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Thiosemicarbazonates of Ruthenium(II): Crystal Structures of [Bis(triphenylphosphine)][bis(*N*-phenyl-pyridine-2-carbaldehyde Thiosemicarbazonato)]ruthenium(II) and [Bis(diphenylphosphino)butane][bis(salicylaldehyde Thiosemicarbazonato)]ruthenium(II)

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Abstract. Reaction of $RuCl_2(PPh_3)_3$ with N-Phenyl-pyridine-2-carbaldehyde thiosemicarbazone ($C_5H_4N-C^2(H)=N^3-N^2H-C^1(=S)-N^1HC_6H_5$, Hpytsc-NPh) in presence of Et_3N base led to loss of $-N^2H-$proton and yielded the complex $[Ru(pytsc\text{-}NPh)_2(Ph_3P)_2]$ (**1**). Similar reactions of precursor $RuCl_2[(p\text{-tolyl})_3P]_3$ with a series of thiosemicarbazone ligands, viz. pyridine-2-carbaldehyde thiosemicarbazone (Hpytsc), salicylaldehyde thiosemicarbazone (H_2stsc), and benzaldehyde thiosemicarbazone (Hbtsc), have yielded the complexes, $[Ru(pytsc)_2\{(p\text{-tolyl})_3P\}_2]$ (**2**), $[Ru(Hstsc)_2\{(p\text{-tolyl})_3P\}]_2$ (**3**), and $[Ru(btsc)_2\{(p\text{-tolyl})_3P\}_2]$ (**4**), respectively. The reactions of precursor $Ru_2Cl_4(dppb)_3$ {dppb = $Ph_2P-(CH_2)_4-PPh_2$} with H_2stsc, Hbtsc, furan-2-carbaldehyde thiosemicarbazone (Hftsc) and thiophene-2-carbaldehyde thiosemicarbazone (Httsc) have formed complexes of the composition, $[Ru(Hstsc)_2(dppb)]$ (**5**), $[Ru(btsc)_2(dppb)]$ (**6**), $[Ru(ftsc)_2(dppb)]$ (**7**), and $[Ru(ttsc)_2(dppb)]$ (**8**). The complexes have been characterized by analytical data, IR, NMR (^1H, ^{31}P) spectroscopy and X-ray crystallography (**1** and **5**). The proton NMR confirmed loss of $-N^2H-$ proton in all the compounds, and ^{31}P NMR spectra reveal the presence of equivalent phosphorus atoms in the complexes. In all the compounds, thiosemicarbazone ligands coordinate to the Ru^{II} atom via hydrazinic nitrogen (N^2) and sulfur atoms. The arrangement around each metal atom is distorted octahedral with *cis*:*cis*:*trans* P, P:N, N:S, S dispositions of donor atoms.

Introduction

Thiosemicarbazones {$R^1R^2C^2=N^3-N^2H-C^1(=S)-N^1R^3R^4$, Chart 1}, exhibit thione−thiol tautomerism, possess several donor atoms and can bind to a metal atom both in neutral as well as in anionic forms and have shown a number of bonding modes [1−8]. Generally, thiosemicarbazones coordinate to transition metals via N^3, S donor atoms (mode **C**), however, exceptional behaviour has been observed in case of Ru^{II} complexes $[Ru(L)_2(PPh_3)_2]$ in which N^2, S (**E**) is the predominant mode of coordination (Chart 1) [9−12].

Recently from our laboratory, thiosemicarbazone chemistry of platinum metals has been reported, and a variety of interesting features such as cyclometallation, synthesis of trinuclear complexes (Cu^{II}-Ru^{II}-Cu^{II}), tricoordination by pyrrole-2-carbaldehyde thiosemicarbazone, were observed [13−15]. In continuation of our interest in PGM-thiosemicarbazone chemistry, a series of ligands as shown in Chart2 have been used for preparing Ru(II) complexes. The complexes are characterized by analytical data, IR, NMR (^1H, ^{31}P) spectroscopy and X-ray crystallography (**1** and **5**). There are only a few mixed ligand complexes of Ru^{II} with thiosemicarbazones and ditertiary phopshines [11, 13].

Experimental Section

Materials and Techniques

The starting ruthenium(II) complexes, $RuCl_2(PPh_3)_3$, $RuCl_2[(p\text{-tolyl})_3P]_2$ [16] and $Ru_2Cl_4(dppb)_3$ [17], were prepared by refluxing $RuCl_3 \cdot xH_2O$ and a suitable phosphine in dry ethanol for 5−6 h. Ligands benzaldehyde thiosemicarbazone, salicylaldehyde thiosemicarbazone, thiophene-2-carbaldehyde thiosemicarbazone, furan-2-carbaldehyde thiosemicarbazone, and pyridine-2-carbaldehyde thiosemicarbazone were prepared by reported methods [18]. Triphenylphosphine (Ph_3P), tri-p-tolylphosphine {(p-tolyl)$_3$P}, bis(diphenylphosphino)methane (dppm), 1,3-bis(diphenyl phosphino)propane (dppp), were procured from Aldrich-Sigma Ltd. Other ligands, 1,2-bis(diphenyl phosphino)ethane (dppe) and 1,4-bis(diphenyl-phosphino)butane (dppb) were prepared as reported in literature [19]. Elemental analysis for C, H and N were carried out using Thermoelectron FLASHEA1112 analyser. The melting points were determined with a Gallenkamp electrically heated ap-

