Ruthenium(II) Diphosphine/Diamine/Diimine Complexes and Catalyzed Hydrogen-Transfer to Ketones

Guibin Ma,[†] Robert McDonald,[†] Michael Ferguson,[†] Ronald G Cavell,[†] Brian O. Patrick,[‡] Brian R. James,*[,‡] and Thomas Q. Hu[#]

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2, Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z1, and Pulp and Paper Research Institute of Canada, Vancouver Laboratory, 3800 Wesbrook Mall, Vancouver, British Columbia, Canada V6S 2L9

Received October 25, 2006

An in situ product, presumed to be $RuCl_2(DPPF)(PPh_3)$, formed in CH_2Cl_2 from a 1:1 mixture of 1,1′-bis(diphenylphosphino)ferrocene (DPPF) and $RuCl_2(PPh_3)_3$, reacts with 1 equiv of a diamine or a diimine (N−N donors) dissolved in MeOH to generate $RuCl_2(DPPF)(N-N)$ complexes: N−N is ethylenediamine (en), *N*,*N*′-dimethyl(ethylenediamine) (dimen), 1,3-diaminopropane (diap), 2,2′-bipyridine (bipy), 1,10-phenanthroline (phen), and 1*S*,2*S*-diaminocyclohexane (1*S*,2*S*-dach). Diethylenetriamine (dien), a tridentate N-donor, generates a monochloro cationic complex. The isolated complexes are *trans*-$RuCl_2$-(DPPF)(en) (**1**), *trans*-$RuCl_2$(DPPF)(dimen) (**2**), [RuCl(DPPF)(dien)]Cl (**3**), *trans*-$RuCl_2$(DPPF)(diap) (**4**), *cis*-$RuCl_2$(DPPF)(bipy) (**5**), *cis*-$RuCl_2$(DPPF)(phen) (**6**), and *trans*-$RuCl_2$(DPPF)(1*S*,2*S*-dach) (**7**). The known complex *trans*-$RuCl_2$(DPPB)(en) (**8**) was similarly made using $RuCl(DPPB)_2(\mu\text{-}Cl)_3$ as precursor, where DPPB is 1,4-bis(diphenylphosphino)butane. Complexes **1**, **2**, **5**, and **8** were characterized crystallographically. Complexes **1**−**8** are effective precursor catalysts in basic 2-propanol solutions for the hydrogen-transfer hydrogenation of acetophenone; the chiral phosphine system (**7**) gives only ∼12% ee at high conversions to 1-phenylethanol, while at 25% conversion the ee reaches 36%. Greater activity for precursor catalyst **1** versus that of **2** qualitatively supports the "metal−ligand bifunctional" mechanism for such diphosphine/diamine systems; however, the "NH-free" diimine bipy and phen systems are as active at 80 °C as the diamine systems and must operate by a different mechanism. Complex **8** is also an effective precursor hydrogen-transfer catalyst for other alkyl−aryl and dialkyl ketones, which were used as model substrates for components of lignin; a substituted styrene was not hydrogenated.

Introduction

The catalytic hydrogenation of unsaturated organics, especially those with polar C═O and C═N bonds, is important in the fine chemical industry, and homogeneous catalysts based on Ru have proven particularly useful for many syntheses.[1,2] Ruthenium homogeneous hydrogenation catalysts have been known for four decades,[3] but it is only relatively recently that Noyori and co-workers have developed highly active catalyst precursors of the type *trans*-$RuCl_2$(diphosphine)(1,2-diamine) for selective hydrogenation of ketones.[4] When the P−P ligand is chiral, and the H_2N---NH_2 ligand is achiral (but optimally chiral), the systems can generate alcohol products with high ee values[4] (or chiral amine products from prochiral ketimines).[1j,2b] The general "metal−ligand bifunctional catalysis" mechanism (or so-called 'ionic hydrogenations') for reduction of ketones[5] was invoked by Noyori's group for these Ru systems[4,6] and implied no direct bonding of the substrate at the Ru, but instead an outer-sphere, H-bonding interaction between an "RuH---NH" unit and the ketone was proposed, with the added H_2 being derived from the metal hydride and an amine proton. Subsequent detailed studies, especially by Morris's group,[1j] have substantiated such a mechanism, particularly for a binap−tmen system (where tmen = $H_2NC(Me)_2C(Me)_2NH_2$) in which the key intermediates involve *trans*-dihydrido species.[1j,7] It is worth noting that hydrogenation of substrates via a mechanism not involving direct bonding of the substrate at the metal was first

* Corresponding author. E-mail: brj@chem.ubc.ca. Tel: 1-604-822-6645.
[†] University of Alberta.
[‡] University of British Columbia.
[#] Pulp and Paper Research Institute.

(1) For example: (a) Zassinovich, G.; Mestroni, G.; Gladiali, S. *Chem. Rev.* **1992**, *92*, 1051. (b) de Graauw, C. F.; Peters, J. A.; van Bekkum, H.; Huskens, J. *Synthesis* **1994**, 1007. (c) James, B. R. *Catal. Today* **1997**, *37*, 209. (d) Palmer, M. J.; Wills, M. *Tetrahedron: Asymmetry* **1999**, *10*, 2045. (e) Kobayashi, S.; Ishitani, H. *Chem. Rev.* **1999**, *99*, 1069. (f) Blaser, H.-U.; Malan, C.; Pugin, B.; Spindler, F.; Steiner, H.; Studer, M. *Adv. Synth. Catal.* **2003**, *345*, 103. (g) Tang, W.; Zhang, X. *Chem. Rev.* **2003**, *103*, 3029. (h) Everaere, K.; Mortreux, A.; Carpentier, J.-F. *Adv. Synth. Catal.* **2003**, *345*, 67. (i) Dorta, R.; Broggini, D.; Kissner, R.; Togni, A. *Chem.−Eur. J.* **2004**, *10*, 4546. (j) Clapham, S. E.; Hadzovic, A.; Morris, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2201. (k) Reetz, M. T.; Li, X.-G. *J. Am. Chem. Soc.* **2006**, *128*, 1044. (l) Gladiali, S.; Alberico, E. *Chem. Soc. Rev.* **2006**, *35*, 226.

(2) (a) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345. (b) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97.

(3) (a) Evans, D.; Osborn, J. A.; Jardine, F. H.; Wilkinson, G. *Nature* **1965**, *208*, 1203. (b) Halpern, J.; Harrod, J. F.; James, B. R. *J. Am. Chem. Soc.* **1966**, *88*, 5150.

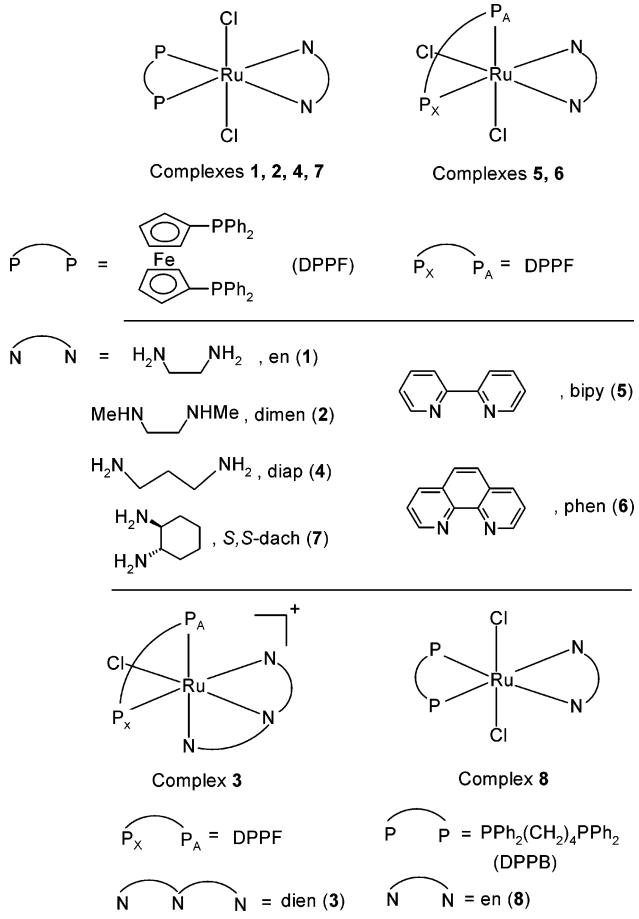
(4) (a) Doucet, H.; Ohkuma, T.; Murata, K.; Yokozawa, T.; Kozawa, M.; Katayama, E.; England, A. F.; Ikariya, T. Noyori, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1703. (b) Ohkuma, T.; Koizumi, M.; Doucet, H.; Pham, T.; Kozawa, M.; Murata, K.; Katayama, E.; Yokozawa, T.; Ikariya, T.; Noyori, R. *J. Am. Chem. Soc.* **1998**, *120* 13529. (c) Mikami, K.; Korenaga, T.; Terada, M.; Ohkuma, T.; Pham, T.; Noyori, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 495.

(5) (a) Magee, M. P.; Norton, J. R. *J. Am. Chem. Soc.* **2001**, *123*, 1778. (b) Bullock, R. M. *Chem.−Eur. J.* **2004**, *10*, 2366. (c) Ikariya, T.; Murata, K.; Noyori, R. *Org. Biomol. Chem.* **2006**, *4*, 393. (d) Samec, J. S. M.; Bäckvall, J.-E.; Andersson, P. G.; Brandt, P. *Chem. Soc. Rev.* **2006**, *35*, 237.

