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Syntheses and structures of ruthenium(II) complexes bearing hybrid phosphine-thioether ligands, $Me_2PCH_2CH_2SR$

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Abstract

Hybrid phosphine-thioether ligands $Me_2PCH_2CH_2SR$ (L) reacted with $[RuCl_2(cym)]_2$ (cym = *p*-cymene) to produce 11 new ruthenium(II) complexes; $[RuCl_2(cym)(L)]$ (**1**–**3** for R = CH_3(Me), C_2H_5(Et) and C_6H_5(Ph), respectively) in toluene, $[RuCl(cym)(L)]^+$ (**4**–**6** for R = Me, Et and Ph, respectively) in ethyl alcohol and $[RuCl_2(L)_2]$ (**7** and **8** for R = Me and Et, respectively and **9**–**11** for R = Ph) in refluxing *n*-butanol. Complexes **1**–**3** in which L acts as a monodentate ligand through phosphorus led to complexes **4**–**6** where L binds to Ru through phosphorus and sulfur in ethyl alcohol at room temperature. Complexes **9**–**11** were separated into three of five possible geometrical isomers by fractional crystallization, *trans*(Cl,Cl′)*trans*(P,P′) (**9**), *cis*(Cl,Cl′)*cis*(P,P′) (**10**) and *trans*(Cl,Cl′)*cis*(P,P′) (**11**), whereas complexes **7** and **8** afforded only the *trans*(Cl,Cl′)*trans*(P,P′) isomer. The crystal structures of complexes **5**, **8**, **9** and **11** were determined by an X-ray diffraction method, suggesting stronger *trans* influence of the dimethylphosphino group than those of the thioether and *p*-cymene moieties. ^{31}P-{H}- and ^{1}H- or ^{13}C-{H}-NMR spectral data are used to characterize the structures of the complexes. The hydride complex $[RuH(cym)(Me_2PCH_2CH_2SEt)]^+$ was also prepared by the treatment of $NaBH_4$ with complex **5**. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structure; Phosphine-thioether ligands; Ruthenium(II) complexes

1. Introduction

While complexes with phosphine-ether hybrid donor ligands have been extensively studied for various transition metals [1], analogous phosphine-thioether ligands have received less attention [2]. Thioethers are considered to be poor donors upon coordination at transition metals [3] and they may act as a hemilabile ligand which provides a potential vacant site for incoming substrates. Most of phosphine-thioether hybrid ligands so far reported are limited to those having a diphenylphosphino group as the phosphine moiety. We have been interested in phosphorus-sulfur mixed-donor ligands $Me_2PCH_2CH_2SR$ (R = H and CH_3) in which the dimethylphosphino moiety carries sterically undemanding and strongly electron-donating methyl groups and found that these molecules act as either monodentate or bidentate ligands depending on transition metal fragments [4–7].

In this paper we report the syntheses of new ruthenium(II) complexes containing $Me_2PCH_2CH_2SR$ (L: R = Me, Et and Ph) and their structural characterization by an X-ray diffraction method and ^{31}P-{^{1}H}- and ^{1}H- or ^{13}C-{^{1}H}-NMR spectra. These complexes can be grouped into the three types, $[RuCl_2(cym)(L)]$ (cym = *p*-cymene), $[RuCl(cym)(L)]^+$ and $[RuCl_2(L)_2]$. To our best knowledge, there is only one structural report of a ruthenium(II) complex containing a P,S hybrid donor ligand, namely, *cis*-$[RuCl_2\{(p\text{-tolyl})_2P(4\text{-DBT})\}_2]$ ((*p*-tolyl)$_2$P(4-DBT) = 4-(di-*p*-tolylphosphino)dibenzothiophene) [8]. Palladium complexes of dialkylphosphine-

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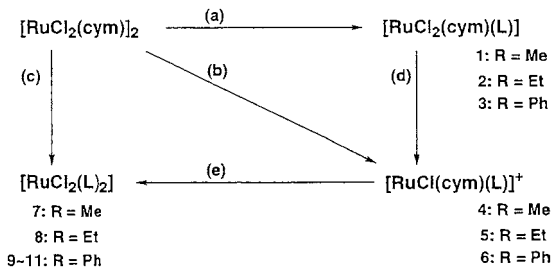
thioether [$PdCl_2(R_2PCH_2CH_2SEt)$] (R = Et, ^{i}Pr) have also appeared [9]. We have communicated a preliminary result on the crystal structure of [RuCl(cym)($Me_2PCH_2CH_2SMe$)]$BPh_4 \cdot 0.5CH_2Cl_2$ [10].

2. Results and discussion

2.1. Synthesis and structure determination by NMR spectroscopy

The preparation of $Me_2PCH_2CH_2SR$ (R = Me: mtdmp, R = Et: etdmp and R = Ph: ptdmp) was always accompanied by the contamination of 1,2-bis(dimethylphosphino)ethane (dmpe) in 5–20% yields. Mtdmp or etdmp could not be separated from dmpe by distillation because their boiling points are similar. Since the mixtures were used for the preparation of ruthenium complexes, the reactions with $[RuCl_2(cym)]_2$ afforded $[RuCl_2(cym)]_2$(μ-dmpe) as a by-product, which was removed by fractional crystallization. On the other hand, the phenyl derivative, ptdmp, was successfully separated from dmpe by distillation.

The reaction of $[RuCl_2(cym)]_2$ with $Me_2PCH_2CH_2SR$ (L) resulted in the formation of three different types of complexes depending upon the choice of solvents (Scheme 1). The reaction (a) in toluene at room temperature afforded $[RuCl_2(cym)(L)]$ (**1–3** for R = Me, Et and Ph, respectively), while reaction (b) in ethyl alcohol at room temperature [RuCl(cym)(L)]X (X = BPh_4 or PF_6) (**4–6** for R = Me, Et and Ph, respectively). Complexes **1–6** are air stable in the solid and even in solution. The phosphorus signals in the ^{31}P-{^1H}-NMR spectra appear at ca. −50, 10 and ca. 51 ppm for the free ligands (L; mtdmp, etdmp and ptdmp), $[RuCl_2(cym)(L)]$ and [RuCl(cym)(L)]X, respectively. The down-field shift of the ^{31}P signals in this order and the difference of chemical shifts ($\Delta\delta$ ca. 41 ppm) between $[RuCl_2(cym)(L)]$ and [RuCl(cym)(L)]X suggested that coordination occurs at phosphorus and that L in $[RuCl_2(cym)(L)]$ binds to Ru in a monodentate manner while L in [RuCl(cym)(L)]X chelates Ru [11]. Recently a similar trend of ^{31}P signals has been noted for



Scheme 1. Synthetic routes of the complexes. (a) 3–4 L, in toluene at room temperature, (b) 4 L, in ethyl alcohol at room temperature, (c) 6–8 L, reflux in *n*-butanol, (d) 1–2 L, reflux in *n*-butanol.

