Inorg. Chem. **2008**, *47*, 1488−1495

Inorganic Chemistry

Article

Synthesis of $Cu^{II}-Ru^{II}-Cu^{II}$ Trinuclear Complexes via Redox Reaction of Copper(I) Across Thiosemicarbazones Coordinated to Ruthenium(II)

Tarlok S. Lobana,[*,†] Gagandeep Bawa,[†] and Ray J. Butcher[‡]

Department of Chemistry, Guru Nanak Dev University, Amritsar – 143 005, and India Department of Chemistry, Howard University, Washington, D.C. 20059

Received September 11, 2007

Pyridine-2-carbaldehyde thiosemicarbazones [$C_5H_4N^1-C(H){=}N^2-N^3H-C({=}S)-N^4HR$, R = H, L^1H_2; CH_3, L^2H_2−Me; CH_2CH_3, L^3H_2−Et] with $Ru(PPh_3)_3Cl_2$ have formed mononuclear Ru^{II} precursors for the generation of trinuclear complexes. The reaction of 2 mol each of L^1H_2, L^2H_2-Me, or L^3H_2-Et with $Ru(PPh_3)_3Cl_2$ in the presence of Et_3N has yielded mononuclear complexes [$Ru(N^3,S-L^1H)_2(PPh_3)_2$] (**1**), [$Ru(N^3,S-L^2H-Me)_2(PPh_3)_2$] (**2**), and [$Ru(N^3,S-L^3H)_2(PPh_3)_2$] (**3**). The addition of 2 equiv of copper(I) chloride solution to complex **1** in acetonitrile has formed a novel trinuclear complex, $(Ph_3P)_2Ru^{II}(L^1)_2Cu^{II}_2Cl_2$ (**4**), in which the pendant amino group ($-N^4H_2$) loses one hydrogen along with the oxidation of Cu^I to Cu^{II}. In this complex, Ru^{II} is bonded to two P, two S, and two N^3 atoms, while each Cu^{II} is coordinated to N^1, N^2, N^4, and Cl atoms. Reaction with copper(I) bromide yielded a similar trinuclear complex, $(Ph_3P)_2Ru(L^1)_2Cu^{II}_2Br_2$ (**5**). From precursors **2** and **3**, analogous complexes $(Ph_3P)_2Ru^{II}(L^2-Me)_2Cu^{II}_2Cl_2$ (**6**), $(Ph_3P)_2Ru^{II}(L^2-Me)_2Cu^{II}_2Br_2$ (**7**), $(Ph_3P)_2Ru^{II}(L^3-Et)_2Cu^{II}_2Cl_2$ (**8**), and $(Ph_3P)_2Ru^{II}(L^3-Et)_2Cu^{II}_2Br_2$ (**9**) have been synthesized. These complexes have been characterized using analytical, spectroscopic, and electrochemical techniques. Single-crystal X-ray crystallography has been carried out for precursor **2** and all of the trinuclear complexes, **4**−**9**. X-band electron spin resonance and UV–vis spectra have confirmed the presence of Cu^{II}. The cyclic voltammetry studies support the Ru^{II}/Ru^{III} redox behavior of this metal in trinuclear complexes.

Introduction

The chemistry of polynuclear transition metal complexes has received a recent surge of interest due to fascinating and versatile properties exhibited by them.[1] Among the methodologies that are used for the construction of polynuclear assemblies of predesigned compositions, the most popular method is stepwise construction of mononuclear transition metal complexes of multidentate ligands in which some of the donor sites are unoccupied, which often serve as efficient building blocks.[2] Thiosemicarbazones (RHC=N−NH−C(=S)−NH_2) represent one class of multidonor ligands which possess several donor atoms and bind to metals as neutral ligands (**1a**) {modes A−D}[3] and anionic ligands (**1b**) {modes A−F}[4–6] (Chart 1). In cases where the R group is pyridyl, or 2-hydroxyphenyl, additional modes G [X = N,[7] X = O[8]] have been identified.

* Author to whom correspondence should be addressed. E-mail: tarlokslobana@yahoo.co.in.
† Guru Nanak Dev University.
‡ Howard University.

(1) (a) Seino, H.; Iwata, N.; Kawarai, N.; Hidai, M.; Mizobe, Y *Inorg. Chem.* **2003**, *42*, 7387. (b) Fandos, R.; Gallego, B.; Otero, A.; Rodriguez, A.; Ruiz, M. J.; Terreros, P.; Pastor, C. *Dalton Trans.* **2006**, 2683. (c) Neot, K. E.; Ong, Y. Y.; Huynh, H. V.; Andyhor, T. S. *J. Mater. Chem.* **2007**, *17*, 1002. (d) Atkins, S. E.; Craig, D. C.; Colbran, S. B. *J. Chem. Soc., Dalton Trans.* **2002**, 2423. (e) Keene, F. R. *Chem Soc. Rev.* **1998**, *27*, 185. (f) Anson, F. C.; Shi, C.; Steiger, B. *Acc. Chem. Res.* **1997**, *30*, 437.

(2) (a) Ward, M. D. *Inorg. Chem.* **1996**, *35*, 1712. (b) Berkelbach, F.; Weyhemuller, T.; Lengen, M.; Garden, M.; Trautwein, A. X.; Weighardt, K.; Chaudhari, P. *J. Chem. Soc., Dalton Trans.* **1997**, 4529. (c) Paw, W.; Eisenberg, R. *Inorg. Chem.* **1997**, *36*, 2287. (d) Majumdar, P.; Peng, S. M.; Goswami, S. *J. Chem. Soc., Dalton Trans.* **1998**, 1569. (e) Das, A. K.; Rueda, A.; Falvello, L. R.; Peng, S. M.; Bhattacharya, S. *Inorg. Chem.* **1999**, *38*, 4365.

(3) Lhuachan, S.; Siripaisarnpipat, S.; Chaichat, N. *Eur. J. Inorg. Chem.* **2003**, 263.

(4) (a) Lobana, T. S.; Sanchez, A.; Casas, J. S.; Castineiras, A.; Sordo, J.; Garcia-Tasende, M. S. *Polyhedron* **1998**, *17*, 3701. (b) Casas, J. S.; Castellano, E. E.; Rodriguez-Arguelles, M. C.; Sanchez, A.; Sordo, J.; Zukerman-Schpector, J. *Inorg. Chim. Acta* **1997**, *260*, 183. (c) Carballo, R.; Castineiras, A.; Perez, T. *Z. Naturforsch., B.: Chem. Sci.* **2001**, *56*, 881. (d) Alonso, R.; Bermejo, E.; Castineiras, A.; Perez, T.; Carballo, R. *Z. Anorg. Allg. Chem.* **1997**, *623*, 818.

(5) Basuli, F.; Peng, S.-M.; Bhattacharya, S. *Inorg. Chem.* **2000**, *39*, 1120.

(6) Ashfield, L. A.; Cowley, A. R.; Dilworth, J. R.; Donnely, P. S. *Inorg. Chem.* **2004**, *43*, 4121.

