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

(p) Synthesis of $[(C_6H_5)_2B(OH)(pz)W(\eta^3\text{-}NNCHCHCHCH_2CHCHCHCH_3)(CO)_2]$ (7b). $Na(C_6H_5)_2B(pz)_2$ (0.16 g, 0.49 mmol) was added to $W(CO)_2(CH_3CN)_2(\eta^3\text{-}C_5H_7)Br$ (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 $[(C_6H_5)_2B(pz)_2W(CO)_2(\eta^3\text{-}C_5H_7)]$ (**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^6), 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): ν(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), $J_{1\text{-}CH_3}$ = 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:

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

k' = Boltzmann constant, $\hbar$ = 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 Kα 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 Kα radiation, and the structures were solved by the Patterson method. All data reduction and structure refinement were performed with the NRCCSDP 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 $RhCl(C_2H_4)$(triphos) (I), where triphos is $MeC(CH_2PPh_2)_3$, gives $RhH(C_2H_4)$(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 $RhCl(^{13}C_2H_4)$(triphos) or $Rh(H)_2Cl$(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 $RhX(C_2H_4)$(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 $RhPh(C_2H_4)$(triphos).

Introduction

We have reported recently[1] 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 implicated 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(triphos)[4] were pre-

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pared by literature methods. $^{13}C_2H_4$ 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.

RhCl(C_2H_4)(triphos). To [Rh(C_2H_4)$_2$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, RhCl(C_2H_4)(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 RhCl(C_2H_4)(triphos)[5] (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). ^{1}H NMR (360 MHz, CD_2Cl_2, 22 °C): δ 1.48 (unresolved q, J_{PH} = 2.1 Hz, CCH_3), 2.31 (v br s, $-CH_2P$), 1.7 (br d, J_{HH} = 10.59 Hz, C_2H_4), 3.12 (br d, J_{HH} = 9.85 Hz, C_2H_4), 6.5–8.0 (br, $-PPh_2$). ^{1}H 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_{PH} = 7.9 Hz, $-CH_2P$, 2 H), 2.19 (m, $-CH_2P$, 4 H), 3.0 (br m, C_2H_4, 2 H), 7.9–6.7 ($-P(C_6H_5)_2$). $^{31}P\{^1H\}$ NMR (146 MHz, CD_2Cl_2, −30 °C): −11 (d of d, J_{PRh} = 111 Hz, J_{PP} = 28 Hz), 46 (d of t, J_{PRh} = 132 Hz, J_{PP} = 28 Hz).

Rh(η^2-triphos)(η^6-PhBPh$_3$). RhCl(C_2H_4)(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. ^{1}H NMR (500 MHz, THF-d_8, 22 °C): δ 2.09 (br s, CCH_3), 2.52–2.4 (3 overlapping multiplets, $-CH_2P$, 6 H), 5.15 (br unresolved t, meta H's of η^6-PhBPh$_3$), 5.40 (v br, ortho H's of η^6-PhBPh$_3$), 7.7–6.7 (para H's of η^6-PhBPh$_3$, $-BPh_3$, and $P(C_6H_5)_2$). $^{31}P\{^1H\}$ NMR (146 MHz, THF-d_8, 22 °C): δ 27.5 (d, J_{PRh} = 195 Hz, 2 P), −30.4 (s, 1 P). Proton chemical shifts for the η^6-PhBPh$_3$ ligand were assigned by comparison to previously reported[6] values for similar compounds.

Reaction of RhCl(C_2H_4)(triphos) with $^{13}C_2H_4$. A sample of RhCl(C_2H_4)(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 $^{13}C_2H_4$ (99 atom %) and flame-sealed. The tube was then shaken for 4 h. $^{13}C\{^1H\}$ NMR (90.8 MHz, CD_2Cl_2, 22 °C): 43.24 ppm (br 5-line multiplet, 2nd order). $^{31}P\{^1H\}$ NMR (146 MHz, −20 °C): δ −11.25 (d of d of d, J_{PRh} = 111 Hz, $J_{CP} \cong J_{PP} \cong$ 25.8 Hz, 2 P), 46.15 (d of t, J_{PRh} = 132, J_{PP} = 27.7 Hz, 1 P).

