Effect of Chelate Ring Size on the Rate of Hydride Transfer from CpRu(P−P)H (P−P = Chelating Diphosphine) to an Iminium Cation

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The rate constants for hydride transfer from CpRu(P−P)H (P−P = bis(diphenylphosphino)-methane (dppm), bis(diphenylphosphino)ethane (dppe), bis(diphenylphosphino)benzene (dpbz), or bis(diphenylphosphino)propane (dppp)) to 1-(1-phenylethylidene)pyrrolidinium tetrafluoroborate have been measured. The bite angles of the hydride complexes CpRu-(dppm)H, CpRu(dppe)H, CpRu(dpbz)H, and CpRu(dppb)H (dppb = bis(diphenylphosphino)-butane) have been determined by X-ray diffraction. Hydride transfer is faster when the chelate ring of the diphosphine is smaller (i.e., CpRu(dppm)H > CpRu(dppe)H ≈ CpRu-(dpbz)H > CpRu(dppp)H ≫ CpRu(dppb)H). Boiling $CpRu(PPh_3)_2Cl$ with dpbz in benzene or toluene results in the formation of $[CpRu(PPh_3)(\eta^2\text{-dpbz})]Cl$ as well as CpRu(dpbz)Cl.

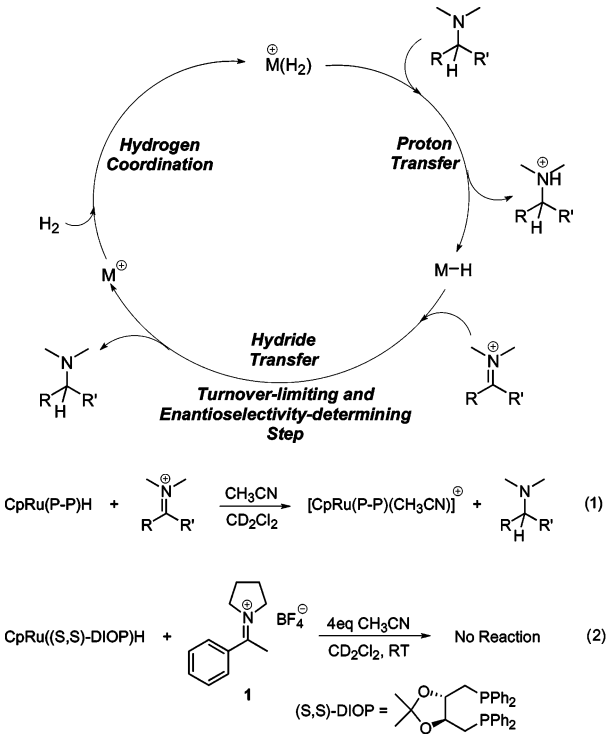
Introduction

We have previously reported[1] the ruthenium-catalyzed hydrogenation of iminium cations (including protonated imines) by an ionic mechanism, involving heterolytic cleavage of H_2 and sequential transfer of H^- and H^+ to the substrates. When chiral diphosphines are employed, C=N bonds can be hydrogenated enantioselectively with ee's up to 60%. As the literature contains few catalysts for the asymmetric hydrogenation of C=N bonds,[2,3] we have studied the mechanism of ours; the transfer of H^- from CpRu(P−P)H to the iminium cation (Scheme 1) has proven to be turnover-limiting and enantioselectivity-determining.[1]

It is possible to stop the reaction after a single H^- transfer if it is carried out in the absence of H_2 and the presence of a coordinating solvent (usually CH_3CN) (eq 1). To screen phosphines for catalytic use, we have measured the rate at which their CpRu(P−P)H complexes undergo this "stoichiometric" hydride transfer. When such an experiment (eq 2) showed CpRu((*S*,*S*)-DIOP)H to be inactive at hydride transfer to 1-(1-phenylethylidene)pyrrolidinium tetrafluoroborate (**1**),[1] we suspected an effect of the size of the chelate ring. (The CpRu hydrides of other chelating diphosphines with one alkyl and two aryl substituents on each phosphorus transfer H^- to **1**.[1])

The effect of chelate ring size on metal-catalyzed C−C bond forming reactions, such as hydroformylation, allylic substitution, hydrocyanation, and the amination of aryl halides, has been reviewed by van Leeuwen and co-workers.[4] The Brookhart group has shown that the kinetic barriers for the migratory insertion of complexes $[Ph_2P(CH_2)_nPPh_2]Pd(CH_3)(CO)^+$ (n = 2−4) decrease with an increase in the P−Pd−P bond angle.[5] Vilar et al. have recently reported a similar influence of chelate ring size on the insertion of isocyanides into the Pd−C bond of (P−P)Pd(CH_3)Cl complexes.[6]

Scheme 1



(1) Magee, M. P.; Norton, J. R. *J. Am. Chem. Soc.* **2001**, *123*, 1778−1779.

(2) (a) Willoughby, C. A.; Buchwald, S. L. *J. Am. Chem. Soc.* **1994**, *116*, 8952−8965. (b) Broger, E. A.; Burkart, W.; Hennig, M.; Scalone, M.; Schmid, R. *Tedrahedron: Asymmetry* **1998**, *9*, 4043−4054. (c) Xiao, D.; Zhang, X. *Angew. Chem., Int. Ed.* **2001**, *40*, 3425−3428.

(3) Review on hydrogenation of imines: Blaser, H.-U.; Spindler, F. Hydrogenation of Imine Groups. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer-Verlag: New York, 1999; Vol. 1, pp 247−265.

(4) (a) van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. *Chem. Rev.* **2000**, *100*, 2741−2769. (b) Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Reek, J. N. H. *Acc. Chem. Res.* **2001**, *34*, 895−904.

(5) Ledford, J.; Shultz, C. S.; Gates, D. P.; White, P. S.; DeSimone, J. M.; Brookhart, M. *Organometallics* **2001**, *20*, 5266−5276.