(7) Kovala-Demertzi, D.; Miller, J. R.; Kourkoumelis, N.; Hadjikakou, S. K.; Demertzis, M. A. *Polyhedron* **1999**, *18*, 1005.

10.1021/ic701780g CCC: $40.75

Published on Web 02/02/2008

Chart 1

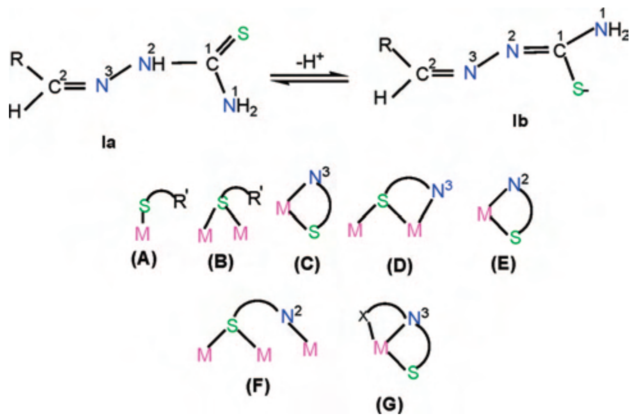
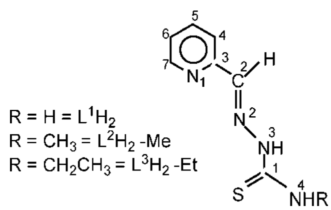


Chart 2



From this laboratory, several mononuclear and dinuclear transition metal complexes with thiosemicarbazones have been reported. [9] It was noted in a mononuclear $[Ru(L^1H)_2(dppb)]$ complex {Chart 2; L^1H_2 = pyridine-2-carbaldehyde thiosemicarbazone; dppb = 1,4-bis(diphenylphosphino)butane} that the thiosemicarbazone ligand binds via N^3; S donor atoms (forming four-membered ring) and some of the donor atoms are still free.[9a] The presence of three uncoordinated donor atoms (N^1, N^2, and N^4) for each ligand and their relative dispositions in space suggested that such complexes might provide a possibility to bind to a second metal ion. In the literature, an analogous ligand, namely, salicylaldehyde thiosemicarbazone, has formed an octanuclear complex, namely, $[\{Ru(bpy)_2(stsc)\}_4Ni_4](ClO_4)_4$ (stsc = trianion of salicylaldehyde thiosemicarbazone), in which it acts as a multidentate ligand.[10]

Keeping in view the above observations, it was planned to investigate polymetallic chemistry using pyridine-based thiosemicarbazones, as shown in Chart 2. Thus, in this paper, a series of trinuclear complexes based on precursors $[Ru(N^3,S-L^1H)_2(PPh_3)_2]$ (**1**), $[Ru(N^3,S-L^2H-Me)_2(PPh_3)_2]$ (**2**), and $[Ru(N^3,S-L^3H-Et)_2(PPh_3)_2]$ (**3**) containing pyridine-2-carbaldehyde thiosemicarbazones are reported.

Results and Discussion

The reaction of 2 equiv of thiosemicarbazones L^1H_2, L^2H_2-Me, or L^3H_2-Et with $RuCl_2(PPh_3)_3$ in the presence of the Et_3N base in methanol has yielded precursors $[Ru(N^3,S-L^1H)_2(PPh_3)_2]$ (**1**), $[Ru(N^3,S-L^2H-Me)_2(PPh_3)_2]$ (**2**), and $[Ru(N^3,S-L^3H-Et)_2(PPh_3)_2]$ (**3**) (Scheme 1). In these precursors, there is deprotonation of the hydrazinic $-N^3H-$ group and the thiosemicarbazone ligands behave as uninegative bidentate anions. The addition of 2 equiv of copper(I) halide, CuX (X = Cl, Br), to 1 equiv of complex **1** in acetonitrile resulted in a rapid change of color from light orange to dark red (maroon), and slow evaporation of the resulting solution formed the red crystalline complexes $(Ph_3P)_2Ru^{II}(L^1)_2Cu^{II}{}_2Cl_2$, **4**, and $(Ph_3P)_2Ru(L^1)_2Cu^{II}{}_2Br_2$, **5**. These reactions involved participation of the pendant, $-N^1H_2$ moiety in binding to Cu^{II}. Similarly, reactions of precursors **2** and **3** with copper(I) halides yielded the heterotrinuclear complexes **6**−**9** (Scheme 1). Complexes have good solubility in the organic solvents, such as dichloromethane and chloroform.

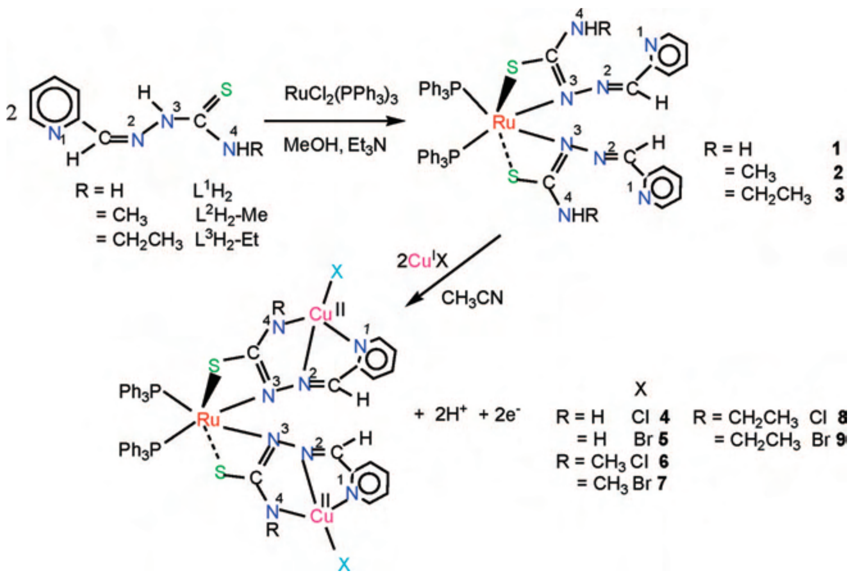
The formation of complexes **4**−**9** involves deprotonation of hydrazinic ($-N^3H-$) and $-N^4HR$ protons (R = H, Me, Et), generating dianions and the oxidation of Cu^I to Cu^{II}. The generation of a dianion from pyridine-2-carbaldehyde thiosemicarbazones (L^1H_2, L^2H_2-Me, and L^3H_2-Et) and its pentacoordination are unprecedented. A plausible mechanism of formation of Cu^{II} and deprotonation of $-N^4HR$ groups is represented in Scheme 2.

