

Interaction of rhodium(I) bisphosphine complexes with semicarbazones to give orthometallated rhodium(III) complexes*

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Interaction of the *cis*-[Rh(PR₃)₂(Solv)₂]PF₆ complexes (R = Ar or R₃ = Ph₂Me, Solv = solvent) under Ar with semicarbazones bearing a phenyl group on the imine-C atom gives the rhodium(III)-hydrido-bis(phosphine)-orthometallated semicarbazone species [RhH(PR₃)₂{(o-C₆H₄(R')C=N-N(H)CONH₂)}]PF₆ (R' = Me or Et), which are characterized generally by elemental analysis, ³¹P{¹H} and ¹H NMR spectroscopy, and mass-spectrometry. The PPh₃-containing complex with R' = Me, structurally characterized by X-ray analysis, reveals coordination of the semicarbazone by the *ortho*-C atom, the imine-N atom, and the amide-carbonyl group. For a semicarbazone containing no Ph group, the rhodium(I) complex [Rh(PR₃)₂(Et(Me)C=N-N(H)CONH₂)]PF₆, containing the η²-semicarbazone bonded *via* the imine-N and carbonyl, is formed. Attempts to hydrogenate the C=N moiety in the complexes or to catalytically hydrogenate the semicarbazones were unsuccessful.

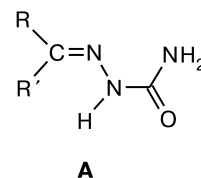
Key words: rhodium, phosphines, orthometallation, semicarbazones, complexes, C–H activation, molecular structure, synthesis.

The findings reported in this paper result from our fundamental interest in the catalytic asymmetric hydrogenation of imines,¹ in particular in the use of [Rh(cod)(PR₃)₂]PF₆ (cod is cycloocta-1,5-diene, R = Ar) as catalyst precursors as they are known to function at ambient conditions of temperature and pressure, where mechanistic investigations are simplified.^{2,3} These precursors react with H₂ in coordinating solvents to generate the *cis,trans,cis*-[Rh(H)₂(PR₃)₂(Solv)₂]PF₆ complexes (Solv is a solvent molecule), while subsequent removal of the H₂ atmosphere readily gives the *cis*-[Rh(PPh₃)₂(Solv)₂]⁺ species in solution;^{4,5} removal of solvent then produces [Rh(PPh₃)₂{(μ-Ph)PPh₂}]₂(PF₆)₂.⁵ The standard imine substrates usually tested are typically of the type Ph(R)C=NCH₂Ph, where R = H, Alk, Ar,¹ while reports on more substituted imines such as oxime ethers and hydrazones are relatively rare.^{6,7}

We decided to study the interaction of these substrates, as well as the semicarbazones R(R')C=N-N(H)CONH₂ (R = Me or Et, with R' = Ph; and R = Me with R' = Et) with the *cis*-[Rh(PR₃)₂(Solv)₂]⁺ species (R = Ar or R₃ = Ph₂Me), with the ultimate aim of catalytically hydrogenating the prochiral imine moiety. The semicarbazone work is described here, in particular synthesis and characterization of the rhodium(III)-hydrido-bis(phosphine)-orthometallated semicarbazone complexes.

R = Ph, R' = Me (*E*-acetophenone semicarbazone);
R = Ph, R' = Et (*E*-propiophenone semicarbazone);
R = Et, R' = Me (*E*-butanone semicarbazone)

More generally, the diverse coordination chemistry of semicarbazones has been thoroughly studied,** especially because of the potential beneficial biological properties of transition metal-semicarbazone and thiosemicarbazone complexes.^{8,9} For the main type of semicarbazone used in our work (A), coordination can occur *via* the imine-N and carbonyl-O atoms to give a five-membered metalcyclic derivative^{10a,11}. If orthometallation also occurs *via* the *ortho*-C atom of the Ph group, then two fused, five-membered metallocycles are formed.^{9,10a,12} Coordination *via* just the imine-N and *ortho*-C atom also generates a five-



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** In the Database of *Chem. Abstracts* the semicarbazone complexes of ~40 elements of the Periodic System were found.

membered metallocycle.¹² Demonstrated also is coordination *via* the enolic form of the semicarbazone, involving the carbonyl-O and an imine-N, this giving a four- or five-membered ring species.¹⁰ These four modes of coordination have been demonstrated crystallographically. In addition, mono-, bis-, and tris-(semicarbazone) metal complexes are known.^{10–13}

To our knowledge, in structures showing the orthometallation of the semicarbazone,^{9,10a,12} the "released" *o*-hydrogen atom has not been found as a metal-coordinated hydride, and indeed this is rare among even the more standard imines (see above).² Our work here presents an example of such a hydrido-orthometallated complex within the class of two fused, five-membered metallocyclic derivatives.