Rh(H)$_2$Cl(triphos) from RhCl(C_2H_4)(triphos) and H_2. A saturated C_6D_6 (0.4 mL) solution of RhCl(C_2H_4)(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. ^{1}H NMR spectroscopy showed C_2H_6 (δ 0.79) and quantitative conversion of the rhodium to RhH$_2$Cl(triphos), which was identified by comparison to an authentic sample.

Rh(H)$_2$Cl(triphos). [Rh(COD)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, RhH$_2$Cl(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 RhH$_2$Cl(triphos) (1.46 g; 95% yield) as an off-white solid. ^{1}H NMR (360 MHz, CD_2Cl_2, 22 °C): δ −7.34 (2nd-order m), 1.52 (unresolved q, J_{PH} = 2.52 Hz, CCH_3), 2.20 (d, J_{PH} = 10.1 Hz, 2 H, $-CH_2P$ trans to Cl), 2.33 (m, 4 H, ($-CH_2P$)$_2$ trans to H), 7.8–6.95 ($P(C_6H_5)_2$). $^{31}P\{^1H\}$ NMR (146 MHz, CD_2Cl_2, 22 °C): δ −0.83 (d of d, J_{PRh} = 79 Hz, J_{PP} = 21 Hz, 2 P), 49.3 (d of t, J_{PRh} = 136 Hz, 1 P).[7]

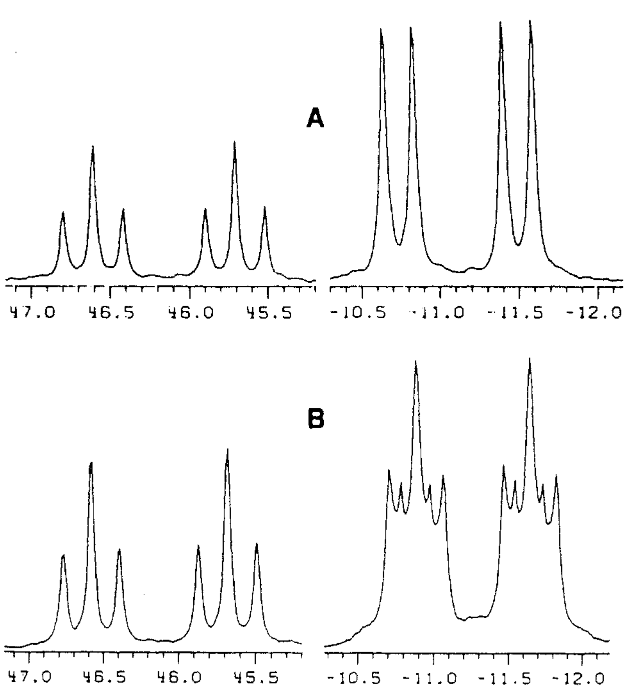

Figure 1. $^{31}P\{^1H\}$ NMR spectra of RhCl(C_2H_4)(triphos) in CH_2Cl_2 at −30 °C: (A) C_2H_4 = $^{12}C_2H_4$ (I); (B) C_2H_4 = $^{13}C_2H_4$ (I*).

