Hydride Transfer from Rhodium Complexes to Triethylborane

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The hydrides HRh(depe)$_2$ and HRh(dmpe)$_2$ (depe = Et$_2$PCH$_2$CH$_2$PEt$_2$, dmpe = Me$_2$PCH$_2$CH$_2$PMe$_2$) have thermodynamic hydride donor abilities comparable to LiHBEt$_3$, as indicated by their ability to transfer a hydride ligand to Et$_3$B to sequentially form [Et$_3$BHBEt$_3$]$^-$ and [HBEt$_3$]$^-$. HRh(depe)$_2$ and HRh(dmpe)$_2$ can be generated from [Rh(dmpe)$_2$](CF$_3$SO$_3$) and [Rh(depe)$_2$](CF$_3$SO$_3$) and hydrogen gas in the presence of a strong base such as potassium *tert*-butoxide or lithium diisopropylamide. This reaction proceeds through the oxidative addition of hydrogen to form the [H$_2$Rh(diphosphine)$_2$](CF$_3$SO$_3$) complexes, followed by deprotonation. The oxidative addition of H$_2$ is favored by diphosphine ligands with electron-donating substituents and large chelate bites. In the present study, the driving force for oxidative addition of H$_2$ follows the order [Rh(dmpe)$_2$](CF$_3$SO$_3$) > [Rh(depe)$_2$](CF$_3$SO$_3$) > [Rh(dppe)$_2$](CF$_3$SO$_3$) with [Rh(dmpe)$_2$](CF$_3$SO$_3$) binding H$_2$ more strongly than [Rh(dppe)$_2$](CF$_3$SO$_3$) (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) by at least 2.7 kcal/mol. The effect of the chelate bite size is larger. [H$_2$Rh(depx)$_2$](CF$_3$SO$_3$) (depx = 1,2-(Et$_2$PCH$_2$)$_2$C$_6$H$_4$) binds H$_2$ more strongly than [Rh(depe)$_2$](CF$_3$SO$_3$) by 12 kcal/mol. An understanding of both hydrogen activation and hydride donor abilities is important for developing powerful hydride donors from H$_2$.

Introduction

The use of hydrogen to form transition metal hydrides that have hydride donor abilities comparable to borohydride reagents is of interest because it offers the possibility of replacing these relatively expensive and energy intensive stoichiometeric reagents with hydrogen.[1] In addition, the formation of B−H bonds from hydrogen could provide attractive routes to the regeneration of borohydrides and other boron compounds that have been proposed for hydrogen storage.[2] Recent advances in our understanding of the factors controlling the thermodynamic[3−5] and kinetic[1,6] hydride donor abilities (hydricities) of transition metal hydrides permit a rational approach to developing molecules that can activate hydrogen and serve as powerful hydride donors.

Previous thermodynamic studies of hydride complexes of the type [HM(diphosphine)$_2$]$^{n+}$ ($n = 0$, M = Co, Rh; $n = 1$, M = Ni, Pd, Pt) demonstrated that they have a range of thermodynamic hydride donor abilities (where the hydride donor ability is defined by the free energy associated with the reaction $\mathrm{HML}_n \rightarrow \mathrm{ML}_n^+ + \mathrm{H}^-$ in acetonitrile) extending over approximately 50 kcal/mol.[7] The less hydridic [HNi(diphosphine)$_2$]$^+$ members of this class of complexes are more compatible with protic environments, and certain nickel derivatives have been shown to exhibit high activities for the electrocatalytic oxidation and production of hydrogen.[8] On the more hydridic end of the scale, HRh(*o*-Ph$_2$PC$_6$H$_4$PPh$_2$)$_2$ was found to be a better hydride donor than complexes of the type [HW(CO)$_4$(L)]$^-$ (where L = CO, P(OMe)$_3$, or PPh$_3$), even though the latter are anionic and further to the left in the periodic table.[7b,9] The relatively good hydride donor abilities of the five-coordinate, 18-electron [HM(diphosphine)$_2$]$^{n+}$ complexes is attributed in part to their ability

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(1) Labinger, J. A. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1991; pp 361−379.

(2) (a) Amendola, S. C.; Sharp-Goldman, S. L.; Janjua, M. S.; Spencer, N. C.; Kelly, M. T.; Petillo, P. J.; Binder, M. *Int. J. Hydrogen Energy* **2000**, *25*, 969−975. (b) Chen, Y.; Fulton, J. L.; Linehan, J. C.; Autrey, T. *J. Am. Chem. Soc.* **2005**, *127*, 3254−3255.

(3) Raebiger, J. W.; Miedaner, A.; Curtis, C. J.; Miller, S. M.; DuBois, D. L. *J. Am. Chem. Soc.* **2004**, *126*, 5502−5514.

(4) Curtis, C. J.; Miedaner, A.; Raebiger, J. W.; DuBois, D. L. *Orgnometallics* **2004**, *23*, 511−516.

(5) Berning, D. E.; Miedaner, A.; Curtis, C. J.; Noll, B. C.; DuBois, M. R.; DuBois, D. L. *Organometallics* **2001**, *20*, 1832−1839.

(6) (a) Labinger, J. A.; Komadina, K. H. *J. Organomet. Chem.* **1978**, *155*, C25−C28. (b) Kao, S. C.; Spillett, C. T.; Ash, C.; Lusk, R.; Park, Y. K.; Darensbourg, M. Y. *Organometallics* **1985**, *4*, 83−91. (c) Kao, S. C.; Gaus, P. L.; Youngdahl, K.; Darensbourg, M. Y. *Organometallics* **1984**, *3*, 1601−1603. (d) Gaus, P. L.; Kao, S. C.; Youngdahl, K.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1985**, *107*, 2428−2434. (e) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 7902−7915. (f) Cheng, T.-Y.; Bullock, R. M. *J. Am. Chem. Soc.* **1999**, *121*, 3150−3155. (g) Cheng, T.-Y.; Brunschwig, B. S.; Bullock, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 13121−13137. (h) Bullock, R. M.; Voges, M. H. *J. Am. Chem. Soc.* **2000**, *122*, 12594−12595. (i) Cheng, T.-Y.; Bullock, R. M. *Organometallics* **2002**, *21*, 2325−2331. (j) Song, J.-S.; Szalda, D. J.; Bullock, R. M. *Organometallics* **2001**, *20*, 3337−3346. (k) Kobayashi, A.; Takatori, R.; Kikuchi, I.; Konno, H.; Sakamoto, K.; Ishitani, O. *Organometallics* **2001**, *20*, 3361−3363.