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However, little is known about the effect of chelate ring size on hydride transfer, although much work has been done on other factors influencing the rate of such transfers from transition-metal hydrides.[7] DuBois and co-workers have determined the equilibrium constants for several H^- transfer reactions of $[HM(diphosphine)_2]PF_6$ (M = Pt, Ni) complexes and have found that a smaller chelate ring favors hydride transfer *thermodynamically*.[8] Knowledge of the *kinetic* effects of chelate ring size is still lacking.

In this paper we report the kinetics of hydride transfer from CpRu(P−P)H, with bidentate phosphines of different chelate ring sizes, to the iminium cation **1**. We also report the structures of these complexes and their influence on the rates of hydride transfer.

Results and Discussion

Preparation of CpRu(P−P)H. The literature contains two general methods of preparing CpRu(P−P)H: (1) the synthesis of CpRu(P−P)Cl and its reduction by CH_3ONa,[9] and (2) the displacement of carbonyl ligands from $CpRu(CO)_2H$ by diphosphines.[10] Method 1 is more convenient because the chlorides CpRu(P−P)Cl (**3**) are air stable; however, method 2 gives better results when the distance between the P atoms is large and bridging is a possibility. We thus prepared CpRu(dppm)H (**2a**), CpRu(dppe)H (**2b**), and CpRu(dpbz)H (**2c**) by method 1; CpRu(dppp)H (**2d**) and CpRu(dppb)H (**2e**) by method 2.

Most **3** are readily prepared by displacing PPh_3 from $CpRu(PPh_3)_2Cl$ with the appropriate diphosphine. However, the preparation of CpRu(dpbz)Cl (**3c**) by this method in boiling benzene (eq 3) gives an interesting byproduct: a light green precipitate, **4**. (The precipitate **4** is not an intermediate in the formation of **3c**: **4** remains after 3 days in boiling benzene, or when the higher-boiling toluene is used as solvent.) The ^1H NMR of **4** shows, in addition to the Cp singlet (δ 4.71), 39 protons in the aromatic region; the $^{31}P\{^1H\}$ NMR reveals a triplet at δ 43.39 and a doublet at δ 72.05, with J = 34.0 Hz. Thus **4** is $[CpRu(PPh_3)(\eta^2\text{-dpbz})]Cl$, analogous to the known $[CpRu(PPh_3)(\eta^2\text{-dppm})]BF_4$[11,12]

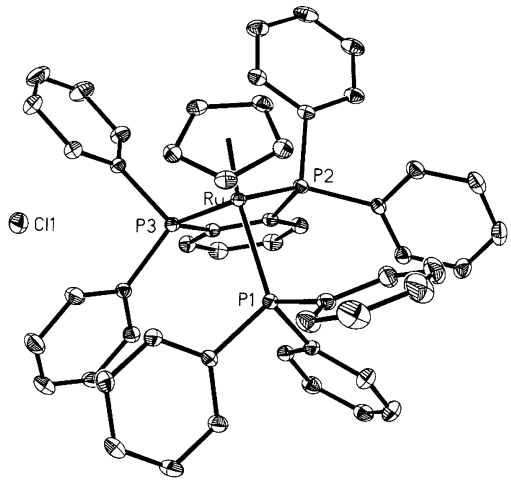
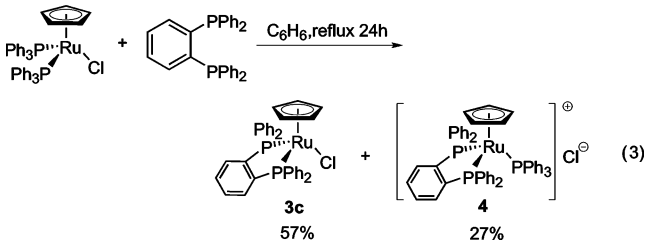


Figure 1. Structure of $[CpRu(PPh_3)(\eta^2\text{-dpbz})]Cl$ (**4**) (20% probability level). Selected bond lengths (Å) and angles (deg): Ru−P1 2.3478(6), Ru−P2 2.2787(7), Ru−P3 2.3136(7), P1−Ru−P2 97.26(2), P1−Ru−P3 97.58(2), P3−Ru−P2 82.87(2).

and $[CpRu(PPh_3)(\eta^2\text{-dppe})]BF_4$[12] (prepared by treating CpRu(dppm)Cl or CpRu(dppe)Cl with PPh_3 and NH_4BF_4 in CH_3OH).



A dimeric or oligommeric structure for **4** in solution cannot be ruled out, although we are not aware of any case where dpbz has served as a bridging ligand. We have been able to grow single crystals of **4**, by slow diffusion of hexanes into a concentrated CH_2Cl_2 solution. X-ray diffraction shows (Figure 1)[13] a monomeric structure in the solid state.

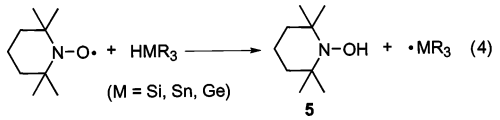
The ruthenium in **4** sits in a very crowded environment, with both the PPh_3 and the dpbz coordinated. The dissociation of the Cl^- in eq 3 parallels its dissociation in polar solvents, such as CH_3OH, C_2H_5OH, and DMSO. Treichel and co-workers have measured the rates of halide ion solvolysis of $CpRuL_2Cl$ (L = PMe_3, $PPhMe_2$, PPh_2Me, $PPh_2(OMe)$, $P(OEt)_3$, $PMe(OMe)_2$; L_2 = dppe) in DMSO and CH_3CN.[14] (They found that a less electron-donating phosphine retards Cl^- dissociation, while silver, ammonium, or sodium salts facilitate it.) However, in nonpolar solvents such as benzene, toluene, or decalin, phosphine dissociation from CpRu(P−P)Cl

