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Arene ruthenium metallacycles containing chelating thioamide ligands

Cansu Alagöz, David J. Brauer, Fabian Mohr *

Fachbereich C – Anorganische Chemie, Bergische Universität Wuppertal, 42119 Wuppertal, Germany

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ABSTRACT

Cationic, chiral arene ruthenium complexes of the type $[Ru(\eta^6\text{-cym})(PPh_3)\{\kappa^2N,S\text{-PhNC(S)R}\}]BPh_4$ were prepared in high yields by refluxing a mixture containing $[(\eta^6\text{-cym})RuCl_2]_2$, Ph_3P, PhNHC(S)R, $NaBPh_4$ and Et_3N in MeOH. A series of seven complexes with different thioamide ligands was prepared and fully characterised by spectroscopic methods including NMR spectroscopy and electrospray mass spectrometry. The solid-state structures of two complexes were determined by single crystal X-ray diffraction.

1. Introduction

Thioamides containing the NHC(S) unit are versatile ligands, which upon deprotonation can coordinate to a given metal either as monoanionic thiolato ligands or as anionic N,S-chelating ligands *via* both N and S atoms forming four-membered metallacycles (Chart 1). To the best of our knowledge, coordination as anionic N-donors solely *via* the nitrogen atom has so far never been reported.

The group of Henderson has reported the synthesis and structural characterisation of various transition metal complexes containing chelating thioamide derivatives including PhNHC(S)NHPh, MeNHC(S)NHCN, $Ph_2NNHC(S)NHPh$ and $PhNHC(S)NR_2$ [1–5]. We have previously examined reactions, structures and anti-tumour activity of various gold(I), platinum(II) and palladium(II) complexes containing anionic S-coordinated thioamide ligands [6–9]. At present, we are also undertaking an investigation of gold(I) complexes containing selenoamide ligands [10,11]. The current interest in organometallic ruthenium complexes with anti-tumour activity [12–16] as well as the lack of known arene ruthenium complexes containing anionic N,S-chelating ligands prompted us to investigate this class of complexes in further detail. The only reported arene ruthenium complexes containing anionic chelating N,S-ligands appear to be the chiral Ru(II) complex $[Ru(\eta^6\text{-}C_6H_6)(Cl)\{\kappa^2N,S\text{-PhMeCHNC(S)Ph}\}]$ containing a chiral thioamide ligand [17] and the Ru(II) complex containing an N,S-chelating triazepine ligand (Chart 2) [18].

We therefore wished to extend this chemistry by preparing some arene ruthenium phosphine complexes containing anionic chelating N-phenyl thioamides of the type $PhNHC(S)NR_2$. The results of the synthesis and structural investigations of some cationic arene ruthenium complexes containing chelating N-phenyl thioamide ligands are presented in this paper.

2. Results and discussion

Refluxing a mixture containing $[(\eta^6\text{-cym})RuCl_2]_2$, Ph_3P, PhNHC(S)R and Et_3N in MeOH gave an orange solution out of which the yellow, cationic Ru(II) complexes $[Ru(\eta^6\text{-cym})(PPh_3)\{\kappa^2N,S\text{-PhNC(S)R}\}]^+$ were isolated as their BPh_4 salts in good yields (Scheme 1).

These air- and moisture-stable compounds are soluble in chlorinated solvents, acetone, acetonitrile and hot MeOH but insoluble in water and Et_2O. Complexes **1**–**7** were fully characterised by spectroscopic methods and, in addition, the solid-state structures of complexes **1** and **2** were determined by X-ray diffraction. The $^{31}P\{^1H\}$ NMR spectra of complexes **1**–**7** all show a singlet resonance at *ca.* 40 ppm, typical for $[Ru(\eta^6\text{-arene})(PPh_3)]$ type complexes. The metal-centered chirality of the complexes is evident from their ^1H NMR spectra, which show doubling of the resonances of the cymene protons (four doublets) and also the isopropyl Me-groups (two doublets). The remaining signals from the thioamide ligands, the PPh_3 group and the BPh_4 anion were unambiguously assigned using 2-D NMR spectra (see Section 3). The deprotonation of the thioamide ligands is confirmed by the absence of an NH signal in the ^1H NMR spectra of the complexes. The positive-ion electrospray mass spectra of complexes **1**–**7** show two signals, one strong corresponding to the molecular ion of the cation, the other,

* Corresponding author.
E-mail address: fmohr@uni-wuppertal.de (F. Mohr).

