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# Synthesis and reaction of ruthenium(II) complexes containing heteroatom donor (O, N, and P) tethered to $\eta^6$-arene ring

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**Abstract**

Synthesis of ruthenium(II) complexes chelated by the $\eta^6$-arene ring and a pendent donor atom (O, N, and P) is described. The alcohol-containing $\eta^6$-arene ruthenium complexes $[Ru\{\eta^6\text{-}C_6H_5(CH_2)_3OH\}(PR_3)Cl_2]$ (**1a** R = Ph; **1b** R = Et) and $[Ru\{\eta^6\text{-}C_6H_5(CH_2)_3OH\}L_2Cl]BF_4$ (**2a** $L_2$ = 2,2′-bipyridine; **2b** $L_2$ = 1,10-phenanthroline; **2c** $L_2$ = 2,2-bis[4(*R*)-phenyl-1,3-oxazolon-2-yl]propane, (*R*)-bpop) were prepared by treatment of $[Ru\{\eta^6\text{-}C_6H_5(CH_2)_3OH\}Cl_2]_2$ with tertiary phosphines or *N*,*N*′-chelate ligands/$NaBF_4$, respectively. Addition of 1 equiv. of $AgBF_4$ to a solution of complexes **1** or **2** gave alcohol chelate complexes $[Ru\{\eta^6\text{:}\eta^1\text{-}C_6H_5(CH_2)_3OH\}(PR_3)Cl]BF_4$ (**3a**–**b**) or $[Ru\{\eta^6\text{:}\eta^1\text{-}C_6H_5(CH_2)_3OH\}L_2](BF_4)_2$ (**4a**–**c**), respectively. Although stable in MeOH, the alcohol–Ru chelate bond of **3** and **4** was cleaved by $Cl^-$ ion. Treatment of **4** with bases ($OH^-$, $R_3N$) led to abstraction of the hydroxy proton to give alkoxy chelate complexes $[Ru\{\eta^6\text{:}\eta^1\text{-}C_6H_5(CH_2)_3O\}L_2]BF_4$ (**5a**–**c**). In $CH_2Cl_2$ acidity of the hydroxy proton in **4c** was revealed to be comparable to that of *N*-methylbenzylammonium cation ($pK_a$ in $H_2O$, ca. 11). Amino chelate complexes $[Ru\{\eta^6\text{:}\eta^1\text{-}C_6H_5(CH_2)_nNH_2\}(PPh_3)Cl]BF_4$ (**7a** $n = 3$; **7b** $n = 2$) were prepared by treatment of ammonium complexes $[Ru\{\eta^6\text{-}C_6H_5(CH_2)_nNH_3Cl\}(PPh_3)Cl_2]$ (**6a** $n = 3$; **6b** $n = 2$) with 1 equiv. of NaOH and $NaBF_4$. **7** were stable to the attack of $Cl^-$ ion. In contrast, the similar treatment of dimethylammonium derivative $[Ru\{\eta^6\text{-}C_6H_5(CH_2)_3NMe_2\text{-}HCl\}(PPh_3)Cl_2]$ (**8**) with KOH gave a non-chelate complex $[Ru\{\eta^6\text{-}C_6H_5(CH_2)_3NMe_2\}(PPh_3)Cl_2]$ (**9**). Phosphorous chelate complexes $[Ru\{\eta^6\text{:}\eta^1\text{-}C_6H_5(CH_2)_3OPPR_2\}Cl_2]$ (**10a** R = Ph; **10b** R = $^i$Pr) were prepared by reaction of $[Ru\{\eta^6\text{-}C_6H_5(CH_2)_3OH\}Cl_2]_2$, $PPR_2Cl$, and $EtN^iPr_2$. Treatment of **10b** with $AgBF_4$ and CO (1 atm) gave the cationic carbonyl complex $[Ru\{\eta^6\text{:}\eta^1\text{-}C_6H_5(CH_2)_3OP^iPr_2\}(CO)Cl]BF_4$ (**11**). © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Arene complexes; Ruthenium complexes; Heteroatom donor complexes; Crystal structure

## 1. Introduction

In recent years, the coordination chemistry of chelated ligands containing mixed functionalities on transition metal centers has been an extremely active area of research [1]. In particular, transition metal complexes with a coordination group which is tethered to the cyclopentadienyl ligand have attracted attention from viewpoints of improving and elucidating catalytic processes such as olefin polymerization [2–4]. Nitrogen [2], oxygen [3], and phosphorous [4] have been used as the coordination atom. Although $\eta^6$-arene ligands are isoelectronic with the $\eta^5$-cyclopentadienyl ligands and the synthesis of modified $\eta^6$-arene ligands seemed to be easier than that of the modified cyclopentadienyl ligands, transition metal complexes with a coordination group tethered to the $\eta^6$-arene ligand have received much less attention [5]. Here we report the synthesis of ruthenium(II) complexes chelated by alcohol, amine, or phosphite donor and $\eta^6$-arene ligand. In spite of the key role as intermediates in homogeneous catalytic [6a,b] as well as biochemical transformations [6c–e], late transition metal alcohol complexes have rarely been subjects of molecular level coordination chemistry because of the weak M–O bond. Studies of the synthesis and properties of moderately stable alcohol complexes are thus of potential interest to development of some catalytic processes. Part of the present work has been published in a preliminary communication [7].

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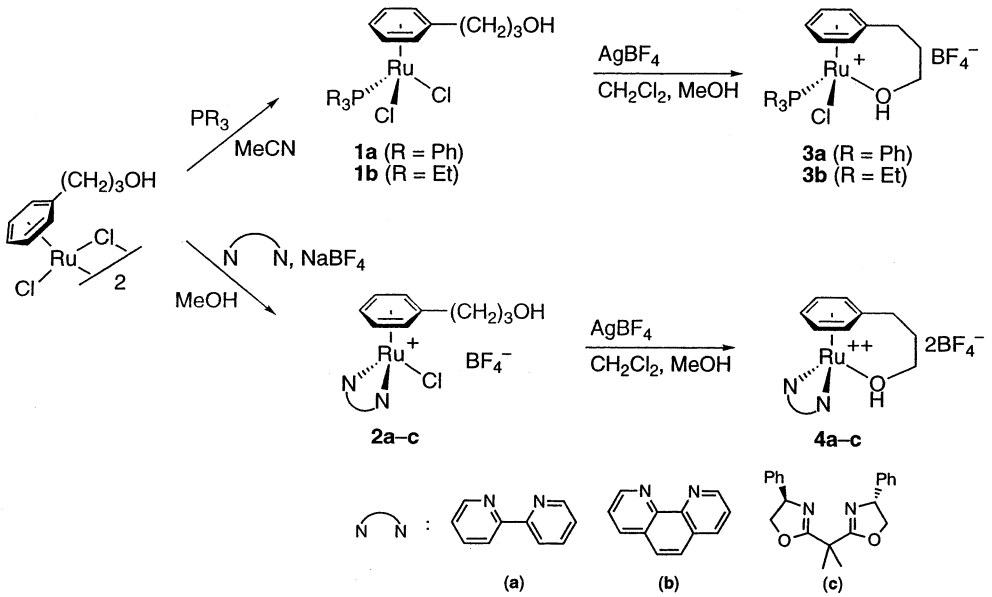



Scheme 1.

