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Pyridine- and pyrimidine-2-thiolate complexes of ruthenium

Mohammad El-khateeb [a,*], Khawla Damer [a], Helmar Görls [b], Wolfgang Weigand [b]

[a] Chemistry Department, Jordan University of Science and Technology, Irbid 22110, Jordan
[b] Institut für Anorganische und Analytische Chemie, Friedrich-Schiller-Universtät Jena, August-Bebel Strasse 2, Jena 07743, Germany

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Abstract

A series of mononuclear ruthenium complexes containing pyridine- and pyrimidine-2-thiolato ligands was prepared and characterized. The new compounds of general formula $CpRu(PPh_3)(\kappa^2S,N\text{-SR})$ (**1**) (SR = pyridine-2-thiolate (**a**), pyrimidine-2-thiolate (**b**)) were prepared directly by reacting the thiolato anions (RS^-) with $CpRu(PPh_3)_2Cl$. Complexes **1** readily react with $NOBF_4$ or CO in THF at room temperature to give $[CpRu(PPh_3)(NO)(\kappa^1S\text{-HSR})][BF_4]_2$ (**2**) and $CpRu(PPh_3)(CO)(\kappa^1S\text{-SR})$ (**3**), respectively. The one-pot reaction of $CpRu(PPh_3)_2Cl$, thiolato anions and bis(diphenylphosphino)ethane (dppe) gave $CpRu(dppe)(\kappa^1S\text{-SR})$ [dppe: $Ph_2PCH_2CH_2PPh_2$ (**4**)]. The complex salts, $[CpRu(PPh_3)_2(\kappa^1S\text{-HSR})]BPh_4$ (**5**) are prepared by mixing $CpRu(PPh_3)_2Cl$, HSR and $NaBPh_4$ at room temperature. The structures of $CpRu(PPh_3)(\kappa^2S,N\text{-Spy})$ (**1a**), $[CpRu(PPh_3)(NO)(\kappa^1S\text{-HSpy})][BF_4]_2$ (**2a**) and $CpRu(PPh_3)(CO)(\kappa^1S\text{-Spy})$ (**3a**), (py = C_5H_4N) have been determined.

Keywords: Ruthenium; Pyridine-2-thiolate; Pyrimidine-2-thiolate; Structures; Chelates; Sulfur; Phosphine ligands; Nitrosyl; Carbonyl; Complexes

1. Introduction

The coordination chemistry of pyridine and pyrimidine thiolates is of great interest in a variety of reactions [1]. This interest is due to the unusual coordination geometry, variety of bonding, and interesting spectral and electrochemical behavior of these complexes [2–4]. The interaction of such ligands with heavy metals, such as gold and platinum, is of special interest because of their antitumor properties with the potential to develop metal-based drugs. To this end, some papers involving platinum (II or IV) and gold (I) complexes of these ligands with tertiary phosphines as co-lignads have been reported in the literature [5–10].

There are two donor atoms in these types of ligands, the S-atom, which is a soft center, and the N-atom, which is considered as a hard center [11,12], enabling these ligands to coordinate to both soft and hard metals. These thiolate ligands interact with metals in several ways, which include S-bonding (κ^1), S-bridging (μ_2), N,S-chelating (κ^2) and N,S-bridging (μ_2) modes [11,12].

Several complexes of ruthenium with pyridine-2-thiolate complexes have been known in the literature [13–21]. In most of these complexes, the thiolato ligand is bonded to the ruthenium in an N,S-chelating (κ^2) mode. Cyclopentadienyl ruthenium complexes containing these thiolate ligands are rare. The complexes $[CpRu(PP)(\kappa^1S\text{-}SC_5H_4NH)]BPh_4$ (PP = $2PEt_3$ [19], dippe [20], dppf [21]) are prepared by reacting the corresponding Ru-chlorides with the HSpy in the presence of BPh_4^-.

We are interested in the synthesis and reactions of ruthenium thiolate complexes [22–24]. This was extended to include the ruthenium heterocyclic thiolate ligands. The complexes CpRu(L)(L′)SR (SR = 2-mercaptobenzimidazolyl, 2-mercaptobenzoxazolyl and 2-mercaptobenzthiazolyl) have been reported [25]. In this paper, we wish to report the synthesis, reactions and characterization of several complexes of cyclopentadienyl ruthenium complexes containing pyridine- and pyrimidine-2-thiolate ligands.

* Corresponding author. Tel.: +962 2 7201000; fax: +962 2 7095014.
E-mail address: kateeb@just.edu.jo (M. El-khateeb).

