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# Hydrogen-Transfer Reactions of the Trihydride $[(MeC(CH_2PPh_2)_3)RhH_3]$: A Simple Route to Rhodium Cis Hydride $\eta^2$-Alkene Complexes

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The number, the disposition, and the nature of the substituents play an important role in determining the product composition of the reactions between the trihydride $[(triphos)RhH_3]$ (1) and mono- or 1,2-disubstituted alkenes (triphos = $MeC(CH_2PPh_2)_3$). In particular, alkenes bearing electron-withdrawing substituents such as $CO_2R$ or Ph stabilize cis hydride $\eta^2$-alkene complexes of the formula $[(triphos)Rh(H)(\eta^2\text{-alkene})]$, whereas electron-rich alkenes do not form $\eta^2$ adducts but are hydrogenated to alkanes by 1. Alkynes are more easily hydrogenated by 1 than comparable alkenes. The crystal structure of $[(triphos)Rh(H)(\eta^2\text{-DMFU})]\cdot C_4H_9OH$ has been determined by X-ray methods (DMFU = dimethyl fumarate). The coordination geometry is a distorted octahedron with rhodium bound to the three phosphorus atoms of triphos, to a hydride ligand, and to the two carbon atoms of a DMFU moiety. The C=C bond distance in the alkene ligand is significantly lengthened by interaction with the metal at a distance of 1.45 (2) Å, thus indicating a remarkable $\pi$-back-bonding contribution. Crystallographic details: space group $P2_12_12_1$ (orthorhombic); $a = 14.277$ (2), $b = 17.065$ (2), $c = 19.429$ (3) Å; $V = 4734$ Å$^3$; $Z = 4$; $R = 0.051$, $R_w = 0.063$ for 3847 observed reflections. The reactions of dimethyl maleate, *cis*-stilbene, and *cis*-4-methyl-2-pentene with a catalytic amount of 1 in tetrahydrofuran have been studied in detail. The former two alkenes are catalytically isomerized to their trans isomers, whereas both double-bond and cis → trans isomerizations occur for *cis*-4-methyl-2-pentene.

## Introduction

Transition-metal complexes stabilized by tripodal polyphosphine ligands are attracting considerable interest because of their effectiveness in a wide range of homogeneous catalytic reactions.[1] In particular, organorhodium compounds of the formula $[(triphos)Rh(R)(C_2H_4)]$ have proven efficient catalyst precursors for hydrogenation and hydroformylation reactions of olefins (triphos = $MeC(CH_2PPh_2)_3$; R = H, Me, Et, Ph).[1c,d] Recent results show that the replacement of ethylene with mono- or disubstituted alkenes may strongly affect the chemistry of the $[(triphos)Rh(R)(\eta^2\text{-alkene})]$ complexes.[1d,2] As an example, $[(triphos)Rh(H)(\eta^2\text{-DMFU})]$ (DMFU = dimethyl fumarate) is a much poorer catalyst for the hydrogenation of 1-hexene as compared to the $\eta^2$-ethylene analogue. It therefore appeared interesting to study systematically the influence of the alkene substituent(s) on the reactivity of organorhodium compounds of the type $[(triphos)Rh(H)(\eta^2\text{-alkene})]$. At a first stage, such a study necessarily requires designing an efficient synthetic route to as many derivatives as possible. Herein, we report on a simple method to accomplish this goal, namely the one-pot reaction of the trihydride $[(triphos)RhH_3]$[3] (1) with either alkenes or alkynes. The ability of 1 to act as a catalyst

Scheme I

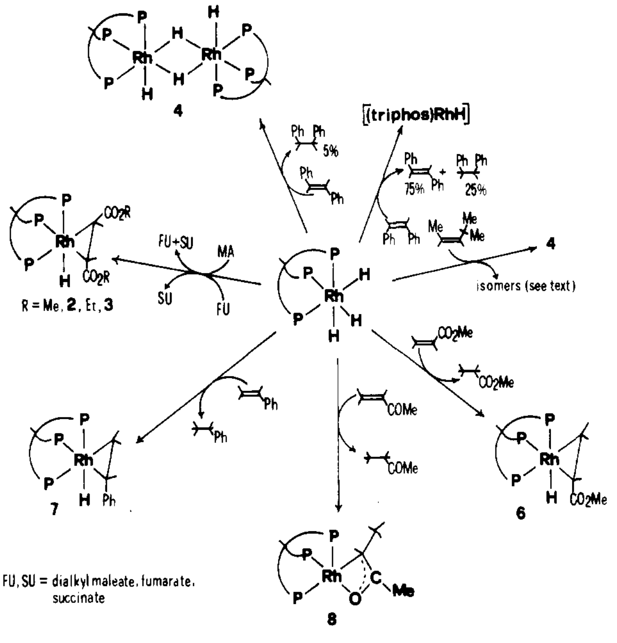

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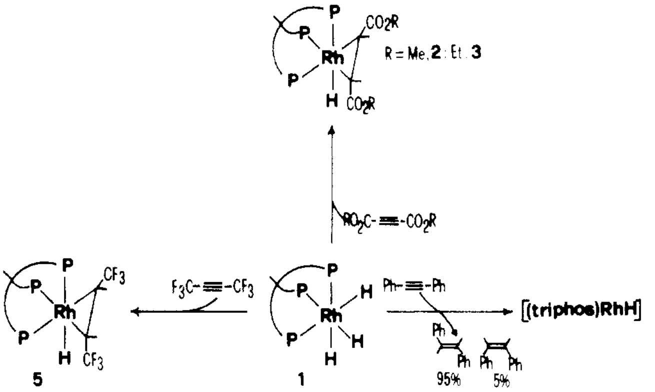
**Table I. $^{31}P\{^1H\}$ NMR Data for the Complexes**[a]

| | | | | chem shift, ppm[c] | | | coupling const, Hz | |
|---|---|---|---|---|---|---|---|---|
| compd | solvent[b] | temp, K | pattern | $\delta(P_A)$ | $\delta(P_M)$ | $\delta(P_Q)$ | $J$(PP) | $J$(PRh) |
| 2 | A | 298 | AMQX | 23.04 | 23.34 | 4.57 | ≅2–3 ($P_AP_M$)<br>30.0 ($P_AP_Q$)<br>29.7 ($P_MP_Q$) | 130.6 ($P_A$Rh)<br>132.6 ($P_M$Rh)<br>80.7 ($P_Q$Rh) |
| 3 | A | 298 | AMQX | 24.55 | 23.79 | 4.29 | ≅1–2 ($P_AP_M$)<br>30.0 ($P_AP_Q$)<br>29.5 ($P_MP_Q$) | 132.2 ($P_A$Rh)<br>131.3 ($P_M$Rh)<br>80.5 ($P_Q$Rh) |
| 5 | B | 298 | $AMQXY_3$[d] | 25.10 | 23.38 | 5.40 | ≅2–3 ($P_AP_M$)<br>30.8 ($P_AP_Q$)<br>30.8 ($P_MP_Q$) | 121.7 ($P_A$Rh)<br>122.1 ($P_M$Rh)<br>78.4 ($P_Q$Rh) |
| 6 | C | 298 | AMQX | 28.86 | 18.62 | 13.37 | 19.8($P_AP_M$)<br>31.6 ($P_AP_Q$)<br>31.6 ($P_MP_Q$) | 139.6 ($P_A$Rh)<br>125.9 ($P_M$Rh)<br>79.1 ($P_Q$Rh) |
| 7 | C | 298 | AMQX[e] | 21.00 | 13.67 | 13.71 | 32.3 ($P_AP_M$)<br>26.8 ($P_AP_Q$)<br>33.0 ($P_MP_Q$) | 130.9 ($P_A$Rh)<br>132.0 ($P_M$Rh)<br>82.7 ($P_Q$Rh) |
| | C | 213 | AMQX | 21.33 | 13.62 | 15.40 | 32.3 ($P_AP_M$)<br>31.9 ($P_AP_Q$)<br>30.2 ($P_MP_Q$) | 131.1 ($P_A$Rh)<br>131.8 ($P_M$Rh)<br>81.7 ($P_Q$Rh) |
| 8 | B | 253 | AMQX | 16.69 | 5.54 | −1.73 | 30.5 ($P_AP_M$)<br>23.3 ($P_AP_Q$)<br>30.9 ($P_MP_Q$) | 144.3 ($P_A$Rh)<br>102.6 ($P_M$Rh)<br>116.9 ($P_Q$Rh) |

[a] The chemical shift values (δ's) are relative to 85% $H_3PO_4$ with positive values being downfield from the standard. [b] Key: A, $C_6D_6$; B, $CD_2Cl_2$; C, THF-$d_8$. [c] In compounds 2–7 $P_Q$ refers to the triphos P atom trans to the hydride ligand, whereas $P_A$ and $P_M$ denote the residual P atoms in the plane containing the rhodium atom and the $\eta^2$-alkene ligand. [d] Y denotes the fluorine atoms of the $CF_3$ substituents. $J(P_AF) = J(P_MF) = 15.7$ Hz. [e] The room-temperature spectrum is slightly second order as far as the phosphorus $P_M$ and $P_Q$ atoms are concerned. The related NMR parameters (δ, $J$) were obtained through a spin simulation procedure (see Experimental Section).

