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Thiosemicarbazonates of ruthenium(II): Crystal structures of [bis(diphenylphosphino)butane]-[bis(pyridine-2-carbaldehydethiosemicarbazonato)] ruthenium(II) and [bis(triphenylphosphine)][bis(benzaldehydethiosemicarbazonato)] ruthenium(II)

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Abstract

The reaction of $Ru_2Cl_4(dppb)_3$ {dppb = Ph_2P–$(CH_2)_4$–PPh_2} with pyridine-2-carbaldehyde thiosemicarbazone {C_5H_4N—C(H)=N^3—N^2H—C(=S)NH_2, Hpytsc}, and that of $RuCl_2(PPh_3)_3$ with benzaldehyde thiosemicarbazone {C_6H_5—C(H)=N^3—N^2H—C(=S)—NH_2, Hbtsc}, in the presence of Et_3N base led to loss of the –N^2H– proton in each case, and yielded [Ru(pytsc)$_2$(dppb)] (**1**) and [Ru(btsc)$_2$(Ph_3P)$_2$] (**2**), respectively. The complexes are characterized with the help of analytical data, IR, NMR (^{1}H, ^{13}C, ^{31}P) and single crystal X-ray study. In both compounds **1** and **2**, the thiosemicarbazone ligands coordinate to Ru(II) via the hydrazinic nitrogen (N^2) and sulfur atoms forming four membered rings, and the pyridyl group is pendant in **1**. The geometry is distorted octahedral with *cis*:*cis*:*trans* P, P:N, N:S, S dispositions of donor atoms. Proton NMR confirmed loss of the –N^2H– proton in both compounds, and the ^{31}P NMR spectra reveal the presence of equivalent phosphorus atoms in both the compounds. Compound **1** represents the first example of a Ru(II)-thiosemicarbazone complex with a chelating diphosphine and it reveals the stability of a seven membered P,P-chelate ring in the presence of a potentially tridentate pytsc$^-$ ligand.
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Keywords: Pyridine-2-carbaldehyde thiosemicarbazone; Benzaldehyde thiosemicarbazone; Ruthenium(II); Seven membered rings

1. Introduction

Thiosemicarbazones {R^1R^2C=N^3—N^2H—C(=S)—NR^3R^4, Chart 1}, which exhibit thione–thiol tautomerism, possess several donor atoms and generally bind to metals via N^2, S or N^3, S donor atoms forming four- or five-membered rings, respectively [1–11]. Apart from the bonding and structural aspects of metal complexes of thiosemicarbazones, they have biochemical implications either in the free or metal-bonded states [1–4]. Chart 1 depicts various thiosemicarbazone ligands (Htsc) and their complexes with ruthenium(II) [5–11], having the general formulas, [Ru(tsc)$_2$(Ph_3P)$_2$] (**3**–**5**) [7,8,11], [Ru(bpy)$_2$(tsc)](ClO_4) (**6**) [10], [Ru(PPh_3)$_2$(Htsc)$_2$]-(ClO_4)$_2$ (**7**) [9], [Ru(Htsc)(PPh_3)$_2$Cl]Cl (**8**) [6], [Ru(tsc)-(PPh_3)$_2$](ClO_4) (**9**) [5] and [Ru(bpy)$_2$(tsc)](ClO_4) (**10**) [10] (bpy = 2,2′-bipyridine). Complexes **3**–**6** involve N^2, S-chelation (four membered rings), while complexes **7**–**10** have N^3, S-chelation (five-membered rings). In complexes **8** and **9**, N^4 of the pyridine ring is also coordinating.