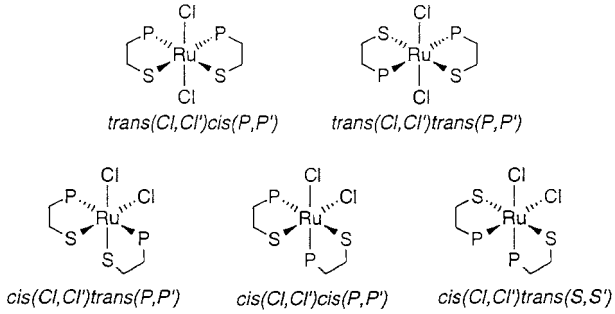


Fig. 1. Five possible geometrical isomers for $[RuCl_2(L)_2]$.

$[RuCl_2(\eta^6\text{-}1,2,3,4\text{-}Me_4C_6H_2)(PPh_2\{(C_6H_3(OMe)_2\text{-}2,6\})]$ (^{31}P-{^1H}-NMR: 19.7 ppm) and $[RuCl(\eta^6\text{-}1,2,3,4\text{-}Me_4C_6H_2)\{PPh_2(2\text{-}o\text{-}C_6H_3\text{-}6\text{-}OMe)\}]$ (^{31}P-{^1H}-NMR: 55.4 ppm), the former bearing a monodentate phosphine and the latter a bidentate one [12]. The chemical shift difference of $\Delta\delta = 35.7$ ppm is close to our observation for $[RuCl_2(cym)(L)]$ and [RuCl(cym)(L)]X.

Complexes **1–3** are transformed into complexes **4–6**, respectively, in ethyl alcohol or methyl alcohol at room temperature (reaction (d) in Scheme 1), while they are intact in toluene, dichloromethane or chloroform. These reactions were monitored by absorption spectra which show isosbestic points. Since the rates of the reactions are independent of the kind of R and the concentration of the complexes and since the addition of excess LiCl does not affect the rates, we propose the mechanism to be an intramolecular ring closure. ^1H-NMR spectra are also consistent with the structures, exhibiting one set of signals for the methyl groups of L and cym in $[RuCl_2(cym)(L)]$, whereas two sets of signals appear for the corresponding methyl groups in [RuCl(cym)(L)]X due to the presence of a chiral center at ruthenium. The crystal structure of [RuCl(cym)(etdmp)]PF_6 was determined by an X-ray diffraction method (see below).

Complexes of the type $[RuCl_2(L)_2]$ (**7**: R = Me, **8**: R = Et and **9–11**: R = Ph) were obtained by reactions of L with $[RuCl_2(cym)]_2$ or $[RuCl(cym)(L)]^+$ in refluxing *n*-butanol (reactions (c) and (e) in Scheme 1). For L = mtdmp or etdmp, $[RuCl_2(L)(dmpe)]$ occured as a by-product. Use of $[RuCl_2(dmso)_4]$ (dmso = dimethyl sulfoxide) in refluxing *n*-butanol instead of $[RuCl_2(cym)]_2$ gave **7–11** in 10–15% yields, while the reactions did not proceed in refluxing ethyl alcohol or methyl alcohol. All the complexes are air stable in solution and in the solid state. Of the five possible geometrical isomers (Fig. 1) of $[RuCl_2(ptdmp)_2]$, *trans*(Cl,Cl′)*trans*(P,P′) (**9**), *cis*(Cl,Cl′)*cis*(P,P′) (**10**) and *trans*(Cl,Cl′)*cis*(P,P′) (**11**) isomers were isolated by fractional crystallization and two of them (**9** and **11**) were characterized by the X-ray diffraction study. The ^{31}P-{^1H}-NMR spectra of complexes **9** and **11** are consis-

tent with the X-ray-derived structures, exhibiting one singlet at 38.81 for **9** and 48.90 ppm for **11**.

Complex **10** exhibits two doublets at 51.69 and 48.49 ppm with $J = 32.6$ Hz in the ^{31}P-$\{^1H\}$-NMR spectrum, suggesting the *cis*(Cl,Cl′)*cis*(P,P′) configuration. The UV–vis absorption spectra of the three isomers (**9**–**11**) differ in the lowest-energy region (19 000–25 000 cm^{-1}) as shown in Fig. 2. The absorption peaks in this region, which are assigned to the d–d transition bands of low-spin d^6 metal complexes [13], shift to higher energy in the order **9** < **11** < **10**. The absorption peaks at 26 170 and 30 630 cm^{-1} of **11** may overlap with charge-transfer bands.

Only a *trans*(Cl,Cl′)*trans*(P,P′) isomer was produced for $[RuCl_2(mtdmp)_2]$ (**7**) and $[RuCl_2(etdmp)_2]$ (**8**) and the structure of **8** was determined by the X-ray analysis. The ^{31}P-$\{^1H\}$-NMR (38.42 ppm (s)) and absorption spectra of the etdmp complex (**8**) are quite similar to those of the *trans*(Cl,Cl′)*trans*(P,P′) isomer of $[RuCl_2(ptdmp)_2]$. The ^{13}C-$\{^1H\}$-NMR spectrum of **8** exhibits a virtual triplet (δ 11.5) and a singlet (δ 13.3) for the methyl groups of PMe_2 and SCH_2CH_3, respectively, indicating that the inversion at the sulfur atom occurs rapidly and the *gauche* chelate conformation of etdmp is also flexible. The ^{31}P-$\{^1H\}$, ^{13}C-$\{^1H\}$-NMR and UV–vis spectra of **7** are quite similar to those of **8**. In contrast to the *trans*(Cl,Cl′)*trans*(P,P′) geometry of the Ru(II) complexes, $[CoCl_2(L)_2]^+$ (L = mtdmp, etdmp) was isolated as a *trans(Cl,Cl′)cis(P,P′)* isomer [6]. The origin of the different geometrical choice for the Ru(II) and Co(III) complexes is not clear at present.

The hydride complex $[RuH(cym)(etdmp)]^+$ prepared by the treatment of $NaBH_4$ with $[RuCl(cym)(etdmp)]^+$ in ethyl alcohol exhibits a doublet at δ −11.18 with

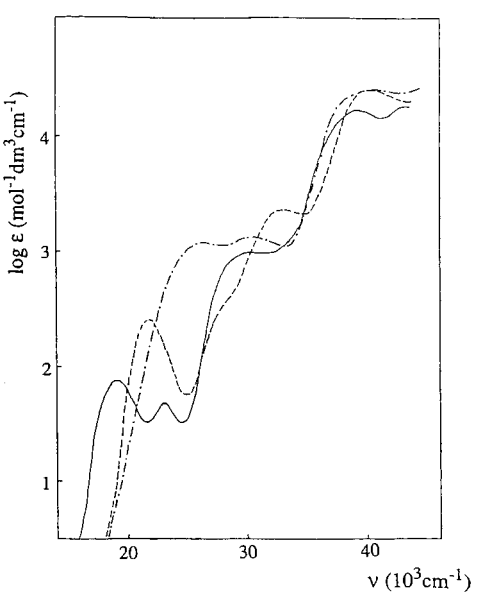


Fig. 2. Absorption spectra of complexes **9** (—), **10** (– · –) and **11** (– – –), in CH_2Cl_2.

