4a and 4c. NMR spectra were recorded with a Bruker Spektrospin 270-MHz spectrometer.

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Reactions of Dihydrido(bicarbonato)bis(triisopropylphosphine)rhodium(III) with Alkynes. Formation of $Rh_2H_2(O_2CO)(PhC\equiv CPh)(P(\textit{i}\text{-}Pr)_3)_3$ and the Stereoselective Hydrogenation of Alkynes to Trans Olefins

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Abstract: A reaction of $RhH_2(O_2COH)(P(\textit{i}\text{-}Pr)_3)_2$ (**1**) with $PhC\equiv CPh$ has been found to give *trans*-stilbene and a novel binuclear rhodium complex $Rh_2H_2(O_2CO)(PhC\equiv CPh)(P(\textit{i}\text{-}Pr)_3)_3$ (**2**). A similar reaction with $MeO_2CC\equiv CCO_2Me$ results both in H_2 evolution and half-hydrogenation, while with $F_3C\equiv CCF_3$ only H_2 evolution is observed. Compound **1** catalyzes the stereoselective half-hydrogenation of alkynes to trans olefins. Complex **2** crystallizes in the monoclinic space group C_{2h}^5—$P2_1/c$, with four formula units in a cell of dimensions a = 17.158 (4) Å, b = 23.916 (3) Å, c = 11.255 (3) Å, β = 103.3 (1)°, and V = 4494 Å^3 ($t \approx -160$ °C). In the solid state **2** consists of a distorted octahedral Rh(III) center and a distorted square-planar Rh(I) center bridged by a bis-bidentate carbonato group.

Cis dihydrides of transition metals have received considerable attention as catalysts for the hydrogenation of unsaturated organic molecules. The reaction proceeds through insertion of the unsaturated molecule into the M–H bond.[2] An alternative reaction of cis dihydrides with π-acids is reductive elimination to produce dihydrogen. Recently we have observed both types of reactions for the cis-dihydrido carbonato and formato compounds RhH_2XL_2 ($X = O_2COH, O_2CH$; $L = P(\textit{i}\text{-}Pr)_3, P(c\text{-}C_6H_{11})_3$).[3] Thus, reaction with CO_2 under ambient conditions leads readily to reduction of the substrate, while reaction with CO results in dihydrogen evolution. Both reactions afford the carbonyl compounds *trans*-$Rh(\eta^2\text{-}O_2COH)(CO)L_2$ and *trans*-$Rh(\eta^2\text{-}O_2CH)(CO)L_2$, respectively. A facile dihydrogen evolution is also observed on treatment of the cationic cis-dihydrido compounds $[RhH_2(S)_2L_2]^+$ (S = solvent, L = phosphine) with CO and *t*-BuNC.[4,5] The square-planar cis-dihydrido compound PtH_2(diphos) (diphos = $(\textit{t}\text{-}Bu)_2P(CH_2)_2P(\textit{t}\text{-}Bu)_2$) reacts with olefins carrying electron-withdrawing substituents, e.g., acrylonitrile and maleic anhydride, to afford the compounds Pt(olefin)(diphos) with evolution of H_2.[6] Recent MO calculations[7] are consistent with this facile reductive elimination of H_2. By contrast, the compound PtH_2(diphos) is inert toward cyclohexene under ambient conditions, while under forcing conditions (100 °C, 80 Kg/cm^2 of H_2) it catalyzes the hydrogenation to give cyclohexane.[6] Apparently the reaction of cis-dihydrido complexes with π-acid is sensitive to the π-acidity of the substrate.

In this paper we examine the types of reactions that occur between the cis-dihydride $RhH_2(\eta^2\text{-}O_2COH)(P(\textit{i}\text{-}Pr)_3)_2$ (**1**)[3] and the alkynes $PhC\equiv CPh$, $MeO_2CC\equiv CCO_2Me$, and $F_3CC\equiv CCF_3$. The reaction with $PhC\equiv CPh$ affords the half-hydrogenation product *trans*-stilbene, together with a new binuclear dihydrido carbonato diphenylacetylene compound characterized by diffraction and spectroscopic methods to be $Rh_2H_2(O_2CO)(PhC\equiv CPh)(P(\textit{i}\text{-}Pr)_3)_3$ (**2**). A similar reaction with $MeO_2CC\equiv CCO_2Me$ results both in H_2 evolution and hydrogenation to give dimethyl fumarate. In contrast, with the stronger π-acid $F_3CC\equiv CCF_3$ only H_2 evolution is observed. As the stereospecific half-hydrogenation of alkynes with homogeneous catalysts to afford trans olefins is rare,[8,9] we also describe our studies of the hydrogenation of $PhC\equiv CPh$ as catalyzed by **1** and **2**.

Results and Discussion

Reaction of $RhH_2(\eta^2\text{-}O_2COH)(P(\textit{i}\text{-}Pr)_3)_2$ with $PhC\equiv CPh$. Reaction of the colorless compound $RhH_2(\eta^2\text{-}O_2COH)(P(\textit{i}\text{-}Pr)_3)_2$ (**1**)[3] with an excess (3 molar equiv) of $PhC\equiv CPh$ in toluene occurs

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Table I. Bond Distances (Å) and Angles (deg) in $Rh_2H_2(O_2CO)(PhC{\equiv}CPh)(P(i\text{-}Pr)_3)_3$

