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Hydrogenation of Benzonitrile to Benzylamine Catalyzed by Ruthenium Hydride Complexes with P−NH−NH−P Tetradentate Ligands: Evidence for a Hydridic−Protonic Outer Sphere Mechanism

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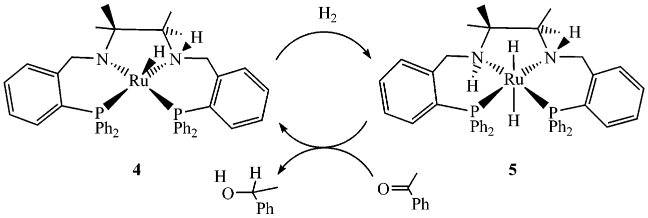
The reaction of $RuHCl(PPh_3)_3$ with the tetradentate ligand $[PPh_2((\textit{ortho}\text{-}C_6H_4)CH_2NHCH_2^{-})]_2$ {eth$P_2(NH)_2$} in THF produces the new complex *trans*-RuHCl{eth$P_2(NH)_2$} (**1**) as a mixture of two isomers. The complex RuHCl{eth$P_2(NH)_2$} (**1**) when activated with KO^tBu/KH is a very active catalyst for the hydrogenation of benzonitrile to benzylamine in toluene, more active than the known catalyst $Ru(H_2)_2H_2(PCy_3)_2$ (**2**). A mixture of **1** and **2** and base also results in efficient conversion of benzonitrile to benzylamine. The complex RuHCl{tme$P_2(NH)_2$} (**3**) where tme$P_2(NH)_2$ is $[PPh_2((\textit{ortho}\text{-}C_6H_4)CH_2NHCMe_2^{-})]_2$ is a less active catalyst for this reaction. These catalyst systems are air sensitive and extremely moisture sensitive. Experimental and theoretical (DFT) evidence is presented for a new mechanism for nitrile hydrogenation: the successive hydrogenation of the CN triple bond and then the CN double bond of the intermediate imine by H^+/H^- transfer from a *trans* dihydride active catalyst. The amido complex RuH{tmeP_2N(NH)} (**4**) has similar activity to **3**/base for the base-free hydrogenation of benzonitrile and is moderately active for the catalytic hydration of benzonitrile. The new complex $RuH(BH_4)$\{eth$P_2(NH)_2$\} (**7**) was prepared by reacting **1** with $NaBH_4$ but is found to be a poor catalyst for nitrile hydration.

Introduction

The hydrogenation of nitriles to primary amines whether catalyzed by heterogeneous[1−4] or homogeneous[5−8] catalysts can result in the formation of side products consisting of imines and secondary and tertiary amines. The side products are the result of reactions of imine intermediates with the product amine. The selectivity to the primary amine can be low for heterogeneous catalysts unless special conditions such as pressures of ammonia[2] or protecting agents are added;[1] nevertheless nitriles are hydrogenated to primary amines on a large scale in industry.[8] In certain cases homogeneous catalysts are very selective (>90%) in producing the primary amine.[1,9−14] The complex $RhH(P^iPr_3)_3$ catalyzes the hydrogenation of benzonitrile exclusively to benzylamine at 23 °C and 5 bar H_2 in THF[13] although the conversion is only 45% due to poisoning of the catalyst by the product unless excess CO_2 is present.[1] The dihydrogen complex $Ru(H_2)_2H_2(PCy_3)_2$ (**2**)[15] was also found to be a catalyst for the hydrogenation of nitriles under mild conditions (see also below).[10] An anionic ruthenium complex[11,12] and a ruthenium amido complex[9] are good catalysts at higher temperatures (80−90 °C) and pressures (6−60 atm). The latter system was proposed to transfer H^+/H^- to the coordinated nitrile (in the inner coordination sphere) to give a coordinated imine that is subsequently hydrogenated to the amine.

Scheme 1. Hydrogenation of Acetophenone Catalyzed by Complexes 4 and 5



The question of inner sphere versus outer sphere reactivity is a topic of great interest.[16,17] The Noyori transfer hydrogenation

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Table 1. Crystallographic Data for RuH(NHCOPh){tmeP$_2$(NH)$_2$} (6) and RuH(BH$_4$){ethP$_2$(NH)$_2$} (7)

	6 (H_2O)	7
formula	$C_{51}H_{55}N_3O_2P_2Ru$	$C_{40}H_{43}BN_2P_2Ru$
fw	904.99	725.59
space group	$P2_1/n$	$P\bar{1}$
T, K	150(2)	150(2)
a, Å	17.693(4)	10.163(2)
b, Å	12.837(3)	15.129(3)
c, Å	20.962(4)	24.273(5)
α, deg	90	99.54(3)
β, deg	112.64(3)	98.42(3)
γ, deg	90	104.56(3)
V, Å^3	4394.1(15)	3492.6(12)
Z	4	4
wavelength, Å	0.71073	0.71073
ρ_{calcd}, mg/m^3	1.368	1.380
R1 (all data)	0.1087	0.1808
wR2	0.1469	0.1328

Table 2. Selected Bond Distances and Angles for RuH(NHCOPh){tmeP$_2$(NH)$_2$} (6)

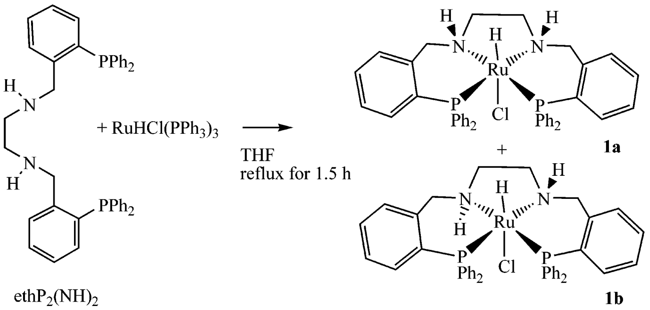
Distances, Å			
Ru(1)−N(3)	2.178(3)	Ru(1)−N(2)	2.179(4)
Ru(1)−N(1)	2.182(4)	Ru(1)−P(1)	2.252(1)
Ru(1)−P(2)	2.255(1)	N(3)−C(45)	1.304(5)
N(2)−C(10)	1.481(6)	N(2)−C(9)	1.526(6)
N(1)−C(7)	1.488(6)	N(1)−C(8)	1.517(6)
C(45)−O(1)	1.269(5)	Ru(1)−H(0)	1.64(4)
Angles, deg			
N(3)−Ru(1)−N(2)	90.2(1)	N(3)−Ru(1)−N(1)	91.1(1)
N(2)−Ru(1)−N(1)	78.3(2)	N(3)−Ru(1)−P(1)	94.34(9)
N(2)−Ru(1)−P(1)	169.5(1)	N(1)−Ru(1)−P(1)	92.1(1)
N(3)−Ru(1)−P(2)	91.86(9)	N(2)−Ru(1)−P(2)	90.5(1)
N(1)−Ru(1)−P(2)	168.4(1)	P(1)−Ru(1)−P(2)	98.89(4)
C(45)−N(3)−Ru(1)	134.4(3)	O(1)−C(45)−N(3)	122.8(4)
O(1)−C(45)−C(46)	117.8(3)	N(3)−C(45)−C(46)	119.4(4)

Table 3. Selected Bond Distances and Angles for RuH(BH$_4$){ethP$_2$(NH)$_2$} (7), Molecule 1

Distances, Å			
Ru(1)−N(2)	2.158(4)	Ru(1)−N(1)	2.170(4)
Ru(1)−P(2)	2.248(2)	Ru(1)−P(1)	2.249(2)
Ru(1)−H(1RU)	1.59(4)	Ru(1)−H(1B)	1.95(5)
H(3B)···H(2C)	2.0		
Angles, deg			
N(2)−Ru(1)−N(1)	80.9(2)	N(2)−Ru(1)−P(2)	90.2(1)
N(1)−Ru(1)−P(2)	169.7(1)	N(2)−Ru(1)−P(1)	170.2(1)
N(1)−Ru(1)−P(1)	89.8(1)	P(2)−Ru(1)−P(1)	98.75(6)
Ru(1)−H(1B)−B(1)	148(4)		

catalyst Ru(η^6-arene)H(NH$_2$CHPhCHPhNHTs) was proposed to add H$^+$/H$^-$ to C═N bonds of imines by the metal−ligand bifunctional outer sphere mechanism.[18] However, the actual hydride acceptor has recently been revealed to be in some cases an iminium C═N bond.[19] Our research group used the outer sphere concept and the RuH···HN motif to find very active ketone and imine H$_2$-hydrogenation catalysts,[20−23] and now one for benzonitrile.

