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Insertions of electrophiles into metal hydride bonds. Reactions of $(C_5Me_5)Rh(PMe_3)H_2$ with activated alkynes to produce η^2 -alkene complexes

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Abstract

The dihydride complex $(C_5Me_5)Rh(PMe_3)H_2$ (1) reacts with the electron deficient alkynes phenylacetylene (PhC=CH), diphenylacetylene (PhC=CPh), methyl propiolate (HC=CE, E = CO_2Me), dimethylacetylenedicarboxylate (EC=CE, DMAD) and hexafluoro-2-butyne (F₃CC=CCF₃) to produce in all cases η^2 -olefin complexes of the hydrogenated alkyne (**2a**–**j**). The complexes (C_5Me_5)Rh(PMe_3)(η^2 -methacrylate) (**2a**, **2b**), (C_5Me_5)Rh(PMe_3)(η^2 -styrene) (**2c**, **2d**) and (C_5Me_5)Rh(PMe_3)(η^2 -cis-stilbene) (**2e**, **2f**) exist as pairs of rotamers that do not interconvert. The reaction of 1 with PhC=CPh also produces (C_5Me_5)Rh(PMe_3)(η^2 -transstilbene) (**2g**) at higher temperatures. Insertion of F₃CC=CCF₃ into 1 occurs stereoselectively to yield (C_5Me_5)Rh(PMe_3)(η^2 -transhexafluoro-2-butene) (**2h**). A mixture of *cis*- and *trans*- insertion products is observed in the reaction of 1 with EC=CE to yield (C_5Me_5)Rh(PMe_3)(η^2 -fumarate) (**2i**) and (C_5Me_5)Rh(PMe_3)(η^2 -maleate) (**2j**) complexes. A crossover experiment using 1 and 1-d₂ with DMAD shows only d₀ and d₂ η^2 -olefin products, demonstrating that both hydrogens come from the same molecule of 1. A second crossover experiment using (C_5Me_5)Rh(PMe_3)(η^2 -fumarate)-d₂ and free dimethylfumarate shows no evidence for incorporation of the free olefin. The vinyl hydride intermediates (C_5Me_5)Rh(PMe_3)(CR=CHR)H are observed below -20° C for R = E and at room temperature for R = CF₃. Cyclic voltammetry of the metal complex 1 and of the substituted alkynes shows irreversible behavior and half-wave redox potentials $E_{1/2}$ are reported. CHCl₃ quenching of the vinyl hydride products from the reaction of 1 with F₃CC=CCF₃ yields crystals of the complex (C_5Me_5)Rh(PMe_3)[*trans*-C(CF₃)=CH(CF₃)]Cl (**5a**) which was established as the *trans* complex by X-ray crystallography. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Rhodium complexes; Hydride complexes; Alkyne complexes; Insertion

1. Introduction

The insertion of unsaturated organic substrates into metal hydride bonds is one of the most fundamental steps in both stoichiometric and catalytic organometallic reactions such as hydrogenation, oligomerization, and polymerization [1]. Olefin insertion into metal hydrides has been well investigated in terms of its relationship to Ziegler–Natta polymerization [2]. The reactions of alkynes with metal hydride complexes have also been well studied, though no general trend has been proposed to explain the assortment of regiochemical and stereochemical outcomes for different systems. Several

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mechanisms have been proposed to account for these experimental results.

Many examples exist of alkyne insertions into metal hydride complexes to give *cis*-products only [3]. Most authors agree that formation of *cis*-products is likely to arise from the four-centered transition state depicted in Eq. (1).

$$\begin{array}{c} \mathsf{R}-\mathsf{C}\equiv\mathsf{C}-\mathsf{R} \\ + \\ \mathsf{L}_{\mathsf{n}}\mathsf{M}-\mathsf{H} \end{array} \longrightarrow \begin{bmatrix} \mathsf{R} \\ \vdots \\ \mathsf{L}_{\mathsf{n}}\mathsf{M}-\cdots+\mathsf{H} \end{bmatrix}^{\mathsf{T}} \xrightarrow{\mathsf{R}} \\ \begin{array}{c} \mathsf{R} \\ \mathsf{L}_{\mathsf{n}}\mathsf{M} \end{array} \xrightarrow{\mathsf{R}} \\ \begin{array}{c} \mathsf{R} \\ \mathsf{L}_{\mathsf{n}}\mathsf{M} \end{array} \xrightarrow{\mathsf{R}} \\ \begin{array}{c} \mathsf{R} \\ \mathsf{R} \\ \mathsf{L}_{\mathsf{n}}\mathsf{M} \end{array} \xrightarrow{\mathsf{R}} \\ \begin{array}{c} \mathsf{R} \\ \mathsf$$

Stereoselective formation of *trans*-insertion products is less common and several different mechanisms have been proposed to account for this phenomenon [4]. Other studies have shown that both *cis*- and *trans*products can be formed depending on the substrate

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used and the reaction conditions [5]. A few reports have observed the interconversion of the vinyl hydride intermediates that ostensibly determine the final stereochemical outcome of the reaction [6], and one has noted isomerization of an η^2 -olefin complex [7]. An additional pathway of terminal alkyne C–H bond activation has also been seen [8].

Disparate mechanistic proposals have been offered to account for competitive formation and/or isomerization of cis- and trans-vinyl complexes, some of which include electron transfer [5c] phosphine-promoted interconversion [6c], and concerted trans-insertion [5a]. Few reasonable mechanisms have been proposed to account for the E/Z interconversion of η^2 -olefin complexes, apart from photochemically induced isomerization. In addition, the reactions of terminal and unsymmetrical alkynes with metal hydride complexes show no consistent trends concerning factors that determine the ultimate regiochemistry of the insertion. In the case of terminal alkynes, insertion can take place to yield either α - or β - substituted vinyl complexes, and both regiochemical outcomes have been observed [9]. A few papers have also reported subsequent insertions of alkynes into the initially formed vinyl complexes to yield butadienyl or even hexatrienyl fragments [10].

In this section are reported the reactions of the dihydride complex $(C_5Me_5)Rh(PMe_3)H_2$ (1) with the five electron-deficient alkynes phenylacetylene (PhC=CH), diphenylacetylene (PhC=CPh), methyl propiolate (HC=CE, E = CO_2Me), dimethylacetylenedicarboxylate (EC=CE, DMAD) and hexafluoro-2-butyne (F_3CC=CCF_3). In all cases the final products were η^2 -alkene complexes of the hydrogenated alkyne. Intermediate vinyl hydride complexes could be observed in the reactions of 1 with dimethylacetylenedicarboxylate and hexafluoro-2-butyne. Mechanistic implications based on kinetic and crossover experiments and electrochemical measurements are discussed.

2. Results

2.1. Reactions of 1 with alkynes

The reactions of 1 with phenylacetylene and with methyl propiolate gave similar results Eq. (2).



Addition of excess HC=CE (E = CO_2Me) to a benzene solution of 1 at 25°C resulted in a rapid color change from light tan to red over the course of a few minutes. Inspection of the solution by ¹H NMR spectroscopy

showed two new methoxy resonances at δ 3.624 (s, 3H) and 3.483 (s, 3H) in a 2.2:1 ratio along with corresponding C₅Me₅ and PMe₃ resonances. In addition, a new group of resonances appeared in the region δ 2.6–1.9 with complex coupling patterns consistent with a π -bound olefin complex. No new hydride resonances were observed. ³¹P{¹H} NMR spectroscopy confirmed the presence of two new products with large $J_{\rm Rh-P}$ couplings (~ 190 Hz) consistent with rhodium in the +1 formal oxidation state [11]. These two products were assigned η^2 -methacrylate rotamers of the complex as $(C_5Me_5)Rh(PMe_3)[\eta^2-CH_2=CH(E)]$ 2a and 2b.