(7) (a) Berning, D. E.; Noll, B. C.; DuBois, D. L. *J. Am. Chem. Soc.* **1999**, *121*, 11432−11447. (b) Price, A. J.; Ciancanelli, R.; Noll, B. C.; Curtis, C. J.; DuBois, D. L.; DuBois, M. R. *Organometallics* **2002,** *21*, 4833−4839. (c) Miedaner, A.; Raebiger, J. W.; Curtis, C. J.; Miller, S. M.; DuBois, D. L. *Organometallics* **2004**, *23*, 2670−2679. (d) Curtis, C. J.; Miedaner, A.; Ellis, W. W.; DuBois, D. L. *J. Am. Chem. Soc.* **2002**, *124*, 1918−1925.

(8) (a) Wilson, A. D.; Newell, R. H.; McNevin, M. J.; Muckerman, J. T.; DuBois, M. R.; DuBois, D. L. *J. Am. Chem. Soc.* **2006**, *128*, 358−366. (b) Curtis, C. J.; Miedaner, A.; Ciancanelli, R. F.; Ellis, W. W.; Noll, B. C.; DuBois, M. R.; DuBois, D. L. *Inorg. Chem.* **2003,** *42*, 216−227.

(9) Ellis, W. W.; Ciancanelli, R.; Miller, S. M.; Raebiger, J. W.; DuBois, M. R.; DuBois, D. L. *J. Am. Chem. Soc.* **2003**, *125*, 12230−12236.

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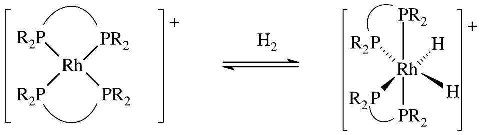
to form stable four-coordinate, 16-electron $[M(diphosphine)_2]^{(n+1)+}$ complexes upon hydride transfer. For this class of hydrides, the second-row transition metals are better hydride donors than either the first- or third-row analogues.[4] The hydride donor abilities also increase as the electron donor abilities of the substituents on the diphosphine ligand increase and the chelate bite sizes decrease.[3,5] Finally, the neutral $HM(diphosphine)_2$ complexes of the cobalt triad of metals are better hydride donors than the analogous positively charged $[HM(diphosphine)_2]^+$ members of the nickel triad, as expected.[7a,10] These trends all suggest that rhodium complexes with small chelate bite sizes and electron-donating substituents should be excellent hydride donors. In this paper, it is shown that $HRh(dmpe)_2$ and $HRh(depe)_2$ have hydride donor abilities similar to $LiHBEt_3$ on the basis of their ability to reversibly transfer their hydride ligand to triethyboron. In addition, these rhodium hydrides are readily generated from hydrogen in the presence of bases such as potassium *tert*-butoxide or lithium diisopropylamide.

Results

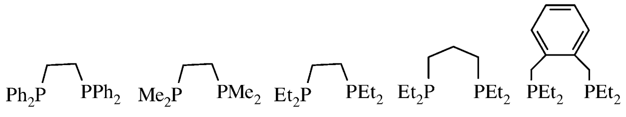
Reaction of $[Rh(diphosphine)_2](CF_3SO_3)$ Complexes with H_2 in the Absence and Presence of Base. The reactions of H_2 with the five $[Rh(diphosphine)_2](CF_3SO_3)$ complexes shown in eq 1 have been studied in both CD_3CN and tetrahydrofuran (THF) by ^1H and ^{31}P NMR spectroscopy. Similar results were obtained for both solvents. No reaction is observed for $[Rh(dppe)_2](CF_3SO_3)$ under 2−3 atm of H_2 as expected from previous reports.[11,12] However, the remaining four $[Rh(diphosphine)_2](CF_3SO_3)$ complexes react rapidly with hydrogen to form dihydride complexes, as indicated by the appearance of new hydride and phosphorus resonances in the ^1H and ^{31}P NMR spectra, respectively (reaction 1, see Experimental Section for spectral data for individual complexes). $[Rh(depp)_2](CF_3SO_3)$ and $[Rh(depx)_2](CF_3SO_3)$ react irreversibly with complete formation of dihydride species. However, under 0.8 atm of hydrogen, only a fraction of $[Rh(depe)_2](CF_3SO_3)$ converts to the dihydride and an equilibrium is established. A rapid reversible reaction was also observed for $[Rh(dmpe)_2](CF_3SO_3)$ consistent with previous work by Chatt and Butter.[12] The equilibrium constant for reaction 1 for $[Rh(depe)_2](CF_3SO_3)$ ($K_{eq} = [H_2Rh^+]/[Rh^+][H_2]$, where the concentration of hydrogen is expressed in atmospheres) was measured to be 0.25 ± 0.05 atm^{-1} by integration of the ^{31}P NMR spectra at 25 °C. For $[Rh(dmpe)_2](CF_3SO_3)$, the equilibrium constant for H_2 addition is 1.7 ± 0.2 atm^{-1}. The slightly higher binding constant for $[Rh(dmpe)_2](CF_3SO_3)$ is expected, because dmpe complexes are generally more electron rich than depe complexes, and both are much more electron rich than $[Rh(dppe)_2](CF_3SO_3)$, which does not react with H_2. The failure to observe H_2 binding by $[Rh(dppe)_2](CF_3SO_3)$ at 2−3 atm is consistent with a binding constant of less than 0.02 atm^{-1} for this complex.

Increasing the chelate bite size of the diphosphine ligand also favors H_2 addition. $[Rh(depp)_2](CF_3SO_3)$ and $[Rh(depx)_2](CF_3SO_3)$ react irreversibly with complete formation of the dihydride species, and in a previous study it was shown that the formation of $[H_2Rh(depx)_2](CF_3SO_3)$ is favored by 11 kcal/mol under 1.0 atm of H_2.[13] A comparison of the free energies for the addition of H_2 to $[Rh(depx)_2](CF_3SO_3)$ and $[Rh(depe)_2](CF_3SO_3)$ indicates that an increase in the natural bite angle[14,15] from 78° to 90° results in an increase in the driving force for H_2 addition by at least 12 kcal/mol. The actual increase arising from the increase in natural bite angle is probably somewhat larger. Ethyl substituents are better electron donors than benzyl substituents, and, as discussed in the preceding paragraph, this substituent effect would tend to partly offset the increase caused by an increase in the bite angle.

