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Interactions of Rh(III)–Dihydrido–Bis(phosphine) Complexes with Semicarbazones

Maria B. Ezhova,[†] Brian O. Patrick,[†] Kapila N. Sereviratne,[†] Brian R. James,*[,†] Francis J. Waller,[‡] and Michael E. Ford[‡]

Department of Chemistry, University of British Columbia, Vancouver, British Columbia V6T 1Z1, Canada, and Air Products & Chemical Inc., Allentown, Pennsylvania 18195-1501

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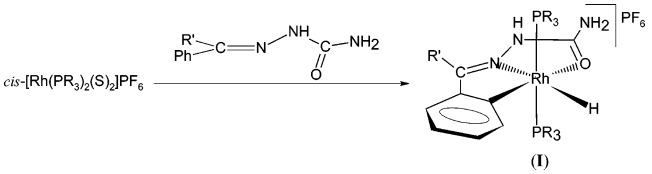
Interaction of *cis,trans,cis*-$[Rh(H)_2(PR_3)_2(acetone)_2]PF_6$ complexes (R = aryl or R_3 = Ph_2Me, Ph_2Et) under H_2 with *E*-semicarbazones gives the Rh(III)–dihydrido–bis(phosphine)–semicarbazone species *cis,trans*-$[Rh(H)_2(PR_3)_2\{R'(R'')C{=}N{-}N(H)CONH_2\}]PF_6$, where R′ and R″ are Ph, Et, or Me. The complexes are generally characterized by elemental analysis, $^{31}P\{^1H\}$ NMR, ^1H NMR, and IR spectroscopies, and MS. X-ray analysis of three PPh_3 complexes reveals chelation of *E*-semicarbazones by the imine-N atom and the carbonyl-O atom. In contrast, the corresponding reaction of $[Rh(H)_2(PPhMe_2)_2(acetone)_2]PF_6$ with acetophenone semicarbazone gives the ortho-metalated-semicarbazone species *cis*-$[RhH(PPhMe_2)_2\{o\text{-}C_6H_4(Me)C{=}N{-}N(H)CONH_2\}]PF_6$. The X-ray structure of *E*-propiophenone semicarbazone is also reported. Rhodium-catalyzed, homogeneous hydrogenation of semicarbazones was not observed even at 40 atm H_2.

Introduction

As part of our long term interest in catalyzed homogeneous hydrogenation of imine derivatives, we recently reported on the room temperature (~20 °C), 1:1 reaction of *cis*-$[Rh(PR_3)_2(solvent)_2]PF_6$ complexes with *E*-semicarbazones (R = aryl or R_3 = Ph_2Me; solvent = acetone, MeOH).[1] When the semicarbazone contained a Ph group on the imine-C atom, the product was the Rh^{III} hydrido-orthometalated species $[RhH(PR_3)_2\{o\text{-}C_6H_4(R')C{=}N{-}N(H)CONH_2\}]PF_6$ containing *trans*-PR_3 ligands, where R′ is Me or Et (see **I** in Scheme 1).[1] The PPh_3 complex with R′ = Me was structurally characterized, including location of the hydride, which had not been reported previously for an orthometalated semicarbazone complex. For a semicarbazone containing no Ph group, the product was a Rh^I–(η^2-semicarbazone) species, exemplified by $[Rh(PPh_3)_2\{Et(Me)C{=}N{-}N(H)CONH_2\}]PF_6$ with the semicarbazone coordinated via the imine-N and carbonyl-O atoms.[1]

Our publication[1] included introductory material describing the well-known chemistry of $[Rh(COD)(PR_3)_2]PF_6$ to generate *cis,trans,cis* (*c,t,c*)-$[Rh(H)_2(PR_3)_2(solvent)_2]PF_6$, and the subsequent removal of H_2 to give *cis*-$[Rh(PR_3)_2(solvent)_2]PF_6$ species;[2,3] these systems have been used to catalyze hydrogenation of imines.[4,5] The several modes of coordination of semicarbazones were also reviewed in one of our publications,[1] including the type shown as **I** in Scheme 1, containing two fused, five-membered rings.

Scheme 1. Formation of the Orthometalated Semicarbazone Complexes[a]



(**I**)

[a] S = solvent, R′ = Me or Et.

* To whom correspondence should be addressed. E-mail: brj@chem.ubc.ca. Fax: (604) 822-2847.
[†] University of British Columbia.
[‡] Air Products & Chemical Inc.

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In studies aimed at the catalytic hydrogenation of semicarbazones, this current paper describes interaction of these substituted imines with the dihydrides *c,t,c*-$[Rh(H)_2(PR_3)_2(acetone)_2]PF_6$ under H_2. The products depend on the nature of R and are either (i) the Rh(III)−dihydrido−bis(phosphine)-η^2-*N,O*-semicarbazone species such as *cis,trans* (*c,t*)-$[Rh(H)_2(PR_3)_2\{Ph(R')C{=}N{-}N(H)CONH_2\}]PF_6$, where R = Ph or R_3 = Ph_2Me or Ph_2Et, and R′ = Me or Et; or (ii) the orthometalated species $[RhH(PR_3)_2\{o\text{-}C_6H_4(Me)C{=}N{-}N(H)CONH_2\}]PF_6$ with *cis*-phosphines when R = $PhMe_2$. The semicarbazones are all of *E*-geometry, as exemplified in Scheme 1.

Experimental Section

General. Reactions of the Rh systems were performed under Ar using standard Schlenk and/or glovebox techniques. All nondeuterated solvents (reagent grade) were dried over CaH_2 or Na, distilled under N_2, stored over sodium/benzophenone ketyl in a vacuum, and vacuum distilled directly into a reaction vessel. Deuterated solvents were dried according to standard procedures[6] and stored under Ar or under vacuum.

NMR spectra were recorded at room temperature in acetone-d_6 (unless noted otherwise) on Bruker AC200 and Bruker AV300 spectrometers, with residual protons of deuterated solvents (^{1}H, relative to external $SiMe_4$), and external $P(OMe)_3$ ($^{31}P\{^1H\}$, δ_P = 141.00 vs 85% aq H_3PO_4) being used as references; *J* values are given in Hz. IR spectra (KBr pellets) were recorded in cm^{-1} on an ATI Mattson Genesis FT-IR spectrometer. Low resolution mass spectral data were measured on a Kratos Concept IIHQ LSIMS instrument (using thioglycerol or 3-nitro-benzyl alcohol as matrix), and are given as *m/z* with relative % intensities. Microanalyses were performed by Mr. P. Borda in this department.

Materials. Phosphines and $RhCl_3{\cdot}3H_2O$ were purchased, respectively, from Strem Chemicals and Colonial Metals, Inc. H_2 (Praxair, Extra Dry) was purified by passage through an Englehard "Deoxo" catalyst. Acetone−, acetophenone−, propiophenone−, and butanone−semicarbazone were synthesized as the *E*-isomer by the standard condensation reaction of the appropriate ketone with semicarbazide in H_2O/EtOH at room temperature.[7] We reported recently ^{1}H and ^{13}C NMR, IR, and MS data for the last three mentioned semicarbazones,[1] and presented here for reference purposes are some spectroscopic data for acetone semicarbazone, $Me_2C{=}NN(H)C(O)NH_2$. ^{1}H NMR (δ, acetone-d_6): 1.90 (s, C*H*$_3$), 1.93 (s, C*H*$_3$), 2.76 (s, N*H*$_2$), 8.55 (s, N*H*). IR: 1686 ($\nu_{C=O}$), 1580 ($\nu_{C=N}$). MS: 115 ($[M]^+$, 45%,), 100 ($[M - 15]^+$, 20%), 72 ($[(Me)_2C{=}NNH_2]^+$, 100%), 57 ($[(Me)_2C{=}NH]^+$, 65%).

The $[Rh(COD)(PR_3)_2]PF_6$ complexes [R_3 = Ph_3 (**1a**), $Ph_2(C_6H_4$-*p*-Me) (**1b**), $(C_6H_4$-*p*-Me)$_3$ (**1c**), $(C_6H_4$-*p*-OMe)$_3$ (**1d**), $(C_6H_4$-*p*-F)$_3$ (**1e**); Ph_2Et (**1f**), Ph_2Me (**1g**), $PhMe_2$ (**1h**)], isolated according to a literature method,[2] were reacted with H_2 in acetone at room temperature to form in situ the corresponding *c,t,c*-$[Rh(H)_2(PR_3)_2(acetone)_2]PF_6$ (**2a**−**h**) species.[2,3] The $^{31}P\{^1H\}$ and high-field ^{1}H NMR data for isolated **1a**−**h**, and for in situ **2a**−**h** were: **1a** (δ_P 27.03, d, J_{RhP} = 145); **1b** (δ_P 26.69, d, J_{RhP} = 146); **1c** (δ_P 24.43, d, J_{RhP} = 145); **1d** (δ_P 26.96, d, J_{RhP} = 146); **1e** (δ_P 25.56, d, J_{RhP} = 147); **1f** (δ_P 21.47, d, J_{RhP} = 143); **1g** (δ_P 12.25, d, J_{RhP} = 144); **1h** (δ_P −2.41, d, J_{RhP} = 145). **2a** (δ_P 45.43, d, J_{RhP} = 118; δ_H −20.72 dt, J_{RhH} = 25.3, J_{PH} = 15.0); **2b** (δ_P 44.82, d, J_{RhP} = 117; δ_H −20.79 dt, J_{RhH} = 25.0, J_{PH} = 15.0); **2c** (δ_P 43.27, d, J_{RhP} = 118; δ_H −20.93 dt, J_{RhH} = 25.5, J_{PH} = 15.3); **2d** (δ_P 40.66, d, J_{RhP} = 116; δ_H −20.98 dt, J_{RhH} = 26.6, J_{PH} = 15.5); **2e** (δ_P 42.73, d, J_{RhP} = 119; δ_H −20.54 dt, J_{RhH} = 24.96, J_{PH} = 15.3); **2f** (δ_P 39.32, d, J_{RhP} = 116; δ_H −21.70 dt, J_{RhH} = 25.2, J_{PH} = 15.9); **2g** (δ_P 24.09, d, J_{RhP} = 114; δ_H −21.31 dt, J_{RhH} = 27.0, J_{PH} = 16.8); **2h** (δ_P 27.57, br d, J_{RhP} = 131; δ_H −17.45 m).