In the present paper, we report the synthesis, spectroscopy and crystal structures of two ruthenium(II) complexes of [Ru(pytsc)$_2$(dppb)] (**1**) and [Ru(btsc)$_2$(Ph_3P)$_2$] (**2**). The

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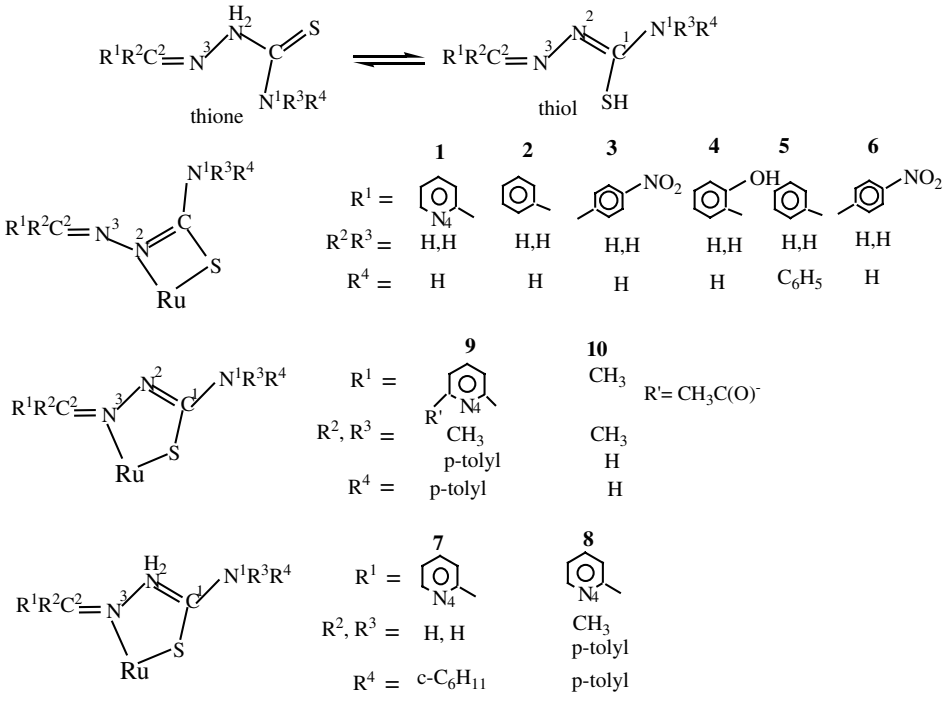


Chart 1.

coordination behaviour of these thiosemicarbazones is investigated under the influence of a potentially P,P-chelating diphosphine ligand $\{(C_6H_5)_2P–(CH_2)_4–P(C_6H_5)_2\}$ in compound **1**, and an unidenate PPh_3 ligand in compound **2**. To the best of our knowledge, compound **1** is the first example of a ruthenium(II)–thiosemicarbazone complex with a diphosphine ligand.

2. Experimental

2.1. Materials and techniques

The starting ruthenium(II) complexes, $RuCl_2(PPh_3)_3$ [12] and $Ru_2Cl_4(dppb)_3$ [13], were prepared by refluxing $RuCl_3 \cdot xH_2O$ and the suitable phosphine in dry ethanol for 5–6 h. Ligands benzaldehyde thiosemicarbazone and pyridine-2-carbaldehyde thiosemicarbazone were prepared by the reported methods [15]. Elemental analysis for C, H and N were carried out using a Thermoelectron FLASHEA1112 analyser. The melting points were determined with a Gallenkamp electrically heated apparatus. UV spectra were recorded using an UV-1601PC Shimadzu. IR spectra were recorded using KBr pellets on a Pye-Unicam SP3-300 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL AL300 FT spectrometer at 300 MHz in $CDCl_3$ with TMS as internal reference. ^{13}C NMR spectra were recorded at 75.45 MHz with TMS as internal reference. ^{31}P NMR spectra were recorded at 121.5 MHz with TMP $\{(CH_3O)_3P\}$ as external reference taken as zero position.

