Rhodium(III)-Cyclometalated-Imine Complexes: Solution Behavior and Reactivity with Molecular Hydrogen

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Acetone solutions of *cis,trans,cis*-$[Rh(H)_2(PPh_3)_2(acetone)_2]PF_6$ and *cis*-$[Rh(PPh_3)_2(acetone)_2]PF_6$ react with the imines RN=CR′(R″), where R = $PhCH_2$, Ph, or C_6H_{11}; R′ = H or Me; and R″ = Ph or *p*-OMe-C_6H_4, to form orthometalated complexes exemplified by $[Rh(H)\{RN{=}CR'(o\text{-}C_6H_4)\}(PPh_3)_2(acetone)]PF_6$ that are generally characterized spectroscopically, and in one case (where R = $PhCH_2$, R′ = Me, and R″ = *p*-OMe-C_6H_4) by X-ray crystallography. These complexes maintain their integrity in acetone solution and show no reaction toward 1 atm H_2 at ambient conditions. In MeOH, the complexes in which R′ = Me simply change to the corresponding MeOH derivative, but when R′ = H they are partially converted to the non-orthometalated, η^1-N-imine species $[Rh(PPh_3)_2(RN{=}CHR'')(MeOH)]PF_6$ (**I**), and in MeOH, stoichiometric hydrogenation of the imine to the corresponding amine occurs via **I**. We have shown recently (*Inorg. Chem.* **2004**, *43*, 4820) that the catalyzed hydrogenation of $PhCH_2N{=}C(H)Ph$ to dibenzylamine using *cis,trans,cis*-$[Rh(H)_2(PPh_3)_2(MeOH)_2]PF_6$ as catalyst precursor in MeOH proceeds via a cationic Rh-(η^1-*N*-imine)(amine) intermediate (**II**), analogous to **I** but with the MeOH replaced by the amine that is formed via hydrolysis of the imine by the presence of adventitious water. Intermediate **I** (R = $PhCH_2$, R″ = Ph) is shown to be somewhat less active than **II** toward H_2, but both intermediates provide viable pathways for hydrogenation of the imine. The orthometalated imine-amine complex $[Rh(H)\{PhCH_2N{=}C(Me)(o\text{-}C_6H_4)\}(PPh_3)_2(NH_2CH_2Ph)]PF_6$, where the benzylamine comes from imine hydrolysis, is also isolated and characterized crystallographically.

Introduction

Our recent studies on the homogeneous H_2-hydrogenation of the imine $PhCH_2N{=}C(H)Ph$ catalyzed by the $[Rh(COD)(PPh_3)_2]PF_6$ (**1**) precursor (when, for example, imine:Rh = 100) have revealed that the active catalyst (the species that reacts with H_2) is a mixed Rh(I)-imine-amine species, the amine benzylamine being formed via an accompanying Rh-catalyzed hydrolysis of the imine by adventitious water.[1] Under stoichiometric conditions (imine:Rh = 1), we now observe quite different chemistry, which is reported here: the imine coordinates with orthometalation in an η^2 fashion via the imine-N and the ortho-C atom of a phenyl group, giving rise to a five-membered metallacycle within a hydrido-Rh(III)-*o*-metalated complex. Such intramolecular activation of a C−H bond of an aryl group of a donor ligand has long been known for platinum metal complexes of a variety of ligands, including N-donors,[2−4] and there are many early examples in Rh and Ir chemistry.[5,6] Our group has recently reported on orthometalation within semicarbazone complexes of Rh (semicarbazone being a substituted imine)[7] and within Ir species containing simple imines such as $PhCH_2N{=}C(H)Ph$,[8] but to our knowledge this work is the first report of orthometalation of simple imines at Rh (specifically imines of the type RN=CR′(R″), where R = $PhCH_2$, Ph, or C_6H_{11}; R′ = H or Me; and R″ = Ph or *p*-OMe-C_6H_4, containing solely alkyl or aryl substituents). Of more interest and relevance, however, are the solution chemistry of these new orthometalated species, their reaction with H_2, and the implications of the findings to catalyzed hydrogenation of the imines, a topic that continues to attract much interest.[9]

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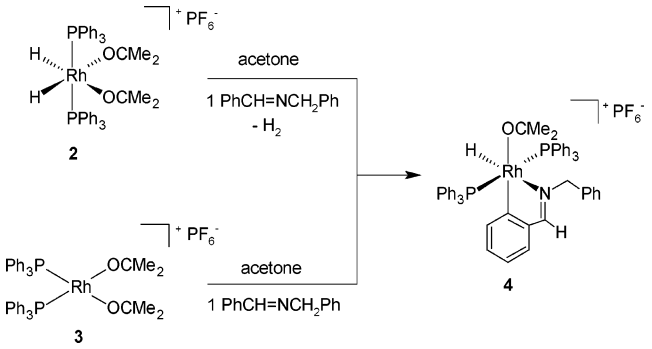

Figure 1. Scheme showing reactions for formation of **4**.

Results and Discussion

Reaction of either *cis,trans,cis*-$[Rh(H)_2(PPh_3)_2(acetone)_2]PF_6$ (**2**) or *cis*-$[Rh(PPh_3)_2(acetone)_2]PF_6$ (**3**)[10,11] with $PhCH_2N{=}C(H)Ph$ (Rh:imine = 1:1) in acetone at room temperature (~20 °C) under Ar affords the Rh(III)-orthometalated complex $[Rh(H)\{PhCH_2N{=}CH(o\text{-}C_6H_4)\}(PPh_3)_2(acetone)]PF_6$ (**4**) (Figure 1), isolated as an off-white solid. Formation of orthometalated complexes via reaction of a simple imine with a Rh(I) species has not been reported in detail, although we have noted the existence of such species[1] and have reported on the Ir analogue of **4** that was isolated from reaction of the imine with the Ir analogue of **2**.[8] The mechanism[3,8] presumably involves displacement of an acetone ligand by imine when the *ortho*-CH group becomes close to the metal, this being accompanied, when **2** is the reactant, by reductive elimination of the hydride ligands as H_2 (detected in the ^1H NMR spectrum at δ_H 4.40 in acetone-d_6); oxidative addition of C−H then generates **4**. Detection of hydride (see below) versus deuteride in the product isolated from reaction of $PhCH_2N{=}CHPh$ with the precursor $[Rh(D)_2(PPh_3)_2(acetone\text{-}d_6)_2]PF_6$ in acetone-d_6 is consistent with the hydrido ligand emanating from the orthometalation process. Of note, reaction of $[RhCl(CO)_2]_2$ with $MeN{=}C(H)Ph$ forms the η^1-N-imine complex *cis*-$RhCl(CO)_2(MeN{=}CHPh)$, presumably because the presence of the electron-withdrawing CO ligands diminishes the tendency for oxidative addition.[3]