***cis,trans*-$[Rh(H)_2(PPh_3)_2\{PhC(Me){=}N{-}N(H)C(O)NH_2\}]PF_6$ (3a).** $[Rh(COD)(PPh_3)_2]PF_6$ (**1a**) (21.6 mg, 0.025 mmol) was reacted with 1 atm H_2 in acetone (0.6 mL) at room temperature for 2.5 h. During this time, the solution color changed from orange to pale yellow when **2a** is formed. *E*-Acetophenone semicarbazone (4.34 mg, 0.025 mmol) was then added; after ∼15 min at room temperature, **3a** is fully formed. All volatile compounds (H_2, solvent, and cyclooctane) were removed under vacuum at room temperature, and the residue was dissolved in CH_2Cl_2 (∼0.5 mL). Addition of hexanes or Et_2O (∼3 mL) precipitated an off-white solid, that was collected and dried under vacuo overnight. Yield 19.0 mg (80%). $^{31}P\{^1H\}$NMR: δ 41.74 (d, J_{RhP} = 119), −143.2 (septet, PF_6^-). ^{1}H NMR: δ −20.48 (ddt, 1H, Rh-*H*, J_{HH} = 11.4, J_{PH} = 13.9, J_{RhH} = 19.2), −17.02 (ddt, 1H, Rh-*H*, J_{HH} = 11.4, J_{PH} = 16.3, J_{RhH} = 19.2), 1.94 (s, 3H, C*H*$_3$), 2.84 (br s, 2H, N*H*$_2$), 6.85 (d, 2H, ═CPh$_{o-H}$, J_{HH} = 8), 7.09 (pseudo-t, 2H, J_{HH} = 8, ═CPh$_{m-H}$), 7.3−7.65 (m, 32H, arom + N*H*). MS: 889 (6%), 804 ($[M - 2H - PF_6]^+$, 7%), 760 ($[Rh(PPh_3)_2(PhC(Me){=}N{-}NH)]^+$, 2%), 627 ($[Rh(PPh_3)_2]^+$, 100%), 287 ($[Rh{=}PPh_2]^+$, 45%). IR: 2187 ($\nu_{Rh-H}$), 2129 ($\nu_{Rh-H}$), 1671 ($\nu_{C=O}$), 1542 ($\nu_{C=N}$). Anal. Calcd for $C_{45}H_{43}N_3OF_6P_3Rh$: C, 56.79; H, 4.55; N, 4.42. Found: C, 56.98; H, 4.61; N, 4.76.

Compound **3a** is formed similarly from a mixture of **1a** and the semicarbazone under H_2, while the reaction can also be carried out in MeOH or CH_2Cl_2. Use of 2 or more equivs of the semicarbazone gave the same product.

Analogous complexes (**4**, **5**, and **6**, respectively) were formed with propiophenone−, acetone−, and butanone−semicarbazone using the same precursor system (**1a**, **2a)** and the above procedure in acetone at room temperature.

***cis,trans*-$[Rh(H)_2(PPh_3)_2\{PhC(Et){=}N{-}N(H)C(O)NH_2\}]PF_6$ (4).** Compound **1a** (50.6 mg, 0.057 mmol) and propiophenone semicarbazone (11.0 mg, 0.057 mmol) were used in this synthesis. Yield 41.5 mg (75%). $^{31}P\{^1H\}$NMR: δ 41.72 (d, J_{RhP} = 120), −143.2 (septet, PF_6^-). ^{1}H: δ -20.65 (ddt, 1H, Rh-*H*, J_{HH} = 11.7, J_{PH} = 13.2, J_{RhH} = 19.2), −17.13 (ddt, 1H, Rh-*H*, J_{HH} = 11.7, J_{PH} = 16.1, J_{RhH} = 18.6), 0.72 (t, 3H, J_{HH} = 7.7, C*H*$_3$), 2.33 (q, 2H, J_{HH} = 7.7, C*H*$_2$), 2.83 (br s, 2H, N*H*$_2$), 6.65 (d, 2H, J_{HH} = 8.0, ═CPh$_{o-H}$), 7.15 (pseudo-t, 2H, J_{HH} = 8.0, ═CPh$_{m-H}$), 7.45−7.6 (m, 32H, arom + N*H*). MS: 820.1 ($[M - PF_6]^+$, 80%), 818 ($[M - 2H - PF_6]^+$, 100%), 626.9 ($[Rh(PPh_3)_2]^+$, 100%). IR: 2083 (ν_{Rh-H}), 1656 ($\nu_{C=O}$), 1536. ($\nu_{C=N}$). Anal. Calcd for $C_{46}H_{45}N_3OF_6P_3Rh$ (**4**)·0.1CH_2Cl_2: C, 56.82; H, 4.68: N, 4.32. Found: C, 56.83; H, 4.54; N, 4.21.

Complex **4** is not stable in acetone; over 24 h, increasing amounts (up to ∼20%) of a new species (**4a**) are formed. $^{31}P\{^1H\}$NMR: δ 42.56 (d, J_{RhP} = 110); −143.2 (septet, PF_6^-). ^{1}H NMR: δ -20.15 (ddt, 1H, Rh-*H*, J_{HH} = 11.3, J_{PH} = 15.2, J_{RhH} = 20.6), −16.48 (ddt, 1H, Rh-*H*, J_{HH} = 11.3, J_{PH} = 15.2, J_{RhH} = 17.9), 0.3 (t, 3H, J_{HH} = 7.6, C*H*$_3$), 2.65 (q, 2H, J_{HH} = 7.6, C*H*$_2$). It was difficult to assign the other ^{1}H signals of **4a**.

***cis,trans*-$[Rh(H)_2(PPh_3)_2\{Me_2C{=}N{-}NHC(O)NH_2\}]PF_6$ (5).** Compound **1a** (16.6 mg, 0.018 mmol) and acetone−semicarbazone (2.17 mg, 0.018 mmol) were used. Yield 12.3 mg (78%). $^{31}P\{^1H\}$ NMR: δ 44.06 (d, J_{RhP} = 117), −143.2 (septet, PF_6^-). ^{1}H NMR: δ -20.5 (ddt, 1H, Rh-*H*, J_{HH} = 11.6, J_{PH} = 15.2; J_{RhH} = 21.4),

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−17.05 (ddt, 1H, Rh-*H*, J_{HH} = 11.6, J_{PH} = 14.0, J_{RhH} = 17.6), 1.39 (s, 3H, C*H*$_3$), 1.49 (s, 3H, C*H*$_3$), 2.81 (br s, 2H, NH$_2$), 7.43−7.52 (m, 14H, arom + N*H*), 7.60−7.72 (m, 17H, arom). MS: 744 ([M − PF_6]$^+$, 5%), 627 ([Rh(PPh$_3$)$_2$]$^+$, 100%). IR: 2066 (ν_{Rh-H}), 1671 ($\nu_{C=O}$), 1543 ($\nu_{C=N}$). Anal. Calcd for $C_{40}H_{41}N_3OF_6P_3Rh$ (**5**)·0.5CH_2Cl_2: C, 52.20; H, 4.55: N, 4.51. Found: C, 52.17; H, 4.62; N, 4.36.

***cis,trans*-[Rh(H)$_2$(PPh$_3$)$_2${Et(Me)C═N−NHC(O)NH$_2$}]PF$_6$ (6).** Compound **1a** (18.4 mg, 0.021 mmol) and butanone−semicarbazone (2.7 mg, 0.021 mmol) were used. Yield 13.1 mg (70%). $^{31}P\{^1H\}$ NMR: δ 43.42 (d, J_{RhP} = 118), −143.2 (septet, PF_6^-). ^{1}H NMR: δ −20.28 (ddt, 1H, Rh-*H*, J_{HH} = 11.3, J_{PH} = 15.0; J_{RhH} = 21.0), −16.50 (ddt, 1H, Rh-*H*, J_{HH} = 11.4; J_{PH} = 15.0; J_{RhH} = 17.3), 0.34 (t, 3H, C*H*$_3$CH$_2$, J_{HH} = 7.5), 1.49 (s, 3H, C*H*$_3$C═), 2.13 (m, 2H, CH$_3$C*H*$_2$), 2.85 (br s, 2H, NH$_2$), 7.4−7.55 (m, 19H, arom + N*H*), 7.55−7.7 (m, 12H, arom). MS: 758 ([M − PF_6]$^+$, 18%), 627 ([Rh(PPh$_3$)$_2$]$^+$, 65%), 307 (31%), 285 (16%), 154 (100%), 136 (64%). IR: 2047 (ν_{Rh-H}), 1667 ($\nu_{C=O}$), 1544 ($\nu_{C=N}$). Anal. Calcd for $C_{41}H_{43}N_3OF_6P_3Rh$ (**6**)·Me_2CO: C, 54.95; H, 5.14; N, 4.37. Found: C, 54.87; H, 5.05; N, 4.52.