Scheme 2



The complex RuHCl{cyP$_2$(NH)$_2$}, where cyP$_2$(NH)$_2$ is the tetradentate P−NH−NH−P ligand (*R*,*R*)-PPh$_2$(*ortho*-C$_6$H$_4$)CH$_2$-NH−C$_6$H$_{10}$−NHCH$_2$(*ortho*-C$_6$H$_4$)PPh$_2$, is a precursor to a highly active asymmetric ketone hydrogenation catalyst.[24] A *trans* dihydride RuH$_2${cyP$_2$(NH)$_2$} is proposed to transfer hydride from ruthenium and proton from nitrogen to the C═O bond of acetophenone in the second coordination sphere.[24,25] We wondered whether nitriles could be hydrogenated in a similar fashion. Since an enantiopure ligand is not required, we investigated the use of the tetradentate P−NH−NH−P ligands ethP$_2$(NH$_2$) ([PPh$_2$(*ortho*-C$_6$H$_4$)CH$_2$NHCH$_2$−]$_2$)[24] and tmeP$_2$-(NH)$_2$ ([PPh$_2$(*ortho*-C$_6$H$_4$)CH$_2$NHCMe$_2$−]$_2$).[25] The second ligand allows the synthesis of well-defined catalysts for ketone hydrogenation: the crystallographically characterized hydrido amido complex *trans*-RuH{tmeP$_2$N(NH)} (**4**) and the dihydride complex *trans*-RuH$_2${tmeP$_2$(NH)$_2$} (**5**) (Scheme 1). These provide additional information on the nitrile hydrogenation reaction and resulted in the discovery of a nitrile hydration catalyst.

Experimental Section

General. All preparations and manipulations were carried out under hydrogen, nitrogen, or argon atmospheres with the use of standard Schlenk, vacuum line, and glove box techniques in dry, oxygen-free solvents. Tetrahydrofuran (THF), toluene, diethyl ether, and hexanes were dried and distilled from sodium benzophenone ketyl. Deuterated solvents were degassed and dried over activated molecular sieves. Potassium t-butoxide and 2-(diphenylphosphino) benzaldehyde were supplied by the Aldrich Chemical Co. Benzonitrile was purchased in 99% pure, anhydrous form from Aldrich, vacuum distilled under argon, and stored over 4 Å molecular sieves under Ar. Cyclohexene was vacuum distilled under argon and stored over 4 Å molecular sieves under Ar. The complexes RuHCl{tmeP$_2$-(NH)$_2$},[25] RuH{tmeP$_2$N(NH)},[25] Ru(COD)(COT),[26] Ru(H$_2$)$_2$H$_2$-(PCy$_3$)$_2$,[27] and RuHCl(PPh$_3$)$_3$[28] were prepared by the literature methods. The tetradentate ligand ethP$_2$(NH)$_2$ was prepared by the literature method.[29] NMR spectra were recorded on a Varian Unity-500 (500 MHz for ^{1}H), a Varian Unity-400 (400 MHz for ^{1}H), or a Varian Gemini 300 MHz spectrometer (300 MHz for ^{1}H and 121.5 for ^{31}P). All ^{31}P chemical shifts were measured relative to 85% H$_3$PO$_4$ as an external reference. ^{1}H chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. All infrared spectra were obtained on a Nicolet

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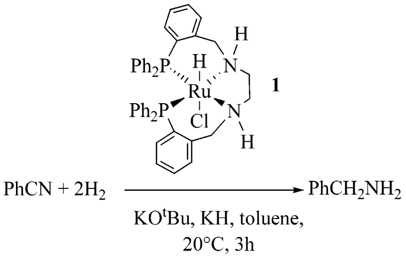
Table 4. Catalytic Hydrogenation of Benzonitrile to Benzylamine[a]

entry	catalyst	base[b]	time (h)	conv (%)
1	**1**	none	18	0
2	**1**	KO^{t}Bu[c]	<18	100
3	**1**	KO^{t}Bu/H$_2$O[d]	18	0
4	**1**	KO^{t}Bu/KH[c,e]	3-6	100
5	**1**	KO^{t}Bu/KH[c,e,f]	3	31
6	KH[d]	KO^{t}Bu[c]	3	0
7	**2**	none	50	95.7
8	**1** + **2**[g]	KO^{t}Bu[c]	3	99.5
9	**3**	KO^{t}Bu	24	10
10	**3** + **2**	KO^{t}Bu	22	99
11	**4**		3	9

[a] 20 °C, 14 atm H$_2$, dry toluene (5 mL), nitrile:Ru = 180:1, [substrate] = 0.18 M, [catalyst] = 1.0 mM. [b] [KO^{t}Bu] = 9 mM. [c] The base is not completely dissolved. [d] 50 mg H$_2$O added. [e] KH (3 mg, 15 mM). [f] With nitrile:cyclohexene:Ru = 180:180:1, only the nitrile is hydrogenated. [g] 0.5 mM of each catalyst, 7 atm H$_2$.

Scheme 3



550 Magna-IR spectrometer. Microanalyses were performed at the University of Toronto.

Synthesis of RuHCl{ethP$_2$(NH)$_2$} (1). RuHCl(PPh$_3$)$_3$ (673 mg, 0.729 mmol) and ethP$_2$(NH)$_2$ (470 mg, 0.772 mmol) were dissolved in THF (12 mL) under a nitrogen atmosphere. The purple solution was refluxed for 1.5 h to give a yellow precipitate. The mixture was filtered and washed with diethyl ether and dried under vacuum to give a yellow powder. The yellow powder was composed of two isomers **1a** and **1b** with different configurations of the nitrogens (yield: 370 mg, 68.1%). Anal. Calcd for C$_{40}$H$_{39}$ClN$_2$P$_2$Ru: C, 64.38; H, 5.27; N, 3.75. Found: C, 63.82; H, 5.58; N, 3.65. ^{1}H NMR (C$_6$D$_6$): δ −17.62 (t, 1H, Ru*H*, $^2J_{HP}$ 23 Hz, **1a**), −18.50 (dd, 1H, Ru*H*, $^2J_{HP}$ 23, 28 Hz, **1b**), 0.88−2.16 (m, 8H, C*H*$_2$, **1a** + **1b**), 2.92−3.34 (m, 8H, HNC*H*$_2$Ph, **1a** + **1b**), 3.51 (m, 1H, N*H*, **1b**), 4.02 (m, 1H, N*H*, **1a**), 4.35 (m, 1H, N*H*, **1b**), 5.49 (m, 1H, N*H*, **1a**), 6.76−7.68 (m, 28H, Ar*H*, **1a**), 6.00−8.25 (m, 28H, Ar*H*, **1b**). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 65.7 (br s, **1a**), 64.26 (d, **1b**), 60.29 (d, $^2J_{PP}$ 26.5 Hz).

Synthesis of RuH(NHCOPh){tmeP$_2$(NH)$_2$} (6). RuH{tmeP$_2$N(NH)} (50 mg, 0.068 mmol), degassed water (50 mg, 3.0 mmol), and benzonitrile (20 mg, 0.20 mmol) were dissolved in THF (3 mL) and refluxed for 3 h under H$_2$. The solvent was removed by vacuum to give a brown residue. Et$_2$O (5 mL) was added to the mixture, and this was stirred overnight to give a yellow precipitate. The mixture was filtered and washed with Et$_2$O (2 mL × 3) and hexane (2 mL × 3) and dried in vacuum to give a yellow solid (41 mg, 68%). A red crystal of RuH(NHCOPh){tmeP$_2$(NH)$_2$} was obtained by the vapor diffusion of hexane into a C$_6$D$_6$ solution of RuH(NHCOPh){tmeP$_2$(NH)$_2$} under Ar after a week. Anal. Calcd for C$_{51}$H$_{53}$N$_3$OP$_2$Ru: C, 69.06; H, 6.02; N, 4.74. Found: C, 69.21; H, 6.35; N, 4.39. ^{1}H NMR (C$_6$D$_6$): δ 10.71 (m, 1H, N*H*···O), 8.60 (t, $^3J_{HH}$ 7 Hz, 2H, Ar*H*), 8.0−6.8 (m, 29H, Ar*H*), 6.03 (t, $^3J_{HH}$ 7.5 Hz, 2H, Ar*H*), 4.81 (s, 1H, N*H*CO), 4.28 (m, 1H, C*H*$_2$), 4.11 (m, 2H, C*H*$_2$), 3.90 (m, 1H, C*H*$_2$), 3.48 (m, 1H, N*H*), 1.28 (s, 3H, C*H*$_3$), 1.20 (s, 3H, C*H*$_3$), 1.10 (s, 3H, C*H*$_3$), 0.83 (s, 3H, C*H*$_3$), −13.66 (dd, 1H, Ru*H*, $^2J_{HP}$ 20.8, 23.6 Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 65.66 (AB), 64.81 (AB, $^2J_{HP}$ = 28.8 Hz). IR (Nujol): 3373 (w, NH), 3284 (w, NH), 1869 (m, RuH), 1590 (m, C═O), 1554 (m, C═N).

