ: 1.06 (s, 3H, Me—Cp); 2.94 (s, 3H, CH_3CN); 4.04, 4.19, 4.33, 4.34 (bs, 2H, Fc); 7.41–7.72 (m, 20H, Ph) ppm. ^{31}P NMR ($CDCl_3$) δ: 44.67 ppm. IR (KBr) (cm^{-1}): 2260 (C≡N); 1134 (BF_4).

3.6. Preparation of [Ru(η-O$_2$)(dppf)Cp*]BF$_4$ (8)

To a suspension of **2** (42 mg, 0.05 mmol) in anhydrous acetone (5 ml) was added $AgBF_4$ (10 mg, 0.05 mmol). The mixture was stirred for 2 h in air. After the reaction mixture had been filtered, the filtrate was diluted with anhydrous ether (5 ml). On storing the solution in a refrigerator overnight, brown crystals (31 mg, 70%) were obtained. M.p. 172°C. Analysis: Found: C, 57.97; H, 5.09%. $C_{44}H_{43}BF_4O_2P_2FeRu$ requires: C, 58.11; H, 4.93%. ^1H NMR (acetone-d_6) δ: 1.25 (s, 3H, C_5Me_5); 4.28 (bs, 2H, Fc-β); 4.51 (bs, 2H, Fc-α); 4.59 (bs, 2H, Fc-β); 5.15 (bs, 2H, Fc-α); 7.46–7.85 (m, 20H, Ph) ppm. ^{13}C NMR (acetone-d_6) δ: 9.43 (Me—Cp); 70.76 (Fc-β); 74.86 (Fc-α); 75.44 (Fc-β); 76.09 (Fc-α); 87.08 (Fc-*ipso*); 108.71 (C_5Me_5); 128.30 (Ph-*ipso*); 129.14, 129.41 (Ph-*m*); 132.17, 133.56 (Ph-*p*); 134.69, 136.82 (Ph-*o*); 135.76 (Ph-*ipso*) ppm. ^{31}P NMR ($CDCl_3$) δ: 38.57 ppm. IR (KBr) (cm^{-1}): 1154 (BF_4); 840 (O—O).

3.7. Reaction of 3–6 with PhC≡CH

A mixture of **3** (55 mg, 0.06 mmol), PhC≡CH (2 drops) and NH_4PF_6 (10 mg, 0.06 mmol) in MeOH (5 ml) was stirred under dinitrogen for 2 h at room temperature. After evaporation, the residue was chromatographed on Al_2O_3 by elution with CH_2Cl_2 to give **9** as orange crystals (24 mg, 42%). Recrystallization from $MeOH/CH_2Cl_2$ gave an analytical sample. M.p. 205°C (dec.). Analysis: Found: C, 72.26; H, 5.23%. $C_{54}H_{48}P_2Ru \cdot 1/2CH_2Cl_2$ requires: C, 72.53; H, 5.47%. IR (KBr) (cm^{-1}): 2077 (C≡C). ^1H NMR ($CDCl_3$) δ: 1.27 (s, 15H, Me); 6.09–7.95 (m, 37H, Ph + Naph) ppm. ^{13}C NMR ($CDCl_3$) δ: 9.77 (C_5Me_5); 94.04 (C_5Me_5); 111.95 (≡*C*Ph); 122–141.5 (m, Ph + Naph + Ru*C*≡) ppm.

Complex **10** was prepared in a similar manner. M.p. 205°C. Analysis: Found: C, 72.26; H, 5.29%. $C_{54}H_{48}P_2Ru \cdot 1/2CH_2Cl_2$ requires: C, 72.53; H, 5.47%. IR (KBr) (cm^{-1}): 2076 (C≡C). ^1H NMR ($CDCl_3$) δ: 1.27 (s, 15H, Me); 6.09–7.95 (m, 37H, Ph + Naph) ppm. ^{13}C NMR ($CDCl_3$) δ: 9.77 (C_5Me_5);

94.04 (C_5Me_5); 111.95 (≡CPh); 122–141.5 (m, Ph + Naph + RuC≡) ppm.

