

N, 7.83. Found: C, 55.82; H, 4.45; N, 7.72.

(p) **Synthesis of** $[(C_6H_5)_2B(OH)(pz)W(\eta^3-$

$NNCHCHCHCH_2CHCHCHCH_3)(CO)_2]$ (**7b**). $Na(C_6H_5)_2B(pz)_2$ (0.16 g, 0.49 mmol) was added to $W(CO)_2(CH_3CN)_2(\eta^3-C_5H_7)Br$ (0.27 g, 0.50 mmol) in 50 mL of CH_2Cl_2 , and the mixture was stirred at 23 °C for 30 min. The solvent was then removed in vacuo, and 1H NMR spectra of the residues showed the presence of $[(C_6H_5)_2B(pz)_2W(CO)_2(\eta^3-C_5H_7)]$ (**5b**) and **7b**. 1H NMR for **5b** (400 MHz, $CDCl_3$): δ 0.50 (d, 1 H, H^2), 0.60 (d, 1 H, H^6), 2.80 (m, 1 H, H^4), 5.29 (d, 1 H, H^7), 5.35 (d, 1 H, H^8), 6.20 (m, 1 H, H^5). The residue was chromatographed through a neutral alumina column, and a yellow band consisting of an unknown organic component was eluted off the column. Elution of the top immobile brown band with CH_3CN produced a gold-yellow band of **7b**. Removal of the solvent under reduced pressure gave a yellow solid, which was recrystallized from a saturated CH_2Cl_2 -hexane solution to yield yellow block-shaped crystals of **7b** (0.063 g, 0.10 mmol). IR (Nujol): $\nu(CO)$ 1950 (s), 1871 (s) cm^{-1} . 1H NMR (400 MHz, $CDCl_3$): δ 1.93 (d, 3 H, CH_3), 2.08 (dt, 1 H, H^1), 2.38 (t, 1 H, H^3), 2.65 (t, 1 H, H^2), 4.62 (dd, 1 H, H^4), 5.30 (d, 1 H, H^5), 6.0-8.2 (16 H, Ph + pz), $J_{1-CH_3} = 6.4$ Hz, $J_{12} = J_{23} = 9.2$ Hz, $J_{34} = 3.5$ Hz, $J_{45} = 15.4$ Hz. Anal. Calcd for $WC_{25}H_{25}O_3N_4B$: C, 47.83; H, 3.98; N, 8.95. Found: C, 47.52; H, 3.86; N, 8.84.

(q) **Solution Dynamics.** A sample of **5a** was dissolved in toluene- d_8 and NMR spectra were recorded over the temperature range -60 to +90 °C. Probe temperatures were calibrated by using the temperature dependence of the differences in the chemical shifts between the 1H resonances of the methyl and hydroxyl groups of methanol below ambient temperature and between the 1H resonances of the methylene and hydroxyl groups of ethylene glycol above ambient temperature. Theoretical line shapes were calculated for a series of rates by using the method of Johnson.²⁹

Exchange rate constants for each temperature were determined by matching the theoretical spectra to experimental spectra. The rate constants k were then used to calculate the energy of activation $\Delta G^\ddagger$ at each temperature T , by using the Eyring equation:

$$k_C = (k'/h)Te^{-\Delta G^\ddagger/RT}$$

$k' =$ Boltzmann constant, $h =$

Planck constant (divided by 2π), $R =$ ideal gas constant

(r) **X-ray Diffraction Study.** Single crystals of **3a**, **5a**, **6a**, and **7b** were sealed in glass capillaries under an inert atmosphere. Data for **3a** were collected at room temperature on a Nicolet R3m/V diffractometer using graphite-monochromated Mo $K\alpha$ radiation. The structure of **3a** was solved by the Patterson method. All data reduction and structural refinement were performed by means of the SHELXTL PLUS package. Data for **5a**, **6a**, and **7b** were collected on a Nonius CAD-4 diffractometer, using graphite-monochromated Mo $K\alpha$ radiation, and the structures were solved by the Patterson method. All data reduction and structure refinement were performed with the NRCSDP package. Crystal data and details of the data collection and structure analysis are summarized in Table V. For all four structures, all non-hydrogen atoms were refined with anisotropic parameters. All hydrogen atoms included in the structure factor calculations were placed in idealized positions.

Supplementary Material Available: Listings of bond lengths and angles, thermal parameters, and H atom positional parameters for **3a**, **5a**, **6a**, and **7b** (18 pages); listings of observed and calculated structure factors (46 pages). Ordering information is given on any current masthead page.

