

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

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The complexes cis, trans, cis-[Rh(H)₂(PPh₃)₂(NH₂CH₂Ph)₂]PF₆ (1) and cis-[Rh(PPh₃)₂(NH₂CH₂Ph)₂]PF₆ (2) are characterized by X-ray crystallography; the structures are maintained in CH₂Cl₂ where the species are in equilibrium under H₂. In MeOH and in acetone, loss of amine and/or H₂ can occur. Traces of 1 and 2 are present after a Rh-catalyzed H₂-hydrogenation of PhCH=NCH₂Ph 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(PPh₃)₂(MeOH)₂]PF₆ (3) precursor, readily formed from [Rh(COD)(PPh₃)₂]PF₆ and 1 atm H_2 at room temperature (room temperature, ~20 °C), catalyzes homogeneously the H₂-hydrogenation of benzylideneamines (PhCH=NR, R = alkyl, aryl) in MeOH at ambient conditions.^{1,2} We have shown recently that, for the imine PhCH=NCH₂Ph, the mixed imine-amine complex cis-[Rh-(PPh₃)₂(PhCH=NCH₂Ph)(PhCH₂NH₂)]PF₆ (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 ³¹P NMR. These have now been identified as cis, trans, cis-[Rh(H)₂(PPh₃)₂(NH₂CH₂Ph)₂]- PF_6 (1) and *cis*-[Rh(PPh₃)₂(NH₂CH₂Ph)₂]PF₆ (2); this article describes the characterization of 1 and 2 in the solid state and their solution structures in CH₂Cl₂, MeOH, and acetone. More generally, catalyzed imine hydrogenation is very solvent-dependent¹ and can be subject to catalyst poisoning by amines,² and so, the findings are important in this area that has industrial significance.³

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(PPh₃)₂(NH₂CH₂Ph)₂]PF₆ (1). A yellow suspension of [Rh(COD)(PPh₃)₂]PF₆ (85 mg, 0.100 mmol) in MeOH (6 mL) was stirred under 1 atm H₂ for 2 h. To the resultant pale yellow solution was added the amine (27 μ L, 0.250 mmol) under H₂, 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 Et₂O (3 × 3 mL), and dried in vacuo. Yield: 50 mg (51%). Anal. Calcd for C₅₀H₅₀N₂P₃F₆Rh: C, 60.74; H, 5.10; N, 2.83. Found: C, 60.38; H, 4.87; N, 2.78. ³¹P{¹H} NMR (CD₂Cl₂): δ 49.55 (d, $J_{RhP} = 116$). ¹H NMR (CD₂Cl₂): δ -17.55 (pseudo-q, 2H, Rh(*H*)₂, $J_{RhH} \approx {}^{2}J_{HP} = 14$), 2.20 (m, 4H, -N*H*₂), 2.80 (m, 4H, -C*H*₂), 6.20 (d, 4H, -CH₂(*o*-C₆*H*₅), ${}^{3}J_{HH} = 5$), 6.95–7.60 (m, 36H, arom-*H*). IR (KBr pellet): ν 2050, 2090 (Rh–H, m), 3336 (N–H, m).

cis-[Rh(PPh₃)₂(PhCH₂NH₂)₂]PF₆ (2)·0.5MeOH. To a red solution of [Rh₂(PPh₃)₄][PF₆]₂ (85 mg, 0.110 mmol Rh)⁴ in MeOH (4 mL) under Ar was added the amine (27 μ L, 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 Et₂O (3 × 3 mL), and dried in vacuo. Yield: 60 mg (55%). Anal. Calcd for C₅₀H₄₈N₂P₃F₆Rh·(0.5CH₃OH): C, 60.48; H, 4.99; N, 2.79. Found: C, 60.27; H, 4.90; N, 2.80. ³¹P{¹H} NMR (CD₂Cl₂): δ 51.81 (d,