RhH(C_2H_4)(triphos) from RhCl(C_2H_4)(triphos) and NaBEt$_4$. To RhCl(C_2H_4)(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 RhH(C_2H_4)(triphos) as a pale orange powder. This material was collected by filtration and dried in vacuo. ^{1}H NMR (500 MHz, C_6D_6, 22 °C): −10.95 (~d of t of d, $J_{PH_{trans}}$ = 174 Hz, $J_{H_{cis}} \cong J_{HRh} \cong$ 13.5 Hz), 1.21 (br s, CCH_3), 2.06 (br s, $-CH_2P$, 2 H), 2.21 (m, $-CH_2P$, 4 H), 2.40 (br s, C_2H_4, 2 H), 3.88 (br m, C_2H_4, 2 H), 7.88–6.67 ($P(C_6H_5)_2$). $^{31}P\{^1H\}$ NMR (146 MHz, THF, 22 °C): δ 15.5 (d of t, J_{PRh} = 83 Hz, J_{PP} = 33 Hz, 1 P), 18.9 (d of d, J_{PRh} = 132 Hz, J_{PP} = 33 Hz, 2 P). Also present in the ^{31}P NMR spectrum were very minor resonances at 10 ppm, identified as RhEt(C_2H_4)(triphos) by comparison to the literature.[8]

RhCl($^{13}C_2H_4$)(triphos) and NaBEt$_4$. A steady stream of N_2 was bubbled through a THF (10 mL) solution of RhCl($^{13}C_2H_4$)(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 $^{31}P\{^1H\}$ NMR spectrum indicated only the production of RhH($^{12}C_2H_4$)(triphos). The $^{13}C\{^1H\}$ 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 RhCl(C_2H_4)(triphos) (I). When 2 equiv of triphos is reacted at 0 °C and under an atmosphere of ethylene with [Rh(C_2H_4)$_2$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

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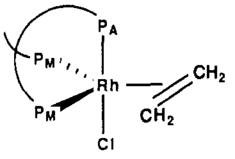

I

ethylene carbon atoms are coplanar. The ^{1}H 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}P{^{1}H} NMR spectra (Figure 1) of I and its ^{13}C-labeled analogue $\mathrm{RhCl(^{13}C_2H_4)(triphos)}$ (I*) reveals that, in both molecules, P_A remains a doublet of triplets (δ 46, $J_{RhP} = 132$ Hz, $J_{PP} = 28$ 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}P{^{1}H} NMR spectrum of I shows a simple doublet of doublets for the P_M nuclei, while I* shows an additional doublet splitting with $J_{PC} \cong 25.8$ Hz. The ^{13}C{^{1}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-termperature* ^{31}P{^{1}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 ^{1}H 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 ^{1}H 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 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.