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Tetraethylborate as an Ethyl Transfer Reagent

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Reaction of $NaBEt_4$ with $RhCl(C_2H_4)(\text{triphos})$ (**I**), where triphos is $MeC(CH_2PPh_2)_3$, gives $RhH(C_2H_4)(\text{triphos})$. Coordinated $^{13}C_2H_4$ in labeled **I** is liberated during the reaction, proving that $NaBEt_4$ is the source of the ethylene coordinated in the product. Compound **I** reacts at 1 atm and 25 °C with $^{13}C_2H_4$ or H_2 to give $RhCl(^{13}C_2H_4)(\text{triphos})$ or $Rh(H)_2Cl(\text{triphos})$, respectively. It is proposed that all three reactions proceed by a mechanism in which one arm of the triphos ligand in **I** dissociates to yield a planar $RhCl(C_2H_4)(\eta^2\text{-triphos})$ transient. Both five-coordinate species $RhX(C_2H_4)(\text{triphos})$ ($X = H, Cl$) are unusual in showing relatively high barriers for both phosphorus site exchange and olefin rotation. In contrast to the reaction of **I** with $NaBEt_4$, the reaction with $NaBPh_4$ stops at $Rh(\eta^2\text{-triphos})(\eta^6\text{-PhBPh}_3)$ and shows no further conversion to $RhPh(C_2H_4)(\text{triphos})$.

Introduction

We have reported recently¹ on a group of Rh(III) trihydride and trimethyl compounds containing the tridentate ligand $MeC(CH_2PPh_2)_3$ ("triphos"). These 18-electron compounds were quite reactive under very mild conditions with CO, with H_2 , and with ethylene. This high reactivity was traced to mechanisms that were initiated by dissociation of one arm of the triphos, a step which we initially found surprising. We report here an examination of the products and mechanisms of some reactions of a Rh(I)/triphos compound. An "arm-off" mechanism is also im-

plicated in these reactions. This work also demonstrates an example of tetraethylborate functioning as an ethyl transfer reagent.

Experimental Section

General Procedures. Pentane, tetrahydrofuran, benzene, and toluene were all dried and distilled prior to use from solutions containing sodium/potassium benzophenone ketyl. Methylene chloride was refluxed over P_2O_5 and distilled prior to use. Sodium tetraphenylborate was purchased from Aldrich. Sodium tetraethylborate (Caution! pyrophoric) was purchased from Alfa. $[Rh(COD)Cl]_2$,² $[Rh(C_2H_4)_2Cl]_2$,³ and $RhH_3(\text{triphos})$ ⁴ were pre-

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(2) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* 1979, 19, 218.

pared by literature methods. $^{13}\text{C}_2\text{H}_4$ was obtained from Cambridge Isotope Laboratory. NMR spectra were recorded on a Bruker AM-500 or a Nicolet NT-360 spectrometer. Where stated, measured gas quantities were supplied with use of a standard calibrated gas manifold. Abbreviations: FPT, freeze-pump-thaw; d, doublet; t, triplet; q, quartet; m, multiplet.

$\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$. To $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$ (0.11 g, 0.28 mmol) in 40 mL of toluene at 0°C , under an atmosphere of C_2H_4 , was added triphos (0.35 g; 0.56 mmol) in 10 mL of toluene. Upon addition of triphos, the homogeneous yellow solution turned deep orange. The solution was stirred at 0°C for an additional 15 min and then at room temperature for 15 min, after which time large amounts of a yellow-orange precipitate, $\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$, were present. The volume of toluene was reduced to 20 mL, and the product was collected by filtration and dried in vacuo to yield $\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$ (0.32 g). The homogeneous orange filtrate was then further reduced in volume (10 mL) and allowed to stand at -20°C overnight. Filtering this solution gave a second batch of product (0.10 g); combined yield 0.42 g (95% yield). ^1H NMR (360 MHz, CD_2Cl_2 , 22°C): δ 1.48 (unresolved q, $J_{\text{PH}} = 2.1$ Hz, CCH_3), 2.31 (v br s, $-\text{CH}_2\text{P}$), 1.7 (br d, $J_{\text{HH}} = 10.59$ Hz, C_2H_4), 3.12 (br d, $J_{\text{HH}} = 9.85$ Hz, C_2H_4), 6.5–8.0 (br, $-\text{PPh}_2$). ^1H NMR (CD_2Cl_2 , -35°C): δ 1.40 (br s, CCH_3), 1.54 (br m, C_2H_4 , 2 H), 2.08 (d, $J_{\text{PH}} = 7.9$ Hz, $-\text{CH}_2\text{P}$, 2 H), 2.19 (m, $-\text{CH}_2\text{P}$, 4 H), 3.0 (br m, C_2H_4 , 2 H), 7.9–6.7 ($-\text{P}(\text{C}_6\text{H}_5)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (146 MHz, CD_2Cl_2 , -30°C): δ -11 (d of d, $J_{\text{PRh}} = 111$ Hz, $J_{\text{PP}} = 28$ Hz), 46 (d of t, $J_{\text{PRh}} = 132$ Hz, $J_{\text{PP}} = 28$ Hz).

