

Anisotropic thermal parameters were used only for the Rh, P, and Cl atoms. The phenyl rings were treated as rigid bodies of D_{6h} symmetry with C-C distances fixed at 1.395 Å and calculated hydrogen atom positions (C-H = 0.96 Å). None of the residual peaks detected in the Fourier difference map allowed us to localize the ethyne hydrogen atoms. Atomic coordinates for all the non-hydrogen atoms are given in Table IV.

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Supplementary Material Available: Final positional parameters for hydrogen atoms (Table V) and refined anisotropic and isotropic temperature factors (Table VI) for **2c**-DMF, the cyclic voltammetric behavior of **2b** in CH_2Cl_2 (Figure 8), and the cyclic voltammogram of **2b** in CH_2Cl_2 after exhaustive two-electron oxidation (Figure 9) (5 pages); a listing of observed and calculated structure factors for **2c**-DMF (13 pages). Ordering information is given on any current masthead page.

Coupling of Two Ethyne Molecules at Rhodium versus Coupling of Two Rhodium Atoms at Ethyne. 2. Implications for the Reactivity. Catalytic and Stoichiometric Functionalization Reactions of Ethyne

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The rhodacyclopentadiene complex $[(\text{triphos})\text{RhCl}(\eta^2\text{-C}_4\text{H}_4)]$ (**3**) has been synthesized by treatment of $[(\text{triphos})\text{RhCl}(\text{C}_2\text{H}_4)]$ (**1**) in CH_2Cl_2 with an excess of ethyne (triphos = $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$). Complex **3** catalyzes under very mild conditions the cyclotrimerization of ethyne to benzene as well as the cyclooligomerization of ethyne with acetonitrile to 2-picoline. A plausible catalysis cycle for both reactions is proposed on the basis of multiform experimental evidence. Complex **3** is a potential synthon for the preparation of a variety of heterocyclic compounds containing the C_4H_4 diene moiety. As an example, **3** reacts with dimethyl acetylenedicarboxylate, carbon disulfide, and *cyclo*-octasulfur, producing dimethyl phthalate, dithiopyrone, and thiophene, respectively. Carbon monoxide reacts with **3** in the presence of TiPF_6 , yielding $[(\text{triphos})\text{Rh}(\eta^4\text{-C}_4\text{H}_4\text{CO})]\text{PF}_6$ (**10**), which contains an unsubstituted cyclopentadienone ligand. By treatment with H_2 , **3** transforms into the η^4 -butadiene derivative $[(\text{triphos})\text{Rh}(\eta^4\text{-C}_4\text{H}_6)]\text{BPh}_4$ (**13**). The chemistry of **3** has been compared to and contrasted with that of the related *perpendicular* $\mu\text{-C}_2\text{H}_2$ complex $[(\text{triphos})\text{Rh}(\mu\text{-Cl})(\mu\text{-}\eta^2, \eta^2\text{-C}_2\text{H}_2)\text{Rh}(\text{triphos})]\text{Cl}$ (**2**). From this study it is concluded that coupling of two or more metal centers at acetylene may lead to inactive complexes for catalytic transformations of acetylene.

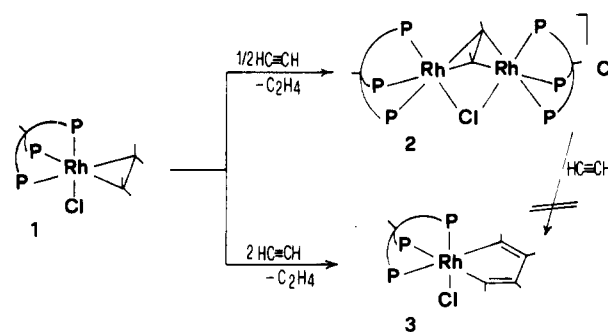
Introduction

In the preceding article,¹ we have shown that the reaction between $[(\text{triphos})\text{RhCl}(\text{C}_2\text{H}_4)]$ (**1**) and ethyne can selectively give either the bridging C_2H_2 dimer $[(\text{triphos})\text{Rh}(\mu\text{-Cl})(\mu\text{-}\eta^2, \eta^2\text{-C}_2\text{H}_2)\text{Rh}(\text{triphos})]\text{Cl}$ (**2**) or the product originated by coupling of two ethyne molecules at the metal, the rhodacyclopentadiene $[(\text{triphos})\text{RhCl}(\eta^2\text{-C}_4\text{H}_4)]$ (**3**) (triphos = $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$) (Scheme I). Along with a detailed characterization of the rhodacyclopentadiene complex, in this paper we compare and contrast the reactions of **2** and **3** with a variety of selected reagents. The two complexes exhibit quite different chemical properties. Distinct reactivities for **2** and **3** are not surprising and could well be predicted in view of their different structures. However, the question is not of trivial importance, since the two compounds form from the same reaction and only a subtle change of the conditions tips the balance in favor of either product.

Results and Discussion

As anticipated in the preceding article,¹ the most convenient way to synthesize the rhodacyclopentadiene com-

Scheme I



plex **3** is to dissolve **1** in dichloromethane previously saturated with ethyne at 0 °C. Addition of a mixture of acetone/*n*-hexane precipitates **3**· $(\text{CH}_3)_2\text{CO}$ as off-white crystals, which are stable in the solid state and in deoxygenated solutions. The complex behaves as a nonelectrolyte in CH_2Cl_2 and EtNO_2 , where it is monomeric as determined by molecular weight measurements. The IR spectrum contains a weak band at 1495 cm^{-1} , which can be assigned to $\nu(\text{C}=\text{C})$ within the metallacycle.³

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The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in CDCl_3 is temperature-invariant in the range $+50$ to -90°C and consists of a first-order AM_2X spin system with $\delta(\text{P}_\text{A})$ 28.91 and $\delta(\text{P}_\text{M})$ -18.52 ($J(\text{P}_\text{A}\text{P}_\text{M}) = 24.0$ Hz, $J(\text{P}_\text{A}\text{Rh}) = 141.1$ Hz, $J(\text{P}_\text{M}\text{Rh}) = 69.6$ Hz). This pattern is typical for octahedral triphos complexes of rhodium containing two chemically equivalent phosphorus nuclei.⁴

