and MS facilities at OSU were partially funded by the National Science Foundation, DMB-8603864 and BSS-8704089, respectively. C.M.A. thanks BASF for the kind donation of COT and Professors L. T. Scott and K. Hafner for helpful discussions.

Registry No. 1, 125519-39-3; 2, 64121-49-9; 3, 125519-40-6; 4, 33056-62-1; 5, 125519-41-7; 6, 125519-42-8; 7, 58396-62-6; 8, 125519-43-9; 9, 125519-44-0; 10, 53407-14-0; 11, 125519-45-1; 12, 125519-46-2; $Fe_2(CO)_9$, 15321-51-4; 1,3-dimercaptopropane, 109-80-8.

Supplementary Material Available: Tables of anisotropic thermal parameters and least-squares planes for 1 and tables of crystal data, positional and anisotropic thermal parameters, and bond angles and distances for 8 (7 pages); listings of observed and calculated structure factor amplitudes for 1 and 8 (37 pages). Ordering information is given on any current masthead page.

Reactions of Binuclear Rhodium Hydrides with Imines: Factors Influencing the Insertion of Carbon–Nitrogen Double Bonds into Rhodium–Hydride Bonds

Michael D. Fryzuk* and Warren E. Piers†

Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC, Canada V6T 1Y6

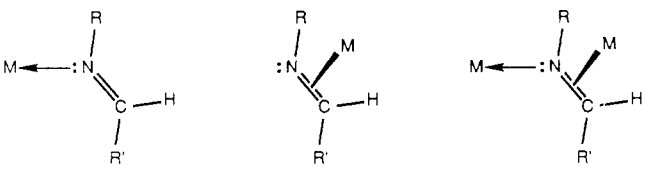
Received July 20, 1989

The reaction of the binuclear rhodium hydride complexes $[(R_2PCH_2CH_2PR_2)Rh]_2(\mu\text{-}H)_2$ (R = Pr^i, **1a**, $[(dippe)Rh]_2(\mu\text{-}H)_2$; R = OPr^i, **1b**, $[(dipope)Rh]_2(\mu\text{-}H)_2$) with simple aldimines (RCH=NR'), the ketimine benzophenone imine (Ph_2C=NH), and the cyclic imine isoquinoline are described. Amido–hydride products of the general formula $[(R_2PCH_2CH_2PR_2)Rh]_2(\mu\text{-}NR'CH_2R)(\mu\text{-}H)$ are produced. The mechanism of this reaction has been investigated by labeling studies and kinetic analysis. Intermediates have been detected and characterized spectroscopically that are consistent with the imine binding through the lone pair on nitrogen and through the π-system of the carbon–nitrogen double bond. On the basis of these studies it is proposed that a necessary condition for migratory insertion of a C=N double bond into a metal hydride is prior coordination through the C=N π-system. Iminium salts of the formula $[PhCH{=}NHR']^+BF_4^-$ react with the hydride dimer **1a** to generate cationic complexes of the formula $\{[(Pr^i_2PCH_2CH_2PPr^i_2)Rh]_2(\mu\text{-}NR'{=}CHPh)(\mu\text{-}H)\}^+BF_4^-$ having the imine bound in the $\mu\text{-}\eta^2\text{-}\sigma$-mode. Further reaction of this material with $LiAl(OBu^t)_3H$ generates the corresponding amido hydride. Attempts at using the hydride dimers **1a** and **1b** as catalyst precursors for the homogeneous hydrogenation of imines were only partially successful, resulting in at best seven turnovers (1 atm, 16 h).

Introduction

Many homogeneous mononuclear organotransition-metal systems mediate the reduction of carbon–carbon multiple bonds.[1] However there are very few examples of those that bring about the hydrogenation of carbon–nitrogen double (C=N) or triple (C≡N) bonds under ambient conditions.[2-6] This observation seems to parallel the known π-complexation chemistry of each type of functional group: for olefins and alkynes, this chemistry is vast,[7] but for imines and nitriles the tendency to σ-donate the lone pair on nitrogen to a metal almost always precludes π-coordination of the C=N or the C≡N group to the metal.[8] Since it is generally accepted that π-coordination of olefins or alkynes to the metal precedes its reduction via migratory insertion of a metal–hydride bond, the lack of homogeneous systems for the hydrogenation of imines or nitriles appears to stem from the fact that this key step is prevented in a cycle involving C=N or C≡N moieties, due to the stronger donating ability of the lone pair compared with that of the C=N or C≡N π-system.

The relatively few known imine transition-metal complexes exhibit σ-bonding through the nitrogen lone pair, i.e., type I. In fact, mononuclear complexes having side-on



I II III

π-bonding imine ligands (type II) have only been reported for the early metals,[8] generally as a result of migratory insertion reactions of isonitriles and metal hydrocarbyls. In systems which hydrogenate imines under ambient conditions, it has been proposed that the nitrogen lone pair is occupied in some manner other than bonding to the metal. For example, this feature is included in the mechanistic proposal for the hydrogenation of aldimines by a cationic rhodium triphenylphosphine complex,[2a] wherein an intermediate in which the imine C=N bond is π-coordinated forms when the lone pair at nitrogen

†NSERC Postgraduate Scholar (1984–1988).

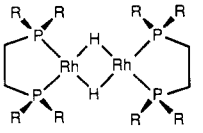
(1) Parshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980; Chapters 3–5.
(2) (a) Longley, C. J.; Goodwin, T.; Wilkinson, G. *Polyhedron* **1986**, *5*, 1625. (b) Grigg, R.; Mitchell, T. R. B.; Tongpenyai, N. *Synthesis* **1981**, 442.
(3) (a) Vastag, S.; Bakos, J.; Torös, S.; Takach, N. E.; King, R. B.; Heil, B.; Marko, L. *J. Mol. Catal.* **1984**, *22*, 283. (b) Vastag, S.; Heil, B.; Torös, S.; Marko, L. *Transition Met. Chem.* **1977**, *2*, 58. (c) Levi, A.; Modena, G.; Scorrano, G. *J. Chem. Soc., Chem. Commun.* **1975**, 6. (d) Kang, G.-J.; Cullen, W. R.; Fryzuk, M. D.; James, B. R.; Kutney, J. P. *J. Chem. Soc., Chem. Commun.* **1988**, 1466.
(4) (a) Radhi, M. A.; Palyi, G.; Marko, L. *J. Mol. Catal.* **1983**, *22*, 195. (b) Radhi, M. A.; Marko, L. *J. Organomet. Chem.* **1984**, *262*, 359.
(5) Baranyai, A.; Ungvary, F.; Marko, L. *J. Mol. Catal.* **1985**, *32*, 343.
(6) Palagyi, J.; Nagy-Magos, Z.; Marko, L. *Transition Met. Chem.* **1985**, *10*, 336.
(7) Lewandos, G. S. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley: New York, 1982; Vol. 1, Chapter 7.
(8) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*, 2nd ed.; University Science Books: Mill Valley, CA, 1987; p 64. For examples of η^2-imines, see: (b) Chamberlain, L. R.; Steffey, B. D.; Rothwell, I. P.; Huffman, J. C. *Polyhedron* **1989**, *8*, 341. (c) Durfee, L. D.; Fanwick, P. E.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 4720 and ref 10 therein.

0276-7333/90/2309-0986$02.50/0

hydrogen-bonds with a coordinated alcohol solvent molecule. Hydrogenation with this catalyst system was effected under very mild conditions (25 °C, 1 atm of H_2). In situ systems comprised of a Rh(I) starting material and a chelating diphosphine ligand have also been reported[3d] to be effective in the asymmetric hydrogenation of imines in alcohol solvent mixtures; however, while mechanistic details have not yet been reported, higher pressures than for the Rh/PPh_3 system previously mentioned are required for any activity. Other homogeneous catalyst systems that bring about the hydrogenation of imines utilize metal carbonyls (M = Fe,[4] Co,[5] and Cr, Mo, or W[6]) as catalyst precursors but require strongly polar solvents, elevated temperatures, and high pressures of H_2. Under these conditions, the nature of the imine–transition-metal interaction is unclear, but there is evidence that the reduction proceeds via an initial protonation of the nitrogen lone pair by the acidic $HM(CO)_n$ catalyst, followed by H transfer to the imine moiety.

The possibility that polynuclear complexes can mediate transformations not possible by mononuclear species is well recognized.[9] The success of heterogeneous catalysts in the hydrogenation of imines[10] suggests that multiple metal binding sites may provide pathways for the reduction of imines and that polynuclear homogeneous catalysts may be effective moderators of this process. Although σ-coordination of the C=N lone pair may be preferred, the presence of an additional metal center nearby could induce π-donation to that center from the C=N bond since the lone pair is already occupied with the other metal center, as in type III. Indeed, π-donation to adjacent metal centers by the C=N double bonds of σ-coordinated diimines (1,4-azadienes) has been observed in many polynuclear complexes;[11] however, similar bonding modes for simple imines are unprecedented.

In this report, the reactions of the binuclear rhodium dihydrides **1a**[12] and **1b**[13] with simple aldimines (RCH=NR'), the ketimine benzophenone imine (Ph_2C=NH), and the cyclic imine isoquinoline are described. The products



R = Pr^i **1a** [(dippe)Rh]$_2$(μ-H)$_2$

R = OPr^i **1b** [(dipope)Rh]$_2$(μ-H)$_2$

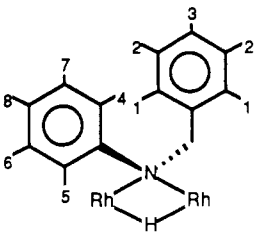
are binuclear amido hydrides in which the μ-amido ligand has arisen from an apparent migratory insertion of the imine substrate into a Rh–H bond of the dihydride. Intermediates observed by low-temperature NMR studies indicate that π-coordination of the imine is involved as part of a complex process wherein both metal centers act congruently. Additional support for this proposal is based on kinetic studies and synthetic work on the characterization of analogues of proposed intermediates in the reaction. A preliminary report of this work has appeared.[14] A subsequent paper will describe the related reactions of these dihydrides with simple organic nitriles.

(9) Burch, R. R.; Shusterman, A. J.; Muetterties, E. L.; Teller, R. G.; Williams, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 3546 and references therein.
(10) (a) Yoshida, T.; Harada, K. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3706. (b) Roe, A.; Montgomery, J. A. *J. Am. Chem. Soc.* **1953**, *75*, 910.
(11) van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151.
(12) Fryzuk, M. D.; Einstein, F. W. B.; Jones, T. *Organometallics* **1984**, *3*, 185.
(13) Fryzuk, M. D. *Can. J. Chem.* **1983**, *61*, 1347.
(14) Fryzuk, M. D.; Piers, W. E. *Organometallics* **1988**, *7*, 2062.

Experimental Section

General Procedures. General techniques and procedures have been described in detail elsewhere.[15] The syntheses of the dihydride dimers **1a**,[12] **1b**,[13] and **1c**[15] have been previously described. *N*-Benzylideneaniline was prepared via a literature procedure;[16] its ^{13}C-labeled isotopomer $(C_6H_5)N{=}^{13}CH(C_6H_5)$ was prepared in the same manner by using ^{13}C-labeled benzaldehyde obtained from MSD Isotopes. *N*-Phenylbenzylamine, *N*-benzylidenemethylamine, *N*-benzylidenebenzylamine, benzophenone imine, and the cyclic imine isoquinoline were all purchased from the Aldrich Chemical Co., distilled under argon prior to use, and stored in the glovebox. Lithium tri-*tert*-butoxyaluminohydride was also purchased from Aldrich. The tetrafluoroborate iminium salts $[(C_6H_5)HN{=}CH(C_6H_5)]BF_4$ and $[(CH_3)HN{=}CH(C_6H_5)]BF_4$ were prepared via protonation of the corresponding imine with HBF_4 (Aldrich, 85% in Et_2O) in diethyl ether. The iminium salts precipitated immediately upon addition of HBF_4 and, after washing twice with 50-mL portions of Et_2O, were dried under vacuum and stored in a glovebox. Purity was found to be >98% via ^{1}H NMR spectroscopy.

Synthesis of [(dippe)Rh]$_2$[μ-(C$_6$H$_5$)N(CH$_2$C$_6$H$_5$)](μ-H) (2a). To a stirred solution of $[(dippe)Rh]_2(\mu\text{-}H)_2$ (**1a**; 0.164 g, 0.22 mmol) in toluene (15 mL) was added solid *N*-benzylideneaniline (0.081 g, 0.44 mmol). Within 5 min, the deep green to orange color change was complete. The toluene was removed in vacuo, and the orange solid remaining was recrystallized from the minimum amount of toluene–hexane (1:2), yielding 0.167 g (82%) of orange crystalline $[(dippe)Rh]_2[\mu\text{-}(C_6H_5)N(CH_2CH_6H_5)](\mu\text{-}H)$ (**2a**). ^{1}H NMR (C_6D_6, ppm):



C-H_1, 8.74 (d, 2 H, $^3J_{H_2}$ = 8.0 Hz); C-H_4 or C-H_5, 8.58 (d, 1 H, ^3J_H = 8.4 Hz); C-H_2, C-H_3, C-H_6, or C-H_7 and C-H_4 or C-H_5, 7.14–7.30 (overlapping multiplets, 5 H); C-H_6 or C-H_7, 7.00 (m, 1 H, $^3J_H \approx$ 7.2 Hz); C-H_8, 6.75 (m, 1 H, $^3J_H \approx$ 7.6 Hz); NCH_2C$_6$H$_5$, 5.32 (br t, 2 H, $^4J_P \approx$ 2.0–3.0 Hz); CH(CH$_3$)$_2$, 2.32, 2.26, 1.78, 1.68 (dsp, $^2J_P \approx$ 2.0–4.0 Hz, ^3J_H = 7.2–8.0 Hz); CH(CH_3)$_2$, 1.52, 1.50, 1.13, 1.06, 0.88, 0.85, 0.64, 0.57 (overlapping dd, ^3J_P = 12.8–14.4 Hz); CH_2CH_2 (resonances buried underneath signals for the methyl groups); Rh-H-Rh, −9.41 (ttt, $^2J_{P_{trans}}$ = 56.4 Hz, $^2J_{P_{cis}}$ = 12.8 Hz, $^1J_{Rh}$ = 23.1 Hz). ^{13}C{^{1}H} NMR (C_6D_6, ppm): C_{ipso}(N), 164.6; C_{ipso}(C), 143.7; other aromatic carbons, 130.3, 128.8, 127.4, 126.3, 126.1, 124.7, 117.8, 111.3; NCH_2C$_6$H$_5$, 66.8; CH(CH$_3$)$_2$, 26.8–28.7 (4 m); CH_2CH_2, 21.8–22.8 (m); CH(CH_3)$_2$, 18.3–22.7 (8 s). ^{31}P{^{1}H} NMR (C_6D_6, ppm; $P_{cis(N)}$ = A, $P_{trans(N)}$ = B, Rh = X): δ_A = 73.9; δ_B = 105.5; $J_{AA'}$ = 33.5 Hz; J_{AB} = 30.3 Hz; $J_{AB'}$ = 2.9 Hz; J_{AX} = 191.3; $J_{ZX'}$ = 5.8 Hz; $J_{BB'}$ = −0.9 Hz; J_{BX} = 166.9 Hz; $J_{BX'}$ = −1.2 Hz; $J_{XX'}$ = 5.6 Hz. Anal. Calcd for $C_{41}H_{75}P_4Rh_2N$: C, 54.01; H, 8.29; N, 1.54. Found: C, 54.30; H, 8.52; N, 1.62.