Results and Discussion

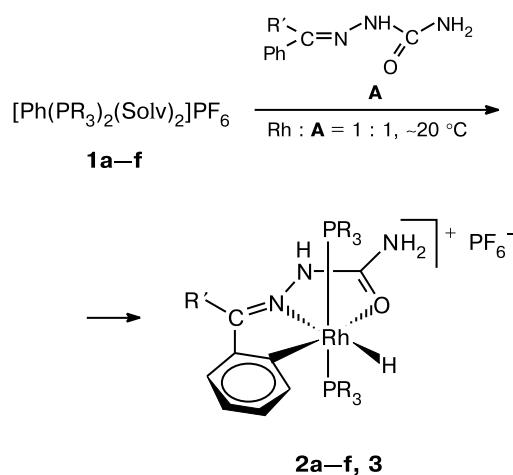
Precursor *cis*-[Rh(PPh₃)₂(Solv)₂]⁺ complexes. The use of [Rh(cod)(PR₃)₂]PF₆ complexes to generate *in situ cis*-[Rh(PR₃)₂(Solv)₂]⁺ (**1**) (R = Ar; Solv = Me₂CO, MeOH) is well documented for R = Ph (**1a**) or *p*-Tol (see above).^{4,5} We have now extended the use of this procedure for the synthesis of the complexes with R₃ = Ph₂(*p*-MeC₆H₄) (**1b**), R = *p*-OMeC₆H₄ (**1c**), *p*-FC₆H₄ (**1d**), and *p*-ClC₆H₄ (**1e**), and R₃ = Ph₂Me (**1f**). Preliminary treatment of these complexes with H₂, followed by gentle heating of the solution under vacuum, yields a red residue; for the R = Ph or *p*-Tol species, the residues have been recently characterized as [Rh(PPh₃)₂](μ-Ph)PPh₃)(PF₆)₂ and the analogous *p*-Tol complex.⁵ The residue is then re-dissolved in acetone or MeOH to generate complexes **1**, species that are readily identified *in situ* by their ³¹P{¹H} NMR data: the triarylphosphine derivatives (**1a–e**) exhibit doublets at δ_p 51–54, with J_{Rh,P} ≈ 200 Hz typical of *cis*-phosphine ligands,⁵ while the more basic Ph₂Me species (**1f**) shows a more upfield shift at δ_p 37.

Preparation and characterization of the orthometallated complexes (2a–f, 3). The *in situ 1a–f* species react over a day at room temperature with *E*-acetophenone semicarbazone to form the orthometallated complexes **2a–f**, respectively, while **1a** forms an analogous complex **3** with the *E*-semicarbazone of propiophenone; the reactions are summarized in Scheme 1, where the semicarbazone Ph group has undergone orthometallation.

The process presumably involves initial formation of a Rh^I complex containing N,O-chelated semicarbazone with loss of acetone ligands (see **4** below), followed by the well recognized oxidative addition of the *ortho*-C–H moiety at the metal.^{2,14}

The ORTEP for the cation of **2a** is shown in Fig. 1, and selected bond lengths and angles are given in Table 1. To our knowledge, **2a** represents the first example of an

Scheme 1



- 2:** R = Ph, R' = Me (**a**); R₃ = Ph₂(*p*-MeC₆H₄), R' = Me (**b**);
R = *p*-OMeC₆H₄, R' = Me (**c**); R = *p*-FC₆H₄, R' = Me (**d**);
R = *p*-ClC₆H₄, R' = Me (**e**); R₃ = Ph₂Me, R' = Me (**f**)
3: R = Ph, R' = Et

orthometallated semicarbazone complex in which the co-hydride ligand is structurally located, although we have also discovered several other examples within the Rh—"standard imine" systems^{2,15} and have reported on analogous Ir systems.^{2b} In examples of the Ru^{II} and Pd^{II}-orthometallated semicarbazones systems,^{10a,12} the hydride is commonly replaced by halide. This is also true for the orthometallated Rh^{III} complex derived from a "standard imine" and RhCl(PPh₃)₃ where again the expected hydride has been replaced by chloride.¹⁶

The distorted octahedral structure of **2a** has *trans*-PPh₃ ligands that are bent toward the hydride as indicated by the P–Rh–H angles (89 and 81°) and the P–Rh–P angle (170.30°); there are possibly weak interactions between the hydride and some protons of the Ph rings as judged by three RhH...HC distances (2.23–2.36 Å, see Table 1) that are less than the van der Waals distance between two H atoms (2.40 Å).^{16,17} Similar, but stronger interactions (H...H = 2.00–2.20 Å) have been suggested for a related orthometallated Rh^{III}-azobenzene system.¹⁶ There is no interaction between the hydride and the H atom at C(2) of the orthometallated ring (H...H 2.80 Å).

The *E*-semicarbazone is chelated *via* the imine-N and -O atoms, and these are co-planar with the orthometallated-C atom and the hydride; the hydride is *trans* to the imine-N (angle N–Rh–H is 176.7°), the C is *trans* to the O atom (angle C(1)–Rh–O is 153.3°), and the system thus has two fused, five-membered metallocycles. The N–Rh–C and N–Rh–O angles (79.7 and 73.6°) are within 4° of those reported for the ortho-metallated (but non-hydride containing) semicarbazone complexes of Rh^{III},⁹ Ru^{II},^{10a} and Pd^{II}.¹²