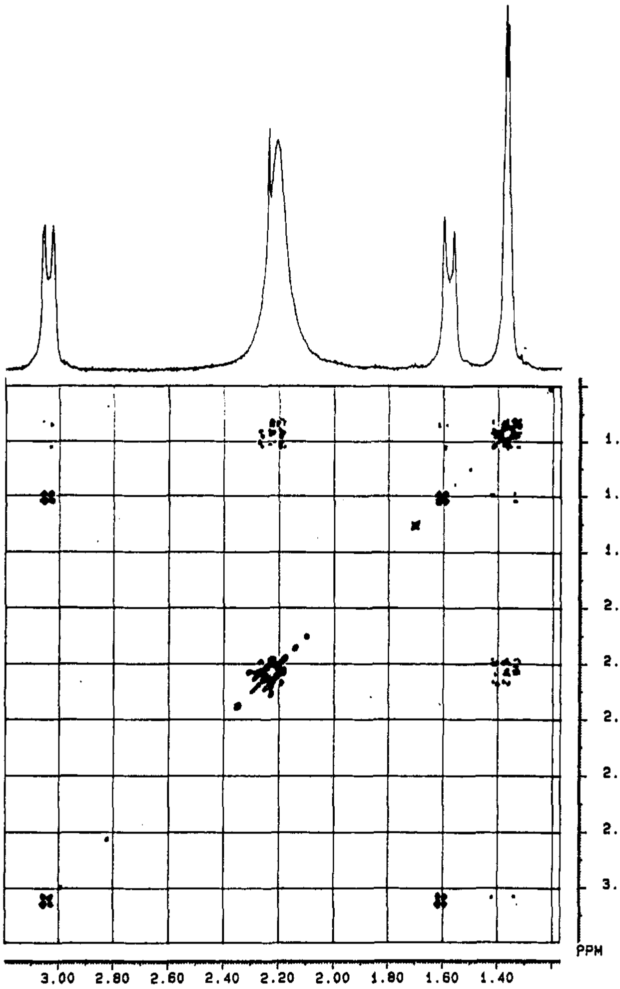

Figure 2. Two-dimensional NOESY experiment for $\mathrm{RhCl(C_2H_4)(triphos)}$ in $\mathrm{CD_2Cl_2}$ at 35 °C and 500 MHz.

Reactivity of $\mathbf{RhCl(C_2H_4)(triphos)}$ with $\mathbf{NaBEt_4}$. Treatment of $\mathrm{RhCl(C_2H_4)(triphos)}$ with $\mathrm{NaBEt_4}$ (eq 1) provides a new route to the known hydrido ethylene complex $\mathrm{RhH(C_2H_4)(triphos)}$[5] (II). Also observed during the course of this reaction was the evolution of gas, which has been identified as C_2H_4 by ^{1}H NMR spectroscopy (δ 5.33, THF-d_8).

$$\mathrm{RhCl(C_2H_4)(triphos) + NaBEt_4 \xrightarrow[-C_2H_4]{THF} RhH(C_2H_4)(triphos)} \quad (1)$$

The ^{31}P{^{1}H} NMR spectrum of II at room temperature shows an AM_2X pattern of a stereochemically rigid species. The ^{1}H 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 $\mathrm{Rh(C_2H_5)(C_2H_4)(triphos)}$ (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-

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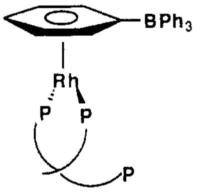
[9] The large separation of the vinylic chemical shifts would cause a high coalescence temperature in the ^{1}H NMR spectrum.

$$\underset{\text{II}}{\mathrm{RhH(C_2H_4)(triphos)}} + \mathrm{C_2H_4} \rightleftarrows \underset{\text{III}}{\mathrm{Rh(C_2H_5)(C_2H_4)(triphos)}} \quad (2)$$

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, is was necessary to label the ethylene group in compound I. Fortunately, I readily exchanges with free ethylene to generate $RhCl(^{13}C_2H_4)$(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 $^{12}C_2H_4$), suggesting they were the resonances for $Rh(Et)(^{13}C_2H_4)$(triphos) with unresolved ^{13}C coupling to phosphorus.

Reactivity of $RhCl(C_2H_4)$(triphos) with $NaBPh_4$. We have investigated $RhCl(C_2H_4)$(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 $Rh(\eta^6\text{-}C_6H_5BPh_3)(\eta^2\text{-triphos})$ (IV). The identity of this compound follows from its $^{31}P\{^1H\}$ NMR spectrum, which shows a doublet at 27 ppm (J_{PRh} = 195 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]



IV

Reactivity of $RhCl(C_2H_4)$(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 $Rh(H)_2Cl$(triphos) and ethane.

While $Rh(H)_2Cl$(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 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.

$$[\mathrm{Rh(COD)Cl}]_2 + 2\mathrm{triphos} \xrightarrow[\text{toluene, 36 h}]{\mathrm{H_2},\ 2000\ \text{psi}} \underset{\text{V}}{\mathrm{Rh(H)_2Cl(triphos)}} \quad (3)$$