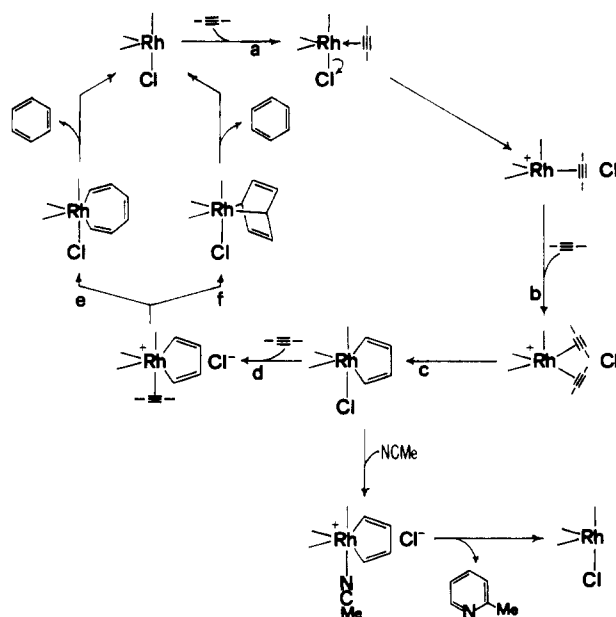
The ^1H NMR spectrum in CD_2Cl_2 is temperature-invariant and exhibits a multiplet at 5.97 ppm corresponding to two hydrogens. A chemical shift correlated 2D NMR (COSY) experiment showed this resonance to be correlated with a resonance at ca. 7.7 ppm in the aromatic hydrogen region. These chemical shifts are consistent with those for the only two other mononuclear C_4H_4 metallacycles, $[\text{CpCo}(\text{PMe}_3)(\text{C}_4\text{H}_4)]^5$ and $[\text{Cp}_2\text{Ti}(\text{C}_4\text{H}_4)]$.³ The higher field signal has been successfully simulated as the AA' part of an $[\text{AMX}]_2\text{Y}$ spin system with the following parameters: $\delta(\text{H}_\text{A}) = \delta(\text{H}_\text{A}') = 5.97$, $J(\text{H}_\text{A}\text{H}_\text{A}') = 4.0$ Hz, $J(\text{H}_\text{A}\text{H}_\text{M}) = J(\text{H}_\text{A}'\text{H}_\text{M}) = 5.7$ Hz, $J(\text{H}_\text{A}\text{H}_\text{M}') = J(\text{H}_\text{A}'\text{H}_\text{M}') = -2.7$ Hz, $J(\text{H}_\text{A}\text{P}_\text{X}) = J(\text{H}_\text{A}'\text{P}_\text{X}) = 3.2$ Hz, $J(\text{H}_\text{A}\text{P}_\text{X}') = J(\text{H}_\text{A}'\text{P}_\text{X}') = 10$ Hz, and $J(\text{P}_\text{X}\text{P}_\text{X}') = 7.1$ Hz (the symbols P_X and P_X' denote the phosphorus trans to the metallacycle carbons). The isochronous resonance of H_M and H_M' at ca. 7.7 ppm is partially masked by the signals of the phenyl hydrogens; nevertheless, selective decoupling experiments allowed us to approximately evaluate $J(\text{H}_\text{M}\text{Rh}) \approx 3$ Hz as well as to confirm the $J(\text{H}_\text{A}\text{H}_\text{M})$ value used in the computer simulation of the H_A resonance. The values of $J(\text{H}_\text{A}\text{Rh})$ and $J(\text{H}_\text{M}\text{Rh})$ are consistent with an assignment of H_A and H_M signals to the α - and β -hydrogens of the metallacycle, respectively. This assignment is also supported by the large coupling constants of H_A and H_A' to the phosphorus nuclei P_X and P_X' .

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** (CD_2Cl_2 , 20°C) exhibits a single resonance at 168.5 ppm for the α -carbons of the C_4H_4 moiety, showing they are chemically (but not magnetically) equivalent. This resonance consists of a dddd pattern and has successfully been simulated as the AA' part of an $\text{AA}'\text{MM}'\text{QX}$ spin system, where M and M' denote the two phosphorus atoms trans to the C_4H_4 ligand, Q denotes the remaining phosphorus, and X is rhodium. The largest coupling constant (109.2 Hz) is $J(\text{C}_\alpha\text{Rh})$. Three different values of $J(\text{C}_\alpha\text{P})$ confirm the magnetic nonequivalence of the phosphorus nuclei in **3** ($J(\text{C}_\alpha\text{P}_\text{M}) = 23.4$ Hz, $J(\text{C}_\alpha\text{P}_\text{M}') = 13.5$ Hz, $J(\text{C}_\alpha\text{P}_\text{Q}) = 7.9$ Hz). In good agreement with previous reports,^{3,6} the resonance of the β -carbon falls at higher field (139.7 ppm) as compared to C_α and consists of an unresolved multiplet. The gate-off decoupled ^{13}C NMR spectrum shows $^1J(\text{C}_\alpha\text{H})$ and $^1J(\text{C}_\beta\text{H})$ to be 150.7 and 154.2, respectively.

On the basis of all of these data, **3** can be readily assigned a structure in which rhodium is octahedrally coordinated by triphos, by the two terminal carbons of a C_4H_4 diene moiety, and by a chloride ligand (Scheme I).