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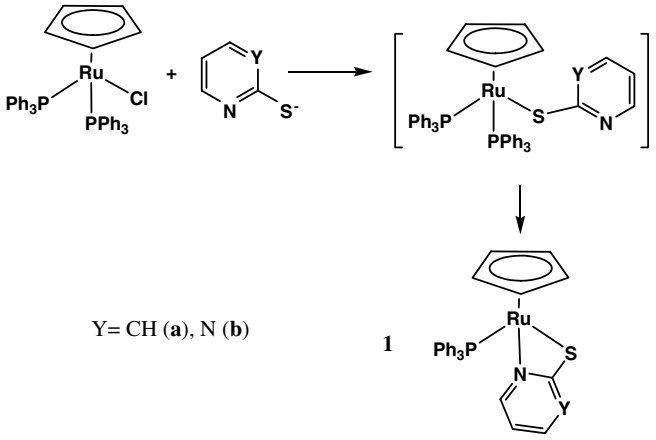
2. Results and discussion

2.1. Synthesis

Treating the chloro complex $CpRu(PPh_3)_2Cl$ with pyridine- or pyrimidine-2-thiolate anions (RS^-) in refluxing THF for 30 min gave the corresponding ruthenium heterocyclic thiolato complexes **1** in good yields (Scheme 1). Solutions of these complexes are orange and sensitive to air. They have been characterized by ^{31}P and ^1H NMR spectroscopy as well as by elemental analysis. The thiolato ligands act as chelate ligands, in which they are bonded to ruthenium through both the S and N-atoms, this has been confirmed by the structure determination of **1a** (Fig. 1). These complexes may be formed from the bis-triphenylphosphine compounds $[CpRu(PPh_3)_2(\kappa^1S\text{-SR})]$, which could not be isolated in these reactions (Scheme 1). This result is not surprising in view of the fact that complexes of the formula $CpRu(PPh_3)_2SR$ have a tendency to lose PPh_3 easily [26] and these heterocyclic thiolate ligands are good chelate ligands [11,12]. Attempts to make the bis-triphenylphosphine compounds $[CpRu(PPh_3)_2(\kappa^1S\text{-SR})]$ by treating the benzonitrile complex $[CpRu(PPh_3)_2NCPh]^+$ with the thiolato anions at room temperature failed. These reactions give only complexes **1** as shown by the ^1H and ^{31}P NMR spectra of the reaction mixture.



Scheme 1.

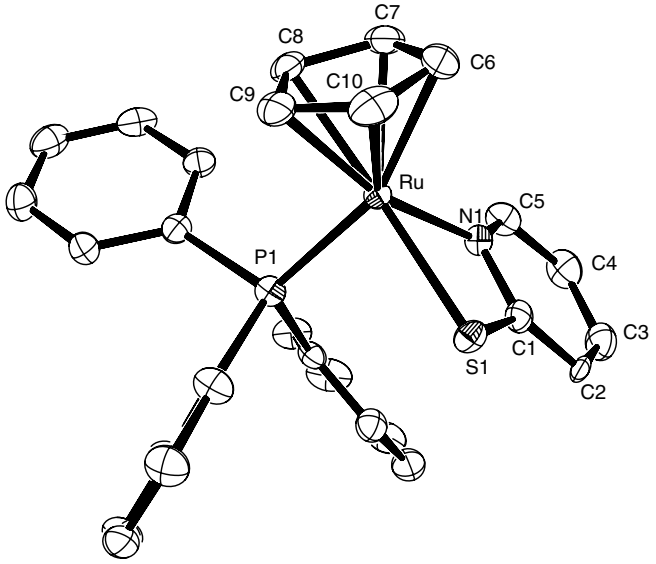
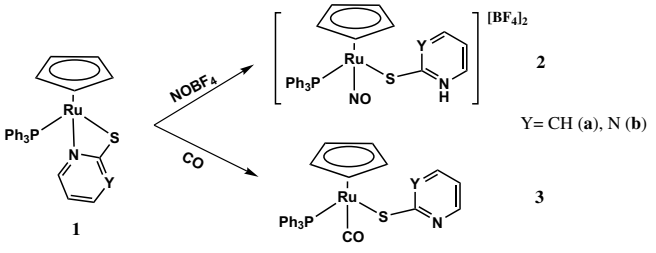


Fig. 1. ORTEP drawing of $CpRu(PPh_3)(\kappa^2S,N\text{-Spy})$, **1a**.

The ^1H NMR spectra of complexes **1** show a singlet in the range of 4.12–4.38 ppm corresponding to the Cp-protons. This peak is similar to those observed for the simple alkyl and aryl thiolate complexes, $CpRu(PPh_3)_2SR$, (4.17–4.38 ppm) [27,28]. The ^{31}P NMR spectra of complexes **1** have a singlet in the range of 50.59–53.21 ppm. This peak is at lower field compared to those of $CpRu(PPh_3)_2SR$ (RS = 2-mercaptobenzothiazole, 2-mercaptobenzoxazolyl and 2-mercaptoimidazolyl) (41.89–42.64 ppm) [25].

Treatment of $CpRu(PPh_3)(\kappa^2S,N\text{-SR})$ (**1**), with $NOBF_4$ in THF at room temperature gave the corresponding nitrosyl complex salts $[CpRu(PPh_3)(NO)(\kappa^1S\text{-HSR})][BF_4]_2$ (Scheme 2).