The IR data for **4** reveal bands for ν_{RhH}, $\nu_{C=N}$, and ν_{CO} for the coordinated acetone. The room-temperature $^{31}P\{^1H\}$ NMR spectrum in acetone-d_6 shows a doublet (δ 40.40, J_{RhP} = 116), the J value being indicative of mutually *trans* phosphines.[1c] The high-field hydride ^1H NMR resonance (δ −12.85, $^2J_{HP} \approx J_{RhH}$ = 13) appears as a pseudo-quartet (ps q) instead of the expected doublet of triplets; such overlapping of triplets has been reported for other *trans*-$Rh(PPh_3)_2$-hydrido moieties.[12] Upfield-shifted δ_H resonances for the orthometalated ring protons and for the N=C*H* signal (δ_H 7.81 versus 8.50 for the free imine) are similar to those reported for the Ir analogue.[8] Thus, in acetone solution, **4** maintains the solid state structure shown in Figure 1 and confirmed crystallographically for a closely related imine complex (**5**, see below).

In CD_3OD, **4** shows different and more complex behavior (Figure 2) that was studied by variable-temperature NMR experiments (Figure S1 in the Supporting Information). The room-temperature $^{31}P\{^1H\}$ NMR spectrum of **4** now indicates the presence of three species: $[Rh(H)\{PhCH_2N{=}CH(o\text{-}C_6H_4)\}(PPh_3)_2(CD_3OD)]PF_6$ (**4′**)[13] (δ 40.52 d, J_{RhP} = 116), *cis*-$[Rh(PPh_3)_2(CD_3OD)_2]PF_6$ (**3′**) (δ 57.02 d, J_{RhP} = 207),[11] and a fluxional species that gives rise to two broad, unresolved resonances centered at δ ~46 and ~55. These resonances resolve at 253 K into an AMX, 8-line pattern (δ 44.55 dd, J_{RhP} = 164, $^2J_{PP}$ = 54; 54.74 dd, J_{RhP} = 214, $^2J_{PP}$ = 54), indicative of a species containing two inequivalent *cis*-phosphines, each *trans* to a different ligand, and this is identified as the imino-solvento complex *cis*-$[Rh(PPh_3)_2(PhCH_2N{=}CHPh)(CD_3OD)]PF_6$ (**I**), shown in Figure 2. Free acetone (δ 2.10) is detected in the room-temperature ^1H NMR spectrum of **4** in CD_3OD (Figure S1), indicating its displacement by CD_3OD to give **4′**, while detection of free imine indicates that **4′** has undergone "reductive elimination" of this ligand, a premise confirmed by the presence of $[Rh(PPh_3)_2(CD_3OD)_2]PF_6$ (**3′**) in the $^{31}P\{^1H\}$ NMR spectrum (Figure S1) in an amount that corresponds to the amount of free imine. The room-temperature ^1H NMR spectrum also shows sharp singlets at δ 4.80 and 4.99 for the benzylic protons of free imine and the orthometalated imine (of **4′**), respectively, as well as a broad signal in the δ 4.7−5.3 region; at 253 K (Figure S1), this broad signal sharpens into a pair of doublets (δ 4.50 d, 5.35 d, $^2J_{HH}$ = 6), showing diastereotopic inequivalence of the benzylic protons within **I**, presumably because of some restricted rotation of the imine moiety at lower temperatures. The C*H*=N resonances of **4′** and **I** are not seen, presumably being masked by the aromatic proton signals. The room-temperature ^1H NMR spectrum also shows a downfield doublet (δ 9.65 d, 2H, $^3J_{HH} \approx 7$) that is not attributable to **3′** or to free imine; the corresponding $^1H-^{13}C$ HETCOR NMR experiment reveals correlation of this signal with resonances corresponding to aromatic C atoms (δ 132), and so the signal is attributed to the *o*-protons of the imine-Ph moiety of **I** being involved in a π-arene interaction with Ph groups of the PPh_3 ligands that causes a shielding of this resonance. A similar shielding was observed for a Rh(I)-imine-amine complex recently reported by our group.[1c] Neither **4′** nor **I** could be isolated pure from a solution mixture of **4′**, **3′,** and **I**, formed either from a solution of **4** in MeOH or from a MeOH solution of **4′** formed directly from reaction of *cis*-$[Rh(PPh_3)_2(MeOH)_2]PF_6$ with 1 equiv of $PhCH_2N{=}C(H)Ph$.

Thus in MeOH, the orthometalation process evident in **4** (and **4′**) is effectively reversed and affords **3′** and **I**, square planar species that can both undergo oxidative addition of H_2 (see below). Such behavior is relevant in that $[Rh(COD)(PPh_3)_2]PF_6$ (**1**) is an effective precursor catalyst for hydrogenation of imines in MeOH solution but not in acetone. In the latter solvent, the integrity of the coordinatively saturated Rh(III) species **4** is

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(13) A prime superscript (e.g., as in **4′**) refers to the CD_3OD/CH_3OH analogue of the corresponding acetone/acetone-d_6 species (e.g., **4**).

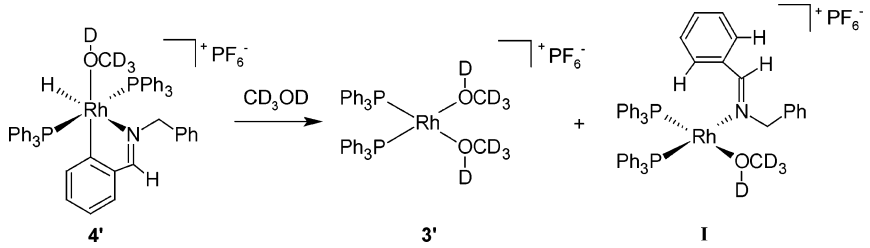


Figure 2. Scheme showing the species generated in a CD_3OD solution of **4** (or **4′**).