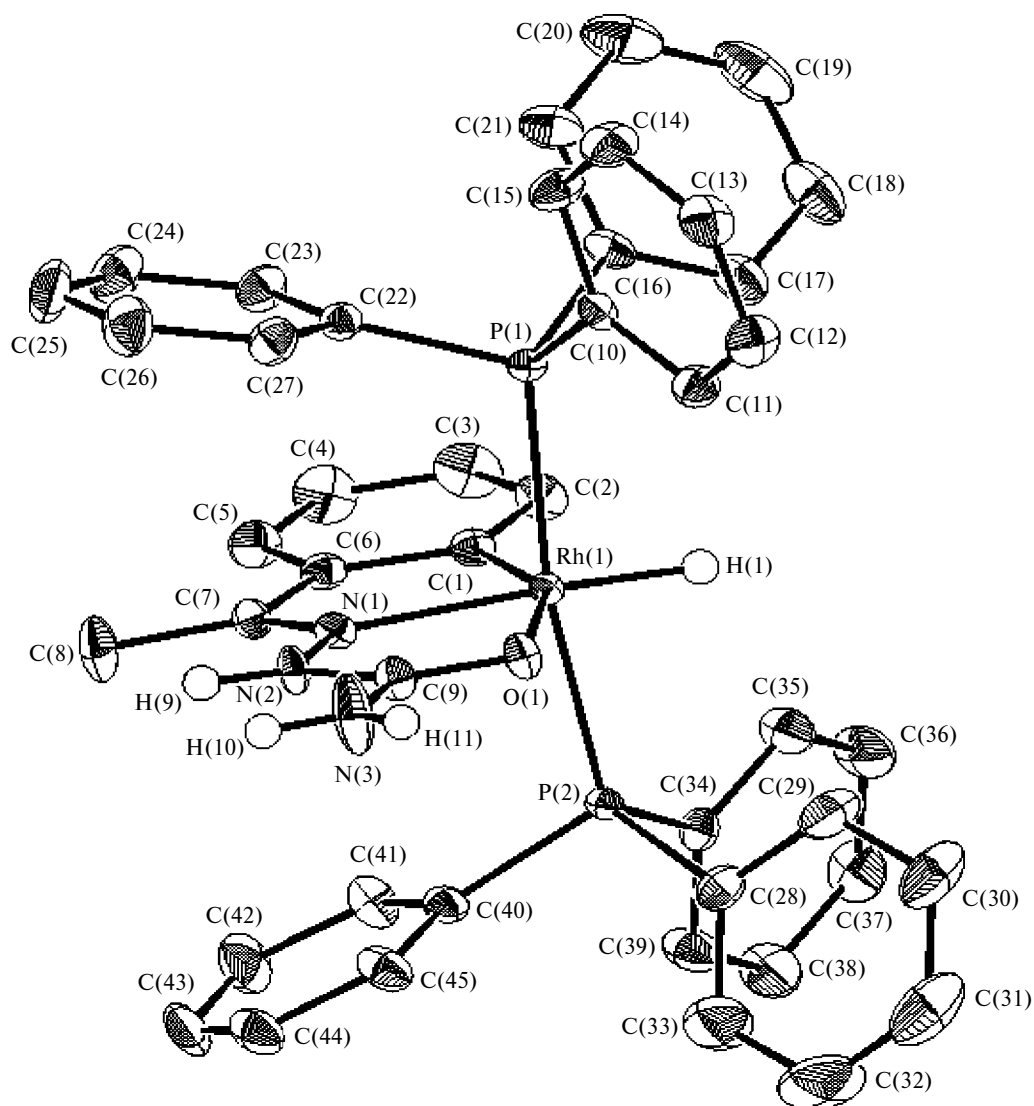


Fig. 1. ORTEP diagram for the cation of $[\text{Rh}(\text{H})(\text{PPh}_3)_2(\text{C}_6\text{H}_4(\text{CH}_3)\text{C}=\text{N}-\text{N}(\text{H})\text{C}(\text{O})\text{NH}_2)]\text{PF}_6$ (**2a**), with 50% probability ellipsoids.

Table 1. Selected bond length (d) and bond angles (ω) in complex **2a**

Bond	$d/\text{\AA}$	Angle	ω/deg
Rh—P(1)	2.3162(8)	P(1)—Rh—P(2)	170.3(2)
Rh—P(2)	2.3218(9)	P(1)—Rh—H(1)	89(1)
Rh—N(1)	2.065(3)	P(2)—Rh—H(1)	81(1)
Rh—O(1)	2.310(2)	C(1)—Rh(1)—H(1)	97(1)
Rh—C(1)	2.009(4)	N(1)—Rh—C(1)	79.7(1)
Rh—H(1)	1.52(4)	O(1)—Rh—H(1)	110(1)
N(1)—C(7)	1.295(4)	N(1)—Rh—O(1)	73.6(1)
C(6)—C(7)	1.471(5)	P(1)—Rh—O(1)	94.46(6)
C(9)—O(1)	1.254(4)	P(2)—Rh—O(1)	90.09(6)
C(9)—N(2)	1.368(4)	Rh—H(1)—H(32)C(35)	120.3
C(9)—N(3)	1.319(5)	Rh—H(1)—H(17)C(17)	121.5
N(1)—N(2)	1.364(4)	Rh—H(1)—H(27)C(29)	107.7
RhH(1)—H(32)C(35)	2.23(4)		
RhH(1)—H(17)C(17)	2.27(4)		
RhH(1)—H(27)C(29)	2.36(4)		

The mass-spectrum of compound **4** shows the parent peak for the cation, and the room temperature ^1H NMR spectrum in acetone is consistent with this formulation. The resonances of the CH_2 and both Me groups of the free semicarbazone (although measured in CDCl_3 , see Experimental) are shifted upfield by upto 0.3 ppm on coordination of the semicarbazone, while the NH_2 signals experience an upfield shift of 3 ppm, which is consistent with $\eta^2\text{-N,O}$ -imine coordination (as are the IR data). The NH signal (δ 8.5 in the free ligand) is again considered to be buried under the peaks for the Ph protons. The elemental analysis for **4** suggests the presence of two acetone solvates per mole of complex, while the solution ^1H NMR data show coordination of the amide carbonyl, and thus the square planar, four-coordinate geometry is strongly preferred. The major MS peak at 279 remains unidentified; the $[\text{Rh}(\text{PPh})\text{EtC}(\text{Me})\text{N} - 2\text{H}]^+$ species corresponds to such a mass but is considered unlikely; perhaps a matrix component is involved.

The room temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum for **4** in acetone exhibits a broad doublet at δ 49.7 ($J_{\text{Rh,P}} = 194$ Hz) resembling those of *cis*- $[\text{Rh}(\text{PPh}_3)_2(\text{Me}_2\text{CO})_2]^+$ (**1a**). However, complex **4** (unlike **1a**) has inequivalent phosphines, and this is demonstrated by the low temperature $^{31}\text{P}\{^1\text{H}\}$ NMR data (Fig. 2). As the temperature is

