Characterization of a Rhodium(III)−Imine−Orthometalated Imine Complex: Reversible C−H Activation of a Coordinated Imine

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Solutions of *cis*-$[Rh(PPh_3)_2(solv)_2]PF_6$ (solv = acetone or MeOH) react at room temperature under Ar with benzophenone imine to yield *cis*-$[Rh(PPh_3)_2(\eta^1\text{-}NH{=}CPh_2)_2]PF_6$ (**3**), but depending on reaction conditions, one of the imine ligands undergoes orthometalation to give $[RhH\{NH{=}C(Ph)(o\text{-}C_6H_4)\}(HN{=}CPh_2)(PPh_3)_2]PF_6$ (**2**) with *trans*-phosphines; this is the first recorded complex containing an imine in its η^1-form and as an η^2-moiety formed via orthometalation. Complexes **2** and **3** are characterized by elemental analysis, ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, and, in the case of **2**, an X-ray crystal structure.

Introduction

As part of our ongoing studies on hydrogenation of imines catalyzed by cationic, Rh(I)-phosphine species as precursors,[1] we reported recently on the room-temperature reaction of imines of the type RN=CR′(R″), where R and R″ are alkyl or aryl groups, and R′ = H or Me, with *cis*-$[Rh(PPh_3)_2(solv)_2]PF_6$ (**1**) and *cis*,*trans*,*cis*-$[Rh(H)_2(PPh_3)_2(solv)_2]PF_6$ complexes (solv = acetone or MeOH; see Scheme S1 in the Supporting Information).[2] In acetone solution, when R″ = Ph (or *p*-OMe-C_6H_4), the products are species exemplified by $[RhH\{RN{=}CR'(o\text{-}C_6H_4)\}(PPh_3)_2(acetone)]PF_6$, in which the imine coordinates with orthometalation in an η^2 fashion via the imine-N and the ortho-C atom of the phenyl group; in MeOH solution, when R′ = H, nonorthometalated species, η^1-species of the type $[Rh(PPh_3)_2(RN{=}CHR'')(MeOH)]PF_6$ can be formed and these provide one pathway for subsequent hydrogenation of the imine by reaction with H_2.[2] In an extension of this work, we have now used benzophenone imine, $HN{=}CPh_2$, as the reactant imine with the Rh complexes, and from the reaction in MeOH or acetone, the initially formed product is the bis(imine) complex *cis*-$[Rh(PPh_3)_2(\eta^1\text{-}NH{=}CPh_2)_2]PF_6$ (**3**), a rare type of species, but this converts partially to $RhH\{HN{=}C(Ph)(o\text{-}C_6H_4)\}(HN{=}CPh_2)(PPh_3)_2]PF_6$ (**2**), containing the imine in its η^1-form and as an η^2-moiety formed via orthometalation; this unique type of complex is readily isolated. The corresponding reaction in CH_2Cl_2 gives solely complex **3**. The interconversion between **2** and **3** is solvent-dependent and represents a further example of reversible C−H activation within these imine systems.[2] The findings are summarized in Scheme 1.

More generally, the orthometalation reaction—activation of a C−H bond in the ortho-position of an aromatic ring by transition metals—continues to be an important class of reactions,[3,4] because of potential applications in diverse areas such as catalysis,[4,5] organic synthesis,[6] and material science.[7]

Experimental Section

General experimental procedures and instrumentation used have been described in a recent publication.[2] The imine, $HN{=}CPh_2$ (an Aldrich product, pure according to GC and ^1H NMR), was used as received. The $[Rh(COD)(PPh_3)_2]PF_6$ precursor, and in situ $[Rh(PPh_3)_2(solv)_2]PF_6$ (**1**), $[Rh(H)_2(PPh_3)_2(solv)_2]PF_6$ (solv = acetone, MeOH), and $[Rh(PPh_3)_2]_2(PF_6)_2$ species, were prepared according to literature procedures.[8,9]