## 2. Results and discussion

### 2.1. Synthesis and structures of alcohol chelate complexes

Cyclohexadiene derivatives with a terminal alcohol functionality $C_6H_7(CH_2)_nOH$ ($n = 2$, 3) were prepared by *Birch reduction* [8] of commercially available $C_6H_5(CH_2)_nOH$. Treatment of $RuCl_3$ with $C_6H_7(CH_2)_3$-OH (5 equiv.) in refluxing ethanol gave orange solids of $\eta^6$-arene ruthenium dichloride $[Ru\{\eta^6\text{-}C_6H_5(CH_2)_3\text{-}OH\}Cl_2]$ in high yield. This was converted to the monomeric neutral phosphine complexes **1a**–**b** or the cationic complexes containing *N*,*N*′-chelate **2a**–**c** when treated with the tertiary phosphines or the *N*,*N*′-donor and $NaBF_4$, respectively (Scheme 1). The solid state structure of **2a** is shown in Fig. 1 (Table 1). Reaction of **1** or **2** with $AgBF_4$ (1 equiv.) in $CH_2Cl_2$ and methanol at r.t. gave the cationic complexes **3a**–**b** or dicationic complexes **4a**–**c**, respectively (Scheme 1). The chelate coordination of the alcohol ligand in **4b** and **4c** was confirmed by X-ray crystallography (Figs. 2 and 3; Tables 2 and 3). The $^1H$ NMR data of **3** and **4c** in $CDCl_3$ or $CD_2Cl_2$ at r.t. showing two diastereotopic $OCH_2$ resonances of the alcohol group[1] were diagnostic for the coordination of alcohol ligand in solution, while only a single $OCH_2$ resonance was observed in **1** and **2**. Reaction of $AgBF_4$ with the shorter side-arm analog $[Ru\{\eta^6\text{-}C_6H_5\text{-}(CH_2)_2OH\}(bpop)Cl]BF_4$ (bpop = 2,2-bis[4(*R*)-phenyl-1,3-oxazolon-2-yl]propane), which was obtained similarly to **2c** starting from $C_6H_7(CH_2)_2OH$, did not afford the corresponding alcohol chelate complex, as suggested by the appearance of only a single $OCH_2$ resonance.

$^1H$ NMR spectra of **4c** measured in $CD_3OD$ were almost the same as those in $CDCl_3$ or $CD_2Cl_2$, suggesting that coordination of the pendent alcohol is maintained even in MeOH. The analogous coordination of the $(CH_2)_3OH$ group of **4a** and **4b** in $CD_3OD$ was also

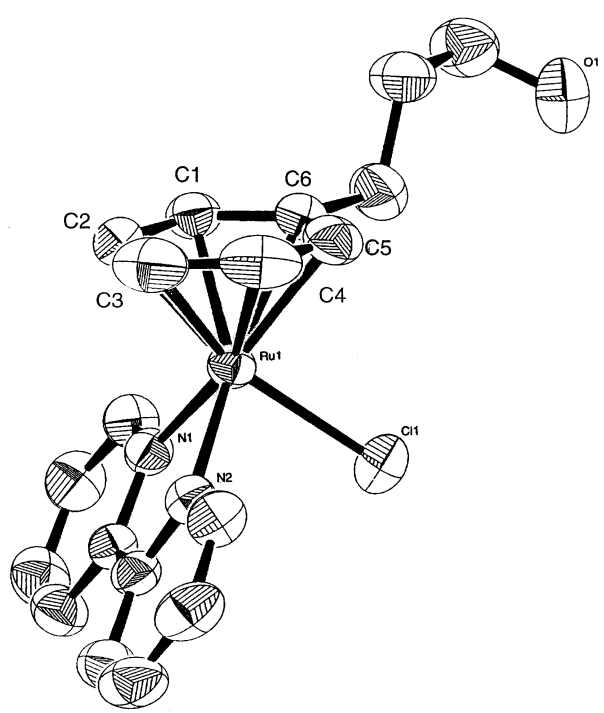



Fig. 1. ORTEP drawing of **2a**. $BF_4$ was omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

[1] The chemical shifts of $OCH_2$ protons in **3** and **4c** are as follows (see Section 3). **3a**: $\delta$ 3.44, 3.78; **3b**: $\delta$ 3.48, 3.92; **4c**: $\delta$ 2.18, 3.55.

Table 1
Selected bond distance (Å) and angle (°) of **2a**

| | |
|---|---|
| Ru(1)–Cl(1) | 2.397(1) |
| Ru(l)–N(1) | 2.077(4) |
| Ru(1)–N(2) | 2.080(4) |
| Ru(1)–C(1) | 2.188(5) |
| Ru(1)–C(2) | 2.158(5) |
| Ru(1)–C(3) | 2.158(5) |
| Ru(1)–C(4) | 2.196(5) |
| Ru(1)–C(5) | 2.192(5) |
| Ru(1)–C(6) | 2.211(5) |
| Cl(1)–Ru(1)–N(1) | 85.2(1) |
| Cl(1)–Ru(1)–N(2) | 84.5(1) |
| N(1)–Ru(1)–N(2) | 76.9(1) |

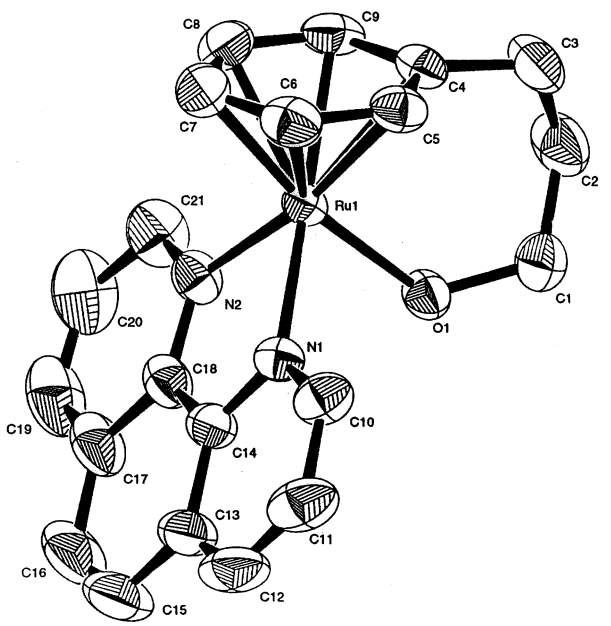



Fig. 2. ORTEP drawing of **4b**. $BF_4$ was omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

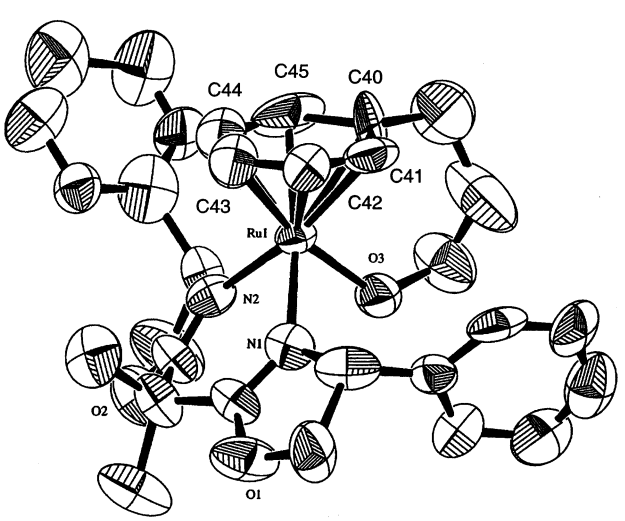



Fig. 3. ORTEP drawing of **4c**. $BF_4$ and $H_2O$ were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

assessed by $^1H$ NMR spectra. Thus, the proton resonances of this group in freely rotating C–C bond in **2a** and **2b** appeared as a typical $A_2M_2X_2$ spin system, while those in **4a** and **4b** appeared as more complex AA′MM′XX′ patterns since the free rotation about the C–C axis is restricted. $^1H$ NMR spectra of **3** measured in $CD_3OD$ were too complex to allow any structure assessment.