In this reaction, the chelate ring is opened and the NO^+ oxidized the Ru center to form the products shown. Unexpectedly, the analysis of the complexes (together with the X-ray structure of **2a**) shows that **2** contain a protonated ligands, instead of thiolate, two BF_4 anions and one water molecule as coordinated solvent. This might be due to the high affinity of the NO^+ salt to water. It absorbed water during the weighing process which took place in air. Water is known to react with NO^+ to produce acidic solution [29]. The formed acid attacks the basic N-atom of the thiolate ligand and converted it to the protonated form. The infrared spectra of complexes **2** display a medium band in the range of 1838–1861 cm^{-1}, for the NO stretching frequency. This peak is higher than those observed for $[CpRu(PPh_3)(NO)SR]^+$ (R = CMe_3, $CHMe_2$, and C_6H_4Me) which show a band in the range of 1817–1821 cm^{-1} [21]. This result reflects weaker σ-donating properties of the heterocyclic protonated ligands compared to that of simple thiolate ligands. The spectra also show a weak band in the range of 3260–3271 cm^{-1} for the N–H stretching frequency. Their ^1H NMR spectra show a singlet peak for the Cp protons in the range 6.22–6.49 ppm, which is shifted downfield from the values of the parent thiolates **1**. This shift may attributes to the reduction of electron density around



Scheme 2.

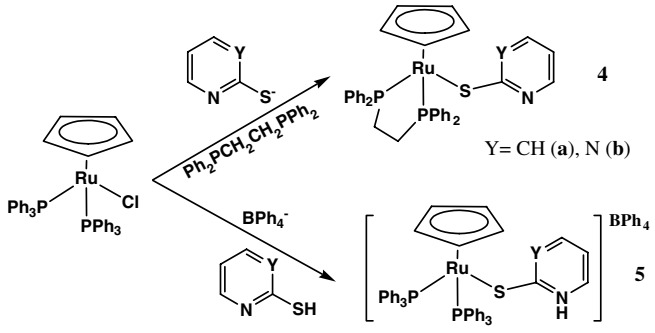
ruthenium center by the nitrosyl-group. This peak appears at higher values compared to the values reported for $[CpRu(PPh_3)(NO)SR]^+$, where R = CMe_3, $CHMe_2$, 4-C_6H_4Me (6.10–6.31 ppm), which is also consistent with a strong π-accepting properties of the heterocyclic ligand compared to the simple thiolate ligands. The NH proton is shown in the NMR spectra of **2** in the range of 9.58–9.62 as a broad peak. The ^{31}P NMR spectra show a peak in the range of 33.68–36.02 ppm.

Complexes **1** react readily with CO-gas at room temperature to give the mixed carbonyl-phosphine complexes **3** as shown in Scheme 2. The IR spectra of **3** display a strong band in the range of 1951–1956 cm^{-1} for the terminal carbonyl group bonded to ruthenium. This range is comparable to those of analogues ruthenium thiolate complexes [25,27]. The ^1H NMR spectra of **3** show a singlet in the range of 4.80–4.82 ppm for the Cp-ring protons, which is also comparable to that of $CpRu(PPh_3)(CO)SR$ [27,28]. Their ^{31}P NMR spectra show only one singlet for the triphenylphosphine ligand in the range of 55.92–56.98 ppm similar to that of $CpRu(PPh_3)(CO)SR$ [28].

The synthesis of $CpRu(dppe)(\kappa^1S\text{-}SR)$ (**4**), which have an S-bonded thiolate ligands, were achieved in good yields by treating $CpRu(PPh_3)_2Cl$ with lithium thiolate anions and excess dppe ligand in refluxing THF for 4 h (Scheme 3).

In complexes **4**, the thiolate ligand is bonded to the Ru-center by the S-atom in a monodentate fashion. This may attributed to the strong chelating ability of the dppe ligand compared to that of the heterocyclic thiolates used in this study. The ^1H NMR spectra of these complexes show a singlet peak for the Cp protons in the 4.76–4.87 ppm range, which is lower than the range reported for heterocyclic thiolate ruthenium complexes (5.00–5.04 ppm) [25] and higher than that of **1** (4.12–4.38 ppm). Their ^{31}P NMR spectra show a single peak in the range of 79.57–79.90 ppm, which are slightly lower than the values for CpRu(dppe)SR, where SR = 2-mercaptobenzimidazolyl, 2-mercaptobenzothiazolyl and 2-mercaptobenoxazolyl (81.08–81.38 ppm) [25].

The complexes $[CpRu(PPh_3)_2(SC_5H_4NH)]BPh_4$ (**5a**) and $[CpRu(PPh_3)_2(SC_4H_3N_2H)]BPh_4$ (**5b**) are prepared following the method of Puerta [19,20] as shown in Scheme 3. The IR spectra of these orange stable complexes show the NH stretching band in the range of 3242–3256 cm^{-1}. Their ^1H NMR spectra show a broad peak in the range of 9.50–9.51 ppm for the nitrogen bound proton. This implies that the heterocyclic thiol is bonded to the metal through the S-atom of the thione form as observed for similar complexes [19,20].