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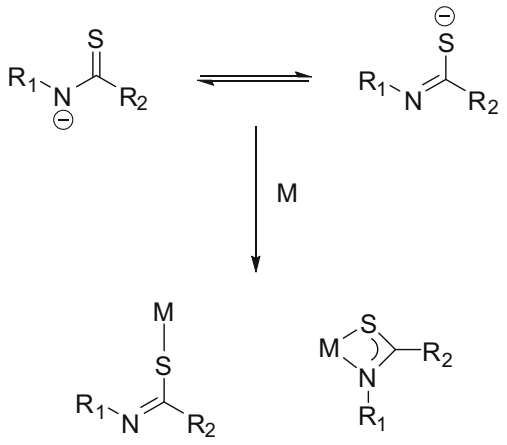


Chart 1.

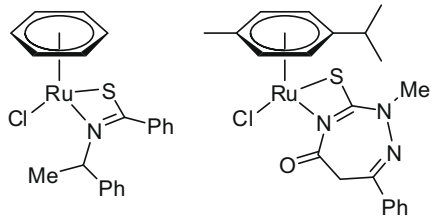


Chart 2.

much weaker, due to loss of the Ph_3P group. The observed isotope patterns of these signals agree well with the computed patterns for the given formulae. The proposed structure of these compounds was confirmed by an X-ray diffraction study of complexes **1** and **2**, shown in Figs. 1 and 2, respectively. Selected bond distances and angles are collected in Tables 1 and 2.

In both complexes, the cations consist of a ruthenium atom coordinated to the deprotonated thioamide *via* the sulphur and nitrogen atoms forming a four-membered metallacycle with an S–Ru–N angle of *ca.* 67°. This angle is similar to that observed in the Ru(II) complex $[Ru\{\kappa^2N,S\text{-}PhNC(S)NPh\}_2(CO)(PPh_3)]$ containing chelating *N,N′*-diphenylthioureido ligands [19] and also similar to that observed in $[Ru(\eta^6\text{-}C_6H_6)(Cl)\{\kappa^2N,S\text{-}PhMeCHNC(S)Ph\}]$ [17]. The trigonal pyramidal coordination sphere about Ru in these complexes is completed by the P-coordinated phosphine and the η^6-coordinated arene. Both the Ru–S and Ru–N bond distances of *ca.* 2.40 and 2.10 Å, respectively are similar to those observed in $[Ru\{\kappa^2N,S\text{-}PhNC(S)NPh\}_2(CO)(PPh_3)]$ [19]. The Ru–P and Ru–arene distances and angles are similar to those reported for other *p*-cymene Ru phosphine complexes [3]. The C–C bond lengths in the *p*-cymene ligands of the complexes alternate in a long-short-long pattern, which is typically observed for arenes coordinated to Ru. The aforementioned chirality of these compounds is also observed in the solid-state structures: Whilst crystals of complex **1** contain a mixture of equal amounts of *R* and *S* enantiomers (an *R* enantiomer is shown in Fig. 1), the crystals of complex **2** contained only the *S* enantiomers. The racemic complex **2** forms separate crystals for both the *R* and *S* enantiomers upon recrystallisation and by chance a crystal of *S* enantiomer happened to have been picked for the diffraction experiment.

In conclusion, we present here the synthesis, spectroscopic properties of the first cationic arene ruthenium(II) complexes containing N,S-chelating thioamide ligands which show metal-centered chirality. Further studies of this class of compounds including their biological activity are currently in progress.

