Reductive Elimination of $[Ph_2C{=}C{=}CHPR_3]BF_4$ from the Rhodium(III)−Allenyl Derivatives $[Rh(acac)\{CH{=}C{=}CPh_2\}(PR_3)_2]BF_4$ (PR_3 = PCy_3, $PiPr_3$)

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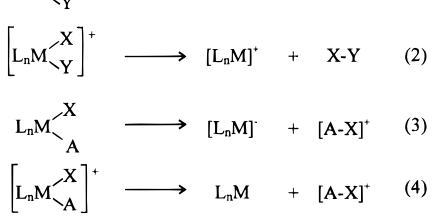
The olefinic unit of the complexes Rh(acac)(cyclooctadiene)(PR_3) (PR_3 = PCy_3 (**1**), $PiPr_3$ (**2**)) is displaced by 1,1-diphenyl-2-propyn-1-ol, to afford Rh(acac)$\{\eta^2$-HC≡CC(OH)$Ph_2\}(PR_3)$ (PR_3 = PCy_3 (**3**), $PiPr_3$ (**4**)). At 60 °C, in toluene as solvent, and in the presence of 1 equiv of phosphine, complexes **3** and **4** evolve into Rh(acac)H$\{C{\equiv}CC(OH)Ph_2\}(PR_3)_2$ (PR_3 = PCy_3 (**5**), $PiPr_3$ (**6**)). At −78 °C, the treatment of complex **5** with $HBF_4{\cdot}OEt_2$ leads to the allenylphosphonium compound [Rh(acac)$\{\eta^2$-CH(PCy_3)=C=$CPh_2\}(PCy_3)]BF_4$ (**7**). The X-ray crystal structure analysis of **7** reveals that the coordination geometry around the rhodium center is almost square-planar with the CH(PCy_3)=C bond disposed perpendicular to the coordination plane of the rhodium center. The allenylphosphonium ligand of **7** is easily displaced by carbon monoxide, to give Rh(acac)(CO)(PCy_3) (**8**) and $[Ph_2C{=}C{=}CHPCy_3]BF_4$ (**9**). At −78 °C, the protonation of complex **6** leads to the five-coordinate rhodium(III)−allenyl derivative [Rh(acac)$\{CH{=}C{=}CPh_2\}(PiPr_3)_2]BF_4$ (**10**), which evolves in solution into [Rh(acac)$\{\eta^2$-CH($PiPr_3$)=C=$CPh_2\}(PiPr_3)]BF_4$ (**11**). For this isomerization first-order constants k_{obs} were obtained in CD_2Cl_2, which give activation parameters of $\Delta H^{\ddagger} = 23 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger} = 2 \pm 2$ cal K^{-1} mol^{-1}. Similarly to **7**, the reaction of complex **11** with carbon monoxide affords Rh(acac)(CO)($PiPr_3$) (**12**) and $[Ph_2C{=}C{=}CHPiPr_3]BF_4$ (**13**).

Introduction

Reductive elimination, the reverse of oxidative addition, leads to the extrusion of an X−Y fragment from a $L_nM(X)(Y)$ (or $[L_nM(X)(Y)]^+$) complex. For mononuclear compounds, these reactions involve a decrease of 2 in the oxidation number of the metallic center and a decrease in coordination number for the metal.[1]

In general, reductive elimination takes place when X and Y are one-electron ligands and, in this way, the X−Y fragments are neutral molecules (eqs 1 and 2). The



extrusion of $[A{-}X]^+$ cations as results of the elimination of a one-electron ligand and a two-electron molecule (eqs 3 and 4) is uncommon. Although, it was not rationalized as a reductive process, eq 3 has been previously observed in a few cases for neutral complexes.[2] In 1985, Rubinskaya and co-workers[2b] reported that the complexes PdI(CH=$CHCO_2R)(PPh_3)_2$, on heating in benzene at 75−80 °C, formed PdI$\{\eta^2$-CH(PPh_3)=$CHCO_2R\}(PPh_3)$ (R = Me, Et). The X-ray investigation of PdI$\{\eta^2$-CH(PPh_3)=$CHCO_2Me\}(PPh_3)$ reveals that the carbon−carbon double bond of the alkenylphosphonium ligand lies in the coordination plane, and therefore, the complex can be regarded as a palladium(0) derivative. Previously, Guerchais and co-workers[2a] had observed that the complex W(η^5-C_5H_5)(CH=CHCN)$(CO)_2(PPh_3)$ similarly evolves into W(η^5-C_5H_5)$(CO)_2\{\eta^2$-CH(PPh_3)=CHCN}.

In the search for transition-metal complexes which are catalytically active for the addition of germanes and stannanes to alkynes, we have recently reported on the reactivity of the (acetylacetonato)rhodium compound Rh(acac)(cyclooctene)(PCy_3), which is formed by ligand displacement from Rh(acac)(cyclooctene)$_2$ and PCy_3.[3] The cyclooctene compound Rh(acac)(cyclooctene)(PCy_3) reacts with $HGeEt_3$ to give Rh(acac)H($GeEt_3$)(PCy_3) and with $HSnPh_3$ to afford Rh(acac)H($SnPh_3$)(PCy_3). The hydrido−germyl complex reacts with methyl propiolate and phenylacetylene to give square-planar complexes, Rh(acac)$\{\eta^2$-CH($GeEt_3$)=CHR}(PCy_3), containing the corresponding germane−olefin. In contrast to the case for Rh(acac)H($GeEt_3$)(PCy_3), the related reactions with Rh(acac)H($SnPh_3$)(PCy_3) lead to rhodium(III) alkenyl−stannyl derivatives, which are stable and do not evolve by reductive elimination of the stannaolefins.[4]

The olefinic unit of Rh(acac)(cyclooctene)(PCy_3) can be also easily displaced by strong π-acceptor ligands

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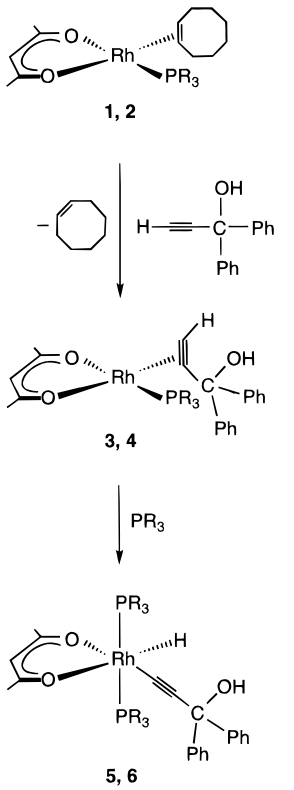
Scheme 1[a]



[a] For **1**, **3**, and **5**, $PR_3 = PCy_3$; for **2**, **4**, and **6**, $PR_3 = PiPr_3$.

such as carbon monoxide, dimethyl acetylenedicarboxylate, and methyl propiolate. Although the bis(phosphine) complex Rh(acac)$(PCy_3)_2$ is not accessible by direct reaction from Rh(acac)(cyclooctene)(PCy_3), it can be prepared by addition of PCy_3 to Rh(acac)$\{\eta^2$-HC≡$CCO_2Me\}(PCy_3)$. Rh(acac)$(PCy_3)_2$ does not react with molecular hydrogen and terminal alkynes by oxidative addition. However, the rhodium(III) compounds Rh(acac)$HX(PCy_3)_2$ (X = H, C≡CR) are obtained by addition of HX to Rh(acac)(cyclooctene)(PCy_3) in the presence of a stoichiometric amount of the phosphine. The protonation of the hydrido−alkynyl derivatives with $HBF_4 \cdot OEt_2$ affords the cationic five-coordinate alkenyl complexes [Rh(acac)$\{(E)$-CH=CHR$\}(PCy_3)_2]BF_4$ (R = Cy, H).[3]

