

Thermodynamic Studies of the Addition of N₂, C₂H₄, and Alkynes to [Rh(P^{*i*}Pr₃)₂Cl]₂

Kun Wang and Alan S. Goldman*

Department of Chemistry, Rutgers—The State University of New Jersey, New Brunswick, New Jersey 08903

Chunbang Li and Steven P. Nolan*

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

Received March 27, 1995[®]

Summary: $[Rh(P^iPr_3)_2Cl]_2$ reacts with various small molecules L' to give complexes $Rh(P^iPr_3)_2ClL'$. The enthalpy of this reaction has been determined calorimetrically and/or by equilibrium methods for $L' = N_2$, C_2H_4 , diphenylacetylene, and 2-butyne. These values, in combination with the previously determined lower limit for the $[Rh(P^iPr_3)_2Cl]_2$ bridge strength, afford lower limits of the Rh-L' BDE's; the lower limits are probably only slightly less than the actual BDE's.

Rhodium phosphine complexes such as Wilkinson's Catalyst have played a major role in the development of "organometallic" catalysis and continue to reveal novel catalytic chemistry. If any species may be designated as the actual catalyst in much of this chemistry, it is bis(phosphine)rhodium chloride; this fragment, for example, is the key player in Rh(PPh₃)₃Cl-catalyzed olefin hydrogenation¹ and in alkane dehydrogenation catalyzed by Rh(PMe₃)₂(CO)Cl.^{2,3} The need to develop a body of reliable organometallic thermodynamic data is particularly important for reactions of such catalytically relevant species. We have recently determined lower limits for the enthalpy of addition of CO, H_2 , and ^tBuNC to RhL₂Cl (L = $P^i Pr_3$).⁴ In this contribution we report the corresponding values for addition of C₂H₄, diphenylacetylene, 2-butyne, and N₂.

Results and Discussion

 $[RhL_2Cl]_2$ (1) reacts in solution with N₂, C₂H₄, and diphenylacetylene, respectively, to give the corresponding adducts RhL_2ClL' (L' = N₂ (2), C₂H₄ (3), and diphenylacetylene (4)),⁵ which can be isolated as crystalline solids.⁶ X-ray structures of $2^{6,7}$ and 3^6 reveal square planar geometries with trans-phosphines; the C_2H_4 ligand of 3 is perpendicular to the molecular plane.⁶ Spectroscopic data indicate that the structure of 4 is analogous to that of 3. Because C_2H_4 and N_2 are gases (and, in the case of N_2 , because the reaction with 1 is quite slow) their addition reactions are not well suited to direct calorimetric measurement. In order to determine their bond disruption enthalpies we exploited a method previously reported for determination of the enthalpy of addition of H₂. ^tBuNC reacts rapidly with complexes 2-4 to displace the respective ligands L'. These reactions (eq 1) were measured calorimetrically, and the resulting values were subtracted from those measured for the direct addition of t BuNC (eq 2) to give the enthalpies of addition of 1 (eq 3).⁸ In the case of L'

$$RhL_{2}ClL'_{(soln)} + {}^{t}BuNC_{(soln)} \rightarrow RhL_{2}Cl({}^{t}BuNC)_{(soln)} + L'_{(soln)}$$
(1)

$$\begin{array}{ccccc} L' & RhL_2ClL' & \Delta H_1 \, (kcal/mol) \\ N_2 & \mathbf{2} & -25.9 \pm 0.5 \\ C_2H_4 & \mathbf{3} & -17.6 \pm 0.3 \\ PhC \equiv CPh & \mathbf{4} & -19.9 \pm 0.5 \end{array}$$

$$\frac{1}{2}[RhL_{2}Cl]_{2(soln)} + {}^{t}BuNC_{(soln)} \rightarrow RhL_{2}Cl({}^{t}BuNC)_{(soln)}$$

$$5$$
(2)
$$\Delta H_{2} = -33.5 \pm 0.5 \text{ kcal/mol}$$

$$\frac{1}{2[\mathrm{RhL}_{2}\mathrm{Cll}]_{2(\mathrm{soln})} + \mathrm{L}'_{(\mathrm{soln})} \rightarrow \mathrm{RhL}_{2}\mathrm{ClL'}_{(\mathrm{soln})}} \quad (3)$$
$$\Delta H_{3} = \Delta H_{2} - \Delta H_{1}$$

