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

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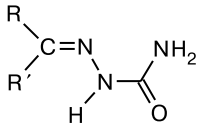
Interaction of the *cis*-$[Rh(PR_3)_2(Solv)_2]PF_6$ complexes (R = Ar or R_3 = Ph_2Me, Solv — solvent) under Ar with semicarbazones bearing a phenyl group on the imine-C atom gives the rhodium(III)-hydrido-bis(phosphine)-orthometallated semicarbazone species $[RhH(PR_3)_2\{(o\text{-}C_6H_4(R')C{=}N{-}N(H)CONH_2\}]PF_6$ (R′ = Me or Et), which are characterized generally by elemental analysis, $^{31}P\{^1H\}$ and ^1H NMR spectroscopy, and mass-spectrometry. The PPh_3-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 $[Rh(PR_3)_2(Et(Me)C{=}N{-}N(H)CONH_2)]PF_6$, containing the η^2-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 $[Rh(cod)(PR_3)_2]PF_6$ (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 H_2 in coordinating solvents to generate the *cis*,*trans*,*cis*-$[Rh(H)_2(PR_3)_2(Solv)_2]PF_6$ complexes (Solv is a solvent molecule), while subsequent removal of the H_2 atmosphere readily gives the *cis*-$[Rh(PPh_3)_2(Solv)_2]^+$ species in solution;[4,5] removal of solvent then produces $[Rh(PPh_3)\{(\mu\text{-}Ph)PPh_2\}]_2(PF_6)_2$.[5] The standard imine substrates usually tested are typically of the type $Ph(R)C{=}NCH_2Ph$, 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 $R(R')C{=}N\text{-}N(H)CONH_2$ (R = Me or Et, with R′ = Ph; and R = Me with R′ = Et) with the *cis*-$[Rh(PR_3)_2(Solv)_2]^+$ species (R = Ar or R_3 = Ph_2Me), 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.



A

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 metallocyclic derivative[10a,11]. If orthometallation also occurs *via* the *o*-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.

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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

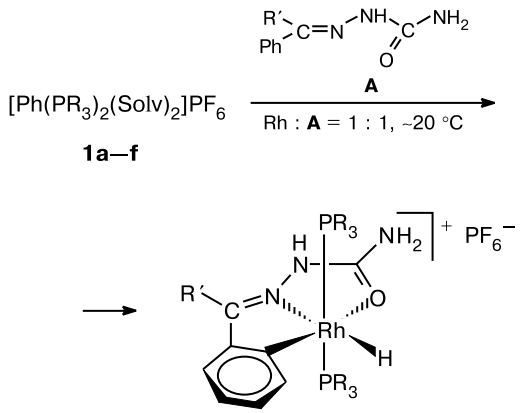
Precursor *cis*-$[Rh(PPh_3)_2(Solv)_2]^+$ complexes. The use of $[Rh(cod)(PR_3)_2]PF_6$ complexes to generate *in situ* *cis*-$[Rh(PR_3)_2(Solv)_2]^+$ (**1**) (R = Ar; Solv = Me_2CO, MeOH) is well documented for R = Ph (**1a**) or *p*-Tol (see above).[4,5] We have now extended the use of this procedure for the synthesis of the complexes with R_3 = $Ph_2(p\text{-}MeC_6H_4)$ (**1b**), R = $p\text{-}OMeC_6H_4$ (**1c**), $p\text{-}FC_6H_4$ (**1d**), and $p\text{-}ClC_6H_4$ (**1e**), and $R_3 = Ph_2Me$ (**1f**). Preliminary treatment of these complexes with H_2, 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 $[Rh(PPh_3)\{(\mu\text{-}Ph)PPh_2\}]_2(PF_6)_2$ 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 $^{31}P\{^1H\}$ NMR data: the triarylphosphine derivatives (**1a—e**) exhibit doublets at δ_P 51—54, with $J_{Rh,P} \approx$ 200 Hz typical of *cis*-phosphine ligands,[5] while the more basic Ph_2Me 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 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 semicarbzones 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 $RhCl(PPh_3)_3$ where again the expected hydride has been replaced by chloride.[16]