Bond Distances

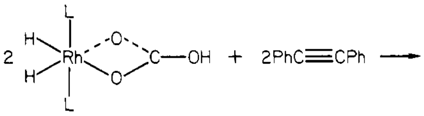
Distances from the Rhodium Atoms			
Rh(1)-P(1)	2.299 (1)	Rh(2)-P(3)	2.208 (1)
Rh(1)-P(2)	2.299 (1)	Rh(2)-O(1)	2.208 (2)
Rh(1)-O(1)	2.324 (2)	Rh(2)-O(3)	2.092 (2)
Rh(1)-O(2)	2.272 (2)	Rh(2)-C(41)	2.037 (3)
Rh(1)-H(1)	1.48 (3)	Rh(2)-C(51)	2.048 (3)
Rh(1)-H(2)	1.42 (3)		
Distances within the Carbonato Ligand			
C(1)-O(1)	1.317 (3)	O(1)···O(2)	2.220 (3)
C(1)-O(2)	1.259 (3)	O(1)···O(3)	2.216 (3)
C(1)-O(3)	1.296 (3)	O(2)···O(3)	2.264 (3)
Distances within the Phosphine Ligands			
P(1)-C(11)	1.861 (3)	C(13)-C(18)	1.527 (5)
P(1)-C(12)	1.853 (3)	C(13)-C(19)	1.518 (5)
P(1)-C(13)	1.862 (3)	C(21)-C(24)	1.530 (4)
P(2)-C(21)	1.865 (3)	C(21)-C(25)	1.526 (4)
P(2)-C(22)	1.858 (3)	C(22)-C(26)	1.530 (4)
P(2)-C(23)	1.868 (3)	C(22)-C(27)	1.530 (4)
P(3)-C(31)	1.855 (3)	C(23)-C(28)	1.531 (4)
P(3)-C(32)	1.861 (3)	C(23)-C(29)	1.535 (4)
P(3)-C(33)	1.859 (3)	C(31)-C(34)	1.532 (5)
P-C(av)	1.860 (5)[a]	C(31)-C(35)	1.517 (5)
C(11)-C(14)	1.531 (4)	C(32)-C(36)	1.528 (4)
C(11)-C(15)	1.535 (4)	C(32)-C(37)	1.535 (4)
C(12)-C(16)	1.528 (4)	C(33)-C(38)	1.530 (4)
C(12)-C(17)	1.524 (5)	C(33)-C(39)	1.524 (4)
		C-C(av)	1.529 (5)
Distances within the PhC≡CPh Ligand			
C(41)-C(51)	1.268 (4)	C(51)-C(52)	1.443 (4)
C(41)-C(42)	1.441 (4)	C(52)-C(53)	1.395 (4)
C(42)-C(43)	1.399 (4)	C(53)-C(54)	1.376 (4)
C(43)-C(44)	1.389 (4)	C(54)-C(55)	1.390 (4)
C(44)-C(45)	1.387 (5)	C(55)-C(56)	1.379 (4)
C(45)-C(46)	1.382 (5)	C(56)-C(57)	1.386 (4)
C(46)-C(47)	1.383 (4)	C(57)-C(52)	1.402 (4)
C(47)-C(42)	1.403 (4)		

Bond Angles

Angles about the Rhodium Atoms and the Carbonato Ligand			
P(1)-Rh(1)-P(2)	170.71 (3)	P(3)-Rh(2)-O(3)	97.84 (6)
P(1)-Rh(1)-O(1)	99.30 (5)	P(3)-Rh(2)-C(41)	96.63 (8)
P(1)-Rh(1)-O(2)	90.18 (5)	P(3)-Rh(2)-C(51)	97.40 (8)
P(1)-Rh(1)-H(1)	89 (1)	O(1)-Rh(2)-O(3)	61.97 (7)
P(1)-Rh(1)-H(2)	86 (1)	O(1)-Rh(2)-C(41)	103.52 (9)
P(2)-Rh(1)-O(1)	88.35 (5)	O(1)-Rh(2)-C(51)	101.39 (9)
P(2)-Rh(1)-O(2)	98.40 (6)	O(3)-Rh(2)-C(41)	152.7 (1)
P(2)-Rh(1)-H(1)	83 (1)	O(3)-Rh(2)-C(51)	159.85 (9)
P(2)-Rh(1)-H(2)	87 (1)	O(1)-C(1)-O(2)	119.1 (2)
O(1)-Rh(1)-O(2)	57.74 (6)	O(1)-C(1)-O(3)	116.1 (2)
O(1)-Rh(1)-H(1)	113 (1)	O(2)-C(1)-O(3)	124.9 (2)
O(1)-Rh(1)-H(2)	172 (1)	Rh(1)-O(1)-Rh(2)	174.44 (9)
O(2)-Rh(1)-H(1)	171 (1)	C(1)-O(1)-Rh(2)	87.9 (2)
O(2)-Rh(1)-H(2)	117 (1)	C(1)-O(1)-Rh(1)	89.7 (2)
H(1)-Rh(1)-H(2)	73 (2)	C(1)-O(2)-Rh(1)	93.5 (2)
P(3)-Rh(2)-O(1)	159.39 (5)	C(1)-O(3)-Rh(2)	93.7 (2)
Angles within the Phosphine Ligands			
Rh(1)-P(1)-C(11)	114.8 (1)	Rh(1)-P(2)-C(21)	118.0 (1)
Rh(1)-P(1)-C(12)	111.5 (1)	Rh(1)-P(2)-C(22)	110.8 (1)
Rh(1)-P(1)-C(13)	118.5 (1)	Rh(1)-P(2)-C(23)	116.0 (1)
C(11)-P(1)-C(12)	103.3 (1)	C(21)-P(2)-C(22)	105.3 (1)
C(11)-P(1)-C(13)	103.1 (1)	C(21)-P(2)-C(23)	101.7 (1)
C(12)-P(1)-C(13)	104.0 (1)	C(22)-P(2)-C(23)	103.6 (1)
P(1)-C(11)-C(14)	112.9 (2)	P(2)-C(21)-C(24)	112.7 (2)
P(1)-C(11)-C(15)	110.2 (2)	P(2)-C(21)-C(25)	112.7 (2)
C(14)-C(11)-C(15)	108.2 (3)	C(24)-C(21)-C(25)	109.3 (3)
P(1)-C(12)-C(16)	115.2 (2)	P(2)-C(22)-C(26)	113.5 (2)
P(1)-C(12)-C(17)	113.3 (2)	P(2)-C(22)-C(27)	114.6 (2)
C(16)-C(12)-C(17)	110.9 (3)	C(26)-C(22)-C(27)	111.0 (3)
P(1)-C(13)-C(18)	112.7 (2)	P(2)-C(23)-C(28)	113.6 (2)
P(1)-C(13)-C(19)	114.0 (2)	P(2)-C(23)-C(29)	110.9 (2)
C(18)-C(13)-C(19)	108.9 (3)	C(28)-C(23)-C(29)	109.3 (3)
Rh(2)-P(3)-C(31)	123.8 (1)	P(3)-C(31)-C(34)	113.9 (2)
Rh(2)-P(3)-C(32)	107.2 (2)	P(3)-C(31)-C(35)	113.6 (2)
Rh(2)-P(3)-C(33)	110.8 (1)	C(34)-C(31)-C(35)	110.9 (3)
C(31)-P(3)-C(32)	105.2 (1)	P(3)-C(32)-C(36)	110.4 (2)
C(31)-P(3)-C(33)	102.4 (1)	P(3)-C(32)-C(37)	116.9 (2)
C(32)-P(3)-C(33)	106.2 (1)	C(36)-C(32)-C(37)	110.5 (3)
		P(3)-C(33)-C(38)	117.0 (2)
		P(3)-C(33)-C(39)	111.1 (2)
		C(38)-C(33)-C(39)	109.3 (3)
Angles within the PhC≡CPh Ligand			
Rh(2)-C(41)-C(42)	136.3 (2)	Rh(2)-C(51)-C(52)	136.6 (2)
Rh(2)-C(41)-C(51)	72.4 (2)	Rh(2)-C(51)-C(41)	71.4 (2)
C(42)-C(41)-C(51)	151.3 (3)	C(52)-C(51)-C(41)	151.9 (3)
C(41)-C(42)-C(47)	120.2 (3)	C(57)-C(52)-C(51)	120.2 (3)
C(41)-C(42)-C(43)	121.3 (3)	C(51)-C(52)-C(53)	121.3 (3)
C(43)-C(42)-C(47)	118.5 (3)	C(53)-C(52)-C(57)	118.5 (3)
C(42)-C(43)-C(44)	120.2 (3)	C(52)-C(53)-C(54)	120.8 (3)
C(43)-C(44)-C(45)	120.6 (3)	C(53)-C(54)-C(55)	120.2 (3)
C(44)-C(45)-C(46)	119.5 (3)	C(54)-C(55)-C(56)	119.9 (3)
C(45)-C(46)-C(47)	120.6 (3)	C(55)-C(56)-C(57)	120.1 (3)
C(46)-C(47)-C(42)	120.6 (3)	C(56)-C(57)-C(52)	120.5 (3)