As a continuation of our work in this field, we have now studied the reactivity of Rh(acac)(cyclooctene)(PCy_3) and the related triisopropylphosphine derivative Rh(acac)(cyclooctene)$(PiPr_3)$ toward 1,1-diphenyl-2-propyn-1-ol. During this study, we have prepared the hydrido−alkynyl complexes Rh(acac)H$\{C{\equiv}CC(OH)Ph_2\}(PR_3)_2$ and observed that their protonations with $HBF_4 \cdot OEt_2$ afford the allenylphosphonium derivatives [Rh(acac)$\{\eta^2$-CH$(PR_3){=}C{=}CPh_2\}(PR_3)]BF_4$. In this paper, we report evidence to prove that the formation of the allenylphosphonium derivatives is a result of the reductive elimination of the allenylphosphonium cation from the cationic (allenyl)rhodium(III) derivatives [Rh(acac)$\{CH{=}C{=}CPh_2\}(PR_3)_2]BF_4$ ($PR_3 = PCy_3$, $PiPr_3$).

Results and Discussion

Synthesis and Characterization of Rh(acac)$\{\eta^2$-HC≡CC(OH)$Ph_2\}(PR_3)$ and Rh(acac)H$\{$C≡CC(OH)$Ph_2\}(PR_3)_2$ ($PR_3 = PCy_3$, $PiPr_3$). These compounds were prepared according to Scheme 1. The olefinic unit of the complex Rh(acac)(cyclooctene)(PCy_3) (**1**) and the related derivative Rh(acac)(cyclooctene)$(PiPr_3)$ (**2**) can be displaced by 1,1-diphenyl-2-propyn-1-ol to afford the π-alkyne compounds Rh(acac)$\{\eta^2$-HC≡CC(OH)$Ph_2\}(PR_3)$ ($PR_3 = PCy_3$ (**3**), $PiPr_3$ (**4**)). The reactions were carried out at −78 °C, in pentane as solvent, and the reaction products were isolated as yellow solids in 71% (**3**) and 63% (**4**) yields.

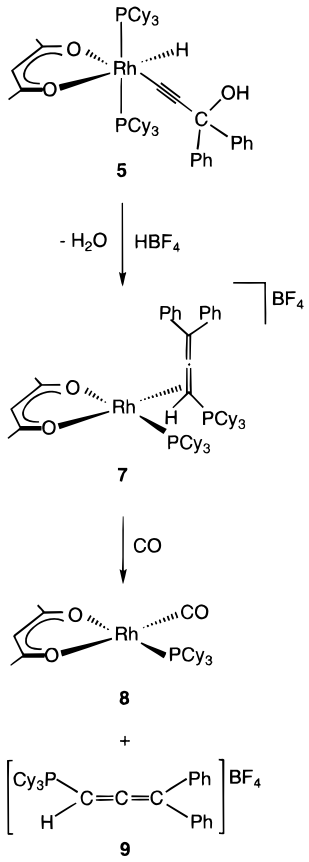
The IR spectra of **3** and **4** display two strong ν(CO) absorptions between 1582 and 1521 cm^{-1}, indicating that the acetylacetonato ligand is coordinated in a κ^2-oxygen bonding mode.[5] The π-coordination of the alkynol is also supported by the IR spectra, in which the C≡C stretching frequency is found at 1831 (**3**) and 1821 (**4**) cm^{-1}, shifted 286 (**3**) and 296 (**4**) cm^{-1} to lower wavenumbers in comparison with the free alkynol (2117 cm^{-1}). In agreement with the square-planar coordination of the rhodium atom, the ^1H NMR spectra display two singlets between 1.83 and 1.53 ppm for the protons of the methyl groups of the acetylacetonato ligand. The resonances due to the OH and HC≡ protons appear at 5.78 and 4.41 ppm (**3**) and at 5.74 and 4.37 ppm (**4**), as singlets. The $^{13}C\{^1H\}$ NMR spectra agree well with the ^1H NMR spectra. Thus, they contain two singlets between 188 and 183 ppm for the carbon atoms of the carbonyl groups of the β-diketonato ligand, and a singlet and a doublet, both at about 27 ppm, for the carbon atoms of the methyl groups of the same ligand. In the $^{13}C\{^1H\}$ NMR spectra of both compounds, the resonance of the HC≡ carbon atom appears at 69.4 ppm as a double doublet with Rh−C and P−C coupling constants of about 16 and 6 Hz, respectively, whereas the other acetylenic carbon atom gives rise at about 90 ppm to a doublet with a Rh−C coupling constant of about 16.5 Hz. The $^{31}P\{^1H\}$ NMR spectra of **3** and **4** contain doublets at 50.6 (**3**) and 60.3 (**4**) ppm with Rh−P coupling constants of 176.5 and 178.3 Hz, respectively.

At 60 °C, in toluene as solvent, and in the presence of 1 equiv of phosphine, complexes **3** and **4** evolve into the six-coordinate hydrido−alkynyl species Rh(acac)H$\{C{\equiv}CC(OH)Ph_2\}(PR_3)_2$ ($PR_3 = PCy_3$ (**5**), $PiPr_3$ (**6**)), which were isolated as white solids in 59% (**5**) and 51% (**6**) yields.

The most noticeable features of the IR spectra of **5** and **6** in KBr are two bands between 2130 and 2109 cm^{-1}, which were assigned to the ν(Rh−H) and ν(C≡C) vibrations. The presence of an alkynyl ligand in these compounds is also supported by the $^{13}C\{^1H\}$ NMR spectra. The signals of the α-C carbon atoms appear at about 97 ppm as double triplets with Rh−C and P−C coupling constants of about 50 and 17 Hz, respectively, while the β-C carbon atoms give rise to doublets at 106.2 (**5**) and 107.3 (**6**) ppm with Rh−C coupling constants of about 10 Hz and the γ-C carbon atoms display singlets at 75.5 (**5**) and 75.7 (**6**) ppm. In the ^1H NMR spectra, the resonances of the hydrido ligands are observed in the high-field region at −19.23 (**5**) and −18.99 (**6**) ppm, as double triplets with Rh−H and P−H coupling constants of about 18 and 12 Hz, respectively. The presence of only one hydrido ligand in **5** and **6** was inferred from the $^{31}P\{^1H\}$ NMR spectra, which contain at 37.7 (**5**) and 47.3 (**6**) ppm doublets with Rh−P coupling constants of 101.9 and 102.9 Hz, respectively, in agree-

(5) Oro, L. A.; Carmona, D.; Esteruelas, M. A.; Foces-Foces, C.; Cano, F. H. *J. Organomet. Chem.* **1986**, *307*, 83.

