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Chemistry of Ruthenium(II) Monohydride and Dihydride Complexes Containing Pyridyl Donor Ligands Including Catalytic Ketone H_2-Hydrogenation[1]

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In this study we determine the changes to the properties of dihydride catalysts for ketone H_2-hydrogenation by successively replacing the amine donors in the known dach complex $RuH_2(PPh_3)_2$(dach) (**2a**), dach = 1,2-(*R*,*R*)-diaminocyclohexane, with one pyridyl group in the corresponding 2-(aminomethyl)pyridine (ampy) complexes $RuH_2(PPh_3)_2$(ampy) (**2b**) and with two pyridyl groups in the complexes $RuH_2(PPh_3)_2$(bipy) (**2c**) and $RuH_2(PPh_3)_2$(phen) (**2d**). The ruthenium monohydride complex, (*OC*-6-54)-$RuHCl(PPh_3)_2$(ampy), (**1b** with Cl trans to H) was prepared by the addition of 1 equiv of ampy to $RuHCl(PPh_3)_3$ in THF. Treatment of the monohydride complex with K[BH(sec-Bu)$_3$] in THF or KO^{t}Bu/H_2 in toluene resulted in the formation of a mixture of at least two isomers of the highly reactive, air-sensitive ruthenium dihydride complex **2b**. One is the cis dihydride (*OC*-6-14)-**2b** or more simply c,t-**2b** with trans PPh_3 groups and another is the cis dihydride c,c-**2b** (*OC*-6-42) that has PPh_3 trans to H and PPh_3 trans to N(pyridyl). The isomer c,c-**2b** slowly converts to c,t-**2b** in solution. The reaction of **1b** with KO^{t}Bu under Ar results in the formation of a mixture that includes a complex with an imino ligand HN=CH-2-py while the same reaction under H_2 leads to c,c-**2b** and then c,t-**2b.** The dach complex c,t-**2a**, reacts with ampy, 2,2′-bipyridine (bipy), and 1,10-phenanthroline (phen) in refluxing THF to form the substituted *cis*-dihydride complexes c,t-**2b**, (*OC*-6-13)-$RuH_2(PPh_3)_2$(bipy) (c,t-**2c** with trans PPh_3 groups) and (*OC*-6-13)-$RuH_2(PPh_3)_2$(phen), c,t-**2d**, respectively. The dihydrides containing amino groups and *cis*-PPh_3 groups, i.e., c,c-**2a** or c,c-**2b**, are active precatalysts for the H_2-hydrogenation of acetophenone (neat or in benzene) under mild reaction conditions, whereas those with *trans*-PPh_3 groups, c,t-**2a** and c,t-**2b** are much less active. The combination of ampy complex **1b** and KO^{t}Bu also provides a catalyst in benzene that is more active than the corresponding dach system. The complexes without amino groups c,t-**2c** and c,t-**2d** are air-stable and inactive as hydrogenation catalysts under comparable conditions. The mechanism of hydrogenation of ketones catalyzed by isomers of **2a**,**b** is thought to be similar and to proceed via a *trans*-dihydride complex, t,c-**2a** or t,c-**2b**, and an amido complex, neither of which are directly observed for the ampy complexes. The dihydride complex c,t-**2b** reacts with formic acid to give (*OC*-6-45)-$RuH(OCHO)(PPh_3)_2$(ampy), **3b**, with formate trans to hydride. The structures of **1b**, c,t-**2b**, c,t-**2c**, and **3b** have been determined by single-crystal X-ray diffraction.

Introduction

The first demonstrations of the N−H effect on the hydrogenation of ketones was the generation of very active catalyst systems by the addition of ethylenediamine and other diamines to $RuCl_2(PPh_3)_3$ and base in 2-propanol as reported by Noyori and co-workers.[2,3] Our own interest in ruthenium hydride and dihydrogen chemistry and, in particular, hydridic−protonic M−H···H−N bonds[4−8] led us to investigate

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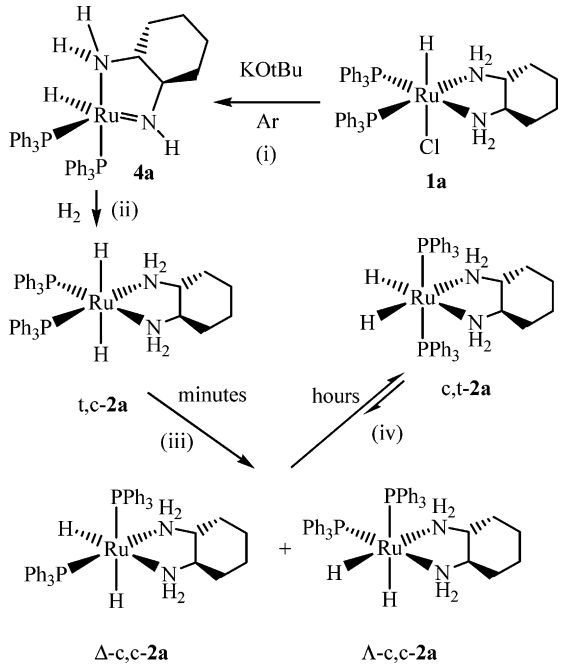
Chart 1. Labels for the Complexes

Complex	N-N
$RuHCl(N\text{-}N)(PPh_3)_2$	
1a N-N = dach	**a** dach
1b N-N = ampy	**b** ampy
$RuH_2(N\text{-}N)(PPh_3)_2$	
2a N-N = dach	**c** bipy
2b N-N = ampy	**d** phen
2c N-N = bipy	
2d N-N = phen	
$RuH(O_2CH)(N\text{-}N)(PPh_3)_2$	
3b N-N = ampy	
$RuH(N\text{-}N\text{-amido})(PPh_3)_2$	
4a N-N = dach	
4b N-N= ampy	

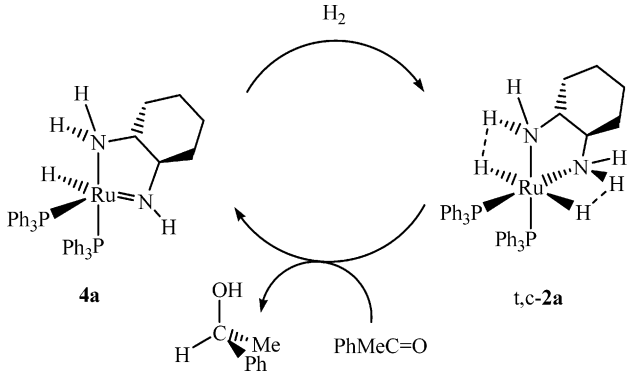
the possible ruthenium monohydride and dihydride species which are expected to be generated in these basic ruthenium(II) dichloride mixtures. We have demonstrated that *trans*-dihydride species of the type $RuH_2(PPh_3)_2$(diamine), diamine = (*R*,*R*)-1,2-diaminocyclohexane (dach),[9] ethylenediamine (en),[9] and 2,3-dimethyl-2,3-diaminobutane (tmen),[10] or *trans*-RuH_2(diphosphine)(diamine)[10,11] and the corresponding amido complexes derived from these dihydrides are exceptionally active catalysts for the hydrogenation of ketones and imines. In this paper we determine the changes to the properties of the catalysts by successively replacing the amine donors in the dach complexes (these complexes are labeled with an **a** below; see Chart 1) with one pyridyl group in corresponding 2-(aminomethyl)pyridine (ampy) complexes (**b**) and with two pyridyl groups in 2,2′-bipyridine (**c**) and phenanthroline (**d**) complexes. The dach and ampy ligands have an amino group that is thought to be crucial for this catalytic mechanism while the last two do not. Therefore, only the dach and ampy complexes are expected to lead to active hydrogenation catalysts, a finding that is verified here.