To a solution of **5** (59 mg, 0.08 mmol) in MeOH (2 ml) and CH_2Cl_2 (5 ml) were added PhC≡CH (2 drops) and NH_4PF_6 (13 mg, 0.08 mmol). The mixture was stirred under dinitrogen for 2 hr at room temperature. After evaporation, the residue was chromatographed on Al_2O_3 by elution with CH_2Cl_2 to give **11** as yellow crystals (35 mg, 52%). Recrystallization from cyclohexane/CH_2Cl_2 gave an analytical sample. M.p. 220°C. Analysis: Found: C, 70.49; H, 6.37%. $C_{49}H_{52}O_2P_2Ru$ requires: C, 70.40; H, 6.27%. ^{1}H NMR ($CDCl_3$) δ: 1.02 (s, 3H, Me); 1.19 (s, 3H, Me); 1.21 (s, 15H, Me—Cp); 1.96, 2.79, 3.05, 4.03 (m, 1H, CH_2); 3.47, 4.39 (m, 1H, CH); 6.93–8.08 (m, 15H, Ph) ppm. IR (KBr) (cm^{-1}): 2072 (C≡C).

Complex **12** was prepared in a similar manner. M.p. 220°C. Analysis: Found: C, 70.53; H, 6.23%. $C_{49}H_{52}O_2P_2Ru$ requires: C, 70.40; H, 6.27%. ^{1}H NMR ($CDCl_3$) δ: 1.02 (s, 3H, Me); 1.19 (s, 3H, Me); 1.21 (s, 15H, Me—Cp); 1.96, 2.79, 3.05, 4.03 (m, 1H, CH_2); 3.47, 4.39 (m, 1H, CH); 6.93–8.08 (m, 15H, Ph) ppm. ^{13}C NMR ($CDCl_3$) δ: 9.35 (C_5Me_5); 26.63, 27.24 (Me); 31.91 (d, J = 28.0 Hz, CH_2); 37.43 (dd, J = 23.9, 5.6 Hz, CH_2); 74.70 (d, J = 11.4 Hz, CH); 80.16 (dd, J = 7.8, 1.6 Hz, CH); 92.90 (C_5Me_5); 107.95 (CMe_2); 111.80 (≡CPh); 122.7–141.4 (Ph + RuC≡) ppm. IR (KBr) (cm^{-1}): 2071 (C≡C).

3.8. Catalytic reaction of PhC≡CH with allyl alcohol

A mixture of PhC≡CH (0.1 ml, 1 mmol), allyl alcohol (4 ml), Cp*[(+)-BINAP]RuCl (54 mg, 0.06 mmol)$_4$ and NH_4PF_6 (16 mg, 0.1 mmol) was heated at 100°C in a sealed tube for 10 h. After evaporation of the allyl alcohol, the residue was chromatographed on SiO_2. Only a trace amount of $PhCH_2COCHCHCH_3$ was isolated however. ^{1}H NMR ($CDCl_3$) δ: 1.87 (dd, J = 7.2, 1.8 Hz, 3H, Me); 3.81 (s, 2H, CH_2); 6.16, 6.92 (m, 1H, CH); 7.24 (m, 5H, Ph) ppm.

3.9. Structure determination

Crystal data for **8**: $C_{44}H_{43}BF_4O_2P_2FeRu$, FW = 909.50; monoclinic, $P21/a$; a = 15.193(6), b = 25.08(1), c = 11.010(6) Å; β = 109.69(4)°; V = 3951(3) Å^3; Z = 4; D_{calc} = 1.53 g cm^{-3}; μ(Mo Kα) = 8.761 cm^{-1}; T = 298 K; crystal size 0.22 × 0.24 × 0.12 mm.

Data collection was performed at room temperature on a Mac Science MXC18K diffractrometer with graphite monochromated Mo Kα radiation and a 18-kW rotating anode generator. Of 8965 reflections collected, 8029 reflections were unique, of which 8606 reflections with $I > 3.00\ \sigma\ (I)$ were used for refinement. The structure was solved using the Dirdif–Patty method with CRYSTAN-G (software package for structure determination) and refined by a full-matrix least-squares procedure. Absorption correction with the ψ-scan method and anisotropical refinements for non-hydrogen atoms were carried out; R = 0.075 and Rw = 0.078.

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