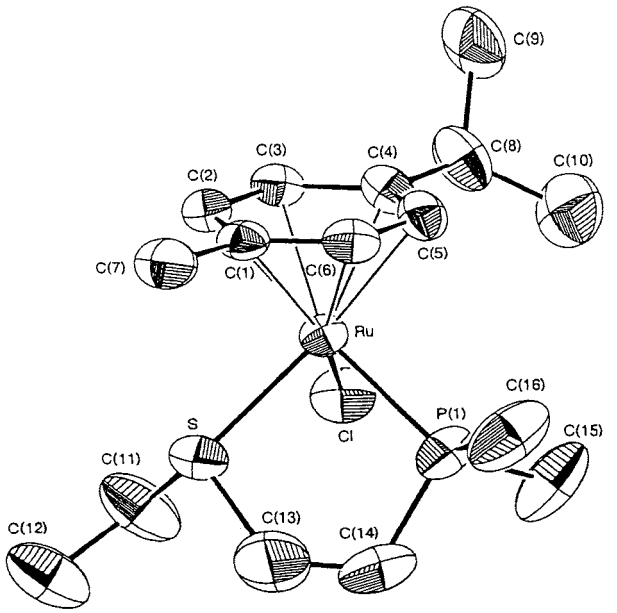


Fig. 3. ORTEP drawing of **5**.

$J = 48$ Hz in the ^1H-NMR and an absorption peak at 1933 cm^{-1} in the IR spectrum due to RuH. The spectral data are comparable to those for $[RuHCl(PPh_3)(C_6Me_6)]$ (δ −8.93 ($J = 53$ Hz), 1950 cm^{-1}) [14] and $[RuH(cym)(dippe)]BPh_4$ (dippe = 1,2-bis(diisopropylphosphino)ethane) (δ −12.82 ($J = 36.6$ Hz), 2045 cm^{-1}) [15]. We treated $[RuCl(cym)(etdmp)]^+$ with PhCCH, CO and CH_3CN to find that no reaction took place.

2.2. Description of the crystal structures

The crystal structures of complexes **5**, **8**, **9** and **11** have been determined by the X-ray diffraction study. The ORTEP drawings of these complexes are shown in Figs. 3–6 and the selected bond lengths and bond angles are summarized in Table 1.

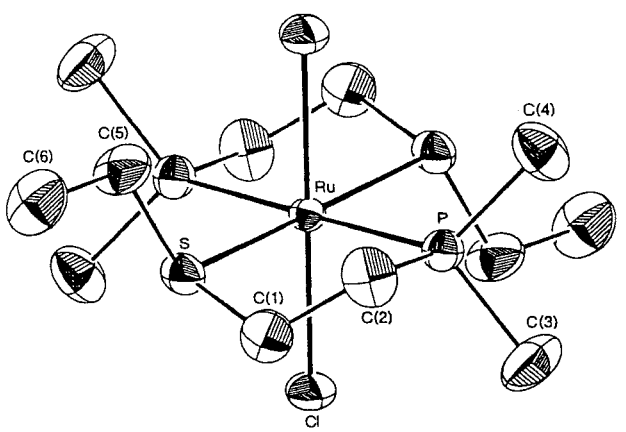


Fig. 4. ORTEP drawing of **8**.

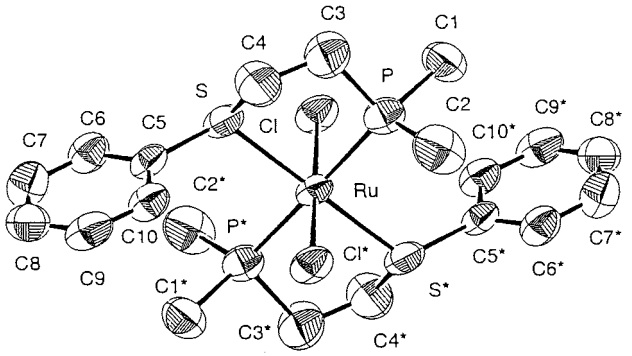


Fig. 5. ORTEP drawing of **9**.

Complex **5** has a three-legged piano stool structure in which etdmp acts as a didentate ligand to form a five-membered chelate ring with a bite angle of 84.52(4)°. The angles at Ru with the three legs do not deviate from a right angle, indicating that the structure is also viewed as a distorted octahedron as cym is regarded as a tridentate ligand. The structural parameters around Ru are quite similar to those for [RuCl(cym)(mtdmp)] [10]. The Ru–P bond lengths of the etdmp and mtdmp complexes are shorter by ca. 0.03 Å than that (2.342(3) Å) of [RuCl(cym){PPh(2-*o*-C_6H_3-6-OMe)(C_6H_3(OMe)$_2$-2,6}] [12]. This shortening may result from less steric congestion at the phosphorus atoms in the former complexes and/or the fact that the methyl-substituted phosphine moiety is a stronger donor than the aryl-substituted phosphine group. The Ru–Cl bond length (2.403(1) Å) in the etdmp complex is comparable to those in the mtdmp complex (2.389 (2) Å) and [RuCl(cym){PPh(2-*o*-C_6H_3-6-OMe)(C_6H_3-(OMe)$_2$-2,6}] (2.401(4) Å). The absolute configurations of the Ru and S atoms in the etdmp complex are

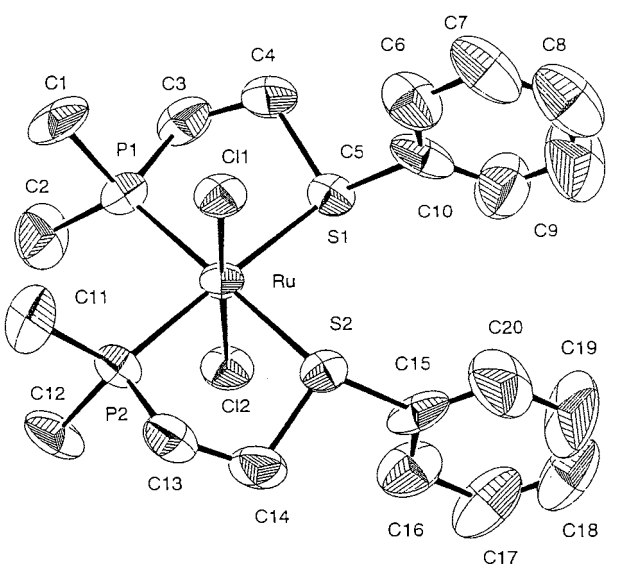


Fig. 6. ORTEP drawing of **11**.