Scheme 1



2: R = Ph, R´ = Me (**a**); $R_3 = Ph_2(p\text{-}MeC_6H_4)$, R´ = Me (**b**); R = $p\text{-}OMeC_6H_4$, R´ = Me (**c**); R = $p\text{-}FC_6H_4$, R´ = Me (**d**); R = $p\text{-}ClC_6H_4$, R´ = Me (**e**); $R_3 = Ph_2Me$, R´ = Me (**f**)
3: R = Ph, R´ = Et

The distorted octahedral structure of **2a** has *trans*-PPh_3 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 Vaals 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 ortho-metallated-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]

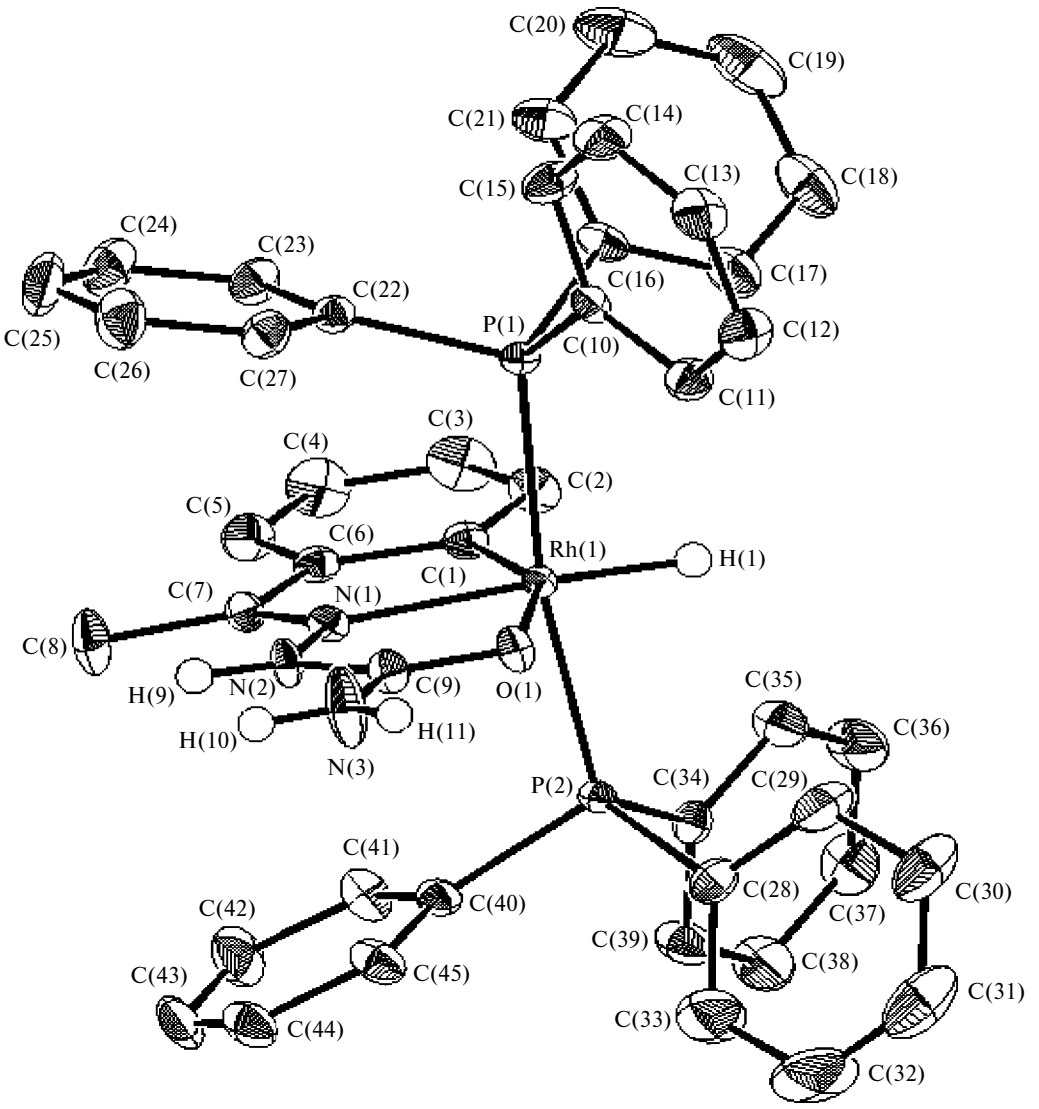


Fig. 1. ORTEP diagram for the cation of $[Rh(H)(PPh_3)_2(C_6H_4(CH_3)C{=}N{-}N(H)C(O)NH_2]PF_6$ (**2a**), with 50% probability ellipsoids.