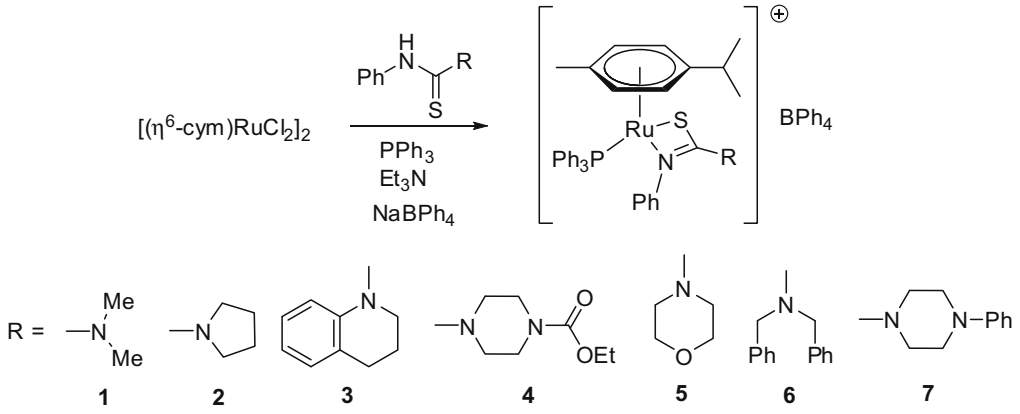
3. Experimental

3.1. General

^1H, ^{13}C and $^{31}P\{^1H\}$ NMR spectra were recorded on a 400 MHz Bruker ARX spectrometer. Chemical shifts are quoted relative to external $SiMe_4$ (^1H, ^{13}C) and 85% H_3PO_4 (^{31}P). Electrospray mass spectra were measured on a Bruker MicroTOF spectrometer in positive-ion mode using solutions of the samples in MeCN. Elemental analyses were performed by staff of the microanalytical laboratory of the University of Wuppertal. All reactions were carried out under aerobic conditions. Chemicals and solvents (HPLC grade) were sourced commercially and used as received. The thioamides were prepared by addition of the appropriate amines to a solution of PhNCS in Et_2O. NMR data for the two new thioamides is given below. $[(\eta^6\text{-cym})RuCl_2]_2$ was prepared as described in Ref. [20].

3.2. PhNHC(S)R3 tetrahydroquinoline

To a solution of 1,2,3,4-tetrahydroquinoline (thq) (1.3 mL, 0.01 mol) in Et_2O (10 mL) PhNCS (1.2 mL, 0.01 mol) was added. After stirring the mixture for 0.5 h, the colourless precipitate was isolated by filtration, washed with pentane and dried in air. Yield: 1.73 g (64%). ^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.77 (br. s, 1H, NH), 7.11–7.45 (m, 9H, NPh, thq), 4.35 (t, J = 6.6 Hz, 2H, NCH_2), 2.80 (t, J = 6.6 Hz, 2H, $ArCH_2$), 2.07 (pent, J = 6.6 Hz, $ArCH_2CH_2CH_2N$). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C): δ = 23.98 ($ArCH_2CH_2$), 26.67 ($ArCH_2$), 49.28 (NCH_2), 123.62 (thq), 124.42



Scheme 1.

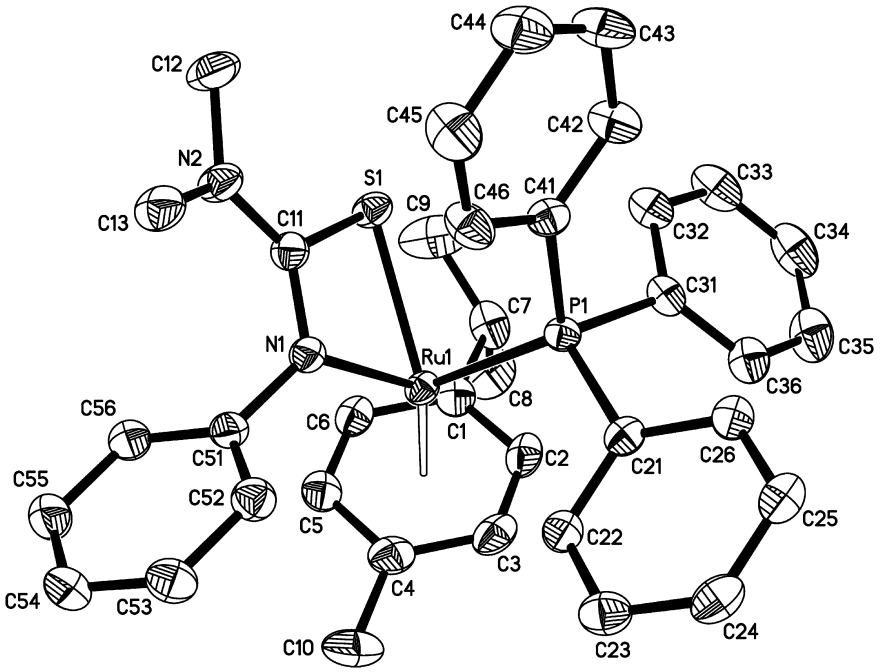


Fig. 1. Molecular structure of complex **1**. Hydrogen atoms and the BPh_4 anion have been omitted for clarity.

