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Unusual Coordination Mode of Thiosemicarbazone Ligand. Synthesis, Structure, and Redox Properties of Some Ruthenium and Osmium Complexes

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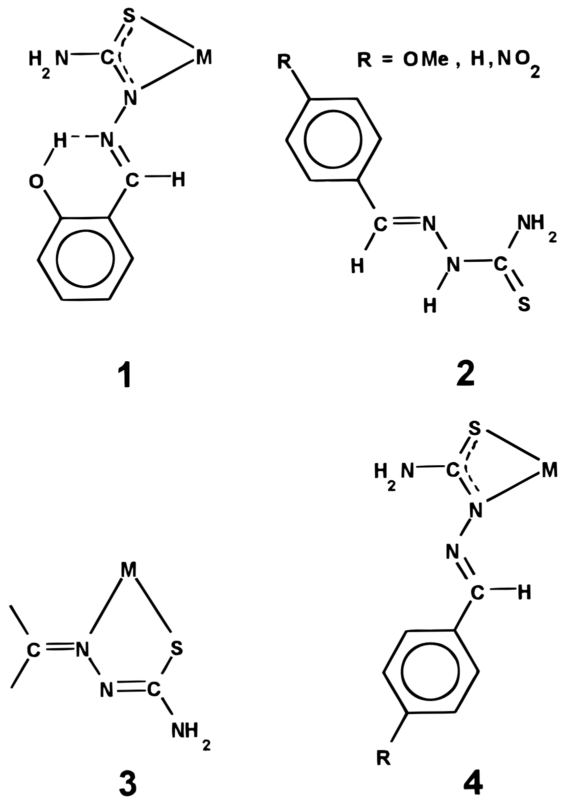
Introduction

In a recent note we reported the unusual coordination mode of salicylaldehyde thiosemicarbazone (**1**, Chart 1) observed in a group of $[M(PPh_3)_2(saltsc)_2]$ complexes (where M = Ru, Os and saltsc = anion of salicylaldehyde thiosemicarbazone).[2] It appeared that two factors might be responsible for such unusual coordination mode of salicylaldehyde thiosemicarbazoe: (i) the steric bulk of the two triphenylphosphine ligands and (ii) intramolecular hydrogen bonding between the phenolic hydrogen and the imine nitrogen. The present work has originated from our attempt to find out the actual driving force behind such coordination mode of the thiosemicarbazone ligand. To do that, the triphenylphosphine ligand is kept unchaned while the thiosemicarbazone ligand has been modified by removing the hydroxy group from the salicylaldehyde fragment to prevent any intramolecular hydrogen bonding. Herein we have used thiosemicarbazones of benzaldehyde and two para substituted benzaldehydes (**2**). The ligands are abbreviated in general as HL-R, where H stands for the dissociable proton and R for the substituent. Ligands of this type are known to bind to a metal ion as a monoanionic bidentate N,S donor forming stable five-membered chelate ring (**3**).[3] However, reaction of these ligands with $[M(PPh_3)_3X_2]$ (where M = Ru, Os and X = Cl, Br) afforded complexes of type $[M(PPh_3)_2(L\text{-}R)_2]$ where the thiosemicarbazone ligand is coordinated as a bidentate N,S donor ligand forming a four-membered chelate ring (**4**). The synthesis, structure and cyclic voltammetric properties of the $[M(PPh_3)_2(L\text{-}R)_2]$ complexes are described here with special reference to the nature of steric interaction responsible for the observed mode of binding of the thiosemicarbazone ligands.

Experimental Section

Materials. $[Ru(PPh_3)_3Cl_2]$ and $[Os(PPh_3)_3Br_2]$ were synthesized following reported procedures.[4] The thiosemicarbazone ligands (HL-R) were prepared by reacting equimolar amounts of thiosemicarbazide and respective para-substituted benzaldehyde in 1:1 ethanol−water mixture. Purification of dichloromethane and preparation of tetraethylammonium perchlorate (TEAP) for electrochemical work were performed as reported in the literature.[5]

Chart 1. Structures **1**−**4**



Preparation of $[Ru(PPh_3)_2(L\text{-}OMe)_2]$. To a solution of HL-OMe (53 mg, 0.25 mmol) in ethanol (40 mL) was added $[Ru(PPh_3)_3Cl_2]$ (100 mg, 0.10 mmol) followed by NEt_3 (26 mg, 0.26 mmol). The mixture was then refluxed for 1 h. Yellow precipitate started to separate out during refluxing. After cooling the solution to room temperature, the precipitate was collected by filtration, washed thoroughly with ethanol and dried in air. Recrystallization of the crude product from 1:1 dichloromethane-hexane solution gave $[Ru(PPh_3)_2(L\text{-}OMe)_2]$ as a yellow crystalline solid. Yield: 69%. Anal. Calcd for $C_{54}H_{50}N_6O_2P_2S_2Ru$: C, 62.25; H, 4.08; N, 8.07. Found: C, 62.35; H, 4.12; N, 8.05.