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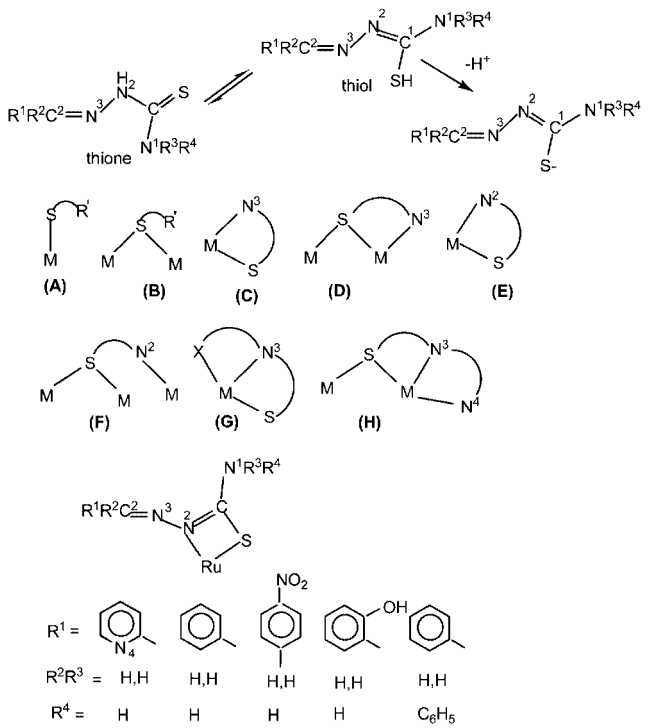

Chart 1.

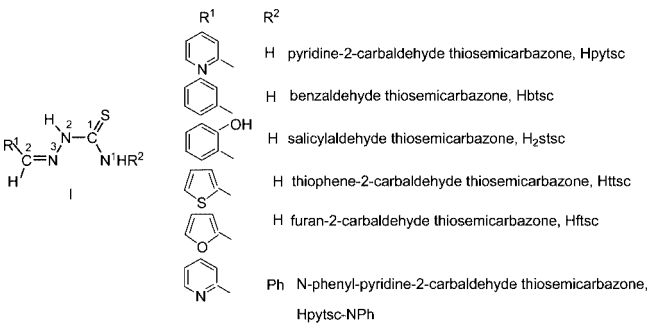

Chart 2.

paratus U.V spectra were recorded using 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. ^{31}P NMR spectra were recorded at 121.5 MHz with TMP $\{(CH_3O)_3P\}$ as external reference taken as zero position.

$[Ru(\eta^2\text{-}N^2, S\text{-}pytsc\text{-}NPh)_2(PPh_3)_2]\cdot 1.5CH_3CN$ (1). To a solution of Hpytsc-NPh (0.019 g; 0.10 mmol) in methanol (20 mL) was added $RuCl_2(PPh_3)_3$ (0.050 g; 0.052 mmol) and Et_3N (0.5 mL) followed by stirring for 2 h, during which clear orange colored solution was formed. The solution was filtered and kept for evaporation, orange crystalline product starts forming after few days. It was recrystallised from acetonitrile. Mp. 150−152 °C, orange, yield, 70 %. Anal. calc. $C_{65}H_{56.50}N_{9.50}P_2RuS_2$; C 64.87 (calc. 65.10); H5.79 (4.71); N 10.97 (11.10) %.

IR bands (KBr, pellets, cm^{-1}) : ν(N-H) 3340s, 3217 (-NH_2-); ν(C-H) 3010w; ν(C=N) + δNH_2 + ν(C=C) 1589s, 1558; ν(P-C_{Ph}) 1089m; ν(C-S) 760s; **^{1}H NMR** ($CDCl_3$, δ): 9.00 (s, C^2H, 2H); 8.52 (d, C^7H, 2H, J = 1.125); 8.34 (s, NHPh, 2H); 6.91−7.51 (m, $C^{4,5,6}$ + Ph-H 36H). **^{31}P NMR**($CDCl_3$, δ): −56.67; $\Delta\delta(\delta_{complex}-\delta_{PPh3}) = 56.7$ $\{\delta_{PPh3} = -113.15\}$.

$[Ru(\eta^2\text{-}N^2, S\text{-}pytsc)_2\{(p\text{-}tolyl)_3P\}_2]$ (2). To a solution of Hpytsc (0.0186 g; 0.1 mmol) in methanol (30 mL) was added solid $RuCl_2\{(p\text{-}tolyl)_3P\}_3$ (0.050 g; 0.046 mmol) followed by NEt_3 base (0.5 mL). The mixture was stirred for 4 h. and yellow solid separated was filtered, washed with methanol, and dried. The $Et_3NH^+Cl^-$ salt remained in the solution. The compound was recrystallized from dichloromethane-acetonitrile mixture. Mp. 180−82 °C, bright orange, yield, 76 %. Anal. calc. $C_{56}H_{56}N_8P_2RuS_2$; C 61.98 (calc. 62.90); H 5.58 (5.2); N 10.57 (10.40) %.

