Amine Products and Catalyst Poisoning in the Homogeneous H_2 Hydrogenation of Imines Catalyzed by the $[Rh(COD)(PPh_3)_2]PF_6$ Precursor

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

Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, British Columbia V6T 1Z1, Canada

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Summary: The H_2 hydrogenations of PhN=CHPh and $PhCH_2N$=CHPh are catalyzed by the precursor $[Rh(COD)(PPh_3)_2]PF_6$. However, the amine product $PhNHCH_2Ph$ poisons the catalyst by coordination to the Rh through an arene moiety, while the other amine product, $(PhCH_2)_2NH$, forms a labile N-bonded species that does not poison the catalyst system.

Transition-metal-catalyzed hydrogenation of imines is an area of intense interest, particularly for production of chiral amines from prochiral ketimine substrates, but the mechanisms are poorly understood.[1,2] One problem is that the more forcing hydrogenation conditions generally required, versus those for the corresponding reductions of C=C and C=O functionalities,[2] complicate mechanistic investigations; however, cationic precursors such as $[Rh(COD)(PPh_3)_2]PF_6$ (**1**)[3] have long been known to catalyze homogeneously the H_2 hydrogenation of aldimines (RCH=NR′) under ambient conditions,[4] and we and others[5] are studying mechanistic aspects of such systems. The strong donor character of the NH group of an amine, with its ability to compete for coordination at the catalytic site (catalyst poisoning), may be one factor contributing to the more difficult hydrogenation of imines.[2] We report here on the hydrogenation of two different aldimines, the findings revealing two limiting cases for the interaction of the product amines with the catalytic center.

Treatment of a suspension of **1** in MeOH with 1 atm of H_2 at room temperature (~20 °C) for 2 h afforded a pale yellow solution of $[Rh(H)_2(PPh_3)_2(MeOH)_2]PF_6$ (**2**).[3,6] For a catalytic run, excess imine (Rh:imine = 1:100) was added to an MeOH solution (10 mL) of **2**, preformed in situ (0.53 mM) under 1 atm of H_2, and the conversion monitored by GC analysis as a function of time. Of the two substrates tested, benzylidenebenzylamine ($PhCH_2N$=CHPh) and benzylideneaniline (PhN=CHPh), only the former was converted to the amine (Figure 1).[7,8] Negligible conversion and formation of a red solution (with trace red solid) during the first 5 min

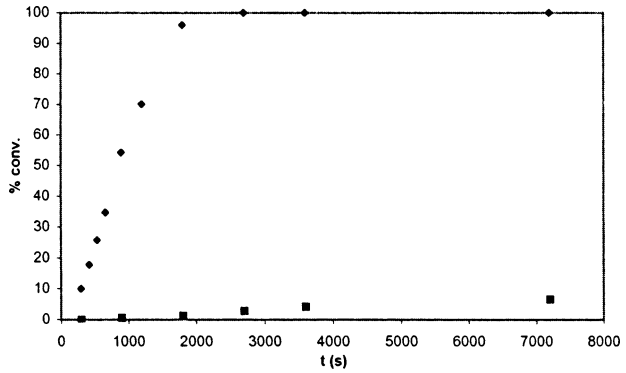
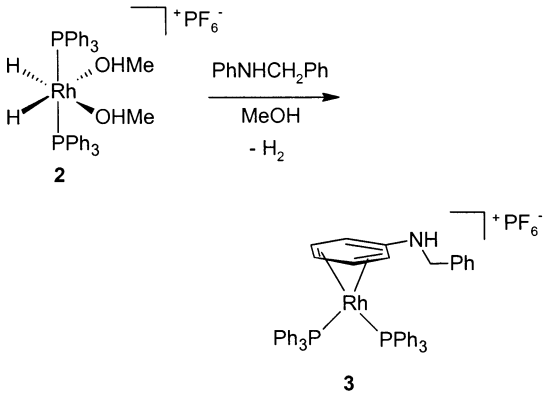


Figure 1. Plots of percent conversion vs time for the hydrogenation of $PhCH_2N$=CHPh (◆) and PhN=CHPh (■) catalyzed by 0.53 mM $[Rh(H)_2(PPh_3)_2(MeOH)_2]PF_6$ (**2**) in MeOH (substrate:catalyst = 100:1, 293 K, 1 atm of H_2).

of reaction were observed for PhN=CHPh; indeed, the room-temperature reaction of **2** with the product amine $PhNHCH_2Ph$ in MeOH under Ar (amine:Rh = 2) gave the red complex $[Rh\{\eta^4\text{-}(C_6H_5)NHCH_2Ph\}(PPh_3)_2]PF_6$ (**3**) containing in the solid state the amine ligand bonded through an η^4-π-arene interaction (eq 1).[9] X-ray-quality



crystals were obtained from evaporation of a CH_2Cl_2/hexanes solution of **3**; Figure 2 shows the structure of the cation, and selected structural parameters are given in the figure legend.[10] The choice of coordination via the aryl rather than the NH moiety of the amine was not expected. The solid isolated from the catalytic mixture

* To whom correspondence should be addressed. Tel.: +1-(604)-822-6645. Fax: +1-(604)-822-2847. E-mail: brj@chem.ubc.ca.