**Scheme II**



precursor for the isomerization of cis-disubstituted alkenes has been studied in detail. This has provided useful mechanistic information on the hydride transfer from rhodium to alkene.

A preliminary communication of part of this work has already appeared.[2]

## Results

The preparations and the principal reactions of the compounds described in this paper are reported in Schemes I and II. Selected NMR spectral data for the new complexes are collected in Table I ($^{31}P\{^1H\}$ NMR) and Table II ($^1H$ NMR).

**Reactions of 1 with 1,2-Disubstituted Alkenes. Dialkyl Maleates and Dialkyl Fumarates (Alkyl = Me, Et).** Stirring 1 in benzene with a 2-fold excess of either dimethyl maleate (DMMA) or diethyl maleate (DEMA) at reflux temperature for 20 min results in the formation of a light brown solution, from which diamagnetic crystals of [(triphos)Rh(H)($\eta^2$-DMFU)] (2) and [(triphos)Rh(H)($\eta^2$-DEFU)] (3) (DEFU = diethyl fumarate) are precipitated by addition of $n$-heptane, respectively. The reactions are accompanied by production of the corresponding dialkyl succinate (60%) and dialkyl fumarate (40%) due to either hydrogenation or isomerization of excess olefin (Scheme I). Compounds 2 and 3 are stable in the solid state and in deareated solutions in which they behave as nonelectrolytes. The IR spectra of 2 and 3 contain $\nu$(Rh—H) as medium-intensity bands at 2020 and 2015 cm$^{-1}$, respectively. A couple of strong absorptions at 1690–1680 and 1680–1670 cm$^{-1}$ are present in the IR spectra of both compounds and are readily assigned to $\nu$(C=O) of uncoordinated ester groups.[4] The $^{31}P\{^1H\}$ NMR spectra ($C_6D_6$, 298 K) are quite similar to each other and consist of temperature-invariant AMQX spin systems. Such a pattern is typical of octahedral rhodium complexes of triphos containing three different ligands trans to each phosphorus.[1d] Notwithstanding, the phosphorus atoms $P_A$ and $P_M$ resonate at very close values of the magnetic field (23.04 and 23.34 ppm); no second-order effect perturbs the spectrum due to the very small values of the $J(P_AP_M)$ coupling constants (~2 Hz). Selective-decoupling experiments show that $P_Q$ is located trans to a hydride ligand (see below). The very similar nature of $P_A$ and $P_M$ is evidenced also by the nearly coincident values of the $T_1$ relaxation times measured with the inversion-recovery method (1.1 (2) and 1.0 (2) s at 298 K, respectively). The presence of a hydride ligand trans to a phosphorus atom in both compounds is clearly shown by the $^1H$ NMR spectra ($CD_2Cl_2$, 298 K), which contain well-resolved resonances in the hydride region. These appear as two largely separated doublets of pseudodoublets, which can be properly simulated as the A portions of AMQRX spin systems (see Table II). The largest coupling constants (2, 181.2 Hz; 3, 182.2 Hz) are evidently $J(HP_Q)$, as the two nuclei are trans to each other.[5] An estimated value of ca. 1–2 Hz for $J(HP_M)$ has been introduced to reproduce the line width of the resonance. Valuable information on the conformation of the alkene ligand that occupies the two remaining coordination sites around rhodium is provided by the analysis of the $^1H$ NMR spectra. Figure 1 shows

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Table II. $^1$H NMR Spectral Data for the Complexes[a]

| compd | assignt | pattern[c] | chem shift, ppm (intens)[b] | coupling const, *J*, Hz | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | HH | HM | HR | HQ | HX |
| 2 | Rh*H* | AMQRX | −11.72 (1 H) | | 4.9 | ≅2 | 181.2 | 8.0 |
| | C*H*$_A$C*H*$_B$ | ABMQRX | 4.55 (1 H) | 8.8 | 2.3 | 2.3 | 4.8 | 9.1 |
| | | | 3.75 (1 H) | | 1.2 | 8.6 | 1.2 | 8.6 |
| | OC*H*$_3$ | A$_3$ | 3.32 (3 H) | | | | | |
| | | | 3.52 (3 H) | | | | | |
| 3 | Rh*H* | AMQRX | −11.70 (1 H) | | 5.0 | ≅0 | 182.2 | 7.3 |
| | C*H*$_A$C*H*$_B$ | ABMQRX | 4.54 (1 H) | 9.1 | 2.3 | 2.3 | 4.9 | 9.2 |
| | | | 3.81 (1 H) | | 1.5 | 1.5 | 7.8 | 9.1 |
| | OC*H*$_2$CH$_3$[d] | ABD$_3$ | 4.08 (1 H) | −10.8 (AB) | | | | |
| | | | | 7.3 (AD) | | | | |
| | | | 3.96 (1 H) | 7.2 (BD) | | | | |
| | OCH$_2$C*H*$_3$ | ABD$_3$ | 1.00 (3 H) | | | | | |
| | OC*H*$_2$CH$_3$[d] | ABD$_3$YY′[e] | 3.74 (1 H) | −10.6 (AB) | | | | |
| | | | | 7.1 (AD) | | | | |
| | | | 3.45 (1 H) | 7.2 (BD) | | | | |
| | OCH$_2$C*H*$_3$ | ABD$_3$YY′[e] | 1.10 (3 H) | | | | | |
| 5 | Rh*H* | AMQRX | −12.08 (1 H) | | 4.8 | ≅0 | 178.2 | 4.8 |
| | C*H*$_A$C*H*$_B$ | br | 3.59 (1 H) | | | | | |
| | | br | 2.93 (1 H) | | | | | |
| 6 | Rh*H* | AMQRX | −11.20 (1 H) | | 5.1 | 5.1 | 179.1 | 12.5 |
| | C*H*$_2$CH | ABDMQRX | 3.40 (1 H) | 6.5 (AB) | 7.1 | ≅0 | 7.1 | 7.0 |
| | | | | 2.0 (AD) | | | | |
| | | | 2.87 (1 H) | 6.6 (BD) | 7.1 | ≅0 | 7.1 | 7.1 |
| | CH$_2$C*H* | ABDMQRX | 1.83 (1 H) | | 6.5 | ≅0 | 6.5 | 8.1 |
| | OC*H*$_3$ | A$_3$ | 3.70 (3 H) | | | | | |
| 7[f] | Rh*H* | AMQRX | −10.89 (1 H) | | 12.1 | ≅0 | 171.4 | 12.1 |
| | C*H*$_2$CH | br | 3.55 (1 H) | | | | | |
| | | | 3.34 (1 H) | | | | | |
| | CH$_2$C*H* | br | 2.12 (1 H) | | | | | |
| 8[g] | CH$_3$C*H* | br | 4.30 (1 H) | 6.0 | | | | |
| | C*H*$_3$CH | br d | 2.06 (3 H) | | | | | |
| | C*H*$_3$C(O) | A$_3$M$_3$X | 2.32 (3 H) | | 10.6 | 10.6 | 10.6 | 20.3 |

[a] All the $^1$H NMR spectra were recorded at 299.945 MHz in CD$_2$Cl$_2$ solutions at ambient temperature (298 K) unless otherwise stated. The resonances due to the hydrogen atoms belonging to the triphos ligand are not reported. [b] The chemical shift values ($\delta$'s) are relative to tetramethylsilane as external standard. [c] The letters A, B, and D refer to hydrogen atoms; the letters M, Q, and R denote the phosphorus donors of the triphos ligand and, finally, the letter X refers to the rhodium nucleus: br = broad, d = doublet. [d] The two CH$_2$ protons of the carbethoxy group form a diastereotopic pair (see text). [e] Y and Y′ represent two heteronuclei to which the H$_A$ nucleus and the three D$_3$ protons are weakly coupled: $|J(H_AY) + J(H_AY')| \cong 6$ Hz; $|J(DY) + J(DY')| \cong 2$–3 Hz (see text). [f] At 213 K. [g] At 223 K.

the experimental and computed spectra of 2 in the 4.60–3.70 ppm region. Two multiplets centered at 4.55 ppm (1 H) and 3.75 ppm (1 H) are assigned to the C–H protons of the disubstituted alkene ligand and have been computed as the AB parts of ABMQRX systems. The nonequivalence of the two C–H hydrogens is consistent with an *E* structure (dimethyl fumarate) of the alkene ligand.[6] In accord with this interpretation, the two hydrogen nuclei exhibit quite different values of the coupling constants to P$_Q$ (i.e. the phosphorus trans to hydride): $J(H_AP_Q) = 4.8$ Hz, $J(H_BP_Q) = 1.2$ Hz. Such a difference may be interpreted in terms of a closer proximity of H$_A$ to P$_Q$ as compared to H$_B$ (through-space interaction).[7] The trans conformation of the alkene ligand is also supported by the different chemical shifts of the two methoxy hydrogens as well as by the $^{13}$C{$^1$H} NMR spectrum (CD$_2$Cl$_2$, 298 K), which exhibits two distinct resonances at 179.82 and 178.24 ppm for the COOCH$_3$ carbon atoms.

