

Unprecedented Chemical Transformation of Semicarbazones Mediated by Wilkinson's Catalyst

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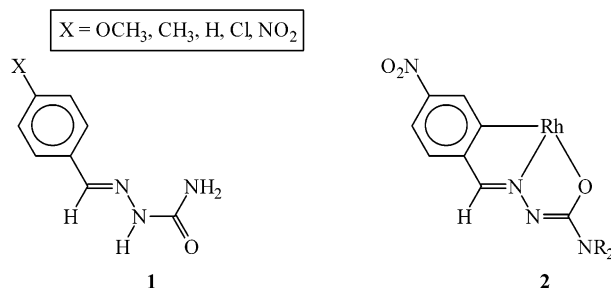
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para-Nitrobenzaldehyde semicarbazone undergoes an unusual chemical transformation upon reaction with [Rh(PPh₃)₃Cl] in the presence of trialkyl and dialkylamines (NR₂R'; R = Et, ⁱPr, ⁿBu; R' = H or R' = R) via dissociation of the C–NH₂ bond and formation of a new C–NR₂ bond (where the NR₂ fragment is provided by the amine). The transformed semicarbazone ligand binds to rhodium as a dianionic C,N,O-donor to afford complexes of type [Rh(PPh₃)₂(CNO–NR₂)Cl] (CNO–NR₂ = the coordinated semicarbazone ligand). Another group of semicarbazones (viz. salicylaldehyde semicarbazone, 2-hydroxyacetophenone semicarbazone, and 2-hydroxynaphthaldehyde semicarbazone) has also been observed to undergo a similar chemical transformation upon reaction with [Rh(PPh₃)₃Cl] under similar experimental conditions as before, and these transformed semicarbazones bind to rhodium as dianionic O,N,O-donors affording complexes of the type [Rh(PPh₃)₂(ONOⁿ–NR₂)Cl] (ONOⁿ–NR₂ = the coordinated semicarbazone ligand; *n* = 1–3). The structure of the [Rh(PPh₃)₂(CNO–NEt₂)Cl] and [Rh(PPh₃)₂(ONO²–NR₂)Cl] complexes has been determined. All the complexes show characteristic ¹H NMR signals. They also show intense absorptions in the visible and ultraviolet region. Cyclic voltammetry on the complexes shows an oxidative response within 0.52–0.97 V versus SCE and a reductive response within –1.00 to –1.27 V versus SCE, where both the responses are believed to be centered on the semicarbazone ligand.

Introduction

There has been considerable interest in the chemistry of transition metal complexes of the semicarbazone and thiosemicarbazone ligands, primarily because of their bioinorganic relevance² and particularly because of their potentially beneficial biological (viz. antibacterial, antimalarial, antiviral, and antitumor) activities.³ However, we have been studying chemistry of the platinum metal complexes of the semicarbazone and thiosemicarbazone ligands with special reference to the variable coordination modes displayed by these

ligands,⁴ and the present report has emerged from this continuous study. For this work, a group of five semicarbazones of *para*-substituted benzaldehydes (**1**) have been chosen as the principal ligand, and rhodium has been selected as the metal.



Our recent studies on the ruthenium complexes of these ligands have shown that they can bind to the metal as a bidentate N,O-donor and, depending on the experimental

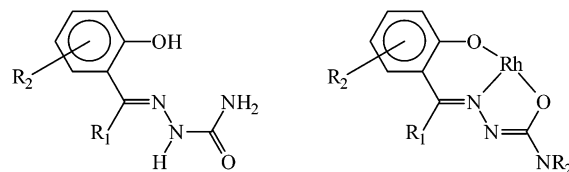
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conditions, afford either four- or five-membered chelate rings.^{4c} The *para*-nitrobenzaldehyde semicarbazone (**1**, X = NO₂) can also coordinate to ruthenium as a tridentate C,N,O-donor affording organometallic complexes.^{4c} Similar C,N,O-tricoordination by such ligands was also observed by others.⁵ The facile formation of organometallic complexes by the benzaldehyde semicarbazones has encouraged us to explore the possibility of synthesizing organorhodium complexes of these ligands, and the Wilkinson's catalyst, viz. [Rh(PPh₃)₃Cl], has been chosen as the rhodium starting material for this purpose because of its ability, as we have already experienced, to form organometallic complexes with C,N,O-donor ligands.⁶ Reaction of [Rh(PPh₃)₃Cl] has been carried out with all five benzaldehyde semicarbazones (**1**) in the presence of a base (NR₂R', R = Et, ⁱPr, ⁿBu; R' = R, H). However, only the reaction with *para*-nitrobenzaldehyde semicarbazone has afforded a family of interesting organorhodium complexes,⁷ where the semicarbazone ligand has been found to undergo an unusual chemical transformation via dissociation of the C–NH₂ bond and formation of a new C–NR₂ bond (where the NR₂ fragment is provided by the base). The transformed ligand remains bound to rhodium(III) as a dianionic tridentate C,N,O-donor (**2**) affording organorhodium complexes of type [Rh(PPh₃)₂(CNO–NR₂)Cl] (where CNO–NR₂ refers to the coordinated ligand in **2**).

In order to check the generality, if any, of the described

transformation, a second group of three potentially tridentate semicarbazones (**3**; viz. salicylaldehyde semicarbazone, 2-hydroxyacetophenone semicarbazone, and 2-hydroxynaphthaldehyde semicarbazone) have been allowed to react with [Rh(PPh₃)₃Cl] under similar experimental conditions. These new semicarbazones have also been observed to undergo similar chemical transformation as before and bind to rhodium(III) as a dianionic tridentate O,N,O-donor (**4**) affording complexes of type [Rh(PPh₃)₂(ONO[–]–NR₂)Cl] (where ONO[–]–NR₂ stands for the coordinated ligand in **4**). The



R ₁	R ₂	R ₁	R ₂	Coordinated Ligand
H	H	H	H	ONO ¹ -NR ₂
CH ₃	H	CH ₃	H	ONO ² -NR ₂
H	5,6-benzo	H	5,6-benzo	ONO ³ -NR ₂
3		4		

chemistry of the [Rh(PPh₃)₂(CNO–NR₂)Cl] and [Rh(PPh₃)₂(ONO[–]–NR₂)Cl] complexes is reported in this paper with special reference to their formation, structure, and electrochemical properties.