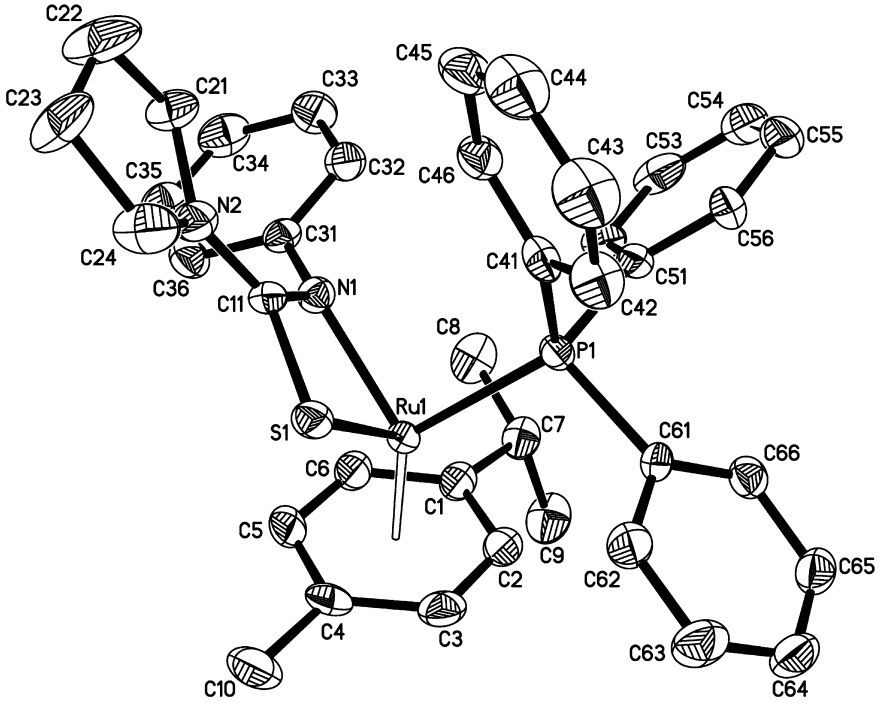


Fig. 2. Molecular structure of complex **2**. Hydrogen atoms and the BPh_4 anion have been omitted for clarity.

(*o*-NPh), 125.61, 126.82 (thq), 128.64 (*m*-NPh), 129.85, 134.92, 138.66 (thq), 139.22 (*ipso*-NPh), 181.19 (C═S).

3.3. PhNHC(S)R4 ethoxycarbonylpiperazine

This was prepared as described above from 1-ethoxycarbonylpiperazine (1.5 mL, 0.01 mol) and PhNCS (1.2 mL, 0.01 mol). Yield: 2.89 g (98%). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.32–7.39 (m, 2H, NPh), 7.31 (br. s, 1H, NH), 7.10–7.20 (m, 3H, NPh), 4.15 (q, J = 7.1 Hz, 2H, OCH_2), 3.78–3.89 (m, 4H, piperazine), 3.52–3.62 (m, 4H, piperazine), 1.26 (t, J = 7.1 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C): δ = 14.53 (Me), 42.68 (NCH_2), 61.67 (OCH_2), 123.42 (*o*-NPh), 125.37 (*p*-NPh), 129.03 (*m*-NPh), 139.83 (*ipso*-NPh), 155.29 (C═O), 183.58 (C═S).

3.4. Preparation of [Ru(η^6-cym)(PPh_3){κ^2N,S-PhNC(S)R}]BPh_4 complexes

A mixture containing [Ru(η^6-cym)Cl_2]$_2$ (0.050 g, 0.082 mmol), thioamide (0.166 mmol) and Ph_3 P (0.043 g, 0.164 mmol) in MeOH

Table 1
Selected bond distances [Å] and angles [deg] for complex **1**.

Ru(1)–S(1)	2.4020(5)	P(1)–C(31)	1.829(2)
Ru(1)–P(1)	2.3469(5)	P(1)–C(41)	1.838(2)
Ru(1)–N(1)	2.1030(17)	N(1)–C(11)	1.319(3)
Ru(1)–C(1)	2.234(2)	N(2)–C(11)	1.341(3)
Ru(1)–C(2)	2.228(2)	N(1)–C(51)	1.430(3)
Ru(1)–C(3)	2.243(2)	C(1)–C(6)	1.436(3)
Ru(1)–C(4)	2.273(2)	C(1)–C(2)	1.409(3)
Ru(1)–C(5)	2.231(2)	C(2)–C(3)	1.423(4)
Ru(1)–C(6)	2.230(2)	C(3)–C(4)	1.403(4)
Cg[a]–Ru(1)	1.7345(10)	C(4)–C(5)	1.439(3)
S(1)–C(11)	1.743(2)	C(5)–C(6)	1.395(3)
P(1)–C(21)	1.821(2)		
S(1)–Ru(1)–N(1)	67.07(5)	C(21)–P(1)–C(31)	105.97(10)
P(1)–Ru(1)–N(1)	90.94(5)	C(21)–P(1)–C(41)	98.52(9)
S(1)–Ru(1)–P(1)	84.841(19)	C(31)–P(1)–C(41)	105.49(10)
Cg–Ru(1)–S(1)	131.87(4)	C(11)–N(1)–C(51)	124.35(17)
Cg–Ru(1)–P(1)	129.10(4)	C(11)–N(1)–Ru(1)	103.48(13)
Cg–Ru(1)–N(1)	131.90(6)	C(51)–N(1)–Ru(1)	126.64(13)
C(11)–S(1)–Ru(1)	80.70(7)	N(1)–C(11)–N(2)	128.81(19)
C(21)–P(1)–Ru(1)	117.37(7)	N(1)–C(11)–S(1)	108.73(15)
C(31)–P(1)–Ru(1)	107.34(7)	N(2)–C(11)–S(1)	122.42(17)
C(41)–P(1)–Ru(1)	120.77(7)		

[a] Cg is the centroid defined by the ring atoms C(1)–C(6).