[a] Standard deviation of a single observation as estimated from agreement among values averaged.

rapidly at room temperature to afford a dark red solution from which we isolated diamagnetic orange-red crystals of $Rh_2H_2(O_2CO)(PhC{\equiv}CPh)(P(i\text{-}Pr)_3)_3$ (**2**) in 70% yield (based on **1**), together with *trans*-stilbene (38%) as the sole hydrogenation product (reaction 1). VPC analysis of the gaseous phase showed



1

$$Rh_2H_2(O_2CO)(PhC{\equiv}CPh)L_3 + CO_2 + trans\text{-}PhCH{=}CHPh + L \quad (1)$$

2

$L = P(i\text{-}Pr)_3$

the presence of CO_2 in approximately 35% yield and no detectable amounts of H_2. No product derived from insertion of the alkyne into the $Rh–O_2COH$ bond, e.g., "$RhCPh{=}CPh(OCO_2H)$", was detected in the IR spectrum of the residue left after separation of **2**. In contrast to $RhCl(PhC{\equiv}CPh)(PPh_3)_2$, from which the alkyne dissociates extensively,[10] the alkyne coordination in **2** is stable in solution at room temperature. Thus, the molecular weight (949) determined cryoscopically in benzene agrees well with the required value (926).

Crystallographic and Spectroscopic Characterization of $Rh_2H_2(O_2CO)(PhC{\equiv}CPh)(P(i\text{-}Pr)_3)_3$ (2). The molecular structure of $Rh_2H_2(O_2CO)(PhC{\equiv}CPh)$ $(P(i\text{-}Pr)_3)_3$ consists of a distorted octahedral Rh(III) center (labeled Rh(1)) and a distorted square-planar Rh(I) center (labeled Rh(2)), with two hydrido and two triisopropylphosphine ligands coordinated to

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[10] Mague, J. T; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1736–1740.

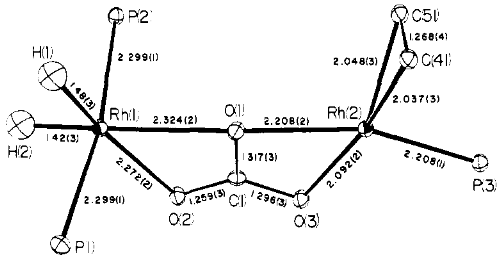

Figure 1. Labeling of atoms and selected distances (Å) about the rhodium atoms of $Rh_2H_2(O_2CO)(PhC{\equiv}CPh)(P(i\text{-}Pr)_3)_3$.

Rh(1) and a diphenylacetylene and a triisopropylphosphine ligand coordinated to Rh(2). A carbonato ligand bridges the two rhodium atoms. Figure 1 shows the inner coordination sphere, labeling scheme, and some bond distances. Figure 2 is a stereodrawing of the molecule, while Figure 3 displays the packing. All intermolecular distances are normal, the shortest between non-hydrogen atoms being 3.509 Å. Table I lists distances and angles.

The bonding mode of the carbonato ligand is unusual, insofar as it is a bridging ligand that also acts as a chelating ligand to both the Rh(I) and Rh(III) metal centers. This bonding mode for a carbonato ligand has been previously observed in $[(CuL)_2CO_3](ClO_4)_2$[11] (L = 2,4,4,9-tetramethyl-1,5,9-triazacyclodec-1-ene) and $[(CuCl(\text{tetramethyl-1,3-propanediamine}))_2CO_3]$.[12] In each of these previous structures there is a crystallographically imposed twofold axis of symmetry that passes through the bridging oxygen atom and the carbon atom of the carbonato bridge. In the current structure the carbonato ligand bridges the two rhodium atoms asymmetrically. The carbonato oxygen atom O(1) directly coordinated to both rhodium atoms is trans to a hydride ligand on atom Rh(1) (O(1)–Rh(1)–H(2) = 172 (1)°) and trans to a triisopropylphosphine ligand on atom Rh(2) (P(3)–Rh(2)–O(1) = 159.39 (5)°). One nonbridging oxygen atom O(2) is trans to a hydride ligand on Rh(1) (O(2)–Rh(1)–H(1) = 171 (1)°), and the analogous oxygen atom O(3) is trans to a diphenylacetylene ligand on Rh(2) (O(3)–Rh(2)–C(41) = 152.7 (1)°; O(3)–Rh(2)–C(51) = 159.9 (1)°). The lengthening of the Rh–O bonds trans to the hydride ligands in comparison with those trans to the diphenylacetylene and the triisopropylphosphine ligands is a function of both the differing trans effects of the ligands and the different oxidation states of the two rhodium atoms. The Rh_2CO_3 fragment is essentially planar, the largest deviation from the best least-squares plane being 0.101 (2) Å for atom O(1).

The coordination geometry about the Rh(III) center is approximately that observed about the Rh(III) center in the parent compound $RhH_2(O_2COH)(P(i\text{-}Pr)_3)_2$.[3] The Rh(III)–P bond lengths of 2.299 (1) and 2.299 (1) Å are very similar to those observed in $RhH_2(O_2COH)(P(i\text{-}Pr)_3)_2$ (2.321 (2) and 2.302 (2) Å) and are slightly shorter than several other reported Rh–P distances ($RhCl(L)(P(i\text{-}Pr)_3)_2$ (L = O_2, N_2, $CH_2{=}CH_2$) (2.348–2.363 Å)),[13,14] while the Rh(I)–P bond length of 2.208 (1) Å is significantly shorter. The Rh(III)–O bond lengths of 2.324 (2) and 2.272 (2) Å are considerably longer than the Rh(I)–O bond lengths of 2.208 (2) and 2.092 (2) Å but similar to the Rh(III)–O bond lengths in $RhH_2(O_2COH)(P(i\text{-}Pr_3)_2$ of 2.279 (2) and 2.306 (3).[3]

The Rh(III)–H bond lengths of 1.42 (3) and 1.48 (3) Å are shorter than the 1.5–1.7 Å distances usual for terminal metal-hydride bonds[15,16] but once again are comparable with the Rh(III)–H distances of 1.41 (3) and 1.47 (3) Å found in $RhH_2(O_2COH)(P(i\text{-}Pr)_3)_2$.

