Articles

Bis(diphenylphosphino)methane Induces Unusual Cyclometalation of Thiophene and Phenyl Rings (R) at the C^2 Carbon of Thiosemicarbazones {R-C^2(H) = N^3-N^2 H-C(=S)-N^1H_2} in Ruthenium(II) Complexes

Tarlok S. Lobana,*[†] Gagandeep Bawa,[†] A. Castineiras,[‡] Ray J. Butcher,[§] and M. Zeller[⊥]

Department of Chemistry, Guru Nanak Dev University, Amritsar-143 005, India, Departmento de Quimica Inorganica, Facultad de Farmacia, Universidad de Santiago, 15782-Santiago, Spain, Department of Chemistry, Howard University, Washington, D.C. 20059, and Department of Chemistry, Youngstown University, Youngstown, Ohio 44555-3663

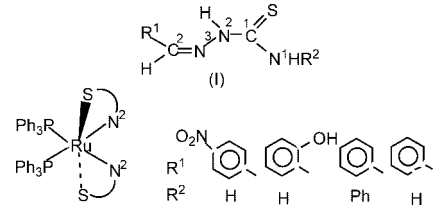
Received August 9, 2007

Reaction of *trans*-[Ru(dppm)$_2$Cl$_2$] (dppm = $Ph_2PCH_2PPh_2$) with thiophene-2-carbaldehyde thiosemicarbazone {C_4H_3S-C^2(H)=N^3-N^2H-C^1(=S)-N^1H_2, H_2L^1} in the presence of Et_3N base formed a complex, [Ru(η^3-C,N^3,S-L^1)(η^2-P,P-dppm)(η^1-P-dppm)] (**1**) (L^1 is dinegative thiophene-2-carbaldehyde thiosemicarbazonate), with an unprecedented cyclometalation of a heterocyclic ring in Ru^{II}-thiosemicarbazone chemistry. In contrast, the thiophene ring did not undergo cyclometalation in complexes of monotertiary phosphines of stoichiometry [Ru(η^2-N^2,S-HL^1)$_2$(PR'_3)$_2$] (R′ = phenyl, **2**; *p*-tolyl, **3**; HL^1 = uninegative thiophene-2-carbaldehyde thiosemicarbazonate). Benzaldehyde thiosemicarbazone {C_6H_5-C(H)=N^3-N^2H-C(=S)-N^1H_2,H_2L^2} with *trans*-[Ru(dppm)$_2$Cl$_2$] displayed cyclometalation and yielded an organometallic complex [Ru(η^3-C,N^3,S-L^2)(η^2-P,P-dppm)(η^1-P-dppm)] (**4**) (L^2 is dinegative benzaldehyde thiosemicarbazonate), similar to complex **1**. The complexes have been characterized using analytical, spectroscopic, and single-crystal X-ray crystallographic (**1**, **3**, **4**) studies. The cyclometalation in complexes **1** and **4** is attributed to the presence of two types of coordination modes of dppm, namely, both η^1-P-dppm and chelating η^2-P,P-dppm in the same complex. These cyclometalation reactions represent the first examples in Ru^{II}-thiosemicarbazone chemistry.

Introduction

The intramolecular activation of aromatic C−H bonds of coordinated ligands by transition metals represents an active area of research due to their applications such as to serve as intermediates in organic and organometallic synthesis, as active catalysts, as liquid crystals, as analytical tools, to allow for resolution of racemic mixtures, and for the design of metal complexes with promising anticancer or photochemical properties.[1] In the literature, thiosemicarbazones (I, Chart 1) have undergone cyclometalation with Rh(III), Pd(II), and Pt(II) by activation of the C−H bond of phenyl and substituted phenyl substituents at the C^2 carbon.[2] However, no cyclometalation

Chart 1



* Corresponding author. E-mail: tarlokslobana@yahoo.co.in.
† Guru Nanak Dev University.
‡ Universidad de Santiago.
§ Howard University.
⊥ Youngstown University.

(1) (a) Main, L.; Nicholson, B. K. *Adv. Met.-Org. Chem.* **1994**, *3*, 1. (b) Spencer, J.; Pfeffer, M. *Adv. Met.-Org. Chem.* **1998**, *6*, 103. (c) Dopont, J.; Pfeffer, M.; Spencer, J. *Eur. J. Inorg. Chem.* **2001**, *1917*. (d) Botella, L.; Najera, C. *Angew. Chem., Int. Ed.* **2002**, *41*, 179. (e) Marcos, M In *Metallomesogens. Synthesis, Properties and Applications*; Serrano J. L., Ed.; VCH: Weinheim, 1996. (f) Urriolabeitia, E. P.; Diaz-de-Villegas, M. D. *J. Chem. Educ.* **1999**, *76*, 77. (g) Albert, J.; Cadena, J. M.; Granell, J. R.; Solans, X.; Font-Bardia, M. *Tetrahedron Asymmetry* **2000**, *11*, 1943. (h) Quiroga, A. G.; Perez, J. M.; Lopez-Solera, I.; Masuguer, J. R.; Luque, A.; Roman, P.; Edwards, A.; Alonso, C.; Navarro-Ranninger, C. *J. Med. Chem.* **1998**, *41*, 1399. (i) Song, D.; Wu, Q.; Hook, A.; Kozin, I.; Wang, S. *Organometallics* **2000**, *20*, 4683.