Reactions of 2 and 3. Binuclear complexes containing $\mu\text{-}\eta^2,\eta^2$ -acetylene ligands may exhibit a rich, ligand-centered chemistry, including hydrogenation to the alkene⁷ and

Scheme II



coupling with further acetylene molecules to give oligomerization products.⁸ In some cases, the $\mu\text{-}\eta^2,\eta^2\text{-C}_2\text{R}_2$ complexes themselves serve as catalysts for acetylene hydrogenation^{7b,9} or functionalization reactions.¹⁰ In turn, compounds of the metallacyclopentadiene type may provide a good starting point for the study of oligomerization¹¹ and cycloaddition reactions of alkynes.^{8c,12,13}

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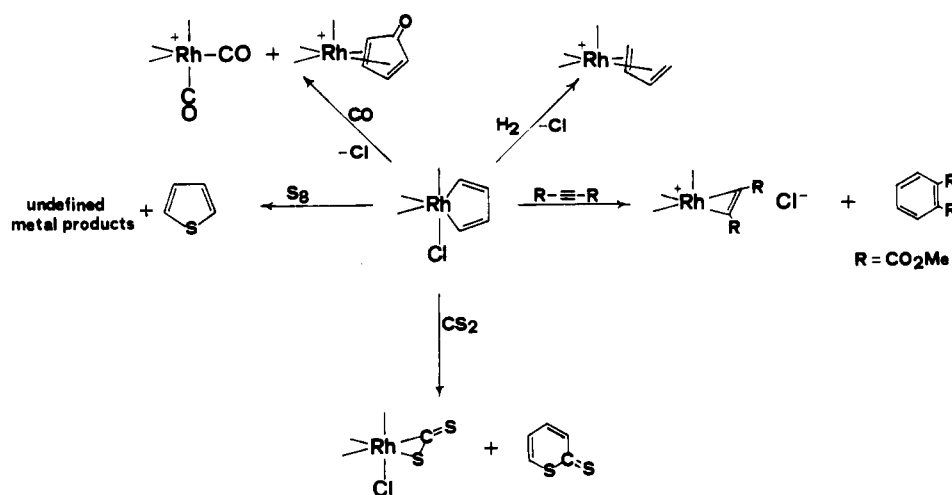
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Scheme III



With this in mind, we carried out the following reactions, which are summarized in Schemes II and III.

Ethyne Cyclotrimerization and Cocyclization with Disubstituted Alkynes. Compound 2 is stable in ethyne-saturated solutions, not converting to 3 even for long reaction times.¹ GC analysis of the reaction mixtures shows no formation of ethyne oligomers or polymers.

In contrast, 3 behaves as a catalyst for the cyclotrimerization of ethyne to benzene. The reaction occurs in CH_2Cl_2 at room temperature with a substrate to catalyst ratio of 200 and produces benzene with a turnover number of 6 (moles of product per mole of catalyst per hour). At the end of the catalysis cycle, 3 is recovered in almost quantitative yield. The reaction is selective, as we have no evidence for formation of other oligomerization or polymerization products of ethyne. Increasing the temperature decreases the turnover number due to partial conversion of the catalyst 3 to the inactive species 2.¹ When the reaction between 3 and excess ethyne is carried out in the presence of a chloride scavenger such as TIPF_6 or NaBPh_4 , only a stoichiometric amount of benzene is produced together with undefined metal products, suggesting that the chloride anion constitutes an essential ingredient in the catalysis cycle. An important role for the chloride ligand can be inferred also by comparing the reactions of ethyne with a catalytic amount of the related complexes $[(\text{triphos})\text{RhCl}(\text{C}_2\text{H}_4)]$ (1), $[(\text{triphos})\text{Rh}(\text{Me})(\text{C}_2\text{H}_4)]^2$ (4), and $[(\text{triphos})\text{Rh}(\text{Ph})(\text{C}_2\text{H}_4)]^2$ (5) under the same conditions employed for the cyclotrimerization reaction assisted by 3. As expected, 1 is as efficient as 3, except for the presence of an induction period necessary for its conversion to the rhodacyclopentadiene complex. In contrast, 4 and 5 show negligible catalytic activity for formation of benzene.

Having found that Cl^- is determinant for the occurrence of the present catalysis cycle, we try now to address the question of its specific role.

The chloride ligand in the parent compound 1 is tightly bound to rhodium, the Rh-Cl bond distance being 2.462 (7) Å.² A strong Rh-Cl bond seems to be maintained in solution, where 1 undergoes a fluxional process on the NMR time scale involving dissociation of the phosphorus trans to Cl. In actuality, a number of reactions assisted by 1 have been proposed to occur by a mechanism in which an arm of triphos dissociates to give a transient $[(\eta^2\text{-triphos})\text{RhCl}(\text{C}_2\text{H}_4)]$ species stabilized by π -donation from the chloride ligand.¹⁴ This is consistent with the fact that $[(\text{triphos})\text{RhX}(\text{C}_2\text{H}_4)]$ is fluxional for X = Cl but static for X = H, alkyl, Ph.² The ethylene ligand in 1 is certainly more labile than chloride, as the complex evolves C_2H_4 in ambient-temperature solutions. The resulting 16-electron $[(\text{triphos})\text{RhCl}]$ fragment decomposes to undefined products unless external ligands are added.^{15,16} When disubstituted alkynes such as dimethylacetylenedicarboxylate (DMAD) and diphenylacetylene (DPA) are used, the stable five-coordinate complexes $[(\text{triphos})\text{Rh}(\pi\text{-alkyne})]\text{BPh}_4$ (alkyne = DMAD (6), DPA (7)) are quantitatively obtained. Compound 6 has been described already.² The IR spectra of 6 and 7 exhibit $\nu(\text{C}\equiv\text{C})$ at 1750 and 1685 cm^{-1} , respectively, which is consistent with a metallacyclopentadiene type structure.^{2,11a} Monitoring the reactions between 1 and disubstituted alkynes in CD_2Cl_2 by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy shows the complex cations $[(\text{triphos})\text{Rh}(\pi\text{-alkyne})]^+$ to form as soon as the alkyne is added, indicating that it is not necessary to use a chloride scavenger. This is an important point, as it permits one to propose a reasonable mechanism for the formation of the rhodacyclopentadiene 3.

The pathway shown in Scheme II implies reaction of the 16-electron $[(\text{triphos})\text{RhCl}]$ fragment with ethyne to give the coordinatively unsaturated $[(\text{triphos})\text{Rh}(\pi\text{-C}_2\text{H}_2)]^+$ transient (step a), which adds a second alkyne molecule (step b). Finally, the rhodacyclopentadiene complex forms via C-C bond formation at rhodium, followed by reentry

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of Cl⁻ into the coordination sphere (step c).