Scheme 2



ment with the mutually *trans* disposition of the phosphine ligands. Under off-resonance conditions these signals split into double doublets due to the P−H coupling. These spectroscopic data agree well with those previously reported for the hydrido−alkynyl complexes Rh(acac)H(C≡CR)(PCy_3)$_2$ (R = Ph, Cy, $SiMe_3$), which were prepared by reaction of **1** with the corresponding alkyne in the presence of tricyclohexylphosphine, as has been previously mentioned.[4] Then, we proposed that the formation of these compounds involves the coordination of phosphine to five-coordinate hydrido−alkynyl intermediates of the type Rh(acac)H(C≡CR)(PCy_3). The formation of **5** and **6**, with **3** and **4** and phosphine as starting materials, is new evidence in favor of this proposal.

Protonation of 5. Treatment of complex **5** with 1 equiv of HBF_4·OEt_2 in dichloromethane at −78 °C leads to a red-orange solution, which changes color to yellow by slow heating to room temperature. From the yellow solution, a yellow solid in 89% yield was obtained by addition of diethyl ether. The solid was characterized as the allenylphosphonium complex [Rh(acac){η^2-CH(PCy_3)=C=CPh_2}(PCy_3)]BF_4 (**7**; see Scheme 2) by elemental analysis, IR and ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectroscopy, and a X-ray diffraction study. Although at −78 °C the solution is red-orange, the spectroscopic data obtained from the solid isolated at this temperature are the same as those of **7**. This complex is also obtained from the reaction of **5** with DBF_4·D_2O, indicating that the hydrido ligand of **5** becomes a part of the allenyl ligand of **7**.

A view of the molecular geometry of **7** is shown in Figure 1. Selected bond distances and angles are listed in Table 1. The coordination around the rhodium center

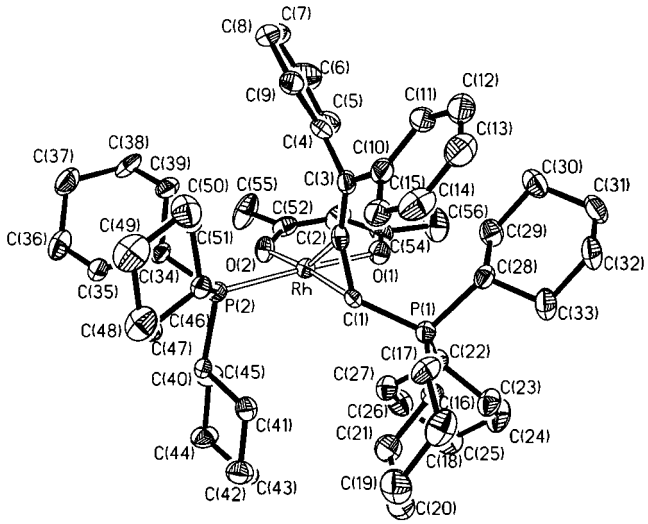


Figure 1. Molecular drawing for the complex [Rh(acac){η^2-CH(PCy_3)=C=CPh_2}(PCy_3)]BF_4 (**7**).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex [Rh(acac){η^2-CH(PCy_3)=C=CPh_2}(PCy_3)]BF_4 (7)

Bond Lengths			
Rh−C(1)	2.130(7)	O(2)−C(52)	1.279(9)
Rh−C(2)	1.969(7)	C(52)−C(53)	1.388(11)
Rh−O(1)	2.083(5)	C(52)−C(55)	1.489(11)
Rh−O(2)	2.040(5)	C(1)−P(1)	1.809(7)
Rh−P(2)	2.285(2)	C(1)−C(2)	1.401(10)
O(1)−C(54)	1.276(9)	C(2)−C(3)	1.344(10)
C(53)−C(54)	1.387(11)	C(3)−C(4)	1.486(10)
C(54)−C(56)	1.512(11)	C(3)−C(10)	1.506(10)
Bond Angles			
P(2)−Rh−O(1)	173.2(2)	Rh−C(2)−C(3)	135.0(6)
P(2)−Rh−O(2)	86.5(2)	C(1)−C(2)−C(3)	148.5(7)
P(2)−Rh−M(1)[a]	95.1(2)	C(2)−C(1)−P(1)	127.2(5)
O(1)−Rh−O(2)	88.4(2)	C(2)−C(3)−C(4)	121.9(7)
O(1)−Rh−M(1)	90.9(3)	C(2)−C(3)−C(10)	120.7(7)
O(2)−Rh−M(1)	166.7(3)	C(4)−C(3)−C(10)	117.5(6)
C(1)−Rh−C(2)	39.7(3)	C(1)−P(1)−C(16)	107.5(3)
Rh−C(1)−C(2)	63.9(4)	C(1)−P(1)−C(22)	113.9(3)
Rh−C(2)−C(1)	76.4(4)	C(1)−P(1)−C(28)	109.6(3)
Rh−C(1)−P(1)	124.2(4)		

[a] M(1) is the midpoint of the allenylphosphonium ligand C(1)−C(2) double bond.

is almost square planar with the C(1)−C(2) double bond disposed perpendicular to the coordination plane of the rhodium. If M(1) is the midpoint of the C(1)−C(2) double bond, the deviations from the best plane are 0.0082(6) Å (Rh), 0.014(2) Å (P(2)), −0.448(5) Å (O(2)), 0.122(5) Å (O(1)), and −0.0011(3) Å (M(1)). The β-diketonato bite angle (O(1)−Rh−O(2) = 88.4(2)°) is similar to the values found in related chelated rhodium complexes,[3,4,6] whereas the P(2)−Rh−M(1) angle (95.1(2)°) slightly deviates from the ideal value of 90°, probably as a result of the steric hindrance experienced by the phosphine and allenylphosphonium ligands, which are mutually *cis*-disposed. The C(1)−C(2) and C(2)−C(3) bond lengths are 1.401(10) and 1.344(10) Å, respectively. The elongation of the C(1)−C(2) bond upon coordination of the allenylphosphonium ligand to the rhodium atom is accompanied by a bending of the C(1)−C(2)−C(3) angle to 148.5(7)°. Although transition-metal allenyl-

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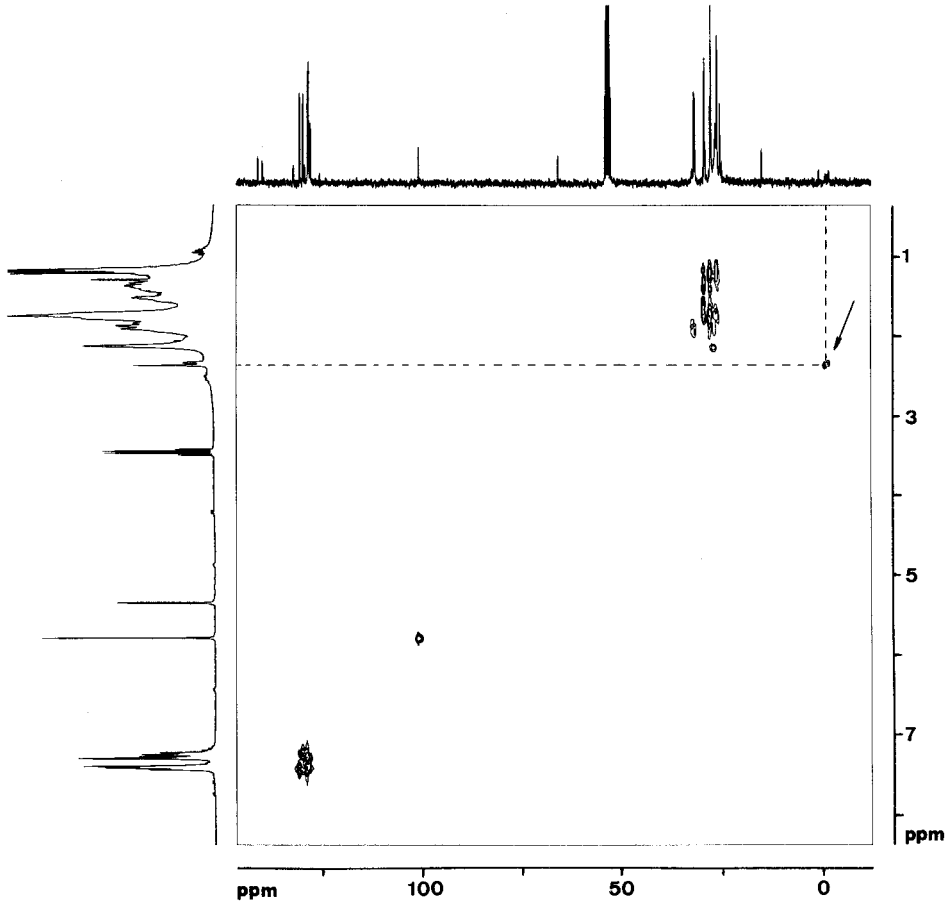