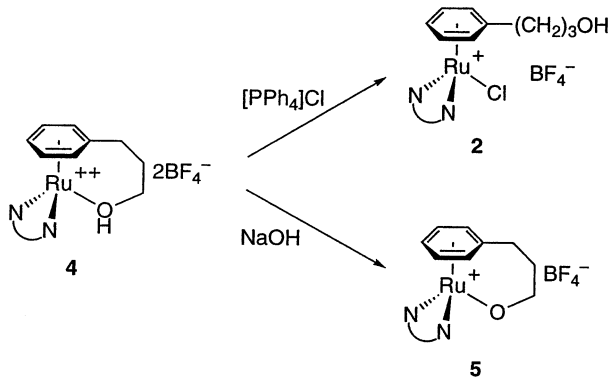
The alcohol chelate complexes **3** and **4** readily reacted with 1 equiv. of $[PPh_4]Cl$ to give the original chloride complexes **1** and **2** in almost quantitative yields. Of particular note was the reaction of **4** with NaOH in MeOH affording alkoxide complexes **5** (Scheme 2). No β-hydrogen elimination giving aldehyde functionalities has been observed in **5**, presumably owing to difficulty for the Ru–O–C–H framework to lie in a plane. The solid state structure of **5a** is shown in Fig. 4 (Table 4). Significantly, the bond distance of Ru–O in **5a** was shorter than that of Ru–O in **4b** by approximately 0.1 Å. There was no difference of the bond angles around the Ru center and the distance between Ru and the arene ring. One molecule of MeOH is contained in the unit cell. The distance between the oxygen of methanol and the Ru-bound alkoxo oxygen

Table 2
Selected bond distance (Å) and angle (°) of **4b**

| | |
|---|---|
| Ru(1)–O(1) | 2.145(3) |
| Ru(1)–N(1) | 2.096(3) |
| Ru(1)–N(2) | 2.096(3) |
| Ru(1)–C(4) | 2.204(4) |
| Ru(1)–C(5) | 2.196(4) |
| Ru(1)–C(6) | 2.165(4) |
| Ru(1)–C(7) | 2.163(5) |
| Ru(1)–C(8) | 2.168(4) |
| Ru(1)–C(9) | 2.189(4) |
| O(1)–Ru(1)–N(1) | 81.0(1) |
| O(1)–Ru(1)–N(2) | 83.2(1) |
| N(1)–Ru(1)–N(2) | 77.9(1) |

Table 3
Selected bond distance (Å) and angle (°) of **4c**

| | |
|---|---|
| Ru(1)–O(3) | 2.11(2) |
| Ru(1)–N(1) | 2.10(2) |
| Ru(1)–N(2) | 2.14(2) |
| Ru(1)–C(40) | 2.24(3) |
| Ru(1)–C(41) | 2.13(3) |
| Ru(1)–C(42) | 2.20(2) |
| Ru(1)–C(43) | 2.18(3) |
| Ru(1)–C(44) | 2.11(4) |
| Ru(1)–C(45) | 2.13(5) |
| O(3)–Ru(1)–N(1) | 85.2(8) |
| O(3)–Ru(1)–N(2) | 81.6(8) |
| N(1)–Ru(1)–N(2) | 82.0(8) |




Scheme 2.

Table 4
Selected bond distance (Å) and angle (°) of **5a**

| | |
|---|---|
| Ru(1)–O(1) | 2.050(5) |
| Ru(1)–N(1) | 2.064(6) |
| Ru(1)–N(2) | 2.107(6) |
| Ru(1)–C(1) | 2.203(8) |
| Ru(1)–C(9) | 2.178(7) |
| Ru(1)–C(2) | 2.179(7) |
| Ru(1)–C(4) | 2.205(7) |
| Ru(1)–C(19) | 2.191(8) |
| Ru(1)–C(18) | 2.185(9) |
| O(1)–Ru(1)–N(1) | 82.5(2) |
| O(1)–Ru(l)–N(2) | 80.9(2) |
| N(1)–Ru(1)–N(2) | 77.6(3) |

iis 2.67 Å, suggesting the existence of the hydrogen bond with regard to these oxygen atoms.

### 2.2. Synthesis of amine chelate complexes

Cyclohexadiene derivatives with nitrogen donor atom were prepared by Birch reduction. However, the reaction of these cyclohexadienes with $RuCl_3$, a common method of preparing arene ruthenium dimer complexes, did not work well. So, the cyclohexadienes with amine were first treated with hydrochloric acid to give the ammonium salts, which were subsequently treated with $RuCl_3$ to give the $\eta^6$-arene dimer complexes containing the ammonium side-chain (Scheme 3). Then these were treated with triphenylphosphine in refluxing MeCN for 2 h to give monomeric complexes **6**, which gave amino chelate complexes **7** upon treatment with sodium hydroxide and $NaBF_4$ (Scheme 3). The two methylene protons geminal to N in **7** were observed non-equivalent. Unlike the failure of the $CH_2CH_2OH$ side-arm to form a stable chelate structure (see above), **7b** with the side-arm of the similar length was stable enough to maintain the coordination of the amine nitrogen.

Treatment of a dimethylamino derivative **8**, synthesized similarly to **6**, with KOH gave a non-chelate complex **9** (Scheme 4). In the $^1H$ NMR spectra of **9** the resonance of the methylene protons geminal to N and the N-methyl resonance appeared as a triplet and a singlet, respectively. This result is in sharp contrast to the reaction of **6a** with sodium hydroxide in the absence of $NaBF_4$ which gave a chelate complex having a chloride counter ion. Moreover, **7** were stable to the attack of $Cl^-$ ion. These results suggest a stronger coordination power of $NH_2$ than $NMe_2$.