(6) Noyori, R.; Ohkuma, T. *Angew. Chem., Int. Ed.* **2001**, *40*, *40.*

10.1021/om060987z CCC: $37.00
Publication on Web 01/19/2007

Scheme 1. Synthesized Complexes 1−8



demonstrated in the late 1960s for some $CoH(CN)_5^{3-}$ systems,[8] an important point commonly overlooked in recent literature.[9]

In studies described in this paper, we selected 1,1′-bis(diphenylphosphino)ferrocene (DPPF) as a "constant" bidentate, P−P ligand (Scheme 1) and varied the bidentate N−N ligand using different diamine and diimine ligands; a tridentate N-donor was also used. The $RuCl_2(DPPF)(N{-}N)$ complexes were synthesized from $RuCl_2(PPh_3)_3$, where N−N is, respectively, ethylenediamine (en, complex **1**), *N*,*N*′-dimethyl(ethylenediamine) (dimen, complex **2**), 1,3-diaminopropane (diap, complex **4**), 2,2′-bipyridine (bipy, complex **5**), 1,10-phenanthroline (phen, complex **6**), and 1*S*,2*S*-diaminocyclohexane (1*S*,2*S*-dach, complex **7**); diethylenetriamine generated [RuCl(DPPF)(dien)]Cl (**3**). Complexes **2**−**7** are new, while **1** has been made previously by a less efficient route, for use as a catalyst precursor for dehydrogenation of diols to lactones.[10] We report also an improved synthetic route for the known complex[11] *trans*-$RuCl_2$(DPPB)(en) (**8**), where DPPB = 1,4-bis(diphenylphosphino)butane, and describe the use of **1**−**8** as catalyst precursors for hydrogen-transfer activity in basic 2-propanol for ketone reduction, in order to gain some insight into reaction mechanisms. Some of the ketone substrates were chosen as models for chromophore units present in lignin, the aim of the hydrogenation being to reduce the degree of conjugation in lignin in a search for new procedures for the bleaching of pulps.[12]

Of note is that DPPF has also been used within the isocyanide-containing complexes *trans*-$RuCl_2(DPPF)(CNR)_2$ in 2-propanol for catalyzed hydrogen-transfer hydrogenation of ketones.[13]

Experimental Section

General Procedures. Unless otherwise noted, all reactions, recrystallizations, and routine manipulations were performed at ambient conditions in an Ar-filled glovebox or by using standard Schlenk techniques under N_2. Acetone, CH_2Cl_2, $CHCl_3$, Et_2O, and EtOH were dried (over B_2O_3, CaH_2, P_2O_5, Na/benzophenone, and Mg, respectively) and were vacuum-transferred before use. Deuterated solvents were obtained from Cambridge Isotope Laboratories (CIL).

NMR spectra were recorded at room temperature (∼20 °C) in CD_2Cl_2 solution, unless otherwise stated, on a Bruker AV 400 instrument (400.0 MHz for ^{1}H, 162.0 MHz for $^{31}P\{^1H\}$, and 100.6 MHz for $^{13}C\{^1H/^{31}P\}$). Residual protonated species in deuterated solvents were used as internal references; all ^{1}H and ^{13}C shifts (s = singlet, d = doublet, t = triplet, sept = septet, m = multiplet, br = broad) are reported relative to external TMS, while $^{31}P\{^1H\}$ NMR shifts are reported relative to external 85% aqueous H_3PO_4; *J* values are given in Hz. IR spectral data for complex **8** (in KBr) were recorded on a Nicolet Magna 750 FTIR spectrometer and, for complexes **1**−**7**, on a Nic-Plan FTIR microscope. Elemental analyses were carried out on a Carlo Erba CHNS-O EA1108 analyzer. UV−vis spectra were recorded on a Hewlett-Packard 8453 DAD spectrophotometer and are presented as λ_{max} (ϵ_{max}, mol L^{-1} cm^{-1}). Conductivity data (presented as Ω^{-1} cm^2 mol^{-1}) were obtained in CH_2Cl_2 using a Thomas Serfass conductance bridge model RCM151B1 (Arthur H. Thomas Co. Ltd.) connected to a 3404 cell (Yellow Springs Instrument Co.); measurements were made at 25 °C using $\sim10^{-3}$ mol L^{-1} solutions of the complexes. Gas chromatography (GC) analyses were performed using a Hewlett-Packard 5890 GC or 5970 MSD instrument, fitted with either an HP-FFAP polar column (50 m × 0.32 mm × 0.52 μm phase thickness) or a chiral CP-Cyclodex (β-cyclodextrin) column (25 m × 0.25 mm × 0.25 μm); the oven temperature ranged from 100 to 220 °C (10 °C/min) with an injection and detector temperature of 220 °C.

Materials. The phosphines (DPPF and DPPB), the amines and imines (en, dimen, dien, diap, bipy, phen, and 1*S*,2*S*-dach), and the ketones, were used as received from Aldrich. $RuCl_3{\cdot}3H_2O$ was donated by Colonial Metals, Inc.; $RuCl_2(PPh_3)_3$[14] and $[RuCl(DPPB)]_2(\mu\text{-}Cl)_3$[15] were synthesized by the literature methods. $[RuCl(p\text{-cymene})]_2(\mu\text{-}Cl)_2$ was obtained from Strem Chemicals.

***trans*-$RuCl_2$(DPPF)(en) (1).** To a rapidly stirred, 10 mL CH_2Cl_2 suspension of $RuCl_2(PPh_3)_3$ (96 mg, 0.1 mmol) was added DPPF (55 mg, 0.1 mmol), the color changing from purple-black to red within a few minutes. The solution was stirred for 30 min, when 50 μL of a MeOH solution of 2 M en (0.1 mmol) was added, giving an immediate color change to yellow-green. After a further 30 min,

(7) (a) Abdur-Rashid, K.; Lough, A. J.; Morris, R. H. *Organometallics* **2001**, *20*, 1047. (b) Abdur-Rashid, K.; Clapham, S. E.; Hadzovic, A.; Harvey, J. N.; Lough, A. J.; Morris, R. H. *J. Am. Chem. Soc.* **2002**, *124*, 15104.

(8) Halpern, J.; Wong, L.-Y. *J. Am. Chem. Soc.* **1968**, *90*, 6665.

(9) James, B. R. *Chem. Eng. News* **2002**, *March 11*, 8.

(10) Zhao, J.; Hartwig, J. F. *Organometallics* **2005**, *24*, 2441.

(11) Queiroz, S. L.; Batista, A. A.; Oliva, G.; Gambardella, M. T. do Pi.; Santos, R. H. A.; MacFarlane, K. S.; Rettig, S. J.; James, B. R. *Inorg. Chim. Acta* **1998**, *267*, *209*.

(12) (a) Hu, T. Q.; Cairns, G. R.; James, B. R. *Holzforschung* **2000**, *54*, 127. (b) Hu, T. Q.; James, B. R. In *Chemical Modification, Properties and Usage of Lignin*; Hu, T. Q., Ed.; Kluwer Publishers: Dordrecht, The Netherlands, 2002; p 247.

(13) Cadierno, V.; Crochet, P.; Diez, J.; Garcia-Garrido, S. E.; Gimeno, J. *Organometallics* **2004**, *23*, 4836.

(14) Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Synth.* **1970**, *12*, 237.

(15) (a) Thorburn, I. S.; Rettig, S. J.; James, B. R. *Inorg. Chem.* **1986**, *25*, 234. (b) Joshi, A. M.; Thorburn, I. S.; Rettig, S. J.; James, B. R. *Inorg. Chim. Acta* **1992**, *198*−*200*, 283. (c) K. S. MacFarlane, K. S.; Thorburn, I. S.; Cyr, P. W.; Chau, D. E. K.-Y.; Rettig, S. J.; James, B. R. *Inorg. Chim. Acta* **1998**, *270*, 130.

the solvent was removed in vacuo and 5 mL of Et_2O was added. The yellow product was filtered off, washed twice with ether (2 × 5 mL), and then dried under vacuum. Yield: 74 mg (94%). ^{1}H NMR (CD_3Cl): 1.55 (br s, 4H, N*H*$_2$), 2.70 (br s, 4H, C*H*$_2$), 4.19 (s, 4H, C$_5$*H*$_4$), 4.62 (s, 4H, C$_5$*H*$_4$), 7.10−7.44 (m, 20H, Ph). ^{31}P{^{1}H} NMR (CD_3Cl): 50.9 (s). ^{13}C{^{1}H} NMR (CD_3Cl): 43.5 (s, *C*H$_2$), 70.4 (t, $^3J_{CP}$ = 2.7, *C*$_5$H$_4$), 76.6 (t, $^2J_{CP}$ = 3.6, *C*$_5$H$_4$), 87.7 (d, $^1J_{CP}$ = 24.4, *C*$_5$H$_4$), 127.6 (t, $^4J_{CP}$ = 4.3, Ph), 129.3 (s, Ph), 134.7 (t, $^2J_{CP}$ = 5.0, Ph), 139.4 (t, $^1J_{CP}$ = 18.7, Ph). ^{13}C{^{1}H,^{31}P} NMR (CD_3Cl): the above ^{13}C{^{1}H} signals became singlets. The NMR data are in excellent agreement with those in the literature[10] (but see Results and Discussion). ESI-MS (THF): *m*/*z* 787 [M + H]$^+$. IR (cm^{-1}): 3329, 3252, 3055, 2938 (ν_{N-H} and ν_{C-H}); 1562, 1482, 1434 ($\nu_{C=C}$, and C−H, N−H bending), 1161, 1094, 1028, 750, 694 (ν_{C-C}, ν_{C-N}, ν_{C-P} and bending). UV−vis: 221 (1.30 × 10^5), 335 sh (3450), 456 (550). Anal. Calcd for $C_{36}H_{36}N_2Cl_2P_2FeRu\cdot 0.5C_4H_{10}O$: C, 55.41; H, 4.98; N, 3.40. Found: C, 55.78; H, 4.89; N, 3.37. (The ether solvate was estimated by intensities of the ^{1}H NMR signals for the ether−CH_3 and en−CH_2 groups.) Rhombus-shaped single crystals of **1** (and **2**, see below) were obtained by slow evaporation of solvent from a CH_2Cl_2 solution of the complex.

Complexes **2**−**6** were synthesized using the same procedure and solvents as described for the synthesis of **1**.