Synthesis of [(dippe)Rh]$_2$[μ-(CH$_3$)N(CH$_2$C$_6$H$_5$)](μ-H) (3a). To a stirred solution of $[(dippe)Rh]_2(\mu\text{-}H)_2$ (**1a**; 0.274 g, 0.37 mmol) in toluene (20 mL) was added neat *N*-benzylidenemethylamine (0.088 g, 0.74 mmol), in one portion. A rapid green to orange color change ensued. The toluene was then removed under reduced pressure, and the resulting orange residue was recrystallized from toluene–hexane (1:5). The orange crystals were washed twice with cold hexane to remove excess imine; yield 0.262 g (82%). ^{1}H NMR (C_6D_6, ppm): H_{ortho}, 8.35 (d, 2 H, $^3J_{H_{meta}}$ = 7.6 Hz); H_{meta} and H_{para}, 7.05–7.18 (m, 3 H); NCH_2C$_6$H$_5$, 5.10 (br t, ^4J_P = 4.8 Hz); NCH_3, 3.80 (br t, 3 H, $^4J_P \approx$ 1.5–2.0 Hz); CH(CH$_3$)$_2$, 1.8–2.2 (4 overlapping dsp, 8 H, ^3J_H = 6.9–7.7 Hz, ^2J_P = 3.7–4.0 Hz); CH(CH_3)$_2$, 1.37, 1.35, 1.33, 1.08, 1.06, 0.88, 0.83 (overlapping dd, 48 H, ^3J_P =

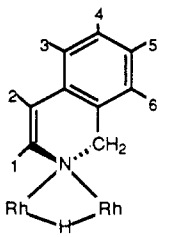
(15) Fryzuk, M. D.; Piers, W. E.; Einstein, F. W. B.; Jones, T. *Can. J. Chem.* **1989**, *67*, 883.
(16) *Organic Syntheses*, 2nd ed.; Gilman, H., Blatt, A. H., Eds.; Wiley: New York, 1941; Collect. Vol. 1, p 80.

12.8–14.4 Hz); PCH_2CH_2P, 1.15–1.25 (m, 8 H); Rh–*H*–Rh, –8.92 (ttt, $^2J_{P_{trans}}$ = 57.2 Hz, $^2J_{P_{cis}}$ = 12.8 Hz, $^1J_{Rh}$ = 22.7 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, ppm): C_{ipso}, 143.8; other aromatic carbons 129.3, 126.2, 125.8; NCH_3, 75.6; N$CH_2(C_6H_5)$, 56.2; phosphine ligand resonances, 18–28. $^{31}P\{^1H\}$ NMR (C_6D_6, ppm): $P_{trans(N)}$, 101.1 (dm, $^1J_{Rh} \approx$ 152 Hz); $P_{cis(N)}$, 75.1 (dm, $^1J_{Rh} \approx$ 195 Hz). Anal. Calcd for $C_{36}H_{75}P_4Rh_2N$: C, 50.77; H, 8.88; N, 1.64. Found: C, 50.67; H, 9.10; N, 1.59.

Synthesis of [(dippe)Rh]$_2$[μ-N(C$H_2C_6H_5$)$_2$](μ-H) (4a). To a stirred solution of [(dippe)Rh]$_2$(μ-H)$_2$ (**1a**; 0.045 g, 0.06 mmol) in toluene (10 mL) was added neat *N*-benzylidenebenzylamine (0.015 g, 0.08 mmol), in one portion. The reaction mixture was stirred until the green to orange color change was complete (10 min), at which time the toluene was removed in vacuo. The remaining solid was recrystallized from toluene–hexane (1:2), yielding a crop of bright orange crystals (0.039 g, 69%) after washing with cold hexane. ^1H NMR (C_6D_6, ppm): H_{ortho}, 8.54 (d, 4 H, $^3J_{H_{meta}}$ = 7.2 Hz); H_{meta}, 7.21 (m, 4 H, $^3J_{H_{para}} \approx$ 7.5 Hz); H_{para}, 7.13 (m, 2 H); N$CH_2(C_6H_5)$, 5.44 (br t, 4 H, ^4J_P = 3.5–4.0 Hz); C$H(CH_3)_2$, 2.35, 1.85 (dsp, 8 H, ^3J_H = 7.6–8.0 Hz, ^2J_P = 3.0–4.0 Hz); CH(CH_3)$_2$, 1.48, 1.06, 0.73, 0.72 (dd, 48 H, ^2J_P = 12.0–14.0 Hz); PCH_2CH_2P, 1.1 (br m, obscured by methyl groups); Rh–*H*–Rh, –9.40 (ttt, $^2J_{P_{trans}}$ = 57.2 Hz, $^2J_{P_{cis}}$ = 12.8 Hz, $^1J_{Rh}$ = 22.0 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, ppm): C_{ipso}, 144.3; other aromatic carbons, 129.2, 125.9, 125.5; NCH_2, 76.1; CH(CH_3)$_2$, 26.4–28.7 (m); PCH_2CH_2, 19.7–21.1 (m); CH(CH_3)$_2$, 18.4, 19.0, 19.0, 19.6 (s). $^{31}P\{^1H\}$ NMR (C_6D_6, ppm): $P_{trans(N)}$, 98.8 (dm, $^1J_{Rh} \approx$ 154 Hz); $P_{cis(N)}$, 74.7 (dm, $^1J_{Rh} \approx$ 199 Hz). Anal. Calcd for $C_{42}H_{79}P_4Rh_2N$: C, 54.37; H, 8.58; N, 1.51. Found: C, 54.26; H, 8.80; N, 1.50.

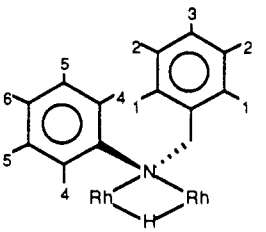
Synthesis of [(dippe)Rh]$_2$[μ-HNCH(C$_6H_5$)$_2$](μ-H) (5a). To a stirred solution of [(dippe)Rh]$_2$(μ-H)$_2$ (**1a**; 0.060 g, 0.082 mmol) in toluene (10 mL) was added neat benzophenone imine (0.022 g, 0.12 mmol), in one portion. The reaction mixture was stirred for an additional 10 min, after which the green to orange color change was complete. The solvent was removed in vacuo, and the remaining orange solid was recrystallized from toluene–hexane (1:3), yielding a crop of orange crystals of [(dippe)Rh]$_2$[μ-HNCH(C$_6H_5$)$_2$](μ-H) (0.052 g, 70%) after washing with cold hexane. ^1H NMR (C_6D_6, ppm): H_{ortho}, 7.78 (d, 4 H, $^3J_{H_{meta}}$ = 7.6 Hz); H_{meta}, 7.20 (m, 4 H); H_{para}, 7.13 (m, 2 H); NCH(C$_6H_5$)$_2$, 6.28 (br t, 1 H, ^4J_P = 5.2 Hz); *H*–N, 4.57 (br s, 1 H); C$H(CH_3)_2$, 2.45, 1.90, 1.81, 1.67 (dsp, 8 H, ^3J_H = 7.5–7.9 Hz, ^2J_P = 2.0–4.0 Hz); CH(CH_3)$_2$, 1.30, 1.21, 1.19, 1.06, 1.05, 1.02, 0.92, 0.92 (overlapping dd, 48 H, ^2J_P = 12.0–14.0 Hz); PCH_2CH_2P, 1.1–1.2 (m, obscured by methyl groups); Rh–*H*–Rh, –8.20 (ttt, $^2J_{P_{trans}}$ = 60.0 Hz, $^2J_{P_{cis}}$ = 12.4 Hz, $^1J_{Rh}$ = 22.2 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, ppm): C_{ipso}, 147.2; other aromatic carbons, 129.2, 127.2, 126.2; NCH(C$_6H_5$)$_2$, 73.7; C$H(CH_3)_2$, 27.8–28.9, CH_2CH_2, CH(CH_3)$_2$, 17.1–25.2 (overlapping signals). $^{31}P\{^1H\}$ NMR (C_6D_6, ppm): $P_{trans(N)}$, 104.3 (dm, $^1J_{Rh} \approx$ 159 Hz); $P_{cis(N)}$, 84.5 (dm, $^1J_{Rh} \approx$ 191 Hz). Anal. Calcd for $C_{41}H_{77}P_4Rh_2N$: C, 53.89; H, 8.49; N, 1.53. Found: C, 54.07; H, 8.37; N, 1.60.

Synthesis of [(dippe)Rh]$_2$(μ-C$_9H_8$N)(μ-H) (6a). To a stirred solution of [(dippe)Rh]$_2$(μ-H)$_2$ (**1a**; 0.140 g, 0.19 mmol) in hexane (15 mL) was added dropwise a solution of isoquinoline (0.074 g, 0.57 mmol) in hexane (5 mL). The green solution of **1a** turned to a red-brown color within 10 min, and hexane was removed in vacuo, leaving a dark red-brown solid. Recrystallization from hexane yielded a crop of red crystals (0.112 g, 68%) after washing with cold hexane. ^1H NMR (C_6D_{12}, ppm):



C–H_4 or C–H_5, 6.83 (m, 1 H, ^3J_H = 6.4 Hz); C–H_4 or C–H_5 and C–H_3 or C–H_6, 6.71 (m, 2 H); C–H_2, 6.52 (d, 1 H, $^3J_{H_2}$ = 7.6); C–H_1, 4.98 (d, 1 H); NCH_2, 5.66 (br t, 2 H, ^4J_P = 2.2 Hz); C$H(CH_3)_2$, 2.07, 2.05, 1.97, 1.85 (overlapping dsp, 8 H, ^3J_H = 7.5–8.0 Hz, ^2J_P = 2.0–4.0 Hz); CH(CH_3)$_2$ and PCH_2CH_2P, 0.9–1.3 (overlapping signals); Rh–*H*–Rh, –9.31 (ttt, $^2J_{P_{trans}}$ = 59.2 Hz, $^2J_{P_{cis}}$ = 13.6 Hz, $^1J_{Rh}$ = 22.9 Hz). $^{13}C\{^1H\}$ NMR (C_6D_{12}, ppm): NCH, 148.7; *C*–*C* (bridgehead carbons), 136.1, 128.7; other aromatic carbons, 125.0, 123.2, 121.5, 119.8, 95.9; NCH_2, 62.2; C$H(CH_3)_2$, 27.4, 27.3, 26.6, 25.5 (m); CH_2CH_2, 20.3 (m); CH(CH_3)$_2$, 21.0, 20.7, 20.6, 19.5, 19.4, 17.9, 17.5, 17.4. $^{31}P\{^1H\}$ NMR (C_6D_{12}, ppm, major regioisomer): $P_{trans(N)}$, 110.5 (dm, $^1J_{Rh} \approx$ 162 Hz); $P_{cis(N)}$, 84.1 (dm, $^1J_{Rh} \approx$ 185 Hz). $^{31}P\{^1H\}$ NMR (C_6D_{12}, ppm, minor regioisomer): $P_{trans(N)}$, 115.7 (dm, $^1J_{Rh} \approx$ 175 Hz); $P_{cis(N)}$, 96.7 (dm, $^1J_{Rh} \approx$ 188 Hz). Anal. Calcd for $C_{37}H_{73}P_4Rh_2N$: C, 51.57; H, 8.54; N, 1.63. Found: C, 51.53; H, 8.50; N, 1.62.

Synthesis of [(dipope)Rh]$_2$[μ-(C$_6H_5$)N(C$H_2C_6H_5$)](μ-H) (2b). To a stirred solution of [(dipope)Rh]$_2$(μ-H)$_2$ (**1b**; 0.150 g, 0.17 mmol) in toluene (10 mL) was added solid *N*-benzylideneaniline (0.063 g, 0.35 mmol), in one portion. The reaction mixture was stirred for 30–45 min, during which a slow red to yellow-brown color change was observed. The toluene was removed under reduced pressure and the oily yellow-brown residue recrystallized from hexane (<1 mL). After a quick wash with 0.5 mL of cold hexane, 0.152 g (84%) of yellow crystals of [(dipope)Rh]$_2$[μ-(C$_6H_5$)N(C$H_2C_6H_5$)](μ-H) was obtained. ^1H NMR (C_7D_8, ppm):



C–H_1, 8.42 (dd, 2 H, $^3J_{H_2}$ = 7.4 Hz, $^4J_{H_3}$ = 1.9 Hz); C–H_4, 7.61 (d, 2 H, $^3J_{H_5}$ = 8.0 Hz); C–H_2 and C–H_3 or C–H_6, 7.01 (m, 3 H); C–H_5, 6.89 (m, 2 H); C–H_3 or C–H_6, 6.58 (m, 1 H); N$CH_2C_6H_5$, 5.01 (br t, 2 H, ^4J_P = 4.5 Hz); OC$H(CH_3)_2$, 5.07, 4.43, 4.40, 3.71 (dsp, 8 H, ^3J_H = 5.8–6.6 Hz, ^3J_P = 2.0–4.0 Hz); OCH(CH_3)$_2$, 1.39, 1.37, 1.30, 1.14, 1.05, 1.02, 1.00, 0.78 (d, 48 H); PCH_2CH_2P, 1.5–1.8 (m, 8 H); Rh–*H*–Rh, –8.32 (ttt, $^2J_{P_{trans}}$ = 84.1 Hz, $^2J_{P_{cis}}$ = 4.8 Hz, $^1J_{Rh}$ = 23.1 Hz). $^{13}C\{^1H\}$ NMR (C_7D_8, ppm): C_{ipso}(N), 165.6 (t, ^3J_P = 3.3 Hz); C_{ipso}(C), 159.9; other aromatic carbons, 142.6, 131.3, 131.1, 126.7, 126.0, 125.9, 121.3, 117.7 (two signals obscured by solvent peaks); N$CH_2C_6H_5$, 63.6; OC$H(CH_3)_2$, 67–70 (4 s); PCH_2CH_2P, 31.5–33 (m); OCH(CH_3)$_2$, 24.6–26 (8 s). $^{31}P\{^1H\}$ NMR (C_7D_8, ppm; $P_{cis(N)}$ = A, $P_{trans(N)}$ = B, Rh = X): δ_A = 73.9; δ_B = 105.5; $J_{AA'}$ = 44.8 Hz; J_{AB} = 39.9 Hz; $J_{AB'}$ = 4.4 Hz; J_{AX} = 191.3; $J_{AX'}$ = 265.1 Hz; $J_{BB'}$ = –3.8 Hz; J_{BX} = 223.3 Hz; $J_{BX'}$ = –2.4 Hz; $J_{XX'}$ = 3.2 Hz. Anal. Calcd for $C_{41}H_{77}O_8P_4Rh_2N$: C, 47.27; H, 7.45; N, 1.34. Found: C, 47.52; H, 7.70; N, 1.40.