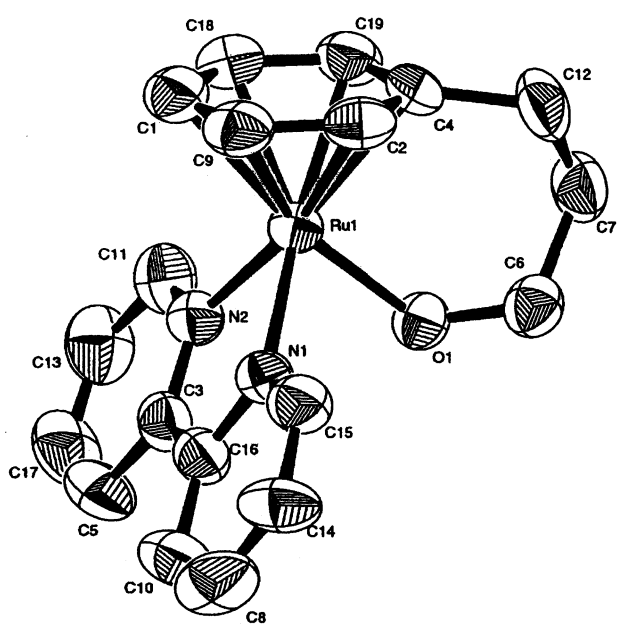
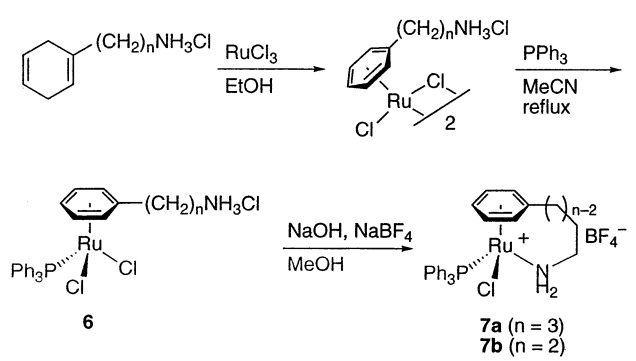
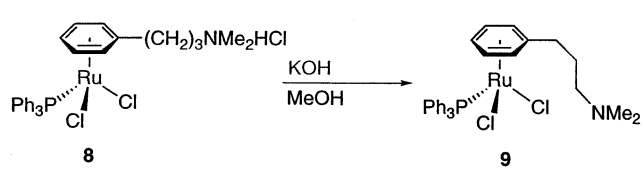



Fig. 4. ORTEP drawing of **5a**. $BF_4$ and MeOH were omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.




Scheme 3.




Scheme 4.

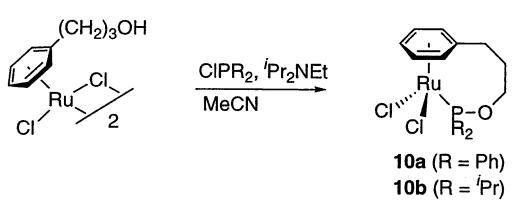
### 2.3. Synthesis of phosphite chelate complexes

Treatment of $[Ru\{\eta^6\text{-}C_6H_5(CH_2)_3OH\}Cl_2]_2$ with chlorophosphine $ClPR_2$ and $EtN^iPr_2$ gave neutral phosphorous chelate complexes **10a** and **10b** (Scheme 5). The use of $K_2CO_3$, KOH, and pyridine as bases did not afford **10**.

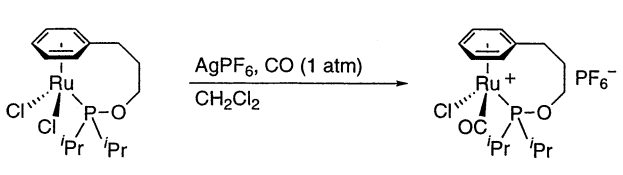
Treatment of the phosphorous chelate complex **10b** with $AgPF_6$ and CO gas (1 atm) in $CH_2Cl_2$ gave carbonyl complex **11** in high yield (Scheme 6). This is shown clearly by the infrared spectrum, where only a single carbonyl stretching band at 2035 $cm^{-1}$ was observed. Mono-substituted arene ruthenium carbonyl complex has to our knowledge not ever been reported. In $CH_2Cl_2$ solution under inert atmosphere **11** was labile to lead to decomposition.

### 2.4. Acidity of hydroxy proton in 4c

Addition of amine to a $CD_2Cl_2$ solution of **4c** resulted in the formation of an equilibrium mixture of **4c** and **5c**, the ratio of the two species being dependent on the amount and basicity of the amine. The rate of interconversion between **4c** and **5c** was confirmed rapid on the NMR time scale; averaging was observed at 25°C for each pair of resonances due to protons of **4c** and the corresponding protons of **5c**. Among these, the averaged position of one of the *meta*-H in $\eta^6$-$C_6H_5R$ ring moved from $\delta$ 6.80 in **4c** to $\delta$ 5.85 in **5c**, when **4c** was titrated with an amine (Fig. 5). This allowed us to assess acid–base equilibrium constants expressed by Eq. (1); a least-squares curve-fitting afforded $K_{eq} = 1.02 \pm 0.13$ for $B = (C_6H_5CH_2)(CH_3)NH$ and $0.43 \pm 0.08$ for $B = (C_6H_5CH_2)_2NH$, suggesting that in $CH_2Cl_2$ the acidity of the coordinating alcohol in **4c** is comparable to those of ammonium salts formed from these amines




Scheme 5.




Scheme 6.

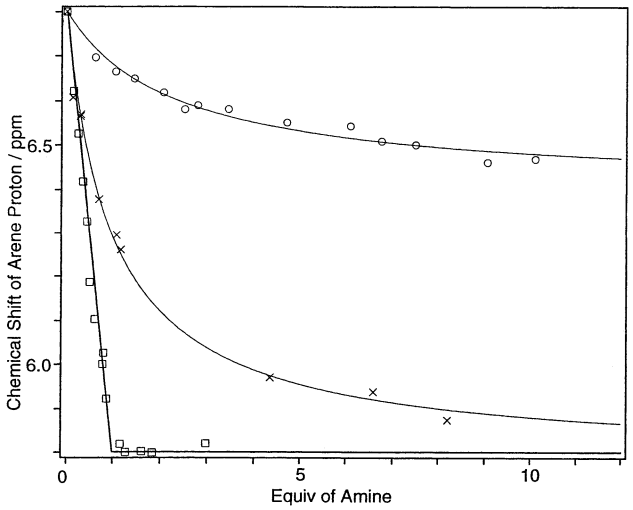
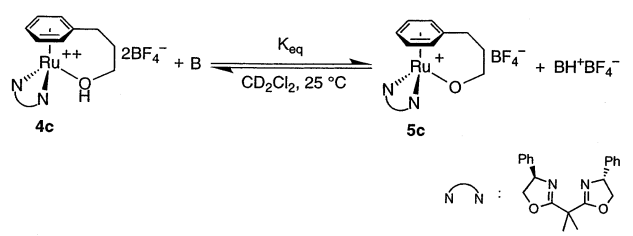



Fig. 5. Variation of chemical shift of *meta*-H in $\eta^6$-$C_6H_5R$ ring as a function of equivalent of amine added to **4c**; triethylamine (□), benzylmethylamine ( × ), and dibenzylamine (○).

($pK_a$ in $H_2O$, ca. 11). Triethylamine was too basic to allow correct estimation of the equilibrium constant.




(1)

### 2.5. Conclusion

The chelate effect exerted by the $\eta^6$-arene ligand and the pendent donor atom was shown useful to stabilize otherwise labile binding of some ligands such as alcohols to a ruthenium center. The present effort may also become suitable for looking into details of coordination behavior of the synthetically important donor groups such as alcohols, alkoxides, amines, and amides in a systematic manner.

## 3. Experimental

General remarks. Most of the commercially available reagents were used without further purification. Solvents were dried by standard methods and distilled prior to use. $^1H$ and $^{31}P$ NMR spectra were recorded with JEOL GSX-270 and GSX-400 spectrometers.