Experimental Section

Materials. Rhodium trichloride was obtained from Arora Matthey, Kolkata, India. Triethylamine, diethylamine, tri-*n*-butylamine, and diisopropylamine were purchased from Aldrich. All other chemicals and solvents were reagent grade commercial materials and were used as received. [Rh(PPh₃)₃Cl] was synthesized by following a reported procedure.⁸ The semicarbazone ligands were prepared by reacting equimolar amounts of semicarbazide hydrochloride, sodium acetate, and the respective aldehyde or ketone in 1:1 ethanol–water mixture. Purification of dichloromethane and acetonitrile and preparation of tetrabutylammonium perchlorate (TBAP) for electrochemical work were performed as before.⁹

Preparation of Complexes. [Rh(PPh₃)₂(CNO–NEt₂)Cl], *para*-Nitrobenzaldehyde semicarbazone (23 mg, 0.11 mmol) was taken in toluene (40 mL) and to it was added triethylamine (70 mg, 0.70 mmol).¹⁰ The flask was purged with a stream of nitrogen for 10 min. Then, [Rh(PPh₃)₃Cl] (100 mg, 0.11 mmol) was added, and the mixture was heated at reflux under a nitrogen atmosphere for 6 h to yield an orange solution. Evaporation of this solution gave a yellowish-orange solid, which was subjected to purification by thin-layer chromatography on a silica plate. With benzene as the eluant (**CAUTION!** Benzene is carcinogenic.), an orange band separated, which was extracted with acetonitrile, and evaporation of this extract gave [Rh(PPh₃)₂(CNO–NEt₂)Cl] as a crystalline orange solid. Yield: 75%.

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(10) Addition of an equivalent quantity of diethylamine (NH₂Et₂) also gave the same product.

The other two $[\text{Rh}(\text{PPh}_3)_2(\text{CNO}-\text{NR}_2)\text{Cl}]$ ($\text{R} = \text{}^i\text{Pr}$ and $\text{}^n\text{Bu}$) complexes were prepared by following the same procedure using, respectively, diisopropylamine and tri-*n*-butylamine instead of triethylamine. The yield was 72% for the $\text{R} = \text{}^i\text{Pr}$ complex and 78% for the $\text{R} = \text{}^n\text{Bu}$ complex.

$[\text{Rh}(\text{PPh}_3)_2(\text{ONO}^1-\text{NEt}_2)\text{Cl}]$. Salicylaldehyde semicarbazone (30 mg, 0.17 mmol) was taken in toluene (40 mL) and to it was added triethylamine (90 mg, 0.90 mmol).¹⁰ The flask was purged with a stream of nitrogen for 10 min. Then, $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ (100 mg, 0.11 mmol) was added, and the mixture was heated at reflux under a nitrogen atmosphere for 8 h to yield an orange solution. Evaporation of this solution gave a yellowish-orange solid, which was subjected to purification by thin-layer chromatography on a silica plate. Using 10:1 benzene–acetonitrile as the eluant, a yellowish-orange band separated, which was extracted with 1:1 dichloromethane–acetonitrile. Upon evaporation of this extract, beautiful yellowish-orange crystals were obtained. As these crystals were found to contain the $[\text{Rh}(\text{PPh}_3)_2\text{Cl}_2]$ complex in addition to $[\text{Rh}(\text{PPh}_3)_2(\text{ONO}^1-\text{NEt}_2)\text{Cl}]$ (vide infra), they were again dissolved in dichloromethane and purified for the second time by thin-layer chromatography on a silica plate. Using only benzene as the eluant, a minor yellow band moved first followed by a major orange band. The orange band was extracted with acetonitrile, and evaporation of this extract gave $[\text{Rh}(\text{PPh}_3)_2(\text{ONO}^1-\text{NEt}_2)\text{Cl}]$ as an orange solid. Yield: 52%.

The other $[\text{Rh}(\text{PPh}_3)_2(\text{ONO}^n-\text{NR}_2)\text{Cl}]$ complexes were prepared by following the same procedure using the appropriate semicarbazone and amine ($\text{NR}_2\text{R}'$) instead of salicylaldehyde semicarbazone and triethylamine, respectively. Each complex was purified by chromatography twice as described. Yields varied in the range 50–55%.

Physical Measurements. Microanalyses (C, H, N) were performed using a Heraeus Carlo Erba 1108 elemental analyzer. IR spectra were obtained on a Shimadzu FTIR-8300 spectrometer with samples prepared as KBr 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. ^1H NMR spectra were recorded in CDCl_3 solution on either a Bruker DRX 500 or a Bruker Avance DPX 300 NMR spectrometer using TMS as the internal standard. Electrochemical measurements were made using a CH Instruments model 600A electrochemical analyzer. 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. All electrochemical experiments were performed under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

Crystallography of $[\text{Rh}(\text{PPh}_3)_2(\text{CNO}-\text{NEt}_2)\text{Cl}]$. Single crystals of $[\text{Rh}(\text{PPh}_3)_2(\text{CNO}-\text{NEt}_2)\text{Cl}]$ were obtained by slow evaporation of an acetonitrile solution of the complex. Selected crystal data and data collection parameters are given in Table 1. Data were collected on an Enraf Nonius CAD-4 diffractometer using graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) by $\theta-2\theta$ scans ($1.78^\circ < \theta < 22.50^\circ$). X-ray data reduction and structure solution and refinement were done using the SHELXS-97 and SHELXL-97 programs.¹¹ The structure was solved by direct methods.