$\text{Rh}(\eta^2\text{-triphos})(\eta^6\text{-PhBPh}_3)$. $\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$ (0.05 g; 0.06 mmol) and NaBPh_4 (0.021 g; 0.06 mmol) were dissolved in a minimum amount of THF- d_8 and transferred to an NMR tube. The tube was then degassed (FPT, three cycles) and flame-sealed. The tube was then placed in a hot water bath (70°C) and refluxed for 20 min. ^1H NMR (500 MHz, THF- d_8 , 22°C): δ 2.09 (br s, CCH_3), 2.52–2.4 (3 overlapping multiplets, $-\text{CH}_2\text{P}$, 6 H), 5.15 (br unresolved t, meta H's of $\eta^6\text{-PhBPh}_3$), 5.40 (v br, ortho H's of $\eta^6\text{-PhBPh}_3$), 7.7–6.7 (para H's of $\eta^6\text{-PhBPh}_3$, $-\text{BPh}_3$, and $\text{P}(\text{C}_6\text{H}_5)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (146 MHz, THF- d_8 , 22°C): δ 27.5 (d, $J_{\text{PRh}} = 195$ Hz, 2 P), -30.4 (s, 1 P). Proton chemical shifts for the $\eta^6\text{-PhBPh}_3$ ligand were assigned by comparison to previously reported⁶ values for similar compounds.

Reaction of $\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$ with $^{13}\text{C}_2\text{H}_4$. A sample of $\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$ (0.066 g; 0.084 mmol) was dissolved in a minimum amount of CD_2Cl_2 and transferred to an NMR tube. This solution was then degassed (FPT, three cycles), and the tube was charged with a 10-fold excess of $^{13}\text{C}_2\text{H}_4$ (99 atom %) and flame-sealed. The tube was then shaken for 4 h. $^{13}\text{C}\{^1\text{H}\}$ NMR (90.8 MHz, CD_2Cl_2 , 22°C): 43.24 ppm (br 5-line multiplet, 2nd order). $^{31}\text{P}\{^1\text{H}\}$ NMR (146 MHz, -20°C): δ -11.25 (d of d of d, $J_{\text{PRh}} = 111$ Hz, $J_{\text{CP}} \approx J_{\text{PP}} \approx 25.8$ Hz, 2 P), 46.15 (d of t, $J_{\text{PRh}} = 132$, $J_{\text{PP}} = 27.7$ Hz, 1 P).

$\text{Rh}(\text{H}_2)\text{Cl}(\text{triphos})$ from $\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$ and H_2 . A saturated C_6D_6 (0.4 mL) solution of $\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$ was transferred to an NMR tube, degassed (FPT, three cycles), and placed under H_2 (1 atm). The tube was then flame-sealed and shaken for 10 min. The tube was then allowed to stand 12 h. ^1H NMR spectroscopy showed C_2H_6 (δ 0.79) and quantitative conversion of the rhodium to $\text{RhH}_2\text{Cl}(\text{triphos})$, which was identified by comparison to an authentic sample.

$\text{Rh}(\text{H}_2)_2\text{Cl}(\text{triphos})$. $[\text{Rh}(\text{COD})\text{Cl}]_2$ (0.5 g; 1 mmol) and triphos (1.3 g; 2 mmol) were placed in 50 mL of toluene. This mixture was then placed in a glass-lined high-pressure reaction vessel that was subsequently charged with H_2 (2000 psi). The mixture was stirred 36 h, after which time the pressure was released and the glass insert was removed from the reaction vessel. The resulting white precipitate, $\text{RhH}_2\text{Cl}(\text{triphos})$ (with a pale yellow supernatant), was collected by filtration, washed with toluene (4×5 mL) and pentane (3×10 mL), and dried in vacuo to yield $\text{RhH}_2\text{Cl}(\text{triphos})$ (1.46 g; 95% yield) as an off-white solid. ^1H NMR (360

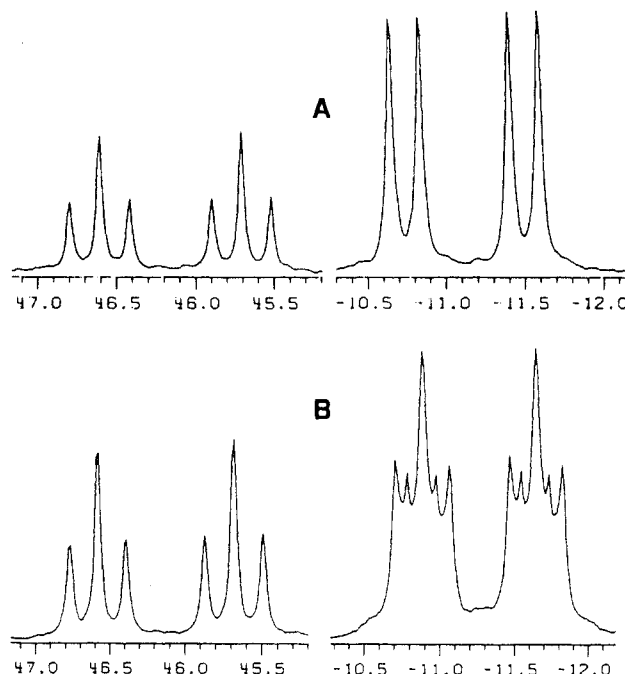


Figure 1. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of $\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$ in CH_2Cl_2 at -30°C : (A) $\text{C}_2\text{H}_4 = ^{13}\text{C}_2\text{H}_4$ (I); (B) $\text{C}_2\text{H}_4 = ^{13}\text{C}_2\text{H}_4$ (I*).