R(Ru)*S*(S) or *S*(Ru)*R*(S) like those in the analogous mtdmp complex. The molecular model study indicates that the observed diastereomer is sterically favoured over the alternative *S*(Ru)*S*(S) or *R*(Ru)*R*(S) isomer, where steric repulsion is expected to occur between cym and a SEt or SMe moiety.

As shown in Fig. 4, the geometry of complex **8** is a slightly distorted octahedron in a *trans*(Cl,Cl′)-*trans*(P,P′) configuration, where an inversion center sits at Ru. Two etdmp ligands coordinate to Ru as bidentate chelates with a common bite angle of 86.38(2)°. The conformation is *gauche* with the P–C–C–S dihedral angle of 51.9(2)°. The Ru–P bond length, 2.3267(6) Å, is comparable to those in complex **5** (2.313(1) Å) and *trans*-[Ru(SPh)$_2$(dmpe)$_2$] (dmpe = $Me_2PCH_2CH_2PMe_2$) (average 2.334 Å) [16]. However, it is longer by 0.10 Å than that (average 2.229(2) Å) in *trans*(Cl,Cl′)*cis*(P,P′)-[RuCl$_2${PPh$_2$(C_6H_3(OMe)$_2$-2,6}] [12], probably due to the stronger *trans* influence of the PMe_2 group than that of OMe. The Ru–S bond length (2.349(1) Å) in complex **8** is fairly shorter than that (average 2.469(1) Å) in *trans*-[Ru(SPh)$_2$(dmpe)$_2$].

The ligand arrangements of the slightly distorted octahedral complexes, **9** and **11**, are *trans*(Cl,Cl′)-*trans*(P,P′) and *trans*(Cl,Cl′)*cis*(P,P′), respectively (Figs. 5 and 6). The intriguing feature of the structure of **9** is the elongation (by 0.06 Å) of the Ru–P bond and the concomitant shortening (0.07 Å) of the Ru–S bond, compared with those of complex **11**. This is probably caused by the stronger *trans* influence of the PMe_2 group than the SPh group. The Ru–Cl bond lengths are similar in these complexes. The structural parameters of **9** are also similar to those in **8**. The S–Ru–P* angles of **9** and S(1)–Ru–S(2) and P(1)–Ru–P(2) angles of **11** are slightly larger than a right angle and the *cis*-positioning of the bulky donor groups may be the reason behind the trend. The five-membered chelates assume a distorted gauche or envelope conformation.

3. Experimental

All reactions were handled under a dinitrogen atmosphere using Schlenk techniques until such time that air-stable ruthenium complexes were formed. All solvents, used in the preparation of phosphines and their complexes, were deaerated by bubbling dinitrogen gas for 20 min immediately before use. The ^{1}H, ^{31}P-{^{1}H} and ^{13}C-{^{1}H}-NMR spectra were recorded on Jeol JNM-A600, Bruker AMX-400 and Hitachi R-90H spectrometers using tetramethylsilane as an internal reference for ^{1}H and ^{13}C-{^{1}H} and 85% H_3PO_4 as an external reference for ^{31}P-{^{1}H}-NMR. Absorption spectra were obtained on a Hitachi U3400 spectrophotometer.

Table 1
Selected bond lengths (Å) and angles (°) for the complexes

Complex ***5***					
Ru–Cl	2.403(1)	Ru–S	2.377(1)	Ru–P(1)	2.313(1)
Ru–C(1)	2.231(3)	Ru–C(2)	2.267(3)	Ru–C(3)	2.273(3)
Ru–C(4)	2.244(3)	Ru–C(5)	2.206(4)	Ru–C(6)	2.198(3)
Cl–Ru–S	90.89(4)	Cl–Ru–P(1)	86.68(4)	S–Ru–P(1)	84.52(4)
Ru–S–C(11)	112.3(2)	Ru–S–C(13)	106.0(2)	C(11)–S–C(13)	102.2(3)
Ru–P(1)–C(14)	107.4(2)	Ru–P(1)–C(15)	119.2(2)	Ru–P(1)–C(16)	116.6(1)
C(14)–P(1)–C(15)	103.3(3)	C(14)–P(1)–C(16)	105.7(3)	C(15)–P(1)–C(16)	103.2(3)
S–C(11)–C(12)	113.4(3)	S–C(13)–C(14)	117.2(5)	P(1)–C(14)–C(13)	115.7(4)
Complex ***8***					
Ru–Cl	2.4336(7)	Ru–S	2.3485(6)	Ru–P	2.3267(6)
Cl–Ru–Cl'	180.0	S–Ru–S'	180.0	P–Ru–P'	180.0
Cl–Ru–S	84.29(2)	Cl–Ru–S'	95.71(2)	Cl–Ru–P	91.12(2)
Cl–Ru–P'	88.88(2)	S–Ru–P	86.38(2)	S–Ru–P'	93.62(2)
Complex ***9***					
Ru–Cl	2.435(2)	Ru–S	2.344(2)	Ru–P	2.335(2)
Cl–Ru–Cl*	180.0	Cl–Ru–S	85.96(5)	Cl–Ru–S*	94.04(5)
Cl–Ru–P	90.04(7)	Cl–Ru–P*	89.96(7)	S–Ru–S*	180.0
S–Ru–P	83.82(7)	S–Ru–P*	96.18(7)	P–Ru–P*	180.0
Complex ***11***					
Ru–Cl(1)	2.429(2)	Ru–Cl(2)	2.433(2)	Ru–S(1)	2.416(2)
Ru–S(2)	2.414(3)	Ru–P(1)	2.276(3)	Ru–P(2)	2.271(3)
Cl(1)–Ru–Cl(2)	178.58(10)	Cl(1)–Ru–S(1)	93.66(8)	Cl(1)–Ru–S(2)	85.35(8)
Cl(1)–Ru–P(1)	91.55(9)	Cl(1)–Ru–P(2)	89.49(9)	Cl(2)–Ru–S(1)	85.54(8)
Cl(2)–Ru–S(2)	93.56(8)	Cl(2)–Ru–P(1)	89.54(9)	Cl(2)–Ru–P(2)	91.33(9)
S(1)–Ru–S(2)	96.34(9)	S(1)–Ru–P(1)	84.70(10)	S(1)–Ru–P(2)	176.73(10)
S(2)–Ru–P(1)	176.79(10)	S(2)–Ru–P(2)	84.77(10)	P(1)–Ru–P(2)	94.4(1)

3.1. Preparation of phosphines

3.1.1. 2-(Methylthio)dimethylphosphinoethane (mtdmp)

The preparation was described previously [5]. ^{1}H-NMR ($CDCl_3$, 90 MHz): δ 2.5–2.7 (m, 2H, CH_2S), 2.13 (s, 3H, SCH_3), 1.5–1.8 (m, 2H, PCH_2), 1.04 (d, ^2J(PH) 2.2 Hz, 6H, PCH_3). ^{31}P-{^{1}H}($CDCl_3$, 36 MHz): −49.56 ppm (s).