Scheme 3.

2.2. Crystal structures

Crystals of **1a**, **2a** and **3a** can be grown by solvent diffraction method (THF:hexane). The ORTEP drawings of these complexes are shown in Figs. 1–3, respectively. Selected bond lengths and angles for these molecules are shown in Table 1. In **1a** the pyridine-2-thiolate ligand is bonded in a chelate form through the S and N atoms, while for **2a** and **3a** this ligand opts for an S-coordination with a pendant N site.

The Ru–S bond length of **1a** (2.4443(7) Å) is comparable to the corresponding Ru–S distance found for the complexes $CpRu(PPh_3)_2SX$ (X = $SSiPr^i_3$: 2.462(3) Å, SC≡CPh: 2.4216(7) Å [30,31]). The corresponding Ru–S dis-

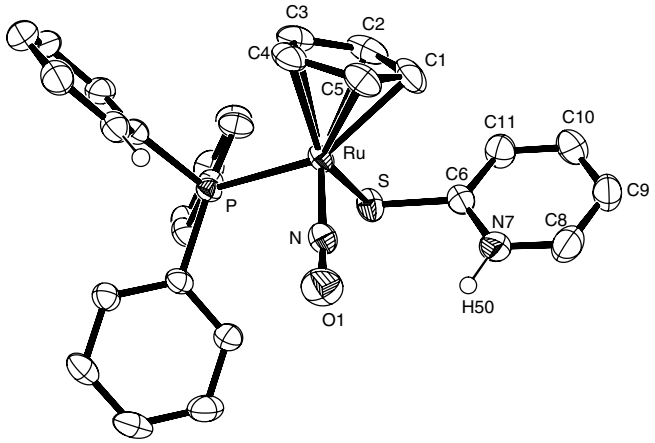


Fig. 2. ORTEP drawing of the cation present in $[CpRu(PPh_3)(NO)(\kappa^1S\text{-}HSPy)]BF_4$, **2a**.

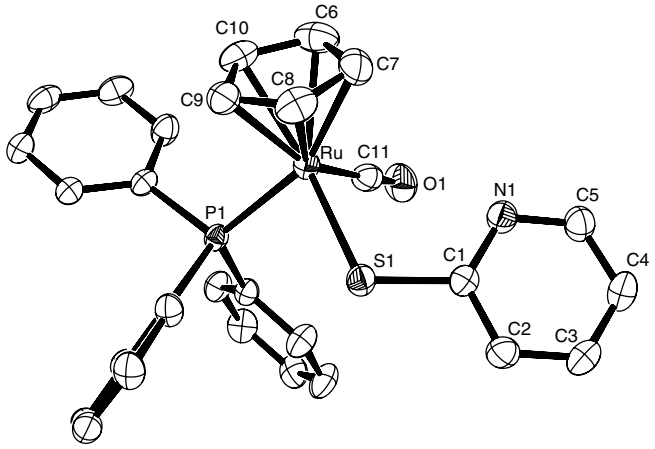


Fig. 3. ORTEP drawing of $CpRu(PPh_3)(CO)(\kappa^1S\text{-Spy})$, **3a**.

Table 1
Selected bond length (Å) and selected bond angles (°) of $CpRu(PPh_3)(\kappa^2S,N\text{-Spy})$ (**1a**) $[CpRu(PPh_3)(NO)(\kappa^1S\text{-HSPy})[BF_4]_2$ (**2a**) and $CpRu(PPh_3)(CO)(\kappa^1S\text{-Spy})$ (**3a**)

1a		**2a**		**3a**	
Ru–C6	2.207(3)	Ru–C1	2.245(3)	Ru–C6	2.230(3)
Ru–C7	2.185(3)	Ru–C2	2.272(3)	Ru–C7	2.239(3)
Ru–C8	2.281(3)	Ru–C3	2.252(3)	Ru–C8	2.256(3)
Ru–C9	2.190(3)	Ru–C4	2.222(3)	Ru–C9	2.254(3)
Ru–C10	2.185(3)	Ru–C5	2.230(3)	Ru–C10	2.237(3)
Ru–P1	2.3035(7)	Ru–P1	2.3802(6)	Ru–P1	2.2973(6)
Ru–S1	2.4443(7)	Ru–S1	2.3927(7)	Ru-S1	2.3918(7)
Ru–N1	2.092(2)	Ru–N1	1.764(2)	Ru–C11	1.882(3)
S1–C1	1.729(3)	S1–C6	1.758(3)	S1–C1	1.765(2)
		N1–O1	1.148(3)	C11–O1	1.113(3)
N1–C1	1.362(4)	N7–C6	1.355(3)	N1–C1	1.341(3)
N1–C5	1.339(4)	N7–C8	1.350(4)	N1–C5	1.346(3)
N1–Ru–P1	90.61(6)	N1–Ru–P1	92.92(7)	C11–Ru–P1	90.98(8)
P1–Ru–S1	91.20(3)	P1–Ru–S1	85.79(2)	P1–Ru–S1	89.04(2)
N1–Ru–S1	66.93(6)	N1–Ru–S1	100.89(7)	C11–Ru–S1	90.42(8)
C1–S1–Ru	80.66(10)	C6–S1–Ru	101.70(7)	C1–S1–Ru	111.67(9)
N1–C1–S1	108.5(2)	N7–C6–S1	120.08(16)	N1–C1–S1	121.34(19)
		O1–N1–Ru	171.3(3)	O1–C11–Ru	178.3(2)

