

# Chemical Control on the Coordination Mode of Benzaldehyde Semicarbazone Ligands. Synthesis, Structure, and Redox Properties of Ruthenium Complexes

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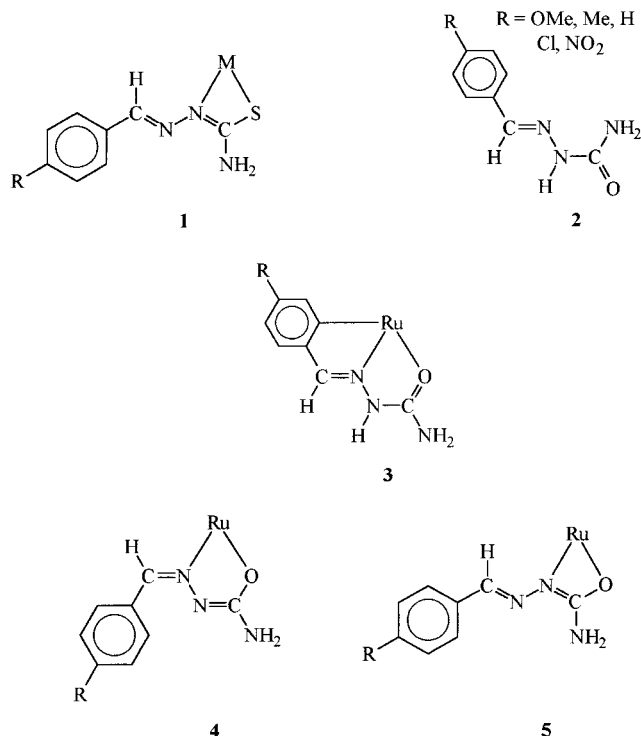
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Reaction of benzaldehyde semicarbazone (HL-R, where H is a dissociable proton and R is a substituent (R = OMe, Me, H, Cl, NO<sub>2</sub>) at the para position of the phenyl ring) with [Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>] and [Ru(PPh<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Cl<sub>2</sub>] has afforded complexes of different types. When HL-NO<sub>2</sub> and [Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>] react in solution at ambient temperature, *trans*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl] is obtained. Its structure determination by X-ray crystallography shows that L-NO<sub>2</sub> is coordinated as a tridentate C,N,O-donor ligand. When reaction between HL-NO<sub>2</sub> and [Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>] is carried out in refluxing ethanol, a more stable *cis* isomer of [Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl] is obtained. The *trans* isomer can be converted to the *cis* isomer simply by providing appropriate thermal energy. Slow reaction of HL-R with [Ru(PPh<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Cl<sub>2</sub>] in solution at ambient temperature yields 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] complexes. A structure determination of 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl] shows that the semicarbazone ligand is coordinated as a bidentate N,O-donor, forming a five-membered chelate ring. When reaction between HL-R and [Ru(PPh<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Cl<sub>2</sub>] is carried out in refluxing ethanol, the 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] complexes are obtained. A structure determination of 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl] shows that a semicarbazone ligand is bound to ruthenium as a bidentate N,O-donor, forming a four-membered chelate ring. All the complexes are diamagnetic (low-spin d<sup>6</sup>, *S* = 0). The *trans*- and *cis*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl] complexes undergo chemical transformation in solution. The 5- and 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] complexes show sharp NMR signals and intense MLCT transitions in the visible region. Cyclic voltammetry of the 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] and 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] complexes show the Ru(II)–Ru(III) oxidation to be within 0.66–1.07 V. This oxidation potential is found to linearly correlate with the Hammett constant of the substituent R.

## Introduction

We have recently observed a very unusual coordination mode of benzaldehyde thiosemicarbazone (**1**) in a series of ruthenium and osmium complexes.<sup>2</sup> This has led us to explore the coordination chemistry of the benzaldehyde semicarbazones **2**, particularly with reference to the different possible coordination modes of these ligands. However, the present study has been restricted only to ruthenium complexes of the benzaldehyde semicarbazones. It is interesting to note here that though transition-metal complexes of the semicarbazone ligands have received some attention,<sup>3</sup> the ruthenium chemistry of the benzaldehyde semicarbazones appears to have remained completely unexplored. The primary objective of this study has been to synthesize ruthenium complexes of benzaldehyde semicarbazones where the semicarbazone ligands are coordinated in different fashions and where the coordination modes can be controlled chemically. During the course of our studies we have found that the coordination mode of the benzaldehyde semicarbazones is very sensitive toward minor variations in the experimental conditions, the nature of the substituent on the benzaldehyde fragment of the ligand, and the ruthenium starting material. In the four types of complexes synthesized for the present study, we have observed three different coordination



modes of the benzaldehyde semicarbazones: (i) C,N,O-tricoordination (**3**), (ii) N,O-coordination forming a stable five-membered chelate (**4**), and (iii) an unusual four-membered

- (1) (a) Jadavpur University. (b) National Taiwan University.  
 (2) (a) Basuli, F.; Peng, S. M.; Bhattacharya, S. *Inorg. Chem.* **1997**, *36*, 5645. (b) Basuli, F.; Ruf, M.; Pierpont, C. G.; Bhattacharya, S. *Inorg. Chem.* **1998**, *37*, 6113. (c) Basuli, F.; Peng, S. M.; Bhattacharya, S. *Inorg. Chem.* **2000**, *39*, 1120.  
 (3) Padhye, S.; Kauffman, G. B. *Coord. Chem. Rev.* **1985**, *63*, 127.

chelate (**5**) formation as an N,O-donor. An account of the chemistry of all these complexes is described in this paper with special reference to synthesis, structure, and electrochemical properties.

### Experimental Section

**Materials.** Commercial ruthenium trichloride was purchased from Arora Matthey, Calcutta, India, and was converted to  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  by repeated evaporation with concentrated hydrochloric acid. Semicarbazide hydrochloride, benzaldehyde, and para-substituted benzaldehydes were purchased from Merck, India. Triphenylphosphine and formaldehyde were purchased from Spectrochem, India. All other chemicals and solvents were reagent grade commercial materials and were used as received.  $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$  and  $[\text{Ru}(\text{PPh}_3)_2(\text{CO})_2\text{Cl}_2]$  were prepared by following a reported procedure.<sup>4</sup> The semicarbazone ligands were prepared by reacting equimolar amounts of semicarbazide hydrochloride, sodium acetate, and the respective para-substituted benzaldehyde in a 1:1 ethanol–water mixture. The purification of acetonitrile and dichloromethane and the preparation of tetrabutylammonium perchlorate (TBAP) for electrochemical work were performed as before.<sup>5</sup>

**Preparations of Complexes. *trans*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl].** A solution of 4-nitrobenzaldehyde semicarbazone (25 mg, 0.12 mmol) in ethanol (60 mL) was carefully layered over a solution of  $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$  (100 mg, 0.10 mmol) in dichloromethane (20 mL). The solutions were allowed to diffuse slowly (~25 days) to afford single crystals of *trans*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl]. Yield: 70%.