We have recently discovered a succession of hydrides generated by reacting (*OC*-6-43)- $RuHCl(dach)(PPh_3)_2$ (**1a**)[12,13] in benzene solution with a strong base under Ar (step i, Scheme 1) and then under H_2 (step ii, Scheme 1). The

Scheme 1. Succession of Dihydrides Produced by Reacting Complex **1a** with Base under H_2



Scheme 2. Catalytic Cycle for the Hydrogenation of Acetophenone by (*R*,*R*)-1,2-Diaminocyclohexane Complexes in Benzene



unstable amido complex $RuH(NHC_6H_{10}NH_2)(PPh_3)_2$, **4a**, is produced in step i. This reacts with 1 atm of H_2 in step ii to produce the *trans*-dihydride (*OC*-6-22)-$RuH_2(dach)(PPh_3)_2$, t,c-**2a**, that isomerizes quickly in step iii to the *cis*-dihydride diastereomers Δ-c,c-**2a** and Λ-c,c-**2a**. The cis, cis isomers slowly isomerize in step iv almost completely until reaching equilibrium with the *cis*-dihydride with *trans*-phosphines, c,t-**2a**.

Despite the instability of **4a** and t,c-**2a**, we demonstrated that these are the active catalysts in the ketone hydrogenation mechanism (Scheme 2). The amido complex **4a** is formed in the catalytic cycle by donation of 1 equiv of H^+/H^- to the ketone from a Ru−H···H−N unit of the *trans*-dihydride. The *trans*-dihydride is regenerated by reaction of **4a** with dihydrogen, presumably via an unstable η^2-dihydrogen ligand, which splits heterolytically into a hydride and a proton. The proton adds to the amido nitrogen to regenerate the N−H group.[10,14] By contrast the more stable *cis*-dihydride

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(12) For the (*OC*-6-*ij*) stereochemical descriptor for octahedral complexes, *i* is the Cahn−Ingold−Prelog priority of the atom trans to the highest priority (1) atom and *j* is the priority of the atom trans to the next highest priority atom along another axis of the octahedron. If there is an ambiguity, then the axis with the maximum difference in numbers of the trans atoms is chosen. E.g. for (*OC*-6-54)-**1b** the priorities are Cl (1), $P(PPh_3)$ (2), N(pyridyl) (3), N(amino) (4), and H (hydride) (5); see ref 13.
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complex c,t-**2a**[9,14] and monohydrides of the type RuHCl(PPh$_3$)$_2$(diamine) and RuHCl(diphosphine)(diamine) are inactive and only function as precatalysts by reaction with base. Therefore the dipolar proton−hydride motif, constituting a hydride (Ru−H) and amine (N−H) coordinated cis on ruthenium(II), plays a crucial role in the molecular recognition of the polar carbon−heteroatom double bond of a ketone and facilitates its reduction by an outer-sphere hydrogenation mechanism. This has been called metal−ligand bifunctional catalysis by Noyori et al.[15] or hydrogenation in the outer sphere with ligand assistance (HOL) by some of us.[16] Yamakawa et al.[17] and our group[10] have shown by use of DFT calculations that this concerted transfer is a low-barrier process. With the Shvo catalyst system, Casey and Johnson have shown experimentally that this outer-sphere transfer involves the concerted transfer of hydride and proton.[18]

In related work, Mizushima et al.[19] have examined the use of chiral ampy-type ligands 2-R^1-6-R^2-C$_5$H$_3$N where R^1 = H, Me, R^2 = CH$_2$NHCHR^{3}Me, and R^3 = phenyl, naphthyl in the asymmetric transfer hydrogenation of aryl−alkyl ketones catalyzed by ruthenium(II) complexes. These were added to either RuCl$_2$(PPh$_3$)$_3$ or RuHCl(PPh$_3$)$_3$ in THF to generate uncharacterized solutions that were used to transfer hydrogen from 2-propanol or HCOOH/NEt$_3$ to the ketones to produce alcohols with up to 86% ee. Baratta et al.[20,21] prepared a 2-(aminomethyl)pyridine complex RuCl(CO){(2-CH$_2$-6-MeC$_6$H$_3$)PPh$_2$}(ampy) that was an active precatalyst for the transfer of hydrogen from 2-propanol to ketones. Brunner's group has examined the use of potentially tridentate ligands with 1-(pyridin-2-yl)ethylamine or Schiff base ligands with amine and pyridyl donors as chiral units in combination with RuCl$_2$(PPh$_3$)$_3$ and KO^{t}Bu as catalyst systems for the asymmetric transfer hydrogenation of ketones.[22,23]

Experimental Section

General Methods. RuCl$_2$(PPh$_3$)$_3$, RuHCl(PPh$_3$)$_3$,[24] and RuH$_2$(PPh$_3$)$_2$(dach), dach = *(R,R)*-1,2-diaminocyclohexane,[14] were synthesized by following literature procedures. Potassium tri-*sec*-butylborohydride, potassium *tert*-butoxide, (*R,R*)-1,2-diaminocyclohexane, 2-(aminomethyl)pyridine, 2,2′-bipyridine, and 1,10-phenanthroline were supplied by Aldrich Chemical Co. All preparations and manipulations were carried out under hydrogen, nitrogen, or argon atmospheres with the use of standard Schlenk, vacuum line, and glovebox techniques in dry, oxygen-free solvents. Tetrahydrofuran (THF), diethyl ether (Et$_2$O), and hexanes were dried and distilled from sodium benzophenone ketyl. Deuterated solvents were degassed and dried over activated molecular sieves. 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. ^{1}H NMR NOE experiments were done at 500 MHz. All infrared spectra were obtained on a Nicolet 550 Magna-IR spectrometer. Microanalyses were performed by Guelph Chemical Laboratories Ltd. or in our Chemistry Department.

Synthesis. RuHCl(PPh$_3$)$_2$(ampy) (1b). A mixture of RuHCl(PPh$_3$)$_3$ (2.0 g, 2.16 mmol) and 2-(aminomethyl)pyridine (240 mg, 2.22 mmol) in THF (5 mL) was stirred for 30 min under an atmosphere of nitrogen. The resulting solution was filtered, and hexanes (10 mL) added to the filtrate, precipitating a yellow solid that was filtered out, washed with hexanes, and dried under vacuum. Yield = 1.51 g of (*OC*-6-54)-**1b**, 70%. Once the product was yellow-green due to the presence of a second isomer t-**1b** with trans PPh$_3$ groups. It is not clear what caused this variation. IR (Nujol): 1941, 2035 cm^{-1} (νRuH), 3140, 3214, 3345 cm^{-1} (νNH). Anal. Calcd for C$_{42}$H$_{39}$ClN$_2$P$_2$Ru: C, 65.49; H, 5.10; N, 3.64. Found: C, 64.94; H, 5.05; N, 3.56. NMR for **1b**: ^{1}H NMR (C$_6$D$_6$) δ 8.00−8.20 ppm (m, pyridyl-H), 6.90−7.10 ppm (m, phenyl-H), 3.85, 3.15, 2.95, 2.05 ppm (m, CH$_2$ and NH$_2$), −16.70 ppm (dd, $^2J_{HP}$ = 24 Hz, 30 Hz, RuH); ^{31}P{^{1}H} NMR (C$_6$D$_6$) δ 70.5 (d), 74.3 (d, $^2J_{PP}$ = 37 Hz). NMR for t-**1b**: ^{1}H NMR (C$_6$D$_6$) δ −11.81 (t, $^2J_{HP}$ = 21.7 Hz, 1H, RuH); ^{31}P{^{1}H} NMR δ 50.8 (s).

RuH$_2$(PPh$_3$)$_2$(ampy) (c,t-2b/c,c-2b). Method a. A solution of potassium tri-*sec*-butylborohydride (350 mg of a 1.0 M solution in THF, 0.39 mmol) was added to a solution of **1b** (300 mg, 0.39 mmol) in THF (2 mL) under a nitrogen atmosphere. The mixture became dark yellow immediately. It was stirred at room temperature for 20 min and filtered using a fine-porosity sintered glass frit. The filtrate was evaporated to dryness under vacuum, and diethyl ether (1.0 mL) was added to the resulting solids. The slurry was stirred vigorously for 10 min, and then hexanes (5 mL) were added. The dark yellow solids were filtered out, washed with hexanes, and dried under vacuum. Yield = 278 mg, 97% as a mixture of isomers c,t-**2b** (81%) c,c-**2b** (17.7%), and (*OC*-6-43)-c,c-**2b** (1.3%).

