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Rhodium–Hydrido–Benzylamine–Triphenylphosphine Complexes: Solid-State and Solution Structures and Implications in Catalyzed Imine Hydrogenation

Paolo Marcazzan, Brian O. Patrick, and Brian R. James*

Department of Chemistry, The University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1

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The complexes *cis,trans,cis*-[Rh(H)$_2$(PPh$_3$)$_2$(NH$_2$CH$_2$Ph)$_2$]PF$_6$ (**1**) and *cis*-[Rh(PPh$_3$)$_2$(NH$_2$CH$_2$Ph)$_2$]PF$_6$ (**2**) are characterized by X-ray crystallography; the structures are maintained in CH_2Cl_2 where the species are in equilibrium under H_2. In MeOH and in acetone, loss of amine and/or H_2 can occur. Traces of **1** and **2** are present after a Rh-catalyzed H_2-hydrogenation of PhCH=NCH$_2$Ph in MeOH, where the amine is generated by hydrolysis of the imine substrate through adventitious water. The findings are relevant to catalyst poisoning in the catalytic process.

Introduction

The *cis,trans,cis*-[Rh(H)$_2$(PPh$_3$)$_2$(MeOH)$_2$]PF$_6$ (**3**) precursor, readily formed from [Rh(COD)(PPh$_3$)$_2$]PF$_6$ and 1 atm H_2 at room temperature (room temperature, ~20 °C), catalyzes homogeneously the H_2-hydrogenation of benzylideneamines (PhCH=NR, R = alkyl, aryl) in MeOH at ambient conditions.[1,2] We have shown recently that, for the imine PhCH=NCH$_2$Ph, the mixed imine−amine complex *cis*-[Rh(PPh$_3$)$_2$(PhCH=NCH$_2$Ph)(PhCH$_2$NH$_2$)]PF$_6$ (**4**) is the species that reacts with H_2 in the key step of the catalytic cycle; the benzylamine is generated via a Rh-promoted hydrolysis of the imine, the source of the adventitious water possibly being the liquid imine.[2] At the end of the catalysis, trace amounts of Rh species were detected by ^{31}P NMR. These have now been identified as *cis,trans,cis*-[Rh(H)$_2$(PPh$_3$)$_2$(NH$_2$CH$_2$Ph)$_2$]PF$_6$ (**1**) and *cis*-[Rh(PPh$_3$)$_2$(NH$_2$CH$_2$Ph)$_2$]PF$_6$ (**2**); this article describes the characterization of **1** and **2** in the solid state and their solution structures in CH_2Cl_2, MeOH, and acetone. More generally, catalyzed imine hydrogenation is very solvent-dependent[1] and can be subject to catalyst poisoning by amines,[2] and so, the findings are important in this area that has industrial significance.[3]

* To whom correspondence should be addressed. E-mail: brj@chem.ubc.ca.

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Experimental Section

General. General experimental procedures were carried out, and reagents were obtained, as described recently elsewhere.[2]

Syntheses. *cis,trans,cis*-[Rh(H)$_2$(PPh$_3$)$_2$(NH$_2$CH$_2$Ph)$_2$]PF$_6$ (1). A yellow suspension of [Rh(COD)(PPh$_3$)$_2$]PF$_6$ (85 mg, 0.100 mmol) in MeOH (6 mL) was stirred under 1 atm H_2 for 2 h. To the resultant pale yellow solution was added the amine (27 μL, 0.250 mmol) under H_2, and the mixture was stirred for 15 min to afford spontaneous precipitation of a white solid that was collected, washed with hexanes (3 mL) and Et_2O (3 × 3 mL), and dried in vacuo. Yield: 50 mg (51%). Anal. Calcd for $C_{50}H_{50}N_2P_3F_6Rh$: C, 60.74; H, 5.10; N, 2.83. Found: C, 60.38; H, 4.87; N, 2.78. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 49.55 (d, J_{RhP} = 116). ^{1}H NMR (CD_2Cl_2): δ −17.55 (pseudo-q, 2H, Rh(*H*)$_2$, $J_{RhH} \approx {}^2J_{HP}$ = 14), 2.20 (m, 4H, −N*H*$_2$), 2.80 (m, 4H, −C*H*$_2$), 6.20 (d, 4H, −CH$_2$(*o*-C$_6$*H*$_5$), $^3J_{HH}$ = 5), 6.95−7.60 (m, 36H, arom-*H*). IR (KBr pellet): ν 2050, 2090 (Rh−H, m), 3336 (N−H, m).