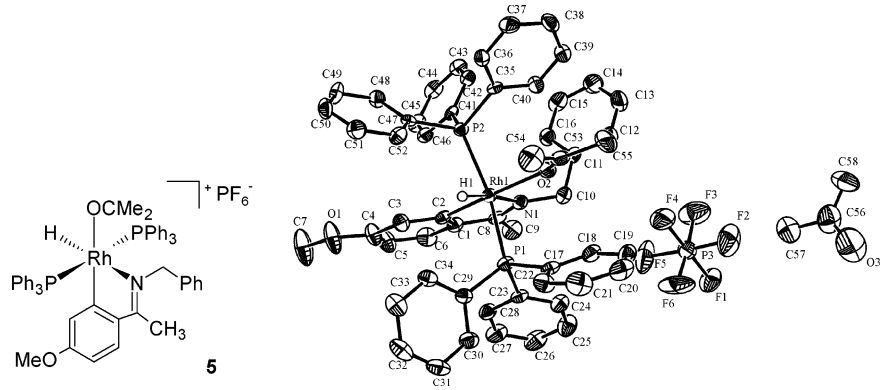


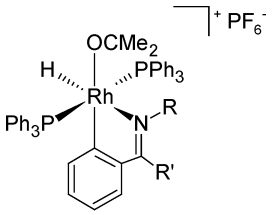
Figure 3. Structural and ORTEP diagram of $[Rh(H)\{PhCH_2N{=}C(Me)(o\text{-}C_6H_3\text{-}p\text{-}OMe\}(PPh_3)_2(acetone)]PF_6{\cdot}Me_2CO$ (**5**) with 50% probability thermal ellipsoids.

maintained, and there is no reactivity toward H_2. However, exposure of a MeOH solution of **4′** to 1 atm H_2 results in quantitative hydrogenation of the coordinated imine within 5 min to afford dibenzylamine and *cis,trans,cis*-$[Rh(H)_2(PPh_3)_2(CD_3OD)_2]PF_6$ (**2′**), as detected by $^{31}P\{^1H\}$ and ^1H NMR spectroscopies.[10,11] Monitoring the H_2-hydrogenation of **4** in MeOH (i.e. **4′**) by variable-temperature NMR spectroscopy showed no evidence for hydrido-imine intermediates. At 243 K, the spectra revealed the presence of **4′**, **2′** (formed from **3′**), **I**, free acetone, and a smaller amount of free imine; as the solution was warmed to 300 K, **I** and **4′** gradually disappeared with concomitant formation of dibenzylamine (δ_{CH2} 4.80) and increased amounts of **2′** and **3′**. The dibenzylamine is, in fact, involved in a labile equilibrium with **3′**, and we have reported earlier on the NMR investigation of this equilibrium.[1a] The only Rh species seen in the final solution at 300 K is **2′**, when all the imine has been converted to free amine.

Attempts to obtain a crystal of **4** suitable for X-ray analysis were unsuccessful, but the ketimine $PhCH_2N{=}C(Me)(p\text{-}MeOC_6H_4)$ similarly underwent the orthometalation reaction with **2** in acetone to give $[Rh(H)\{PhCH_2N{=}C(Me)(o\text{-}C_6H_3\text{-}p\text{-}OMe\}(PPh_3)_2(acetone)]PF_6$ (**5**), which was characterized crystallographically (Figure 3); selected structural parameters are given in Table 2. The complex crystallizes as a two-component twin with one acetone molecule in the asymmetric unit. The geometry at the Rh is essentially octahedral with *trans*-phosphines, the acetone being *trans* to the metalated *o*-carbon and the refined, located Rh-H hydrogen atom being *trans* to the imine-N atom. As for the related Ir complex $[Ir(H)\{PhCH_2N{=}CH(o\text{-}C_6H_4)\}(PPh_3)_2(acetone)]PF_6$, the large C(53)−O−Rh angle of 137.9° and the P(1)−Rh−P(2) angle of 166.8° indicate that the acetone-Me groups are subject to steric repulsions by the Rh-$(PPh_3)_2$ moiety. The structure of **5** is generally very similar to that of the Ir complex noted above, with the five-membered cyclometalated rings being essentially planar. The N(1)−C(8) imine bond is 0.18 Å shorter than the N(1)−C(10) single bond, while the Rh−O bond length of 2.19 Å likely reflects a *trans*-influence of the *ortho*-C ligand, although we have been unable to find any structural data on a Rh-acetone moiety (the Rh−O distances within related orthometalated Rh-semicarbazone complexes[7] are in the range 2.207−2.310 Å). The solid state IR of **5** reveals the ν_{Rh-H}, $\nu_{C=N}$, and $\nu_{C=O}$ bands. The room-temperature $^{31}P\{^1H\}$ and ^1H NMR spectra of **5** in acetone-d_6 correspond closely to those of **4**, with the former showing also the "extra" resonances for the imine Me and OMe protons. Interestingly, and in contrast with **4**, complex **5** upon dissolution in MeOH simply forms the MeOH-solvated analogue **5′** (δ_P 40.33 d, $J_{RhP} = 117.8$; δ_H −12.70 ps q, $J_{RhH} \approx {}^2J_{HP} = 13$) and displays none of the behavior associated with the

Table 1. Crystallographic Data for 5 and 9*

	5	**9***
formula	$C_{58}H_{59}NO_3F_6P_3Rh$	$C_{59.50}H_{60}N_2O_{1.50}F_6P_3Rh$
fw	1127.88	1136.92
cryst color, habit	colorless, needle	red, irregular
cryst size (mm)	0.30 × 0.07 × 0.07	0.40 × 0.30 × 0.20
space group	$P2_1/c$	$P2_1/n$
a (Å)	10.060(1)	16.5613(5)
b (Å)	19.129(2)	17.8073(4)
c (Å)	27.912(3)	18.7853(5)
β (deg)	91.600(5)	107.822(2)
V (Å^3)	5369(1)	5274.2(2)
Z	4	4
D_{calcd} (g cm^{-3})	1.395	1.432
μ (mm^{-1})	0.473	0.481
total no. of reflns	157 997	48 378
no. of unique reflns	30 620	12 155
R_{int}	0.071	0.047
no. of variables	697	660
R1	0.044 ($I > 2\sigma(I)$, 16 036 obs reflns)	0.032 ($I > 3\sigma(I)$, 8601 obs reflns)
wR2	0.104 (all data)	0.090 (all data)
GOF	0.94 (all data)	1.12 (all data)



7 (R = Ph, R' = H)
8 (R = C_6H_{11}, R' = H)
9 (R = CH_2Ph, R' = Me)
10 (R = CH_2Ph, R' = Ph)

Figure 4. Complexes **7**−**10**.