Method b. Toluene (2 mL) was added to a mixture of RuHCl(PPh$_3$)$_2$(ampy) (300 mg, 0.39 mmol) and KO^{t}Bu (50 mg, 0.44 mmol) under a flow of hydrogen and the mixture stirred for 2 h under H$_2$ (1 atm). The resulting mixture was filtered, and evaporated to dryness, and hexanes (10 mL) were added, precipitating a dark yellow solid. This was filtered out, washed with hexanes, and dried under vacuum. Yield = 215 mg, 75% as isomers c,t-**2b** (73%) and c,c-**2b** (27%). IR (Nujol): 1902, 1912, 1930 cm^{-1} (ν_{RuH}), 3294, 3300, 3353 cm^{-1} (ν_{NH}). Anal. Calcd for C$_{42}$H$_{40}$N$_2$P$_2$Ru: C, 68.56; H, 5.48; N, 3.81. Found: C, 68.09; H, 5.66; N, 3.44. NMR (see Table 1) results are as follows. c,t-**2b**: ^{1}H NMR (C$_6$D$_6$) δ −18.2 (td, $^2J_{HP}$ = 27 Hz, $^2J_{HH}$ = 7 Hz, 1H, RuH), −16.3 (td, $^2J_{HP}$ = 27 Hz, $^2J_{HH}$ = 7 Hz, 1H, RuH), 1.7 (t, $^2J_{HH}$ = 6 Hz, 2H, NH$_2$), 2.7 (t, $^2J_{HH}$ = 6 Hz, 2H, CH$_2$), 5.8−8.1 (m, 34H); ^{31}P{^{1}H} NMR δ 67.7 (s). c,c-**2b**: ^{1}H NMR (C$_6$D$_6$) δ −5.2 (ddd, $^2J_{HP}$ = 99 and 36 Hz, $^2J_{HH}$ = 6 Hz, RuH), −14.9 (dt, $^2J_{HP}$ = 26 Hz, $^2J_{HH}$ = 6 Hz, RuH); ^{31}P{^{1}H} δ 83.1 (br), 57.8 (br). (*OC*-6-43)-c,c-**2b**: ^{1}H NMR (C$_6$D$_6$) δ −4.97 (ddd, $^2J_{HP}$ = 96 and 38 Hz, $^2J_{HH}$ = 6 Hz), −16.3 (ddd, $^2J_{HP}$ = 30 and 18.5 Hz, $^2J_{HH}$ = 6 Hz). Upon standing overnight in C$_6$D$_6$, all of the isomer c,c-**2b** completely isomerized to c,t-**2b**.

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Table 1. NMR Properties of Isomers of Dihydrides **2a**,**b** in C_6D_6

	ampy	dach[a]	
trans-H, *cis*-PPh_3	t,c-**2b**	t,c-**2a**	
δ_H (ppm)		−5.45 (t)	
$^2J_{HP}$ (Hz)		18	
δ_P (ppm)		86.5 (s)	
cis-H, *cis*-PPh_3	c,c-**2b**	Λ-c,c-**2a**	Δ-c,c-**2a**
δ_H (ppm)	−5.2 (ddd)	−5.6 (ddd)	−5.5 (ddd)
$^2J_{HPtrans}$ (Hz)	99	100	103
$^2J_{HPcis}$ (Hz)	36	32	34
$^2J_{HH}$ (Hz)	6	6	6
δ_H (ppm)	−14.9 (td)	−15.4 (dt)	−15.4 (dt)
$^2J_{HP}$ (Hz)	26	23	23
$^2J_{HH}$ (Hz)	6	6	6
δ_P (ppm)	57.8 (d)	55.5	57.7
δ_P (ppm)	83.1 (d)	84.6	84.4
$^2J_{PP}$ (Hz)	14	14	14
cis-H, *trans*-PPh_3	c,t-**2b**	c,t-**2a**	
δ_H (ppm)	−18.2 (td)	−18.3 (t)	
J_{HP} (Hz)	27	27	
J_{HH} (Hz)	7		
δ_H (ppm)	−16.3 (td)		
J_{HP} (Hz)	27		
J_{HH} (Hz)	7		
δ_P (ppm)	67.6 (s)	66.0 (s)	

[a] Reference 9.

Reaction of 1b with KO^{t}Bu. $RuHCl(PPh_3)_2$(ampy) (31 mg, 0.04 mmol) and KO^{t}Bu (10 mg, 0.08 mmol) were mixed under N_2, C_6D_6 (0.5 mL) was added, and the mixture was stirred for 30 min. It turned blue-black. The ^{1}H NMR spectrum contained evidence of an imino-ampy hydride species along with several others: ^{1}H NMR (C_6D_6) 10.45 ppm (d, $^3J_{HH}$ = 6 Hz, py-CH═NH), −11.65 ppm (br, RuH); $^{31}P\{^1H\}$ NMR (C_6D_6) 62.0 ppm (s). There are several other unidentified species with ^{1}H resonances at −12.85 ppm (br s), −15.45 ppm (br t, J = 24 Hz), and −16.90 ppm (t, J = 29 Hz) and $^{31}P\{^1H]$ resonances at 49.5 ppm (m), 56.0 ppm (s), 61.0 ppm (m), 67.5 ppm (t, J = 25 Hz), 71.0 ppm (t, J = 25 Hz), and 77.0 ppm (s).

$RuH_2(PPh_3)_2$(bipy) (c,t-2c). THF (5 mL) was added to a mixture of $RuH_2(PPh_3)_2$(dach) (300 mg, 0.40 mmol) and 2,2′-bipyridine (61 mg, 0.39 mmol), and the solution was refluxed for 3 h under an argon atmosphere, resulting in a dark green solution. After the solution was cooled to room temperature, hexanes (20 mL) were added resulting in the precipitation of a deep violet solid, which was filtered out, washed with hexanes, and dried under vacuum. Yield = 232 mg, 76%. IR (Nujol): 1877, 1921 cm^{-1} (ν_{RuH}). Anal. Calcd for $C_{46}H_{40}N_2P_2Ru$: C, 70.48; H, 5.14; N, 3.57. Found: C, 70.0; H, 5.0; N, 3.6. NMR: ^{1}H NMR (C_6D_6) δ −13.71 (t, $^2J_{HP}$ = 28 Hz, 2H, RuH), 6.10−8.52 (m, 38H); $^{31}P\{^1H\}$ NMR δ 63.7 (s).

$RuH_2(PPh_3)_2$(phen) (c,t-2d). THF (5 mL) was added to a mixture of $RuH_2(PPh_3)_2$(dach) (300 mg, 0.40 mmol) and 1,10-phenanthroline (72 mg, 0.40 mmol), and the solution was refluxed for 3 h under an argon atmosphere, resulting in a violet solution. After the solution was cooled to room temperature, hexanes (30 mL) were added resulting in the precipitation of a violet solid, which was filtered out, washed with hexanes, and dried under vacuum. Yield = 265 mg, 82%. NMR: ^{1}H NMR (C_6D_6) δ −13.3 (t, $^2J_{HP}$ = 27.4 Hz, 2H, RuH), 5.85−8.68 (m, 38H); $^{31}P\{^1H\}$ NMR δ 64.5 (s). Anal. Calcd for $C_{48}H_{40}N_2P_2Ru$: C, 71.36; H, 4.99; N, 3.47. Found: C, 71.2; H, 4.8; N, 3.4.

$RuH(HCO_2)(PPh_3)_2$(ampy) (3b). Formic acid (10 mg) was added to a solution of $RuH_2(PPh_3)_2$(ampy) (200 mg, 0.27 mmol) in THF (1 mL) and the mixture stirred for 30 min. Hexanes (10 mL) were then added, resulting in the precipitation of a pale yellow solid, which was filtered out, washed with hexanes, and dried under vacuum. Yield = 132 mg, 65%. NMR: ^{1}H NMR (C_6D_6) δ −18.8 (t, $^2J_{HP}$ = 26 Hz, 1H, RuH), 1.8 (br, 1H, NH), 3.5 (br, 1H, CH), 3.8 (br, 1H, CH), 5.9−8.7 (m, 34H), 8.5 (br, 1H, NH), 9.3 (s, 1H, CH); $^{31}P\{^1H\}$ δ 74.5 (d), 65.5 (d, $^2J_{PP}$ = 36 Hz). The structure was verified by single-crystal X-ray diffraction (see Supporting Information).