***trans*-RuCl$_2$(DPPF)(dimen) (2).** Yield: 73 mg (90%). ^{1}H NMR (CD_2Cl_2): 1.58 (br s, 2H, N*H*), 2.01 (d, 6H, C*H*$_3$), 2.92 (br, s, 4H, C*H*$_2$), 4.10 (s, 4H, C$_5$*H*$_4$), 4.26 (s, 4H, C$_5$*H*$_4$), 7.10−7.44 (m, 20H, Ph). ^{31}P{^{1}H} NMR: 44.5 (br s). ^{13}C{^{1}H}: 37.8 (s, *C*H$_2$), 51.9 (s, *C*H$_3$), 69.8 (s, *C*$_5$H$_4$), 76.0 (t, *C*$_5$H$_4$), 88.2 (t, *C*$_5$H$_4$), 126.9 (d, Ph), 128.2 (t, Ph), 128.9 (s, Ph), 129.8 (s, Ph), 135.0 (s, Ph), 135.6 (s, Ph). ESI-MS (THF): *m*/*z* 815 [M + H]$^+$. IR (cm^{-1}): 3292, 3269, 3058, 2919 (ν_{N-H} and ν_{C-H}), 1482, 1433, 1397 ($\nu_{C=C}$, and C−H, N−H bending), 1183, 1180, 1038, 937, 820, 700 (ν_{C-C}, ν_{C-N}, ν_{C-P} and bending). UV−vis: 220 (1.09 × 10^5), 339 sh (1800), 464 (350). Anal. Calcd for $C_{38}H_{40}N_2Cl_2P_2FeRu$: C, 56.03; H, 4.91; N, 3.44. Found: C, 56.04; H, 4.93; N, 3.40.

[Ru(DPPF)(dien)Cl]Cl (3). Yield: 54 mg (65%). ^{1}H NMR: 2.00 (s, 1H, N*H*), 2.12 (s, 4H, N*H*$_2$), 2.33−2.86 (m, 8H, C*H*$_2$), 3.29 (s, 1H), 3.91(s, 1H), 3.99 (s, 1H), 4.21 (s, 2H), 4.49 (s, 1H), 4.66 (s, 1H), 6.03 (s, 1H) (the 7 signals from δ 3.29−6.03 correspond to the C$_5$*H*$_4$ protons), 7.10−7.44 (m, 20H, Ph). ^{31}P{^{1}H} NMR: 52.8 (d, $^2J_{PP}$ = 36.5), 37.7 (d, $^2J_{pp}$ = 36.5). ^{13}C{^{1}H} NMR: 42.7 (s, NH$_2$*C*H$_2$), 53.3 (s, *C*H$_2$NH), 69.3 (d, *C*$_5$H$_4$), 76.1 (d, *C*$_5$H$_4$), 91.7 (t, *C*$_5$H$_4$), 126.6 (m, Ph), 127.7 (m, Ph), 128.8 (m, Ph), 131.7 (m, Ph), 134.5 (m, Ph), 137.5 (m, Ph). ESI-MS (THF): *m*/*z* 795 [M − Cl]$^+$. IR (cm^{-1}): 3341, 3234, 3054 (ν_{N-H} and ν_{C-H}), 1573, 1481, 1431 ($\nu_{C=C}$, and C−H, N−H bending), 1149, 1087, 972, 817, 745, 700 (ν_{C-C}, ν_{C-N}, ν_{C-P} and bending). UV−vis: 221 (7.34 × 10^4), 349 sh (2500), 459 (1000). Λ_M = 10.9 Ω^{-1} cm^2 mol^{-1}. Anal. Calcd for $C_{38}H_{41}N_3Cl_2P_2FeRu$: C, 55.02; H, 4.95; N, 5.07. Found: C, 54.77; H, 5.07; N, 4.92.

trans-RuCl$_2$(DPPF)(diap) (4). Yield: 76 mg (95%). ^{1}H NMR: 1.59 (s, 4H, N*H*$_2$), 2.82 (s, 6H, C*H*$_2$), 4.17 (s, 4H, C$_5$*H*$_4$), 4.59 (s, 4H, C$_5$*H*$_4$), 7.10−7.44 (m, 20H, Ph). ^{31}P{^{1}H} NMR: 49.4 (s). ^{13}C{^{1}H} NMR: 29.1 (s, CH$_2$*C*H$_2$CH$_2$), 39.4 (s, NH$_2$*C*H$_2$), 70.7 (t, *C*$_5$H$_4$), 76.5 (t, *C*$_5$H$_4$), 86.4 (t, *C*$_5$H$_4$), 127.7 (m, Ph), 128.5 (m, Ph), 129.3 (s, Ph), 131.5 (m, Ph), 133.1 (m, Ph), 135.4 (m, Ph). ESI-MS (THF): *m*/*z* 800 [M + H]$^+$. IR (cm^{-1}): 3329, 3313, 3243, 3054, 2927 (ν_{N-H} and ν_{C-H}), 1560, 1482, 1434 ($\nu_{C=C}$, and C−H, N−H bending), 1092, 750, 695 (ν_{C-C}, ν_{C-N}, ν_{C-P} and bending). UV−vis: 221 (1.37 × 10^5), 340 sh (2330), 456 (430). Anal. Calcd for $C_{37}H_{38}N_2Cl_2P_2FeRu$: C, 55.50; H, 4.75; N, 3.50. Found: C, 55.79; H, 5.01; N, 3.38.

***Cis*-RuCl$_2$(DPPF)(bipy) (5).** Yield: 84 mg (95%). ^{1}H NMR: 3.44 (s, 1H), 4.19 (s, 1H), 4.29 (s, 1H), 4.39 (s, 1H), 4.52 (s, 2H), 5.01 (s, 1H), 6.02 (s, 1H) (the 7 signals from δ 3.44−6.02 correspond to the C$_5$*H*$_4$ protons), 6.80−8.50 (m, 20H, Ph). ^{31}P{^{1}H} NMR: 44.2 (d, $^2J_{pp}$ = 30.0), 38.6 (d, $^2J_{PP}$ = 30.0). ^{13}C{^{1}H,^{31}P} NMR: 65.0, 69.7, 70.3, 73.1, 75.1, 76.9, 77.8, 84.8 (s, *C*$_5$H$_4$), 121.6, 123.4, 125.2, 125.3, 125.8, 125.9, 126.0, 126.1, 126.5, 127.5, 127.6, 127.8, 128.7, 130.0, 131.7, 133.2, 133.5, 133.6, 133.7, 133.8, 136.6, 150.2, 151.3, 157.4 (s, Ph and bipy rings). ESI-MS (THF): *m*/*z* 847 [M − Cl]$^+$. IR (cm^{-1}): 3099, 3076, 3050 (ν_{N-H} and ν_{C-H}), 1482, 1443, 1432 ($\nu_{C=C}$, and C−H bending), 1164, 1091, 1039, 751, 696 (ν_{C-C}, ν_{C-N}, ν_{C-P} and bending). UV−vis: 220 (7.30 × 10^4), 303 (1.58 × 10^4), 456 (4490), 545 sh (2200). $\Lambda_M \approx 0$. Anal. Calcd for $C_{44}H_{36}N_2Cl_2P_2FeRu$: C, 59.89; H, 4.08; N, 3.17. Found: C, 60.27; H, 4.45; N, 3.16. Red, hexagon-shaped single crystals of **5** were obtained by slow evaporation of solvent from a CH_2Cl_2 solution of the complex.

***Cis*-RuCl$_2$(DPPF)(phen) (6).** Yield: 81 mg (94%) ^{1}H NMR: 3.37(s, 1H), 4.14 (s, 1H), 4.26 (s, 1H), 4.36 (s, 1H), 4.41 (s, 1H), 4.50 (s, 1H), 5.06 (s, 1H), 6.12 (s, 1H) (the signals between 3.30 and 6.20 are due to the eight C$_5$*H*$_4$ protons), 6.70−8.30 (m, 28H, Ph). ^{31}P{^{1}H} NMR: δ 43.6 (d, $^2J_{PP}$ = 30.6), 37.4 (d, $^2J_{PP}$ = 30.6). ^{13}C{^{1}H,^{31}P} NMR: 66.1, 70.7, 71.3, 73.8, 74.1, 76.2, 78.0, 79.0, 85.6 (s, *C*$_5$H$_4$), 122.6, 124.5, 124.9, 126.3, 126.6, 127.0, 127.6, 128.5, 128.8, 129.6, 129.8, 130.0, 131.0, 132.9, 134.4, 134.7, 134.9, 137.7, 148.2, 151.3, 152.4, 156.1, 158.5 (s, Ph and phen rings). ESI-MS (THF): *m*/*z* 871 [M − Cl]$^+$. IR (cm^{-1}): 3099, 3046, 3017 (ν_{N-H} and ν_{C-H}), 1585, 1482, 1431 ($\nu_{C=C,}$ and C−H bending), 1152, 1091, 1038, 846, 694 (ν_{C-C}, ν_{C-N}, ν_{C-P} and bending). UV−vis: 220 (1.04 × 10^5), 274 (3.66 × 10^4), 442 (5250), 547 sh (1570). $\Lambda_M \approx 0$. Anal. Calcd for $C_{46}H_{36}N_2Cl_2P_2FeRu$: C, 60.93; H, 3.97; N, 3.09. Found: C, 60.58; H, 4.11; N, 3.12.

***trans*-RuCl$_2$(DPPF)(1*S*,2*S*-dach) (7).** The synthesis follows that given for **1**, except that after evaporation of the CH_2Cl_2, 2-propanol was added to precipitate the product, which was then washed with MeOH (5 mL) and dried under vacuum. Yield: 50.0 mg, 60%. ^{1}H NMR: 1.04 (m, 4H), 1.55 (s, 4H), 1.71(d, 2H), 2.43 (d, 2H), 2.65 (m, 4H), 4.20 (s, 2H, C$_5$*H*$_4$), 4.23 (s, 2H, C$_5$*H*$_4$), 4.57 (s, 2H, C$_5$*H*$_4$), 4.71 (s, 2H, C$_5$*H*$_4$), 7.20−7.60 (m, 12H, Ph ring), 7.87 (d, 8H, Ph ring); trace peaks at 1.17 (d), 2.18 (s), and 4.00 (sept) are due to 2-propanol. ^{31}P{^{1}H} NMR: 51.4 (s). ^{13}C{^{1}H,^{31}P} NMR: 24.9, 36.1, 57.5 (1*S*,2*S*-cyclohexyl ring), 70.2, 70.4, 76.5, 76.8, 88.9 (s, *C*$_5$H$_4$), 127.5, 127.7, 128.9, 129.2, 129.4, 132.2, 132.3, 134.6, 134.9, 139.3, 139.4 (s, Ph rings). ESI-MS (THF): *m*/*z* 805.1 [M − Cl]$^+$. IR (cm^{-1}): 3329, 3053, 2935, 2858 (ν_{N-H} and ν_{C-H}), 1565, 1481, 1433 ($\nu_{C=C}$, and C−H, N−H bending), 1185, 1178, 1092, 1028, 746, 697 (ν_{C-C}, ν_{C-N}, ν_{C-P} and bending). Anal. Calcd for $C_{40}H_{42}N_2Cl_2P_2FeRu$: C, 57.15; H, 5.00; N, 3.33. Found: C, 57.27; H, 5.04; N, 3.11.