After ∼20 days in acetone, **6** is partially (∼40%) converted to **6a**. $^{31}P\{^1H\}$ NMR: δ 43.57 (d, J_{RhP} = 118), −143.2 (septet, PF_6^-). ^{1}H NMR: δ −20.48 (ddt seen as m, 1H, Rh-*H*), −16.55 (ddt seen as m, 1H, Rh-*H*, overlapping with hydride of **6**), 0.66 (t, 3H, J_{HH} = 7.6, C*H*$_3$CH$_2$), 1.54 (s, 3H, C*H*$_3$C═), 1.71 (q, 2H, J_{HH} = 7.6, CH$_3$C*H*$_2$).

From the *c,t,c*-[Rh(H)$_2$(PR$_3$)$_2$(acetone)$_2$]$^+$ precursors (**2b**−**2g**), prepared analogously in situ in acetone, the dihydrido−acetophenone semicarbazone complexes were isolated (**3b**−**e**) or formed in situ (**3f**, **3g**). Reaction of **2h** with acetophenone semicarbazone gave the isolated hydrido-orthometalated complex **8**.

***cis,trans*-[Rh(H)$_2$(PPh$_2$C$_6$H$_4$-*p*-Me)$_2${Ph(Me)C═N−NHC(O)NH$_2$}]PF$_6$ (3b).** Compound **1b** (15.3 mg, 0.017 mmol) and acetophenone−semicarbazone (3.00 mg, 0.017 mmol) were used here. Yield 11.6 mg (70.5%). $^{31}P\{^1H\}$ NMR: δ 41.08 (d, J_{Rh-P} = 120), −143.2 (septet, PF_6^-). ^{1}H NMR: δ −20.5 (ddt, 1H, Rh-*H*, J_{HH} = 11.7; J_{PH} = 13.2; J_{RhH} = 19.7), −17.05 (ddt, 1H, Rh-*H*, J_{HH} = 11.7, J_{PH} = 15.6, J_{RhH} = 19.1), 1.90 (s, 3H, C*H*$_3$C═), 2.38 (s, 6H, *p*-C*H*$_3$), 2.85 (br s, 2H, NH$_2$), 6.88 (d, 2H, J_{HH} = 7.5, ═CPh$_{o-H}$), 7.09 (pseudo-t, 2H, J_{HH} = 8.0, ═CPh$_{m-H}$), 7.25−7.6 (m, 30H, arom + N*H*). MS: 931 (70%), 832 ([M − PF_6 − 2H]$^+$, 7.5%), 655 ([Rh(PPh$_2$C$_6$H$_4$-*p*-Me)$_2$]$^+$, 100%). IR: 2064 (ν_{Rh-H}), 1670 ($\nu_{C=O}$), 1538 ($\nu_{C=N}$). Anal. Calcd for $C_{51}H_{55}N_3OF_6P_3Rh$: C, 57.62; H, 4.84; N, 4.29. Found: C, 57.40; H, 4.84; N, 4.50.

***cis,trans*-[Rh(H)$_2$(P(C$_6$H$_4$-*p*-Me)$_3$)$_2${Ph(Me)C═N−NHC(O)NH$_2$}]PF$_6$ (3c).** Compound **1c (**21.2 mg, 0.022 mmol) and the semicarbazone (3.89 mg, 0.022 mmol) were used. Yield 16 mg (70.2%). $^{31}P\{^1H\}$ NMR: δ 39.85 (d, J_{RhP} = 119), −143.2 (septet, PF_6^-). ^{1}H NMR: δ −20.59 (ddt, 1H, Rh-*H*, J_{HH} = 12.6, J_{PH} = 15.9, J_{RhH} = 19.7), −17.13 (ddt, 1H, Rh-*H*, J_{HH} = 12.6, J_{PH} = 16.0; J_{RhH} = 19.1), 1.48 (s, 3H, C*H*$_3$C═), 2.31 (s, 6H, *p*-C*H*$_3$), 2.40 (s, 12H, *p*-C*H*$_3$), 6.92 (d, 2H, J_{HH} = 7.5, ═CPh$_{o-H}$), 7.12 (pseudo-t, 2H, J_{HH} = 7.7, ═CPh$_{m-H}$), 7.2−7.7 (m, 26H, arom + N*H*). MS: 888 ([M − 2H − PF_6]$^+$, 10%), 711 ([Rh(P(C$_6$H$_4$-*p*-Me)$_3$)$_2$]$^+$, 100%). IR: 2092 (ν_{Rh-H}), 1661 ($\nu_{C=O}$), 1600 ($\nu_{C=N}$). Anal. Calcd for $C_{51}H_{55}N_3OF_6P_3Rh$ (**3c**)·1.5H_2O: C, 57.63; H, 5.50; N, 3.95. Found: C, 57.50; H, 5.25; N, 3.83.

***cis,trans*-[Rh(H)$_2$(P(C$_6$H$_4$-*p*-OMe)$_3$)$_2${Ph(Me)C═N−NHC(O)NH$_2$}]PF$_6$ (3d).** Compound **1d (**18.7 mg, 0.018 mmol) and the semicarbazone (3.13 mg, 0.018 mmol) were used. Yield 12.3 mg (61.8%). $^{31}P\{^1H\}$ NMR: δ 37.57 (d, J_{RhP} = 119), −143.2 (septet, PF_6^-). ^{1}H NMR: δ −20.63 (ddt, 1H, Rh-*H*, J_{HH} = 10.5, J_{PH} = 16.1, J_{RhH} = 19.7), −17.2 (ddt, 1H, Rh-*H*, J_{HH} = 10.5, J_{PH} = 16.4, J_{RhH} = 19.5), 1.91 (s, 3H, C*H*$_3$C), 2.83 (br s, 2H, NH$_2$), 3.84 (s, 18H, OC*H*$_3$), 6.95−7.05 (m, 12H, arom), 7.15 (pseudo-t, J_{HH} = 7.74, 2H, ═CPh$_{m-H}$), 7.25−7.55 (m, 16H, arom + N*H*). MS: 986.2 ([M − PF_6]$^+$, 100%). A satisfactory elemental analysis could not be obtained.

***cis,trans*-[Rh(H)$_2$(P(C$_6$H$_4$-*p*-F)$_3$)$_2${Ph(Me)C═N−NHC(O)NH$_2$}]PF$_6$ (3e).** Compound **1e** (19.7 mg, 0.020 mmol) and the semicarbazone (3.52 mg, 0.020 mmol) were used. Yield 15.5 mg (73.5%). $^{31}P\{^1H\}$ NMR: δ 39.30 (d, J_{RhP} = 119), −143.2 (septet, PF_6^-). ^{1}H NMR: δ −20.36 (ddt, 1H, Rh-*H*, J_{HH} = 11.5, J_{PH} = 13.7, J_{RhH} = 19.4), −17.03 (ddt, 1H, Rh-*H*, J_{HH} =11.5, J_{PH} =16.1, J_{RhH} = 18.9), 2.10 (s, 3H, C*H*$_3$), 2.91 (br s, 2H, N*H*$_2$), 6.92 (d, 2H, J_{HH} = 8.0, ═CPh$_{o-H}$), 7.17 (pseudo-t, 2H, J_{HH} = 8.0, ═CPh$_{m-H}$), 7.25−7.65 (m, 26H, arom + N*H*). MS: 912 ([M − PF_6]$^+$, 9%), 735 ([Rh(P(C$_6$H$_4$-*p*-F)$_3$)$_2$]$^+$, 100%), 596 (25%), 323 (60%). IR: 2062 (ν_{Rh-H}), 1669 ($\nu_{C=O}$), 1588 ($\nu_{C=N}$). Anal. Calcd for $C_{45}H_{36}N_3OF_{12}P_3Rh$: C, 51.01; H, 3.52; N, 3.97. Found: C, 50.70; H, 3.60; N, 4.08.

***cis,trans*-[Rh(H)$_2$(PPh$_2$Et)$_2${Ph(Me)C═N−NHC(O)NH$_2$}]PF$_6$ (3f).** Compound **1f** (20.0 mg, 0.025 mmol) and the semicarbazone (4.50 mg, 0.025 mmol) were used in this in situ synthesis. $^{31}P\{^1H\}$ NMR: δ 38.14 (d, J_{RhP} = 116), −143.2 (septet, PF_6^-). ^{1}H NMR: δ −21.33 (ddt, 1H, Rh-*H*, J_{HH} = 11.9, J_{PH} = 15.2, J_{RhH} = 20.9), −17.81 (ddt, 1H, Rh-*H*, J_{HH} = 11.9, J_{PH} = 15.5, J_{RhH} = 20.0), 0.97 (pseudo-pentet, 6H, C*H*$_3$CH$_2$P, J_{HH} = 7.5, J_{PH} = 9.1), 1.77 (s, 3H, C*H*$_3$C═), 2.11 (m, 2H, CH$_3$C*H*$_2$P), 2.41 (m, 2H, CH$_3$C*H*$_2$P), 3.48 (br s, 2H, N*H*$_2$), 7.04 (d, 2H, J_{HH} = 6.8, ═CPh$_{o-H}$), 7.25 (pseudo-t, 2H, J_{HH} = 6.9, ═CPh$_{m-H}$), 7.34−7.66 (m, 22H, arom + N*H*).