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Table 1. Crystallographic Data for	1	and	2
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_	1	2
formula	C52H54N2F6P3Cl4Rh	C _{50.5} H ₅₀ N ₂ O _{0.5} F ₆ P ₃ Rh
fw	1158.59	1002.74
cryst color, habit	colorless, chip	red, blocks
cryst size (mm ³)	$0.15 \times 0.15 \times 0.10$	$0.38 \times 0.30 \times 0.25$
space group	<i>C</i> 2/ <i>c</i> (No. 15)	C2/c (No. 15)
a (Å)	13.7776(9)	29.3124(7)
b(A)	21.9566(14)	21.0184(5)
<i>c</i> (Å)	19.2997(14)	18.1676(4)
β (deg)	95.948(4)	124.853(2)
$V(Å^3)$	5806.9(7)	9185.2(4)
Ζ	4	8
$\mu \text{ (mm}^{-1}\text{)}$	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 $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

 $J_{\text{RhP}} = 177$). In CD₃OD: δ 52.21 (d, $J_{\text{RhP}} = 176$). ¹H NMR (CD₂-Cl₂): 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 CH2Cl2/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 Ka 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 ($3.7^{\circ} < 2\theta < 55.7^{\circ}$) and 22397 (5.9° < 2θ < 55.9°) reflections, respectively. The structures were solved by direct methods⁶ 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 CH₂Cl₂ or hexane. The SQUEEZE function8 in PLATON9 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 PF3 on each; one PF₃ 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 leastsquares refinement (function minimized: $\sum w(F_0^2 - F_c^2)^2$) was based on 6625 observed reflections ($I > 0.00\sigma(I)$) and 349 variables



Figure 1. ORTEP diagram of the cation cis, trans, cis-[Rh(H)₂(PPh₃)₂(NH₂-CH₂Ph₂]⁺ (1) with 50% probability thermal ellipsoids.

for **1**, and on 9302 observed reflections $(I > 0.00\sigma(I))$ and 590 variables for **2**. All calculations were performed using the teXsan¹⁰ crystallographic software package and SHELXL-97.¹¹

Results and Discussion

Reaction of a MeOH solution of *cis,trans,cis*-[Rh(H)₂-(PPh₃)₂(MeOH)₂]PF₆ (**3**), generated in situ from [Rh(COD)-(PPh₃)₂]PF₆,¹² with ~2 equiv of PhCH₂NH₂ at room temperature under 1 atm H₂ for 15 min results in the displacement of the MeOH ligands and the formation of *cis,trans,cis*-[Rh-(H)₂(PPh₃)₂(NH₂CH₂Ph)₂]PF₆ (**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*-PPh₃ 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

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Scheme 1. Reaction Scheme for the Formation of cis, trans, cis-[Rh(H)₂(PPh₃)₂(NH₂CH₂Ph)₂]PF₆ (1) and cis-[Rh(PPh₃)₂(NH₂CH₂Ph)₂]PF₆ (2)



Table 2. Selected Bond Distances and Angles for cis,trans,cis-[Rh(H)₂(PPh₃)₂(NH₂CH₂Ph)₂]PF₆ (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)

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 ³¹P{¹H} doublet (δ_P 49.55, J_{RhP} = 116) is typical for *trans*-PPh₃ ligands coupled to Rh,¹² while the high-field ¹H resonance for the equivalent cishydrides ($\delta_{\rm H}$ –17.55, $J_{\rm RhH} \approx {}^2J_{\rm PH} = 14$) appears as a pseudoquartet 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 $\delta_{\rm H}$ shift for the hydrides of 1 versus that of the analogous bis-alcohol complex 3 ($\delta_{\rm H}$ –21.20) is consistent with the relative *trans*influence of the ligands ($RNH_2 > ROH$).¹⁶ The ¹H NMR doublet at δ 6.20 (${}^{3}J_{\rm HH} = 5$) 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⁻¹³C 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(PPh₃)₂(NH₂CH₂Ph)₂]PF₆ (2) (Scheme 1), a species that was more readily isolated from reaction of 2 equiv of PhCH₂NH₂ with *cis*-[Rh(PPh₃)₂(MeOH)₂]PF₆, this being generated in situ by dissolution of [Rh₂(PPh₃)₄][PF₆]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 squareplanar 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*-PPh₃ ligands^{3,4} while the Rh^I–N lengths are