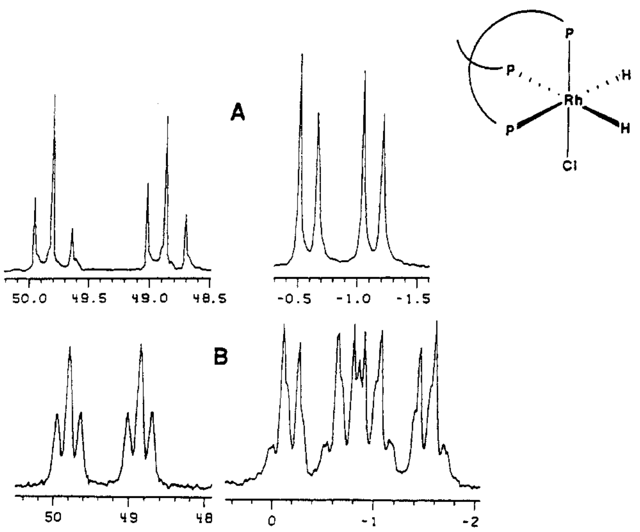
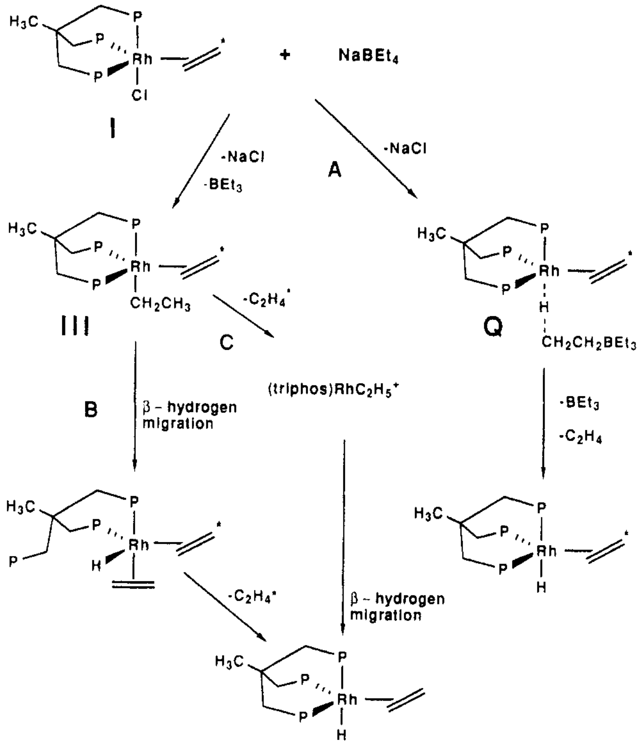


Figure 3. ^{31}P NMR spectra for $Rh(H)_2Cl$(triphos) in CH_2Cl_2 at 22 °C: (A) ^1H-decoupled spectrum; (B) selectively decoupled (0–10 ppm) spectrum.

Scheme I



Discussion

Reaction of $RhCl(C_2H_4)$(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-

$$\mathrm{RhCl(C_2H_4)(triphos)} + \mathrm{NaBEt_4} \xrightarrow[-\mathrm{NaCl}]{\mathrm{THF}} \mathrm{RhH(C_2H_4)(triphos)} + \mathrm{C_2H_4} \quad (4)$$

tional, could occur within the ion pair Q of Scheme I and bears a formal similarity to the Hofmann elimination (eq 5, B being a Brønsted base). Evidence for the ethyl

$$R_3NC_2H_5^+ + B^- \rightarrow R_3N + BH + C_2H_4 \quad (5)$$

transfer process was found in the ^{31}P NMR spectrum of reaction solutions, which always displayed residual resonances for the *intermediate* ethyl ethylene compound III. However, this was not sufficient support for this mechanism, since we and others[8] have shown that II readily reacts with free ethylene to generate III. Strong support for the ethyl transfer mechanism was obtained by distinguishing the two ethylenes by starting with RhCl($^{13}C_2H_4$)(triphos). A hydride transfer process (path A) should produce RhH($^{13}C_2H_4$)(triphos). None of this product is observed. In the operative ethyl transfer process, two options remain. The reaction *could* proceed through the ethyl ethylene compound III to an intermediate bis(ethylene) hydride complex. This intermediate (path B) might lose $^{12}C_2H_4$ or $^{13}C_2H_4$ with comparable facility, to yield a 50:50 mixture of labeled and unlabeled II. The fact that reaction between I* and NaBEt$_4$ yields exclusively the unlabeled compound II verifies not only that the ethylene ligand must be derived from the BEt_4^- anion but also that the two C_2 fragments remain inequivalent throughout the mechanism. This is best accommodated by path C, where (triphos)RhC$_2$H$_5^+$ could be solvated (THF) or could contain a β-agostic ethyl group.