tance of **2a** (2.3927(7) Å) and of **3a** (2.3918(7) Å) are shorter than that of **1a** but are comparable to the distances found for $CpRu(PPh_3)(CO)Y$ ($Y = SSO_2Ph$: 2.383(3) Å, SSO_2Pr^n: 2.3972 Å, SCO_2Bu^n: 2.3719(7) Å) [32,33]. The Ru–P distance in **1a** (2.3035(7) Å) and in **3a** (2.2973(6) Å) lie within the same range observed for similar systems (*i.e.* $CpRu(PPh_3)_2SC{\equiv}CPh$: 2.3174(7) Å, 2.3440(8) Å; $CpRu(PPh_3)_2SCO_2Bu^n$: 2.3194(6) and 2.3190(6) Å; $CpRu(PPh_3)(CO)SCO_2Bu^n$: 2.290(7) Å; $CpRu(PPh_3)(CO)SSO_2\text{-}4\text{-}C_6H_4Me$: 2.315(2) Å) [31,33,34]. However, the Ru–P bond distance in **2a** (2.3802(6) Å) is longer than those of **1a** and **3a** and also longer that of the corresponding distance in $[CpRu(PPh_3)(NO)SBu^t]^+$ of 2.369(2) Å [35]. The Ru–N bond lengths of 2.092(2) Å for **1a** is quite longer than the corresponding distance in **2a** (1.764(2) Å), indicating the stronger π-acceptor properties of the nitrosyl ligand. The latter distance is comparable to that reported for $[CpRu(PPh_3)(NO)SBu^t]^+$ of 1.753(6) Å [35]. The Ru–N–O (171.3(3)°) and the Ru–C–O (178.3(2)°) bond angles are reasonably linear and are similar to those found in analogous systems [33,35]. The angles around the ruthenium center (S–Ru–P, S–Ru–N(C) and N(C)–Ru–P) are around 90°, consistent with a pseudo-octahedral structure for these complexes. The sulfur atom in these complexes has an sp^3 hybridization as predicted from the Ru–S–C(py) angles.

3. Experimental

3.1. General

All reactions and manipulations were carried out under nitrogen atmosphere using vacuum and Schlenk line techniques. Hexane, tetrahydrofuran and diethyl ether were dried by refluxing over sodium/benzophenone and freshly distilled prior to use. 2-Mercaptopyrimidine, 2-mercaptopyridine and nitrosonium tetraflouroborate (ACROS) were used as received. $CpRu(PPh_3)_2Cl$ was prepared as reported [36]. Infrared spectra were recorded on a Perkin Elmer AC 2000 FT-IR spectrometer in CH_2Cl_2 solution. ^1H and ^{31}P NMR spectra were recorded using a Bruker Avance 200 or 400 MHz spectrometer. Chemical shifts are quoted in ppm downfield of TMS (^1H) and phosphoric acid (^{31}P) and referenced using the chemical shifts of residual solvent resonances. Elemental analyses were performed by the Institute of Organic and Macromolecular Chemistry, FSU-Jena. Melting points were recorded on a polarization-microscope (Axiolab) connected to a heating unit (THMS-600) using the software Linkam LNP and CI 93.

3.2. General procedure for the preparation of $CpRu(PPh_3)(\kappa^2\text{-}S,N\text{-}SR)$ (*1*)

A 3-neck flask equipped with a reflux condenser was charged with 50 mL THF and thiol (0.90 mmol). The solution was cooled to −78 °C in an ethanol/dry ice bath and methyllithium (0.56 mL, 0.90 mmol) was added. After 10 min the cooling bath was replaced by a water bath and the solution was warmed to 40 °C. $CpRu(PPh_3)_2Cl$ (0.50 g, 0.72 mmol) was added and the resulting mixture was refluxed for 30 min. The volatiles were removed under vacuum and the resulting solid was extracted with toluene. The extract was layered with hexane and cooled over night to give orange crystals of the product which were separated and washed several times with cold hexane.

3.2.1. $CpRu(PPh_3)(\kappa^2\text{-}S,N\text{-}Spy)$ (*1a*)

Yield: 73%, m.p.: 148–151 °C. ^1H NMR (C_6D_6): 4.26 (s, 5H, Cp), 5.82 (m, 1H, C_5NH_4), 6.16 (m, 1H, C_5NH_4), 6.34 (m, 1H, C_5NH_4), 7.02 (m, 9H, PPh_3), 7.34 (m, 6H, PPh_3), 7.55 (m, 1H, C_5NH_4). ^{31}P NMR (C_6D_6): 56.86. Anal. Calc. for ($C_{28}H_{24}NPRuS$): C, 62.44; H, 4.49; S, 5.95; N, 2.60. Found: C, 61.72; H, 4.49; S, 5.55; N, 2.47%.