***trans*-RuCl$_2$(DPPB)(en) (8).** Two procedures were used to synthesize **8**: (i). To [RuCl(DPPB)]$_2$(μ-Cl)$_3$ (123.3 mg, 0.2 mmol of Ru) dissolved in 5 mL of CH_2Cl_2 was added 0.1 mL of an EtOH solution of 2 M en (0.2 mmol). The color changed from red to green when the solution was stirred for 2 h. The solvent was then removed under vacuum to give a residue, to which 5 mL of EtOH was added; the remaining solid was filtered off, washed with more EtOH (10 mL), and dried under vacuum. Yield: 94 mg (71%). (ii) [RuCl(DPPB)]$_2$(μ-Cl)$_3$ (0.123.3 mg) was suspended in EtOH (10 mL), and 1 equiv of en was added as the mixture was stirred and heated to ∼ 50 °C for 10 h, when the color changed from red to green. The solid product was filtered off, washed with EtOH (2 × 5 mL), and dried under vacuum. Yield: 84 mg (64%). The ^{1}H and ^{31}P{^{1}H} NMR data in $CDCl_3$ were in excellent agreement with the literature data.[11] ESI-MS (THF): *m*/*z* 659, [M + H]$^+$. IR (cm^{-1}): 3052, 2922 (ν_{N-H} and ν_{C-H}), 1566, 1509, 1449, 1434 ($\nu_{C=C}$, and C−H, N−H bending), 1028, 898, 876, 743, 534 (ν_{C-C}, ν_{C-N}, ν_{C-P} and bending). Anal. Calcd for $C_{30}H_{36}N_2Cl_2P_2Ru$: C, 54.67; H, 5.47; N, 4.25. Found: C, 54.61; H, 5.50; N, 4.24. Block single crystals of **8** were obtained by slow evaporation of the solvents from a mixed CH_2Cl_2/EtOH solution (1:1 v/v) of the complex.

Table 1. Crystal Data and Structure Refinement Details for Complexes 1, 2, 5, and 8

empirical formula	$C_{36}H_{36}N_2P_2Cl_2FeRu\cdot 2CH_2Cl_2$ (**1**)	$C_{38}H_{40}N_2P_2Cl_2FeRu\cdot CH_2Cl_2$ (**2**)	$C_{44}H_{36}N_2P_2Cl_2FeRu\cdot 2CH_2Cl_2$ (**5**)	$C_{30}H_{36}N_2P_2Cl_2Ru$ (**8**)
fw	956.28	899.41	1052.36	658.52
cryst color, habit	yellow, block	yellow, block	red, block	green, block
cryst syst	triclinic	monoclinic	orthorhombic	monoclinic
cryst dimens	0.25 × 0.24 × 0.17 mm	0.50 × 0.26 × 0.11 mm	0.56 × 0.49 × 0.25 mm	0.30 × 0.20 × 0.10 mm
space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$Pna2_1$/ (No. 33)	$P2_1/c$ (No. 14)
unit cell dimens				
a (Å)	11.3221(13)	14.8147(19)	13.0207(18)	13.584(1)
b (Å)	11.8585(14)	14.895(2)	16.928(2)	12.8507(7)
c (Å)	16.4254(19)	17.335(2)	19.903(3)	18.122(1)
α (deg)	102.8433(16)			
β (deg)	103.6783(17)	92.937(9)		111.750(3)
γ (deg)	104.7914(16)			
volume (Å^3)	1975.8(4)	3820.3(9)	4386.8(11)	2928.4(3)
Z	2	4	4	4
calcd density (g cm^{-3})	1.607	1.564	1.593	1.494
temp, K	193.2(1)	193.2(1)	193.2(1)	173.2(1)
μ(Mo Kα), (mm^{-1})	1.267	1.170	1.150	0.850
θ range for data collection (deg)	2.57 to 26.39	10.02 to 12.5	11.05 to 28.8	2.27 to 27.87
index ranges	$-14 \le h \le 14$ $-14 \le k \le 14$ $-20 \le l \le 20$	$-17 \le h \le 0$ $-17 \le k \le 0$ $-20 \le l \le 20$	$-16 \le h \le 16$ $-21 \le k \le 21$ $-24 \le l \le 24$	$-17 \le h \le 16$ $-16 \le k \le 15$ $-21 \le l \le 22$
no. of reflns collected	23533	7000	9391	26014
no. of indep reflns	8067	6724	9086	6633
no. of data/restraints/params	8067/4/448	6724/0/429	9086/0/524	6633/0/350
goodness-of-fit on F^2	1.064	1.032	1.062	1.082
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0483$ $wR_2 = 0.1386$	$R_1 = 0.0638$ $wR_2 = 0.1642$	$R_1 = 0.0619$ $wR_2 = 0.1516$	$R_1 = 0.045$ $wR_2 = 0.139$
largest diff peak and hole	2.077 and −1.381 e/Å^3	0.939 and −0.701 e/Å^3	0.873 and −0.722 e/Å^3	0.77 and −1.15 e/Å^3

Crystal Structure Determination. Suitable crystals were mounted on glass fibers by means of mineral oil, and the data were collected using graphite-monochromated Mo Kα radiation (0.71073 Å). Data collections were performed on a Bruker PLATFORM/SMART 1000 CCD diffractometer (for compound **1**), a Siemens P4/RA diffractometer (for **2** and **5**), and a Rigaku/ADSC area detector diffractometer (for **8**). The structures of **1**, **2**, and **5** were solved at the University of Alberta, and that of **8** at the University of British Columbia. The structures were solved by direct methods using SHELXL-86 (for **1** and **2**),[16] SIR97 (for **8**),[16] or the Patterson search/structure expansion (DIRDIF-99) (for **5**),[17] and were refined using full-matrix least-squares on F^2 (SHELXL-93) (for **1**, **2**, and **5**)[16] and F^2 (SHELXL-97) (for **8**).[18] All the non-hydrogen atoms in the four structures were refined with anisotropic displacement parameters. The selected crystal data and structure refinement details for **1**, **2**, **5**, and **8** are listed in Table 1.

General Procedure for the Catalytic Studies. The procedure used follows standard literature methods, the hydrogen-transfer experiments being carried out in standard Schlenk glassware.[4,19] All reactions were set up in a dry glovebox under N_2 using 10^{-5} M catalyst in 2-propanol (10 mL) and a molar ratio of catalyst/KOH/substrate = 1:20:1000, and the magnetically stirred reaction mixture was heated at 80 °C for selected times. For the high-pressure H_2 experiments, catalyst, base, solvent, and substrate were placed (inside the dry glovebox) in a glass sleeve containing a magnetic stir-bar; the sleeve was then placed and sealed in a Parr reactor autoclave (30 mL capacity), which was subsequently purged with H_2 and filled to a selected H_2 pressure. The reaction mixture was then stirred and heated at 80 °C, usually for 24 h. The pressure was then released, and a 0.1 mL reaction sample was collected and diluted with 1 mL of ethyl acetate and acetone (4:1 v/v). The reaction products were isolated and identified by GC by comparison with data for known compounds.

Results and Discussion

Synthesis and Characterization of Complexes. Complexes **1**, **2**, and **4**−**7**, of formulation $RuCl_2$(DPPF)(N−N) [N−N = en (**1**), dimen (**2**), diap (**4**), bipy (**5**), phen (**6**), and 1*S*,2*S*-dach (**7**)], and [RuCl(DPPF)(dien)]Cl (**3**) (see Scheme 1) were synthesized from $RuCl_2(PPh_3)_3$ via consecutive substitution reactions. Addition of 1 equiv of DPPF to a CH_2Cl_2 solution of $RuCl_2(PPh_3)_3$ under aerobic conditions resulted in a rapid color change from blackish-purple to red, presumably due to formation of $RuCl_2$(DPPF)(PPh_3), analogous to formation of the corresponding DPPB complex;[11,15b] subsequent addition of 1 equiv of diamine, dien, or diimine resulted in further color changes, and straightforward workup of the solutions gave good to high yields of high-purity products: complexes **1**−**4** and **7** are yellow, while **5** and **6** are red. The ligand substitution reactions could be readily monitored by the $^{31}P\{^1H\}$ signal of the PPh_3 generated. Complex **1** has been synthesized recently in lower yield using $[RuCl_2(C_6H_6)]_2$ as precursor.[10]

The attempted synthesis of *trans*-$RuCl_2$(DPPB)(en) (**8**) from $RuCl_2(PPh_3)_3$ via the same procedure was unsatisfactory in that a pure product could not be isolated from a mixture of Ru(II) complexes that were formed in solution; however, pure **8** was obtained when $[RuCl(DPPB)]_2(\mu\text{-}Cl)_3$[15] was used as the precursor. The green complex **8** has been made previously, in a similar yield, from $RuCl_2$(DPPB)(PPh_3).[11]

The electrospray mass spectra in THF solution of complexes **1**, **2**, **4**, and **8**, which have *trans*-chlorides (see below), show a

(16) (a) Sheldrick, G. M. *Acta Crystallogr.* **1990**, *A46*, 467. (b) Sheldrick, G. M. *SHELXL-93, Program for crystal structure determination*; University of Göttingen: Germany, 1993. (c) *SIR9*: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.

(17) (a) Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Garcia-Granda, S.; Israel, R.; Gould, R. O.; Smits, J. M. M. *DIRDIF-99*; University of Nijmegen, The Netherlands, 1999. (b) Flack, H. D. *Acta Crystallogr.* **1983**, *A39*, 876. (c) Flack, H. D.; Bernardinelli, G. *Acta Crystallogr.* **1999**, *A55*, 908. (d) Flack, H. D.; Bernardinelli, G. *J. Appl. Crystallogr.* **2000**, *33*, 1143. The Flack parameter refines to a value near zero for the correct configuration of the structure and to a value of about one for the inverted configuration.