### 3.1. Preparation of complexes

#### 3.1.1. $[Ru\{\eta^6\text{-}C_6H_5(CH_2)_3OH\}Cl_2]_2$

To a solution of hydrated ruthenium trichloride (1.28 g, 5.1 mmol) in ethanol (62 ml) was added $C_6H_7(CH_2)_3$-

OH (3.5 g, 25 mmol) and the mixture was refluxed for 4 h. The orange precipitate was filtered off, washed with ether, and dried in vacuo to give the chloride dimer (1.42 g, 90%). $^1$H NMR ($CD_3CN$): $\delta$ 1.83 (tt, $J = 6.2$, 7.7 Hz, 2H), 2.61 (t, $J = 7.7$ Hz, 2H), 3.58 (brs, 2H), 5.46 (d, $J = 5.9$ Hz, 2H), 5.61 (t, $J = 5.5$ Hz, 1H), 5.70 (t, $J = 5.9$ Hz, 2H). *Anal.* Calc. for $C_{18}H_{24}Cl_4O_2Ru_2$: C, 35.08; H, 3.92. Found: C, 35.31; H, 3.77.

### 3.1.2. [Ru{$\eta^6$-$C_6H_5(CH_2)_3OH$}$(PPh_3)Cl_2$] (**1a**)

To a suspension of [Ru{$\eta^6$-$C_6H_5(CH_2)_3OH$}$Cl_2$]$_2$ (1.03 g, 3.33 mmol/Ru) in acetonitrile (50 ml) was added triphenylphosphine (873 mg, 3.33 mmol) and the mixture was stirred for 14 h at r.t. to give an orange suspension. The suspension was filtered off to give orange powders **1a** (1.07 g). The filtrate was evaporated and recrystallization from $CH_2Cl_2$/n-hexane gave orange–red crystalline **1a** (516 mg). Total 1.58 g (83%). $^1$H NMR ($CDCl_3$): $\delta$ 1.98 (m, 2H), 2.81 (t, $J = 5.0$ Hz, 2H), 3.80 (brt, $J = 5.4$ Hz, 2H), 4.54 (brt, $J = 4.5$ Hz, 1H), 5.14 (t, $J = 4.6$ Hz, 2H), 5.37 (d, $J = 5.9$ Hz, 2H), 7.30–7.77 (m, 15H). $^{31}$P NMR ($CDCl_3$): $\delta$ 28.80 (s). *Anal.* Calc. for $C_{27}H_{27}Cl_2OPRu$: C, 56.85; H, 4.77. Found: C, 56.67; H, 4.70.

### 3.1.3. [Ru{$\eta^6$-$C_6H_5(CH_2)_3OH$}$(PEt_3)Cl_2$] (**1b**)

This was prepared similarly to **1a** (84%). $^1$H NMR ($CDCl_3$): $\delta$ 1.14 (dt, $J = 15.1$, 7.8 Hz, 9H), 1.96–2.12 (m, 8H), 2.76 (t, $J = 7.3$ Hz, 2H), 3.83 (t, $J = 5.9$ Hz, 2H), 5.13 (m, 1H), 5.44 (s, 4H). $^{31}$P NMR ($CDCl_3$): $\delta$ 28.57 (s). *Anal.* Calc. for $C_{15}H_{27}Cl_2OPRu$: C, 42.26; H, 6.38. Found: C, 42.10; H, 6.19.

### 3.1.4. [Ru{$\eta^6$-$C_6H_5(CH_2)_3OH$}(bipy)Cl]$BF_4$ (**2a**)

To a suspension of [Ru{$\eta^6$-$C_6H_5(CH_2)_3OH$}$Cl_2$]$_2$ (500 mg, 1.62 mmol/Ru) in acetonitrile (60 ml) was added 2,2′-bipyridine (253 mg, 1.62 mmol) and the mixture was stirred for 2 h at r.t., followed by addition of $NaBF_4$ (178 mg, 1.62 mmol). After stirring for further 14 h, the mixture was filtered and the solvent was evaporated. The residue was recrystallized from MeCN/ether to give an orange crystalline product (629 mg, 77%). $^1$H NMR ($CD_3OD$): $\delta$ 1.88 (m, 2H), 2.67 (t, $J = 7.8$ Hz, 2H), 3.63 (t, $J = 6.4$ Hz, 2H), 5.83 (t, $J = 5.7$ Hz, 1H), 5.95 (d, $J = 6.5$ Hz, 2H), 6.21 (t, $J = 6.4$ Hz, 2H), 7.74 (m, 2H), 8.23 (td, $J = 7.8$, 1.4 Hz, 2H), 8.49 (d, $J = 8.4$ Hz, 2H), 9.49 (d, $J = 4.9$ Hz, 2H). *Anal.* Calc. for $C_{19}H_{20}BClF_4N_2ORu$: C, 44.25; H, 3.91; N, 5.43. Found: C, 44.54; H, 3.85; N, 5.67.

### 3.1.5. [Ru{$\eta^6$-$C_6H_5(CH_2)_3OH$}(phen)Cl]$BF_4$ (**2b**)

This was prepared similarly to **2a** (68%). $^1$H NMR ($CD_3OD$): $\delta$ 1.91 (m, 2H), 2.70 (t, $J = 7.8$ Hz, 2H), 3.64 (t, $J = 6.1$ Hz, 2H), 5.85 (t, $J = 5.9$ Hz, 1H), 6.08 (d, $J = 6.5$ Hz, 2H), 6.32 (t, $J = 6.1$ Hz, 2H), 8.08 (dd, $J = 5.4$, 3.0 Hz, 2H), 8.20 (s, 2H), 8.49 (dd, $J = 8.4$, 1.6 Hz, 2H), 9.84 (dd, $J = 5.3$, 0.95 Hz, 2H). *Anal.* Calc. for $C_{21}H_{20}BClF_4N_2ORu$: C, 46.73; H, 3.73; N, 5.19. Found: C, 46.48; H, 3.57; N, 5.21.

### 3.1.6. [Ru{$\eta^6$-$C_6H_5(CH_2)_3OH$}(bpop)Cl]$BF_4$ (**2c**)

This was prepared in MeOH (80 ml) using [Ru{$\eta^6$-$C_6H_5(CH_2)_3OH$}$Cl_2$]$_2$ and (*R*)-bpop. After stirring for 5.5 h, the mixture was poured into a separatory funnel containing $CH_2Cl_2$ and water. The crude product obtained by separation and evaporation of $CH_2Cl_2$ was purified by column chromatography (Wako C-200 silica gel, ether and $CH_3CO_2Et/CH_2Cl_2$ (3/2)) to give 559 mg (62%) of orange solids **2c**. $^1$H NMR ($CDCl_3$): $\delta$ 1.45 (m, 1H), 1.58 (m, 1H), 1.73 (s, 3H), 1.76 (m, 1H), 1.82 (s, 3H), 2.33 (m, 1H), 3.50 (brt, $J = 6.1$ Hz, 2H), 4.27 (dd, $J = 6.8$, 8.4 Hz, 1H), 4.41 (dd, $J = 4.6$, 8.6 Hz, 1H), 4.76–4.85 (m, 3H), 4.99 (d, $J = 6.5$ Hz, 1H), 5.24 (dd, $J = 8.4$, 10.5 Hz, 1H), 5.36 (dd, $J = 5.7$, 5.9 Hz, 1H), 5.54 (dd, $J = 4.6$, 10.0 Hz, 1H), 6.02 (dd, $J = 5.4$, 5.7 Hz, 1H), 6.14 (dd, $J = 6.8$, 10.5 Hz, 1H), 7.38–7.64 (m, 10H). *Anal.* Calc. for $C_{30}H_{34}BClF_4N_2O_3Ru{\cdot}0.5H_2O$: C, 51.26; H, 5.02; N, 3.99. Found: C, 51.18; H, 4.94; N, 3.98.