MHz, CD_2Cl_2 , 22°C): δ -7.34 (2nd-order m), 1.52 (unresolved q, $J_{\text{PH}} = 2.52$ Hz, CCH_3), 2.20 (d, $J_{\text{PH}} = 10.1$ Hz, 2 H, $-\text{CH}_2\text{P}$ trans to Cl), 2.33 (m, 4 H, $-\text{CH}_2\text{P}$ trans to H), 7.8–6.95 ($\text{P}(\text{C}_6\text{H}_5)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (146 MHz, CD_2Cl_2 , 22°C): δ -0.83 (d of d, $J_{\text{PRh}} = 79$ Hz, $J_{\text{PP}} = 21$ Hz, 2 P), 49.3 (d of t, $J_{\text{PRh}} = 136$ Hz, 1 P).⁷

$\text{RhH}(\text{C}_2\text{H}_4)(\text{triphos})$ from $\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$ and NaBEt_4 . To $\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$ (0.05 g; 0.063 mmol) stirred in THF (10 mL) was added a THF solution of NaBEt_4 (0.01 g; 0.063 mmol). Upon addition of NaBEt_4 gas evolution could be observed if stirring was stopped. The solution was stirred 10 min, after which time pentane (60 mL) was added to precipitate $\text{RhH}(\text{C}_2\text{H}_4)(\text{triphos})$ as a pale orange powder. This material was collected by filtration and dried in vacuo. ^1H NMR (500 MHz, C_6D_6 , 22°C): δ -10.95 (~d of t of d, $J_{\text{PHtrans}} = 174$ Hz, $J_{\text{Hdd}} \approx J_{\text{HRh}} \approx 13.5$ Hz), 1.21 (br s, CCH_3), 2.06 (br s, $-\text{CH}_2\text{P}$, 2 H), 2.21 (m, $-\text{CH}_2\text{P}$, 4 H), 2.40 (br s, C_2H_4 , 2 H), 3.88 (br m, C_2H_4 , 2 H), 7.88–6.67 ($\text{P}(\text{C}_6\text{H}_5)_2$). $^{31}\text{P}\{^1\text{H}\}$ NMR (146 MHz, THF, 22°C): δ 15.5 (d of t, $J_{\text{PRh}} = 83$ Hz, $J_{\text{PP}} = 33$ Hz, 1 P), 18.9 (d of d, $J_{\text{PRh}} = 132$ Hz, $J_{\text{PP}} = 33$ Hz, 2 P). Also present in the ^{31}P NMR spectrum were very minor resonances at 10 ppm, identified as $\text{RhEt}(\text{C}_2\text{H}_4)(\text{triphos})$ by comparison to the literature.⁸

$\text{RhCl}(^{13}\text{C}_2\text{H}_4)(\text{triphos})$ and NaBEt_4 . A steady stream of N_2 was bubbled through a THF (10 mL) solution of $\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$ (0.05 g; 0.063 mmol). To this solution was added NaBEt_4 (0.01 g; 0.063 mmol), and the solution was flushed with N_2 for 15 min to mix the reagents and remove excess ethylene. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum indicated only the production of $\text{RhH}(\text{C}_2\text{H}_4)(\text{triphos})$. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum showed only a resonance due to solvent, C_6D_6 ; no signal due to ^{13}C -enriched material was present.

Results

Synthesis and Characterization of $\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$ (I). When 2 equiv of triphos is reacted at 0°C and under an atmosphere of ethylene with $[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$, a deep orange solution of I^5 is produced. Compound I is obtained in 95% yield as a light orange powder whose spectroscopic properties are consistent with a trigonal-bipyramidal structure in which two P atoms, Rh, and both

(3) Cramer, R. *Inorg. Synth.* 1974, 15, 14.

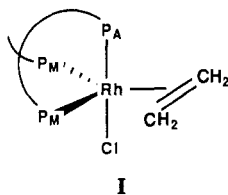
(4) Geerts, R. L.; Huffman, J. C.; Westerberg, D. E.; Folting, K.; Caulton, K. G. *New J. Chem.* 1988, 12, 455.

(5) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *J. Chem. Soc., Chem. Commun.* 1986, 777.

(6) (a) Haines, L. M.; Nolte, M. J.; Gafner, G. *J. Chem. Soc. D* 1969, 1406. (b) Schrock, R. R.; Osborn, J. A. *Inorg. Chem.* 1970, 9, 2339.

(7) Cf. the data for the iridium analogue: Janser, P.; Venanzi, L. M.; Bachechi, F. *J. Organomet. Chem.* 1985, 296, 229.