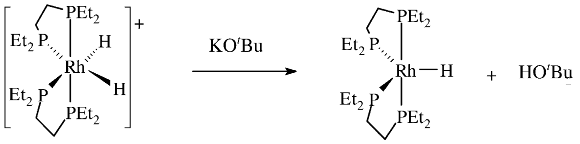


(1)

$K_{eq} = [RhH_2^+]/P_{H_2}[Rh^+]$



dppe **dmpe** **depe** **depp** **depx**



(2)

$[H_2Rh(depe)_2](CF_3SO_3)$ and $[H_2Rh(dmpe)_2](CF_3SO_3)$ are deprotonated by potassium *tert*-butoxide in tetrahydrofuran (reaction 2). For $[H_2Rh(dmpe)_2](CF_3SO_3)$, this reaction results in an equilibrium, whereas for $[Rh(depe)_2](CF_3SO_3)$ this reaction goes to completion. When lithium di(isopropyl)amide is used as a base, the reaction goes to completion for both compounds. The combination of these reactions with reaction 1 is the heterolytic cleavage of hydrogen. These monohydride products both exhibit a doublet of pentets at −11.6 ppm ($^2J_{PH} = 15$ Hz, $^1J_{RhH} = 15$ Hz, $HRh(dmpe)_2$) and −12.2 ppm ($^2J_{PH} = 14$ Hz, $^1J_{RhH} = 13$ Hz, $HRh(depe)_2$) in the ^1H NMR spectra and a doublet in the ^{31}P NMR spectra. These spectral features are consistent with five-coordinate $HRh(diphosphine)_2$ complexes. The same products are obtained by treatment of $[Rh(depe)_2](CF_3SO_3)$ and $[Rh(dmpe)_2](CF_3SO_3)$ with butyllithium in THF. The latter reaction is quantitative and provides a convenient method for the in situ generation of $HRh(depe)_2$ and $HRh(dmpe)_2$. Although solutions of $LiAlH_4$ in THF also reduce $[Rh(depe)_2](CF_3SO_3)$ and $[Rh(dmpe)_2](CF_3SO_3)$ to the corresponding monohydrides, these reactions are not as clean as the deprotonation and butyllithium routes. No reactions are observed when $[Rh(dmpe)_2](CF_3SO_3)$ and $Rh(depe)_2](CF_3SO_3)$ are treated with bis(triphenylphosphin)iminium borohydride ($PPNBH_4$) in THF for two weeks, suggesting that borohydride is not sufficiently hydridic to transfer a hydride ligand to these rhodium complexes.

Hydride Transfer Reactions from Rhodium to Boron. Titration of $HRh(dmpe)_2$ with BEt_3 in THF results in a hydride resonance that shifts from −0.37 ppm (B/Rh ratio = 0.37) to −2.75 ppm (B/Rh ratio = 6.2) with a sharp break at a 2.0/1.0 ratio (Figure 1). At the same time, ^{31}P NMR spectra indicate formation of $[Rh(dmpe)_2]^+$ with a chemical shift identical to that of $[Rh(dmpe)_2](CF_3SO_3)$ and no evidence for a coordinated triethylborohydride ligand. The variation in the position of the

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(10) Ciancanelli, R. F.; Noll, B. C.; DuBois, D. L.; DuBois, M. R. *J. Am. Chem. Soc.* **2002**, *124*, 2984−2992.

(11) Collman, J. P. *Acc. Chem. Res.* **1968**, *1*, 136−143.

(12) Chatt, J.; Butter, S. A. *Chem. Commun.* **1967**, 501.

(13) Raebiger, J. W.; DuBois, D. L. *Organometallics* **2005**, *24*, 110−118.

(14) Casey, C. P.; Whiteker, G. T. *Isr. J. Chem.* **1990**, *30*, 299−304.

(15) Van Leeuwen, P. W. N. M.; Kamer, P. C. J.; Reek, J. N. H.; Dierkes, P. *Chem. Rev.* **2000**, *100*, 2741−2769.

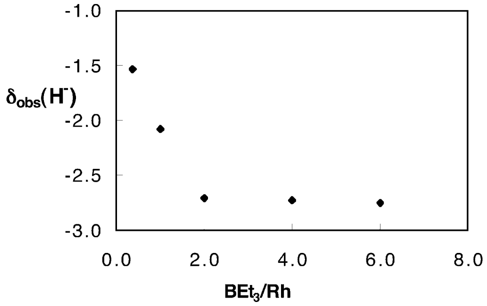


Figure 1. Plot of the chemical shift of the hydride resonance assigned to $[Et_3BHBEt_3]^-$ as a function of the BEt_3/Rh ratio.

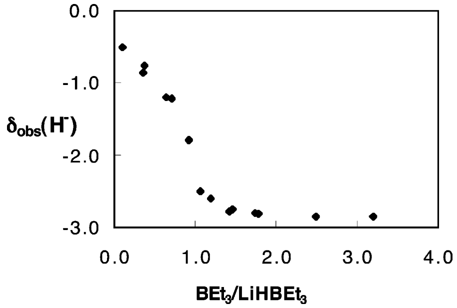
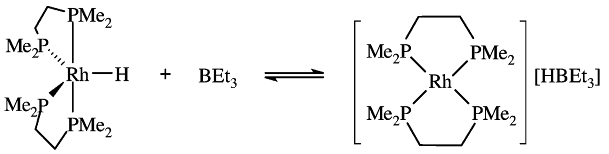


Figure 2. Plot of the chemical shift of the hydride resonance assigned to $[Et_3BHBEt_3]^-$ as a function of the $BEt_3/LiHBEt_3$ ratio.