***cis,trans*-[Rh(H)$_2$(PPh$_2$Me)$_2${PhC(Me)═N−NHC(O)NH$_2$}]PF$_6$ (3g).** Compound **1g** (10.0 mg, 0.013 mmol) and PhC(Me)═N−N(H)CONH$_2$ (2.35 mg, 0.013 mmol) were placed in an NMR tube equipped with a J-Young valve, and then ∼0.6 mL of dry, degassed acetone-d_6 was condensed into this tube. The resulting solution was exposed to 1 atm of H_2 at room temperature, and after 2 h ∼45% of **1g** had reacted to form **3g**: $^{31}P\{^1H\}$ NMR: δ 21.44 (d, J_{RhP} = 114), −143.2 (septet, PF_6^-). ^{1}H NMR: δ −20.99 (ddt, 1H, Rh-*H*, J_{HH} = 11.9, J_{PH} = 17.3, J_{RhH} = 21.5), −17.81 (ddt, 1H, Rh-*H*, J_{HH} = 11.9, J_{PH} = 16.1, J_{RhH} = 21.5), 1.91 (s, 3H, C*H*$_3$C), 1.48 (br s, 6H, P−C*H*$_3$), 7.1−7.5 (m, 26H, arom + N*H*).

After 2 days, **1g** was no longer present, but most of **3g** had "decomposed" to a species with δ_P 33.82 (dd, J_{RhP} = 180, J_{PP} = 64) and 37.11 (dd, J_{RhP} = 193, J_{PP} = 64), considered to be [Rh(PPh$_2$Me)$_2${PhC(Me)═N−N(H)CONH$_2$}]PF$_6$ (**7**). No hydride ^{1}H NMR signals were seen. An MS of this solution showed peaks at 680 ([M − PF_6]$^+$, 3%), 503 ([Rh(PPh$_2$Me)$_2$]$^+$, 7%), and 154 (100%).

[Rh(H)(PPhMe$_2$)$_2${*o*-C$_6$H$_4$C(Me)═N−NHC(O)NH$_2$}]PF$_6$ (8). The procedure to generate **8** was identical to the one used for the preparation of **3a**, but with the reactants **1h** (36.1 mg, 0.057 mmol) and PhC(Me)═NNHC(O)NH$_2$ (10.1 mg**,** 0.057 mmol). The product solution was then treated with Et_2O (∼1 mL), when an oily layer became evident. The acetone/ether solution was decanted from the oil and pumped to dryness. The residue was redissolved in a C_6H_6 (15 mL)/CH_2Cl_2 (2 mL) mixture, and the solution concentrated to precipitate a light yellow solid. Yield 11.5 mg (28.7%). $^{31}P\{^1H\}$ NMR (in situ): δ 20.94 (dd, J_{RhP} = 129.9, J_{PP} = 32), 21.10 (dd, J_{RhP} = 122, J_{PP} = 32), −143.2 (septet, PF_6^-). ^{1}H NMR (in situ): δ -18.7 (ddd, 1H, $J_{trans-PH}$ = 20.1, J_{cis-PH} = 15.7, J_{RhH} = 32.2, Rh-*H*), 1.16 (d, 3H, J_{PH} = 10.7, PC*H*$_3$), 1.43 (d, 3H, J_{PH} = 10.7, PC*H*$_3$), 1.69 (d, 3H, J_{PH} = 11.7, PC*H*$_3$), 1.81 (d, 3H, J_{PH} = 11.7, PC*H*$_3$), 2.60 (s, 3H, C*H*$_3$C). MS: 655 (10%), 592 ([M − Me − F_6]$^+$, 6%), 556 ([M − PF_6]$^+$, 15%), 379 ([Rh(PPhMe$_2$)$_2$]$^+$ 100%).

Table 1. Crystallographic Data for Propiophenone Semicarbazone and the Complexes $[Rh(H)_2(PPh_3)_2(Ph(Me)C{=}N{-}NHC(O)NH_2)]PF_6$ (**3a**), $[Rh(H)_2(PPh_3)_2(Ph(Et)C{=}N{-}NHC(O)NH_2)]PF_6$ (**4**), and $[Rh(H)_2(PPh_3)_2(Me_2C{=}N{-}NHC(O)NH_2)]PF_6$ (**5**)

	propiophenone semicarbazone	**3a**[a]	**4**·$2CH_2Cl_2$	**5**·Me_2CO
formula	$C_{10}H_{13}N_3O$	$C_{45}H_{43}N_3OF_6P_3Rh$	$C_{48}H_{49}N_3OF_6Cl_4P_3Rh$	$C_{43}H_{47}N_3O_2F_6P_3Rh$
fw	191.23	951.64	1135.56	947.68
cryst size (mm^3)	0.50 × 0.20 × 0.10	0.40 × 0.20 × 0.20	0.35 × 0.20 × 0.10	0.25 × 0.15 × 0.15
cryst syst	orthorhombic	triclinic	triclinic	triclinic
space group	*Pccn* (No. 56)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	17.885(2)	12.9890(3)	12.7688(6)	12.6183(9)
b, Å	15.005(3)	14.1950(5)	14.4322(8)	12.7951(5)
c, Å	7.4444(8)	14.732(1)	14.842(1)	14.244(1)
α (deg)	90.00	67.437(2)	97.986	79.465(2)
β (deg)	90.00	77.667(2)	104.637	73.471(2)
γ (deg)	90.00	70.973(3)	98.751	83.606(3)
V, $Å^3$	1998(1)	2359.1(2)	2570.1(3)	2163.3(2)
Z	8	2	2	2
D_{calc} (g cm^{-3})	1.271	1.340	1.467	1.455
μ (cm^{-1})	0.86	5.23	6.93	
R_{int}	0.050	0.052	0.044	0.044
total reflns	18044	20165	23670	19061
unique reflns	2774	8987	11351	9042
no. variables	139	554	651	543
R, *Rw* (F^2, all data)	0.065; 0.091	0.066; 0.124	0.067; 0.109	0.056; 0.089
R, *Rw* (F, $I > n\sigma(I)$)[b]	0.034; 0.042	0.046; 0.117	0.039; 0.048	0.032; 0.041
refln/param ratio	17.70	16.22	17.44	16.65
GOF	1.04	1.06	1.26	1.13

[a] An unresolved molecule of CH_2Cl_2 that was not modeled was also present in the lattice. [b] $n = 2$ for **3a**, and 3 for the other structures.

Anal. Calcd for $C_{25}H_{33}N_3OP_3F_6Rh$ (**8**)·$0.6C_6H_6$: C, 45.91; H, 4.93; N, 5.62. Found: C, 45.84; H, 5.61; N, 5.29.

Attempted Hydrogenation of Acetophenone−Semicarbazone. Hydrogenation of the semicarbazone (∼ 0.1 M) was attempted using a solution of $[Rh(COD)(PPh_3)_2]PF_6$ (∼10^{-3} M) at room temperature under 1−40 atm H_2, the Rh precursor having been pretreated with 1 atm H_2 prior to addition of the semicarbazone to form *c*,*t*,*c*-$[Rh(H)_2(PR_3)_2(solvent)_2]PF_6$ (in acetone and MeOH) or $[(Ph_3P)Rh(\mu\text{-}PhPPh_2)]_2[PF_6]_2$ in CH_2Cl_2.[2,3] The experiments at ambient conditions and at high pressure were carried out with stirring in a Schlenk tube, and a small-scale Parr autoclave, respectively. After 24 h, the volatile fraction (distilled under vacuum) of the product mixture, and the residue (after dissolution in DMSO-d_6), were analyzed by GC (on a Hewlett-Packard instrument; HP-17 (25 m), $T_1 = 80$ °C, $t_1 = 3$ min, $R = 20$ °C/min, $T_2 = 220$ °C, $t_2 = 15$ min) and ^{1}H NMR; no hydrogenation products (from C=N or C=O reduction) or hydrogenolysis products (e.g., $Ph(Me)CHNH_2$) were detected, and most of the semicarbazone was recovered.

X-ray Crystallographic Analysis. Colorless, prism crystals of *cis*,*trans*-$[Rh(H)_2(PPh_3)_2PhC(Me){=}N{-}N(H)C(O)NH_2\}]PF_6$ (**3a**), *cis*,*trans*-$[Rh(H)_2(PPh_3)_2\{PhC{-}(Et){=}N{-}N(H)C(O)NH_2\}]\ PF_6$ (**4**), and *cis*,*trans*-$[Rh(H)_2(PPh_3)_2\{Me_2C{=}N{-}NHC(O)NH_2\}]PF_6$ (**5**) were grown by slow evaporation of solutions of the complexes in 1:1 hexane/CH_2Cl_2 (**3a**, **4**) or 1:1 hexane/acetone (**5**); a crystal of propiophenone−semicarbazone was grown from an EtOH solution. Measurements on the crystals were made at 173(1) K (for **3a**, **5**) or 198(1) K (for **4** and the semicarbazone) on a Rigaku/ADSC CCD with graphite monochromated Mo Kα radiation (0.71069 Å). Some crystallographic data and principle parameters from the refinement of the crystals are given in Table 1. The final unit cell parameters were based on 11 063 reflections for **3a**, 13 307 reflections for **4**, 11 509 reflections for **5**, and 9066 reflections for the semicarbazone, with 2θ in the general range 4.1−60.1°. The data were collected and processed using the *d***TREK* program,[8] and the structure was solved by direct methods[9] and expanded using Fourier techniques.[10] The non-H atoms were refined anisotropically, while the H atoms attached to the Rh and the N atoms were refined isotropically, and the other H atoms were included in fixed positions. All calculations were performed using the *teXsan* crystallographic software package.[11] One region in the asymmetric unit cell of **3a** contained large residual electron density peaks consistent with a CH_2Cl_2 molecule. Subsequent refinements (as CH_2Cl_2), however, proved to be unsatisfactory, as this region appears to be only partially occupied, the solvent molecule being significantly disordered. As a result, the SQUEEZE function[12] found in PLATON[13] was employed. The atoms of the disordered solvent molecule were removed, and a refinement was carried out, resulting in large, unassigned residual peaks in the void space. SQUEEZE then identifies any void spaces in the unit cell, uses the original data to find unassigned electron density peaks in these spaces, and then produces a new, "corrected" data set that eliminates this residual electron density from the spaces, leaving the remainder of the structure unchanged, but containing a void space (i.e., no atoms or residual electron density). This new data set is used in subsequent refinements. SQUEEZE calculated electron density equivalent to 27 electrons (or slightly more than one-half of a CH_2Cl_2 molecule) in a void space of 338 $Å^3$. The refinement improved from R1 = 0.065 with the partially modeled CH_2Cl_2 molecule (and from R1 = 0.096 with no solvent modeled) to 0.046.