(8) Bianchini, C.; Meli, A.; Peruzzini, M.; Vizza, F.; Fujiwara, Y.; Jin-toku, T.; Taniguchi, H. *J. Chem. Soc., Chem. Commun.* 1988, 299.



ethylene carbon atoms are coplanar. The ^1H NMR spectrum (22 °C) of I shows a single triphos methyl resonance (1.48 ppm) and a broad resonance (2.31 ppm) for the methylene protons in the backbone of the triphos ligand. The ethylene protons appear as two inequivalent sets at 1.7 and 3.12 ppm, with each resonance split into a doublet. Selective homonuclear decoupling experiments established that this doublet splitting is due to geminal coupling on the order of 10 Hz. The orientation of the CC vector of the ethylene molecule is best established by ^{31}P and ^{13}C NMR spectroscopy. A comparison of the low-temperature (−30 °C) $^{31}\text{P}\{^1\text{H}\}$ NMR spectra (Figure 1) of I and its ^{13}C -labeled analogue $\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$ (I*) reveals that, in both molecules, P_A remains a doublet of triplets (δ 46, $J_{\text{RhP}} = 132$ Hz, $J_{\text{PP}} = 28$ Hz), while the P_M patterns in I and I* are quite distinct; this is a result of large transoid but small cis J_{PC} values. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of I shows a simple doublet of doublets for the P_M nuclei, while I* shows an additional doublet splitting with $J_{\text{PC}} \approx 25.8$ Hz. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of I* shows a single second-order multiplet at δ 43 ppm for the ethylene carbons of I*, showing they are chemically (but not magnetically) equivalent. This excludes a structure where the ethylene CC axis is parallel to the RhCl axis. Olefin rotation is not rapid at this temperature. A more detailed description of the spectroscopy and fluxionality of I is in order, since it is somewhat unusual.

While the low-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of I is a well-resolved AM_2X pattern, at room temperature the P_M signals collapse to a broad doublet with no resolvable phosphorus coupling and the P_A signal is a broad resonance with no discernable Rh/P or P/P coupling. This suggests a fluxional process that involves the dissociation of P_A . The room-temperature ^1H NMR spectrum of this material is also indicative of a fluxional species. While it appears that the ethylene molecule is static (showing two well-resolved resonances), the single broad resonance for the methylene protons in the backbone of the triphos ligand suggests that these protons are undergoing site exchange. At 60 °C in toluene- d_8 the ^1H NMR signals of the ethylene hydrogens for I show no appreciable change and the broad triphos methylene resonance narrows only slightly. To investigate whether or not the fluxional process of phosphorus site exchange in I also involved ethylene site exchange,⁹ two further experiments were performed. The first was a two-dimensional NOESY experiment (Figure 2), performed at 35 °C to enhance any ethylene rotation that might occur. Strong, off-diagonal peaks are present between the two ethylene resonances at 3.05 and 1.60 ppm. This result is indicative of chemical site exchange and/or through-space dipolar magnetic coupling between the geminal protons. To separate these two contributions, a direct NOE difference experiment was performed. The NOE difference experiment between the two ethylene resonances showed an average NOE enhancement of 63% at 30 °C and 75% at 35 °C. Both of these values are greater than the maximum 50% possible as a result of through-space coupling. This supports the

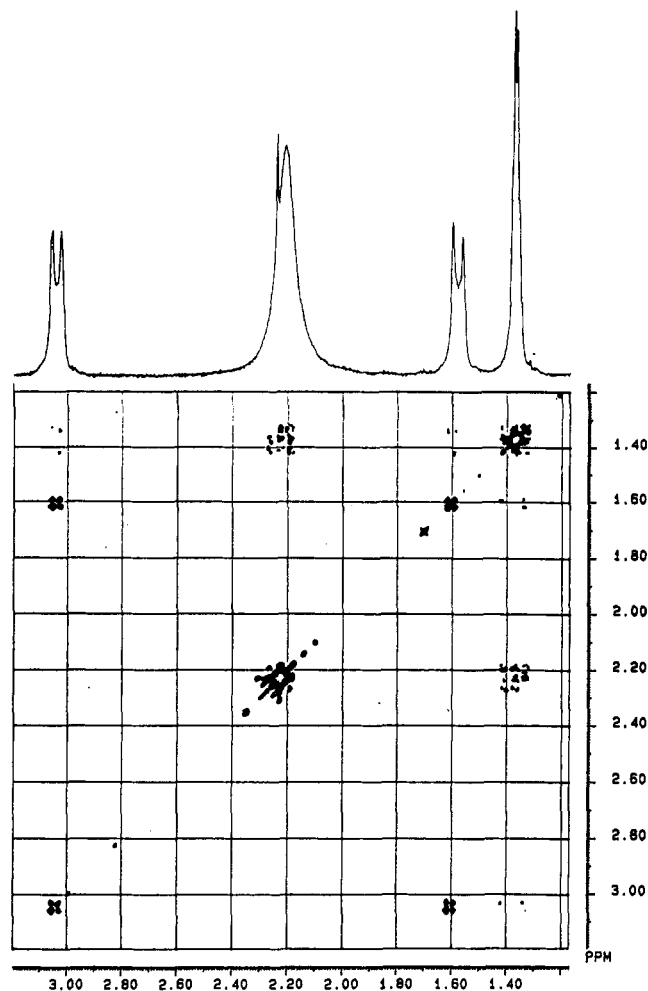
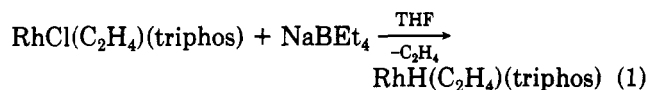