*3.2.2. CpRu(PPh$_3$)(κ^2-S,N-Spym) (**1b**)*

Yield: 81%, m.p.: 205–207 °C. ^{1}H NMR (acetone-d_6): 4.38 (s, 5H, Cp), 6.27 (t, 1H, $C_4N_2H_3$), 7.28 (m, 9H, PPh_3), 7.39 (m, 6H, PPh_3), 7.56 (t, 1H, $C_4N_2H_3$), 8.56 (d, 1H, $C_4N_2H_3$). ^{31}P NMR (acetone-d_6): 50.59. Anal. Calc. for ($C_{27}H_{23}N_2PRuS$): C, 60.10; H, 4.30; S, 5.94; N, 5.19. Found: C, 59.24; H, 4.69; S, 4.83; N, 5.83%.

*3.3. General procedure for the preparation of [CpRu(PPh$_3$)(NO)(κ^{1}S-SR)][BF$_4$]$_2$ · H$_2$O (**2**)*

A 100 mL Schlenk flask was charged with 15 mL of THF, ruthenium thiolate complex CpRu(PPh_3)(κ^2*S*,*N*-SR) (**1**), (0.25 mmol) and $NOBF_4$ (0.060 g, 0.50 mmol) were added. The mixture was stirred for 2 h, an orange precipitate was formed. The supernatant was removed and the precipitate was washed with hexane. The complexes were recrystallized from absolute ethanol/hexanes to give dark red crystals.

*3.3.1. [CpRu(PPh$_3$)(NO)(κ^{1}S-Spy)][BF$_4$]$_2$ · H$_2$O (**2a**)*

Yield: 91%, m.p.: 229–230 °C. IR (KBr): $\nu_{(NH)} = 3271\ cm^{-1}$, $\nu_{(NO)} = 1838\ cm^{-1}$. ^{1}H NMR (acetone-$d_6$): 6.48 (s, 5H, Cp), 7.59 (m, 16H, $PPh_3 + C_5NH_4$), 8.15 (d, 1H, C_5NH_4), 8.30 (t, 1H, C_5NH_4), 8.60 (d, 1H, C_5NH_4); 9.58 (br, 1H, N*H*). ^{31}P NMR (acetone-d_6): 34.37. Anal. Calc. for ($C_{28}H_{24}N_2OPRuSB_2F_8 \cdot H_2O$): C, 44.24; H, 3.45; S, 4.22; N, 3.68. Found: C, 43.83; H, 3.45; S, 3.84; N, 3.51%.

*3.3.2. [CpRu(PPh$_3$)(NO)(κ^{1}S-Spy)][BF$_4$]$_2$ · H$_2$O (**2b**)*

Yield: 79%, m.p.: 235–237 °C. IR (KBr): $\nu_{(NH)} = 3260\ cm^{-1}$, $\nu_{(NO)} = 1849\ cm^{-1}$. ^{1}H NMR (acetone-$d_6$): 6.38 (s, 5H, Cp), 7.66 (m, 15H, PPh_3), 7.12 (d, 1H, $C_4N_2H_3$), 7.29 (t, 1H, $C_4N_2H_3$), 8.66 (d, 1H, $C_4N_2H_3$); 9.62 (br, 1H, N*H*). ^{31}P NMR (acetone-d_6): 35.03. Anal. Calc. for ($C_{27}H_{23}N_3SOPRuB_2F_8.H_2O$): C, 42.60; H, 3.31; S, 4.21; N, 5.52. Found: C, 41.99; H, 3.75; S, 4.02; N, 4.92%.

*3.4. General procedure for the preparation of CpRu(PPh$_3$)(CO)(κ^{1}S-SR) (**3**)*

A 100 mL Schlenk flask was charged with 15 mL of THF, ruthenium thiolate complex CpRu(PPh_3)(κ^2-*S*,*N*-SR) (**1**), (0.25 mmol). CO was bubbled through the resulting solution for half an hour and the mixture was stirred under CO-atmosphere for additional 3 h. The volatiles were removed under vacuum and the resulting yellow solid was redissolved in a minimum amount of THF and chromatoghraphed on silica. Elution with hexane removes the produced PPh_3 then with (1:1 v:v) ratio of THF/hexane gave a yellow band of the product which was collected and dried under vacuum. The complexes were recrystallized from THF/hexane to give yellow crystals.

*3.4.1. CpRu(PPh$_3$)(CO)(κ^{1}S-Spy) (**3a**)*

Yield: 91%, m.p.: 229–230 °C. IR (CH_2Cl_2): $\nu_{CO} = 1951\ cm^{-1}$. ^{1}H NMR (C_6D_6): 4.80 (s, 5H, Cp), 6.45 (m, 1H, C_5NH_4), 6.77 (m, 2H, C_5NH_4), 6.99 (m, 9H, PPh_3), 7.62 (m, 6H, PPh_3), 8.43 (m, 1H, C_5NH_4). ^{31}P NMR (C_6D_6): 56.98. Anal. Calc. for ($C_{29}H_{24}NOPRuS$): C, 61.47; H, 4.27; S, 5.66; N, 2.47. Found: C, 61.52; H, 4.33; S, 5.35; N, 2.39%.