In a similar way, the cyclotrimerization reaction leading to benzene may initially occur either by displacement of chloride ligand from **3** by ethyne (step d) or via an η^2 -triphos transient. Whether the successive reductive elimination of benzene proceeds via metallacycloheptatriene (step e) or 7-metallanorbornadiene^{11f} (step f) is hard to assess in the absence of detected intermediates. In effect, Diels–Alder addition of alkynes to the diene moiety of metallacyclopentadienes generally occurs between electron-rich diene moieties and alkynes exhibiting a much more dienophilic character than ethyne.^{11j}

Indeed, a Diels–Alder mechanism cannot be excluded for the reaction of **3** with the electrophilic DMAD. The reaction occurs at reflux temperature in CH₂Cl₂, giving dimethyl phthalate and the complex cation [(triphos)Rh(π -DMAD)]⁺ (Scheme III).^{11g,j} Only a stoichiometric amount of arene is produced even in the presence of large amounts of ethyne and DMAD, due to the great stability of **6**, which reacts neither with ethyne nor with DMAD.

A similar stability in the presence of alkynes is shown by **2**, which does not undergo bridge-exchange reactions when reacted with excesses of DMAD or DPA even at reflux temperature.

Cycloooligomerization of Ethyne with Acetonitrile. The capability of **3** to act as a catalyst precursor for the cyclotrimerization of ethyne prompted us to investigate the potential of this complex as a synthon for the preparation of heterocyclic compounds containing the C₄H₄ diene moiety. Indeed, **3** catalyzes the cocyclization of ethyne with CH₃CN to give 2-methylpyridine.^{12b-i}

In a typical run, **3** is dissolved in CH₂Cl₂ containing an excess of ethyne (200:1) and CH₃CN (1000:1) at room temperature. Along with 2-picoline (turnover number 4), some benzene is produced (turnover number 1). After the reaction is quenched by substituting nitrogen for ethyne, ca. 60% of **3** was recovered. ³¹P NMR spectroscopy shows formation of some unidentified rhodium complexes.

As in the cyclotrimerization reaction of ethyne, the chloride ligand in **3** plays a determinant role for the occurrence of a catalytic cycle for this reaction. In fact, only a stoichiometric amount of 2-picoline is produced when chloride is removed from **3** by addition of either NaBPh₄ or TlPF₆. Accordingly, the mechanism proposed for the cyclotrimerization reaction can be reasonably extended to the cocyclization with acetonitrile (Scheme II).

No reaction is observed between **2** and C₂H₂/CH₃CN mixtures.

Reactions with CS₂ and S₈. Reactions of **3** with either carbon disulfide in CH₂Cl₂ or *cyclo*-octasulfur in THF produce dithiopyrone and thiophene, respectively (Scheme III).¹²ⁱ Both reactions are stoichiometric even in the presence of large excesses of CS₂ or S₈-C₂H₂ mixtures. The absence of catalytic activity is again attributed to the stability of the metal species that forms after the cocyclization reaction. As a matter of fact, in the case of CS₂, red crystals of the known η^2 -CS₂ complex [(triphos)RhCl(η^2 -CS₂)]¹⁶ (**8**) can be isolated, which do not react with C₂H₂. An intractable mixture of undefined rhodium products containing sulfur and triphos is obtained from the reaction with S₈. Dithiopyrone and thiophene form also by reaction of CS₂ or S₈ with **3** in the presence of a chloride scavenger such as NaBPh₄, thus indicating that a free coordination site at the metal, here provided by chloride removal, is a necessary requisite for substrate-C₄H₄ moiety coupling reactions.

Carbon disulfide and *cyclo*-octasulfur react also with the μ -C₂H₂ dimer **2**, liberating ethyne and yielding the η^2 -CS₂

complex **8** and undefined sulfur-containing rhodium complexes, respectively.

Reactions with CO. Another reagent that proves able to cleave the μ - η^2 , η^2 -C₂H₂ bridge in **2** is carbon monoxide. As a result, 2 equiv of the known five-coordinate carbonyl [(triphos)RhCl(CO)]¹⁵ (**9**) is formed while C₂H₂ is evolved. The reaction occurs by bubbling CO into a CH₂Cl₂ solution of **2**.

A much more interesting reaction is observed between CO and **3** in CH₂Cl₂ to give the η^4 -cyclopentadienone complex [(triphos)Rh(η^4 -C₄H₄CO)]PF₆ (**10**).^{11g,12a,e,13} Unlike the functionalization reactions of the Rh-C₄H₄ moiety reported above, the formation of the addition product **10** occurs only by removing chloride from **3** with TlPF₆ (in the absence of halide scavengers only traces of **10** are detected by ³¹P NMR spectroscopy).

In a typical run, carbon monoxide is bubbled into a THF solution of **3** at 0 °C and then solid TlPF₆ is added with stirring. After TlCl is filtered off, *n*-heptane is added until precipitation of a microcrystalline compound occurs. The composition of the crude product depends on the time of CO bubbling. The quantitative transformation of **3** takes place in 40–50 min, but in this case, the crop of cyclopentadienone complex is contaminated by variable amounts of the known dicarbonyl [(triphos)Rh(CO)₂]PF₆ (**11**),^{15b} likely through a simple displacement reaction. Pure samples of **10** can be obtained by repeated recrystallizations from CH₂Cl₂ and ethanol. The complex is stable in deoxygenated solutions, where it behaves as a 1:1 electrolyte.

The structural formulation for **10**, as given in Scheme III, is strongly supported by its spectroscopic characterization. The IR spectrum contains a medium-intensity band at 1647 cm⁻¹, which can be readily assigned to ν -(C=O) of the cyclopentadienone ligand.^{13g,h,17d,e} No ν -(C=C) absorption is found in the 1600–1300-cm⁻¹ region, thus suggesting that the cyclopentadienone ligand is coordinated to the metal via the diene moiety.