Crystallography of $[\text{Rh}(\text{PPh}_3)_2(\text{ONO}^2-\text{NEt}_2)\text{Cl}]$. Single crystals of $[\text{Rh}(\text{PPh}_3)_2(\text{ONO}^2-\text{NEt}_2)\text{Cl}]$ were obtained by slow evapora-

Table 1. Crystallographic Data for $[\text{Rh}(\text{PPh}_3)_2(\text{CNO}-\text{NEt}_2)\text{Cl}]$ and $[\text{Rh}(\text{PPh}_3)_2(\text{ONO}^2-\text{NEt}_2)\text{Cl}]$

empirical formula	$\text{C}_{50}\text{H}_{47}\text{ClN}_5\text{O}_3\text{P}_2\text{Rh}$	$\text{C}_{134}\text{H}_{124}\text{Cl}_4\text{N}_6\text{O}_4\text{P}_6\text{Rh}_3$
fw	965.41	2518.74
space group	monoclinic, $I2/a$	triclinic, $P\bar{1}$
$a, \text{ \AA}$	24.288(5)	12.1627(1)
$b, \text{ \AA}$	17.010(5)	16.4398(2)
$c, \text{ \AA}$	25.114(5)	16.5077(2)
$\alpha, \text{ deg}$	90.00(5)	112.3859(5)
$\beta, \text{ deg}$	114.370(5)	105.4037(4)
$\gamma, \text{ deg}$	90.00(5)	90.9540(5)
$V, \text{ \AA}^3$	9451(4)	2916.56(6)
Z	4	1
$\lambda, \text{ \AA}$	0.71069	0.71073
crystal size, mm^3	$0.20 \times 0.20 \times 0.20$	$0.10 \times 0.10 \times 0.07$
$T, \text{ K}$	293	150
$\mu, \text{ mm}^{-1}$	0.532	0.652
$R1^a$	0.0860	0.0530
$wR2^b$	0.1666	0.1268
GOF^c	1.086	1.040

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

tion of the 1:1 dichloromethane–acetonitrile extract obtained from the first chromatographic purification of the complex (see synthetic procedure). Selected crystal data and data collection parameters are given in Table 1. Data were collected on a Nonius Kappa CCD diffractometer using graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) by ϕ and ω scans ($1.75^\circ < \theta < 27.50^\circ$). X-ray data reduction and structure solution and refinement were done as already stated. These crystals were found to contain a square planar $[\text{Rh}(\text{PPh}_3)_2\text{Cl}_2]$ complex molecule per two molecules of the $[\text{Rh}(\text{PPh}_3)_2(\text{ONO}^2-\text{NEt}_2)\text{Cl}]$ complex. As the observed structural parameters for the $[\text{Rh}(\text{PPh}_3)_2\text{Cl}_2]$ fragment compare well with those reported earlier,¹² the structural discussion in the text includes only the $[\text{Rh}(\text{PPh}_3)_2(\text{ONO}^2-\text{NEt}_2)\text{Cl}]$ complex.

Results and Discussion

Reaction of $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ was carried out with all the semicarbazones (**1**) in refluxing toluene in the presence of NEt_3 . However, only the reaction with *para*-nitrobenzaldehyde semicarbazone proceeded smoothly to afford an orange complex in decent yield.⁷ Preliminary characterizations (microanalysis, IR, and NMR) on this complex failed to indicate any unambiguous formulation for it. Identity of the complex has been revealed by its structure determination by X-ray crystallography. The structure is displayed in Figure 1, and selected bond parameters are listed in Table 2. The structure shows that during the course of the synthetic reaction the *para*-nitrobenzaldehyde semicarbazone has undergone an interesting chemical transformation, viz. the NH_2 group of the semicarbazone has been replaced by a NEt_2 group provided by the base (NEt_3). The modified semicarbazone is coordinated to rhodium, via dissociation of two protons, as a dianionic C,N,O-donor ligand. Ortho-metalation has taken place from the phenyl ring of the modified semicarbazone. Two triphenylphosphines and a chloride are also bound to the metal center. This complex is therefore formulated as $[\text{Rh}(\text{PPh}_3)_2(\text{CNO}-\text{NEt}_2)\text{Cl}]$, where $\text{CNO}-\text{NEt}_2$ represents the coordinated semicarbazone. The

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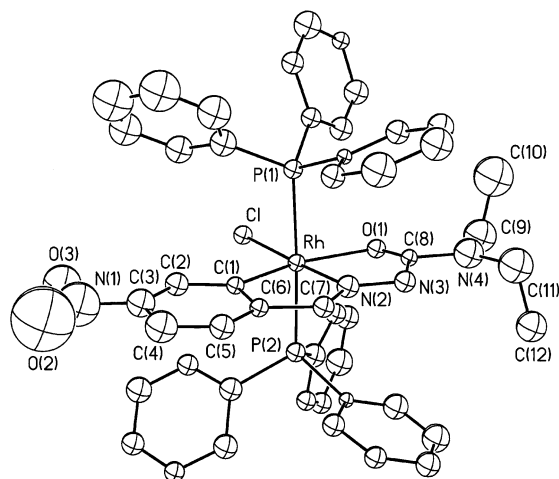


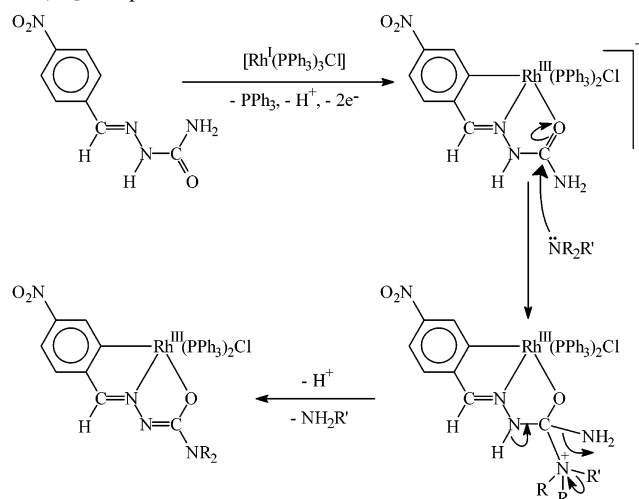
Figure 1. View of the $[\text{Rh}(\text{PPh}_3)_2(\text{CNO}-\text{NEt}_2)\text{Cl}]$ complex.