IR bands (KBr, pellets, cm^{-1}) : ν(N-H) 3444w, 3437s (-NH_2-); ν(C-H) 3012w; ν(C=N) + δNH_2 + ν(C=C) 1592sh, 1600s, 1581s; ν(P-C) 1085s; ν(C-S), 808s. **^{1}H NMR** ($CDCl_3$, δ): 8.67 (s, C^2H, 2H), 6.53 (d, C^7H, 1H), 7.44−7.54 (m, $C^{5,6}$H, 4H), 6.76−7.44 (m, Ph-H + C^4), 5.45 (s, -NH_2, 4H), 2.2 (s, -CH_3, 18H). **^{31}P NMR**($CDCl_3$, δ): −58.74, $\Delta\delta(\delta_{complex}-\delta_{(p\text{-}tolyl)3P}) = 56.86$; $\{\delta_{(p\text{-}tolyl)3P} = -115.6\}$.

Compounds **3** and **4** were prepared by a method similar to **2**.

$[Ru(\eta^2\text{-}N^2, S\text{-}Hstsc)_2\{(p\text{-}tolyl)_3P\}_2]$ (3). Mp. 182−185 °C, yellow, yield, 76 %. Anal. Calc. for $C_{58}H_{56}N_6O_2P_2RuS_2$: C 63.30 (calc. 63.50); H 5.35 (5.10); N 7.54 (7.66) %.

IR bands (KBr, pellets, cm^{-1}): ν(N-H) 3377s; ν(C-C) 3012w; ν(C=N) + δNH_2 1622sh, 1600s, 1581s; ν(C-S), 808s; ν(P-C) 1085s. **^{1}H NMR** ($CDCl_3$, δ): 10.65 (s, -OH, 2H), 8.78 (s, C^2H, 2H), 7.13−7.19 (m, m, p-Ph+$C^{4,5,6,7}$), 6.78−6.85 (m, O-H), 4.75(s, -NH_2, 4H), 2.20 (s, -CH_3, 18H). **^{31}P NMR**($CDCl_3$, δ): −58.41, $\Delta\delta(\delta_{complex}-\delta_{(p\text{-}tolyl)3P}) = 57.19$.

$[Ru(\eta^2\text{-}N^2, S\text{-}btsc)_2\{(p\text{-}tolyl)_3P\}_2]$ (4). Mp. 155−160 °C, yellow, yield, 60 %. Anal. calc. for $C_{58}H_{58}N_6P_2S_2Ru$: C 65.26 (calc. 65.10); H 5.52 (5.40); N 8.30 (7.80) %.

IR bands (KBr, pellets, cm^{-1}) : ν(N-H) 3376s, 3233 (-NH_2); ν(C=N) + δNH_2 + ν(C=C) 1605s, 1592sh; ν(P-C) 1085s; ν(C-S) 824s; **^{1}H NMR** ($CDCl_3$, δ): 8.64 (s, C^2H, 2H), 7.25 (s, C^6H, 2H), 7.07 (m, C^{4+8}H, 2H), 6.8 (dd, C^5H, 2H), 5.15 (s, -NH_2, 4H), 2.20 (s, -CH_3, 18H), 7.07−7.19 (m, o, m-H, 24H), 6.78 (d, m-H, 12H); **^{31}P NMR**($CDCl_3$, δ) : −57.36, $\Delta\delta(\delta_{complex}-\delta_{p\text{-}tolyl)3P}) = 58.24$.

$[Ru(\eta^2\text{-}N^2, S\text{-}Hstsc)_2(dppb)]$ (5). To a solution of H_2stsc (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 24 h. The yellow solid formed was filtered, washed with methanol and dried ($Et_3NH^+Cl^-$ remained in mother liquor being soluble). Crystals were grown from dichloromethane-acetonitrile-methanol. Mp. 218−220 °C, color, yellow, yield, 62 %. Anal. calc. for $C_{45}H_{44.50}N_6O_4P_2RuS_2$: C 55.8 (calc. 56.2); H 4.8 (4.60); N 9.2 (8.8) %.

IR bands (KBr, pellets, cm^{-1}): ν(N-H) 3479b, 3375s, 3292s (-NH_2); ν(C=N) + δNH_2 + ν(C=C) 1618sh, 1589s, 1514s; ν(P-C_{Ph}) 1091s; ν(C-S) 810s; ^{1}H NMR ($CDCl_3$, δ): 10.65 (s, -OH, 2H), 8.93 (s, C^2H, 2H), 7.60 (s br, C^5H, 2H), 6.8 (m, $C^{7,8}$H, 4H), 7.07−7.60(m, C^4H + PhH), 4.76 (s, -NH_2, 4H), 2.8 (s, -CH_2, 2H), 2.51 (s, -CH_2, 2H). ^{31}P NMR ($CDCl_3$, δ) : −57.54 ppm, $\Delta\delta(\delta_{complex}-\delta_{dppb}) = 66.35$ ppm. ($\delta_{dppb} = -123.89$ ppm).

Compounds **6**, **7**, **8** were prepared similarly.

$[Ru(\eta^2\text{-}N^2, S\text{-}btsc)_2(dppb)]$ (6). Mp. 175−177 °C, yellow, yield, 55 %. Anal. calc. for $C_{44}H_{44}N_6P_2S_2Ru$: C 59.2 (calc. 59.90); H 5.04 (5.00); N 10.05 (9.53) %.