*3.4.2. CpRu(PPh$_3$)(CO)(κ^{1}S-Spym) (**3b**)*

Yield: 79%, m.p.: 235–237 °C. IR (KBr): $\nu_{CO} = 1956\ cm^{-1}$. ^{1}H NMR (C_6D_6): 4.82 (s, 5H, Cp), 6.10 (t,1H, $C_4N_2H_3$), 6.60 (t, 1H, $C_4N_2H_3$), 7.01 (m, 9H, PPh_3), 7.60 (m, 6H, PPh_3), 8.21 (d, 1H, $C_4N_2H_3$). ^{31}P NMR (C_6D_6): 55.92. Anal. Calc. for ($C_{28}H_{23}N_2OPRu$): C, 59.25; H, 4.08; S, 5.56; N, 4.90. Found: C, 59.90; H, 4.44; S, 5.99; N, 5.39%.

*3.5. General procedure for the preparation of CpRu(dppe)(κ^1-S-SR) (**4**)*

A three neck flask equipped with a reflux condenser was charged with 50 mL THF and thiol (0.89 mmol). The solution was cooled to −78 °C in an ethanol/dry ice bath and methyllithium (0.56 mL, 0.90 mmol) was added. After 10 min the cooling bath was replaced by a water bath and the solution was warmed up to 40 °C. CpRu(PPh_3)$_2$Cl (0.50 g, 0.72 mmol) and bis(diphenylphosphino)ethane (0.40 g, 1.03 mmol) was added and the resulting mixture was refluxed for 4 h. The volatiles were removed under vacuum and the remaining solid was dissolved in toluene (10.0 mL) and allowed to stand, the supernatant was taken and concentrated under vacuum to about 4.0 mL then 30.0 mL of cooled hexane was added, an orange–yellow precipitate was formed which was collected by removing the mother liquor and washed several times with cooled hexane and dried in vacuum.

*3.5.1. CpRu(dppe)(κ^{1}S-Spy) (**4a**)*

Yield: 93%, m.p.: 181–183 °C. ^{1}H NMR (acetone-d_6): 1.20 (m, 2H, Ph_2PCH_2), 2.82 (m, 2H, Ph_2PCH_2), 4.87 (s, 5H, Cp), 6.84 (d, 1H, C_5NH_4), 7.05 (t, 1H, C_5NH_4), 7.32 (m, 20H, PPh_3), 7.73 (t, 1H, C_5NH_4), 8.53 (d, 1H, C_5NH_4). ^{31}P NMR (acetone-d_6): 79.57. Anal. Calc. for ($C_{36}H_{33}NP_2RuS$): C, 64.1; H, 4.93; S, 4.75; N, 2.08. Found: C, 63.7; H, 5.17; S, 5.87; N, 1.90%.

*3.5.2. CpRu(dppe)(κ^{1}S-Spym) (**4b**)*

Yield: 94%, m.p.: 178–180 °C. ^{1}H NMR (acetone-d_6): 1.23 (m, 2H, Ph_2PCH_2), 2.85 (m, 2H, Ph_2PCH_2), 4.87 (s, 5H, Cp), 6.87 (d, 1H, $C_4N_2H_3$), 7.35 (m, 20H, PPh_3), 7.78 (t, 1H, $C_4N_2H_3$), 8.58 (d, 1H, $C_4N_2H_3$). ^{31}P NMR (acetone-d_6): 79.63. Anal. Calc. for ($C_{35}H_{32}N_2P_2RuS$): C, 62.2; H, 4.79; S, 4.74; N, 4.15. Found: C, 61.9; H, 4.46; S, 5.15; N, 4.65%.

3.6. General procedure for the preparation of $[CpRu(PPh_3)_2(\kappa^1S\text{-}SHR)]BPh_4$ (**5**)

A 100 mL Schlenk flask was charged with 15 mL of THF, ruthenium chloride $CpRu(PPh_3)_2Cl$ (0.50 g, 0.72 mmol), HSR (1.00 mmol) and $NaBPh_4$ (0.25 g, 0.72 mmol). The mixture was stirred for 2 h at room temperature, an orange precipitate was formed. The supernatant was removed and the precipitate was washed with hexane. The complexes were recrystallized from THF/hexane to give orange crystals.