The Rh(I) center in $Rh_2H_2(O_2CO)(PhC{\equiv}CPh)(P(i\text{-}Pr)_3)_3$ has Rh–P (2.208 (1) Å) and Rh–O (2.092 (2)–2.208 (2) Å) bond distances similar to those about the Rh(I) center in $Rh_2(CO_3)(PPh_3)_5$[17] (Rh–P = 2.183 (5)–2.208 (3) Å and Rh–O = 2.104 (7)–2.138 (7) Å). In the present compound the longer bond distance of 2.208 (2) Å for Rh(2)–O(1) probably results from the bridging nature of this oxygen atom. The C–O bond lengths in the carbonato ligand (C(1)–O(1) = 1.317 (3) Å, C(1)–O(2) = 1.259 (3) Å, C(1)–O(3) = 1.296 (3) Å) are comparable with those observed in $Rh_2(CO_3)(PPh_3)_5$,[17] carbonates,[18] and $Mo_2(\mu\text{-}O_2CO)(CO)_2(PMe_2Ph)_6$.[19]

The Rh(I) interaction with the diphenylacetylene ligand is that expected for an η^2-alkyne ligand bonded to one metal center,[20,21] the Rh–C bond lengths being Rh(2)–C(41) = 2.037 (3) Å and Rh(2)–C(51) = 2.048 (3) Å and the C–C acetylenic linkage being C(41)–C(51) = 1.268 (4) Å. The phenyl rings of the coordinated acetylene are bent from the C(41)–C(51) bond axis, away from the Rh atom, with angles of C(41)–C(51)–C(52) = 151.9 (3)° and C(51)–C(41)–C(42) = 151.3 (3)°. The bond distances from the acetylenic carbon atoms to their phenyl rings are C(41)–C(42) = 1.441 (4) Å and C(51)–C(52) = 1.443 (4) Å. All other bond distances and angles in the structure are normal.

The structure of **2**, as deduced crystallographically, is consistent with IR studies of the solid and with NMR studies of the compound in solution. The IR spectrum (Nujol mull) of **2** shows two ν(Rh–H) bands at 2090 and 2140 cm^{-1}. The ν(C≡C) absorption observed at 1870 cm^{-1} is considerably lower than that (1916 cm^{-1}) found for $RhCl(PhC{\equiv}CPh)(PPh_3)_2$[10] but higher than those (1740–1825 cm^{-1}) of the corresponding compounds of the zerovalent nickel triad $M(PhC{\equiv}CPh)L_2$ (L = PPh_3, t-BuNC).[22]

The ^1H NMR spectrum of **2** measured in benzene-d_6 exhibits two hydrido signals at δ −24.12 and −24.13, both as double triplets of equal intensity. The magnitudes of the coupling constants of both signals are essentially equal, J_{H-P} and J_{H-Rh} being 14.3 and 27.0 Hz, respectively. These values are comparable with those of the parent compound **1** (J_{H-P} = 13.1 Hz, J_{H-Rh} = 26.3 Hz).[3] Consistently the methyl proton signal of the two $P(i\text{-}Pr)_3$ ligands attached to the Rh(III) center is observed at δ 1.16 as an apparent quartet because of virtual coupling ($^3J_{H-P} + {}^5J_{H-P}$ = 14.5 Hz, J_{H-H} = 7.3 Hz). The corresponding signal of the third $P(i\text{-}Pr)_3$ group, the one attached to the Rh(I) center, appears at δ 1.14 as a doublet of doublets (J_{H-P} = 11.7 Hz, J_{H-H} = 7.8 Hz). As expected, the intensity ratio of the former methyl proton signal to the latter is approximately 2. The relative intensity of the aromatic ortho proton signal (δ 8.32) and the methyl proton signals of $P(i\text{-}Pr)_3$ (4:56) is consistent with the molecular formula of **2**.

The ^{13}C NMR spectrum of **2** (benzene-d_6) shows signals from the carbonato and alkyne carbon atoms at δ 170.0(s) and 89.9 (br d, J_{C-Rh} = 18.3 Hz), respectively. As expected from the ^1H NMR spectrum, both methyl and methine carbon atoms show two signals at δ 20.3 (s) and 20.0 (s) and δ 25.0 (t, $^1J_{C-H} + {}^3J_{C-P}$ = 22.1 Hz) and 24.8 (d, J_{C-P} = 25.0 Hz), respectively. The lower field signals of the respective carbon atoms are assignable to the two mutually trans $P(i\text{-}Pr)_3$ ligands coordinated to a Rh(III) moiety, while the higher field signals arise from the third $P(i\text{-}Pr)_3$ ligand bonded to the Rh(I) center.

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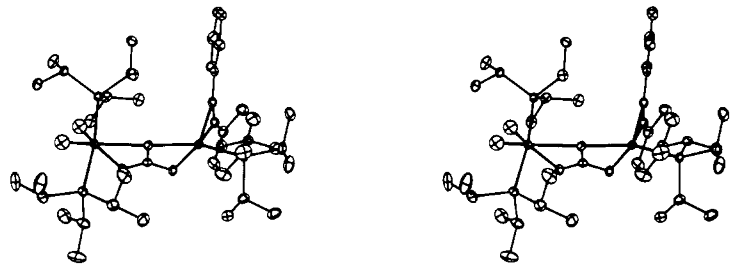
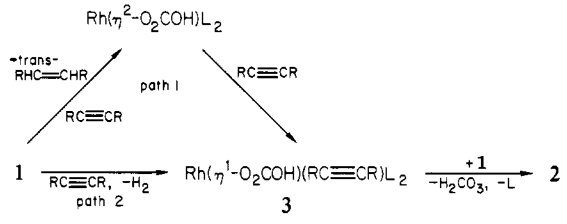


Figure 2. Stereoscopic view of the $Rh_2H_2(O_2CO)(PhC{\equiv}CPh)(P(i\text{-}Pr)_3)_3$ molecule.