IR bands (KBr, pellets, cm^{-1}) : ν(N-H) + ν(O-H), 3457m, 3360−3300m, 3150w, ν(C=N) + δNH_2 + ν(C=C) + δ(OH_2), 1585s, 1573sh, 1562sh; ν(P-C) 1093s; ν(C-S) 817s. ^{1}H NMR ($CDCl_3$, δ) : 8.80 (s, C^2H, 2H), 8.52 (d, C^7H, 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-, 8H); ^{31}P NMR ($CDCl_3$, δ) : −58.213 ppm, $\Delta\delta(\delta_{complex}-\delta_{ligand}) = 65.48$ ppm.

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[Ru(η^2-N^2, S-ftsc)$_2$(dppb)] (7): Mp. 198−200 °C, yellow-brown, yield, 55 %. Anal. calc. for $C_{40}H_{40}N_6O_2P_2RuS_2$: C 55.80 (calc. 55.60); H 4.54 (calc. 4.60); N 9.40 (calc. 9.73).

IR bands (KBr, pellets, cm^{-1}) : ν(N-H), 3483b, 3367s; (-NH_2), ν(C=N) + δNH_2 + ν(C=C) 1573s, 1508b; ν(P-C_{Ph}) 1093s; ν(C-S) 815s. **^{1}H NMR** ($CDCl_3$, δ) : 8.60(s, C^2H, 2H), 7.62 (m, C^6H, 2H), 6.9−7.40 (m, PhH,), 6.45 (d, C^4H, 2H), 6.36 (dd, C^5H, 2H), 5.07 (s, -NH_2, 4H), 2.86 (s, -CH_2, 2H), 2.51 (s, -CH_2, 2H). ^{31}P NMR ($CDCl_3$, δ) : −68.78 ppm, $\Delta\delta(\delta_{complex}-\delta_{dppb)} = 56.97$.

[Ru(η^2-N^2, S-ttsc)$_2$(dppb)] (8): Mp. 196−200 °C, yellow-brown, yield, 60 %. Anal. calc. for $C_{40}H_{40}N_6P_2RuS_4$: C 53.89 (calc. 53.60); H 5.10 (4.50); N 9.40 (9.38) %.

IR bands (KBr, pellets, cm^{-1}) : ν(N-H), 3477s, 3365s, (-NH_2), ν(C=N) + δNH_2 + ν(C=C) 1568s, 1488s, ν(P-C_{Ph}) 1089s; ν(C-S) 815s. **^{1}H NMR** ($CDCl_3$, δ) : 8.92 (s, C^2H, 2H), 7.25 (s, C^6H, 2H), 7.22−7.05 (m, PhH), 7.07 (d, C^4H, 2H), 6.95 (dd, C^5H, 2H), 5.07 (s, -NH_2, 4H), 2.48 (s, -CH_2, 2H), 2.87 (s, -CH_2, 2H). **^{31}P NMR** ($CDCl_3$, δ) : −57.72 ppm, $\Delta\delta(\delta_{complex}-\delta_{dppb}) = 66.16$.

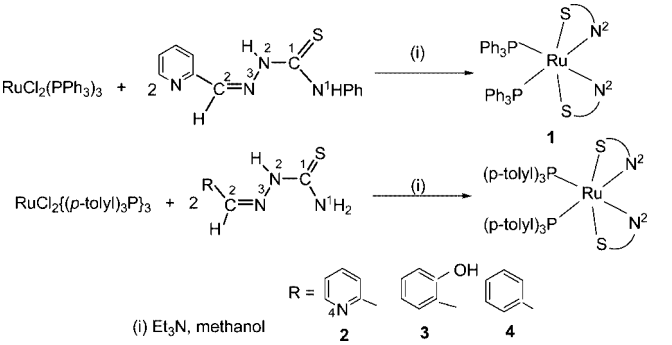
X-ray Crystallography

A single crystal of compound **1** was mounted on a Oxford Diffraction Gemini, whereas that of complex **5** was mounted on CCD area detector diffractometer both equipped with a graphite monochromator and Mo-Kα radiator (λ = 0.71073 Å). The unit cell dimensions and intensity data were measured at 200(2) K (**1**) and 273(2) K (**5**). The structures were solved by the direct methods, and refined by the full matrix least square based on F^2 with anisotropic thermal parameters for the non-hydrogen atoms using CCD (**1**) and Bruker Smart (**5**) for data collection, and SHELXL 97 (data reduction and computing molecular graphics, structure solution and (structure refinement) for complex **1**.