Table 2. Selected Bond Distances and Bond Angles for $[\text{Rh}(\text{PPh}_3)_2(\text{CNO}-\text{NEt}_2)\text{Cl}]$ and $[\text{Rh}(\text{PPh}_3)_2(\text{ONO}^2-\text{NEt}_2)\text{Cl}]$

$[\text{Rh}(\text{PPh}_3)_2(\text{CNO}-\text{NEt}_2)\text{Cl}]$			
Bond Distances (Å)			
Rh–C(1)	1.989(12)	Rh–O(1)	2.189(9)
Rh–P(1)	2.371(3)	Rh–P(2)	2.360(3)
Rh–Cl	2.381(4)	Rh–N(2)	1.968(10)
C(7)–N(2)	1.328(15)	N(2)–N(3)	1.351(14)
C(8)–N(3)	1.35(2)	C(8)–O(1)	1.26(2)
C(8)–N(4)	1.384(19)	C(9)–N(4)	1.47(2)
C(11)–N(4)	1.43(2)		
Bond Angles (deg)			
P(2)–Rh–P(1)	177.61(14)	N(2)–Rh–C(1)	83.1(5)
N(2)–Rh–Cl(1)	177.2(2)	N(2)–Rh–O(1)	76.3(5)
C(1)–Rh–O(1)	159.4(5)		
$[\text{Rh}(\text{PPh}_3)_2(\text{ONO}^2-\text{NEt}_2)\text{Cl}]$			
Bond Distances (Å)			
Rh(1)–N(1)	1.974(3)	Rh(1)–O(1)	1.996(2)
Rh(1)–O(2)	2.034(2)	Rh(1)–P(1)	2.3833(11)
Rh(1)–P(2)	2.3786(10)	Rh(1)–Cl(1)	2.3795(10)
O(1)–C(1)	1.324(4)	C(7)–N(1)	1.306(5)
N(1)–N(2)	1.398(4)	C(9)–N(2)	1.340(5)
C(9)–O(2)	1.303(5)	C(9)–N(3)	1.358(5)
C(10)–N(3)	1.364(6)	C(12)–N(3)	1.460(6)
Bond Angles (deg)			
P(1)–Rh(1)–P(2)	177.79(4)	N(1)–Rh(1)–O(1)	95.18(12)
N(1)–Rh(1)–Cl(1)	173.37(10)	N(1)–Rh(1)–O(2)	80.78(12)
O(1)–Rh(1)–O(2)	175.41(10)		

CNOP_2Cl coordination sphere around rhodium is a distorted octahedron, as reflected in all the bond parameters around the metal center. The tricoordinated semicarbazone, rhodium, and chloride have constituted one equatorial plane, and the two PPh_3 ligands have taken up the axial positions and, hence, they are mutually trans. The Rh–C, Rh–N, Rh–P, and Rh–Cl distances are all quite normal, as usually observed in complexes of rhodium(III) containing these bonds.^{6,13} However, the Rh–O(1) length is a bit longer than usual.^{13b,14} The observed C(8)–O(1) distance is intermediate between C=O and C–O. The C(8)–N(3) distance similarly indicates a bond order which is between a single and double

Scheme 1. Probable Steps in the Formation of the $[\text{Rh}(\text{PPh}_3)_2(\text{CNO}-\text{NR}_2)\text{Cl}]$ Complexes



bond. The observed intermediacy in bond orders in the O(1)–C(8)–N(3) fragment is attributable to the possible charge delocalization over this fragment.

The observed chemical transformation of *para*-nitrobenzaldehyde semicarbazone is not only unusual but also, to our knowledge, unprecedented. Encouraged by this result, reaction of the *para*-nitrobenzaldehyde semicarbazone with $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ was also carried out in the presence of another trialkylamine (N^nBu_3) and two dialkylamines (NHR_2 , R = Et, ^iPr) in order to check whether the semicarbazone reacts with these amines and undergoes a similar transformation. Each of these reactions indeed gave the expected complex of type $[\text{Rh}(\text{PPh}_3)_2(\text{CNO}-\text{NR}_2)\text{Cl}]$ (R = Et, ^iPr , ^nBu). It is interesting to note here that the same $[\text{Rh}(\text{PPh}_3)_2(\text{CNO}-\text{NEt}_2)\text{Cl}]$ complex is obtained using diethylamine or triethylamine. Elemental (C, H, N) analytical data of all these complexes agree well with their formulations (Table S1). As all the $[\text{Rh}(\text{PPh}_3)_2(\text{CNO}-\text{NR}_2)\text{Cl}]$ complexes have been prepared by following similar procedures and as they show similar properties (*vide infra*), the other two $[\text{Rh}(\text{PPh}_3)_2(\text{CNO}-\text{NR}_2)\text{Cl}]$ (R = ^iPr , ^nBu) complexes are assumed to have a similar structure as $[\text{Rh}(\text{PPh}_3)_2(\text{CNO}-\text{NEt}_2)\text{Cl}]$.

The mechanism of the interesting chemical transformation of *para*-nitrobenzaldehyde semicarbazone is not completely clear to us. However, that the observed transformation has been mediated by the metal center is apparent from the fact that treatment of the *para*-nitrobenzaldehyde semicarbazone with the base ($\text{NR}_2\text{R}'$) alone in refluxing toluene (for 6 h) failed to bring about any such transformation. The sequences illustrated in Scheme 1 thus seem probable. In the initial step, the semicarbazone coordinates to trivalent rhodium as a monoanionic C,N,O-donor via loss of one phenyl proton. This particular coordination mode of the *para*-nitrobenzaldehyde semicarbazone was observed in its ruthenium complex.^{4c} However, isolation of this intermediate has not been possible in the present case. Nucleophilic attack by the amine ($\text{NR}_2\text{R}'$) at the carbonyl carbon then takes place, which is believed to be the crucial step. The carbonyl carbon in the uncoordinated ligand (**1**) is similar to that in urea, and hence, it does not appear to be electropositive enough so as