It may be pointed out here that the formation of complexes **4**−**9** occurs in the presence and absence of air, and the reaction is instantaneous, with the color of the solution of the precursors changing from the light orange to the dark red after the addition of copper(I) halides. It rules out the oxidation of Cu^I by air in the reaction systems. Further, the addition of $CuCl_2$ in place of CuCl to precursors did not form similar trinuclear complexes; rather, the transfer of thiosemicarbazonate from Ru^{II} to Cu^{II} has been identified, by isolating a compound characterized as $[CuCl_2(L^1H_2)]$. Silver(I) chloride, being insoluble in CH_3CN, did not react with precursor **1**. The addition of AuCl does show an initial color change from light orange to red, but it reverts to the original color. The color change is believed to be due to the formation of Au^{II} momentarily, making it difficult to establish its formation using spectroscopic techniques. The addition of $HgCl_2$ to precursor **1** led to the formation of an octahedral complex, $Hg(L^1H)_2$ (L^1H is a uninegative anion), confirmed by X-ray crystallography to be the same as that reported earlier by a different reaction.[9d] Further, there was no reaction with copper(I) halides when the 2-pyridyl group was changed to 3-pyridyl, phenyl, or thiophene at the C^2 carbon.

IR and Electron Spin Resonance (ESR) Spectral Studies. The spectra of the free ligands reveal bands in the region 3500−3150 cm^{-1} attributed to the ν(N−H) of $-NH_2$, and at 3200–3150 cm^{-1} assigned to the imino −NH− group (see the Experimental Section). The ν(C–H) bands due to the aromatic ring are observed for all of the complexes in the region near 3050 cm^{-1}. Further, $\delta(NH_2) + \nu(C{=}N) +$

(8) (a) Kovala-Demertzi, D.; Yadav, P. N.; Demertzis, M. A.; Jasiski, J. P.; Andreadaki, F. J.; Kostas, I. D. *Tetrahedron Lett.* **2004**, *48*, 2923. (b) Garcia-Tojal, J.; Lezama, L.; Pizarro, J. L.; Insausti, M.; Arriortua, M. I.; Rojo, T. *Polyhedron* **1999**, *18*, 3703.
(9) (a) Lobana, T. S.; Bawa, G.; Butcher, R. J.; Liaw, B.-J.; Liu, C. W. *Polyhedron* **2006**, *25*, 2897. (b) Lobana, T. S.; Bawa, G.; Castineiras, A.; Butcher, R. J. *Inorg. Chem. Commun.* **2007**, *10*, 506. (c) Lobana, T. S.; Rekha; Butcher, R. J.; Failes, T. W.; Turner, P. *J. Coord. Chem.* **2005**, *58*, 1369. (d) Lobana, T. S.; Rekha; Castineiras, A. *Inorg. Chem. Commun.* **2005**, *8*, 1094. (e) Lobana, T. S.; Rekha; Butcher, R. J. *Transition Met. Chem. (Dordrecht, Neth.)* **2004**, *29*, 291. (f) Lobana, T. S.; Rekha; Butcher, R. J.; Castineiras, A.; Bermejo, E.; Bharatam, P. V. *Inorg. Chem.* **2006**, *45*, 1535.
(10) Pal, I.; Basuli, F.; Mak, T. C. W.; Bhattacharya, S. *Angew. Chem., Int. Ed.* **2001**, *40*, 2923.

Scheme 1



Scheme 2

$$Cu^{+} \longrightarrow Cu^{2+} + e^{-}$$

$$\text{-}N^{4}HR \longrightarrow N^{4}R^{-} + H^{+} \quad (R = H, Me, Et)$$

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 at around 830 cm^{-1} shifted to low energy (at ~810 cm^{-1}) as compared with the similar free ligand bands, and this is consistent with its single-bond character in the anionic form. The presence of PPh_3 in complexes **1–9** is confirmed by the presence of a characteristic ν(P−C) band in the range 1076–1085 cm^{-1}. Further, the X-band ESR spectra of each of the microcrystalline complexes showed one signal centered at g = 2.096 and 2.095 in **4** and **5**, respectively, and it confirmed the presence of Cu^{II} in the trinuclear complexes. The ESR spectra at low temperature (120 K) and in the solution state (CH_2Cl_2) were essentially unchanged. Similarly, complexes **6–9** showed ESR signals centered at g = 2.088, 2.089, 2.0758, and 2.0353, respectively.

Descriptions of the Crystal Structures. Precursors. Among the precursors (**1−3**), precursor **2** formed good-quality crystals, and its X-ray structure is first discussed here. Figure 1a shows the molecular structure of complex **2** with the numbering scheme. It crystallized in the monoclinic space group. Ruthenium(II) is coordinated to two anionic L^2H_2−Me ligands via N^3 and S-donor atoms, thus forming four-membered chelate rings with a bite angle N^3−Ru−S of 65.80(6)° and 66.20(6)°. The Ru^{II}−N^3 bond distances are 2.161(2) and 2.1693(19) Å, and the Ru^{II}−S distances are 2.4205(7) and 2.465(7) Å. The other two sites are occupied by P donor atoms of two PPh_3 ligands with Ru−P distances of 2.3008(7) and 2.3034(7) Å. The cis N−Ru−N {81.25(8)°} angle is less than 90°, whereas the other cis angle, P−Ru−P {98.89(2)°}, is more than 90°. The trans angle S−Ru−S {159.03(2)°} deviates largely from linearity. The geometry of the complex is thus distorted octahedral. All of the bond parameters around Ru^{II} are comparable to literature reports.[11] The presence of water shown by elemental analysis was confirmed by X-ray crystallography. It forms two hydrogen bonds; the O of water is bonded to the amino hydrogen of the $-NHCH_3$ moiety, with an O⋯H distance of 2.240(4) Å, while pyridine N is bonded to the H of H_2O with a N⋯H distance of 2.045(4) Å (Figure 1b).

Structures of Trinuclear $Ru^{II}Cu^{II}_2$ Complexes. The structures of trinuclear complexes **4−9** have been revealed by X-ray crystallography. Compounds **4−9** crystallized in triclinic crystal systems with the $P\bar{1}$ space group in each case. Table 1 shows the crystallographic data for these complexes; Table 2 deals with the comparison of important bond parameters. Since the complexes have similar structures, a detailed description of only complex $(Ph_3P)_2Ru^{II}(L^1)_2Cu^{II}_2Cl_2$ (**4**) is given here, and the structures of other complexes are discussed with reference to it. Protons of the phenyl rings have been removed for clarity.

In complex **4**, each thiosemicarbazone ligand behaves as a dianion, and two such dianions are connecting one Ru^{II} and two Cu^{II} ions forming the trinuclear complex. The ligand coordinates to the Ru metal center via N^3 and S-donor atoms with S−Ru−N^3 bite angles of 66.36(7) and 66.19(7)° (Figure 2a), and the geometry is distorted octahedral with *trans*-S−Ru−S and *cis*-P−Ru−P bond angles of 156.09(3)° and 98.23(3)°, respectively. The Ru−S, Ru−P, and Ru−N^3 bond lengths, 2.4500(9) and 2.4564(10) Å, 2.2975(10) and 2.2993(9) Å, and 2.112(3) and 2.133(2) Å, respectively, are characteristic of Ru^{II} complexes.[11] Each Cu^{II} metal ion is coordinated to the N^1, N^2, N^4, and Cl atoms. The trans bond angles, 160.25(11)° and 159.28(12)° (N^4−Cu−N^1) and 177.49(9)°

(11) (a) Maji, M.; Chatterjee, M.; Ghosh, S.; Chattopadhyay, S. K.; Mak, T. C. W.; Wu, B. M. *J. Chem. Soc., Dalton Trans.* **1999**, 135. (b) Gupta, P.; Dinda, R.; Ghosh, S.; Sheldrick, W. S. *Polyhedron* **2003**, *22*, 447. (c) Mishra, D.; Naskar, S.; Drew, M. G. B.; Chattopadhyay, S. K. *Polyhedron* **2005**, *24*, 1861. (d) Basuli, F.; Ruf, M.; Pierpont, C. G.; Bhattacharya, S. *Inorg. Chem.* **1998**, *37*, 6113. (e) Basuli, F.; Peng, S. M.; Bhattacharya, S. *Inorg. Chem.* **1997**, *36*, 5645. (f) Maji, M; Ghosh, S.; Chattopadhyay, S. K.; Mak, T. C. W. *Inorg. Chem.* **1997**, *36*, 2938.