Results and Discussion

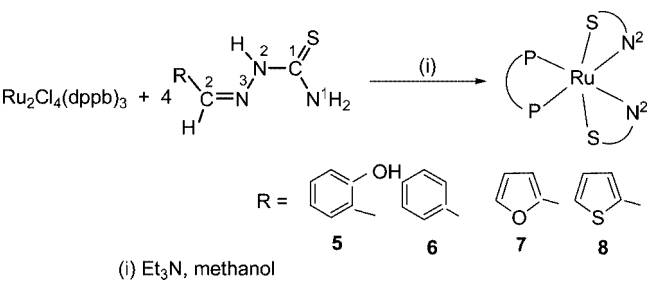
Synthesis and General Comments

Scheme 1 shows the formation of complexes **1**−**4**. Reaction of $RuCl_2(PPh_3)_3$ complex with two moles of Hpytsc-NPh ligand in the presence of Et_3N (excess) in methanol resulted in a clear solution which upon evaporation yielded a dark orange crystalline product of stoichiometry, [Ru(pytsc-NPh)$_2$-(PPh_3)$_2$] (**1**). Similarly, reactions of [$RuCl_2${(*p*-tolyl)$_3$P}$_3$] with a series of thiosemicarbazones, viz. Hpytsc, H_2stsc and Hbtsc in presence of excess Et_3N resulted in the formation of complexes, [Ru(η^2-N^2, S-pytsc)$_2${(*p*-tolyl)$_3$P}$_2$] (**2**), [Ru(η^2-N^2, S-Hstsc)$_2${(*p*-tolyl)$_3$P}$_2$] (**3**), and [Ru(η^2-N^2, S-btsc)$_2${(*p*-tolyl)$_3$P}$_2$] (**4**) which have same composition as **1**. It is inferred that complexes with the pyridyl, 2-hydroxyphenyl, and phenyl substituents at C^2 carbon (**2**−**4** respectively), or phenyl substituent at N^1 nitrogen (**1**), all have the same stoichiometry independent of nature of phosphine used, and based on x-ray crystallography of **1** (vide infra), each complex has N^2,S-chelation. Complexes **2**−**4** though soluble in dichloromethane, chloroform and acetonitrile did not form suitable crystals as they slowly decomposed in the solution state.



Scheme 1. (i) Et_3N, methanol

Reaction of $Ru_2Cl_4(dppb)_3$ (green) with salicyladehyde thiosemicarbazone (H_2stsc) in 1:4 ratio {$Ru_2Cl_4(dppb)_3$:H_2stsc} in presence of Et_3N (excess) in methanol yielded a yellow product, [Ru(η^2-N^2, S-Hstsc)$_2$(dppb)] (**5**) (Scheme 2). Similar reaction with a series of other thiosemicarbazone ligands yielded complexes, [Ru(η^2-N^2, S-btsc)$_2$(dppb)] (**6**), [Ru(η^2-N^2, S-ftsc)$_2$(dppb)] (**7**), and [Ru(η^2-N^2, S-ttsc)$_2$-(dppb)] (**8**). The composition of complexes **5**−**8** is similar to complexes **1**−**4**, as two thiosemicarbazone ligands, and one dppb ligand (replaces two R_3P) are coordinating to Ru(II). Thus the presence of 2-hydroxyphenyl, phenyl, thiophene, and furan substituents at C^2 (**5**−**8** respectively) do not alter bonding pattern of either thio-ligands or dppb, and bonding is similar to that of [Ru(η^2-N^2, S-pytsc)$_2$(dppb)] [11]. Complexes **5**−**8** all have chelating dppb forming seven-membered rings and N^2, S-chelating thio-ligands (based on X-ray crystallography of **5**) which are rare examples in ruthenium-thiosemicarbazone chemistry [11].



Scheme 2. (i) Et_3N, methanol

It may be pertinent to spell out here that bis(diphenylphosphino)methane (dppm) yielded [Ru(η^3-C, N^3, S-ttsc)-(η^2-P, P-dppm)(η^1-P-dppm)], [Ru(η^3-C, N^3, S-btsc)-(η^2-P, P-dppm)(η^1-P-dppm)] involving C-H activation of thiophene and phenyl rings at C^2 carbon, and [Ru(η^3-O, N^3, S stsc)(η^2-P, P-dppm)(η^1-P-dppm)] with activation of −OH group of salicylaldehyde thiosemicarbazone [13]. The behaviour of dppb is different from dppm as noted above. The attempt to prepare complexes with $(CH_2)_2$ and $(CH_2)_3$ alkane spacers connecting Ph_2P groups (dppe, dppp respectively) did not succeed.

IR Spectroscopy

The IR spectra of the complexes reveal the presence of ν(N−H) bands due to (NH_2) group in the range 3278−3495 cm^{-1}. The bands in the region 3100−3150 cm^{-1} expected due to N^2H group in the free ligands [18] are found to be absent in the spectra of their complexes **1**−**8**, and thus supporting the anionic form of the ligands. The ν(C−H) bands due to the aromatic ring are observed for all the complexes in the region near 3050 cm^{-1}. Further, δ(NH_2), ν(C=N) and ν(C-C) vibration modes are unresolved, and are assigned in the range 1635−1515 cm^{-1}. However, the thioamide bands due to the ν(C−S) mode shifted to the low energy (at ~810 cm^{-1}) as compared with the similar free ligand bands, and it is consistent with its single bond character in the anionic form [18]. The presence of phosphine ligands in all the complexes is confirmed by the presence of a characteristic ν(P-C) band in the range, 1095−1099 cm^{-1}.