Table 2. Selected Bond Distances and Angles for [Rh(H){PhCH$_2$N=C(Me)(*o*-C$_6$H$_3$-*p*-OMe}(PPh$_3$)$_2$(acetone)]PF$_6$·Me$_2$CO (5) (estimated standard deviations in parentheses)

bond	length (Å)	bond	angle (deg)
Rh(1)−P(1)	2.3313(8)	P(1)−Rh(1)−C(2)	88.92(7)
Rh(1)−P(2)	2.3529(7)	P(2)−Rh(1)−N(1)	99.56(6)
Rh(1)−N(1)	2.1597(19)	P(2)−Rh(1)−O(2)	92.15(5)
Rh(1)−O(2)	2.1937(18)	P(2)−Rh(1)−H(1)	85.0(6)
Rh(1)−C(2)	2.001(2)	N(1)−Rh(1)−H(1)	171.4(7)
Rh(1)−H(1)	1.564(17)	N(1)−Rh(1)−C(2)	79.86(9)
N(1)−C(8)	1.296(3)	N(1)−Rh(1)−O(2)	92.11(8)
N(1)−C(10)	1.479(3)	N(1)−C(8)−C(1)	115.8(2)
O(2)−C(53)	1.223(3)	C(2)−C(1)−C(8)	117.0(2)
C(53)−C(54)	1.496(4)	P(2)−Rh(1)−C(2)	88.18(7)
C(53)−C(55)	1.498(4)	O(2)−C(53)−C(54)	122.6(3)
C(8)−C(1)	1.465(3)	O(2)−C(53)−C(55)	120.1(3)
C(8)−C(9)	1.521(3)	C(53)−O(2)−Rh(1)	137.93(19)
C(1)−C(2)	1.414(3)	Rh(1)−C(2)−C(1)	113.62(19)
C(10)−C(11)	1.527(3)	Rh(1)−C(2)−C(3)	128.52(19)
		Rh(1)−N(1)−C(8)	113.53(17)
bond	angle (deg)	Rh(1)−N(1)−C(10)	124.54(16)
P(1)−Rh(1)−P(2)	166.86(3)	C(53)−O(2)−Rh(1)	137.93(19)
O(2)−Rh(1)−C(2)	171.90(9)	Rh(1)−C(2)−C(1)	113.62(19)
P(1)−Rh(1)−N(1)	92.54(6)	Rh(1)−C(2)−C(3)	128.52(19)
P(1)−Rh(1)−O(2)	92.52(5)	Rh(1)−N(1)−C(8)	113.53(17)
P(1)−Rh(1)−H(1)	82.4(7)	Rh(1)−N(1)−C(10)	124.54(16)

chemistry of **4′** shown in Figure 2. Consistent with this, no reaction is observed when exposing a MeOH solution of **5** (or **5′**) to 1 atm H_2.

The orthometalated complex [Rh(H){CH$_3$N=CH(*o*-C$_6$H$_4$)}(PPh$_3$)$_2$(acetone)]PF$_6$ (**6**), formed from the imine MeN=C(H)Ph, was also isolated and characterized spectroscopically as for **4**, and its solution behavior is similar to that of **4**: in acetone, the solid state structure is maintained, while in CD_3OD, chemistry corresponding to that of Figure 2 is seen (i.e., formation of **6′**, the "reverse" of orthometalation, and reactivity toward H_2). Analogous orthometalated species [Rh(H){RN=CR′(*o*-C$_6$H$_4$)}(PPh$_3$)$_2$(acetone-d_6)]PF$_6$, **7**−**10**, were synthesized in situ in acetone-d_6 from the precursor imines PhN=C(H)Ph, C$_6$H$_{11}$N=C(H)Ph, PhCH$_2$N=C(Me)Ph, and PhCH$_2$N=CPh$_2$, respectively (Figure 4); their NMR spectra were assigned as for complexes **4**−**6**, and in the case of **7**, the high-field hydride ^{1}H resonance is seen as the expected doublet of triplets because of a sufficient difference in the J_{RhH} and $^2J_{HP}$ values (16 and 13 Hz, respectively). Of key interest, species **9′** and **10′** (the MeOH derivatives of **9** and **10** that can be made in situ in MeOH from *cis*-[Rh(PPh$_3$)$_2$(MeOH)$_2$]$^+$ and 1 equiv of the imine), like **5′** with the Me substituent at the imine-C atom, are essentially stable as such in MeOH (but see below for **9′**), while **7′** and **8′** (the MeOH analogues of **7** and **8**) that have the H atom at the imine-C atom show the same complex behavior in MeOH as **4′** and **6′** (cf. Figure 2). Thus, the labile chemistry noted in MeOH is seen only for the imine systems that contain the N=CH moiety, but it is unclear why this governs the "reverse orthometalation". There is no evidence for incorporation of deuterium into **4′**, **3′**, or **I** in the observed chemistry of Figure 2, and thus cleavage of the Rh−C bond by protons/deuterons is ruled out, implying that direct reductive elimination from the *cis*-Rh(H)-C moiety occurs (or alternatively the oxidative addition of the imine is less complete in MeOH). Possibly some H-bonding interaction between the MeOH and the H atom of the imine N=CH increases the acidity of the H atom, decreases the basicity of the imine, and thus decreases the propensity for oxidative addition to the Rh(I). A contributing factor is also likely to be the somewhat higher donor number of MeOH versus that of acetone (20 versus 17),[14] a feature that has been demonstrated within the related *cis,trans,cis*-[Ir(H)$_2$(PPh$_3$)$_2$(solvent)$_2$]BF$_4$ species.[15]

The labile chemistry noted in MeOH is also reflected in the catalytic hydrogenation of the different imines in this solvent. As noted above, hydrogenation of **4′** in MeOH gives dibenzylamine and *cis,trans,cis*-[Rh(H)$_2$(PPh$_3$)$_2$(MeOH)$_2$]PF$_6$ (**2′**); this solution can then be treated with a further equivalent of PhCH$_2$N=CHPh, and under H_2 the imine is again reduced to the amine via the partial formation of **4′** and the chemistry of Figure 2. Thus, via a series of stoichiometric hydrogenations, the net process is a catalyzed imine hydrogenation via [Rh(PPh$_3$)$_2$(PhCH$_2$N=CHPh)(MeOH)]PF$_6$ (**I**). Of note, if excess imine is used under the same conditions in MeOH, catalytic hydrogenation occurs via [Rh(PPh$_3$)$_2$(PhCH$_2$N=CHPh)(NH$_2$CH$_2$Ph)]PF$_6$ (**II**), the amine being formed via a Rh-catalyzed hydrolysis of the imine by adventitious water.[1] The rate (turnover)-determining step of the catalytic process is oxidative addition of H_2 to **II** with a rate constant that we will define as k_{II}, whose value at 30 °C has been determined[1b] as ∼45 M^{-1} s^{-1}. An estimate of the corresponding k_I value for oxidative addition of H_2 to **I** at ∼20 °C can be made as follows. Integration of the ^{31}P{^{1}H} resonances of the species present in a solution of **4′** at this temperature ([Rh]$_{total}$ = 0.022 M) shows a 4:1 ratio of **I**:**4′** and much smaller amounts of **3′** (see Figures 2 and S1), and thus the [**I**] is ∼0.017 M; when the solution is shaken under 1 atm H_2 (which is effectively maintained at a constant solution concentration of ∼1.5 × 10^{-3} M[1b]), the imine is converted to amine with $t_{1/2} \approx 90$ s, corresponding to a k_I value of ∼8 M^{-1} s^{-1} at room temperature. Although the kinetic activation parameters have not been measured for these systems, it is almost certain that reactivity to give amine via **II** is more favorable than via **I** (probably by a factor of ∼3, as rate constants for oxidative addition of H_2 to such systems typically double with a 10 °C increase in temperature).[16] The difference in oxidative addition reactivity (see Figure 5) seems reasonable considering the higher basicity of benzylamine versus that of CD_3OD/MeOH. An important

(14) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper Collins: New York, 1983; p 340.
(15) Crabtree, R. H.; Mellea, M. F.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* **1982**, *104*, 107.
(16) James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973; Chapter XII.