(2) (a) Acharya, R.; Dutta, S.; Basuli, F.; Peng, S.-M.; Lee, G.-H.; Falvello, L. R.; Bhattacharya, S. *Inorg. Chem.* **2006**, *45*, 1252. (b) Vila, J. M.; Pereira, M. T.; Ortigueira, J. M.; Grana, M.; Lata, D.; Suarez, A.; Fernandez, J. J.; Fernandez, A.; Lopez-Torres, M.; Adams, H. *J. Chem. Soc., Dalton Trans.* **1999**, 4193. (c) Yadav, P. N.; Demertzis, M. A.; Kovala-Demertzi, D.; Castineiras, A.; West, D. X. *Inorg. Chim. Acta* **2002**, *32*, 204. (d) Martinez, J.; Pereira, M. T.; Buceta, I.; Alberdi, G.; Amoeda, A.; Fernanadez, J. J.; Lopez-Torres, M.; Vila, J. M. *Organometallics* **2003**, *22*, 5581. (e) Martinez, J.; Adiro, L. A.; Antelo, J. M.; Teresa-Pereira, M.; Fernandez, J. J.; Vila, J. M. *Polyhedron* **2006**, *25*, 2848. (f) Amoedo, A.; Grana, M.; Martinez, J.; Pereira, T.; Lopez-Torres, M.; Fernandez, A.; Fernanadez, J. J.; Vila, J. M.; *Eur. J. Inorg. Chem.*, **2002**, 613. (g) Vazquez-Garcia, D.; Fernanadez, A.; Fernanadez, J. J.; Lopez-Torres, M.; Suarez, A.; Ortigueira, J. M.; Vila, J. M.; Adams, H. *J. Organomet. Chem.* **2000**, *59*, 5–199.

10.1021/om700804s CCC: $40.75
Publication on Web 12/29/2007

Chart 2

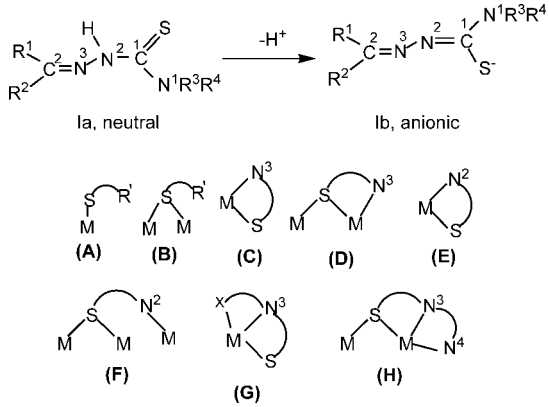
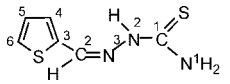
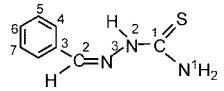


Chart 3


thiophene-2-carbaldehyde thiosemicarbazone (H_2L^1)


benzaldehyde thiosemicarbazone (H_2L^2)

occurred in Ru^{II}-thiosemicarbazone complexes with aryl rings as substituents at the C^2 carbon (Chart 1).[3] Further, there is only one report of cyclometalation of a heterocyclic ring in metal-thiosemicarbazone chemistry.[4]

The chemistry of transition metals with thiosemicarbazones (I, Chart 1; Ia, Ib, Chart 2) has received a recent upsurge for a variety of reasons, such as biochemical applications, catalytic properties, and analytical applications, in addition to displaying bonding and structural diversity (modes A to H, Chart 2).[5] In view of our interest in Ru^{II} chemistry with N and S donor ligands,[6] it was desired to investigate interaction of Ru^{II} with thiosemicarbazones having heterocyclic rings at the C^2 carbon with mono- and ditertiary phosphines as coligands. For this purpose, thiophene-2-carbaldehyde thiosemicarbazone (C_4H_3S-$C(H)$=N^3-N^2H-C(=S)-N^1H_2,H_2L^1, Chart 3) was selected on an arbitrary basis, along with bis(diphenylphosphino)methane (dppm), triphenylphosphine, and tri-*p*-tolylphosphine as coligands for carrying out reactions with ruthenium(II) substrates. The reaction chemistry has been extended to benzaldehyde

(3) (a) Lobana, T. S.; Bawa, G.; Butcher, R. J.; Liaw, B.-J.; Liu, C. W. *Polyhedron* **2006**, *25*, 2897. (b) Mishra, D.; Naskar, S.; Drew, M. G. B.; Chattopadhyay, S. K. *Polyhedron* **2005**, *24*, 1861. (c) Basuli, F.; Ruf, M.; Pierpont, C. G.; Bhattacharya, S. *Inorg. Chem.* **1998**, *37*, 6113. (d) Basuli, F.; Peng, S. M.; Bhattacharya, S. *Inorg. Chem.* **1997**, *36*, 5645.

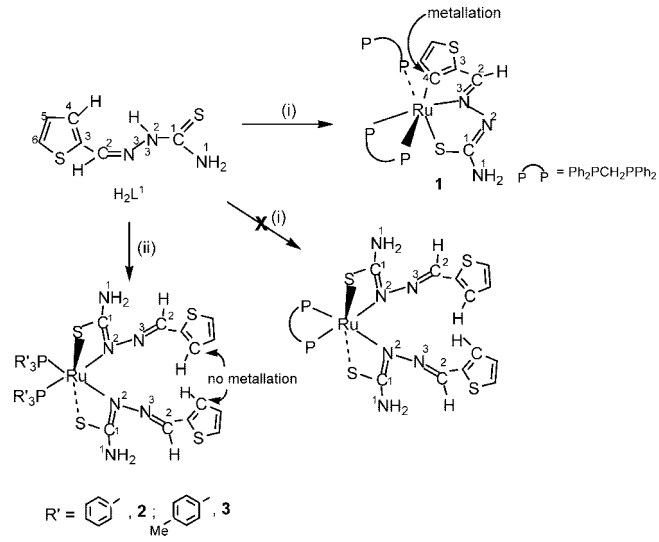
(4) Adrio, L.; Antelo, J. M.; Ortigueira, J. M.; Lata, D.; Pereira, M. T.; Lopez-Torres, M.; Vila, J. M. *Z. Anorg. Allg. Chem.* **2007**, *633*, 1875.