BH resonance is attributed to a rapid equilibrium between BEt_3, $[HBEt_3]^-$, and $[Et_3BHBEt_3]^-$ in THF. That is, both reactions 3 and 4 are occurring. At low B/Rh ratios, $[HBEt_3]^-$ is the dominant boron species, but at high B/Rh ratios $[Et_3BHBEt_3]^-$ is the dominant species. Reaction 3 also proceeds in the opposite direction. When $LiEt_3BH$ is added to $[Rh(dmpe)_2](CF_3SO_3)$, $HRh(dmpe)_2$ is formed. This indicates that reaction 3 is a true equilibrium with $HRh(dmpe)_2$, having a hydride donor ability comparable to that of $LiHBEt_3$, "superhydride" in THF. Efforts to obtain reliable equilibrium constants for reaction 3 were complicated by the existence of reaction 4, ion pairing (common in THF), and an apparent disproportionation reaction of $LiHBEt_3$ to form $LiBEt_4$ and LiH_2BEt_2. The latter reaction has been reported previously.[16]



(3)

$[Et_3BH]^- + BEt_3 \Leftrightarrow [Et_3BHBEt_3]^-$ (4)

To confirm that the hydride resonance with a variable chemical shift in the preceding experiment arose from the reaction of triethyl boron with triethylborohydride, lithium triethylborohydride was titrated with triethylborane. The observed chemical shift of the hydride resonance is a function of $BEt_3/LiHBEt_3$ ratio, with an equivalence point occurring at a 1.0/1.0 ratio (Figure 2), consistent with the formation of $Li[Et_3BHBEt_3]$. A ^{11}B NMR spectrum recorded at a 1:1 BEt_3 to $LiHBEt_3$ ratio shows a single resonance at 8.7 ppm with respect to $BF_3{\cdot}Et_2O$. The same chemical shift is observed at a 2.0 B/Rh ratio in Figure 1. The slight difference in the hydride chemical shifts for the $[Et_3BHBEt_3]^-$ anion at high $BEt_3/LiHBEt_3$ ratios shown in Figure 2 compared to those at high $BEt_3/HRh(dmpe)_2$ ratios in Figure 1 (0.1 ppm) is attributed to the different cations ($[Rh(dmpe)_2]^+$ vs Li^+) and concentrations, leading to slightly different ion pairing.

It was also found that $HRh(depe)_2$ transfers a hydride to BEt_3 to form an equilibrium mixture of products, similar to reactions 3 and 4 for $HRh(dmpe)_2$, and again the reverse reaction is observed, confirming a true equilibrium. These studies indicated that $HRh(depe)_2$ is a slightly poorer hydride donor than $HRh(dmpe)_2$. The sequence of reactions 5−8 have been used to determine more quantitatively the difference in hydride donor abilities of these two complexes. It can be seen from eq 9 that this difference is the sum of the free energies associated with the ligand exchange reactions 6 and 7, for which equilibrium constants of 6.2 and 2.9, respectively, have been determined at 25 °C. As a result, $HRh(dmpe)_2$ is a 1.7 kcal/mol better hydride donor than $HRh(depe)_2$. In eq 9, a lower value of $\Delta G^\circ_{H^-}$ indicates a better hydride donor.

$$HRh(depe)_2 \rightarrow [Rh(depe)_2]^+ + H^- \tag{5}$$

$$[Rh(depe)_2]^+ + 2\ dmpe \Leftrightarrow [Rh(dmpe)_2]^+ + 2\ depe \tag{6}$$

$$HRh(dmpe)_2 + 2\ depe \Leftrightarrow HRh(depe)_2 + 2\ dmpe \tag{7}$$

$$HRh(dmpe)_2 \rightarrow [Rh(dmpe)_2]^+ + H^- \tag{8}$$

$$\Delta G^\circ_{H^-}(dmpe) = \Delta G^\circ_{H^-}(depe) - RT \ln K_{eq}(6) - RT \ln K_{eq}(7) \tag{9}$$

Discussion

The development of catalysts that can efficiently activate hydrogen and serve as hydride transfer agents requires an understanding of the factors controlling the activation of hydrogen as well as those controlling hydride transfer. The activation of hydrogen by these catalysts should be fast and reversible. For example, in the storage of hydrogen, it is desirable to rapidly bind and release hydrogen with a relatively small swing in hydrogen pressures to avoid large losses in efficiency. A common mode of activation of hydrogen is oxidative addition to a transition metal. As pointed out by Goldman and co-workers, our understanding of the factors that govern the thermodynamics of this and related oxidative addition reactions is limited.[17] In addition, the results are sometimes contradictory. For instance the influence of ancillary halogen ligands is different for different metals,[18,19] and different results have been reported for even the same metal.[18,20] Goldman and co-workers' study of H_2 addition to (X-PCP)Ir(CO) complexes (where X-PCP is a series of 2,6-(R_2PCH_2)-4-(X)-C_6H_2 ligands containing para substituents on the bound arene ring) demonstrated that π-bonding effects can lead to a situation in which increased electron density on the metal disfavors the addition of H_2. In other systems, it has been observed that increasing

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[16] (a) Jia, G.; Lough, A. J.; Morris, R. H. *J. Organomet. Chem.* **1993**, *461*, 147−156. (b) Fryzuk, M. D.; Lloyd, B. R.; Clentsmith, G. K. B.; Rettig, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 4332−4334.

[17] Krogh-Jespersen, K.; Czerw, M.; Zhu, K.; Singh, B.; Kanzelberger, M.; Darji, N.; Achord, P. D.; Renkema, K. B.; Goldman, A. S. *J. Am. Chem. Soc.* **2002**, *124*, 10797−10809.

[18] Vaska, L.; Werneke, M. F. *Ann. N. Y. Acad. Sci.* **1971**, *172*, 546−562.

[19] Hascall, T.; Rabinovich, D.; Murphy, V. J.; Beachy, M. D.; Friesner, R. A.; Parkin, G. *J. Am. Chem. Soc.* **1999**, *121*, 11402−11417.

[20] Strohmeier, W. *J. Organomet. Chem.* **1971**, *32*, 137−143.

the electron density at the metal center favors oxidative addition of H_2. For example, Chatt and Butter reported that $[Rh(dmpe)_2]^+$ reacts with H_2, but $[Rh(dppe)_2]^+$ does not.[12] It is also known that Vaska's complex, $IrCl(PPh_3)_2(CO)$, adds hydrogen, whereas the analogous rhodium complex does not.[11,21] This has also been attributed to greater electron density at Ir compared to Rh.[11] In the present study, the driving force for $[Rh(diphosphine)_2](CF_3SO_3)$ complexes to undergo oxidative addition of H_2 follows the order $[Rh(dmpe)_2](CF_3SO_3) > [Rh(depe)_2](CF_3SO_3) > [Rh(dppe)_2](CF_3SO_3)$. On the basis of the equilibrium constants for H_2 binding by these complexes, $[Rh(dmpe)_2](CF_3SO_3)$ binds H_2 more strongly than $[Rh(depe)_2](CF_3SO_3)$ by 1.1 kcal/mol, and $[Rh(depe)_2](CF_3SO_3)$ binds hydrogen more strongly than $[Rh(dppe)_2](CF_3SO_3)$ by at least 1.6 kcal/mol. This order suggests that increasing the electron donor ability of the diphosphine ligand favors oxidative addition of H_2 for this class of complexes.