***cis*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl]. Method A.** A finely powdered solid sample of *trans*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl] (100 mg, 0.15 mmol) was placed in a three-necked flask. Dry nitrogen gas was passed through the flask for ~5 min. The solid was then heated at 155 °C (sand bath) under an atmosphere of nitrogen for ~15 min with occasional stirring to afford *cis*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl]. This solid was then cooled to room temperature under nitrogen. The yield was quantitative.

**Method B.** To a suspension of  $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$  (100 mg, 0.10 mmol) in ethanol (40 mL) was added 4-nitrobenzaldehyde semicarbazone (25 mg, 0.12 mmol). The resulting mixture was heated at reflux for 3 h. *cis*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl] started to separate out as a dark microcrystalline solid during the reflux. After the solution was cooled to room temperature, the precipitate was collected by filtration, washed thoroughly with ethanol, and dried in air. Yield: 60%.

**5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl].** These complexes were all prepared by following a general procedure. Specific details are given below for a particular complex.

**5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl].** A solution of 4-nitrobenzaldehyde semicarbazone (30 mg, 0.14 mmol) in ethanol (60 mL) was carefully layered over a solution of  $[\text{Ru}(\text{PPh}_3)_2(\text{CO})_2\text{Cl}_2]$  (100 mg, 0.13 mmol) in dichloromethane (20 mL). The solutions were allowed to diffuse slowly (~30 days) to afford single crystals of 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl]. Yield: 70%.

**4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl].** These complexes were all prepared by following a general procedure. Specific details are given below for a particular complex.

**4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl].** To a hot solution of 4-nitrobenzaldehyde semicarbazone (30 mg, 0.14 mmol) in ethanol (40 mL) was added  $[\text{Ru}(\text{PPh}_3)_2(\text{CO})_2\text{Cl}_2]$  (100 mg, 0.13 mmol). The mixture was refluxed for 24 h to produce an orange solution. On evaporation of the solvent, a yellow residue was obtained, which was purified by chromatography through a silica gel column. Using 1:10 acetonitrile–toluene as the eluent, a yellow band was eluted, which was collected, and evaporation of the eluate gave 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl] as a crystalline yellow solid. Yield: 65%.

**Physical Measurements.** Microanalyses (C, H, N) were performed using a Perkin-Elmer 240C elemental analyzer. IR spectra were obtained on a Perkin-Elmer 783 spectrometer with samples prepared as KBr

**Table 1.** Crystallographic Data for *trans*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl], 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl], and 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl] Complexes

	[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-NO <sub>2</sub> )Cl]	5-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-NO <sub>2</sub> )(CO)Cl]	4-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-NO <sub>2</sub> )(CO)Cl]·0.5CH <sub>2</sub> Cl <sub>2</sub> ·0.75C <sub>6</sub> H <sub>6</sub>
empirical formula	C <sub>44</sub> H <sub>37</sub> N <sub>4</sub> O <sub>3</sub> ·P <sub>2</sub> ClRu	C <sub>45</sub> H <sub>37</sub> ClN <sub>4</sub> O <sub>4</sub> P <sub>2</sub> Ru	C <sub>50</sub> H <sub>42.50</sub> Cl <sub>2</sub> N <sub>4</sub> O <sub>4</sub> P <sub>2</sub> Ru
fw	868.26	896.25	997.29
space group	monoclinic, P2 <sub>1</sub> /c	triclinic, P1̄	triclinic, P1̄
a, Å	9.7178(10)	10.212(2)	16.9298(2)
b, Å	17.4695(23)	13.011(2)	17.6296(2)
c, Å	23.109(3)	17.218(3)	17.9285(1)
α, deg	90	111.17(2)	74.937(1)
β, deg	91.864(12)	91.12(2)	67.473(1)
γ, deg	90	106.337(13)	80.209(1)
V, Å <sup>3</sup>	3921.0(8)	2028.3(6)	4758.00(8)
Z	4	2	4
λ, Å	0.710 73	0.710 73	0.710 73
cryst size, mm	0.50 × 0.45 × 0.40	0.50 × 0.20 × 0.20	0.22 × 0.16 × 0.08
T, K	295	293(2)	295(2)
μ, cm <sup>-1</sup>	5.847	5.80	5.57
R indices	R <sub>F</sub> = 0.036 <sup>a</sup> R <sub>w</sub> = 0.040 <sup>b</sup>	R1 = 0.0297 <sup>c</sup> wR2 = 0.0794 <sup>d</sup>	R1 = 0.0647 <sup>e</sup> wR2 = 0.1538 <sup>f</sup>
GOF	1.26 <sup>e</sup>	1.032 <sup>f</sup>	1.048 <sup>f</sup>

<sup>a</sup>  $R_F = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup>  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$ . <sup>c</sup>  $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>d</sup>  $wR2 = [\sum \{w(F_o^2 - F_c^2)^2\} / \sum \{w(F_o^2)\}]^{1/2}$ . <sup>e</sup>  $GOF = [\sum w(|F_o| - |F_c|)^2 / (M - N)]^{1/2}$ , where  $M$  is the number of reflections and  $N$  is the number of parameters refined. <sup>f</sup>  $GOF = [\sum w(F_o^2 - F_c^2)^2 / (M - N)]^{1/2}$ , where  $M$  is the number of reflections and  $N$  is the number of parameters refined.

pellets. Electronic spectra were recorded on a JASCO V-570 spectrophotometer. Magnetic susceptibilities were measured using a PAR 155 vibrating-sample magnetometer fitted with a Walker Scientific L75FBAL magnet. <sup>1</sup>H NMR spectra were obtained on a Bruker drx500 NMR spectrometer using TMS as the internal standard. The FAB mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using argon/xenon (6 kV, 10 mA) as the FAB gas. Solid-state thermal investigations were carried out with the help of a Shimadzu DT-30 thermal analyzer. Electrochemical measurements were made using a PAR Model 273 potentiostat. A platinum-disk working electrode, a platinum-wire auxiliary electrode, and an aqueous saturated calomel reference electrode (SCE) were used in a three-electrode configuration. Dinitrogen gas was purified by successively bubbling it through alkaline dithionite and concentrated sulfuric acid. All electrochemical experiments were performed under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials. An RE 0089 X-Y recorder was used to trace the voltammograms.