(18) Sheldrick, G. M. *SHELXL-97, Program for crystal structure determination*; University of Göttingen: Germany, 1997.

(19) For example: (a) James, B. R.; Morris, R. H. *J. Chem. Soc., Chem. Commun.* **1978**, 929. (b) Mizushima, E.; Yamaguchi, M.; Yamagishi, T. *J. Mol. Catal. A* **1999**, *148*, 69. (c) Lindner, E.; Warad, I.; Eichele, K.; Mayer, H. A. *Inorg. Chim. Acta* **2003**, *350*, 49.

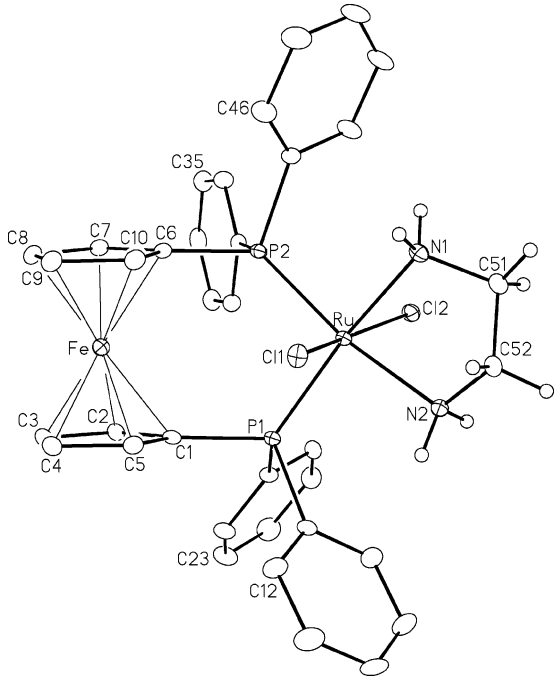


Figure 1. ORTEP diagram of *trans*-$RuCl_2$(DPPF)(en) (**1**) with 20% probability Gaussian ellipsoids; H atoms on phenyl and cyclopentadienyl rings not shown.

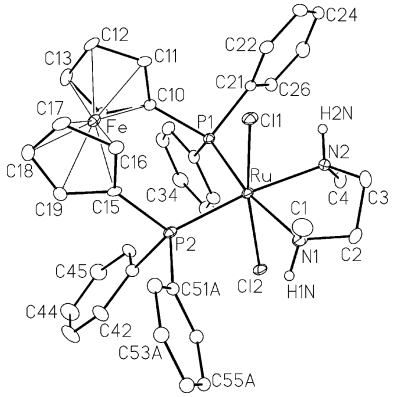


Figure 2. ORTEP diagram of *trans*-$RuCl_2$(DPPF)(dimen) (**2**) with 20% probability Gaussian ellipsoids; H atoms not shown except for those on the N atoms.

peak corresponding to monoprotonated $RuCl_2$(DPPF)(diamine) species, while complexes **5** and **6**, which have *cis*-chlorides (see below), reveal a peak corresponding to [RuCl(DPPF)(diamine)]$^+$. There is no general pattern in the MS data, however, in that **7** (a *trans*-dichloro species) gives a major peak for [RuCl(DPPF)(dach)]$^+$. Complex **3**, the ionic species [RuCl(DPPF)(dien)]Cl, containing the tridentate dien ligand, gives a major MS peak corresponding to that of the cation.

Crystal Structures of *trans*-$RuCl_2$(DPPF)(en) (1), *trans*-$RuCl_2$(DPPF)(dimen) (2), *cis*-$RuCl_2$(DPPF)(bipy) (5), and *trans*-$RuCl_2$(DPPB)(en) (8). The X-ray diffraction analyses of **1**, **2**, and **8** (Figures 1, 2, and 4, respectively) reveal *trans*-dichloro structures, with the bidentate ligands necessarily being *cis*; selected bond lengths and angles are listed in Tables 2, 3, and 5, respectively. The geometry at the metal is distorted octahedral, as seen by the P−Ru−P angles (in the 95.1−95.9° range), the N−Ru−N angles (78.3−79.9°), and the Cl−Ru−Cl angles (165.5−167.3°). These angles and the average Ru−ligand bond lengths to Cl, N, and P are close to those determined previously in structures of other *trans*- and *cis*-$RuCl_2$(diphosphine)(diamine or diimine) complexes, where the diphosphine is chiral

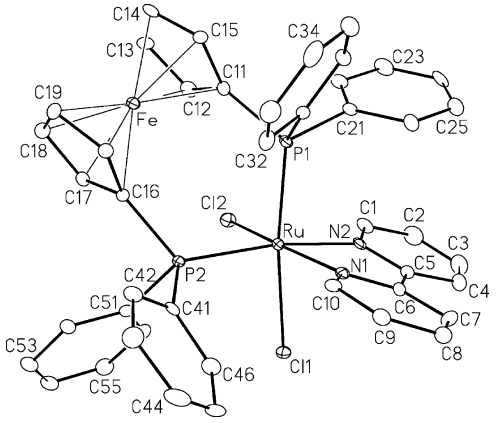


Figure 3. ORTEP diagram of *cis*-$RuCl_2$(DPPF)(bipy) (**5**) with 20% probability Gaussian ellipsoids; H atoms not shown.

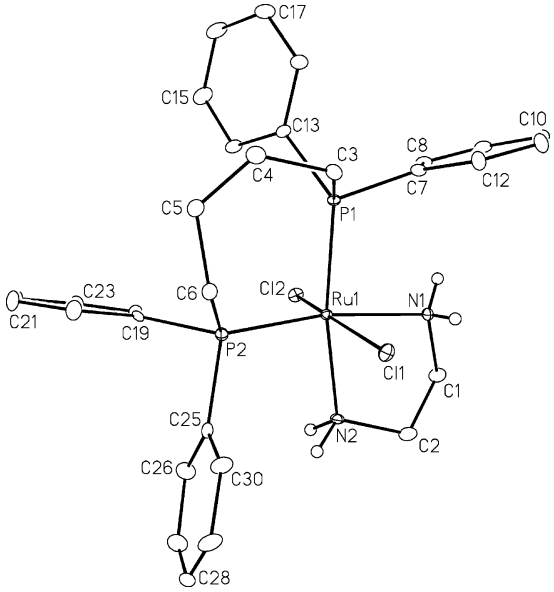


Figure 4. ORTEP diagram of *trans*-$RuCl_2$(DPPB)(en) (**8**) with 20% probability Gaussian ellipsoids; H atoms not shown except for those on the N atoms.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for *trans*-$RuCl_2$(DPPF)(en) (1) with Estimated Standard Deviations in Parentheses

Ru−N(1)	2.167(3)	Cl(1)−Ru−Cl(2)	166.31(4)
Ru−N(2)	2.171(3)	Cl(1)−Ru−P(1)	87.40(4)
Ru−Cl(1)	2.4030(10)	Cl(1)−Ru−P(2)	96.61(4)
Ru−Cl(2)	2.4279(10)	Cl(1)−Ru−N(1)	83.68(10)
Ru−P(1)	2.2957(10)	Cl(1)−Ru−N(2)	84.06(9)
Ru−P(2)	2.2865(9)	Cl(2)−Ru−P(1)	104.05(4)
Fe−C(1)	2.068(4)	Cl(2)−Ru−P(2)	89.74(4)
Fe−C(2)	2.053(4)	Cl(2)−Ru−N(1)	83.95(10)
Fe−C(3)	2.048(4)	Cl(2)−Ru−N(2)	87.70(9)
Fe−C(4)	2.031(4)	P(1)−Ru−P(2)	95.87(4)
Fe−C(5)	2.029(4)	P(1)−Ru−N(1)	168.53(10)
Fe−C(6)	2.039(4)	P(1)−Ru−N(2)	93.65(9)
Fe−C(7)	2.048(4)	P(2)−Ru−N(1)	92.33(10)
Fe−C(8)	2.050(4)	P(2)−Ru−N(2)	170.47(9)
Fe−C(9)	2.051(4)	N(1)−Ru−N(2)	78.28(13)
Fe−C(10)	2.030(4)	Ru−N(1)−C(51)	111.0(2)
		Ru−N(2)−C(52)	111.1(2)

or nonchiral and the N−N donor is chiral or nonchiral;[4a,11,20,21] the major interest in the chiral systems is their use as catalysts, particularly for asymmetric hydrogen-transfer hydrogenation of ketones.[4a,20] For all the *trans*-dichloro complexes, including **1**, **2**, and **8**, the Ru−Cl distances are all within 0.025 Å of each other. The crystal structure of **5** (Figure 3) revealed *cis*-

Table 3. Selected Bond Lengths (Å) and Angles (deg) for *trans*-$RuCl_2$(DPPF)(dimen) (2) with Estimated Standard Deviations in Parentheses[a]

Ru−N(1)	2.229(6)	Cl(1)−Ru−Cl(2)	167.34(7)
Ru−N(2)	2.205(7)	Cl(1)−Ru−P(1)	87.78(7)
Ru−Cl(1)	2.422(2)	Cl(1)−Ru−P(2)	97.53(8)
Ru−Cl(2)	2.419(2)	Cl(1)−Ru−N(1)	86.73(18)
Ru−P(1)	2.307(2)	Cl(2)−Ru−P(1)	104.14(7)
Ru−P(2)	2.294(2)	Cl(2)−Ru−P(2)	85.74(7)
		Cl(2)−Ru−N(1)	80.84(18)
Ru−N(1)−C(1)	120.9(5)	Cl(2)−Ru−N(2)	90.45(19)
Ru−N(2)−C(4)	118.0(5)	P(1)−Ru−P(2)	95.42(7)

[a] Other bond lengths and bond angles are within 0.02 Å and 3°, respectively, of the corresponding values given for complex **1** in Table 2.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for *cis*-$RuCl_2$(DPPF)(bipy) (5) with Estimated Standard Deviations in Parentheses