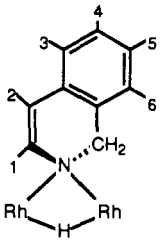
Synthesis of [(dipope)Rh]$_2$[μ-(CH$_3$)N(C$H_2C_6H_5$)](μ-H) (3b). To a stirred solution of [(dipope)Rh]$_2$(μ-H)$_2$ (**1b**; 0.065 g, 0.08 mmol) in toluene (10 mL) was added neat *N*-benzylidenemethylamine (0.027 g, 0.24 mmol), in one portion. Stirring was continued for 10 min, during which time a red to yellow-brown color change occurred. The toluene was then removed under reduced pressure, and the oily residue remaining was redissolved in hexane (0.5–1.0 mL). When the solution was cooled, a crop of oily yellow crystals was isolated in 61% yield (0.045 g). ^1H NMR (C_6D_6, ppm): H_{ortho}, 8.36 (d, 2 H, $^3J_{H_{meta}}$ = 7.4 Hz); H_{meta}, 7.25 (m, 2 H); H_{para}, 7.15 (m, 1 H); NC$H_2C_6H_5$, 5.04 (br t, 2 H, ^4J_P = 4.8 Hz); OC$H(CH_3)_2$, 5.12, 4.97, 4.84, 4.66 (dsp, 8 H, ^3J_H = 6.2–6.6 Hz, ^3J_P = 2.0–4.0 Hz); NCH_3, 3.99 (br t, 3 H, $^4J_P \approx$ 2–3 Hz); PCH_2CH_2P, 1.6–1.9 (m, 8 H); OCH(CH_3)$_2$, 1.51, 1.50, 1.48, 1.36, 1.34, 1.32, 1.32, 1.22 (d, 48 H); Rh–*H*–Rh, –7.33 (ttt, $^2J_{P_{trans}}$ = 75.8 Hz, $^2J_{P_{cis}}$ = 4.9 Hz, $^1J_{Rh}$ = 22.2 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, ppm): C_{ipso}, 143.4; other aromatic carbons, 129.9, 126.4, 125.9; NCH_2, 72.7; NCH_3, 56.5 (t, *J* = 2.8 Hz); OC$H(CH_3)_2$, 69.7, 69.1 (2), 68.7; PCH_2CH_2P, 32.0–32.8 (m); OCH(CH_3)$_2$, 24.9–25.8 (8 overlapping singlets). $^{31}P\{^1H\}$ NMR (C_6D_6, ppm): $P_{trans(N)}$, 202.2 (dm, $^1J_{Rh} \approx$ 204 Hz); $P_{cis(N)}$, 177.8 (dm, $^1J_{Rh} \approx$ 272 Hz). Anal. Calcd for $C_{36}H_{74}O_8P_4Rh_2N$: C, 44.18; H, 7.62; N, 1.43. Found: C, 43.83; H, 7.93; N, 1.48.

Synthesis of [(dipope)Rh]$_2$[μ-N(C$H_2C_6H_5$)$_2$](μ-H) (4b). To a stirred solution of [(dipope)Rh]$_2$(μ-H)$_2$ (**1b**; 0.038 g, 0.04 mmol) in toluene was added *N*-benzylidenebenzylamine (0.026 g, 0.13 mmol), in one portion. The reaction mixture was stirred for 2 h, during which a slow red to yellow-brown color change occurred.

The toluene was completely removed in vacuo and the oily residue dissolved in hexane (0.5 mL). When the solution was cooled, a crop of oily yellow crystals was obtained in 63% yield (0.029 g). ^{1}H NMR (C_6D_6, ppm): H_{ortho}, 8.27 (d, 4 H, $^3J_{H_{meta}}$ = 7.6 Hz); H_{meta}, 7.05 (m, 4 H); H_{para}, 7.00 (m, 2 H); $NCH_2C_6H_5$, 5.26 (br t, 4 H, ^4J_P = 4.8 Hz); $OCH(CH_3)_2$, 4.75, 4.28 (dsp, 8 H, ^3J_H = 6.2–6.6 Hz, ^2J_P = 2.0–3.0 Hz); PCH_2CH_2P, 1.65 (dm, 4 H, $J_P \approx 30$ Hz, $J_H \approx 8$ Hz); PCH_2CH_2P, 1.58 (dm, 4 H, $J_P \approx 30$ Hz); $OCH(CH_3)_2$, 1.38, 1.27, 1.09, 0.98 (d, 48 H); Rh-*H*-Rh, −7.44 (ttt, $^2J_{P_{trans}}$ = 78.4 Hz, $^2J_{P_{cis}}$ = 3.8 Hz, $^1J_{Rh}$ = 21.8 Hz). ^{13}C{^{1}H} NMR (C_6D_6, ppm): C_{ipso}, 144.2; other aromatic carbons, 129.5, 125.7, 125.3; NCH_2, 71.6; $OCH(CH_3)_2$, 68.6, 68.5; PCH_2CH_2P, 31.2–32.6 (m); $OCH(CH_3)_2$, 25.3, 25.2, 24.7, 24.6. ^{31}P{^{1}H} NMR (C_6D_6, ppm): $P_{trans(N)}$, 200.3 (dm, $^1J_{Rh} \approx 204$ Hz); $P_{cis(N)}$, 176.7 (dm, $^1J_{Rh} \approx 268$ Hz). Anal. Calcd for $C_{42}H_{79}O_8P_4Rh_2N$: C, 47.78; H, 7.54; N, 1.33. Found: C, 48.00; H, 7.53; N, 1.40.

Synthesis of [(dipope)Rh]$_2$[μ-HNCH(C_6H_5)$_2$](μ-H) (5b). To a stirred solution of [(dipope)Rh]$_2$(μ-H)$_2$ (**1b**; 0.045 g, 0.05 mmol) in toluene (10 mL) was added neat benzophenone imine (0.028 g, 0.15 mmol), in one portion. Stirring was continued for 5 min, during which time a red to yellow-orange color changed occurred. After rotary evaporation of the toluene, the oily residue was redissolved in hexane (0.5 mL). When the solution was cooled, a crop of yellow crystals was isolated, yielding 0.025 g (46%) after washing with cold hexane. ^{1}H NMR (C_6D_6, ppm): H_{ortho}, 7.95 (d, 4 H, $^3J_{H_{meta}}$ = 7.4 Hz); H_{meta}, 7.24 (m, 4 H); H_{para}, 7.11 (m, 2 H); $NCH(C_6H_5)_2$, 6.70 (br t, ^4J_P = 8.8 Hz); $OCH(CH_3)_2$, 5.06, 4.90, 4.60, 4.59 (dsp, 8 H, ^3J_H = 6.2–6.6 Hz, ^2J_P = 2.0–3.0 Hz); N*H*, 4.07 (br t, 1 H, $^3J_P \approx$ 4–5 Hz); PCH_2CH_2P, 1.88, 1.60 (dm, 8 H); $OCH(CH_3)_2$, 1.42, 1.37, 1.35, 1.26, 1.23, 1.21, 1.16 (d, 48 H); Rh-*H*-Rh, −7.53 (ttt, $^2J_{P_{trans}}$ = 76.2 Hz, $^2J_{P_{cis}}$ = 4.0 Hz, $^1J_{Rh}$ = 21.2 Hz). ^{31}C{^{1}H} NMR (C_6D_6, ppm): C_{ipso}, 148.1; other aromatic carbons, 128.9, 127.6, 126.2; $NCH(C_6H_5)_2$, 72.1; $CH(CH_3)_2$, 68.5–70.7; CH_2CH_2, 32.1 (m); $OCH(CH_3)_2$, 24.9–25.5 (overlapping singlets). ^{31}P{^{1}H} NMR (C_6D_6, ppm): $P_{trans(N)}$, 197.4 (dm, $^1J_{Rh} \approx 205$ Hz); $P_{cis(N)}$, 177.5 (dm, $^1J_{Rh} \approx 260$ Hz). Anal. Calcd for $C_{41}H_{77}O_8P_4Rh_2N$: C, 46.27; H, 7.45; N, 1.34. Found: C, 46.40; H, 7.53; N, 1.44.

Synthesis of [(dipope)Rh]$_2$(μ-C_9H_8N)(μ-H) (6b). To a stirred solution of [(dipope)Rh]$_2$(μ-H)$_2$ (**1b**; 0.081 g, 0.09 mmol) was added a solution of isoquinoline (0.036 g, 0.30 mmol) in hexane (5 mL), in one portion. After the mixture was stirred for a further 30 min, a red to yellow color change was complete; concentrating the reaction mixture to ~1 mL in volume, followed by cooling, led to a crop of yellow crystals (0.082 g, 88%). ^{1}H NMR (C_6D_{12}, ppm):



C-*H*$_4$ or C-*H*$_5$, 6.85 (m, 1 H); C-*H*$_4$ or C-*H*$_5$, 6.76 (m, 1 H); C-*H*$_2$, C-*H*$_3$, and C-*H*$_6$, 6.56 (m, 3 H); C-*H*$_1$, 5.0 (d, 1 H, $^3J_{H_1}$ = 7.4 Hz); NCH_2, 4.75 (br t, 2 H, $^4J_P \approx 4$ Hz); $OCH(CH_3)_2$, 4.95, 4.89, 4.81, 4.62 (overlapping dsp, 8 H, ^3J_H = 6.4–6.6 Hz, ^2J_P = 2.0–3.0 Hz); PCH_2CH_2P, 1.35–1.65 (m, 8 H); $OCH(CH_3)_2$, 1.23–1.32 (5 overlapping d, 30 H); $OCH(CH_3)_2$, (3 overlapping d, 18 H); Rh-*H*-Rh, −8.10 (ttt, $^2J_{P_{trans}}$ = 76.0 Hz, $^2J_{P_{cis}}$ = 5.4 Hz, $^1J_{Rh}$ = 23.3 Hz). ^{13}C{^{1}H} NMR (C_6D_{12}, ppm): *C*-H, 143.2, 120.6, 119.2, 118.3, 116.4, 93.7 (the two quaternary bridgehead carbons were not observed); NCH_2, 57.2; $OCH(CH_3)_2$, 64.8, 64.1, 63.9, 63.3 (s); PCH_2CH_2P, 24.8–28; $OCH(CH_3)_2$, 19.0–21.5 (overlapping resonances). ^{31}P{^{1}H} NMR (C_6D_{12}, ppm): $P_{trans(N)}$, 201.0 (dm, $^1J_{Rh} \approx 211$ Hz); $P_{cis(N)}$, 177.2 (dm, $^1J_{Rh} \approx 252$ Hz).

Synthesis of [(dippp)Rh]$_2$[μ-HNCH(C_6H_5)$_2$](μ-H) (5c). To a solution of [(dippp)Rh]$_2$(μ-H)$_2$ (**1c**; 0.062 g, 0.08 mmol) in toluene (10 mL) was added benzophenone imine (0.150 g, ~10 equiv), in one portion. The reaction mixture was stirred at 50 °C for 16 h, which brought about a green to red-orange color change. The toluene was removed in vacuo and the residue recrystallized from toluene–hexane (1:2). The crystals were washed twice with cold hexane (1 mL) to remove excess imine; yield 0.059 g (77%). ^{1}H NMR (C_6D_6, ppm): H_{ortho}, 7.83 (d, 4 H, $^3J_{H_{meta}}$ = 7.3 Hz); H_{meta}, 7.15 (m, 4 H); H_{para}, 7.06 (m, 2 H); $NCH(C_6H_5)_2$, 6.05 (br t, 1 H, $^4J_P \approx 6$ Hz); N*H*, 3.87 (br s); $CH(CH_3)_2$, 2.31, 1.6–1.8 (overlapping dsp, 8 H, ^3J_H = 7.6–8.0 Hz, ^2J_P = 3.0–4.0 Hz); $PCH_2CH_2CH_2P$, $CH(CH_3)_2$, 0.8–1.4 (overlapping multiplets, 60 H); Rh-*H*-Rh, −10.00 (ttt, $^2J_{P_{trans}}$ = 57.9 Hz, $^2J_{P_{cis}}$ = 11.6 Hz, $^1J_{Rh}$ = 22.0 Hz). ^{31}P{^{1}H} NMR (C_6D_6, ppm): $P_{trans(N)}$, 41.4 (dm, $^1J_{Rh} \approx 161$ Hz); $P_{cis(N)}$, 27.2 (dm, $^1J_{Rh} \approx 190$ Hz). Anal. Calcd for $C_{43}H_{81}P_4Rh_2N$: C, 54.84; H, 8.67; N, 1.49. Found: C, 54.59; H, 8.72; N, 1.35.