Reaction of *cis*-$[Rh(PPh_3)_2(solv)_2]PF_6$ (1) with 2 Equiv of $HN{=}CPh_2$. An acetone solution (4 mL) of $[Rh(COD)(PPh_3)_2]PF_6$ (42 mg, 0.0475 mmol) was reacted with 1 atm H_2 for 2 h to form $[Rh(H)_2(PPh_3)_2(acetone)_2]PF_6$ in situ. The H_2 and the volatile materials (solvent, cyclooctane) were removed under vacuum at ∼40 °C overnight, and the resulting dark red residue of $[Rh(PPh_3)_2]_2(PF_6)_2$[9] was then redissolved in MeOH (∼2 mL) under Ar to form $[Rh(H)_2(PPh_3)_2(MeOH)_2]PF_6$. Imine (17.3 mg, 0.095 mmol) was then added, and the reaction was monitored by ^1H and $^{31}P\{^1H\}$ NMR. After 1 h, the two species $[RhH\{NH{=}C(Ph)(o\text{-}C_6H_4)\}(\eta^1\text{-}HN{=}CPh_2)(PPh_3)_2]PF_6$ (**2**) and *cis*-$[Rh(PPh_3)_2(\eta^1\text{-}NH{=}CPh_2)_2]PF_6$ (**3**) (see below) were ob-

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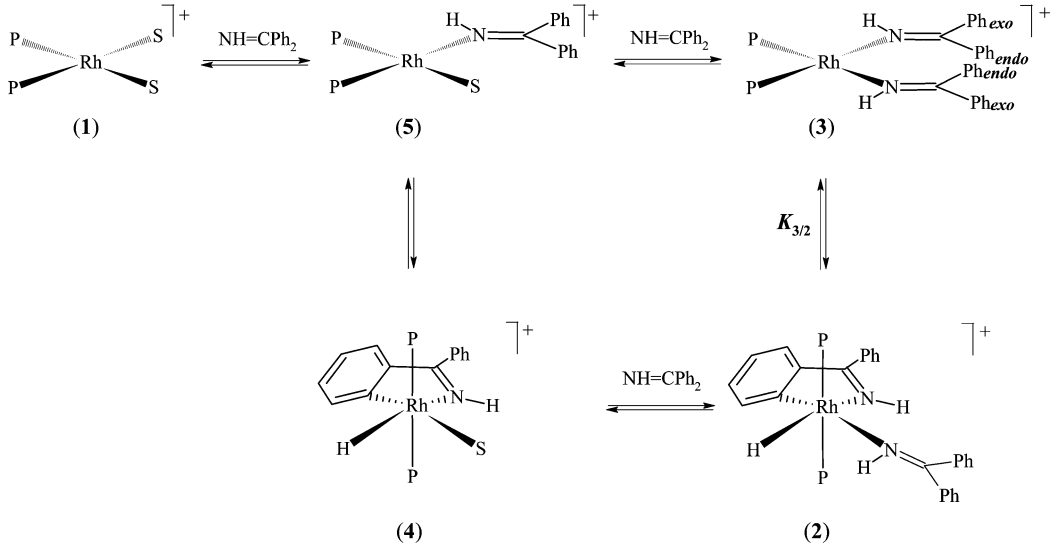
Scheme 1. Formation of Benzophenone-Imine Complexes and Derived Orthometalated Species 2−5[a]



[a] P = PPh_3; S = solvent (acetone or MeOH).

served in a ratio of ∼1:25, but after 24 h, the colorless, crystalline solid **2** precipitated from the solution. The solid was filtered off, washed with 1:15 MeOH/hexanes (1 mL), and dried in a vacuum. Yield: 38 mg (72%). $^{31}P\{^1H\}$ NMR (CD_3OD): δ 45.2 (d, $J_{RhP} = 117$), −143.2 (septet, PF_6^-). ^1H NMR (CD_3OD): δ −11.98 (dt, 1H, Rh*H*, $^2J_{HP} = 9.6$, $J_{RhH} = 11.6$), 6.28 (d, 1H, *m*-(*o*-C_6H_4), $^3J_{HH} = 7.1$), 6.52 (dd, 1H, *m*-(*o*-C_6H_4), $^3J_{HH} = 7.1$), 6.70 (pseudo t, 1H, *p*-(*o*-C_6H_4), $^3J_{HH} = 7.1$), 6.84 (d, 1H, *o*-(*o*-C_6H_4), $^3J_{HH} = 7.1$), 7.1−7.8 (m, ∼47H, $H_{arom.}$+ 2N*H*). MS: 809 ($[Rh(PPh_3)_2(HNCPh_2)]^+$, 40%), 627 ($[Rh(PPh_3)_2]^+$, 100%), 287 ($[RhPPh_2-H]^+$, 45%), 217 (89%), 91 (55%). IR: 3056 (ν_{N-H}), 2134 (ν_{Rh-H}), 1570 ($\nu_{C=N}$). Anal. Calcd for $C_{62}H_{52}N_2P_3F_6Rh$: C, 65.61; H, 4.62; N, 2.47. Found: C, 65.67; H, 4.73; N, 2.59.