***cis*-[Rh(PPh$_3$)$_2$(PhCH$_2$NH$_2$)$_2$]PF$_6$ (2)·0.5MeOH.** To a red solution of [Rh$_2$(PPh$_3$)$_4$][PF$_6$]$_2$ (85 mg, 0.110 mmol Rh)[4] in MeOH (4 mL) under Ar was added the amine (27 μL, 0.250 mmol), and the resultant yellow solution was stirred for 2 h. The volume was then reduced to ~1 mL to afford precipitation of a yellow solid that was collected, washed with hexanes (3 mL) and Et_2O (3 × 3 mL), and dried in vacuo. Yield: 60 mg (55%). Anal. Calcd for $C_{50}H_{48}N_2P_3F_6Rh\cdot(0.5CH_3OH)$: C, 60.48; H, 4.99; N, 2.79. Found: C, 60.27; H, 4.90; N, 2.80. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 51.81 (d,

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Table 1. Crystallographic Data for **1** and **2**

	1	**2**
formula	$C_{52}H_{54}N_2F_6P_3Cl_4Rh$	$C_{50.5}H_{50}N_2O_{0.5}F_6P_3Rh$
fw	1158.59	1002.74
cryst color, habit	colorless, chip	red, blocks
cryst size (mm^3)	0.15 × 0.15 × 0.10	0.38 × 0.30 × 0.25
space group	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)
a (Å)	13.7776(9)	29.3124(7)
b (Å)	21.9566(14)	21.0184(5)
c (Å)	19.2997(14)	18.1676(4)
β (deg)	95.948(4)	124.853(2)
V ($Å^3$)	5806.9(7)	9185.2(4)
Z	4	8
μ (mm^{-1})	0.614	0.540
total reflns	27616	40023
unique reflns	6625	9302
R_{int}	0.071	0.057
no. variables	349	590
R1 ($I > 2\sigma(I)$)	0.060 (4488 obsd reflns)	0.042 (7083 obsd reflns)
wR2	0.168 (all data)[a]	0.120 (all data)[b]
GOF	0.96 (all data)	1.03 (all data)

[a] $w = 1/[\sigma^2(F_o^2) + (0.0996P)^2]$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$. [b] $w = 1/[\sigma^2(F_o^2) + (0.0588P)^2 + 0.5327P]$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

$J_{RhP} = 177$). In CD_3OD: δ 52.21 (d, $J_{RhP} = 176$). ^1H NMR (CD_2Cl_2): δ 2.50 (br t, 4H, $-NH_2$), 3.45 (br t, 4H, $-CH_2$), 6.90−7.70 (m, 40H, arom-*H*).

X-ray Crystallographic Analysis. X-ray quality crystals of **1** and **2**, respectively, were grown from CH_2Cl_2/hexanes and from MeOH solutions of the complexes. Measurements were made at 173(2) K on a Rigaku/ADSC CCD area detector with graphite monochromated Mo Kα radiation (0.71073 Å). Some crystallographic data for **1** and **2** are shown in Table 1. Data were collected and processed using the d*TREK program.[5] The final unit-cell parameters for **1** and **2** were based on 14423 ($3.7° < 2\theta < 55.7°$) and 22397 ($5.9° < 2\theta < 55.9°$) reflections, respectively. The structures were solved by direct methods[6] and expanded using Fourier techniques.[7] Compound **1** crystallizes with a CH_2Cl_2 molecule in the asymmetric unit; additional residual electron density peaks were found but could not be modeled as either CH_2Cl_2 or hexane. The SQUEEZE function[8] in PLATON[9] was used to correct the raw data for the residual density. All non-H-atoms of the cations of **1** and **2** were refined anisotropically. Within **1**, the N−H and Rh−H H-atoms were refined isotropically, while other H-atoms were included in fixed positions. Within **2**, the associated PF_6 counterion resides on two positions with one-half PF_3 on each; one PF_3 fragment is disordered and was modeled in two orientations. In addition, one-half molecule of MeOH also crystallized in the asymmetric unit of **2**. Some atoms in the disordered PF_3 fragment were refined isotropically, while the H-atoms of the MeOH involved in H-bonding were refined isotropically, but all other H-atoms were included in calculated positions. The final cycle of full-matrix least-squares refinement (function minimized: $\sum w(F_o^2 - F_c^2)^2$) was based on 6625 observed reflections ($I > 0.00\sigma(I)$) and 349 variables for **1**, and on 9302 observed reflections ($I > 0.00\sigma(I)$) and 590 variables for **2**. All calculations were performed using the teXsan[10] crystallographic software package and SHELXL-97.[11]