(5) (a) Casas, J. S.; Garcia-Tasende, M. S.; Sordo, *J. Coord. Chem. Rev.* **2000**, *209*, 197. (b) West, D. X.; Liberta, A. E.; Padhye, S. B.; Chikate, R. C.; Sonawane, P. B.; Kumbhar, A. S.; Yerande, A. S. *Coord. Chem. Rev.* **1993**, *123*, 49. (c) Baylak, S.; Balaban, A.; Turker, A. R.; Erk, B. *J. Anal. Chem.* **2006**, *61*, 476. (d) Mahajan, R. K.; Kaur, I.; Lobana, T. S. *Talanta* **2003**, *59*, 101. (e) Kovala-Demertzi, D.; Demertzis, M. A.; Varagi, V.; Papageorgiou, A.; Mourelatos, D.; Mioglou, E.; Iakovidou, Z.; Kotsis, A. *Chemotherapy* **1998**, *44*, 421.

(6) (a) Lobana, T. S.; Kaur, P. J.; Castineiras, A. *J. Coord. Chem.* **2005**, *58*, 429. (b) Lobana, T. S.; Verma, R.; Indian, J. *Chem. Sect. A* **2003**, *42*, 534. (c) Lobana, T. S.; Verma, R.; Singh, R.; Castineiras, A. *Transition Met. Chem.* **1998**, *23*, 25. (d) Lobana, T. S.; Singh, R. *Polyhedron* **1995**, *14*, 907. (e) Tiekink, E. R. T.; Lobana, T. S.; Singh, R. *J. Cryst. Spectrosc. Res.* **1991**, *21*, 205.

(7) (a) Chakravarty, A. R.; Cotton, F. A.; Schwotzer, W. *Inorg. Chim. Acta* **1984**, *84*, 179. (b) Stephenson, T. A.; Wilkinson, G. J. *J. Inorg. Nucl. Chem.,* **1966**, *28*, 945.

Scheme 1[a]



[a] 1/2$RuCl_2$(dppm)$_2$, toluene (i); 1/2$RuCl_2(PR_3)_2$, MeOH (ii); Et_2N (i, ii).

thiosemicarbazone {C_6H_5-$C(H)$=N^3-N^2H-C(=S)-N^1H_2,H_2L^2, Chart 3} with dppm as a coligand.

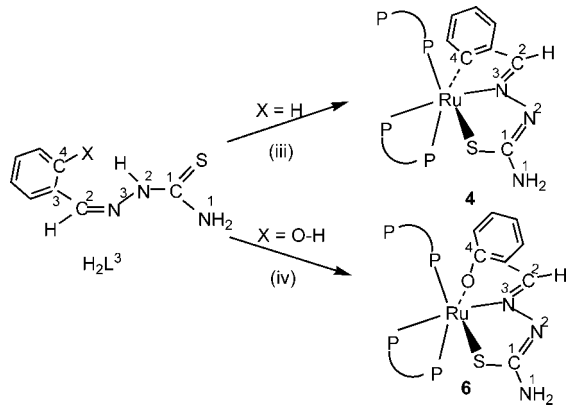
In this paper, we report four complexes (**1**−**4**), viz., [Ru(η^3-C,N^3,S-L^1)(η^2-P,P-dppm)(η^1-P-dppm)] (**1**), [Ru(η^2-N^2,S-HL^1)$_2$(PR'_3)$_2$] (R′ = phenyl, **2**; *p*-tolyl, **3**), and [Ru(η^3-C,N^3,S-L^2)(η^2-P,P-dppm)(η^1-P-dppm)] (**4**), two of which (**1**, **4**) have undergone cyclometalation. The formation of complexes **1** and **4** involving C−H activation of thiophene and phenyl rings represents the first examples in Ru^{II}-thiosemicarbazone chemistry.

Results and Discussion

Synthesis. Reactions of thiophene-2-carbaldehyde thiosemicarbazone {C_4H_3S-$C^2(H)$=N^3-N^2H-C^1(=S)-N^1H_2,H_2L^1} were carried out with the three Ru^{II} precursors, namely, [Ru(dppm)$_2$Cl$_2$] {dppm = bis(diphenylphosphino)methane}; [$RuCl_2(PPh_3)_3$], and [$RuCl_2$\{(*p*-tolyl)$_3$P\}$_3$] {(*p*-tolyl)$_3$P = tri-*p*-tolylphosphine}. Reaction of *trans*-Ru(dppm)$_2$$Cl_2$[7a] with 2 equiv of H_2L^1 in the presence of Et_3N base yielded a complex of unusual stoichiometry, [Ru(dppm)$_2$(L^1)] (**1**) (Scheme 1). However, reactions of H_2L^1 with precursors [$RuCl_2$-$(PPh_3)_3$][7b] and [$RuCl_2$\{(*p*-tolyl)$_3$P\}$_3$] have yielded complexes [Ru(HL^1)$_2$(PPh_3)$_2$] (**2**) and [Ru(HL^1)$_2$\{(*p*-tolyl)$_3$P\}$_2$] (**3**) (Scheme 1). Compound **1** is stoichiometrically different from compounds **2** and **3**, as it contains only one thiosemicarbazone ligand and two dppm ligands. The IR spectral data revealed the presence of thiosemicarbazone and phosphine ligands, but no structural information could be obtained.