Reaction of RuHCl{tmeP$_2$(NH)$_2$} and Ru(H$_2$)$_2$H$_2$(PCy$_3$)$_2$ with KO^{t}Bu, H$_2$, and Benzonitrile. RuHCl{tmeP$_2$(NH)$_2$}[25] (8 mg, 1 × 10^{-2} mmol), Ru(H$_2$)$_2$H$_2$(PCy$_3$)$_2$[27] (7 mg, 1 × 10^{-2} mmol), and KO^t-Bu (2 mg, 2 × 10^{-2} mmol) were mixed in a pressure NMR tube under Ar. C$_6$D$_6$ (1 mL) was added to make a yellow-brown solution. ^{1}H NMR (C$_6$D$_6$) hydride region: δ −5.2 (m, *trans*-Ru(H)$_2${tmeP$_2$(NH)$_2$}[25]), −7.9 (br s, Ru(H$_2$)$_2$H$_2$(PCy$_3$)$_2$), −9.2 (br s, unknown), −12.5 (br s, Ru$_2$H$_6$(PCy$_3$)$_4$[15]), −23.9 (dd, $^2J_{HP}$ 24.9 Hz, RuH{tmeP$_2$N(NH)}[25]). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 58.4 (s, Ru$_2$H$_6$(PCy$_3$)$_4$), 61.1 (d, $^2J_{PP}$ 24.3 Hz, RuH{tmeP$_2$N(NH)}[25]), 65.4 (d, RuH{tmeP$_2$N(NH)}), 76.2 (s, Ru(H$_2$)$_2$H$_2$(PCy$_3$)$_2$), 77.7 (s, Ru(H)$_2${tmeP$_2$(NH)$_2$}). It was then frozen by cooling in liquid N$_2$, H$_2$ gas was added, and the mixture was warmed up to room temperature to give a yellow brown solution. ^{1}H NMR (C$_6$D$_6$) hydride region: δ −5.3 (t, $^2J_{HP}$ 17.7 Hz, Ru(H)$_2${tmeP$_2$(NH)$_2$}), −7.9 (br s, Ru(H$_2$)$_2$H$_2$(PCy$_3$)$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 9.7 (s, PCy$_3$), 76.3 (s, Ru(H$_2$)$_2$H$_2$(PCy$_3$)$_2$), 77.7 (s, Ru(H)$_2${tmeP$_2$(NH)$_2$}). Benzonitrile (25 mg, 0.24 mmol) was added under Ar. After freezing and adding H$_2$ gas, the mixture was warmed up to room temperature. A red solution was obtained after shaking. The mixture was examined by NMR immediately. ^{1}H NMR (C$_6$D$_6$) hydride region: δ −10.9 (t, $^2J_{HP}$ 27.5, Ru(PhCN)$_2$H$_2$(PCy$_3$)$_2$), −13.66 (dd, 1H, Ru*H*, $^2J_{HP}$ 20.8, 23.6 Hz, RuH(PhCONH){tmeP$_2$(NH)$_2$}). ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ: 9.7 (s, PCy$_3$), 42.9 (s, Ru(PhCN)$_2$H$_2$(PCy$_3$)$_2$), 65.66 (AB, RuH(PhCONH){tmeP$_2$(NH)$_2$}), 64.81 (AB, $^2J_{HP}$ 28.8 Hz, RuH(PhCONH){tmeP$_2$(NH)$_2$}).

Synthesis of RuH(BH$_4$){ethP$_2$(NH)$_2$} (7). RuHCl{ethP$_2$(NH)$_2$} (**1**) (75 mg, 0.1 mmol) was suspended in benzene (10 mL). NaBH$_4$ (100 mg, 2.7 mmol) in ethanol (10 mL) was added. A yellow clear solution was formed. The mixture was stirred for 30 min at 65 °C and one additional hour at room temperature. The solvent was evaporated to give a white residue. Benzene (10 mL) was added, and the mixture was stirred for 30 min. A yellow solution was obtained after filtering the mixture through Celite to remove sodium chloride. After evaporation of most of the solvent, hexane (10 mL) was added to give a white precipitate. The mixture was filtered and washed with hexane (1 mL × 3) and dried in vacuum to give a light yellow solid (70 mg, 96.5%). Two isomers **7a** (35%) and **7b** (65%) were observed by NMR. A yellow crystal of RuH(BH$_4$){ethP$_2$(NH)$_2$} was obtained by the vapor diffusion of hexane into a C$_6$D$_6$ solution of **7** under Ar after 3 days. Anal. Calcd for C$_{51}$H$_{53}$N$_3$OP$_2$Ru: C, 69.06; H, 6.02; N, 4.74. Found: C, 69.21; H, 6.35; N, 4.39. ^{1}H NMR (C$_6$D$_6$): δ −14.26 (t, **7a,** Ru*H*, $^2J_{HP}$ 25.8 Hz,), −0.97 (br, B*H*$_4$, **7a**+**7b**), 0.88 (m, 2H, **7a,** C*H*$_2$), 1.95 (m, 2H, **7a** C*H*$_2$), 3.30−3.60 (m, 2H, **7a** HNC*H*$_2$Ph), 3.90 (m, 1H, **7a** N*H*), 4.38 (m, 1H, **7a** N*H*), 5.08 (m, 2H, **7a** HNC*H*$_2$Ph), 6.69−8.15 (m, 56H, Ar*H*, **7a**+**7b**), −15.08 (dd, **7b** Ru*H*, $^2J_{HP}$ 21.8 Hz, 25.6 Hz), 1.22 (m, 1H, **7b** C*H*$_2$), 1.43 (m, 1H, **7b** C*H*$_2$), 2.25 (m, 1H, **7b** C*H*$_2$), 2.38 (m, 1H, **7b** C*H*$_2$), 2.70 (br, 1H, **7b** N*H*), 4.10 (br s, 1H, **7b** N*H*). ^{31}P NMR (C$_6$D$_6$): δ 65.43 (s, **7a**), 66.4 (d, $^2J_{PP}$ 32 Hz, **7b**), 64.7 (d, $^2J_{PP}$ 32 Hz, **7b**).

Catalysis. The toluene utilized for the hydrogenation reactions was dried and distilled over sodium and further stirred with KH under argon for 18 h immediately prior to use. The KH/toluene mixture was then filtered through a Celite plug to remove undissolved solids. The substrates were passed through a plug of alumina immediately prior to use. All catalyst and substrate solutions were prepared in an argon drybox. The atmosphere was tested immediately prior to preparation of catalyst solutions and was found to contain minimal amounts of oxygen and water.

Hydrogenation reactions were done at a constant pressure of 14 atm of H$_2$ gas using a 50 mL Parr hydrogenation reactor. The temperature was maintained at 20 °C using a constant temperature water bath. The Parr reactor was flushed several times with

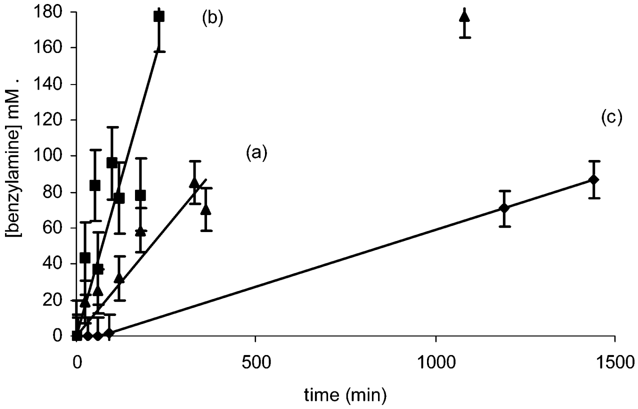


Figure 1. Hydrogenation of benzonitrile in toluene catalyzed by (a) **1**/KO^{t}Bu (entry 2, Table 4); (b) **1**/KO^{t}Bu/KH (entry 4); (c) **2** (entry 7). The error bars reflect the variation in several experiments.