L'	RhL_2ClL'	$\Delta H_2 - \Delta H_1 (\text{kcal/mol})$
N_2	2	-7.6 ± 0.7
C_2H_4	3	-15.9 ± 0.6
PhC≡CPh	4	-13.6 ± 0.7

= PhC=CPh the addendum is not volatile. Thus the addition reaction could be directly measured, and doing so served as an internal consistency check for the method. The directly measured enthalpy of eq 4

Abstract published in Advance ACS Abstracts, July 1, 1995.
 (1) Halpern, J. Inorg. Chim. Acta. 1981, 50, 11-19 and references therein.

^{(2) (}a) Maguire, J. A.; Boese, W. T.; Goldman, A. S. J. Am. Chem. Soc. **1989**, 111, 7088-7093. (b) Maguire, J. A.; Boese, W. T.; Goldman, M. E.; Goldman, A. S. Coord. Chem. Rev. **1990**, 97, 179-192.

^{(3) (}a) Maguire, J. A.; Goldman, A. S. J. Am. Chem. Soc. **1991**, 113, 6706-6708. (b) Maguire, J. A.; Petrillo, A.; Goldman, A. S. J. Am. Chem. Soc. **1992**, 114, 9492-9498.

⁽⁴⁾ Wang, K.; Rosini, G. P.; Nolan, S. P.; Goldman, A. S. J. Am. Chem. Soc. **1995**, 117, 5082-5088.

⁽⁵⁾ The closely related tricyclohexylphosphine analogs of these complexes were first reported by Van Gaal et al. (a) Van Gaal, H. L. M.; Moers, F. G.; Steggerada, J. J. J. Organomet. Chem. 1974, 65, C43-C45. (b) Van Gaal, H. L. M.; Van Den Bekerom, F. L. A. J. Organomet. Chem. 1977, 134, 237-248.

⁽⁶⁾ Busetto, C.; D'Alfonso, A.; Maspero, F.; Pergo, G.; Zazzetta, A. J. Chem. Soc., Dalton Trans. 1977, 1828-1834.

$$\frac{1}{2}[RhL_{2}Cl]_{2(soln)} + PhC \equiv CPh_{(soln)} \rightarrow 1$$

$$(PhC \equiv CPh)RhL_{2}Cl_{(soln)} \quad (4)$$

$$4$$

$$\Delta H_{4(\text{calcd})} = \Delta H_2 - \Delta H_1 = -13.6 \pm 0.7 \text{ kcal/mol}$$

$$\Delta H_{4(\text{expt})} = -14.2 \pm 0.4 \text{ kcal/mol}$$

was found to be -14.2 ± 0.4 kcal/mol, equal within the limits of experimental error to the value of $\Delta H_2 - \Delta H_1$. (We will take ΔH_4 to be the average of the two values, i.e., -13.9 ± 0.8 kcal/mol.) These results are indicated in Scheme 1.

The similar BDE's calculated for addition of PhC=CPh and C_2H_4 imply that it might be possible to spectroscopically observe an equilibrium between the two addenda. This is found to be the case. A variable temperature ³¹P NMR study of reaction 5 in toluene over

$$(PhC=CPh)RhL_{2}Cl_{(soln)} + C_{2}H_{4(soln)} =$$

$$4$$

$$(C_{2}H_{4})RhL_{2}Cl_{(soln)} + PhC=CPh_{(soln)} (5)$$

$$3$$

 $\Delta H_{5(\text{calorimetry})} = [\Delta H_3(L' = C_2 H_4)] - \Delta H_4 = -2.0 \pm 1.0 \text{ kcal/mol}$

$$\Delta H_{5(\text{NMR})} = 0.1 \pm 0.2 \text{ kcal/mol}$$

the temperature range 0-50 °C was conducted. A van't Hoff plot gave a value for ΔH_5 of 0.1 ± 0.2 kcal/mol ($\Delta S = -5.3 \pm 0.6$ eu). This result is outside the limits of experimental error of the calorimetric data, but the deviation is fairly small, and, considering the very different nature of the two techniques, we do not consider it to be a very serious discrepancy. It may suggest, however, that the actual error limits are slightly greater than those calculated.