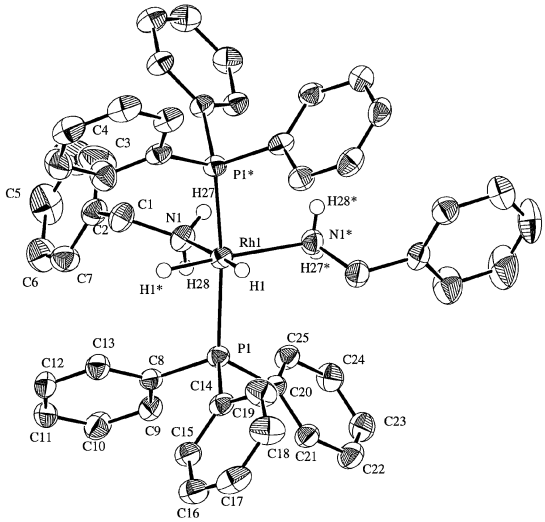

Figure 1. ORTEP diagram of the cation *cis,trans,cis*-$[Rh(H)_2(PPh_3)_2(NH_2CH_2Ph)_2]^+$ (**1**) with 50% probability thermal ellipsoids.

Results and Discussion

Reaction of a MeOH solution of *cis,trans,cis*-$[Rh(H)_2(PPh_3)_2(MeOH)_2]PF_6$ (**3**), generated in situ from $[Rh(COD)(PPh_3)_2]PF_6$,[12] with ∼2 equiv of $PhCH_2NH_2$ at room temperature under 1 atm H_2 for 15 min results in the displacement of the MeOH ligands and the formation of *cis,trans,cis*-$[Rh(H)_2(PPh_3)_2(NH_2CH_2Ph)_2]PF_6$ (**1**) in ∼50% isolated yield (Scheme 1).

The structure of the cation is shown in Figure 1, with selected bond lengths and angles given in Table 2. The complex resides on a 2-fold rotation axis, and the geometry at the Rh(III) is close to octahedral. The Rh−P distance within the *trans*-PPh_3 ligands (2.293 Å) and the Rh−H bond length (1.47 Å) are typical of those found in Rh(III) complexes,[13,14] while the phosphine ligands are bent towards the hydrides as indicated by the P−Rh−H angles (86.9° and 82.4 °) and the P−Rh−P angle (165.6 °). The Rh−N distance (2.239 Å) is ∼0.2 Å longer than an estimated average Rh^{III}−N bond length,[15] presumably because the amine is trans to the high trans-influence hydride ligand.[16] The geometry of the coordinated amine is essentially identical to that in the mixed Rh^I−imine−amine complex such as **4** (see Introduction) but where the phosphine is P(*p*-tolyl)$_3$ and the

(5) *d*TREK*: *Area Detector Software*, version 7.11; Molecular Structure Corporation: The Woodlands, TX, 2001.
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(9) *PLATON*: Spek, A. L. *A Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 1998.
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Scheme 1. Reaction Scheme for the Formation of *cis,trans,cis*-$[Rh(H)_2(PPh_3)_2(NH_2CH_2Ph)_2]PF_6$ (**1**) and *cis*-$[Rh(PPh_3)_2(NH_2CH_2Ph)_2]PF_6$ (**2**)