(6) Owen, G. R.; Vilar, R.; White, A. J. P.; Williams, D. J. *Organometallics* **2002**, *21*, 4799−4807.
(7) (a) Labinger, J. A. Nucleophilic Reactivity of Transition Metal Hydrides. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; pp 361−379. (b) Labinger, J. A.; Komadina, K. H. *J. Organomet. Chem.* **1978**, *155*, C25−C28. (c) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem.* **1978**, *100*, 7902−7915. (d) Kao, S. C.; Gaus, P. L.; Youngdahl, K.; Darensbourg, M. Y. *Organometallics* **1984**, *3*, 1601−1603. (e) Kao, S. C.; Spillett, C. T.; Ash, C.; Lusk, R.; Park, Y. K.; Darensbourg, M. Y. *Organometallics* **1985**, *4*, 83−91. (f) Gaus, P. L.; Kao, S. C.; Youngdahl, K.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1985**, *107*, 2428−2434. (g) Martin, B. D.; Warner, K. E.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 33−39. (h) Smith, K.-T.; Norton, J. R.; Tilset, M. *Organometallics* **1996**, *15*, 4515−4520. (i) Hembre, R. T.; McQueen, S. *J. Am. Chem. Soc.* **1994**, *116*, 2141−2142. (j) Hembre, R. T.; McQueen, J. S. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 65−67. (k) Cheng, T.-Y.; Bullock, R. M. *Organometallics* **1995**, *14*, 4031−4033. (l) Cheng, T.-Y.; Brunschwig, B. S.; Bullock, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 13121−13137. (m) Cheng, T.-Y.; Bullock, R. M. *Organometallics* **2002**, *21*, 2325−2331. (n) Sarker, N.; Bruno, J. W. *J. Am. Chem. Soc.* **1999**, *121*, 2174−2180.
(8) Berning, D. E.; Noll, B. C.; DuBois, D. L. *J. Am. Chem. Soc.* **1999**, *121*, 11432−11447.
(9) Bruce, M. I.; Humphrey, M. G.; Swincer, A. G.; Wallis, R. C. *Aust. J. Chem.* **1984**, *37*, 1747−1755.
(10) White, C.; Cesarotti, E. *J. Organomet. Chem.* **1985**, *287*, 123−125.
(11) Bruce, M. I.; Humphrey, M. G.; Patrick, J. M.; White, A. H. *Aust. J. Chem.* **1983**, *36*, 2065−2072.
(12) Ashby, G. S.; Bruce, M. I.; Tomkins, I. B.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1003−1016.
(13) The solvent molecule is severely disordered, and a suitable model cannot be constructed for the solvate. The program SQUEEZE (see van der Sluis, P.; Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, 194−201) was used to refine the solvent molecule as a diffuse contribution to overall scattering without specific atom positions; however, the empirical formula, density, and absorption coefficient reflect the full formula.
(14) (a) Treichel, P. M.; Komar, D. A.; Vincenti, P. J. *Inorg. Chim. Acta* **1984**, *88*, 151−152. (b) Treichel, P. M.; Vincenti, P. J. *Inorg. Chem.* **1985**, *24*, 228−230.

is generally more facile,[15] so the Cl^- dissociation in eq 3 is surprising.

Most of the hydrides **2** proved to be stable in halogenated solvents, but **2d**, regardless of the batch or the synthetic methods used to prepare it, gave CpRu(dppp)Cl within minutes in CD_2Cl_2.[16,17] This type of halogenation is known to be a radical process[18] and potentially retarded by radical inhibitors, so we examined the stability of **2d** in the presence of several such inhibitors. After 1 day with a suspension of hydroquinone (only slightly soluble) in CD_2Cl_2, about 85% of the **2d** remained, but 4-*tert*-butylcatechol, which has better solubility in halogenated solvents, reacted immediately with **2d** (to give complex products that were not identified). However, TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) proved unreactive toward **2d** and efficient at preventing its reaction with CD_2Cl_2: no significant decomposition of **2d** in CD_2Cl_2 solution was observed after 30 h in the presence of 1% (by weight) TEMPO.

The fact that TEMPO does not itself abstract $H^\bullet$ from **2d** warrants comment. TEMPO abstracts $H^\bullet$ from group 14 organometallic hydrides (e.g., Bu_3SnH) at 80 °C,[19] forming the hydroxylamine **5** (eq 4). As the O−H bond dissociation energy (BDE) of **5** in benzene is 69 kcal/mol[20] and the Ru−H BDE value for **2d** can be estimated at 65 cal/mol,[21] $H^\bullet$ abstraction from **2d** by TEMPO should be thermodynamically favorable. The reason it does not occur at an appreciable rate must be kinetic: the cyclopentadienyl ring and dppp ligand in **2d** must make the hydride ligand inaccessible to a bulky radical like TEMPO.



(4)

Kinetics of Hydride Transfer from the Hydride Complexes 2 to the Iminium Cation 1. When H^- transfer to **1** from any of the hydride complexes **2a**−**d** is carried out in the presence of CH_3CN, the cation **6** results (eq 5). Monitoring the disappearance of the Cp signal of the hydride **2b** by ^1H NMR in the presence of excess **1** (10 equiv) gave a pseudo-first-order rate constant k_{obs}. Variation of [**1**] from 0.10 to 0.26 M (Table S-1, Figure 2) showed that k_{obs} for **2b** was linear with [**1**], implying that the hydride transfer reaction in eq 5 is second-order overall (eq 6). The rate constant k for **2b** was calculated from the slope of Figure 2 and inserted in Table 1.