Preparation of $[Ru(PPh_3)_2(L\text{-}H)_2]$. This was prepared by following the same above procedure using HL-H instead of HL-OMe. Yield: 72%. Anal. Calcd for $C_{52}H_{46}N_6P_2S_2Ru$: C, 63.61; H, 4.69; N, 8.56. Found: C, 63.70; H, 4.73; N, 8.51.

Preparation of $[Ru(PPh_3)_2(L\text{-}NO_2)_2]$. This was prepared by following the same procedure as in $[Ru(PPh_3)_2(L\text{-}OMe)_2]$, using HL-$NO_2$ instead of HL-OMe. Yield: 75%. Anal. Calcd for $C_{52}H_{44}N_8O_4P_2S_2Ru$: C, 58.26; H, 4.11; N, 10.45. Found: C, 58.32; H, 4.13; N, 10.42.

Preparation of $[Os(PPh_3)_2(L\text{-}NO_2)_2]$. To a solution of HL-$NO_2$ (50 mg, 0.22 mmol) in warm ethanol (40 mL) were added $[Os(PPh_3)_3Br_2]$ (100 mg, 0.09 mmol) and NEt_3 (25 mg, 0.25 mmol). The mixture was refluxed for 2 h to produce a brownish-red solution. On partial evaporation of the solvent, a precipitate separated out which was collected by filtration, washed with cold ethanol, and dried in air. Recrystallization of the crude product from 1:1 dichloromethane−hexane solution gave $[Os(PPh_3)_2(L\text{-}NO_2)_2]$ as a dark crystalline solid.

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(1) (a) Jadavpur University. (b) University of Colorado.

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Table 1. Crystallographic Data for [Ru(PPh$_3$)$_2$(L-NO$_2$)$_2$]

empirical formula	$C_{52}H_{44}N_8O_4P_2S_2Ru$
fw	1072.08
space group	triclinic, $P\bar{1}$
a, Å	11.4528(13)
b, Å	11.996(2)
c, Å	18.347(2)
α, deg	98.560(13)
β, deg	94.313(10)
γ, deg	103.531(10)
V, Å^3	2407.5(6)
Z	2
ρ_{calcd}, g cm^{-3}	1.479
ρ_{obsd}, g cm^{-3}	1.440
λ, Å	0.710 73
crystal size, mm	0.54 × 0.31 × 0.18
T, °C	20
μ, mm^{-1}	0.535
R1^a	0.0241
wR2^b	0.0594
GOF on F^2 ^{c}	1.036

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

Yield: 64%. Anal. Calcd for $C_{52}H_{44}N_8O_4P_2S_2Os$: C, 53.79; H, 3.79; N, 9.65. Found: C, 53.72; H, 3.90; N, 9.73.

Preparation of [Os(PPh$_3$)$_2$(L-H)$_2$]. To a solution of HL-H (42 mg, 0.23 mmol) in ethanol (40 mL) was added [Os(PPh$_3$)$_3$Br$_2$] (100 mg, 0.09 mmol) followed by NEt$_3$ (24 mg, 0.24 mmol). Upon stirring at ambient temperature for 3 h a yellow microcrystalline solid separated out which was collected by filtration, washed with ethanol, and dried in air. Recrystallization of the crude product from 1:1 dichloromethane−hexane solution gave [Os(PPh$_3$)$_2$(L-H)$_2$] as a yellow crystalline solid. Yield: 63%. Anal. Calcd for $C_{52}H_{46}N_6P_2S_2Os$: C, 58.32; H, 4.30; N, 7.85. Found: C, 58.41; H, 4.30; N, 7.93.

Preparation of [Os(PPh$_3$)$_2$(L-OMe)$_2$]. This was prepared by following the same above procedure using HL-OMe instead of HL-H. Yield: 67%. Anal. Calcd for $C_{54}H_{50}N_6O_2P_2S_2Os$: C, 57.35; H, 4.42; N, 7.43. Found: C, 57.52; H, 4.47; N, 7.48.