### 3.1.7. [Ru{$\eta^6$:$\eta^1$-$C_6H_5(CH_2)_3OH$}$(PPh_3)Cl$]$BF_4$ (**3a**)

To a solution of **1a** (1.42 g, 2.49 mmol) in $CH_2Cl_2$ (50 ml) was added a solution of $AgBF_4$ (485 mg, 2.49 mmol) in MeOH (3 ml) and the mixture was stirred for 15 min. The suspension was filtered and the solvent was evaporated. Recrystallization from MeOH gave 1.34 g (82%) of an orange crystalline product. $^1$H NMR ($CD_2Cl_2$): $\delta$ 2.22 (m, 2H), 2.73 (m, 2H), 3.44 (m, 1H), 3.78 (m, 1H), 4.38 (t, $J = 5.1$ Hz, 1H), 4.79 (m, 1H), 5.04 (t, $J = 4.9$ Hz, 1H), 5.37 (m, 1H), 6.01 (t, $J = 4.9$ Hz, 1H), 6.31 (d, $J = 5.9$ Hz, 1H), 7.47–7.56 (m, 15H). $^{31}$P NMR ($CD_2Cl_2$): $\delta$ 33.69 (s). *Anal.* Calc. for $C_{27}H_{27}BClF_4NOPRu{\cdot}CH_3OH$: C, 51.43; H, 4.78. Found: C, 51.12; H, 4.89.

### 3.1.8. [Ru {$\eta^6$:$\eta^1$-$C_6H_5(CH_2)_3OH$}$(PEt_3)Cl$]$BF_4$ (**3b**)

The initial procedure was similar to that for **3a**. Recrystallization from $CH_2Cl_2$/n-hexane gave an orange crystalline product (83%). $^1$H NMR ($CD_2Cl_2$): $\delta$ 1.10 (dt, $J = 15.7$, 5.1 Hz 9H), 1.82–2.08 (m, 6H), 2.18 (m, 1H), 2.56–2.67 (m, 1H), 2.69–2.78 (m, 1H), 3.48 (m, 1H), 3.92 (m, 1H), 4.07 (t, $J = 4.9$ Hz, 1H), 4.95 (t, $J = 5.1$ Hz, 1H), 5.49 (d, $J = 5.9$ Hz, 1H), 5.82 (t, $J = 5.4$ Hz, 4H), 5.88 (t, $J = 5.9$ Hz, 1H), 6.29 (d, $J = 5.9$ Hz, 1H). $^{31}$P NMR ($CD_2Cl_2$): $\delta$ 32.10 (s). *Anal.* Calc. for $C_{15}H_{27}BClF_4NOPRu$: C, 37.72; H, 5.70. Found: C, 38.03; H, 5.49.

### 3.1.9. [Ru {$\eta^6$:$\eta^1$-$C_6H_5(CH_2)_3OH$}(bipy)]$(BF_4)_2$ (**4a**)

To a solution of **2a** (200 mg, 0.388 mmol) in MeOH (30 ml) was added a solution of $AgBF_4$ (76 mg, 0.388

mmol) in MeOH (2 ml) and the mixture was stirred for 14 h. The suspension was filtered and the solvent was evaporated. Recrystallization from MeOH/ether gave an orange crystalline product (29%). $^1$H NMR ($CD_3OD$): $\delta$ 2.29 (m, 2H), 2.91 (m, 2H), 3.70 (m, 2H), 5.41 (t, $J = 5.8$ Hz, 1H), 6.22 (d, $J = 6.5$ Hz, 2H), 6.50 (t, $J = 6.1$ Hz, 2H), 7.88 (m, 2H), 8.35 (td, $J = 9.1$, 1.2 Hz, 2H), 8.56 (d, $J = 8.4$ Hz, 2H), 9.68 (d, $J = 4.9$ Hz, 2H) *Anal.* Calc. for $C_{19}H_{20}B_2F_8N_2ORu$: C, 40.24; H, 3.55; N, 4.94. Found: C, 40.48; H, 3.39; N, 4.94.

*3.1.10. [Ru {$\eta^6$:$\eta^1$-$C_6H_5(CH_2)_3OH$}(phen)]$(BF_4)_2$ (**4b**)*

This was prepared similarly to **4a** (22%). $^1$H NMR ($CD_3OD$): $\delta$ 2.29 (m, 2H), 2.95 (m, 2H), 3.62 (m, 2H), 5.36 (t, $J = 5.7$ Hz, 1H), 6.36 (d, $J = 6.2$ Hz, 2H), 6.64 (t, $J = 6.4$ Hz, 2H), 8.21 (dd, $J = 8.1$, 5.3 Hz, 2H), 8.27 (s, 2H), 8.96 (dd, $J = 8.4$, 1.6 Hz, 2H), 10.04 (dd, $J = 5.4$, 1.1 Hz, 2H). *Anal.* Calc. for $C_{21}H_{20}B_2F_8N_2ORu$: C, 42.67; H, 3.41; N, 4.74. Found: C, 42.66; H, 3.42; N, 4.78.

*3.1.11. [Ru{$\eta^6$:$\eta^1$-$C_6H_5(CH_2)_3OH$}(bpop)]$(BF_4)_2$ (**4c**)*

This was prepared from **2c** in $CH_2Cl_2$ and $AgBF_4$ in MeOH. Recrystallization from MeOH/ether gave an orange crystalline product (74%). $^1$H NMR ($CDCl_3$): $\delta$ 1.43 (m, 1H), 1.37 (s, 3H), 1.79 (m, 1H), 1.89 (s, 3H), 2.05 (m, 1H), 2.18 (m, 1H), 2.41 (m, 1H), 3.55 (m, 1H), 4.48–4.57 (m, 2H), 4.63 (t, $J = 5.9$ Hz, 2H), 4.77 (d, $J = 5.9$ Hz, 1H), 4.78 (brs, 1H), 5.19 (dd, $J = 8.4$, 10.5 Hz, 1H), 5.30–5.40 (m, 4H), 5.97 (dd, $J = 6.9$, 10.4 Hz, 1H), 6.89 (t, $J = 5.9$ Hz, 1H), 7.32–7.64 (m, 10H). *Anal.* Calc. for $C_{30}H_{34}B_2F_8N_2O_3Ru{\cdot}2H_2O$: C, 46.12; H, 4.90; N, 3.59. Found: C, 45.98; H, 4.53; N, 3.62.

*3.1.12. [Ru{$\eta^6$:$\eta^1$-$C_6H_5(CH_2)_3O$}(bipy)]$BF_4$ (**5a**)*

To a solution of **4a** (80 mg, 0.141 mmol) in MeOH (7 ml) was added NaOH (6 mg, 0.15 mmol) and the mixture was stirred for 1 min at 0°C. The solvent was evaporated under vacuum. The residue was extracted with $CH_2Cl_2$, and the solvent evaporated. The remaining solids were recrystallized from MeOH/ether to give 46 mg (69%) of orange crystalline product **5a**. $^1$H NMR ($CD_3OD$): $\delta$ 2.17 (m, 2H), 2.72 (m, 2H), 3.47 (m, 2H), 5.38 (t, $J = 5.8$ Hz, 1H), 5.66 (d, $J = 5.7$ Hz, 2H), 6.12 (t, $J = 6.2$ Hz, 2H), 7.74 (m, 2H), 8.22 (td, $J = 7.8$, $J = 1.6$ Hz, 2H), 8.47 (d, $J = 8.4$ Hz, 2H), 9.39 (d, $J = 4.9$ Hz, 2H) *Anal.* Calc. for $C_{19}H_{19}BF_4N_2ORu{\cdot}H_2O$: C, 45.89; H, 4.26; N, 5.63. Found: C, 45.81; H, 4.32;N, 5.64.