Complex **10** is fluxional on the NMR time scale in room-temperature solutions, as shown by the ³¹P{¹H} NMR spectrum in CD₂Cl₂, which exhibits a single resonance at δ 16.29 ppm (*J*(PRh) = 124.1 Hz) for the three phosphorus atoms of triphos. Such a fluxionality is quite frequently observed for five-coordinate triphos complexes and is attributed to a fast non-bond-breaking interconversion between trigonal-bipyramidal and square-pyramidal structures.⁴ The complex becomes stereochemically rigid below -100 °C, as shown in Figure 1, which illustrates the variable-temperature spectra in the +20 to -105 °C range. Even at the lowest temperature, the spectrum is not completely resolved, as it consists of two broad bands with no discernable phosphorus and rhodium couplings; nevertheless, one can reasonably assume that the spectrum is going to show an AM₂X spin system with the M₂ resonance at lower field. A similar ³¹P NMR behavior is displayed by the η -8,9,10-trinorbornadiene complex [(triphos)Rh(nbd)]SO₃CF₃ (**12**) as well as the butadiene derivative [(triphos)Rh(η^4 -C₄H₆)]BPh₄ (**13**) (see below). An X-ray analysis showed **12** to contain a five-coordinate rhodium atom in a distorted-square-pyramidal arrangement.¹⁸ The midpoints of the diolefinic double bonds and two of the

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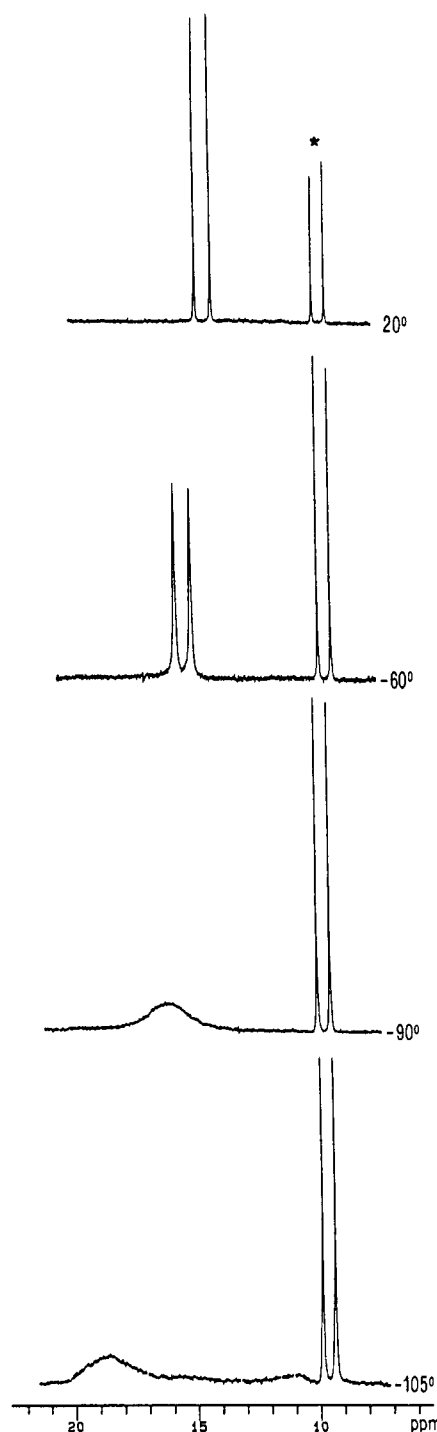


Figure 1. Variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of a 3:1 mixture of 10 and 11 (*) in CD_2Cl_2 (121.42 MHz, 85% H_3PO_4 reference).

three phosphorus atoms of triphos occupy equatorial sites, while the third one lies in the axial plane.

Conclusive evidence for the presence in 10 of a cyclopentadienone ligand coordinated to rhodium via the two double bonds is provided by the ^1H NMR spectrum in CD_2Cl_2 . As expected, the room-temperature spectrum shows 10 to be fluxional. The six CH_2 protons of triphos originate a unique resonance centered at 2.6 ppm, while the resonance of the central CH_3 group is a quartet ($J(\text{HP}) = 3.5$ Hz). The spectrum contains two pseudosextuplets of equal intensity (2 H) at 6.06 and 4.38 ppm, which a COSY experiment showed to be correlated with each other. The chemical shifts are in the proper range for hydrogens

belonging to cyclic enone compounds.^{13b,k} The lower field signal is attributed to the symmetric pair of hydrogens closer to the $\text{C}=\text{O}$ group^{13k} and has been computed as the AA' part of an $[\text{AM}]_2\text{X}_3\text{Y}$ spin system with the following parameters: $J(\text{H}_\text{A}\text{H}_\text{M}) = J(\text{H}_\text{A}'\text{H}_\text{M}') = 4.4$ Hz, $J(\text{H}_\text{A}\text{P}_\text{X}) = J(\text{H}_\text{A}'\text{P}_\text{X}') = 1.8$ Hz. In turn, the higher field signal constitutes the MM' part with $J(\text{H}_\text{M}\text{P}_\text{X}) = J(\text{H}_\text{M}'\text{P}_\text{X}') = 1.4$ Hz. Calculated values of ca. 0.5 Hz for $J(\text{H}_\text{A}\text{Rh})$ and $J(\text{H}_\text{M}\text{Rh})$ have been introduced to exactly reproduce the line shape of the signal. When the temperature is decreased to -105°C , the alkyl chains of triphos become rigid and give rise to a series of resonances between 2.4 and 2.0 ppm while the resonances of the dienone hydrogens remain practically unshifted but broaden, showing no discernable coupling constants.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in CD_2Cl_2 at room temperature is in agreement with the structure of the complex as well as with its fluxionality. Resonances at δ 177.6 (br, singlet), 89.7 (doublet, $J(\text{CRh}) = 5.4$ Hz), and 74.1 (pseudoquintet, $J(\text{CP}) \simeq J(\text{CRh}) \simeq 5.9$ Hz) can be attributed to the carbonyl carbon and to the other two types of cyclopentadienone ring carbons, respectively.^{17a-d} A reasonable mechanism for the formation of 10 involves carbon monoxide insertion across the $\text{Rh}-\text{C}$ bonds of 3 to give a metallacyclohexadienone intermediate, which then collapses, in a reductive-elimination step, to the η^4 -cyclopentadienone complex.