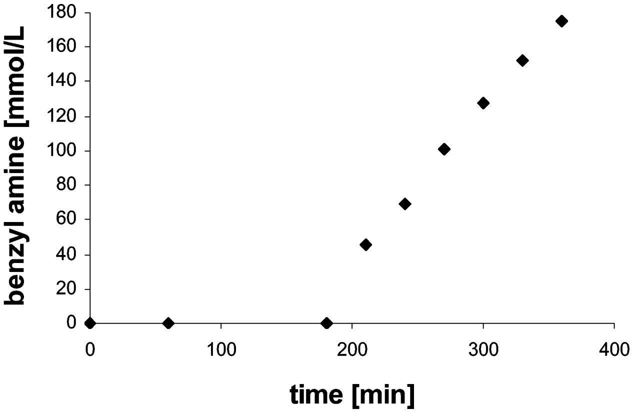
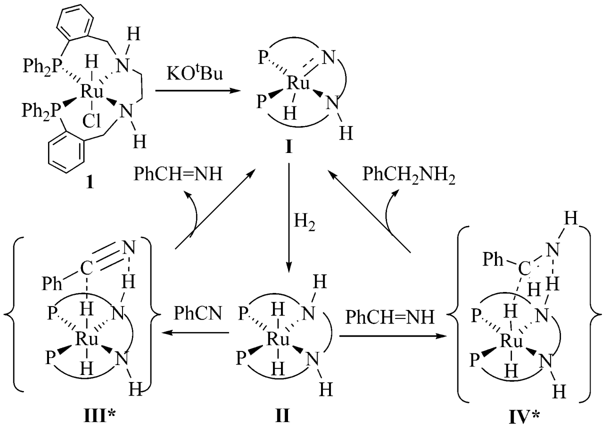


Figure 2. Hydrogenation in toluene (7 atm) of benzonitrile using RuHCl{ethP$_2$(NH)$_2$}/KO^{t}Bu for the first 180 min and then adding Ru(H$_2$)$_2$H$_2$(PCy$_3$)$_2$.

Scheme 4. Proposed Hydrogenation Mechanism[a]



[a] Only the drawing of **1** shows the complete ligand structure.

hydrogen gas at the pre-set pressure prior to adding the components of the reaction mixture. The benzonitrile (103 mg, 1.0 mmol), KO^{t}Bu (5 mg), and KH (3 mg), suspended in toluene (4 mL), were added to the reactor first, followed immediately by a suspension of RuHCl{ethP$_2$(NH)$_2$} (4 mg, 5×10^{-3} mmol) in toluene (1 mL). The ruthenium complex had somewhat variable solubility, possibly due to the presence of the two isomers. Aliquots of the reaction mixture were quickly withdrawn with a syringe under a flow of hydrogen at timed intervals by venting the Parr reactor. Samples were added to CHCl$_3$ in air to destroy the catalyst and terminate the reaction. Concentrations of benzonitrile and benzyl amine were determined by gas chromatography with a Chrompack capillary column (Chirasil-Dex CB 25 m*0.25 mm) and H$_2$ as carrier gas at a column pressure of 6 psi, an oven temperature of 110 °C, an injector temperature of 250 °C, and an FID at 275 °C. The retention times for benzonitrile and benzylamine are 4.2 and 5.5 min, respectively.

X-ray Diffraction Structure Determination of RuH(NHCOPh){tmeP$_2$(NH)$_2$} (6) and RuH(BH$_4$){ethP$_2$(NH)$_2$} (7). Crystals suitable for X-ray diffraction were obtained by vapor diffusion. Data were collected on a Nonius Kappa-CCD diffractometer using Mo K radiation (λ 0.71073 Å). The CCD data were integrated and scaled using the DENZO-SMN software package, and the structure was solved and refined using SHELXTL V6.0. The crystallographic data are listed in Table 1 and selected bond distances and angles in Tables 2 and 3. The hydrides were located and refined with isotropic thermal parameters.

Hydration of Benzonitrile Catalyzed by RuH{tmeP$_2$N(NH)} or RuH(BH$_4$){enP$_2$(NH)$_2$}. RuH{tmeP$_2$N(NH)} or RuH(BH$_4$){enP$_2$(NH)$_2$} (4 mg, 0.005 mmol), degassed water (180 mg, 10 mmol), and benzonitrile (100 mg, 1.0 mmol) were mixed in acetone-d_6 (1 mL). The mixtures were heated at 80 °C. The conversion to benzamide was determined by ^{1}H NMR spectroscopy.

Computation. All calculations were performed using Gaussian03.[30] The calculations were done on a workstation with two 2.8 GHz Opteron X2 with 4 GB of RAM and Red Hat Linux Enterprise Edition. All calculations used the rMPW1PW91 density functional method. Ruthenium was treated with the SDD basis set to include relativistic effects and an effective core potential, and H, C, N, and P were treated with the triple-ζ basis set 6-311++G** which includes diffuse functionals and additional p orbitals on H as well as additional d orbitals on C, N, and P. The structures were optimized in the gas phase at 1 atm of pressure and 298 K. Full vibrational analyses were performed on the optimized structure to obtain values of ΔH, ΔG, and ΔS. The QST2 or QST3 method was utilized to locate transition states. All transition states were found to have one imaginary frequency. IRC calculations were used to show that the reactants led to the products via these transition states.

Solvation by toluene was modeled using the polarized continuum model (PCM). Single point energy calculations were performed on the gas-phase optimized structures. The following modifications to the PCM model were used: the bondi radii were used to specify explicit hydrogen atoms, and "scfvac" was added to calculate $\Delta G_{\text{solvation}}$. The default solvent parameters included in Gaussian03 were used for toluene.

The initial DFT studies utilized the simple models for the catalysts, RuH(NHCH$_2$CH$_2$NH$_2$)(PH$_3$)$_2$ and RuH$_2$(en)(PH$_3$)$_2$. These results were then extended to a more complete model of the catalysts. Here tetradentate ligands were employed with PPh$_2$ groups replaced by PH$_2$ groups, i.e., RuH(PH$_2$C$_6$H$_4$CH$_2$NCH$_2$−CH$_2$-NHC$_6$H$_4$PH$_2$) **A** and *trans*-RuH$_2$({PH$_2$C$_6$H$_4$CH$_2$NHCH$_2$−}$_2$) **B**. Acetonitrile was used to model benzonitrile to reduce the size of the calculation.

Results

Preparation of *trans*-RuHCl{ethP$_2$(NH)$_2$} (1). This complex is prepared in 68% yield as a yellow powder by reacting RuHCl(PPh$_3$)$_3$ with the tetradentate ligand ethP$_2$(NH)$_2$,[24] by the same method used for making RuHCl{cyP$_2$(NH)$_2$} (Scheme 2).[24]

The ^{1}H and ^{31}P NMR spectra of RuHCl{ethP$_2$(NH)$_2$} (**1**) signal the presence of two isomers **1a** and **1b** that are very similar to those of the reported complex RuHCl{tmeP$_2$(NH)$_2$} (**3a** and **3b**).[25] Isomer **1a** exhibits a broad peak at 65.7 ppm in

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[30] Frisch, M. J., et al. *Gaussian 03*, revision D.01; 2003. See the Supporting Information for the complete author list.

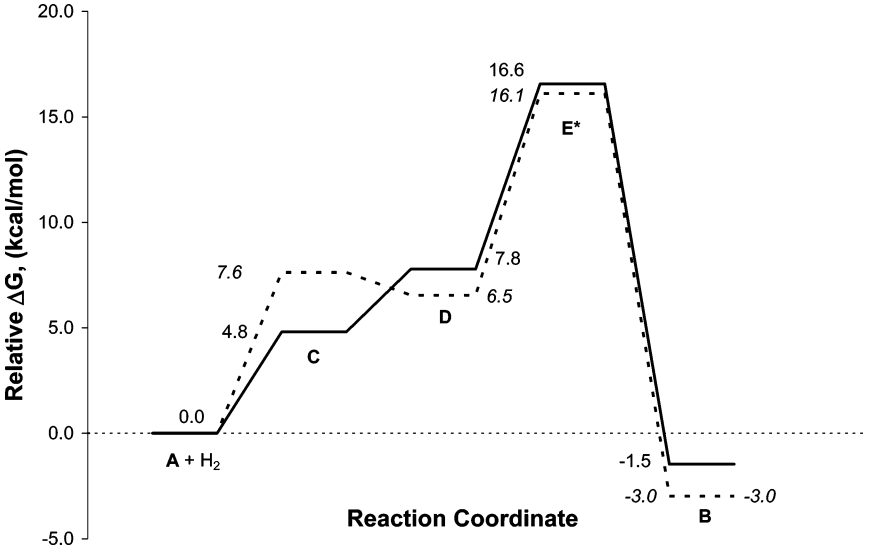


Figure 3. Reaction coordinate diagram (free energies at 298 K) for the reaction of the amido complex **A** with dihydrogen in the gas phase (—) and with toluene solvation (···).