**Crystallography of *trans*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl].** Single crystals of *trans*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl] were obtained by slow diffusion of an ethanol solution of HL-NO<sub>2</sub> into a dichloromethane solution of  $[\text{Ru}(\text{PPh}_3)_3\text{Cl}_2]$ . Selected crystal data and data collection parameters are given in Table 1. The unit cell dimensions were determined by a least-squares fit of 25 centered reflections ( $19.00 \leq \theta \leq 29.60^\circ$ ). Data were collected on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.710 73 \text{ \AA}$ ) by  $\theta$ - $2\theta$  scans with a maximum  $2\theta = 50^\circ$ . Three standard reflections, used to check the crystal stability toward X-ray exposure, showed no significant intensity variation over the course of data collection. X-ray data reduction, structure solution, and refinement were done using the NRCVAX package. The structure was solved by direct methods.

**Crystallography of 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl].** Single crystals of 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl] were obtained by slow diffusion of an ethanol solution of HL-NO<sub>2</sub> into a dichloromethane solution of  $[\text{Ru}(\text{PPh}_3)_2(\text{CO})_2\text{Cl}_2]$ . Selected crystal data and data collection parameters are given in Table 1. Data were collected on a Siemens Smart CCD diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.710 73 \text{ \AA}$ ) by  $\omega$  scans within the angular range  $1.74 < \theta < 24.98^\circ$ .

(4) (a) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 945. (b) Ahmad, A.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1972**, 843.

(5) (a) Sawyer, D. T.; Roberts, J. L., Jr. *Experimental Electrochemistry for Chemists*; Wiley: New York, 1974; pp 167–215. (b) Walter, M.; Ramaley, L. *Anal. Chem.* **1973**, *45*, 165.

**Table 2.** Microanalytical Data for the Complexes

compd	microanal. data <sup>a</sup> (%)		
	C	H	N
<i>trans</i> -[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-NO <sub>2</sub> )Cl]	60.87 (60.86)	4.30 (4.26)	6.43 (6.45)
<i>cis</i> -[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-NO <sub>2</sub> )Cl]	60.64 (60.86)	4.23 (4.26)	6.42 (6.45)
5-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-OMe)(CO)Cl]	62.73 (62.69)	4.53 (4.54)	4.79 (4.77)
5-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-Me)(CO)Cl]	63.88 (63.85)	4.64 (4.63)	4.89 (4.86)
5-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-H)(CO)Cl]	63.51 (63.49)	4.49 (4.47)	4.97 (4.94)
5-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-Cl)(CO)Cl]	61.07 (61.02)	4.19 (4.18)	4.78 (4.74)
5-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-NO <sub>2</sub> )(CO)Cl]	60.32 (60.30)	4.35 (4.32)	6.29 (6.25)
4-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-OMe)(CO)Cl]	62.73 (62.69)	4.55 (4.54)	4.79 (4.77)
4-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-Me)(CO)Cl]	63.87 (63.85)	4.65 (4.63)	4.83 (4.86)
4-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-H)(CO)Cl]	63.52 (63.49)	4.50 (4.47)	4.95 (4.94)
4-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-Cl)(CO)Cl]	61.03 (61.02)	4.20 (4.18)	4.77 (4.74)
4-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-NO <sub>2</sub> )(CO)Cl]	60.32 (60.30)	4.31 (4.32)	6.24 (6.25)

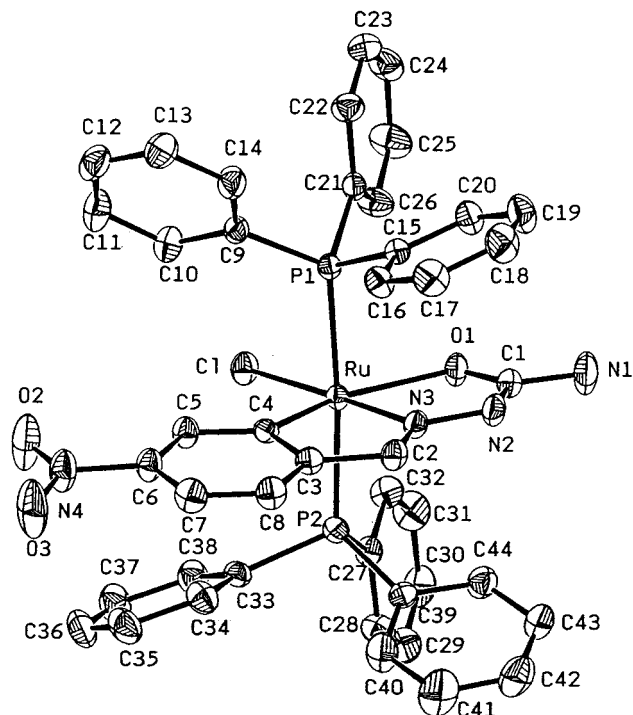
<sup>a</sup> Calculated values are given in parentheses.

X-ray data reduction, structure solution, and refinement were done using the SHELXTL-PLUS package. The structure was solved by direct methods.

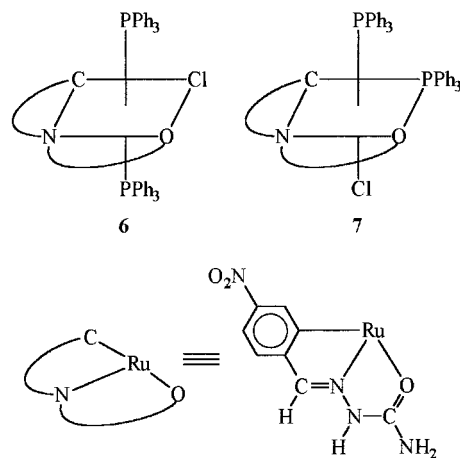
**Crystallography of 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl]·0.5CH<sub>2</sub>Cl<sub>2</sub>·0.75C<sub>6</sub>H<sub>6</sub>.** Single crystals of 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl] were grown by slow diffusion of benzene into a dichloromethane solution of the complex. Selected crystal data and data collection parameters are given in Table 1. Data were collected on a Siemens Smart CCD diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) by  $\omega$  scans within the angular range  $1.20 < \theta < 26.37^\circ$ . X-ray data reduction, structure solution, and refinement were done using the SHELXTL-PLUS package. The structure was solved by direct methods.