Equilibrium Measurements for the Equilibrium 1a + Isoquinoline ⇄ 6a. Sample Preparation. [(dippe)Rh]$_2$[μ-(C_9H_8N)](μ-H) (**6a**; 0.120 g, 0.139 mmol) was dissolved in cyclohexane-d_{12} (0.30 mL). The resulting deep red solution was distributed evenly among three sealable 5-mm NMR tubes. Similarly, a solution of isoquinoline (0.020 g, 0.16 mmol) in toluene-d_8 (0.30 mL) was added in even portions to each of the three NMR tubes. To the first tube was added a further 0.40 mL of cyclohexane-d_{12} (C_6D_{12}:C_7D_8 = 5:1); the second sample was augmented with 0.20 mL of cyclohexane-d_{12} and 0.20 mL of toluene-d_8 (C_6D_{12}:C_7D_8 = 1:1), while the third sample was made up to volume with 0.40 mL of toluene-d_8 (C_6D_{12}:C_7D_8 = 1:5). The tubes were fitted with needle valves, attached to a vacuum line, degassed, and sealed under about 0.9 atm of argon at −78 °C. Each sample contained 4.65×10^{-5} mol of [(dippe)Rh]$_2$[μ-(C_9H_8N)](μ-H) and 5.2×10^{-5} mol of isoquinoline in a total sample volume of 0.75 mL.

Equilibrium Measurements. Measurement of the equilibrium constant at various temperatures was carried out by integration of the appropriate peaks in the ^{31}P{^{1}H} NMR spectra. The samples were placed in a thermostated probe and allowed to equilibrate at each temperature for 10 min before pulsing began. The ^{31}P{^{1}H} spectra were collected at constant temperature by using a 73° pulse, a 4-s relaxation delay, and broad-band decoupling. The ratio of phosphorus-containing constituents was determined via integration of the appropriate peaks; no corrections for NOE effects were made. The possibility of intensity anomalies due to relaxation time differences was ruled out when a separate experiment yielded T_1 values of between 1.5 and 2.5 s for each phosphorus nucleus in the spectrum.

Equilibrium Measurements for the Equilibrium: 1b + Isoquinoline → 6b. Sample Preparation. [(dipope)Rh]$_2$[μ-(C_9H_8N)](μ-H) (**6b**; 0.036 g, 0.036 mmol) was dissolved in pure *n*-hexane (0.30 mL) and the solution loaded into a sealable 5-mm NMR tube. A solution of isoquinoline (0.006 g, 0.05 mmol) in toluene-d_8 (0.30 mL) was added to the tube and a 180° needle valve attached. The assemblage was connected to a vacuum line and the sample degassed via two freeze–pump–thaw cycles. The tube was sealed under ~0.9 atm of argon.

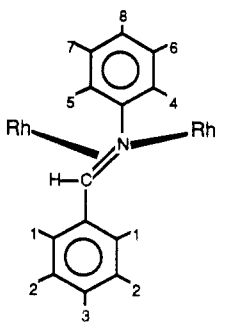
Equilibrium Measurements. These were carried out in a procedure identical with that described above for the dippe system.

Kinetic Measurements. [(dippe)Rh]$_2$(μ-H)$_2$ + *N*-Benzylideneaniline. Kinetic measurements of the reaction of [(dippe)Rh]$_2$(μ-H)$_2$ (**1a**) with *N*-benzylideneaniline were made by following the reaction by ^{31}P{^{1}H} NMR spectroscopy. Samples were prepared by loading a sealable 5-mm NMR tube with 0.25 mL of a stock solution of **1a** in toluene-d_8 (0.494 g in 5.00 mL of C_7D_8, 1.35×10^{-1} M) and a further 0.25 mL of toluene-d_8. The tube was then fitted with a 45° needle valve and attached to a vacuum line. The sample was degassed via two freeze–pump–thaw cycles and cooled to −78 °C. *N*-Benzylideneaniline (0.10 mL of a stock solution containing 1.257 g in 5.00 mL of C_7D_8, 1.39 M) was added through the needle valve via syringe under a strong flow of argon. The tube was then sealed without delay under about 0.85 atm of argon and placed in a thermostated probe set at 204.0, 209.0, 214.0, or 218.0 K. While the sample thermally equilibrated, a spectrum was collected; if observable amounts of the final amido-hydride product **2a** were present, the run was aborted. After an equilibration period of 10 min, spectra were collected at convenient intervals. Time points were taken as the midpoint of FID collection periods and calculated on the basis of the number of scans collected, the time at the start of data collection, and an acquisition time of 0.4096 s. The ratio of components in solution was determined from the ratios of appropriate integrals; anomalies due to differences in T_1 values were ruled out when

a separate experiment revealed similar T_1 values for all phosphorus-containing components in solution. When the first step in the reaction was complete, the probe was warmed rapidly to 244.0, 248.5, 254.0, or 258.0 K. After a 10-min equilibration period, the second step was followed in a manner analogous to that described above for the first step. Kinetic runs were repeated at least twice.

[(dippe)Rh]$_2$(μ-D)$_2$ + *N*-Benzylideneaniline. This experiment was carried out in a procedure identical with that described above. Samples were prepared by dissolving **1a**-d_2 (0.026 g, 0.035 mmol) in toluene-d_8 (0.4 mL) and loading into a sealable 5-mm NMR tube equipped with a 180° needle valve. After the tube was attached to a vacuum line and degassed, a solution of *N*-benzylideneaniline (0.025 g, 0.14 mmol) in toluene-d_8 (0.2 mL) was added via syringe under a strong flow of argon. The tube was sealed under 0.9 atm of argon, and the reaction's two steps were followed at 209 and 254 K, respectively.

Synthesis of {[(dippe)Rh]$_2$[μ-(C$_6$H$_5$)N=CH(C$_6$H$_5$)](*μ*-H)}BF$_4$ (7a). The dihydride [(dippe)Rh]$_2$(μ-H)$_2$ (**1a**; 0.200 g, 0.27 mmol) and the iminium salt generated from *N*-benzylideneaniline and HBF$_4$ (0.073 g, 0.27 mmol) were loaded into a small reactor bomb equipped with a magnetic stirbar. The bomb was attached to a vacuum line, evacuated, and cooled to −78 °C. THF (∼10 mL) was vacuum-transferred into the vessel. An immediate orange-brown color obtained, different from the characteristic deep green of **1a**; while it was warmed to room temperature, the solution became deep red-purple. Although gas evolution was not visually observed, a slight buildup of pressure in the reaction vessel was apparent. THF was removed in vacuo once the reaction mixture was warmed to room temperature, and the residue was recrystallized from the minimum amount of THF–toluene. ^{1}H NMR ((CD$_3$)$_2$CO, ppm):



C–*H*$_1$, 8.69 (d, 2 H, $^3J_{H_2}$ = 8.0 Hz); C–*H*$_4$ or C–*H*$_5$, 7.94 (br s, 1 H); C*H*=N, 7.78 (br t, 1 H, J_P = 1.5 Hz); C–*H*$_3$, 7.40 (t, 1 H, $^3J_{H_2}$ = 7.4 Hz); C–*H*$_4$ or C–*H*$_5$, 7.34 (br s, 1 H); C–*H*$_6$, C–*H*$_7$, and C–*H*$_8$, 7.23 (br m, 3 H); C–*H*$_2$, 7.14 (m, 2 H); C*H*(CH$_3$)$_2$ and PC*H*$_2$C*H*$_2$P, 1.8–2.5 (overlapping broad m, 16 H); CH(C*H*$_3$)$_2$, 1.41, 1.29, 1.07 (3), 0.75 (3) (overlapping dd, 48 H, ^3J_H = 6.4–7.2 Hz, ^2J_P = 11.6–16.4 Hz); Rh–*H*–Rh, −9.01 (ttt, $^2J_{P_{trans}}$ = 50.1 Hz, $^2J_{P_{cis}}$ = 13.6 Hz, $^1J_{Rh}$ = 23.6 Hz). ^{31}P{^{1}H} NMR ((CD$_3$)$_2$CO, ppm, +30 °C): P$_{trans(N)}$, 107.7 (br dm, $^1J_{Rh}$ ≈ 163 Hz); P$_{cis(N)}$, 91.3 (br dm, $^1J_{Rh}$ ≈ 157 Hz). ^{31}P{^{1}H} NMR ((CD$_3$)$_2$CO, ppm, −45 °C): P$_{trans(N)}$, 110.0 (dd, $^1J_{Rh}$ = 166.3 Hz, ^2J_P = 31.2 Hz); P$_{trans(N)}$, 106.4 (dd, $^1J_{Rh}$ = 159.8 Hz, ^2J_P = 29.6 Hz); P$_{cis(N)}$, 92.8 (dm, $^1J_{Rh}$ = 182.5 Hz); P$_{cis(N)}$, 89.7 (dm, $^1J_{Rh}$ = 140.9 Hz). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO, ppm): *C*H=N, 93.6 (s, ^1J_H = 168.4 Hz). Anal. Calcd for C$_{41}$H$_{76}$P$_4$Rh$_2$NBF$_4$: C, 49.26; H, 7.66; N, 1.40. Found: C, 49.46; H, 7.85; N, 1.30.

Synthesis of {[(dippe)Rh]$_2$[μ-(CH$_3$)N=CH(C$_6$H$_5$)](*μ*-H)}BF$_4$ (8a). The dippe dihydride **1a** (0.153 g, 0.21 mmol) and the iminium salt generated from *N*-benzylidenemethylamine and HBF$_4$ (0.043 g, 0.21 mmol) were loaded into a small reactor bomb equipped with a magnetic stirbar. The vessel was evacuated and cooled to −78 °C. Pure THF (10 mL) was vacuum-transferred into the vessel. Although reaction was immediate, as evidenced by a green to red-brown color change, the mixture was stirred at −78 °C until all the solid was dissolved prior to warming to room temperature (30 min). After the solution was warmed, the THF was removed in vacuo and the remaining oily dark red solid was recrystallized from THF–toluene, yielding 0.150 g (77%) of red-purple crystals. ^{1}H NMR ((CD$_3$)$_2$CO, ppm): *H*$_{ortho}$, 8.41 (d, 2 H, $^3J_{H_{meta}}$ = 7.4 Hz); C*H*=N, 7.70 (br t, 1 H, J_P ≈ 2.0 Hz); *H*$_{para}$, 7.34 (t, 1 H, $^3J_{H_{meta}}$ = 7.2 Hz); *H*$_{meta}$, 7.09 (m, 2 H); NC*H*$_3$, 3.65 (s, 3 H); dippe ligand resonances are broad, C*H*(CH$_3$)$_2$, 2.4, 1.9 (8 H); PC*H*$_2$C*H*$_2$P, 2.2, 1.8 (8 H); CH(C*H*$_3$)$_2$, 0.9–1.4 (48 H); Rh–*H*–Rh, −9.45 (m). ^{31}P{^{1}H} NMR (THF, ppm, +30 °C): P$_{trans(N)}$, 107.1 (br dm, $^1J_{Rh}$ ≈ 163 Hz, ^2J_P ≈ 29 Hz); P$_{cis(N)}$, 92.4 (br dm, $^1J_{Rh}$ ≈ 169 Hz). ^{31}[^{1}H} NMR (THF, ppm, −50 °C): P$_{trans(N)}$, 109.4 (dd, $^1J_{Rh}$ = 159.6 Hz, ^2J_P = 29.1 Hz); P$_{trans(N)}$, 105.5 (br dd, $^1J_{Rh}$ = 166.2 Hz, ^2J_P = 26.6 Hz); P$_{cis(N)}$, 95.3 (dm, $^1J_{Rh}$ = 183.0 Hz); P$_{cis(N)}$, 90.1 (dm, $^1J_{Rh}$ = 143.9 Hz). ^{13}C{^{1}H} NMR ((CD$_3$)$_2$CO, ppm): *C*$_{ipso}$, 139.6; other aromatic carbons, 129.5, 128.9, 128.1; *C*H=N, 102.8; NC*H*$_3$, 57.9; ligand resonances, 18–30.

Reaction of {[(dippe)Rh]$_2$[μ-(C$_6$H$_5$)N=CH(C$_6$H$_5$)](*μ*-H)}BF$_4$ (7a) and LiAlH(OBu^t)$_3$. The μ-imine hydride complex **7a** (0.052 g, 0.052 mmol) was dissolved in THF (10 mL). To this stirred solution was added solid LiAlH(OBu^t)$_3$ (0.015 g, 0.057 mmol) in small portions over a period of 5 min. The solution slowly turned from deep red to green-orange. THF was removed under reduced pressure, and the residue was extracted with hexane (3 × 10 mL portions). The extracts were filtered through a pad of Celite and concentrated to ∼3 mL. Cooling led to the precipitation of an orange powder consisting of >95% pure [(dippe)Rh]$_2$[μ-(C$_6$H$_5$)-N(CH$_2$C$_6$H$_5$)](*μ*-H) (**2a**; 0.37 g, 78%).

This reaction was also carried out in an NMR tube at low temperature. Complex **7a** (0.046 g, 0.046 mmol) was dissolved in THF and loaded into a sealable 5-mm NMR tube equipped with a 180° needle valve. The assemblage was connected to a vacuum line and degassed; the sample was then cooled to −78 °C, and a THF solution containing 2 equiv of LiAlH(OBu^t)$_3$ was syringed into the tube under a strong flow of argon. The tube was sealed immediately and the reaction monitored by ^{31}P{^{1}H} NMR spectroscopy.

Hydrogenation Procedures for the Attempted Hydrogenation of *N*-Benzylideneaniline. Use of [(dippe)Rh]$_2$(μ-H)$_2$ (1a) as Catalyst Precursor. The dihydride [(dippe)Rh]$_2$(μ-H)$_2$ (**1a**; 0.020 g, 0.027 mmol) and *N*-benzylideneaniline (0.098 g, 20 equiv) were dissolved in THF (5.0 mL), and the solution was loaded into a small reactor bomb. The solution was degassed on a vacuum line, placed under 4 atm of dihydrogen, and stirred at room temperature for 14 h. The solvent and excess dihydrogen were removed in vacuo, and the residue was analyzed via ^{1}H NMR spectroscopy. Only traces of *N*-phenylbenzylamine were detected, corresponding to <3% hydrogenation.

Use of [(dippe)Rh]$_2$(H)$_4$ as Catalyst Precursor. The dihydride [(dippe)Rh]$_2$(μ-H)$_2$ (**1a**; 0.020 g, 0.027 mmol) was dissolved in THF (4.0 mL) and the solution loaded into a small reactor bomb. The solution was degassed and placed under 1 atm of dihydrogen, converting the dihydride into the tetrahydride adduct instantly.[15] Under a strong flow of dihydrogen, a solution of *N*-benzylideneaniline (0.098 g, 20 equiv) in THF (1.0 mL) was syringed into the reaction vessel. The solution was stirred for 12 h and worked up in a procedure analogous to that described above. ^{1}H NMR spectroscopy of the residue indicated ∼35% conversion of the imine to the amine, corresponding to approximately seven turnovers. Again, a similar procedure with [(dippe)Rh]$_2$(μ-H)$_2$ (**1b**) as catalyst precursor was performed; no hydrogenation was detected.