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

Bond	d/Å	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 Rh—H bond length (1.52 Å) is in the expected range. Of interest, a Cambridge Database search reveals only two structures of mononuclear Rh^{III} complexes that contain two five-membered metallocycles and a hydride (with Rh—H equal to 1.361 and 1.464 Å), generated in both cases by Rh insertion into an sp^3-C—H bond,[18,19] unlike the sp^2-carbon system of **2a**. There is one structure of a Rh—H complex with one five-membered metallocycle formed *via* insertion of Rh into an sp^2-CH bond; here, in a Rh^{III} complex with *trans*-$P(C_6H_{11})_3$ ligands, the hydride (Rh—H is 1.65 Å) is *trans* to an N atom of azobenzene, while chloride and the orthometallated C atom are the other two ligands.[16]

The other bond lengths are unexceptional: the Rh—P bond distances,[15,16,18] and the Rh—O, Rh—N, and Rh—C bond lengths are in the ranges reported for orthometallated rhodium—semicarbazone complexes.[9,16] The C=O, C=N, N—N, C(9)—N(2), and C(9)—N(3) bond lengths of the coordinated acetophenone semicarbazone again agree well with the corresponding values within other metal-semicarbazones complexes.[9,10a,12,13]

The solid state IR spectrum shows the ν(Rh—H), ν(C=O), and ν(C=N) bands in the expected regions, and the mass-spectrum gives a signal for the parent molecular cation.

The room temperature NMR data for complex **2a** in acetone-d_6 show that the structure in this solvent is the same as in the solid state. The $^{31}P\{^1H\}$ data give the expected doublet, with a $J_{Rh,P}$ value consistent with equivalent, *trans*-phosphines.[4,5] The ^1H NMR shows the high-field doublet of triplets for the hydride, with $J_{P,H}$ values typical of a hydride *cis* to *trans* phosphines;[4,5] signals for the orthometallated Ph ring protons are shifted 0.5 to 1.0 ppm upfield in comparison to those for the Ph protons of the free semicarbazone, while signals for the Me and amino protons are also shifted upfield (~0.7 and 3.6 ppm, respectively). The NH proton signal, which is seen at δ 9.45 in the free acetophenone semicarbazone, is not detected for complex **2a** and is likely buried under the aromatic proton signals (see below).

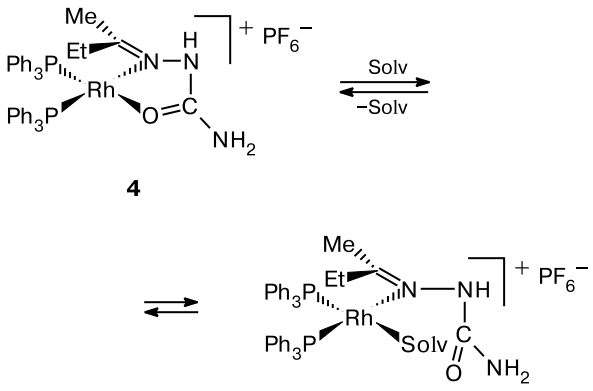
Complex **2a** is stable in acetone, MeOH, and CH_2Cl_2, but its corresponding synthesis in the last two solvents requires a long reaction time (several days *vs.* 1 day in acetone). The synthetic orthometallation reaction is not reversed on treating **2a** with 1 atm H_2 for 24 h at room temperature in any of the three solvents.

Of particular interest, a recent paper[9] reports on a stoichiometric reaction of benzaldehyde semicarbazone with tri- or dialkylamines that occurs at the Rh of $RhCl(PPh_3)_3$. The amide NH_2 is replaced by the new dialkylamine fragment, and the product is the orthometallated Rh^{III} complex akin to **2a**, but with R′ = H and the new dialkylamine moiety instead of the NH_2 (see Scheme 1); also the "expected" hydride ligand from the ortho-metallation has again been replaced by the chloro ligand of the Rh complex.