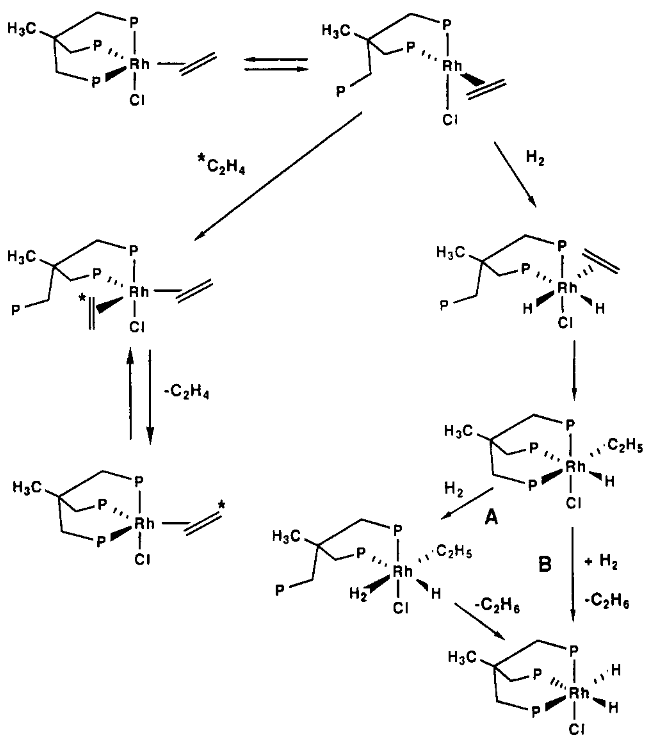
Comparison to NaBPh$_4$. While phenyl transfer from BPh_4^- to a transition metal has been observed often[10] and alkyl transfer from tetraalkylborates has been observed for lead systems,[11] this appears to be the first example of alkyl group transfer from a BEt_4^- anion to a transition metal.[12] It is therefore surprising that the reaction which has been documented on several occasions for transition-metal systems, phenyl group transfer from BPh_4^- (eq 6),[10b]

$$[(CpRu(CO)_2)_2Cl]PF_6 + NaBPh_4 \xrightarrow{\text{room temp}} CpRu(CO)_2Ph + CpRu(CO)_2Cl \quad (6)$$

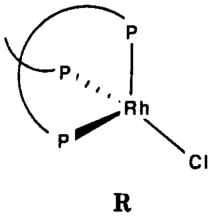
does not occur for RhCl(C$_2$H$_4$)(triphos). Instead, the zwitterionic complex Rh(η^2-triphos)(η^6-PhBPh$_3$) (IV) is formed.[13] Analogous η^6-BPh_4^- compounds of rhodium are known.[6] Rh[P(OMe)$_3$]$_2$(BPh$_4$) has been structurally characterized.[6b] Although IV would seem to be a reasonable intermediate along the reaction pathway to phenyl transfer,[14] we have not been able to induce phenyl transfer in this species. One possible explanation is that phenyl transfer would yield a pseudotetrahedral phenyl complex prior to recoordination of the displaced ethylene. Clearly, the energetics of this process are unfavorable.

Synthesis and Reactivity of RhCl(C$_2$H$_4$)(triphos). Initial attempts to synthesize RhCl(C$_2$H$_4$)(triphos) from [Rh(C$_2$H$_4$)$_2$Cl]$_2$ and triphos in toluene gave vigorous gas evolution and insoluble products. However, the synthesis proceeds in high yield at 0 °C under an atmosphere of ethylene.