2.2. Synthesis of [Ru(pytsc)$_2$(dppb)] (1)

To a solution of Hpytsc (0.022 g; 0.12 mmol) in methanol (30 mL) was added solid $[Ru_2Cl_4(dppb)_3]$ (0.05 g; 0.03 mmol) followed by addition of NEt_3 (0.5 mL). The mixture was stirred for about 15 h. The red solid that formed was filtered, washed with methanol and dried. Crystals were grown from dichloromethane–acetonitrile–methanol. Yield: 51%, m.p. 172 °C. *Anal.* Calc. for $C_{42}H_{42}N_8P_2S_2Ru \cdot 2H_2O \cdot CH_3CN$: C, 54.6; H, 5.48; N, 13.02. Found: C, 54.0; H, 5.04; N, 13.25%. Main IR peaks (KBr, cm^{-1}): $\nu(NH_2) + \nu(OH_2)$ 3457m, 3360–3300m, 3150w; $\nu(C{=}N) + \delta NH_2 + \nu(C{=}C) + \delta(OH_2)$ 1585s, 1573sh, 1562sh; $\nu(C{=}S)$ 1047s; $\nu(P–C)$ 1093s; electronic spectra (CH_2Cl_2, $\lambda_{max/nm}$, ε/L mol^{-1} cm^{-1}) 391.50 (17600), 328.50 (24580), 245 (40000). ^{1}H NMR ($CDCl_3$): $\delta = 8.80$ (s, C^{2}H, 2H), 8.52 (d, C^{7}H, 2H), 7.10–7.66 (m, Ph–H + C^{4,5,6}H, 26H), 5.46 (s, NH_2, 4H), 1.26–2.89 (–CH_2–, 8 H) ppm; ^{13}C NMR ($CDCl_3$), $\delta = 182.0$ (C^1), 155.2 (C^3), 149.0 (C^7), 145.2 (C^2), 138.6–140.6 (*i*-C), 135.8 (C^5), 132.5 (*o*-C), 126.9–128.6 (*m*- and *p*-C), 122.4 (C^6), 120.7 (C^4), 30.1, 23.4 {–$(CH_2)_4$-carbons} ppm; ^{31}P NMR ($CDCl_3$), $\delta = -57.413$ ppm, $\Delta\delta(\delta_{complex} - \delta_{ligand}) = 66.48$ ppm.

2.3. Synthesis of [Ru(btsc)$_2$(Ph$_3$P)$_2$] (2)

This complex was prepared by the literature method [9]. To a solution of Hbtsc (0.0186 g; 0.1 mmol) in methanol (30 mL) was added solid $RuCl_2(Ph_3P)_3$ (0.05 g; 0.05 mmol) followed by NEt_3 base (0.5 mL). The mixture was stirred for 2 h and the yellow solid which separated was filtered,

washed with methanol and dried. The compound was recrystallized from dichloromethane–methanol solution. Yield: 60% m.p. 170 °C. Main IR peaks (KBr, cm^{-1}), $\nu(NH_2)$ 3483s, 3361s; $\nu(C{=}N) + \delta NH_2 + \nu(C{=}C)$ 1600s, 1577; $\nu(C{=}S)$ 1050s, 754 s; $\nu(P–C)$ 1087s. ^1H NMR ($CDCl_3$) $\delta = 8.88$ (s, C^2H, 2H), 5.03 (s, NH_2, 4H), 6.97–7.90 (m, $C^{2,4–6,8}H + 40H$, Ph). ^{13}C NMR ($CDCl_3$) 179.46 (C^1), 147.28 (C^2), 136.06 (C^3), 128.49 ($C^{4,8}$), 127.23 (C^5), 137.24 (*i*-C), 134.2 (t, *o*-C), 128.27 (d, *p*-C), 126.75 (t, *m*-C). ^{31}P NMR ($CDCl_3$), $\delta = -56.015$ ppm, $\Delta\delta(\delta_{complex} - \delta_{ligand}) = 57.13$ ppm.