Complex **4** crystallized with 2 CH_2Cl_2 molecules per asymmetric unit, one having chlorine atoms disordered over two sites with relative populations refined to 0.90 and 0.10; the semicarbazone

(8) *d***TREK: Area Detector Software*, version 4.13; Molecular Structure Corporation, The Woodlands, TX, 1996−1998.

(9) Altomare, A.; Burla, M. C.; Cammalli, G.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Poidori, G.; Spagna, A. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(10) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits J. M. M. *The DIRDIF-94 Program System*; Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1994.

(11) *teXsan: Crystal Structure Analysis Package*; Molecular Structure Corporation; The Woodlands, TX, 1985 and 1992.

(12) *SQUEEZE*: Sluis, P. v.d.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194.

(13) Spek, A. L. *PLATON: A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 1998.

ethyl group of **4** was also disordered, the two fragments being distributed equally over two sites.

Results and Discussion

The $[Rh(COD)(PR_3)_2]PF_6$ (1a−h) and *c,t,c*-$[Rh(H)_2(PR_3)_2(acetone)_2]PF_6$ (2a−h) Complexes. Although the reactivity of $[Rh(COD)(PPh_3)_2]PF_6$ with H_2 to give *c,t,c*-$[Rh(H)_2(PPh_3)_2(solvent)_2]PF_6$ has been thoroughly investigated,[2,3] listed in the Experimental Section are some in situ $^{31}P\{^1H\}$ and the high-field ^1H NMR data for analogous systems containing other phosphine ligands; data are given for the bis(acetone) species with $R_3 = Ph_3$ (**2a**), $Ph_2(C_6H_4$-*p*-Me) (**2b**), $(C_6H_4$-*p*-Me$)_3$ (**2c**), $(C_6H_4$-*p*-OMe$)_3$ (**2d**), $(C_6H_4$-*p*-F$)_3$ (**2e**), Ph_2Et (**2f**), Ph_2Me (**2g**), and $PhMe_2$ (**2h**). For **2a**−**e**, the δ_P doublets appear between 46 and 40 ppm, while species with the more basic phosphines, PPh_2Me (**2g**) and $PPhMe_2$ (**2h**), not unreasonably show a more upfield shift (at δ_P 24 and 27, respectively); a similar trend is seen for **1a**−**f** vs **1g** and **1h**, and is also evident within the corresponding *cis*-$[Rh(PR_3)_2(solvent)_2]^+$ species.[1] (The data for **2f** and **1f**, containing Ph_2Et, surprisingly are closer to, but are at the higher field end of, those of the tris(arylphosphine) systems.) As expected, the J_{RhP} values for the *trans*-phosphine species **2** (114−131 Hz) are always less than for the corresponding *cis*-phosphine species **1** (143−145 Hz).[1,3,5,14]

Qualitatively, the rate of reaction of **1** with H_2 at room temperature to fully form **2** decreases when an electron-withdrawing *p*-fluorine is substituted into PPh_3 ($t_{1/2}$ ~3 h vs ~0.5 h), this being consistent with a rate-determining oxidative addition of H_2 to **1** or to the presumed intermediate $[Rh(PR_3)_2(acetone)_2]^+$ species. However, in apparent contradiction, the presence of a more basic phosphine, such as PPh_2Me (vs PPh_3) also decreases the rate of formation of **2** ($t_{1/2}$ ~1 h), and this is thought to be due to an increase in the rate of loss of H_2 from the dihydride, as **2g** decomposes (on removing the H_2 atmosphere) to $[Rh(PPh_2Me)_2(acetone)_2]PF_6$ relatively rapidly ($t_{1/2}$ ~1 h) compared to the **2a**−**e** systems. Correspondingly, reaction of the most basic $PPhMe_2$ species (**1h**) with H_2 is the slowest ($t_{1/2}$ ~10 h), and the **2h** product now exhibits a broadened doublet (δ_P 27.6), implying again perhaps a faster "off-rate"; indeed, **2h** loses H_2 more rapidly ($t_{1/2}$ ~0.5 h) than does **2g**. Quantitative kinetic data are required for a more detailed understanding of the overall reaction of **1** to generate **2**, where steric effects appear to play a role.

Dihydrido−Bis(phosphine)−Semicarbazone Rh(III) Complexes: *cis,trans*-$[Rh(H)_2(PR_3)_2(\eta^2$-*N,O*-semicarbazone)$]PF_6$ (3a−g, 4−6). The in-situ **2a** species reacts in a few minutes with *E*-acetophenone−semicarbazone in acetone at room temperature to form in high yield the dihydrido−semicarbazone complex **3a**, which is air-stable in solution or in the solid state even in the absence of H_2; the reaction is simple replacement of the acetone by the chelating semicarbazone still in the *E*-configuration, and the species has *trans*-PPh_3 ligands and *cis*-hydrides (Scheme 2).

An ORTEP for the cation of **3a** is shown in Figure 1, and selected bond distances and angles are given in Table 2. The

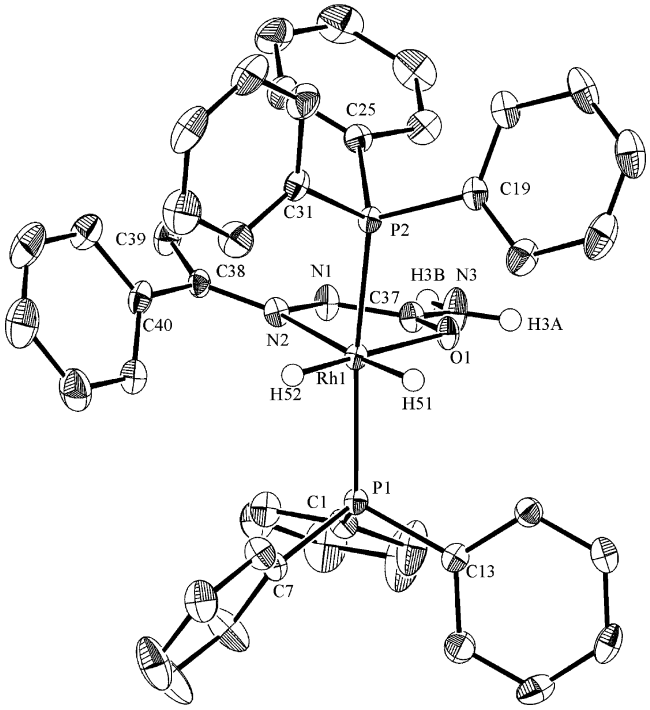
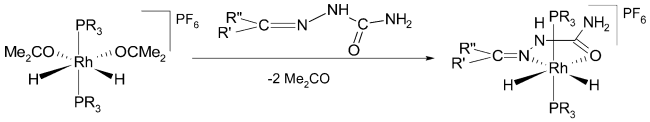


Figure 1. ORTEP diagram of the *cis,trans*-$[Rh(H)_2(PPh_3)_2\{PhC(Me)=N-N(H)C(O)NH_2\}]^+$ cation of **3a**, with 50% probability thermal ellipsoids.

Scheme 2. Formation of the Dihydrido−Semicarbazone Complexes **3a** (R = Ph, R′ = Ph, R″ = Me), **3b** ($R_3 = Ph_2C_6H_4$-*p*-Me, R′ = Ph, R″ = Me), **3c** ($R = C_6H_4$-*p*-Me, R′ = Ph, R″ = Me), **3d** (R = C_6H_4-*p*-OMe, R′ = Ph, R″ = Me), **3e** ($R = C_6H_4$-*p*-F, R′ = Ph, R″ = Me), **3f** ($R_3 = Ph_2Et$, R′ = Ph, R″ = Me), **3g** ($R_3 = Ph_2Me$, R′ = Ph, R″ = Me), **4** (R = Ph, R′ = Ph, R″ = Et), **5** (R = Ph, R′ = R″ = Me), **6** (R = Ph, R′ = Et, R″ = Me)



2a-g **3a-g, 4-6**

η^2-*N,O*-coordination mode of a semicarbazone is very common,[15] but we are unaware of any other metal dihydrido−semicarbazone complexes, although a monohydridic $[OsH(CO)(PPh_3)_2(\eta^2$-*N,O*-semicarbazone derivative$)]^+$ has been structurally characterized.[16a] More common are η^3-*C,N,O*-semicarbazone-type species containing two fused metallocycle rings, formed via (i) orthometalation of a Ph substituent on the imine C atom (see Scheme 1),[1,16b,c,17] or (ii) donation from an *ortho*-N- or O-donor substituent on this Ph group.[18] The closest analogues of **3a**−**g, 4**−**6** are the *cis,trans*-$[Rh(H)_2(PR_3)_2(N-N)]^+$ complexes, also containing a five-membered metallocycle, where N−N is a chelated, unsaturated (imine type) N-donor.[19]

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(15) A search of the Chemical Abstracts database revealed that metal−semicarbazone complexes (with ligand/metal ratios = 1−3) are known with ~40 elements of the periodic table.