The $^1$H NMR spectrum of the DEFU derivative 3 in the 4.60–3.70 ppm region is similar to that of 2 except that it contains the signals of the CH$_2$ groups of the ethoxy substituents. Each pair of methylene protons constitutes a diastereotopic pair due to the asymmetric centers at the alkene carbons.[8] As a matter of fact, the resonances of these CH$_2$ groups can be computed as the AB part of the ABD$_3$ spin systems. A detailed computer analysis of both patterns shows that the H$_A$ component of the higher field AB system is also weakly coupled to two heteronuclei, most likely rhodium and P$_Q$ with $|J(H_AY) + J(H_AY')| \approx 6$ Hz. In a similar way, the D$_3$ portion of the same ABD$_3$ pattern appears to feel the magnetic effects of some heteronuclei, as the line shape of its resonance can be nicely reproduced only by introducing an additional coupling constant of 2–3 Hz. We are inclined to assign this ABD$_3$ system to the

Table III. Selected Bond Lengths (Å) and Angles (deg) for [(triphos)Rh(H)($\eta^2$-DMFU)][a]

| | | | |
|---|---|---|---|
| Rh–P1 | 2.296 (3) | O1–C5 | 1.46 (2) |
| Rh–P2 | 2.394 (3) | O2–C3 | 1.22 (1) |
| Rh–P3 | 2.297 (3) | O3–C4 | 1.25 (2) |
| Rh–C1 | 2.16 (1) | O4–C4 | 1.32 (2) |
| Rh–C2 | 2.17 (1) | O4–C6 | 1.45 (2) |
| C1–C2 | 1.45 (2) | P–C[b] | 1.85 (2) |
| C1–C3 | 1.43 (2) | C11–C21 | 1.59 (2) |
| C2–C4 | 1.42 (2) | C11–C32 | 1.60 (2) |
| O1–C3 | 1.35 (1) | C11–C43 | 1.55 (2) |
| Rh–C1–C2 | 70.8 (6) | P1–Rh–P2 | 88.3 (1) |
| Rh–C2–C1 | 69.9 (6) | P1–Rh–P3 | 89.7 (1) |
| C1–Rh–P1 | 113.6 (3) | P2–Rh–P3 | 90.8 (1) |
| C1–Rh–P2 | 99.9 (3) | C1–C2–C4 | 120.9 (8) |
| C1–Rh–P3 | 154.4 (1) | C2–C1–C3 | 119.6 (8) |
| C2–Rh–P1 | 150.7 (1) | O1–C3–O2 | 119.5 (8) |
| C2–Rh–P2 | 105.2 (3) | O3–C4–O4 | 123.3 (8) |
| C2–Rh–P3 | 115.6 (3) | | |

[a] Esd's in the last significant figure in parentheses. [b] Average value; the standard deviation of the mean is given in parentheses.

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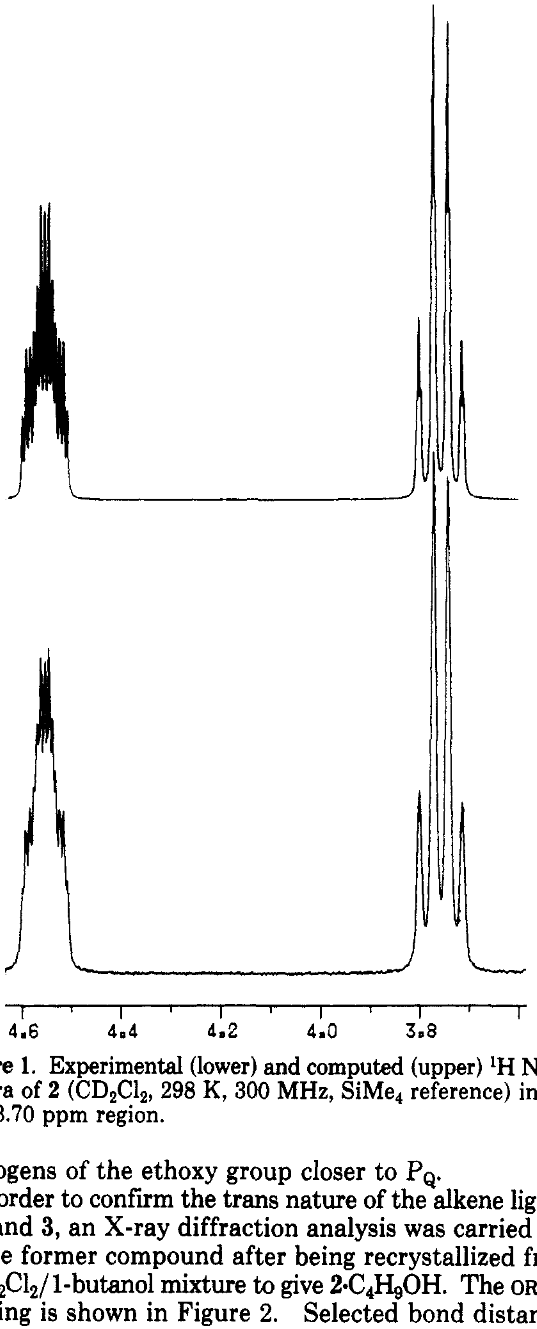

**Figure 1.** Experimental (lower) and computed (upper) $^1$H NMR spectra of **2** ($CD_2Cl_2$, 298 K, 300 MHz, $SiMe_4$ reference) in the 4.60–3.70 ppm region.

hydrogens of the ethoxy group closer to $P_Q$.

In order to confirm the trans nature of the alkene ligand in **2** and **3**, an X-ray diffraction analysis was carried out on the former compound after being recrystallized from a $CH_2Cl_2$/1-butanol mixture to give **2**·$C_4H_9OH$. The ORTEP drawing is shown in Figure 2. Selected bond distances and angles are reported in Table III.

The structure consists of discrete mononuclear [(triphos)Rh(H)($\eta^2$-DMFU)] molecules with 1-butanol solvent molecules in the lattice. In keeping with the chemical-physical characterization of the complex, the coordination geometry around the rhodium center is a distorted octahedron with the metal bound to the three phosphorus atoms of triphos, to a hydride ligand, and to the two carbons of a DMFU moiety. The Rh–P distances are nonequivalent. In particular, the Rh–P bond trans to the hydride ligand is longer (2.394 (3) Å) then the other two (average 2.296 (3) Å).[9] The latter separations are comparable with those found in $[(\text{triphos})RhH_2(Au(PPh_3))_3]^{2+}$ (average 2.313 (5) Å)[10] or in complex **1** (average 2.304 (6) Å)[3] but significantly shorter than that in [(triphos)Rh(Cl)($C_2H_4$)] (average 2.361 (9) Å).[1d] Both Rh–C(alkene) (average 2.16 (1) Å) and C–C(alkene) (1.45 (2) Å) distances are also comparable to those found in [(triphos)Rh(Cl)($C_2H_4$)] (average 2.19 (2) and 1.49 (4) Å, respectively).[4,11] From these observations, if we assume values of 1.54 and 1.34 Å as distances in single and double bonds, respectively, the C–C(alkene) separation found in **2**·$C_4H_9OH$ lies midway between the two, indicating an appreciable amount of $\pi$ back-bonding.[12] The other bond lengths in the DMFU ligand fall in the expected range.[4,13] The conformation of the alkene is the trans one, consistent with the solution behavior. Any intramolecular or intermolecular metal–oxygen contact can be ruled out, as we have suggested, on the basis of the IR spectra.

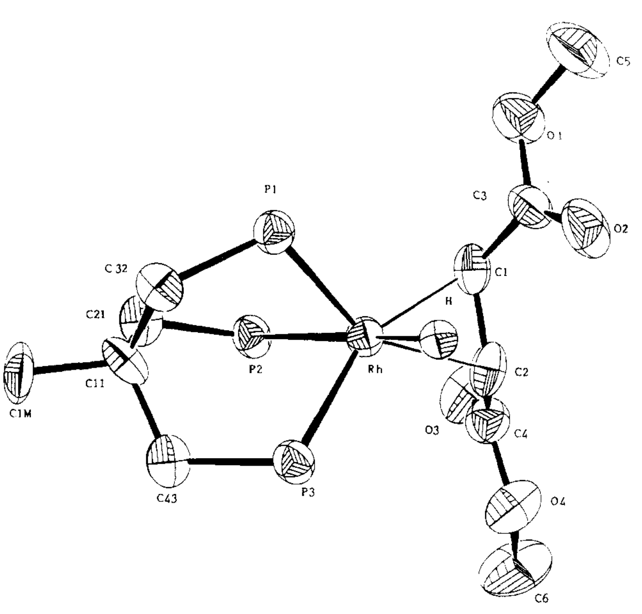

**Figure 2.** ORTEP drawing of the complex [(triphos)Rh(H)($\eta^2$-DMFU)]. The phenyl rings of the triphos ligand are omitted for clarity.