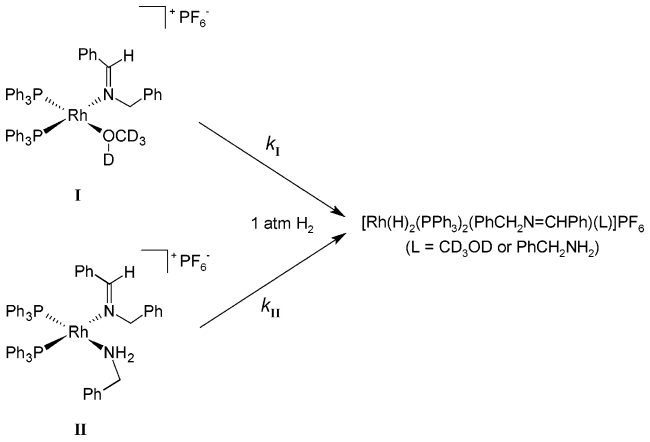


Figure 5. Oxidative addition of H_2 to species **I** and **II**. The supposed dihydrido products have not been detected (see ref 1b).

result from this study is the demonstration that Rh-catalyzed imine hydrogenation can, in principle, occur *without* the need for hydrolysis of imine to amine. Under catalytic conditions in MeOH,[1] the ketimine $PhCH_2N{=}C(Me)Ph$ was hydrogenated much more slowly than the aldimine $PhCH_2N{=}C(H)Ph$, with conversions of only ~4 and ~40% after 1 and 40 h, respectively. Ketimines are invariably hydrogenated more slowly than a corresponding aldimine because of increased steric bulk around the N=C moiety,[17] but whether the hydrogenation of $PhCH_2N{=}C(Me)Ph$ occurs via a solvent-η^1-imine intermediate such as **I** or an η^1- amine-η^1-imine species such as **II** is unclear, particularly as an orthometalated species (**9***) containing also η^1-benzylamine has been isolated (see below). With the more heavily substituted imine $PhCH_2N{=}CPh_2$, no catalytic hydrogenation is observed under ambient conditions in MeOH, while we have reported earlier[1a] that the corresponding hydrogenation of $PhN{=}C(H)Ph$ is inhibited by catalyst poisoning, the amine product $PhNHCH_2Ph$ coordinating to the Rh via the N-phenyl group (η^4 in the solid state and η^6 in solution).

When the MeOH solution of $[Rh(H)\{PhCH_2N{=}CMe(o\text{-}C_6H_4)\}(PPh_3)_2(acetone)]PF_6$ (**9′**) was left at room temperature for about a week "under vacuo", a small crystal formed, and this proved by X-ray analysis (Figure 6) to be $[Rh(H)\{PhCH_2N{=}C(Me)(o\text{-}C_6H_4)\}(PPh_3)_2(NH_2CH_2Ph)]PF_6$ (**9***), where the MeOH ligand of **9′** has been replaced by benzylamine, the amine hydrolysis product of the imine. We have reported elsewhere on this metal-catalyzed hydrolysis reaction,[1,8] and indeed in the Rh-catalyzed hydrogenation of $PhCH_2N{=}CHPh$ the active catalyst is **II**, as noted above. Whether **9*** is a catalyst precursor for hydrogenation of $PhCH_2N{=}C(Me)Ph$ will remain unknown until a reliable synthetic method is realized for this complex. The structure of **9*** (Table 3) is similar to that of complex **5** but where the acetone has been replaced by the amine; the key bond lengths and angles are close to those in **5**, and even the $Rh{-}N(2)_{amine}$ distance is the same as the Rh−O distance in **5**. We have noted recently the close correspondence in the structures of the Ir complexes $[Ir(H)\{PhCH_2N{=}CH(o\text{-}C_6H_4)\}(PPh_3)_2(L)]PF_6$, where L = acetone or benzylamine.[8]

(17) James, B. R. *Catal. Today* **1997**, *37*. 209.

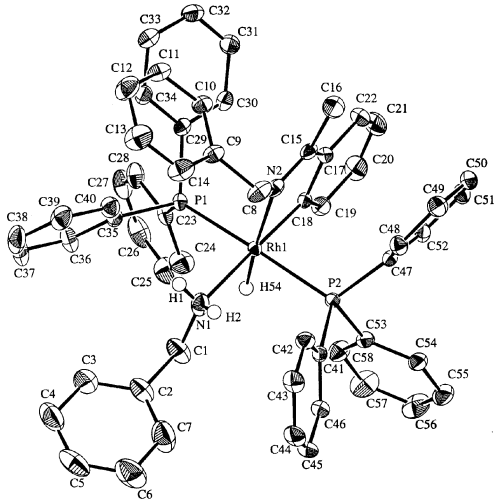


Figure 6. ORTEP diagram of the cation $[Rh(H)\{PhCH_2N{=}C(Me)(o\text{-}C_6H_4)\}(PPh_3)_2(NH_2CH_2Ph)]^+$ of complex **9*** with 50% probability thermal ellipsoids.