## Results and Discussion

**Synthesis and Characterization.** Semicarbazones of five para-substituted benzaldehydes (**2**) have been used in the present study. The ligands are abbreviated in general as HL-R, where H stands for any dissociable proton and R for the para substituent in the benzaldehyde fragment. The reaction of all five ligands has been first carried out with [Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>] in two different ways. However, it has been observed that only one semicarbazone with a strong electron-withdrawing substituent (viz. HL-NO<sub>2</sub>) has afforded a characterizable product from these reactions. This may be attributed to the enhanced acidity of this ligand, which appears to be the primary requirement for such reactions. When an ethanol solution of the semicarbazone ligand (HL-NO<sub>2</sub>) is allowed to diffuse slowly into a solution of [Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>] in dichloromethane at ambient temperature, a reddish brown crystalline product is obtained. Elemental C,H,N analytical data (Table 2) indicate that this complex has the [Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl] composition. Magnetic susceptibility measurements show that it is diamagnetic, which corresponds to the +2 oxidation state of ruthenium (low-spin  $d^6$ ,  $S = 0$ ) in this complex. As ruthenium(II) usually remains hexacoordinated in its complexes, the semicarbazone ligand appears to serve as a monoanionic tridentate ligand in this complex, coordinating to ruthenium as shown in **3**. Thus, the [Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl] complex may exist in the two geo-

**Figure 1.** Structure of *trans*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl].

metrical isomeric forms **6** and **7**, which will be henceforth referred to as the *trans* and *cis* isomers, respectively, with regard to the mutual disposition of the two PPh<sub>3</sub> ligands. To find out



the actual coordination mode of the semicarbazone ligand in this complex and the stereochemistry of this complex as well, its structure has been determined by X-ray crystallography. The structure is shown in Figure 1, and selected bond parameters are listed in Table 3. The semicarbazone ligand is indeed coordinated to ruthenium as a tridentate C,N,O-donor, forming two five-membered chelate rings with bite angles of  $79.88(14)^\circ$  (C–Ru–N) and  $75.98(12)^\circ$  (N–Ru–O). Metalation of the phenyl ring has taken place from the ortho carbon. The semicarbazone ligand, ruthenium, and the chloride are pseudo-planar with the coordinated chloride *trans* to the semicarbazone nitrogen. The two PPh<sub>3</sub> ligands have occupied mutually *trans* positions. Therefore, this complex is the *trans* isomer of [Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl] (**6**). The RuCNOP<sub>2</sub>Cl core is distorted octahedral in nature, as reflected in the bond parameters around ruthenium. Bond distances within the semicarbazone ligand, particularly the C–O bond order ( $1.228(5) \text{ \AA}$ ), together with

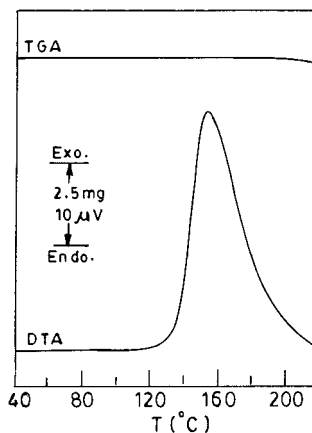


**Table 3.** Selected Bond Distances and Bond Angles for *trans*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl], 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl], and 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl] Complexes

<i>trans</i> -[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-NO <sub>2</sub> )Cl]			
Bond Distances (Å)			
Ru—P(1)	2.3592(11)	O(1)—C(1)	1.228(5)
Ru—P(2)	2.3762(11)	N(1)—C(1)	1.336(5)
Ru—Cl	2.4526(10)	N(2)—N(3)	1.391(4)
Ru—O(1)	2.310(3)	N(2)—C(1)	1.372(6)
Ru—N(3)	1.962(3)	N(3)—C(2)	1.287(5)
Ru—C(4)	2.009(4)	C(2)—C(3)	1.445(6)
		C(3)—C(4)	1.425(5)
Bond Angles (deg)			
P(1)—Ru—P(2)	175.68(4)		
Cl—Ru—N(3)	176.26(10)		
O(1)—Ru—C(4)	155.83(12)		
O(1)—Ru—N(3)	75.98(12)	P(2)—Ru—Cl	86.77(4)
N(3)—Ru—C(4)	79.88(14)	P(2)—Ru—O(1)	93.73(8)
P(1)—Ru—Cl	91.36(4)	P(2)—Ru—N(3)	90.42(10)
P(1)—Ru—O(1)	90.46(8)	P(2)—Ru—C(4)	87.44(11)
P(1)—Ru—N(3)	91.60(10)	Cl—Ru—O(1)	101.72(7)
P(1)—Ru—C(4)	89.71(11)	Cl—Ru—C(4)	102.45(10)
5-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-NO <sub>2</sub> )(CO)Cl]			
Bond Distances (Å)			
Ru—C(1)	1.879(3)	N(1)—C(3)	1.290(3)
Ru—O(2)	2.067(2)	N1—N2	1.382(3)
Ru—N(1)	2.115(2)	N(2)—C(2)	1.328(4)
Ru—P(1)	2.3872(8)	N(3)—C(2)	1.361(4)
Ru—P(2)	2.3896(8)	C(2)—O(2)	1.270(3)
Ru—Cl(1)	2.4015(9)	C(1)—O(1)	1.077(3)
Bond Angles (deg)			
C(1)—Ru—N(1)	170.16(10)		
P(1)—Ru—P(2)	178.17(3)		
O(2)—Ru—Cl(1)	168.76(5)		
O(2)—Ru—N(1)	76.43(18)	N(1)—Ru—Cl(1)	92.34(6)
C(1)—Ru—O(2)	93.73(10)	P(2)—Ru—Cl(1)	90.52(3)
O(2)—Ru—P(1)	89.74(5)	C(1)—Ru—P(1)	88.68(8)
C(1)—Ru—P(2)	89.92(8)	N(1)—Ru—P(1)	91.00(6)
N(1)—Ru—P(2)	90.19(6)	O(2)—Ru—P(2)	89.18(5)
C(1)—Ru—Cl(1)	97.50(9)	P(1)—Ru—Cl(1)	90.83(3)
4-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-NO <sub>2</sub> )(CO)Cl]·0.5CH <sub>2</sub> Cl <sub>2</sub> ·0.75C <sub>6</sub> H <sub>6</sub>			
Bond Distances (Å)			
Ru(1)—C(1)	1.811(5)	O(2)—C(2)	1.297(5)
Ru(1)—O(2)	2.258(3)	N(1)—C(2)	1.327(6)
Ru(1)—P(1)	2.4029(13)	N(2)—C(2)	1.333(6)
Ru(1)—N(2)	2.077(4)	N(2)—N(3)	1.358(5)
Ru(1)—P(2)	2.4038(13)	N(3)—C(3)	1.289(6)
Ru(1)—Cl(1)	2.4235(12)	C(3)—C(4)	1.443(7)
Bond Angles (deg)			
C(1)—Ru(1)—O(2)	164.1(2)		
P(1)—Ru(1)—P(2)	173.27(5)		
N(2)—Ru(1)—Cl(1)	163.56(11)		
C(1)—Ru(1)—N(2)	104.2(2)	O(2)—Ru(1)—Cl(1)	103.23(9)
N(2)—Ru(1)—O(2)	60.33(13)	P(2)—Ru(1)—Cl(1)	89.53(4)
N(2)—Ru(1)—P(1)	88.23(11)	C(1)—Ru(1)—P(1)	93.9(2)
C(1)—Ru(1)—P(2)	92.6(2)	O(2)—Ru(1)—P(1)	89.43(9)
O(2)—Ru(1)—P(2)	83.84(9)	N(2)—Ru(1)—P(2)	88.67(11)
C(1)—Ru(1)—Cl(1)	92.3(2)	P(1)—Ru(1)—Cl(1)	91.77(4)

the presence of the N—H proton clearly indicate that the semicarbazone ligand is bound to ruthenium in the keto form (3). While the Ru—C, Ru—P, and Ru—Cl bond distances are quite normal,<sup>6</sup> the Ru—N bond is a bit shorter, which points to the strong  $\pi$ -interaction between the imine nitrogen and

(6) (a) McGuiggan, M. F.; Pignolet, L. H. *Inorg. Chem.* **1982**, *21*, 2523.  
(b) Fox, G. A.; Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1991**, *30*, 2895.