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 pellets. Electronic spectra were recorded on a Shimadzu UV-1601 spectrophotometer. Magnetic susceptibilities were measured using a PAR 155 vibrating sample magnetometer. ^{1}H NMR spectra were obtained on a Brucker AC-200 NMR spectrometer using TMS as the internal standard. 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. A platinum-wire gauze electrode was used in the coulometric experiments. A RE 0089 X-Y recorder was used to trace the voltammograms. Electrochemical measurements were made under a dinitrogen atmosphere. All electrochemical data were collected at 298 K and are uncorrected for junction potentials.

Crystallography of [Ru(PPh$_3$)$_2$(L-NO$_2$)$_2$]. Single crystals were grown by slow diffusion of hexane into a dichloromethane solution of the complex. Selected crystal data and data collection parameters are given in Table 1. The unit cell dimensions were determined by a least-squares fit of 8192 centered reflections ($0 < \theta < 31°$). Data were collected on a Siemens Smart CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å) by ω scans within the angular range $1.77 < \theta < 31.21°$. Fifty 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, and structure solution and refinement were done using the SHELXS-97 package.[6] The structure was solved by the direct method. Final cycles of refinement converged with discrepancy indices R1 = 0.0241 and wR2 = 0.0594.

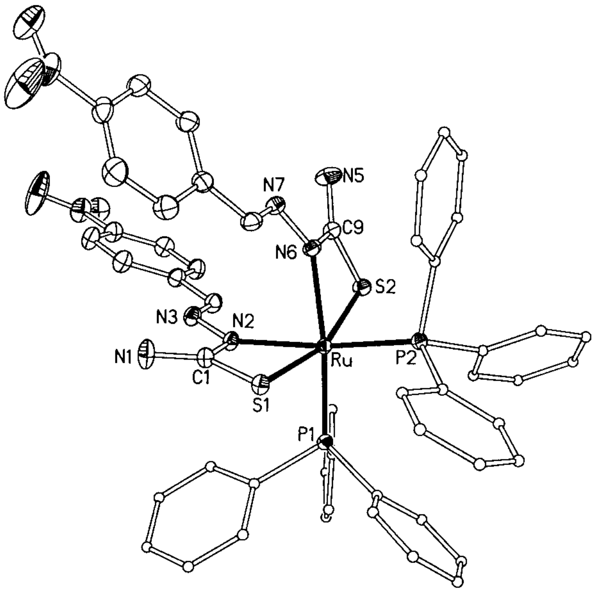

Figure 1. View of the [Ru(PPh$_3$)$_2$(L-NO$_2$)$_2$] molecule.

Table 2. Selected Bond Distances and Bond Angles for [Ru(PPh$_3$)$_2$(L-NO$_2$)$_2$]

Bond Distances (Å)			
Ru−S1	2.4436(4)	C1−N1	1.3338(16)
Ru−S2	2.4371(4)	C1−N2	1.3328(15)
Ru−P1	2.2911(5)	C2−N3	1.2881(16)
Ru−P2	2.3066(5)	C9−S2	1.7149(13)
Ru−N2	2.1563(10)	C9−N6	1.3292(16)
Ru−N6	2.2064(11)	C9−N5	1.3398(16)
C1−S1	1.7226(13)	C10−N7	1.2857(17)

Bond Angles (deg)			
S1−Ru−S2	162.774(11)	N2−Ru−N6	80.42(4)
P2−Ru−N2	165.42(3)	N6−Ru−P2	91.82(3)
P1−Ru−N6	165.71(3)	N2−Ru−S2	101.32(3)
N2−Ru−S1	66.33(3)	N2−Ru−P1	90.58(3)
N6−Ru−S2	65.47(3)	P2−Ru−S2	86.392(16)
P1−Ru−P2	99.241(16)	N6−Ru−S1	99.58(3)
P1−Ru−S2	105.991(15)	P2−Ru−S1	103.273(16)
P1−Ru−S1	86.738(16)		

Results and Discussion

The thiosemicarbazone ligands react smoothly with [Ru(PPh$_3$)$_3$Cl$_2$] in refluxing ethanol in the presence of NEt$_3$ to afford the [Ru(PPh$_3$)$_2$(L-R)$_2$] complexes in decent yields. [Os(PPh$_3$)$_2$(L-NO$_2$)$_2$] was synthesized similarly, but we allowed a longer reaction time. The other two osmium complexes, viz. [Os(PPh$_3$)$_2$(L-OMe)$_2$] and [Os(PPh$_3$)$_2$(L-H)$_2$], were obtained by simply stirring the reactants in ethanol at ambient temperature. Refluxing in these two cases gave products of unidentified composition. All six [M(PPh$_3$)$_2$(L-R)$_2$] complexes are diamagnetic, which corresponds to the bivalent state of the metals (low-spin d^6, $S = 0$) in these complexes.