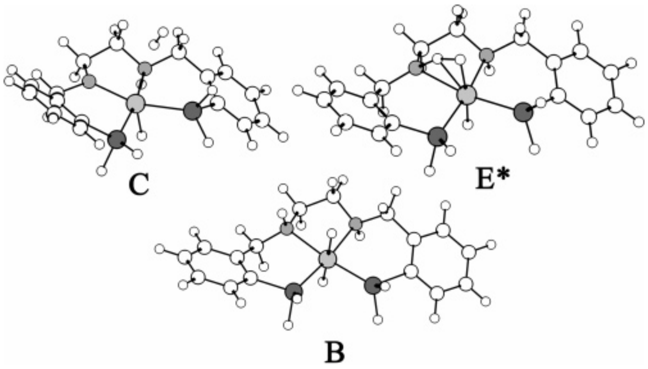


Figure 4. Calculated structures of the end-on dihydrogen adduct **C** (Ru···H 3.48; H−H 0.74, Ru−N(amido) 2.01 Å), the transition state for the heterolytic splitting of H_2 **E*** (Ru···H 1.80, H···H 1.02, H···N 1.40, Ru−N(amido) 2.17 Å), and the dihydride product **B** (Ru−H 1.69, H···H 2.48, H···N 1.02, Ru−N 2.18 Å).

the $^{31}P\{^1H\}$ NMR spectrum and a triplet for the hydride at −17.6 ppm in the ^1H NMR. This spectrum is very similar to that of the crystallographically characterized isomer **3a** which has two NH hydrogen atoms *syn* to the hydride ligand. Isomer **1b** exhibits two doublets at 64.26 and 60.29 ppm in the ^{31}P NMR spectrum and a doublet of doublets for the hydride at −18.50 ppm with P−H coupling constants ($^2J_{HP}$ 23, 28 Hz) appropriate for mutually *cis* hydride and phosphorus nuclei. This spectrum is similar to that of **3b**, so therefore isomer **1b**, like **3b**, is proposed to have one NH hydrogen *syn* to the chloride and the other NH *syn* to the hydride.

Hydrogenation of Benzonitrile. Table 4 outlines the development of the catalytic system with **1** (Scheme 3) and a comparison to the known homogeneous catalyst **2**. Complex **1** in toluene under 14 atm H_2 at 20 °C is not a catalyst for PhCN hydrogenation (entry 1, Table 4). However, when activated with KO^{t}Bu under these conditions, it becomes an active catalyst for the selective hydrogenation of benzonitrile to benzylamine (Table 4, entry 2; Figure 1). There is no conversion when wet benzonitrile (entry 3) or wet toluene solvent is used or when isopropanol is used as the solvent. The addition of potassium hydride to remove traces of water improved the rate of conversion (entry 4; Figure 1), making this a very active catalyst for benzonitrile hydrogenation. The base is not completely dissolved, and the rate is somewhat variable. The selectivity to the primary amine is >99% under these conditions. The catalyst only hydrogenates the nitrile in a nitrile/cyclohexene mixture (entry 5). Without **1** there is no hydrogenation (entry 6). The **1**/base combination is more active and selective[9] than the known catalyst **2** at 20 °C (entry 7). However, the system with **1** does not hydrogenate acetonitrile, presumably because of the acidity of its CH bonds.

When a combination of the bis dihydrogen complex $Ru(H_2)_2H_2(PCy_3)_2$ (**2**) and complex **1** in 1:1 ratio is used as a catalyst for the hydrogenation of benzonitrile in benzene at the lower pressure of 7 atm H_2 pressure, the conversion reaches 99.5% in 3 h (Table 4, entry 8). Complex **1** with base is not active at 7 atm H_2, but when **2** is added, the hydrogenation proceeds rapidly (Figure 2), at a rate much greater than that of **1** or **2** alone. In the absence of **1**, complex **2** has an induction period of about 90 min before the hydrogenation of substrate starts. This induction period is not affected by the presence of KO^{t}Bu or benzylamine product. Therefore, there seems to be a synergic effect of the combination of **1** and **2** on the rate of hydrogenation.

Catalytic Hydrogenation of Benzonitrile with a Combination of $Ru(H_2)_2H_2(PCy_3)_2$ and RuHCl{tmeP$_2$(NH)$_2$} or RuH{tmeP$_2$N(NH)}. Complex **3** with the methylated diamine backbone is a less active catalyst for nitrile hydrogenation (entry 9, Table 4). The combination of $Ru(H_2)_2H_2(PCy_3)_2$ and RuHCl{tmeP$_2$(NH)$_2$} with base is more active, with a conversion of 99% after 22 h (entry 10). The rates of these reactions are less than those involving **1**, presumably because the bulky methylated backbone of **3** interferes with catalysis.

To eliminate the influence of base and to simplify the system, the hydridoamido complex RuH{tmeP$_2$N(NH)}[25] (**4**) was also tested for benzonitrile hydrogenation. There is 9% conversion after 3 h (Table 4, entry 11), comparable with the result for complex **3** with base (Table 4, entry 9).

In order to better understand the mechanism of the combined catalysts for the hydrogenation of benzonitrile, a reaction was carried out in a pressure NMR tube. The known compounds RuHCl{tmeP$_2$(NH)$_2$},[25] $Ru(H_2)_2H_2(PCy_3)_2$,[27] and KO^{t}Bu in a molar ratio of 1:1.1:1.8 were mixed under Ar in C_6D_6 to produce a red solution. The known compounds RuH{tmeP$_2$(N(NH)} (**4**), *trans*-RuH$_2${tmeP$_2$(NH)$_2$} (**5**),[25] the dimeric species $Ru_2H_6(PCy_3)_4$,[15] and $Ru(H_2)_2H_2(PCy_3)_2$ are detected by ^1H and ^{31}P

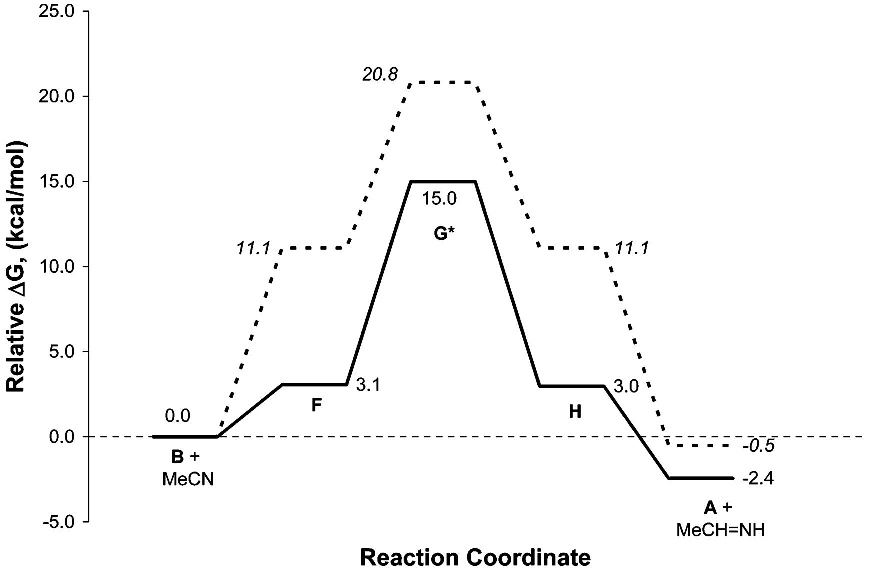


Figure 5. Reaction of acetonitrile with the *trans*-dihydride complex **B** via the hydrogen-bonded nitrile adduct **F** and the transition state **G*** to give the amido complex **A** plus imine via the hydrogen-bonded imine adduct **H**. The solid line refers to free energies at 298 K for the system in the gas phase, and the dotted line, for the system with toluene solvation.

NMR. This observation is explained by the transfer of dihydrogen from the dihydrogen complex **2** to the amido complex **4** to produce the dihydride **5** and the dimer. Then, this red solution was reacted with hydrogen to give a yellow-brown solution containing only **5** and **2** and some free PCy_3. Therefore, the synergetic effect might, in part, result from complex **2** supplying dihydrogen rapidly to **4** so that the active dihydride **5** can form. However, theory predicts that the activation of dihydrogen by **4** is not the turnover limiting step, and so there may be another, as yet unidentified, explanation for this synergic effect. The addition of benzonitrile led to a dark red solution with benzylamine formation and the formation of the complex $RuH(PhCONH)\{tmeP_2(NH)_2\}$ (**6**), resulting from the reaction of the complex **4** or **5** with benzonitrile and traces of water (see below).