Table 2
Selected bond distances [Å] and angles [deg] for complex **2**.

Ru(1)–S(1)	2.4020(9)	P(1)–C(51)	1.825(3)
Ru(1)–P(1)	2.3602(8)	P(1)–C(41)	1.832(4)
Ru(1)–N(1)	2.088(3)	N(1)–C(11)	1.316(5)
Ru(1)–C(1)	2.293(4)	N(2)–C(11)	1.345(5)
Ru(1)–C(2)	2.193(4)	N(1)–C(31)	1.437(4)
Ru(1)–C(3)	2.215(4)	C(1)–C(6)	1.407(5)
Ru(1)–C(4)	2.253(3)	C(1)–C(2)	1.432(5)
Ru(1)–C(5)	2.234(3)	C(2)–C(3)	1.409(6)
Ru(1)–C(6)	2.236(4)	C(3)–C(4)	1.428(6)
Ru(1)–Cg[a]	1.7317(14)	C(4)–C(5)	1.412(6)
S(1)–C(11)	1.742(3)	C(5)–C(6)	1.420(6)
P(1)–C(61)	1.823(3)		
S(1)–Ru(1)–N(1)	67.33(8)	C(61)–P(1)–C(51)	103.40(16)
P(1)–Ru(1)–N(1)	90.11(8)	C(61)–P(1)–C(41)	107.22(17)
S(1)–Ru(1)–P(1)	85.91(3)	C(51)–P(1)–C(41)	97.89(15)
Cg–Ru(1)–S(1)	128.80(6)	C(11)–N(1)–C(31)	126.0(3)
Cg–Ru(1)–P(1)	131.00(6)	C(11)–N(1)–Ru(1)	103.4(2)
Cg–Ru(1)–N(1)	131.86(10)	C(31)–N(1)–Ru(1)	126.4(2)
C(11)–S(1)–Ru(1)	80.10(12)	N(1)–C(11)–N(2)	128.3(3)
C(61)–P(1)–Ru(1)	107.16(10)	N(1)–C(11)–S(1)	109.1(2)
C(51)–P(1)–Ru(1)	120.97(12)	N(2)–C(11)–S(1)	122.6(3)
C(41)–P(1)–Ru(1)	118.62(11)		

[a] Cg is the centroid defined by the ring atoms C(1)–C(6).

(15 mL) and Et_3N (1 mL) was heated to reflux for *ca.* 5 min. To the hot solution was added solid $NaBPh_4$ (0.058 g, 0.169 mmol), which caused precipitation of a yellow solid on cooling. The product was isolated by filtration, washed with H_2O, a little cold MeOH, Et_2O and was subsequently dried in vacuum.

Using this procedure the following compounds were prepared.

3.5. [Ru(η^6-cym)(PPh$_3$){κ^2N,S-PhNC(S)NMe$_2$}]BPh$_4$ (**1**)

Yield: 0.141 g (87%) yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.33–7.54 (m, 23H, Ph_3Ph, *o*-BPh_4), 7.28 (t, *J* = 8.1 Hz, 2H, *m*-NPh), 7.12 (dt, *J* = 7.6, 1.0 Hz, 1H, *p*-NPh), 6.99 (t, *J* = 7.6 Hz, 8H, *m*-BPh_4), 6.85 (t, *J* = 7.1 Hz, 4H, *p*-BPh_4), 6.71 (d, *J* = 8.6 Hz, 2H, *o*-NPh), 5.27 (d, *J* = 6.6 Hz, 1H, cym), 4.87 (d, *J* = 5.6 Hz, 1H, cym), 4.77 (d, *J* = 6.6 Hz, 1H, cym), 4.67 (d, *J* = 6.1 Hz, 1H, cym), 2.25 (sept, *J* = 7.1 Hz, 1H, Me_2CH), 2.15 (s, 6H, NMe_2), 1.31 (s, 3H, Me), 1.17 (d, *J* = 6.6 Hz, 3H, Me_2CH), 1.07 (d, *J* = 6.6 Hz, 3H, Me_2CH). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = 40.54. ES-MS: *m/z* = 677 [M]$^+$. Anal. Calc. for $C_{61}H_{60}BN_2PSRu$ (996.06): C, 73.55; H, 6.07; N, 2.81. Found: C, 73.44; H, 5.99; N, 2.75%.