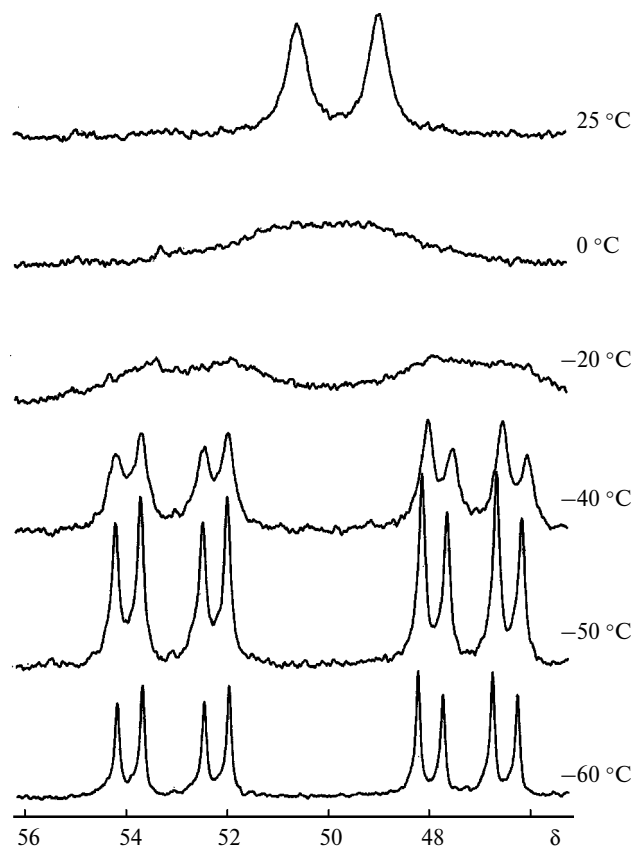


Fig. 2. Variable temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **4** in acetone- d_6 .

decreased to -60 °C, the doublet first collapses to a broad signal, which then resolves to the expected eight-line ABX pattern: δ 53.01 (dd, $J_{\text{Rh,P}} = 207$ Hz, $J_{\text{P,P}} = 60$ Hz); 47.49 (dd, $J_{\text{Rh,P}} = 178.8$ Hz, $J_{\text{P,P}} = 60$ Hz); a comparison with the literature data²⁰ suggests that the higher-field shift should be assigned to the P atom *trans* to the imine-N atom. The room temperature spectrum is attributed to a labile equilibrium involving competitive coordination of acetone (Solv) with the carbonyl of the semicarbazone (see Scheme 2).

More generally, there are many examples of Rh metallocycles formed *via* the activation of the $\text{sp}^2\text{-C-H}$ ^{16,21,22} and $\text{sp}^3\text{-C-H}$ ^{18,23,24} bonds within a range of ligand systems. In addition to being possible intermediates in catalytic hydrogenations (our interest), such complexes may possess physical properties with practical applications. For example, some Rh^{III} complexes containing orthometallated imine ligands have useful photochemical properties,²² while some Pd^{II} and Ni^{II} complexes with a five- or six-membered orthometallated ring possess nonlinear optical properties.²⁵

Experimental

Materials, reagents, and instrumentation. All syntheses were performed under Ar using standard Schlenk and/or dry-box techniques. The solvents (acetone, ether, and hexanes) were dried using Na-benzophenone ketyl, degassed, and condensed into a reaction flask under vacuum immediately prior to use; MeOH was purified by refluxing over Mg chips; CH_2Cl_2 was dried with molecular sieves, and deuterated solvents were dried and degassed prior to use.

Phosphines were purchased from Strem Chemicals. Hydrogen (Praxair, Extra Dry) was purified by passing through the Englehard Deoxo catalyst. The $[\text{Rh}(\text{cod})(\text{PR}_3)_2]\text{PF}_6$ complexes ($\text{R} = \text{Ph}$, *p*- OMeC_6H_4 , *p*- FC_6H_4 , *p*- ClC_6H_4 ; $\text{R}_3 = \text{Ph}_2\text{Me}$, $\text{Ph}_2(p\text{-MeC}_6\text{H}_4)$) were prepared according to a literature method.⁴ The $[\text{Rh}(\text{PR}_3)_2(\text{Solv})_2]^+$ ($\text{Solv} = \text{MeOH}$, Me_2CO) species were generated *in situ* by removing the H_2 atmosphere over the solutions containing the corresponding *cis,trans,cis*- $[\text{Rh}(\text{H})_2(\text{PR}_3)_2(\text{Solv})_2]\text{PF}_6$ species according to the literature procedure.^{4,5}

NMR spectra were recorded on Bruker AC-200 and Bruker AV-300 spectrometers, with residual protons of deuterated solvents (^1H , relative to external SiMe_4), solvent carbon (^{13}C , relative to external SiMe_4), and external $\text{P}(\text{OMe})_3$ ($^{31}\text{P}\{^1\text{H}\}$, $\delta_{\text{P}} 141.00$ vs. 85% aq. H_3PO_4) being used as references; data were recorded at room temperature (-20 °C). The $^o\text{C}_6\text{H}_4$ notation used represents assignments of the orthometallated ring protons. IR spectra (in KBr pellets) were recorded on an ATI Mattson Genesis FT-IR spectrometer. Mass spectral data were measured on a Kratos Concept IIIHQ liquid secondary-ion instrument using thioglycerol or 3-nitrobenzylalcohol matrix. Microanalyses were performed by P. Borda in the analytical Laboratory of the Chemistry Department, University of British Columbia.

Semicarbazones. These were prepared as the *E*-isomers by the standard condensation reaction of the appropriate ketone

with semicarbazide in H₂O/EtOH at room temperature.²⁶ The three semicarbazones have been reported previously, but the degree of their characterization has been variable;^{27,28} given below are more complete data. There is good agreement with the available, more limited literature data.