X-ray Structure Analysis. Crystals were obtained by the slow diffusion of either diethyl ether or hexanes into THF or benzene solutions of the desired compounds under a nitrogen atmosphere. Data were collected on a Nonius Kappa-CCD diffractometer using

Table 2. Summary of X-ray Parameters for the Complexes

	1b	c,t-**2b**	c,t-**2c**	**3b**
formula	$C_{42}H_{39}ClN_2P_2Ru$	$C_{42}H_{40}N_2P_2Ru$	$C_{46}H_{40}N_2P_2Ru$	$C_{49}H_{46}N_2O_2P_2Ru$
M_r	770.21	735.77	783.81	857.89
cryst size, mm	0.25 × 0.24 × 0.20	0.40 × 0.35 × 0.35	0.32 × 0.16 × 0.06	0.24 × 0.20 × 0.18
cryst class	triclinic	orthorhombic	monoclinic	monoclinic
space group	P-1	P2(1) 2(1) 2(1)	C2/c	P2(1)/c
temp, K	150	150	150	150
a, Å	10.8591(1)	9.885(1)	9.7052(2)	27.0614(4)
b, Å	18.4542(3)	16.3564(2)	16.3191(7)	17.0984 (4)
c, Å	22.6775(3)	22.3784(4)	23.399(1)	18.4155(7)
α, deg	81.380(1)	90	90	90
β, deg	82.400(1)	90	90.205(3)	101.098(1)
γ, deg	79.001(1)	90	90	90
V, Å^3	4385.4(1)	3618.3(4)	3706.0(2)	8361.6(4)
Z	4	4	4	8
D_{calc}, g cm^{-3}	1.167	1.351	1.405	1.363
μ(Mo Kα), mm^{-1}	0.518	0.554	0.545	0.493
F(000)	1584	1520	1616	3552
range θ, deg	2.55−27.51	3.00−27.48	2.59−27.47	2.55−27.50
no. of reflcns	46 671	32 449	15 388	46 851
no. of indpdt reflcns	19 453	8257	4230	18 815
R1 [$I > 2\sigma(I)$][a]	0.0395	0.0290	0.0361	0.0507
wR2 (all data)[b]	0.1333	0.0631	0.0779	0.1192
goodness of fit	1.067	1.034	1.028	1.015
no. of ref params	890	434	236	1041
max peak, e Å^{-3}	0.694	0.461	0.372	0.641

[a] $R1 = \Sigma(F_o - F_c)/\Sigma(F_o)$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table 3. Selected Bond Distances and Angles for the Known Complex c,t-**2a** and the New Complexes c,t-**2b** and c,t-**2c**

	c,t-**2a**[14]	c,t-**2b**	c,t-**2c**[a]
Ru(1)−H(1Ru)	1.53(2)	1.56(2)	1.59(2)[b]
Ru(1)−H(2Ru)	1.62(3)	1.56(3)	
Ru(1)−N(1)	2.225(3)	2.235(2)	2.126(2)[b]
Ru(1)−P(2)	2.2497(8)	2.2504(6)	
Ru(1)−P(1)	2.2512(7)	2.2661(6)	2.2843(6)[b]
Ru(1)−N(2)	2.284(2)	2.141(2)	
N(1)−H(1NB)	0.82(3)		
N(1)−H(1NA)	0.87(3)		
N(2)−H(2NA)	0.99(3)		
N(2)−H(2NB)	0.84(3)		
H(1Ru)−Ru(1)−H(2Ru)	83(1)	92(1)	86(2)
H(1Ru)−Ru(1)−N(1)	96(1)	97.2(9)	99.0(9)[b]
H(2Ru)−Ru(1)−N(1)	177(1)	170.6(9)	174.3(9)[b]
H(1Ru)−Ru(1)−P(2)	83(1)	80(1)	
H(2Ru)−Ru(1)−P(2)	80(1)	85(1)	
N(1)−Ru(1)−P(2)	97.34(8)	98.62(6)	99.99(5)[b]
H(1Ru)−Ru(1)−P(1)	82(1)	79(1)	81.3(9)[b]
H(2Ru)−Ru(1)−P(1)	83(1)	81(1)	83.1(9)[b]
N(1)−Ru(1)−P(1)	99.14(9)	98.46(6)	96.87(5)[b]
P(2)−Ru(1)−P(1)	158.21(3)	154.96(2)	158.57(3)[b]
H(1Ru)−Ru(1)−N(2)	172(1)	174.1(9)	
H(2Ru)−Ru(1)−N(2)	105(1)	93.6(9)	
N(1)−Ru(1)−N(2)	76.6(1)	77.14(7)	75.9(1)
P(2)−Ru(1)−N(2)	99.72(8)	102.06(5)	
N(1)−Ru(1)−N(2)	97.89(7)	77.14(7)	

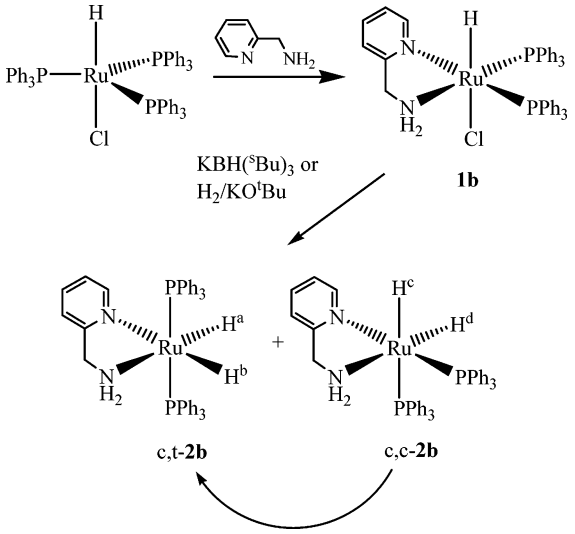
[a] There is a second bond distance or angle related by symmetry with the same distance or angle (H(1Ru)#1 = H(1Ru)#1, N(1)#1 = N(1)#1, P(1)#1 = P(1)#1). [b] There is a second, equivalent bond distance or angle because of the symmetry.

Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The CCD data were integrated and scaled using the DENZO-SMN software package, and the structures were solved and refined using SHELXTL V5.0 (see Tables 2 and 3). The hydrides were located and refined with isotropic thermal parameters.

Catalytic Hydrogenation of Neat Acetophenone. Acetophenone (1.0 g) was added under a flow of hydrogen gas to 5 mg of **1b** and 5 mg of KO^{i}Pr in a 500 mL Schlenk flask. The flask was then cooled to liquid nitrogen temperature, filled with H_2 gas, closed, and allowed to warm to room temperature. The mixture was then vigorously stirred for 1 h. A ^{1}H NMR spectrum of the mixture indicated complete conversion of the ketone to phenylethanol. Similar results were obtained using the isomer mixture c,t-**2b**/c,c-**2b** as a catalyst without added KO^{i}Pr.

Catalytic Hydrogenation of Acetophenone in Benzene. Reactions were done at 5 atm of H_2 using a 50 mL Parr hydrogenator reactor. A constant temperature (20 °C) was maintained by use of a Fisher Scientific Isotemp 1016D water bath. All solutions were handled under a nitrogen atmosphere. Standard solutions of acetophenone and catalyst precursors were prepared in benzene while that of potassium *tert*-butoxide was made up in 2-propanol.

Scheme 3. Preparation of the RuHCl and RuH_2 Complexes



The solution of the ketone, followed by the solution of the ruthenium complex and then the base (if required), was injected into the already-thermostated reactor at 5 atm H_2 pressure to give a final working volume of 5 mL with concentrations of 0.17 M acetophenone and 0.00024 M Ru with 15 equiv of base per Ru when required. The reaction time was measured from the time of the injection of the precatalyst solution. The amount of acetophenone remaining and 1-phenylethanol produced after 1 h and 20 min was determined by gas chromatography (see Table 4).

Deuteration Studies. A weighed sample of the desired compound was dissolved in the required deuterated solvent in a NMR tube under an argon atmosphere. The tube was then fitted with an adapter, by which it was connected to a vacuum line. The sample was cooled to liquid nitrogen temperature, degassed, and closed. After being warmed to room temperature, the NMR tube was filled with D_2 gas at 1 atm pressure and then flame-sealed.