3.6. [Ru(η^6-cym)(PPh$_3$){κ^2N,S-PhNC(S)R2}]BPh$_4$ (**2**)

Yield: 0.114 g (68%) yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.35–7.56 (m, 23H, Ph_3Ph, *o*-BPh_4), 7.27 (t, *J* = 7.6 Hz, 2H, *m*-NPh), 7.13 (t, *J* = 7.1, 1.0 Hz, 1H, *p*-NPh), 7.00 (t, *J* = 7.1 Hz, 8H, *m*-BPh_4), 6.85 (t, *J* = 7.1 Hz, 4H, *p*-BPh_4), 6.70 (d, *J* = 7.1 Hz, 2H, *o*-NPh), 5.34 (d, *J* = 5.6 Hz, 1H, cym), 4.80 (d, *J* = 6.1 Hz, 1H, cym), 4.72 (d, *J* = 6.1 Hz, 1H, cym), 4.64 (d, *J* = 5.6 Hz, 1H, cym), 2.63 (br. s, 4H, NCH_2), 2.26 (sept, *J* = 6.6 Hz, 1H, Me_2CH), 1.59 (br. s, 2H, CH_2), 1.41 (br. s, 2H, CH_2), 1.32 (s, 3H, Me), 1.19 (d, *J* = 7.1 Hz, 3H, Me_2CH), 1.05 (d, *J* = 7.1 Hz, 3H, Me_2CH). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = 40.00. ES-MS: *m/z* = 703 [M]$^+$, 441 [M−*PPh*$_3$]$^+$. Anal. Calc. for $C_{63}H_{62}BN_2PSRu$ (1022.10): C, 74.03; H, 6.11; N, 2.74. Found: C, 73.64; H, 6.23; N, 2.66%.

3.7. [Ru(η^6-cym)(PPh$_3$){κ^2N,S-PhNC(S)R3}]BPh$_4$ (**3**)

Yield: 0.109 g (62%) yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.36–7.51 (m, 23H, Ph_3Ph, *o*-BPh_4), 7.06 (t, *J* = 7.6 Hz, 2H, *m*-NPh), 7.00 (t, *J* = 7.1 Hz, 8H, *m*-BPh_4), 6.95 (m, 1H, thq), 6.87 (m, 5H, *p*-BPh_4, thq), 6.77 (t, *J* = 7.6 Hz, 1H, *p*-NPh), 6.53 (m, 3H, *o*-NPh, thq), 5.66 (m, 1H, thq), 5.32 (d, *J* = 6.6 Hz, 1H, cym), 5.14 (d, *J* = 6.1 Hz, 1H, cym), 4.84 (d, *J* = 6.6 Hz, 1H, cym), 4.61 (d, *J* = 6.1 Hz, 1H, cym), 3.26 (m, 1H, thq), 2.98 (m, 1H, thq), 2.48 (m, 1H, thq), 2.33 (sept, *J* = 7.1 Hz, 1H, Me_2CH), 1.76 (m, 1H, thq), 1.63 (m, 1H, thq), 1.25 (s, 3H, Me), 1.18 (d, *J* = 7.1 Hz, 3H, Me_2CH), 1.12 (d, *J* = 7.1 Hz, 3H, Me_2CH). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = 40.73. ES-MS: *m/z* = 765 [M]$^+$ 503 [M−*PPh*$_3$]$^+$. Anal. Calc. for $C_{68}H_{64}BN_2PSRu \cdot H_2O$ (1102.19): C, 74.10; H, 6.04; N, 2.54. Found: C, 74.44; H, 6.23; N, 2.58%.

3.8. [Ru(η^6-cym)(PPh$_3$){κ^2N,S-PhNC(S)R4}]BPh$_4$ (**4**)