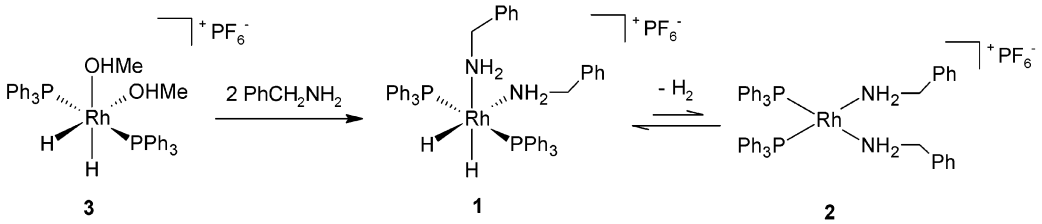

Table 2. Selected Bond Distances and Angles for *cis,trans,cis*-$[Rh(H)_2(PPh_3)_2(NH_2CH_2Ph)_2]PF_6$ (**1**) with Estimated Standard Deviations in Parentheses

bond	length (Å)	bond	angle (deg)
Rh(1)−P(1)	2.2927(10)	P(1)−Rh(1)−N(1)	91.76(11)
Rh(1)−N(1)	2.239(3)	N(1)−Rh(1)−N(1*)	94.33(19)
Rh(1)−H(1)	1.47(3)	P(1)−Rh(1)−P(1*)	165.63(5)
N(1)−C(1)	1.489(5)	N(1)−Rh(1)−H(1)	174.5(12)
C(1)−C(2)	1.513(5)	N(1*)−Rh(1)−H(1)	91.1(12)
		P(1)−Rh(1)−H(1)	86.9(13)
		P(1*)−Rh(1)−H(1)	82.4(13)
		P(1)−Rh(1)−N(1*)	98.01(11)
		C(1)−N(1)−Rh(1)	114.7(2)

Table 3. Selected Bond Distances and Angles for *cis*-$[Rh(PPh_3)_2(NH_2CH_2Ph)_2]PF_6$ (**2**) with Estimated Standard Deviations in Parentheses

bond	length (Å)	bond	angle (deg)
Rh(1)−P(1)	2.2063(8)	P(1)−Rh(1)−N(1)	178.17(10)
Rh(1)−P(2)	2.2483(8)	P(2)−Rh(1)−N(2)	173.47(11)
Rh(1)−N(1)	2.202(3)	P(1)−Rh(1)−P(2)	93.88(3)
Rh(1)−N(2)	2.146(3)	P(1)−Rh(1)−N(2)	92.50(10)
N(1)−C(37)	1.486(4)	P(2)−Rh(1)−N(1)	87.70(10)
N(2)−C(44)	1.475(6)	C(37)−N(1)−Rh(1)	120.0(2)
		C(44)−N(2)−Rh(1)	120.0(3)
		N(1)−Rh(1)−N(2)	85.95(14)

amine is trans to the phosphine; in this mixed complex, the Rh−N distance is 2.209 Å.[2] For complex **1**, IR bands are seen for ν(Rh−H) and ν(N−H).

The structure of **1** is maintained in CH_2Cl_2 under H_2 (see additional details elsewhere in this paper) as shown by room temperature NMR data: the $^{31}P\{^1H\}$ doublet (δ_P 49.55, J_{RhP} = 116) is typical for *trans*-PPh_3 ligands coupled to Rh,[12] while the high-field ^1H resonance for the equivalent *cis*-hydrides (δ_H −17.55, $J_{RhH} \approx {}^2J_{PH} = 14$) appears as a pseudo-quartet instead of the expected doublet of triplets. This overlapping of triplets has been seen previously with corresponding dihyride complexes containing unsaturated N-donor ligands.[13,17] The more downfield δ_H shift for the hydrides of **1** versus that of the analogous bis-alcohol complex **3** (δ_H −21.20) is consistent with the relative *trans*-influence of the ligands (RNH_2 > ROH).[16] The ^1H NMR doublet at δ 6.20 ($^3J_{HH} = 5$) is assigned to the *ortho*-H atoms of the amine benzylic rings, likely involved in a π-arene interaction with one phosphine-Ph group: a similar assignment was made for the imine−amine complex **4**, where a $^1H-^{13}C$ HETCOR NMR experiment established that these protons correlate with aromatic C-atoms.[2]

Complex **1** in CD_2Cl_2 under Ar loses H_2 reversibly to generate *cis*-$[Rh(PPh_3)_2(NH_2CH_2Ph)_2]PF_6$ (**2**) (Scheme 1), a species that was more readily isolated from reaction of 2 equiv of $PhCH_2NH_2$ with *cis*-$[Rh(PPh_3)_2(MeOH)_2]PF_6$, this being generated in situ by dissolution of $[Rh_2(PPh_3)_4][PF_6]_2$ in MeOH.[4] The reaction is again simple replacement of MeOH ligands by amines. The structure of the cation of **2** (Figure 2, Table 3) reveals the expected, essentially square-planar geometry at the Rh(I) center. The Rh^I-P distances are within ±0.05 Å of those found in other Rh(I) complexes containing *cis*-PPh_3 ligands[3,4] while the Rh^I-N lengths are 0.03−0.09 Å shorter than those in complex **1**. The Rh−N−C angles of **2**, compared to those of **1**, have opened up by ∼5 °, presumably because of less steric constraint.