A similar result was obtained by reacting 1 with phenylacetylene (Eq. (2)). Addition of 1 equiv. of PhC=CH to a benzene solution of 1 resulted in no color change, and NMR spectroscopy confirmed that no reaction had occurred at room temperature. Heating the mixture at 80°C for 2 h caused the solution to become bright red. ¹H NMR spectroscopy revealed two new ortho-phenyl resonances at δ 7.501 (d, J = 8.6 Hz, 2H) and 7.444 (d, J = 8.6 Hz, 2H) accompanied by new pairs of C₅Me₅ and PMe₃ resonances in a 2.4:1 ratio. The characteristic η^2 -olefin resonances were observed in the region δ 2.1–3.8. Homonuclear decoupling experiments in this region, however, showed that only two η^2 -olefin resonances for each product were present within this region. Irradiation at δ 1.67 resulted in the simplification of two of these resonances, confirming the existence of a third peak masked by the C₅Me₅ resonances. Again no new hydrides were seen, and the ³¹P{¹H} NMR spectrum showed two new products with coupling constants indicative of Rh in the +1 formal oxidation state. These two products were assigned as rotamers of the η^2 -styrene complex $(C_5Me_5)Rh(PMe_3)[\eta^2-CH_2=CH(Ph)]$ 2c and 2d. These products were also observed previously in the thermal reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ (3) with styrene [12].

The reaction of **1** with diphenylacetylene was somewhat more complicated (Eq. (3)).



Addition of excess PhC=CPh to a benzene solution of 1 led to no reaction at room temperature and a very slow reaction at 70°C. After 140 h at 70°C two major products could be identified in a 3:1 ratio with new *ortho*-phenyl aromatic resonances at δ 7.786 (d, J = 7.4 Hz, 4H) and 7.567 (d, J = 7.2 Hz, 4H) and corresponding

 η^2 -olefin peaks at 3.730 (d, J = 2 Hz, 2H) and 3.391 (dd, J = 7.3, 2.4 Hz, 2H). New C₅Me₅ and PMe₃ resonances were also visible. The ${}^{31}P{}^{1}H$ NMR spectrum exhibited large Rh–P couplings ($J_{Rh-P} = 196$, 208 Hz) for the two doublet resonances of the products. These two complexes were assigned as rotamers of the η^2 -cis-stilbene complex $(C_5Me_5)Rh(PMe_3)[\eta^2-cis-CH(Ph)=CH(Ph)]$ 2e and 2f. After heating the mixture at 105°C for 2 days, however, a major new product could be detected with inequivalent η^2 -olefin resonances at δ 4.325 (dd, J = 10.6, 2 Hz, 1H) and 4.013 (td, J = 10.6, 2 Hz, 1H), a C₅Me₅ resonance at δ 1.521 (d, J = 1.7 Hz, 15H) and a PMe₃ resonance at δ 0.673 (d, J = 8.4 Hz, 9H). The ³¹P{¹H} NMR spectrum showed a new doublet at $\delta - 4.046$ (d, J = 210Hz). Continued heating for 6 days at 105°C resulted in formation of this species as the primary product along with a decrease in 2e and 2f. Based on the inequivalent η^2 -olefin resonances, this complex was assigned as the *trans*-stilbene complex $(C_5Me_5)Rh(PMe_3)[\eta^2-trans-$ CH(Ph) = CH(Ph)] 2g.

In order to confirm the identity of the products in the reaction with diphenylacetylene, (C₅Me₅)Rh(PMe₃)(Ph)-H was treated with cis- and trans-stilbene. Heating a hexane solution of (C5Me5)Rh(PMe3)(Ph)H at 65°C with excess trans-stilbene led to loss of benzene and coordination of the free alkene. ¹H and ³¹P{¹H} NMR spectra were identical to those for 2g above and allowed recording of the ${}^{13}C{}^{1}H$ NMR spectrum in the absence of the additional unknown products. When the same reaction was carried out with cis-stilbene, however, ¹H and ${}^{31}P{}^{1}H$ NMR spectra showed exclusive formation of the trans-stilbene complex 2g along with the observation of a white crystalline material precipitating from the hexanes solution. ¹H NMR identified the white material as trans-stilbene, with no spectral evidence for any cis-stilbene remaining in solution. A control experiment of thermolysis of a hexanes solution of *cis*-stilbene at 65°C overnight resulted in no detectable isomerization. The origin of this E/Z interconversion of the free olefin is unknown, but is apparently catalyzed by the rhodium complex.

The reaction of 1 with hexafluoro-2-butyne at room temperature was instantaneous (Eq. (4)).



When gaseous $F_3CC=CCF_3$ was condensed into a frozen benzene solution of 1 on the high-vacuum line, an immediate color change to dark yellow was observed upon thawing the sample, accompanied by the thickening of the solution to a viscous fluid¹. Careful removal of the volatiles left a dark orange-brown solid which was dissolved in C₆D₆ and filtered. Examination of the ¹H NMR spectrum revealed two new products in a 2.5:1 ratio with hydride resonances at $\delta - 13.120$ (dd, J = 46, 27 Hz, 1H) and -13.950 (dd, J = 49, 28 Hz, 1H) and a complex multiplet at δ 7.11, due to overlapping vinylic hydrogens. A ³¹P{¹H} NMR spectrum showed two doublets at δ 3.523 and 2.358 with small $J_{\text{Rh-P}}$ couplings (146 and 140 Hz) indicating the presence of rhodium in the +3oxidation state. These two products were assigned as vinyl $(C_5Me_5)Rh(PMe_3)[C(CF_3)=CH$ hvdride complexes (CF₃)]H 3a and 3b. In order to determine the stereochemistry of the trifluoromethyl groups, ¹⁹F NMR spectra were recorded. Previous work by Clark [5c] and others [14] demonstrated that vicinal through-space ¹⁹F-¹⁹F coupling is much larger for cis-trifluoromethyl groups $({}^{5}J_{\rm F-F} > 10$ Hz) than for *trans*-trifluoromethyl groups (${}^{5}J_{\rm F-F}$ < 3 Hz). Inspection of the 19 F NMR spectrum showed a pair of resonances for each isomer: δ 20.765 (br s) and 19.260 (d, J = 8.6 Hz) for **3a**; and δ 17.134 (t, J = 8.7 Hz) and 15.278 (br s) for **3b**. The absence of a large quartet coupling for each resonance suggested that the geometry about the double bond was trans, and consequently 3a and 3b were assigned as rotamers. After 1 day at 25°C, a new product could be observed growing in. A ¹H NMR spectrum exhibited new C₅Me₅ and PMe₃ resonances along with a complex pattern at δ 2.439 (m, 2H). ${}^{31}P{}^{1}H$ NMR spectra showed the new product to be a Rh^I complex ($J_{Rh-P} = 187$ Hz) and ¹⁹F NMR spectroscopy showed resonances at δ 20.156 (dt, J = 9.6, 3 Hz) and 17.513 (d, J = 9.6 Hz), again indicating a trans-arrangement of the CF₃ substituents. This product was assigned to be the η^2 -hexafluoro-2-butene complex $(C_5Me_5)Rh(PMe_3)[\eta^2$ -trans-CH(CF₃)=CH(CF₃)] (**2h**). Heating the sample at 100°C for 5 h resulted in quantitative formation of 2h. A crystal structure of the chloride complex $(C_5Me_5)Rh(PMe_3)[C(CF_3)=C(CF_3)H]Cl$ (4a) was obtained by quenching the initial mixture of vinyl hydride complexes 3a and 3b with CHCl₃. Fig. 1 shows an ORTEP drawing of the molecule, confirming the trans geometry of the vinyl group.

The reaction of 1 with dimethyl acetylenedicarboxylate was also rapid (Eq. (5)).

¹ This may be due to oligomerization or polymerization of the $F_3CC_2CF_3$, catalyzed by some metal species. For references on polymerization of this alkyne, see: Ref. [13].