Table 3. Selected Bond Distances and Angles for $[Rh(H)\{PhCH_2N{=}C(Me)(o\text{-}C_6H_4)\}(PPh_3)_2(NH_2CH_2Ph)]PF_6$ (9*) (estimated standard deviations in parentheses)

bond	length (Å)	bond	angle (deg)
Rh(1)−P(1)	2.3499(6)	P(2)−Rh(1)−N(1)	92.29(7)
Rh(1)−P(2)	2.3344(6)	P(2)−Rh(1)−N(2)	91.49(5)
Rh(1)−N(1)	2.224(2)	P(1)−Rh(1)−C(18)	88.50(6)
Rh(1)−N(2)	2.162(2)	P(2)−Rh(1)−C(18)	86.79(6)
Rh(1)−C(18)	1.999(2)	N(2)−Rh(1)−H(54)	175(1)
Rh(1)−H(54)	1.43(2)	N(2)−Rh(1)−N(1)	101.70(8)
N(2)−C(15)	1.288(3)	N(2)−Rh(1)−C(18)	79.45(8)
N(2)−C(8)	1.478(3)	N(2)−C(15)−C(16)	124.9(2)
N(1)−C(1)	1.509(4)	N(2)−C(15)−C(17)	116.0(2)
C(1)−C(2)	1.509(4)	C(15)−C(17)−C(18)	116.4(2)
C(15)−C(16)	1.511(3)	C(8)−N(2)−C(15)	121.0(2)
C(15)−C(17)	1.467(3)	N(2)−C(8)−C(9)	115.1(2)
C(8)−C(9)	1.512(3)	N(1)−C(1)−C(2)	114.3(2)
C(17)−C(18)	1.411(3)	Rh(1)−C(18)−C(17)	114.3(2)
		Rh(1)−C(18)−C(19)	128.0(2)
bond	angle (deg)	Rh(1)−N(2)−C(15)	113.8(1)
P(1)−Rh(1)−P(2)	169.30(2)	C(8)−N(2)−C(15)	121.0(2)
N(1)−Rh(1)−C(18)	178.55(9)	N(2)−C(8)−C(9)	115.1(2)
P(1)−Rh(1)−N(1)	92.22(7)	N(1)−C(1)−C(2)	114.3(2)
P(1)−Rh(1)−N(2)	97.08(5)	Rh(1)−C(18)−C(17)	114.3(2)
P(1)−Rh(1)−H(54)	85(1)	Rh(1)−C(18)−C(19)	128.0(2)
P(2)−Rh(1)−H(54)	86(1)	Rh(1)−N(2)−C(15)	113.8(1)

Experimental Section

Unless stated otherwise, synthetic procedures were performed at room temperature (~20 °C) using standard Schlenk techniques under an atmosphere of dry Ar. The liquid imines $PhCH_2N{=}CHPh$ and $CH_3N{=}CHPh$ from Aldrich were purified by distillation; the solid imines $PhCH_2N{=}C(Me)Ph$, $PhCH_2N{=}C(Me)\text{-}p\text{-}C_6H_4OMe$, $PhCH_2N{=}CPh_2$, and $PhN{=}CHPh$, and the liquid $C_6H_{11}N{=}CHPh$ were synthesized in this laboratory previously by Drs. D. E. Fogg, K. S. MacFarlane, and M. B. Ezhova.[18] The $[Rh(COD)(PPh_3)_2]PF_6$ (**1**) and corresponding *cis,trans,cis*-$[Rh(H)_2(PPh_3)_2(solvent)_2]PF_6$ (**2**, **2′**) and *cis*-$[Rh(PPh_3)_2(solvent)_2]PF_6$ (**3**, **3′**) precursors (solvent = acetone, MeOH) were prepared according to literature procedures.[9,10] Other reagents were purchased from commercial sources and used as supplied. Solvents were dried over the appropriate agents and distilled under N_2 prior to use. NMR spectra were recorded on Bruker AV 300 (300 MHz for ^1H, 121 MHz for $^{31}P\{^1H\}$, 75 MHz for ^{13}C) and AV 400 (400 MHz for ^1H, 162 MHz for ^{31}P-

(18) (a) Fogg, D. E. Ph.D. Dissertation, The University of British Columbia, Vancouver, 1994. (b) MacFarlane, K. S.; Ezhova, M. B. Unpublished results.

{^{1}H}, 100 MHz for ^{13}C) spectrometers. Residual solvent proton (^{1}H, relative to external $SiMe_4$ δ 0.00) and external $P(OMe)_3$ (^{31}P{^{1}H}, δ 141.00 versus external 85% aqueous H_3PO_4) were used as references. All J values are given in Hz. Infrared spectra were recorded on an ATLI Mattson Genesis Series FTIR spectrophotometer, and IR bands (KBr pellet) are reported in cm^{-1}. Elemental analyses were performed by Mr. P. Borda of this department using a Carlo Erba 1108 analyzer.

[*N*,*o*-*C*-(*N*-Benzylidenebenzylaminato)]hydrido(acetone)bis(triphenylphosphine)rhodium(III) Hexafluorophosphate, [Rh(H){PhCH$_2$N=CH(*o*-C$_6$H$_4$)}(PPh$_3$)$_2$(acetone)]PF$_6$ (4). To a pale yellow solution of $[Rh(H)_2(PPh_3)_2(acetone)_2]PF_6$ (**2**) (0.113 mmol) or a red solution of $[Rh(PPh_3)_2(acetone)_2]PF_6$ (**3**) (0.116 mmol) in acetone (3 mL) was added $PhCH_2N{=}CHPh$ (22.0 μL, 0.116 mmol) under Ar and the mixture stirred for 2 h. The volume was then reduced under vacuum to ~1 mL to afford spontaneous precipitation of an off-white solid that was collected by filtration, washed with Et_2O (3 × 4 mL), and dried in vacuo. Yield: 0.090 g (75%). ^{31}P{^{1}H} NMR (acetone-d_6): δ 40.40 (d, J_{RhP} = 116). ^{1}H NMR (acetone-d_6): δ −12.85 (ps q, 1H, Rh-*H*, $J_{RhH} \approx {}^2J_{HP}$ = 13), 2.10 (s, 6H, free C*H*$_3$COC*H*$_3$), 5.25 (s, 2H, C*H*$_2$), 6.52 (t, 1H, *p*-(*o*-C$_6$*H*$_4$), $^3J_{HH}$ = 6.5), 6.72 (d, 1H, *o*-(*o*-C$_6$*H*$_4$), $^3J_{HH}$ = 6.5), 6.95 (m, 2H, *m*-(*o*-C$_6$*H*$_4$), $^3J_{HH}$ = 6.5), 7.01−7.79 (m, 35H, aromatics), 7.81 (s, 1H, =C*H*). IR (KBr): ν 2096 (Rh−H), 1660 (C=O), 1611, 1576 (C=N), Anal. Calcd for $C_{53}H_{49}NOF_6P_3Rh$: C, 62.06; H, 4.81; N, 1.37. Found: C, 62.0; H, 4.9; N, 1.5.