The observation of three O_2CO bands (1535 (s), 1328 (s), 828 (s) cm^{-1}) for **2** is certainly different from that found for the η^1,η^1-bridging carbonate $Rh_2(\mu\text{-}O_2CO)(CO)_2(P(i\text{-}Pr)_3)_4$ (1533, 1300, 1275, 829 cm^{-1}).[3] The band positions are rather similar but do not correspond exactly to those of the η^2,η^2-carbonates $Cu_2Cl_2(\mu\text{-}O_2CO)(Me_2N(CH_2)_3NMe_2)_2$ (1560, 1380, 895, 730 cm^{-1})[12] and $Cu_2(\mu\text{-}O_2CO)L_2^+$ (L = 2,4,4,7-tetramethyl-1,5,9-triazacyclodec-1-ene) (1570, 1350, 830, 730 cm^{-1}).[11]

Reaction Scheme and Reaction of $RhH_2(\eta^2\text{-}O_2COH)(P(i\text{-}Pr)_3)_2$ with Other Alkynes. The compound $RhH_2(\eta^2\text{-}O_2COH)(P(i\text{-}Pr)_3)_2$ (**1**) was found to be an efficient catalyst for half-hydrogenation of $PhC{\equiv}CPh$ to give *trans*-stilbene (vide infra). Therefore, it is reasonable to assume that the formation of $Rh_2H_2(O_2CO)(PhC{\equiv}CPh)(P(i\text{-}Pr)_3)_3$ (**2**) (reaction 1) proceeds through an incipient reduction of the alkyne by **1** to give *trans*-stilbene and $Rh(\eta^2\text{-}O_2COH)L_2$ (L = $P(i\text{-}Pr)_3$) and subsequent coordination of $PhC{\equiv}CPh$ to the latter to afford a transient alkyne compound $Rh(\eta^1\text{-}O_2COH)(PhC{\equiv}CPh)L_2$ (**3**) (path 1 in eq 2). Oxidative addition of the bicarbonato OH bond of **1** to **3**, followed by reductive elimination of H_2CO_3 and dissociation of L from the adduct leads to the formation of **2**. A facile transformation of the square-planar bicarbonato Rh(I) species *trans*-$Rh(\eta^1\text{-}O_2COH)(CO)(P(i\text{-}Pr)_3)_2$ into $Rh_2(\mu\text{-}\eta^1,\eta^1\text{-}O_2CO)(CO)_2(P(i\text{-}Pr)_3)_4$ is known.[3,5]



(2)

R = Ph; L = $P(i\text{-}Pr)_3$

When **1** was treated with 0.5 mol of $PhC{\equiv}CPh$ at room temperature for 3 h, compound **2** (0.13 mol) and *trans*-stilbene (0.17 mol) were isolated, together with unreacted **1** (0.35 mol), but no H_2 was found. This is consistent with the proposed scheme (path 1 in eq 2) and excludes an alternative path involving H_2 evolution (path 2 in eq 2) and half-hydrogenation of the alkyne with **2**, since the latter reaction, in a separate experiment, was confirmed to be rather slow (vide infra).

Reductive elimination of cis-dihydrido ligands is facilitated by the presence of an electron-accepting trans ligand in a square-planar d^8 complex,[7] and this is also true in the reaction of the d^6 complex **1** with CO.[3] Consistently both hydrogenation of an alkyne and reductive elimination of H_2 take place when **1** is treated with $MeO_2CC{\equiv}CCO_2Me$. Thus, on addition of 2 mol of $MeO_2CC{\equiv}CCO_2Me$ to a toluene solution of **1**, the colorless solution turns red and gas evolution is observed. VPC analysis of the vapor phase shows the evolution of H_2 (10% based on **1**) and CO_2 (52%). The reddish oily residue obtained by concentration of the reaction mixture was purified by chromatography on Al_2O_3. Elution with a mixture of acetone–toluene gave dimethyl fumarate (29%) and a small amount of uncharacterized red crystals (**4**).

In contrast to the facile half-hydrogenation of $PhC{\equiv}CPh$ and $MeO_2CC{\equiv}CCO_2Me$ with **1**, a similar reaction with $F_3CC{\equiv}CCF_3$ proceeds exclusively through reductive elimination of H_2 from **1**. Thus treatment of a suspension of **1** in *n*-hexane with 2 mol of $F_3CC{\equiv}CCF_3$ at room temperature results in evolution of H_2 (92% based on **1**) and CO_2 (65%). From the orange solution orange crystals (**5**) are obtained (35%). These remain uncharacterized from elemental analyses and spectral data (see Experimental Section).

Catalytic Half-Hydrogenation of $PhC{\equiv}CPh$. We have shown that the hydrogenation of $PhC{\equiv}CPh$ and $MeO_2CC{\equiv}CCO_2Me$ with **1** gives *trans*-stilbene and dimethyl fumarate. The selective half-hydrogenation of internal alkynes to give trans olefins is remarkable, since cis hydrogenation seems to be general with Rh(I) catalysts, e.g., $RhCl(PPh_3)_3$,[23] $[Rh(diene)L_2]^+$ (L = phosphine),[24] and $[RhH(P(OCH_3)_3)_2]_n$ (n = 2, 3).[25] The homogeneous catalysts for trans hydrogenation of $PhC{\equiv}CPh$ so far reported are $RhCl_3(py)_3\text{·}NaBH_4\text{·}DMF$[8] and $Rh_2(\mu\text{-}H)_2(P(O\text{-}i\text{-}C_3H_7)_3)_4$.[9] Therefore, we have studied the hydrogenation of $PhC{\equiv}CPh$ as catalyzed by **1** and **2**.

Hydrogenation of $PhC{\equiv}CPh$ catalyzed with **1** (1 mol %) in toluene proceeds under ambient conditions (20 °C, 1 atm of H_2) without an induction period. After absorption of 1 mol of H_2 *trans*-$PhCH{=}CHPh$, *cis*-$PhCH{=}CHPh$, and $PhCH_2CH_2Ph$ were obtained in a 31:3:1 ratio. The hydrogenation rates of $PhC{\equiv}CPh$ and *trans*-$PhCH{=}CHPh$ are 6.6 and 4×10^{-2} mol/mol of **1**/min, respectively. The IR spectrum of the concentrated reaction mixture indicates the absence of any Rh compounds other than **1**.