Addition of excess EC=CE ($E = CO_2Me$) to a benzene solution of 1 resulted in an immediate color change to dark red. Inspection of the ¹H NMR spectrum showed formation of a major product with inequivalent methoxy resonances at δ 3.509 (s, 3H) and 3.413 (s, 3H) and inequivalent vinylic hydrogens at δ 3.492 (ddd, J = 11.3, 9.5, 2 Hz, 1H) and 3.383 (dd, J = 11.3, 2 Hz, 1H). A minor product was also detected with a new methoxy peak at δ 3.631(s, 6H) which integrated as two OMe groups relative to its corresponding C₅Me₅ and PMe₃ resonances. A resonance at δ 2.404 (dd, J = 8.8, 2 Hz, 2H) showed that the vinylic hydrogens for this material were also equivalent. The ³¹P{¹H} NMR spectrum indicated that both of the new materials were Rh^I complexes by their large coupling constants $(J_{Rh-P} =$ 191, 182 Hz). These two products were assigned as the η^2 -dimethyl fumarate complex (C₅Me₅)Rh(PMe₃)[η^2 *trans*-CH(E)=CH(E)] **2i** and the η^2 -dimethyl maleate complex $(C_5Me_5)Rh(PMe_3)[\eta^2-cis-CH(E)=CH(E)]$ 2j. These materials could be separated by thin-layer chro-



Fig. 1. ORTEP drawing of $(C_5Me_5)Rh(PMe_3)(trans-CCF_3=CHCF_3)Cl$. Ellipsoids are shown at the 50% level, and hydrogen atoms (except on vinyl ligand) have been omitted for clarity. Selected distances (Å) and angles (°): Rh–Cl(1), 2.414(3); Rh–Cl(5), 2.05(1); C(14)–C(15), 1.81(3); C(15)–C(16), 1.11(3); C(16)–C(17), 1.60(4); Rh–Cl(5)–C(16), 155(3), C(14)–C(15)–C(16), 90(2); C(15)–C(16)–C(17), 109(3).

matography and isolated (see Section 5). No evidence for interconversion of isomers was detected after several days in solution at room temperature.

2.2. Intermediates in alkyne insertion reactions

In an attempt to observe the intermediate vinyl hydride complexes, the reaction was repeated at low temperature. Addition of 5 equiv. of EC=CE to a frozen d₈-toluene solution of 1 was performed under a nitrogen purge and the solution warmed to -78° C and gently swirled to mix the components. The NMR tube was immediately transferred to the pre-cooled NMR probe $(-40^{\circ}C)$ and ¹H and ³¹P{¹H} NMR spectra recorded. Two new products could be detected by ³¹P{¹H} NMR spectroscopy at δ 11.103 (d, J = 148.3) and 8.336 (d, J = 145.4 Hz) with small J_{Rh-P} values, indicating Rh^{III} complexes. Although incomplete ¹H NMR data were obtained due to DMAD impurities, new hydride resonances could be seen at $\delta - 11.467$ (dd, J = 47.6, 23.2 Hz, 1H) and -13.744 (dd, J = 48.2, 10.13)29.3 Hz, 1H), confirming that the new materials were the expected vinyl hydride complexes (C₅Me₅)Rh- (PMe_3) [trans-C(E)=CH(E)]H (3c) and $(C_5Me_5)Rh$ - $(PMe_3)[cis-C(E)=CH(E)]H$ (3d). Smaller ¹H and ³¹P{¹H} NMR resonances were also detected for complexes 2i and 2j. As the sample was slowly allowed to warm, the resonances for 3c and 3d decreased with a



Fig. 2. ${}^{31}P{}^{1}H$ NMR spectra of (a) 1, (b) $1-d_2$, and (c) mixture of 1 and $1-d_2$ showing that 1 and $1-d_2$ do not undergo H/D exchange.

concomitant increase in 2i and 2j. The stereochemical assignments for the two vinyl hydride complexes 3c and 3d is somewhat tentative, and is primarily based on the observation that the total amount of *trans*-material (i.e. [3c] + [2i]) and the total amount of *cis*-material (i.e. [3d] + [2j]) each remained constant throughout the reaction.

The origin of the vinylic hydrogens in the products **2i** and **2j** was probed with a deuterium crossover experiment. A mixture of $1-d_0$ and $1-d_2$ showed distinct resonances in the ${}^{31}P{}^{1}H{}$ NMR spectrum due to an intrinsic isotopic shift [15] and demonstrated that H/D exchange does not occur between the two complexes (Fig. 2(a)–(c)). Addition of DMAD to this solution exhibited ${}^{31}P{}^{1}H{}$ NMR resonances for only **2i**-d₀, **2i**-d₂, **2j**-d₀, and **2j**-d₂ (Fig. 3(a)–(d)) with no d₁ products detectable. Consequently, both hydrogens in products **2i** or **2j** came from the same molecule of dihydride complex **1**.

In order to determine if free olefin was generated prior to formation of **2i** and **2j** or if intermolecular olefin exchange was occurring, the following deuterium labeling study was carried out. **1**-d₂ was allowed to react with DMAD in the presence of free dimethyl fumarate. Inspection of the ³¹P{¹H} NMR spectrum showed formation of **2i**-d₂ and **2j**-d₂, but no **2i**-d₀ or **2j**-d₀. This observation demonstrated that olefin exchange in this complex is slow. Also, no free dimethyl fumarate or dimethyl maleate can be involved, since none of the d₀-olefin was incorporated into the η^2 olefin products.

The electrochemistry of complex 1 and the substituted acetylenes was investigated. Cyclic voltammograms for PhC=CH, PhC=CPh, HC=CE, EC=CE and $F_3CC \equiv CCF_3$ and $(C_5Me_5)Rh(PMe_3)H_2$ were recorded in THF solvent (TBA+PF₆⁻ supporting electrolyte) using a glassy-carbon working electrode against an internal $Fe(C_5H_5)_2$ reference (E° for ferrocene = 0.400 V). Reversible couples were not obtained even at sweep rates up to 5 V s⁻¹. Typical sweep rates were 200-500 mV s⁻¹. In order to approximate the midpoint between the measured reduction wave and the unobserved oxidation couple the half-wave potential $E_{1/2}$ was defined as the midpoint of the measured reduction peak current and the baseline current (see Fig. 4). Complex 1 also showed an irreversible oxidation wave, and its $E_{1/2}$ was determined as for the acetylenes. Reduction potentials for the substituted acetylenes along with the oxidation potential for 1 are reported in Table 1.

The reaction of **1** with HC=CE was found to be bimolecular. Reaction of **1** (0.027 M) with HC=CE (0.054 M) was found to fit a second order plot of $\ln\{([M]_0 - [M])/2[M]\}$ versus time and was linear over 5 half-lives ($k_{obs} = 5.9(5) \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$). Similar reactions in the presence of a radical initiator (TBP, di-tert-



Fig. 3. ³¹P{¹H} NMR spectra of (a) 1 + DMAD, (b) $1-d_2 + DMAD$, (c) mixture of 2i, 2i-d₂, 2j, and 2j-d₂, (d) reaction of $1 + 1-d_2$ from Fig. 2(c) with DMAD.

butyl peroxide) or in the presence of a radical spin trapping agent (PBN, α-phenyl-*N*-tert-butyl nitrone) showed comparable rates ($k_{\text{TBP}} = 4.3(7) \times 10^{-4} \text{ M}^{-1}$ s⁻¹, $k_{\text{PBN}} = 5.8(7) \times 10^{-4} \text{ M}^{-1}$ s⁻¹, see Section 5), demonstrating that free radical species are not involved.