Figure 2. HETCOR NMR spectrum of [Rh(acac){η^2-CH(PCy_3)=C=CPh_2}(PCy_3)]BF_4 (**7**) in CD_2Cl_2 at 293 K.

phosphonium complexes have not been previously reported, one can find examples of structurally characterized M(η^2-R_2C=C=CR_2) compounds.[7] For these compounds the degree of elongation of the coordinated carbon−carbon double bond agrees well with that found in **7** (between 0.10 and 0.03 Å), and the elongation is also accompanied by a similar bending of the allene ligand (between 160 and 140°).

In agreement with the sp^2 character of C(1), the value of the C(2)−C(1)−P(1) angle is 127.2(5)°. The rhodium−allenylphosphonium coordination exhibits Rh−C distances of 2.130(7) Å (Rh−C(1)) and 1.969(7) Å (Rh−C(2)), which agree well with those found in rhodium(I)−olefin complexes (mean values 2.10 Å).[8] The P(1)−C(1) bond length of 1.809(7) Å is close to that observed in W(η^5-C_5H_5)$(CO)_2${η^2-CH(PPh_3)=CHCN} (1.802(3) Å)[2a] and is significantly greater than the values found for P=C double bonds (for example, 1.640(6) Å in $(CH_3)_3$-P=CH_2)[9] or for partial phosphorus−carbon double bonds (between 1.68 and 1.78 Å).[2a]

In addition, it should be mentioned that the Rh−O(2) bond distance (O *trans* to C(1)−C(2), 2.040(5) Å) is about 0.04 Å shorter than the Rh−O(1) bond length (O *trans* to P(2), 2.083(5) Å), probably as a result of the different *trans* influences of the allenylphosphonium and phosphine ligands. The same situation, with similar Rh−O bond lengths, has been found in the related rhodium(I) complex Rh(acac){η^2-CH($GeEt_3$)=$CHCO_2Me$}(PCy_3).[4]

In agreement with the κ^2-oxygen coordination bonding mode of the acetylacetonato ligand in **7**, and the salt character of the compound, the IR spectrum in KBr shows two strong ν(CO) bands at 1576 and 1522 cm^{-1} and an absorption due to the $[BF_4]^-$ anion centered at 1056 cm^{-1}. In the $^{13}C\{^1H\}$ NMR spectrum, the most noticeable resonances are those corresponding to the α-, β-, and γ-C carbon atoms of the allenylphosphonium ligand. The resonance due to C(1) appears at −1.2 ppm as a doublet of doublets of doublets with Rh−C, P(1)−C, and P(2)−C coupling constants of 13.8, 54.3, and 2.3 Hz, respectively. The resonance corresponding to C(2) is observed at 162.7 ppm, also as a doublet of doublets of doublets but with a Rh−C coupling constant of 24.7 Hz and the same value (5.9 Hz) for the P(1)−C and P(2)−C coupling constants. The resonance due to C(3) appears at 132.2 ppm as a doublet with a Rh−C coupling constant of 6.0 Hz. According to the HETCOR spectrum shown in Figure 2, the *H*C(PCy_3)=C resonance appears in the ^1H NMR spectrum at 2.25 ppm, as a doublet of doublets of doublets with P(1)−H, Rh−H, and P(2)−H coupling constants of 8.4, 2.7, and 2.5

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Hz, respectively. The $^{31}P\{^1H\}$ NMR spectrum shows two doublets at 44.4 (P(2)) and 39.9 (P(1)) ppm, with Rh−P coupling constants of 158.8 and 5.3 Hz.

The allenylphosphonium ligand of **7** is easily displaced by carbon monoxide. By passage of a slow stream of this gas through a dichloromethane solution of **7** the previously reported carbonyl complex Rh(acac)(CO)(P-Cy_3)[3] (**8**) and the salt $[Ph_2C{=}C{=}CHPCy_3]BF_4$ (**9**) are formed.

Salt **9** was isolated as a white solid in 75% yield and characterized by elemental analysis and IR and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. The presence of the allenyl unit in the compound is supported by the C=C=C stretching frequency in the IR spectrum at 1928 cm^{-1} and three doublets in the $^{13}C\{^1H\}$ NMR spectrum at 215.9 (J_{PC} = 3.2 Hz), 113.6 (J_{PC} = 13.3 Hz), and 73.3 (J_{PC} = 78.3 Hz) ppm for the β-, γ-, and α-C allenyl carbon atoms, respectively, which are in agreement with the $^{13}C\{^1H\}$ data reported for other allene−phosphine derivatives.[10] In the ^1H NMR spectrum the most noticeable resonance is at 6.38 ppm, and it appears as a doublet with a P−H coupling constant of 7.8 Hz. This signal was assigned to the C*H*PCy_3 proton. The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 30.2 ppm.

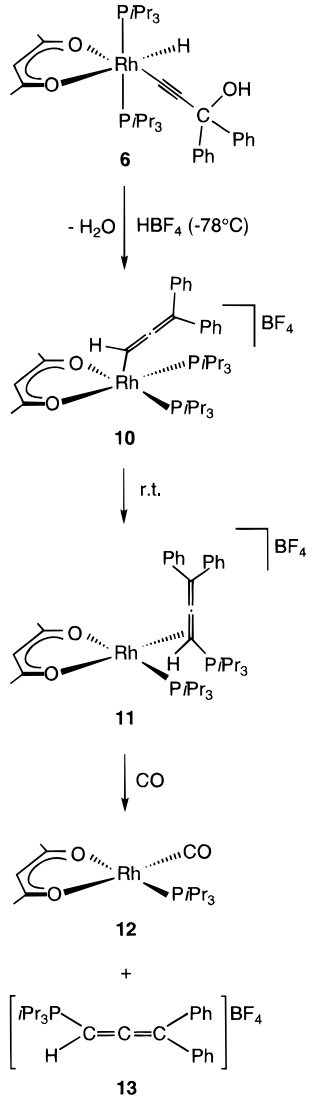
In addition, it should be mentioned that the resonances of α- and β-carbon atoms of the allenyl unit in the $^{13}C\{^1H\}$ NMR spectrum of compound **7** show an unusually long slide toward high field, as a result of the coordination to the rhodium atom. The same phenomenon has been previously observed for the coordination of simple allene ligands.[6h,11]

Protonation of 6. Treatment of complex **6** with 1 equiv of $HBF_4{\cdot}OEt_2$ in dichloromethane at −78 °C leads to a red-orange solution, from which the allenyl complex $[Rh(acac)\{CH{=}C{=}CPh_2\}(P\textit{i}Pr_3)_2]BF_4$ (**10**; see Scheme 3) was isolated as a red-orange solid in 63% yield, by addition of diethyl ether.