Yield: 0.152 g (84%) yellow solid. ^{1}H NMR (400 MHz, acetone-d_6, 25 °C): δ = 7.51–7.64 (m, 15H, Ph_3P), 7.40 (t, *J* = 7.6 Hz, 2H, *m*-NPh), 7.31–7.37 (m, 8H, *o*-BPh_4), 7.21 (t, *J* = 7.6 Hz, 1H, *p*-NPh), 7.08 (d, *J* = 7.6 Hz, 2H, *o*-NPh), 6.92 (t, *J* = 7.1 Hz, 8H, *m*-BPh_4), 6.77 (t, *J* = 7.1 Hz, 4H, *p*-BPh_4), 5.81 (d, *J* = 6.1 Hz, 1H, cym), 5.49 (d, *J* = 5.6 Hz, 1H, cym), 5.35 (d, *J* = 5.6 Hz, 1H, cym), 5.21 (d, *J* = 6.1 Hz, 1H, cym), 4.02 (q, *J* = 7.1 Hz, 2H, OCH_2), 3.06–3.23 (m, 4H, piperazine), 2.81 (t, *J* = 5.6 Hz, 4H, piperazine), 2.50 (sept, *J* = 6.6 Hz, 1H, Me_2CH), 1.56 (s, 3H, Me), 1.26 (d, *J* = 6.6 Hz, 3H, Me_2CH), 1.14–1.19 (m, 3H, Me_2CH, CH_3CH_2). ^{31}P{^{1}H} NMR (162 MHz, acetone-d_6, 25 °C): δ = 40.37. ES-MS: *m/z* = 790 [M]$^+$, 528 [M−*PPh*$_3$]$^+$. Anal. Calc. for $C_{66}H_{67}BN_3O_2PSRu$ (1109.18): C, 71.47; H, 6.09; N, 3.79. Found: C, 71.49; H, 6.27; N, 3.43%.

3.9. [Ru(η^6-cym)(PPh$_3$){κ^2N,S-PhNC(S)NR5}]BPh$_4$ (**5**)

Yield: 0.154 g (91%) yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.35–7.55 (m, 23H, Ph_3Ph, *o*-BPh_4), 7.29 (t, *J* = 7.6 Hz, 2H, *m*-NPh), 7.16 (t, *J* = 7.6, 1.0 Hz, 1H, *p*-NPh), 7.00 (t, *J* = 7.1 Hz, 8H, *m*-BPh_4), 6.86 (t, *J* = 7.1 Hz, 4H, *p*-BPh_4), 6.74 (d, *J* = 7.6 Hz, 2H, *o*-NPh), 5.23 (d, *J* = 6.1 Hz, 1H, cym), 4.77 (d, *J* = 6.1 Hz, 1H, cym), 4.72 (d, *J* = 5.6 Hz, 1H, cym), 4.61 (d, *J* = 5.6 Hz, 1H, cym), 3.28 (m, 4H, CH_2O), 2.68 (m, 4H, NCH_2), 2.26 (sept, *J* = 6.6 Hz, 1H, Me_2CH), 1.27 (s, 3H, Me), 1.19 (d, *J* = 6.6 Hz, 3H, Me_2CH), 1.05 (d, *J* = 6.6 Hz, 3H, Me_2CH). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = 39.89. ES-MS: *m/z* = 719 [M]$^+$. Anal. Calc. for $C_{63}H_{62}BN_2OPSRu$ (1038.10): C, 72.89; H, 6.02; N, 2.70. Found: C, 72.83; H, 6.12; N, 2.43%.

3.10. [Ru(η^6-cym)(PPh_3){κ^2N,S-PhNC(S)NR6}]BPh_4 (**6**)

Yield: 0.081 g (44%) yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.33–7.54 (m, 23H, Ph_3Ph, *o*-BPh_4), 7.24 (m, 6H, *m*-NPh, Bz), 7.08 (m, 3H, *p*-NPh, Bz), 7.00 (t, J = 7.1 Hz, 8H, *m*-BPh_4), 6.80–6.91 (m, 8H, *p*-BPh_4, Bz), 6.48 (d, J = 7.6 Hz, 2H, *o*-NPh), 5.33 (d, J = 6.1 Hz, 1H, cym), 4.86 (d, J = 6.1 Hz, 1H, cym), 4.69 (d, J = 6.6 Hz, 1H, cym), 4.60 (d, J = 6.6 Hz, 1H, cym), 3.97 (AB quart, J = 15.8 Hz, 4H, NCH_2), 2.29 (sept, J = 7.1 Hz, 1H, Me_2CH), 1.26 (s, 3H, Me), 1.20 (d, J = 7.1 Hz, 3H, Me_2CH), 1.03 (d, J = 7.1 Hz, 3H, Me_2CH). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = 36.86. ES-MS: m/z = 829 $[M]^+$, 567 $[M-PPh_3]^+$. Anal. Calc. for $C_{73}H_{68}BN_2PSRu$ (1148.25): C, 76.36; H, 6.07; N, 5.97. Found: C, 76.64; H, 6.36; N, 5.77%.