3. Discussion

Although the stereochemical outcome of alkyne insertions into metal-hydride bonds has been well studied, many conflicting explanations have been invoked to account for the disparate results. In cases where cis-insertion occurs exclusively, a four-membered concerted transition state has been frequently invoked. When trans-insertion is observed, the proposed mechanisms to account for E/Z isomerization are diverse. Clark et al. showed that an electron transfer mechanism was the most likely for their $trans-Pt(PR_3)H_2$ system based on EPR results and electrochemical measurements [5c]. Otsuka and Nakamura proposed a concerted four-membered transition state that results in direct formation of a *trans*-vinyl hydride complex [5a]. Bergman and Huggins examined the insertion of alkynes into the Ni-CH₃ bond of a series of Ni(acac)-(PR₃)CH₃ complexes and concluded that phosphine



Fig. 4. Sample cyclic voltammograms of HC=CCO₂Me showing estimation of $E_{1/2}$ referenced to ferrocene.

Table 1

Irreversible oxidation and reduction potentials for $(C_5Me_5)Rh(PMe_3)H_2$ (1) and for substituted alkynes $R^1C\equiv CR^2$ in THF/TBAPF₆

$R^1 =$	$R^2 =$	$E_{1/2}$ (V) ^a	ΔG° (kcal mol ⁻¹)
Ph	Н	-2.65	51.9
MeO ₂ C	Н	-2.45	50.7
Ph	Ph	-2.39	49.4
CO ₂ Me	CO_2Me	-1.49	28.6
CF ₃	CF ₃	-1.03	18.0
1	-	+0.25	_

^a All values are referenced to reversible $Fe(C_5H_5)_2$ couple at $E_o = 0.400$ V. $E_{1/2}$ are one electron reductions in all cases except for 1 which is a one electron oxidation.

loss followed by alkyne coordination and methyl migration to the least hindered alkyne carbon atom produced vinyl derivatives that could rapidly interconvert stereochemistry, leading to the observation of both kinetic and thermodynamic products [6c]. In this case, the E/Zisomerization was proposed to occur via a zwitterionic vinyl intermediate that could be stabilized by σ bases such as free phosphine.

The observation of a mixture of E/Z isomers in the reaction of 1 with DMAD could be accommodated by an electron-transfer mechanism (Scheme 1). If single electron transfer from the metal complex 1 to the



Scheme 1.

electron-deficient alkyne were to occur, the ion-paired intermediate **A** could then undergo a proton transfer from the metal hydride cation radical to the alkynyl anion radical, leading to the neutral cage pair **B** which contains a vinyl radical. Rapid E/Z isomerization of this radical species prior to cage collapse is consistent with the mixture of *cis*- and *trans*-vinyl hydride materials observed in this reaction and also with the predominance of the *trans*-stereoisomer. In this scheme, the initial ratio of η^2 materials that are formed, as is observed experimentally. Alternatively, H atom transfer from **1** to the acetylene could occur, giving the same vinyl radical intermediate.

To examine the feasibility of this mechanistic proposal, the electrochemistry of the substituted alkynes and the metal complex 1 was investigated by cyclic voltammetry. Reversible couples were not obtained even at the fastest sweep rates (5 V s⁻¹), and irreversible values are reported as half-wave potentials $E_{1/2}$ (see Table 1). The oxidation potential for complex 1 was measured to be +0.25 V versus NHE and was also irreversible. Reduction potentials for the series of alkynes ranged from -1.03 V (F₃CC=CCF₃) to -2.65 V (PhC=CH). From these redox values, ΔG for each reaction was calculated from the relationship $\Delta G =$ nFE_{rxn} , where $E_{\text{rxn}} = E_{1/2}^{\text{ox}}(1) + E_{1/2}^{\text{red}}(\text{alkyne})$. As these electron transfers are all uphill, they represent minimum kinetic barriers for the rate of reaction. It is clear that electron transfer rates calculated from these free energies are far too slow to be responsible for the reactions studied, and based on these $E_{1/2}$ values outer sphere electron transfer is not deemed a plausible mechanism in these cases².

In the series of reactions studied here, all possible stereochemical outcomes are observed depending upon the acetylene substrate. Diphenylacetylene reacts with 1 to give *cis*-products only, with the observation of the *trans*-stilbene adduct 2g only under severe conditions. In contrast, hexafluoro-2-butyne gives stereospecifically the *trans*-vinyl hydride and η^2 -olefin complex, while dimethyl acetylenedicarboxylate gives a mixture of *E* and *Z* products both at the vinyl hydride and the η^2 -olefin stages. The rational for this range of behavior remains unclear. However, it seems apparent from these experiments that the stereochemical outcome of the reaction is fixed by the stereoselectivity of the initial insertion to produce the *E* and/or *Z* vinyl hydride complex(es). Since vinyl hydride intermediates are not

² Due to the fact that irreversible couples were obtained, the measured potentials are only taken as upper limits for the actual reversible values. As a result, rates that are calculated based on these irreversible electrochemical potentials cannot be slower, but may indeed be faster. It is unlikely, however, that the $E_{1/2}$ values differ substantially from the reversible values, and therefore initial electron transfer is kinetically too slow to explain the observed rates of reaction.



observed in the reaction with diphenylacetylene, the *cis*-insertion adduct must form exclusively.

Although dihydride 1 is a coordinatively saturated 18 electron complex, it is known to react bimolecularly with D_2 , PMe₃ and CS₂ [15,16]. In order to account for the associative rate dependence on these substrates, the possibility of $\eta^5 \rightarrow \eta^3$ ring slippage and hydride to ring migration pre-equilibria were proposed. Of these reactions, the insertion of CS_2 into the metal hydride bond of 1 is the most closely related to the insertion chemistry of the alkynes. Based on detailed kinetic studies in these systems it was proposed that hydride to ring migration to produce the intermediate $(\eta^4-C_5Me_5H)$ -Rh(PMe₃)H occurred, producing a vacant coordination site and allowing pre-coordination of free substrate. This mechanism accounts for the associative nature of these reactions, which would otherwise require loss of a ligand (i.e. PMe_3 or H_2) prior to reaction with the substrate. Rates of H₂ loss and PMe₃ exchange are slow, and alternative pathways are required to explain the rapid reaction of 1 with alkynes and CS_2 .

In order to accommodate the observed stereochemical outcomes in the reactions of **1** with PhC=CPh, EC=CE and $F_3CC=CCF_3$, the possibility of hydrogen atom transfer from **1** to the alkyne to form a vinyl radical species was considered. The observation of only *cis*-materials for the reaction of **1** with PhC=CPh, however, is inconsistent with this mechanism as the diphenyl vinyl radical formed would be expected to isomerize quickly to give *trans*-products. Also, the lack of crossover in the reaction of **1**-d₂ with DMAD argues against free vinyl radical intermediates, as does the inability to trap the vinyl radical with a spin trapping agent.

A second proposal that allows for the observation of *cis*- and *trans*-materials would be formation of only the

cis-vinyl hydride intermediate (C₅Me₅)Rh(PMe₃)(cis-CR=CHR)H as the kinetic product via acetylene insertion. A separate equilibration of the vinyl hydride would then yield the thermodynamically more stable (C₅Me₅)Rh(PMe₃)(trans-CR=CHR)H (and (C₅Me₅)Rh-(PMe₃)-(*trans*-η²-CHR=CHR)) materials in competition with $(C_5Me_5)Rh(PMe_3)(cis-\eta^2-CHR=CHR)$ from CpRh(PMe₃)(cis-CR=CHR)H. Potential mechanisms for isomerization of vinyl hydride intermediates are shown in Scheme 2. Scheme 2a illustrates an organometallic equivalent to an allylic rearrangement, effectively a [1,3] sigmatropic H-shift. The rhodium carbene intermediate C can freely rotate around C_{α} -C_B producing the trans-vinyl hydride intermediates and ultimately the *trans*- η^2 -olefin materials. A similar mechanism in Scheme 2b forms a rhodium carbene hydride intermediate **D** that places a negative charge on C_{β} which is stabilized by the attached substituent. For the cases R = Ph and CO_2Me , a resonance stabilized anion is formed (a benzylic anion for R = Ph, and an enolate anion for $R = CO_2Me$) while in the $R = CF_3$ case the anion is stabilized by the inductive effect of an electron withdrawing group. This latter pathway seems most reasonable and consistent with the observations.