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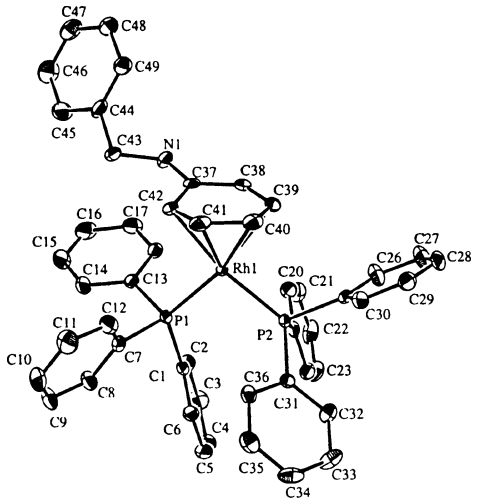


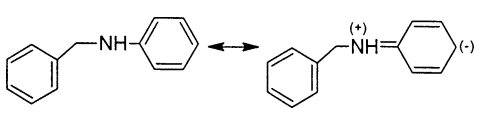
Figure 2. ORTEP diagram of the cation of **3**, $[Rh\{\eta^4\text{-}(C_6H_5)NHCH_2Ph\}(PPh_3)_2]^+$, with 50% probability thermal ellipsoids. Selected bond distances (Å) and angles (deg): Rh(1)−P(1) = 2.2636(8), Rh(1)−P(2) = 2.2421(7), Rh(1)−C(37) = 2.524(3), Rh(1)−C(38) = 2.442(3), Rh(1)−C(39) = 2.288(3), Rh(1)−C(40) = 2.287(4), Rh(1)−C(41) = 2.310(4), Rh(1)−C(42) = 2.291(3), N(1)−C(37) = 1.354(4), N(1)−C(43) = 1.468(4), C(37)−C(38) = 1.405(4), C(38)−C(39) = 1.388(4), C(39)−C(40) = 1.416(5), C(40)−C(41) = 1.392(5), C(41)−C(42) = 1.416(5), C(42)−C(37) = 1.430(5); P(1)−Rh(1)−P(2) = 94.98(3), P(1)−Rh(1)−C(37) = 105.30(7), P(1)−Rh(1)−C(38) = 129.33(7), P(1)−Rh(1)−C(39) = 163.24(9), P(1)−Rh(1)−C(40) = 152.61(9), P(1)−Rh(1)−C(41) = 118.75(9), P(1)−Rh(1)−C(42) = 98.37(8), P(2)−Rh(1)−C(37) = 144.30(7), P(2)−Rh(1)−C(38) = 112.61(7), P(2)−Rh(1)−C(39) = 94.09(7), P(2)−Rh(1)−C(40) = 102.24(10), P(2)−Rh(1)−C(41) = 131.75(9), P(2)−Rh(1)−C(42) = 165.90(8), C(37)−N(1)−C(43) = 124.0(3).

described above was also **3**, formed following hydrogenation of 1−2 equiv of the imine; the Rh center is "sequestered" and the catalytic activity poisoned by the coordinated amine. While Rh^I−π-arene complexes are common, those adopting η^4 hapticities are rare.[11−14] The shorter Rh(1)−C(*n*) (*n* = 39−42) distances show that the arene is coordinated through the C(39)−C(40) and C(41)−C(42) bonds, while the longer Rh(1)−C(37) and Rh(1)−C(38) distances are consistent with the C(37)−C(38) bond being noncoordinating; the C−C bond distances within the η^4-phenyl do not, however, differ significantly, and this has precedents within other Rh^I−η^4-phenyl structures.[14] IR bands are seen for ν(C−N) and ν(N−H).[9]

The room-temperature $^{31}P\{^1H\}$ NMR spectrum of **3** in CD_2Cl_2 (δ 46.61 d, J_{RhP} = 211 Hz) shows that the complex is stable in noncoordinating or weakly coordinating media, the J_{RhP} value being typical for cis phosphines within Rh^I−π-bound arene complexes.[13,15,16] The three upfield-shifted resonances for the π-arene protons in a 1:2:2 ratio in the room-temperature ^1H NMR spectrum in CD_2Cl_2[9] indicate equivalence of the two meta and the two ortho protons in an η^6 coordination mode; for η^4-hapticity, as in the solid state, five different upfield-shifted resonances would be expected. The mutually coupled CH_2 and NH resonances of the coordinated amine are observed at δ 3.83 and 4.08, respectively, upfield of those of the free amine (δ 4.36 and 7.30, respectively). The four upfield-shifted resonances for the C atoms of the coordinating ring in an approximate 1:2:2:1 ratio (para, ortho, meta, and ipso C, respectively) in the room-temperature $^{13}C\{^1H\}$ spectrum in CD_2Cl_2[9] are also consistent with the η^6 coordination mode.