Ru−N(1)	2.086(6)	Cl(1)−Ru−Cl(2)	92.08(7)
Ru−N(2)	2.118(6)	Cl(1)−Ru−P(1)	172.91(7)
Ru−Cl(1)	2.4876(19)	Cl(1)−Ru−P(2)	89.71(7)
Ru−Cl(2)	2.433(2)	Cl(1)−Ru−N(1)	82.38(18)
Ru−P(1)	2.289(2)	Cl(2)−Ru−P(1)	90.94(7)
Ru−P(2)	2.345(2)	Cl(2)−Ru−P(2)	87.05(7)
N(1)−C(6)	1.355(11)	Cl(2)−Ru−N(1)	167.3(2)
N(2)−C(1)	1.329(11)	Cl(2)−Ru−N(2)	89.9(2)
		P(1)−Ru−P(2)	96.86(7)
		P(1)−Ru−N(1)	93.36(18)
		P(2)−Ru−N(1)	104.3(2)
		N(1)−Ru−N(2)	78.0(3)

[a] The bond lengths and angles within the coordinated DPPF are within 0.02 Å and 3°, respectively, of the corresponding values given for complex **1** in Table 2.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for *trans*-$RuCl_2$(DPPB)(en) (8) with Estimated Standard Deviations in Parentheses[a]

Ru(1)−N(1)	2.185(3)	N(2)−Ru(1)−N(1)	78.7(1)
Ru(1)−N(2)	2.172(3)	N(2)−Ru(1)−P(2)	93.51(9)
Ru(1)−Cl(1)	2.4228(9)	N(2)−Ru(1)−P(1)	170.60(8)
Ru(1)−Cl(2)	2.4332(9)	N(1)−Ru(1)−P(1)	92.26(9)
Ru(1)−P(1)	2.2888(9)	P(2)−Ru(1)−P(1)	95.12(3)
Ru(1)−P(2)	2.2791(9)	N(1)−Ru1−Cl(1)	84.0(1)
P(1)−C(3)	1.852(4)	P(1)−Ru(1)−Cl(1)	91.26(3)
P(2)−C(6)	1.832(4)	P(2)−Ru(1)−Cl(2)	103.57(3)
C(4)−C(5)	1.516(6)	P(1)−Ru(1)−Cl(2)	96.32(3)
		Cl(1)−Ru(1)−Cl(2)	165.57(3)
Ru(1)−P(1)−C(3)	117.7(1)	C(3)−C(4)−C(5)	116.1(3)
Ru(1)−P(2)−C(6)	113.5(1)	C(4)−C(5)−C(6)	116.4(3)

[a] The bond lengths and angles within the coordinated en are within 0.02 Å and 3°, respectively, of the corresponding values given for complex **1** in Table 2.

dichloride ligands, with one chlorine necessarily being *trans* to a P atom and one *trans* to a N atom; the Ru−Cl bond length for the chlorine *trans* to phosphorus (2.488 Å) is about 0.055 Å longer than for that *trans* to nitrogen, in line with the expected *trans*-effect.[22] More generally, differences in the Ru−Cl bond of the *cis*-dichloro complexes are in the 0.05−0.09 Å range.[4a,11,20,21] Such $RuCl_2$(P−P)(N−N) structures have been discussed extensively,[4a,11,20,21] and, at least in one set of complexes, the *trans*- and *cis*-species have been shown to be the kinetic and thermodynamic products, respectively.[11]

The two planar, cyclopentadienyl rings of ferrocene within structures **1**, **2**, and **5** are eclipsed and are essentially coplanar, the average torsion angle (H−C---C−H) between the C−H of one ring and the most adjacent one of the other ring being 8.39° (for **1**), 8.00° (for **2**), and 13.6° (for **5**); the corresponding P−C−C−P torsion angles are 8.04°, 9.06°, and 19.7°. In the solution ^{1}H NMR spectra of **1** and **2** at room temperature, two signals are seen for the ferrocene rings (see below), implying that the small twist seen in the solid state is not evident in solution. For complex **5**, there is more splitting of the ferrocene-^{1}H signals (see below), consistent with the greater twist evident in the solid state.

NMR Characterization. The ^{31}P{^{1}H} and ^{1}H solution spectra (in CD_2Cl_2 or CD_3Cl) of each complex (**1**−**8**) revealed the presence of just a single species. The ^{31}P{^{1}H} NMR spectra in CD_2Cl_2 of the structurally characterized *trans*-dichloro complexes **1**, **2**, and **8** show a singlet in the δ 44.5−50.9 range, consistent with a regular octahedral structure containing a C_2 axis (see Scheme 1), essentially that of the solid-state structure without the minor distortions. Complexes **4** and **7** similarly show ^{31}P{^{1}H} singlets at δ 49.4 and 51.4, respectively, and are thus also assumed to have *trans*-dichloro structures. In contrast, solutions of complexes **3**, **5**, and **6** show a typical AX doublet of doublets pattern in their ^{31}P{^{1}H} NMR spectra. For **5** and **6** (which were nonelectrolytes in CH_2Cl_2), the spectra are very similar with equal intensity doublets centered, respectively, at δ ~44 and ~38 with $^2J_{PP}$ values of 30.6 Hz; presumably both **5** and **6** in solution have the *cis*-dichloro structure (see Scheme 1), consistent with the solid-state structure determined for **5**. Complex **3** is a 1:1 electrolyte as expected, as evidenced by conductivity data in CH_2Cl_2 (Λ_M = 10.9 Ω^{-1} cm^2 mol^{-1}).[23] The dien ligand is tridentate, enforcing a *cis*-disposition of the P atoms in a structure like that shown in Scheme 1 for **5** and **6**, but with one chloride replaced by a dien N atom; the ^{31}P{^{1}H} data for **3** (δ 52.8 and 38.6, $^2J_{PP}$ = 35.5 Hz) are similar to those of **5** and **6**, suggesting that the Cl *trans* to P_A is replaced (see Scheme 1).

Of note, it is the bidentate-diimine ligand systems, **5** and **6**, that generate the *cis*-dichloro species, while the bidentate-diamine species (**1**, **2**, **4**, **7**, and **8**) exist as *trans*-dichloro species. Presumably the rigid diimines, compared to the more flexible diamines, have considerably less steric interaction with *cis*-chlorides (see Figure 3, for **5**) than with *trans*-dichlorides (cf. Figure 3 vs Figures 1 and 2 for complexes **1** and **2**). Attempts to synthesize $RuCl_2$(DPPF)(2,2′-biquinoline) with the bulkier diimine were unsuccessful. Of note, within the series of $RuCl_2$(DPPB)(N−N) complexes, when N−N is bipy or phen, both the *cis*- and *trans*-dichloro species have been isolated, the former

(20) For example: (a) Gao, J.-X.; Ikariya, T.; Noyori, R. *Organometallics* **1996**, *15*, 1087. (b) Akotsi, O. M.; Metera, K.; Reid, R. D.; McDonald, R.; Bergens, S. H. *Chirality* **2000**, *12*, 514. (c) Doherty, S.; Newman, C. R.; Hardacre, C.; Nieuwenhuyzen, M.; Knight, J. G. *Organometallics* **2003**, *22*, 1452. (d) Lindner, E.; Mayer, H. A.; Warad, I.; Eichele, K. *J. Organomet. Chem.* **2003**, *665*, 176. (e) Lindner, E.; Warad, I.; Eichele, K.; Mayer, H. A. *Inorg. Chim. Acta* **2003**, *350*, *49*. (f) Leong, C. G.; Akotsi, O. M.; Ferguson, M. J.; Bergens, S. H. *Chem. Commun.* **2003**, 750 and 1779 (correction). (g) Baratta, W.; Herdtweck, E.; Siega, K.; Toniutti, M.; Rigo, P. *Organometallics* **2005**, *24*, 1660. (h) de Araujo, M. P.; de Figueiredo, A. T.; Bogado, A. L.; Poelhsitz, G. V.; Ellena, J.; Castellano, E. E.; Donnici, C. L.; Comasseto, J. V.; Batista, A. A. *Organometallics* **2005**, *24*, 6159.

(21) For example: (a) Song, J.-H.; Cho, D.-J.; Jeon, S.-J.; Kim, Y.-H.; Kim, T.-J.; Jeong, J. H. *Inorg. Chem.* **1999**, *38*, 893. (b) Santra, P. K.; Sinha, C.; Sheen, W.-J.; Liao, F.-L.; Lu, T.-H. *Polyhedron* **2001**, *20*, 599. (c) Korenaga, T.; Aikawa, K.; Terada, M.; Kawauchi, S.; Mikami, K. *Adv. Synth. Catal.* **2001**, *343*, 284. (d) Butler, I. R.; Coles, S. J.; Fontani, M.; Hursthouse, M. B.; Lewis, E.; Abdul Malik, K. L. M.; Meunier, M.; Zanello, P. *J. Organomet. Chem.* **2001**, *637*−*639*, 538. (e) Wong, W.-K.; Chen, X.-P.; Guo, J.-P.; Chi, Y.-G.; Pan, W.-X.; Wong, W.-Y. *J. Chem. Soc., Dalton Trans.* **2002**, 1139. (f) Nachtigal, C.; Al-Gharabli, S.; Eichele, K.; Lindner, E.; Mayer, H. A. *Organometallics* **2002**, *21*, 105. (g) Harvey, B. G.; Arif, A. M.; Ernst, R. D. *Polyhedron* **2004**, *23*, 2725. (h) Santiago, M. O.; Batista, A. A.; de Araújo, M. P.; Donnici, C. L.; Moreira, I. de S.; Castellano, E. E.; Ellena, J.; Santos, S. dos; Queiroz, S. *Transition Met. Chem.* **2005**, *30*, 170.

(22) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1988; p 1299.

(23) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, *81*.

being the thermodynamic product;[11] this is consistent with the DPPB ligand being less bulky and more flexible that DPPF. Although only *trans*-$RuCl_2$(DPPB)(en) has been isolated (ref 11 and this work), the overall findings imply that the *cis*-isomer should be isolable under appropriate conditions.