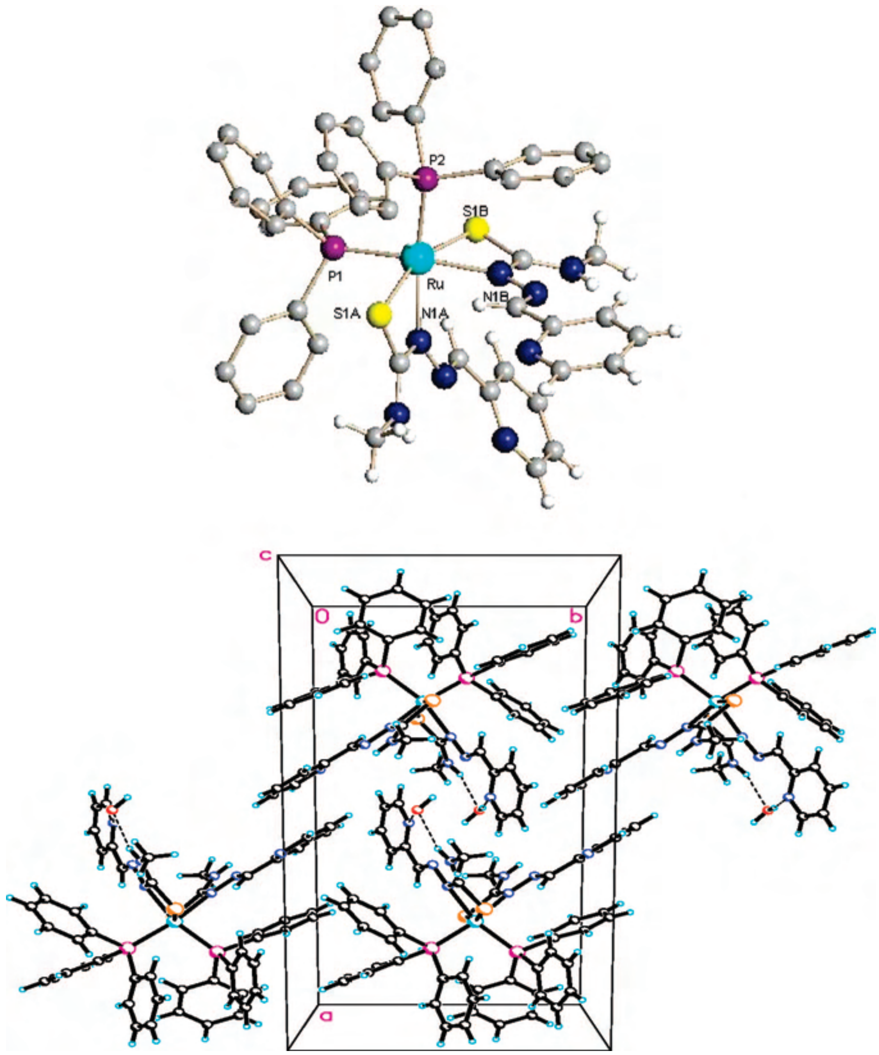


Figure 1. (a) Structure of complex $[Ru(L^1H\text{-}Me)_2PPh_3)_2]$, **2**, with numbering scheme. (b) Packing diagram for complex **2**.

and 166.47(8)° ($N^2-Cu-Cl$), reveal distorted square-planar geometry around the Cu^{II} metal center. The $Cu-N^4$ bond distance between Cu and imido ($-N^4H^-$) nitrogen atoms is the shortest, 1.939(3) Å, while other Cu−N distances, 1.962(2) and 2.011(3) Å, are longer. Acetonitrile lies in the lattice with one of its three hydrogens having weak contact with chlorine. Two such trinuclear units dimerize via long-range Cu···Cl interactions {2.9984(9) and 3.1970(11) Å, sum of van der Waals radii = 3.10–3.30 Å},[12] and it results in the formation of a hexanuclear cluster (Figure 2b).

On changing the halide from chloride to bromide, complex **5** is obtained. The structure of complex **5** shows the bonding around Ru^{II} and Cu^{II} centers to be identical to that of complex **4** (Figure 3). The metal-donor (Ru^{II}/Cu^{II}) bond lengths are also comparable with those of complex **4** (Table 2). It may be mentioned here that, in this case also, long-range Cu···Br (~3.0 Å) interactions result in a hexanuclear structure. Acetonitrile is present as a solvent of crystallization. The coordination to Cu^{II} significantly shortens the C^1-N^4 and N^2-N^3 bond distances (1.37 and 1.32 Å, respectively) of complex **6** (Figure 4) vis-à-vis complex **2** (1.43 and 1.37 Å).

It can be observed from the comparison, Table 2, that the bond parameters for complexes **4−9** do not vary significantly; thus, there is no significant effect of change of the halide from chloride to bromide or by substituting $-NH_2$ by bulky substituents $-NHCH_3$ or $-NHC_2H_5$ on bond parameters except for variation in the P−Ru−P angle, which opens up in complexes **8** and **9**. The *trans*-N−Cu−X bond angles for two Cu's in a trinuclear complex are unequal, while the *trans*-N−Cu−N bond angles are nearly the same (Table 2).

Solution State Behavior. Trinuclear complexes **4−9** did not show any NMR signal, and it confirmed the presence of Cu^{II}, as shown by ESR. The Ru^{II} precursors **1−3** are diamagnetic and, so, are NMR-active. Important signals are listed in the Experimental Section. Each of the free ligands (L^1H_2, L^2H_2-Me, and L^3H_2-Et) show a peak at low fields ($\delta\sim10$ ppm) due to the presence of a hydrazinic proton ($-N^3H-$), and this peak was absent in the spectra of complexes **1−3**, thus confirming deprotonation of the ligands. In the ^{31}P NMR spectra, each of the complexes showed a

(12) Huheey, J. E.; Keiter, E. A.; Keiter, R. L. *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed.; Harper Collins: NewYork, 1993.