If the $[Rh(PPh_3)_2]_2(PF_6)_2$ was dissolved in CH_2Cl_2 (2 mL) rather than MeOH, prior to reaction with the imine, only the bis(imine) complex (**3**) is formed; addition of hexanes (∼1 mL) gave a dark red solid, which was filtered off, washed with hexanes, and dried overnight in a vacuum. Yield: 29 mg (55%).$^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 46.8 (d, $J_{RhP} = 167$), −143.2 (septet, PF_6^-). ^1H NMR (CD_2Cl_2): δ 6.12 (d, 4H, *o*-H_{PhP}, $^3J_{HH} = 7.6$), 7.05−7.20 (m, 15H, $H_{arom.}$), 7.23 (t, 4H, *m*-H_{PhP}, $^3J_{HH} = 7.1$), 7.35 (t, 2H, *p*-H_{PhC}, $^3J_{HH} = 7.5$), 7.45 (m, 15H, $H_{arom.}$), 7.65 (t, 4H, *m*-H_{PhC}, $^3J_{HH} = 7.4$), 7.75 (br s, 2H, N*H*), 7.85 (t, 2H, *p*-H_{PhC}, $^3J_{HH} = 7.3$), 8.20 (d, 4H, *o*-H_{PhC}, $^3J_{HH} = 7.1$). IR: 3275 (ν_{N-H}), 1590 ($\nu_{C=N}$). Anal. Calcd for $C_{62}H_{52}N_2P_3F_6Rh$: C, 65.61; H, 4.62; N, 2.47. Found: C, 64.95; H, 4.90; N, 2.40. The low C analysis results from the presence of CH_2Cl_2 that could not be removed even on prolonged drying under vacuum (CH_2Cl_2 was detected at δ_H 5.60 in an acetone-d_6 solution of **3**); inclusion of 0.15−0.20 mol of CH_2Cl_2 per mole of complex allows for analytical data in excellent agreement with the experimental values.

If the $[Rh(PPh_3)_2]_2(PF_6)_2$ was dissolved in acetone-d_6 to generate *cis*-$[Rh(PPh_3)_2(acetone)_2]PF_6$ and this was similarly reacted with 2 equiv of imine, close to complete formation of **3** over 1 h was followed by partial conversion to **2** (after 2 days, **3**:**2** ≈ 2.5).

In Situ Reactions of *cis*-[Rh(PPh$_3$)$_2$(solv)$_2$]PF$_6$ (1) with 1 or 0.5 Equiv of HN=CPh$_2$. $[Rh(PPh_3)_2]_2(PF_6)_2$, obtained from $[Rh(COD)(PPh_3)_2]PF_6$ (20 mg, 0.023 mmol) as described above, was dissolved in 0.6 mL of CD_3OD, and $HN=CPh_2$ (4.12 mg, 0.023 mmol) was added to the solution under Ar in a glovebox; the reaction was monitored at room temperature by ^1H and $^{31}P\{^1H\}$ NMR. For the corresponding reaction in acetone-d_6, the imine addition was done in two stages (2 × 2.06 mg), each stage being monitored.