Table 3. Selected Bond Distances and Angles for cis-[Rh(PPh₃)₂(NH₂CH₂Ph)₂]PF₆ (**2**) with Estimated Standard Deviations in Parentheses

bond	length (Å)	bond	angle (deg)
Rh(1)-P(1) Rh(1)-P(2) Rh(1)-N(1) Rh(1)-N(2) N(1)-C(37) N(2)-C(44)	2.2063(8) 2.2483(8) 2.202(3) 2.146(3) 1.486(4) 1.475(6)	$\begin{array}{c} P(1)-Rh(1)-N(1) \\ P(2)-Rh(1)-N(2) \\ P(1)-Rh(1)-P(2) \\ P(1)-Rh(1)-N(2) \\ P(2)-Rh(1)-N(1) \\ C(37)-N(1)-Rh(1) \\ C(44)-N(2)-Rh(1) \\ N(1)-Rh(1)-N(2) \end{array}$	178.17(10) 173.47(11) 93.88(3) 92.50(10) 87.70(10) 120.0(2) 120.0(3) 85.95(14)
		N(1) = Kn(1) = N(2)	85.95(14)

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 \sim 5 °, presumably because of less steric constraint.

The structure of **2** is retained in CD_2Cl_2 and in CD_3OD solutions, where a ³¹P{¹H} doublet is seen in the room temperature NMR spectra, the J_{RhP} value of ~175 Hz being typical for *cis*-PPh₃ 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 CD₃-OD under Ar undergoes partial (reversible) loss of H₂ to form 2, and a *trans*-Rh(PPh₃)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(PPh₃)₂(NH₂CH₂Ph)(MeOH)]PF₆ (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 CD₃OD, presumably because of hydride exchange with the solvent (an intermediate with hydrogenbonding between *cis*-disposed hydride and MeOH ligands

Figure 2. ORTEP diagram of the cation cis-[Rh(PPh₃)₂(NH₂CH₂Ph₂]⁺ (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 hydrogena- $(tion)^{2,3}$ exists as a mixture of 1, 2, and 5 certainly shows that benzylamine may compete for (i.e., poison) the Rh catalyst. When PhCH=NCH₂Ph 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 H₂ 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 CD₃OD under H_2 , catalytic hydrogenation occurs via complete formation of 4 as described elsewhere,² although here $\mathbf{1}$ 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 PhCH₂NH₂, however, does inhibit the catalysis.²

Addition of 1 equiv of PhCH=NCH₂Ph to a CD₂Cl₂ solution of **2** under Ar again results in partial formation (~50%) of the mixed species **4**. Exposure of this solution to 1 atm H₂, 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 CD₂Cl₂ and CD₃OD: both complexes quantitatively rearrange (via loss of H₂ and/or amine) into a species **6** that is either *cis*-[Rh(PPh₃)₂(NH₂-CH₂Ph)(acetone)]PF₆ or *cis*-[Rh(PPh₃)₂{NH₂CH₂(η^2 -C₆H₅)}]-PF₆ (eq 1).¹⁸ Free benzylamine and H₂, displaced from either **1** or **2**, were detected in the ¹H NMR spectrum [δ (CH₂) 4.55 s, δ (H₂) 4.15], but attempts to isolate **6** were unsuccessful.



The 8-line AMX pattern seen in the ³¹P{¹H} NMR spectrum reveals inequivalent cis phosphines, each trans to a different ligand, and both protons within each of the CH₂ and NH₂ 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 H₂ or 1 equiv of PhCH=NCH₂-Ph, and no catalyzed imine hydrogenation was observed in this solvent. As the bis(amine) and bis(acetone)¹² species readily oxidatively add H₂, 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 H₂ 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=NCH₂Ph a nontrivial problem. The generality of such findings within other imine substrates remains to be established.

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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. ³¹P{¹H} NMR (acetone-*d*₆): δ 47.46 (dd, $J_{RhP} = 167$, ² $J_{PP} = 49$), 52.44 (dd, $J_{RhP} = 183$, ² $J_{PP} = 49$). ¹H NMR (acetone-*d*₆): δ 2.90 (d, 1H, ² $J_{HH} = 12$, $-NH_2$), 3.16 (d, 1H, ² $J_{HH} = 12$, $-NH_2$), 4.50 (d, 1H, ² $J_{HH} = 12$, $-CH_2$), 4.75 (d, 1H, ² $J_{HH} = 12$, $-CH_2$), 6.23 (d, 2H, ³ $J_{HH} = 8$, $-CH_2$ -(*o*-C₆ H_5) or η^2 -Ph, see text), 7.05–7.65 (m, 33H, arom-*H*).

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