Figure 2. Two-dimensional NOESY experiment for $\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$ in CD_2Cl_2 at 35 °C and 500 MHz.

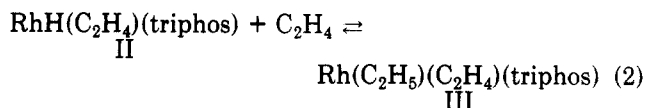
hypothesis that the off-diagonal peaks contain a contribution from site exchange and confirms that the ethylene ligand is undergoing site exchange, but at a rate insufficient to cause coalescence at 360 MHz.

Reactivity of $\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$ with NaBEt_4 . Treatment of $\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$ with NaBEt_4 (eq 1) provides a new route to the known hydrido ethylene complex $\text{RhH}(\text{C}_2\text{H}_4)(\text{triphos})$ ⁵ (II). Also observed during the



course of this reaction was the evolution of gas, which has been identified as C_2H_4 by ^1H NMR spectroscopy (δ 5.33, $\text{THF}-d_8$). The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of II at room temperature shows an AM_2X pattern of a stereochemically rigid species. The ^1H NMR spectrum also requires the surprising conclusion of nonfluxional character: there are triphos resonances (including three inequivalent methylene δ 's) along with two multiplets at 2.2 and 3.88 ppm for the ethylene ligand and a doublet of triplets of doublets, centered at δ −10.95, for the hydride ligand. Besides the resonances for II in the ^{31}P NMR spectrum, there exist two non-first-order multiplets (intensity <2%) near 10 ppm. These resonances increase substantially upon addition of excess ethylene to the NMR tube and are assigned, by comparison to the literature,⁸ to the stereochemically rigid ethyl complex $\text{Rh}(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_4)(\text{triphos})$ (III). Since these two compounds are thus in labile equilibrium, at 25 °C (eq 2) it was necessary to establish whether III was in fact an intermediate in the formation of II and not simply pro-

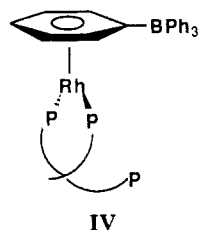
(9) The large separation of the vinylic chemical shifts would cause a high coalescence temperature in the ^1H NMR spectrum.



duced by reaction of II with liberated ethylene. Such an experiment would also help distinguish between two possible mechanisms for eq 1: (1) ethyl group transfer from BEt_4^- to Rh or (2) direct hydride abstraction from BEt_4^- by Rh. To accomplish this, it was necessary to label the ethylene group in compound I. Fortunately, I readily exchanges with free ethylene to generate $\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$ (I*).

Reacting I* with 1 equiv of NaBEt_4 in THF yields only the unlabeled compound II as determined by ^{31}P and ^{13}C NMR spectroscopy. This shows that the ethylene ligand in II is derived from BEt_4^- and not from the ethylene initially present in I. Support for the hypothesis that the ethyl ethylene compound III is an intermediate in the formation of II comes from the fact that an effort was made during this reaction to remove liberated ethylene (thereby preventing the formation of III from II and free C_2H_4), yet minor resonances for III were still apparent in the ^{31}P NMR spectrum. These resonances were also significantly broader than those previously observed for III (containing $^{12}\text{C}_2\text{H}_4$), suggesting they were the resonances for $\text{Rh}(\text{Et})(\text{C}_2\text{H}_4)(\text{triphos})$ with unresolved ^{13}C coupling to phosphorus.

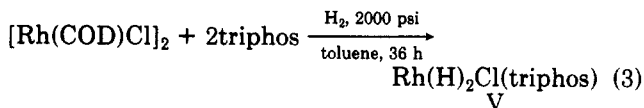
Reactivity of $\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$ with NaBPh_4 . We have investigated $\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$ as a partner for phenyl transfer from NaBPh_4 . Reaction of I with NaBPh_4 in THF-d_8 at 70 °C for 20 min does not effect phenyl transfer. Instead, ethylene is displaced to produce $\text{Rh}(\eta^6\text{-C}_6\text{H}_5\text{BPh}_3)(\eta^2\text{-triphos})$ (IV). The identity of this



compound follows from its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, which shows a doublet at 27 ppm ($J_{\text{PRh}} = 195 \text{ Hz}$, 2 P) and a singlet near the chemical shift of free triphos at -30.4 ppm (1 P), characteristic of a pendant phosphine arm. The ^1H NMR spectrum shows two high-field resonances at 5.15 and 5.4 ppm for the η^6 -bound phenyl group, which compares well with similar compounds reported previously.⁶

Reactivity of $\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$ (I) toward H_2 . In an effort to better understand the mechanism of reactions of I, its reaction with H_2 was explored. When a solution of I is exposed to H_2 for 12 h, ^1H NMR spectroscopy reveals a quantitative conversion of I to $\text{Rh}(\text{H})_2\text{Cl}(\text{triphos})$ and ethane.