Assuming that the *cis*-vinyl hydrides are the kinetic products formed in these reactions as shown in Scheme 3, several specific relationships between equilibrium constants and relative rates must be true. If the rate of equilibration of vinyl hydride complexes is fast relative to k_1 and k_2 , then $K_{eq} \ll 1$ for R = Ph, $K_{eq} \sim 1$ for R = E, and $K_{eq} \gg 1$ for $R = CF_3$. On the other hand, it is possible that k_1 is faster than equilibration when R = Ph (leading to *cis*-olefin product), but equilibration is faster than k_1 for $R = CF_3$ (leading to *trans*-olefin



Scheme 3.

product). For $R = CO_2Me$, equilibration appears to be more rapid than reductive elimination since the same ratio of *cis/trans* vinyl hydride intermediates is seen throughout the reaction.

The least satisfying explanation is to simply propose different mechanistic pathways for each substrate. This may be possible, however, given the extremely different nature of the acetylenes used. Perhaps stereospecific cis-insertion occurs for diphenylacetylene, while stereospecific trans-insertion occurs for hexafluoro-2butyne. Both pathways would have to be competitive in the reaction of 1 with DMAD, leading to both *cis*- and trans-materials. There is ample precedent supporting a four centered transition state leading to cis-stereochemistry for the vinyl hydride materials. In order to accommodate *trans*-stereochemistry, a perpendicular insertion into the metal hydride shown in E below has been invoked to explain the concerted formation of transvinyl hydride materials without isomerization of an initially formed cis-vinyl hydride complex.



This mechanism is attractive in that it involves the same intermediate η^2 -alkyne complex and differs only in the orientation of the C=C bond in relation to the metal hydride. Smaller substrates such as F₃CC=CCF₃ may be able to achieve this transition state geometry while bulkier alkynes such as PhC=CPh cannot. If distinct paths are responsible for the observation of different stereochemical outcomes in this series of reactions, these two pathways that differ only in the trajectory of the bound alkyne seem to be the most reasonable. The direct insertion pathway also accounts for the lack of crossover in the reaction of 1-d₂ with DMAD.

Previous work studying the insertion of DMAD into the metal hydride bond of $(C_5Me_5)Rh(PMe_3)(Ph)H$ supports this proposal. Both *cis*- and *trans*-isomers of the complex $(C_5Me_5)Rh(PMe_3)[C(E)=CH(E)](Ph)$ were isolated and structurally characterized [17]. Since this vinyl complex has no metal hydride, the allylic rearrangement discussed above is not possible, and proposing a zwitterionic mechanism to account for the observed stereochemistry (leading to an intermediate similar to **D**) seems unlikely as these materials are stereochemically stable and do not interconvert. This closely related system lends support to the notion of a 'direct' insertion of the acetylene into the metal hydride bond that determines the E/Z stereochemistry about the double bond.

4. Conclusions

The complex $(C_5Me_5)Rh(PMe_3)H_2$ reacts with the electron poor acetylenes PhC=CH, EC=CH, PhC=CPh, EC=CE and F₃CC=CCF₃ to give η^2 -olefin complexes of the hydrogenated alkynes. PhC=CH and EC=CH react similarly to each yield two species assigned as rotamers. Stereoselective cis-insertion (two rotamers) is observed for PhC=CPh at 70°C, with isomerization to the transcomplex only occurring above 100°C. A mixture of cisand *trans*-products is seen in the reaction with EC=CE and stereoselective trans-insertion occurs in the reaction with F₃CC=CCF₃. Vinyl hydride intermediates are detected at -40° C for the EC=CE reaction and at room temperature for the reaction with $F_3CC=CCF_3$. The stereochemistry of the η^2 -olefin complexes is likely to be determined by the initial stereochemistry of the vinyl hydride intermediates.

Cyclic voltammetry measurements give irreversible reduction potentials for the series of acetylenes and the irreversible oxidation potential for **1**. Based on these $E_{1/2}$ values, electron transfer is tentatively ruled out as the first step in the insertion mechanism for all of the alkynes except hexafluoro-2-butyne (and perhaps dimethyl acetylenedicarboxylate).

5. Experimental

5.1. General considerations

All operations and routine manipulations were performed under an atmosphere of nitrogen, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres dri-lab. Benzene, THF, and hexanes were distilled from dark purple solutions of benzophenone ketyl and stored in glass ampules fitted with Teflon sealed vacuum line adapters. Alkane solvents were made olefin-free by stirring over H₂SO₄, washing with aqueous KMnO₄ and water, and distilling from dark purple solutions of tetraglyme/benzophenone ketyl. Phenylacetylene, methyl propiolate, dimethyl acetylenedicarboxylate, dimethyl fumarate, cis-stilbene, *trans*-stilbene, Red-Al (sodium bis(2-methoxyethoxy) aluminum hydride), sodium borohydride and sodium borodeuteride were purchased from Aldrich and distilled before use. Bis-triphenylphosphino iminium chloride (PPN⁺Cl⁻) and diphenylacetylene were purchased from Strem Chemicals and used as received. Hexafluoro-2-butyne was purchased from PCR gases and used as received.

¹H, ¹³C{¹H}, and ³¹P{¹H} spectra were recorded on Bruker AMX400 or Bruker WP200 NMR spectrometers. ¹⁹F NMR (470 MHZ) were obtained on a Varian VXR500S spectrometer. All ¹H NMR chemical shifts are reported in ppm (δ) relative to TMS (tetramethylsilane) and referenced to the residual solvent resonances (benzene, δ 7.15; chloroform, δ 7.24; acetone, δ 2.04; THF, δ 3.58, 1.73; toluene, δ 2.10). ¹³C{¹H} NMR chemical shifts are referenced to residual C_6D_6 (δ 128.00). ³¹P{¹H} NMR chemical shifts are referenced to external 10% H₃PO₄ (δ 0.00). ¹⁹F NMR chemical shifts are referenced to external F_3CCO_2H (δ 0.00). All temperatures for variable temperature NMR spectroscopy were calibrated relative to the chemical shift differences in the NMR spectra of known standards (4% methanol in methanol- d_4). Analyses were obtained from Desert Analytics. PPN⁺BH₄⁻ and PPN⁺BD₄⁻ were prepared by the method of Bau [18]. The complexes (C_5Me_5) - $Rh(PMe_3)Cl_2$, $(C_5Me_5)Rh(PMe_3)Br_2$ [19], (C_5Me_5) - $Rh(PMe_3)H_2$, $(C_5Me_5)Rh(PMe_3)(PMe_3)(C_2H_4)$ [20], and (C₅Me₅)Rh(PMe₃)(Ph)H [21], have all been prepared previously.