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Table 2. Selected Bond Distances (Å) and Angles (deg) for Propiophenone Semicarbazone and the Cations of Complexes **3a**, **4**, and **5** with Estimated Standard Deviations in Parentheses

propiophenone semicarbazone[a]		**3a**		**4**[a]		**5**	
N1−C7	1.289(1)	N2−C38	1.295(5)	N3−C38	1.274(4)	N1−C38	1.283(3)
O1−C10	1.234(1)	O1−C37	1.255(5)	O1−C37	1.246(3)	O1−C37	1.253(3)
C7−C8	1.511(1)	C38−C39	1.506(6)	C38−C45A	1.49(1)	C38−C39	1.491(4)
C1−C7	1.481(2)	C38−C40	1.483(6)	C38−C39	1.488(5)	C38−C40	1.493(4)
N2−C10	1.372(1)	N1−C37	1.353(5)	N2−C37	1.363(4)	N2−C37	1.353(3)
N3−C10	1.337(1)	N3−C37	1.327(5)	N1−C37	1.326(4)	N3−C37	1.329(3)
N1−N2	1.374(1)	N1−N2	1.383(4)	N2−N3	1.398(4)	N1−N2	1.400(3)
		Rh−P1	2.3081(10)	Rh−P1	2.3005(7)	Rh−P1	2.3131(7)
		Rh−P2	2.3046(10)	Rh−P2	2.3031(7)	Rh−P2	2.2982(7)
		Rh−H51	1.50(4)	Rh−H1	1.52(3)	Rh−H1	1.51(2)
		Rh−H52	1.56(4)	Rh−H2	1.48(4)	Rh−H2	1.49(3)
		Rh−O1	2.233(2)	Rh−O1	2.226(2)	Rh−O1	2.207(2)
		Rh−N2	2.226(3)	Rh−N3	2.188(2)	Rh−N1	2.187(2)
N2−N1−C7	119.03(9)	N1−N2−C38	116.6(3)	N2−N3−C38	117.6(3)	N2−N1−C38	116.0(2)
N1−N2−C10	118.08(9)	N2−N1−C37	120.1(3)	N3−N2−C37	118.5(3)	N1−N2−C37	118.8(2)
C1−C7−C8	119.96(9)	C39−C38−C40	119.3(4)	C39−C38−C45A	109.2(5)	C39−C38−C40	117.2(2)
O1−C10−N2	120.53(9)	O1−C37−N1	121.3(4)	O1−C37−N2	121.4(3)	O1−C37−N2	121.4(2)
N2−C10−N3	116.1(1)	N1−C37−N3	116.4(4)	N1−C37−N2	116.7(3)	N2−C37−N3	116.2(2)
		P1−Rh−P2	169.12(4)	P1−Rh−P2	163.30(3)	P1−Rh−P2	168.02(2)
		P1−Rh−O1	89.89(7)	P1−Rh−O1	96.19(5)	P1−Rh−O1	93.41(5)
		P1−Rh−N2	97.80(8)	P1−Rh−N3	97.26(7)	P1−Rh−N1	93.29(6)
		O1−Rh−N2	74.61(10)	O1−Rh−N3	75.14(8)	O1−Rh−N1	75.41(7)
		N2−Rh−H52	105.9(16)	N3−Rh−H2	101(1)	N1−Rh−H1	103(1)
		P2−Rh−H51	83.1(16)	P1−Rh−H1	83(1)	P2−Rh−H2	88(1)
		P1−Rh−H51	86.1(16)	P2−Rh−H1	82(1)	P1−Rh−H2	84(1)
		P2−Rh−H52	87.2(16)	P1−Rh−H2	83(1)	P2−Rh−H1	84(1)
		P2−Rh−H52	88.9(16)	P2−Rh−H2	89(1)	P1−Rh−H1	87(1)
		H51−Rh−H52	76(2)	H1−Rh−H2	84(2)	H1−Rh−H2	80(1)
		O1−Rh−H52	178.7(15)	O1−Rh−H2	176(1)	O1−Rh−H1	179(1)
		N2−Rh−H51	175.6(16)	N3−Rh−H1	175(1)	N1−Rh−H2	176(1)

[a] The atom labelings for the semicarbazone and for **4** correspond to equivalent atoms.

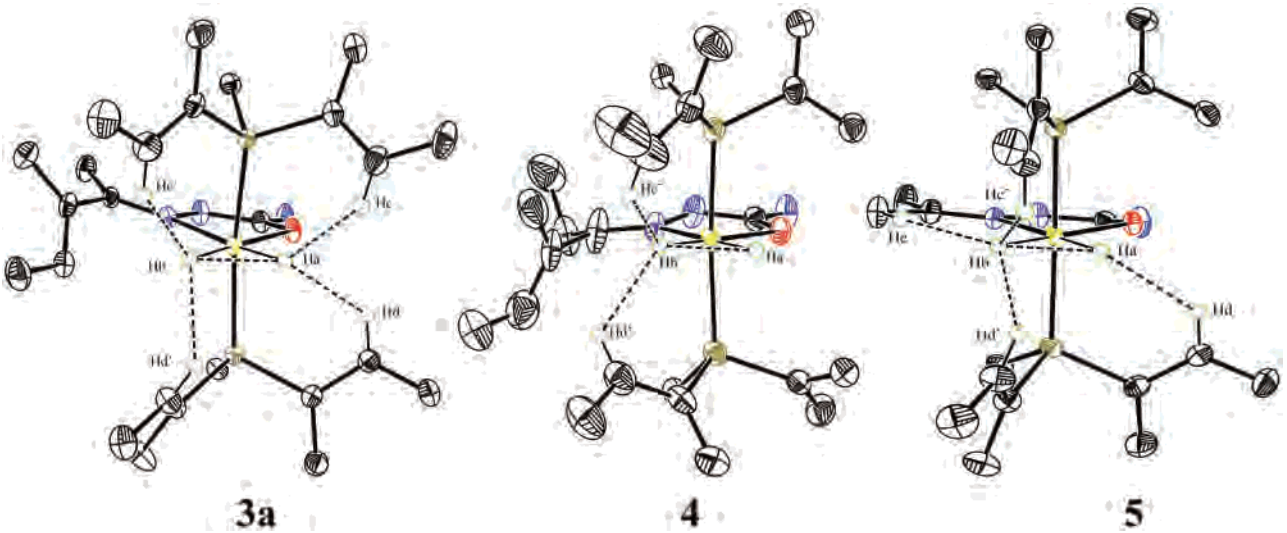

Figure 2. Diagrams showing RhH···HC interactions in the cations of **3a**, **4**, and **5**; sections of the phenyl groups have been omitted for clarity.

In the distorted octahedral structure of **3a**, the *trans*-PPh_3 ligands lean towards the hydrides as indicated by the P−Rh−P angles (169.12°) and the P−Rh−H angles (83.1−88.9°); intramolecular RhH···HC interactions between the hydride and some Ph ring protons may play a role (Figure 2). Two trifurcated arrangements of the type $(sp^2)CH\cdots H_{Rh}\cdots H_{Rh}$ between Ph ring protons of different phosphines and the metal−hydrides are present (Table 3). These interactions

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Table 3. Calculated RhH···HC Distances (Å)

	Ha···Hb	Ha···Hc	Ha···Hd	Hb···Hc′	Hb···Hd′	Hb···He
3a	1.89(5)	2.04	2.27	1.98	2.32	
4	2.01(5)			1.96	2.19	
5	1.92(4)		2.37	2.14	2.25	2.20

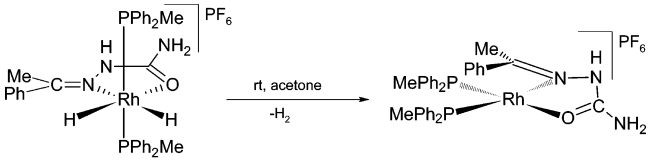
(from 1.89 to 2.32 Å) vary from strong to weak considering the van der Waals distance between two H atoms is 2.40 Å,[20,21] and are similar to interactions (H···H = 2.00−2.20 Å) found in a related orthometalated Rh^{III}−azobenzene system,[20] but are stronger than those found in the hydrido-orthometalated acetophenone−semicarbazone complex **I** shown in Scheme 1.[1]

The chelated semicarbazone within the five-membered ring and the hydrides are essentially coplanar. The hydrides are trans to the imine-N and O-atoms, with N−Rh−H and O−Rh−H angles of 175.6° and 178.7°, respectively. The N−Rh−O angle (74.61°) is close to those found in the η^2-*N,O*-acetophenone−semicarbazone of the cationic hydrido-bis(phosphine) Os(II) species(74.52°),[16a] a cationic chloro−bis(phosphine) Ru(II) species (76.43°),[16b] and the orthometalated hydrido−bisphosphine−hydrido−Rh species **I** (Scheme 1) (73.6°).[1] The H−Rh−H angle (76°) is smaller than the corresponding angle in the *cis,trans*-$[Rh(H)_2(PR_3)_2(N-N)]^+$ complexes (89.1−90.5°),[19a,b] and is, in fact, closer to the angle of other *cis,trans*-$[Rh(H)_2(PR_3)_2(N)_2]^+$ species where N is a monodentate, unsaturated N-donor.[19c,d] The Rh−H bond length (1.50 Å) is in the expected range,[1,19a,b,d,e] and the Rh−P bond distances are similar to those in other complexes containing *trans*-PPh_3 ligands.[1,16c,20] The Rh−O bond (2.233 Å) is somewhat shorter, and the Rh−N bond (2.226 Å) somewhat longer, than those reported for **I** (2.310 and 2.065 Å, respectively).[1] The other bond lengths and angles within the coordinated semicarbazone agree well with corresponding values for other metal−acetophenone−semicarbazones complexes.[16−18] The crystallographic data given for the free propiophenone−semicarbazone, and the chelated form in complex **4** (see below) (Table 2), imply that the geometry of a semicarbazone changes remarkably little upon coordination.