The unusual stoichiometry led to investigate the structure of complex **1** using X-ray crystallography (*vide infra*), which revealed that the thiophene ring is cyclometalated to Ru^{II} and it completed the charge balance required for the stoichiometry. Interestingly, complex **3**, with two monotertiary phosphines and two uninegative HL^1 moieties, did not involve cyclometalation of the thiophene ring, and stoichiometry of complex **2** suggested a bonding pattern similar to that of complex **3**. In complex **1**, the thiosemicarbazone ligand involves activation of the C^4−H bond of the thiophene ring, as well as deprotonation of the hydrazinic (−N^2H−) nitrogen (Scheme 1). Thus the L^1 moiety is dinegative and coordinates via C^4, N^3, S donor atoms. In contrast, complexes **2** and **3** involved deprotonation of −N^2H−

Scheme 2[a]



[a] $RuCl_2(dppm)_2$, Et_3N, toluene (iii, iv).

protons and two uninegative HL^1 moieties bind to Ru^{II} via N^2, S donor atoms in each complex.

The cyclometalation in complex **1** is believed to be due to the presence of two dppm ligands that are differently bonded (one η^2-P,Pdppm and the second, η^1-P-dppm) (*vide infra*). In order to check the generality of the influence of dppm on cyclometalation, another thiosemicarbazone ligand, namely, benzaldehyde thiosemicarbazone{C_6H_5-C(H)=N^3-N^2H-C(=S)-N^1H_2, H_2L^2}, with R^1 = Ph and R^2 = H in place of R^1 = thiophene and R^2 = H, has been reacted with a $Ru(dppm)_2Cl_2$ precursor in the presence of Et_3N. Interestingly, the stoichiometry turned out to be [$Ru(L^2)(dppm)_2$] (**4**) similar to that of compound **1**. Its X-ray crystal structure determination (*vide infra*) has revealed cyclometalation of the phenyl ring (Scheme 2). This behavior is different from that observed in compound [$Ru(\eta^2$-N^2,S-$HL^2)_2(PPh_3)_2$] (**5**) when PPh_3 was used. In the latter complex two units of the uninegative HL^2 ligand are chelating to the Ru^{II} center via N^2, S donor atoms.[3a] It may be noted here that with the salicylaldehyde thiosemicarbazone (HOC_6H_4-C^2(H)=N^3-N^2H-C^1(=S)-N^1H_2,H_2L^3) a similar complex, [$Ru(\eta^3$-O,N^3,S-$L^3)(\eta^2$-P,P-dppm)(η^1-P-dppm)] (**6**), was isolated. It involved activation of a −O−H bond at the C^4 carbon, forming a Ru−O bond (Scheme 2). No similar activation occurred in the PPh_3 complex [$Ru(\eta^2$-N^2, S-$HL^3)_2(PPh_3)_2$] (**7**) (HL^3 = uninegative N^2,S-chelating salicylaldehyde thiosemicarbazonate).[3d]

Crystal Structures. Among four complexes, crystal structures of **1**, **3**, and **4** are obtained and described in this section. Crystallographic data are given in Table 1. The X-ray structure of complex **3** shows that Ru^{II} is coordinated to two thiophene-2-carbaldehyde thiosemicarbazone ligands and two *p*-tolyl phosphine ligands. The thiophene rings of the both the thiosemicarbazones are pendant and the ligands bind to the metal center via N^2,S-donor atoms, thus forming four-membered chelate rings. The other two coordinating sites around Ru^{II} are occupied by phosphine ligands. The donor atoms around Ru^{II} center occupy *cis*; *cis*; *trans*; *N, N*; *P*, *P*; *S*, *S* positions (Figure 1). The bond distances as well as bond angles (Ru−N, 2.178 Å; Ru−S, 2.424 Å; Ru−P, 2.297 Å; N−Ru−N, 79.91°; P−Ru−P, 101.788°; S−Ru−S, 159.56°; N−Ru−S, 65.96°, approximate values) are in the range comparable to literature reports of ruthenium complexes with similar geometry and coordination.[3]

In contrast, complex **1** has one thiosemicarbazone ligand and two dppm ligands coordinated to Ru^{II}. The absence of any anion (chlorine) in the molecule demands that the thiosemicarbazone ligand be dinegative for maintaining charge balance. Ru^{II} is coordinated to two dppm ligands, one of which is P,P-chelating with Ru−P distances of 2.292(1) and 2.314(1) Å, whereas the other dppm ligand is coordinating through only one P atom at a longer Ru−P distance of 2.368(1) Å, with one pendant PPh_2 group. The thiosemicarbazone ligand is coordinating to Ru^{II} via N^3,S donor atoms with Ru−S1 and Ru−N1 distances of 2.437(1) and 2.067(3) Å respectively. The bond distances are comparable with the literature values.[3] This completes the five binding sites around the Ru^{II} center, and the sixth site is occupied by the C^4 carbon of the thiophene ring after activation of the C^4−H bond. This has led to the formation of an organometallic complex, [$Ru(\eta^3$-C^4,N^3,S-$L^1)(\eta^2$-P,P-dppm)(η^1-P-dppm)] (**1**) (Figure 2). The Ru1−C3 bond length of 2.076(3) Å is comparable with the literature reports.[8] The angles around the Ru^{II} center reveal severely distorted octahedral geometry {N1−Ru−S1, 79.21(8)°; trans angles P1−Ru−P3, P4−Ru−N, and S−Ru−C3 of 174.36(3)°, 161.92(9)°, and 156.92(11)°, respectively}. The thiosemicarbazone ligand thus forms two five-membered chelate rings with bite angles C3−Ru−N1 = 78.95(13)° and N1−Ru−S1 = 79.21(8)°, respectively. Complex **1** is unusual in the context that no cyclometalation has ever been reported in ruthenium(II)- thiosemicarbazone chemistry. Further, it also represents the first example of a thiophene-2-carbaldehyde thiosemicarbazone (H_2L^1) acting as a tridentate dianion.