5.2. Reaction of 1 with phenylacetylene

20 mg (C₅Me₅)Rh(PMe₃)Cl₂ (0.052 mmol) was converted to the dihydride 1 using PPN+BH₄- and dissolved in C_6D_6 in a reseatable NMR tube. 6 µl (0.056 mmol) PhC=CH was injected under a nitrogen atmosphere and the solution heated to 80°C for 2 h. The solution turned red. The volatile components were removed under vacuum leaving a dark red oil. NMR spectroscopy showed two products. $(C_5Me_5)Rh$ - $(PMe_3)(\eta^2$ -styrene) Rotamer 1. ¹H NMR (C₆D₆): δ 7.444 (d, J = 8.6 Hz, 2H), 7.1–7.25 (obsc, 2H), 7.003 (t, J = 8.6 Hz, 1H), 3.427 (dtd, J = 10.8, 10.1, 2.2 Hz, $1H_{vinvl}$, 2.145 (d, J = 10 Hz, $1H_{vinvl}$), 1.67 (obsc, $1H_{vinvl}$), 1.565 (d, J = 2 Hz, 15H), 0.840 (d, J = 8.2 Hz, 9H). ³¹P{¹H} NMR (C₆D₆): δ - 6.318 (d, J = 208 Hz). ¹³C{¹H} NMR (C₆D₆): δ 147.79 (s), 130.26 (s), 123.01 (s), 95.87 (t, J = 3.4 Hz), 46.80 (dd, J = 14.4, 2.5 Hz), 24.37 (dd, J = 16.3, 3.4 Hz), 16.55 (d, J = 25.4 Hz), 10.30 (s). Rotamer 2. ¹H NMR (C_6D_6): δ 7.501 (d, J = 8.6 Hz, 2H), 7.1–7.25 (obsc, 2H), 7.055 (t, J = 8.6Hz, 1H), 3.779 (ddd, J = 11.6, 7.6, 2.8 Hz, $1H_{vinvl}$), 2.198 (d, J = 11.6 Hz, $1H_{vinvl}$), 1.810 (d, J = 2 Hz, 15H), 1.67 (obsc, 1 H_{vinvl}), 0.624 (d, J = 8.9 Hz, 9H). ³¹P{¹H} NMR (C₆D₆): $\delta = -0.494$ (d, J = 199 Hz). ¹³C{¹H} NMR (C_6D_6): δ 150.15 (s), 132.32 (s), 123.82 (s), 95.63 (t, J = 3.4 Hz), 49.67 (dd, J = 14.3, 1.7 Hz), 28.48 (dd,J = 16, 3.4 Hz), 18.00 (d, J = 24.7 Hz), 10.413 (s).

5.3. Reaction of 1 with diphenylacetylene

10 mg (C_5Me_5)Rh(PMe_3)Cl₂ (0.026 mmol) was converted to the dihydride 1 using Red–Al and dissolved in C_6D_6 in a resealable NMR tube. 47 mg PhC=CPh (0.26 mmol) was added under nitrogen. The solution was heated at 70°C for 6 days. The solution turned red. Examination of the solution by ¹H and ³¹P{¹H} NMR spectroscopy revealed two major products. (C_5Me_5)-

 $Rh(PMe_3)(\eta^2$ -cis-stilbene) Rotamer 1. ¹H NMR (C₆D₆): δ 7.567 (d, J = 7.2 Hz, 4H), 6.9–7.3 (obsc, 4H), 6.815 $(t, J = 7.8 \text{ Hz}, 2\text{H}), 3.391 \text{ (dd}, J = 7.3, 2.4 \text{ Hz}, 2\text{H}_{vinvlic}),$ 1.467 (d, J = 2.6 Hz, 15H), 0.821 (d, J = 8.6 Hz, 9H). ³¹P{¹H} NMR (C₆D₆): δ 1.710 (d, J = 196 Hz). Rotamer 2. ¹H NMR (C₆D₆): δ 7.786 (d, J = 7.4 Hz, 4H), 6.9-7.3 (obsc, 4H), 6.718 (t, J = 7.2 Hz, 2H), 3.730 (d, J = 2 Hz, $2H_{vinvlic}$), 1.732 (d, J = 1.6 Hz, 15H), 0.542 (d, J = 8.3 Hz, 9H). ³¹P{¹H} NMR (C₆D₆): $\delta - 9.083$ (d, J = 208 Hz). After heating at 105°C for 2 days a new major product was formed. $(C_5Me_5)Rh(PMe_3)(\eta^2 - trans$ stilbene) ¹H NMR (C₆D₆): δ 7.995 (d J = 7.4 Hz, 4H), 6.9-7.3 (obsc, 4H), 6.862 (t, J = 7.4 Hz, 2H), 4.325 (dd, J = 10.6, 2 Hz, 1H_{vinylic}), 4.013 (td, J = 10.6, 2 Hz, $1H_{vinvlic}$), 1.521 (d, J = 1.7 Hz, 15H), 0.673 (d, J = 8.4Hz, 9H). ³¹P{¹H} NMR (C₆D₆): δ - 4.046 (d, J = 210 Hz). The product could be isolated as a red oil by chromatography on silica gel, but the oil decomposes upon standing at room temperature under nitrogen.

5.4. Reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with trans-stilbene

20 mg $(C_5Me_5)Rh(PMe_3)(C_2H_4)$ (0.058 mmol) was dissolved in C₆H₆ and photolyzed using a $\lambda > 345$ nm filter for 2 days. ³¹P{¹H} NMR spectroscopy showed 95% conversion the phenyl hvdride to (C₅Me₅)Rh(PMe₃)(Ph)H along with some formation of $(C_5Me_5)Rh(PMe_3)_2$. The benzene was removed under vacuum and the yellow solid dissolved in hexanes. 71 mg trans-stilbene (0.394 mmol) was added under nitrogen and the solution was heated to 65°C for 10 h. Examination of the ³¹P{¹H} NMR spectrum showed formation of $(C_5Me_5)Rh(PMe_3)(\eta^2 - trans - stilbene)$ as the major product. The solution was taken to dryness and dissolved in $C_6D_6.\ ^1H$ and $^{31}P\{^1H\}$ NMR spectra were identical to those of the final product obtained from the reaction of 1 with PhC=CPh (vide supra). ¹³C{¹H} NMR (C₆D₆): δ 150.00 (t, J = 2 Hz), 147.37 (d, J = 2.5 Hz), 130.58 (s), 129.24 (s), 128.51 (s), 127.62(s), 123.88 (s), 123.07 (s), 96.43 (t, J = 3.8 Hz), 45.98 (dd, J = 14, 3 Hz), 44.03 (dd, J = 16, 2 Hz), 18.09 (d, J = 26 Hz), 10.23 (s).

5.5. Reaction of $(C_5Me_5)Rh(PMe_3)(Ph)H$ with cis-stilbene

20 mg (C_5Me_5)Rh(PMe₃)(C_2H_4) (0.058 mmol) was dissolved in C_6H_6 and photolyzed using a $\lambda > 345$ nm filter for 2 days. ³¹P{¹H} NMR spectroscopy showed 95% conversion to phenyl hydride along with some formation of (C_5Me_5)Rh(PMe₃)₂. The solution was taken to dryness under vacuum and the yellow solid dissolved in hexanes. 60 µl *cis*-stilbene (0.337 mmol) was added via a syringe under nitrogen and the solution was heated to 65°C for 4 h. A white crystalline precipitate was observed. Examination of the ${}^{31}P{}^{1}H{}$ NMR spectrum showed formation of $(C_5Me_5)Rh(PMe_3)(\eta^2-trans-stilbene)$ as the major product. The solution was taken to dryness and dissolved in C_6D_6 . ¹H NMR spectroscopy revealed that all of the *cis*-stilbene had been converted to *trans*-stilbene.