Reaction of [(dippe)Rh]$_2$[μ-(C$_6$H$_5$)N(CH$_2$C$_6$H$_5$)](*μ*-H) (2a) with Dihydrogen. The amido–hydride **2a** (0.032 g, 0.035 mmol) was dissolved in toluene-d_8 (∼0.5 mL) and the solution loaded into a sealable 5-mm NMR tube fitted with an 180° needle valve. The assemblage was attached to a vacuum line with access to pure dihydrogen and the sample degassed with two freeze–pump–thaw cycles. The sample tube was cooled to −196 °C and dihydrogen admitted to ∼0.9 atm; the tube was sealed, thawed, and monitored periodically via ^{1}H NMR spectroscopy. Signals due to *N*-phenylbenzylamine slowly appeared and were identified through comparison with a spectrum of an authentic sample (Aldrich). After ∼3 days, the peaks due to **2a** had disappeared, leaving only those of the free amine and the tetrahydride adduct of **1a**.

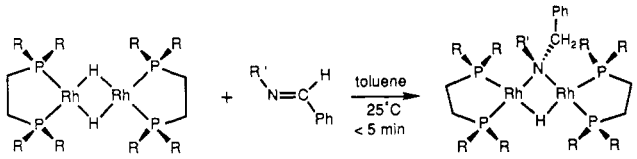
Spectroscopic Monitoring of Reactions between 1a and Imines. The following method was used to monitor the reactions of the dihydrides with various imines at low temperatures. A solution of **1a** or **1b** was loaded into a sealable 5-mm NMR tube equipped with a 180° needle valve. The assemblage was attached to a vacuum line, cooled to −78 °C, and degassed. A solution of the imine was then added via syringe through the needle valve

port under a strong flow of argon. The tube was sealed under a partial vacuum (~0.9 atm of argon) and, without agitating, taken to the NMR spectrometer. The sample was shaken vigorously and transferred into the precooled probe as quickly as possible (<5 s). After suitable equilibration periods, depending on the nature of the experiment, spectra were collected.

Attempted "Trapping" of 8a. A toluene solution of *N*-benzylideneaniline (2 equiv, 1 mL) was added via syringe to a solution of **1a** (~0.050 g) in toluene (5 mL) cooled to −78 °C. The reaction mixture was stirred for 2 h at temperatures never exceeding −60 °C to ensure complete formation of the brown-green intermediate. At this point, the trapping agent, CCl_4 (1 mL) or ethylene (1 atm), was introduced into the reaction vessel. After they were stirred for a further 30 min at low temperature in the presence of these reagents, the solutions were slowly warmed to room temperature. The reaction mixture containing CCl_4 turned black-brown upon warming, with significant deposits of metal observed. The solution to which ethylene had been admitted was worked up by removal of the solvent and excess ethylene in vacuo followed by recrystallization of the residue from toluene–hexane. $^{31}P\{^1H\}$ NMR spectroscopy revealed the presence of only **2a** and the μ-vinyl hydride complex $[(dippe)Rh]_2(\mu\text{-}\eta^2\text{-}\sigma\text{-}CH{=}CH_2)(\mu\text{-}H)$.

Results and Discussion

Synthesis and Properties of Binuclear Rhodium Amido Hydrides. The dihydrides $[(dippe)Rh]_2(\mu\text{-}H)$ (**1a**) and $[(dipope)Rh]_2(\mu\text{-}H)_2$ (**1b**) react rapidly with simple aldimines (R′N=CH(Ph); R′ = C_6H_5, CH_3, $CH_2C_6H_5$) to afford the binuclear products $[(R_2PCH_2CH_2PR_2)Rh]_2[\mu\text{-}(R')NCH_2(C_6H_5)](\mu\text{-}H)$ (R = Pr^i, **2a–4a**; R = OPr^i, **2b–4b**) in good yield (eq 1). This reaction may be extended to

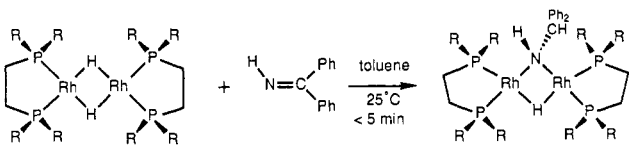


R = Pr^i, **1a**
R = OPr^i, **1b**

R′	R	
C_6H_5	Pr^i	**2a**
C_6H_5	OPr^i	**2b**
CH_3	Pr^i	**3a**
CH_3	OPr^i	**3b**
CH_2Ph	Pr^i	**4a**
CH_2Ph	OPr^i	**4b**

(1)

the ketimine benzophenone imine (eq 2). In each case,



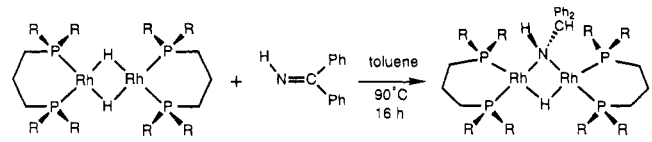
R = Pr^i, **1a**
R = OP^i, **1b**

R = Pr^i, **5a**
R = OPr^i, **5b**

(2)

the products are produced in quantitative yield as determined by $^{31}P\{^1H\}$ NMR spectroscopy. Isolated yields, though not maximized in some cases, vary from about 50 to 90% depending on the solubilities of the products. The amido hydrides incorporating the dipope ligand were found to be highly soluble even in nonpolar hydrocarbon solvents such as hexane, and thus isolated yields were generally lower for these complexes. Qualitatively, reactions involving **1b** and imines were slower than those between **1a** and imines; in addition, reaction rates appeared to be influenced by the steric bulk of the substituent on nitrogen in the imine, with bulkier groups impeding the reactions significantly. For example, at roughly the same concentrations, the reaction of **1a** with *N*-benzylidenemethylamine was more rapid than that with *N*-benzylidenebenzylamine by a factor of about 10. Steric bulk on the imine carbon atom had less of an effect; the ketimine benzophenone imine reacted rapidly with both **1a** and **1b** to form the amido hydride products **5a** and **5b**. In all reactions only 1 equiv of imine adds to the dihydrides; thus, in most cases, a 2–4-fold excess of imine was employed to facilitate the reactions.

The dihydride dimer $[(dippp)Rh]_2(\mu\text{-}H)_2$ (**1c**), which incorporates the three-carbon-backbone ligand 1,3-bis(diisopropylphosphino)propane, $Pr^i_2P(CH_2)_3PPr^i_2$, is virtually inert toward reaction with these imines, with the exception of benzophenone imine. Even at elevated temperatures (~90 °C) and with use of large excesses of imine, **1c** failed to react with *N*-benzylideneaniline or *N*-benzylidenemethylamine. When such conditions were employed with benzophenone imine, a slow reaction ensued and the dippp amido hydride product **5c** was isolated in 77% yield after 16 h of reaction time (eq 3).



R = Pr^i, **1c** R = Pr^i, **5c**

(3)

The amido hydride products are bright orange (dippe "**a**" series) or yellow (dipope "**b**" series) crystalline solids. The complexes are all air-sensitive both in solution and in the solid state. Complex **2a** is stable toward water and methanol, however. In addition to moisture stability, **2a** exhibits high thermal stability in solution in spite of the bulkiness of the μ-amido ligand, which normally destabilizes the bridging mode of ligation for such ligands,[17] and the presence of β-hydrogens in the amido ligand, which would facilitate decomposition pathways for this molecule. Nevertheless, toluene solutions of **2a** may be heated at 120 °C for at least 4 days without spectroscopically detectable decomposition, although the solution darkens gradually throughout heating. Heating at 150 °C for 10 h results in less than 10% decomposition.

Though quite stable toward decomposition under thermal duress, hydrogen–deuterium exchange from the solvent into the μ-amido ligand benzyl and ortho phenyl positions was observed at temperatures between 100 and 120 °C. A similar process, along with exchange into the triisopropyl phosphite methyl positions, was observed for exchange between D_2 and $[\{(Pr^iO)_3P\}_2Rh]_2[\mu\text{-}NMe(p\text{-}Cl\text{-}C_1H_4)](\mu\text{-}H)$;[18] presumably a similar mechanism is operative.

The amido hydrides were fully characterized via multinuclear NMR spectroscopy and elemental analyses. The spectroscopic data for these complexes are comparable to those observed for the related, structurally characterized amido hydride $[\{(Pr^iO)_3P\}_2Rh]_2[\mu\text{-}NMe(p\text{-}Cl\text{-}C_6H_4)](\mu\text{-}H)$, formed via hydrogenation of the bridging isocyanide ligand in $[\{(Pr^iO)_3P\}Rh]_2[\mu\text{-}CN(p\text{-}Cl\text{-}C_6H_4)](\mu\text{-}H)_2$.[18] The similarities to this compound imply that all of our amido hydride products possess the same square-planar geometry at each rhodium center. Although the ^1H NMR spectra do not distinguish the proposed square-planar geometry from a structure with tetrahedral rhodium centers, certain

(17) Lappert, M. F.; Power, P. P.; Sanger, A. P.; Srivastava, R. C. *Metal and Metalloid Amides*; Wiley: New York, 1979; p 468.
(18) McKenna, S. T.; Andersen, R. A.; Muetterties, E. L. *Organometallics* **1986**, *5*, 2233.
(19) Reference deleted in proof.

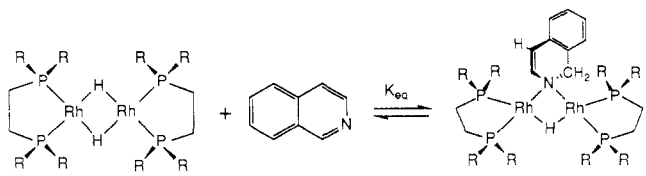
features of the $^{31}P\{^1H\}$ spectra support the square-planar structure (vide infra).

Diagnostic features of the ^1H NMR spectra of these compounds are the signals due to the benzylic protons of the amido ligand. In all of the amido hydride complexes, this signal is a broad triplet, which collapses to a singlet upon broad-band decoupling of phosphorus. The magnitude of this four-bond coupling is 2–4 Hz, except in compounds **5a** and **5b**, where more substantial couplings of 5.2 and 8.8 Hz, respectively, are observed. A similar coupling was observed in the signals due to the *N*-methyl groups in complexes **3a** and **3b**. In the $^{13}C\{^1H\}$ NMR spectra, the benzylic carbons (and the N-alkyl carbons of **3a** and **3b**) resonate in the region 65–75 ppm, appearing as slightly broad singlets ($w_{1/2} \approx 8$ Hz) with no apparent fine structure originating from coupling to either phosphorus or rhodium.

In all the amido hydride complexes but **2a** and **2b**, the aromatic region of the ^1H NMR spectrum is uncomplicated. In **2a**, however, the *N*-phenyl ring experiences restricted rotation about the C_{ipso}–N bond and thus there are five separate environments for the protons on this ring. This phenomenon was also observed for the *N*-phenyl group in the complex $[\{Pr^iO)_3P\}_2Rh]_2[\mu\text{-NMe}(p\text{-Cl-}C_6H_4)](\mu\text{-H})$.[18] In this complex free rotation was observed at room temperature, but upon cooling of the sample the rotation was frozen out and separate signals for each of the five proton environments were observed. In the spectrum of **2a**, the five separate resonances are observed at room temperature, indicating that the barrier to rotation is higher than that calculated for $[\{Pr^iO)_3P\}_2Rh]_2[\mu\text{-NMe}(p\text{-Cl-}C_6H_4)](\mu\text{-H})$.[18] Although heating a sample of **2a** did result in the coalescence of the signals due to the ortho (8.58 and ~7.2 ppm) and the meta (~7.2 and 7.00 ppm) protons of the ring, the high-temperature limit was not reached. This corresponds to a $\Delta G^{\ddagger}$[20] value of approximately 16.7 (5) kcal/mol (100 °C) compared to that of 12.0 kcal/mol (−15 °C) reported for $[\{Pr^iO)_3P\}_2Rh]_2[\mu\text{-NMe}(p\text{-Cl-}C_6H_4)](\mu\text{-H})$.[18] The *N*-phenyl ring in **2b** also experiences hindered rotation, but with a lower barrier of $\Delta G^{\ddagger}$ = 9.8 (4) kcal/mol (−60 °C). The differences in the barriers to rotation of the ring likely reflect differences in the steric bulk of the ancillary ligands in each complex. Since the *N*-phenyl ring lies in the idealized mirror plane of these molecules, more steric crowding of the molecular core results in a higher barrier to free rotation about the C_{ipso}–N bond. Consistent with the above discussion is the observation of 10 singlets in the region of the $^{13}C\{^1H\}$ NMR spectrum of **2a** for aromatic carbon resonances, rather that the eight expected should free rotation about the C_{ipso}–N bond be facile at room temperature.

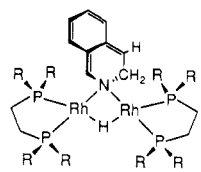
The $^{31}P\{^1H\}$ NMR spectra of these complexes are also diagnostic and have been discussed in some detail by other workers.[18] Although complex, the spectra arising from the AA′BB′XX′ spin system are interpretable. As has been observed in other systems,[18,21,22] a large four-bond $J_{AA'}$ coupling comparable in magnitude to the two-bond J_{AB} coupling is found. It is likely due to the fact that the large bridging amido ligand forces P_A and $P_{A'}$ into closer conjunction with the Rh–Rh vector such that they are nearly opposed across this vector.[18] For example, in $[\{Pr^iO)_3P\}_2Rh]_2[\mu\text{-NMe}(p\text{-Cl-}C_6H_4)](\mu\text{-H})$, the P_A–Rh–Rh′ angle was 145.1°.[18] This structural feature greatly enhances coupling between these two nuclei. The same rationale explains why the three-bond $J_{AX'}$ coupling of P_A to the distal rhodium is larger than the analogous coupling of P_B to $Rh_{X'}$. Other four-bond couplings (i.e., $J_{AB'}$ and $J_{BB'}$) are small.