*3.1.13. [Ru{$\eta^6$:$\eta^1$-$C_6H_5(CH_2)_3O$}(phen)]$BF_4$ (**5b**)*

This was prepared similarly to **5a** (62%). $^1$H NMR ($CD_3OD$): $\delta$ 2.16 (m, 2H), 2.77 (m, 2H), 3.40 (m, 2H), 5.34 (t, $J = 5.7$ Hz, 1H), 5.82 (d, $J = 5.9$ Hz, 2H), 6.25 (t, $J = 6.1$ Hz, 2H), 8.04 (dd, $J = 8.1$, 5.1 Hz, 2H), 8.18 (s, 2H), 8.81 (dd, $J = 8.4$, 0.81 Hz, 2H), 9.74 (dd, $J = 5.1$, 1.4 Hz, 2H). *Anal.* Calc. for $C_{21}H_{19}BF_4N_2ORu{\cdot}H_2O$: C, 48.39; H, 4.06; N, 5.37. Found: C, 48.04; H, 3.85; N, 5.38.

*3.1.14. [Ru{$\eta^6$:$\eta^1$-$C_6H_5(CH_2)_3O$}(bpop)]$BF_4$ (**5c**)*

This was prepared similarly to **5a** (91%). $^1$H NMR ($CDCl_3$): $\delta$ 1.42 (m, 1H), 1.68 (m, 1H), 1.68 (s, 3H), 1.83 (s, 3H), 1.98 (m, 1H), 2.13 (m, 1H), 2.82 (dd, $J = 8.1$, 11.9 Hz, 1H), 3.36 (dd, $J = 6.9$, 12.3 Hz, 1H), 4.05 (d, $J = 5.4$ Hz, 1H), 4.20–4.30 (m, 3H), 4.39 (dd, $J = 6.5$, 8.9 Hz, 1H), 4.84 (dd, $J = 8.9$, 10.8 Hz, 1H), 5.19 (dd, $J = 8.4$, 10.8 Hz, 1H), 5.26 (dd, $J = 6.5$, 10.8 Hz, 1H), 5.46 (t, $J = 5.9$ Hz, 1H), 5.92 (dd, $J = 8.9$, 10.8 Hz, 1H), 6.12 (dd, $J = 5.4$, 5.9 Hz, 1H), 7.33–7.59 (m, 10H). *Anal.* Calc. for $C_{30}H_{33}BF_4N_2O_3Ru{\cdot}H_2O$: C, 53.34; H, 5.22; N, 4.15. Found: C, 53.37; H, 5.00; N, 4.16.

*3.1.15. [Ru{$\eta^6$:$\eta^1$-$C_6H_5(CH_2)_3NH_2$}$(PPh_3)Cl$]$BF_4$ (**7a**)*

To a solution of hydrated ruthenium trichloride (2.28 g, 8.9 mmol) in ethanol (200 ml) was added $C_6H_7(CH_2)_3NH_3Cl$ (7.73 g, 45 mmol) and the mixture was refluxed for 4 h. The brown precipitate was filtered off, washed with ether, and dried in vacuo to give the chloride dimer (3.02 g, 99%). To the suspension of $[Ru\{\eta^6\text{-}C_6H_5(CH_2)_3NH_3Cl\}Cl_2]_2$ (1.00 g, 2.90 mmol/Ru) in MeCN (80 ml) was added triphenylphosphine (773 mg, 2.95 mmol) and the mixture was stirred for 11 h at r.t. to give an orange suspension. The suspension was filtered off to give orange powders **6a** (92%). To the suspension of **6a** (495 mg, 0.82 mmol) in MeOH (100 ml) was added a solution of NaOH (33 mg, 0.82 mmol) in MeOH (5 ml) and the mixture was stirred for 15 min at r.t. Then, $NaBF_4$ (159 mg, 0.82 mmol) was added to the suspension and the mixture was stirred for 15 h at r.t. The suspension was filtered and the filtrate was evaporated. The residue was recrystallized with hot MeOH to give 244 mg (0.39 mmol, 48%) of orange crystalline product **7a**. $^1$H NMR ($CDCl_3$): $\delta$ 1.99 (brs, 1H), 2.17–2.33 (m, 2H), 2.51 (m, 2H), 4.08 (brs, 1H), 4.24 (brs, 1H), 5.45 (brs, 1H), 5.81–5.84 (m, 2H), 6.02 (d, $J = 5.9$ Hz, 1H), 7.53–7.57 (m, 15H). $^{31}$P NMR ($CDCl_3$): $\delta$ 36.13 (s). *Anal.* Calc. for $C_{27}H_{28}BClF_4NPRu$: C, 52.24; H, 4.55; N, 2.26. Found: C, 52.02; H, 4.63; N, 2.26.

*3.1.16. [Ru{$\eta^6$:$\eta^1$-$C_6H_5(CH_2)_2NH_2$}$(PPh_3)Cl$]$BF_4$ (**7b**)*

This was prepared similarly to **7a** (42%). $^1$H NMR ($CDCl_3$): $\delta$ 2.18 (s, 1H), 2.60–2.67 (m, 1H), 3.35–3.44 (m, 1H), 3.92 (brs, 2H), 4.32 (q, $J = 5.4$ Hz, 1H), 4.85 (brs, 1H), 5.44 (t, $J = 5.4$ Hz, 1H), 5.61 (d, $J = 5.4$ Hz, 1H), 5.96 (d, $J = 5.4$ Hz, 1H), 6.15 (t, $J = 5.9$ Hz, 1H), 7.52–7.61 (m, 15H). $^{31}$P NMR ($CDCl_3$): $\delta$ 34.54 (s). *Anal.* Calc. for $C_{26}H_{26}BClF_4NPRu{\cdot}H_2O$: C, 49.98; H, 4.52; N, 2.24. Found: C, 49.97; H, 4.39; N, 2.32.

*3.1.17. [Ru{η⁶-$C_6H_5(CH_2)_3NMe_2$}($PPh_3Cl_2$] (**9**)*

Complex **8** was prepared similarly to **6a** (90%). To the suspension of **8** (570 mg, 0.91 mmol) in MeOH (50 ml) was added a solution of KOH (51 mg, 0.91 mmol) in MeOH (5 ml) and the mixture was stirred for 10 min at r.t. The solution was evaporated, and the residue was extracted with AcOEt. Recrystallization with benzene/n-hexane gave 279 mg (0.46 mmol, 51%) of orange crystalline product **9**. $^1$H NMR ($CDCl_3$): $\delta$ 1.75 (m, 2H), 2.13 (s, 6H), 2.26 (t, $J=7.3$ Hz, 2H), 2.57 (t, $J=7.8$ Hz, 2H), 4.48 (t, $J=5.4$ Hz, 1H), 5.10 (t, $J=5.4$ Hz, 2H), 5.22 (d, $J=7.8$ Hz, 2H), 7.28–7.74 (m, 15H). $^{31}$P NMR ($CDCl_3$): $\delta$ 28.35 (s). *Anal.* Calc. for $C_{29}H_{29}Cl_2NPRu$: C, 58.29; H, 5.40; N, 2.34. Found: C, 58.06; H, 5.11; N, 2.32.