It is also known that chelate bite angles exert a strong influence on the rates and selectivities of a wide variety of catalytic reactions.[22,23] For example, the rates of olefin insertion reaction into M−H or M−C bonds of M(diphosphine)(R)(olefin) complexes (where M = Pd or Pt) are orders of magnitude higher for complexes containing ligands with large bite angles compared to those with small bite angles.[24,25] A similar trend has been observed for reductive elimination reactions (the reverse of oxidative addition reactions). Examples include the elimination of nitriles from Pd(diphosphine)(R)(CN) complexes and hydrocarbons from $(diphosphine)MR_2$ complexes (M = Ni, Pd).[26−28] If thermodynamic studies were to parallel these kinetic studies, one would expect that oxidative addition reactions might be favored by small chelate bite sizes. However, it is also known that addition of H_2 to the $[Rh(Ph_2P(CH_2)_nPPh_2]^+$ cation is reversible for $n = 3$, but for $n = 1$ or 2 no reaction is observed.[29]

The 12 kcal/mol increase in driving force for the oxidative addition of H_2 to $[Rh(depx)_2](CF_3SO_3)$ compared to $[Rh(depe)_2](CF_3SO_3)$ clearly demonstrates a strong chelate bite size effect on the oxidative addition of H_2 to square planar d^8 metal complexes. The origin of this effect can be attributed to the lowering of the energy of the lowest unoccupied molecular orbital as the bite size increases. This drop in orbital energy is caused by an increasingly large tetrahedral distortion that occurs as the ligand bite size increases. Such a distortion has been documented by extensive structural studies of nickel, palladium, and platinum complexes.[3,7a,30] Previous theoretical studies have shown that this tetrahedral distortion results in a decrease in the antibonding overlap between the phosphorus σ orbitals and the d_{xy} orbital of the metal complex as the chelate bite size increases.[30] In addition, this orbital rehybridizes and becomes more suitably oriented for interaction with the hydrogen σ orbital. At the same time, the filled d_{xz} and d_{yz} orbitals increase in energy. The result is a geometry that is better optimized for interaction with H_2.

A detailed study of the heats for the oxidative addition reaction of tetrachloro-1,2-benzoquinone to $[M(dppv)_2]^+$ complexes (where M = Co, Rh, and Ir and dppv = *cis*-1,2-bis(diphenylphosphino)ethylene) found the order Co > Ir > Rh.[31] If the trend described by Blake and co-workers on the effect of the metal are combined with the chelate bite and substituent effects described in the preceding paragraphs, one would expect cobalt complexes containing diphosphine ligands with large bite angles and electron-donating substituents to bind H_2 very strongly. However, our interest in this project was in complexes that could reversibly activate H_2 at or near 1 atm pressure and that could be used to generate hydride donor complexes that are sufficiently hydridic to form B−H bonds. The $[Rh(dmpe)_2](CF_3SO_3)$ and $[Rh(depe)_2](CF_3SO_3)$ complexes appear to have the desired features for reversible hydrogen activation and for hydride transfer to boron.

The generation of hydridic reagents (i.e., reagents able to donate H^-) from molecular hydrogen intrinsically involves the heterolytic cleavage of hydrogen and the protonation of a base. This is achieved for $[Rh(dmpe)_2](CF_3SO_3)$ and $[Rh(depe)_2](CF_3SO_3)$ by following the oxidative addition of hydrogen (reaction 1) with the deprotonation of the resulting dihydride species (reaction 2). Potassium phenoxide is not a sufficiently strong base to deprotonate either $[H_2Rh(dmpe)_2](CF_3SO_3)$ or $[H_2Rh(depe)_2](CF_3SO_3)$, and lithium diisopropylamide completely deprotonates both to form the corresponding monohydrides. Potassium *tert*-butoxide deprotonates $[H_2Rh(depe)_2](CF_3SO_3)$ quantitatively, but $[H_2Rh(dmpe)_2](CF_3SO_3)$ exhibits an equilibrium. As a result, the acidity of $[H_2Rh(dmpe)_2](CF_3SO_3)$ is comparable to that of *tert*-butyl alcohol in THF. Ideally, these comparisons should be made in acetonitrile, because there is a large body of pK_a and hydricity data on similar complexes in this solvent.[32] However, attempts to carry out these deprotonation reactions in either acetonitrile or benzonitrile were unsuccessful because of competing reactions of the generated monohydride species with these solvents.

The final step in demonstrating that transition metal hydrides generated from hydrogen can have hydride donor abilities comparable to borohydride reagents is the transfer of a hydride ligand from the transition metal hydride to boron. Of course the generation of $[BH_4]^-$ from solutions of BH_3 in THF is one possibility. However, commercially available solutions are stabilized by the addition of $[BH_4]^-$ ions. To avoid this complication, we selected BEt_3 as our hydride acceptor. The formation of $[HBEt_3]^-$ would represent the formation of an even more hydridic reagent than $[BH_4]^-$. The selection of $HRh(depe)_2$ and $HRh(dmpe)_2$ as potential hydride donors was guided by the considerations outlined in the Introduction.

Borohydride reagents are typically used to generate transition metal hydrides, and BH_4^- salts are the most widely used reagents for this purpose. However, because of their greater hydride donor ability, Et_3BH^- salts have frequently been used to generate more hydridic transition metal hydrides.[33] As

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[21] Vaska, L.; Diluzio, J. W. *J. Am. Chem. Soc.* **1962**, *84*, 679−680.

[22] Freixa, Z.; van Leeuwen, P. W. N. M. *J. Chem. Soc., Dalton Trans.* **2003**, 1890−1901.

[23] Kamer, P. C. J.; van Leeuwen, P. W. N. M.; Reek, J. N. H. *Acc. Chem. Res.* **2001**, *34*, 895−904.

[24] Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079−2090.

[25] Dekker, G. P. C. M.; Elsevier, C. J.; Vrieze, K.; van Leeuwen, P. W. N. M.; Roobeek, C. F. *J. Organomet. Chem.* **1992**, *430*, 357−372.

[26] Marcone, J. E.; Moloy, K. G. *J. Am. Chem. Soc.* **1998**, *120*, 8257−8528.

[27] Kohara, T.; Yamamoto, T.; and Yamaoto, A. *J. Organomet. Chem.* **1980**, *192*, 265−274.