In more strongly coordinating media, **3** partially dissociated the amine; at room temperature in acetone-d_6, about half the complex dissociates to form *cis*-$[Rh(PPh_3)_2(acetone)_2]^+$ (**4**; δ_P 54.19, d, J_{RhP} = 202 Hz)[6] and free amine. The corresponding room-temperature ^1H NMR data support the dissociation reaction, the resonances for **3** being seen at values 0.15−0.30 ppm downfield-shifted from those recorded in CD_2Cl_2.

Complex **3** dissociates similarly in CD_3OD, with the exception that **3** now exists as two different isomers in about a 2:1 ratio. The room-temperature $^{31}P\{^1H\}$ spectrum shows the resonance of *cis*-$[Rh(PPh_3)_2(alcohol)_2]^+$ (δ 57.02 d, J_{RhP} = 207 Hz)[6] and a doublet for each isomer of **3** (δ 46.71 d, J_{RhP} = 211 Hz; δ 47.45 d, J_{RhP} = 212 Hz; ∼2:1); the corresponding ^1H NMR spectrum reveals two sets of upfield-shifted resonances for the η-arene moieties, as well as two upfield-shifted singlets for the amine CH_2 protons (the NH proton of the coordinated amine is not detected because of exchange with the deuterated solvent). For the major isomer, resonances are seen at δ 3.81 (s, 2H, CH_2), 5.21 (t, ^1H, $^3J_{HH}$ = 7 Hz, *p*-(η^6-Ph)), 5.51 (d, 2H, $^3J_{HH}$ = 7 Hz, *o*-(η^6-Ph)), 5.92 (pseudo t, 2H, $^3J_{HH}$ = 7 Hz, *m*-(η^6-Ph)); for the minor isomer "corresponding" resonances are seen at δ 3.33, 5.23, 5.55, and 6.02 with the same splitting patterns and *J* values as for the major isomer. The nature of the second isomer is unclear. The 0.48 ppm difference in the δ(CH_2) resonances suggests that one isomer may coordinate the amine through the benzylic arene; resonance structures of the type shown in eq 2 could be



(2)

involved with the relative contributions of the forms perhaps being dependent on H-bonding interactions

(9) In a solution of $[Rh(H)_2(PPh_3)_2(MeOH)_2]PF_6$ (**2**; 0.074 g, 0.084 mmol) in MeOH (5 mL), a solution of the amine (0.031 g, 0.168 mmol) in MeOH (1 mL) was cannulated under Ar and the resulting deep red solution stirred for 2 h at room temperature. Volume reduction to ∼1 mL afforded a red solid that was collected, washed with Et_2O (3 × 2 mL), and dried in vacuo. Yield: 0.060 g (75%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 46.61 (d, J_{RhP} = 211 Hz). ^1H NMR (CD_2Cl_2): δ 3.83 (d, 2H, CH_2, $^3J_{HH}$ = 5 Hz), 4.08 (t, 1H, N*H*, $^3J_{HH}$ = 5 Hz), 5.09 (t, 1H, *p*-(η^6-Ph), $^3J_{HH}$ = 6 Hz), 5.42 (d, 2H, *o*-(η^6-Ph), $^3J_{HH}$ = 7 Hz), 5.94 (pseudo t, 2H, *m*-($^6\eta$-Ph), $^3J_{HH} \approx$ 6 Hz), 7.15−7.70 (m, 35H, aromatics). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 48.60 (*C*H_2), 90.35 (*o*-η^6-Ph), 91.47 (*p*-η^6-Ph), 104.66 (*m*-η^6-Ph), 115.12 (*ipso*-η^6-Ph). IR (KBr pellet): ν 1567 (C−N, m), 3388 cm^{-1} (N−H, s). Anal. Calcd for $C_{49}H_{43}NP_3F_6Rh$: C, 61.58; H, 4.54; N, 1.47. Found: C, 61.40; H, 4.54; N, 1.65. X-ray-quality crystals were obtained from evaporation of a CH_2Cl_2/hexanes solution of **3**.