The X-ray structure of complex **4** (Figure 3) is similar to that of complex **1**, the only difference being that Ru is cyclometalated to a phenyl ring instead of a thiophene ring. X-ray shows the presence of a toluene molecule as the solvent of crystallization in complex **4**. Bond parameters of organometallic complex [$Ru(\eta^3$-C^4, N^3,S-$L^2)(\eta^2$-P,P-dppm)(η^1-P-dppm)] (**4**) are only marginally different from those of complex **1**.

An analysis of P−Ru−P angles of complexes **1** and **3**−**7** (Table 2) shows that the P−Ru−P angle of **1** is much shorter than that of **3** or **4**, and thus dppm creates less steric effect on the thiophene-2-carbaldehyde thiosemicarbazone ligand, which adopts an N^3,S mode versus usual N^2,S chelation and brings the thiophene ring close to the Ru-metal center, paving the way for cyclometalation, and hence only one H_2L^1 as dianion, $(L^1)^{2-}$, is binding to the metal center. One PPh_2 end of the second dppm ligand completes the sixth coordination site with a pendant PPh_2 group. The behavior is similar for the cyclometalated complex **4**. In summary, the small P−Ru−P bond angle of dppm has played a crucial role in inducing unusual cyclometalation of the thiophene ring in complexes **1** and **4**.

Thus the presence of two dppm ligands in the complex has a tendency to activate the C−H bonds of the aryl/heterocyclic ring substituent at C^2. In the case where a more acidic group such as −OH is present, then its deprotonation is followed by coordination of the O atom to the metal center.

Spectroscopy. ^{1}H NMR spectra of complexes **1**−**4** showed the absence of a signal due to the $-N^2H-$ proton (9.45 and 10.22 ppm for free ligands, H_2L^1, and H_2L^2, respectively[9]), thus supporting its deprotonation in all the complexes. The C^2H signal (8.01 ppm, H_2L^1) shifts downfield in complexes **2** and **3**, while thiophene ring signals shift upfield on coordination in complexes. The signals due to phosphine ligands are well

(8) Wada, S.; Yuge, H.; Miyamoto, T. K. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **2003**, *C59*, m369.

(9) Lobana, T. S.; Sanchez, A.; Casas, J. S.; Castineiras, A.; Sordo, J.; Garcia-Tasende, M. S.; Vazquez-Lopez, E. M. *J. Chem. Soc., Dalton Trans* **1997**, 4289.

Table 1. Crystal Data and Data Collection and Refinement for 1, 3, and 4

	1	3	4
formula	$C_{56}H_{49}N_3P_4RuS_2$	$C_{54}H_{54}N_6P_2RuS_4$	$C_{58}H_{51}N_3P_4RuS \cdot 1/2C_7H_8$
molecular wt	1053.05	1078.28	1093.10
color	reddish brown	clear	red
size, mm	0.30, 0.29, 0.05	0.53, 0.14, 0.14	0.40, 0.35, 0.14
symmetry, space group	monoclinic, $P2_1/c$	monoclinic, $P2(1)/n$	monoclinic, $P2(1)/n$
a, Å	10.558(3)	13.5877(5)	14.6639(14)
b, Å	30.638(8)	29.3587(12	24.436(2)
c, Å	17.027(3)	14.6203(6)	15.0151(15)
α, deg	90.00	90	90.00
β, deg	111.308(13)	114.3530(10	93.161(2)
γ, deg	90.00	90	90.00
V, Å^3	5131(2)	5313.3(4)	5372.0(9)
Z	4	4	2
D_{calc}, g cm^{-3}	1.363	1.348	1.353
Data Collection and Refinement			
diffractometer	Bruker SMART CCD1000	CCD area detector	Bruker AXS SMART APEX CCD
λ(Mo Kα), Å	0.71073	0.71073	0.71073
monochromater	graphite	graphite	graphite
scan type	ω	φ and ω	ω
μ, mm^{-1}	0.552	0.554	0.492
2θ, range, deg	2.4, 25.7	2.58, 28.51	1.59, 28.28
temp, K	293(2)	298(2)	100 (2)
no. of data collected	48737	61264	123073
no. of unique data	7682	15522	13352
no. of params/restraints	596/0	610/0	663/62
R_1 [$I > 2\sigma(I)$]	0.0499	0.0347	0.0492
wR_2 (all data)	0.1440	0.0869	0.1250

resolved and identified in complexes **2** and **3**. In complex **1** also the C^2H signal shows a downfield shift (8.83 ppm); however, the thiophene ring protons merge with the phenyl rings of the dppm ligands (6.39–7.77 ppm). The CH_2 protons of the free dppm ligand appear as a triplet centered at 2.8 ppm, and they become a multiplet centered at around 2.9 ppm in complex **1**. The NH_2 protons appear as single peaks in complexes **2** and **3**, while these merge with signals due to rings of thiophene and phenyl in complexes **1** and **4**.

The ^{31}P NMR spectra of complexes **2** and **3** showed only one signal each, which support equivalence of PR_3 ligands in the complexes. Their coordination shifts (∼56 ppm) are similar to literature reports.[3] However, the presence of more than one signal in the ^{31}P NMR spectra of complexes **1** and **4** indicates that the phosphorus atoms in these complexes are not equivalent.