In CD_3OD after 1 h, four Rh-containing species are seen, **1**−**3**, and a new one (**4**), in an approximate ratio of 6:4:2:1, as judged by intensities of the $^{31}P\{^1H\}$ signals; for **4**, δ_P 43.0 (d, $J_{RhP} = 116$), −143.2 (septet, PF_6^-). In acetone-d_6, with 0.5 equiv of $HN=CPh_2$, just one product (**4**) was observed after 1 h (**4**:**1** ≈ 1), and there were trace ^1H signals of the free imine. $^{31}P\{^1H\}$ NMR: δ 43.6 (d, $J_{RhP} = 116$), −143.2 (septet, PF_6^-). ^1H NMR: δ −11.78 (dt, 1H, Rh*H*, $^2J_{HP} = 9.5$, $J_{RhH} = 10.6$), 6.41 (br d, 2H, *o*-C_6H_4, $J_{HH} \approx 6.9$), 6.67 (pseudo t, 1H, *o*-C_6H_4, $J_{HH} \approx 6.6$), 6.78 (pseudo t, 1H, $J_{HH} \approx 7.7$), 6.88 (pseudo t, 1H, *p*-H_{PhC}, $J_{HH} \approx 7.7$), 7.0−8.0 (m, 33H, H_{arom} + 1N*H*), 8.3 (d, 2H, *o*-H_{PhC}, $^2J_{HH} = 6.8$). Species **4** is formulated as [RhH{HN=CPh(*o*-C_6H_4)}$(PPh_3)_2$(solv)]PF_6 containing *trans*-phosphines. Various mixtures of **1**−**4** (in amounts that varied with reaction time) were observed using 0.5 equiv of imine in CD_3OD, or 1.0 equiv of imine in acetone-d_6.

In Situ Reaction of *cis,trans,cis*-[Rh(H)$_2$(PPh$_3$)$_2$(solv)$_2$]-PF$_6$ with 2 Equiv of HN=CPh$_2$. $[Rh(COD)(PPh_3)_2]PF_6$ (15 mg, 0.017 mmol) was used with 1 atm H_2 for the in situ preparation of the dihydride in acetone-d_6 or in CD_3OD (0.6 mL). The imine (6.17 mg, 0.034 mmol) was added to the dihydride solution in a glovebox, and the reaction mixture was then exposed to H_2 again at room temperature. The reaction progress was followed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy. In the acetone-d_6 system after 1 h, **2** and **3** were present in a ratio of 1:2.3, this changing to 1:3 after 24 h. In CD_3OD after 0.5 h, only **3** was evident, but after 24 h, complex **2** had precipitated out. Neither system showed the presence of H_2-NC(H)Ph_2, the imine hydrogenation product.

Catalytic Hydrogenation of Benzophenone Imine. $[Rh(COD)(PPh_3)_2]PF_6$ (5 mg, 0.0056 mmol) and the imine (20.6 mg, 0.114 mmol) were dissolved in MeOH (10 mL), and the solution was stirred under 1 atm H_2 for 24 h; GC analysis (HP-5890 instrument with an HP-17 column) revealed ∼5% conversion to $H_2NC(H)Ph_2$. Analysis by NMR of an acetone-d_6 or CD_3OD solution of the residue, obtained after removing the MeOH under vacuum, showed the presence of the amine (δ_{CH} 5.20), unreacted imine, and initially just species **3**, although this slowly partially converted to **2**.

Crystallographic Analysis of Complex 2. Colorless, needle crystals of [RhH{NH=C(Ph)(*o*-C_6H_4)}(HN=CPh_2)-$(PPh_3)_2]PF_6$ (**2**) were grown by layering hexanes over a MeOH solution of the reacting mixture of **1** and 2 equiv of imine (see above). X-ray measurements were made at 173(1) K on a Rigaku/ADSC CCD area detector with graphite-monochromated Mo Kα radiation (0.71069 Å). Some crystallographic

Table 1. Crystallographic Data for 2

formula	$C_{62}H_{52}N_2F_6P_3Rh$
fw	1134.88
cryst color, habit	colorless, needle
cryst size (mm)	0.15 × 0.10 × 0.05
cryst syst	orthorhombic
space group	$Pna2_1$ (No. 33)
a (Å)	27.571(1)
b (Å)	18.5892(7)
c (Å)	12.1020(5)
V (Å^3)	6202.6(4)
Z	4
D_{calcd} (g cm^{-3})	1.215
μ (cm^{-1})	4.07
total no. of reflns	48 827
no. of unique reflns	10 723
R_{int} (Friedels not merged)	0.135
no. of variables	597
R1	0.0.062 ($I > 2.00\ \sigma(I)$, 6888 obs reflns)
wR2	0.155 (all data)
GOF	0.96 (all data)

data are shown in Table 1. Data were processed using the d*TREK program[10] and integrated using the CrystalClear[11] software package. The structure was solved by direct methods[12] and expanded using Fourier techniques.[13] The material crystallized with lattice solvent (MeOH and/or hexanes) that could not be modeled reasonably, so the SQUEEZE function found in PLATON[14] was used. All calculations were performed using the teXsan crystallographic software.[15] Further details on the collection of data and the refinement of the structure are available in the Supporting Information.