In another competition experiment, a mixture of 38 mM (MeC=CMe)Rh(PⁱPr₃)₂Cl (6) and 45 mM diphenylacetylene in C_6D_6 (eq 6) at room temperature was

$$(MeC \equiv CMe)RhL_2Cl_{(soln)} + PhC \equiv CPh_{(soln)} \neq \mathbf{6}$$

$$(PhC \equiv CPh)RhL_2Cl_{(soln)} + MeC \equiv CMe_{(soln)} \quad (6)$$

$$\mathbf{4}$$



monitored by both ¹H and ³¹P NMR spectroscopy. An equilibrium constant of 40(5) was measured; thus the Rh-alkyne BDE of 4 is about 2.2 kcal/mol greater than that in **6** (if $\Delta S = 0$ is assumed). In a reciprocal experiment only a small fraction (ca. 2% of the total rhodium concentration) of diphenylacetylene was displaced by MeC=CMe when a solution of **4** was treated with a 20-fold excess of MeC=CMe in C₆D₆; however, several unidentified species were observed (possibly due to replacement of PⁱPr₃ by 2-butyne) and the results of this experiment are considered less meaningful.

Acetylenes typically bind more strongly than olefins,⁹ particularly in the case of coordinatively unsaturated complexes like 4. The greater (or at least comparable) binding affinity of C_2H_4 in this case would not seem likely to result from steric factors; the phenyl groups of diphenylacetylene would be expected to lie in the plane perpendicular to the P-Rh-P axis to avoid interaction with the bulky $P^i Pr_3$ ligands, while the $C_2 H_4$ hydrogen atoms could not do so.⁶ Molecular mechanics (MM2) calculations support this hypothesis: if the Rh-L'(C-C midpoint) distance is fixed at 2.01 Å,⁶ and L is varied from PH_3 to PMe_3 to P^iPr_3 , the calculated energy increases significantly less when $L' = PhC \equiv CPh$ than when L' is either MeC=CMe or C_2H_4 . Accordingly, visual inspection of the calculated models ($L = P^i P r_3$) reveals significant crowding when L' is 2-butyne or C_2H_4 , whereas the diphenylacetylene ligand neatly resides in a "cleft" between the two triisopropylphosphines.

The greater bonding affinity of RhL₂Cl for the olefin is not surprising if simple molecular orbital interactions are considered. If the complexes are viewed as d⁸ square-planar, with olefin or acetylene perpendicular to the RhP₂Cl plane,⁶ the empty d(Rh) orbital is the x^{2} y^{2} (see Scheme 2 for labeling of axes). For both olefin and acetylene, σ -bond formation involves the $\pi_{||}$ orbital while the d_{xz}(Rh) orbital is of correct symmetry to backdonate into the $\pi_{||}^{*}$ orbital. However, the d_{xy} orbital of Rh and the π_{\perp} orbital of alkyne are both filled and therefore their interaction should weaken the Rh– alkyne bond. It has previously been suggested that D(M-alkyne) - D(M - alkene) may be less for late than

⁽⁷⁾ The N_2 ligand of $RhL_2Cl(N_2)$ was originally characterized as binding in a "side-on" fashion⁶, but was later shown to be bound "end-on": Thorn, D. L.; Tulip, T. H.; Ibers, J. A. J. Chem. Soc., Dalton Trans. **1979**, 2022–2025.

⁽⁸⁾ The ratio of solution to gas volume in the calorimetry cell is approximately 16 (4 mL: 0.25 mL). Since the solubility of ethylene in benzene is fairly high (ca. 0.14 M/atm at 20 °C,^a in good agreement with a value reported for toluene, 3.19 cm³ (C₂H₄)/(cm³(toluene) atm) at 22 °C,^b virtually all ethylene produced will remain in solution at equilibrium (ca. 98%); the actual percentage remaining in solution will of course be higher if equilibrium is not reached. The solubility of N₂ is considerably lower (0.124 cm³(N₂)/(cm³(benzene) atm);^c at equilibrium roughly equal amounts of N₂ will be in gas and solution. However, as the heat of solution of N₂ is undoubtedly very small (slightly positive as indicated by the observation that N₂ solubility in benzene increases with increasing temperature^d), this should have no significant effect on the determined reaction enthalpy. (a) Gerrard, W. Solubility of Gases and Liquids; Plenum Press: New York, 1976; p 141. (b) Waters, J. A.; Mortimer, G. A.; Clements, H. E. J. Chem. Eng. Data 1970, 15, 174-176. (c) Landolt-Bornstein. Zahlenwerte und Funktionen, 6th ed.; Springer-Verlag: Berlin, 1962; Vol. 2, Part 2b. (d) Burrows, G.; Preece, F. H. Trans. Faraday Soc. 1963, 59, 1293.