2.3.1. Ligand NMR data

Hpytsc (dmso-d_6): ^1H NMR, $\delta = 11.57$ (s, N^2H, 1H), 8.47 (s, C^2H, 1H), 7.2–8.06 (6H, $C^{4,5,6,7} + Ph–H$) ppm. ^{13}C NMR 178.05 (C^1), 152.17 (C^3), 148.42 (C^2), 142.38 (C^7), 135.56 (C^5), 123.09 (C^6), 119.73 (C^4) ppm; Hbtsc [17] ^1H NMR $\delta = 7.27$, 6.60 (s, N^1H_2, 2H), 10.22 (s, N^2H, 1H), 9.26 (s, C_2H, 1H), 7.69 (m, $C^{4,8}H$, 2H), 7.43 (m, $C^{5,6,7}H$, 3H). ^{13}C NMR 178.86 (C^1), 143.94 (C^2), 133.99 (C^3), 130.87 (C^6), 128.96 ($C^{4,8}$), 127.54 ($C^{5,7}$); ^{31}P NMR of dppb: $\delta = -123.89$ ppm; ^{31}P NMR of PPh_3, $\delta = -113.15$ ppm.

2.4. X-ray crystallography

Suitable crystals of **1** and **2** were mounted on X-ray diffractomers (Bruker APEX II for **1**; CCD area detector for **2**), each equipped with graphite monochromators and a Mo Kα radiation source ($\lambda = 0.71073$ Å). The unit cell dimensions and intensity data were measured at 293 K. The structures were solved by direct methods and refined by full-matrix least-square methods based on F^2 with anisotropic thermal parameters for non-hydrogen atoms, using Bruker SMART (data collection and cell refinement), Bruker SHELXTL (data reduction and computing molecular graphics), SHELXS-97 (structure solution) and SHELXL-97 (structure refinement)] [16]. An empirical absorption correction was applied. Calculated positions for the H atoms were used in structure factor (SF) calculations. ω scans were to 56° (2θ). In compound **1**, one of the pyridine groups in each pytsc ligand was found to be disordered and these atoms were treated in an equal population model. One of the terminal pyridyl groups displayed disorder. During refinement the disorder in this group was resolved. Selected crystal data for compounds **1** and **2** are given in Table 1.

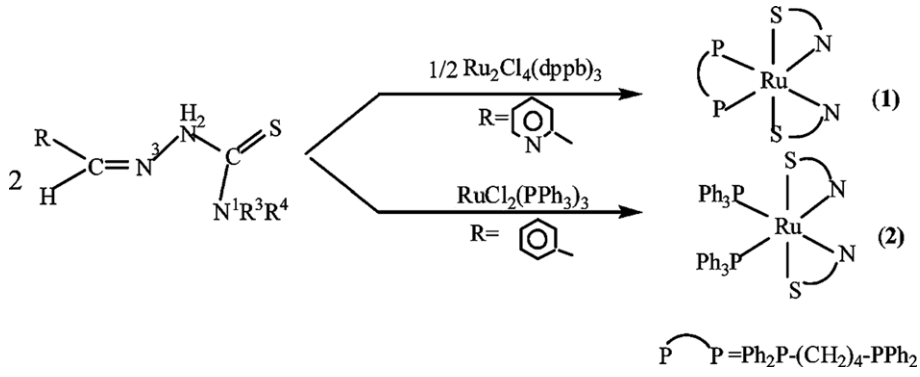
Table 1
Crystal data and refinement details for **1** and **2**

	1	**2**
Empirical formula	$C_{42}H_{44.5}N_8O_{1.5}P_2RuS_2$	$C_{52}H_{46}N_6P_2RuS_2$
M	912.49	982.08
T (K)	293(2)	293(2)
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
a (Å)	9.7303(6)	12.715(3)
b (Å)	12.8038(8)	12.864(3)
c (Å)	19.3406(11)	16.286(4)
α (°)	85.2610(10)	72.184(5)
β (°)	84.9840(10)	72.621(5)
γ (°)	70.4980(10)	65.146(4)
V (Å^3)	2258.9(2)	2256.0(10)
Z	2	2
D_{calc} (g cm^{-3})	1.348	1.446
μ (mm^{-1})	0.552	0.556
Reflections collected	31 048	16 506
Unique reflections [R_{int}]	11 175 [0.0478]	10 455 [0.0740]
Reflections with [$I > 2\sigma(I)$]	6181	5602
Final *R* indices [$I > 2\sigma(I)$]	$R = 0.0448$, $wR = 0.1238$	$R = 0.0778$, $wR = 0.1274$