The corresponding orthometallated acetophenone semicarbazone complexes containing *para*-substituents at the P-aryl rings, **2b**, **2d**, and **2e,** were similarly isolated, while **2c** and **2f** (see Scheme 1) were made *in situ*; their spectroscopic data (especially the high-field, doublet of triplets signal for the hydride at $\delta_H \sim -10.5$) correspond to those of **2a** and their structures are assumed to be the same. The $^{31}P\{^1H\}$ doublets for triarylphosphines species (**2b—e**) are at δ_P 37—41, while for the more basic PPh_2Me species (**2f**) the doublet is more upfield at δ_P 21.5; the $J_{Rh,P}$ values (112—122 Hz) are again consistent with *trans*-P atoms. Like **2a**, the isolated compounds are completely air-stable in the solid state, and in solution under Ar. The propiophenone semicarbazone derivative (**3**) was correspondingly isolated and characterized. Of note, for **3**, the isolated **2e**, and the *in situ* species **2c** and **2f**, the NH proton was detected in the ^1H NMR spectra in the range δ_H 6.28—6.60, ~3 ppm upfield from the resonance for the respective, free semicarbazones; as for **2a**, the δ_{NH} signal for **2b** and **2d** is likely buried under the aromatic proton signals. The elemental analysis for **2e** is not very satisfactory but, with the inclusion of one H_2O solvate molecule per mole of complex, the elemental analysis becomes in excellent agreement with that calculated (C, 46.03; H, 3.18; N, 3.58 %). Similarly, the elemental analysis for **3** agrees well after the inclusion of 0.25 CH_2Cl_2 per mole of complex, and there was qualitative ^1H NMR data for the presence of this solvent.

Formation of $[Rh(PPh_3)_2\{EtC(Me)=N—NHC(O)NH_2\}]PF_6$ (4). Semicarbazones that do not have a Ph substituent at the imine-C atom cannot form orthometallated species, and the reaction of **1a** with 1 or 2 equiv. of butanone semicarbazone in acetone at room temperature produces a dark red, 1 : 1 Rh^I—semicarbazone chelate complex (**4**) that was isolated as a bis(acetone) solvate species (Scheme 2).

Scheme 2



The mass-spectrum of compound **4** shows the parent peak for the cation, and the room temperature ^{1}H 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 η^2-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 ^{1}H 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 $[Rh(PPh)EtC(Me)N - 2\ H]^+$ species corresponds to such a mass but is considered unlikely; perhaps a matrix component is involved.

The room temperature $^{31}P\{^1H\}$ NMR spectrum for **4** in acetone exhibits a broad doublet at δ 49.7 ($J_{Rh,P}$ = 194 Hz) resembling those of *cis*-$[Rh(PPh_3)_2(Me_2CO)_2]^+$ (**1a**). However, complex **4** (unlike **1a**) has inequivalent phosphines, and this is demonstrated by the low temperature $^{31}P\{^1H\}$ NMR data (Fig. 2). As the temperature is 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, $J_{Rh,P}$ = 207 Hz, $J_{P,P}$ = 60 Hz); 47.49 (dd, $J_{Rh,P}$ = 178.8 Hz, $J_{P,P}$ = 60 Hz); a comparison with the literature data[20] 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).

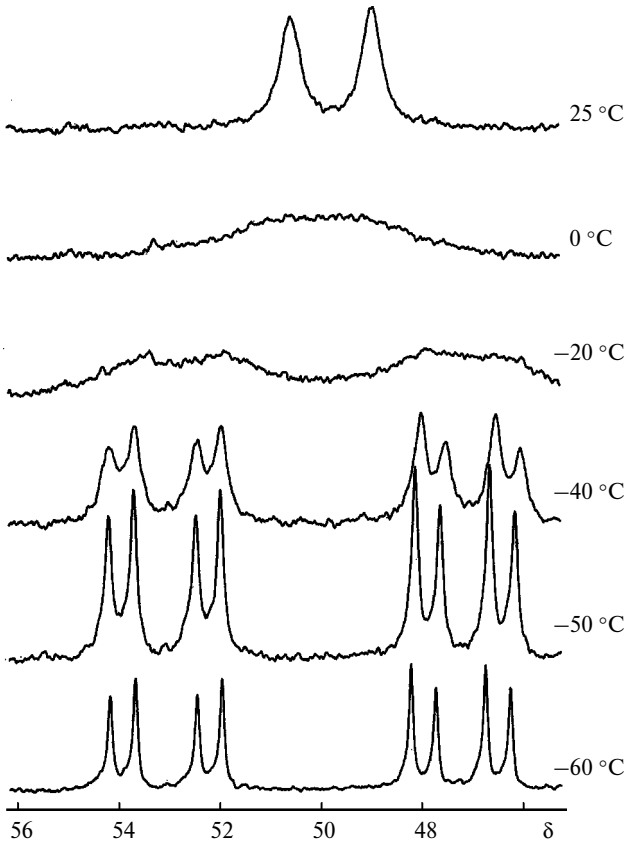


Fig. 2. Variable temperature $^{31}P\{^1H\}$ NMR spectra of **4** in acetone-d_6.