3.1.2. 2-(Ethylthio)dimethylphosphinoethane (etdmp)

Etdmp was prepared by a method similar to that for mtdmp using (2-chloroethyl)ethylsulfide instead of (2-chloroethyl)methylsulfide. (90%) The crude product was found to be a mixture of etdmp and 1,2-bis-(dimethylphosphino)ethane (5–10%, ^{31}P-{^{1}H} −46.39 ppm) according to the NMR spectra. Since it was difficult to separate etdmp from the mixture by distillation because of the similar boiling points, the crude product was used for the preparation of complexes without further purification. However, the isolation and purification of the desired complexes were performed successfully as will be described later in this section. ^{1}H-NMR ($CDCl_3$, 90 MHz): δ 2.4–2.8 (m, 4H, CH_2S, SCH_2CH_3), 1.5–1.8 (m, 2H, PCH_2), 1.27 (t, ^3J(HH) 7.4, SCH_2CH_3), 1.05 (d, ^2J(PH) 2.0 Hz, 6H, PCH_3). ^{31}P-{^{1}H}-NMR ($CDCl_3$, 36 MHz): −50.66 ppm (s).

3.1.3. 2-(Phenylthio)dimethylphosphinoethane (ptdmp)

To a dark-blue liquid ammonia solution (200 cm^3) of sodium metal (2.35 g, 0.102 mol), in a dry ice–acetone bath, was added tetramethyldiphosphine [17] (6.3 g, 0.052 mol) drop-wise with mechanical stirring. After stirring for 1 h, 2-chloroethyl phenyl sulfide (17.9 g, 0.104 mol) was added portion-wise to the resulting yellow orange solution, yielding a colourless solution. After stirring it for 1 h the liquid ammonia was slowly evaporated to dryness. Diethyl ether (100 cm^3) was added to the residue with stirring and insoluble materials were filtered off. The filtrate was first evaporated at 45°C at atmospheric pressure to remove the solvent and then at 40°C at 4 mmHg to remove the side-product, dmpe, together with a small amount of unreacted 2-chloroethyl phenyl sulfide (1.76 g). The resulting oily product was found to be nearly pure ptdmp according to the NMR spectrum and was used for preparing metal complexes without further purification. (13.1 g, 64%) ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.2–7.4 (m, 5H, SC_6H_5), 2.98–3.04 (m, 2H, CH_2S), 1.67–1.73 (m, 2H, PCH_2), 1.04 (d, ^2J(PH) 2.0 Hz, 6H, PCH_3), ^{31}P-{^{1}H} ($CDCl_3$, 162 MHz) −49.63 ppm (s).

3.2. Preparation of complexes

3.2.1. [$RuCl_2$(cym)(mtdmp-κP)] **1**

To a toluene solution (30 cm^3) of [$RuCl_2$] (0.31 g, 0.50 mmol) was added mtdmp (0.33 g, 2.4 mmol) with stirring. The solution was stirred at room temperature (r.t.) for 3 h and filtered, yielding orange precipitates (0.09 g, 24%) which were characterized as [$RuCl_2$(cym)]$_2$(μ-dmpe) by the elemental analysis and ^{1}H-NMR spectrum. Found: C, 41.18; H, 5.79. $C_{26}H_{44}Cl_4P_2Ru_2$ requires C, 40.95; H, 5.82%. ^{1}H-NMR (CD_2Cl_2, 90 MHz): δ 5.5 (br, 8H, C_6H_4), 2.75 (spt, ^3J(HH) 6.8, 2H, Me_2CH), 2.18 (m, 4H, PCH_2), 2.02 (s, 6H, $C_6H_4CH_3$), 1.55 (filled-in d, J 20.6, 12H, PCH_3), 1.20 (d, ^3J(HH) 6.8Hz, 12H, $(CH_3)_2CH$). The filtrate was evaporated under reduced pressure to dryness. The residue (complex **1**) was washed with hexane and air-dried. (0.32 g, 72%). Found: C, 40.89; H, 6.14%. $C_{15}H_{27}Cl_2PRuS$: requires C, 40.73; H, 6.15%. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 5.4 (br, 4H, C_6H_4), 2.84 (spt, ^3J(HH) 6.9, 1H, Me_2CH), 2.6–2.8 (m, 2H, SCH_2), 2.2–2.4 (m, 2H, PCH_2), 2.15 (s, 3H, SCH_3), 2.08 (s, 3H, $C_6H_4CH_3$), 1.57 (d, ^2J(HP) 10.8, 6H, PCH_3), 1.23 (d, ^3J(HH) 7.0 Hz, 6H, $(CH_3)_2CH$), ^{31}P-{^{1}H}-NMR ($CDCl_3$, 162 MHz): 9.54 ppm (s). The complex is soluble in chloroform, dichloromethane, or toluene, slightly soluble in diethyl ether and insoluble in hexane.

3.2.2. [$RuCl_2$(cym)(etdmp-κP)] **2**

The complex was prepared by a method similar to that for **1** using etdmp (73%). Found: C, 41.82; H, 6.56%. $C_{16}H_{29}Cl_2PRuS$ requires C, 42.11; H, 6.40%. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 5.5–5.6 (m, 4H, C_6H_4), 2.81 (spt, ^3J(HH) 6.9, 1H, Me_2CH), 2.7–2.8 (m, 2H, CH_2S), 2.59 (q, ^3J(HH) 7.4, 2H, SCH_2Me), 2.3–2.4 (m, 2H, PCH_2), 2.07 (s, 3H, $C_6H_4CH_3$), 1.60 (d, ^2J(HP) 10.8, 6H, PCH_3), 1.27 (t, ^3J(HH) 7.43, 3H, SCH_2CH_3), 1.23 (d, ^3J(HH) 7.0Hz, 6H, $(CH_3)_2CH$). ^{31}P-{^{1}H}-NMR ($CDCl_3$, 162 MHz): 10.34 ppm (s). The solubility of the complex is similar to that of **1**.