^{(9) (}a) Otsuka, S.; Nakamura, A. Advances in Organometallic Chemistry; Academic Press: New York, 1976; Vol. 14, pp 245-283.
(b) Crabtree, R. H. The Organometallic Chemistry of the Transition Metals, 2nd ed.; John Wiley & Sons: New York, 1994; pp 111-112.

Table 1. Enthalpy of Addition of L' to 1 in Solution and the Corresponding Minimum Rh-L' BDE's (kcal/mol)

<u> </u>			
L'	$\Delta H (eq 3)$	min Rh–L' BDE ^a	
CO	$-39.3(7)^{b}$	48.2^{b}	
^t BuNC	$-33.5(5)^{b}$	42.4^{b}	
\mathbf{H}_2	$-23.6(6)^{b}$	$32.5^{b,c}$	
C_2H_4	-15.9(6)	24.8	
PhC≡CPl	h $-13.9(8)^d$	22.8^{d}	
MeC≡CM	Ie -11.7(9)	20.6	
\mathbf{N}_2	-7.6(7)	16.5	

^a Minimum enthalpy of addition of L' to monomeric RhL₂Cl based on a minimum bridge strength of 1 of 17.8 kcal/mol (see ref 4). ^b Values from ref 4. ^c Minimum enthalpy of H₂ addition; this corresponds to an average Rh-H BDE of 68.4 kcal/mol. d Average of values obtained from direct (eqs 1 and 2) and indirect (eq 3) measurement.

for early transition metals;¹⁰ similar MO-based considerations may be applicable generally.

Comparison with Thermodynamics of Relevant Systems. The bridge strength of 1 was previously determined to be at least 17.8 kcal/mol. While only a minimum value could be measured, on the basis of the estimated bridge strength of a closely related complex $[Rh(P(4-Tol)_3)_2Cl]_2$ (19.7 kcal/mol)¹¹ and the observed reactivity of 1,12 we believe the actual value is not much greater. Addition of one-half of the minimum bridge strength to ΔH_3 gives the corresponding lower limits for the absolute Rh-L' BDE's. These values along with results from our previous study are shown in Table 1.

Thermodynamic measurements of other metalnitrogen bonds have been made. Kubas and Hoff¹³ reported the following $M-N_2$ BDE's in $M(CO)_3(PCy_3)_2$ -(N₂) (kcal/mol): Cr, 19.3; Mo, 19.0; W, 23.5; these values assume that the agostic interactions found in $M(CO)_3$ - $(PCy_3)_2$ are equal to 10 kcal/mol. $Ru(dmpe)N_2$ was studied by Scaiano et al.14 using photoacoustic calorimetry, and the Ru-N₂ BDE was found to be 18.8 ± 2.0 kcal/mol. Using kinetic methods, Turner¹⁵ determined the $Ni-N_2$ BDE in $Ni(CO)_3N_2$ to be 10 kcal/mol. The lower limit of the Rh-N₂ BDE (16.5 kcal/mol) in 2 is thus consistent with other reported examples of metal-N₂ BDE's.

Addition of olefins and acetylenes to organometallic compounds is the subject of a large body of studies which have been reviewed.^{16,17} The values reported in this work are not unusual. For example, $\Delta H = -11.8$ kcal/ mol for the addition of C_2H_4 to Vaska's complex vs -9.3kcal/mol for the addition of C₂H₂.¹⁸ In view of the importance of bis(phosphine)rhodium chloride in olefin hydrogenation and alkane dehydrogenation catalysis, a comparison of the enthalpy of binding of ethene with that of the addition of H_2 is worth noting. H_2 is found to add more readily by 7.7 kcal/mol (this value or any other differences in addition enthalpies resulting from this work are independent of the estimate of the bridge strength of 1). For alkenes other than ethene, the difference is presumably significantly greater for steric reasons.¹⁹ Extrapolating such a comparison to complexes with different phosphines can only be done tentatively. With that proviso, we note that the greater binding enthalpy of H_2 is consistent with the mechanism proposed for Rh(PMe₃)₂(CO)Cl-catalyzed alkane photodehydrogenation:² the intermediate Rh(PMe₃)₂Cl(alkene)- H_2 is proposed to lose alkene, which should be thermodynamically more favorable than loss of H₂.