3. Results and discussion

3.1. Synthesis and IR spectroscopy

Scheme 1 shows the formation of complexes **1** and **2**. Reaction of $Ru_2Cl_4(dppb)_3$ {dppb = $Ph_2P–(CH_2)_4–PPh_2$} with pyridine-2-carbaldehyde thiosemicarbazone {$C_5H_4N–C(H){=}N^3–N^2H–C(=S)NH_2$, Hpytsc}, and that of $RuCl_2(PPh_3)_3$ with benzaldehyde thiosemicarbazone {$C_6H_5–C(H){=}N^3–N^2H–C(=S)–NH_2$, Hbtsc}, in the presence of Et_3N base led to loss of the $–N^2H–$ proton in each case, and yielded [Ru(pytsc)$_2$(dppb)] (**1**) and [Ru(btsc)$_2$(Ph_3P)$_2$] (**2**) [9], respectively. Both the complexes



Scheme 1.

are soluble in dichloromethane, chloroform, acetone or toluene, but partially soluble in acetonitrile. The compounds are stable in air in the solid state; however in solution phase the complexes turn green on standing for a long time.

Due to the presence of H_2O in complex **1**, the ν(N–H) region has broad signals at 3457m, 3360–3300m and 3150w, and these peaks are attributed to ν(N–H) + ν(O–H). However in complex **2**, the ν(N–H) region shows sharp peaks at 3483s and 3361s. The free ligands show very strong signals due to ν(N–H) of the hydrazinic –N^2H– group in the region 3140–3150 cm^{-1} [14,18]. Thus in complex **2**, it is unequivocally established that deprotonation of the N^2H proton occurs after complexation; and in complex **1** due to obscuring of the ν(N–H) region by water, deprotonation of the N^2H proton appears less apparent. It may be pointed out here that in a series of complexes of copper(I) with neutral thiosemicarbazones, ν(N–H) of the hydrazinic –N^2H– group was clearly visible though shifted from the free ligand position [19]. Other important IR peaks are listed in the Section 2. The thioamide bands ν(C=S) + ν(C–N) appear in the range 1050–803 cm^{-1} (cf. free ligands, 1060–817 cm^{-1}), and on complexation, these shift to either lower energy or higher energy, but the shifts are not significant. The appearance of characteristic ν(P–C_{Ph}) bands at around 1090 cm^{-1} indicates the presence of Ph_3P and dppb in the complexes.

3.2. Crystal structures

The atomic numbering schemes for **1** and **2** are given in Figs. 1 and 2 respectively, and selected bond angles and bond lengths are listed in Table 2. Compounds **1** and **2** crystallized in triclinic crystal systems with the space group $P\bar{1}$ in each case. In compound **1**, the thiosemicarbazone ligand in its deprotonated form (pytsc$^-$) is chelating via its N^2, S-donor atoms, thus forming four membered chelate rings with average Ru(II)–N and Ru(II)–S distances of 2.202 Å and 2.418 Å, respectively, and the pyridyl group is pendant. The diphosphine ligand (dppb) is also chelating via its P,P donor atoms with an average Ru–P distance of 2.264 Å (Tables 2 and 3). The donor atoms around the Ru(II) center occupy *cis*:*cis*:*trans* N,N:P,P:S,S positions. The angles around the Ru(II) center lie in the range, 65–163°, with a N^2–Ru–S bite angle of 65.85°, N–Ru–N angle of 83.07° and *trans* S(1)–Ru–S(2) angle of 163.30°. The diphosphine ligand dppb forms a seven membered chelate ring with a P–Ru–P angle of 94.54°. Similarly, compound **2** has average Ru(II)–N, Ru(II)–S and Ru–P distances of 2.145, 2.410 and 2.301 Å, respectively. The average bond angles for N^2–Ru–S, N–Ru–N, S–Ru–S, P–Ru–P are 65.80°, 78.80°, 162.54° and 105.37°, respectively. The geometry of both the complexes is distorted octahedral.