3.2.3. [$RuCl_2$(cym)(ptdmp-κP)] **3**

To a toluene solution (30 cm^3) of [$RuCl_2$(cym)]$_2$ (0.31 g, 0.50 mmol) was added ptdmp (0.41 g, 2.1 mmol) with stirring. The solution was stirred at r.t. for a further 3 h, yielding an orange powder that was filtered and washed with hexane and air-dried. (0.47 g, 93%). Found: C, 48.32; H, 5.38; S, 5.60%. $C_{20}H_{29}Cl_2PRuS$ requires C, 47.62; H, 5.79; S, 6.36%. ^{1}H-NMR ($CDCl_3$, 400 MHz) δ 7.1–7.4 (m, 5H, SC_6H_5), 5.4(br, 4H, C_6H_4), 2.76 (spt, ^3J(HH) 6.9, 1H, Me_2CH), 3.09–3.14 (m, 2H, CH_2S), 2.3–2.4 (m, 2H, PCH_2), 2.01 (s, 3H, $C_6H_4CH_3$), 1.56 (d, ^2J(HP) 10.8, 6H, PCH_3), 1.19 (d, ^3J(HH) 7.0 Hz, 6H, $(CH_3)_2CH$). ^{31}P-{^{1}H} ($CDCl_3$, 162 MHz) 10.40 ppm (s). The complex is soluble in chloroform or dichloromethane, slightly soluble in diethyl ether and insoluble in hexane or toluene.

3.2.4. [RuCl(cym)(mtdmp)]$B(C_6H_5)_4$ **4**

To an ethyl alcohol solution (30 cm^3) of [$RuCl_2$(cym)]$_2$ (0.31 g, 0.50 mmol) was added mtdmp (0.21 g, 1.5 mmol) with stirring. The solution was stirred at r.t. for 3 h and then filtered, yielding an orange powder of [$RuCl_2$(cym)]$_2$(μ-dmpe) (0.06 g, 16%). The filtrate was dried under reduced pressure. The residue was washed with diethyl ether and extracted with ethyl alcohol (5 cm^3). The solution was mixed with the ethyl alcohol solution saturated with $NaB(C_6H_5)_4$, yielding yellow precipitates. The powdered precipitates were recrystallized from a mixture of acetone and water to afford orange–yellow crystals. (0.52 g, 72%). Found: C, 64.49; H, 6.47%. $C_{39}H_{47}BClPRuS$ requires C, 64.51; H, 6.52%. ^{1}H-NMR (DMSO-d_6, 600 MHz): δ 6.40 (t, ^3J(HH) 5.5, 2H, C_6H_4), 5.71 (d, ^3J(HH) 6.2, 1H, C_6H_4), 5.48 (d, ^3J(HH) 6.2, 1H, C_6H_4), 2.6–2.8 (m, 3H, CH_2S, Me_2CH), 2.41 (s, 3H, SCH_3), 2.0–2.1 (m, 2H, PCH_2), 1.95 (s, 3H, $C_6H_4CH_3$), 1.84 (d, ^2J(HP) 11.4, 3H, PCH_3), 1.67 (d, ^2J(HP) 12.5, 3H, PCH_3), 1.14 (d, ^3J(HH) 6.6, 3H, $(CH_3)_2CH$), 1.10 (d, ^3J(HH) 7.0 Hz, 3H, $(CH_3)_2CH$). ^{31}P-{^{1}H}-NMR ($CDCl_3$, 36 MHz): 51.24 ppm (s). The complex is soluble in dimethyl sulfoxide, dichloromethane or acetone and insoluble in diethyl ether, ethyl alcohol or water.

3.2.5. [RuCl(cym)(etdmp)]PF_6 **5**

The complex was prepared by a method similar to that for complex **4**, using etdmp and $NaPF_6$. The recrystallization was performed from a mixture of dichloromethane and diethyl ether to afford orange–yellow crystals. (69%) Found: C, 33.89; H, 5.12%. $C_{16}H_{29}ClF_6P_2RuS$ requires C, 33.96; H, 5.17%. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 6.12 (m, 2H, C_6H_4), 5.64 (d, ^3J(HH) 6.4, 1H, C_6H_4), 5.49 (d, ^3J(HH) 6.4, 1H, C_6H_4), 3.0–3.2 (m, 1H, Me_2CH), 2.5–2.7 (m, 4H, CH_2S, SCH_2CH_3), 2.0–2.2 (m, 2H, PCH_2), 2.11 (s, 3H, $C_6H_4CH_3$), 1.94 (d, ^2J(HP) 10.5, 3H, PCH_3), 1.81 (d, ^2J(HP) 12.0, 3H, PCH_3), 1.34 (t, ^3J(HH) 7.4, 3H, SCH_2CH_3), 1.25 (d, ^3J(HH) 6.8, 3H, $(CH_3)_2CH$), 1.21 (d, ^3J(HH) 6.9 Hz, 3H, $(CH_3)_2CH$). ^{31}P-{^{1}H}-NMR ($CDCl_3$, 162 MHz) 50.96 ppm (s). The complex is soluble in dichloromethane, chloroform or acetone, slightly soluble in ethyl alcohol and insoluble in diethyl ether or water.

3.2.6. [RuCl(cym)(ptdmp)]$B(C_6H_5)_4$ **6**

To an ethyl alcohol solution (30 cm^3) of [$RuCl_2$(cym)]$_2$ (0.31 g, 0.50 mmol) was added ptdmp (0.33 g, 1.7 mmol) with stirring. The solution was stirred overnight and dried under reduced pressure. The residue was extracted with ethyl alcohol (5 cm^3). The ethyl alcohol solution of $NaB(C_6H_5)_4$ was added to the extract, yielding yellow powdered precipitates. The precipitates were recrystallized from a mixture of dichloromethane and diethyl ether to afford orange–

yellow crystals. (0.56 g, 71%). ^{1}H-NMR (DMSO-d_6, 400 MHz): δ 7.6–7.7 (m, 2H, SC_6H_5), 7.4–7.5 (m, 3H, SC_6H_5), 6.4 (br, 2H, C_6H_4), 5.9 (br, 1H, C_6H_4), 5.69 (d, ^3J(HH) 6.1, 1H, C_6H_4), 3.17 (spt, J 6.9, 1H, Me_2CH), 2.5–2.7 (m, 2H, CH_2S), 2.0–2.2 (m, 2H, PCH_2), 1.97 (d, ^2J(HP) 12.4, 3H, PCH_3), 1.96 (s, 3H, $C_6H_4CH_3$), 1.72 (d, ^2J(HP) 11.4, 3H, PCH_3), 1.13 (d, ^3J(HH) 6.9, 3H, $(CH_3)_2CH$), 1.11 (d, ^3J(HH) 7.0 Hz, 3H, $(CH_3)_2CH$). ^{31}P-{^{1}H}-NMR (DMSO-d_6, 162 MHz): 51.32 ppm (s). The complex is soluble in dichloromethane or acetone and insoluble in diethyl ether, ethyl alcohol, or water.