[28] Brown, J. M.; Guiry, P. J. *Inorg. Chim. Acta* **1994**, *220*, 249−259.

[29] (a) James, B. R.; Mahajan, D. *Can. J. Chem.* **1980**, *58*, 996. (b) Zhou, Z.; Facey, G.; James, B. R.; Alper, H. *Organometallics* **1996**, *15*, 2496−2503.

[30] Miedaner, A.; Haltiwanger, R. C.; DuBois, D. L. *Inorg. Chem.* **1991**, *30*, 417−427.

[31] Mondal, J. U.; Bulls, R.; Blake, D. M. *Inorg. Chem.* **1982**, *21*, 1668−1670.

[32] (a) Kristjánsdóttir, S. S.; Norton, J. R. In *Transition Metal Hydrides: Recent Advances in Theory and Experiment*; Dedieu, A., Ed.; VCH: New York, 1991; pp 309−359. (b) Izutsu, K. *Acid−Base Dissociation Constants in Dipolar Aprotic Solvents*, IUPAC Chemical Data Series, No. 35; Blackwell Scientific Publications: Oxford, 1990.

[33] (a) Crabtree, R. H.; Hlatky, G. G. *Inorg. Chem.* **1982**, *21*, 1273−1275. (b) Dawson, D. M.; Meetsma, A.; Roedelof, J. B.; Teuben, J. H. *Inorg. Chim. Acta* **1997**, *259*, 237−239.

discussed in the Results section, hydride transfer to BEt_3 to form first $[Et_3BHBEt_3]^-$ and then $[HBEt_3]^-$ is observed for both $HRh(dmpe)_2$ and $HRh(depe)_2$ as well as the reverse reactions. At high B to Rh ratios, the hydride species formed contains two borons per hydride transferred, as indicated by the formation of a species with a chemical shift of 2.8 ppm (see Figure 1). This same species is also observed for mixtures of BEt_3 and $LiHBEt_3$ with ratios greater than 1.0 (Figure 2). At B to Rh ratios less than 2.0, increasing amounts of $[HBEt_3]^-$ are formed, as indicated by a positive shift in hydride resonance and the shift of the ethyl resonances toward those observed for pure $LiHBEt_3$. This indicates that $HRh(dmpe)_2$ is capable of transferring a hydride ligand to $[Et_3BHBEt_3]^-$ to form $[HBEt_3]^-$. For $HRh(dmpe)_2$, equilibrium 3 lies further to the right than for $HRh(depe)_2$. This is expected, because $HRh(dmpe)_2$ is a better hydride donor than $HRh(depe)_2$ by 1.7 kcal/mol, as confirmed by reactions 6 and 7. These results demonstrate that $HRh(dmpe)_2$ and $HRh(depe)_2$ have hydride donor abilities comparable to those of $LiHBEt_3$ and greater than those of $[Et_3BHBEt_3]^-$ in THF.

The combination of reactions 1−3 is reaction 10, the heterolytic cleavage of H_2 by triethyl boron and potassium *tert*-butoxide to form potassium triethylborohydride and butanol. Because reactions 1−3 are all reversible for $[Rh(dmpe)_2](CF_3SO_3)$, this cycle represents an energetically efficient way of generating potassium triethylborohydride from hydrogen. Although these steps can be carried out independently in a stepwise manner, attempts to observe this reversible transformation catalytically in a single solution have not been successful. If reactions 1 and 2 are performed first in an NMR tube and Et_3B is added, the formation of $HBEt_3^-$ is observed. In contrast, if potassium *tert*-butoxide, $[Rh(dmpe)_2](CF_3SO_3)$, and BEt_3 are all mixed in an NMR tube and then H_2 is added, the formation of $HBEt_3^-$ is not observed. This is attributed to the formation of a strong adduct between triethylborane and the *tert*-butoxide anion. This is not surprising, and for the development of a catalytic system it will be necessary to select a base and conditions so that the base interacts much more strongly with a proton than with boron.

$$BEt_3 + KO^tBu + H_2 \rightarrow KHBEt_3 + HO^tBu \qquad (10)$$

Summary

These studies demonstrate that the rhodium hydrides $HRh(depe)_2$ and $HRh(dmpe)_2$ have thermodynamic hydride donor abilities comparable to $LiHBEt_3$, so-called “superhydride”. These hydrides can be generated from hydrogen gas in the presence of a strong base. These results raise the interesting possibility of using hydrogen and a base to carry out reactions that typically require borohydride reagents. A stepwise process for generating potassium triethylborohydride from H_2, potassium *tert*-butoxide, and triethylborane has been demonstrated. In addition, the relative hydride donor abilities of $HRh(dmpe)_2$ and $HRh(depe)_2$ were determined using a potentially useful new method based on facile exchange of diphosphine ligands. Finally, the results presented here, in combination with previous results on oxidative addition reactions of $[Rh(diphosphine)_2]^+$ cations,[29] demonstrate that chelate bites sizes (or natural bite angles) have a large effect on the thermodynamic driving force for the oxidative addition of H_2. An understanding of both hydrogen activation and hydride donor abilities is important for developing powerful hydride donors from H_2.

Experimental Section

General Procedures. NMR spectra were recorded on a Varian Inova 400 MHz spectrometer. ^1H chemical shifts are reported relative to tetramethylsilane using residual solvent protons as a secondary reference. ^{31}P chemical shifts are reported relative to external phosphoric acid, and all ^{31}P NMR spectra were proton decoupled unless stated otherwise. ^{11}B chemical shifts are reported relative to external $BF_3{\cdot}Et_2O$, and all ^{11}B NMR spectra were proton decoupled unless stated otherwise. All syntheses were performed under an inert atmosphere using standard Schlenk techniques or in a glovebox. Solvents were distilled under nitrogen using standard procedures. Potassium *tert*-butoxide was purified by sublimation. $[Rh(diphosphine)_2]CF_3SO_3$ complexes were prepared using literature methods.[3,29] Bis(1,5-cyclooctadiene)rhodium(I) triflate, $[Rh(COD)_2]CF_3SO_3$, was purchased from Strem Chemicals, Inc. The ligand α,α′-bis(diethylphosphino)xylene (depx) was prepared as previously described.[3]