**Figure 2.** Thermogram of *trans*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl].

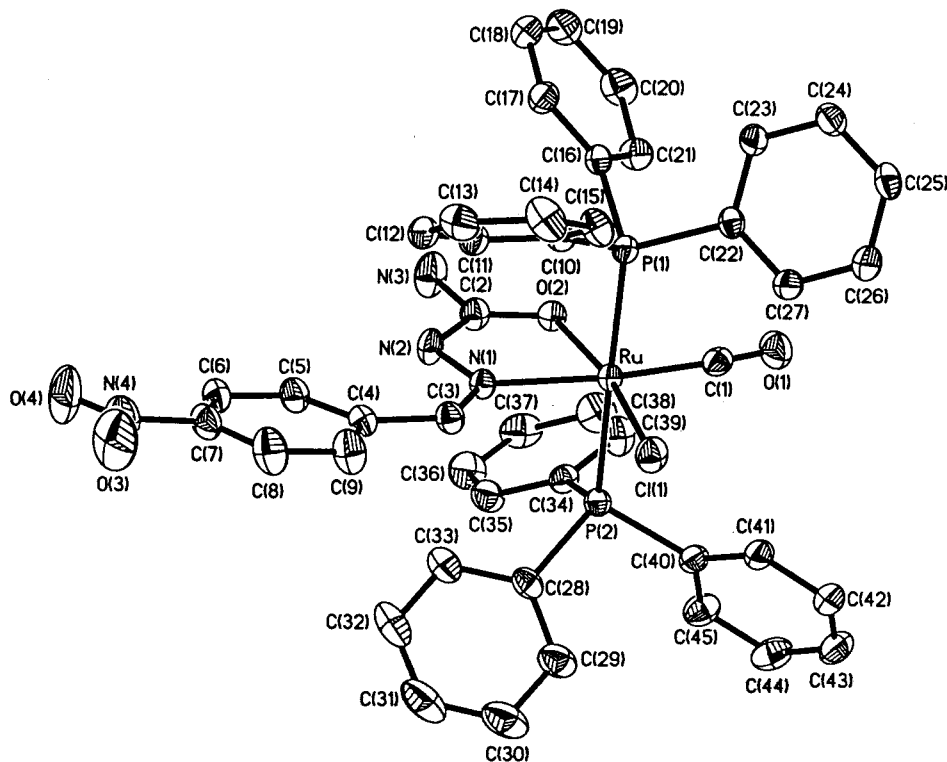
ruthenium.<sup>7</sup> The Ru—O length is noticeably large, indicating the expected weak bonding between the carbonyl oxygen and ruthenium. It may be noted here that such cyclometalation of benzaldehyde semicarbazone appears to be unprecedented in the literature.

In complexes of ruthenium(II) containing the Ru(PPh<sub>3</sub>)<sub>2</sub> fragment, the PPh<sub>3</sub> ligands usually take up mutually cis positions for favorable  $d\pi(\text{Ru})-d\pi(\text{P})$  interactions.<sup>8</sup> The *trans*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl] complex thus appears to be the kinetically controlled product under the rather mild reaction conditions followed for its synthesis. This also points to the possible existence of a thermodynamically stable cis isomer of this complex. To test this hypothesis, the *trans*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl] complex has been subjected to thermogravimetric analysis. An exothermic phase transition has indeed been observed for this complex at 155 °C (Figure 2). This indicates that a thermally induced stereochemical change, which is likely to be a trans to cis isomerization with regard to the relative disposition of the two PPh<sub>3</sub> ligands, must be taking place. Encouraged by this result, the *trans*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl] complex was simply heated at 155 °C to afford a dark solid. This new complex is also found to be diamagnetic, and its microanalytical data agree well with the expected composition, viz. [Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl]. Mass spectra of the complex also support this formulation. The molecular ion (M) is observed at  $m/z$  868, and some other peaks at  $m/z$  833 (M — Cl), 606 (M — PPh<sub>3</sub>), and 571 (M — PPh<sub>3</sub> — Cl) are also observed. The infrared spectrum of this complex is qualitatively similar to that of the *trans*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl] complex. Apart from strong vibrations near 520, 695, and 745  $\text{cm}^{-1}$  due to the Ru(PPh<sub>3</sub>)<sub>2</sub> fragment,<sup>9</sup> each complex shows a  $\nu(\text{N—H})$  stretch near 3200  $\text{cm}^{-1}$ , a  $\nu(\text{C=O})$  stretch near 1650  $\text{cm}^{-1}$ , and a  $\nu(\text{Ru—Cl})$  stretch near 330  $\text{cm}^{-1}$ . Structural characterization of this complex has not been possible because its single crystals could not be grown, even after many attempts. However, from the characterization data it is clear that this complex is the cis isomer of [Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl] (7). To explore the possibility of obtaining the *cis*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl] complex directly from the reaction between the reactants, a reaction of the semicarbazone (HL-NO<sub>2</sub>) with [Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>] has been carried out in refluxing ethanol. The reaction proceeds

(7) Das, A. K.; Rueda, A.; Falvello, L. R.; Peng, S. M.; Bhattacharya, S. *Inorg. Chem.* **1999**, *38*, 4365.

(8) (a) Pramanik, A.; Bag, N.; Lahiri, G. K.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1990**, 3823. (b) Menon, M.; Bag, N.; Chakravorty, A. *J. Chem. Soc., Dalton Trans.* **1995**, 1417.

(9) (a) Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1991**, *30*, 1511. (b) Sinha, P. K.; Falvello, L. R.; Peng, S. M.; Bhattacharya, S. *Polyhedron*, in press.



**Figure 3.** Structure of 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl].

smoothly to afford a dark crystalline solid. Characterizations (elemental analysis, magnetic susceptibility measurement, mass spectrum, and IR spectrum) of this complex show that it is identical with the *cis*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl] complex obtained from the solid-state isomerization reaction. Therefore, the *cis*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl] complex can be obtained directly from the reaction of HL-NO<sub>2</sub> with [Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>] or via the formation of the *trans* isomer.