Experimental Section

General Procedures. All manipulations were conducted under an argon atmosphere either in a Vacuum Atmospheres Dry-Lab glovebox or by using standard Schlenk techniques. Nitrogen (99.99% grade) and ethylene (99.5% grade) were purchased from JWS Technologies, Inc., and used without further purification. 2-Butyne and tert-butyl isocyanide were purchased from Aldrich and freeze-pump-thawed prior to use. C_6D_6 (99.5 atom % d, Cambridge Isotope Laboratories) was dried over Na and vacuum distilled prior to use. All other solvents were either distilled from dark purple solutions of benzophenone ketyl or dried over molecular sieves. $[Rh(P^{i}Pr_{3})_{2}Cl]_{2}(1)$ was synthesized according to Werner.²⁰ ('BuNC) $Rh(P^{i}Pr_{3})_{2}Cl$ (5) was synthesized as reported earlier.4

NMR spectra were recorded on either a Varian VXR-200 or XL-400 MHz spectrometer. ³¹P NMR chemical shift values are expressed in reference to 85% H₃PO₄. IR spectra were recorded on a Mattson Cygnus 100 FTIR spectrometer.

Only materials of high purity as indicated by IR and NMR spectroscopy were used in the calorimetric experiments. Calorimetric measurements were performed using a Calvet calorimeter (Setaram C-80) which was periodically calibrated using the TRIS reaction²¹ or the enthalpy of solution of KCl in water.²² The experimental enthalpies for these two standard reactions compared very closely to literature values. This calorimeter and the experimental procedures used have been previously described.23 Typical procedures are described below. Experimental enthalpy data are reported with 95% confidence limits.

Solution Calorimetry: Calorimetric Measurement of Reactions Between *t*-BuNC and $L'Rh(P^iPr_3)_2Cl$ ($L' = N_2$ (2), C_2H_4 (3), and PhC=CPh (4)). The procedures for the measurement of this type of reactions are similar and represented by that of 4.

The mixing vessels of the Setaram C-80 were cleaned, dried in an oven maintained at 120 °C, and then taken into the glovebox. A 20-25 mg sample of 4 was accurately weighed into the lower vessel; it was closed and sealed with 1.5 mL of mercury. A 4 mL amount of a stock solution of tert-butyl isocyanide (25 μ L of the isocyanide in 20 mL of freshly dried and distilled benzene) was added, and the remainder of the cell was assembled, removed from the glovebox, and inserted in the calorimeter. The reference vessel was loaded in an

⁽¹⁰⁾ Calhorda, M.; Carrondo, M.; Dias, A.; Galvão, A.; Garcia, M.;

⁽¹⁰⁾ Calmorda, M., Carrondo, M.; Dias, A.; Galvao, A.; Garcia, M.;
Martins, A.; Piedade, M.; Pinhiro, C.; Romao, C.; Simões, J.; Veiros, L. Organometallics 1991, 10, 483-494.
(11) (a) Pribula, A. J.; Drago, R. S. J. Am. Chem. Soc. 1976, 98, 2784-2788.
(b) Drago, R. S.; Miller, J. G.; Hoselton, M. A.; Farris, R. D.; Desmond, M. J. J. Am. Chem. Soc. 1983, 105, 444-449.
(12) Shih K.; Goldman A. S. Organometallics 1009, 0, 2200-2200.

⁽¹²⁾ Shih, K.; Goldman, A. S. Organometallics 1993, 9, 3390-3392. (13) (a) Gonzales, A. A.; Zhang, K.; Nolan, S. P.; Vega, R. L. d. I.;
 Mukerjee, S. L.; Hoff, C. D.; Kubas, G. J. Organometallics 1988, 7,
 2429-2435. (b) Zhang, K.; Gonzales, A. A.; Mukerjee, S. L.; Chou,
 S.-J.; Hoff, C. D.; Kuba-Martin, K. A.; Barnhart, D.; Kubas, G. J. J. Am. Chem. Soc. 1991, 113, 9170-9176.