5.6. Reaction of 1 with methyl propiolate

10 mg $(C_5Me_5)Rh(PMe_3)Cl_2$ (0.026 mmol) was converted to the dihydride 1 using Red-Al. The tan oil was dissolved in C_6D_6 and placed in a resealable NMR tube. 11.5 µl HC=CE (0.129 mmol) was added under nitrogen atmosphere. The solution became red after several minutes. Examination of the solution by NMR spectroscopy revealed two products. (C_5Me_5) - $Rh(PMe_3)(\eta^2-methylacrylate)$ Rotamer 1. ¹H NMR (C₆D₆): δ 3.624 (s, 3H), 2.58 (m, 1H_{vinylic}), 2.420 (dd, J = 9.9, 1.7 Hz, $1H_{vinylic}$), 1.925 (d, J = 8 Hz, $1H_{vinylic}$), 1.806 (d, J = 2.3 Hz, 15H), 0.683 (d, J = 8.6 Hz, 9H). ³¹P{¹H} NMR (C₆D₆): δ -0.924 (d, J=192 Hz). ¹³C{¹H} NMR (C₆D₆): δ 176.35 (s), 96.13 (t, J = 4 Hz), 50.03 (s), 35.59 (d, J = 16 Hz), 28.79 (dd, J = 16, 3 Hz), 16.16 (d, J = 26 Hz), 10.10 (s). Rotamer 2. ¹H NMR (C₆D₆): δ 3.483 (s, 3H), 2.60 (m, 1H_{vinvlic}), 2.49 (m, $1H_{vinvlic}$, 1.92 (m, $1H_{vinvlic}$), 1.699 (d, J = 1.5 Hz, 15H), 1.125 (d, J = 9 Hz, 9H). ³¹P{¹H} NMR (C₆D₆): δ -5.510 (d, J = 199 Hz). ¹³C{¹H} NMR (C₆D₆): δ 177.12 (s), 95.92 (t, J = 3 Hz), 50.30 (s), 36.93 (d. J = 16Hz), 32.87 (d, J = 16 Hz), 17.86 (d, J = 25 Hz), 10.10 (s).

5.7. Kinetic studies of 1 with methyl propiolate

Three solutions of **1** in 0.84 ml C_6D_6 (0.020 M in **1**) were freeze-pump-thaw degassed three times. Three stock solutions containing the following were prepared: (i) 0.0875 g EC=CH in 5 ml C_6D_6 ([EC=CH] = 0.208 M), (ii) 0.0991 g α -phenyl-*N*-tert-butyl nitrone (PBN) in 2 ml of solution (i) above ([PBN] = 0.280 M), (iii) 0.0876 g EC=CH, 0.0168 g tert-butyl peroxide (TBP) in 5 ml C_6D_6 ([TBP] = 0.023 M). All three stock solutions were thoroughly degassed. For each kinetic experiment, 250 µl of the appropriate stock solution was injected into a C_6D_6 solution of **1** under a nitrogen atmosphere and room temperature ¹H NMR spectra immediately recorded at 5 min intervals for at least 5 half-lives.

5.8. Reaction of 1 with dimethyl acetylenedicarboxylate

20 mg (C_5Me_5)Rh(PMe_3)Cl₂ (0.052 mmol) was converted to the dihydride 1 using PPN⁺BH₄⁻. The tan oil was dissolved in d₈-toluene in a resealable NMR tube and freeze-pump-thaw degassed three times. The tube was frozen in liquid nitrogen and 32 µl dimethyl acetylenedicarboxylate (0.26 mmol) was injected into

the tube while under a stream of nitrogen. The tube was warmed to -78° C in a dry ice/acetone bath and swirled gently to mix the components. The sample was quickly transferred to the pre-cooled $(-40^{\circ}C)$ NMR probe and monitored by ${}^{31}P{}^{1}H$ NMR spectroscopy as the probe was warmed in 10° (C) increments. Four new products were observed by ¹H and ³¹P{¹H} NMR spectroscopy. $(C_5Me_5)Rh(PMe_3)[trans-C(R)CH(R)]H$ ¹H NMR (d_8 -toluene, 235 K): δ 3.464 (s, 3H), 3.368 (s, 3H), 1.767 (s, 15H), 1.040 (d, J = 10.4 Hz, 9H), -11.467 (dd, J = 47.6, 23.2 Hz, 1H). ³¹P{¹H} NMR (d₈-toluene, 235 K): δ 11.103 (d, J = 148.3 Hz). $(C_5Me_5)Rh(PMe_3)[cis-C(R)CH(R)]H^{-1}H^{-1}H^{-1}MR^{-1}(d_8$ toluene, 235 K): δ 1.623 (s, 15H), 1.167 (d, J = 10.3 Hz, 9H), -13.744 (dd, J = 48.2, 29.3 Hz, 1H). ³¹P{¹H} NMR (d₈-toluene, 235 K): δ 8.336 (d, J = 145.4 Hz). $(C_5Me_5)Rh(PMe_3)(\eta^2-maleate)$ ¹H NMR $(d_8-toluene,$ 235 K): δ 1.875 (s. 15H), 0.528 (d. J = 8.3 Hz, 9H). ³¹P{¹H} NMR (d₈-toluene, 235 K): δ 3.267 (d, J = 180.9 Hz). $(C_5Me_5)Rh(PMe_3)(\eta^2-fumarate)$ ¹H NMR (d₈-toluene, 235 K): δ 1.633 (s, 15H), 1.091 (d, J = 10.4Hz, 9H). ³¹P{¹H} NMR (d_8 -toluene, 235 K): δ 1.440 (d, *J* = 189.7 Hz).

5.9. Chromatographic separation of $(C_5Me_5)Rh$ -(PMe_3)(η^2 -maleate) and $(C_5Me_5)Rh(PMe_3)(\eta^2$ -fumarate) complexes

100 mg $(C_5Me_5)Rh(PMe_3)Cl_2$ (0.260 mmol) was converted to the dihydride 1 using Red-Al. The tan solid was dissolved in benzene and 100 µl DMAD added slowly under a nitrogen atmosphere. The mixture was allowed to stir for 15 min. The benzene was removed under vacuum leaving a dark red oil. The oil was dissolved in THF and chromatographed on thick layer silica plates using a 1:1 benzene/THF mixture. Two bands could be observed. The leading yellow-orange band was determined to be the fumarate complex $(C_5Me_5)Rh(PMe_3)$ [trans-CH(R)CH(R)], and the second vellow band was determined to be the maleate complex (C₅Me₅)Rh(PMe₃)[cis-CH(R)CH(R)] by NMR spectroscopy. $(C_5Me_5)Rh(PMe_3)(\eta^2-fumarate)$ ¹H NMR (C₆D₆): δ 3.509 (s, 3H), 3.413 (s, 3H), 3.478 (ddd, J = 11.3, 9.5, 2 Hz, 1H_{vinvlic}), 3.356 (dd, J = 11.3, 2 Hz, $1H_{vinvlic}$), 1.696 (d, J = 2.5 Hz, 15H), 1.061 (d, J = 9.2Hz, 9H). ³¹P{¹H} NMR (C₆D₆): δ - 4.087 (d, J = 191 Hz). ¹³C{¹H} NMR (C₆D₆): δ 176.51 (s), 175.11 (s), 96.49 (t, J = 4 Hz), 49.98 (s), 49.77 (s), 39.20 (dd, J = 16, 4 Hz), 36.50 (d, J = 16 Hz), 16.94 (d, J = 26Hz), 9.25 (s). $(C_5Me_5)Rh(PMe_3)(\eta^2-maleate)$ ¹H NMR (C_6D_6) : δ 3.631 (s, 6H), 2.404 (dd, J = 8.8, 2 Hz, $2H_{vinylic}$, 1.766 (d, J = 2.6 Hz, 15H), 0.600 (d, J = 8.6Hz, 9H). ³¹P{¹H} NMR (C₆D₆): δ - 1.959 (d, J = 182 Hz). ${}^{13}C{}^{1}H$ NMR (C₆D₆): δ 49.87 (s), 34.92 (dd, J = 16, 2 Hz), 14.86 (d, J = 25 Hz), 13.94 (s).

5.10. Crossover experiment between d_2 -(C_5Me_5)-Rh(PMe_3)(η^2 -fumarate) and free dimethyl fumarate

A sample of $(C_5Me_5)Rh(PMe_3)D_2$ was prepared by reacting 9 mg $(C_5Me_5)Rh(PMe_3)Br_2$ (0.019 mmol) with PPN⁺BD₄⁻. The dideuteride 1-d₂ was dissolved in d₈-toluene and 11.2 mg dimethyl fumarate (0.0778 mmol) added under a nitrogen atmosphere. The solution was placed in an NMR tube capped with a rubber septum and cooled to $-20^{\circ}C$ in the NMR probe. ³¹P{¹H} NMR spectra showed no reaction had occurred. The sample was removed from the probe and 4.7 µl DMAD (0.038 mmol) injected through the septum. The tube was inverted three times and quickly returned to the NMR probe. ³¹P{¹H} NMR spectra revealed that no crossover between the d₂-(C₅Me₅) Rh(PMe₃)(η^2 -fumarate) complex and free dimethyl fumarate had taken place.