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Table 3. ^1H NMR Data of the Complexes

compd	chemical shift in ppm			
	PPh ₃	semicarbazone		
		aromatic proton ^a	azomethine proton	R
[Rh(PPh ₃) ₂ (CNO–NEt ₂)Cl]	7.17–7.56	6.60(d, 8), 7.46(d, 8), 7.91(s)	6.56	0.76, 2.99
[Rh(PPh ₃) ₂ (CNO–N ⁱ Pr ₂)Cl]	7.21–7.55	6.59(d, 8), 7.83(s)	6.50	0.87
[Rh(PPh ₃) ₂ (CNO–N ^t Bu ₂)Cl]	7.22–7.54	6.57(d, 8), 7.91(s)	6.54	0.87, 1.08, 2.76, 2.94
[Rh(PPh ₃) ₂ (ONO ¹ –NEt ₂)Cl]	7.21–7.67	6.03(t, 7), 6.09(d, 7), 6.66(d, 8), 6.74(t, 7)	6.52	0.60, 2.91
[Rh(PPh ₃) ₂ (ONO ¹ –N ⁱ Pr ₂)Cl]	7.21–7.64	6.03(t, 6), 6.11(d, 7), 6.66(d, 9), 6.73(t, 8)	6.50	0.90, 1.08
[Rh(PPh ₃) ₂ (ONO ¹ –N ^t Bu ₂)Cl]	7.20–7.73	6.04(t, 6), 6.10(d, 6), 6.66(d, 8), 6.74(t, 7)	6.48	0.81, 0.97, 2.83
[Rh(PPh ₃) ₂ (ONO ² –NEt ₂)Cl]	7.20–7.64	6.09(qn, 4), 6.56(d, 8), 6.70(d, 4)	1.81 ^b	0.61, 2.93
[Rh(PPh ₃) ₂ (ONO ² –N ⁱ Pr ₂)Cl]	7.19–7.70	6.09(qn, 4), 6.56(d, 8), 6.70(d, 4)	1.80 ^b	0.87, 1.06
[Rh(PPh ₃) ₂ (ONO ² –N ^t Bu ₂)Cl]	7.20–7.75	6.09(qn, 4), 6.57(d, 8), 6.70(d, 3)	1.79 ^b	0.85, 0.93, 2.84
[Rh(PPh ₃) ₂ (ONO ³ –NEt ₂)Cl]	7.13–7.70	6.84(d, 9), 7.01(t, 7), 7.40(t, 8)		0.67, 2.92
[Rh(PPh ₃) ₂ (ONO ³ –N ⁱ Pr ₂)Cl]	7.07–7.63	6.84(d, 9), 7.01(t, 7), 7.40(t, 8)		0.79
[Rh(PPh ₃) ₂ (ONO ³ –N ^t Bu ₂)Cl]	7.13–7.73	6.84(d, 9), 7.02(t, 7), 7.40(t, 8)		0.85, 1.06, 2.86

^a Multiplicity (s = singlet, d = doublet, t = triplet, qn = quintet) of the signal and the coupling constant (in Hz) are given in parentheses. ^b Methyl signal.

to initiate an attack by the amine (NR₂R'). Coordination of the semicarbazone ligand to trivalent rhodium as a monoanionic C,N,O-donor in the first step must have enhanced the electrophilicity of the carbonyl carbon to such an extent that it undergoes facile attack by the nucleophile (NR₂R'). The nitro group in the phenyl ring also appears to play a vital role in this reaction. Being a strong electron-withdrawing group, it enhances dissociability of the phenyl protons and thus favors formation of the Rh–C bond, which is also responsible, to some extent, for increasing the electropositive nature of the carbonyl carbon. Indirect evidence of the influence of the nitro group comes from the fact that reactions of [Rh(PPh₃)₃Cl] with semicarbazones of other *para*-substituted benzaldehydes (**1**, X ≠ NO₂), where the substituent is less electron-withdrawing than the nitro group (e.g., OCH₃, CH₃, H, and Cl), do not afford a similar product.⁷ Thus, the observed transformation of the *para*-nitrobenzaldehyde semicarbazone appears to be directed by the combined influence of the nitro group in it and its coordination to rhodium(III) in the initial step.

All the [Rh(PPh₃)₂(CNO–NR₂)Cl] complexes are diamagnetic, which corresponds to the trivalent state of rhodium (low-spin d⁶, S = 0) in these complexes. ^1H NMR spectra of these complexes show all the expected signals (Table 3). The signals from the phenyl protons of the PPh₃ ligands are observed as broad signals within 7.1–7.6 ppm. The azomethine proton signal is observed near 6.5 ppm. Among the three expected aromatic proton signals (one singlet and two doublets) from the nitro–phenyl ring of the CNO–NR₂ ligand, two (one singlet and one doublet) are clearly observed within 6.57–7.91 ppm in all the three complexes, while the third (doublet) signal is observed in only one complex. It could not be detected in the other two complexes because of its overlap with the PPh₃ signals. Signals for the alkyl groups of the NR₂ fragment of the CNO–NR₂ ligands are also observed as broad peaks in the expected region. The ^1H NMR spectral data of the [Rh(PPh₃)₂(CNO–NR₂)Cl] complexes are therefore consistent with their compositions.

Infrared spectra of the [Rh(PPh₃)₂(CNO–NR₂)Cl] complexes show sharp bands near 745, 695, and 520 cm⁻¹ due