The structure of **2** is retained in CD_2Cl_2 and in CD_3OD solutions, where a $^{31}P\{^1H\}$ doublet is seen in the room temperature NMR spectra, the J_{RhP} value of ∼175 Hz being typical for *cis*-PPh_3 ligands coupled to Rh.[3,12] The corresponding ^1H NMR spectra also identify **2** as the only species present in solution.

Complex **1** on dissolution at room temperature in CD_3OD under Ar undergoes partial (reversible) loss of H_2 to form **2**, and a *trans*-$Rh(PPh_3)_2$ species (δ_P 46.09 d, J_{RhP} = 118 Hz). This is almost certainly the amine−MeOH species *cis,trans,cis*-$[Rh(H)_2(PPh_3)_2(NH_2CH_2Ph)(MeOH)]PF_6$ (**5**), as in the presence of excess amine this species is reconverted to **1**. Of note, the high-field hydride resonances for **1** and **5** are not seen in CD_3OD, presumably because of hydride exchange with the solvent (an intermediate with hydrogen-bonding between *cis*-disposed hydride and MeOH ligands

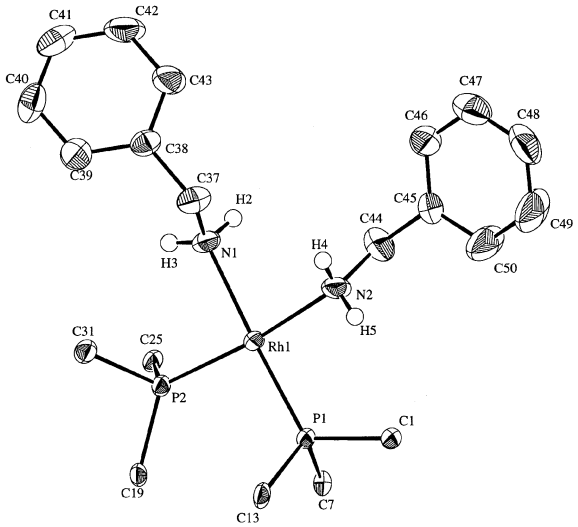

Figure 2. ORTEP diagram of the cation *cis*-$[Rh(PPh_3)_2(NH_2CH_2Ph)_2]^+$ (**2**) with 50% probability thermal ellipsoids.

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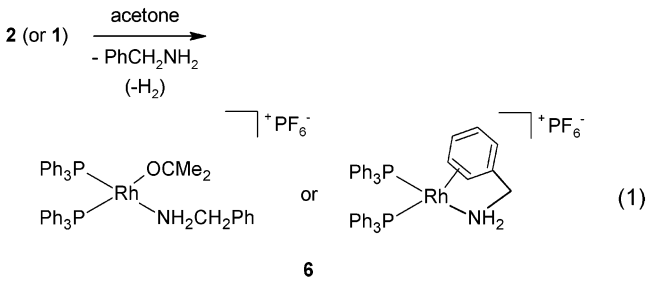
is readily envisioned). Thus, the fact that **1** dissolved in MeOH (the favored solvent for catalyzed imine hydrogenation)[2,3] exists as a mixture of **1**, **2**, and **5** certainly shows that benzylamine may compete for (i.e., poison) the Rh catalyst. When $PhCH{=}NCH_2Ph$ is added (Rh/imine = 1:1) to a CD_3OD solution of **2** stored under Ar, the imine−amine complex **4**[2] (∼30% formation), unreacted imine, and **2** are detected. Exposure of this solution to 1 atm H_2 for 5 min results in complete conversion of the imine to the dibenzylamine product and generation of **1**. Similarly, if excess imine (10 equiv) is added to **2** (or **1**) in CD_3OD under H_2, catalytic hydrogenation occurs via complete formation of **4** as described elsewhere,[2] although here **1** is the final species remaining in solution. Thus in MeOH, the presence of up to 2 equiv of benzylamine per Rh is innocuous to the catalysis, and indeed 1 equiv is essential for formation of the key imine−amine species. Addition of >2 equiv of $PhCH_2NH_2$, however, does inhibit the catalysis.[2]