Hydrogenation with **2** also takes place under conditions similar to those employed for **1** to afford *trans*-$PhCH{=}CHPh$; no $PhCH_2CH_2Ph$ was detected after absorption of 0.9 mol of H_2. Prolonged hydrogenation, however, affords $PhCH_2CH_2Ph$. The catalysis of **2** differs from that of **1** in several respects: (1) the hydrogenation rate with **2** (3.0×10^{-1} mol/mol of **2**/min) is much slower than with **1** and (2) there is an induction period (~100 min), suggesting that **2** is not an active species. The reaction of compound **2** with H_2 was therefore studied. An orange-red solution of **2** in toluene reacts slowly with H_2 under ambient conditions to give a dark brown solution, together with some precipitation of metallic Rh. From the solution we isolated **1** (15%) and $PhCH_2CH_2Ph$ (91%). An attempt to isolate other Rh compounds from the concentrated dark oily residue failed. The IR spectrum of the oil, however, suggests the presence of $Rh_2(CO)_3(P(i\text{-}Pr)_3)_3$ (ν(CO) 1955, 1770, 1732 cm^{-1}).[4,5]

Compound **1** may be produced through reduction of the coordinated alkyne in **2** and H_2 addition to a Rh(I) moiety to give *trans*-$PhCH{=}CHPh$ and $Rh_2H_4(OCO_2)(P(i\text{-}Pr)_3)_3$ and subsequent reductive elimination of hydrido and carbonato ligands from the latter to give **1** and a highly coordinatively unsaturated species "$RhHP(i\text{-}Pr)_3$" (eq 3).

$$\mathbf{2} \xrightarrow[trans\text{-}PhCH=CHPh]{2H_2} RhH_2L_2\text{–}OCO_2\text{–}RhH_2L \rightarrow \mathbf{1} + \text{“}RhHL\text{”} \qquad (3)$$

$$L = P(i\text{-}Pr)_3$$

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This coordinatively unsaturated Rh(I) compound probably decomposes to afford metallic Rh. An alternative route involving hydrolysis of the carbonato ligand in **2** by a trace of H_2O present in the reaction mixture to give **1** and $Rh(OH)(PhC\equiv CPh)(P(i\text{-}Pr)_3)_2$ is unlikely since **2** may be recovered quantitatively after stirring a solution of **2** in toluene with an excess of H_2O for 5 h.

A Rh(I) hydride $RhH(P(i\text{-}Pr)_3)_3$, which readily adds H_2 to give *trans*-$RhH_3(P(i\text{-}Pr)_3)_2$,[26] also serves as an active catalyst for the half-hydrogenation of $PhC\equiv CPh$ to afford *trans*-$PhCH{=}CHPh$, the rate being 2.8 mol/mol of Rh/min. The yields of *cis*-$PhCH{=}CHPh$ and $PhCH_2CH_2Ph$ are less than 1% of that for *trans*-$PhCH{=}CHPh$. In the presence of free $P(i\text{-}Pr)_3$, the species "$RhH(P(i\text{-}Pr)_3)$", formed through the reaction of **2** with H_2 (eq 3), should afford $RhH(P(i\text{-}Pr)_3)_n$ (n = 2, 3).[26] A mixture of **2** and free $P(i\text{-}Pr)_3$ therefore should show activity for the half-hydrogenation of $PhC\equiv CPh$ comparable with that observed for **1** or $RhH(P(i\text{-}Pr)_3)_3$. In fact the activity of **2** is enhanced in the presence of 1 mol of free $P(i\text{-}Pr)_3$, the rate being 4.3 mol/mol of **2**/min. Furthermore, the induction period observed for the catalysis of **2** is absent for this system. The product ratio of *trans*-$PhCH{=}CHPh$, $PhCH_2CH_2Ph$, and *cis*-$PhCH{=}CHPh$ is essentially that obtained for **1**. These studies suggest that the active species involved in the catalysis of **2** is **1** produced as indicated in eq 3.

Compound **1** also catalyzes an isomerization of *cis*-$PhCH{=}CHPh$ to the trans olefin. Under conditions similar to those employed for the hydrogenation, but in the absence of H_2, the rate of cis–trans isomerization (0.8 mol/mol of **1**/min) is much slower than that of 6.6 mol/mol of **1**/min for the hydrogenation of $PhC\equiv CPh$. Moreover, even at the initial stage of the hydrogenation *trans*-$PhCH{=}CHPh$ is obtained as the major product; the rates of *trans*- and *cis*-$PhCH{=}CHPh$ formation are 5.0 and 1.6 mol/mol of **1**/min, respectively. Thus cis–trans isomerization is not a major factor in the selective formation of the trans olefin. Formation of trans-vinylic metal compounds from transition-metal hydrides and internal alkynes, e.g., $IrH(NCC\equiv CCN)(CO)(PPh_3)_3$[27] and $(\eta^5\text{-}C_5H_5)_2MoH_2(F_3CC\equiv CCF_3)$,[28] may proceed through cis addition of M–H to the coordinated alkyne and subsequent intramolecular isomerization of the cis isomer via the dipolar intermediate $M^{+}{=}CR{-}{}^{-}CHR$.[29-31] Therefore, it is possible that the stereoselective hydrogenation of $RC\equiv CR$ (R = Ph, MeO_2C) with **1** to afford the trans olefin occurs mainly through the isomerization to the trans isomer of the incipiently bound cis vinylic compound $RhH(cis\text{-}CR{=}CHR)(O_2COH)(P(i\text{-}Pr)_3)_2$, with subsequent reductive elimination of trans olefin. Presumably electron-donating ligands (e.g., $P(i\text{-}Pr)_3$) and electron-withdrawing substituents (e.g., Ph, CO_2Me) of alkynes provide a low-energy process that leads to the dipolar intermediate.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of N_2. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on a JEOL JNM-4H-100 spectrometer and ^{19}F NMR spectra on a JEOL JNM-C-60HL spectrometer. IR spectra were measured on a Hitachi Model 295 spectrometer. Quantitative analysis of CO_2 and H_2 were carried out by the method described previously.[5,31,32]

Reactions of $RhH_2(\eta^2\text{-}O_2COH)(P(i\text{-}Pr)_3)_2$ (1) with Alkynes. I. $PhC\equiv CPh$. To a toluene solution (10 mL) of **1** (0.17 g, 0.35 mmol) was added $PhC\equiv CPh$ (0.19 g, 1.06 mmol) at room temperature. Immediately the colorless solution turned orange-red and CO_2 gas (35%) was evolved. The concentrated residue of the reaction mixture was washed with n-hexane and subsequently recrystallized from toluene–n-hexane to afford $Rh_2H_2(O_2CO)(PhC\equiv CPh)(P(i\text{-}Pr)_3)_3$ (**2**) as orange crystals (0.12 g, 70%). Anal. Calcd for $C_{42}H_{75}O_3P_3Rh_2$: C, 54.43; H, 8.16. Found: C, 54.48; H, 7.95. Concentration of the n-hexane washing gave a mixture of *trans*-stilbene and unreacted $PhC\equiv CPh$. The yield of the former, as assessed from the ^1H NMR intensity ratio of olefinic (δ 6.9 in CCl_4) and aromatic proton signals of the mixture, was 38% (based on the Rh(III) dihydride). *cis*-Stilbene and bibenzyl were not detected. Similarly a mixture of **1** (0.10 g, 0.21 mmol) and $PhC\equiv CPh$ (0.02 g, 0.11 mmol) was treated to give **2**, *trans*-stilbene, and unreacted **1** in 26, 17, and 35% yield (based on **1**), respectively.