Acetophenone semicarbazone. Yield was 97 %. M.p. 195.5–197 °C. Found (%): C, 61.09; H, 6.29; N, 23.33. C₉H₁₁N₃O. Calculated (%): C, 61.00; H, 6.26; N, 23.71. IR, ν/cm⁻¹: 1695 (C=O); 1584 (C=N). ¹H NMR (DMSO-d₆), δ: 2.20 (s, 3 H, Me); 6.60 (s, 2 H, NH₂); 7.30–7.40 (m, 3 H, H arom.); 7.80–7.90 (m, 2 H, H arom.); 9.45 (s, 1 H, NH). ¹³C NMR (DMSO-d₆), δ: 13.46 (s, 1 C, Me); 128.07, 128.29 (both s, 2 C each, C arom.); 128.55 (s, 1 C, C arom.); 138.38 (s, 1 C, C=C_{imine}); 144.29 (s, 1 C, C=N); 157.66 (s, 1 C, C=O). MS, m/z (I_{rel} (%)): 177 [M]⁺ (42), 133 [M – CO – NH₂]⁺ (100), 119 [M – N – CO – NH₂]⁺ (35), 103 [PhC(Me) – H]⁺ (25), 77 [Ph⁺] (60).

Propiophenone semicarbazone. Yield was 98%. M.p. 176.5–178 °C. Found (%): C, 62.93; H, 6.89; N, 21.94. C₁₀H₁₃N₃O. Calculated (%): C, 62.81; H, 6.85; N, 21.97. IR, ν/cm⁻¹: 1695 (C=O); 1583 (C=N). ¹H NMR (DMSO-d₆), δ: 1.00 (t, 3 H, Me); 2.75 (q, 2 H, CH₂); 6.50 (s, 2 H, NH₂); 7.30–7.40 (m, 3 H, H arom.); 7.80–7.90 (m, 2 H, H arom.); 9.50 (s, 1 H, NH). ¹³C NMR (DMSO-d₆), δ: 10.59 (s, 1 C, Me); 18.95 (s, 1 C, CH₂); 126.09 (s, 3 C, C arom.); 128.48 (s, 2 C, C arom.); 137.18 (s, 1 C, C=C, imine); 148.29 (s, 1 C, C=N); 157.47 (s, 1 C, C=O). MS, m/z (I_{rel} (%)): 191 [M – 2 H]⁺ (45); 162 [M – Et]⁺ (15); 147 [M – Et – NH]⁺ (100); 130 [M – Et – NH₂ – O]⁺ (35); 119 [M – Et – CO – NH]⁺ (50); 77 [Ph⁺] (55).

Butanone semicarbazone. Yield was 70%. M.p. 148–150 °C. Found (%): C, 47.05; H, 8.62; N, 32.17. C₅H₁₁N₃O. Calculated (%): C, 46.49; H, 8.58; N, 32.53. IR, ν/cm⁻¹: 1645 (C=O); 1584 (C=N). ¹H (CDCl₃), δ: 1.15 (t, 3 H, CH₃CH₂); 1.85 (s, 3 H, MeC=); 2.20 (q, 2 H, MeCH₂); 5.80 (br.s, 2 H, NH₂); 8.50 (s, 1 H, NH). ¹³C NMR (CDCl₃), δ: 10.56 (s, 1 C, CH₃CH₂); 15.29 (s, 1 C, CH₃C=); 31.88 (s, 1 C, CH₂CH₂); 151.65 (s, 1 C, C=O); 158.48 (s, 1 C, C=N). MS, m/z (I_{rel} (%)): 129 [M]⁺ (85); 114 [M – Me]⁺ (15); 100 [M – Et]⁺ (55); 86 [Et(Me)C=NNH₂]⁺ (60); 85 [M – C(O)NH₂]⁺ (35); 69 [EtC=NN]⁺ (40).

Synthesis of orthometallated complexes. (O,N,ortho-C-Acetophenonesemicarbazonato)(hydrido)bis(triphenylphosphine)rhodium(III) hexafluorophosphate, [Rh(H)(PPh₃)₂{o-C₆H₄(Me)C=N–N(H)CONH₂}]PF₆ (2a). Complex [Rh(cod)(PPh₃)₂]PF₆ (55.5 mg, 0.063 mmol) in acetone (5 mL) was reacted with 1 atm H₂ at ~20 °C for 2 h to form an *in situ* sample of *cis,trans,cis*-[Rh(H)₂(PPh₃)₂(Me₂CO)₂]⁺. Hydrogen and the volatile materials (solvent, cyclooctane) were then removed under vacuum at –40 °C for 12 h, and the dark red residue was then redissolved in acetone (~3 mL) to form [Rh(PPh₃)₂(Me₂CO)₂]⁺ (**1a**).⁵ Acetophenone semicarbazone (11.2 mg, 0.063 mmol) was then added, and the mixture was stirred at –20 °C for 1 day, when the colour changed to pale yellow. Addition of Et₂O (~3 mL) precipitated a white solid that was collected and dried under vacuo for 12 h; yield of **2a** was 41 mg (68%). An alternative procedure for isolation of **2a** was removal of solvent from the reaction mixture, dissolution of the residue in minimal amount of dichloromethane, and precipitation by addition of hexanes. Crystals of **2a** were grown by layering hexanes over a dichloromethane solution of the complex.

Complex 2a. Found (%): C, 57.09; H, 4.46; N, 4.56. C₄₅H₄₁F₆N₃OP₃Rh. Calculated (%): C, 56.91; H, 4.35; N, 4.43. IR, ν/cm⁻¹: 2002 m (Rh–H); 1656 s (C=O); 1577 s (C=N). ¹H NMR (acetone-d₆), δ: –10.65 (dt, 1 H, RhH, J_{P,H} = 10 Hz, J_{Rh,H} = 15 Hz); 1.53 (s, 3 H, Me); 3.00 (br.s, 2 H, NH₂); 6.33 (t, 1 H, ^oC₆H₄, J_{H,H} = 8 Hz); 6.66 (m, 2 H, ^oC₆H₄, J_{H,H} = 8 Hz); 6.82 (d, 1 H, ^oC₆H₄, J_{H,H} = 8 Hz); 7.50–8.00 (m, ~30 H, PPh₃). ³¹P{¹H} NMR (acetone-d₆), δ: 41.13 (d, J_{Rh,P} = 118 Hz); –143.2 (septet, PF₆⁻, J_{P,H} = 708 Hz). MS, m/z (I_{rel} (%)): 804 [M – PF₆]⁺ (60); 627 [Rh(PPh₃)₂]⁺ (95); 542 [M – PPh₃ – PF₆]⁺ (100); 287 [Rh(PPh₂)]⁺ (68).