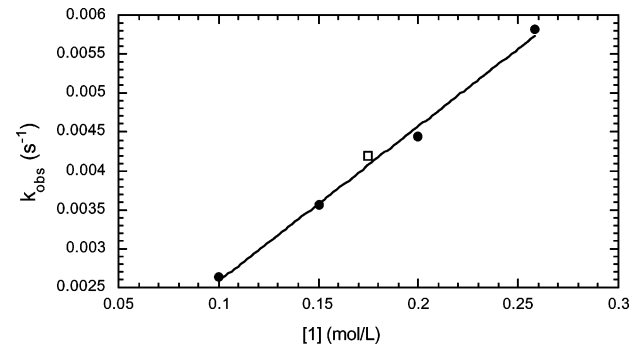
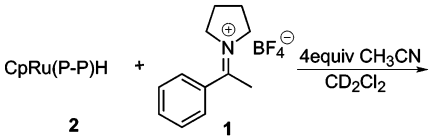


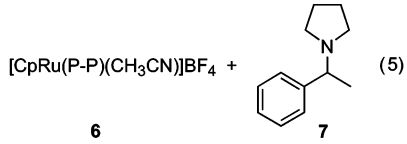
Figure 2. Plot of k_{obs} vs [**1**] for hydride transfer from **2b** to the iminium cation **1** at 300 K with MeCN present (●). (The value of k_{obs} without MeCN present is also displayed in this figure (□).)

Table 1. Rates of Hydride Transfer from CpRu(P−P)H to the Iminium Cation 1 at 300 K in CD_2Cl_2

complex	chelating ligand	bite angle P−Ru−P (deg)	rate constant k ($M^{-1}\,s^{-1}$)
2a	dppm	72.01(3)	$6.4(3) \times 10^{-1}$ [a]
2b	dppe	84.497(16)	$2.0(1) \times 10^{-2}$
2c	dpbz	84.22(4)	$2.1(2) \times 10^{-2}$
2d	dppp	91.9(1) [b]	$2.8(2) \times 10^{-3}$
2e	dppb	93.96(3)	no reaction ($<4 \times 10^{-6}$)

[a] Average of two kinetic experiments with different concentrations of **1** and **2a**. [b] See ref 31.





(5)

$$-\frac{d[2]}{dt} = k_{obs}[2] = k[1][2] \qquad (6)$$

Without CH_3CN k_{obs} does not change appreciably (Figure 2), although the amine **7** becomes coordinated instead of the CH_3CN. [22] The rate-determining step in reaction 5 is clearly H^- transfer, with CH_3CN serving as an efficient trap. Sixteen-electron half-sandwich ruthenium diphosphine complexes, with and without agostic interactions, have been isolated and structurally characterized. They are particularly stable when a Cp* ring and bulky phosphine ligands such as $(^iPr)_2PCH_2CH_2P(^iPr)_2$ or two $PMe(^iPr)_2$ are both present,[23] but can also be made when there is a less bulky diphosphine.[24] (Sixteen-electron complexes with less bulky diphosphines are more reactive.)

The k_{obs} value for **2c** was obtained by monitoring the appearance of the coordinated CH_3CN signal of **6c**,

(15) Davies, S. G.; McNally, J. P.; Smallridge, A. J. *Adv. Organomet. Chem.* **1990**, *30*, 1−76, and references therein.

(16) The fact that the dppp hydride **2d** is more reactive toward CD_2Cl_2 than **2a** and **2b** is probably due to the more negative potential of **2d**,[17] which enables it to initiate a radical chain more easily by electron transfer to the solvent.

(17) Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875−883.

(18) (a) Shackleton, T. A.; Mackie, S. C.; Fergusson, S. B.; Johnson, L. J.; Baird, M. C. *Organometallics* **1990**, *9*, 2248−2253. (b) Brown, T. L. In *Organometallic Radical Processes*; Trogler, W. C., Ed.; Journal of Organometallic Chemistry Library 22; Elsevier: New York, 1990; pp 67−107, and references therein.

(19) Lucarini, M.; Marchesi, E.; Pedulli, G. F.; Chatgilialoglu, C. *J. Org. Chem.* **1998**, *63*, 1687−1693.

(20) Mahoney, L. R.; Mendenhall, G. D.; Ingold, K. U. *J. Am. Chem. Soc.* **1973**, *95*, 8610−8614.

(21) The BDE of $CpRu(CO)_2H$ has been reported as 65 kcal/mol, and phosphine substitution usually has a negligible effect on M−H energies. See: (a) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711−6717; correction, *J. Am. Chem. Soc.* **1990**, *112*, 2843. (b) Kristjánsdóttir, S. S.; Norton, J. R. Acidity of Hydrido Transition Metal Complexes in Solution. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1992; pp 309−359.

(22) Iimura, M.; Magee, M. P.; Norton, J. R. Unpublished work.

(23) Jiménez-Tenorio, M.; Mereiter, K.; Puerta, M. C.; Valerga, P. *J. Am. Chem. Soc.* **2000**, *122*, 11230−11231.

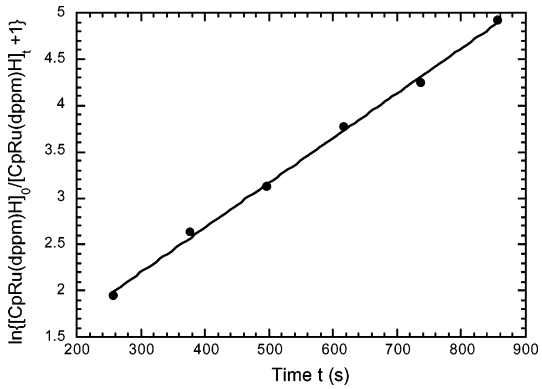


Figure 3. Plot of $\ln\{([RuH]_0/[RuH]_t) + 1\}$ vs time t for hydride transfer from **2a** to the iminium cation **1** at 300 K in CD_2Cl_2 with MeCN present. Initially [**2a**] = 7.5×10^{-3} M, [**1**] = 1.5×10^{-2} M.