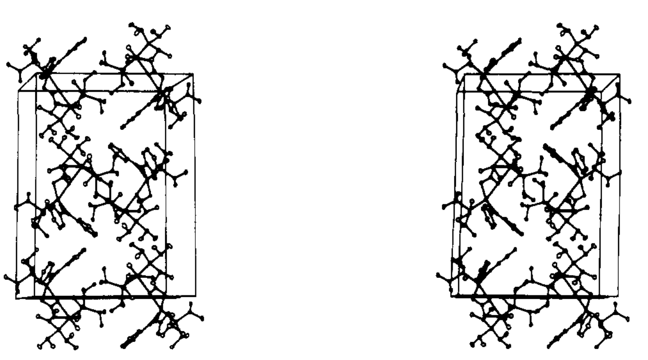

Figure 3. Stereoscopic view of the unit-cell contents of $Rh_2H_2(O_2CO)(PhC\equiv CPh)(P(i\text{-}Pr)_3)_3$.

II. $MeO_2CC\equiv CCO_2Me$. A solution of **1** (0.79 g, 1.6 mmol) in toluene (50 mL) was treated with $MeO_2CC\equiv CCO_2Me$ (0.5 g, 3.5 mmol) at room temperature. The colorless solution turned red immediately. The amounts of H_2 and CO_2 evolved were 10 and 52%, respectively, based on **1**. The concentrated reaction mixture was chromatographed on Al_2O_3. Elution with a mixture of acetone–toluene (1:20 volume ratio), followed by evaporation of the eluent gave dimethyl fumarate (0.066 g, 29%). Subsequent elution with acetone–toluene (1:10) gave a small amount of a red solid. Recrystallization from ether–n-hexane gave red crystals of **4** (0.02 g). IR (cm^{-1}) 1950 (w), 1738 (vs), 1717 (vs), 1630 (s), 1595 (m), 1435 (vs), 1400 (m), 1350 (s), 825 (w) ; ^1H NMR (δ) CH_3, 1.16 (dd, 18 H, J_{H-P} = 12.3 Hz, J_{H-H} = 7.2 Hz), 1.26 (dd, 18 H, J_{H-P} = 13.4 Hz, J_{H-H} = 7.2 Hz, CH, 1.98 (m, 3 H), 2.54 (m, 3 H); CH_3O, 3.49 (s, 3 H), 3.54 (s, 6 H), 3.27 (dd, J = 8.4 Hz, J = 2.0 Hz); ^{13}C NMR (δ) CH_3, 19.8 (s), CH, 24.4 (d, J_{C-P} = 24.8 Hz), 24.8 (d, J_{C-P} = 22.7 Hz), CH_3O, 51.0 (s), 52.8 (s), CO and OCO_2, 164.8 (s), 172.9 (s), 185.8 (s), 186.0 (s), 36.9 (d, J = 17.6 Hz), 102.0 (s). Anal. Found: C, 44.48; H, 6.50, P, 4.38.

III. $F_3CC\equiv CCF_3$. To a suspension of **1** (0.14 g, 0.29 mmol) in n-hexane (10 mL) was introduced gaseous $F_3CC\equiv CCF_3$ (13 mL) at room temperature. The mixture was stirred for 2 h to give an orange solution. VPC analysis of the gaseous phase showed evolution of CO_2 and H_2 in 60 and 92%, respectively. Concentration of the reaction mixture gave a viscous oil to which ether was added to induce crystallization. Recrystallization from n-hexane gave orange crystals of **5** (0.05 g). IR (cm^{-1}) 1880 ($\nu_{C\equiv C}$); ^1H NMR (δ) CH_3, 1.12 (dd, 6 H, J_{H-P} = 14.4 Hz, J_{H-H} = 7.4 Hz), 1.21 (q, 12 H, $^3J_{H-P} + {}^5J_{H-P}$ = 13.6 Hz, J_{H-H} = 6.8 Hz), 1.22 (q, 24 H, $^3J_{H-P} + {}^5J_{H-P}$ = 13.0 Hz, J_{H-P} = 6.5 Hz), CH, 1.7–2.4 (m, 7 H); ^{13}C NMR (δ) CH_3, 19.3 (s), 19.5 (s), 20.2 (s), CH, 22.2 (t, $^1J_{C-P} + {}^3J_{C-P}$ = 17.7 Hz), 24.3 (d, J_{C-P} = 22.1 Hz), 25.1 (t, $^1J_{C-}P$ + $^3J_{C-P}$ = 20.6 Hz), 30.1 (b), 31.9 (b), 111.1 (b), 121.5 (s), 169.4 (s), 171.6 (s), ^{31}P NMR (δ from H_3PO_4) 35.0 (d, J_{P-Rh} = 110.3 Hz), 59.3 (d, J_{P-Rh} = 115.2 Hz), 70.6 (d, J = 176.7 Hz). Anal. Found: C, 42.44; H, 7.08; F, 21.45; P, 9.35.

Reactions of $Rh_2H_2(O_2CO)(PhC\equiv CPh)(P(i\text{-}Pr)_3)_3$ (2). I. With H_2. An orange-red solution of **2** (0.20 g, 0.21 mmol) in toluene (10 mL) was stirred under H_2 (1 atm) at room temperature for 12 h. The dark brown solution was filtered to remove traces of metallic rhodium. The amount of metal separated increased with increasing reaction time. The dark brown oily residue obtained by concentration of the filtrate was dissolved in n-hexane and was kept at −40 °C to separate $PhCH_2CH_2Ph$ (0.035 g, 91%) as colorless crystals. On further cooling of the mother liquor to −70 °C colorless crystals were obtained (0.015 g, 15%). These were identified as $RhH_2(\eta^2\text{-}O_2COH)(P(i\text{-}Pr)_3)_2$ (**1**) by IR spectroscopy (ν(Rh–H) 2120, 2140; $\nu(O_2CO)$ 1338, 1587 cm^{-1}). The concentration of the filtrate gave a dark brownish oil that contained $Rh_2(CO)_3(P(i\text{-}Pr)_3)_3$ as deduced from the ν(CO) bands which were identical with those found for an authentic sample.[4,5]

II. With H_2O. A mixture of **2** (0.03 g, 0.3 mmol) and H_2O (0.5 mL) in toluene (5 mL) was stirred at room temperature for 5 h. The mixture was concentrated to dryness to recovery **2** quantitatively. The IR spectrum of the concentrated residue did not indicate the formation of $RhH_2(\eta^2\text{-}O_2COH)(P(i\text{-}Pr)_3)_2$ (**1**).