Scheme II



We propose that the facile (4 h, 25 °C, 1 atm) exchange of $^{13}C_2H_4$ with RhCl(C$_2$H$_4$)(triphos) proceeds through the mechanism outlined on the left-hand side of Scheme II, in which I is in equilibrium with a four-coordinate, square-planar Rh^I complex generated through dissociation of one arm of the phosphine. This intermediate is then trapped by a second molecule of ethylene, at which point the original ethylene ligand could dissociate and generate I*. Support for the occurrence of an "arm-off" preequilibrium comes from the facile reaction of I with H$_2$. When I is placed under an atmosphere of H$_2$, Rh(H)$_2$Cl(triphos) (V) and ethane are the only observed products. This can proceed as outlined on the right-hand side of Scheme II. The final step may actually be preceded by the formation of an η^2-H$_2$ complex (path A), thereby avoiding the need to generate a pseudotetrahedral Rh^I intermediate (R)



R

following reductive elimination of ethane (path B). The synthesis of Rh(H)$_2$Cl(triphos) from [Rh(COD)Cl]$_2$ also involves hydrogenation of coordinated olefin (to cyclooctane).

The arm-off preequilibrium at the top of Scheme II also provides an initial step for the ethyl transfer reaction of Scheme I, where the ethyl anion transfer can take place to the unsaturated species RhCl(C$_2$H$_4$)(η^2-triphos).

Conclusion

This work has implicated "arm-off" processes of the η^3-MeC(CH$_2$PPh$_2$)$_3$ ligand in both fluxionality and net reactions (C$_2$H$_4$ exchange, hydrogenolysis, and "Et$^-$" transfer). We have reported elsewhere[1] numerous other

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[10] (a) Clark, H. C.; Dixon, K. R. *J. Am. Chem. Soc.* **1969**, *91*, 596. (b) Haines, R. J.; du Preez, A. L. *J. Chem. Soc., Dalton Trans.* **1972**, 944. (c) Sacconi, L.; Dapporto, P.; Stoppioni, P. *Inorg. Chem.* **1976**, *15*, 325. (d) Albano, P.; Aresta, M.; Manasser, M. *Inorg. Chem.* **1980**, *19*, 1069.

[11] Honeycutt, J. B.; Riddle, J. M. *J. Am. Chem. Soc.* **1961**, *83*, 369.

[12] For the most recent contribution on phenyl transfer, see: Siegmann, K.; Pregosin, P.; Venanzi, L. M. *Organometallics* **1989**, *8*, 2659.

[13] This compound has a J_{PRh} value that is very large compared to those of a wide range of Rh(I) complexes (compare, for example, RhH(C$_2$H$_4$)(triphos) at 83 and 132 Hz). However, a very similar species, the Rh(C$_6$H$_6$)(*trans*-1,2-bis((diphenylphosphino)methyl)cyclobutane) cation, shows J_{PRh} = 201 Hz. See: Townsend, J. M.; Blount, J. F. *Inorg. Chem.* **1981**, *20*, 269.

[14] Precoordination of BPh_4^- in Rh(diphos)(η-BPh$_4$) is proposed to allow for the phenyl migration at 70 °C to give Rh(C$_6$H$_5$)(diphos).[10d]