More generally, there are many examples of Rh metallocycles formed *via* the activation of the sp^2-C—H[16,21,22] and sp^3-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 $[Rh(cod)(PR_3)_2]PF_6$ complexes (R = Ph, *p*-$OMeC_6H_4$, *p*-FC_6H_4, *p*-ClC_6H_4; R_3 = Ph_2Me, $Ph_2(p\text{-}MeC_6H_4)$) were prepared according to a literature method.[4] The $[Rh(PR_3)_2(Solv)_2]^+$ (Solv = MeOH, Me_2CO) species were generated *in situ* by removing the H_2 atmosphere over the solutions containing the corresponding *cis*,*trans*,*cis*-$[Rh(H)_2(PR_3)_2(Solv)_2]PF_6$ 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 (^{1}H, relative to external $SiMe_4$), solvent carbon (^{13}C, 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; data were recorded at room temperature (~20 °C). The $^oC_6H_4$ 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 IIHQ 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 H_2O/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. $C_9H_{11}N_3O$. Calculated (%): C, 61.00; H, 6.26; N, 23.71. IR, ν/cm^{-1}: 1695 (C=O); 1584 (C=N). ^{1}H NMR (DMSO-d_6), δ: 2.20 (s, 3 H, Me); 6.60 (s, 2 H, NH_2); 7.30—7.40 (m, 3 H, H arom.); 7.80—7.90 (m, 2 H, H arom.); 9.45 (s, 1 H, NH). ^{13}C NMR (DMSO-d_6), 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 $[M - CO - NH_2]^+$ (100), 119 $[M - N - CO - NH_2]^+$ (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. $C_{10}H_{13}N_3O$. Calculated (%): C, 62.81; H, 6.85, N, 21.97. IR, ν/cm^{-1}: 1695 (C=O); 1583 (C=N). ^{1}H NMR (DMSO-d_6), δ: 1.00 (t, 3 H, Me); 2.75 (q, 2 H, CH_2); 6.50 (s, 2 H, NH_2); 7.30—7.40 (m, 3 H, H arom.); 7.80—7.90 (m, 2 H, H arom.); 9.50 (s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 10.59 (s, 1 C, Me); 18.95 (s, 1 C, CH_2); 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 $[M - 2H]^+$ (45); 162 $[M - Et]^+$ (15); 147 $[M - Et - NH]^+$ (100); 130 $[M - Et - NH_2 - O]^+$ (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. $C_5H_{11}N_3O$. Calculated (%): C, 46.49; H, 8.58; N, 32.53. IR, ν/cm^{-1}: 1645 (C=O); 1584 (C=N). ^{1}H ($CDCl_3$), δ: 1.15 (t, 3 H, C$\underline{H}_3$CH$_2$); 1.85 (s, 3 H, MeC=); 2.20 (q, 2 H, MeC$\underline{H}_2$); 5.80 (br.s, 2 H, NH_2); 8.50 (s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 10.56 (s, 1 C, $\underline{C}H_3CH_2$); 15.29 (s, 1 C, $\underline{C}H_3C$=); 31.88 (s, 1 C, $CH_3\underline{C}H_2$); 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 $[Et(Me)C{=}NNH_2]^+$ (60); 85 $[M - C(O)NH_2]^+$ (35); 69 $[EtC{=}NN]^+$ (40).