Results

Synthesis of the Ruthenium(II) Monohydride and Dihydride Complexes. The yellow monohydride complex RuHCl(PPh$_3$)$_2$(ampy), **1b**, is prepared by reaction of RuHCl(PPh$_3$)$_3$ with 2-(aminomethyl)pyridine (Scheme 3). It contains mutually *cis*-phosphines with the hydride trans to the chloride ligand, as deduced by its solution ^{1}H and ^{31}P NMR spectra.

The X-ray structure of **1b** is shown in Figure 1. Selected bond distances and angles are listed in Table 2. The structure is that of a distorted octahedron, with the hydride trans to the chloride ligand. The ruthenium−nitrogen bond distances

Table 4. Hydrogenation of Acetophenone Catalyzed by Ruthenium Complexes

entry	precatalyst[a]	ketone/solvent	other reagents	ketone:Ru:base	time/conversion to CMePh(H)OH
1	c,c-RuH$_2$(dach)L$_2$/c,t-RuH$_2$(dach)L$_2$ = 30/70	MePhCO (4 g)	3 atm H_2	5000:1	<8 h/100%[14]
2	c,c-RuH$_2$(ampy)L$_2$/c,t-RuH$_2$(ampy)L$_2$ = 18/82	MePhCO (1 g)	3 atm H_2	2000:1	1 h/100%
3	t-RuHCl(ampy)L$_2$	MePhCO (1 g)	3 atm H_2, KO^{i}Pr	2000:1:8	1 h/100%
4	c,t-RuH$_2$(bipy)L$_2$	MePhCO (1 g)	3 atm H_2	100:1	24 h/0%
5	c,t-RuH$_2$(phen)L$_2$	MePhCO (1 g)	3 atm H_2	100:1	24 h/0%
6	c,c-RuH$_2$(ampy)L$_2$/c,t-RuH$_2$(ampy)L$_2$ = 7/83	MePhCO (0.17 M)/C$_6$H$_6$	5 atm H_2	709:1	1.3 h/12%
7	t-RuHCl(dach)L$_2$	MePhCO (0.17 M)/C$_6$H$_6$	5 atm H_2, KO^{t}Bu	709:1:17	1.3 h/55%
8	t-RuHCl(ampy)L$_2$	MePhCO (0.17 M)/C$_6$H$_6$	5 atm H_2, KO^{t}Bu	709:1:17	1.3 h/98%
9	t-RuHCl(bipy)L$_2$	MePhCO (0.17 M)/C$_6$H$_6$	5 atm H_2, KO^{t}Bu	709:1:17	3 h/0%

[a] L = PPh$_3$.

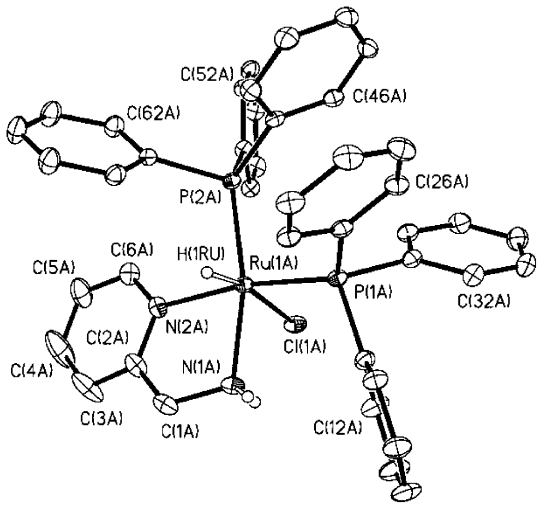


Figure 1. Structure and atomic numbering of $RuHCl(PPh_3)_2$(ampy), **1b**.

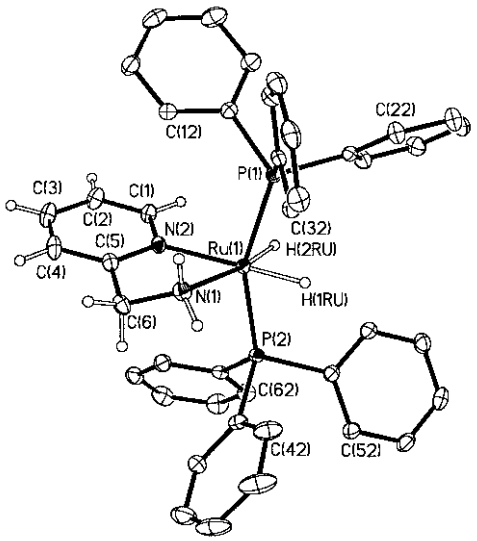


Figure 2. Structure and atomic numbering of c,t-$RuH_2(PPh_3)_2$(ampy), c,t-**2b**.

Ru(1A)−N(1A) and Ru(1A)−N(2A) are similar at 2.163(2) and 2.171(2) Å, respectively. This is unlike what is observed for the dihydride complexes (below), in which the ruthenium−nitrogen distances involving the pyridyl groups are typically much shorter than those involving the amine moieties.

Isomers of the dihydride RuH_2(ampy)$(PPh_3)_2$ are obtained by the addition of KHB^sBu_3 to **1b** in THF or by the reaction of **1b** with H_2 (1 atm) and KO^{t}Bu in toluene (Scheme 3). At first the ^{1}H and ^{31}P{^{1}H} NMR spectra of the reaction mixtures in C_6D_6 show the presence of two or three isomers, with the isomer c,t-**2b**, containing *cis*-hydrides and *trans*-phosphines, predominating relative to those containing *cis*-hydrides and *cis*-phosphines, namely the isomers (*OC*-6-42)-c,c-**2b** (unless otherwise indicated this isomer will simply be called isomer c,c-**2b**) and (*OC*-6-43)-c,c-**2b** (<2%). With warming or over the course of 20 h at room temperature, the minor dihydride isomers in solution are converted to c,t-**2b**. No *trans*-dihydride species t,c-**2b** was detected in solution at room temperature.

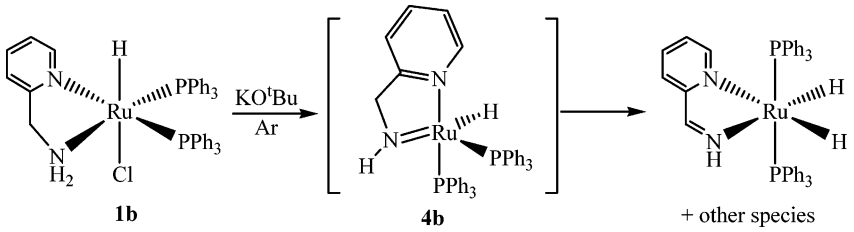
The hydride region of the ^{1}H NMR spectrum of c,t-**2b** shows two sets of triplet of doublet patterns at −18.2 and −16.3 ppm in a 1:1 ratio (Table 1). The ^{31}P{^{1}H} NMR spectrum shows a sharp singlet at 67.7 ppm, indicative of equivalent phosphorus nuclei, while the hydride-coupled ^{31}P spectrum shows a doublet of doublet pattern. A comparison of the proton NMR spectrum of c,t-**2b** with those of c,t-$RuH_2(PPh_3)_2$(dach) and c,t-$RuH_2(PPh_3)_2$(bipy) (below) indicates that the hydride chemical shifts at −18.2 and −16.3 ppm (labeled H^a and H^b, respectively, in Scheme 3) are likely due to their locations trans to the amino and pyridyl moieties of the bidentate ligand, respectively. The assignment of the hydride chemical shifts was verified by a ^{1}H NMR NOE experiment. Irradiation of the hydride with a resonance at −18.2 ppm (H^a) shows a large increase in the intensity of the other hydride resonance at −16.3 ppm (H^b). On the other hand, irradiation at −16.3 ppm shows a correspondingly large increase in the hydride intensity at −18.2 ppm, as well as an increase in the NH_2 signal at 1.7 ppm. Likewise, irradiation of the NH_2 signal produces a large increase in the intensity of the H^b signal but no change in the signal of H^a.