Crystal Structures of Complexes

Crystal structures of complexes **1** and **5** along with their numbering schemes are given in Figures 1 and 2 respectively. The crystallographic data and important bond parameters are given in Tables 1 and 2, respectively. Compounds **1** and **5** crystallised in orthorhombic and monoclinic space groups, respectively. In compound **1**, Ru^{II} is coordinated to two N-phenyl pyridine-2-carbaldehyde thiosemicarbazone ligands which coordinate as uninegative anions (after removal of N^2H proton) via N^2, S donor atoms with Ru-N^2 distances, 2.1688(13), 2.1933(13) Å, and Ru-S bond distances, 2.4186(4), 2.4303(4) Å. The other two sites are occupied by PPh_3 ligands {Ru-P, 2.3114(4) and 2.3223 Å}. The Ru-N and Ru-S distances are comparable with those of complexes reported earlier (Table 3). The S-Ru-S {164.688(15)°} and P-Ru-N {164.51(4); 162.58(4)°} trans angles deviate significantly from linearity and N^2, S chelation (four membered ring) leads to small N-Ru-S bite angles, 65.30(4)° and 65.97(4)°. The cis-N-Ru-N {83.30(5)°} angle is acute whereas the other *cis* angle, P-Ru-P {100.90(16)°} is obtuse. The geometry around Ru^{II} is thus *cis*: *cis*: *trans*::N, N: P, P: S, S, distorted octahedral. Com-

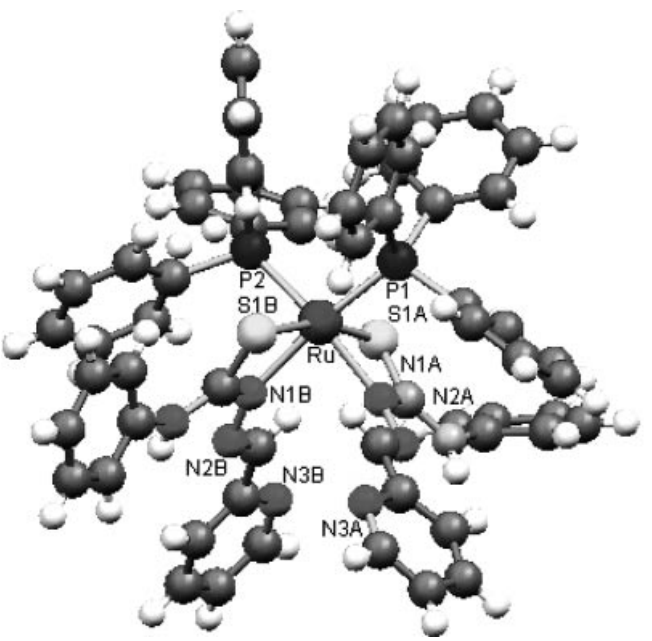


Figure 1. Structure of complex [Ru(η^2-N^2, S-pytsc-NPh)$_2$(PPh_3)$_2$] (**1**) with numbering scheme.

Table 1. Crystal data and refinement details for **1** and **5**.

	1	**5**
Empirical formula	$C_{65}H_{56.50}N_{9.50}P_2RuS_2$	$C_{45}H_{44.50}N_6O_4P_2RuS_2$
M	1197.83	960.50
T /K	200(2)	273(2) K
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1/n$
Unit cell dimensions		
a /Å	11.5587(2)	20.3013(4)
b /Å	18.3504(2)	17.6890(3)
c /Å	27.7472(3)	26.5755(5)
β /°		104.2350(10)
V /Å^3	5885.37(14)	9250.5(3)
Z	4	8
D_{calcd} /g·cm^{-3}	1.352	1.379
μ /mm^{-1}	0.441	0.546
F(000)	2476	3956
Crystal size /mm	0.12 x 0.38 x 0.51	0.5 x 0.3 x 0.3
Reflections collected	18945	78535
Unique reflections	14262	22965 [*R*(int) = 0.0251]
Data/ Restraints/ parameters	18945/ 10/ 733	22965/ 0/ 1081
Index ranges	$-14\le h\le 16$, $-27\le k\le 22$, $-38\le l\le 42$	$-27\le h\le 19$, $-23\le k\le 23$, $-35\le l\le 35$

Table 2. Selected bond lengths and bond angles of complexes **1** and **5**.

Compound **1**			
Ru-N(1A)	2.169(1)	Ru-P(2)	2.322(1)
Ru-N(1B)	2.193(1)	Ru-S(1A)	2.419(1)
Ru-P(1)	2.311(1)	Ru-S(1B)	2.430(1)
N(1A)-Ru-N(1B)	83.30(5)	N(1A)-Ru-P(1)	88.91(4)
N(1B)-Ru-P(1)	162.58(4)	N(1A)-Ru-(P2)	164.51(4)
N(1B)-Ru-P(2)	90.22(4)	P(1)-Ru-(P2)	100.90(2)
N(1A)-Ru-S(1A)	65.97(4)	N(1B)-Ru-(S1A)	101.64(4)
N(1A)-Ru-(S1B)	103.17(4)	N(1B)-Ru-(S1B)	65.30(4)
P(1)-Ru-(S1B)	101.69(2)	P(2)-Ru-(S1B)	86.70(2)
S(1A)-Ru-S(1B)	164.69(2)		
Compound **5**			
Ru(1)-N(5)	2.179(3)	Ru(1)-S(1)	2.422(1)
Ru(1)-N(2)	2.225(3)	Ru(1)-S(2)	2.431(1)
Ru(1)-P(2)	2.269(1)	S(1)-C(1)	1.725(4)
Ru(1)-P(1)	2.270(1)	S(2)-C(13)	1.726(4)
N(5)-Ru(1)-P(2)	161.39(9)	P(1)-Ru(1)-S(1)	105.18(4)
N(2)-Ru(1)-P(2)	92.02(9)	N(5)-Ru(1)-S(2)	65.69(9)
N(5)-Ru(1)-P(1)	91.72(9)	N(2)-Ru(1)-S(2)	99.90(9)
N(2)-Ru(1)-P(1)	168.41(9)	P(2)-Ru(1)-S(2)	97.12(3)
P(1)-Ru(1)-P(2)	95.00(3)	P(1)-Ru(1)-S(2)	88.39(3)
N(5)-Ru(1)-S(1)	102.09(9)	S(1)-Ru(1)-S(2)	162.40(4)
N(2)-Ru(1)-S(1)	65.18(9)		

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Table 3. A comparison of bond lengths /Å and bond angles /° of **1** and **5** with literature data.