It is worth noting that **2**·$C_4H_9OH$ was synthesized from DMMA, and it is the same as that obtained with DMFU (see below). Therefore, the complexation of the olefin by the [(triphos)RhH] fragment occurs with its complete isomerization.

In a similar way, the ethyl analogue **3** can be quantitatively obtained also by stirring **1** in refluxing benzene with 2 equiv of DEFU. Interestingly, unlike dialkyl maleates, only traces of alkyl succinates are formed.

***cis*- and *trans*-Stilbene.** Under the conditions employed for the reactions with dialkyl maleates and fumarates, treatment of **1** with 2 equiv of *cis*-stilbene results in the formation of *trans*-stilbene (75%) and 1,2-diphenylethane (25%) (Scheme I). By addition of *n*-heptane, a gray powder precipitates, which contains rhodium and triphos in a ca. 1:1 ratio. No precise formula can be assigned to this product, which, on the basis of $^{31}$P NMR spectroscopy, appears as a mixture of various compounds originating from degradation of the [(triphos)RhH] moiety.

A quite different result is obtained when **1** is reacted with 2 equiv of *trans*-stilbene. Practically no hydrogenation of alkene occurs (<5%), whereas red crystals of the known tetrahydride [(triphos)Rh(H)($\mu$-H)$_2$(H)Rh(triphos)] (**4**) form in 90% yield (Scheme I).[1f]

***cis*-4-Methyl-2-pentene.** The reaction of **1** with 2 equiv of *cis*-4-methyl-2-pentene proceeds midway between the

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(9) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Ramirez, J. A.; Vacca, A.; Zanobini, F. *Organometallics* **1989**, *8*, 2179.

(10) Albinati, A.; Demartin, F.; Janser, P.; Rhodes, L. F.; Venanzi, L. M. *J. Am. Chem. Soc.* **1989**, *111*, 2115.

(11) Carr, S. W.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1987**, 1763.

(12) Guggenberger, L. J.; Cramer, R. *J. Am. Chem. Soc.* **1972**, *94*, 3779.

(13) (a) Agnes, G.; Bassi, I. W.; Benedicenti, C.; Intrito, R.; Calcaterra, M.; Santini, C. *J. Organomet. Chem.* **1977**, *129*, 401. (b) Bassi, I. W.; Calcaterra, M. *J. Organomet. Chem.* **1976**, *110*, 129.

reactions with *cis*- and *trans*-stilbene. The tetrahydride 4 is isolated in 60% yield, while the excess olefin is essentially isomerized to *trans*-4-methyl-2-pentene and 2-methyl-2-pentene (see below).

**Reactions of 1 with Disubstituted Alkynes.** Disubstituted alkynes such as dialkyl acetylenedicarboxylate (alkyl = Me, Et), hexafluorobut-2-yne, and diphenylacetylene are readily hydrogenated to alkene by 1.[6] In a typical procedure, 1 is stirred in benzene with a slight excess of alkyne either at room or at reflux temperature. Addition of *n*-heptane precipitates 2, 3, or [(triphos)Rh(H)($F_3C(H)C{=}C(H)CF_3$)] (5) in ca. 90% yield. In agreement with the results presented in the preceding section, no defined metal product is obtained from the reaction with diphenylacetylene, whereas most of the alkyne is hydrogenated to *trans*-stilbene (Scheme II).

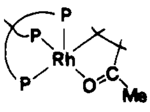
The novel cis hydride $\eta^2$-alkene complex 5 shows $\nu$(Rh–H) at 2040 cm$^{-1}$ and $\nu$(C–F) at 1290, 1265, and 1250 cm$^{-1}$. The $^{31}P\{^1H\}$ NMR spectrum ($CD_2Cl_2$, 298 K) consists of a temperature-invariant $AMQXY_3$ spin system and is similar to those of the fumarate derivatives 2 and 3 except for exhibiting additional couplings of $P_A$ and $P_M$ to the fluorine nuclei (Y nuclei) of the $CF_3$ groups ($J(P_AF)$ = $J(P_MF)$ = 15.7 Hz). The phosphorus atom $P_Q$ is located trans to a hydride ligand ($J(P_QH)$ = 178.2 Hz), the $^1H$ NMR resonance of which consists of two largely separated pseudotriplets (Table II). Like the dialkyl fumarate analogues, the signal of the hydride ligand has been computed as the A part of an AMQRX spin system. No coupling of hydride to fluorine is observed. The two alkene C–H hydrogens are not equivalent (*E* structure) and give rise to two unresolved broad multiplets centered at 3.59 and 2.93 ppm. On the basis of all of these data, compound 5 is assigned a structure in which the metal center is octahedrally coordinated by the three phosphorus atoms of triphos, by hydride, and by a $\eta^2$-bonded *trans*-1,2-(trifluoromethyl)ethylene ligand (Scheme II).

**Reactions of 1 with Monosubstituted Alkenes. Methyl Acrylate and Styrene.** The cis hydride $\eta^2$-alkene complexes [(triphos)Rh(H)($H_2C{=}C(H)CO_2Me$)] (6) and [(triphos)Rh(H)($H_2C{=}C(H)Ph$)] (7) are obtained as well-shaped crystals by reacting 1 in benzene with 2 equiv of methyl acrylate or styrene, respectively. The excess alkene is almost quantitatively hydrogenated to alkane (Scheme I).

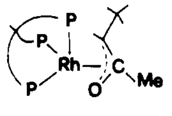
Compounds 6 and 7 are stable in both the solid state and deareated solutions, in which they behave as nonelectrolytes. The presence of a hydride ligand in both compounds is shown by medium-intensity IR absorptions at 1965 (6) and 1955 cm$^{-1}$ (7). The IR spectrum of 6 contains $\nu$(C=O) and $\nu$(C—O—C) of the uncoordinated ester group at 1665 and 1160 cm$^{-1}$, respectively.[4] A reinforced phenyl vibration at 1595 cm$^{-1}$ is diagnostic for the phenyl substituent of styrene. The methyl acrylate derivative is rigid on the NMR time scale over the temperature range 193–333 K in THF-$d_8$. The three phosphorus atoms of triphos give rise to an AMQX pattern as expected because of the three different ligating groups trans to each phosphorus. The higher field resonance ($P_Q$) is assigned to the phosphorus atom trans to the hydride ligand. The resonance of the hydride ligand can be properly simulated as the A part of an AMQRX spin system. The alkene hydrogens constitute the ABD portion of an ABDMQRX spin system with $\delta(H_A)$ = 3.40 ppm, $\delta(H_B)$ = 2.87 ppm, and $\delta(H_D)$ = 1.83 ppm. The higher field signal is assigned to the C–H hydrogen.

On the basis of all of these data, a structure can be assigned to 6 in which the rhodium center is coordinated by triphos, a hydride ligand, and a $\eta^2$-bonded methyl acrylate molecule in an octahedral environment. The same structure can be assigned to the styrene derivative 7 over the temperature range 213–298 K. In fact, the $^{31}P\{^1H\}$ NMR spectrum (THF-$d_8$) exhibits an AMQX pattern, while the $^1H$ NMR spectrum in the hydride region ($CD_2Cl_2$, 213 K) contains two largely separated pseudotriplets. Such a resonance can be computed as the A part of an AMQRX pattern with $J(HP_Q)$ = 171.4 Hz. As found for the methyl acrylate derivative, the alkene hydrogens constitute an ABD spin system, D being the C–H proton (see Table II).

**Methyl Vinyl Ketone.** Treatment of 1 in refluxing benzene with a 2-fold excess of methyl vinyl ketone results in the formation of pale yellow crystals of [(triphos)Rh($\eta^3$-(Me)CHC(Me)O)] (8). Methyl ethyl ketone is detected by GC in the reaction mixture due to hydrogenation of excess olefin. Compound 8 is stable in the solid state as well as in deareated solutions, in which it behaves as a nonelectrolyte. Unlike all of the other products obtained by reacting 1 with alkenes, 8 does not contain a terminal hydride ligand. In fact, neither the IR spectrum exhibits absorptions in the 2200–1600-cm$^{-1}$ region nor the $^1H$ NMR spectrum ($CD_2Cl_2$, 303–183 K) exhibits resonances in the hydride region. The compound is slightly fluxional on the NMR time scale in ambient-temperature solutions, as shown by the $^{31}P\{^1H\}$ NMR spectrum ($CD_2Cl_2$, 273 K), which consists of three poorly resolved doublets centered at 16.78 ppm ($J$(PRh) = 101.5 Hz), 5.97 ppm ($J$(PRh) = 143.6 Hz), and −2.02 ppm ($J$(PRh) = 118.1 Hz). When the temperature is lowered by only 20 °C, the spectrum is fully resolved, showing a typical AMQX spin system with a negligible temperature dependence of the chemical shifts. Below 253 K the spectrum is temperature-invariant. The contemporaneous absence of charge and hydride ligand provides evidence that migration of hydride from rhodium to $\eta^2$-alkene has occurred during the reaction of 1 with methyl vinyl ketone. In principle, the hydride ligand can migrate either to the $CH_2$ carbon or to the CH carbon. In both cases, a $\sigma$-alkyl Rh(I) complex is expected to form, which, however, cannot be stable per se due to its electron-deficient nature. In actuality, a stabilizing interaction seems to be provided by the ketonic C=O group. This, in fact, is bonded to rhodium as shown by $\nu$(C=O), which is shifted to low energy by ca. 145 cm$^{-1}$ as compared to that of free methyl vinyl ketone (1535 vs 1680 cm$^{-1}$).[14] Further experimental evidence supporting hydride migration to alkene is provided by the reaction of 8 with strong protic acids such as $HOSO_2CF_3$, which leads to the formation of free methyl ethyl ketone. On the basis of this preliminary experimental evidence, compound 8 may be described either as in A or as in B.