3.2.7. *trans(Cl,Cl′)trans(P,P′)-[RuCl$_2$(mtdmp)$_2$]* **7**

The suspension of $[RuCl_2(cym)]_2$ (0.31 g, 0.50 mmol) in n-butanol (20 cm^3) was treated with mtdmp (0.64 g, 4.7 mmol) and the mixture was refluxed overnight, yielding an orange–yellow solution. The solvent was evaporated under reduced pressure. The residue was extracted with diethyl ether. Removal of diethyl ether from the solution yielded an orange powder which was washed with hexane. The composition of the orange complex was determined to be [RuCl$_2$(mtdmp)(dmpe)] based on the elemental analysis. Found: C, 29.19; H, 6.40%, $C_{11}H_{29}C_{l2}P_3RuS$ requires C, 28.83; H, 6.38%. (0.084 g, 18%). The residue of the diethyl ether extraction was dissolved in dichloromethane and filtered. The filtrate was evaporated to dryness and the residue was recrystallized from a mixture of dichloromethane and diethyl ether to afford orange–yellow crystals. (0.23 g, 52%). Found: C, 27.05; H, 5.94%. $C_{10}H_{26}Cl_2P_2RuS_2$ requires C, 27.03; H, 5.90%. ^{13}C-{^{1}H}-NMR ($CDCl_3$, 23 MHz): δ 36.7(virtual t, J(PC) 21.0, CH_2S), 27.2 (virtual t, J(PC) 23.8 Hz, PCH_2), 18.7 (s, SCH_3), 11.0 (m, PCH_3). ^{31}P-{^{1}H}-NMR ($CDCl_3$, 162 MHz): 39.93 ppm (s). The complex is soluble in dichloromethane, acetone or n-butanol and insoluble in diethyl ether, hexane or water.

3.2.8. *trans(Cl,Cl′)trans(P,P′)-[RuCl$_2$(etdmp)$_2$]* **8**

The complex was prepared by a method similar to that for complex **7** using etdmp to afford [RuCl$_2$(etdmp)(dmpe)] (yield 18%), found C, 31.00; H, 6.65%, $C_{11}H_{29}Cl_2P_3RuS$ requires C, 30.51; H, 6.62% and complex **8** (yield 59%), found: C, 30.67; H, 6.30%, $C_{12}H_{30}Cl_2P_2RuS_2$ requires C, 30.51; H, 6.40%. ^{13}C-{^{1}H}-NMR ($CDCl_3$, 23 MHz): δ 33.1 (m, CH_2S), 29.0 (s, SCH_2CH_3), 27.8 (virtual t, J(PC) 23.6, PCH_2), 13.3 (s, SCH_2CH_3), 11.5 (virtual t, J(PC) 25.8 Hz, PCH_3). ^{31}P-{^{1}H}-NMR ($CDCl_3$, 162 MHz): 38.42 ppm (s). The solubility of complex **8** is similar to that of complex **7**.

3.2.9. *trans (Cl,Cl′) trans (P,P′) - [RuCl$_2$ (ptdmp)$_2$]* **9**, *cis-(Cl,Cl′)cis(P,P′)-[RuCl$_2$(ptdmp)$_2$]* **10** *and trans(Cl,Cl′)-cis(P,P′)-[RuCl$_2$(ptdmp)$_2$]* **11**

Treatment of $[RuCl_2(cym)]_2$ (0.31 g, 0.50 mmol) and ptdmp (0.81 g, 4.1 mmol) in n-butanol (3 cm^3) under a refluxed condition overnight yielded red and yellow precipitates. The suspension was allowed to stand at −15°C overnight and filtered. The precipitates was mixed with a small amount of ethyl alcohol to extract yellow complex, leaving red precipitates. The red precipitates were recrystallized from a mixture of dichloromethane and diethyl ether to afford red crystals of complex **9**. (0.074 g, 13%). Found: C, 42.23; H, 5.09; S, 11.35%. $C_{20}H_{30}Cl_2P_2RuS_2$ requires C, 42.25; H, 5.32; S, 11.28%. ^{1}H-NMR ($CDCl_3$, 90 MHz): δ 7.8–8.0 (m, 2H, SC_6H_5), 7.2–7.4 (m, 3H, SC6H$_5$), 2.9–3.2 (m, 2H, CH_2S), 1.6–2.0 (m, 2H, PCH_2), 1.1–1.4 (m, 6H, PCH_3). ^{31}P-{^{1}H}-NMR ($CDCl_3$, 162 MHz): 38.81 ppm (s). UV–vis 513 nm (ε 73): 433(44), 330(890). The complex is soluble in dichloromethane, or chloroform and insoluble in ethyl alcohol, n-butanol or diethyl ether.

The yellow ethyl alcohol extract was concentrated to a small volume just before crystals appeared and allowed to stand at −15°C to yield yellow crystals of complex **10**. (0.14 g, 25%). Found: C, 42.17; H, 5.15; S, 11.12%. $C_{20}H_{30}Cl_2P_2RuS_2$ requires C, 42.25; H, 5.32; S, 11.28%. ^{31}P-{^{1}H}-NMR ($CDCl_3$, 162 MHz): 51.69 (d, ^2J(PP) 32.6), 48.49 (d, ^2J(PP) 32.6 Hz). UV–vis: 456 nm (ε 258), 349sh (320), 300 (2100). The complex is soluble in dichloromethane or chloroform, slightly soluble in ethyl alcohol or n-butanol and insoluble in diethyl ether.

When the n-butanol filtrate of the starting reaction mixture was evaporated to dryness, an orange complex was extracted from the residue with diethyl ether. The extract was evaporated to dryness. The residue was washed with hexane and recrystallized from toluene to afford orange crystals of complex **11**. (0.042 g, 7%). Found: C, 41.98; H, 5.03; S, 11.42%. $C_{20}H_{30}Cl_2P_2RuS_2$ requires C, 42.25; H, 5.32; S, 11.28%. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.6–7.7 (m, 2H, SC_6H_5), 7.1–7.3 (m, 3H, SC_6H_5), 3.1–3.3 (m, 2H, CH_2S), 2.1–2.2 (m, 2H, PCH_2), 1.62(filled-in d, J(HP) 9.3 Hz, 6H, PCH_3), ^{31}P-{^{1}H}-NMR ($CDCl_3$, 162 MHz) 48.90 ppm (s). UV–vis 382 nm (ε 1150): 326 (1250). The complex is soluble in dichloromethane, chloroform or n-butanol, slightly soluble in diethyl ether and insoluble in hexane.