The solid-state IR spectrum of **3a** shows ν_{Rh-H}, $\nu_{C=O}$, and $\nu_{C=N}$ bands in the appropriate regions, and the mass spectrum gives a signal for the molecular cation minus two hydrogens.

$^{31}P\{^1H\}$ and ^1H NMR spectra of **3a** in acetone-d_6 show that the solid-state structure is maintained in solution. The δ_P doublet for the P atoms is seen at 41.74, in the region found for other Rh(III) semicarbazone complexes with phosphine ligands,[1,16c] and the J_{RhP} value (119 Hz) is consistent with equivalent *trans*-phosphines.[1−3,22] The ^1H NMR data show two high-field ddt signals for inequivalent hydrides due to coupling to the Rh, a H atom and two equivalent P atoms, with appropriate J_{HH}, J_{PH}, and J_{RhH} values.[1−3,19c,d,22] The ^1H signals (in acetone-d_6) for the *o*- and *m*-protons of the Ph ring of the coordinated acetophenone

Scheme 3. Decomposition of **3g** via Loss of H_2[a]



3g **7**

[a] rt = room temperature.

semicarbazone, seen as a doublet and pseudo-triplet, respectively, are shifted 0.5−0.6 ppm upfield in comparison to those of the free semicarbazone,[1] while signals for the Me and NH_2 protons are shifted <0.1 ppm downfield. The assignment of the NH proton signal (for example, seen at δ 9.45 in free acetophenone semicarbazone,[1] and δ 8.55 in acetone semicarbazone) is difficult, as it appears to overlap in the δ 7.30−7.65 region the aromatic signals of the PPh_3 ligands, and that of the *p*-proton of the semicarbazone-Ph; the δ_{NH} signal is included with those of these aromatic protons (see Experimental Section), although it is impossible to quantify the integration for 1 NH proton in the presence of the 31 aromatic protons (30 from the two PPh_3 ligands plus the *p*-H of the semicarbazone-Ph). The problem of locating δ_{NH} was encountered with all the semicarbazone complexes.

Dihydrido−bis(phosphine)−acetophenone semicarbazone complexes, **3b**−**e**, analogous to **3a** but having a *p*-substituent in a phosphine-aryl ring were similarly isolated (Scheme 2), while complexes containing an alkyl substituted phosphine, **3f** and **3g**, were made in situ in acetone. Their spectroscopic data, especially the two high-field ddt ^1H signals in the ranges δ_H −20.3 ± 0.7 and −17.5 ± 0.3 for the hydrides, imply the same type structure as **3a**. Similarly, the $^{31}P\{^1H\}$ data for **3b**−**g** show doublets at δ_P 21−41, with J_{RhP} values of 114−120 Hz, and there is a trend of the δ_P values with phosphine basicity similar to that noted for **1a**−**g** and **2a**−**g**. Again, the isolated and in situ complexes are air-stable, although the in situ **3g** decomposes very slowly and irreversibly at room temperature with loss of H_2 to the Rh(I)−semicarbazone complex $[Rh(PPh_2Me)_2\{PhC(Me)=N-N(H)CONH_2\}]PF_6$ (**7**, Scheme 3), as evidenced by the absence of ^1H NMR hydride signals, and the ABX pattern in $^{31}P\{^1H\}$ spectrum; we have recently isolated an analogous butanone−semicarbazone complex, $[Rh(PPh_3)_2\{EtC(Me)=N-N(H)CONH_2\}]PF_6$, which has δ_P values ∼20 ppm above those for **7**, but with very similar J_{RhP} and J_{PP} values, the higher field δ_P value (δ_P = 33.82 for **7**) being assigned to the P atom trans to the imine-N atom.[1]

To give satisfactory characterization data required the addition of 1.5 mol of H_2O in the formulation for **3c**, 0.1 mol of CH_2Cl_2 for **4**, 0.5 mol CH_2Cl_2 for **5**, 1.0 mol of Me_2CO for **6**, and 0.6 mol C_6H_6 for **8**, while a good elemental analysis could not be obtained for **3d**. Water was seen qualitatively for **3c** in the ^1H NMR (δ 2.85), while the crystal structures of **3a**, **4**, and **5** revealed the presence of 1 or 2 mol of solvate per molecule (Table 1). The ^1H NMR signals for the NH_2 group were not seen for **3c**, **3g**, and **8** (see below). These Rh−semicarbazone complexes certainly reveal

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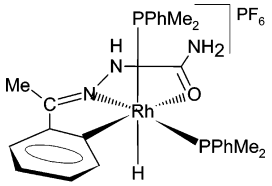
(22) Partridge, M. G.; Messerle, B. A.; Field, L. D. *Organometallics* **1995**, *14*, 3527.

a propensity to retain solvate molecules. IR data were not recorded for **3d** or **8** because of the limited material available.

Of note, when the **1h**/**2h** precursor (where the phosphine is $PPhMe_2$) was reacted with acetophenone semicarbazone, the product isolated was the orthometalated Rh(III) complex $[Rh(H)(PPhMe_2)_2\{o\text{-}C_6H_4C(Me)=N-NHC(O)NH_2\}]PF_6$ (**8**), which is well characterized: the one high-field ^1H NMR ddd signal at δ_H −18.7, and the ABX pattern in the $^{31}P\{^1H\}$ spectrum with appropriate J_{RhH}, J_{PH}, and J_{PP} values are consistent with the geometry shown. Complex **8** could be formed from the initially formed dihydride species (**3h**, cf. Scheme 2) with subsequent loss of H_2, or directly via *cis*-$[Rh(PPhMe_2)_2(acetone)_2]PF_6$, particularly as **2h** is prone to lose H_2 (see above). We have reported elsewhere[1] (see Introduction) that *cis*-$[Rh(PR_3)_2(acetone)_2]PF_6$ species (R = aryl or R_3 = Ph_2Me) react with semicarbazones to form orthometalated complexes with *trans*-phosphines (see Scheme 1); with the less bulky $PPhMe_2$, the *cis*-phosphine isomer **8** is favored, and is the first example of an orthometalated Rh(III)−hydrido−semicarbazone complex containing *cis*-phosphines. Of note, ^1H NMR data reveal that the four



8

phosphine-Me groups are inequivalent (each seen as a doublet in the δ 1.16−1.81 region, J_{PH} = 10.7 or 11.7 Hz), presumably because of restricted rotation about the Rh−P bond; in the analogous orthometalated semicarbazone complex with *trans*-PPh_2Me ligands, the Me groups are equivalent.

The propiophenone−, acetone−, and butanone−semicarbazone analogues of **3a**, namely complexes **4**−**6** (Scheme 2), were also isolated and well characterized, including X-ray crystallographic analysis of **4** and **5** (Figures 3 and 4, respectively, and Table 2). The ORTEP for *E*-propiophenone−semicarbazone is presented in Figure 5, with selected bond length and angles also given in Table 2.

Complexes **4** and **5** have octahedral distortions such as those in **3a**, and again, intramolecular RhH···HC interactions are evident (Figure 2, Table 3): interactions in **4** and **5** again involve the hydrides and a Ph ring proton, while in **5** there is also an interaction of a hydride with the proton of the semicarbazone-Me group. The chelate rings are again coplanar with the hydrides, and all the geometrical parameters are close to those of **3a**. The data in Table 2 show that the bond lengths and angles of the free and coordinated propiophenone semicarbazone are essentially the same, and this applies also on comparing data for **5** with those for free acetone semicarbazone.[23] (Propiophenone semicarbazone crystallizes in an orthorhombic crystal system, while both the acetone and benzaldehyde semicarbazones crystallize in a monoclinic system.)[23] Worth noting also is that all four structures (**3a**, **4**, **5**, and the free ligand) show strong

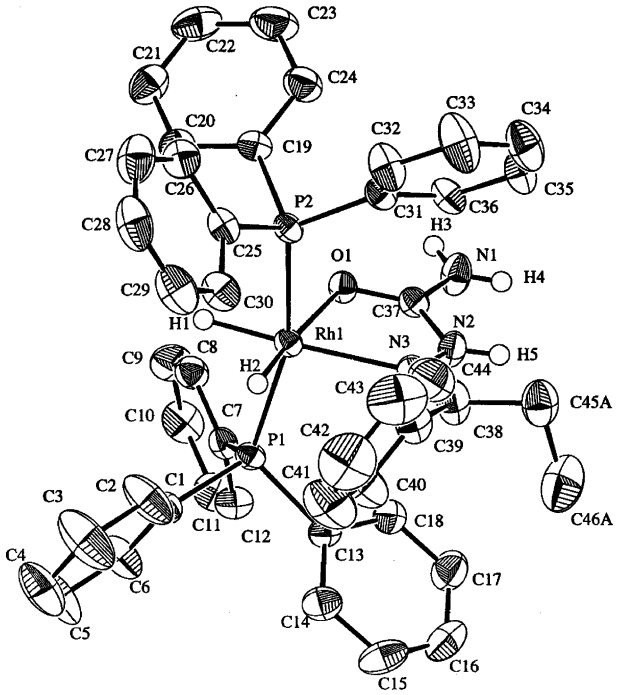


Figure 3. ORTEP diagram of the *cis*,*trans*-$[Rh(H)_2(PPh_3)_2\{PhC(Et)=N-N(H)C(O)NH_2\}]^+$ cation of **4**, with 50% probability thermal ellipsoids; only one of the disordered positions of the Et group is shown.

intermolecular H-bonding between the O-atom and the H-atom of the NH_2 of the neighboring semicarbazone moiety.