Reactions of the Dihydrides 1a and 1b with Isoquinoline. In addition to the reactions described above, the dihydrides **1a** and **1b** also react with the cyclic imine isoquinoline (eq 4). Analysis of the crude reaction mixture



(4)

by NMR spectroscopy showed the product to be >95% pure; a small amount (<5%) of another material was observed by $^{31}P\{^1H\}$ NMR spectroscopy, but its identity was not pursued. Assignment of the structures of **6a** and **6b** to the indicated regioisomer was made on the basis of ^1H NMR evidence; in particular, the observation of two doublets for the vicinal vinyl protons in the heterocyclic ring obviates the other possible regioisomer **6′**, which would have a distinct pattern of resonances in the proton NMR spectrum.



R = Pr^i or OPr^i, **6′**

The $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were consistent with both structures and had features similar to the spectra of the amido hydrides discussed above. Like complexes **2a,b**–**5a,b** amido hydrides **6a** and **6b** are quite air-sensitive but, in contrast, exhibit thermal instability in solution. In fact, as shown in eq 4, the system is at a measurable equilibrium at room temperature, the position of which is dependent on the nature of the solvent at constant temperature. The temperature dependence of the equilibrium constant in each system was studied by dissolution of pure **6a** or **6b** in an appropriate solvent mixture along with a known amount of isoquinoline (~1 equiv). The concentrations of **1a**/**1b** and **6a**/**6b** were determined via integration of the appropriate peaks in the $^{31}P\{^1H\}$ NMR spectra at various temperatures, while the concentration of isoquinoline was calculated by difference.[23] In the synthetic experiments, it was clear that the above reactions did not proceed in aromatic solvents. Indeed, only when the reactions were carried out in aliphatic solvents, such

(20) (a) $\Delta G^{\ddagger}$ values for exchange processes observed via NMR spectroscopy were calculated by using the value for the rate constant k_c ($k_c = \pi(\Delta\nu_c)/2^{1/2}$, where $\Delta\nu_c$ = the chemical shift separation in hertz at coalescence, is estimated roughly from the separation just prior to coalescence temperature, T_c) at the coalescence temperature[20b] in the Eyring equation: $\Delta G^{\ddagger} = -RT_c \ln(\pi(\Delta\nu_c)h/kT_c)$ (R = gas constant; h = Planck's constant; k = Boltzmann's constant; transmission coefficient 1). Estimates of T_c were made visually and therefore have an error of approximately ±3 K. (b) Thomas, W. A. *Annu. Rev. NMR Spectrosc.* **1968**, *1*, 43.

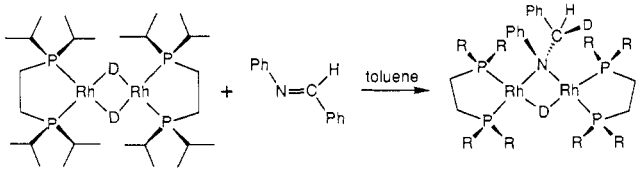
(21) Fryzuk, M. D.; Piers, W. E. *Polyhedron* **1988**, *7*, 1001.

(22) McKenna, S. T.; Muetterties, E. L. *Inorg. Chem.* **1987**, *26*, 1296.

(23) (a) For the equilibrium **1a** + **7** ⇌ **6a** in a 1:1 mixture of cyclohexane-d_{12}–toluene-d_8, $\Delta H°$ = −10.3 (±0.5) kcal/mol and $\Delta S°$ = −26.0 (±2.0) eu. For the equilibrium **1b** + **7** ⇌ **6b** in a 1:1 mixture of *n*-hexane–toluene-d_8, $\Delta H°$ = −9.2 (±0.5) kcal/mol and $\Delta S°$ = −22.9 (±2.0) eu. (b) van't Hoff plots and a table containing values of $\Delta G°$ and K at various temperatures are included as supplementary material.

as hexane, were we able to isolate **6a** and **6b**. These observations were borne out in the measurement of the equilibrium constants for eq 4. As the proportion of aromatic solvent (toluene-d_8) in the mixture increases, the equilibrium constant as defined above decreases; for example, in the equilibrium of **1a** plus isoquinoline with **6a**, the values obtained for K_{eq} in 5:1, 1:1, and 1:5 mixtures of cyclohexane-d_{12}–toluene-d_8 were 179.5, 83.1, and 64.1 (293 K), respectively.[23b] The instability of these benzocycloamides in aromatic solvents may reflect the steric crowding at the bimetallic core, which is relieved upon deinsertion due to the isoquinoline being better solvated in the presence of an aromatic solvent.

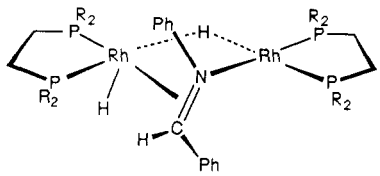
Mechanistic Studies. Reaction of 1a with *N*-Benzylideneaniline at Low Temperature. Mechanistically, the reaction of **1a** with *N*-benzylideneaniline is apparently straightforward. By simple product analysis, the amido hydrides appear to have resulted from a migratory insertion of an imine carbon–nitrogen bond into a bridging hydride ligand. Indeed, when the dideuterides **1a**-d_2 and **1b**-d_2 were allowed to react with any of the imines, the label appeared as one deuterium in the benzylic position of the μ-amido ligand, while one deuterium was retained in the bridging position (eq 5). However, when



1a-d_2 R = Pr^i, **2a**-d_2 (5)

the reactions were carried out at low temperature and monitored via NMR spectroscopy, an intermediate was observed, the nature of which provides evidence for a more complex process that involves both metal centers.

As previously reported,[14] the $^{31}P\{^1H\}$ NMR (162.21 MHz) spectra of the proceeding reaction between **1a** and *N*-benzylideneaniline reveal the presence of an intermediate formed at low temperatures. At −70 °C, near the beginning of the reaction, the spectrum consists of the doublet characteristic of the dihydride **1a** and four faint resonances not attributable to the product **2a**. After approximately 1 h, these signals have grown in almost completely, still with no trace of the peaks due to **2a**. At temperatures at or below −50 °C, this intermediate, A, is stable in solution



R = Pr^i, A

but is unstable at higher temperatures even in the solid state. Thus, when the sample is warmed to −20 °C, the intermediate begins to decompose to **2a**, and after about 45 min, the amido hydride has formed almost completely, with no trace of other phosphorus-containing products. A spectroscopically similar reaction course was observed in the analogous reaction involving **1b** and *N*-benzylideneaniline.

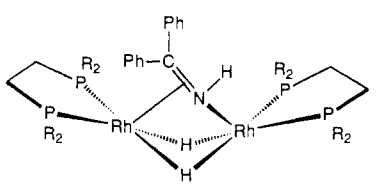
The $^1H\{^{31}P\}$ NMR spectrum of A also indicates a highly unsymmetrical structure in that the complex has 16 separate environments for the methyl groups of the dippe ligands as evidenced by the 16 doublets in the upfield region of the spectrum. The aromatic region is also complex. A broad singlet at 4.90 ppm, integrated to one proton, can be assigned to the imine proton; notably, it is shifted significantly upfield from the resonance of the free imine at 8.16 ppm. The most important structural information the ^1H NMR spectrum has to offer is found in the hydride region, in which signals for one terminal hydride ligand (−11.45 ppm, d, $^1J_{Rh}$ = 18.4 Hz) and one bridging hydride (−13.79 ppm, br t, $^1J_{Rh}$ = 19.6–20.4 Hz) are observed, indicating that the first step in this reaction involves the rearrangement of the $Rh_2(\mu\text{-}H)_2$ core of the dihydride by the imine. Again, similar features are observed in the ^1H NMR spectrum of the intermediate formed from the dipope dimer **1b** and *N*-benzylideneaniline. In the $^{13}C\{^1H\}$ NMR spectrum of labeled A, generated from **1a** and $(C_6H_5)N{=}^{13}CH(C_6H_5)$, a broad signal ($w_{1/2} \approx 20$ Hz) at 62.4 ppm was observed and assigned to the imine carbon; no large P–C or Rh–C couplings were apparent. In addition, a large $^1J_{^{13}C-H}$ coupling constant of 151.3 Hz (doublet) suggested that the imine carbon remains sp^2 hybridized in the intermediate. These data are consistent with our structural proposal for this intermediate A, which contains a bridging imine ligand in the previously unknwon μ-η^2-σ bonding mode. The intermediate's structure is analogous to that of a family of μ-η^2-σ-vinyl hydride complexes previously characterized in our laboratories.[12] The large upfield shifts for the resonances due to both the imine proton (vide supra) and the imine carbon (62.4 vs 160.0 ppm for the free imine) can be accounted for by π-coordination of the imine C=N bond to rhodium. Upfield shifts of similar magnitude are observed in the resonances for the β-protons and the β-carbon nuclei in the vinyl hydride complex $[(dippe)Rh]_2(\mu\text{-}\eta^2\text{-}\sigma\text{-}CH{=}CH_2)(\mu\text{-}H)$.[12,21]

The μ-η^2-σ-imine dihydride intermediate A is a potentially interesting compound because of the unprecedented bonding mode of the μ-imine ligand. Unfortunately, attempts at isolating this species at low temperature were only partially successful. While it could be precipitated from a concentrated solution in hexane at −78 °C, even as a solid it decomposed to the amido hydride product upon warming. This extreme sensitivity precluded further characterization in our hands. Attempts were also made to trap the intermediate by reacting it with halogenated solvents or ethylene after it had formed at −78 °C, the purpose being to remove or modify the terminal hydride ligand. These reactions, however, resulted only in decomposition and no reaction for CCl_nH_{4-n} and ethylene, respectively. However, further evidence as to the validity of our structural proposal has been obtained through the synthesis of cationic analogues of the intermediate that are stable and isolable via conventional techniques (vide infra).

Reaction of 1a with Benzophenone Imine at Low Temperature. A plausible reaction trajectory for the formation of A involves σ-coordination of the imine via the nitrogen lone pair to one coordinatively unsaturated rhodium center followed by π-donation from the C=N bond to the adjacent metal and cleavage of a Rh–H bond. While monitoring the reaction between **1a** and benzophenone imine ($Ph_2C{=}NH$) at low temperature, we obtained spectroscopic evidence for such a pathway. In a more complex reaction course, two observable species are formed, one of which is an intermediate analogous to that formed in the reaction of **1a** and *N*-benzylideneaniline en route to the amido hydride product. A series of $^{31}P\{^1H\}$ NMR spectra recorded at various times and temperatures during the reaction is shown in Figure 1. In contrast with

the **1a**–*N*-benzylideneaniline reaction, it was not possible to isolate each step in this reaction and thus peaks for all components are present during the course of the reaction. Nonetheless, the sequence in which each intermediate appears is clear. Almost immediately after a 2–3-fold excess of benzophenone imine is added at −78 °C, the dihydride disappears and four new signals arise (Figure 1A). As the reaction proceeds, this species B decomposes to a second, unsymmetrical (four phosphorus environments) intermediate, which, as seen in the corresponding ^{1}H NMR spectra, is analogous in structure to the intermediate A (vide supra). The appearance of signals due to the amido hydride product **5a** occurs virtually simultaneously (Figure 1B,C). Upon completion of the reaction this complex mixture of components has all gone to product; as seen in Figure 1D, the reaction is quantitative. Parenthetically, it should be noted that at low temperatures the signals due to **5a** are broad and coalescing presumably due to the freezing out of rotation about the N–C bond in the μ-amido ligand; this spectral behavior was confirmed by a separate low-temperature experiment (the rotational barrier is $\Delta G^{\ddagger}$ = 9.1 (3) kcal/mol).

Monitoring this reaction in a similar fashion via ^{1}H NMR spectroscopy further clarifies the process. In particular, the hydride region of the spectrum is informative; early in the reaction, signals for two bridging hydrides are observed at −3.75 and −5.04 ppm, with large trans H–P couplings apparent, consistent with intermediate B. As the reaction proceeds, these signals disappear, while new resonances grow in at −11.51 and −15.69 ppm; these latter resonances are due to the bridging and terminal hydride ligands, respectively, of the μ-η^2-σ-iminyl dihydride species A. The hydride signals of **1a** (−4.63 ppm) and **5a** (−7.88 ppm) do not interfere with the resonances for the intermediates. In this sequence, the first intermediate is formed prior to the μ-η^2-σ-iminyl dihydride species A and contains two bridging hydrides and four inequivalent phosphorus nuclei. In addition, a signal at 11.0 ppm is assigned to the nitrogen-bound imine proton. While these data do not allow for unambiguous assignment of structure, a reasonable proposal involves coordination of the imine to one rhodium center via the nitrogen lone pair with concomitant π-bonding to the proximal rhodium atom (structure B).



R = Pr^i, B

It represents the species present just prior to Rh–H bond cleavage to form the second observable intermediate containing the terminal hydride ligand. A structure with such π-bonding is similar in structure to many observed and proposed $[P_2Rh]_2(\mu\text{-}X)(\mu\text{-}H)_2$[9,18,22,24] complexes found in the chemistry of the dihydrides **1a**, **1b**, and $[\{(Pr^iO)_3P\}_2Rh]_2(\mu\text{-}H)_2$.[25]

Kinetic Studies and Proposed Mechanism. Scheme I shows a proposed mechanistic sequence for this reaction, incorporating all of the results discussed above. In the reaction between **1a** and *N*-benzylideneaniline the first intermediate (i.e. analogous to B) was not detected, reducing the process to two kinetically isolable steps. Both

Scheme I

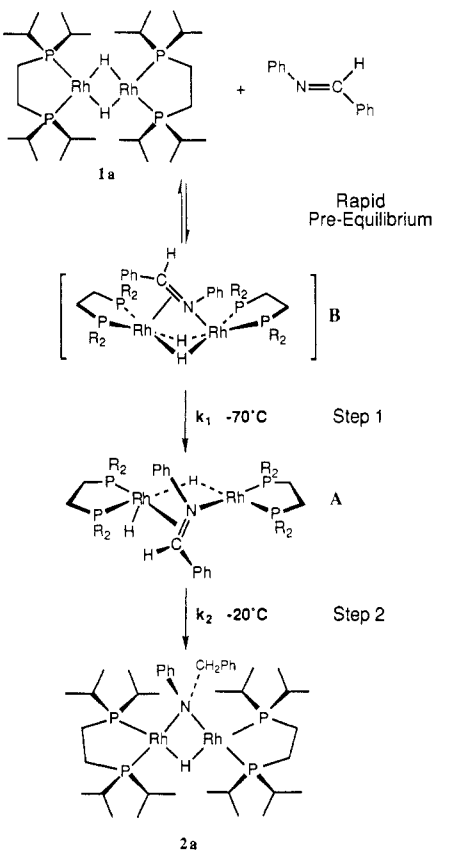


Table I. Rate Constants and Eyring Plot Data for 1a + *N*-Benzylideneaniline → A

temp[a]	rate const,[b] k_1	ln (k_1/T)	$1/T$[c]
204	3.13×10^{-3}	−11.08	4.90×10^{-3}
209	4.39×10^{-3}	−10.77	4.78×10^{-3}
214	1.14×10^{-2}	−9.84	4.67×10^{-3}
218	1.26×10^{-2}	−9.76	4.59×10^{-3}

[a] In K. [b] In L mol^{-1} s^{-1}. [c] In K^{-1}.