Reaction of H_2 Gas with $[Rh(diphosphine)_2](CF_3SO_3)$ Complexes. $[Rh(dmpe)_2](CF_3SO_3)$. An NMR tube capped with a rubber septum and containing a 0.043 M solution of $[Rh(dmpe)_2](CF_3SO_3)$ in acetonitrile-d_3 (1.0 mL) was equilibrated in a constant-temperature bath at 25.0 ± 0.2 °C. The solution was purged with H_2 gas (0.82 atm, ambient pressure, Golden, CO) using a needle for 15 min. The NMR tube was removed from the bath and inserted into an NMR probe maintained at 25.0 ± 0.2 °C. ^{31}P NMR spectra were recorded and integrated to determine the ratio of $[H_2Rh(dmpe)_2](CF_3SO_3)$ to $[Rh(dmpe)_2](CF_3SO_3)$. Using the data obtained from four separate experiments an equilibrium constant of 2.1 ± 0.1 atm^{-1} was obtained ($K = [H_2Rh^+]/[Rh^+]P_{H2}$, uncertainty reported at 2σ). Spectral data for $[Rh(dmpe)_2](CF_3SO_3)$: ^1H NMR (acetonitrile-d_3): δ 1.73 (m, 8 H, PCH_2CH_2P), 1.46 (m, 24 H, PCH_2CH_3). ^{31}P NMR (acetonitrile-d_3): δ 36.25 (d, $^1J_{RhP} = 123$ Hz). Spectral data for $[H_2Rh(dmpe)_2](CF_3SO_3)$ (under H_2): ^1H NMR (acetonitrile-d_3): δ 1.7 (br m, 8 H, PCH_2CH_2P), 1.47 (br s, 24 H, PCH_3), −10.27 (br d, splitting = 145 Hz, Rh*H*). ^{31}P NMR (acetonitrile-d_3): δ 26.42 (br d), 38.0 (br d). Purging the NMR tubes with N_2 results in spectra identical to that of $[Rh(dmpe)_2](CF_3SO_3)$.

$[Rh(depe)_2](CF_3SO_3)$. An experiment identical to that described for $[Rh(dmpe)_2](CF_3SO_3)$ was performed with $[Rh(depe)_2](CF_3SO_3)$. From these data an equilibrium constant of 0.23 ± 0.02 atm^{-1} was calculated. Spectral data for $[Rh(depe)_2](CF_3SO_3)$: ^1H NMR (acetonitrile-d_3): δ 1.93 and 1.75 (two m, 24 H, PCH_2CH_2P and PCH_2CH_3), 1.07 (m, 24 H, PCH_2CH_3). ^{31}P NMR (acetonitrile-d_3): δ 63.18 (d, $^1J_{RhP} = 126$ Hz). Spectral data for $[H_2Rh(depe)_2](CF_3SO_3)$ (under H_2): ^1H NMR (acetonitrile-d_3): δ 1.95 and 1.78 (br m, 24 H, PCH_2CH_2P and PCH_2CH_3), 1.07 (m, 24 H, PCH_2CH_3), −10.7 (br d, splitting = 132 Hz, Rh*H*). ^{31}P NMR (acetonitrile-d_3): δ 47.5 (br m), 64.5 (br m).

$[Rh(depp)_2](CF_3SO_3)$. For this complex the reaction with H_2 is quantitative. Spectral data for $[Rh(depp)_2](CF_3SO_3)$: ^1H NMR (acetonitrile-d_3): δ 2.0 (m, 4 H, $PCH_2CH_2CH_2P$), 1.80 and 1.73 (two m, 24 H, $CH_2PCH_2CH_3$), 1.12 (m, 24 H, PCH_2CH_3). ^{31}P NMR (acetonitrile-d_3): δ 5.02 (d, $^1J_{RhP} = 126$ Hz). Spectral data for $[H_2Rh(depp)_2](CF_3SO_3)$: ^1H NMR (acetonitrile-d_3): δ 2.2−1.4 (br ms, $PCH_2CH_2CH_2PCH_2CH_3$), 1.47 (br s, PCH_2CH_3), −10.82 (AA′ portion of an AA′MM′XX′Z spin system, Rh*H*). ^{31}P NMR (acetonitrile-d_3): δ 15.00 (apparent dt), −6.20 (complex m). This complex may also be a diphosphine-bridged complex (see ref 27).

$[Rh(dppe)_2](CF_3SO_3)$ and $[Rh(depx)_2](CF_3SO_3)$. No reaction of the well-known $[Rh(dppe)_2](CF_3SO_3)$ complex with H_2 was observed under 2−3 atm of H_2. The irreversible addition of H_2 to $[Rh(depx)_2](CF_3SO_3)$ was reported previously.[13]

Heterolytic Cleavage of H_2 with Potassium *tert*-Butoxide and $[Rh(dmpe)_2](CF_3SO_3)$. Potassium *tert*-butoxide (0.015 g, 0.13 mmol) was added to a solution of $[Rh(dmpe)_2](CF_3SO_3)$ in THF (0.043 M, 1.0 mL, 0.043 mmol) in an NMR tube, and the tube was shaken to produce a clear solution. A ^{31}P NMR spectrum was recorded on this solution after 30 min. The only resonances observed were those for unreacted [Rh(dmpe)$_2$](CF$_3$SO$_3$). After purging the sample with hydrogen for 15 min, ^{1}H and ^{31}P NMR spectra were again recorded. Resonances assigned to [Rh(dmpe)$_2$](CF$_3$SO$_3$) (5%) and HRh(dmpe)$_2$ (95%) were observed. ^{1}H NMR (THF, external lock): δ -11.61 (doublet of pentets, $^2J_{PH} = 15$ Hz, $^1J_{RhH} = 15$ Hz, *H*Rh). ^{31}P NMR (THF, external lock): δ 32.95 (d, $^1J_{RhP} = 124$ Hz, [Rh(dmpe)$_2$](CF$_3$SO$_3$), 5%), 23.32 (d, $^1J_{RhP} = 139$ Hz, HRh(dmpe)$_2$, 95%).

Heterolytic Cleavage of H$_2$ with Potassium *tert*-Butoxide and [Rh(depe)$_2$](CF$_3$SO$_3$). A similar reaction was repeated using potassium *tert*-butoxide (0.015 g, 0.13 mmol) and a solution of [Rh(depe)$_2$](CF$_3$SO$_3$) in THF (0.043 M, 1.0 mL, 0.043 mmol). In this case the conversion to HRh(depe)$_2$ was quantitative. ^{1}H NMR (THF, external lock): δ -12.17 (doublet of pentets, $^2J_{PH} = 14$ Hz, $^1J_{RhH} = 13$ Hz, *H*Rh). ^{31}P NMR (THF, external lock): δ 54.32 (d, $^1J_{RhP} = 140$ Hz).