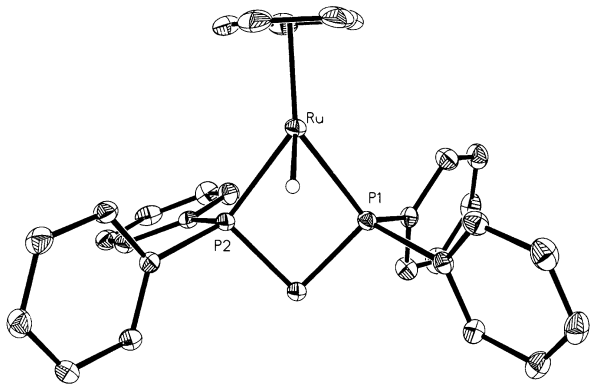


Figure 4. Molecular structure of CpRu(dppm)H (**2a**) (20% probability level). Selected bond lengths (Å) and angle (deg): Ru−P1 2.2435(9), Ru−P2 2.2399(9), P1−Ru−P2 72.01(3).

because the Cp of **6c** has a ^{1}H NMR chemical shift (δ 4.635) very close to that of the Cp of **2c** (δ 4.639). Variation of [**1**] from 0.10 to 0.25 M (Table S-2, Figure S-2) also showed a linear relationship between k_{obs} and [**1**], confirming that the hydride transfer is a second-order reaction. The rate constant k for **2c** has been calculated from the slope of Figure S-2 and is shown in Table 1.

Measuring the kinetics of H^- transfer to **1** from **2d** required the addition of TEMPO to suppress H/Cl exchange between **2d** and CD_2Cl_2. (A control experiment with the stable hydride **2b** showed that the presence of TEMPO had no effect on the rate of hydride transfer.[25]) The kinetics behavior of **2d** was similar to that of **2b** (Table S-3, Figure S-3). The rate constant k for **2d** was calculated from the slope of Figure S-3 and is shown in Table 1.

The transfer of hydride to **1** from **2a** was so fast that it was difficult to measure k_{obs} under pseudo-first-order conditions (the reaction of **2a** with **1** was complete within minutes). The rate constant was measured using a 1:2 ratio of [**2a**] to [**1**]. Under these conditions, a second-order reaction between **2a** and **1** will behave according to eq 7,[26] where $[RuH]_t$ is the concentration of **2a** at time t, $[RuH]_0$ is the initial concentration of **2a**, and k is the second-order rate constant.

$$\ln\{1 + (\Delta_0[RuH]_0/[\mathbf{2a}]_0[RuH]_t)\} = \ln([\mathbf{1}]_0/[\mathbf{2a}]_0) + k\Delta_0 t \quad (7)$$

$$\Delta_0 = [\mathbf{1}]_0 - [\mathbf{2a}]_0$$

When $[\mathbf{1}]_0 = 2[\mathbf{2a}]_0$, $\Delta_0 = [\mathbf{2a}]_0$, eq 7 can be rewritten as eq 8.

$$\ln\{1 + ([RuH]_0/[RuH]_t)\} = \ln 2 + k[\mathbf{2a}]_0 t \quad (8)$$

Experimental data confirm a linear relationship between $\ln\{1 + [RuH]_0/[RuH]_t\}$ and t (Figure 3). Furthermore, the y-intercept (0.744 ± 0.072) is consistent with ln 2 in eq 8, again confirming that H^- transfer from **2** to **1** is a second-order reaction.[27] The rate constant k for **2a** has been derived from the slope ($k[\mathbf{2a}]_0$) and is shown in Table 1.

Structures of Hydride Complexes CpRu(P−P)H (2). The literature contains surprisingly little crystallographic information about half-sandwich ruthenium phosphine hydrides. Structures had been reported for the bisphosphine complexes $CpRu(PPh_3)_2H$[28] and $CpRu(PMe_3)_2H$[29] and for the chelating diphosphine complexes CpRu(dppf)H (dppf = bis(diphenylphosphino)ferrocene)[30] and **2d**.[31]

Crystals of **2a** were obtained during a study of the mechanism of ionic hydrogenation.[32] Crystals of **2b**, **2c**, and **2e** were grown by adding CH_3OH to a saturated benzene solution of the hydrides. Thermal ellipsoid plots of the solid-state structures of **2a**, **2b**, **2c**, and **2e** are shown in Figures 4−7. (Figure 6 shows only one of the two independent molecules of **2c** in a unit cell.[33])

The coordination spheres of Ru in all these hydride complexes adopt pseudo-octahedral geometries. (All the hydride ligands were located except the one in **2e**.) The Ru−P distances of these hydrides (from 2.21 Å in **2c** to 2.25 Å in **2e**) are similar to those found in the structures previously reported. The only significant differences are in the P−Ru−P angles, which vary from 72.01(3)° in **2a** to 93.96(3)° in **2e**. Relevant bite angles are shown in Table 1.

Relationship between Chelate Bite Angle and Hydride Transfer Rate. As Table 1 shows, k decreases

(24) Aneetha, H.; Jiménez-Tenorio, M.; Puerta, M. C.; Valerga, P.; Sapunov, V. N.; Schimid, R.; Kirchner, K.; Mereiter, K. *Organometallics* **2002**, *21*, 5334−5346. Extensive earlier theoretical work on such systems is cited therein.

(25) $k_{obs} = 3.6(1) \times 10^{-3}$ s^{-1} when [**2b**] = 1.5×10^{-2} M, [**1**] = 1.5×10^{-1} M; $k_{obs} = 3.5(2) \times 10^{-2}$ s^{-1} when [**2b**] = 1.5×10^{-2} M, [**1**] = 1.5×10^{-1} M, with 1% (by weight) TEMPO.