Table 1. Crystallographic Data for Complexes **2**, **4−9**

	2	**4**	**5**	**6**	**7**	**8**	**9**
empirical formula	$C_{52}H_{50}N_8OP_2RuS_2$	$C_{50.67}H_{43}Cl_2Cu_2N_{8.34}P_2RuS_2$	$C_{52}H_{45}Br_2Cu_2N_9P_2RuS_2$	$C_{54}H_{49}Cl_2Cu_2N_9OP_2RuS_2$	$C_{53}H_{47.50}Br_2Cu_2N_{8.50}P_2RuS_2$	$C_{54}H_{50}Cl_2Cu_2N_8P_2RuS_2$	$C_{54}H_{50}Br_2Cu_2N_8P_2RuS_2$
M	1030.13	1193.71	1310.00	1249.13	1317.52	1236.13	1325.05
T (K)	173(2)	93(2)	93(2)	173(2)	173(2)	296(2)	296(2) K
cryst syst	monoclinic	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space group	*P*21/*C*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	23.454(2)	9.1513(18)	9.2077(17)	9.5925(7)	9.486(2)	12.9527(10)	12.886(2)
b (Å)	11.6204(10)	13.245(3)	13.349(3)	13.2815(10)	13.286(3)	15.3932(14)	15.5562(8)
c (Å)	18.2898(15)	22.354(4)	22.401(4)	22.5555(17)	22.641(5)	16.1930(14)	16.2100(19)
α (deg)	90	76.802(4)	77.548(3)	76.5540(10)	76.918(3)	114.585(8)	114.636(8)
β (deg)	100.804(2)	85.834(4)	84.583(3)	86.5440(10)	87.9443(3)	96.333(7)	96.241(11)
γ (deg)	90	71.727(3)	70.755(3)	72.5920(10)	73.013(3)	99.163(7)	99.009(8)
V (Å^3)	4896.4(7)	2505.0(8)	2537.6(8)	2666.7(3)	2656.8(10)	2841.9(4)	2862.0(6)
Z	4	2	2	2	2	2	2
D_{calcd} (g cm^{-3})	1.397	1.583	1.714	1.556	1.647	1.445	1.538
μ (mm^{-1})	0.518	1.438	2.891	1.355	2.762	1.270	2.564
reflns collected	26003	20005	19145	30485	29171	41345	38135
ind. reflns	13539 [*R*(int) = 0.0667]	11709 [*R*(int) = 0.0521]	11792 [*R*(int) = 0.0238]	14954 [*R*(int) = 0.0131]	14365 [*R*(int) =0.0383]	18572 [R_{int}= 0.0514]	18183 [R_{int} = 0.0131]
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0441, wR2 = 0.0842	R1 = 0.0518, wR2 = 0.0900	R1 = 0.0675, wR2 = 0.1394	R1 = 0.0257, wR2 = 0.0659	R1 = 0.0376, wR2 = 0.0992	R1 = 0.0431, wR2 = 0.0901	R1 = 0.0257, wR2 = 0.0659

Table 2. Comparison of Important Bond Parameters of Complexes **4–9**

	4 (Cl)	**5** (Br)	**6** (Cl)	**7** (Br)	**8** (Cl)	**9** (Br)
a. Important Bond Lengths (Å) of Complexes **4–9**						
Ru−N3 (hydrazinic)	2.112 (3), 2.133 (2)	2.124 (5), 2.140 (5)	2.1224 (14), 2.1304 (13)	2.126 (2), 2.121 (2)	2.1231 (11), 2.1200 (11)	2.1150 (16), 2.1267 (16)
Ru−S	2.4564 (10), 2.4500 (9)	2.4449 (15), 2.4502 (15)	2.4238 (8), 2.4533 (4)	2.4212 (9), 2.4500 (10)	2.4360 (5), 2.4257 (4)	2.4220 (6), 2.4363 (5)
Ru−P	2.2975 (10), 2.2993 (9)	2.2960 (15), 2.2969 (16)	2.2980 (4), 2.2996 (4)	2.3022 (8), 2.2994 (9)	2.3339 (4), 2.3265 (4)	2.3151 (6), 2.3303 (6)
Cu−N4 (amino)	1.961 (3), 1.939 (3)	1.944 (5), 1.941 (5)	1.9617 (14), 1.9615 (15)	1.972 (3), 1.973 (3)	1.9480 (12), 1.9766 (10)	1.9653 (15), 1.9493 (14)
Cu−N2 (azomethine)	1.959 (3), 1.962 (2)	1.961 (5), 1.963 (5)	1.9657 (13), 1.9622 (14)	1.954 (3), 1.960 (2)	1.9347 (10), 1.9486 (11)	1.9350 (15), 1.9398 (14)
Cu−N1 (pyridine)	2.042 (3), 2.011 (3)	2.015 (6), 2.017 (6)	2.0292 (14), 2.0242 (16)	2.028 (3), 2.037 (3)	2.0337 (11), 2.0343 (11)	2.0397 (15), 2.0346 (16)
Cu−X	2.2164 (11), 2.2298 (9)	2.3409 (11), 2.3605 (11)	2.2334 (5), 2.2499 (5)	2.3818 (7), 2.3613 (6)	2.107 (3), 2.2453 (8)	2.291 (4), 2.3298 (15)
b. Important Bond Angles (deg) of Complexes **4–9**						
P−Ru−P	98.23 (3)	98.05 (6)	98.155 (16)	98.52 (3)	105.725 (14)	105.70 (2)
N−Ru−N	82.19 (10)	82.39 (19)	81.79 (5)	82.49 (10)	79.07 (4)	78.93 (6)
S−Ru−S	156.09 (3)	157.06 (5)	154.429 (14)	154.32 (3)	157.762 (14)	157.36 (2)
N3−Ru−S (bite angle)	66.36 (7), 66.19 (7)	66.20 (14), 66.15 (13)	66.42 (4), 66.84 (4)	66.70 (7), 66.47 (7)	66.34 (2), 66.61 (2)	66.72 (3), 66.40 (3)
N1B−Cu−N4B	159.28 (12), 160.25 (11)	160.2 (2), 160.1 (2)	159.92 (6), 159.39 (6)	159.56 (12), 159.95 (11)	160.44 (5), 159.63 (5)	159.66 (7), 159.87 (7)
N2B−Cu−X	166.47 (8), 177.74 (9)	167.10 (15), 177.71 (16)	165.59 (4), 177.53 (4)	165.95 (7), 177.24 (7)	171.81 (9), 179.02 (3)	167.03 (11), 179.02 (3)