Mechanism of Hydrogenation. Conventional mechanisms of nitrile hydrogenation involve hydride migration to a κ^1-N σ-bonded or κ^2-NC π-bonded NCPh ligand.[5,9] The high activity and selectivity of the catalyst system **1**/base point to a different mechanism: the successive hydrogenation of the CN triple bond and then the CN double bond in outer sphere reactions (Scheme 4). The cycle is entered via the reaction of complex **1** with base to produce the hydridoamido complex **I**. Heterolytic splitting of dihydrogen across the ruthenium amido bond generates catalyst **II** as in the ketone hydrogenation mechanism. A possible, new step is the outer sphere transfer of hydride from ruthenium and proton from nitrogen to the nitrile CN bond on going from **II** to the unstable imine intermediate PhCH═NH and **I** via transition state **III***. The imine intermediate must then be immediately hydrogenated in a similar H^-/H^+ transfer via transition state **IV*** (an HOL mechanism[23]) to account for the high selectivity of the catalyst. The high hydrogenation activity of the dihydride species with a coordinatively saturated and 18 electron ruthenium(II) center is more consistent with an outer sphere mechanism than an inner sphere one where a donor of the tetradentate ligand would have to dissociate to allow the nitrile to coordinate to the metal and be attacked by the hydride. In keeping with this idea, the C═C bond of cyclohexene is not hydrogenated under these conditions.

Catalysts **I** and **II** have not yet been directly observed for the $ethP_2(NH)_2$ ligand system but are well characterized for the $tmeP_2(NH)_2$ system. The complexes **4** and **5** with the latter ligand are also nitrile hydrogenation catalysts, although they are much less active than **1**/base, giving 9% conversion after 3 h (entry 11, Table 4) and 16% after 18 h. They are also much less active ketone hydrogenation catalysts than ones with the $cyP_2(NH)_2$ ligands, presumably because of steric interference in the catalytic process by the methyl groups in the backbone of the $tmeP_2(NH)_2$ ligand.[25] An alternative mechanism might involve anionic hydride complexes as has been proposed for ruthenium triphenylphosphine systems.[11,12] However, we have no NMR evidence for such species.

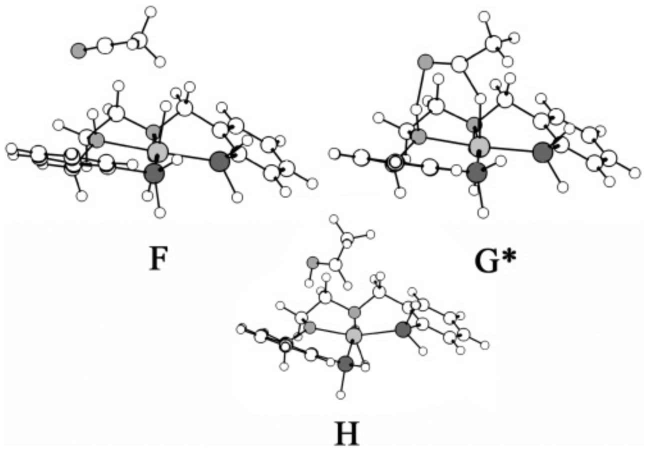


Figure 6. Calculated structures of the hydrogen-bonded imine adduct (**F**, C−N(nitrile) 1.15, N(nitrile)···H 2.31, H−N(amine) 1.01; Ru−N(amine) 2.19, Ru−H 1.70, H(hydride)···C(nitrile) 3.15 Å, C−C−N(nitrile) 178°), the transition state for outer sphere transfer of hydride from Ru and proton from amine (**G***; dimensions of the 6-membered RuHCNHN ring: Ru−H 1.78, H···C 1.50, C−N 1.19, N(nitrile)···H 1.78, H−N(amine) 1.05, N(amine)−Ru 2.14 Å, C−C−N 142°), and the adduct of the newly born imine with the amido complex **A** (**H**, Ru···HC 3.1, H−C 1.10, C−N 1.27, N−H 1.02, H(imine)···N(amido) 2.24, N(amido)−Ru 2.02 Å, C−C−N 123°).

DFT Calculations. Scheme 4 is supported by DFT calculations[30] using the MPW1PW91 functional on the simplified complexes $RuH(PH_2C_6H_4CH_2NCH_2{-}CH_2NHC_6H_4PH_2)$ **A** and *trans*-$RuH_2(\{PH_2C_6H_4CH_2NHCH_2{-}\}_2)$ **B** as models for the

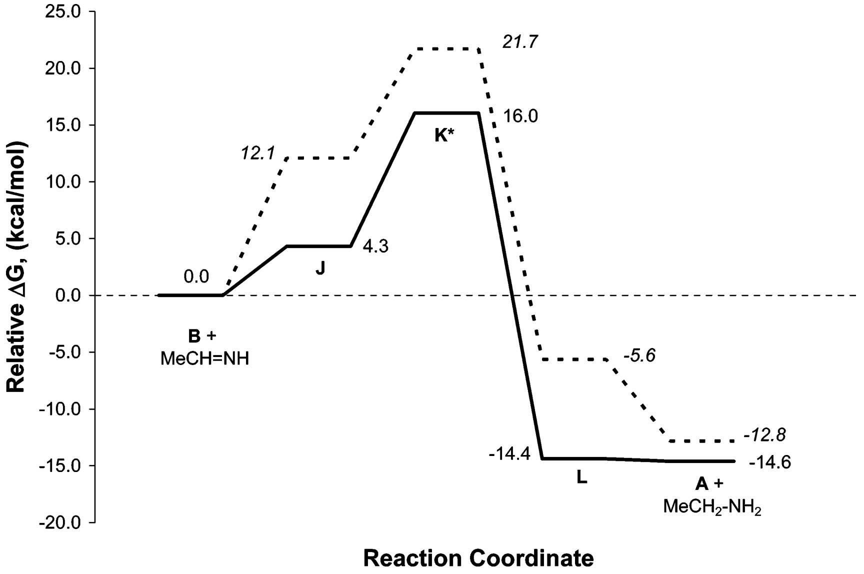


Figure 7. Reaction of the imine MeCH═NH with the *trans*-dihydride complex **B** via the hydrogen-bonded imine adduct **J** and the transition state **K*** to give the amido complex **A** plus the amine $MeCH_2NH_2$ via the hydrogen-bonded amine adduct **L**. The solid line refers to free energies at 298 K for the system in the gas phase, and the dotted line, for the system with toluene solvation.

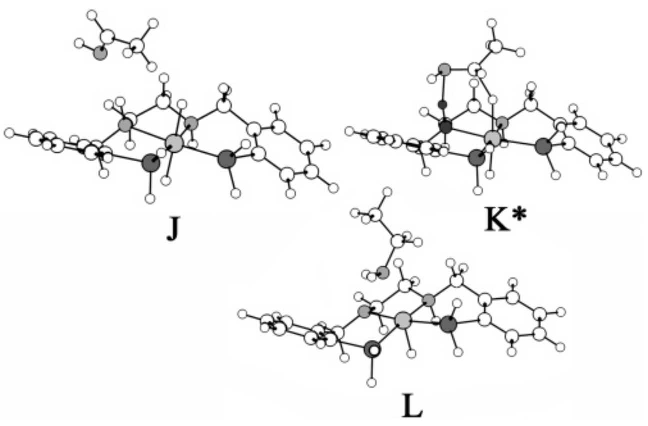
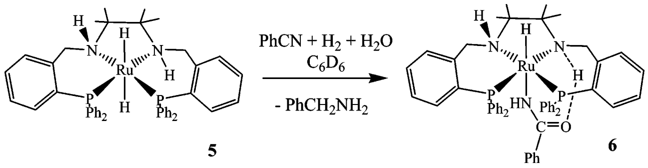


Figure 8. Calculated structures of the hydrogen-bonded imine adduct (**J**, C−N(imine) 1.27, N(imine)···H(amine) 2.10, H−N(amine) 1.02; Ru−N(amine) 2.19, Ru−H 1.69, H(hydride)···C(imine) 4.0 Å), the transition state for outer sphere transfer of hydride from Ru and proton from amine (**K***; dimensions of the 6-membered RuHCNHN ring: Ru−H 1.77, H..C 1.57, C−N 1.32, N···H 1.74, H−N 1.06, N−Ru 2.14 Å), and the adduct of the newly born amine with the amido complex **A** (**L**, Ru···N(amine product) 2.32, N(amido)−Ru 2.12 Å).

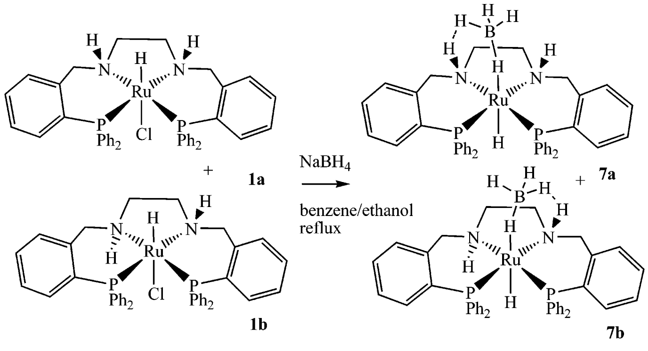
amido catalyst **I** and the dihydride catalyst **II**, respectively, of Scheme 4 and CH_3CN as a substitute for benzonitrile. It is unlikely that this substitition will greatly change the energetics of polar bond hydrogenation. The reason that acetonitrile is not hydrogenated by our catalyst system is due to the reactivity of the C−H bonds of the acetonitrile (work in progress) in a side reaction that poisons the catalyst, not because of a much higher hydrogenation activation energy for acetonitrile than benzonitrile.