The preparation of **2a** can also be carried out in MeOH or in CH₂Cl₂, when the precursors are [Rh(PPh₃)₂(MeOH)₂]⁺ or [Rh(PPh₃){(μ-Ph)PPh₂}]₂²⁺, respectively (see above), but the reactions with the semicarbazone are much slower, taking several days for completion.

Other [Rh(PR₃)₂(Me₂CO)₂]⁺ precursor species (**1b–f**) were prepared analogously *in situ* in acetone, and their room temperature ³¹P{¹H} NMR data, together with those for **1a**, are summarized in the Results and Discussion section. From these precursors, four other orthometallated complexes (**2b**, **2d**, **2e**, and **3**) were isolated and characterized by procedures identical to those described above for **2a**, and using 0.063 mmole of each of the respective precursors and semicarbazones, while two others (**2c** and **2f**) were just formed *in situ*, *i.e.* prior to addition of ether. The yields and analytical data for **2b–e** and **3** are summarized below, NMR data again being recorded in acetone-d₆.

(O,N,o-C-Acetophenonesemicarbazonato)(hydrido)bis[diphenyl(p-methylphenyl)phosphine]rhodium(III) hexafluorophosphate, [Rh(H)(PPh₂(p-MeC₆H₄))₂{o-C₆H₄(Me)C=N–NHC(O)NH₂}]PF₆ (2b). Yield 63%. Found (%): C, 57.55; H, 4.73; N, 4.39. C₄₇H₄₅F₆N₃OP₃Rh. Calculated (%): C, 57.74; H, 4.64; N, 4.30. IR, ν/cm⁻¹: 2009 m (Rh–H); 1638 s (C=O); 1576.3 s (C=N). ¹H NMR, δ: –10.70 (dt, 1 H, RhH, J_{P,H} = 10.4 Hz, J_{Rh,H} = 15.3 Hz); 1.50 (s, 3 H, Me); 2.28 (s, 6 H, p-Me); 2.88 (br.s, 2 H, NH₂); 6.31 (t, 1 H, ^oC₆H₄, J_{H,H} = 7.1 Hz); 6.62 (d, 1 H, ^oC₆H₄, J_{H,H} = 8.5 Hz); 6.66 (t, 1 H, ^oC₆H₄, J_{H,H} = 7.1 Hz); 6.81 (d, 1 H, ^oC₆H₄, J_{H,H} = 7.6 Hz); 6.90–7.80 (m, 28 H, H arom.). ³¹P{¹H} NMR, δ: 40.7 (d, J_{Rh,P} = 116.6 Hz); –143.2 (septet, PF₆⁻). MS, m/z (I_{rel} (%)): 832 [M – PF₆]⁺ (45); 655 [Rh{PPh₂(p-MeC₆H₄)}₂]⁺ (100); 556 [M – PPh₂(p-MeC₆H₄)]⁺ (90); 301 (40), 136 (40).

(O,N,o-C-Acetophenonesemicarbazonato)(hydrido)bis[tri(p-methoxyphenyl)phosphine]rhodium(III) hexafluorophosphate, [Rh(H){P(p-OMeC₆H₄)₃}₂{o-C₆H₄(Me)C=N–NHC(O)NH₂}]PF₆ (2c). ¹H NMR, δ: –10.84 (dt, 1 H, RhH, J_{P,H} = 11 Hz, J_{Rh,H} = 16.5 Hz); 2.08 (s, 3 H, MeC); 2.88 (br.s, 2 H, NH₂); 3.80 (s, 12 H, OMe); 3.83 (s, 6 H, OMe); 6.28 (br.s, 1 H, NH); 6.36 (t, 1 H, ^oC₆H₄); 6.64 (d, 1 H, ^oC₆H₄); 6.68 (t, 1 H, ^oC₆H₄); 6.82 (d, 1 H, ^oC₆H₄); 6.90–7.80 (m, 24 H, H arom.). ³¹P{¹H} NMR, δ: 36.7 (d, J_{Rh,P} = 121.5 Hz); –143.2 (septet, PF₆⁻).

(O,N,o-C-Acetophenonesemicarbazonato)(hydrido)bis[tri(p-fluorophenyl)phosphine]rhodium(III) hexafluorophosphate, [Rh(H){P(p-FC₆H₄)₃}₂{o-C₆H₄(Me)C=N–NHC(O)NH₂}]PF₆ (2d). Yield 59%. Found (%): C, 51.03; H, 3.42; N, 3.79. C₄₅H₃₅F₁₂N₃OP₃Rh. Calculated (%): C, 51.11; H, 3.34; N, 3.97. ¹H NMR, δ: –10.77 (dt, 1 H, RhH, J_{P,H} = 10.8 Hz, J_{Rh,H} = 15.0 Hz); 1.67 (s, 3 H, Me); 2.90 (br.s, 2 H, NH₂); 6.46 (t, 1 H, ^oC₆H₄, J_{H,H} = 7 Hz); 6.68 (d, 1 H, ^oC₆H₄, J_{H,H} = 8 Hz); 6.73 (t, 1 H, ^oC₆H₄, J_{H,H} = 7.4 Hz); 6.92 (d, 1 H, ^oC₆H₄, J_{H,H} = 7.7 Hz); 7.12 (t, 2 H, H arom., J_{H,H} = 8.4 Hz); 7.23 (t, 10 H,

H arom., $J_{\text{H,H}} = 8.8$ Hz); 7.55 (m, 10 H, H arom.); 7.70 (m, 2 H, H arom.). $^{31}\text{P}\{^1\text{H}\}$ NMR, δ : 38.51 (d, $J_{\text{Rh,P}} = 118$ Hz); -143.2 (septet, PF_6^-). MS, m/z (I_{rel} (%)): 912 $[\text{M} - \text{PF}_6]^+$ (25); 735 $[\text{Rh}\{\text{P}(p\text{-FC}_6\text{H}_4)_3\}_2]^+$ (65); 596 $[\text{Rh}\{\text{P}(p\text{-FC}_6\text{H}_4)_3\}\{\text{C}_6\text{H}_4(\text{Me})\text{C}=\text{NNHC}(\text{O})\text{NH}_2\}]^+$ (100); 323 $[\text{Rh}\{\text{P}(p\text{-FC}_6\text{H}_4)_2\} - \text{H}]^+$ (50).