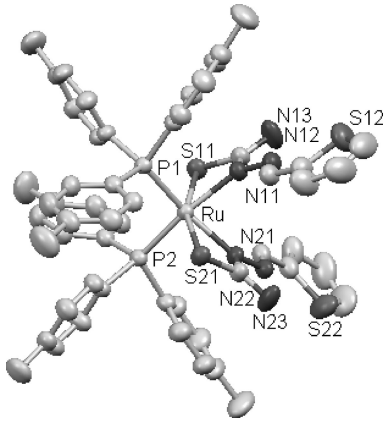


Figure 1. Molecular diagram of complex **3** with numbering scheme. Selected bond lengths [Å] and angles [deg]: Ru−N11 2.1752(15), Ru−N21 2.1812(14), Ru−P1 2.2913(5), Ru−P2 2.3031, Ru−S21 2.4155(5), Ru−S11 2.4320(5), S11−C11 1.721(2); N11−Ru−N21 79.91(6), N11−Ru−P1 91.67(4), S11−Ru−S21 159.563(17), N21−Ru−P1 161.35(4), N21−Ru−P2 161.34(5), N21−Ru−P2 90.56, P1−Ru−P2 101.788(17), N(21)−Ru−S(21) 66.02(4) N(11)−Ru−S(11) 65.90(4).

Thus, the spectrum of complex **4** has shown four signals, which are assigned as follows: the signal at −133.80 ppm due to the pendant P of the η^1-dppm, at –116.50 ppm due to the coordinated P of η^1-dppm, and two other peaks at −99.47 and –72.85 ppm due to chelated dppm. The spectrum of complex **1** showed peaks centered at around −82.72 ppm due to chelated dppm and at −115.50 ppm due to the coordinated P atom of η^1-dppm.

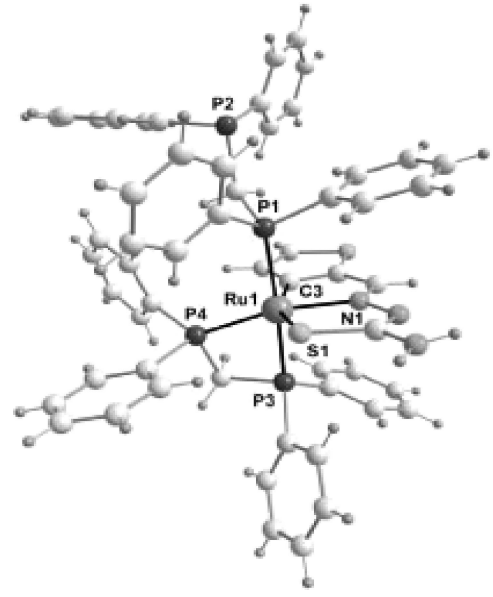


Figure 2. Molecular diagram of complex **1**. Selected bond lengths (Å) and angles (deg): Ru1−N1 2.067(3), Ru1−C3 2.076(3), Ru1−P4 2.2918(11), Ru1−P3 2.3138(11), Ru1−P1 2.3684(11), Ru1−S1 2.4369(11); N1−Ru1−C3 78.95(13), N1−Ru1−P4 161.92(9), C3−Ru1−P4 93.85(11), N1−Ru−P3 91.82(9), C3−Ru1−P3 88.95(10), P4−Ru−P3 71.33(4), N1−Ru1−P1 91.58(9), C3 Ru1 P1 87.29(10), P4 Ru1 P1 104.73(4), P3−Ru1−P1 174.36(3), N1−Ru1−S1 79.21(8), C3−Ru1−S1 156.92(11), P4−Ru1−S1 109.21(4), P3−Ru1−S1 99.10(4), P1−Ru1−S1 85.95(3), C3−Ru−N1 78.95(13).

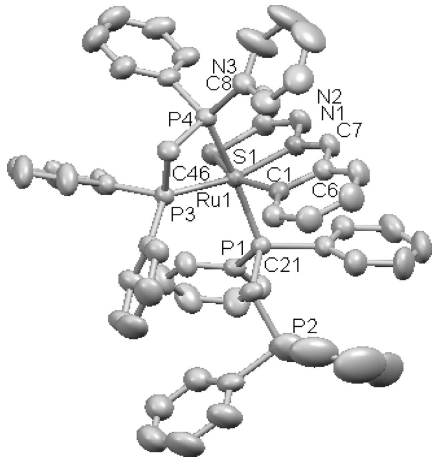


Figure 3. Molecular diagram of complex [Ru(η^3-C^4, N^3,S-L^2)(η^2-P,P-dppm)(η^1-P-dppm)] (**4**) with numbering scheme. Selected bond lengths (Å) and angles (deg): Ru1−N1 2.058(2), Ru1−C1 2.086(3), Ru1−P4 2.3384(8), Ru1−P3 2.3045(7), Ru1−P1 2.3392(8), Ru1−S1 2.4385(8); N1−Ru1−C1 78.90(10), N1−Ru1−P3 162.58(7)), C1 Ru1 P3 97.27(8), N1−Ru1−P4 92.80(7), C1−Ru1−P4 88.03(8), P3−Ru1−P4 69.99(3)), N1−Ru1−P1 93.62(7), C1−Ru1−P1 84.91(8),P3−Ru1−P1 103.02(3),P4−Ru1−P1 169.38(3),N1−Ru1−S1 79.37(7),P4−Ru1−P1 169.38(3),N1−Ru1−S1 79.37(7),C1−Ru1−S1 157.58(8),P3−Ru1−S1 105.13(3),P4−Ru1−S1 98.52(3),P1−Ru1−S1 90.98(3).

Table 2. Comparison of P−Ru−P Angles (deg)

complex[a]	mode	P−Ru−P	remark	ref
1	C^4, N^3, S	71.33(4)	C−H activation	this work
3	N^2, S	101.79(2)	no C−H activation	this work
4	C^4, N^3, S	69.99(3	C−H activation	this work
5	N^2, S	105.37(7)	no C−H activation	3a
6	O, N^3, S	70.10(7)	O−H activation	10
7	N^2, S	105.95(7)	no O−H activation	3d

[a] [Ru(η^3-C,N^3,S-L^1)(η^2-P,P-dppm)(η^1-P-dppm)] (**1**), [Ru(η^2-N^2,S-HL^1)$_2$(PR′$_3$)$_2$] (R′ = phenyl, **2**; *p*-tolyl, **3**), [Ru(η^3-C,N^3,S-L^2)(η^2-P,P-dppm)(η^1-P-dppm)] (**4**), [Ru(η^2-N^2,S-HL^2)$_2$(PPh$_3$)$_2$] **5**, [Ru(η^3-O,N^3,S-L^3)(η^2-P,P-dppm)(η^1-P-dppm)] **6**, [Ru(η^2-N^2,S-HL^3)$_2$(PPh$_3$)$_2$] **7**.