5.11. Crossover experiment between (C_5Me_5) -Rh $(PMe_3)H_2/(C_5Me_5)Rh(PMe_3)D_2$ and DMAD

A sample of $(C_5Me_5)Rh(PMe_3)D_2$ was prepared by reacting 9 mg $(C_5Me_5)Rh(PMe_3)Br_2$ (0.019 mmol) with PPN⁺BD₄⁻. A similar sample of $(C_5Me_5)Rh(PMe_3)H_2$ was prepared by reacting 9 mg $(C_5Me_5)Rh(PMe_3)Br_2$ (0.019 mmol) with PPN⁺BH₄⁻. The two materials were dissolved in d₈-toluene and mixed. ³¹P{¹H} NMR spectra showed no scrambling had occurred. The solution was placed in an NMR tube capped with a rubber septum and cooled to $-20^{\circ}C$ in the NMR probe. The sample was removed from the probe and 4.7 µl DMAD (0.038 mmol) injected through the septum. The tube was inverted three times and quickly returned to the NMR probe. ³¹P{¹H} NMR spectra revealed formation of **2i**, **2i**-d₂, **2j**, and **2j**-d₂ with no evidence for d₁ materials.

5.12. Reaction of 1 with hexafluoro-2-butyne

20 mg (C₅Me₅)Rh(PMe₃)Cl₂ (0.052 mmol) was converted to the dihydride 1 using Red-Al and dissolved in THF in a reseatable NMR tube. The solution was subjected to three freeze-pump-thaw degas cycles. ~100 torr $F_3CC=CCF_3$ (3.21 mmol) was introduced into the high-vacuum line (approx. volume 600 ml) and condensed into the frozen resealable NMR tube. Upon warming to room temperature, the solution turned yellow and thickened to a viscous fluid. Removal of the volatile components under high vacuum left a brown solid which was extracted with C_6D_6 and filtered through a cotton-plugged pipette, yielding a bright yellow solution. NMR spectroscopy showed formation of two products. $(C_5Me_5)Rh(PMe_3)[trans-C(CF_3)CH (CF_3)$]H. Rotamer 1. ¹H NMR (C₆D₆): δ 7.11 (m, $1H_{vinvlic}$), 1.662 (d, J = 2 Hz, 15H), 0.892 (d, J = 10 Hz,

9H), -13.120 (dd, J = 46, 27 Hz, 1H). ³¹P{¹H} NMR (C₆D₆): δ 3.523 (d, J = 146 Hz). ¹⁹F NMR (C₆D₆): δ 20.765 (br s), 19.260 (d, J = 8.7 Hz). Rotamer 2. ¹H NMR (C₆D₆): δ 7.11 (m, 1H_{vinylic}), 1.578 (d, J = 2 Hz, 15H), 0.807 (d, J = 9 Hz, 9H), -13.950 (dd, J = 49, 28 Hz, 1H). ³¹P{¹H} NMR (C₆D₆): δ 2.358 (d, J = 140Hz). ¹⁹F NMR (C₆D₆): δ 17.134 (t, J = 8.7 Hz), 15.278 (br s). After heating the above mixture at 100°C for 5 h a new product is formed quantitatively. (C_5Me_5)- $Rh(PMe_3)(\eta^2$ -trans-hexafluoro-2-butene). ¹H NMR (C₆D₆): δ 2.439 (m, 2H_{vinylic}), 1.614 (d, J = 2 Hz, 15H), 0.816 (d, J = 9 Hz, 9H). ³¹P{¹H} NMR (C₆D₆): δ -5.480 (d, J = 187 Hz). ¹⁹F NMR (C₆D₆): δ 20.156 (dt, J = 9.6, 3 Hz), 17.513 (d, J = 9.6 Hz).

5.13. Electrochemistry of $(C_5Me_5)Rh(PMe_3)H_2$ and substituted alkynes

Cyclic voltammetric measurements were carried out on a Princeton Applied Research 173 potentiostat and PAR 175 sweep generator and a Houston 2000 XY recorder. A single-compartment, three-electrode cell containing a glassy-carbon (3.2 mm diameter) working electrode, a platinum wire auxiliary electrode, and a silver wire reference electrode was used for all measurements. In a typical experiment, several mg of the alkyne or of 1 with 200 mg $TBA^+PF_6^-$ as the supporting electrolyte (0.11 M) was placed in the cell and purged with nitrogen for 5 min. Dry, degassed THF (5 ml) was introduced and cyclic voltammograms recorded immediately. For the measurement of $E_{1/2}$ for F₃CC=CCF₃, the gas cylinder was attached to a syringe needle and the alkyne slowly bubbled into the degassed THF/ $TBA^+PF_6^-$ solution for 30 s.

5.14. X-ray structural determination of (C_5Me_5) -Rh (PMe_3) [trans-CH (CF_3) CH (CF_3)]Cl

A small yellow crystal of the complex was mounted on a glass fiber with epoxy and placed in the cold stream $(-20^{\circ}C)$ of the diffractometer. 25 reflections with values of χ between 5 and 70° were centered and used for cell determination. Data were collected in a primitive monoclinic crystal system, and data reduction showed absences consistent with space group $P2_1/c$. Solution of the Patterson map allowed placement of the rhodium atom, and use of the program DIRDIF allowed location of all remaining atoms. An absorption correction was applied following isotropic refinement with the program DIFABS. In the final model, hydrogens were placed in idealized positions and all non-hydrogen atoms were refined anisotropically with the exception of C16, which tended towards non-positive definite refinement. Data collection and refinement parameters are given in Table 2.

Table 2

Summary of crystallographic data for $(C_5Me_5)Rh(PMe_3)[trans-CCF_3=CHCF_3]Cl$

Crystal parameters	
Chemical formula	RhPC ₁₇ H ₂₅ F ₆ Cl
Formula weight	512.7072
Crystal system	$P2_1/c$
Space group (no.)	14
Ζ	4
a (Å)	9.834(6)
b (Å)	12.527(7)
<i>c</i> (Å)	16.737(5)
β (°)	91.53(3)
$V(Å^3)$	2061(3)
$\rho_{\rm calc} \ ({\rm g} \ {\rm cm}^{-3})$	1.652
Crystal dimensions (mm)	$1.1 \times 2.2 \times 3.4$
Temperature (°C)	-20
Measurement of intensity data	
Diffractometer	Enraf–Nonius CAD4
Radiation (monochrom.)	Mo, 0.71073 Å (graphite)
Scan type	$2 heta/\omega$
Takeoff angle (°)	2.6
Total bkgd time	(scan time)/2
Scan rate (° min^{-1})	2–16.5
Scan range (°)	$0.7 + 0.35 \tan \theta$
2θ Range (°)	4-40
Data collected	$+h,+k,\pm l$
Number of data collected	3607
Number of unique data $F^2 > 3\sigma(F^2)$	1850
Number of parameters varied	235
$\mu (\mathrm{cm}^{-1})$	10.722
Systematic absences	h0l, l odd; 0k0, k odd
Absorption correction	differential
Range of transmission factors	0.78-1.18
Equiv. data	$0k1 = 0k\overline{1}$
Agreement between equiv. data (F_{o})	0.0467
$R(F_{o})$	0.0568
$R_{\rm w}(F_{\rm o})$	0.0590
Goodness-of-fit	1.779

6. Supplementary material

Supplementary material available includes tables of crystallographic data, atomic coordinates, bond distances and angles, and anisotropic thermal parameters for 4a (8 pages).

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