The hydride region of the ^{1}H NMR spectrum of c,c-**2b** shows a doublet of doublet of doublet pattern at −5.2 ppm for the hydride H^c trans to phosphorus ($^2J_{HP}^{trans}$ 99 Hz). The second hydride (H^d) shows a doublet of triplet pattern at −14.9 ppm with $^2J_{HP}^{cis}$ couplings. The structure of c,c-**2b** was assigned on the basis of a ^{1}H NOE experiment. Upon irradiation of the hydride with the chemical shift corresponding to H^c there was an increase in the intensity of the hydride resonance corresponding to H^d and the NH_2 resonance at 4.50 ppm. Upon irradiation of H^d there was a corresponding NOE enhancement of H^c; however, there was no increase in the intensity of the NH_2 resonance. These observations are consistent with the structure of c,c-**2b** as shown in Scheme 3.

The solid-state (Nujol) infrared spectrum of **2b** shows three ν_{Ru-H} peaks at 1902, 1912, and 1930 cm^{-1} and three ν_{N-H} bands at 3294 (w), 3300 (w), and 3353 cm^{-1}. Only c,t-**2b** formed X-ray-quality crystals upon layering a benzene solution of the mixture of isomers with hexanes. The structure is shown in Figure 2, and the bond lengths are listed in Table 3. The Ru−H bond lengths are both 1.56(3) Å. The Ru(1)−N(1)(pyridyl) bond length of 2.141(2) Å is much shorter than that of Ru(1)−N(2)(amino) with a bond length of 2.284(2) Å.

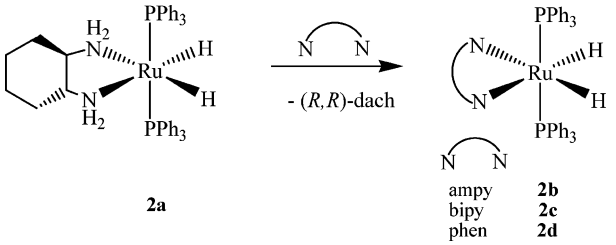
Observation of a Diimine Species. The reaction of the monohydride complex **1b** with KO^{t}Bu in THF under Ar results in a dark blue solution due to the formation of a hydride diimine species (Scheme 4) as well as several other products. The diimine may be produced by β-hydride migration from the methylene group of the undetected intermediate hydrido−amido complex **4b**. A distinctive singlet at 10.4 and triplet at −11.7 ppm in the ^{1}H NMR spectrum and a singlet in the ^{31}P{^{1}H} spectrum are also consistent with the dihydride structure shown in Scheme 4. Other diimine complexes such as the bipyridine complex c,t-

Scheme 4. Reaction of Complex **1b** with Base Producing Imine Complexes, Probably via an Amido Complex **4b**



1b **4b**

Scheme 5. Reaction of *c,t*-$RuH_2(PPh_3)$(dach) with Pyridyl-Donor Ligands To Give the Dihydrides **2b**−**d**



2a

2c and the phenanthroline complex c,t-**2d** (see below) also have this deep color, probably because of metal to diimine charge-transfer transitions.

When this solution containing the diimine species is reacted with 1 atm of H_2(g), the dihydride isomers, $RuH_2(PPh_3)_2$(ampy), shown in Scheme 3, are generated. This might be evidence that the conversion of **4b** to the diimine is reversible as discussed below.

Reactions of $RuH_2(PPh_3)_2$(dach) with Pyridyl-Donor Ligands. The diamine ligand in the complex *c,t*-$RuH_2(PPh_3)_2$(dach) (c,t-**2a**)[14] can be displaced by a range of bidentate ligands containing nitrogen donor groups upon heating or under reflux in THF solutions (Scheme 5). Thus, the addition of 1 equiv of ampy to a THF solution of $RuH_2(PPh_3)_2$(dach) under a nitrogen or argon atmosphere and warming to 50 °C resulted in the gradual formation of the *cis*-dihydride complex, $RuH_2(PPh_3)_2$(ampy), c,t-**2b**.

When *c,t*-$RuH_2(PPh_3)_2$(dach) is refluxed in THF with 1 equiv of 2,2′-bipyridine or 1,10-phenanthroline under an inert atmosphere, the substituted dihydride complexes *c,t*-$RuH_2(PPh_3)_2$(bipy) (c,t-**2c**) or *c,t*-$RuH_2(PPh_3)_2$(phen) (c,t-**2d**) are formed quantitatively, as dark green and violet solutions, respectively, which both yield deep violet crystals upon addition of hexanes. Unlike complexes c,t-**2a** and c,t-**2b** which are very air-sensitive, complexes c,t-**2c** and c,t-**2d** are air-stable as solids, while their solutions are only moderately air-sensitive, requiring at least several hours for decomposition at room temperature. The hydride regions of the ^{1}H NMR spectra of c,t-**2c** and c,t-**2d** show triplets at −13.7 ppm ($^2J_{HP}$ = 28 Hz) and −13.3 ppm ($^2J_{HP}$ = 27 Hz), respectively, while the $^{31}P\{^1H\}$ NMR spectra show sharp singlets at 63.7 and 64.5 ppm, respectively. The deshielding of the hydride chemical shifts in these two complexes relative to that observed for the diamine complex $RuH_2(PPh_3)_2$(dach) with *trans*-PPh_3 (−18.2 ppm) is apparently characteristic of the imine ligands in the former two complexes. Solid-state infrared spectra of c,t-**2c** and c,t-**2d** show two sharp ν_{Ru-H} peaks as expected for a *cis*-dihydride stereochemistry.

The single-crystal X-ray structure of c,t-**2c** is shown in Figure 3. The structure is similar to those of c,t-**2a** and c,t-**2b**[14] with mutually trans phosphine ligands and cis hydrides. The Ru−H bond lengths of 1.59(2) Å are similar to the 1.56(3) and 1.57(3) Å (average) distances observed in c,t-**2b** and c,t-**2a**, respectively. However, the Ru−N distances of 2.129(2) Å are much shorter than the 2.255(3) Å average distance observed in the diamine complex c,t-**2a** but similar to 2.141(2) Å observed for the Ru−N(2)(pyridyl) bond in c,t-**2b**.

Reactions of the Dihydrides with Deuterium Gas. Upon exposure of a solution of **2b** to an atmosphere of D_2 gas in C_6D_6, the ^{1}H NMR spectrum of the solution shows the slow incorporation of deuterium into the hydrides and NH_2 positions (Scheme 6). For the major isomer, c,t-**2b**, two isotopomers were observed to have resonances at −16.36 (triplet of doublets) and −16.33 ppm (triplet). These correspond to the resonance of H^a of the starting $RuH_2(PPh_3)_2$(ampy) complex and the isotopomer $RuHD(PPh_3)_2$(ampy) resulting from the replacement of the hydride located trans to the NH_2 group with deuteride. On the other hand, a series of six triplets between −18.16 and −18.32 ppm was observed for H^b, the hydride located trans to the pyridyl group. These include the resonances for $RuH_2(PPh_3)_2(pyCH_2NH_2)$ and the series of isotopomers $RuH_2(PPh_3)_2(pyCH_2NHD)$ and $RuH_2(PPh_3)_2(pyCH_2ND_2)$, as well as the corresponding HD isotopomers $RuHD(PPh_3)_2(pyCH_2NH_2)$, $RuHD(PPh_3)_2(pyCH_2NHD)$, and $RuHD(PPh_3)_2(pyCH_2ND_2)$.