The gas-phase and toluene-phase free energies and structures of the species in each step of the reaction are plotted in Figures 3−8. Calculations utilizing the even more simplified models $RuH(PH_3)_2(HNCH_2CH_2NH_2)$ and *trans*-$RuH_2(PH_3)_2$(en) give very similar results. The geometry calculated for the structure **A** (Ru−N(amido) 2.01, Ru−N(amine) 2.18, Ru−H 1.57, Ru−P(*trans* to amido) 2.24, Ru−P(*trans* to amine) 2.22 Å) matches

Scheme 5



Scheme 6



well the observed structure of RuH{$tmeP_2N(NH)$}[25] (Ru−N(amido) 2.001(2), Ru−N(amine) 2.164(2), Ru−H 1.54(3), Ru−P(*trans* to amido) 2.2495(7), Ru−P(*trans* to amine) 2.2303(7) Å). Similarly, that of **B** (Ru−N(amine) 2.18, Ru−H 1.69, Ru−P 2.21 Å) agrees with the observed structure *trans*-RuH_2{$tmeP_2(NH)_2$}[25] (Ru−N(amine) 2.196(2) and 2.182(2), Ru−H 1.6, Ru−P 2.2265(6) and 2.2205(6) Å).

Each of the three steps in the catalytic cycle of Scheme 4, dihydrogen splitting, nitrile hydrogenation, and imine hydrogenation, have similar free energies of activation (15−17 kcal/mol) in the gas phase. When solvation is included by use of the PCM model, the nitrile and imine hydrogenation steps have activation free energies of 21−22 kcal/mol, higher than that of the H_2 splitting reaction at 16 kcal/mol. Therefore, the substrate hydrogenation steps are predicted to be the rate-limiting steps. This contrasts with the hydrogenation of ketones where the H_2

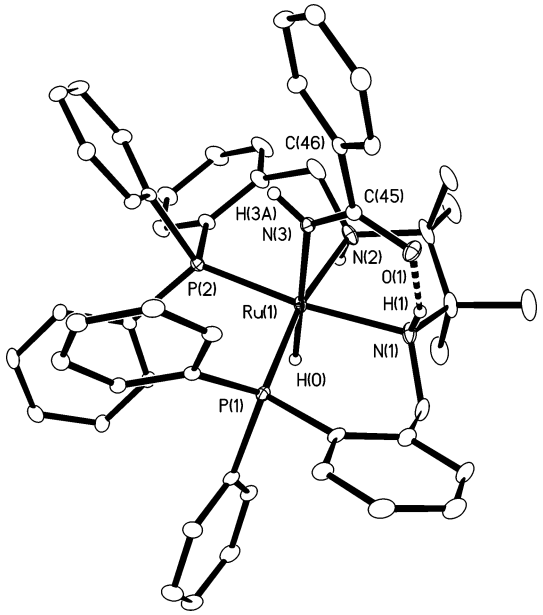


Figure 9. Molecular structure of RuH(NHCOPh){tmeP$_2$(NH)$_2$} (**6**).

splitting step is turn-over limiting.[31] Overall, the hydrogenation of acetonitrile to the ethylamine is calculated to be exothermic by 20 kcal/mol in the gas phase and 19 kcal/mol in solution.

In the H_2 splitting step of Scheme 4 (Figures 3 and 4), the amido complex **A** reacts with dihydrogen to give successively more unstable adducts, first end-on (**C**) (Figure 4) and then side-on (**D**, Ru−H 1.83, H−H 0.81, Ru−N(amido) 2.12 Å). The transition state **E*** lies 16 kcal/mol ($\Delta G^{\ddagger}$) above the reactants with or without solvation by toluene. The $\Delta H^{\ddagger}$ value is 7.0 kcal/mol. This agrees with the experimental values of 14.5 and 7.6, respectively, for the complex RuH(NHCMe$_2$CMe$_2$NH$_2$)(PPh$_3$)$_2$.[31] This transition state has an imaginary vibrational mode (1248.43*i* cm^{-1}) that involves the heterolytic splitting of the H−H bond toward producing the aminedihydride complex **B**. The heterolytic splitting of dihydrogen using the simplified models RuH(PH$_3$)$_2$(HNCH$_2$CH$_2$NH$_2$) and *trans*-RuH$_2$(PH$_3$)$_2$(en) has already been thoroughly investigated using the B3LYP functional with comparable results.[31,32]

The reaction of acetonitrile with the dihydride catalyst **B** involves three steps (Figures 5 and 6). First, a hydrogen-bonded nitrile adduct is formed (**F**). Then in a novel, concerted process, the hydride from ruthenium and proton from an amine hydrogen of the ligand are transferred to the nitrile triple bond in the outer coordination sphere of the metal via transition state **G*** (this corresponds to **III*** in Scheme 4). The transition state **G*** lies 15 ($\Delta G^{\ddagger}$, gas phase) or 21 ($\Delta G^{\ddagger}$, toluene) kcal/mol above the reactants. An animation of the vibrational mode with the imaginary frequency (290*i* cm^{-1}) shows the carbon and nitrogen of the CN bond moving toward the hydride and proton, respectively, while the carbon of the CN bond moves to accept the hydride. This produces the hydrogen-bonded imine adduct **H**.

In a set of steps similar to that of nitrile hydrogenation, the imine MeCH=NH reacts with dihydride **B** to produce the amine product MeCH$_2$NH$_2$ and regenerate the amido catalyst **A** (Figures 7 and 8). The transition state **K*** (437*i* cm^{-1}) lies 16 ($\Delta G^{\ddagger}$ gas phase) or 22 kcal/mol ($\Delta G^{\ddagger}$ toluene) above the reactants. This corresponds to transition state **IV*** in Scheme 4. Yamakawa and co-workers proposed a similar transition state for the hydrogenation of CH$_2$=NH by Ru(C$_6$H$_6$)H(NH$_2$CH$_2$CH$_2$O)[33] at 9.8 kcal/mol above reactants, but we are not aware of a report about the outer sphere hydrogenation of a nitrile.

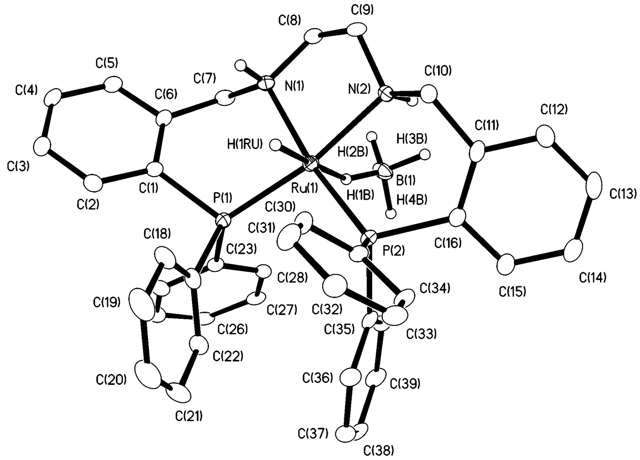
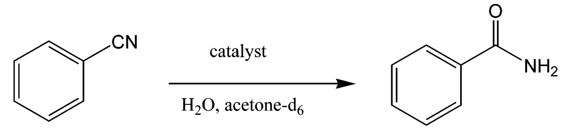


Figure 10. Molecular structure of RuH(BH$_4$){enP$_2$(NH)$_2$} (**7**, isomer b).

Scheme 7



Poisoning of the Catalyst by Water. As indicated above, an NMR scale reaction of dihydrido complex **5** with hydrogen and benzonitrile led to the formation of the amidato complex **6** along with benzylamine (Scheme 5). Complex **6** can also be prepared by the reaction of the amido complex **4** with water and benzonitrile.