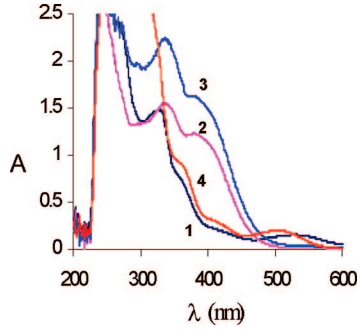


Figure 4. UV−vis spectrum of complexes **1**–**4**.

The electronic absorption spectra of complexes **1**, **2**, and **3** showed bands at 323, 338, and 336 nm, respectively, due to the ligand-based $\pi-\pi^*$ transitions. This band is at higher energy in complex **4**. In complexes **2** and **3**, coordination of thiosemicarbazone is via N^2,S atoms and the bands at 380 and 385 nm may be assigned to n−π^* transitions centered on the C^2=N^3 moiety. This band undergoes a blue shift in complexes **1** and **4** (359 and 357 nm) because the coordination mode changes from N^2,S (**2**, **3**) to N^3,S (**1**, **4**) (Figure 4). An additional band appears in the visible region (at 530 and 500 nm) in spectra of complexes **1** and **4**, which is attributed to d−π^* transitions.

Conclusion

Cyclometalation of thiophene and phenyl rings in ruthenium(II)-thiosemicarbazone complexes [Ru(η^3-C,N^3,S-L^1)(η^2-P,P-dppm)(η^1-P-dppm)], **1** (H$_2$L^1 = thiophene-2-carbaldehyde thiosemicarbazone), and [Ru(η^3-C, N^3,S-L^2)(η^2-P, P-dppm)(η^1-P-dppm)], **4** (H$_2$L^2 = benzaldehyde thiosemicarbazone), is attributed to the short P−Ru−P angle (∼70°) of the chelating dppm ligand versus the large P−Ru−P angle (∼101°) in the complex [Ru(η^2-N^2,S-HL^1)$_2${(*p*-tolylphosphine)$_3$P}$_2$], **3**, and other complexes (**5**, **7**). The short P−Ru=P angle changed modes from usual N^2,S in **3** and other similar complexes to N^3,S in **1** and **4**. This brought the thiophene/phenyl rings in close proximity of the metal, which led to their metalation. In both complexes **1** and **4**, the sixth site is opccupied by one end (PPh$_2$) of the dppm ligand. Interestingly, using salicylaldehyde thiosemicarbazone (H$_2$L^3), complex [Ru(η^3-O,N^3,S-L^3)(η^2-P,P-dppm)(η^1-P-dppm)] (**6**), similar to **1** and **4**, resulted but contained a Ru−O bond, as the 2-position of the phenyl in H$_2$L^3 contains a hydroxy (−OH) group. In ruthenium(II) thiosemicarbazone chemistry, cyclometalated complexes **1** and **4** are the first examples.

Experimental Section

General Methods and Instrumentation. The starting materials Ru(dppm)$_2$Cl$_2$, Ru(PPh$_3$)$_3$Cl$_2$, and Ru(*p*-tolylphoshine)$_3$Cl$_2$ were prepared according to published methods.[7] The thiosemicarbazone ligands were also prepared by general published methods.[9] The following reagents were obtained from commercial sources: RuCl$_3$·*x*H$_2$O, thiophene-2-carbaldehyde, benzaldehyde, thiosemicarbazide, and phosphines. (Sigma-Aldrich). For ^{31}P NMR, (MeO)$_3$P is reference taken at zero position.

Preparation of [Ru(η^3-C^4,N^3,S-L^1)(η^2-P,P-dppm)(η^1-P-dppm)] (1). To a solution of H$_2$L^1 (0.02 g, 0.10 mmol) in toluene was added Ru(dppm)$_2$Cl$_2$ (0.05 g, 0.05 mmol) followed by Et$_3$N (1 mL), and the contents were refluxed for 5 h, during which a bright red solution was formed. Et$_3$NH$^+$Cl$^-$ separated in toluene solution was filtered off, and the filtrate was kept for evaporation. The compound formed was recrystallized using an acetonitrile−dichloromethane mixture (2:1). Yield: 0.03 g, 56%, mp 235–240 °C (dec). C, H, N Calcd for C$_{56}$H$_{49}$N$_3$P$_4$RuS$_2$: C 63.8, H 4.65, N 4.00. Found: C 63.4, H, 4.99, N 4.02. IR bands (KBr pellets, cm^{-1}): ν(N−H), 3516b, 3448sh, 3334w (−NH$_2$), ν(C=N) + δNH$_2$ + νC=C) 1588s, 1508b; ν(C−S), 840s; ν(P−C$_{Ph}$) 1089s. ^{1}H NMR (CDCl$_3$, δ ppm): 8.83 (s, C^{2}H), 6.56–7.78 (m, NH$_2$ + thiophene ring + Ph groups), 2.9 (m, CH$_2$). ^{31}P NMR (CDCl$_3$, δ ppm): −115.48, −82.83, and −55.0 ppm, $\Delta\delta$ ($\delta_{complex} - \delta_{dppm}$) = 14.74, 47.38, 75.22 ppm. δ_P for dppm, −130.15 ppm.