Complex	Ru-N	Ru-S	Ru-P	S-Ru-S	N-Ru-N	P-Ru-P	N-Ru-S	Ref.
1	2.180	2.424	2.316	164.68	83.30	100.90	65.45	This work
5	2.202	2.426	2.269	162.40	–	95.00	65.50	This work
$Ru(pytsc)_2(dppb)$	2.202	2.418	2.264	163.30	83.07	94.54	65.85	[11]
$Ru(pytsc\text{-}NMe)_2(PPh_3)_2$	2.165	2.423	2.302	159.03	81.25	98.89	66.00	[14]
$Ru(Hstsc)_2(PPh_3)_2$	2.152	2.426	2.323	161.23	–	105.95	65.74	[10]

plexes **2**, **3**, **4** with similar composition are assigned similar structures.

In complex **5**, two uninegative salcylaldehyde thiosemicarbazonato ligands are coordinating to Ru^{II} via N^2, S donor atoms, and 2-hydroxyphenyl groups remain pendant. The Ru-N {2.179(3) and 2.225(3)} and Ru-S {2.4219(10), 2.4309(10) Å} distances lie in the usual range [9–11]. The other two sites are occupied by P,P-chelating dppb ligand with a seven membered chelate ring and with Ru-P distances of 2.2690(9) and 2.2700(9) Å. It may be observed from Table 3 that the Ru-P distances of both the dppb complexes are short as compared with those of monoteriary phosphine complexes, and this difference is attributed to the chelate effect of dppb. The P-Ru-P angle, 95.00(3)°, is smaller than the similar angle in complex **1**, but is comparable with that of $Ru(\eta^2\text{-}N^2, S\text{-}pytsc)_2(dppb)$ [11]. This is due to the presence of bulky PPh_3 ligands adjacent to each other in complex **1** which causes this angle to deviate towards the higher side. All other angles lie in the usual range. Since the stoichiometry of complexes **6**–**8** is similar and are believed to have similar structures.

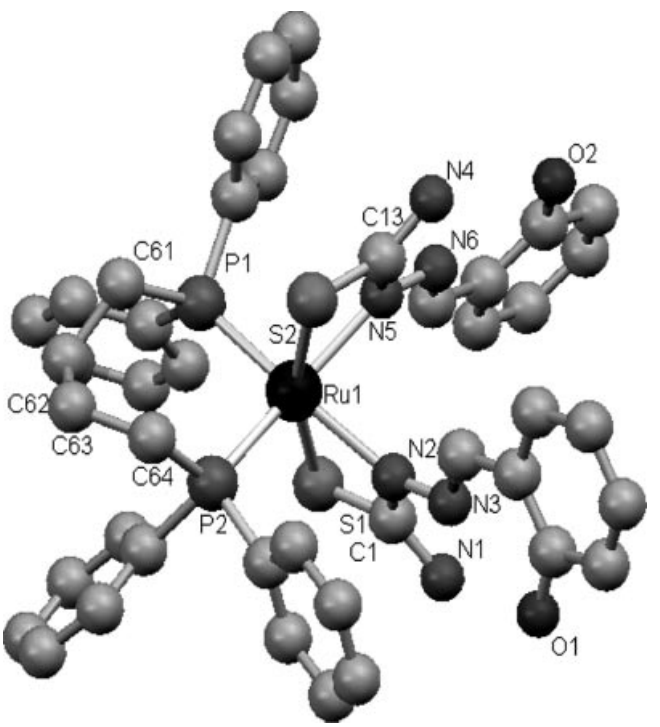

Figure 2. Structure of Complex $[Ru(\eta^2\text{-}N^2, S\text{-}Hstsc)_2(\eta^2\text{-}P, P\text{-}dppb)]$ (**5**) with numbering scheme (hydrogen atoms removed for clarity).

NMR Spectroscopy

The signals due to N^2H protons in the free ligands (9–11 ppm) were absent in the complexes **1**–**8**, and it showed that the ligands are uninegative. The NH_2 protons appear as single peaks in all the complexes due to free rotation of N^1H_2 group along $C^1\text{-}N^1$ bond axis, instead of two broad peaks observed in the free ligands, due to the restricted rotation of N^1H_2 group along $C^1\text{-}N^1$ bond axis, at room temperature [18]. All other protons appear in the aromatic region as given in the experimental section.

The ^{31}P NMR spectrum of each of complexes **1**–**4** showed a single peak each in the range, −56.67 to −58.74 ppm, with the coordination shifts of 56–58 ppm. The dppb containing complexes **5**–**8** also showed a single peak each with coordination shifts of around ~66 ppm (c.f. experimental section). The presence of a single peak in spectra of complexes show the presence of equivalent phosphorus atoms. The coordination shifts of complexes **1**–**4** are smaller as compared to those diphosphine complexes **5**–**8** [11], thus confirming that dppb ligand binds more strongly than the monotertiary phosphines, in conformity with the structural data [11].