On comparing the bond parameters of **1** and **2**, the most striking difference is found in their Ru–N and Ru–P distances. Interestingly, the Ru–P distances of **1** are shorter and its Ru–N distances are longer as compared to those of **2**. This shows the chelating effect of the dppb ligand which forms stronger Ru(II)–P bonds as compared to Ru(II)–PPh_3 bonds, which in turn affect the Ru(II)–N bonds *trans* to Ru–P bonds. The Ru–P distance for **1** is the shortest among all the complexes listed in Table 3. The Ru–S bonds remain unaffected by this change as can be seen by comparing the bonds in both the compounds. The C–S distances in both the compounds are similar, in

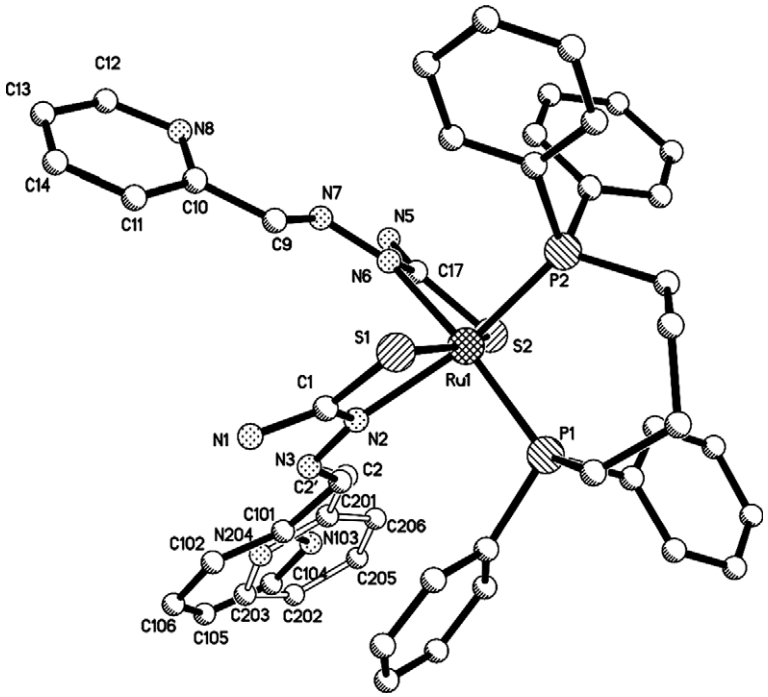


Fig. 1. The structure of [Ru(pytsc)$_2$(dppb)] (**1**) with the atomic numbering scheme.

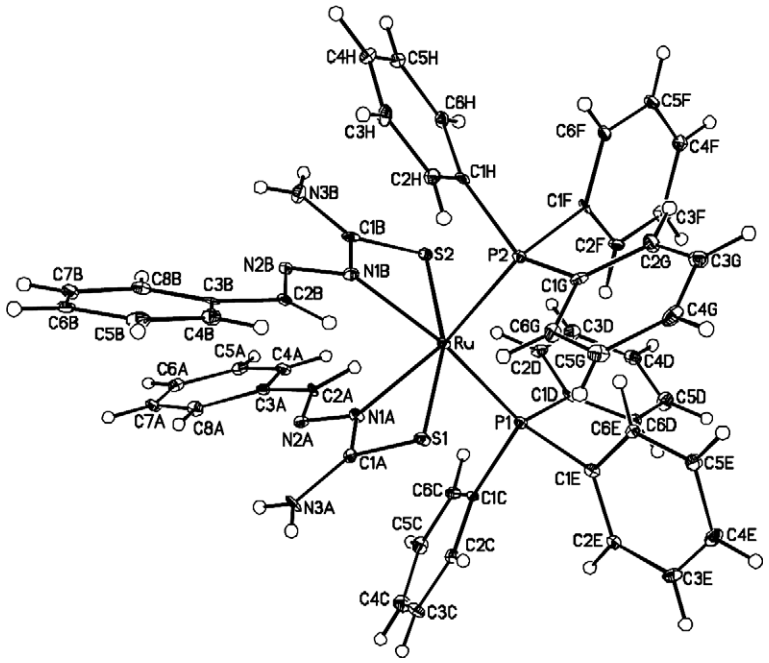


Fig. 2. The structure of $[Ru(btsc)_2(PPh_3)_2]$ (**2**) with the atomic numbering scheme.