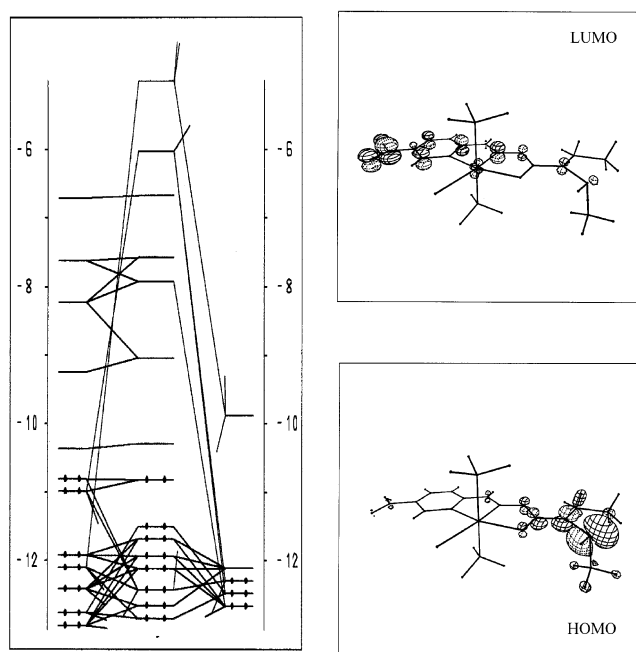
to the coordinated PPh₃ ligands.^{4a,6,15} Strong bands are also observed near 1434, 1411, 1329, 1306, 1280, 1227, 1190, and 1094 cm⁻¹ in all these complexes, which are absent in the infrared spectrum of [Rh(PPh₃)₃Cl], and hence, these bands are attributed to the coordinated semicarbazone ligand. Electronic spectra of the [Rh(PPh₃)₂(CNO–NR₂)Cl] complexes have been recorded in dichloromethane solution. Each complex uniformly shows three intense absorptions, two in the visible region and one in the ultraviolet region (Table 4). The absorption in the ultraviolet region is believed to be due to a transition within the ligand orbitals. Among the two absorptions in the visible region, the higher energy transition (near 380 nm) is relatively less intense, while the lower energy transition (near 490 nm) is much more intense. To have an insight into the nature of transitions in the visible region, qualitative EHMO calculations have been performed¹⁶ on computer generated models of the [Rh(PPh₃)₂(CNO–NR₂)Cl] complexes, where phenyl rings of the triphenylphosphines were replaced by hydrogen. The results of these calculations have been found to be similar for all the complexes. A partial MO diagram for a representative complex is shown in Figure 2, and the composition of some selected molecular orbitals of it is given in Table 5. The highest occupied molecular orbital (HOMO) is concentrated almost entirely (≥90%) on the NR₂ fragment of the semicarbazone ligand. The next couple of filled orbitals (HOMO – 1, HOMO – 2, etc.), however, have significant (≥45%) contribution from the rhodium t₂-orbitals. The lowest unoccupied molecular orbital (LUMO) has a major (≥95%) contribution from the semicarbazone ligand and is localized mostly (≥55%) on the nitro group. The next couple of vacant orbitals (LUMO + 1, LUMO + 2, etc.) also have major contributions from the semicarbazone ligand. The lower energy absorption (near 490 nm) may therefore be assigned to a transition from the HOMO concentrated on one fragment (NR₂) of the semicarbazone ligand to the LUMO localized on another fragment (NO₂) of the same ligand, which is an allowed transition and thus accounts for its high intensity. The second absorption near 380 nm, which is of much less

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Table 4. Electronic Spectral and Cyclic Voltammetric Data

compd	electronic spectral data ^a λ_{max} , nm (ϵ , M ⁻¹ cm ⁻¹)	cyclic voltammetric data ^b	
		$E_{1/2}$, V (ΔE_p , mV)	E_{pc} , V
[Rh(PPh ₃) ₂ (CNO–NEt ₂)Cl]	488(12000), 380 ^c (5400), 300(32900)	0.97(80)	–1.27
[Rh(PPh ₃) ₂ (CNO–N ⁱ Pr ₂)Cl]	494(14600), 374 ^c (6100), 298(38800)	0.95(80)	–1.11
[Rh(PPh ₃) ₂ (CNO–N ⁿ Bu ₂)Cl]	490(11100), 380 ^c (5700), 300(31200)	0.96(70)	–1.00
[Rh(PPh ₃) ₂ (ONO ¹ –NEt ₂)Cl]	404(9300), 388 ^c (8900), 324(27300), 314(27000), 296(26000)	0.73(70)	–1.18
[Rh(PPh ₃) ₂ (ONO ¹ –N ⁱ Pr ₂)Cl]	410(9200), 388(6500), 326(21900), 316(21700), 294(22400)	0.71(80)	–1.26
[Rh(PPh ₃) ₂ (ONO ¹ –N ⁿ Bu ₂)Cl]	410(10500), 390(9700), 326(33000), 316(32900), 296(32900)	0.74(68)	–1.02
[Rh(PPh ₃) ₂ (ONO ² –NEt ₂)Cl]	406 ^c (8300), 388(9200), 326 ^c (27900), 312(30400), 294 ^c (28900)	0.69(70)	–1.08
[Rh(PPh ₃) ₂ (ONO ² –N ⁱ Pr ₂)Cl]	408(7300), 388(9300), 326 ^c (21600), 314(26600), 296(24300)	0.69(73)	–1.14
[Rh(PPh ₃) ₂ (ONO ² –N ⁿ Bu ₂)Cl]	412(6300), 390(6800), 326 ^c (21800), 314(23400), 296(23400)	0.72(64)	–1.24
[Rh(PPh ₃) ₂ (ONO ³ –NEt ₂)Cl]	442(8400), 418(7700), 326(20000), 292(32000), 264(39300)	0.58(70)	–1.15
[Rh(PPh ₃) ₂ (ONO ³ –N ⁱ Pr ₂)Cl]	444 ^c (8000), 422(9100), 328(21000), 294(27600), 266(34700)	0.52(80)	–1.04
[Rh(PPh ₃) ₂ (ONO ³ –N ⁿ Bu ₂)Cl]	450(7900), 426(7200), 328 ^c (22000), 294(33400), 266(32000)	0.55(80)	–1.13

^a In dichloromethane solution. ^b Solvent, 1:9 dichloromethane–acetonitrile; supporting electrolyte, TBAP; 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⁻¹. ^c Shoulder.

**Figure 2.** Partial molecular orbital diagram of [Rh(PPh₃)₂(CNO–NEt₂)Cl].

intensity, may be attributed to a transition taking place from the HOMO – 1 to one of the vacant orbitals and hence may be regarded as a metal-to-ligand charge-transfer (MLCT) transition.

Electrochemical properties of the [Rh(PPh₃)₂(CNO–NR₂)Cl] complexes have been studied by cyclic voltammetry in 1:9 dichloromethane–acetonitrile (0.1 M TBAP) solution. Each complex shows one oxidative response on the positive side of SCE and one reductive response on the negative side. Voltammetric data are given in Table 4, and a selected voltammogram is shown in Figure 3. Keeping the results of the EHMO calculations (vide supra) in view, both the oxidative and reductive responses are assigned to oxidation and reduction of the coordinated semicarbazone ligand. The oxidation is reversible in nature, with a peak-to-peak separation (ΔE_p) of 70–80 mV, and the anodic peak-current (i_{pa}) is almost equal to the cathodic peak-current (i_{pc}). The reductive response is irreversible in nature. One-electron stoichiometry of both the redox couples has been established by comparing

their current heights (i_{pa} for oxidative response and i_{pc} for the reductive response) with those of the standard ferrocene–ferrocenium couple under identical experimental conditions.