Molecular structure of a representative complex, viz. [Ru(PPh$_3$)$_2$(L-NO$_2$)$_2$], was determined by X-ray crystallography. The structure is shown in Figure 1 and selected bond distances and angles are in Table 2. The coordination sphere around ruthenium is N$_2$P$_2$S$_2$ with a cis-cis-trans geometry, respectively. The two PPh$_3$ ligands occupy cis positions as usually observed

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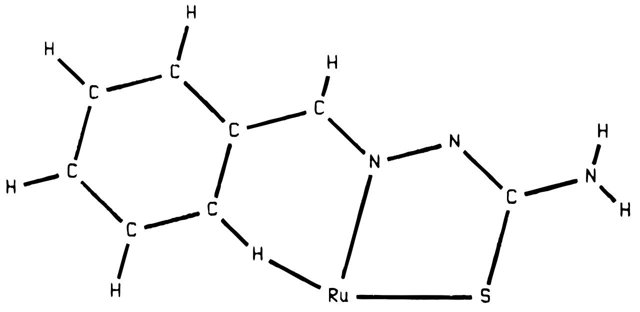
Chart 2. Structures **5** and **6**



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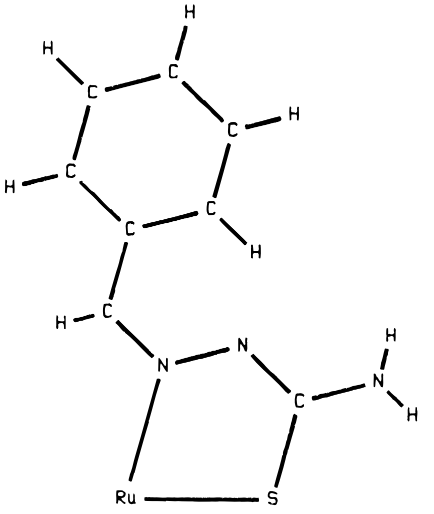

6

in bis-triphenylphosphine complexes of ruthenium(II)[7] and the thiosemicabazone ligands are coordinated as shown in **4** with a bite angle of ∼66°. This has resulted in significant distortion of the $RuN_2P_2S_2$ core from ideal octahedral geometry, which is reflected in the three trans angles and twelve cis angles. The observed bond distances and angles are quite normal and compare well with those of the previous structure.[2]

Formation of the four-membered chelate ring, even after removal of hydroxy group from the phenyl ring (**1**) to prevent intramolecular hydrogen bonding, points to the other possibility that steric interaction of the thiosemicarbazone ligands with the triphenylphosphines has forced them to take up such a coordination mode. To have an insight into the exact nature of possible steric interactions, a computer model of $[M(PPh_3)_2(L\text{-}H)_2]$ was constructed[8] forcing a five-membered chelate ring formation by the thiosemicarbazone ligands (as in **3**) and assuming these ligands to be planar in this coordination mode. A cis-cis-trans geometry of the $N_2P_2S_2$ coordination sphere, as observed in the crystal structure, was also assumed. In the solid state, free benzaldehyde thiosemicarbazone ligands have the structure as shown in 2.[9] Five-memberded chelate ring formation (as in **3**) can only take place via rotation about the C−N(hydrazinic) single bond, followed by tautomerization to the thiol form and dissociation of the thiolate proton upon complexation. Our modeling studies show that in this coordination mode, the phenyl ring of thiosemicarbazone ligand comes in contact with the metal (**5**, Chart 2). A stable five-membered chelate ring formation is possible only when relative disposition of the phenyl ring and the azomethine hydrogen is interchanged (**6**). This requires significant conformational change (rotation about the C═N double bond!) with respect to the free ligand structure. Both these geometries of the thiosemicarbazone ligand were taken into consideration. Steric interaction between the two thiosemicarbazone ligands and that of the thiosemicarbazone ligand and a triphenylphosphine were scrutinized separately. This exercise shows that there is actually no steric interaction between the triphenylphosphines and the thiosemicabazone ligands or between the two thiosemicarbazone ligands coordinated as in **6**. However, there is significant steric interaction between the two thiosemicabazone ligands as well as between the metal and these ligands, where both ligands are coordinated as in **5** (Figure 2) which indicates that such coordination mode is not possible. In fact we were unable to find a single example of a structurally characterized benzaldehyde thiosemicarbazone complex where the ligand is coordinated as in **5**. A recent report on a nickel comlex of a similar ligand showed that the ligands underwent stereochemical change and coordinated as in **6**.[10] The observed coordination mode of the bezaldehyde thiosemicarbazone ligands in the present study appears to result from the combined effect of restricted rotation around the C═N bond and steric interaction of the phenyl ring of the thiosemicarbazone ligand with the metal. Considering the structure of the uncoordinated ligand, the observed coordination mode appears to be quite