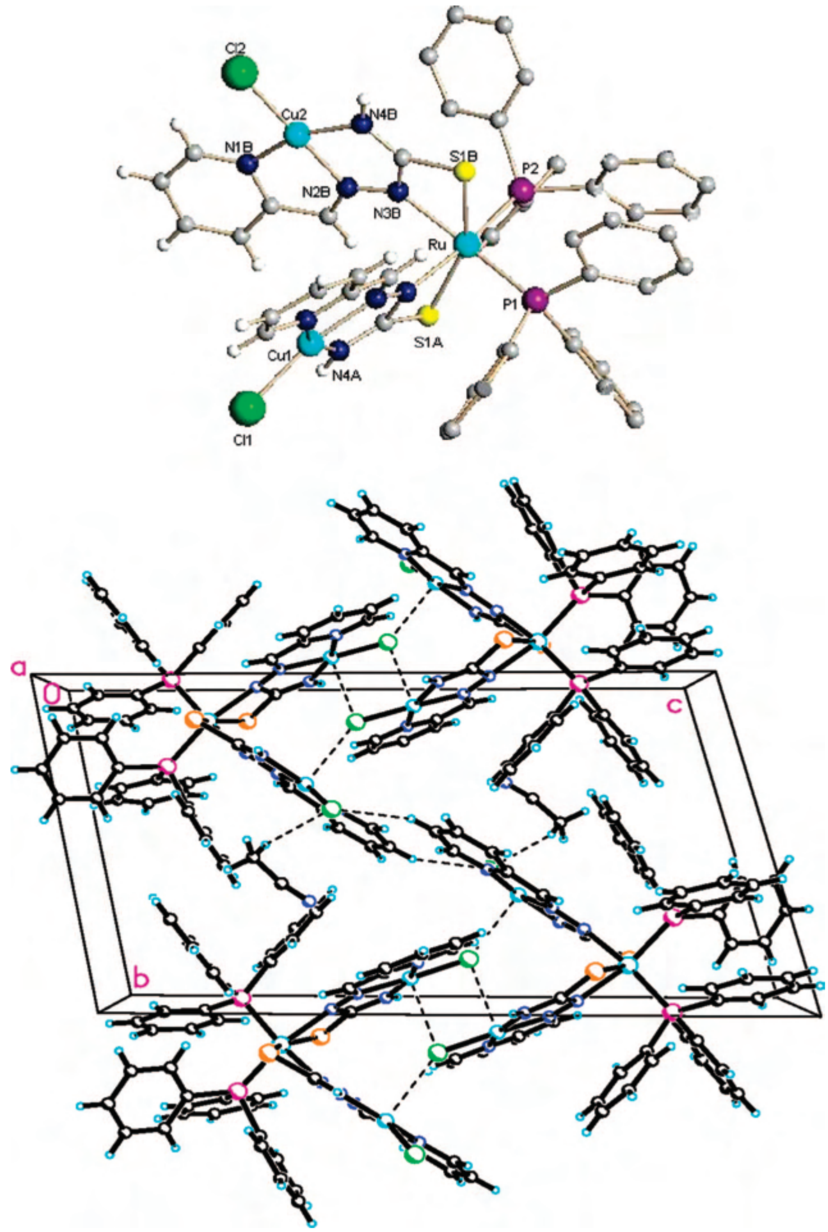


Figure 2. (a) Structure of complex $[(Ph_3P)_2Ru^{II}(L^1)_2Cu^{II}_2Cl_2]$ **4** with numbering scheme. (b) Packing diagram of complex **4**.

single peak depicting the equivalence of two PPh_3 ligands in each complex. The coordination shifts are comparable with other complexes containing tertiary phosphines.[9a,13]

The electronic absorption spectral data of complexes **1**−**9** in dichloromethane are listed in Table 3. Each of the mononuclear complexes **1**–**3** showed two bands in the ranges 390–398 ($n-\pi^*$) and 328–337 nm ($\pi-\pi^*$), respectively. Trinuclear complexes **4**−**9** showed three bands in the ranges 500–502 (d−d transitions), 421–442 ($n-\pi^*$), and 320–327 nm ($\pi-\pi^*$). From these data, it is noted that the peaks due to $\pi-\pi^*$ transitions in complexes **1**–**3** do not undergo significant shifts in trinuclear complexes **4**−**9**, while the peaks due to $n-\pi^*$ transitions in mononuclear complexes undergo significant red shifts in trinuclear complexes. The latter shift is attributed to the change in the dentacy of

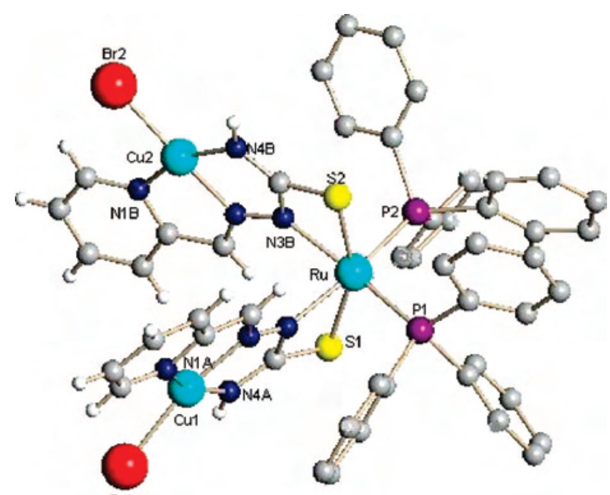


Figure 3. Structure of complex $[(Ph_3P)_2Ru^{II}(L^1)_2Cu^{II}_2Cl_2]$, **5**, with numbering scheme.

(13) (a) Lobana, T. S.; Kaur, P.; Castineiras, A. *J. Coord. Chem.* **2005**, *58*, 429. (b) Lobana, T. S.; Verma, R.; Singh, R.; Castineireas, A. *Transition Met. Chem. (Dordrecht, Neth.)* **1998**, *23*, 25.

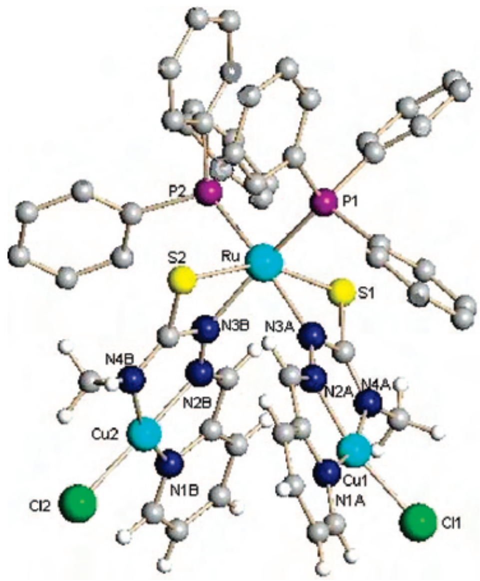


Figure 4. Structure of complex $[(Ph_3P)_2Ru^{II}(L^2\text{-}Me)_2Cu^{II}_2Cl_2]$, **6**, with numbering scheme.