The IR spectrum of **10** in KBr strongly supports the presence of the allenyl ligand, showing the C=C=C stretching frequency at 1885 cm^{-1}. This spectrum also contains two ν(CO) bands at 1569 and 1523 cm^{-1} in agreement with the κ^2-oxygen coordination bonding mode of the acetylacetonato group. Furthermore, the spectrum shows an absorption due to the $[BF_4]^-$ anion with T_d symmetry centered at 1055 cm^{-1}, indicating that, although the metallic center of **10** is coordinatively unsaturated, the anion is not coordinated to the rhodium atom.

The presence of the allenyl ligand in **10** is also supported by the $^{13}C\{^1H\}$ NMR spectrum at −40 °C, which shows two singlets at 189.6 and 119.0 ppm for the β- and γ-C carbon atoms, respectively, and a double triplet at 67.1 ppm with Rh−C and P−C coupling constants of 35.5 and 8.3 Hz for the α-C carbon atom. The $^{13}C\{^1H\}$ NMR spectrum also supports the square-pyramidal geometry proposed in Scheme 3. In agreement with the apical position of the allenyl group, the spectrum shows singlets for both carbonyl and both methyl carbon atoms of the acetylacetonato ligand, at

Scheme 3



185.8 and 26.8 ppm, respectively. The ^1H NMR spectrum at −40 °C agrees well with the $^{13}C\{^1H\}$ NMR spectrum at the same temperature, containing only one singlet at 1.70 ppm for the methyl protons. The resonance of the RhCH= proton appears at 7.22 ppm as a double triplet with Rh−H and P−H coupling constants of 3.3 and 9.3 Hz, respectively. In accordance with the presence of two chemically equivalent phosphine ligands in **10**, the $^{31}P\{^1H\}$ NMR spectrum at −40 °C shows a doublet at 41.1 ppm, with an Rh−P coupling constant of 135.7 Hz.

The related alkenyl complex $[Rh(acac)\{(E)\text{-}CH{=}CHCy\}(PCy_3)_2]BF_4$, which was prepared similarly to **10** by protonation of the hydrido−alkynyl compounds $Rh(acac)H(C{\equiv}CCy)(PCy_3)_2$ with $HBF_4{\cdot}OEt_2$, also has a square-pyramidal geometry with the η^1-carbon ligand in the apical position, as was established by X-ray diffraction analysis.[3] However, in the stannyl−allenyl complex $Rh(acac)(SnPh_3)\{CH{=}C{=}CPh_2\}(PCy_3)$, the allenyl ligand occupies a site of the base of the pyramid.[4]

There are a variety of η^1-allenyl transition-metal complexes known, but most have been prepared by oxidative addition of propargyl or allenyl halides to electron-rich metal centers.[12] Werner has observed that the osmium alkynyl−hydrido complexes $OsHCl\{C{\equiv}CC(OH)Ph_2\}(NO)(PR_3)_2$ react with acidic alumina to afford

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the allenylosmium(II) derivatives $OsCl_2\{CH{=}C{=}CPh_2\}(NO)(PR_3)_2$ (PR_3 = P*i*Pr$_3$, PPh*i*Pr$_2$).[13] Fisher has also reported that the allenylidene complex $Cr(CO)_5\{{=}C{=}C{=}C(C_6H_4NMe_2\text{-}p)_2\}$ adds phosphine at the α-C carbon atom to give $Cr(CO)_5\{\eta^1\text{-}C(PR_3){=}C{=}C(C_6H_4NMe_2\text{-}p)_2\}$ (PR_3 = PMe_3, $PHPh_2$, PH_2Me).[14] In the same sense, Gimeno has observed that $[Ru(\eta\text{-}C_9H_7)\{C{\equiv}CC(PMe_3)Ph_2\}(dppm)]PF_6$ isomerizes in tetrahydrofuran solution to the thermodynamically stable product $[Ru(\eta\text{-}C_9H_7)\{C(PMe_3){=}C{=}CPh_2\}(dppm)]PF_6$,[15] and we have described that the deprotonation of α,*β*-unsaturated alkoxycarbene, (alkylthio)carbene, and 2-azaallenyl complexes also yields allenyl derivatives.[16]

At room temperature, complex **10** evolves in dichloromethane as solvent into the allenylphosphonium−rhodium(I) derivative $[Rh(acac)\{\eta^2\text{-}CH(P\mathit{i}Pr_3){=}C{=}CPh_2\}(P\mathit{i}Pr_3)]BF_4$ (**11**; see Scheme 3), which was isolated as a yellow solid in 90% yield by addition of diethyl ether.

In the IR spectrum of **11**, the most noticeable features are the two *ν*(CO) bands of the acetylacetonato ligand at 1575 and 1520 cm^{-1} and the absorption due to the $[BF_4]^-$ anion with T_d symmetry centered at 1053 cm^{-1}. In the ^{1}H NMR spectrum the C*H*(P*i*Pr$_3$) resonance appears at 2.32 ppm as a doublet of doublets of doublets with P−H, Rh−H, and P′−H coupling constants of 9.0, 3.0, and 2.1 Hz, respectively. The $^{13}C\{^1H\}$ NMR spectrum shows the resonances due to the α-, *β*-, and *γ*-C carbon atoms of the allenylphosphonium ligand at −1.7, 162.2, and 132.8 ppm. The first resonance appears as a doublet of doublets of doublets with P−C, Rh−C, and P′−C coupling constants of 56.5, 14.0, and 2.9 Hz. The second resonance is also observed as a doublet of doublets of doublets, but with a Rh−C coupling constant of 25.2 Hz, and the same value (6.1 Hz) for the P−C and P′−C coupling constants, whereas the third resonance is a doublet with a Rh−C coupling constant of 5.8 Hz. The $^{31}P\{^1H\}$ NMR spectrum shows two doublets at 54.6 (P*i*Pr$_3$) and 50.8 ppm (CHP*i*Pr$_3$), with Rh−P coupling constants of 158.8 and 6.2 Hz, respectively.