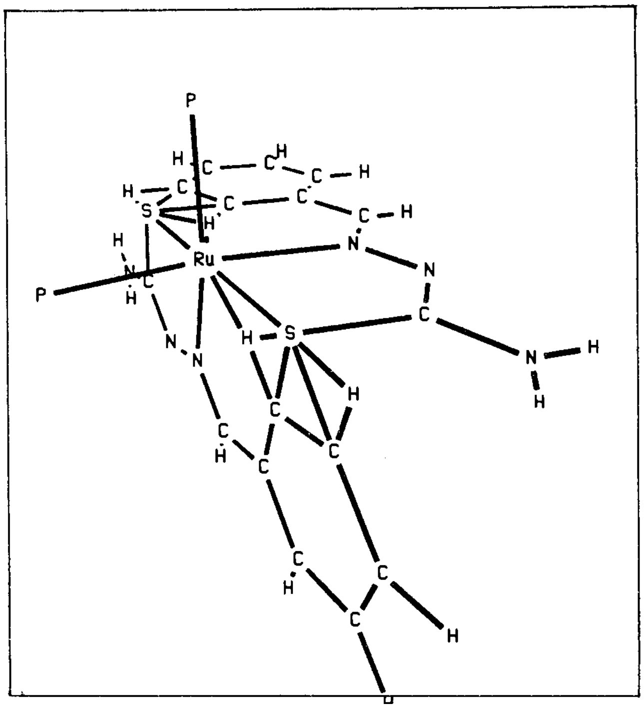

Figure 2. Steric interaction between the benzaldehyde thiosemicarbazone ligands. The phenyl rings of the triphenylphosphines have been omitted for clarity.

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[10] Tian, Y. P.; Duan, C. Y.; Lu, Z. L.; You, X. Z.; Fun, H. K.; Sivakumar, K. *Polyhedron* **1996**, *15*, 2263.

Table 3. Electronic Spectral and Cyclic Voltammetric Data

	electronic spectral data[a]		cyclic voltammetric data[b]	
compound	color	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	$E_{1/2}$, V (ΔE_p, mV)	E_{pa} value
$[Ru(PPh_3)_2(L\text{-}OMe)_2]$	yellow	371 (24 000), 316 (30 600), 273[c] (40 000), 229 (79 000)	0.25 (90)	0.94
$[Ru(PPh_3)_2(L\text{-}H)_2]$	yellow	378 (20 150), 322 (26 000), 232 (84 000)	0.30 (60)	1.03
$[Ru(PPh_3)_2(L\text{-}NO_2)_2]$	red	480 (20 000), 390 (23 900), 316 (19 200), 233 (74 700)	0.39 (60)	1.20
$[Os(PPh_3)_2(L\text{-}OMe)_2]$	greenish-yellow	648[c] (900), 356[c] (29 900), 320 (44 100), 270 (39 400), 224 (52 800)	0.08 (60)	0.92
$[Os(PPh_3)_2(L\text{-}H)_2]$	yellow	376[c] (13 700), 330 (20 800), 256[c] (25 800), 224 (53 300)	0.11 (60)	0.96
$[Os(PPh_3)_2(L\text{-}NO_2)_2]$	brownish-red	450[c] (12 700), 370 (18 000), 310 (16 700), 256[c] (24 000), 224 (48 700)	0.21 (60)	1.04

[a] In dichloromethane solution. [b] Solvent, acetonitrile; supporting electrolyte, TEAP; reference electrode, SCE; $E_{1/2} = 0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; $\Delta E_p = E_{pa} - E_{pc}$; scan rate, 50 mV s^{-1}. [c] Shoulder.