(10) Crystal data for **3**: space group $P2_1/c$, a = 13.5394(8) Å, b = 18.4378(7) Å, c = 18.0210(7) Å, β = 104.352(1)°, Z = 4, ρ_c = 1.521 g/cm^3, R = 0.040, R_w = 0.086.

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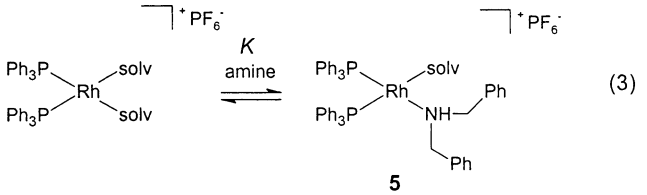
between the NH moiety and MeOH. In the presence of excess amine (2:1), no dissociation of amine from **3** is observed, and **3** is seen as a single isomer (δ 46.71 d, $J_{RhP} = 211$ Hz). Exposure of solutions of **3** to 1 atm H_2 at room temperature gave no hydrogenation of the coordinated arene: **3** in CD_2Cl_2 remains unaltered (cf. eq 1), while in MeOH or acetone, free amine and the respective $[Rh(H)_2(PPh_3)_2(solvent)_2]^+$ (**2**) are the only species detected. The coordinated amine is labile in coordinating media under 1 atm of H_2 but, in the presence of excess amine, **3** is formed under catalysis conditions, and this clearly suppresses catalytic activity (cf. Figure 1).

A quite different interaction with **2** is seen at room temperature under Ar with dibenzylamine, the hydrogenation product of $PhCH_2N{=}CHPh$ (amine:Rh = 2). The NMR data are consistent with the labile equilibrium shown in eq 3, set up after loss of H_2 from **2**. At



(3)

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<243 K, the $^{31}P\{^1H\}$ NMR spectrum is resolved into an AMX eight-line pattern (δ 43.38 dd, $J_{RhP} = 169$ Hz, $^2J_{PP} = 55$ Hz; δ 58.15 dd, $J_{RhP} = 217$ Hz, $^2J_{PP} = 55$ Hz) consistent with the presence of **5**; comparison with literature data[17] leads us to assign the more downfield resonance with the larger J_{RhP} value to the phosphine trans to MeOH and the upfield resonance to that trans to the amine. With an increase of temperature, the equilibrium shifts to the left-hand side and *cis*-$[Rh(PPh_3)_2(CD_3OD)_2]^+$ (δ 57.02 d, $J_{RhP} = 207$ Hz)[6] is fully formed at ~330 K; at intermediate temperatures, broader resonances are seen, and at ~280 K the resonances broaden into the baseline and are nondetectable. The data at 280 K correspond to a K value of ~50 M^{-1}, with **5** having a lifetime of ~3.0×10^{-4} s. The corresponding ^1H NMR spectra reveal a set of two doublets (δ 3.58, 4.01, 2d, $^2J_{HH} = 12$ Hz), indicating inequivalence of the benzylic protons in **5**, and the resonance of the same protons in the free amine (δ 3.79 s, CH_2).

In terms of the catalysis illustrated in Figure 1, the $(PhCH_2)_2NH$ amine generated does not inhibit the hydrogenation; even on complete hydrogenation of $PhCH_2N{=}CHPh$, the concentration of accumulated amine (0.053 M) gives a **5**/$[Rh(PPh_3)_2(MeOH)_2]^+$ value of ~2, and both of these labile species have appropriate solvent sites where the imine substrate could be activated for subsequent hydrogenation. The difference between the amines is the CH_2 "spacer", and this leads to binding through the arene (no spacer) or through the N-atom (spacer). Electronic (versus steric) factors are likely to be more important, with conjugated resonance contributions perhaps favoring arene binding (see eq 2), and also $PhN(H)CH_2Ph$ is a weaker base than $(PhCH_2)_2NH$ as an N-donor. That the corresponding imines both bind to *cis*-$[Rh(PPh_3)_2(solvent)_2]^+$ to form ortho-metalated species of the type $[Rh(H)(PPh_3)_2(RN{=}CH(o\text{-}C_6H_4))(solvent)]^+$ with η^1(N) and η^1(C) bonding (R = Ph, CH_2Ph)[8] tends to rule out steric factors as important in the difference observed in the bonding of the corresponding amines. Inhibition of catalytic hydrogenation of an imine by catalyst poisoning through the amine product was predictable, but binding of the amine via an arene moiety was not.

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Supporting Information Available: Tables giving crystallographic data for **3**, including crystal data and structure refinement details, atomic coordinates, bond distances and angles, and torsion angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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