Complex **6** was isolated as a yellow powder, crystallized, and characterized by X-ray crystallography (Figure 9). The ruthenium is octahedral with the hydride ligand situated *trans* to a benzamidate ligand. There is a strong intramolecular hydrogen bond (H(1)−O(1) 2.1 Å) between the amide and the amine group of the tetradentate ligand defining a six member ring of Ru(1)−N(3)−C(45)−O(1)−H(1)−N(1). The short C(45)−N(3) distance of 1.304(5) Å is consistent with some double bond character. A preliminary crystal structure of the complex RuH(NHCOPh){ethP$_2$(NH)$_2$} showed the same similar features. Neither this complex nor complex **6** is an active catalyst for nitrile hydrogenation, and so they represent poisoned catalyst structures. The complex RuTp(PPh$_3$)(H$_2$O)(NHC(O)CH$_3$)[34] has an acetoamido ligand in a six member Ru−N−C−O−H−O ring involving a *cis* aqua ligand; the bond distances are very similar to those of **6**. The former complex is prepared by the reaction of the hydrido nitrile complex RuTp(PPh$_3$)H(NCCH$_3$) with water. The hydride that is *cis* to the nitrile is thought to assist in activating the water.

Complex **6** exhibits a doublet of doublets at 10.71 ppm in the ^{1}H NMR spectrum for the NH involved in the hydrogen

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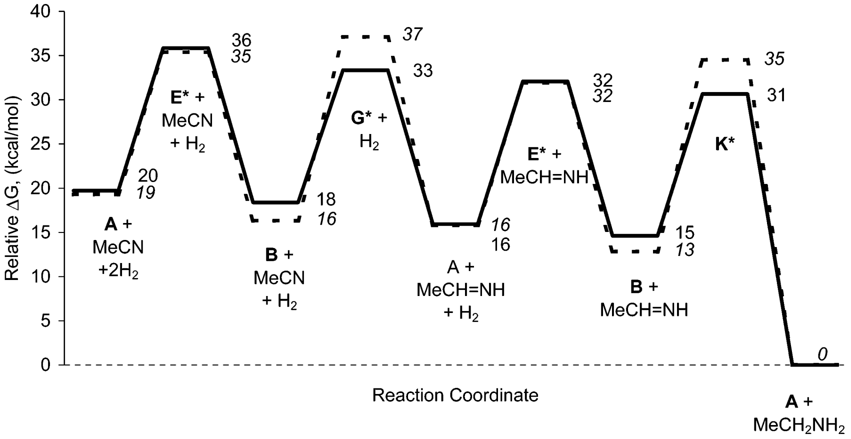

Figure 11. Reaction coordinate diagram for the hydrogenation of acetonitrile to ethylamine catalyzed by the model complex $RuH(PH_2C_6H_4-CH_2NCH_2CH_2NHC_6H_4PH_2)$. The solid line refers to free energies of the system at 298 K while the dotted line refers to that with toluene solvation.

Table 5. Hydration of Benzonitrile in Acetone-d_6

catalyst	[cat.] (M)	[sub] (M)	[H_2O] (M)	*T* (°C)	*t* (h)	conv %
RuH{tmeP_2N(NH)}	5×10^{-3}	1.1	10	80	40	25
$RuHBH_4${eth$P_2(NH)_2$}	5×10^{-3}	1.0	10	80	44	7
KOH	5×10^{-3}	1.1	10	80	44	7

bond with the amide, a singlet at 4.81 ppm for the proton of the NH group of the amide, a multiplet at 3.48 ppm for the other NH, and a doublet of doublets at −13.66 ppm for the Ru−H. There is an AB pattern at 65.66 and 64.81 ppm in the $^{31}P\{^1H\}$ NMR spectrum. The IR absorptions at 1590 cm^{-1} (m) and 1554 cm^{-1} (m) are similar to those of a Pt amide complex reported by Maresca et al.[35] while the complex $RuTp(PPh_3)(H_2O)(NHC(O)CH_3)$ displays a carbonyl absorption at 1540 cm^{-1}.[34]

Preparation and Structure of $RuH(BH_4)$\{eth$P_2(NH)_2$\} (7). The identification of the structure of complex **6** suggested to us the possibility that such ruthenium complexes could serve as catalysts for the hydration of benzonitrile to benzamide. Since KOH or KO^tBu/H_2O will catalyze the hydration of benzonitrile, we sought ruthenium catalysts that would operate under base-free conditions. $RuH(BH_4)$(binap)(diamine) was prepared by Ohkuma et al. as a catalyst for hydrogenation of simple ketones under base-free conditions,[36] and we have used similar complexes $RuH(BH_4)$(binap)(P-nor) for base-free tandem asymmetric Michael addition−hydrogenation[37] and complexes $RuH(BH_4)$(binop)(diamine) for this base-free tandem reaction as well as for asymmetric transfer hydrogenation reactions.[38] A suspension of complex **1** in benzene was heated at 65 °C with an excess of $NaBH_4$ in ethanol. The light yellow complex *trans*-$RuH(BH_4)$\{eth$P_2(NH)_2$\} (**7**) is obtained in 96% yield as a mixture of isomers (Scheme 6). The structure of one enantiomer of **7b** as determined by X-ray crystallography is shown in Figure 10. There are two enantiomers in the unit cell. One has the *R*, *R* configuration at the stereogenic nitrogen atoms while the other (Figure 10) has the *S*, *S* configuration. The boron hydride accepts a dihydrogen bond[39,40] from one NH with an H···H distance of about 2.0 Å.

The two isomers in benzene-d_6 solution are in a ratio of **7a**:**7b** = 1:2 according to the NMR spectra. The NMR patterns are very similar to those of isomers **1a** and **1b**. Therefore, we assign isomer **7a** to a structure in which the N−H hydrogens are both syn to the hydride. This has a triplet at −14.26 ppm with a coupling constant $^2J_{HP}$ = 25.8 Hz in the ^1H NMR spectrum and a singlet at 65.43 ppm in the $^{31}P\{^1H\}$ NMR spectrum. Isomer **7b** gives a doublet of doublets at −15.08 ppm ($^2J_{HP}$ = 21.8 Hz, 25.6 Hz) in the ^1H NMR spectrum and two doublets at 66.4 and 64.7 ppm ($^2J_{PP}$ = 32 Hz) in the $^{31}P\{^1H\}$ NMR spectrum. The BH_4^- moiety gives a broad signal at −0.97 ppm in the ^1H NMR, very similar to the resonance of $RuH(BH_4)$(binap)(1,2-diamine) complexes.[36]

Nitrile Hydration. Complexes **4** and $RuH(BH_4)$\{eth$P_2(NH)_2$\} were tested as nitrile hydration catalysts (Scheme 7, Table 5). Complex **4** is a moderately active catalyst at 80 °C in comparison to others reported in the literature.[41−49] It produced more benzamide than that observed for the control reaction using a similar concentration of KOH as the catalyst. However, it deactivated over time so that the complete conversion was not obtained. The complex $RuH(BH_4)$\{eth$P_2(NH)_2$\} gave a similar conversion to KOH and is a poor catalyst.

Conclusions

In the presence of base, the complexes RuHCl\{eth$P_2(NH)_2$\} (**1**) and RuHCl\{tme$P_2(NH)_2$\} (**3**) are active in the catalytic hydrogenation at 14 atm H_2 of benzonitrile to benzylamine, with **1** being more active than **3**, probably for steric reasons. The dihydrogen complex $Ru(H_2)_2H_2(PCy_3)_2$, **2**, has a synergic effect when mixed with **1** or **3** and base, making an even more active system. The complexes with tetradentate ligand systems are extremely moisture sensitive in the presence of KO^tBu and

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PhCN and form stable benzamide complexes such as RuH(NHCOPh){tme$P_2(NH)_2$}. When KH is used to remove the trace amount of water in the catalytic hydrogenation of benzonitrile with RuHCl{eth$P_2(NH)_2$} and base, the hydrogenation is particularly rapid and selective. A mechanism is proposed that involves the successive outer sphere transfer of dihydrogen first to the CN triple bond and then to the CN double bond. This is the first demonstration that nitrile hydrogenation can proceed via an outer sphere mechanism. The overall theoretical reaction coordinate diagram (Figure 11) predicts that the activation energy for the dihydrogen splitting will be similar to that of nitrile hydrogenation and imine hydrogenation in the gas phase while the predicted activation energies for the outer sphere hydrogenation steps are greater than H_2 splitting when solvation is taken into account. There are difficulties in conducting kinetic runs that prevent the testing of these conclusions for the present system. Future experimental and theoretical work will probe reactions of the amido complex **4** with the acidic C−H bonds of acetonitrile in order to explain the catalyst poisoning by this substrate.

The complex RuH{tmeP_2N(NH)} (**4**) is a poorly active base-free nitrile hydrogenation catalyst and moderately active hydration catalyst while the borohydride complex is not active. Limitations of our catalyst systems for nitrile hydrogenation to be overcome are their high water and oxygen sensitivity and their intolerance to nitriles with acidic groups.

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Supporting Information Available: X-ray crystallographic files for complexes **6** and **7**. Details of the DFT calculations and the complete ref 30. This material is available free of charge via the Internet at http://pubs.acs.org.

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