Addition of 1 equiv of $PhCH{=}NCH_2Ph$ to a CD_2Cl_2 solution of **2** under Ar again results in partial formation (∼50%) of the mixed species **4**. Exposure of this solution to 1 atm H_2, however, results in the hydrogenation of only the imine contained in complex **4**, with complete conversion of all the Rh into **1**; consistent with this, there is no reaction of **1** with 1 equiv of imine. These observations indicate further that, although **2** (and **1**) are themselves a "dead-end" for catalysis, hydrogenation can still occur if the mixed species is formed.

In acetone solution at rt under Ar, **1** and **2** display behavior very different from that in CD_2Cl_2 and CD_3OD: both complexes quantitatively rearrange (via loss of H_2 and/or amine) into a species **6** that is either *cis*-$[Rh(PPh_3)_2(NH_2CH_2Ph)(acetone)]PF_6$ or *cis*-$[Rh(PPh_3)_2\{NH_2CH_2(\eta^2\text{-}C_6H_5)\}]PF_6$ (eq 1).[18] Free benzylamine and H_2, displaced from either **1** or **2**, were detected in the ^1H NMR spectrum [$\delta(CH_2)$ 4.55 s, $\delta(H_2)$ 4.15], but attempts to isolate **6** were unsuccessful.



The 8-line AMX pattern seen in the $^{31}P\{^1H\}$ NMR spectrum reveals inequivalent cis phosphines, each trans to a different ligand, and both protons within each of the CH_2 and NH_2 groups of the coordinated amine are inequivalent in the ^1H NMR, presumably because of restricted rotation about the Rh−N bond.[2] An upfield-shifted doublet resonance for 2 protons in the aromatic region (δ 6.23) is similar to that observed for **1** and could be assigned to the *o*-protons of the benzylamine moiety of the mixed amine/acetone species, in which case the downfield resonance would be assigned to the P-atom trans to acetone, and the upfield resonance to the P-atom trans to the amine.[19] However, in situ **6** in acetone was unreactive toward 1 atm H_2 or 1 equiv of $PhCH{=}NCH_2Ph$, and no catalyzed imine hydrogenation was observed in this solvent. As the bis(amine) and bis(acetone)[12] species readily oxidatively add H_2, nonreactivity of the amine/acetone species toward H_2 would be surprising. Thus, **6** is more likely a bidentate benzylamine adduct containing η^2-coordination of the phenyl group, in which case the δ 6.23 signal would be assigned to the protons of the η^2-moiety.

Acetone is clearly a stronger donor ligand than MeOH within these Rh systems and does not allow for ready formation of the mixed imine−amine species that is necessary for the catalytic hydrogenation.[2] Further, dihydrides are readily formed at 1 atm H_2 by Rh(I)−bis(amine) and Rh(I)−amine(solvent) species in MeOH, but not in acetone. Such marked solvent effects, coupled with the requirement for adventitious water, make optimization of conditions for hydrogenation of $PhCH{=}NCH_2Ph$ a nontrivial problem. The generality of such findings within other imine substrates remains to be established.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support.

Supporting Information Available: X-ray crystallographic data for the structures of **1** and **2** in CIF format. This material is available free of charge at http://pubs.acs.org.

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(18) The in situ characterization of species **6** follows. $^{31}P\{^1H\}$ NMR (acetone-d_6): δ 47.46 (dd, J_{RhP} = 167, $^2J_{PP}$ = 49), 52.44 (dd, J_{RhP} = 183, $^2J_{PP}$ = 49). ^1H NMR (acetone-d_6): δ 2.90 (d, 1H, $^2J_{HH}$ = 12, $-NH_2$), 3.16 (d, 1H, $^2J_{HH}$ = 12, $-NH_2$), 4.50 (d, 1H, $^2J_{HH}$ = 12, $-CH_2$), 4.75 (d, 1H, $^2J_{HH}$ = 12, $-CH_2$), 6.23 (d, 2H, $^3J_{HH}$ = 8, $-CH_2$-(*o*-C_6H_5) or η^2-Ph, see text), 7.05−7.65 (m, 33H, arom-*H*).

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