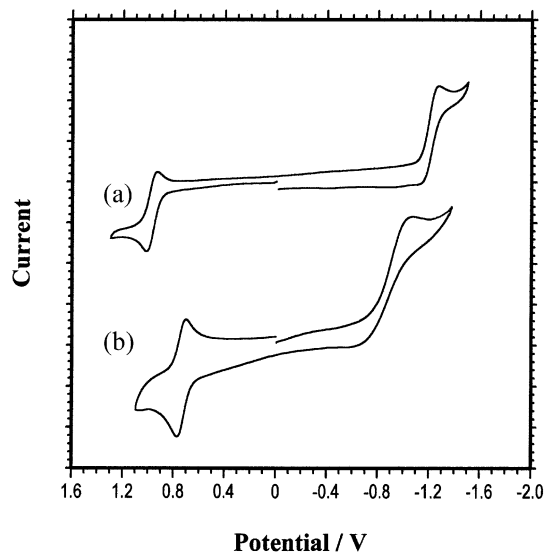
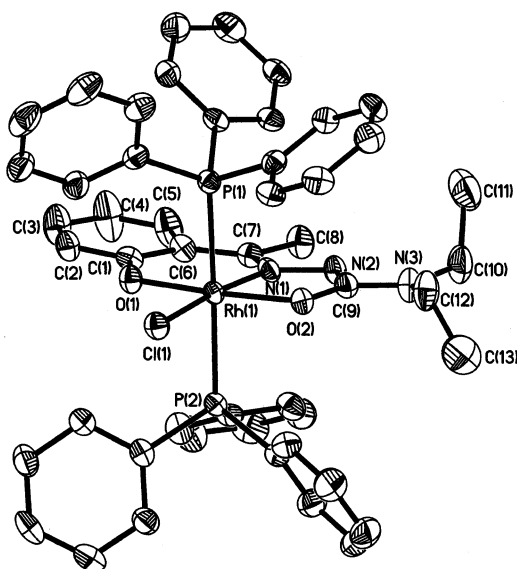
The observed chemical transformation of the *para*-nitrobenzaldehyde semicarbazone, which is believed to be initiated by its coordination to trivalent rhodium in a tridentate fashion via loss of one proton (Scheme 1), prompted us to explore other semicarbazone ligands with similar abilities for more of such reactions. A new group of potentially tridentate semicarbazone ligands (**3**, viz. salicylaldehyde semicarbazone, 2-hydroxyacetophenone semicarbazone, and 2-hydroxynaphthaldehyde semicarbazone) have been selected for this exploration. These semicarbazones are known to serve as O,N,O-donor ligands via loss of two protons.^{2,17} During their reaction with [Rh(PPh₃)₃Cl] in the presence of a base (NR₂R'; R = Et, ⁱPr, ⁿBu and R' = R or H), these ligands are also found to undergo similar chemical transformation as before and afford another group of complexes of type [Rh(PPh₃)₂(ONOⁿ–NR₂)Cl], where ONOⁿ–NR₂ refers to the transformed semicarbazones bound to the metal ion as tridentate O,N,O-donor ligands (**4**). Formation of these complexes has been authenticated by structure determination of one member of this family, viz. [Rh(PPh₃)₂(ONO²–NEt₂)Cl], by X-ray crystallography. The structure is shown in Figure 4, and relevant bond parameters are given in Table 2.

The structure shows that the NH₂ group of the semicarbazone ligand has been replaced by a NEt₂ group and the modified semicarbazone ligand is bound to rhodium as a tridentate O,N,O-donor. The coordinated chloride is sharing the same equatorial plane with the semicarbazone and rhodium, and the PPh₃ ligands have occupied the remaining two axial positions. The NO₂P₂Cl coordination sphere around rhodium is a distorted octahedron. The Rh–P and Rh–Cl distances compare well with those in the previous structure. The Rh–O(1) and C(1)–O(1) distances are quite normal, as observed in structurally characterized complexes of rhodium(III) bound to phenolate oxygen.^{13b,18} However,

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 (17) Thangadurai, T. D.; Natarajan, K. *Transition Met. Chem.* **2001**, *26*, 717.
 (18) Dutta, S.; Peng, S. M.; Bhattacharya, S. *Inorg. Chem.* **2000**, *39*, 2231.

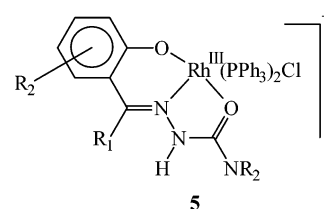
Table 5. Composition of Selected Molecular Orbitals

compd	contributing fragments	% contributions of fragments					
		HOMO	HOMO - 1	HOMO - 2	LUMO	LUMO + 1	LUMO + 2
[Rh(PPh ₃) ₂ (CNO-NEt ₂)Cl]	Rh		78%	49%	2%	2%	3%
	Cl		5%	2%			
	CNO-NEt ₂	100%	17%	49%	98%	98%	97%
[Rh(PPh ₃) ₂ (ONO ¹ -NEt ₂)Cl]	Rh		83%	45%	4%		
	Cl		5%	2%			
	ONO ¹ -NEt ₂	100%	12%	53%	96%	100%	100%
[Rh(PPh ₃) ₂ (ONO ² -NEt ₂)Cl]	Rh		81%	50%	3%		
	Cl		4%	2%			
	ONO ² -NEt ₂	100%	15%	48%	97%	100%	100%
[Rh(PPh ₃) ₂ (ONO ³ -NEt ₂)Cl]	Rh		42%	75%	3%		
	Cl			4%			
	ONO ³ -NEt ₂	100%	58%	21%	97%	100%	100%

**Figure 3.** Cyclic voltammograms of (a) [Rh(PPh₃)₂(CNO-NEt₂)Cl] and (b) [Rh(PPh₃)₂(ONO¹-NⁿBu₂)Cl] in 1:9 dichloromethane-acetonitrile solution (0.1 M TBAP) at a scan rate of 50 mV s⁻¹.**Figure 4.** View of the [Rh(PPh₃)₂(ONO²-NEt₂)Cl] complex.

lengths of the other bonds in the Rh(ONO²-NEt₂) fragment are observed to be significantly different from those of the corresponding bonds in the Rh(CNO-NEt₂) fragment of the previous structure, and this difference is attributable to the

difference in ligand nature and size of the chelate rings. The observed chemical transformation of these semicarbazone ligands (**3**) is believed to be initiated by their coordination of rhodium(III) as a monoanionic O,N,O-donor via dissociation of only the phenolic proton (**5**). Such a coordination mode of these semicarbazone ligands (**3**) is well documented in the literature.^{3e} Attack of the amine (NR₂R') at the carbonyl



carbon then takes place, which is followed by other steps as shown before in Scheme 1. As all the [Rh(PPh₃)₂(ONOⁿ-NR₂)Cl] complexes have been synthesized similarly and they show similar properties (vide infra), the other [Rh(PPh₃)₂(ONOⁿ-NR₂)Cl] complexes are assumed to have similar structure as [Rh(PPh₃)₂(ONO²-NEt₂)Cl].