In the above reactions with [Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>], the semicarbazone ligand (HL-NO<sub>2</sub>) has served as a tridentate C,N,O-donor and proton loss has taken place from the phenyl ring, while the N-H proton has remained intact. This has prompted us to look for a different ruthenium starting material which will undergo complexation by the benzaldehyde semicarbazone but cyclometalation of the phenyl ring of benzaldehyde semicarbazones will not take place and the ligands will be able to function as bidentate N,O-donors via loss of the N-H proton. With this strategy in mind, we planned to try [Ru(PPh<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Cl<sub>2</sub>] as the new starting material because its reactivity pattern is known to be different from that of [Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>].<sup>10</sup> When an ethanol solution of the semicarbazone ligand has been allowed to slowly diffuse into a solution of [Ru(PPh<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Cl<sub>2</sub>] in dichloromethane, crystalline complexes of the type [Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] have been obtained. It may be mentioned here that yields of the R ≠ NO<sub>2</sub> complexes are significantly lower (20–30%) than that of the R = NO<sub>2</sub> complex. Elemental analytical data of the complexes (Table 2) agree well with this composition. The complexes were found to be diamagnetic, indicating the bivalent state of ruthenium. Hence, the semicarbazone ligands must serve as monoanionic bidentate ligands. The structure of a representative complex, viz. [Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl], has been determined by X-ray crystallography in order to find out the coordination mode of the semicarbazone ligand as well as the stereochemistry of these complexes. The structure

is shown in Figure 3, and selected bond parameters are listed in Table 3. The semicarbazone ligand is indeed coordinated to ruthenium as a bidentate N,O-donor, via dissociation of the N-H proton, forming a five-membered chelate ring as shown in **4** with a bite angle of 76.43(18)°. The CO and chloride are respectively *trans* to the nitrogen and oxygen of the semicarbazone. The phosphine ligands have taken up mutually *trans* positions. As mentioned earlier, in complexes of ruthenium(II) having the Ru(PPh<sub>3</sub>)<sub>2</sub> moiety, the PPh<sub>3</sub> ligands always prefer to occupy mutually *cis* positions for better  $\pi$ -interaction. However, in these complexes the presence of CO, which is a stronger  $\pi$ -acid ligand, has probably forced the bulky PPh<sub>3</sub> ligands to take up mutually *trans* positions for steric reasons. The CNOP<sub>2</sub>Cl coordination sphere around ruthenium is distorted octahedral in nature, as reflected in the bond parameters around ruthenium. The Ru-C and C-O bond lengths in the Ru(CO) fragment are quite normal, as observed in structurally characterized carbonyl complexes of ruthenium(II).<sup>11</sup> The Ru-N, Ru-O, Ru-P, and Ru-Cl distances are all quite normal.<sup>6,12</sup> Bond lengths within the five-membered chelate ring indicates that the negative charge, formed upon dissociation of the N-H proton, is delocalized over the O(2)-C(2)-N(2)-N(1) backbone. It is interesting to note here that during the formation of the five-membered chelate ring (**4**), the semicarbazone ligand goes through a conformational change, relative to the free ligand structure (**2**), around the C=N bond. As all the [Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] complexes have been synthesized similarly and they show similar properties (*vide infra*), the other four [Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] complexes are assumed to have a similar structure. This group of complexes will be henceforth referred to as 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] (where 5 stands for the size of the chelate ring) to distinguish them from the other family of linkage isomers of these complexes, which are discussed below.

(10) Seddon, E. A.; Seddon, K. R. *The Chemistry of Ruthenium*; Elsevier: Amsterdam, The Netherlands, 1984.

(11) (a) Yamazaki, H.; Aoki, K. *J. Organomet. Chem.* **1976**, *122*, C54. (b) Clark, G. R. *J. Organomet. Chem.* **1977**, *134*, 51.

(12) Bhattacharya, S.; Pierpont, C. G. *Inorg. Chem.* **1994**, *33*, 6038.

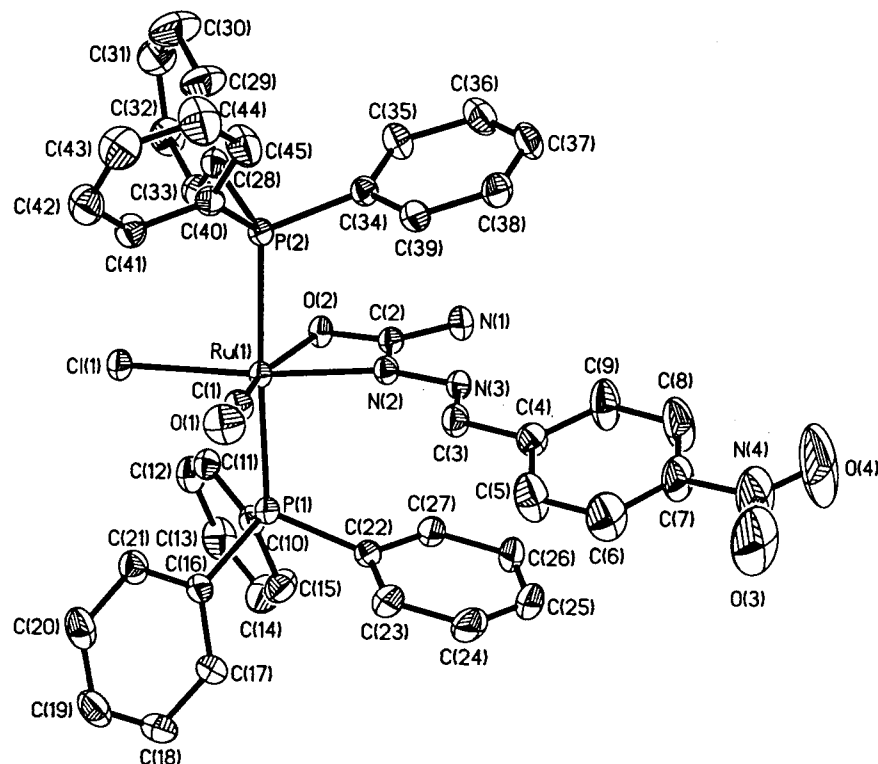


Figure 4. Structure of 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl].