Synthesis of orthometallated complexes. (*O,N,ortho-C*-Acetophenonesemicarbazonato)(hydrido)bis(triphenylphosphine)rhodium(III) hexafluorophosphate, $[Rh(H)(PPh_3)_2\{o\text{-}C_6H_4(Me)C{=}N{-}N(H)CONH_2\}]PF_6$ (2a). Complex $[Rh(cod)(PPh_3)_2]PF_6$ (55.5 mg, 0.063 mmol) in acetone (5 mL) was reacted with 1 atm H_2 at ~20 °C for 2 h to form an *in situ* sample of *cis,trans,cis*-$[Rh(H)_2(PPh_3)_2(Me_2CO)_2]^+$. 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 $[Rh(PPh_3)_2(Me_2CO)_2]^+$ (**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 Et_2O (~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. $C_{45}H_{41}F_6N_3OP_3Rh$. 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). ^{1}H NMR (acetone-d_6), 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, NH_2); 6.33 (t, 1 H, $^oC_6H_4$, $J_{H,H}$ = 8 Hz); 6.66 (m, 2 H, $^oC_6H_4$, $J_{H,H}$ = 8 Hz); 6.82 (d, 1 H, $^oC_6H_4$, $J_{H,H}$ = 8 Hz); 7.50—8.00 (m, ~30 H, PPh_3). ^{31}P{^{1}H} NMR (acetone-d_6), δ: 41.13 (d, $J_{Rh,P}$ = 118 Hz); −143.2 (septet, PF_6^-, $J_{P,H}$ = 708 Hz). MS, *m/z* (I_{rel} (%)): 804 $[M - PF_6]^+$ (60); 627 $[Rh(PPh_3)_2]^+$ (95); 542 $[M - PPh_3 - PF_6]^+$ (100); 287 $[Rh(PPh_2)]^+$ (68).

The preparation of **2a** can also be carried out in MeOH or in CH_2Cl_2, when the precursors are $[Rh(PPh_3)_2(MeOH)_2]^+$ or $[Rh(PPh_3)\{(\mu\text{-}Ph)PPh_2\}]_2^{2+}$, respectively (see above), but the reactions with the semicarbazone are much slower, taking several days for completion.

Other $[Rh(PR_3)_2(Me_2CO)_2]^+$ precursor species (**1b—f**) were prepared analogously *in situ* in acetone, and their room temperature ^{31}P{^{1}H} 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-d_6.

(*O,N,o-C*-Acetophenonesemicarbazonato)(hydrido)bis[diphenyl(*p*-methylphenyl)phosphine]rhodium(III) hexafluorophosphate, $[Rh(H)\{PPh_2(p\text{-}MeC_6H_4)\}_2\{o\text{-}C_6H_4(Me)C{=}N{-}NHC(O)NH_2\}]PF_6$ (2b). Yield 63%. Found (%): C, 57.55; H, 4.73; N, 4.39. $C_{47}H_{45}F_6N_3OP_3Rh$. 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). ^{1}H 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, NH_2); 6.31 (t, 1 H, $^oC_6H_4$, $J_{H,H}$ = 7.1 Hz); 6.62 (d, 1 H, $^oC_6H_4$, $J_{H,H}$ = 8.5 Hz); 6.66 (t, 1 H, $^oC_6H_4$, $J_{H,H}$ = 7.1 Hz); 6.81 (d, 1 H, $^oC_6H_4$, $J_{H,H}$ = 7.6 Hz); 6.90—7.80 (m, 28 H, H arom.). ^{31}P {^{1}H} NMR, δ: 40.7 (d, $J_{Rh,P}$ = 116.6 Hz); −143.2 (septet, PF_6^-). MS, *m/z* (I_{rel} (%)): 832 $[M - PF_6]^+$ (45); 655 $[Rh\{PPh_2(p\text{-}MeC_6H_4)\}_2]^+$ (100); 556 $[M - PPh_2(p\text{-}MeC_6H_4)]^+$ (90); 301 (40), 136 (40).

(*O,N,o-C*-Acetophenonesemicarbazonato)(hydrido)bis[tri(*p*-methoxyphenyl)phosphine]rhodium(III) hexafluorophosphate, $[Rh(H)\{P(p\text{-}OMeC_6H_4)_3\}_2\{o\text{-}C_6H_4(Me)C{=}N{-}NHC(O)NH_2\}]PF_6$ (2c). ^{1}H 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, NH_2); 3.80 (s, 12 H, OMe); 3.83 (s, 6 H, OMe); 6.28 (br.s, 1 H, NH); 6.36 (t, 1 H, $^oC_6H_4$); 6.64 (d, 1 H, $^oC_6H_4$); 6.68 (t, 1 H, $^oC_6H_4$); 6.82 (d, 1 H, $^oC_6H_4$); 6.90—7.80 (m, 24 H, H arom.). ^{31}P{^{1}H} NMR, δ: 36.7 (d, $J_{Rh,P}$ = 121.5 Hz); −143.2 (septet, PF_6^-).