Table 2
Selected bond lengths (Å) and bond angles (°) for **1** and **2**

1			
Ru(1)–N(2)	2.187(4)	Ru(1)–S(1)	2.4096(10)
Ru(1)–N(6)	2.218(3)	Ru(1)–S(2)	2.4270(10)
Ru(1)–P(1)	2.2582(9)	S(1)–C(1)	1.680(5)
Ru(1)–P(2)	2.2696(10)	S(2)–C(17)	1.718(4)
N(2)–Ru(1)–N(6)	83.06(12)	P(1)–Ru(1)–S(1)	91.20(3)
N(2)–Ru(1)–P(1)	92.07(9)	P(2)–Ru(1)–S(1)	97.49(4)
N(6)–Ru(1)–P(1)	163.99(8)	N(2)–Ru(1)–S(2)	101.64(13)
N(2)–Ru(1)–P(2)	162.42(13)	N(6)–Ru(1)–S(2)	65.55(9)
N(6)–Ru(1)–P(2)	94.57(9)	P(1)–Ru(1)–S(2)	100.83(3)
P(1)–Ru(1)–P(2)	94.54(3)	P(2)–Ru(1)–S(2)	93.10(4)
N(2)–Ru(1)–S(1)	66.06(13)	S(1)–Ru(1)–S(2)	163.30(4)
N(6)–Ru(1)–S(1)	100.62(9)		
2			
Ru–N(1A)	2.141(5)	Ru–S(1)	2.4083(17)
Ru–N(1B)	2.149(5)	Ru–S(2)	2.4131(17)
Ru–P(1)	2.2977(19)	S(1)–C(1A)	1.700(7)
Ru–P(2)	2.3044(18)	S(2)–C(1B)	1.712(7)
N(1A)–Ru–N(1B)	78.8(2)	N(1B)–Ru–S(1)	99.52(14)
N(1A)–Ru–P(1)	89.16(15)	P(1)–Ru–S(1)	87.19(6)
N(1B)–Ru–P(1)	162.18(14)	P(2)–Ru–S(1)	104.52(6)
N(1A)–Ru–P(2)	162.46(15)	N(1A)–Ru–S(2)	100.73(4)
N(1B)–Ru–P(2)	89.02(15)	N(1B)–Ru–S(2)	65.85(14)
P(1)–Ru–P(2)	105.37(7)	P(1)–Ru–S(2)	104.21(6)
N(1A)–Ru–S(1)	65.75(14)	P(2)–Ru–S(2)	85.43(6)
S(1)–Ru(1)–S(2)	162.54(6)		

the range 1.68–1.71 Å, which is shorter than a C–S single bond of 1.81 Å but longer than a C–S double bond of 1.62 Å, indicating a partial double bond character [20].

The second major difference lies in the P–Ru–P bond angle which is smaller for **1** as compared to that in **2**, and this is attributed to the presence of bulky PPh_3 ligands adjacent to each other which causes this angle to deviate towards the higher side. As a matter of fact, the P–Ru–P bond angle of **1** is the smallest among all the Ru(II) complexes of thiosemicarbazones reported to date. The N–Ru–N bond angle in **1** is bigger than that in **2**, and this variation is attributed to the scissoring effect of P–Ru–P angles. The S–Ru–S bond angles in both the complexes are comparable and are similar to other complexes reported in the literature (Table 3). From Table 3, it may be noted that parameters of **2** are very close to those of complexes **3**–**5**, but different from those of **1**. Complexes **1**–**5**, forming four-membered rings, have a bite angle of ca. 66°, which is small relative to the bite angles (ca. 81°) of complexes (**7**–**9**) which form five-membered rings.