Results and Discussion

An equilibrium between the bis(imine) species, *cis*-$[Rh(PPh_3)_2(\eta^1\text{-}NH{=}CPh_2)_2]PF_6$ (**3**), and mono(imine)-orthometalated imine species, $[RhH\{NH{=}C(Ph)(o\text{-}C_6H_4)\}(\eta^1\text{-}HN{=}CPh_2)(PPh_3)_2]PF_6$ (**2**), is evident from the methods used for their syntheses. First, it is worth noting that the hydrogenation of the $[Rh(COD)(PPh_3)_2]PF_6$ precursor to give $[Rh(H)_2(PPh_3)_2(solv)_2]PF_6$ is much more rapidly achieved in acetone rather than in MeOH solution, and the subsquent dark red residue isolated is $[Rh(PPh_3)_2]_2(PF_6)_2$, the cation being in fact $[(PPh_3)Rh(\mu\text{-}PhPPh_2)_2Rh(PPh_3)]^{2+}$;[9] this dimer exists as such in CH_2Cl_2, but in MeOH or acetone is converted to *cis*-$[Rh(PPh_3)_2(solv)_2]PF_6$ (**1**).[8,9]

Reaction of **1** with 2 equiv of benzophenone imine in MeOH or in acetone at room temperature gives rapid, in situ formation of a 25:1 mixture of **3** and **2**; in MeOH, **2** eventually precipitates out as a colorless, crystalline solid in 72% yield, while in acetone the system slowly equilibriates to a 5:2 mixture of **3**:**2**. Similarly, if **2** is dissolved in acetone or MeOH, it converts over 2 days to the 5:2 ratio of **3**:**2** (after 1 h, the ratio was 1:2). Thus, the bis(imine) complex **3** is first formed and then is converted slowly and partially to the orthometalated-imine(imine) species **2**, with a $K_{3/2}$ equilibrium constant of ~2.5 at ~20 °C in acetone or MeOH (see Scheme 1). We have noted recently reversible orthometalation of the imine $PhCH_2N{=}C(H)Ph$ at a corresponding Rh center in MeOH, but this system involved a monoimine-(methanol) species.[2] In this current work, in CH_2Cl_2, only **3** is formed, and this suggests that the weak intermolecular interactions involving the hydrido ligand of **2** with H atoms of the phenyl groups of the *trans*-PPh_3 ligands (see below) perhaps assist in stabilizing the orthometalated form in the polar solvents. Complex **3** was readily isolated in 55% yield from the CH_2Cl_2 solution.

Complexes **2** and **3** are well characterized by elemental analyses, NMR data, and, in the case of **2**, X-ray crystallography. The ORTEP for the cation of **2** is shown in Figure 1, and selected bond lengths and angles are given in Table 2. The structure shows an η^2-N-imine moiety coordinated via the imine-N atom and orthometalated-C atom (C_{ortho}), which thus exists as a five-membered metallocycle, this being essentially coplanar with the hydride and the η^1-N atom of a second imine. The hydride is trans to the orthometalated imine-N atom, and the C_{ortho} atom is trans to the η^1-imine-N atom. The N−Rh−C angle (79.3°) of the metallocycle and the C_{ortho}−Rh−H angle (102°) are similar to those of other related cyclometalated Rh-imine systems[2,16,17] and to the corresponding angles of the same orthometalated benzophenone in several Os(II)-P^{i}Pr$_3$ species.[18] The distorted octahedral structure shows *trans*-PPh_3 ligands that are bent slightly toward the hydride and orthometalated-C atom, as indicated by the C−Rh−P (87.6° and 88.1°), H−Rh−P (92° and 83°), and P1−Rh−P2 (172°) angles, and two weak interactions between the hydride on Rh and protons of the phenyl group on the P atom (H1−H11 = 2.264 Å, H1−H26 = 2.094 Å). Similar bending of the PPh_3 ligands and weak interactions with a Rh-hydride have been noted in related complexes containing cyclometalated imine[16] and cyclometalated azobenzene moieties.[17]