While $\text{Rh}(\text{H})_2\text{Cl}(\text{triphos})$ (V) is produced quantitatively from I, we find that a superior synthesis (i.e., higher yield) is the one-pot approach outlined in eq 3. The ^1H NMR



spectrum of the product displays a second-order multiplet for the hydride ligands, a single triphos methyl resonance, and three inequivalent sets of methylene resonances for the backbone of the triphos ligand. The ^{31}P NMR spectrum for V (Figure 3) is quite definitive, showing an A_2MX

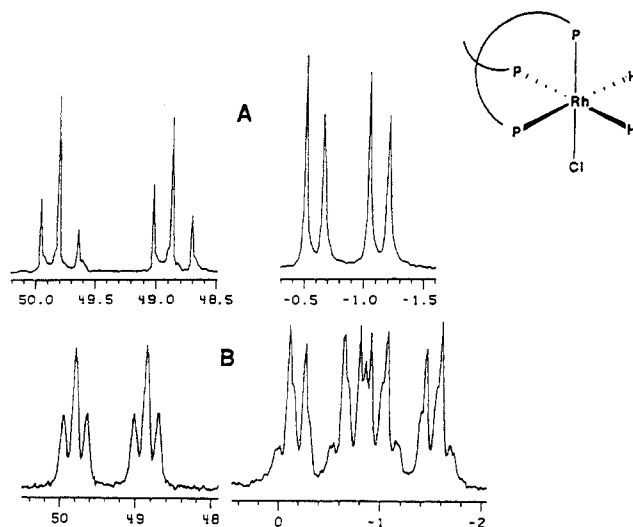
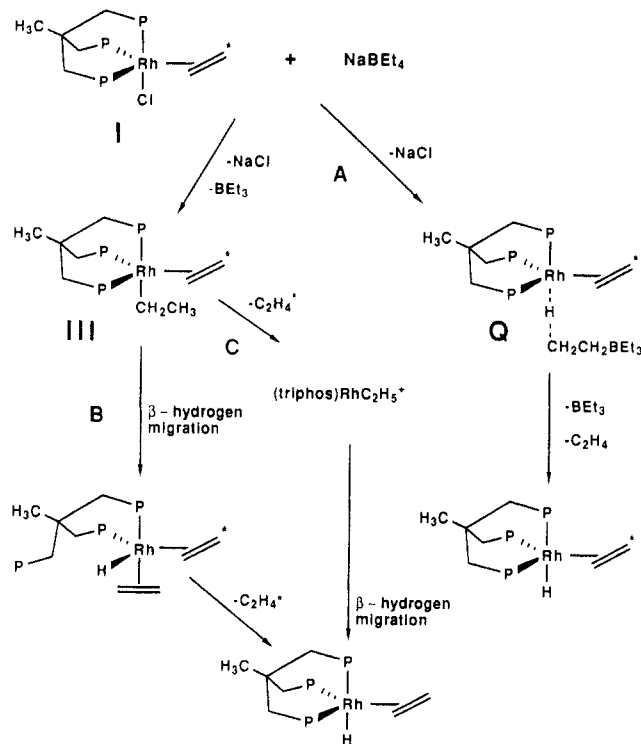


Figure 3. ^{31}P NMR spectra for $\text{Rh}(\text{H})_2\text{Cl}(\text{triphos})$ in CH_2Cl_2 at 22 °C: (A) ^1H -decoupled spectrum; (B) selectively decoupled (0–10 ppm) spectrum.

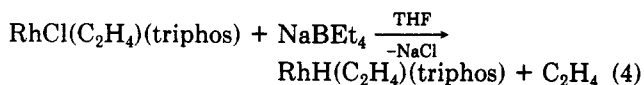
Scheme I



spin system. When the hydride ligands are allowed to couple in the ^{31}P NMR spectrum, the P_A resonance is only slightly broadened, while the P_M resonance becomes an elaborate second-order multiplet. These results are consistent with magnetically inequivalent trans hydride and phosphine ligands.