A



B

Valuable information for discriminating between structures A and B is provided by the analysis of the $^1H$ NMR spectrum ($CD_2Cl_2$, 223 K) in the 4.5–1.5 ppm region. In addition to the signals of the six $CH_2$ hydrogens of the alkyl chains of triphos, the spectrum exhibits a broad singlet at 4.30 ppm (1 H, $w_{1/2}$ = 18 Hz), a well-resolved multiplet at 2.32 ppm (3 H), and a rather broad doublet

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[14] (a) Deeming, A. J.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1973**, 1849. (b) Lundquist, E. G.; Huffman, J. C.; Folting, K.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1165.

at 2.06 ppm. The last signal is partially superimposed on the resonance of an hydrogen belonging to an alkyl chain of triphos. After the intensity due to one hydrogen is substracted, (this can be precisely determined from the intensity of the resonance of the $CH_3$ group of triphos, which falls at 1.50 ppm), the doublet is integrated as three hydrogens. The multiplet centered at 2.32 ppm can be reasonably assigned to a $CH_3$ group. This gives rise to an $A_3M_3X$ spin system, where A, M, and X denote H, P, and Rh, respectively. The fortuitous coincidence of the coupling constants of the three equivalent hydrogens of the $CH_3$ group to the phosphorus atoms of triphos ($J(HP)$ = 10.6 Hz) and the $J(HRh)$ value of 20.3 Hz are responsible for the observed dq pattern. A chemical shift correlated 2D NMR (COSY) experiment shows that the broad singlet at 4.30 ppm (1 H) assigned to a CH hydrogen and the broad doublet at 2.06 ppm (3 H) assigned to a $CH_3$ group are correlated with each other. The two components of the doublet are separated by ca. 6 Hz. Such a coupling constant may be assigned to $J(HH)$, whereas the broadness of the CH and $CHCH_3$ resonances is likely due to some additional coupling to heteronuclei (Rh, P). In conclusion, the spectroscopic data are more consistent with structure B than with structure A; i.e., the hydride migration has occurred at the less substituted carbon atom. In this respect, it is worth mentioning that the protonation of $[(C_5H_5)Rh(PMe_3)(\eta^2\text{-styrene})]$ by $CF_3COOH$ has been reported to occur at the $CH_2$ carbon of styrene, producing an $\eta^3$-benzyl complex.[15] Structure B is also supported by the Markovnikov addition of hydride to *cis*-4-methyl-2-pentene (see below).

**Isomerization Studies.** Surveying the above reactions, one may readily infer that **1** is a potential catalyst precursor for the cis → trans and/or double-bond isomerization of alkenes. In order to confirm this hypothesis, we have studied the reactions of DMMA, *cis*-stilbene, and *cis*-4-methyl-2-pentene with a catalytic amount of **1** (substrate to catalyst ratio 30, THF, 65 °C, 1 h, nitrogen atmosphere).

The reaction with DMMA produces 60.7% DMFU, which is somewhat far from the thermodynamic equilibrium composition (99.6% for DMFU). The termination metal product of the catalysis cycle is the cis hydride DMFU complex **2**, as shown by $^{31}P\{^1H\}$ NMR spectroscopy. The latter compound behaves as a catalyst precursor for the isomerization of DMMA to DMFU with a slightly better rate, likely due to the absence of the induction time necessary to convert **1** to **2**.

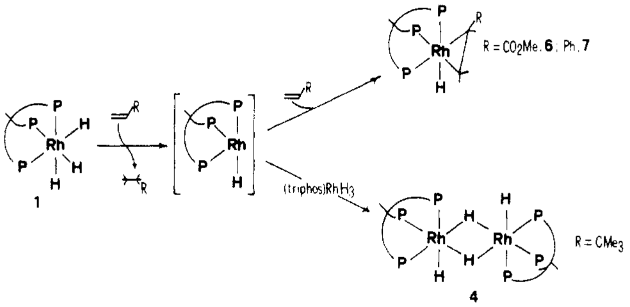
The reaction between **1** and *cis*-stilbene produces 1,2-diphenylethane in an almost stoichiometric amount, while the cis–trans equilibrium is practically achieved (97.3 vs 99.4% for the trans isomer). In accord with the result of the 1:2 reaction, no definite termination product containing rhodium is isolated.

**Table IV. Isomerization of *cis*-4-Methyl-2-pentene by Rhodium Hydride Catalyst Precursors**[a]

| | amt, % | | | | | |
|---|---|---|---|---|---|---|
| catalyst | *cis*-4M-2P | *trans*-4M-2P | 4M-1P | 2M-2P | 2M-1P | ratio[b] |
| **9** | 6.0 | 40.2 | 0.8 | 47.2 | 5.8 | 0.8 |
| **1** | 7.8 | 57.7 | 2.2 | 30.9 | 1.4 | 1.9 |
| **4** | 11.0 | 72.1 | 3.6 | 12.2 | 1.1 | 5.9 |
| equil compositn | 3.0 | 7.6 | 0.5 | 74.5 | 14.4 | 0.1 |

[a] Reaction conditions: substrate to metal mole ratio, 30; amount of catalyst precursor, 7 × $10^{-2}$ mmol; amount of THF, 8 mL; nitrogen atmosphere; time, 1 h; oil bath temperature, 65 °C. *cis*-4-Methyl-2-pentene is abbreviated to *cis*-4M-2P; the other methylpentenes are similarly designated. [b] *trans*-4M-2P to 2M-2P ratio.

**Scheme III**



Along with some hydrogenation to 2-methylpentane (0.6%), both geometrical and positional isomerization processes occur during the reaction of **1** with *cis*-4-methyl-2-pentene. The main products of the reaction are the trans isomer and the double bond isomerization isomer 2-methyl-2-pentene. 4-Methyl-1-pentene and 2-methyl-1-pentene complete the isomeric mixture. The termination metal product is the tetrahydride **4**. In an attempt to establish the role of the latter complex in the catalysis cycle, we have reacted **4** with *cis*-4-methyl-2-pentene under the same conditions used for **1**, obtaining a somewhat different product composition; particularly the *trans*-4-methyl-2-pentene to 2-methyl-2-pentene ratio is now higher (5.9 vs 1.9). Interestingly, **4** is recovered intact after the catalysis cycle. Table IV summarizes the experimental data for the reactions of *cis*-4-methyl-2-pentene with **1** and **4**, together with the results obtained by use of $[(triphos)Rh(H)(C_2H_4)]$ (**9**) as precursor to the known isomerization catalyst [(triphos)RhH].

## Discussion

**Reactions between 1 and Alkenes or Alkynes.** It has been already reported by us that the trihydride **1** is thermally unstable in refluxing THF or benzene, evolving dihydrogen and converting to the tetrahydride **4**.[1f] The formation of the latter complex proceeds through coupling of the unsaturated [(triphos)RhH] fragment, formed in situ by intramolecular $H_2$ elimination, with an intact molecule of **1**.

We have now found that **1** reacts with alkenes or alkynes, yielding different products depending on the nature of the unsaturated hydrocarbon. In particular, it is apparent from our results that alkynes are more easily hydrogenated by **1** than alkenes (this comparison is correct since we have used substrates bearing substitutents of the same type). This finding is in line with several preceding studies, according to which, in alkene/alkyne mixtures, the alkyne function is preferentially reduced because of its greater bonding ability with the metal center.[1f,16] As a matter of fact, in the reaction of **1** with a 1:1 mixture of dimethyl acetylenedicarboxylate and dimethyl maleate in refluxing benzene, only the alkyne is hydrogenated.

The reactions of **1** with alkenes are influenced by a number of factors, including the number, the disposition, and the nature of the substituents.

Monosubstituted alkenes are quantitatively hydrogenated by **1**. However, the nature of the metal products strongly depends on the bonding ability of the alkene, which, in turn, depends on the electronic and steric effects

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(15) Werner, H.; Feser, R. *J. Organomet. Chem.* **1982**, *232*, 351.