The bond lengths at the Rh are unexceptional,[16,17] and the C=N bond length in the η^2-imine (1.314 Å) is close to others reported for benzophenone imine orthometalated at Os(II) centers (1.305, 1.291, 1.26 Å).[18] The C=N bond length of the η^1-imine (1.288 Å) is the same as that found in $[Rh\{PPh_2(CH_2)_2PPh_2\}(\eta^1\text{-imine})_2]^+$ for a cyclic imine,[19] the only other structurally characterized Rh(I)-η^1-imine complex of which we are aware, although such moieties are known with Rh(I)-tridentate, pincer-type imine systems.[20] Complex **2** is the first reported to contain an imine in its η^1-form and as an η^2-moiety formed via orthometalation. Further, we are unaware of any X-ray structural data on other metal-monohy-

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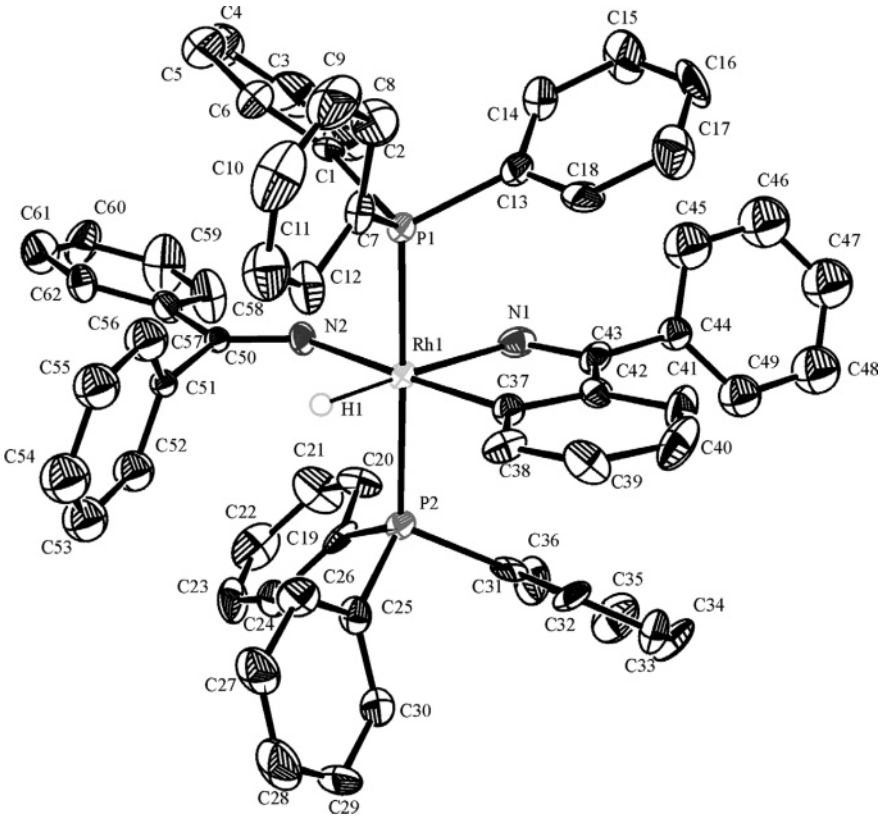

Figure 1. ORTEP diagram for the cation of $[RhH\{NH{=}C(Ph)(o\text{-}C_6H_4)\}(HN{=}CPh_2)(PPh_3)_2]PF_6$ (**2**), with 50% probability ellipsoids.