Conclusion

For a variety of substituents (R^1) at C^2 carbon, the coordination mode of thioligands under discusion remained N^2, S-chelation, even though some ligands possessed donor atoms in R^1 substituents. Also the substituents at N^1 did not alter the N^2, S-chelation mode. Bulky dppb chelates in all the complexes investigated in this paper in line with the earlier observations [11]. The complexes remain stable in solution state as revealed by their NMR spectroscopy.

Supplementary data is available from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-12336033; E-Mail: **deposit@ccdc.cam.ac.uk**) on request quoting the deposition number CCDC 693618 and 693619 for compounds **1** and **5** respectively.

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References

[1] D. X. West, S. Padhye, P. B. Sonawane, *Struct. Bonding (Berlin)* **1991**, *76*, 4.

[2] S. Padhye, G. B. Kauffman, *Coord. Chem. Rev.* **1985**, *63*, 127.
[3] D. X. West, A. E. Liberta, S. B. Padhye, R. C. Chikate, P. B. Sonawane, A. S. Kumbhar, R. G. Yerande, *Coord. Chem. Rev.* **1993**, *123*, 49.
[4] J. S. Casas, M. S. Garcia-Tasende, J. Sordo, *Coord. Chem. Rev.* **2000**, *209*, 197.
[5] a) L. J. Ashfield, A. R. Cowley, J. R. Dilworth, P. S. Donnelly, *Inorg. Chem*. **2004**, *43*, 4121; b) A. R. Cowley, J. R. Dilworth, P. S. Donnelly, E. Labisbal, A. Sousa, *J. Am. Chem. Soc*. **2002**, *124*, 5270; (c) T. S. Lobana, S. Khanna, R. J. Butcher, A. D. Hunter, M. Zeller, *Inorg. Chem.* **2007**, *46*, 5826.
[6] a) D. Kovala-Demertzi, M. A. Demertzis, V. Varagi, A. Papageorgiou, D. Mourelatos, E. Mioglou, Z. Lakovidou, A. Kotsis, *Chemotherapy* **1998**, *44*, 421; b) D. Kovala-Demertzi, J. R. Miller, N. Kourkoumelis, S. K. Hadjikakou, M. A. Demertzis, *Polyhedron* **1999**, *18*, 1005; (c) D. Kovala-Demertzi, M. A. Demertzis, A. Castineiras, D. X. West, *Polyhedron* **1998**, *17*, 3739; d) A. G. Quiroga, J. M. Perez, I. Lopez-Solera, J. R. Masaguer, A. Luque, P. Roman, A. Edwards, C. Alonso, C. Novarro-Ranninger, *J. Med. Chem*. **1998**, *41*, 1399.
[7] D. Kovala-Demertzi, M. A. Demertzis, J. R. Miller, C. Papadopoulou, C. Dodorou, G. Filousis, *J. Inorg. Biochem*. **2001**, *86*, 555; b) K. I. Goldberg, J. Valdez-Martinez, G. Espinosa-Perez, L. J. Ackerman, D. X. West, *Polyhedron* **1999**, *18*, 1177.
[8] L. Papathanasis, M. A. Demertzis, P. N. Yadav, D. Kovala-Demertz, C. Prentjas, A. Castiñeiras, S. Skoulika, D. X. West, *Inorg. Chim. Acta* **2004**, *357*, 4113.
[9] F. Basuli, M. Ruf, C. G. Pierpont, S. Bhattacharya, *Inorg. Chem*. **1998**, *37*, 6113.
[10] F. Basuli, S. M. Peng, S. Bhattacharya, *Inorg. Chem*. **1997**, *36*, 5645.
[11] T. S. Lobana, G. Bawa, R. J. Butcher, B.-J. Liaw, C.-W. Liu, *Polyhedron* **2006**, *25*, 2897.
[12] (a) F. Basuli, S. M. Peng, S. Bhattacharya, *Inorg. Chem.* **2000**, *39*, 1120; (b) D. Mishra, S. Naskar, M. G. B. Drew, S. K. Chattopadhyay, *Polyhedron* **2005**, *24*, 1861.
[13] T. S. Lobana, G. Bawa, A. Castineiras, M. Zeller, R. J. Butcher, *Organometallics* **2008**, *27*, 175.
[14] T. S. Lobana, G. Bawa, R. J. Butcher, *Inorg. Chem.* **2008**, *47*, 1488.
[15] T. S. Lobana, G. Bawa, A. Castineiras, R. J. Butcher, *Inorg. Chem. Comm.* **2007**, *10*, 506.
[16] T. A. Stephenson, G. J. Wilkinson, *J. Inorg. Nucl. Chem*. **1966**, *28*, 945.
[17] M. Bressan, P. Rigo, *Inorg. Chem*. **1975**, *14*, 2286; (b) T. S. Lobana, R. Singh, *Polyhedron* **1995**, *14*, 907
[18] T. S. Lobana, A. Sanchez, J. S. Casas, A. Castineiras, J. Sordo, M. S. Garcia-Tasenda, E. M. Vazquez-Lopez, *J. Chem. Soc. Dalton Trans.* **1997**, 4289.
[19] A. M. Aguion, *J. Org. Chem*. **1964**, *20*, 1660.

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