Preparation of [Ru(η^2-N^2,S-HL^1)$_2$(PPh$_3$)$_2$] (2). To a solution of H$_2$L^1 (0.018 g; 0.10 mmol) in methanol (30 mL) was added solid [RuCl$_2$(PPh$_3$)$_2$] (0.05 g; 0.05 mmol) followed by addition of NEt$_3$ (0.5 mL). The mixture was stirred for about 4 h. The yellow solid formed was filtered, washed with methanol, and dried. Yield: 0.045 g, 75%, mp 190 °C. C, H, N Calcd for C$_{48}$H$_{40}$N$_6$S$_4$P$_2$Ru: C 58.06, H 4.03, N 8.45. Found: C 58.36, H 4.53, N 8.05. Main IR peaks (KBr, cm^{-1}): ν(NH$_2$) 3479s, 3357s; ν(C=C) 3050w; ν(C=N) + δNH$_2$ 1575s, 1496s; ν(C−S) 758s; ν(P−C) 1085s. ^{1}H NMR(CDCl$_3$): δ 8.65 (s, C^{2}H, 2H), 7.37 (s, C^{6}H, 2H), 6.46 (d, C^{4}H, 2H), 6.37(dd, C^{5}H, 2H), 5.07(s, −NH$_2$, 4H), 7.28–7.31 (m, *o*-Ph,12H), 7.13–7.17 (m, *p*-Ph, 6H), 6.98–7.03 (m, *m*-H, 12H) ppm. ^{31}P NMR (CDCl$_3$): δ −56.27 ppm, $\Delta\delta$ ($\delta_{complex} - \delta_{PPh3}$) = 56.88 ppm.

(10) See Supporting Information.

Preparation of [Ru(η^2-N^2,S-HL^1)$_2$(*p*-tolylphosphine)$_2$] (3). This was prepared by the same method as used for **2**. Yield: 0.050 g, 73%, mp 181 °C. H, N Calcd for $C_{54}H_{54}N_6P_2RuS_4$: C 60.11, H 5.01, N 7.79. Found: C 60.04, H 5.00, N 8.10. Main IR peaks (KBr, cm^{-1}): $\nu(NH_2)$ 3483w, 3460s; ν(C═C) 3014w; ν(C═N) + δNH_2 591sh, 1573 s; ν(C−S) 806 s; ν(P−C) 1087s. ^{1}H NMR($CDCl_3$): δ 8.84 (s, C^{2}H, 2H), 7.25 (s, C^{6}H, 2H), 7.07 (d, C^{4}H, 2H), 6.95 (dd, C^{5}H, 2H), 5.05(s, $-NH_2$, 4H), 2.21 (s, $-CH_3$, 18H), 7.14–7.19 (m, *o*-H, 12H), 6.78 (d, *m*-H, 12H) ppm. ^{31}P NMR ($CDCl_3$): δ −58.63 ppm, $\Delta\delta$ ($\delta_{complex} - \delta_{p\text{-}tolyl}$) = 56.97 ppm.

Preparation of [Ru(η^3-C^4,N^3,S-L^2)(η^2-P,P-dppm)(η^1-P-dppm)] (4). To a solution of H_2L^2 (0.02 g, 0.10 mmol) in toluene was added $Ru(dppm)_2Cl_2$ (0.05 g, 0.05 mmol) followed by Et_3N (1 mL), and the contents were refluxed for 5–6 h, during which a bright red solution was formed. $Et_3NH^+Cl^-$ separated in the toluene solution was filtered off, and filtrate was kept for evaporation. Red-colored crystals formed after a few days. Yield: 0.03 g, 70%, mp 240–245 °C. C, H, N Calcd for $C_{58}H_{51}N_3P_4RuS \cdot 1/2C_7H_8$ C 67.52, H 4.82, N 3.84. Found: C 67.66, H, 4.82, N 4.02. IR bands (KBr pellets, cm^{-1}): ν(N−H), 3524b, 3440sh, 3324w ($-NH_2$), ν(C═N) + δNH_2 + ν(C═C) 1569s, 1518b; ν(C−S) 835s; $\nu(P-C_{Ph})$ 1090s. ^{1}H NMR ($CDCl_3$, δ ppm): 7.75 (t, C^{2}H), 6.40–7.59 m, NH_2 + Ph groups), 2.9 (m, CH_2). ^{31}P NMR ($CDCl_3$, δ ppm): −133.80, –116.50, −99.47, and –72.85 ppm, $\Delta\delta$ ($\delta_{complex} - \delta_{dppm}$) = −3.65, 13.65, 30.68, 57.3 ppm.

Structural Analysis of Complexes 1, 3, and 4. Crystals suitable for X-ray diffraction were obtained in an acetonitrile−dichloromethane mixture (**1** and **3**) or toluene (**4**). X-ray data was collected on Bruker SMART CCD-1000 (**1**), CCD area detector (**3**), and Bruker Smart APEX CCD diffractometers (**4**) equipped with graphite monochromaters (λ = 0.71073 Å). The data were processed with SAINT and corrected for absorption using SADABS or multiscan. The structure was solved by direct methods and refined by full matrix least-squares technique using the programs SHELXS-97 (**1** and **3**) and SHELXTL 6.14 (**4**). Positional and anisotropic atomic displacement parameters were refined for all non-hydrogen atoms.

X-ray crystal data in CIF format {CCDC numbers 653832, 653833, and 664627 for **1**, **3**, and **4**, respectively} is available from the Cambridge Crystallographic Data Centre.

Acknowledgment. Financial support from CSIR, New Delhi (F. No. 9/254 (155)/2004-EMR I), is gratefully acknowledged.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

OM700804S