Compounds **1**–**5** are analogous with four membered rings formed by the thiosemicarbazone, the steric bulk of the phosphines appears to favour N^2, S chelation irrespective of the substituents on the C^2 or N^1 atoms. Compound **7** has N^3, S chelation with five membered ring formation, despite the presence of bulky PPh_3 ligands in the *cis* position, and it is apparent that the presence of bulky groups at the N^1 atom appears to disfavour N^2, S chelation. In **8** and **9** the steric effect of PPh_3 is less demanding in view of the presence of one thiosemicarbazone ligand in each complex and this leads to a large P–Ru–P bond angle and also both have bulky R groups at N^1 and this leads to N^3, S chelation. As regards compound **6** and **10**, each have two bipyridine ligands and the only difference lies in the presence of substituents at the C^2 carbon while the substituents at $N^1$are identical (R^3, $R^4 = H$). This difference leads to N^2, S chelation in **6** and N^3, S chelation in **10**.

Table 3
Comparison of bond lengths (Å) and bond angles (°) of **1**, **2** and related complexes

	Ru–N	Ru–S	Ru–P	S–Ru–S	N–Ru–N	P–Ru–P	N–Ru–S	Ref.
1	2.202	2.418	2.264	163.30	83.07	94.54	65.85	this work
2	2.145	2.410	2.301	162.54	78.80	105.37	65.80	this work
3	2.181	2.440	2.299	162.77	80.42	99.24	65.90	[7]
4	2.152	2.426	2.323	161.23		105.95	65.74	[8]
5	2.140	2.439	2.314	160.65	80.50	97.76	65.45	[11]
7	2.146	2.369	2.382	170.81	81.4	101.74	81.65	[9]
8	2.035	2.386	2.399			175.2	83.3	[6]
9	1.981	2.398	2.371			165.8	81.5	[5]

3.3. NMR spectroscopy

The signals due to N^2H protons in the free ligands (see Section 2) were absent in the complexes **1** and **2**, and it showed that the ligands are uninegative. The NH_2 protons appear as single peaks in both the complexes due to free rotation of the N^1H_2 group along the C^1–N^1 bond axis, instead of two broad peaks as observed in the free ligands, due to the restricted rotation of the N^1H_2 group along the C^1–N^1 bond axis at room temperature [18]. All other protons appear in the aromatic region as multiplets and overlapping signals. The ^{13}C NMR spectra of both the compounds showed bands due to tsc^- anions and phosphine ligands (cf. Section 2). The C^1 carbons of both ligands move downfield, and it shows coordination via the S-donor atom, and likewise C^2 and C^3 move downfield, but the shift is small. All other tsc^- carbons show much smaller shifts. Various signals due to *ipso*, *ortho*, *meta* and *para* carbons of the phosphine ligands are resolved in the complexes. Finally, the ^{31}P NMR spectra of **1** and **2** showed coordination shifts $\{\Delta\delta(\delta_{complex}-\delta_{ligand})\}$ of 66.48 and 57.13 ppm, respectively, revealing that both the phosphorus atoms are equivalent in each case, and that the dppb ligand binds more strongly than PPh_3, in conformity with the structural data.

4. Conclusion

Compound **1** represents the first example of a ruthenium(II) complex with a chelating diphosphine, forming a stable seven membered P,P-chelate ring in the presence of a potentially tridentate pyridine-2-carbaldehyde thiosemicarbazonate anion coordinating via N^2, S-donor atoms, which is stable in solid and solution states. For R = Ph and py at the C^2 carbon of the tsc^- ligands, the mode of coordination remains same, viz., N^2, S.

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Appendix A. Supplementary material

Supplementary data is available from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44 1233 6033, e-mail:deposit@ccdc.cam.ac.uk on request quoting the deposition number CCDC 298895 for (**1**) and 298896 for (**2**). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.04.018.

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