The microanalytical data of these [Rh(PPh₃)₂(ONOⁿ-NR₂)Cl] complexes are in good agreement with their compositions (Table S1). ¹H NMR spectra of these complexes (Table 3) are also consistent with their compositions. In addition to broad signals for the triphenylphosphines (7.0–7.8 ppm), some of the expected signals from the coordinated semicarbazones have been clearly located while others could not be observed due to their overlap with the triphenylphosphine signals. The signal for the azomethine proton is observed in the [Rh(PPh₃)₂(ONO¹-NR₂)Cl] complexes around 6.5 ppm, but the same could not be detected in the [Rh(PPh₃)₂(ONO³-NR₂)Cl] complexes. In the [Rh(PPh₃)₂(ONO²-NR₂)Cl] complexes, a distinct methyl signal is observed near 1.8 ppm. Signals for the NR₂ fragment were observed in all these complexes in the expected region as before.

Infrared spectra of the [Rh(PPh₃)₂(ONOⁿ-NR₂)Cl] complexes are mostly similar to those of the [Rh(PPh₃)₂(CNO-NEt₂)Cl] complexes. Electronic spectra of these complexes, recorded in dichloromethane solution, show several intense absorptions in the visible and ultraviolet region (Table 4). The absorptions in the ultraviolet region are assignable to transitions within the ligand orbitals. To understand the origin of the absorptions in the visible region, EHMO calculations

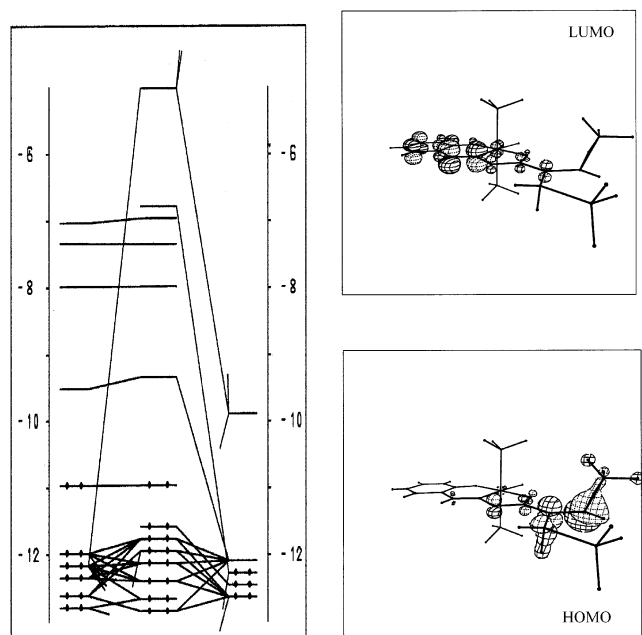


Figure 5. Partial molecular orbital diagram of $[Rh(PPh_3)_2(ONO^1-NEt_2)Cl]$.

have been performed on these complexes, which have afforded qualitatively similar results for all the complexes. The composition of some selected molecular orbitals of three representative complexes is given in Table 5, and a partial MO diagram for one complex is shown in Figure 5. The HOMO is primarily concentrated on the NR_2 fragment of the semicarbazone ligand, while the HOMO - 1 and HOMO - 2 have significant (42–83%) contributions from the metal d-orbitals. The LUMO is delocalized over the arylimine fragment, and the next few vacant orbitals (LUMO + 1, LUMO + 2, etc.) are localized on different parts of the semicarbazone ligand. The lowest energy absorption in the visible region may therefore be attributed to a transition from the HOMO concentrated on one part of the semicarbazone ligand to the LUMO localized on another part of the same ligand. The higher energy absorptions in the visible region may be assigned to transitions from the lower filled orbitals to the higher vacant orbitals.

The cyclic voltammetric behavior of the $[Rh(PPh_3)_2(ONO^n-NR_2)Cl]$ complexes, studied in 1:9 dichloromethane–acetonitrile (0.1 M TBAP) solution, is qualitatively similar to that of the $[Rh(PPh_3)_2(CNO-NR_2)Cl]$ complexes. Each $[Rh(PPh_3)_2(ONO^n-NR_2)Cl]$ complex shows one reversible oxidative response on the positive side of SCE and one irreversible reductive response on the negative side (Table 4, Figure 3), and in view of the results of the EHMO calculations, both the responses are assigned to ligand(semicarbazone)-centered redox reactions.

Conclusions

The present study reveals that reactivity of semicarbazone ligands gets modified considerably upon its coordination to an electropositive metal center and the coordinated semicarbazone ligand undergoes unusual chemical transformation via initial attack of nucleophiles to the carbonyl carbon. This study also shows that ligands of this type are likely to display interesting metal mediated chemical transformations upon reaction with nucleophiles of different types, and such possibilities are currently under exploration.

Acknowledgment. Financial assistance received from the Council of Scientific and Industrial Research, New Delhi [Grant 01(1675)/00/EMR-II], is gratefully acknowledged. The authors thank Professor B. C. Ranu and Professor S. Lahiri of the Department of Organic Chemistry, Indian Association for the Cultivation of Science, Kolkata, for their help. Thanks are also due to the RSIC at Central Drug Research Institute, Lucknow, India, for the C,H,N analysis data and the Bose Institute, Kolkata 700054, for NMR spectral measurements. The authors thank the reviewers for their critical comments and constructive suggestions, which have been helpful in preparing the revised version.

Supporting Information Available: Table containing microanalytical data of the $[Rh(PPh_3)_2(CNO-NR_2)Cl]$ and $[Rh(PPh_3)_2(ONO^n-NR_2)Cl]$ complexes (Table S1). X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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