Heterolytic Cleavage of H$_2$ with Lithium Diisopropylamide and [Rh(dmpe)$_2$](CF$_3$SO$_3$). A similar reaction was repeated using lithium diisopropylamide (0.015 g, 0.14 mmol) and a solution of [Rh(dmpe)$_2$](CF$_3$SO$_3$) in THF (0.043 M, 1.0 mL, 0.043 mmol). In this case the conversion to HRh(dmpe)$_2$ was quantitative.

Generation of HRh(dmpe)$_2$ from [Rh(dmpe)$_2$](CF$_3$SO$_3$) and Butyllithium. A solution of butyllithium (2.5 M, 17 μL, 0.043 mmol) in THF was added to a solution of [Rh(dmpe)$_2$](CF$_3$SO$_3$) in THF (0.043 M, 1.0 mL, 0.043 mmol) in an NMR tube. The tube was shaken to produce a clear solution, and after 30 min ^{1}H and ^{31}P NMR spectra were recorded. The quantitative formation of HRh(dmpe)$_2$ was observed. A similar reaction of [Rh(depe)$_2$](CF$_3$SO$_3$) with butyllithium also quantitatively produces HRh(depe)$_2$.

Titration of HRh(dmpe)$_2$ with Triethylborane. A solution of HRh(dmpe)$_2$ in THF (0.171 M, 1.0 mL, 0.171 mmol) in an NMR tube was titrated with 9, 24, 48, 98, and 148 μL of triethylborane. This corresponds to BEt$_3$ to Rh ratios of 0.37, 1.00, 2.00, 4.08, and 6.16, respectively. This titration was followed by ^{1}H and ^{31}P NMR spectroscopy. Both indicated a disappearance of HRh(dmpe)$_2$ and the formation of [Rh(dmpe)$_2$]$^+$. At a 2.00 BEt$_3$ to Rh ratio only [Rh(dmpe)$_2$]$^+$ was observed. Concurrent with these changes to the rhodium species was the appearance of a resonance at -1.53 ppm in the ^{1}H NMR spectrum at a BEt$_3$ to Rh ratio of 0.37 that grew in intensity and shifted in a negative direction as this ratio increased. A plot of the shift of this resonance versus the BEt$_3$ to Rh ratio is shown in Figure 1. At a 1.0/1.0 BEt$_3$/HRh ratio the [Rh$^+$]/[HRh] was 2.5/1.0, and the ^{11}B NMR spectrum showed a new broad resonance (half-height width of ~150 Hz) at 9.0 ppm. Additional resonances were observed at -14.0 ppm (20% unassigned) and -16.6 ppm (5% assigned to BEt$_4$]$^-$) after 24 h. Similar results were obtained for the reaction carried out between HRh(depe)$_2$ and BEt$_3$, but at the same BEt$_3$ to Rh ratios, less hydride transfer from Rh to B was observed.

Reaction of LiHBEt$_3$ with [Rh(dmpe)$_2$](CF$_3$SO$_3$). A solution of LiHBEt$_3$ in THF (1.0 M, 200 mL, 0.20 mmol) was added to a solution of [Rh(dmpe)$_2$](CF$_3$SO$_3$) in THF (0.043 M, 1.0 mL, 0.043 mmol). Both HRh(dmpe)$_2$ and [Rh(dmpe)$_2$](CF$_3$SO$_3$) were observed by ^{31}P NMR spectroscopy in a 2.2/1.0 ratio ([HRh]/[Rh$^+$]) after 10 min, and this ratio persisted for at least 24 h. In separate experiments, smaller amounts resulted in smaller conversions and larger amounts in larger conversions. At a 1.0/1.0 LiHBEt$_3$/Rh ratio the [HRh]/[Rh$^+$] was 0.77/1.00. Similar results were obtained for [Rh(depe)$_2$](CF$_3$SO$_3$), but conversion to HRh(depe)$_2$ was more complete at the same LiHBEt$_3$/Rh ratios.

Titration of LiHBEt$_3$ with BEt$_3$. Aliquots of triethylborane were added to a solution of LiHBEt$_3$ in THF (1.0 mL, 1.0 M, 1.0 mmol). This titration was followed by ^{1}H NMR spectroscopy. A broad triplet and a broad quartet assigned to the ethyl group on boron were observed, consistent with a rapidly exchanging system. In addition, a hydride resonance was observed with chemical shifts gradually changing with addition of BEt$_3$ from -0.76 to -2.85 ppm. A plot of the shift of this resonance versus the BEt$_3$ to LiHBEt$_3$ ratio is shown in Figure 2. A ^{11}B NMR spectrum recorded at a 1/1 ratio exhibited a single resonance at 8.7 ppm assigned to [Et$_3$BHBEt$_3$]$^-$ and a small resonance at -16.6 pm (5%) assigned to [BEt$_4$]$^-$.

Ligand Exchange Reactions. Reaction of depe with [Rh(dmpe)$_2$](CF$_3$SO$_3$). Bis(diethylphosphino)ethane (depe, 20 μL, 0.086 mmol) was added to a solution of [Rh(dmpe)$_2$](CF$_3$SO$_3$) in acetonitrile-*d*$_3$ (0.043 M, 1.0 mL, 0.043 mmol). A ^{31}P NMR spectrum recorded after 10 min indicated a rapid redistribution of the two ligands and the presence of all three possible rhodium species ([Rh(dmpe)$_2$](CF$_3$SO$_3$), [Rh(depe)(dmpe)](CF$_3$SO$_3$), and [Rh(depe)$_2$](CF$_3$SO$_3$)) as well as uncoordinated depe and dmpe ligands. This ratio remained constant for at least 4 days. Integration of the ^{31}P NMR spectrum was used to determine the ratios of rhodium species and ligand species. From these data for four experiments, an equilibrium constant of 6.2 ± 0.3 was determined for the equilibrium constant $K = \{[\text{depe}]^2[\text{Rh(dmpe)}_2{}^+]/[\text{dmpe}]^2[\text{Rhdepe})_2{}^+]\}$ for eq 6. A similar procedure was used to determine an equilibrium constant of 2.9 ± 0.3 for eq 7, where $K = \{[\text{dmpe}]^2[\text{HRh(depe)}_2]/[\text{depe}]^2[\text{HRhdmpe})_2]\}$.

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