Table 3. UV−Visible Data of Complexes **1**−**9**

complex	λ_{max}(nm) with ϵ ($mol^{-1}\ dm^{-3}\ cm^{-1}$) in parentheses (solvent, CH_2Cl_2)
1	390 (1.797×10^3), 328 (3.329×10^3)
2	395 (2.658×10^3), 336 (2.552×10^3)
3	398 (1.811×10^3), 337 (1.954×10^3)
4	500 (3.28×10^3), 423 (2.10×10^3), 320 (3.24×10^3)
5	501 (1.88×10^3), 421 (1.23×10^3), 321 (2.219×10^3)
6	502 (1.65×10^3), 427 (1.13×10^3), 320 (2.019×10^3)
7	502 (2.157×10^3), 442 (1.27×10^3)
8	500 (2.05×103), 439 (1.246×10^3), 327 (0.68×10^3)
9	501 (2.03×103), 436 (1.236×10^3)

the thiosemicarbazones from two (**1**−**3**) to five (**4**−**9**). The square-planar geometry around each Cu center is supported by the appearance of additional bands in the range 500–502 nm, which are assigned to d−d transitions.[14]

Electrochemical Studies. The cyclic voltammogram of precursor **1** in acetonitrile displayed the Ru^{II}/Ru^{III} redox couple at $E_{1/2} = 0.414$ V with a peak-to-peak separation (ΔE_p) value of 63 mV. The $E_{1/2}$ value is quite close to literature reports of the Ru^{II}/Ru^{III} redox couple with a similar environment around Ru^{II}, for example, $[Ru(PPh_3)_2(L)_2]$ ($E_{1/2}$, 0.39 V; ΔE_p, 60 mV and $E_{1/2}$, 0.30 V; ΔE_p, 60 mV; L = η^2-N^3, S-bonded thiosemicarbazone ligands).[11a,b] The cyclic voltammeteric behavior of trinuclear complex, **4**, is qualitatively similar with that of parent complex **1**, showing $E_{1/2}$ at 0.551 V (ΔE_p, 81 mV) for chloride complex **4**. The shift in $E_{1/2}$ to higher potential, vis-à-vis that of precursor **1**, is attributed to the deprotonation of the thiosemicarbazone and subsequent binding to Cu(II). Trinuclear compex **5** shows a similar trend ($E_{1/2}$ at 0.516 V; ΔE_p, 95 mV). Cu^{II}/Cu^{I} showed a quasi-reversible redox potential at $E_{1/2}$ and $\Delta E_p = -0.310$ V and 191 mV (**4**) and −0.350 V and 120 mV (**5**).[15]

Conclusion

The generation of pyridine-2-carbaldehyde thiosemicarbazones as pentacoordinated dianions $\{(L^1)^{2-}, (L^2\text{−}Me)^{2-}$, and $(L^3\text{−}Et)^{2-}\}$ via the redox reaction of copper(I) halides across thiosemicarbazones coordinated to Ru^{II} have generated novel trinuclear complexes with $Ru^{II}Cu^{II}_2$ cores. The formation of complexes **4**−**9** reveals that the precursors, **1**−**3**, could be suitable analytical reagents/sensors for the detection/determination of copper(I) halides. Further trinuclear complexes might be useful in material science.

Experimental Section

Chemicals. All solvents, $RuCl_3 \cdot xH_2O$, pyridine-2-carbaldehyde, thiosemicarbazide, and N-methyl and N-ethyl thiosemicarbazides are commercially available and were used without further purification.

Physical Measurements. Elemental analyses for C, H, and N were carried out using a thermoelectron FLASHEA1112 analyzer. The melting points were determined with a Gallenkamp electrically heated apparatus. UV−visible spectra were recorded using a UV-1601PC Shimadzu apparatus. The melting points were determined with a Gallenkamp electrically heated apparatus. The IR spectra were recorded using KBr pellets on a Pye-Unicam SP3-300 spectrophotometer. X-band ESR spectra were recorded using a Bruker spectrometer. ^1H NMR spectra were recorded on a JEOL AL300 FT spectrometer at 300 MHz in $CDCl_3$ with TMS as the internal reference. The ^{31}P NMR spectra were recorded at 121.5 MHz with H_3PO_4 as the external reference. Cyclic voltammograms were recorded on an Autolab Electrochemical System equipped with PGSTAT20 apparatus driven by GPES software employing a platinum working electrode and an SCE reference electrode. All solutions were 10^{-3} mmol L^{-1}, and the supporting electrolyte was 10^{-1} mmol L^{-1} of tetraethyl ammonium perchlorate.

Synthesis. $RuCl_2(PPh_3)_3$ was prepared by a literature procedure.[16] The ligands L^1H_2, L^2H_2−Me, and L^3H_2−Et were synthesized by conventional procedures.[17]

$Ru(L^1H)_2(PPh_3)_2$, 1. To a solution of L^1H_2–Me (0.019 g; 0.10 mmol) in methanol (20 mL) was added $RuCl_2(PPh_3)_3$ (0.050 g, 0.05 mmol) and Et_3N (0.5 mL), followed by stirring for 2 h; during stirring, the orange-colored precipitates of the complex started separating and were filtered and dried. The complex is soluble in chloroform, dichloromethane, acetonitrile, and toluene. Yield: 60%. mp: 170–172 °C. Elem anal. found: C, 59.89; H, 4.57; N, 11.17. $C_{50}H_{44}N_8P_2S_2Ru$ requires: C, 60.53; H, 4.47; N, 11.39 (%). IR bands (KBr pellets, cm^{-1}): $\nu(NH_2)$ 3276s, 3163, ν(C=N) + δNH_2+ ν(C=C) 1585s, 1562sh; ν(C−S) 1047s, 824s, ν(P−C) 1085s. ^1H NMR ($CDCl_3$, ppm): δ 8.82 (s, C^2H, 2H), 8.54 (d, C^7H, 2H, J = 4.8), 7.50–7.53 (m, $C^{4,5,6}$, 6H), 5.40(s, NH_2, 4H), 6.98–7.35 (m, Ph−H, 30H). ^{31}P NMR($CDCl_3$): δ 52.1 ppm. Coordination shift $\Delta\delta(\delta_{complex} - \delta_{PPh3}) = 56.8$ ppm.

$Ru(L^2H\text{−}Me)_2(PPh_3)_2 \cdot H_2O$, 2. To a solution of L^2H_2–Me (0.019 g; 0.10mmol) in methanol (20 mL) was added $RuCl_2(PPh_3)_3$ (0.050 g; 0.05 mmol) and Et_3N (0.5 mL), followed by stirring for 2 h, during which a clear orange-colored solution was formed. The solution was filtered and kept for evaporation; an orange crystalline product started forming after a few days. Yield: 65%. mp: 190 °C.

(14) Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier Publishers: New York, 1984.
(15) (a) Naik, A. D.; Reddy, P. A. N.; Nethaji, M.; Chakravarty, A. R. *Inorg. Chim. Acta* **2003**, *349*, 149. (b) Dhar, S.; Chakravarty, A. R. *Inorg. Chem.* **2003**, *42*, 2483.
(16) Stephenson, T. A.; Wilkinson, G. J. *J. Inorg. Nucl. Chem.* **1966**, *28*, 945.
(17) (a) Klayman, D. L.; Bartosevich, J. F.; Griffin, C. J.; Mason, J.; Scovill, J. P. *J. Med. Chem.* **1979**, *22*, 855. (b) 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.