3.11. [Ru(η^6-cym)(PPh_3){κ^2N,S-PhNC(S)R6}]BPh_4 (**7**)

Yield: 0.113 g (63%) yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.36–7.56 (m, 23H, Ph_3Ph, *o*-BPh_4), 7.30 (t, J = 7.6 Hz, 2H, *m*-NPh), 7.22 (t, J = 7.6 Hz, 2H, pipNPh), 7.17 (t, J = 7.6, 1.0 Hz, 1H, *p*-NPh), 6.99 (t, J = 7.6 Hz, 8H, *m*-BPh_4), 6.82–6.90 (m, 5H, *p*-BPh_4, pipNPh), 6.71–6.79 (m, 4H, *o*-NPh, pipNPh), 5.34 (d, J = 6.6 Hz, 1H, cym), 4.78 (d, J = 5.6 Hz, 1H, cym), 4.74 (d, J = 6.6 Hz, 1H, cym), 4.62 (d, J = 5.6 Hz, 1H, cym), 2.76–2.89 (m, 8H, pip), 2.28 (sept, J = 7.1 Hz, 1H, Me_2CH), 1.27 (s, 3H, Me), 1.19 (d, J = 7.1 Hz, 3H, Me_2CH), 1.06 (d, J = 7.1 Hz, 3H, Me_2CH). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, 25 °C): δ = 39.86. ES-MS: m/z = 794 $[M]^+$, 532 $[M-PPh_3]^+$. Anal. Calc. for $C_{69}H_{67}BN_3PSRu$ (1113.21): C, 74.45; H, 6.07; N, 3.77. Found: C, 74.15; H, 6.02; N, 3.67%.

Table 3
Crystallographic and refinement data for complexes **1** and **2**.

Empirical formula	$C_{61}H_{60}BN_2PRuS$	$C_{64}H_{63}BCl_3N_2PRuS$
Formula weight	996.02	1141.42
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1$
a (Å)	11.3402(4)	10.4223(5)
b (Å)	11.6669(4)	25.3367(13)
c (Å)	20.1877(7)	10.8180(5)
α (°)	75.6634(5)	90
β (°)	79.6546(5)	104.3471(6)
γ (°)	80.1345(6)	90
V (Å^3)	2523.0(3)	2767.6(4)
Z	2	2
$D_{calc.}$ (g cm^{-3})	1.311	1.370
Θ range (°)	1.84–29.88	1.94–29.91
Limiting indices	$-15 \leqslant h \leqslant 11$, $-10 \leqslant k \leqslant 15$, $-27 \leqslant l \leqslant 28$	$-13 \leqslant h \leqslant 14$, $-35 \leqslant k \leqslant 34$, $-14 \leqslant l \leqslant 4$
Reflections collected	19708	21381
Unique	12862	14011
$[R_{(int)}]$	0.0401	0.0510
Observed $[I > 2\sigma(I)]$	11217	12696
Crystal size (mm)	0.68 × 0.34 × 0.10	0.52 × 0.20 × 0.10
μ (mm^{-1})	0.425	0.537
Transmission	0.95864–0.85136	0.95579–0.79244
R_1 (all data)	0.0534	0.0549
wR_2 (all data)	0.1359	0.1276
Goodness-of-fit on F^2	1.079	1.056
Parameters	609	671
ΔF map (e Å^{-3})	1.101 to −1.654	1.176 to −1.393
Flack parameter	–	−0.04(2)

3.12. X-ray crystallography

Crystals of complexes **1** and **2** suitable for X-ray diffraction were obtained by slow diffusion of ether into a CH_2Cl_2 solution of the compound. The crystals were fastened with epoxy glue to glass fibres. After cooling the crystals to −100 °C with a Siemens LT-2A device, data were measured using a Bruker P4-SMART diffractometer employing graphite monochromatised Mo Kα radiation (λ = 0.71073 Å). For each compound a series of φ and ω scans were used to generate 1650 CCD frames from which the reflections were harvested and the cell constants in Table 1 were determined. The intensities were corrected by integration for absorption and scaled. Direct methods (SHELXS) [21] yielded the positions of most of the non-hydrogen atoms, and the structures were completed with standard difference Fourier techniques. While the locations of hydrogen atoms were apparent from the ΔF maps, these atoms were idealized and their parameters were constrained during refinement. Initial refinement of complex **2** gave unusually large thermal parameters for the C(23) atom of the pyrrolidino group and a ΔF synthesis showed that this atom was disordered over two sites. Presumably the pyrrolidino ring adopts an envelope conformation with the flap atom C(23) occurring alternatively above and below the plane of the other four ring atoms. Accordingly, the C(23) atom was split and appropriate constraints of ring geometry and positions of the idealized hydrogen atoms were applied in the least-squares process. This model converged with the flap atom essentially evenly divided [occupancies 0.48(3) and 0.52(3)] on the two sides of the ring. Important crystallographic and refinement details are listed in Table 3. SHELXL, and PLATON were used for the data refinement and additional geometrical calculations [21,22].

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Appendix A. Supplementary material

CCDC 709684 and 709685 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.12.015.

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