The observation of these isotopomers also confirms that the chemical shift at −18.23 ppm in c,t-**2b** is due to the hydride ligand (H^a) trans to the NH_2 moiety, since deuteration of the amine hydrogens located trans to the hydride would

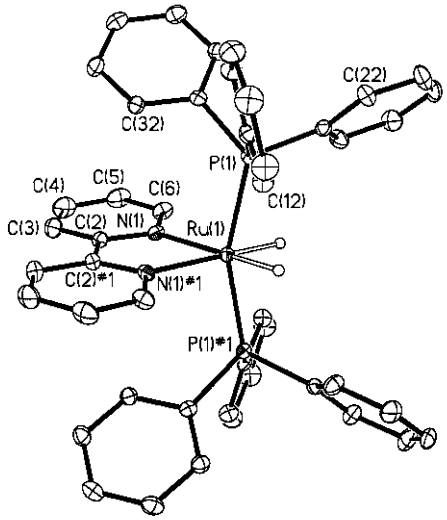
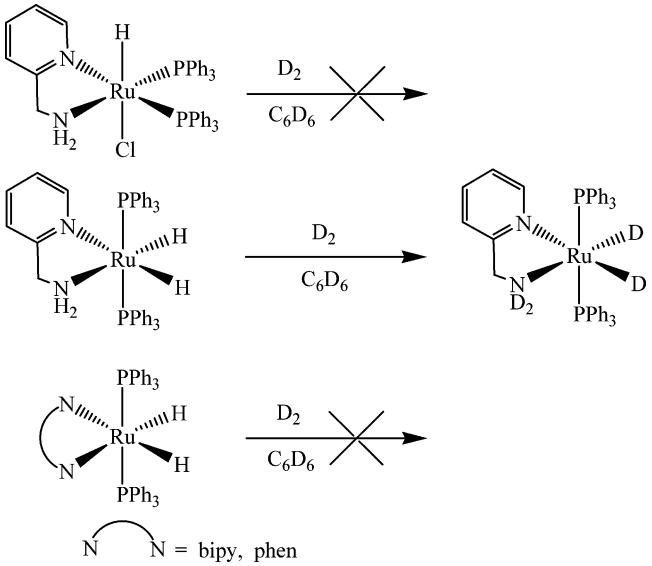


Figure 3. Structure and atomic numbering of $RuH_2(PPh_3)_2$(bipy), c,t-**2c**.

Scheme 6. Isomers of Dihydride **2b** Undergoing H/D Exchange with D_2 Gas While Complexes **1b**, c,t-**2c**, and c,t-**2d** Do Not



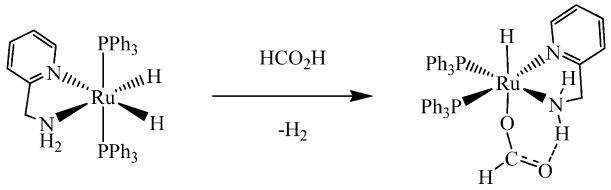
result in a large change in the hydride chemical shift as observed; the change would be small if it were located in the cis position. The incorporation of deuterium into the hydrides of c,c-**2b** resulted in a broadening of the hydride resonances and a decrease in their intensities.

There was no incorporation of deuterium into the monohydride complex **1b** or into dihydride complexes c,t-**2c** and c,t-**2d** upon exposure of their solutions to deuterium gas for several days.

Reaction of $RuH_2(PPh_3)_2$(ampy) with Formic Acid. The dihydrides are very reactive toward acids. The compound $RuH(HCO_2)(PPh_3)_2$(ampy), **3b**, was prepared by the addition of formic acid to a THF solution of c,t-**2b** (Scheme 7). The hydride region of the ^1H NMR spectrum shows a triplet at −18.8 ppm while the formate hydrogen presents a sharp singlet at 9.34 ppm. Two NH hydrogens are observed at 1.8 and 8.5 ppm. The extensive deshielding of the latter proton signal is clearly indicative of a strong hydrogen bond between one of the amine hydrogens and the noncoordinated formato oxygen that is also observed in the X-ray crystal structure (Supporting Information). The complex $RuH(HCO_2)(PPh_3)_2$-$(NH_2CMe_2CMe_2NH_2)$ has a very similar structure.[10] The trans configuration of the complex and the hydrogen-bonded carbonyl groups are important features of the transition state structure for ketone hydrogenation catalyzed by the corresponding *trans*-dihydride complex t,c-**2b** as in Scheme 9 (see below).

Catalytic Hydrogenation of Acetophenone. Like the dach dihydride complexes c,c/c,t-**2a**, the mixture of ampy dihydride isomers c,c/c,t-**2b** is a very active catalyst for the hydrogenation of neat acetophenone to 1-phenylethanol at room temperature and 3 atm H_2 (Table 4, entries 1 and 2). An active catalyst system is also obtained starting from complex **1b** and KO^{i}Pr (entry 3). On the other hand, there was no detection of phenylethanol when a mixture of acetophenone and the bipyridine or phenanthroline complexes (c,t-**2c** or c,t-**2d**) was stirred under hydrogen gas (3 atm) for 24 h (Table 4, entries 4 and 5). The activity of a

Scheme 7. Formation of the Formate Complex **3b**



mixture of isomers c,c-**2b** and c,t-**2b** mixture (Table 4, entry 6) is less than that of a **1b**/KO^{t}Bu mixture in benzene (entry 8). The ampy complex **1b** is an even more active precatalyst than the dach complex **1a** (entry 8 vs entry 7). The complex $RuHCl(bipy)(PPh_3)_2$[25] that has cis phosphines but no amino group is not a precatalyst for the hydrogenation of acetophenone in benzene in the presence of an excess of KO^{t}Bu (entry 9).

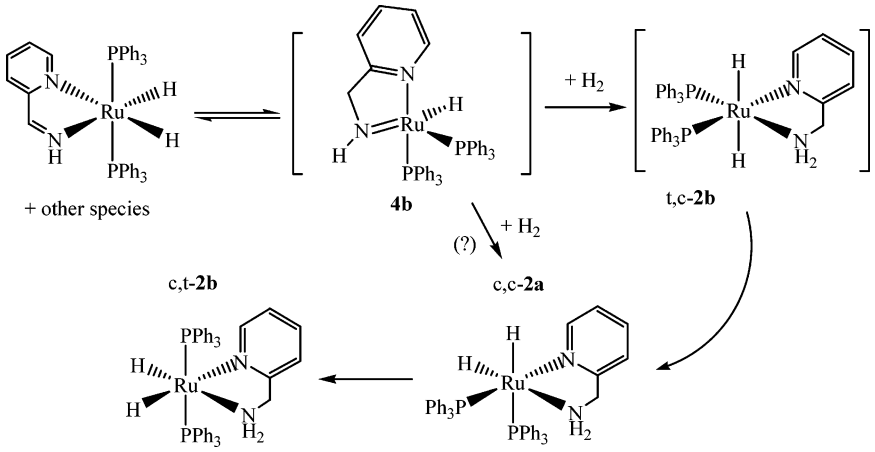
Discussion

In past work we have identified amido complexes[10,11,26] (e.g. $RuH(NHC_6H_{10}NH_2)(PPh_3)_2$, **4a**,[9] in Scheme 1) as the key reactants in the formation of dihydrides and in the cycle for the catalytic hydrogenation of ketones (Scheme 2). Our attempts to generate the corresponding amido complex **4b** as in Scheme 4 resulted in the formation of a mixture of species including a diimine complex that is presumably formed by β-hydride elimination from the CH_2 group of the coordinated ampy ligand. The ethylenediamine ligand in $RuHCl(en)(PPh_3)_2$, upon treatment with base, also undergoes this reaction to form dimeric complexes containing a bridging diimine NHCHCHNH ligand.[9] Conversely, the complex $RuHCl(NH_2CMe_2CMe_2NH_2)(PPh_3)_2$, with a diamine ligand that lacks hydrogens β to the metal, reacts with KO^{t}Bu to give the stable amido complex $RuH(NHCMe_2CMe_2NH_2)$-$(PPh_3)_2$.[10] Nevertheless, the mixture that included this diimine reacted with dihydrogen to give a succession of dihydride isomers (Scheme 8) similar to that produced by the reaction of amido **4a** with dihydrogen (Scheme 1). Therefore, the diimine species could serve as a reservoir of the amido complex **4b** if both are in equilibrium as in Scheme 8. By analogy to the reactions shown in Scheme 1, this amido complex **4b** would react with H_2 to first produce the, as yet, unobserved *trans*-dihydride $RuH_2(ampy)(PPh_3)_2$, t,c-**2b.** As in the case of the dach *trans*-dihydride complex t,c-**2a** (Scheme 1), t,c-**2b** would quickly isomerize to the *cis*-dihydride c,c-**2b** (Scheme 8). This isomer, in turn, converts within less than 20 h into pure c,t-**2b** that is stable in benzene under N_2 for at least several days. However, at this stage we cannot rule out the direct reaction of **4b** with H_2 to give c,c-**2b**, a reaction that would bypass the formation of a *trans*-dihydride.