Discussion

Reaction of $\text{RhCl}(\text{C}_2\text{H}_4)(\text{triphos})$ with NaBEt_4 . The surprising production of a hydride compound from the reaction between I and NaBEt_4 (eq 4) could occur by two



different mechanisms (Scheme I): (1) ethyl group transfer from BEt_4^- or (2) hydride abstraction from an ethyl group of BEt_4^- (path A). The latter reaction, while unconven-

examples of this "arm-off" process. That such a process is tenable is further supported by our isolation of Rh-(η^6 -PhBPh₃)(η^2 -triphos) as a ground-state "arm-off" species. Finally, the fact that RhX(C₂H₄)(triphos) is fluxional (by an "arm-off" mechanism) for X = Cl but static for X = H, C₂H₅ indicates that the resulting 16-electron η^2 -triphos species are stabilized by π -donation from the chloride ligand. The broad conclusion from all of these results is the reminder that the chelate effect enhances thermodynamic stability of coordinate bonds but

that such bonds may nevertheless be kinetically labile.¹⁵

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(15) After this work was submitted for publication, we were informed of a full paper in press expanding upon the work in ref 8. See: Bianchini, C.; Frediani, P.; Meli, A.; Peruzzini, M.; Ramirez, J. A.; Vissa, F. *Organometallics* 1990, 9, 226.

A New Family of (Arene)osmium(0) and -osmium(II) Complexes

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The arene carbonyl complex [(mes)OsCl₂(CO)] (3), which is obtained from [(mes)OsCl₂]_n (1) and CO in CH₂Cl₂, reacts with CH₃MgI and CH₃Li to give the monomethyl- and dimethylosmium(II) compounds [(mes)OsCH₃(CO)I] (4) and [(mes)Os(CH₃)₂(CO)] (5) in good yields. Treatment of 5 with [CPh₃]PF₆ leads to the formation of [(mes)OsH(C₂H₄)(CO)]PF₆ (6), which by deprotonation with NaH gives the osmium(0) complex [(mes)Os(C₂H₄)(CO)] (7). With [(mes)Os(CD₃)₂(CO)] (5-*d*₆) as starting material, the deuterated compound [(mes)Os(C₂D₄)(CO)] (7-*d*₄) has similarly been prepared, which proves that neither the solvent nor the particular reagent is involved in the two reaction steps. The synthesis of the dihydrido complexes [(mes)OsH₂(CO)] (10), [(C₆H₆)OsH₂(CO)] (13), and [(C₆Me₆)RuH₂(CO)] (14) has been achieved by treatment of the corresponding dichloro or diiodo derivatives with sodium in liquid ammonia in presence of *tert*-butyl alcohol as a proton source. Reaction of 10 with HBF₄ in CH₂Cl₂ produces the BF₄ salt of the [(mes)-OsH₃(CO)]⁺ cation (15), which reacts with CO to give [(mes)OsH(CO)₂]BF₄ (16). Deprotonation of 16 with NaH or NaNH₂ in THF leads to the formation of the dicarbonyl compound [(mes)Os(CO)₂] (17). The related olefin osmium(0) complexes [(mes)Os(C₂H₄)₂] (18) and [(mes)Os(C₇H₈)] (19) have been prepared from 1 and ethylene or norbornadiene, respectively, in presence of Na₂CO₃ and ethanol. By use of 3 and 4 as starting materials, the monocarbonylosmium(II) compounds [(mes)OsH(CO)Cl] (9) and [(mes)-OsCH₃(CO)H] (8) have also been synthesized.

Introduction

Following our original work on (arene)ruthenium(0) and -osmium(0) complexes of the general type [(C₆R₆)ML₂] (L = PR₃ or P(OR)₃) and [(C₆R₆)M(PR₃)L] (L = P(OR)₃, CO, C₂H₄, etc.), which proved to be strong nucleophiles,^{1,2} we have recently also prepared a variety of dihydrido- and dialkylruthenium(II) and -osmium(II) compounds [(C₆R₆)MX₂(PR₃)] (X = H, alkyl)^{3,4} to compare their reactivities with those of the corresponding metal(0) derivatives. During attempts to insert unsaturated molecules such as CO, CO₂, or C₂H₄ into the Ru-H bonds of the

(arene)ruthenium complexes [(C₆R₆)RuH₂(PR₃)] (PR₃ = PMe₃, *P-i*-Pr₃) in benzene or toluene as the solvent, we observed that under photolytic conditions H₂ is eliminated and the aryl hydrido compounds [(C₆R₆)RuH(C₆H₄Y)(PR₃)] (Y = H, Me) are formed.⁵ This result was reminiscent of the pioneering work by Bergman⁶ and Graham,⁷ who showed that 16-electron fragments of the general type [(C₅R₅)Ir(L)] (R = H, Me; L = PR₃, CO) are able to react with aromatic as well as with aliphatic hydrocarbons by oxidative addition. As according to Bergman there were no severe conditions necessary to abstract H₂ from [(C₅Me₅)IrH₂(PMe₃)]⁸ and as this result was in full agreement with our own studies on the behavior of [(C₆R₆)RuH₂(PR₃)]⁵ we were very surprised to learn that both under thermal and photolytic conditions the analogous osmium dihydride [(C₆H₆)OsH₂(*P-i*-Pr₃)] was completely inert. Even prolonged irradiation with UV light of 2537 Å in benzene or toluene did not lead to the for-

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