*3.1.18. [Ru{η⁶:η¹-$C_6H_5(CH_2)_3OPPh_2$}$Cl_2$] (**10a**)*

To a suspension of [Ru{η⁶-$C_6H_5(CH_2)_3OH$}$Cl_2$]$_2$ (1.034 g, 3.36 mmol/Ru) in MeCN (100 ml) was added chlorodiphenylphosphine (0.602 ml, 3.36 mmol) and the mixture was stirred for 1 h at r.t. to give a red solution. A solution of ethyldiisopropylamine (0.585 ml, 3.36 mmol) in MeCN (90 ml) was added dropwise to the red solution at 0°C for 1.5 h. and then the mixture was stirred at r.t. for 24 h. The solvent was removed under vacuum, and the residue was extracted with $CH_2Cl_2/H_2O$. Recrystallization with hot $CH_2Cl_2$ gave orange powders **10a** (44%). $^1$H NMR ($CDCl_3$): $\delta$ 2.19 (m, 2H), 2.80 (t, $J=5.4$ Hz, 2H), 4.85 (dt, $J=16.7$, 6.1 Hz, 2H), 5.14 (d, $J=5.4$ Hz, 2H),5.76 (t, $J=6.1$ Hz, 2H), 6.27 (t, $J=6.6$ Hz, 1H), 7.36–7.93 (m, 10H). $^{31}$P NMR ($CDCl_3$): $\delta$ 119.01 (s). *Anal.* Calc. for $C_{21}H_{21}Cl_2OPRu$: C, 51.25; H, 4.30. Found: C, 50.95; H, 4.10.

*3.1.19. [Ru{η⁶:η¹-$C_6H_5(CH_2)_3OP^iPr_2$}$Cl_2$] (**10b**)*

This was prepared similarly to **10a** (25%). $^1$H NMR ($CDCl_3$): $\delta$ 1.27 (m, 12H), 2.09 (tt, $J=6.4$, 5.4 Hz, 2H), 2.77 (t, $J=6.4$ Hz, 2H), 3.04 (m, 2H), 4.27 (dt, $J=13.8$, 5.4 Hz, 2H), 5.55 (d, $J=4.9$ Hz, 2H), 5.77 (t, $J=5.9$ Hz, 2H), 6.20 (t, $J=6.2$ Hz, 1H). $^{31}$P NMR ($CDCl_3$): $\delta$ 156.97 (s). *Anal.* Calc. for $C_{15}H_{25}Cl_2OPRu$: C, 42.46; H, 5.94. Found: C, 42.25; H, 5.71.

*3.1.20. [Ru{η⁶:η¹-$C_6H_5(CH_2)_3OP^iPr_2$}(CO)Cl]$PF_6$ (**11**)*

To a suspension of $AgPF_6$ (25.8 mg, 0.102 mmol) and **10b** (43.3 mg, 0.102 mmol) in $CH_2Cl_2$ (10 ml) was bubbled CO gas for 3 min at r.t. The yellow suspension was filtered and the solvent was removed under vaccum. The yellow powder was washed with ether to give **11** (89%). $^1$H NMR ($CD_2Cl_2$): $\delta$ 1.16–1.34 (m, 12H), 2.12–2.36 (m, 2H), 2.61–2.76 (m, 1H), 3.00–3.15 (m, 3H), 4.14–4.23 (m, 1H), 4.44–4.59 (m, 1H), 6.37–6.41 (m, 2H), 6.64 (d, $J=6.2$ Hz, 1H), 6.67 (t, $J=6.6$ Hz, 1H), 6.87–6.91 (m, 1H). $^{31}$P NMR ($CD_2Cl_2$): $\delta$ 168.09 (s). IR (KBr) 2035 cm$^{-1}$. *Anal.* Calc. for $C_{16}H_{25}ClOF_6P_2Ru$: C, 35.21; H, 4. 62. Found: C, 35.03; H, 4.70.

*3.2. Crystal structure determination*

All data were obtained on a Rigaku AFC-5R (**2a**, **4b**, and **4c**) or R-AXIS RAPID (**5a**) diffractometer with graphite-monochromated Mo Kα radiation. All calculations were carried out with the TEXAN crystallographic software package of Molecular Structure Corp. The structures of **2a**, **4b**, **4c**, and **5a** were solved by direct methods and refined by full-matrix least-squares procedures, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$. The non-hydrogen atoms were refined anisotropically. Part of the hydrogens was positioned by stereochemical consideration.

Crystal data for **2a**: $C_{19}H_{20}BClF_4N_2ORu$, $M=515.71$, monoclinic, space group $P2_1/n$ (no. 14), $a=8.505(2)$, $b=9.390(2)$, $c=24.879(3)$ Å, $V=2922.7(9)$ Å$^3$, $Z=4$, $F(000)=1032$, $D_c=1.724$ g cm$^{-3}$, $m$(Mo Kα) = 9.73 cm$^{-1}$, 257 variable refined with 3443 reflections with $I>3\sigma(I)$ to $R=0.038$, $R_w=0.038$.

Crystal data for **4b**: $C_{21}H_{20}B_2F_8N_2ORu$, $M=591.08$, triclinic, space group $P\bar{1}$ (no. 2), $a=10.002(2)$, $b=11.714(2)$, $c=9.722(2)$ Å, $V=1117.7(4)$ Å$^3$, $Z=2$, $F(000)=588$, $D_c=1.756$ g cm$^{-3}$, $m$(Mo Kα) = 7.86 cm$^{-1}$, 316 variable refined with 4874 reflections with $I>3\sigma(I)$ to $R=0.043$, $R_w=0.064$.

Crystal data for **4c**: $C_{30}H_{34}B_2F_8N_2O_3Ru\cdot 2H_2O$, $M=781.32$, monoclinic, space group $P2_1$ (no. 4), $a=9.304(1)$, $b=19.063(2)$, $c=10.485(2)$ Å, $V=1745.6(4)$ Å$^3$, $Z=2$, $F(000)=796$, $D_c=1.486$ g cm$^{-3}$, $m$(Mo Kα) = 5.31 cm$^{-1}$, 479 variable refined with 2563 reflections with $I>3\sigma(I)$ to $R=0.099$, $R_w=0.124$.

Crystal data for **5a**: $C_{19}H_{19}BF_4N_2ORu\cdot CH_3OH$, $M=511.29$, monoclinic, space group $P2_1/c$ (no. 14), $a=9.5919(5)$, $b=14.0615(7)$, $c=15.4174(9)$ Å, $V=2078.4(2)$ Å$^3$, $Z=4$, $F(000)=960$, $D_c=1.531$ g cm$^{-3}$, $m$(Mo Kα) = 8.00 cm$^{-1}$, 271 variable refined with 3323 reflections with $I>3\sigma(I)$ to $R=0.074$, $R_w=0.079$.

## 4. Supplementary material

Crystallographic details, atomic coordinates, anisotropic displacement parameters, bond lengths and angles, and structure factors for **2a**, **4b**, **4c**, and **5a** are available from the authors on request.

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