(*O,N,o*-C-Acetophenonesemicarbazonato)(hydrido)bis(tri-*p*-chlorophenyl)phosphine]rhodium(III) hexafluorophosphate, $[\text{Rh}(\text{H})\{\text{P}(p\text{-ClC}_6\text{H}_4)_3\}_2\{o\text{-C}_6\text{H}_4(\text{Me})\text{C}=\text{N}-\text{NHC}(\text{O})\text{NH}_2\}]\text{PF}_6$ (2e**). Yield 51%. Found (%): C, 46.11; H, 3.29; N, 3.31. $\text{C}_{45}\text{H}_{35}\text{Cl}_6\text{F}_6\text{N}_3\text{O}_3\text{P}_3\text{Rh}$. Calculated (%): C, 46.74; H, 3.05; N, 3.63. ^1H NMR, δ : -10.74 (dt, 1 H, RhH, $J_{\text{P,H}} = 10.3$ Hz, $J_{\text{Rh,H}} = 14.6$ Hz); 1.60 (s, 3 H, Me); 3.25 (br.s, 2 H, NH_2); 6.47 (t, 1 H, $^o\text{C}_6\text{H}_4$, $J_{\text{H,H}} = 7$ Hz); 6.53 (br.s, 1 H, NH); 6.68 (d, 1 H, $^o\text{C}_6\text{H}_4$, $J_{\text{H,H}} = 8$ Hz); 6.75 (t, 1 H, $^o\text{C}_6\text{H}_4$, $J_{\text{H,H}} = 7.5$ Hz); 6.92 (d, 1 H, $^o\text{C}_6\text{H}_4$, $J_{\text{H,H}} = 7.7$ Hz); 7.45–7.75 (m, 24 H, H arom.). $^{31}\text{P}\{^1\text{H}\}$ NMR, δ : 40.41 (d, $J_{\text{Rh,P}} = 118$ Hz); -143.2 (septet, PF_6^-). MS, m/z (I_{rel} (%)): 1010 $[\text{M} - \text{H} - \text{PF}_6]^+$ (10); 833 $[\text{Rh}\{\text{P}(p\text{-ClC}_6\text{H}_4)_3\}_2 - \text{H}]^+$ (21); 644 $[\text{Rh}\{\text{P}(p\text{-ClC}_6\text{H}_4)_3\}\{\text{C}_6\text{H}_4(\text{Me})\text{C}=\text{NNHC}(\text{O})\text{NH}_2\} - \text{H}]^+$ (100).**

(*O,N,o*-C-Acetophenonesemicarbazonato)(hydrido)bis(methylidiphenyl)phosphine]rhodium(III) hexafluorophosphate, $[\text{Rh}(\text{H})(\text{PPh}_2\text{Me})_2\{o\text{-C}_6\text{H}_4(\text{Me})\text{C}=\text{N}-\text{NHC}(\text{O})\text{NH}_2\}]\text{PF}_6$ (2f**). ^1H NMR, δ : -11.58 (m, 1 H, RhH, $J_{\text{P,H}} = 14.7$ Hz, $J_{\text{Rh,H}} = 17.9$ Hz); 1.18 (s, 6 H, *p*-Me); 2.15 (s, 3 H, MeC); 2.83 (br.s, 2 H, NH_2); 6.48 (br.s, 1 H, NH); 6.84–7.65 (m, 24 H, 20 H arom. and 4 $^o\text{C}_6\text{H}_4$). $^{31}\text{P}\{^1\text{H}\}$ NMR, δ : 21.52 (d, $J_{\text{Rh,P}} = 112.3$ Hz); -143.2 (septet, PF_6^-).**

(*O,N,o*-C-Propiophenonesemicarbazonato)(hydrido)bis(triphenylphosphine)rhodium(III) hexafluorophosphate, $[\text{Rh}(\text{H})(\text{PPh}_3)_2\{o\text{-C}_6\text{H}_4(\text{Et})\text{C}=\text{N}-\text{NHC}(\text{O})\text{NH}_2\}]\text{PF}_6$ (3**). Yield 65.8%. Found (%): C, 56.34; H, 4.56; N, 4.32. $\text{C}_{46}\text{H}_{43}\text{F}_6\text{N}_3\text{O}_3\text{P}_3\text{Rh} \cdot 0.25 \text{CH}_2\text{Cl}_2$. Calculated (%): C, 56.40; H, 4.46; N, 4.27. IR: ν/cm^{-1} : 2045 br m (Rh–H); 1670 s (C=O); 1513 s (C=N). ^1H NMR, δ : -10.85 (dt, 1 H, RhH, $J_{\text{P,H}} = 11$ Hz, $J_{\text{Rh,H}} = 15$ Hz); 0.52 (t, 3 H, Me); 1.88 (q, 2 H, CH_2); 2.80 (br.s, 2 H, NH_2); 6.30 (t, 1 H, $^o\text{C}_6\text{H}_4$, $J_{\text{H,H}} = 8$ Hz); 6.42 (d, 1 H, $^o\text{C}_6\text{H}_4$, $J_{\text{H,H}} = 8$ Hz); 6.60 (br.s, 1 H, NH); 6.73 (t, 1 H, $^o\text{C}_6\text{H}_4$, $J_{\text{H,H}} = 10$ Hz); 6.92 (d, 1 H, $^o\text{C}_6\text{H}_4$, $J_{\text{H,H}} = 8$ Hz); 7.10–8.10 (m, 30 H, PPh_3). $^{31}\text{P}\{^1\text{H}\}$ NMR, δ : 41.58 (d, $J_{\text{Rh,P}} = 117$ Hz); -143.2 (septet, PF_6^-). MS, m/z (I_{rel} (%)): 818 $[\text{M} - \text{PF}_6]^+$ (45); 627 $[\text{Rh}(\text{PPh}_3)_2]^+$ (85); 556 $[\text{M} - \text{PPh}_3 - \text{PF}_6]^+$ (100); 287 $[\text{Rh}\{\text{PPh}_3\}_2 - \text{H}]^+$ (75).**