normal as it does not involve any change in ligand geometry. It is interesting to note here that benzaldehyde thiosemicarbazone ligands are recently reported to coordinate copper as a monodentate S-donor ligand where the thiosemicarbazone ligands retained their stereochemistry as in the free ligand.[11]

The C_2 symmetry observed in the structure of $[Ru(PPh_3)_2(L\text{-}NO_2)_2]$ is also reflected in the ^1H NMR spectrum of this complex recorded in $CDCl_3$ solution. The azomethine proton shows a distinct signal at 8.78 ppm and the resonance due to the two amine hydrogens are observed at 5.21 ppm. The four phenyl protons of the L-NO_2 ligand show two doublets (2H each), as expected, at 7.55 and 8.11 ppm. The PPh_3 protons appear within 6.9−7.4 ppm but could not be clearly observed due to overlap of signals. ^1H NMR spectra of the other two $[Ru(PPh_3)_2(L\text{-}R)_2]$ complexes show similar features. For example in $[Ru(PPh_3)_2(L\text{-}H)_2]$, the azomethine proton signal (1H) is observed at 8.84 ppm and the amine proton signal (2H) is observed at 5.03 ppm. In $[Ru(PPh_3)_2(L\text{-}OMe)_2]$ the above two signals appear at 8.83 and 4.96 ppm respectively. The methyl signal of the OMe group is observed at 3.80 ppm and the phenyl protons of the L-OMe ligand are observed as two doublets (2H each) at 6.80 and 7.42 ppm. ^1H NMR spectra of the $[Os(PPh_3)_2(L\text{-}R)_2]$ complexes are almost identical to their respective ruthenium analogues. The ^1H NMR spectral data thus indicate that all six $[M(PPh_3)_2(L\text{-}R)_2]$ complexes have similar structure. Infrared spectra of these complexes are also in support of their isostructural nature. The $[M(PPh_3)_2(L\text{-}R)_2]$ complexes are soluble in solvents such as acetonitrile, dichloromethane, and chloroform, producing solutions of different colors (Table 3). Electronic spectra of these complexes, recorded in dichloromethane solution, show several intense absorptions in the visible region (Table 3) which are probably due to allowed metal-to-ligand charge-transfer transitions.

Cyclic voltammetry on the $[M(PPh_3)_2(L\text{-}R)_2]$ complexes in acetonitrile solution shows two oxidative responses on the positive side of SCE (Table 3). The first response is reversible in nature while the second one is irreversible. They are assigned to $M^{II}-M^{III}$ oxidation and $M^{III}-M^{IV}$ oxidation, respectively. The oxidation potentials in the osmium complex are lower than those in the corresponding ruthenium analogue, as usually observed.[2,7a] Potentials of both oxidations are observed to be sensitive to the nature of substituent R in the thiosemicarbazone ligand. The oxidation potentials are lowest for $[Os(PPh_3)_2(L\text{-}OMe)_2]$ and highest for $[Ru(PPh_3)_2(L\text{-}NO_2)_2]$, as expected. The one-electron nature of the $M^{II}-M^{III}$ oxidation has been verified by constant potential coulometry. The oxidized solutions containing $[M^{III}(PPh_3)_2(L\text{-}R)_2]^+$ are green in color for R=H and OMe and light brown for R=NO_2. They display identical voltammograms as their precursors (except that the $M^{II}-M^{III}$ couple appears as a reductive response). Coulometric reduction of the oxidized complexes quantitatively afforded the respective $[M^{II}(PPh_3)_2(L\text{-}R)_2]$ complexes identified by their characteristic electronic spectra. The one-electron nature of the $M^{III}-M^{IV}$ oxidation has been established by comparing its current height (i_{pa}) with that of the $M^{II}-M^{III}$ couple.

The present study reveals that steric bulk of triphenylphosphine had nothing to do with the observed "unusual coordination mode" of the benzaldehyde thiosemicarbazone ligands and the expected five-membered chelate ring formation by these ligands could not take place because of the steric interaction between the metal and aryl group of these thiosemicarbazone ligands. In view of the structure of these free thiosemicarbazones and their stereochemical rigidity with respect to the C=N bond, the observed coordination mode actually appears to be the "most usual" for such ligands. Replacement of the aryl group of these thiosemicarbazone ligands with less bulky alkyl groups, in order to favor five-membered chelate ring formation, is currently under progress.

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Supporting Information Available: Tables containing crystal data and details of structure determination, atomic coordinates, anisotropic thermal parameters, and bond distances and angles and figures showing the steric interactions (22 pages). Ordering information is given on any current masthead page.

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