{*N*,*o*-*C*-[*N*-(*p*-MeO-Phenylmethylbenzylaminato)]}hydrido(acetone)bis(triphenylphosphine)rhodium(III) Hexafluorophosphate, [Rh(H){PhCH$_2$N=C(Me)(*o*-C$_6$H$_3$-*p*-OMe)}(PPh$_3$)$_2$(acetone)]PF$_6$ (5). This complex was prepared as a light brown solid from a solution of $[Rh(H)_2(PPh_3)_2(acetone)_2]PF_6$ (**2**) (0.100 mmol) and the imine $PhCH_2N{=}C(Me)C_6H_4$-*p*-OMe (0.024 g, 0.100 mmol) according to the procedure given for **4**. Yield: 0.070 g (65%). ^{31}P{^{1}H} NMR (acetone-d_6): δ 40.43 (d, J_{RhP} = 117). ^{1}H NMR (acetone-d_6): δ −12.51 (ps q, 1H, Rh-*H*, $J_{RhH} \approx {}^2J_{HP}$ = 13), 1.95 (s, 3H, C(C*H*$_3$)), 2.10 (s, 6H, free C*H*$_3$COC*H*$_3$), 2.99 (s, 3H, *p*-OC*H*$_3$), 5.40 (s, 2H, C*H*$_2$), 6.08 (s, 1H, *m*-(*o*-C$_6$*H*$_3$−), 6.60 (d, 1H, *o*-(*o*-C$_6$*H*$_3$−), $^3J_{HH}$ = 7), 6.85 (d, 1H, *m*-(*o*-C$_6$*H*$_3$−), $^3J_{HH}$ = 7), 6.95−7.70 (m, 35H, aromatics). IR (KBr): ν 2105 (Rh−H), 1670 (C=O), 1600, 1576 (C=N). Anal. Calcd for $C_{55}H_{53}NO_2F_6P_3Rh$: C, 61.75; H, 4.99; N, 1.31. Found: C, 61.35; H, 5.3; N, 1.7. An X-ray quality crystal of **5** was obtained by slow evaporation of an acetone/Et_2O solution (1:1 vol) of the compound.

[*N*,*o*-*C*-(*N*-Benzylidenemethylaminato)]hydrido(acetone)bis(triphenylphosphine)rhodium(III) Hexafluorophosphate, [Rh(H){CH$_3$N=CH(*o*-C$_6$H$_4$)}(PPh$_3$)$_2$(acetone)]PF$_6$ (6). To a solution of $[Rh(PPh_3)_2(acetone)_2]PF_6$ (**3**) (0.096 mmol) in acetone (3 mL) was added $CH_3N{=}CHPh$ (12.0 μL, 0.097 mmol) under Ar and the mixture stirred for 2 h. The volume was then reduced to ~1 mL followed by addition of Et_2O (4 mL) to precipitate a creamy-white solid that was collected by filtration, washed with Et_2O (3 × 3 mL), and dried in vacuo. Yield: 0.065 g (70%). ^{31}P{^{1}H} NMR (acetone-d_6): δ 42.10 (d, J_{RhP} = 116). ^{1}H NMR (acetone-d_6): δ −12.58 (ps q, 1H, Rh-*H*, $J_{RhH} \approx {}^2J_{HP}$ = 13), 2.10 (s, 6H, free C*H*$_3$COC*H*$_3$), 3.79 (s, 3H, C*H*$_3$N), 6.54 (t, 1H, *p*-(*o*-C$_6$*H*$_4$), $^3J_{HH}$ = 6.5), 6.83−7.00 (m, 3H, *m*,*o*-(*o*-C$_6$*H*$_4$), $^3J_{HH}$ = 6.5), 7.15−7.70 (m, 30H, aromatics), 7.74 (s, 1H, =C*H*). IR (KBr): ν 2101 (Rh−H), 1666 (C=O), 1618, 1578 (C=N). Anal. Calcd for $C_{47}H_{45}NO\,F_6P_3Rh$: C, 59.44; H, 4.78; N, 1.47. Found: C, 59.1; H, 4.9; N, 1.5.

In Situ Characterization of [Rh(H){RN=CR′(*o*-C$_6$H$_4$)}(PPh$_3$)$_2$(acetone-*d*$_6$)]PF$_6$. An NMR tube equipped with an airtight J Young PTFE valve was charged with the precursor *cis*-$[Rh(PPh_3)_2(acetone\text{-}d_6)_2]PF_6$ (~0.01 mmol) and a 1:1 mol equiv of the respective imine, and the solvent was added via vacuum-transfer. The resulting red solution was then analyzed by NMR spectroscopy. **R = Ph, R′ = H** (**7**): ^{31}P{^{1}H} NMR (acetone-d_6): δ 39.91 (d, J_{RhP} = 116). ^{1}H NMR (acetone-d_6): δ −13.12 (dt, 1H, Rh-*H*, J_{RhH} = 16, $^2J_{HP}$ = 13), 6.40 (t, 1H, *p*-(*o*-C$_6$*H*$_4$), $^3J_{HH}$ = 7), 6.65 (d, 1H, *o*-(*o*-C$_6$*H*$_4$), $^3J_{HH}$ = 7), 6.80 (m, 2H, *m*-(*o*-C$_6$*H*$_4$)), 7.20−7.70 (m, 35H, aromatics), 8.00 (s, ^{1}H, =C*H*). **R = C$_6$H$_{11}$, R′ = H** (**8**): ^{31}P{^{1}H} NMR (acetone-d_6): δ 38.40 (d, J_{RhP} = 117). ^{1}H NMR (acetone-d_6): δ −12.82 (ps q, 1H, Rh-*H*, $J_{RhH} \approx {}^2J_{HP}$ = 13), 1.20−1.90 (m, 10H, C$_6$(H)*H*$_{10}$), 4.30 (pt, 1H, C$_6$(*H*)H$_{10}$, $^3J_{HH}$ = 10), 6.45 (t, 1H, *p*-(*o*-C$_6$*H*$_4$), $^3J_{HH}$ = 7), 6.52 (d, 1H, *o*-(*o*-C$_6$*H*$_4$), $^3J_{HH}$ = 7), 6.95 (t, 1H, *m*-(*o*-C$_6$*H*$_4$), $^3J_{HH}$ = 7), 7.05−7.90 (m, 31H, *m*-(*o*-C$_6$*H*$_4$) and aromatics), 8.10 (s, 1H, =C*H*). **R = PhCH$_2$, R′ = Me** (**9**): ^{31}P{^{1}H} NMR (acetone-d_6): δ 40.33 (d, J_{RhP} = 117). ^{1}H NMR (acetone-d_6): δ −12.42 (ps q, 1H, Rh(*H*), $J_{RhH} \approx {}^2J_{HP}$ = 13), 1.95 (s, 3H, C(C*H*$_3$)), 5.45 (s, 2H, C*H*$_2$), 6.50 (t, 1H, *p*-(*o*-C$_6$*H*$_4$), $^3J_{HH}$ = 7), 6.65 (d, 1H, *o*-(*o*-C$_6$*H*$_4$), $^3J_{HH}$ = 7), 6.85 (m, 2H, *m*-(*o*-C$_6$*H*$_4$), $^3J_{HH}$ = 7), 6.90−7.80 (m, 35H, aromatics). **9′**, the CD_3OD derivative of **9**, was made in situ in CD_3OD from *cis*-$[Rh(PPh_3)_2(CD_3OD)_2]^+$ and 1 equiv of $PhCH_2N{=}C(Me)Ph$ (see text); after one week, a crystal that deposited from the solution was subjected to X-ray analysis and determined to have the structure [Rh(H){PhCH$_2$N=C(Me)(*o*-C$_6$H$_4$)}(PPh$_3$)$_2$(NH$_2$CH$_2$Ph)]PF$_6$ (**9***). There was insufficient material for further characterization. **R = PhCH$_2$, R′ = Ph** (**10**): ^{31}P{^{1}H} NMR (acetone-d_6): δ 38.54 (d, J_{RhP} = 118). ^{1}H NMR (acetone-d_6): δ −12.61 (ps q, 1H, Rh-(*H*), $J_{RhH} \approx {}^2J_{HP}$ = 13), 5.13 (s, 2H, C*H*$_2$), 5.94 (d, 1H, *o*-(*o*-C$_6$*H*$_4$), $^3J_{HH}$ = 7), 6.40 (t, 1H, *p*-(*o*-C$_6$*H*$_4$), $^3J_{HH}$ = 7), 6.45 (m, 2H, *m*-(*o*-C$_6$*H*$_4$), $^3J_{HH}$ = 7), 7.00−7.75 (m, 40H, aromatics).