3.6.1. $[CpRu(PPh_3)_2(\kappa^1S\text{-}SHpy)]BPh_4$ (**5a**)

Yield: 73%, m.p.: 148–151 °C. IR (CH_2Cl_2): ν_{NH}: 3242 cm^{-1}. ^1H NMR ($CDCl_3$): 4.38 (s, 5H, Cp), 6.84 (m, 1H, C_5NH_4), 6.99 (t, 1H, C_5NH_4), 7.02 (m, 1H, C_5NH_4), 7.11–7.50 (m, 50H, $BPh_4 + PPh_3$), 7.80 (d, 1H, C_5NH_4), 9.51 (br, 1H, N*H*). ^{31}P NMR ($CDCl_3$): 42.24. Anal. Calc. for ($C_{70}H_{60}BNP_2RuS$): C, 74.99; H, 5.39; S, 2.86; N, 1.24. Found: C, 74.36; H, 5.49; S, 2.44; N, 0.99%.

3.6.2. $[CpRu(PPh_3)_2(\kappa^1S\text{-}SHpym)]BPh_4$ (**5b**)

Yield: 81%, m.p.: 205–207 °C. IR (CH_2Cl_2): ν_{NH}: 3256 cm^{-1}. ^1H NMR ($CDCl_3$): 4.44 (s, 5H, Cp), 5.99 (t, 1H, $C_4N_2H_3$), 6.73 (m, 2H, $C_4N_2H_3$), 6.85–7.26 (m, 50H, $BPh_4 + PPh_3$), 9.50 (br, 1H, N*H*). ^{31}P NMR ($CDCl_3$): 44.00. Anal. Calc. for ($C_{69}H_{59}BN_2P_2RuS$): C, 73.86; H, 5.30; S, 2.86; N, 2.50. Found: C, 74.45; H, 5.50; S, 2.42; N, 2.29%.

3.6.3. Crystallographic analysis of $CpRu(PPh_3)(\kappa^2S,N\text{-}Spy)$ (**1a**), $[CpRu(PPh_3)(NO)(\kappa^1S\text{-}HSpy)][BF_4]_2$ (**2a**), and $CpRu(PPh_3)(CO)(\kappa^1S\text{-}Spy)$ (**3a**)

Single crystals suitable for the X-ray diffraction studies of complexes **1a**, **2a**, and **3a** were obtained by recrystallization of each of these compounds from THF/hexane mixtures. Detailed crystallographic data for these complexes are shown in Table 2. The geometric and intensity data were collected on a KappaCCD diffractometer. The structures were solved by direct methods using SHELXS [37] and refined by full-matrix least-squares on $|F_o|^2$ using SHELX-97 [38]. All of the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed into calculated positions [38].

Supplementary materials

CCDC 615798, 619944 and 615799 contain the supplementary crystallographic data for **1a**, **2a** and **3a**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Table 2
Selected crystal data and refinement parameters for $CpRu(PPh_3)(\kappa^2S,N\text{-Spy})$, (**1a**) $[CpRu(PPh_3)(NO)(\kappa^1S\text{-HSPy})][BF_4]_2$ (**2a**) and $CpRu(PPh_3)(CO)(\kappa^1S\text{-Spy})$ (**3a**)

	1a	**2a**	**3a**
Empirical formula	$C_{28}H_{24}NPRuS$	$C_{28}H_{27}B_2F_8N_2O_2PRuS$	$C_{29}H_{24}NOPRuS$
Formula weight (g/mol)	538.58	761.24	566.59
Crystal size (mm)	$0.06 \times 0.05 \times 0.05$	$0.1 \times 0.1 \times 0.1$	$0.06 \times 0.06 \times 0.05$
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	*Pbcn*	$P\bar{1}$	$P\bar{1}$
Volume (Å^3)	4668.97(15)	1545.6(2)	1230.61(7)
Z	4	2	2
Unit cell dimensions			
a (Å)	23.7256(3)	9.5370(10)	8.4860(2)
b (Å)	10.7436(2)	10.2710(10)	10.2093(4)
c (Å)	18.3170(4)	16.1070(10)	15.1283(6)
α (°)	90	96.740(5)	101.983(2)
β (°)	90	97.793(5)	98.848(2)
δ (°)	90	94.374(5)	101.394(2)
Index range	$-29 \leqslant h \leqslant 30$	$-13 \leqslant h \leqslant 13$	$-10 \leqslant h \leqslant 9$
	$-12 \leqslant k \leqslant 13$	$-14 \leqslant k \leqslant 14$	$-13 \leqslant k \leqslant 12$
	$-23 \leqslant l \leqslant 23$	$0 \leqslant l \leqslant 22$	$-17 \leqslant l \leqslant 19$
Radiation type	Mo Kα	Mo Kα	Mo Kα
Density (Mg/m^3)	1.532	1.636	1.529
μ (mm^{-1})	0.846	0.705	0.810
θ (°)	2.08–27.48	2.24–30.05	2.50–27.47
λ (Å)	0.71073	0.71073	0.71073
Goodness of fit	1.024	1.018	0.992
Data/restraints/parameters	5314/0/289	9012/3/416	5585/0/307
$R[F^2 > 2\sigma(F^2)]$	0.0321	0.361	0.0322
$\omega R(F^2)$[a]	0.0853	0.0477	0.0750

[a] $\omega = 1/[\sigma^2(F_o^2) + (0.0598P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

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