Table 2. Selected Bond Angles (deg) and Distances (Å) for the Cation of Complex 2

angle		bond	
P1−Rh1−P2	172.09(8)	Rh1−P1	2.3509(19)
C37−Rh1−H1	102(2)	Rh1−P2	2.3387(19)
N2−Rh1−C37	176.8(3)	Rh1−N1	2.178(7)
N1−Rh1−C37	79.3(3)	Rh1−N2	2.131(6)
N2−Rh1−H1	81(2)	Rh1−H1	1.46(6)
N1−Rh1−H1	176(3)	C37−Rh1	2.020(7)
N2−Rh1−N1	97.6(2)	N1−C43	1.314(9)
C37−Rh1−P1	87.62(19)	N2−C50	1.288(9)
C37−Rh1−P2	88.1(2)		
H1−Rh1−P1	92(3)		
H1−Rh1−P2	83(3)		

drido-η^1-imine complexes, which in any case are quite rare.[21]

The H atoms attached to the imine N atoms were not located, but there was crystallographic evidence for their presence (see Supporting Information), and the geometries of the coordinated η^1- and η^2-imines (as well as ^{1}H NMR data, see below) unequivocally establish their presence. The nonlocation of such H atoms by X-ray analysis is not unusual.[18a,c]

The solid state IR spectrum of **2** shows bands assignable to $\nu_{C=N}$, ν_{Rh-H}, and ν_{N-H} (but see below), while the highest mass fragment in the LSIMS mass spectrum corresponded to $[Rh(PPh_3)_2(HNCPh_2)]^+$. The room-temperature $^{31}P\{^1H\}$ NMR spectrum of **2** (in CD_3OD) consists of a doublet (δ 45.2, $J_{RhP} = 117$ Hz), the J value being indicative of mutually *trans*-phosphines.[2,8,9,16] The high-field hydride ^{1}H NMR resonance (a doublet of triplets at δ −11.98, $J_{RhH} = 11.6$, $^2J_{HP} = 9.6$) is consistent with a *trans*-$Rh(PPh_3)_2$-hydrido moiety.[2] The ^{1}H signals of the orthometalated-Ph ring (seen as two doublets, a doublet of doublets, and a pseudo-triplet) are shifted upfield compared with the broad signal at δ 7.1−7.8 for the other 45 aromatic protons, and such shifts have been noted previously in related Rh and Ir imine systems.[2,16,22] The imine-N*H* proton signals must be buried under the broad signal of the 45 aromatic protons, where it is impossible to quantify the integration for the 2 NH protons (for **3**, $\delta_{NH} = 7.75$, see below).

The NMR spectroscopic data for complex **3** are consistent with the formulation *cis*-$[Rh(PPh_3)_2(\eta^1\text{-}NH{=}CPh_2)_2]PF_6$, this being present as a single isomer with equivalent phosphines and equivalent imines. The J_{RhP} value for the $^{31}P\{^1H\}$ NMR doublet in CD_2Cl_2 is 167 Hz, the same as that reported for a crystallographically characterized $[Rh\{PPh_2(CH_2)_2PPh_2\}(\eta^1\text{-imine})_2]^+$ complex that necessarily has *cis*-phosphorus atoms.[19]

Assignment of the ^{1}H NMR signals was aided by an ^{1}H−^{1}H COSY experiment that revealed correlations between (a) the doublet at δ 6.12 with the triplets at δ 7.23 and 7.35, and (b) the doublet at δ 8.20 and the triplets at δ 7.65 and 7.85; each of these correlation sets corresponds to 10 protons and is thus assigned to phenyl

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groups labeled as either *exo* and *endo* on the imine C atoms (see Scheme 1). The phenyl groups of coordinated NH=CPh_2 are mutually orthogonal, as seen in the structures of **2** (Figure 1) and an Os complex;[21d] in **3**, as defined, the two *exo* phenyls will be closer to a PPh_3 ligand of the square planar complex, and the set of ^1H signals at the higher field is tentatively attributed to the *exo*-phenyl protons. The noncorrelated broad ^1H signal at δ 7.75 is assigned to the imine-N*H* protons; this value (and that for **2**) is some 1.0−3.7 ppm at higher field than those reported for η^1-NH=CPh_2 complexes (or an orthometalated derivative) of Os(II) and Ru(II).[18,21] This observation, together with the ν_{N-H} value for **2** (3056 vs 3120−3386 cm^{-1} for the Os and Ru complexes[18,21]), suggests there might be interactions between the NH protons and those of the phenyl groups at the P atom, although the ν_{N-H} value for **3** (3275 cm^{-1}) is normal; unfortunately, the NH protons of **2** were not located crystallographically, and so there is no evidence for such interactions in the solid state.