Reactions with H_2 . While the dimer 2 in CH_2Cl_2 does not react with H_2 (1 atm) at room temperature, the rhodacyclobutadiene 3 forms the η^4 -buta-1,3-diene complex $[(\text{triphos})\text{Rh}(\text{C}_4\text{H}_6)]^+$, which can be isolated as yellow crystals of tetraphenylborate salt 13. Although some 13 forms by direct reaction of 3 with H_2 , the reaction is faster and cleaner when chloride is preliminarily removed from 3. Alternatively, 13 is prepared by the straightforward reaction of 1 in CH_2Cl_2 with buta-1,3-diene, followed by NaBPh_4 addition. The latter route to 13 indirectly supports the structure of the product obtained by hydrogenation of 3.

Compound 13 is air-stable in both the solid state and solution, where it behaves as a 1:1 electrolyte. As anticipated in the previous section, 13 is fluxional on the NMR time scale. The room-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in CD_2Cl_2 consists of an unresolved signal at 12.6 ppm. The complex becomes stereochemically rigid at -50°C , showing an AM_2X spin system with $\delta(\text{P}_\text{A})$ 6.67, $\delta(\text{P}_\text{M})$ 15.76, $J(\text{P}_\text{A}\text{P}_\text{M}) = 22.4$ Hz, $J(\text{P}_\text{A}\text{Rh}) = 154.4$ Hz, and $J(\text{P}_\text{M}\text{Rh}) = 107.4$ Hz. In the slow-exchange limit, the spectrum defines the solution-state structure as square-pyramidal where rhodium is coordinated by the midpoints of the butadiene double bonds.

The ^1H NMR spectrum in CD_2Cl_2 at -50°C is poorly informative, as it exhibits unresolved resonances at 5.56 (2 H) and 1.93 ppm (4 H) for the CH and CH_2 protons of the coordinated diene, respectively. When the temperature is decreased to -100°C , two signals of equal intensity appear for the CH_2 hydrogens (1.95 and 1.88 ppm), indicating that the unique resonance observed at -50°C is just due to a fortuitous coincidence of the chemical shifts. In actuality, the structure for 13, shown in Scheme III, would imply magnetic nonequivalence of the CH_2 hydrogens.^{19a-c} A well-resolved ^1H NMR spectrum of 13 is obtained at room temperature (20°C). The portion of the spectrum

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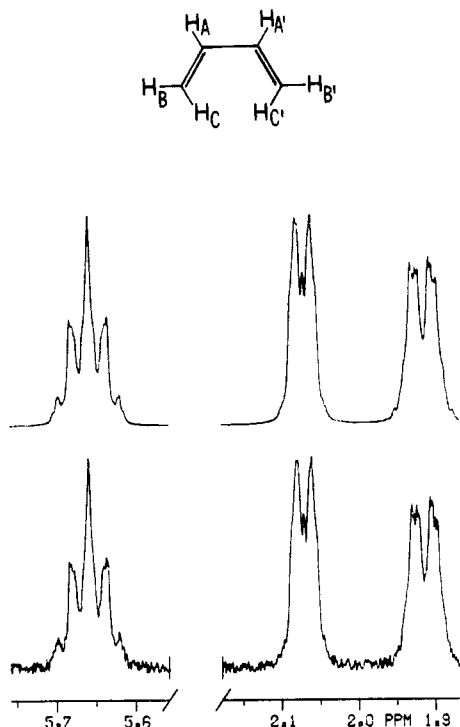


Figure 2. Experimental (lower) and computed (upper) ^1H NMR resonances for the butadiene hydrogens in **13** (299.945 MHz, 20 $^\circ\text{C}$, CD_2Cl_2 , TMS reference).

relative to the C_4H_6 hydrogens is reported in Figure 2 together with the computed spectrum. The butadiene hydrogens give rise to an $[\text{ABC}]_2$ spin system with $\delta(\text{H}_\text{A})$ 5.66, $\delta(\text{H}_\text{B})$ 2.07, and $\delta(\text{H}_\text{C})$ 1.91.²⁰ No coupling to phosphorus or rhodium nuclei is observed. Both chemical shifts and coupling constants fall in the proper range for related $\eta^4\text{-C}_4\text{H}_6$ complexes such as $[\text{Co}(\eta^4\text{-C}_4\text{H}_6)(\text{PMe}_3)_3]\text{BPh}_4$,^{19b} $[\text{Fe}(\eta^4\text{-C}_4\text{H}_6)(\text{PMe}_3)_3]$,^{19c} and $[(\text{triphos})\text{Co}(\eta^4\text{-C}_4\text{H}_6)]\text{-BPh}_4$.^{19a} Interestingly, the structure of the last complex has been described as distorted square pyramidal with the metal center bonded to the midpoints of the diolefin double bonds.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in CD_2Cl_2 at $-50\text{ }^\circ\text{C}$ is consistent with the proposed structure for **13**, as it shows the carbons of the $\eta^4\text{-C}_4\text{H}_6$ moiety to constitute two equivalent pairs (CH , δ 91.8; CH_2 , δ 42.0).^{19b,d}

Conclusions

The present work sheds some light on an area of prime importance in organometallic chemistry and homogeneous catalysis, namely oligomerization, cyclooligomerization, and functionalization reactions of acetylene.

The use of tripodal polyphosphine ligands has allowed us to isolate a novel example of unsubstituted metallacyclopentadiene. The complex is stable enough to permit one to study its role in several homogeneous catalytic and stoichiometric reactions involving ethyne.

From our results it is concluded that oligomerization, cyclooligomerization, and reductive dimerization reactions of ethyne occurring via metallacyclopentadiene intermediates require creation of a free coordination site at the metal.