3.2.10. *[RuH(cym)(etdmp)]PF$_6$*

To an ethyl alcohol solution (50 cm^3) of [RuCl(cym)(etdmp)]PF$_6$ (0.50 g, 0.89 mmol) was added an ethyl alcohol solution (20 cm^3) of $NaBH_4$ with stirring. The solution was stirred at r.t. for 1 h and the colour changed from orange to red immediately. The resulting precipitates were removed by centrifugation and the supernatant solution was evaporated to dryness. The residue was mixed with THF to extract an orange brown complex. The undissolved material was removed by centrifugation and the supernatant was evaporated to dryness. The residue was washed with hexane and

dried in vacuo. (0.37 g, 78%). Found: C, 36.00; H, 5.42; S, 6.03%. $C_{16}H_{30}F_6P_2RuS$ requires C, 36.16; H, 5.69; S, 6.03%. ^{1}H-NMR (THF-d_6, 400 MHz): δ 6.06 (d, ^3J(HH) 6.2, 1H, C_6H_4), 5.95 (d, ^3J(HH) 5.9, 1H, C_6H_4), 5.64 (d, ^3J(HH) 6.0, 2H, C_6H_4), 2.95 (spt, ^3J(HH) 6.9, 1H, Me_2CH), 2.6–2.9 (m, 4H, CH_2S, SCH_2Me), 2.1–2.3 (m, 2H, PCH_2), 2.14 (s, 3H, $C_6H_4CH_3$), 1.70 (d, ^2J(HP) 10.0, 3H, PCH_3), 1.59 (d, ^2J(HP) 11.2, 3H, PCH_3), 1.21 (d, ^3J(HH) 6.3, 3H, $(CH_3)_2CH$), 1.19 (d, ^3J(HH) 6.3, 3H, $(CH_3)_2CH$), 1.13 (t, ^3J(HH) 7.4, 3H, SCH_2Me), −11.18 (d, ^2J(HP) 48 Hz, 1H, RuH). ^{31}P-{^{1}H}-NMR ($CDCl_3$, 162 MHz): 57.77(s), −143.4 ppm (spt, PF_6). IR (KBr pellet): ν(RuH) 1933, $\nu(PF_6)$ 836, 558 cm^{-1}. The complex is unstable in air and decomposes in dichloromethane or chloroform. The complex is soluble in ethyl alcohol, THF or DME and insoluble in toluene or hexane.

3.3. Crystallography

All crystals selected for data collection were mounted on the top of a glass fiber with epoxy resin. Intensity data were collected on a Rigaku AFC-5 (**5** and **8**) and AFC-7R (**9** and **11**) automated four-circle diffractometer using graphite-monochromatized Mo–K_α radiation ($\lambda = 0.71069$ Å). The unit-cell parameters were determined by a least-squares refinement of the setting angles for 25 reflections with 2θ angles in the range of $29° < 2\theta < 30°$ (**5** and **8**) and $22° < 2\theta < 25°$ (**9** and **11**). Crystallographic data and experimental details are summarized in Table 2. Three standard reflections were monitored at every 150 reflections throughout the data collection and no significant deterioration of the crystals was observed. The absorption correction was made for **5** and **8** by a Gaussian integration method and an empirical absorption correction was applied for **9** and **11** based on ψ scan data of several suitable reflections with χ values closed to 90°. The structures of **5** and **8** were solved by direct methods [18] and a subsequent Fourier synthesis and those of **9** and **11** were solved by heavy-atom Patterson methods [19] and expanded using Fourier techniques. The structures were refined on F by full-matrix least-squares method using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were located from a difference-Fourier map or

Table 2
Crystallographic data and experimental details

Complex	**5**	**8**	**9**	**11**
Formula	$C_{16}H_{29}ClF_6P_2RuS$	$C_{12}H_{30}Cl_2P_2RuS_2$	$C_{20}H_{30}Cl_2P_2RuS_2$	$C_{27}H_{38}Cl_2P_2RuS_2$
FW	565.93	472.41	568.51	660.64
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/a$ (No. 14)	Cc (No. 9)
a (Å)	12.529(2)	8.254(2)	8.561(3)	15.42(1)
b (Å)	13.512(2)	12.003(2)	14.548(4)	16.733(5)
c(Å)	14.097(2)	10.034(2)	10.264(4)	14.22(1)
β (°)	106.68(1)	90.69(2)	110.16(3)	122.52(4)
Z	4	2	2	4
V (Å^3)	2286.1(5)	994.0(3)	1200.0(7)	3094(3)
μ(Mo–K_α) (cm^{-1})	10.63	13.95	11.88	9.32
Transmission factor	0.654–0.702	0.628–0.705	0.893–1.000	0.947–1.000
Crystal color	Orange	Orange	Red	Yellow
Crystal habit	Prismatic	Prismatic	Prismatic	Prismatic
Crystal size (mm^3)	0.30 × 0.40 × 0.50	0.30 × 0.30 × 0.50	0.65 × 0.50 × 0.20	0.45 × 0.50 × 0.40
D_{calc} (g cm^{-3})	1.64	1.58	1.57	1.42
T (K)	298	298	296	296
Scan range (°)	1.50 + 0.50 tan θ	1.52 + 0.50 tan θ	1.47 + 0.30 tan θ	1.78 + 0.30 tan θ
Scan mode	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
Scan speed (° min^{-1})	8	8	16	16
$2\theta_{max}$ (°)	60	60	55	50
No. reflections measured	7213	2892	2997	2945
No. reflections observed [a]	4894	2512	2386	2403
R [b]	0.040	0.026	0.071	0.037
R_w [c]	0.047	0.034	0.095	0.045
S	1.74	1.52	3.52	2.26
Largest difference peak (e Å^{-3})	0.71	0.56	0.61	0.71
Largest difference hole (e Å^{-3})	−0.90	−0.82	−2.14	−0.34

[a] $|F_o| > 3\sigma(|F_o|)$ for **5** and **8**, $|I_o| > 3\sigma(|I_o|)$ for **9** and **11**.
[b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[c] $R_w = [\Sigma\, w||F_o| - |F_c||^2/\Sigma\, w|F_o|^2]^{1/2}$, $w = [\sigma^2(F_o) + \{0.015(F_o)\}^2]^{-1}$ for **5** and **8**, $w = 4(F_o)^2\{\sigma^2(F_o^2)\}^{-1}$ for **9**, $w = [\sigma^2(F_o) + \{0.009(F_o)\}^2]^{-1}$ for **11**.

placed at the calculated positions and fixed during the structural refinement. The calculations were performed using XTAL 3.2 [20] (**5** and **8**) and TEXSAN [21] crystallographic software (**9** and **11**) packages.

4. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 114821-114824 for complexes **5**, **8**, **9** and **11**, respectively. Copies of this information may be obtained free of charge from the Director, CCDC, 12, Union Road, Cambridge CB2 1EZ (Fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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