The ^{1}H NMR spectra for the eight cyclopentadienyl (Cp) protons of the DPPF ligand provide information of the degree of deformity of the ferrocene rings. For CD_2Cl_2 solutions of the *trans*-dichloro complexes, **1**, **2**, and **4**, two equal intensity singlets are observed in the δ 4.1−4.6 range, each corresponding to four protons, presumably, for example, for **1** (see Figure 1) on C atoms C2, C5, C7, and C10 and on C atoms C3, C4, C8, and C9; these data are consistent with the solid-state structures determined for **1** and **2**, where the two ferrocene rings are eclipsed and are essentially coplanar. The structure of **4** is presumably similar. The corresponding ^{1}H spectrum for *trans*-$RuCl_2$(DPPF)(1*S*,2*S*-dach) (**7**) is different in that four singlets of two protons each are seen in the δ 4.2−4.7 range, implying that in a structure that must be similar to that of **1** (Figure 1) the C2- and C5-protons must be magnetically slightly different than those on C7 and C10, and similarly the C3/C4 protons differ from the C8/C9 set; five ^{13}C resonances are seen for the C atoms of the two Cp rings.

The ^{1}H NMR spectra for the eight Cp protons of the ionic monochloro complex **3** and the *cis*-dichloro complexes **5** and **6** are more complex, with signals covering the range δ 3.2−6.2. For **3** and **5**, seven resonances are seen with one at δ 4.21 and 4.52, respectively, having twice the intensity of the others; for **6**, eight signals of equal intensity are observed. The ^{1}H−^{1}H COSY spectrum of **6** (Figure S1) shows clearly the eight resonances, and the cross-peaks confirm that signals 1, 2, 3, and 4 come from one ring and that signals 5, 6, 7, and 8 come from the other ring. The more complex spectra are consistent with less symmetrical structures (cf. the above crystal structure section). For all the complexes **1**−**7**, the expected $^3J_{HH}$ coupling for the Cp protons is not resolved, and the resonances are seen as singlets.

Generally, the more flexible amine-containing structures reveal, as expected, a lower number of ^{13}C resonances than do the more rigid imine-containing species. For complexes **1**−**4**, three singlet ^{13}C resonances are seen for the Cp carbon atoms, which correspond to the three types of Cp-carbons; for example, for **1**, signals at δ 70.4, 76.6, and 87.7 must correspond to C3,C4,C8,C9; C2,C5,C7,C10; and C1,C6, respectively (Figure 1), and an APT measurement (Attached Proton Test) confirmed these assignments. For **7**, five resonances are seen at δ 70.2, 70.4, 76.5, 76.8, and 88.9, suggesting that the two sets of close singlets (e.g., at δ 70.2/70.4 and at 76.5/76.8) are each seen as one singlet for complexes **1**−**4**. The *cis*-complexes **5** and **6** have less symmetry and show eight and nine resonances, respectively; for example, for **6**, there are two sets of singlets at δ 66.1, 71.3, 74.1, 78.0 and at δ 70.7, 73.8, 76.2, 79.0, which correspond to the eight C−H carbons of the two Cp rings, and a singlet at δ 85.6 that is characteristic of the two C−P carbons.

Similar complications arise when trying to assign ^{13}C{^{1}H} signals for the phenyl carbon atoms. Complex **1** shows essentially four signals (corresponding to the four types of carbons), which are in excellent agreement with values in the literature,[10] where, however, the multiplicity of the ^{13}C{^{1}H} signals was not discussed (note that this complex is incorrectly numbered in the Experimental Section of ref 10); the doublet and triplet patterns are necessarily due to coupling to P atoms, and this was shown in our work by measuring the ^{13}C{^{1}H,^{31}P} signals, which are all singlets (the triplets must result from some sort of virtual coupling between the two P atoms). Complexes **2**−**4** show six ^{13}C{^{1}H} signals, but the spectra are complicated, as the resonances are a mixture of singlets, doublets, triplets, and multiplets because of coupling to P atoms. In the ^{13}C{^{1}H,^{31}P} data for **7**, the phenyl carbons appear as two sets of six singlets (with a maximum of 0.3 ppm between each pair of corresponding singlets), presumably implying magnetic inequivalence of the two phenyl substituents at each P atom. The ^{13}C{^{1}H}-phenyl region for complexes **5** and **6** is more complicated because of the presence of the bipy/phen ligands.

Table 6. Catalyzed Hydrogen-Transfer Hydrogenation of Acetophenone[a]

precursor catalysts *t*=*trans*, *c*=*cis*	conversion (%)
t-$RuCl_2$(DPPF)(en) (**1**)	91; 32[b]
t-$RuCl_2$(DPPF)(dimen) (**2**)	90;[c] 16[b]
[RuCl(DPPF)(dien)]Cl (**3**)	75; 29[b]
t-$RuCl_2$(DPPF)(diap) (**4**)	86
c-$RuCl_2$(DPPF)(bipy) (**5**)	82
c-$RuCl_2$(DPPF)(phen) (**6**)	91
t-$RuCl_2$(DPPF)(1*S*,2*S*-dach) (**7**)	92; 69[d]
t-$RuCl_2$(DPPB)(en) (**8**)	93; 95[e]
[RuCl(*p*-cymene)]$_2$(μ-Cl)$_2$	45; 61[f]

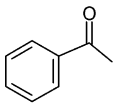
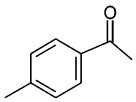
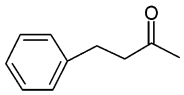
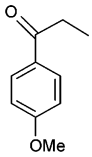
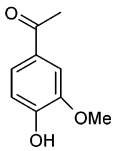
[a] Experimental conditions (see Experimental Section), unless stated otherwise: under N_2, 80 °C for 24 h, Cat:Base:S = 1:20:1000. [b] At 35 °C. [c] 48 h. [d] At 45 °C. [e] Under 1 atm H_2. [f] 0.1 mL of 2.0 M en (0.2 mmol) added.

The absorption spectra of complexes **1**−**6** were measured in CH_2Cl_2 solution; free DPPF has absorption maxima at 221 and 251 nm, with respective ϵ values of 4.03×10^4 and 2.56×10^4 mol L^{-1} cm^{-1}. The complexes reveal three UV−vis absorption maxima (for **5** and **6**) or two absorption maxima and a shoulder band (for **1**−**4**, see Figure S2). On the basis of literature data,[24] the shoulder peaks (335−349 nm) are tentatively assigned to charge transfer from the Ru(II) to a ligand (presumably the P atom donors). The intense absorption at ∼220 nm essentially arises from the DPPF, but the increased molar extinction coefficients of the complexes (vs that of free DPPF) suggest that metal-to-ligand charge transfer may also contribute to this peak. The relatively weak absorption maxima around 460 nm for complexes **1**−**4** and small shoulders at 545 and 547 nm for **5** and **6** may be d−d transitions. For **5** and **6**, the bipy- and phen-containing species, the more intense absorption bands at 456 and 442 nm, respectively, are almost certainly metal-to-imine MLCT bands,[24] and these give rise to the red color of these complexes compared with the yellow colors of **1**−**4**. The absorption bands at 303 and 274 nm for **5** and **6**, respectively, are thought to be $\pi \rightarrow \pi^*$ transitions of the aromatic imine ligands.[24]

Catalytic Transfer Hydrogenation of Ketones. Complexes of formulation $RuCl_2$(P−P)(N−N) have been widely used as hydrogenation precursor catalysts, using either H_2 or 2-propanol as the hydrogen source (see Introduction and refs 1j, 4, 6, 7, 20). Complexes **1**−**8** were similarly tested for hydrogenation of acetophenone by hydrogen-transfer from a basic solution of 2-propanol (eq 1, Table 6), using the complex (10.0 μmol), added KOH (0.2 mmol), and the ketone (1.2 g, 10.0 mmol) in 2-propanol (10 mL) at 80 °C, i.e., a catalyst/base/substrate (Cat/Base/S) ratio of 1:20:1000. The data indicate that complexes **1**−**8** are all reasonably efficient hydrogen-transfer catalysts under a nitrogen atmosphere. The complexes are air-stable in

(24) (a) Ford, P. C.; Rudd, D. P.; Gaunder, R.; Taube. H. *J. Am. Chem. Soc.* **1968**, *90*, 1187. (b) Clarke, R. E.; Ford, P. C. *Inorg. Chem.* **1970**, *9*, 227. (c) Silva, H. A. S.; Carlos, R. M.; Camargo, A. J.; Picchi, C. M. C.; de Almeida Santos, R. H.; McGarvey, B. R. Franco, D. W. *Inorg. Chim. Acta* **2004**, *357*, 3147.

Table 7. Transfer-Hydrogenation of Substrates Catalyzed by Complex 8[a]

substrate	structure	conversion (%)
Acetophenone		100 [b] 6 [c] 91 [d]
4-Methylacetophenone		89 99 [b]
4-Phenyl-2-butanone		96 100 [b]
4-Methoxypropiophenone		71 96 [b]
Acetovanillone		10 [b]

[a] Experimental conditions: as in footnote *a* of Table 6, unless noted otherwise. [b]Under 700 psi H_2. [c]0.02 M KOH, no Ru catalyst. [d] 0.66 M KOH, no Ru catalyst.

the solid state and in solution, but the catalysis requires an oxygen-free environment; exposure of the reacting systems to air completely inhibited the catalysis.

$$PhCOCH_3 + (CH_3)_2CH(OH) \xrightarrow[80\ ^\circ C,\ N_2]{\text{catalyst, KOH}} PhCH(OH)CH_3 + (CH_3)_2CO \quad (1)$$

A "blank" experiment in the absence of a Ru complex (using 0.02 M KOH in 2-propanol, S/Base = 50) showed just 6% conversion of acetophenone after 24 h, although at higher [KOH] (0.66 M KOH and 1.0 M acetophenone, S/Base = 1.5), 91% conversion was observed (see Table 7). Such metal-free, base-catalyzed conversions are well documented.[25]

Conversion versus time plots for the four DPPF-containing precursor catalysts **1**, **2**, **5**, and **6** (N−N = en, dimen, bipy, and phen, respectively) are shown in Figure 5. The systems give ~50% conversions after 1−3 h, and the relative activity sequence up to ~10 h is en ~ phen > bipy ~ dimen. The activities of the imine-containing species **5** and **6** are thus comparable to those of the amine species **1** and **2**, showing that active hydrogens on the N atoms are not essential for hydrogenation and that mechanisms other than ionic hydrogenation,[1j,4−7] such as the more classical "hydride" or "unsaturated" mechanisms,[1j,6,20b,26,27] must be operative in these Ru(II) systems. Such findings for "NH-free" active Ru(II) systems are not novel and have been discussed.[20f,h] The imine ligands are not reduced to amine; further, there is no induction period at the beginning

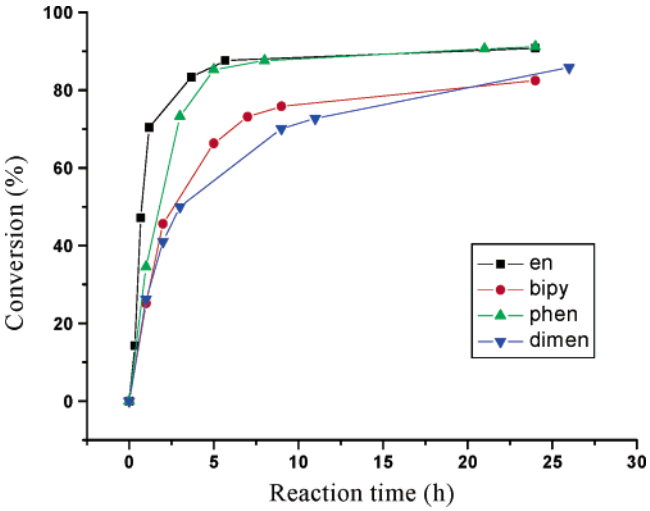


Figure 5. Conversion versus reaction time for conditions given in the Experimental Section. Precursor catalyst systems shown are for complex **1** (black line), **2** (blue line), **5** (red line), and **6** (green line).

of the hydrogenations (see Figure 5), and so the imine systems are not considered to involve any extraneously formed amine ligand.