Another result of this work comes from a comparison of the preparations and chemistry of **2** and **3**. Both compounds form by addition of ethyne to the 16-electron

fragment $[(\text{triphos})\text{RhCl}]$ and can be selectively produced by slightly varying the reaction conditions. However, while the rhodacyclopentadiene complex is a good catalyst precursor for several reactions of ethyne, the *perpendicular* acetylene dimer **2** and its *parallel* derivative $[(\text{triphos})\text{-Rh}(\mu\text{-}\eta^1, \eta^1\text{-C}_2\text{H}_2)(\mu\text{-Cl})_2\text{Rh}(\text{triphos})]^{2+}$ are a dead end for such reactions.¹

In summary, our results suggest that if one wishes to attempt metal-assisted functionalization reactions of ethyne, one must take care of any potential parameter affecting the initial interaction of the hydrocarbon with the metal center. In fact, the nature of the primarily generated product could be of critical importance in determining the following course of the reaction.

Experimental Section

General Data. THF, acetone, and CH_2Cl_2 were purified by distillation over LiAlH_4 , K_2CO_3 , and P_2O_5 under nitrogen just prior to use, respectively. All the other solvents and chemicals employed were reagent grade and were used as received. The compounds $[(\text{triphos})\text{RhX}(\text{C}_2\text{H}_4)]$ ($\text{X} = \text{Cl}, \text{Me}, \text{Ph}$)² and $[(\text{triphos})\text{Rh}(\mu\text{-}\eta^2, \eta^2\text{-C}_2\text{H}_2)(\mu\text{-Cl})\text{Rh}(\text{triphos})]\text{Cl}$ ¹ were prepared according to published procedures. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrophotometer using samples milled in Nujol between KBr plates. Conductivities were measured with an ORION Model 990101 conductance cell connected to a Model 101 conductivity meter. The conductivity data were obtained at sample concentrations of ca. 1×10^{-3} M in nitroethane solutions. Molecular weight determinations were executed by the previously described method.²¹

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at 299.945 and 75.429 MHz, respectively, on a Varian VXR 300 spectrometer. Peak positions are relative to tetramethylsilane as external reference. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Varian VXR 300 instrument operating at 121.42 MHz. Chemical shifts are relative to external 85% H_3PO_4 with downfield values reported as positive. Two-dimensional NMR spectra were recorded by using the Varian program COSY with optimized window functions. Simulation of NMR spectra was achieved by using an updated version of the DAVINS program.²² The initial choices of shifts and coupling constants were refined by iterative least-squares calculation with use of the experimental digitized spectrum. The final parameters gave a satisfactory fit between experimental and calculated spectra, the agreement factor R being 2.80%. All the calculations have been performed with a Toshiba T-3100e computer.

GC analyses were performed on a Shimadzu GC-8A gas chromatograph fitted with a thermal conductivity detector and a 6-ft 0.1% SP-1000 80/100 Carbowax C $1/8$ -in. stainless-steel column (Supelco Inc.). Quantification was achieved with a Shimadzu C-R6A Chromatopac coupled with the chromatograph, operating by an automatic correct area normalization method. GC/MS spectra were collected by using a Hewlett-Packard Model 5970A chromatograph equipped with a mass detector.

Synthesis of the Complexes. All reactions and manipulations were routinely performed under a nitrogen atmosphere by using Schlenk-line techniques. The solid compounds were collected on sintered-glass frits and washed with appropriate solvents before being dried under a stream of nitrogen.

$[(\text{triphos})\text{RhCl}(\eta^2\text{-C}_4\text{H}_6)]$ (3**).** Ethyne was bubbled through a solution of $[(\text{triphos})\text{RhCl}(\text{C}_2\text{H}_4)]$ (**1**; 1.2 g, 1.5 mmol) in CH_2Cl_2 (100 mL) for 1 h at $0\text{ }^\circ\text{C}$. There was a gradual color change from orange to light red. Ethyne was replaced with nitrogen, and after 15 min the solution warmed to room temperature. $^{31}\text{P}\{^1\text{H}\}$ NMR analysis of the solution indicated **3** as the main product (97%). Acetone (50 mL) was added to the reaction mixture. On concentration to 10 mL, off-white crystals of **3** as the acetone adduct began to form. The precipitation was completed by adding *n*-hexane (5 mL). The crystals were filtered off and washed with

(20) The following parameters have been used to simulate the experimental spectrum: $^3J(\text{H}_\text{A}\text{H}_\text{A}') = -5.36\text{ Hz}$, $^3J(\text{H}_\text{A}\text{H}_\text{B}) = 6.67\text{ Hz}$, $^4J(\text{H}_\text{A}\text{H}_\text{B}') = 0.58\text{ Hz}$, $^3J(\text{H}_\text{A}\text{H}_\text{C}) = 8.97\text{ Hz}$, $^4J(\text{H}_\text{A}\text{H}_\text{C}') = -1.74\text{ Hz}$, $^5J(\text{H}_\text{B}\text{H}_\text{B}') = 0.68\text{ Hz}$, $^2J(\text{H}_\text{B}\text{H}_\text{C}) = 0.62\text{ Hz}$, $^5J(\text{H}_\text{B}\text{H}_\text{C}') = 2.54\text{ Hz}$, $^5J(\text{H}_\text{C}\text{H}_\text{C}') = 1.52\text{ Hz}$.

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n-pentane; yield 90%. Anal. Calcd for $C_{48}H_{49}ClOP_3Rh$ ($3 \cdot (CH_3)_2CO$): C, 66.02; H, 5.66; Rh, 11.79. Found: C, 66.08; H, 5.59; Rh, 11.68.

Reaction of 3 with C_2H_2 . In a typical reaction 3 (0.005 mmol) was dissolved in 10 mL of CH_2Cl_2 containing about a 200-fold excess of ethyne at 20 °C. The solution was sampled after 2 h, and the GC and/or GC-MS analysis showed the formation of benzene (rate (moles per mole of catalyst per hour) 6). $^{31}P\{^1H\}$ NMR spectroscopy showed compound 3 to be the only rhodium complex present in solution during and at the end of the catalytic cycle. When the reaction was performed at reflux temperature, benzene production was initially observed; then it rapidly stopped due to transformation of 3 into the inactive species 2 (40%) and $[(triphos)RhCl_3]^{15b}$ (12%).