The isomerization of **10** into **11** was followed by ^{1}H NMR spectroscopy by measuring the disappearance of the CH resonance of the acetylacetonato ligand as a function of time. As shown in Figure 3, the decrease of **10** (with the corresponding increase of **11**) in dichloromethane-d_2 is an exponential function of time, in agreement with a first-order process. The values obtained for the first-order rate constant k_{obs} in the temperature range studied are reported in Table 2. The activation parameters of the reaction were obtained from the Eyring analysis shown in Figure 4, giving values of $\Delta H^{\ddagger} = 23 \pm 2$ kcal mol^{-1} and $\Delta S^{\ddagger} = 2 \pm 2$ cal K^{-1} mol^{-1}. The activation entropy is nearly zero, suggesting that the isomerization is intramolecular and,

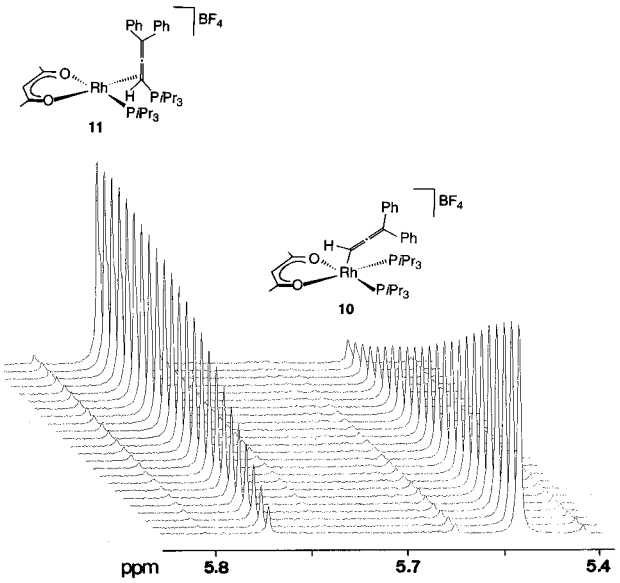

Figure 3. Stacked ^{1}H NMR spectra illustrating the isomerization of complex **10** to **11** in CD_2Cl_2 at 309 K.

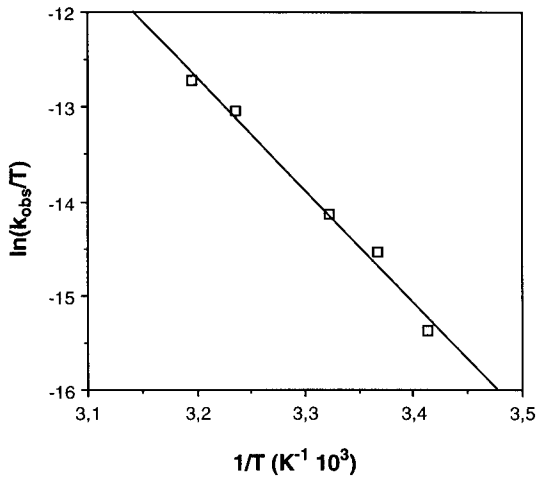

Figure 4. Eyring plot of the first-order rate constants (k_{obs}) for the isomerization of **10** to **11** in CD_2Cl_2.

Table 2. Rates of Isomerization of Complex 10 to 11 in CD_2Cl_2

temp (K)	k_{obs} (10^5 s^{-1})
313	93.1 ± 5.5
309	67.1 ± 4.0
301	21.7 ± 1.3
297	16.0 ± 0.9
293	6.2 ± 0.4

therefore, that the reductive elimination of the allenylphosphonium cation is a concerted process. In agreement with this, we have also observed that the formation of **11** is not affected by the presence of tricyclohexylphosphine.

Although attempts to isolate a compound related to **10** with tricyclohexylphosphine have been unsuccessful, even at −78 °C, it is reasonable to assume that the formation of **7** by protonation of **5** also goes through a five-coordinate allenyl intermediate, $[Rh(acac)\{CH{=}C{=}CPh_2\}(PCy_3)_2]^+$, which rapidly isomerizes into **7**. Two differences seem to exist between tricyclohexylphosphine and triisopropylphosphine. The first phosphine appears to have a larger cone angle and a greater donor power than the second one.[17]

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(16) Esteruelas, M. A.; Gómez, A. V.; Lahoz, F. J.; López, A. M.; Oñate, E.; Oro, L. A. *Organometallics* **1996**, *15*, 3423.

The allenylphosphonium ligand of **11** can be displaced by carbon monoxide, to afford Rh(acac)(CO)(P*i*Pr$_3$) (**12**) and [Ph$_2$C=C=CHP*i*Pr$_3$]BF$_4$ (**13**). Salt **13** was isolated as a white solid in 68% yield. The spectroscopic data obtained for **13** agree well with those of **9**. The presence of the allenyl unit is supported by the C=C=C stretching frequency in the IR spectrum at 1932 cm^{-1} and three doublets in the ^{13}C{^{1}H} NMR spectrum at 217.0 (J_{PC} = 3.2 Hz), 114.6 (J_{PC} = 12.9 Hz), and 72.8 (J_{PC} = 79.7 Hz) ppm for the β-, γ-, and α-C allenyl carbon atoms, respectively. In the ^{1}H NMR spectrum the C*H*P*i*Pr$_3$ resonance appears at 6.21 ppm, as a doublet with a P−H coupling constant of 7.8 Hz. The ^{31}P{^{1}H} NMR spectrum shows a singlet at 40.8 ppm.

Concluding Remarks

This study has revealed that the protonation of the hydrido−alkynyl complexes Rh(acac)H{C≡CC(OH)Ph$_2$}(PR$_3$)$_2$ (PR$_3$ = PCy$_3$, P*i*Pr$_3$) with HBF$_4$·OEt$_2$ leads to the allenyl derivatives [Rh(acac){CH=C=CPh$_2$}(PR$_3$)$_2$]BF$_4$, as a result of the dehydration of the alkynyl group in the acid medium and the migration of the hydrido ligand to the α-C carbon atom of the alkynyl. The five-coordinative allenyl derivatives evolve by reductive elimination of [Ph$_2$C=C=CHPR$_3$]$^+$ into the square-planar allenylphosphonium complexes [Rh(acac){η^2-CH(PR$_3$)=C=CPh$_2$}(PR$_3$)]BF$_4$. The isomerization is intramolecular, suggesting that the reductive elimination of the allenylphosphonium cation is a concerted process.

Experimental Section

All reactions were carried out under an atmosphere of argon by using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting materials Rh(acac)(C$_8$H$_{14}$)(PR$_3$) (R = Cy (**1**), *i*Pr (**2**)) were prepared by a published method.[3] The reagent 1,1-diphenyl-2-propyn-1-ol was a commercial product from ABCR.

IR spectra were recorded on a Perkin-Elmer 883 spectrometer and the NMR spectra on Varian UNITY 300, Varian GEMINI 2000 300 MHz, and Bruker ARX 300 instruments. The probe temperature of the NMR spectrometers was calibrated against a methanol standard. The ^{13}C NMR signals were assigned by DEPT experiments (vt = virtual triplet; $N = {}^3J_{PH} + {}^5J_{PH}$ or ${}^1J_{PC} + {}^3J_{PC}$, respectively). C and H analyses were carried out with a Perkin-Elmer 2400 CHNS/O microanalyzer.