(26) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*, 2nd ed.; McGraw-Hill: New York, 1995; p 25, eq 2−34.

(27) Two experiments with different initial concentrations gave the same second-order rate constants within experimental error: $k_2 = 6.5(2) \times 10^{-1}$ s^{-1} M^{-1} when [**2a**] = 7.5×10^{-3} M, [**1**] = 1.5×10^{-2} M; $k_2 = 6.3(3) \times 10^{-1}$ s^{-1} M^{-1} when [**2a**] = 1.0×10^{-2} M, [**1**] = 2.0×10^{-2} M.

(28) Smith, K. T.; Rømming, C.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 8681−8689.

(29) (a) Lemke, F. R.; Brammer, L. *Organometallics* **1995**, *14*, 3980−3987. (b) Brammer, L.; Klooster, W. T.; Lemke, F. R. *Organometallics* **1996**, *15*, 1721−1727.

(30) Bruce, M. I.; Butler, I. R.; Cullen, W. R.; Koutsantonis, G. A.; Snow, M. R.; Tiekink, E. R. T. *Aust. J. Chem.* **1988**, *41*, 963−969.

(31) Litster, S. A.; Redhouse, A. D.; Simpson, S. J. *Acta Crystallogr.* **1992**, *C48*, 1661−1663.

(32) Single crystals of **2a** for structure analysis were grown from a saturated solution of **2a**, a slight excess of **1** (1.5 equiv), and an excess of free amine **7** (ca. 7 equiv) at −35 °C.[22]

(33) The aromatic ring in the backbone of the other molecule is disordered.

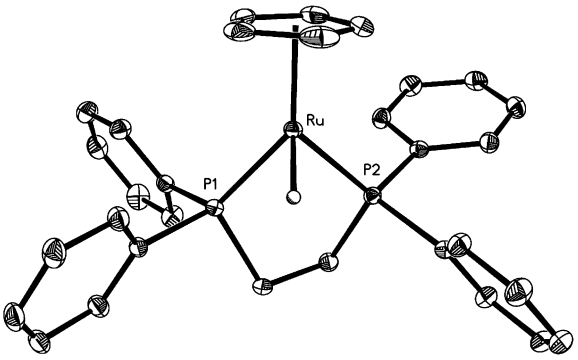


Figure 5. Molecular structure of CpRu(dppe)H (**2b**) (20% probability level). Selected bond lengths (Å) and angle (deg): Ru−P1 2.2365(4), Ru−P2 2.2322(4), P1−Ru−P2 84.497(16).

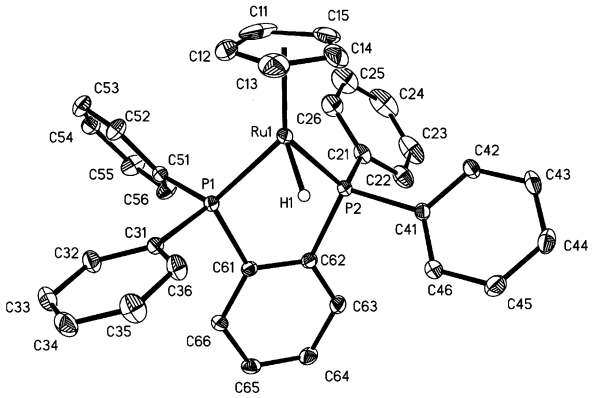


Figure 6. Molecular structure of CpRu(dpbz)H (**2c**) (20% probability level). Selected bond lengths (Å) and angles (deg): Ru1−P1 2.2138(9), Ru1−P2 2.2147(10), P1−C61 1.834(4), P2−C62 1.841(4), C61−C62 1.382(5), P1−Ru1−P2 84.22(4), Ru1−P1−C61 110.29(12), P1−C61−C62 115.9(3), C61−C62−P2 115.3(3), C62−P2−Ru1 110.61(13).

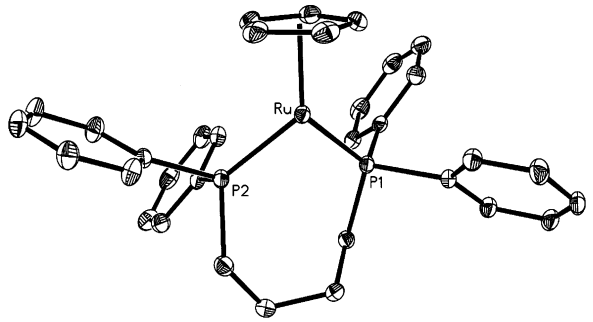


Figure 7. Molecular structure of CpRu(dppb)H (**2e**) (20% probability level). Selected bond lengths (Å) and angle (deg): Ru−P1 2.2452(8), Ru−P2 2.2463(8), P1−Ru−P2 93.96(3).

by at least an order of magnitude for each additional carbon in the backbone of the chelating diphosphine ligand. One possible explanation is steric: more space is available for the approach of the iminium cation when the chelate ring is smaller. A wider bite angle (P−Ru−P) should retard hydride transfer. Table 1 shows that there is little increase in bite angle between hydride **2d** (91.9(1)°) and hydride **2e** (93.96(3)°), probably because there is little room for expansion beyond the 90° of an octahedral geometry. However, the rate constant for hydride transfer (k) declines significantly ($2.8(2) \times 10^{-3}$ M^{-1} s^{-1} for **2d**, no reaction for **2e**), perhaps because of increasing steric repulsion from the longer "backbone" between the phosphorus atoms.