Crystal Structure Determinations. Measurements were made at 173(0.2) K on a Bruker X8 APEX and on a Rigaku/ADSC CCD area detector diffractometer for **5** and **9***, respectively, with graphite-monochromated Mo Kα radiation (0.71073 Å). Some crystallographic data for **5** and **9*** are shown in Table 1.

Data for **5** were collected and integrated using the Bruker SAINT[19] software package and corrected for absorption effects using the multiscan technique (SADABS[20]). The material crystallizes as a two-component twin, with the two components related by a 2.2° rotation about the (1,0,0) axis. The structure was solved by direct methods[21] using an *hkl*f4 format data set including corrected twin overlaps, and final refinements were carried out using an *hkl*f5 format data set containing all reflections for both twin components. The ratio of both twin components is roughly 1:1. All non-hydrogen atoms were refined anisotropically. Four F atoms of the PF_6 anion were disordered and were modeled in two orientations. The Rh-H hydrogen atom was located in a difference map and refined isotropically, while all other hydrogen atoms were included in calculated positions but not refined. The material crystallizes with one molecule of acetone in the asymmetric unit. The final cycle of full-matrix least-squares refinement on F^2 was based on 30 620 reflections and 697 variable parameters (least-squares function minimized $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/[\sigma^2(F_o^2) + (0.0359P)^2 + 0.00P]$ and $P = (F_o^2 + 2F_c^2)/3$), and converged to R1 = 0.094, wR2 = 0.104, GOF = 0.94.

Data for **9*** were collected and processed using the d*TREK[22] program. The structure was again solved by direct methods[21] and expanded using Fourier techniques.[23] The material crystallizes with 1.5 molecules of MeOH in the asymmetric unit. All solvent atoms were refined isotropically, while the rest were refined anisotropically. The N-H and Rh-H hydrogen atoms were refined isotropically; the rest were included in fixed positions. Neutral atom scattering factors were taken from

(19) *SAINT*: Version 6.02; Bruker AXS Inc.: Madison, WI, 1999.
(20) *SADABS*: Bruker Nonius area detector scaling and absorption correction, Version 2.05; Bruker AXS Inc.: Madison, WI.
(21) *SIR97*: Altomare, A.; Burla, M. C.; Cammalli, G.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, A. *J. Appl. Cryst*. **1999**, *32*, 115.
(22) *d*TREK*: Area Detector Software, version 4.13; Molecular Structure Corporation: The Woodlands, TX, 1996−1998.
(23) *DIRDIF94*: 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.

Cromer and Waber,[24] and anomalous dispersion effects were included in F_{calc},[25] the values of $\Delta f'$ and $\Delta f''$ being those of Creagh and McAuley.[26] Values for the mass attenuation coefficients are those of Creagh and Hubbell,[27] and all calculations were performed using the teXsan program.[28] The final cycle of full-matrix least-squares refinement on F^2 was based on 11 765 observed reflections ($I > 0.00\sigma(I)$) and 660 variable parameters (using $\sum w(F_o^2 - F_c^2)^2$, where $w = 1/\sigma^2(F_o^2)$) and converged to R1 = 0.056, wR2 = 0.090, GOF = 1.12.

Conclusions

Simple imines of the type RN=C(H)R″ or RN=C(R′)-R″, where R, R′, and R″ are solely alkyl or aryl substituents, react in a 1:1 stoichiometry with cationic Rh(I)-$(PPh_3)_2$ species to form (via the usual C_{ortho}−H activation) orthometalated complexes containing a five-membered ring, when a suitable phenyl substituent (R′ or R″) is available at the imine-C atom. The complexes are stable as such in acetone solution (and show no reactivity toward 1 atm H_2), but in MeOH solution those that contain a H atom at the imine-C are converted partially to a cationic, mixed η^1-*N*-imine/MeOH species that provides a pathway for reaction of the orthometalated complexes with H_2; this reaction generates amine in a stoichiometric reaction and is relevant in the Rh-catalyzed hydrogenation of the imines, where we have previously reported that a cationic, mixed η^1-*N*-imine/amine species is an important catalytic intermediate. Characterized also is a cationic, Rh-orthometalated imine complex containing also an amine ligand, the amine being formed by hydrolysis of the imine. The studies derive from our ongoing efforts to gain a more detailed understanding of catalyzed imine hydrogenations, particularly on the role of the solvent.

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Supporting Information Available: $^{31}P\{^1H\}$ and ^1H spectra of **4** in CD_3OD at 298 and 253 K (Figure S1), and X-ray crystallographic data for the structures of **5** and **9*** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*, Vol. IV; The Kynoch Press: Birmingham, England, Table 2.2 A, 1974.

(25) Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

(26) Creagh, D. C.; McAuley, W. J. In *International Tables for Crystallography*, Vol. C; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, 1992; Table 4.2.6.8, pp 219−222.

(27) Creagh, D. C.; Hubbell, J. H. In *International Tables for Crystallography*, Vol. C; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, 1992; Table 4.2.4.3, pp 200−206.

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