Preparation of Rh(acac){η^2-HC≡CC(OH)Ph$_2$}(PCy$_3$) (3). A solution of compound **1** (148.2 mg, 0.25 mmol) in 15 mL of pentane was cooled to −78 °C, and then a stoichiometric amount of 1,1-diphenyl-2-propyn-1-ol (52.1 mg, 0.25 mmol) was added. After the mixture was stirred for 1 h, a yellow solid was formed. The solid was separated by decantation, washed with pentane, and dried *in vacuo*. Yield: 123 mg (71%). Anal. Calcd for C$_{38}$H$_{52}$O$_3$PRh: C, 66.08; H, 7.59. Found: C, 65.69; H, 7.24. IR (KBr, cm^{-1}): ν(OH) 3395, ν(C≡C) 1831, ν(CO)$_{acac}$ 1574 and 1521. ^{1}H NMR (300 MHz, C$_6$D$_6$, 293 K): δ 8.10 (d, 4H, J_{HH} = 7.5 Hz, H_{o-Ph}), 7.20 (br, 4H, H_{m-Ph}), 7.05 (br, 2H, H_{p-Ph}), 5.78 (s, 1H, O*H*), 5.12 (s, 1H, C*H* of acac), 4.41 (s, 1H, *H*C≡), 1.83 and 1.53 (both s, 6H, C*H*$_3$ of acac), 1.80−1.11 (m, 33H, C$_6$*H*$_{11}$). ^{31}P{^{1}H} NMR (121.4 MHz, C$_6$D$_6$, 293 K): δ 50.6 (d, J_{RhP} = 176.5 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, toluene-d_8, 233 K): δ 187.4 and 183.9 (both s, *C*O of acac), 149.1 and 147.2 (both s, $C_{ipso-Ph}$), 127.8, 127.6, 127.5, 126.8, and 126.7 (all s, $C_{o,m,p-Ph}$), 99.8 (s, *C*H of acac), 90.1 (d, J_{RhC} = 16.0 Hz, HC≡*C*), 75.1 (s, *C*−OH), 69.4 (dd, J_{RhC} = 15.9 Hz, J_{PC} = 5.9 Hz, H*C*≡C), 31.7 (d, J_{PC} = 24.8 Hz, PCy$_3$), 29.9, 29.1, 28.1, 27.9, and 26.8 (all s, PCy$_3$), 27.4 (d, J_{PC} = 5.5 Hz, *C*H$_3$ of acac), 26.9 (s, *C*H$_3$ of acac).

Preparation of Rh(acac){η^2-HC≡CC(OH)Ph$_2$}(P*i*Pr$_3$) (4). This compound was prepared as described for **3**, using **2** (118.1 mg, 0.25 mmol) and 1,1-diphenyl-2-propyn-1-ol (52.1 mg, 0.25 mmol) as starting materials: yellow solid. Yield: 90 mg (63%). Anal. Calcd for C$_{29}$H$_{40}$O$_3$PRh: C, 61.05; H, 7.07. Found: C, 60.74; H, 6.85. IR (KBr, cm^{-1}): ν(OH) 3255, ν(C≡C) 1821, ν(CO)$_{acac}$ 1582 and 1521. ^{1}H NMR (300 MHz, C$_6$D$_6$, 293 K): δ 8.08 (d, 4H, J_{HH} = 6.9 Hz, H_{o-Ph}), 7.19 (dd, 4H, J_{HH} = $J_{HH'}$ = 6.9 Hz, H_{m-Ph}), 7.05 (dd, 2H, J_{HH} = 6.9 Hz, H_{p-Ph}), 5.74 (s, 1H, O*H*), 5.13 (s, 1H, C*H* of acac), 4.37 (s, 1H, *H*C≡), 1.79 (m, 3H, PC*H*CH$_3$), 1.77 and 1.56 (both s, 6H, C*H*$_3$ of acac), 0.99 (dd, 18H, J_{PH} = 12.9 Hz, J_{HH} = 7.2 Hz, PCHC*H*$_3$). ^{31}P{^{1}H} NMR (121.4 MHz, C$_6$D$_6$, 293 K): δ 60.3 (d, J_{RhP} = 178.3 Hz). ^{13}C{^{1}H} NMR (75.4 MHz, C$_6$D$_6$, 293 K): δ 187.4 and 184.2 (both s, *C*O of acac), 147.9 (br, $C_{ipso-Ph}$), 127.7 (s, C_{o-Ph}), 127.6 (s, C_{m-Ph}), 126.7 (s, C_{p-Ph}), 99.7 (s, *C*H of acac), 89.6 (d, J_{RhC} = 17.4 Hz, HC≡*C*), 75.4 (s, *C*-OH), 69.4 (dd, J_{RhC} = 15.5 Hz, J_{PC} = 5.9 Hz, H*C*≡C), 27.5 (d, J_{PC} = 5.3 Hz, *C*H$_3$ of acac), 26.9 (s, *C*H$_3$ of acac), 22.6 (d, J_{PC} = 23.2 Hz, P*C*HCH$_3$), 19.4 (s, PCH*C*H$_3$).

Preparation of Rh(acac){C≡CC(OH)Ph$_2$}H(PCy$_3$)$_2$ (5). To a solution of PCy$_3$ (70.1 mg, 0.25 mmol) in 15 mL of toluene was added **3** (141.6 mg, 0.25 mmol). After the mixture was stirred for 30 min at 60 °C, a solid was formed. The solvent was removed *in vacuo*, and the residue was treated with pentane to give a white solid. Yield: 143 mg (59%). Anal. Calcd for C$_{56}$H$_{85}$O$_3$P$_2$Rh: C, 69.26; H, 8.82. Found: C, 69.07; H, 8.51. IR (KBr, cm^{-1}): ν(OH) 3480, ν(RhH) 2120, ν(C≡C) 2130, ν(CO)$_{acac}$ 1599 and 1512. ^{1}H NMR (300 MHz, CDCl$_3$, 293 K): δ 7.59 (d, 4H, J_{HH} = 8.1 Hz, H_{o-Ph}), 7.15 (m, 6H, $H_{m,p-Ph}$), 5.13 (s, 1H, C*H* of acac), 1.91−0.92 (m, 66H, C$_6$*H*$_{11}$), 1.88 and 1.67 (both s, 6H, C*H*$_3$ of acac), −19.23 (dt, 1H, J_{RhH} = 18.0 Hz, J_{PH} = 12.1 Hz, RhH), signal of OH not observed. ^{31}P{^{1}H} NMR (121.4 MHz, CDCl$_3$, 293 K): δ 37.7 (d, J_{RhP} = 101.9 Hz, dd in off-resonance). ^{13}C{^{1}H} NMR (75.4 MHz, CDCl$_3$, 293 K): δ 187.9 and 184.1 (both s, *C*O of acac), 148.2 (s, $C_{ipso-Ph}$), 127.2 (s, C_{o-Ph}), 126.9 (s, C_{m-Ph}), 126.1 (s, C_{p-Ph}), 106.2 (d, J_{RhC} = 9.8 Hz, RhC≡*C*), 99.4 (s, *C*H of acac), 97.2 (dt, J_{RhC} = 50.3 Hz, J_{PC} = 16.8 Hz, Rh*C*≡C), 75.5 (s, *C*−OH), 33.3 (vt, N = 18.9 Hz, PCy$_3$), 29.2 and 29.1 (both s, PCy$_3$), 28.5 (s, *C*H$_3$ of acac), 27.9 (m, PCy$_3$), 26.7 (s, PCy$_3$).