There is, however, good evidence for *electronic* control of H^- transfer rates as a function of the other ligands present. Bullock and co-workers have reported that, when $Ph_3C^+BF_4^-$ is the hydride acceptor, the rate of H^- transfer is significantly enhanced when CO is replaced by a tertiary phosphine: *trans*-$CpMo(CO)_2(PMe_3)H$ is 10^4 times as reactive as $CpMo(CO)_3H$.[7k,l]

Tabulated parameters ($E_L = 0.43$ V for dppm, 0.36 V for dppe) for estimating the potentials of octahedral complexes[34] imply a more positive potential for **2a** than for **2b**, suggesting that the energy of the highest occupied Ru orbital (the HOMO) increases in the order **2a** < **2b** < **2d** < **2e**. Indeed, CV measurements (anodic peak potentials of irreversible oxidation waves) on **2a**, **2b**, and **2d** show $E = -0.04$ V for **2a**, -0.09 V for **2b**, and -0.22 V for **2d**,[17] in agreement with the predicted order of the HOMO for **2a**, **2b**, and **2d**.[16]

However, the hydride donor ability of a hydride complex is more closely related to the energy of the orbital left behind after hydride transfer than it is to the energy of its own HOMO. For example, the hydride donor abilities of $(P-P)_2MH^+$ (M = Ni, Pt) toward a generic substrate S^+ (eq 9) correlate with the reduction potentials (II/I) of $(P-P)_2M^{2+}$;[8] these potentials measure the energy of the acceptor orbital (the LUMO) of the coordinatively unsaturated, 16-electron **8**. Larger chelate bites distort **8** from planarity, lowering the energy of its LUMO and making the equilibrium constant for eq 9 less favorable.[8]

$$(P-P)_2MH^+ + S^+ \rightleftharpoons (P-P)_2M^{2+} + S\text{-}H \qquad (9)$$
$$M = Ni, Pt \qquad\qquad \mathbf{8}$$

The rate of hydride transfer from **2** to **1** is independent of [CH_3CN], so its rate-determining step is probably the forward reaction in eq 10, forming the *coordinatively unsaturated*, 16-electron, intermediates **9**. Such complexes prefer a pyramidal geometry, with a LUMO that will be raised in energy by the additional bending imposed by a smaller chelate ring[24] (and by the stabilizing agostic interactions[23] that such a ring may make possible). The energy of the LUMO of **9** will thus, as with **8**, decrease as the size of its chelate ring increases.

$$CpRu(P-P)H + S^+ \rightleftharpoons CpRu(P-P)^+ + S\text{-}H \qquad (10)$$
$$\mathbf{9}$$

Experimental Section

General Procedures. All air-sensitive compounds were prepared and handled under a N_2/Ar atmosphere using standard Schlenk and inert-atmosphere box techniques. Toluene and hexanes were deoxygenated and dried over two successive activated alumina columns under argon.[35] Benzene was distilled from Na and benzophenone under a nitrogen atmosphere. CD_2Cl_2 was dried over CaH_2, degassed by three freeze−pump−thaw cycles, and then purified by vacuum transfer at room temperature. $CpRu(PPh_3)_2Cl$,[36] CpRu(dppm)H (**2a**),[9] CpRu(dppe)H (**2b**),[9] CpRu(dppp)H (**2d**),[10] CpRu(dppb)H (**2e**),[10] and 1-(1-phenylethylidene)pyrrolidinium tetrafluoroborate[37] (**1**) were prepared as described in the literature.

(34) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271−1285.
(35) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518−1520.
(36) Bruce, M. I.; Windsor, N. J. *Aust. J. Chem.* **1977**, *30*, 1601−1604.

Table 2. Summary of Crystallographic Data

	4·C_6H_{14}	**2a**·CH_2Cl_2	**2b**·C_6H_6	**2c**	**2e**(−H)
empirical formula	$C_{59}H_{58}ClP_3Ru$	$C_{31}H_{30}Cl_2P_2Ru$	$C_{37}H_{36}P_2Ru$	$C_{35}H_{30}P_2Ru$	$C_{33}H_{33}P_2Ru$
fw	996.48	636.46	643.67	613.60	592.60
temp, K	293(2)	293(2)	243(2)	293(2)	293(2)
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	9.7432(6)	9.7901(5)	11.7095(6)	11.0831(7)	10.6447(5)
b, Å	23.3215(16)	17.0869(10)	18.9662(9)	27.3950(17)	19.8601(9)
c, Å	20.5948(14)	17.2365(10)	14.3963(7)	18.6843(11)	13.3136(6)
α, deg	90	90	90	90	90
β, deg	94.0850(10)	95.2370(10)	107.3910(10)	92.2170(10)	98.7860(10)
γ, deg	90	90	90	90	90
V, Å^3	4667.8(5)	2871.3(3)	3051.0(3)	5668.7(6)	2781.5(2)
Z	4	4	4	8	4
d_{calc}, g/cm^3	1.418	1.472	1.401	1.438	1.415
λ(Mo Kα), Å	0.71073	0.71073	0.71073	0.71073	0.71073
μ, mm^{-1}	0.537	0.862	0.643	0.689	0.699
no. of data collected	31 301	19 076	20 068	33 512	18 736
no. of unique data	10 391	6469	6851	12 872	6319
no. of data/restraints/params	10391/0/524	6469/0/330	6851/0/366	12 872/0/694	6319/0/326
GOP on F^2	1.028	1.028	1.029	1.011	1.030
R1, wR2 ($I > 2\sigma(I)$)	0.0366, 0.0724	0.0449, 0.1176	0.0250, 0.0633	0.0531, 0.1347	0.0358, 0.0937
R1, wR2 (all data)	0.0667, 0.0791	0.0694, 0.1285	0.0291, 0.0652	0.0671, 0.1437	0.0548, 0.1017