(*O,N,o-C*-Acetophenonesemicarbazonato)(hydrido)bis[tri(*p*-fluorophenyl)phosphine]rhodium(III) hexafluorophosphate, $[Rh(H)\{P(p\text{-}FC_6H_4)_3\}_2\{o\text{-}C_6H_4(Me)C{=}N{-}NHC(O)NH_2\}]PF_6$ (2d). Yield 59%. Found (%): C, 51.03; H, 3.42; N, 3.79. $C_{45}H_{35}F_{12}N_3OP_3Rh$. Calculated (%): C, 51.11; H, 3.34; N, 3.97. ^{1}H 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, NH_2); 6.46 (t, 1 H, $^oC_6H_4$, $J_{H,H}$ = 7 Hz); 6.68 (d, 1 H, $^oC_6H_4$, $J_{H,H}$ = 8 Hz); 6.73 (t, 1 H, $^oC_6H_4$, $J_{H,H}$ = 7.4 Hz); 6.92 (d, 1 H, $^oC_6H_4$, $J_{H,H}$ = 7.7 Hz); 7.12 (t, 2 H, H arom., $J_{H,H}$ = 8.4 Hz); 7.23 (t, 10 H,

H arom., $J_{H,H}$ = 8.8 Hz); 7.55 (m, 10 H, H arom.); 7.70 (m, 2 H, H arom.). $^{31}P\{^1H\}$ NMR, δ: 38.51 (d, $J_{Rh,P}$ = 118 Hz); −143.2 (septet, PF_6^-). MS, *m/z* (I_{rel} (%)): 912 $[M - PF_6]^+$ (25); 735 $[Rh\{P(p\text{-}FC_6H_4)_3\}_2]^+$ (65); 596 $[Rh\{P(p\text{-}FC_6H_4)_3\}\{C_6H_4(Me)C{=}NNHC(O)NH_2\}]^+$ (100); 323 $[Rh\{P(p\text{-}FC_6H_4)_2\} - H]^+$ (50).

(*O,N,o-C*-Acetophenonesemicarbazonato)(hydrido)bis[tri(*p*-chlorophenyl)phosphine]rhodium(III) hexafluorophosphate, $[Rh(H)\{P(p\text{-}ClC_6H_4)_3\}_2\{o\text{-}C_6H_4(Me)C{=}N{-}NHC(O)NH_2\}]PF_6$ (2e). Yield 51%. Found (%): C, 46.11; H, 3.29; N, 3.31. $C_{45}H_{35}Cl_6F_6N_3OP_3Rh$. Calculated (%): C, 46.74; H, 3.05; N, 3.63. ^1H NMR, δ: −10.74 (dt, 1 H, RhH, $J_{P,H}$ = 10.3 Hz, $J_{Rh,H}$ = 14.6 Hz); 1.60 (s, 3 H, Me); 3.25 (br.s, 2 H, NH_2); 6.47 (t, 1 H, $^oC_6H_4$, $J_{H,H}$ = 7 Hz); 6.53 (br.s, 1 H, NH); 6.68 (d, 1 H, $^oC_6H_4$, $J_{H,H}$ = 8 Hz); 6.75 (t, 1 H, $^oC_6H_4$, $J_{H,H}$ = 7.5 Hz); 6.92 (d, 1 H, $^oC_6H_4$, $J_{H,H}$ = 7.7 Hz); 7.45—7.75 (m, 24 H, H arom.). $^{31}P\{^1H\}$ NMR, δ: 40.41 (d, $J_{Rh,P}$ = 118 Hz); −143.2 (septet, PF_6^-). MS, *m/z* (I_{rel} (%)): 1010 $[M - H - PF_6]^+$ (10); 833 $[Rh\{P(p\text{-}ClC_6H_4)_3\}_2 - H]^+$ (21); 644 $[Rh\{P(p\text{-}ClC_6H_4)_3\}\{C_6H_4{-}(Me)C{=}NNHC(O)NH_2\} - H]^+$ (100).