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Table II. Summary of Crystal Data and Intensity Collection

compound	$Rh_2H_2(O_2CO)(PhC{\equiv}CPh)(P(i\text{-}Pr)_3)_3$
formula	$C_{42}H_{75}O_3P_3Rh_2$
fw	962.80
temp, °C	$\sim -160^a$
a, Å	17.158 (4)
b, Å	23.916 (3)
c, Å	11.255 (3)
β, deg	103.31 (1)
V, $Å^3$	4494
Z	4
d(calcd), g/cm^3	1.37
space group	C_{2h}^5-$P2_1/c$
cryst dimens, mm	0.23 × 0.32 × 0.36
cryst shape	parallelpiped with faces of forms {100}, {010}, {$\bar{1}$11}
cryst vol, mm^3	0.003 25
radiatn	Mo K_1 (λ(Mo $K\alpha_1$) = 0.709 30 Å) from monochromator
linear abs coeff, cm^{-1}	6.29
transmissn factors	0.846–0.874
takeoff angle, deg	3.1
scan speed	2° in 2θ/min
scan range, deg	1.0 below $K\alpha_1$ to 0.9 above $K\alpha_2$
background counts	10 s total with rescan option^b
2θ limits, deg	4.0–56.0
final no. of variables	459
no. of observns	11 182
$R(F^2)$	0.046
$R_w(F^2)$	0.073
$R(F)$ $F_o^2 > 3\sigma(F_o^2)$	0.032
$R_w(F)$ $F_o^2 > 3\sigma(F_o^2)$	0.036
error in observn of unit weight, $electrons^2$	1.26

[a] The low-temperature system is based on a design by: Huffman, J. C. Ph.D. Thesis, Indiana University, 1974. [b] The diffractometer was run under the Vanderbilt disk-oriented system (Lenhert, P. G. *J. Appl. Crystallogr.* 1975, *8*, 568–470).

Catalytic Hydrogenation of PhC≡CPh. A Schlenk flask (50 mL), sealed with a serum cap and connected with a liquid paraffin leveling manometer, was used for the hydrogenation. The flask was filled with H_2 (1 atm), and then successively two 5-mL toluene solutions, one containing the catalyst (5×10^{-3} M) and the other containing PhC≡CPh (5×10^{-1} M), were added by syringe. The latter solution also contained naphthalene (5×10^{-2} M) as an internal reference for the product analysis. The hydrogenation was carried out at 20 ± 0.5 °C under 1 atm. of H_2. The reaction products were analyzed quantitatively by vapor phase chromatography with Triton X or Apiezon L or both as columns.

Catalytic Isomerization of *cis*-PhCH=CHPh with $RhH_2(\eta^2\text{-}O_2COH)(P(i\text{-}Pr)_3)_2$ (1). To an NMR tube cooled to −70 °C was added a benzene-d_6 solution (0.2 mL) of **1** (5×10^{-3} M) and then a benzene solution (0.2 mL) of *cis*-PhCH=CHPh (9.4×10^{-1} M) that also contained dibenzyl ether as an internal standard ($\delta(CH_2)$ 4.52). The frozen mixture was melted just before the ^1H NMR measurement. The isomerization of *cis*-PhCH=CHPh was followed by the intensity increase of cis olefinic proton signal (δ 6.57).

X-ray Data Collection. Crystals of $Rh_2H_2(O_2CO)(PhC{\equiv}CPh)(P(i\text{-}Pr)_3)_3$ suitable for X-ray diffraction were obtained upon recrystallization from toluene–hexane. These crystals were manipulated in an inert atmosphere (Ar or N_2). Preliminary film work revealed the material to be monoclinic with systematic absences (*h*0*l*, *l* = 2*n* + 1; 0*k*0, *k* = 2*n* + 1) strongly indicative of the centrosymmetric space group C_{2h}^5—$P2_1/c$.

Lattice parameters were obtained and intensity data collected on a Picker FACS-I diffractometer in a manner previously described.[33] Details relevant to the present structure appear in Table II.

The positions of the two rhodium atoms were found by direct methods.[34] All remaining non-hydrogen atoms were obtained from a single Fourier synthesis. After two cycles of isotropic and one cycle of anisotropic least-squares refinement all hydrogen atoms, including the two hydrido ligands, were apparent on a difference electron density map. All phenyl and isopropyl hydrogen atoms were placed in idealized positions (C–H = 0.95 Å, tetrahedral or trigonal angles) with idealized thermal parameters (*B* = 1.0 $Å^2$ greater than the equivalent *B* of the atom to which it is attached) and held fixed during subsequent refinement.

Initial cycles of refinement were based on *F*, using only those reflections having $F_o^2 > 3\sigma(F_o^2)$. Final refinements were carried out on F_o^2, using all unique data including those with $F_o^2 \leq 0$. The positions and isotropic thermal parameters of the hydrido ligands were refined, along with all non-hydrogen atoms in the final cycles of anisotropic refinement, which converged to values of $R(F^2) = 0.046$ and $R_w(F^2) = 0.073$ for 11182 observations and 459 variables. The corresponding agreement indices on *F* for those 8946 reflections for which $F_o^2 > 3\sigma(F_o^2)$ are 0.032 and 0.036, respectively. The largest peak on a final difference electron density map is of height 0.76 (12) e/$Å^3$ and is near the Rh(III) center. An analysis of $\sum w(F_o^2 - F_c^2)^2$ as a function of F_o^2, setting angles, and Miller indices showed no unexpected trends. Final positional and thermal parameters are collected in Table III.[35] Table IV[35] lists parameters for the non-hydridic hydrogen atoms. Table V gives the value of $10|F_o|$ and $10|F_c|$. A negative entry for $|F_o|$ indicates $F_o^2 < 0$.

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Registry No. **1**, 71380-76-2; **2**, 86747-89-9; $Rh_2(CO)_3(P(i\text{-}Pr)_3)_3$, 74521-39-4; *trans*-PhCH=CHPh, 103-30-0; $MeO_2CC{\equiv}CCO_2Me$, 762-42-5; $F_3CC{\equiv}CCF_3$, 692-50-2; $PhCH_2CH_2Ph$, 103-29-7; *cis*-PhCH=CHPh, 645-49-8; dimethyl fumarate, 624-49-7.

Supplementary Material Available: Table III, positional and thermal parameters, Table IV, a listing of parameters for the non-hydridic hydrogen atoms, and Table V, a listing of $10|F_o|$ and $10|F_c|$ (40 pages). Ordering information is given on any current masthead page.

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(33) See for example: Waters, J. M.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3273–3277.

(34) Main, P.; Fiske, S. J.; Hulls, S. E.; Lessinger, L.; Germain, G.; Declercq, J.-P.; Woolfson, M. M. "Multan 80. A System of Computer Programmes for the Automatic Solution of Crystal Structures from X-ray Diffraction Data", Universities of York, England, and Louvain, Belgium.

(35) Supplementary material.