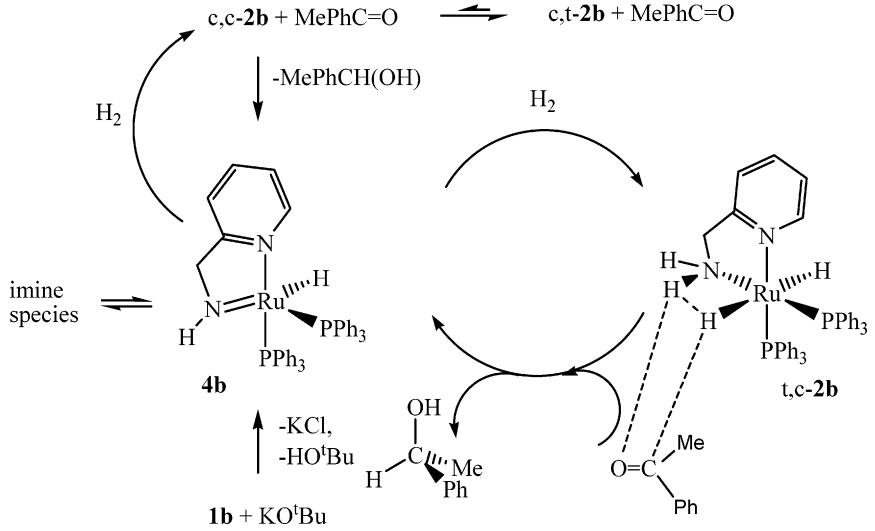
If the steps of Scheme 8 are reversible, then the mechanism of the slow reaction of D_2 with c,c-**2b** and c,t-**2b** can be explained. The prior elimination of H_2 to form the amido complex **4b** followed by reaction with D_2, would produce

(25) Hallman, P. S.; McGarvey, B. R.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 3143−3150.
(26) Li, T.; Churlaud, R.; Lough, A. J.; Abdur-Rashid, K.; Morris, R. H. *Organometallics* **2004**, *23*, 6239−6247.

Scheme 8. Succession of Dihydrides Produced by Reacting the Diimine Mixture of Scheme 4 with Dihydrogen



Scheme 9. Proposed Steps in Catalyst Activation and Function



the isotopomers $RuHD(NHDCH_2py)(PPh_3)_2$. The elimination of HD or H_2 from these compounds and reaction with **4b** would eventually result in the formation of the other isotopomers that are observed by ^1H NMR. The lack of reactivity of D_2 with complexes **2c**,**d** can be explained by the fact that they do not have N−H bonds and cannot form amido complexes. Therefore, they do not react with D_2 as observed. These complexes clearly do not eliminate H_2 to produce a ruthenium(0) intermediate such as $Ru(N-N)(PPh_3)_2$ since this would also be expected to react with D_2. This also argues against Ru(0) species as intermediates in the catalytic hydrogenation mechanism involving complexes **2a** and **b**.

The isomeric dihydride complexes $RuH_2(ampy)(PPh_3)_2$ (c,t-**2b**/c,c-**2b**) have properties quite similar to those of dach (c,t-**2a**/c,c-**2a**). Their ^1H (hydride) and ^{31}P chemical shifts and coupling constants are very similar (Table 1). A difference is that the ampy complex isomerizes completely to the c,t-isomer over time while the dach complex remains as a 92:8 c,t:c,c mixture.[9] The pyridyl-donor ligands ampy, bipy, and phen form more stable complexes than the dach ligand since the dach ligand in c,t-**2a** is substituted quantitatively by these ligands to produce the corresponding dihydrides c,t-**2b**, c,t-**2c**, and c,t-**2d**. The Ru−N distances of these compounds appear to reflect this increase in stability (Table 3). The Ru−pyridyl distances (2.12−2.14 Å in c,t-**2b** and c,t-**2c**) are shorter than those to amino nitrogens (2.25−2.23 Å in c,t-**2a** and c,t-**2b**).

The mechanism of the hydrogenation reaction is thought to involve two very reactive species, the *trans*-dihydride isomer t,c-$RuH_2(ampy)(PPh_3)_2$, **2b**, and the amido complex $RuH(NHCH_2py)(PPh_3)_2$, **4b** (Scheme 9). In the ketone hydrogenation step, the dihydride transfers a hydride from ruthenium and a proton from the amino group to the ketone to generate the alcohol and the amido complex **4b**. The fact that the bipyridine or phenanthroline complexes (c,t-**2c** and c,t-**2d**) are catalytically inactive provides evidence for the importance of the amino group in the hydrogenation of ketones as first discovered by Noyori and co-workers.[2] The structure of the formate complex **3b** (Scheme 7) illustrates the possible geometry of the transition state for H^+/H^- transfer where the carbonyl oxygen is hydrogen-bonded to the amino NH and an oxygen instead of a hydrogen is attached to the carbonyl carbon.

In the dihydrogen activation step, the amido complex **4b** is proposed to split heterolytically an η^2-dihydrogen ligand into a hydride on ruthenium and a proton on nitrogen to regenerate the *trans*-dihydride complex as shown in Scheme

8. The higher reactivity of the ampy amido complex **4b** with dihydrogen compared to that of the dach amido complex **4a** might explain why the ampy catalysts are more active than the dach catalysts in the hydrogenation of acetophenone (Table 4, entry 8 vs entry 7). At least for **4a**, this is the turnover-limiting step in the catalytic cycle. As shown in Scheme 9, we cannot rule out a second catalytic cycle where **4b** reacts with H_2 to give c,c-**2b**, which in turn reacts with ketone to give the alcohol product and regenerate the amido catalyst.

The routes into the catalytic cycle are also similar for the dach (Scheme 2) and ampy (Scheme 9) complexes. The *cis*-dihydride with *cis*-PPh_3 groups, c,c-**2b**, reacts quickly with acetophenone to enter the catalytic cycle via **4b** while the *cis*-dihydride with *trans*-PPh_3 groups, c,t-**2b**, needs an activation step, probably isomerization to c,c-**2b** to enter the cycle. This is consistent with the result shown in Table 4, entry 4, where pure c,t-**2b** is a catalytically inactive complex. Therefore, active catalysts of this type should have a *cis*-phosphine configuration. However, this is not the only requirement since the use of the complex RuHCl(bipy)-$(PPh_3)_2$ with *cis*-PPh_3 ligands does not lead to a catalyst (entry 9, Table 4). The activity of a mixture of isomers c,c-**2b** and c,t-**2b** (Table 4, entry 6) is less than that of a **1b**/KO^tBu mixture in benzene (entry 7). Presumably this latter mixture under H_2 leads to a larger fraction of dihydride isomers with *cis*-PPh_3 groups (Scheme 8).

Another difference between the ampy and dach complexes is the qualitatively faster rate of dehydrochlorination of the hydrido chloro complex **1b** versus that of **1a**. The formation of isomers of the dihydride $RuH_2(ampy)(PPh_3)_2$ (c,t-**2a**/c,c-**2a**) by the addition of KHB^sBu_3 to **1a** (Scheme 3) or KO^tBu/H_2 to **1a (**Scheme 3, Scheme 9**)** is much faster than similar reactions for the formation of $RuH_2(PPh_3)_2$(dach), **2b**, from $RuHCl(PPh_3)_2$(dach), **1b**. The ampy ligand clearly facilitates this dehydrochlorination reaction.

Conclusions

There are similarities and differences between the complexes of 2-(aminomethyl)pyridine and (*R*,*R*)-*trans*-diaminocyclohexane. The structures and properties of the hydrido−chloro and *cis*-dihydride complexes are similar. For both nitrogen-donor ligands, the dihydride isomer with *trans*-PPh_3 groups is more stable than those with *cis*-PPh_3. However it is the later that are the active hydrogenation catalysts. The ampy-amido complex **4b** that is proposed in Schemes 4, 8, and 9 is very unstable compared to the dach-amido complex **4a** and decomposes to an imine-containing complex as well as to other species. The high reactivity of such an amido complex **4b** might translate into a faster reaction with dihydrogen compared to the dach amido complex **4a**. This would explain the higher catalytic activity of the ketone hydrogenation catalysts containing the ampy ligand compared to those containing the dach ligand. The use of bipyridine or phenanthroline ligands that lack an amino N−H group produces catalytically inactive compounds as expected on the basis of a key step in the proposed mechanism for ketone hydrogenation—the transfer of the proton from nitrogen and hydride from ruthenium to the ketone carbonyl in the outer coordination sphere.

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Supporting Information Available: Crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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