Presumably, the hydrogenations catalyzed by *trans*-$RuCl_2$(P−P)(en) operate via the bifunctional mechanism in which the "RuH−NH" unit plays a key role.[1j,4−7] Although we have no definitive data to support this premise, we can select "fortuitous" data for systems based on complexes **1** and **2** (the en and dimen species) that appear to! For example, for the first 2 h at 80 °C (Figure 5), conversions achieved using **1** are about twice those achieved with **2**, a factor consistent with the fact that **1** statistically has twice as many H atoms available compared to **2** for forming the required H-bonded reaction intermediates. To the best of our knowledge, our report is the first to describe such Ru(II)−diphosphine−diamine complexes with the varying amine donor groups being $-NH_2$ and −NHMe, and further detailed kinetic studies are planned with these diamine and diimine systems.

The activities of the *cis*-dichloro species **5** and **6** under N_2 are similar to those of *cis*-$RuCl_2$(DPPB)(N−N), where N−N = bipy or phen, when these were used under similar hydrogen-transfer conditions *but* also under 1 atm H_2 (78% conversion after 3 h).[20h] Under an Ar atmosphere, the DPPB systems showed lower activity: for example, the bipy system gave 50% conversion after 24 h[20h] versus the 82% for *cis*-$RuCl_2$(DPPF)(bipy) (**5**) (Table 6). The activities of complexes **1**−**7** for acetophenone reduction are less than those of the corresponding isocyanide complexes, *trans*-$RuCl_2$(DPPF)$(CNR)_2$, under corresponding conditions.[13]

The effect of using an atmosphere of H_2 above the hydrogen-transfer conditions for reduction of acetophenone was also studied with *trans*-$RuCl_2$(DPPB)(en) (**8**). Some experimental data are shown in Table 6 and Figure S3, where there is little difference in the conversions after 2 or 24 h; the presence of H_2 is thus not essential for the reduction, which is in contrast to data reported for the $RuCl_2$(DPPB)(diimine) systems.[20h] Data for reduction of 4-methylacetophenone, 4-phenyl-2-butanone,

(25) For example: (a) Le Page, M. D.; James, B. R. *Chem. Commun.* **2000**, 1647. (b) Crochet, P.; Gimeno, J.; Garcia-Granda, S.; Borge, J. *Organometallics* **2001**, *20*, 4369. (c) Thoumazet, C.; Melaimi, M.; Ricard, L.; Mathey, F.; Floch, P. L. *Organometallics* **2003**, *22*, 1580.

(26) Standfest-Hauser, C.; Slugovc, C.; Mereiter, K.; Schmid, R.; Kirchner, K.; Xiao, L.; Weissensteiner, W. *J. Chem. Soc., Dalton Trans.* **2001**, 2989.

(27) (a) James, B. R. *Adv. Organomet. Chem.* **1979**, *17*, 319. (b) Johnstone, R. A. W.; Wilby, A. H.; Entwistle, I. D. *Chem. Rev.* **1985**, *85*, 129.

and 4-methoxypropiophenone (see Table 7) similarly reveal that H_2 is not essential.

There was no reduction of the C═C bond in styrene or the lignin model compound 3,4-dimethoxystyrene when this substrate was tested under the same hydrogen-transfer conditions (under N_2), further demonstrating the general selectivity of the $RuCl_2$(P−P)(N−N) systems for reduction of the polar C═O bond.[1h,4,19b,20e,25b,c] However, there are exceptions; for example, both the olefinic C═C and the C═O bonds are reduced in the catalyzed hydrogen-transfer hydrogenation of *trans*-4-phenyl-3-buten-2-one using *trans*-$RuCl_2$(DPPP)(1,2-diaminobenzene) as catalyst, where DPPP = 1,3-(diphenylphosphino)propane.[20d]

Of complexes **1**−**8**, only **7** contains a chiral diamine moiety (1*S*,2*S*-dach), and use of this complex as catalyst precursor did induce some enantiomeric excess into the alcohol product formed from acetophenone. The measured ee values are higher at lower temperatures, and the higher values were recorded at lower conversions. For example, a maximum ee value of 36% was noted at ∼25% conversion at 45 °C, while empirically the *R*/*S* ratio decreases almost linearly with reaction time at both 80 and 45 °C (with similar slopes; see Figure S4); use of the *S*,*S*-form of the diamine generated the *R*-alcohol, not an unusual finding.[28]

Of complexes **1**−**8**, *trans*-$RuCl_2$(DPPB)(en) (**8**) marginally shows the highest activity (93% for the conditions shown in Table 6) for hydrogen-transfer hydrogenation of acetophenone. This catalyst system was thus tested with several alkyl−aryl ketones, selected as model substrates for carbonyl components of lignin (see Table 7); *p*-Me and *p*-OMe substituents in the aryl moiety do not seriously inhibit the hydrogenation, but introduction of a *p*-OH group likely does, as evidenced by the ineffective reduction of acetovanillone, The phenyl-substituted dialkyl ketone, 4-phenyl-2-butanone, was readily reduced.

Reetz and Li have recently reported use of the *p*-cymene-containing precursor $[RuCl(C_{10}H_{14})]_2(\mu\text{-}Cl)_2$ in the presence of BINOL-derived diphosphonites for extremely effective asymmetric hydrogen-transfer hydrogenation (from 2-propanol) of ketones; it is notable that these systems do not require the presence of ancillary diamine ligands.[1k] In addition, Deng's group[29a] and Noyori's group[29b] have earlier used the same precursor in the presence of a chiral diamine (with no diphosphine) for similar ketone hydrogenation in either aqueous media using sodium formate[29a] or basic 2-propanol[29b] as hydrogen donor. We tested this precursor alone in the absence of a diphosphine and in the presence of en (Table 6): conversions after 24 h were, respectively, 45% and 61%, showing that addition of en does promote activity, at least for a phosphine-free, nonchiral system.

Conclusions

Five new complexes of the type *cis*- or *trans*-$RuCl_2$(P−P)(N−N) are reported, where P−P = DPPF and N−N = a diamine or diimine ligand; the cationic complex [RuCl(DPPF)(dien)]Cl is also described, as well as improved syntheses for *trans*-$RuCl_2$(DPPF)(en) and *trans*-$RuCl_2$(DPPB)(en). Crystal structures are presented for these two ethylenediamine complexes as well as for *trans*-$RuCl_2$(DPPF)(dimen) and *cis*-$RuCl_2$(DPPF)(bipy). Preliminary data are presented on the use of the eight complexes as precursor catalysts for transfer hydrogenation (from 2-propanol) of acetophenone and some related ketones; the catalysis is effective under either a nitrogen or a hydrogen atmosphere, although yields of the 1-phenylethanol product are typically marginally higher when H_2 is used. There is little difference between the activities of the diamine and diimine systems, implying that classical "hydride" and/or "unsaturated" mechanistic pathways may be competitive with any bifunctional mechanism that might be operating in the diamine systems (i.e., where the H_2 is derived from a metal-hydride and an amine proton).

Use of the precursor catalyst *trans*-$RuCl_2$(DPPF)(1*S*,2*S*-dach), containing the chiral diamine, does generate chirality in the alcohol product, but only to a maximum extent of 36% at the low conversion of 25%.

Acknowledgment. The authors thank the Natural Sciences and Engineering Research Council (NSERC) of Canada for financial support in terms of a Discovery Grant (to R.G.C.) and a Strategic Project Grant (to B.R.J. and T.Q.H.), and Colonial Metals, Inc. for a gift of $RuCl_3 \cdot 3H_2O$.

Note Added after ASAP Publication. In the version of this paper that was published on the Web on Jan 19, 2007, the β values for compounds **2** and **8** (92.937(9) and 111.750(3), respectively) were incorrectly shown as being α values. This was due to a production error. The version of the table that now appears is correct.

Supporting Information Available: Crystallographic data (as CIF files) for complexes *trans*-$RuCl_2$(DPPF)(en) (**1**), *trans*-$RuCl_2$(DPPF)(dimen) (**2**), *cis*-$RuCl_2$(DPPF)(bipy) (**5**), and *trans*-$RuCl_2$(DPPB)(en) (**8**). Figures S1−S4. These materials are available free of charge via the Internet at http://pubs.acs.org.

OM060987Z

(28) (a) Ito, M.; Hirakawa, M.; Murata, K.; Ikariya, T. *Organometallics* **2001**, *20*, 379. (b) Ohkuma, T.; Koizumi, M.; Muniz, K.; Hilt, G.; Kabuto, C.; Noyori, R. *J. Am. Chem. Soc*. **2002**, *124*, 6508.

(29) (a) Ma, Y.; Liu, H.; Chen, L.; Cui, X.; Zhu, J.; Deng, J. *Org. Lett.* **2003**, *5*, 2103. (b) Yamakawa, M.; Yamada, I.; Noyori, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 2818.