⁽¹⁴⁾ Belt, S. T.; Scaiano, J. C.; Whittlesey, M. K. J. Am. Chem. Soc.

^{1993, 115, 1921-1925.} (15) Turner, J. J.; Simpson, M. B.; Poliakoff, M.; Maier, W. B. J.

Am. Chem. Soc. 1983, 105, 3898–3904. (16) Mondal, J. U.; Blake, D. M. Coord. Chem. Rev. 1982, 47, 205-238

⁽¹⁷⁾ Hartley, F. R. Chem. Rev. 1973, 73, 163-190.

⁽¹⁸⁾ Vaska, L. Acc. Chem. Res. 1968, 1, 335-344.

⁽¹⁹⁾ See for example: Hughes, R. P. In Comprehensive Organome-*Callic Chemisry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 5, pp 418-424. (20) Werner, H.; Wolf, J.; Hohn, A. J. Organomet. Chem. **1985**, 287,

^{395-407.}

⁽²¹⁾ Ojelund, G.; Wadsö, I. Acta Chem. Scand. 1968, 22, 1691-1699. (22) Kilday, M. V. J. Res. Natl. Bur. Stand. (U.S.) 1980, 85, 467-481

⁽²³⁾ Nolan, S. P.; Hoff, C. D.; Landrum, J. T. J. Organomet. Chem. 1985, 282, 357-362.

identical fashion with the exception that no organorhodium complex was added to the lower vessel. After the calorimeter had reached thermal equilibrium at 30.0 °C (about 2 h), the calorimeter was inverted, thereby allowing the reactants to mix. After the reaction had reached completion and the calorimeter had once again reached thermal equilibrium (ca. 2 h), the vessels were removed from the calorimeter. Conversion to $(t-BuNC)Rh(P^iPr_3)_2Cl$ (5) was found to be quantitative under these reaction conditions. The enthalpy of reaction, -15.6 ± 0.4 kcal/mol, represents the average of five individual calorimetric determinations.

In order to consider all species in solution, the enthalpies of solution of 4 had to be directly measured. This was performed by using a procedure similar to the one described above with the exception that no isocyanide was added to the reaction cell. This enthalpy of solution represents the average of five individual determinations and is 4.3 ± 0.2 kcal/mol.

(N₂)Rh(PⁱPr₃)₂Cl (2). Compound 2 was made by modification of a reported method.⁶ Compound 1 (350 mg, 0.38 mmol) was dissolved in 30 mL of toluene, and the solution was stirred under 1 atm of N₂ at room temperature. The formation of **2** was monitored by ³¹P NMR spectroscopy, and conversion was found to be complete after 30 h. The solvent was removed *in vacuo*, and the product was recrystallized from toluene/ hexanes (330 mg, 90% yield). ¹H NMR (C₆D₆, 200 MHz): δ 1.31 (q, (³J_{P-H} + ⁵J_{P-H})/2 = J_{H-H} = 6.6 Hz, 36 H), 2.45 (m, 6 H). ³¹P NMR (C₆D₆, 162 MHz): δ 42.55 (d, J_{Rh-P} = 122.06 Hz). IR (toluene): 2105.2 cm⁻¹ (s).

(C₂H₄)Rh(PⁱPr₃)₂Cl (3). Compound 3 was prepared by modification of a literature method.⁶ Compound 1 (350 mg, 0.38 mmol) was dissolved in 30 mL of toluene, and C₂H₄ was bubbled through the solution for 30 seconds. The initially purple solution turned bright yellow immediately. The solvent was removed *in vacuo*, and the product was recrystallized from toluene/hexanes (330 mg, 90% yield). ¹H NMR (C₆D₆, 400 MHz): δ 1.26 (q, (³J_{P-H} + ⁵J_{P-H})/2 = J_{H-H} = 6.6 Hz, 36 H), 2.32 (m, 6 H), 2.62 (pseudo q, 4 H, C₂H₄). ³¹P NMR (C₆D₆, 162 MHz): δ 34.1 (d, J_{Rh-P} = 120.03 Hz). IR (CH₂Cl₂): 1603.7 cm⁻¹ (w).