examples of this "arm-off" process. That such a process is tenable is further supported by our isolation of Rh(η^6-PhBPh$_3$)(η^2-triphos) as a ground-state "arm-off" species. Finally, the fact that RhX(C$_2$H$_4$)(triphos) is fluxional (by an "arm-off" mechanism) for X = Cl but static for X = H, C$_2$H$_5$ 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)OsCl$_2$(CO)] (**3**), which is obtained from [(mes)OsCl$_2$]$_n$ (**1**) and CO in CH$_2$Cl$_2$, reacts with CH$_3$MgI and CH$_3$Li to give the monomethyl- and dimethylosmium(II) compounds [(mes)OsCH$_3$(CO)I] (**4**) and [(mes)Os(CH$_3$)$_2$(CO)] (**5**) in good yields. Treatment of **5** with [CPh$_3$]PF$_6$ leads to the formation of [(mes)OsH(C$_2$H$_4$)(CO)]PF$_6$ (**6**), which by deprotonation with NaH gives the osmium(0) complex [(mes)Os(C$_2$H$_4$)(CO)] (**7**). With [(mes)Os(CD$_3$)$_2$(CO)] (**5**-d_6) as starting material, the deuterated compound [(mes)Os(C$_2$D$_4$)(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)OsH$_2$(CO)] (**10**), [(C$_6$H$_6$)OsH$_2$(CO)] (**13**), and [(C$_6$Me$_6$)RuH$_2$(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 HBF$_4$ in CH$_2$Cl$_2$ produces the BF$_4$ salt of the [(mes)OsH$_3$(CO)]$^+$ cation (**15**), which reacts with CO to give [(mes)OsH(CO)$_2$]BF$_4$ (**16**). Deprotonation of **16** with NaH or NaNH$_2$ in THF leads to the formation of the dicarbonyl compound [(mes)Os(CO)$_2$] (**17**). The related olefin osmium(0) complexes [(mes)Os(C$_2$H$_4$)$_2$] (**18**) and [(mes)Os(C$_7$H$_8$)] (**19**) have been prepared from **1** and ethylene or norbornadiene, respectively, in presence of Na$_2$CO$_3$ and ethanol. By use of **3** and **4** as starting materials, the monocarbonylosmium(II) compounds [(mes)OsH(CO)Cl] (**9**) and [(mes)OsCH$_3$(CO)H] (**8**) have also been synthesized.

Introduction

Following our original work on (arene)ruthenium(0) and -osmium(0) complexes of the general type [(C$_6$R$_6$)ML$_2$] (L = PR$_3$ or P(OR)$_3$) and [(C$_6$R$_6$)M(PR$_3$)L] (L = P(OR)$_3$, CO, C$_2$H$_4$, 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 [(C$_6$R$_6$)MX$_2$(PR$_3$)] (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, CO$_2$, or C$_2$H$_4$ into the Ru–H bonds of the (arene)ruthenium complexes [(C$_6$R$_6$)RuH$_2$(PR$_3$)] (PR$_3$ = PMe$_3$, P-*i*-Pr$_3$) in benzene or toluene as the solvent, we observed that under photolytic conditions H$_2$ is eliminated and the aryl hydrido compounds [(C$_6$R$_6$)RuH(C$_6$H$_4$Y)(PR$_3$)] (Y = H, Me) are formed.[5] This result was reminiscent of the pioneering work by Bergman[6] and Graham,[7] who showed that 16-electron fragments of the general type [(C$_5$R$_5$)Ir(L)] (R = H, Me; L = PR$_3$, 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 H$_2$ from [(C$_5$Me$_5$)IrH$_2$(PMe$_3$)][8] and as this result was in full agreement with our own studies on the behavior of [(C$_6$R$_6$)RuH$_2$(PR$_3$)],[5] we were very surprised to learn that both under thermal and photolytic conditions the analogous osmium dihydride [(C$_6$H$_6$)OsH$_2$(P-*i*-Pr$_3$)] 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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(1) Werner, H.; Werner, R. *Angew. Chem.* **1978**, *90*, 721; *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 683. (b) Werner, H.; Werner, R. *J. Organomet. Chem.* **1979**, *174*, C67. (c) Werner, H.; Werner, R. *J. Organomet. Chem.* **1980**, *194*, C7. (d) Werner, R.; Werner, H. *Chem. Ber.* **1982**, *115*, 3781. (e) Werner, R.; Werner, H. *Chem. Ber.* **1983**, *116*, 2074. (f) Werner, H.; Roder, K. *J. Organomet. Chem.* **1989**, *367*, 339.

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