Formation of a five-membered chelate ring by the benzaldehyde semicarbazones is particularly interesting, because similar ring formation by the corresponding thiosemicarbazones has not yet been observed.<sup>2</sup> This has prompted us to modify the synthetic route so that a four-membered ring, analogous to that formed by the benzaldehyde thiosemicarbazone ligands (**1**), can be formed. When [Ru(PPh<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Cl<sub>2</sub>] is reacted with the semicarbazone ligands in refluxing ethanol, complexes of composition identical to that above, viz. [Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl], are obtained. However, properties displayed by these complexes (vide infra) are found to be different from those displayed by the 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] complexes. The composition of these complexes has been established by their microanalytical data (Table 2). These complexes are also diamagnetic, which corresponds to the +2 state of ruthenium in these complexes. Besides a few minor differences, the infrared spectra of these complexes are qualitatively similar to those of their respective 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] analogues. All these preliminary characterization data indicate that these complexes are isomers of the previous group of 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] complexes. To find out the coordination mode of the semicarbazones in these complexes, the structure of [Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl] has been determined by X-ray crystallography. This particular complex was chosen for structural characterization because of the proper comparison of structural data with the previous structure. The structure is shown in Figure 4, and selected bond distances and angles are presented in Table 3. The semicarbazone ligand is coordinated to ruthenium as a bidentate N,O-donor, forming a four-membered chelate ring (as shown in **5**) with a bite angle of 60.33(13)°. The two PPh<sub>3</sub> ligands are again trans. The semicarbazone, ruthenium, CO, and chloride constitute the equatorial plane as before. However, in this complex the CO is trans to the semicarbazone oxygen and the Cl is trans to the semicarbazone nitrogen. While the Ru–P and Ru–Cl distances are not very different from those in the previous structure, the Ru–C, Ru–N, and Ru–O distances are

clearly different. In particular, the Ru–O bond is noticeably longer. The difference in bond lengths within the two chelate rings is attributable to the difference in ring sizes. As all the [Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] complexes belonging to this family have been prepared similarly and they display similar properties (vide infra), the other four complexes are assumed to have a structure similar to that of [Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl], and this second family of [Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl] complexes will henceforth be referred to as 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] to indicate the difference in chelate ring size of the coordinated semicarbazone.

In view of the structure of uncoordinated benzaldehyde semicarbazones (**2**),<sup>13</sup> the four-membered chelate ring formation (**5**) appears quite usual because it does not involve any conformational change in the ligand frame, while the five-membered chelate ring formation (**4**) seems to be less favorable, as it involves restricted rotation around a C=N bond. However, the reaction conditions used for the synthesis of the 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] complexes are rather mild compared to those used for the preparation of the 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] complexes. The observed ease of formation of the thermodynamically less favorable five-membered chelate ring is probably due to kinetic reasons.

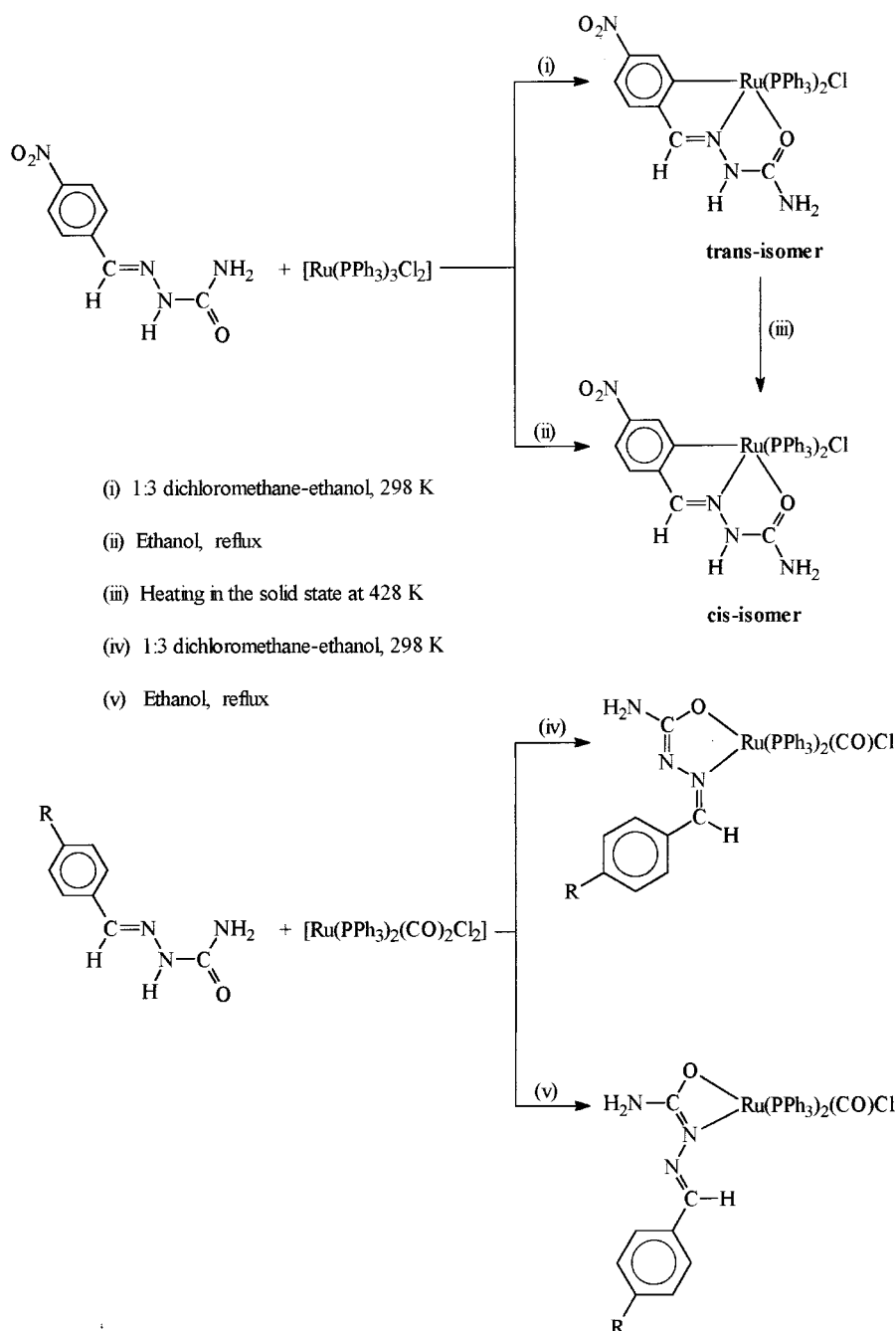
**Solution Properties.** The *trans*- and *cis*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)-Cl] complexes have been observed to undergo chemical transformation in solution, characterized by a gradual change in solution color, and the exact nature of these transformations is not yet clear. This has vitiated their study in solution. The 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] and 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] complexes are stable in solution. <sup>1</sup>H NMR spectra of these complexes, recorded in CDCl<sub>3</sub> solution, show all the expected signals. For example, in 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl] four signals are expected from the coordinated semicarbazone ligand (one singlet (2H) for the NH<sub>2</sub>, one singlet (1H) for the

(13) Naik, D. V.; Palenik, G. J. *Acta Crystallogr., Sect. B* **1974**, *30*, 2396.