Table II. Rate Constants and Eyring Plot Data for A → 2a

temp[a]	rate const,[b] k_2	ln (k_2/T)	$1/T$[c]
244	1.65×10^{-4}	−14.21	4.10×10^{-3}
248.5	3.24×10^{-4}	−13.55	4.02×10^{-3}
254	6.92×10^{-4}	−12.81	3.94×10^{-3}
258	1.20×10^{-3}	−12.28	3.88×10^{-3}

[a] In K. [b] In s^{-1}. [c] In K^{-1}.

steps in this reaction were conveniently followed kinetically by $^{31}P\{^1H\}$ NMR spectroscopy, and the results of these studies are congruent with the mechanistic pathway proposed in Scheme I. The first step was found to be cleanly second order under the conditions employed, first order in both **1a** and *N*-benzylideneaniline. A graph of second-order data at various temperatures is shown in Figure 2, while an Eyring plot is given in Figure 3. Activation parameters for this step are $\Delta H^{\ddagger}$ = 10.1 (±0.5) kcal/mol and $\Delta S^{\ddagger}$ = −19.8 (±2.0) eu. Note that these results do not preclude a rapid preequilibrium step forming the first intermediate in unobservable quantities. The second step, found to be first order in the rate of disappearance of the intermediate, was followed after warming the sample to temperatures around −20 °C. Figure 4 gives a plot of first-order data at these temperatures, and Figure 5 shows the corresponding Eyring plot. Activation parameters for the second step are $\Delta H^{\ddagger}$ = 17.3 (±0.5) kcal/mol and $\Delta S^{\ddagger}$ = −3.6 (±0.5) eu. Rate constants at various temperatures

(24) Burch, R. R.; Muetterties, E. L.; Shultz, A. J.; Gebert, E. G.; Williams, J. M. *J. Am. Chem. Soc.* **1981**, *103*, 5517.
(25) Sivak, A. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1979**, *101*, 4878.

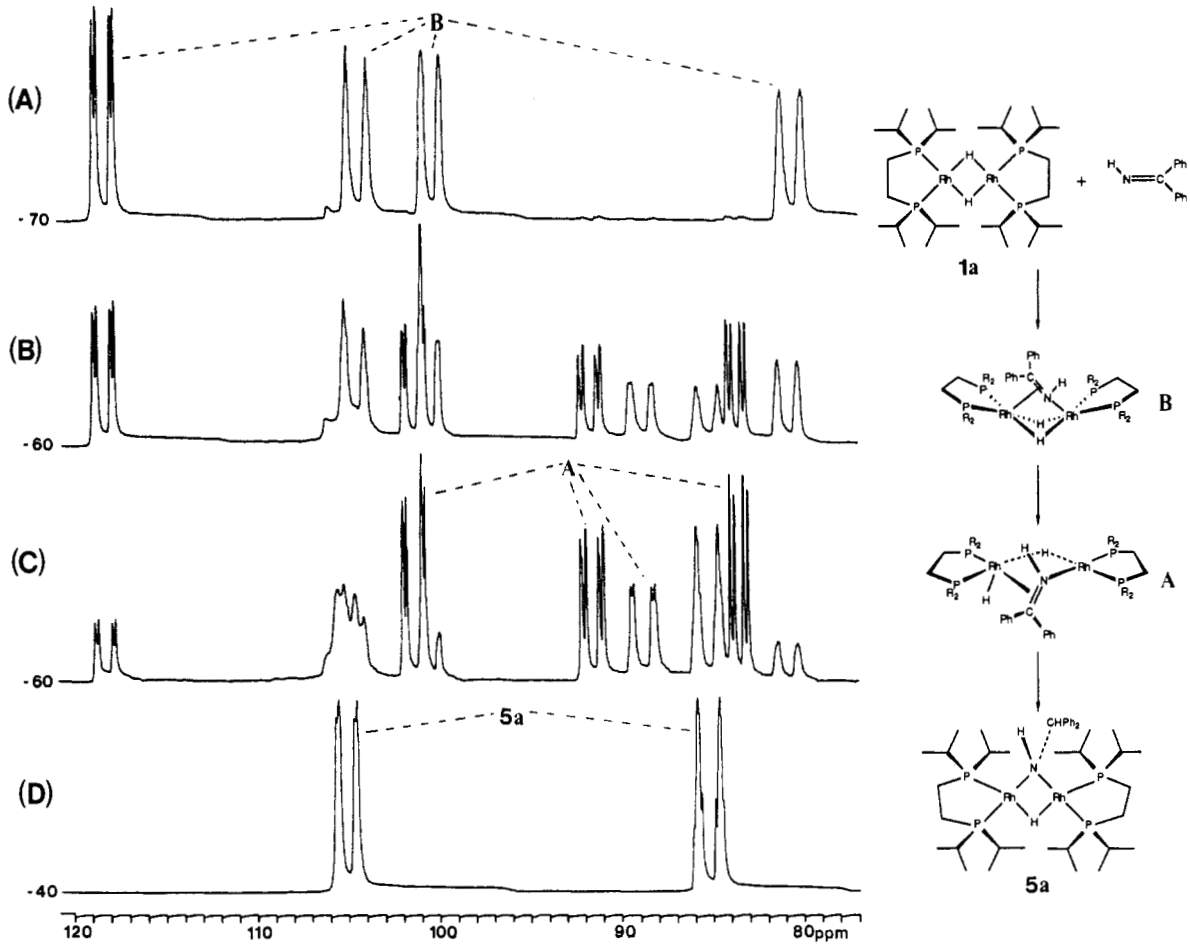


Figure 1. $^{31}P\{^1H\}$ NMR spectra (162.2 MHz, C_7D_8) as a function of temperature and time for the reaction of **1a** with benzophenone imine. Spectrum A is at −70 °C and shows the immediate formation of intermediate B. In spectra B and C, the intermediate A is shown growing in at −60 °C. Spectrum D is due to the final product **5a** and was taken at −40 °C. All of these spectra were recorded over a period of about 45 min while warming the sample to the indicated temperatures.

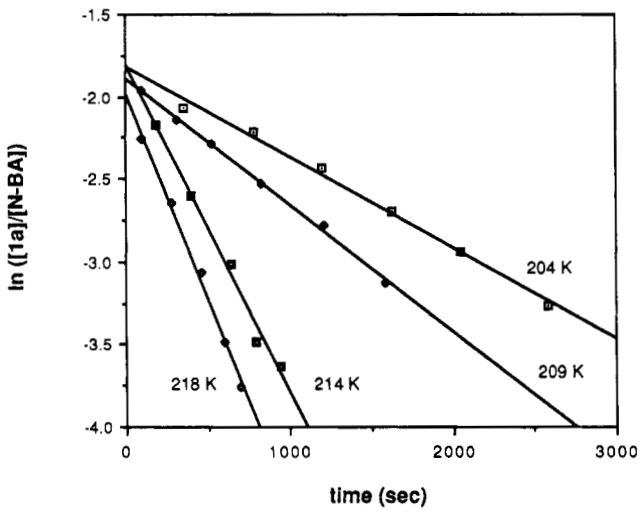


Figure 2. Second-order rate data obtained at the indicated temperatures for the first step in the reaction between **1a** and *N*-benzylideneaniline.

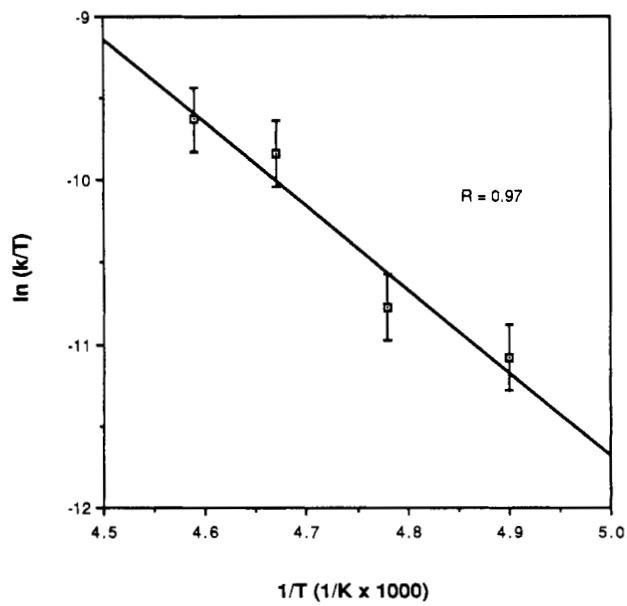


Figure 3. Eyring plot for the first step in the reaction between **1a** and *N*-benzylideneaniline. Data are taken from Figure 2.

for steps 1 (k_1) and 2 (k_2) are given in Table I and II, respectively.

Kinetic analysis of the reaction involving the dideuteride **1a**-d_2 with *N*-benzylideneaniline revealed a small kinetic isotope effect (k_H/k_D) of 1.41 (5) for step 1 and a more substantial value of 2.24 (3) for step 2 of the reaction. The latter k_H/k_D value is within the range of 1.4–2.7 predicted for the primary isotope effect on the insertion of ethylene into the Nb–H bond of $Cp^*_2Nb(H)(\eta^2\text{-}C_2H_4)$.[26] While the two reactions are quite different, if delivery of the hydride to the imine carbon in A takes place via the four-center transition state commonly invoked for olefin insertion reactions, the kinetic isotope effects should be comparable.

(26) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670.

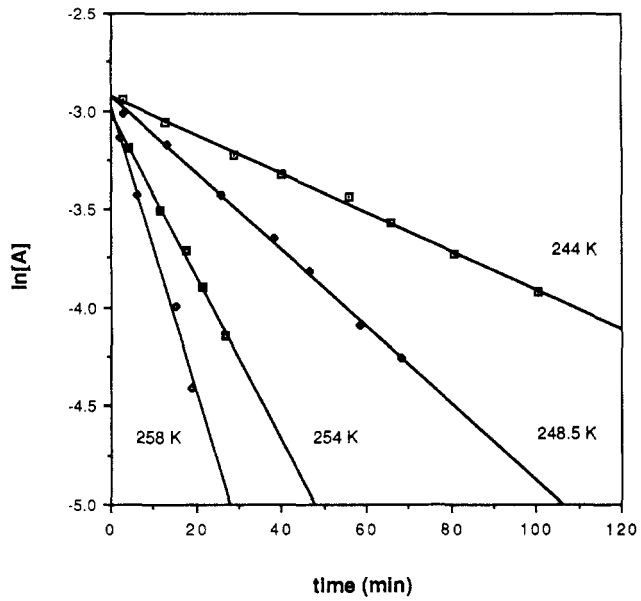


Figure 4. First-order rate data obtained at the indicated temperatures for the second step in the reaction between **1a** and *N*-benzylideneaniline. The disappearance of intermediate A was followed as a function of time by $^{31}P\{^1H\}$ NMR spectroscopy.

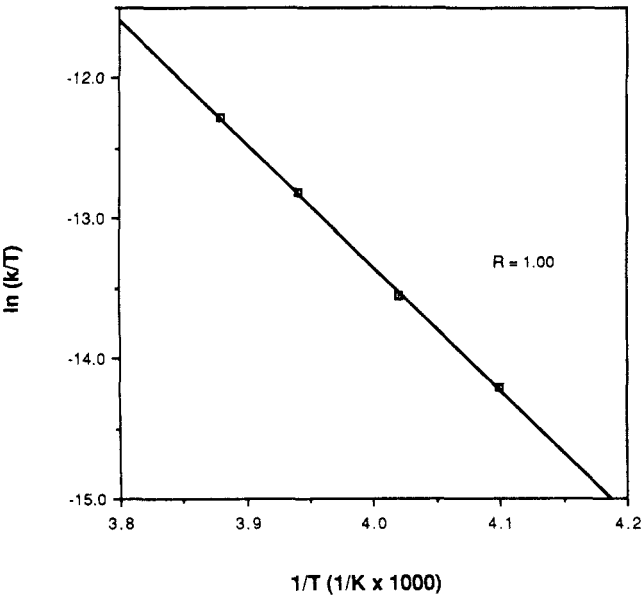
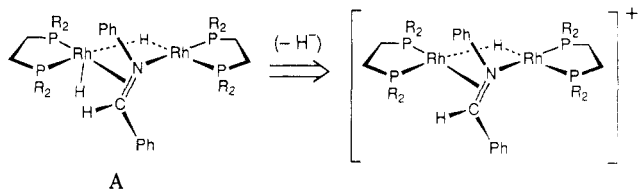


Figure 5. Eyring plot for the second step in the reaction between **1a** and *N*-benzylideneaniline. Data are taken from Figure 4.

The small k_H/k_D value of 1.41 observed for the first step is similar in magnitude to primary isotope effects observed in reactions that involve the migration of a μ-H ligand into a terminal position as the rate-determining step of the reaction.[27] The fact that in certain reactions (i.e. that of **1a** and benzophenone imine) we observe the intermediate occurring just prior to hydride migration is indicative of this step's rate-determining role in the overall reaction.