Spectroscopic data for **4**−**6** are readily assigned as for **3a**. Of interest, however, **4** and **6** in acetone-d_6 very slowly convert partially to species **4a** and **6a**, respectively, that appear to be isomers, as evidenced by the ^{31}P and ^1H NMR data. For **4a**, the high-field ^1H ddt and $^{31}P\{^1H\}$ doublet of **4** are simply shifted slightly (<1 ppm downfield), while more significant changes are seen in the ^1H resonances of the Et group: the CH_3 signal is shifted 0.42 ppm upfield, and the CH_2 signal downfield by 0.32. For **6a**, there are similar small differences from the data for **6**, the most significant again being in the CH_3 and CH_2 resonances of the Et group (0.32 ppm downfield and 0.4 ppm upfield, respectively); the signal of the Me at the imine-C atom shifts just 0.05 ppm downfield. The most obvious rationale is that **4a** and **6a** are isomers containing the *Z*-form of the imine component, but we have been unable to isolate these isomers. We did not detect such behavior for the other semicarbazone complexes with Me and Ph groups on the imine-C atom, but the suspected isomerization reactions are extremely slow, and further studies are required to draw more definitive conclusions; it is unlikely that the presence of an Et group is essential. An isomerization would require rotation about the C=N bond, and this could be promoted via η^2-coordination of the imine moiety; such a coordination mode for a simple, nonchelated imine is unknown within Pt metal systems, although it has been established for some chelated, α,β-unsaturated imines.[24]

Our initial goal in this project was catalytic hydrogenation of the semicarbazones, but disappointingly no such catalysis

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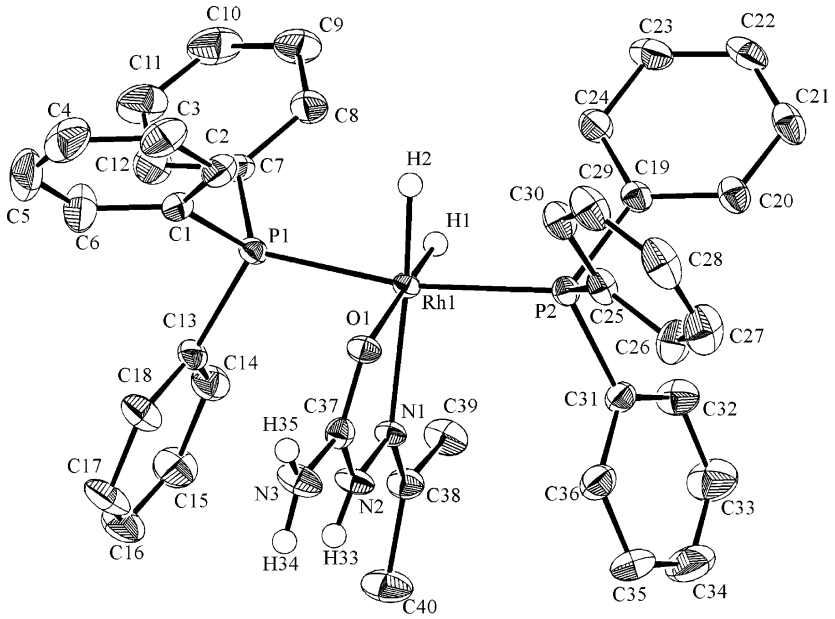

Figure 4. ORTEP diagram of the *cis,trans*-$[Rh(H)_2(PPh_3)_2\{Me_2C{=}N{-}N(H)C(O)NH_2\}]^+$ cation of **5**, with 50% probability thermal ellipsoids.

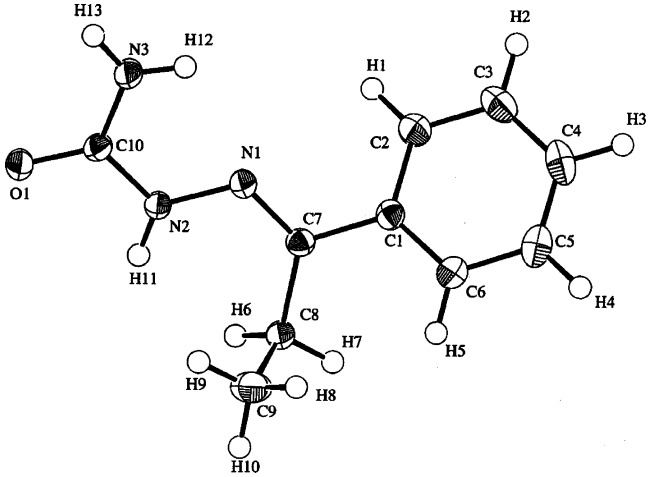

Figure 5. ORTEP diagram of *E*-$PhC(Et){=}N{-}N(H)C(O)NH_2$, with 50% probability thermal ellipsoids.

was observed, at least for the acetophenone semicarbazone tested with the $[Rh(H)_2(PPh_3)_2(solvent)_2]^+$ species (**2a**), including the system in MeOH, often the optimum solvent for Rh-catalyzed hydrogenation of "standard" imines.[5] The Rh(III)−dihydride species **3a** containing the five-membered, chelated semicarbazone shows no inclination to transfer hydrogen to the imine or carbonyl functionality, and appears to be kinetically and thermodynamically stable; as noted, **3a** is a simple substitution product of the labile precursor **2a**, where presumably the high trans-effect of the hydride ligands labilizes the solvent ligands, this rendering a usually classically substitution-inert Rh(III) species more labile. As noted above, **3g** (the analogue of **3a** but containing PPh_2Me) does irreversibly slowly lose H_2 to generate **7** (Scheme 3), and so it is difficult to draw similar conclusions for quite closely analogous systems. Further, we noted in the Introduction that reaction of the $[Rh(PPh_3)_2(solvent)_2]^+$ with acetophenone semicarbazone gives the orthometalated species $[Rh(H)(PPh_3)_2\{o\text{-}C_6H_4C(Me){=}N{-}NH{-}C(O)NH_2\}]^+$ (**I**, Scheme 1);[1] this species does not react with H_2 to generate, for example, **3a**, and also shows no catalytic activity for hydrogenation of the semicarbazone.[1] Here there are two fused five-membered rings rendering a high ground-state stability. Whether η^2-coordination of the C=N moiety is essential for successful hydrogenation (as commonly required for olefinic substrates) remains an unanswered question,[5] but if **4a** and **6a** are the *Z*-isomers of **4** and **6**, respectively, then such coordination at least within a transition state seems feasible.

Conclusions

The studies reveal that *E*-semicarbazones react at room temperature with the *cis,trans,cis*-$[Rh(H)_2(PR_3)_2(solvent)_2]PF_6$ complexes (solvent = Me_2CO or MeOH; R = aryl or R_3 = Ph_2Me, Ph_2Et) under H_2 by replacing the solvent molecules with formation of a product with a five-membered η^2-*N,O*-semicarbazone ring; these are the first reported dihydrido−semicarbazone complexes, and they are generally air-stable, although *cis,trans*-$[Rh(H)_2(PPh_2Me)_2\{PhC(Me){=}N{-}NHC(O)NH_2\}]PF_6$ slowly loses H_2 irreversibly to form $[Rh(PPh_2Me)_2\{PhC(Me){=}N{-}NHC(O)NH_2\}]PF_6$. In contrast, treatment of the reactant complex, where R is the less bulky $PPhMe_2$, with acetophenone−semicarbazone generates the orthometalated, hydrido−Rh(III) complex, *cis*-$[Rh(H)(PPhMe_2)_2\{o\text{-}C_6H_4C(Me){=}N{-}NHC(O)NH_2\}]PF_6$. We have reported earlier that the corresponding orthometalated hydrido complexes with more bulky *trans*-phosphines can be synthesized by reaction of a semicarbazone with the *cis*-$[Rh(PR_3)_2(solvent)_2]PF_6$ species. The orthometalated species do not react with H_2 to form the dihydrido species, and none of the above-mentioned species catalyzes the hydrogenation of acetophenone semicarbazone.

In summary, the following types of cationic Rh−semicarbazone species have now been synthesized from the well-known $[Rh(H)_2(PR_3)_2(solvent)_2]^+$ or $[Rh(PR_3)_2(solvent)_2]^+$ precursors: *cis*-$[Rh(PR_3)_2(\eta^2\text{-}N,O\text{-semicarbazone})]^+$, *cis,trans,cis*-$[Rh(H)_2(PR_3)_2(\eta^2\text{-}N,O\text{-semicarbazone})]^+$, and the

orthometalated *cis*- and *trans*-[Rh(H)(PR_3)$_2$(η^3-*C*,*N*,*O*-semicarbazone-H}]$^+$ complexes; the product formed depends on the nature of the phosphine and the semicarbazone, but details of the factors governing their formation and their interconversions remain to be established.

Acknowledgment. We thank the NSERC (Natural Sciences and Engineering Research Council of Canada) and ESTAC (Environmental Science and Technology Alliance Canada) for financial support.

Supporting Information Available: X-ray crystallographic data for the structures of complexes **3a**, **4**, and **5**, and propiophenone−semicarbazone in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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