(*O,N*-Butanonesemicarbazonato)bis(triphenylphosphine)rhodium(III) hexafluorophosphate, $[\text{Rh}(\text{PPh}_3)_2\{\text{C}_2\text{H}_5(\text{Me})\text{C}=\text{N}-\text{NHC}(\text{O})\text{NH}_2\}]\text{PF}_6$ (4**). Addition of 2.32 mg (0.018 mmol) of butanone semicarbazone (or twice this amount) to an acetone solution (3 mL) of **1a**, formed from 15.8 mg (0.018 mmol) of $[\text{Rh}(\text{cod})(\text{PPh}_3)_2]\text{PF}_6$, resulted in no visible change to the red solution, which was then stirred at -20 °C for 2 h. Then the acetone was removed in vacuum and the residue re-dissolved in $\sim 1\text{--}2$ mL of CH_2Cl_2 . Addition of hexanes (1 mL) gave a red solid that was collected, and dried under vacuo overnight. Yield of complex **4** was 8.2 mg (45%). Found (%): C, 55.76; H, 5.57; N, 4.76. $\text{C}_{41}\text{H}_{41}\text{F}_6\text{N}_3\text{O}_3\text{P}_3\text{Rh} \cdot 2 \text{Me}_2\text{CO}$. Calculated (%): C, 55.47; H, 5.25; N, 4.13. IR, ν/cm^{-1} : 1601 m (C=O, semicarbazone); 1543 m (C=N). ^1H NMR (acetone- d_6), δ : 0.97 (t, 3 H, CH_3CH_2); 1.92 (q, 2 H, MeCH_2); 1.75 (s, 3 H, $\text{CH}_3\text{--C}=\text{N}$); 2.85 (br.s, 2 H, NH_2); 7.15–7.70 (m, 30 H, H arom.). $^{31}\text{P}\{^1\text{H}\}$ NMR (acetone- d_6), δ : 49.7 (br.d, $J_{\text{Rh,P}} = 194$ Hz); -143.2 (septet, PF_6^-). MS,**

m/z (I_{rel} (%)): 756 $[\text{M} - \text{PF}_6]^+$ (3); 627 $[\text{Rh}(\text{PPh}_3)_2]^+$ (20); 279 (?) (100).

Reactivity of $[\text{Rh}(\text{H})(\text{PPh}_3)_2\{o\text{-C}_6\text{H}_4(\text{Me})\text{C}=\text{N}-\text{N}(\text{H})\text{CONH}_2\}]\text{PF}_6$ (2a**) toward H_2 .** Complex **2a** (~ 10 mg) was dissolved in acetone, methanol, or CH_2Cl_2 , and the solution was exposed to H_2 (1 atm) at -20 °C. No reaction was observed by ^1H or $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. Attempts to hydrogenate acetone semicarbazone using **1a** or **2a** as a catalyst with 1–40 atm H_2 at -20 °C in acetone or methanol were unsuccessful.

X-ray diffraction study. X-ray diffraction data on a clear, platelet crystal of **2a** ($0.50 \times 0.25 \times 0.08$ mm 3) were collected at 173 K on a Rigaku/ADSC CCD area detector instrument with graphite monochromated Mo- $K\alpha$ radiation (0.71069 Å). Crystals of **2a**, $\text{C}_{45}\text{H}_{41}\text{N}_3\text{O}_3\text{F}_6\text{P}_3\text{Rh} \cdot 2 \text{CH}_2\text{Cl}_2$ ($M = 1119.52$), are triclinic, space group $P\bar{1}$ (No. 2), $a = 12.786(1)$, $b = 14.096(2)$, $c = 14.7520(9)$ Å, $\alpha = 96.764(4)^\circ$, $\beta = 101.491(5)^\circ$, $\gamma = 105.089(4)^\circ$, $V = 2474.9(4)$ Å 3 , $d_{\text{calc}} = 1.502$ g cm $^{-3}$, $Z = 2$. Of the 21,307 reflections collected, 9536 were unique ($R_{\text{int}} = 0.049$). Data were collected and processed using the d*TREK²⁹ program and corrected for Lorentz and polarization effects. The structure was solved by direct methods³⁰ and expanded using Fourier techniques.³¹ The non-hydrogen atoms were refined anisotropically; the coordinated H atom was refined isotropically, and the rest were included in fixed positions. Two CH_2Cl_2 molecules were found in the asymmetric unit. The final cycle of full-matrix least-squares refinement was based on 9531 reflections and 620 variable parameters. All calculations were performed using the teXsan crystallographic software.³² The final reliability factors were $R_1 = 0.042$ (based on reflections with $I > 3\sigma(I)$) and $wR_2 = 0.119$ (on F^2 , all data). The complete tables of bond lengths, bond angles, atomic coordinates, and thermal parameters were deposited with the Cambridge Crystallographic Data Centre (CCDC-228477).

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