(16) (a) Parshall, G. W. *Homogeneous Catalysis*; Wiley-Interscience: New York, 1980. (b) James, B. R. *Homogeneous Hydrogenations*; Wiley-Interscience: New York, 1973. (c) Burch, R. R.; Muetterties, E. L.; Day, V. W. *Organometallics* **1982**, *1*, 186.

of the substituent. Alkenes bearing an electron-withdrawing substituent such as $CO_2Me$ or Ph do stabilize the [(triphos)RhH] moiety, forming cis hydride $\eta^2$-alkene derivatives. In contrast, electron-rich alkenes such as 3,3-dimethylbut-1-ene are not able to form stable $\eta^2$ adducts, although the hydrogen transfer occurs (Scheme III).[1f] As is shown in Scheme III, only half of the alkene is reduced, while the tetrahydride **4** forms quantitatively.

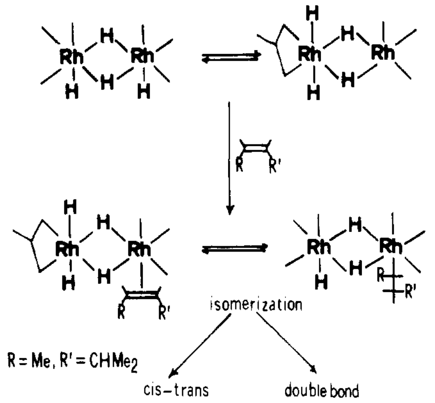
Stable cis hydride $\eta^2$-alkene complexes can also be obtained by reacting **1** with alkenes bearing two electron-withdrawing substituents ($CO_2R$; electrophilic alkenes). However, the steric hindrance of the substituents seems to play an important role, since no $\eta^2$ adduct with either *cis*- or *trans*-stilbene is isolated. In particular, the tetrahydride **4** forms by reaction with *trans*-stilbene, whereas no definite metal product can be isolated when *cis*-stilbene is used. Understanding the reaction with *cis*-stilbene is more complicated, since we would have expected to isolate a complex of the type [(triphos)Rh(H)($\eta^2$-*trans*-stilbene)]. Such a species likely forms as the kinetic product, which might be unstable in refluxing benzene, thus rapidly degrading to unknown products. In actuality, this hypothesis is supported by the following experimental evidence. The $\pi$-alkyne complex [(triphos)Rh($\pi$-PhC≡CPh)]$BPh_4$ (**10**) reacts in THF with $LiHBEt_3$ at 0 °C, affording a white microcrystalline product this is analyzed as [(triphos)Rh(H)(PhCH=CHPh)] (**11**; IR 1972 $cm^{-1}$ ($\nu$(Rh–H)), 1595 $cm^{-1}$ (additional phenyl vibration)) and decomposes in the GC injector at 250 °C, producing *trans*-stilbene. The stability of **11** in solution is so low as to preclude a meaningful spectroscopic characterization except for the $^1H$ NMR spectrum in THF-$d_8$, which exhibits the typical resonance pattern of the hydride ligand trans to phosphorus in [(triphos)Rh(H)($\eta^2$-alkene)] compounds ($\delta$(Rh–H) −11.76 ppm, $J(HP_{trans})$ = 165.3 Hz).

Alkenes bearing electron-releasing substituents such as *cis*-4-methyl-2-pentene, although adopting the less encumbered cis conformation, neither form $\eta^2$-alkene complexes nor are easily hydrogenated. These two facts reasonably imply that the [(triphos)RhH] fragment preferentially coordinates electrophilic alkenes (this is in accord with the electron-rich character of the $ML_4$ $d^8$ system).

**Isomerization Reactions of Cis-Disubstituted Alkenes Catalyzed by 1.** In view of the results presented in the preceding sections, there is little doubt that in the isomerization reactions of DMMA and *cis*-stilbene the trihydride **1** behaves as the precursor to the catalyst [(triphos)RhH]. The latter fragment can be generated either by thermal decomposition or by hydrogen transfer to alkene. Once formed, the [(triphos)RhH] system coordinates the cis olefin, which successively is isomerized to the trans isomer through the classical hydride migration/$\beta$-H elimination mechanism.[17] The lower rate of isomerization of DMMA as compared to that of *cis*-stilbene may be due to the higher stability of the corresponding cis hydride $\eta^2$-alkene derivative.

The isomerization reaction of *cis*-4-methyl-2-pentene appears mechanistically more complicated. In fact, from a perusal of the data summarized in Table IV, one may readily infer that the two catalyst systems [(triphos)RhH] and the tetrahydride **4** are working separately. Obviously, only the [(triphos)RhH] system works when the catalyst precursor is [(triphos)Rh(H)($C_2H_4$)] (**9**). In this case, the experimental data are consistent with the selective formation of a $\sigma$-alkyl intermediate via Markovnikov addition of hydride to alkene (see the low amount of 4-methyl-1-pentene, namely the isomer deriving from the anti-Markovnikov path).[1a,b] This alkyl intermediate evolves to the double-bond isomerization products (2-methyl-2-pentene and 2-methyl-1-pentene, 53.0%) and to the trans isomer (40.2%).

Scheme IV



The Markovnikov addition appears as the favored pathway also by using catalyst **4**, but now the formation of the trans isomer greatly prevails over the double-bond isomerization (72.1 vs 13.3%). The large departure from the equilibrium composition[18] indicates compound **4** to be an active catalyst precursor for the geometrical isomerization of cis olefins.

The sequence shown in Scheme IV accounts well for the isomerization reaction of 4-methyl-2-pentene assisted by **4**. Such a mechanism has a couple of precedents in the isomerization reactions of alkenes catalyzed by [(triphos)Rh($\mu$-$H_3$)Rh(triphos)]($BPh_4$)$_2$[1f] and [HRh(P(O-*i*-$C_3H_7$)$_3$)$_2$]$_2$.[16c,19]

## Experimental Section

**General Data.** Tetrahydrofuran (THF) and benzene were purified by distillation over $LiAlH_4$ and sodium, respectively, under nitrogen just prior to use. All the other solvents and chemicals employed were reagent grade and were used as received. The compounds [(triphos)Rh$H_3$][3] (**1**), [(triphos)RhH($C_2H_4$)][1c] (**9**), and [(triphos)RhCl($C_2H_4$)][1d] were prepared according to published procedures. Hexafluorobut-2-yne was purchased from Strem Chemicals. All the other alkynes and alkenes were purchased from Aldrich. Infrared spectra were recorded on a Perkin-Elmer 1600 Series FTIR spectrophotometer using samples mulled in Nujol between KBr plates. Proton and $^{13}C\{^1H\}$ 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. $^{31}P\{^1H\}$ 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. 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. GC analyses were performed on a Shimadzu GC-8A gas chromatograph fitted with a thermal conductivity detector and with a 10-ft 10% SP-2100 100/120 Supelcoport or a 6-ft 0.1% SP-1000 80/100 Carbopack C $^1/_8$-in. stainless-steel column (Supelco Inc.). Quantification was achieved with a Shimadzu C-R6A Chromatopac coupled with the chromatograph, operating with an automatic correct area normalization method.

Simulation of NMR spectra was achieved by using an updated version of the LAOCN4 program.[20] The initial choices of shifts

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(17) Doherty, N. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 2670.

(18) Sparke, M. B.; Turner, L.; Wenham, A. J. M. *J. Catal.* **1965**, *4*, 332.

(19) Sivak, A. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1979**, *101*, 4878.

and coupling constants were refined by successive iterations, the assignment of the experimental lines being performed automatically. The final parameters gave a fit to the observed line positions better than 0.5 Hz.

**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.

**Synthesis of [(triphos)Rh(H)($\eta^2$-DMFU)] (2). Method A.** A stirred mixture of 1 (0.36 g, 0.5 mmol) and DMMA (0.13 mL, 1 mmol) in benzene (30 mL) was heated at reflux temperature for 20 min. The resulting red-brown solution was allowed to reach room temperature and GC analyzed (DMFU 40%, DMSU 60%) before *n*-heptane (30 mL) was added. The solution gave on standing sandy crystals in 85% yield, which were filtered off and washed with diethyl ether and *n*-pentane. Anal. Calcd for $C_{47}H_{48}O_4P_3Rh$: C, 64.68; H, 5.54; Rh, 11.79. Found: C, 65.01; H, 5.63; Rh, 11.36.

**Method B.** Compound 2 can also be prepared in 92% yield by reaction of 1 (0.36 g, 0.5 mmol) with a 2-fold excess of DMFU (0.16 g, 1 mmol) under the same reaction conditions. Only traces of DMSU were detected by GC analysis of the reaction mixture.

**Method C.** Stirring 1 (0.36 g, 0.5 mmol) in benzene (30 mL) with a 15% excess of dimethyl acetylenedicarboxylate (0.07 mL, 0.57 mmol) for 3 h gave an orange-brown solution. Addition of *n*-heptane (30 mL) led to the precipitation of 2 in 87% yield.