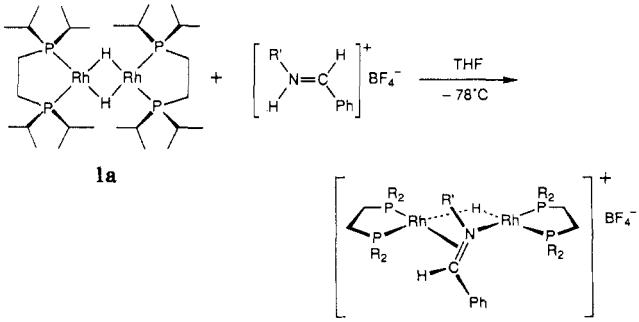
In summary, a likely pathway for the production of the intermediate A involves coordination by the lone pair on the imine nitrogen to one coordinately unsaturated rhodium center in **1a**, followed by π-donation of the C=N double bond to the adjacent rhodium atom with rate-determining rupture of the $Rh_2(\mu\text{-}H)_2$ four-center, electron core of the dihydride molecule to form A. This pathway to A is suggested by the observance of the first intermediate in the **1a**–benzophenone imine reaction, with structure B. The second step of the reaction, taking place subsequent to generation of A, may be formally analyzed as an insertion of the C=N double bond into the newly formed terminal Rh–H bond, producing **2a**. Although we cannot distinguish unambiguously between migratory insertion of the terminal hydride versus the bridging hydride, the isotope effect is more easily explained by the former. The very low value of −3.6 eu for $\Delta S^{\ddagger}$ also suggests a reactant-like transition state for this step; i.e., very little rearrangement of A occurs prior to reaching the transition state. We also note that this insertion is very facile, proceeding rapidly even at −20 °C, suggesting that one π-coordination of C=N is induced, migratory insertion is favored.

Reactions of the Dihydride 1a with Iminium Salts. Since the attempts to isolate A were unsuccessful (vide supra), an atlernative strategy was employed in seeking supporting evidence for its structure. The instability of this intermediate is seemingly due to the fact that it is biased toward migratory insertion because of the presence of both a terminal hydride ligand and the μ-π-imine. It was therefore reasoned that a cationic compound without the terminal hydride would perhaps be stable and isolable (eq 6). The observation that the dihydride **1a** reacts with



(6)

a variety of Brønsted acids to evolve dihydrogen and yield complexes with the conjugate base of the acid in a bridging position[28] suggested that **1a** might react with the iminium salt of *N*-benzylideneaniline to give the desired complex. Protonation of this aldimine with 1 equiv of tetrafluoroboric acid (HBF_4) led to isolation of the iminium salt $[PhCH{=}NHPh]^+BF_4^-$, which upon reaction with the dippe dimer **1a** gave a dark purple solution from which purple, analytically pure crystals of the cationic μ-imine hydride complex **7a** were isolated (eq 7). An analogous reaction obtains when the tetrafluoroborate iminium salt of *N*-benzylidenemethylamine is reacted with **1a**, producing **8a**.



R = Pr^i, R′ = Ph, **7a**
R = Pr^i, R′ = CH_3, **8a**

(7)

The NMR spectral data obtained for these complexes are consistent with the structural formulation in eq 7.

(27) Several examples are described in: Rosenberg, E. *Polyhedron* **1989**, *8*, 383.

(28) (a) Fryzuk, M. D.; Jang, M.-L.; Einstein, F. W. B.; Jones, T. *Can. J. Chem.* **1986**, *64*, 174. (b) Piers, W. E. Ph.D. Thesis, University of British Columbia, 1988.

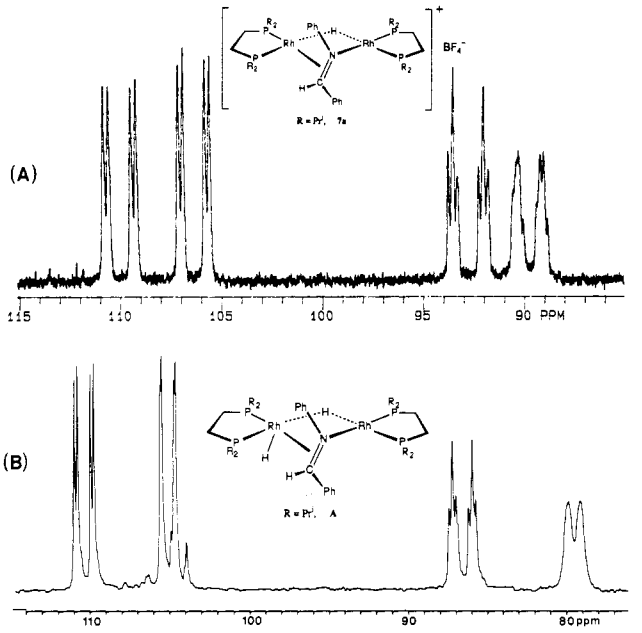
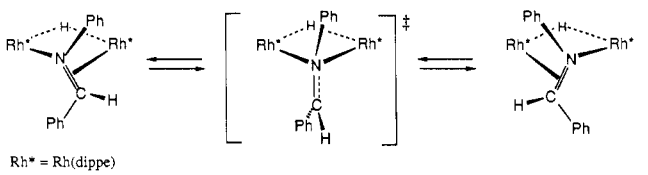


Figure 6. Comparison of the $^{31}P\{^1H\}$ NMR spectra for the cationic μ-η^2-σ-imine complex **7a** and the intermediate A observed in the reaction of **1a** with *N*-benzylideneaniline at low temperature: (A) 121.4-MHz $^{31}P\{^1H\}$ NMR spectrum in C_7D_8 at −30 °C; (B) 162.4-MHz $^{31}P\{^1H\}$ NMR spectrum in C_7D_8 at −70 °C.

Scheme II



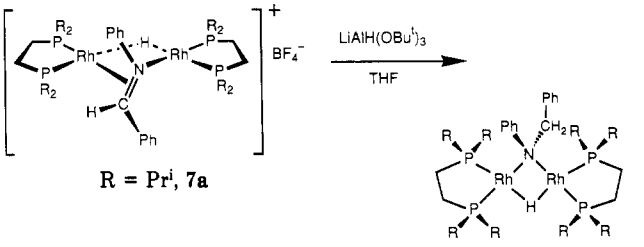
Rh* = Rh(dippe)

Particularly diagnostic are the temperature-dependent $^{31}P\{^1H\}$ spectra. At +30 °C, two broad doublets of multiplets are observed, similar in shape to the patterns observed for the amido hydride complexes. As the sample is cooled, each doublet coalesces (15 °C, $\Delta G^{\ddagger}$ = 12.8 (5) kcal/mol) and reemerges as two other signals, until at −30 °C the low-temperature limit spectrum is reached. Notably, this low-temperature spectrum is remarkably similar to the spectrum of the intermediate A, as seen in Figure 6. This is good evidence that the two complexes are related structurally and further supports the structural assignment for the μ-η^2-σ-imine dihydride intermediates in the dihydride–imine reactions. That the cationic μ-imine hydride complexes exhibit such fluxional behavior is not surprising given that the isoelectronic alkenyl hydride complexes previously characterized in our laboratory undergo a well-documented[29] "windshield wiper" fluxionality. Indeed, the $^{31}P\{^1H\}$ spectral behavior[21] of [(dippe)Rh]$_2$(μ-η^2-σ-CH=CH$_2$)(μ-H) is similar to that of the μ-imine hydrides **7a** and **8a**. By analogy then, the fluxional process proposed for **7a** (and **8a**, R′ = CH_3) is a similar "windshield wiper" process that equilibrates the four phosphorus environments observed at low temperatures into the two seen at ambient temperature (Scheme II).

Of interest in the ^{13}C and ^1H NMR spectra of these cationic complexes are the resonances due to the imine carbon and proton atoms in the bridging imine ligand. The carbon signals occur at 93.3 and 102.8 ppm for **7a** and **8a**, respectively. These chemical shifts are somewhat higher than the range of 68–80 ppm observed for the chemical shifts of the β-carbons in the μ-alkenyl hydride complexes; however, the magnitude of the upfield shifts of these nuclei when compared to those of the free ligands in both types of compounds is comparable. The resonances in the ^1H NMR spectrum for the imine proton (7.78 and 7.70 ppm for **7a** and **8a**, respectively) are close to the range of 6–7 ppm observed for the syn-β proton in the alkenyl hydrides.[12]

The chemistry of these cationic μ-imine hydride complexes is potentially interesting but is largely unexplored to date. A general observation is that they are thermally unstable in solution, particularly in strong donor solvents. Though moderately stable in THF or acetone for short periods of time (<24 h), the complex **7a** decomposes rapidly in acetonitrile. The fate of the organic ligand in this decomposition is unclear, but the organometallic species produced is a highly symmetrical compound which exhibits a sharp doublet in the ^{31}P NMR spectrum and a ^1H NMR spectrum very similar to that of the free dippe ligand. A likely possibility for this product is the mononuclear cationic species [(dippe)Rh(CH$_3$CN)$_2$]$^+$, although further characterization is necessary. This compound is also generated in the decomposition of **8a**.

The reactivity of these cationic complexes toward nucleophiles is an area of obvious interest. Of particular relevance to this work is the reaction of **7a** with a mild hydride reagent in an attempt to generate the proposed intermediate A by transfer of the hydride to one of the rhodium centers. When treated with a slight excess of LiAlH(OBu^t)$_3$ in THF at room temperature, the amido hydride **2a** was isolated in 78% yield (eq 8). When this



R = Pr^i, **7a**

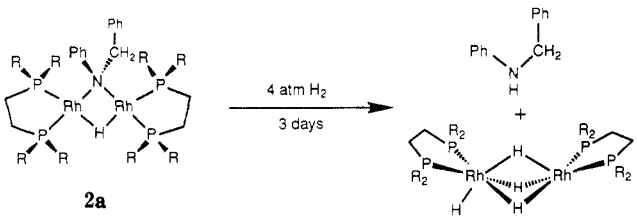
2a (major product)

(8)

reaction was monitored spectroscopically (^{31}P NMR spectroscopy) at low temperature, however, a variety of species were observed. The major product was still the amido hydride **2a**, but other unidentified products were also formed. Intermediates were also detected, including significant amounts of the intermediate A. The presence of other species is not surprising in light of the number of potential sites of reactivity in the molecule. In addition to the two metal centers, direct attack of the μ-imine ligand, at either carbon or nitrogen, is also feasible. In addition, the bulky nature of the hydride reagent employed probably hampered attack as the metal centers. Nonetheless, detection of A provides further, albeit circumstantial, evidence as to the validity of the mechanistic proposal for the reaction of **1a** and **1b** with imines. Further characterization and study of these cationic dimers are currently underway.

(29) (a) Shapley, J. R.; Richter, S. I.; Tachikawa, M.; Keister, J. R. *J. Organomet. Chem.* **1975**, *94*, C43–C46. (b) Gerlach, R. F.; Duffy, D. N.; Curtis, M. D. *Organometallics* **1983**, *2*, 1172. (c) Iggo, J. A.; Mays, M. J.; Raithby, P. R.; Hendrick, K. *J. Chem. Soc., Dalton Trans.* **1983**, 205. (d) King, R. B.; Treichel, P. M.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3600. (e) Al-Obaidi, Y. N.; Baker, P. K.; Green, M.; White, N. D.; Taylor, G. E. *J. Chem. Soc., Dalton Trans.* **1981**, 2321. (f) Caddy, P.; Green, M.; Smart, L. E.; White, N. *J. Chem. Soc., Chem. Commun.* **1978**, 839. (g) Keister, J. R.; Shapley, J. R. *J. Organomet. Chem.* **1975**, *85*, C29. (h) Deeming, A. J.; Hasso, S.; Underhill, M. *J. Organomet. Chem.* **1974**, *80*, C53. (i) Guy, J. J.; Reichert, B. E.; Sheldrick, G. M. *Acta Crystallogr.* **1976**, *B32*, 3319. (j) Clauss, A. D.; Tachikawa, M.; Shapley, J. R.; Pierpont, C. G. *Inorg. Chem.* **1981**, *20*, 1528.

Attempted Homogeneous Hydrogenation of Imines. The initial impetus for these studies was to investigate the activity of the dihydrides **1a,b** toward the hydrogenation of imines. As the above discussions indicate, the anticipated effect of multiple metal bonding sites on the insertion of a C=N bond into a M-H was realized. Unfortunately, this same feature had a deleterious effect on another of the steps necessary in the catalytic cycle, that being the hydrogenolysis of the bridging amido group. While the reaction of **2a** with dihydrogen does proceed to produce free amine and the tetrahydride (eq 9), the rate



2a

(9)

of the reaction is prohibitively slow, requiring about 3 days to complete in the NMR tube (with efficient stirring the reaction is faster but remains too slow for practical purposes). In the presence of excess imine substrate and 4 atm of dihydrogen neither of the dihydrides **1a,b**, exhibited significant activity in the production of *N*-phenylbenzylamine. Raising the dihydrogen pressure to 100 atm had little effect. It thus appears that a pathway involving binuclear intermediates is rendered kinetically inert upon formation of the μ-amido hydride "intermediate", at least in these systems.

When the tetrahydride adduct of **1a**[15] was formed prior to addition of the imine substrate and used as the catalyst precursor, some hydrogenation was observed. Approximately seven turnovers occurred over a 16-h period. Eventually, however, the amine production halted due to a buildup of **2a**. In this reaction, the possibility of catalysis by small amounts of a mononuclear species must be considered;[15] when the mononuclear complex [(dippe)Rh(η^3-C_3H_5)], the precursor to **1a**, was used as catalyst precursor, hydrogenation was more efficient. The results, however, were not impressive enough to pursue.

Conclusions

The synthesis and characterization of a family of binuclear amido hydrides have been accomplished via the reaction of the binuclear rhodium dihydrides **1a** and **1b** and imines. Mechanistic studies on these reactions revealed that both metal centers are involved in the reduction of the C=N double bond. Through the observation of intermediates we were able to propose a reaction trajectory incorporating initial σ-coordination of the imine to one metal with subsequent (or concomitant) π-coordination of the imine to the adjacent rhodium site. Following rate-limiting cleavage of a bridging Rh–H–Rh bond, facile insertion of the carbon–nitrogen double bond into a terminal Rh–H bond was observed. These observations suggest that two or more metal centers acting in concert may provide a means for the facile homogeneous catalytic reduction of imines. Unfortunately, in these systems final release of free amine via hydrogenolysis does not occur rapidly, rendering these compounds unlikely catalyst precursors for this transformation. This undoubtedly is due to the presence of the electron-rich diphosphines used in this study, which probably inhibits reductive elimination of the amine. However, often poor catalysts are the most amenable to mechanistic study, and we are satisfied that the present study provides fundamental insights into the reduction of the C=N bonds of imines by two metal centers.

Acknowledgment. We thank the NSERC of Canada for financial support in the form of an operating grant to M.D.F. and a postgraduate fellowship to W.E.P. This work was also partially funded by a University grant from Imperial Oil of Canada. Johnson-Matthey is also acknowledged for a generous loan of $RhCl_3 \cdot xH_2O$.

Supplementary Material Available: Figures and a table giving equilibrium data for **6a** and **6b** in aromatic/nonaromatic solvent mixtures (3 pages). Ordering information is given on any current masthead page.