Reaction of 3 with DMAD. A mixture of 3 (0.09 g, 0.1 mmol) and a 10-fold excess of DMAD (0.14 g, 1 mmol) in CH_2Cl_2 (5 mL) was stirred for 2 h at reflux temperature. The formation of dimethyl phthalate and the known cation $[(triphos)Rh(\pi-DMAD)]^+$ was ascertained by GC/MS and ^{31}P NMR analysis, respectively. Stoichiometric amounts of dimethyl phthalate were also produced by using excess ethyne.

Reaction of 3 with MeCN under C_2H_2 . Complex 3 (0.005 mmol) was dissolved in 10 mL of CH_2Cl_2 containing MeCN (5 mmol) and ethyne (1 mmol) at 20 °C. The solution was analyzed after 2 h by GC and GC/MS methods, showing the formation of benzene (rate (moles per mole of catalyst per hour) 1) and of 2-picoline (rate 4). At the end of the catalysis cycle the presence of 3 (50–60%) along with some $[(triphos)RhCl(MeCN)_2]^{2+}$ was ascertained by $^{31}P\{^1H\}$ NMR spectroscopy.

Reaction of 3 with S_8 . A mixture of 3 (0.09 g, 0.1 mmol) and S_8 (0.51 g, 0.2 mmol) in THF (10 mL) was heated at reflux temperature for 3 h. Thiophene was produced during the reaction, as shown by GC/MS and 1H NMR spectroscopy. $^{31}P\{^1H\}$ NMR spectroscopy revealed the formation of several unidentified rhodium complexes.

Reaction of 3 with CS_2 . A mixture of 2 (0.31 g, 0.2 mmol) and a large excess of CS_2 (3 mL) in CH_2Cl_2 (30 mL) was heated at reflux temperature for 1 h. The resulting solution was concentrated to 5 mL and then eluted with a 3:1 mixture of benzene-*n*-heptane. Red crystals of $[(triphos)RhCl(\eta^2-CS_2)]$ (8) were obtained in 80% yield.

Reaction of 3 with CS_2 . A mixture of 3 (0.09 g, 0.01 mmol) and CS_2 (0.6 mL, 10 mmol) in CH_2Cl_2 (5 mL) was heated at reflux temperature for 1 h. The formation of dithiopyrone and the complex $[(triphos)RhCl(\eta^2-CS_2)]$ was ascertained by GC/MS and $^{31}P\{^1H\}$ NMR analyses.

Reaction of 2 with CO. A solution of 2 (0.31 g, 0.2 mmol) in CH_2Cl_2 (20 mL) was heated at reflux temperature under a CO

atmosphere for 1 h. Addition of ethanol (20 mL) and slow concentration under nitrogen gave yellow crystals of the known $[(triphos)RhCl(CO)]$ (9).

Reaction of 3 with CO. A solution of 3 (0.26 g, 0.3 mmol) in THF (30 mL) was treated with a stoichiometric amount of $TiPF_6$ at 0 °C under a CO atmosphere for 40 min. Addition of *n*-heptane (20 mL) and slow concentration under nitrogen gave an orange crystalline precipitate. This was characterized as a mixture of $[(triphos)Rh(CO)_2]PF_6$ (11; 15%) and $[(triphos)Rh(\eta^4-C_4H_4CO)]PF_6$ (10). Recrystallization from CH_2Cl_2 -ethanol gave a pure sample of 10. Anal. Calcd for $C_{46}H_{43}F_6OP_4Rh$: C, 58.00; H, 4.55; Rh, 10.80. Found: C, 57.83; H, 4.51; Rh, 10.49. $\Lambda_M = 77 \Omega^{-1} cm^2 mol^{-1}$.

Synthesis of $[(triphos)Rh(\eta^4-C_4H_6)]BPh_4$ (13). Butadiene was bubbled through a CH_2Cl_2 (30 mL) solution of 1 (0.79 g, 1 mmol) for 1 h. There was a color change from orange to lemon yellow. On addition of $NaBPh_4$ (0.34 g, 1 mmol) in ethanol (20 mL) yellow crystals precipitated; yield 85%. Anal. Calcd for $C_{69}H_{66}BP_3Rh$: C, 75.28; H, 5.95; Rh, 9.35. Found: C, 75.16; H, 5.85; Rh, 9.21. $\Lambda_M = 53 \Omega^{-1} cm^2 mol^{-1}$.

Reaction of 3 with H_2 . Hydrogen was bubbled through a solution of 3 (0.09 g, 0.1 mmol) in CH_2Cl_2 (5 mL) at room temperature for 1 h. $^{31}P\{^1H\}$ NMR spectroscopy evidenced the presence of the complex cation $[(triphos)Rh(\eta^4-C_4H_6)]^+$, which was precipitated as the tetraphenylborate salt by addition of $NaBPh_4$ in ethanol; yield 55%.

Synthesis of $[(triphos)Rh(\pi-PhC\equiv CPh)]BPh_4$ (7). Diphenylacetylene (0.36 g, 2 mmol) was dissolved in a CH_2Cl_2 (30 mL) solution of 1 (0.79 g, 1 mmol). There was a color change from orange to red. After 1 h, addition of $NaBPh_4$ (0.34 g, 1 mmol) in ethanol (20 mL) and partial evaporation of the solvent precipitated red crystals, which were collected by filtration and washed with ethanol and petroleum ether; yield 92%. Anal. Calcd for $C_{79}H_{66}BP_3Rh$: C, 77.45; H, 5.68; Rh, 8.40. Found: C, 77.13; H, 5.65; Rh, 8.31. $\Lambda_M = 50 \Omega^{-1} cm^2 mol^{-1}$. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 20 °C): A_3X system, 33.58 ppm, $J(PRh) = 107.7$ Hz. 1H NMR (CD_2Cl_2 , 20 °C): $\delta(CH_3)$ 1.78, q, $J(HP) = 3.2$ Hz; $\delta(CH_2)$ 2.67, d, $J(HP) = 8.4$ Hz.

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Supplementary Material Available: Experimental and computed 1H NMR resonances due to the α -hydrogens of the C_4H_4 moiety in 3 (Figure 3) and $^{13}C\{^1H\}$ NMR resonances due to the α -carbons of the C_4H_4 moiety in 3 (Figure 4) (2 pages). Ordering information is given on any current masthead page.