The crystals of 2·$C_4H_9OH$ were obtained by recrystallization of 2 from a 1:2 $CH_2Cl_2$/1-butanol mixture under nitrogen. Anal. Calcd for $C_{51}H_{58}O_5P_3Rh$: C, 64.69; H, 6.17; Rh, 10.87. Found: C, 64.47; H, 6.01; Rh, 10.64.

**Synthesis of [(triphos)Rh(H)($\eta^2$-DEFU)] (3).** This compound was obtained as sandy crystals in 85–95% yield by following procedures analogous to those employed above for the syntheses of 2. Anal. Calcd for $C_{49}H_{52}O_4P_3Rh$: C, 65.33; H, 5.82; Rh, 11.42. Found: C, 65.71; H, 6.01; Rh, 11.24.

**Reaction of 1 with *cis*-Stilbene.** A stirred mixture of 1 (0.36 g, 0.5 mmol) and *cis*-stilbene (0.18 mL, 1 mmol) in benzene (30 mL) was heated at reflux temperature for 1 h. *trans*-Stilbene (75%) and 1,2-diphenylethane (25%) were detected by GC tests of the resulting solution. On addition of *n*-heptane (30 mL) a gray powder, containing undefined rhodium products, precipitated.

**Reaction of 1 with *trans*-Stilbene.** By a procedure analogous to that reported above, red crystals of [(triphos)Rh(H)($\mu$-H)$_2$(H)Rh(triphos)] (4) precipitated in 90% yied. A small amount (<5%) of 1,2-diphenylethane was detected by GC analysis.

**Reaction of 1 with Diphenylacetylene.** No identifiable products were obtained by reaction of 1 (0.36 g, 0.5 mmol) with a 15% excess of diphenylacetylene (0.10 g, 0.57 mmol) in benzene (30 mL) at reflux temperature for 1 h. *trans*- and *cis*-Stilbene, 95 and 5%, respectively, were detected in solution.

**Reaction of 1 with *cis*-4-Methyl-2-pentene.** By the same procedure used for *cis*-stilbene, red crystals of 4 precipitated in 60% yield. GC tests carried out on the solution evidenced both hydrogenation and partial isomerization of *cis*-4-methyl-2-pentene.

**Synthesis of [(triphos)Rh(H)($\eta^2$-$F_3C(H)C{=}C(H)CF_3$)] (5).** Hexafluorobut-2-yne was bubbled through a suspension of 1 (0.36 g, 0.5 mmol) in benzene (30 mL) at room temperature for 30 min. The solid dissolved to give a yellow solution. When *n*-heptane (30 mL) was added and the mixture stood overnight, yellow crystals precipitated in 86% yield, which were filtered off and washed with *n*-pentane. Anal. Calcd for $C_{45}H_{40}F_6P_3Rh$: C, 60.68; H, 4.53; Rh, 11.55. Found: C, 60.81; H, 4.59; Rh, 11.48.

**Synthesis of [(triphos)Rh(H)($\eta^2$-$H_2C{=}C(H)CO_2Me$)] (6).** A suspension of 1 (0.36 g, 0.5 mmol) in benzene (30 mL) in the presence of methyl acrylate (0.09 mL, 1 mmol) was heated at reflux temperature for 1 h. The resulting orange-red solution was allowed to reach room temperature. Addition of *n*-heptane (30 mL) and slow concentration gave off-white crystals in 75% yield, which were filtered off and washed with *n*-pentane. Methyl propionate was detected in solution by GC. Anal. Calcd for $C_{45}H_{46}O_2P_3Rh$: C, 66.34; H, 5.69; Rh, 12.63. Found: C, 66.61; H, 5.74; Rh, 12.58.

Table V. Experimental Data for the X-ray Diffraction Study of [(triphos)[Rh(H)($\eta^2$-DMFU)]•$C_4H_9OH$

| | |
|---|---|
| formula | $C_{51}H_{58}O_5P_3Rh$ |
| mol wt | 946.84 |
| cryst dimens, mm | 0.3 × 0.2 × 0.2 |
| data collecn $T$, °C | 21 |
| cryst syst | orthorhombic |
| space group | $P2_12_12_1$ |
| $a$, Å | 14.277 (2) |
| $b$, Å | 17.065 (2) |
| $c$, Å | 19.429 (3) |
| $V$, Å$^3$ | 4734 |
| $Z$ | 4 |
| $\rho$(calcd), g cm$^{-3}$ | 1.329 |
| $\mu$, cm$^{-1}$ | 5.02 |
| radiation | Mo K$\alpha$ (graphite monochromated, $\lambda$ = 0.71069 Å) |
| measd rflns | $+h,+k,+l$ |
| $\theta$ range, deg | $2.30 \leq \theta \leq 25.0$ |
| scan type | $\omega/2\theta$ |
| scan width, deg | 1.00 + 0.35 tan $\theta$ |
| max counting time, s | 70 |
| bkdg time, s | 0.5 × scan time |
| max scan speed, deg min$^{-1}$ | 10.1 |
| prescan rejection limit | 0.5 (2$\sigma$) |
| prescan acceptance limit | 0.055 (40$\sigma$) |
| horiz receiving slit, mm | 1.85 + tan $\theta$ |
| vert receiving slit, mm | 4.00 |
| no. of indep data collected | 4598 |
| no. of obsd rflns ($n_v$) ($\lvert F_o\rvert^2 > 2.5\sigma(\lvert F\rvert^2)$) | 3847 |
| no. of params refined ($n_o$) | 336 |
| $R^a$ | 0.051 |
| $R_w{}^b$ | 0.063 |

[a] $R = \sum\lVert F_o\rvert - (1/k)\lvert F_c\rVert/\sum\lvert F_o\rvert$. [b] $R_w = [\sum w(\lvert F_o\rvert - (1/k)\lvert F_c\rvert)^2/\sum w(\lvert F_o\rvert^2)]^{1/2}$.

**Synthesis of [(triphos)Rh(H)($\eta^2$-$H_2C{=}C(H)Ph$)] (7).** The method reported above for 6 was successfully used for the preparation of this yellow compound in 80% yield, except for substitution of styrene (0.12 mL, 1 mmol) for methyl acrylate. Ethylbenzene was detected in solution by GC. Anal. Calcd for $C_{49}H_{48}P_3Rh$: C, 70.67; H, 5.81; Rh, 12.36. Found: C, 70.73; H, 5.84; Rh, 12.28.

**Synthesis of [(triphos)Rh($\eta^3$-(Me)CHC(Me)O)] (8).** This compound was obtained as yellow crystals in a fashion identical with that described for 6, by use of methyl vinyl ketone (0.08 mL, 1 mmol) instead of methyl acrylate; yield 82%. Methyl ethyl ketone was detected in solution by GC. Anal. Calcd for $C_{45}H_{46}P_3RhO$: C, 67.67; H, 5.81; Rh, 12.88. Found: C, 67.73; H, 5.84; Rh, 12.73.

**Synthesis of [(triphos)Rh($\pi$-PhC≡CPh)]BPh$_4$ (10).** A $CH_2Cl_2$ (10 mL) solution of diphenylacetylene (0.18 g, 1 mmol) was added to [(triphos)RhCl($C_2H_4$)] (0.79 g, 1 mmol) in $CH_2Cl_2$ (20 Ml). On addition of NaBPh$_4$ (0.34 g, 1 mmol) in ethanol (30 mL) and slow concentration red crystals precipitated. They were filtered off and washed with ethanol and *n*-pentane. Anal. Calcd for $C_{79}H_{69}BP_3Rh$: C, 77.45; H, 5.68; Rh, 8.40. Found: C, 77.12; H, 5.54; Rh, 8.27. $\Lambda_M$ = 52 $\Omega^{-1}$ cm$^2$ mol$^{-1}$. $^{31}$P{$^1$H} NMR (CDCl$_3$, 298 K): A$_3$X pattern, $\delta$ 33.58 ppm, $J$(RhP) = 107.7 Hz. IR: 1690 cm$^{-1}$ ($\nu$(C≡C)).

**Reaction of 10 with LiHBEt$_3$.** A 4-fold excess of LiHBEt$_3$ (1 M in THF) was syringed into a THF (20 mL) solution of 10 (0.3 g, 0.25 mmol) at 0 °C. There was a color change from red to yellow. Ethanol (2 mL) was added. After 10 min addition of *n*-heptane (50 mL) led to the precipitation of [(triphos)Rh(H)(PhCH=CHPh)] (11) as a white solid, which was collected by filtration and washed with *n*-pentane. Anal. Calcd for $C_{56}H_{51}P_3Rh$: C, 73.12; H, 5.59; Rh, 11.18. Found: C, 72.88; H, 5.44; Rh, 11.01.