Elem anal. found: C, 60.80; H, 4.99; N, 11.17. Required for $C_{52}H_{48}N_8OP_2S_2Ru\cdot H_2O$: C, 60.60; H, 4.85; N, 10.80. IR bands (KBr pellets, cm^{-1}): $\nu(NH_2)$ 3271s, 3172 ν(C=N) + δNH_2+ ν(C=C) 1585s, 1564s; ν(C=S) 1047s, 844s, ν(P−C) 1076s. ^{1}H NMR ($CDCl_3$, ppm): δ 8.82 (s, C^2H, 2H), 8.50 (s, C^7H, 2H), 7.50–7.44–7.51 (m, $C^{4,5,6}$, 6H), 6.99–7.51 (m, Ph−H, 30H), 6.10 (d, NH, 2H, J = 4.8), 2.70 (d, −NH*CH$_3$*, 6H, J = 5.1). ^{31}P NMR($CDCl_3$): δ 52.9 ppm. $\Delta\delta(\delta_{complex}-\delta_{PPh3})$ = 57.5 ppm.

$Ru(L^3H-Et)_2(PPh_3)_2$, 3. Compound **3** was prepared by a method similar to that for complex **2**. Yield: 66%. mp: 175 °C. Elem anal. found: C, 62.78; H, 5.36; N, 10.87. $C_{54}H_{52}N_8P_2S_2Ru$ requires: C, 62.36; H, 5.00; N, 10.77 (%). ^{1}H NMR ($CDCl_3$, ppm): δ 8.84 (s, C^2H, 2H), 8.50 (d, C^7H, 2H, J = 1.125), 7.45–7.54 (m, $C^{4,5,6}$, 6H), 6.99–7.30 (m, Ph−H, 30H), 6.18 (t, *NH*CH_2, 2H, J = 1.57), 3.16 (m, *CH$_2$*CH_3, 4H, J = 6.8), 0.92 (t, CH_2*CH$_3$*, 6H, J = 7.2). ^{31}P NMR($CDCl_3$): δ 53.0 ppm. $\Delta\delta(\delta_{complex}-\delta_{PPh3})$ = 57.7 ppm.

$Ru(L^1)_2(PPh_3)_2Cu_2Cl_2\cdot 0.3CH_3CN$, 4. To a solution of complex **1** (0.050 g; 0.05 mmol) in acetonitrile (10 mL) was added dropwise a solution of copper(I) chloride (0.010 g; 0.10 mmol) in acetonitrile (5 mL), when a distinct color change from bright yellow to dark red occurred. The solution was kept undisturbed in a closed culture tube for about 2 days, when dark red crystals were formed. Yield: 0.045 g, 75%. mp: 204–206 °C. Elem anal. found: C, 51.20; H, 3.05; N, 9.91. $C_{50}H_{42}N_8P_2S_2RuCu_2Cl_2\cdot{}^1/_3CH_3CN$ requires: C, 51.00; H, 3.50; N, 9.98. IR bands (KBr pellets, cm^{-1}): ν(N−H) 3400m, 3375w; ν(C−H), 3050m; ν(C=N) + δNH_2 + ν(C=C), 1650s, 1598s, 1577m; ν(P−C), 1095s; ν(C−S), 825s.

Complexes **5**−**9** were prepared similarly.

$Ru(L^1)_2(PPh_3)_2Cu_2Br_2\cdot CH_3CN$, 5. Yield: 75%. mp: 205–207 °C. Elem anal. found: C, 48.00; H, 4.00; N, 10.10. $C_{50}H_{42}N_8P_2S_2RuCu_2Br_2\cdot CH_3CN$ requires: C, 47.60; H, 3.43; N, 9.60. IR bands (KBr pellets, cm^{-1}): ν(N−H) 3400, 3395w, ν(C−H), 3050m; ν(C=N) + δNH_2 + ν(C=C), 1650b, 1598s, 1577m; ν(P−C) 1093s; ν(C−S) 850sh.

$Ru(L^2-Me)_2(PPh_3)_2Cu_2Cl_2\cdot CH_3CN$, 6. Yield: 75%. mp: 205–207 °C. C, H, N calcd for $C_{54}H_{49}Cl_2Cu_2N9P_2RuS_2$: C 47.60, H, 3.43, N, 9.60. Found: C, 48.00; H, 4.00; N, 10.10. IR bands (KBr pellets): ν(C−H), 3050m; ν(C=N) + δNH_2 + ν(C=C), 1600s, 1573s, 1541s; ν(P−C) 1081s; ν(C−S), 821s.

$Ru(L^2-Me)_2(PPh_3)_2Cu_2Br_2\cdot 0.5CH_3CN$, 7. Yield: 75%. mp: 205–207. Elem anal. found: C, 48.20; H, 3.13; N, 10.82. $C_{52}H_{46}Br_2Cu_2N_8P_2RuS_2\cdot 0.5CH_3CN$ requires: C, 48.29; H, 3.06; N, 11.07. IR bands (KBr pellets): ν(C−H), 3048m; ν(C=N) + ν(C=C), 1610s, 1575s; ν(P−C) 1080s; ν(C−S), 825s.

$Ru(L^3-Et)_2(PPh_3)_2Cu_2Cl_2$, 8. Yield: 80%. mp: 208–210 °C. Elem anal. found: C, 51.97; H, 4.13; N, 9.32. $C_{54}H_{50}Cl_2Cu_2N_8P_2RuS_2$ requires: C, 52.30; H, 4.04; N, 9.60. IR bands (KBr pellets): ν(C−H), 3048m; ν(C=N) + ν(C=C), 1610s, 1575s; ν(P−C) 1080s; ν(C−S), 850s.

$Ru(L^3-Et)_2(PPh_3)_2Cu_2Br_2$, 9. Yield: 80%. mp: 208–210 °C. Found: C, 48.78; H, 4.03; N, 8.32. $C_{54}H_{50}Br_2Cu_2N_8P_2RuS_2$ requires: C, 48.90; H, 3.77; N 8.45. IR bands (KBr pellets): ν(C−H), 3050m; ν(C=N) + δNH_2 + ν(C=C), 1600s, 1573s, 1541s; ν(P−C) 1081s; ν(C−S), 839s.

X-Ray Crystallographic Studies. Single crystals of complexes were mounted on a CCD area detector diffractometer (**2**, **4**−**7**) and an Oxford Diffraction Gemini apparatus (**8** and **9**), equipped with a graphite monochromator and a Mo Kα radiator (λ = 0.71073 Å). The unit cell dimensions and intensity data were measured at 93(2) K for **4** and **5**; 173(2) K for **2**, **6**, and **7**; and 296(2) K for **8** and **9**. The structure was solved by direct methods and refined by full matrix least-squares 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).[18] An empirical ψ absorption correction was applied. X-ray crystal data in CIF format are available as Supporting Information.

Acknowledgment. Financial support from CSIR, New Delhi (F. No. 9/254 (155)/2004-EMR II), to G.B. is gratefully acknowledged. We thank Prof. R. K. Mahajan for electrochemical data collection and Prof. P. K. Bhardwaj, IIT Kanpur, for ESR studies.

Supporting Information Available: X-ray crystal data in CIF format {CCDC numbers 658590 for **2**; 620554, 620555, and 632183 for **4**, **5**, and **6**, respectively; and 658591–658593 for complexes **7**−**9**}. This material is available free of charge via the Internet at http://pubs.acs.org.

IC701780G

(18) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Gottingen; Gottingen, Germany, 1997.