CpRu(η^2-dpbz)Cl (3c) and [CpRu(PPh_3)(η^2-dpbz)]Cl (4). Under a nitrogen atmosphere 300 mL of benzene was added to a mixture of $CpRu(PPh_3)_2Cl$ (1.162 g,1.6 mmol) and dpbz (734 mg, 1.64 mmol), giving an orange-red solution. While the solution was boiled for 24 h, a light green precipitate formed, which was removed by filtration after the mixture was cooled to room temperature. The volume of the orange filtrate was reduced to 40 mL, then hexanes were added to cause precipitation. Solvent was removed by cannula, and the orange solid was washed with hexanes three times, then dried under vacuum to give 591 mg of the orange powder **3c** (57% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.62 (s, Cp, 5H), 6.92−6.96 (m, Ar, 4H), 7.09−7.13 (m, Ar, 4H), 7.22−7.27 (m, Ar, 2H), 7.36−7.42 (m, Ar, 8H), 7.67−7.69 (m, Ar, 2H), 7.90−7.94 (m, Ar, 4H). ^{31}P NMR (121.1 MHz, $CDCl_3$): δ 75.21 (s). Its LRMS (FAB^+) showed a parent ion peak at *m/e* 648.1 (^{102}Ru), with the appropriate isotopic distribution. Anal. Calcd for $C_{35}H_{29}P_2RuCl$: C, 64.87; H, 4.51; Cl, 5.47. Found: C, 64.75; H, 4.70; Cl, 5.47. The light green solid after first filtration was washed with bezene twice and hexanes three times, then dried under vacuum to afford 400 mg of **4** as a light green powder (27% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.71 (s, Cp, 5H), 6.33−6.38 (m, Ar, 4H), 6.40−6.50 (m, Ar, 2H), 6.80−6.90 (m, Ar, 2H), 6.95−7.05 (m, Ar, 12H), 7.07−7.12 (m, Ar, 4H), 7.19−7.26 (m, Ar, 7H), 7.30−7.34 (m, Ar, 4H), 7.66−7.67 (m, Ar, 4H). ^{31}P NMR (121.1 MHz, $CDCl_3$): δ 43.39 (t, J_{P-P} = 34.0 Hz), 72.05 (d, J_{P-P} = 34.0 Hz). Its LRMS(FAB^+) showed *m/e* 875.1 for [CpRu(PPh_3)(η^2-dpbz)]$^+$ (^{102}Ru) and *m/e* 613.1 for [CpRu(η^2-dpbz)]$^+$ (^{102}Ru) with the appropriate isotopic distribution. Anal. Calcd for $C_{53}H_{44}P_3RuCl$: C, 69.92; H, 4.87; Cl, 3.89. Found: C, 70.10; H, 4.97; Cl, 3.60.

CpRu(η^2-dpbz)H (2c). Sodium (110 mg, 4.78 mmol) was added to a suspension of 575 mg of CpRu(dpbz)Cl (**3c**) (0.66 mmol) in 30 mL of CH_3OH. Boiling the resulting mixture for 2 h gave a yellow suspension, from which (after cooling to room temperature) the solvent was removed by cannula. The solid was washed with CH_3OH three times, then dried under vacuum to give 242 mg of yellow powder **2c** (48% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ −13.36 (t, RuH, J_{P-H} = 33.2 Hz, 1H), 4.63 (s, Cp, 5H), 7.16−7.27 (m, Ar, 18H), 7.32−7.34 (m, Ar, 2H), 7.52−7.56 (m, Ar, 4H). ^{31}P NMR (CD_2Cl_2): δ 90.26 (s). Its LRMS (FAB^+) showed a parent ion peak at *m/e* 613.6 (^{102}Ru), with the appropriate isotopic distribution. Anal. Calcd for $C_{35}H_{30}P_2Ru$: C, 68.51; H, 4.93. Found: C, 67.82; H, 4.77.

NMR Measurements of Rate Constants for Hydride Transfer from the Hydride Complexes 2a−d to the Iminium Cation 1. In a typical experiment, **2b** (11.3 mg, 20 μmol) and **1** (52.2 mg, 200μmol) were placed in a vial in an inert atmosphere box. CD_2Cl_2 (1.0 mL) containing CH_3CN (4.2 μL, 80 μmol) was added by a gastight syringe, and the solution was immediately transferred to a J. Young NMR tube. The first ^{1}H NMR spectrum was recorded within 5 min, and single-pulse spectra were taken every 120 s for three to five half-lives. The height of the Cp resonance of the hydride (δ 4.66) was compared to that of residual $CDHCl_2$ (δ 5.32). Zero-filling was used to ensure adequate digital resolution. The probe temperature (300 K) was calibrated using anhydrous methanol.[38]

For **2a** the procedure was similar except that 2 equiv of **1** was used. For **2d**, 1% (by weight) TEMPO was dissolved in CD_2Cl_2 before CD_2Cl_2 was added to the starting materials. For **2c** hexamethylcyclotrisiloxane was used as internal standard, and the reaction was monitored by observing the growth of the signal of coordinated CH_3CN (δ 0.99) in the product [CpRu(dpbz)(CH_3CN)]BF_4 (**6c**). For **2e** <5% reaction was observed after 24 h with excess **1** (0.15 M), implying $k_{obs} < 6 \times 10^{-7}$ s^{-1} and $k < 4 \times 10^{-6}$ M^{-1} s^{-1}.

X-ray Structure Determinations. Crystal data collection and refinement parameters are summarized in Table 2. Data were collected on a Bruker P4 diffractometer equipped with a SMART CCD detector. The structures were solved using direct methods and standard difference map techniques and refined by full-matrix least-squares procedures using SHELXTL. Hydrogen atoms on carbon were included in calculated positions.

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Supporting Information Available: Complete details of the crystallographic study (PDF and CIF), kinetic data, and plots of these data. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0303404

(37) Leonard, N. J.; Paukstelis, J. V. *J. Org. Chem.* **1963**, *28*, 3021−3024.

(38) (a) van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679−680. (b) Raidford, D. S.; Fisk, C. L.; Becker, E. D. *Anal. Chem.* **1979**, *51*, 2050−2051.