(**PhC=CPh**)**Rh**(**P**^{*i*}**Pr**₃)₂**Cl** (4). Compound 1 (350 mg, 0.38 mmol) was dissolved in 30 mL of toluene, and 136 mg (0.76 mmol) of diphenylacetylene was added. The initially purple solution turned bright yellow immediately. The mixture was stirred for 30 min, and the solvent was removed *in vacuo*. The product was recrystallized from toluene/hexanes (430 mg, 90% yield). ¹H NMR (C₆D₆, 200 MHz): δ 1.20 (q, (³*J*_{P-H} + ⁵*J*_{P-H})/2 = *J*_{H-H} = 6.6 Hz, 36 H), 2.27 (m, 6 H), 8.27 (d, 4 H, *Ph*), 7.21 (t, 4 H, *Ph*), 7.05 (d, 2 H, *Ph*). ³¹P NMR (C₆D₆, 162 MHz): δ 32.59 (d, *J*_{Rh-P} = 116.13 Hz).

Reaction of (N₂)Rh(PⁱPr₃)₂Cl (2) with *t***-BuNC.** A 0.45 mL amount of 25 mM 2 in C₆D₆ was treated with 1.5μ L (0.013 mmol) of *t*-BuNC in an NMR tube. The color of the solution changed from brownish-yellow to bright yellow immediately upon shaking, and the evolution of gas was observed. The ³¹P NMR spectrum was observed immediately, and 2 had completely disappeared with the formation of 5 which was confirmed by IR, ¹H, and ³¹PNMR. Excess (>1.1 equiv) *t*-BuNC led to uncharacterized species.

Reaction of (C₂H₄)Rh(PⁱPr₃)₂Cl (3) with *t***-BuNC. A 0.45 mL amount of 25 mM 3 in C₆D₆ was treated with 1.5 \muL (0.013 mmol) of** *t***-BuNC in an NMR tube. The NMR tube was shaken gently, and the evolution of gas was observed. The ³¹P NMR spectrum was recorded immediately, and 3 was found to have disappeared completely with the formation of 5. Free C₂H₄ was found in the ¹H NMR spectrum. As in the reaction of 2, excess (>1.1 equiv)** *t***-BuNC led to uncharacterized species.**

Reaction of (PhC=CPh)Rh(P^{*i*}**Pr**₃)₂**Cl (4) with** *t*-**BuNC.** A 0.45 mL amount of 25 mM 4 in C₆D₆ was treated with 1.5 μ L (0.013 mmol) of *t*-BuNC in an NMR tube. The NMR tube was shaken gently before the ³¹P NMR spectrum was recorded, and complete conversion to **5** was observed within about 15 min. Free diphenylacetylene was observed in the ¹H NMR spectrum. Excess (>1.1 equiv) *t*-BuNC also leads to uncharacterized species in this reaction.

Reaction of C₂H₄ with (PhC=CPh)Rh(PⁱPr₃)₂Cl (4). A 0.6 mL amount of a 66 mM solution of 4 in toluene was put in a J. Young NMR tube (which contained a sealed capillary of PPh₃ in acetone- d_6) and placed under 840 Torr of C₂H₄. Variable temperature ³¹P NMR spectroscopy was used to obtain a van't Hoff plot.

Reaction of Diphenylacetylene with (MeC=CMe)Rh. (**P**ⁱ**Pr**₃)₂**Cl (6).** Compound **6** was generated in situ by reacting 2 equiv of 2-butyne with **1**. ¹H NMR (C₆D₆, 400 MHz): δ 1.32 (q, (³J_{P-H} + ⁵J_{P-H})/2 = J_{H-H} = 6.5 Hz, 36 H), 2.33 (m, 6 H), 2.01 (s, 6 H, C₂Me₂). ³¹P NMR (C₆D₆, 162 MHz): δ 34.83 (d, J_{Rh-P} = 122.62 Hz), IR (C₆D₆): 1953.8 cm⁻¹ (s). A mixture of 38 mM **6** and 45 mM diphenylacetylene in C₆D₆ equilibrated at room temperature and was monitored with both ¹H and ³¹P NMR spectroscopy.

Acknowledgment. Support for this research by the National Science Foundation (Grants CHE-9121695 to A.S.G. and CHE-9305492 to S.P.N.) and the Louisiana Education Quality Support Fund is gratefully acknowledged.

OM950225W