On reacting *cis*-[$Rh(PPh_3)_2(solv)_2$]PF_6 (**1**) with 1 equiv of benzophenone imine in MeOH or acetone at room temperature under Ar, a new species believed to be [RhH{NH=C(Ph)(*o*-C_6H_4)}$(PPh_3)_2$(solv)]PF_6 (**4**) was observed along with **2** and **3** and unreacted **1** (see Scheme 1). With use of just 0.5 equiv of the imine in acetone solution, **4** was the only product observed after 1 h and was formed in situ in ∼50% yield, the maximum possible: the $^{31}P\{^1H\}$ doublet with J_{RhP} = 116 Hz (again revealing *trans*-PPh_3 ligands), combined with the ^1H signals (high-field doublet of triplets and upfield-shifted resonances of aromatic protons attributable to a cyclometalated imine), is consistent with the above formulation, which is a possible precursor to **2** by displacement of the acetone by an η^1-imine (Scheme 1). The NMR data are very similar to those for the analogous, isolated [MH{RN=CR′(*o*-C_6H_4)}$(PPh_3)_2$(acetone)]PF_6 species (M = Rh or Ir; R and R′ = alkyl or aryl).[2,22]

Scheme 1 summarizes the essential chemistry incorporating production of **2**−**4** from **1**, although **2** was isolated using $[Rh(PPh_3)_2]_2(PF_6)_2$ as precursor. The mono-η^1-imine(solvento) species (**5**) was not observed, but these have been detected in MeOH solutions of a corresponding Rh system with the imine, $PhCH_2N$=CH(Ph), and were formed from the corresponding hydrido(orthometalated imine) species.[2] In the present HN=CPh_2 system, **5** in acetone must be relatively rapidly converted into the hydrido-orthometalated species **4**. Our earlier paper recognized the reversible orthometalation process within 1:1 imine/Rh systems,[2] while the findings here establish similar behavior in 2:1 imine/Rh systems, although the processes are solvent-dependent. More generally, formation of five-membered cyclometalated Rh(III)-hydrido complexes from a range of Rh(I) precursors is usually thermodynamically favored.[3,4,23] The Rh(I)-bis(imine) complex (**3**) may be stabilized somewhat by the presence of the second strongly π-accepting HN=CPh_2 ligand.

The in situ reaction of *cis,trans,cis*-[$Rh(H)_2(PPh_3)_2(solv)_2$]PF_6 (solv = CD_3OD or acetone-d_6) with 2 equiv of HN=CPh_2 under H_2 gave findings qualitatively similar to those found for the corresponding reaction with *cis*-[$Rh(PPh_3)_2(solv)_2$]PF_6 (**1**), in terms of formation of the equilibrium mixture of **2** and **3**. No $H_2NC(H)Ph_2$, the hydrogenation product, was seen, and neither **2** or **3** reacts with H_2; for the latter system presumably the strongly electron-deficient imine impedes possible oxidative addition to Rh(I). Under catalytic conditions in MeOH (imine:Rh = 20) at ambient temperature and 1 atm H_2, only ∼5% conversion to the amine was seen after 24 h. Under corresponding catalytic conditions, we have shown previously that the imine $PhCH_2N$=C(H)Ph can be hydrogenated rapidly via a *cis*-[$Rh(PPh_3)_2(PhCH_2N$=CHPh)(L)]PF_6 intermediate, where L is MeOH (a species akin to **5**) or $PhCH_2NH_2$ (formed by hydrolysis of the imine by adventitious water).[1,2] There was no evidence in the current work for such hydrolysis of the imine (to give NH_3 and acetone), and the slow catalytic hydrogenation likely results from the bulky phenyl substituents. Of note, benzophenone imine has been hydrogenated using [$Rh(COD)(PPh_3)_2$]PF_6 as catalyst precursor with 14 atm H_2 at 100 °C, but which specific solvent was used from a list of THF, MeOH, or CH_2Cl_2 cannot be ascertained from the report.[24] Formation of a species such as **2** must now be considered as a possible intermediate in catalyzed reactions of any imine that contains a phenyl substituent on the imine-carbon atom.

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Supporting Information Available: Scheme S1 and some details on the crystallographic refinement data for the structure of **2**; the X-ray data are also available in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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