**Table 4.** Electronic Spectral and Cyclic Voltammetric Data for the 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] and 4-[[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] Complexes

compd	electronic data <sup>a</sup>	cyclic voltammetric data <sup>b</sup>
	$\lambda_{\max}$ , nm ( $\epsilon$ , M <sup>-1</sup> cm <sup>-1</sup> )	$E_{1/2}$ , V ( $\Delta E_p$ , mV)
5-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-OMe)(CO)Cl]	380 (2400), 308 <sup>c</sup> (7900), 272 <sup>c</sup> (10 700), 234 (20 300)	0.82 (80)
5-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-Me)(CO)Cl]	380 (1500), 304 <sup>c</sup> (7200), 270 <sup>c</sup> (10 000), 224 (22 600)	0.85 (70)
5-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-H)(CO)Cl]	382 (13 100), 306 <sup>c</sup> (13 200), 270 <sup>c</sup> (15 100), 236 (29 100)	0.89 (60)
5-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-Cl)(CO)Cl]	378 (7900), 304 <sup>c</sup> (15 200), 272 <sup>c</sup> (19 000), 234 (39 800)	0.92 (80)
5-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-NO <sub>2</sub> )(CO)Cl]	411 (6600), 266 <sup>c</sup> (20 500), 229 (32 500)	1.07 (60)
4-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-OMe)(CO)Cl]	346 (11 400), 271 (23 500), 232 (36 100)	0.66 (70)
4-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-Me)(CO)Cl]	352 <sup>c</sup> (9100), 341 <sup>c</sup> (9000), 265 <sup>c</sup> (17 100), 212 (52 200)	0.70 (80)
4-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-H)(CO)Cl]	352 <sup>c</sup> (10 200), 269 <sup>c</sup> (24 100), 232 (46 600)	0.73 (60)
4-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-Cl)(CO)Cl]	361 (8600), 271 <sup>c</sup> (25 100), 229 (50 500)	0.75 (70)
4-[Ru(PPh <sub>3</sub> ) <sub>2</sub> (L-NO <sub>2</sub> )(CO)Cl]	448 (11 900), 280 <sup>c</sup> (25 200), 229 (53 700)	0.86 (60)

<sup>a</sup> In dichloromethane solution. <sup>b</sup> Conditions and definitions: solvent, acetonitrile; supporting electrolyte, TBAP; working electrode, platinum; reference electrode, SCE;  $E_{1/2} = 0.5(E_{pa} + E_{pc})$ , where  $E_{pa}$  and  $E_{pc}$  are anodic and cathodic peak potentials;  $\Delta E_p = E_{pa} - E_{pc}$ ; scan rate, 50 mV s<sup>-1</sup>. <sup>c</sup> Shoulder.

**Scheme 1**



azomethine proton, and two doublets (2H each) for the two phenyl protons), and all of them are observed at 3.71, 6.78, 7.81, and 8.08 ppm, respectively. Similarly, in 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl] the same four signals are again expected from the coordinated semicarbazone ligand, which are clearly observed at 4.58, 6.34, 7.11, and 8.05 ppm, respectively. The triphenylphosphine protons are observed as overlapping signals at 7.15–7.60 ppm in 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] and at 7.20–7.85 ppm in 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl]. The 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] and 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] complexes are soluble in common organic solvents such as dichloromethane, chloroform, acetonitrile, etc., producing yellow solutions, except for the R = NO<sub>2</sub> complexes. The solution of the 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl] complex is reddish orange, and that of the 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl] complex is orange. Electronic spectra of both the 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] and 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] complexes have been recorded in dichloromethane solution. All the complexes show intense absorptions in the ultraviolet and visible regions (Table 4). The absorptions in the ultraviolet region are assignable to transitions within the ligand orbitals. The absorptions in the visible region are probably due to metal-to-ligand charge-transfer transitions.

The electrochemical properties of the 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] and 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] complexes were studied in acetonitrile solution (0.1 M TEAP) by cyclic voltammetry. Each complex shows one metal-centered oxidative response on the positive side of the SCE (Table 4). The oxidative response, observed in the range of 0.66–1.07 V (all potentials are referenced to SCE), is assigned to the ruthenium(II)–ruthenium(III) oxidation. This oxidation is reversible, with a peak-to-peak separation of 60–80 mV, and the anodic peak current ( $i_{pa}$ ) is almost equal to the cathodic peak current ( $i_{pc}$ ). The one-electron nature of this oxidation has been established by comparing its current height with that of the standard ferrocene/ferrocenium couple under identical experimental conditions. Potentials of the ruthenium(II)–ruthenium(III) oxidation in both the 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] and 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] complexes are found to be sensitive to the nature of the substituent R in the semicarbazone ligands. The potentials increase with increasing electron-withdrawing character of R, and the plots of the oxidation potentials vs Hammett substituent constants ( $\sigma$ ) of R<sup>14</sup> ( $\sigma$  values of the substituents: OMe, –0.27; Me, –0.17; H, 0.00; Cl, 0.23; NO<sub>2</sub>, 0.78) are linear. The slopes of these lines, which are known as the reaction constants ( $\rho$ )<sup>15</sup> and are a

measure of the sensitivity of the oxidation potentials to R, are respectively 0.23 for the 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] complexes and 0.18 for the 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] complexes. It is interesting to note here that the substituent has a greater influence on the oxidation potential in the 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] complexes, where it is seven bonds away from ruthenium, than in the 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] complexes, where it is eight bonds away from ruthenium. It is also interesting to note that a single substituent which is seven or eight bonds away from the electroactive metal center can still influence the metal-centered redox potentials in a predictable manner.

## Conclusions

This present study shows that the coordination mode of benzaldehyde semicarbazone and the stereochemistry of its complexes are noticeably sensitive toward several experimental parameters. This has been reflected in the reaction of the benzaldehyde semicarbazones with [Ru(PPh<sub>3</sub>)<sub>3</sub>Cl<sub>2</sub>] and [Ru(PPh<sub>3</sub>)<sub>2</sub>(CO)<sub>2</sub>Cl<sub>2</sub>] under different experimental conditions, which is summarized in Scheme 1.

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**Supporting Information Available:** Figures giving the mass spectrum of *cis*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl], electronic spectra of 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-Me)(CO)Cl] and 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-Me)(CO)Cl], cyclic voltammograms of 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl] and 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl], and a least-squares plot of Ru(II)–Ru(III) potentials vs  $\sigma$  for 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] and 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-R)(CO)Cl] and tables containing crystal data and details of structure determination, atomic coordinates, anisotropic thermal parameters, and bond distances and angles for *trans*-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)Cl], 5-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl], and 4-[Ru(PPh<sub>3</sub>)<sub>2</sub>(L-NO<sub>2</sub>)(CO)Cl]·0.5CH<sub>2</sub>Cl<sub>2</sub>·0.75H<sub>2</sub>O. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (14) Hammett, L. P. *Physical Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1970.
- (15) Mukherjee, R. N.; Rajan, O. A.; Chakravorty, A. *Inorg. Chem.* **1982**, *21*, 785.