**Catalytic Runs.** In a typical isomerization reaction the substrate (2.1 mmol), THF (8 mL), and a stirring bar were placed in a reaction vessel fitted with a reflux condenser and with a side arm with a rubber septum under anaerobic conditions. The vessel was immersed in a constant-temperature oil bath (65 °C). The catalyst (0.07 mmol) was added. The solution was sampled after 1 h, and the samples were analyzed by GC and, eventually, by

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**Table VI. Positional Parameters for the Atoms of [(triphos)Rh(H)($\eta^2$-DMFU)]•$C_4H_9OH$**

| atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| Rh | −0.09663 (5) | 0.15921 (4) | 0.17859 (4) |
| P1 | −0.18259 (18) | 0.11319 (15) | 0.26994 (13) |
| P2 | −0.14864 (18) | 0.04818 (14) | 0.11376 (13) |
| P3 | 0.03097 (17) | 0.09005 (15) | 0.21759 (14) |
| O1 | −0.29342 (57) | 0.32018 (47) | 0.16579 (46) |
| O2 | −0.15181 (62) | 0.36527 (44) | 0.19485 (48) |
| O3 | −0.09237 (71) | 0.20954 (57) | −0.01341 (40) |
| O4 | 0.05216 (64) | 0.23908 (58) | 0.02527 (48) |
| C1 | −0.16626 (74) | 0.25186 (54) | 0.12181 (50) |
| C2 | −0.06657 (81) | 0.24880 (58) | 0.10259 (50) |
| C3 | −0.19972 (74) | 0.31701 (59) | 0.16397 (57) |
| C4 | −0.04058 (77) | 0.23016 (64) | 0.03292 (55) |
| C5 | −0.33345 (103) | 0.38568 (86) | 0.20374 (109) |
| C6 | 0.09335 (125) | 0.22233 (118) | −0.04222 (76) |
| C1M | −0.09702 (98) | −0.12212 (59) | 0.26602 (66) |
| C11 | −0.09868 (79) | −0.03656 (56) | 0.23754 (53) |
| C21 | −0.13918 (74) | 0.01612 (59) | 0.29864 (48) |
| C32 | −0.16491 (74) | −0.03400 (58) | 0.17277 (52) |
| C43 | 0.00401 (72) | −0.01617 (54) | 0.21903 (56) |
| C111 | −0.18145 (69) | 0.17009 (60) | 0.35027 (52) |
| C211 | −0.17840 (89) | 0.25225 (74) | 0.34572 (64) |
| C311 | −0.17497 (113) | 0.29300 (93) | 0.40724 (81) |
| C411 | −0.17759 (111) | 0.26125 (90) | 0.46910 (81) |
| C511 | −0.18043 (110) | 0.18217 (89) | 0.47472 (81) |
| C611 | −0.18231 (86) | 0.13533 (71) | 0.41417 (62) |
| C121 | −0.30992 (70) | 0.09761 (59) | 0.25826 (49) |
| C221 | −0.35580 (98) | 0.14169 (79) | 0.20793 (73) |
| C321 | −0.45334 (117) | 0.13092 (97) | 0.20017 (83) |
| C421 | −0.50289 (121) | 0.07659 (88) | 0.24331 (80) |
| C521 | −0.45791 (107) | 0.03164 (89) | 0.29074 (77) |
| C621 | −0.35879 (91) | 0.04625 (75) | 0.30184 (65) |
| C112 | −0.26074 (74) | 0.04890 (62) | 0.06355 (54) |
| C212 | −0.33949 (88) | 0.00759 (73) | 0.08399 (65) |
| C312 | −0.42041 (107) | 0.01184 (87) | 0.04513 (79) |
| C412 | −0.42202 (119) | 0.05628 (99) | −0.01553 (84) |
| C512 | −0.34047 (108) | 0.09648 (89) | −0.03399 (79) |
| C612 | −0.26236 (96) | 0.09176 (82) | 0.00561 (70) |
| C122 | −0.07060 (73) | 0.00425 (63) | 0.04921 (56) |
| C222 | 0.01362 (87) | 0.03786 (72) | 0.03565 (63) |
| C322 | 0.07920 (107) | 0.00368 (89) | −0.01137 (78) |
| C422 | 0.05207 (117) | −0.06466 (94) | −0.04449 (82) |
| C522 | −0.03095 (112) | −0.09668 (92) | −0.03168 (81) |
| C622 | −0.09553 (100) | −0.06424 (75) | 0.01421 (65) |
| C113 | 0.14384 (79) | 0.09325 (66) | 0.17233 (60) |
| C213 | 0.17058 (90) | 0.16382 (80) | 0.14283 (67) |
| C313 | 0.25367 (132) | 0.16961 (111) | 0.10440 (94) |
| C413 | 0.31114 (130) | 0.10424 (104) | 0.09752 (91) |
| C513 | 0.28834 (128) | 0.03444 (105) | 0.12576 (92) |
| C613 | 0.20126 (104) | 0.02736 (86) | 0.16534 (73) |
| C123 | 0.07137 (72) | 0.11128 (61) | 0.30491 (51) |
| C223 | 0.05120 (91) | 0.18240 (74) | 0.33728 (64) |
| C323 | 0.08036 (116) | 0.19887 (93) | 0.40443 (79) |
| C423 | 0.12879 (117) | 0.14428 (94) | 0.44180 (85) |
| C523 | 0.15021 (110) | 0.06948 (90) | 0.41322 (80) |
| C623 | 0.11988 (106) | 0.05164 (89) | 0.34220 (76) |
| CS1 | −0.40842 (345) | −0.14794 (249) | 0.35098 (237) |
| CS2 | −0.36526 (343) | −0.20822 (294) | 0.29279 (257) |
| CS3 | −0.37878 (361) | −0.17977 (284) | 0.21863 (283) |
| CS4 | −0.43971 (360) | −0.62935 (288) | 0.17008 (222) |
| OS5 | −0.51576 (314) | −0.20182 (242) | 0.12702 (205) |

GC–MS. The equilibrium compositions for both DMMA and *cis*-stilbene were determined experimentally.

**X-ray Data Collection and Structure Determination.** Crystals suitable for X-ray diffraction of compound **2** were obtained by crystallization from a $CH_2Cl_2$/1-butanol mixture, which gave **2**·$C_4H_9OH$. A prismatic sandy crystal was mounted at random orientation on a glass fiber. An Enraf-Nonius CAD4 diffractometer was used both for the unit cell and space group determination and for data collection. Unit cell dimensions were obtained by a least-squares fit of the $2\theta$ values of 25 high-order reflections ($9.0 \leq \theta \leq 16.0°$) with use of the CAD4 centering routines. From systematic absences the space group was unambigously determined as $P2_12_12_1$. Crystallographic and other relevant data collection parameters are listed in Table V. Data were measured with variable span speed to ensure constant statistical precision for the collected intensities. Three standard reflections (−4,−5,5; −4,5,−5; 4,5,−5) were used to check the stability of the crystal and of the experimental conditions and measured every 1 h; no significant variation was detected. The orientation of the crystal was checked by measuring three reflections (2,2,10; −4,−5,5; −4,5,−5) every 300 measurements. Data have been corrected for Lorentz and polarization factors, with use of the data reduction programs of the CAD4-SDP package.[21] An empirical absorption correction was applied by using azimuthal ($\psi$) scans of four "high $\chi$" angle reflections ($\chi > 86.3°$): 161; 202; 2,10,2; 2,12,2. Transmission factors were in the range 0.999–0.980. Intensities were considered as observed if $|F_o|^2 > 2.5\sigma|F|^2$, while $F_o$ = 0.0 was given to those reflections having negative net intensities. The structure was solved by a combination of Patterson and Fourier methods and refined by block-diagonal least squares (the function minimized was $\sum[w(F_o - (1/k)F_c)^2]$) with use of a Cruickshank weighting scheme[22] and scattering factors taken from ref 23. Corrections for the real and imaginary parts of the anomalous dispersion were also taken into account.[24] Anisotropic temperature factors were used for all atoms except those of the phenyl rings.

The final difference maps revealed a disordered molecular of 1-butanol; its contribution was taken into account and refined (with isotropic thermal parameters) even though only an approximate geometry was obtained with atoms showing the expected high thermal parameters.

Upon convergence (no parameter/shift $>0.2\sigma(p)$) the Fourier difference map showed a peak (approximately 0.6 e/Å$^3$) that was found in an acceptable position for the terminal hydride (Rh–H = 1.67 Å). The nature of this peak was confirmed by using the program HYDEX,[25] which minimizes the interaction energy between the hydride and the other ligands, thus giving a Rh–H separation of 1.72 Å. However, an attempt to refine the hydride positional parameters did not lead to an acceptable convergence.

**Supplementary Material Available:** Refined anisotropic and isotropic temperature factors (Table SVII) and calculated hydrogen positions (Table SVIII) for **2**·$C_4H_9OH$ and an ORTEP view of **2** with numbering scheme (phenyl ring carbons have been given the three digits *nmz* (*n* = 1–6, *m* = number of the ring, *z* = number of the bonded phosphorus)) (3 pages); a listing of observed and calculated structure factors (19 pages). Ordering information is given on any current masthead page.

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