(*O,N,o-C*-Acetophenonesemicarbazonato)(hydrido)bis[(methyldiphenyl)phosphine]rhodium(III) hexafluorophosphate, $[Rh(H)(PPh_2Me)_2\{o\text{-}C_6H_4(Me)C{=}N{-}NHC(O)NH_2\}]PF_6$ (2f). ^1H NMR, δ: −11.58 (m, 1 H, RhH, $J_{P,H}$ = 14.7 Hz, $J_{Rh,H}$ = 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 $^oC_6H_4$). $^{31}P\{^1H\}$ NMR, δ: 21.52 (d, $J_{Rh,P}$ = 112.3 Hz); −143.2 (septet, PF_6^-).

(*O,N,o-C*-Propiophenonesemicarbazonato)(hydrido)bis(triphenylphosphine)rhodium(III) hexafluorophosphate, $[Rh(H)(PPh_3)_2\{o\text{-}C_6H_4(Et)C{=}N{-}NHC(O)NH_2\}]PF_6$ (3). Yield 65.8%. Found (%): C, 56.34; H, 4.56; N, 4.32. $C_{46}H_{43}F_6N_3OP_3Rh \cdot 0.25\ CH_2Cl_2$. 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, $J_{P,H}$ = 11 Hz, $J_{Rh,H}$ = 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, $^oC_6H_4$, $J_{H,H}$ = 8 Hz); 6.42 (d, 1 H, $^oC_6H_4$, $J_{H,H}$ = 8 Hz); 6.60 (br.s, 1 H, NH); 6.73 (t, 1 H, $^oC_6H_4$, $J_{H,H}$ = 10 Hz); 6.92 (d, 1 H, $^oC_6H_4$, $J_{H,H}$ = 8 Hz); 7.10—8.10 (m, 30 H, PPh_3). $^{31}P\{^1H\}$ NMR, δ: 41.58 (d, $J_{Rh,P}$ = 117 Hz); −143.2 (septet, PF_6^-). MS, *m/z* (I_{rel} (%)): 818 $[M - PF_6]^+$ (45); 627 $[Rh(PPh_3)_2]^+$ (85); 556 $[M - PPh_3 - PF_6]^+$ (100); 287 $[Rh\{PPh_2\} - H]^+$ (75).

(*O,N*-Butanonesemicarbazonato)bis(triphenylphosphine)rhodium(III) hexafluorophosphate, $[Rh(PPh_3)_2\{C_2H_5(Me)C{=}N{-}NHCONH_2\}](PF_6)$ (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 $[Rh(cod)(PPh_3)_2]PF_6$, 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 ~1—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. $C_{41}H_{41}F_6N_3OP_3Rh \cdot 2\ Me_2CO$. 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, $C\underline{H}_3CH_2$); 1.92 (q, 2 H, $MeC\underline{H}_2$); 1.75 (s, 3 H, $C\underline{H}_3{-}C{=}$); 2.85 (br.s, 2 H, NH_2); 7.15—7.70 (m, 30 H, H arom.). $^{31}P\{^1H\}$ NMR (acetone-d_6), δ: 49.7 (br.d, $J_{Rh,P}$ = 194 Hz); −143.2 (septet, PF_6^-). MS, *m/z* (I_{rel} (%)): 756 $[M - PF_6]^+$ (3); 627 $[Rh(PPh_3)_2]^+$ (20); 279 (?) (100).

Reactivity of $[Rh(H)(PPh_3)_2\{o\text{-}C_6H_4(Me)C{=}N{-}N(H)CONH_2\}]PF_6$ (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 $^{31}P\{^1H\}$ 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** (0.50×0.25×0.08 mm^3) were collected at 173 K on a Rigaku/ADSC CCD area detector instrument with graphite monochromated Mo-Kα radiation (0.71069 Å). Crystals of **2a**, $C_{45}H_{41}N_3OF_6P_3Rh \cdot 2\ CH_2Cl_2$ (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, α = 96.764(4)°, β = 101.491(5)°, γ = 105.089(4)°, V = 2474.9(4) Å^3, d_{calc} = 1.502 g cm^{-3}, Z = 2. Of the 21,307 reflections collected, 9536 were unique (R_{int} = 0.049). Data were collected and processed using the d*TREK [29] program and corrected for Lorentz and polarization effects. The structure was solved by direct methods[30] 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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