Preparation of Rh(acac){C≡CC(OH)Ph$_2$}H(P*i*Pr$_3$)$_2$ (6). This compound was prepared as described for **5**, using P*i*Pr$_3$ (46 mL, 0.25 mmol) and **4** (142.6 mg, 0.25 mmol) as starting materials: white solid. Yield: 93 mg (51%). Anal. Calcd for C$_{38}$H$_{61}$O$_3$P$_2$Rh: C, 62.46; H, 8.42. Found: C, 62.27; H, 8.19. IR (KBr, cm^{-1}): ν(OH) 3342, ν(C≡C) 2119, β(RhH) 2109, ν(CO)$_{acac}$ 1598 and 1515. ^{1}H NMR (300 MHz, C$_6$D$_6$, 293 K): δ 7.88 (d, 4H, J_{HH} = 7.7 Hz, H_{o-Ph}), 7.17−7.06 (m, 6H, $H_{m,p-Ph}$), 5.14 (s, 1H, C*H* of acac), 2.69 (s, 1H, O*H*), 2.35 (m, 6H, PC*H*CH$_3$), 1.85 and 1.63 (both s, 6H, C*H*$_3$ of acac), 1.25 (dvt, 18H, N = 13.5 Hz, J_{HH} = 6.9 Hz, PCHC*H*$_3$), 1.21 (dvt, 18H, N = 13.5 Hz, J_{HH} = 6.6 Hz, PCHC*H*$_3$), −18.99 (dt, 1H, J_{RhH} = 18.6 Hz, J_{PH} = 12.6 Hz, RhH). ^{31}P{^{1}H} NMR (121.4 MHz, C$_6$D$_6$, 293 K): δ 47.3 (d, J_{RhP} = 102.9 Hz, dd in off-resonance). ^{13}C{^{1}H} NMR (75.4 MHz, C$_6$D$_6$, 293 K): δ 188.8 and 185.0 (both s, *C*O of acac), 148.9 (s, $C_{ipso-Ph}$), 127.7 (s, C_{o-Ph}), 127.2 (s, C_{m-Ph}), 126.5 (s, C_{p-Ph}), 107.3 (d, J_{RhC} = 9.6 Hz, RhC≡*C*), 99.9 (s, *C*H of acac), 96.7 (dt, J_{RhC} = 47.0 Hz, J_{PC} = 17.4 Hz, Rh*C*≡C), 75.7 (s, *C*−OH), 28.9 and 28.0 (both s, *C*H$_3$ of acac), 23.6 (vt, N = 20.3 Hz, P*C*HCH$_3$), 19.2 and 19.1 (both s, PCH*C*H$_3$).

Preparation of [Rh(acac){η^2-CH(PCy$_3$)=C=CPh$_2$}(PCy$_3$)]BF$_4$ (7). A solution of **5** (242.8 mg, 0.25 mmol) in 5 mL of dichloromethane was cooled to −78 °C, and then a stoichiometric amount of HBF$_4$·OEt$_2$ (37 μL, 0.27 mmol) was added. A change from yellow to red-orange occurred almost instantaneously. The solution turns yellow by slow heating to room

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temperature. The solvent was removed *in vacuo*, and the residue was washed with diethyl ether to give a yellow solid. Yield: 232 mg (89%). Anal. Calcd for $C_{56}H_{84}BF_4O_2P_2Rh$: C, 64.62; H, 8.13. Found: C, 64.52; H, 7.91. IR (KBr, cm^{-1}): $\nu(CO)_{acac}$ 1576 and 1522, $\nu(BF_4)$ 1056. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.40−7.12 (m, 10H, Ph), 5.78 (s, 1H, C*H* of acac), 2.25 (ddd, 1H, J_{PH} = 8.4 Hz, J_{RhH} = 2.7 Hz, $J_{P'H}$ = 2.5 Hz, C*H*(PCy_3)), 2.02 (br, 6H, CH_3 of acac), 1.78−1.04 (m, 66H, C_6H_{11}). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 44.4 (d, $^1J_{RhP}$ = 158.8 Hz, Rh(*P*Cy_3)), 39.9 (d, $^2J_{RhP}$ = 5.3 Hz, CH(*P*Cy_3)). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 187.4 (br, *C*O of acac), 162.7 (ddd, J_{RhC} = 24.7 Hz, J_{PC} = $J_{P'C}$ = 5.9 Hz, CH(PCy_3)=*C*=C), 141.1 and 140.1 (both s, $C_{ipso-Ph}$), 132.3 (d, J_{RhC} = 6.0 Hz, CH(PCy_3)=C=*C*), 130.7, 129.9, 128.7, 128.5, 128.3, and 128.0 (all s, $C_{o,m,p-Ph}$), 101.0 (s, *C*H of acac), 33.0 (br, PCy_3), 32.2 (d, J_{PC} = 23.0 Hz, PCy_3), 29.7 and 29.6 (both s, PCy_3), 28.2 (d, J_{PC} = 9 Hz, PCy_3), 28.1 (d, J_{PC} = 9.6 Hz, PCy_3), 26.0 (br, *C*H_3 of acac), 26.6 and 25.8 (both s, PCy_3), −1.2 (ddd, J_{PC} = 54.3 Hz, J_{RhC} = 13.8 Hz, $J_{P'C}$ = 2.3 Hz, *C*H(PCy_3)=C=C).

Reaction of 7 with CO. A stream of CO was passed through a solution of compound **7** (260.2 mg, 0.25 mmol) in 10 mL of dichloromethane for 5 min. A change from yellow to light yellow occurred almost instantaneously. Then the solvent was removed *in vacuo*, and the addition of pentane caused the precipitation of a white solid, which was washed with pentane. The pentane solution was concentrated *in vacuo* to produce a residue, which was identified as Rh(acac)(CO)(PCy_3) (**8**).[3] The white solid was identified as [Ph_2C=C=CHPCy_3]BF_4 (**9**). Yield: 105 mg (75%). Anal. Calcd for $C_{33}H_{44}BF_4P$: C, 70.97; H, 7.94. Found: C, 70.60; H, 7.64. IR (KBr, cm^{-1}): ν(C=C=C) 1928, $\nu(BF_4)$ 1066. ^1H NMR (300 MHz, $CDCl_3$, 293 K): δ 7.45−7.27 (m, 10H, Ph), 6.38 (d, J_{PH} = 7.8 Hz, C*H*PCy_3), 2.51−1.10 (m, 33H, C_6H_{11}). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$, 293 K): δ 30.2 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, $CDCl_3$, 293 K): δ 215.9 (d, J_{PC} = 3.2 Hz, C=*C*=CH), 132.4 (d, J_{PC} = 5.5 Hz, $C_{ipso-Ph}$), 129.2 and 128.5 (both s, $C_{o,m,p-Ph}$), 113.6 (d, J_{PC} = 13.3 Hz, *C*=C=CH), 73.3 (d, J_{PC} = 78.3 Hz, C=C=*C*H), 31.0 (d, J_{PC} = 41.4 Hz, PCy_3), 26.6, 26.5, 26.4, 26.2, and 25.2 (all s, PCy_3).

Preparation of [Rh(acac)(CH=C=CPh_2)(P*i*Pr_3)$_2$]BF_4 (10). A solution of **6** (182.7 mg, 0.25 mmol) in 5 mL of dichloromethane was cooled to −78 °C, and then a stoichiometric amount of HBF_4·OEt_2 (37 μL, 0.27 mmol) was added. A change from yellow to red-orange occurred almost instantaneously. The solvent was removed *in vacuo*, and the residue was washed with diethyl ether at −78 °C to give a red-orange solid. Yield: 126 mg (63%). Anal. Calcd for $C_{38}H_{60}BF_4O_2P_2Rh$: C, 57.01; H, 7.55. Found: C, 56.54; H, 7.09. IR (KBr, cm^{-1}): ν(C=C=C) 1885, $\nu(CO)_{acac}$ 1569 and 1523, $\nu(BF_4)$ 1055. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.8−7.4 (m, 10H, Ph), 7.22 (dt, 1H, J_{PH} = $J_{P'H}$ = 9.3 Hz, J_{RhH} = 3.3 Hz, RhC*H*=C=C), 5.52 (s, 1H, C*H* of acac), 2.81 (m, 6H, PC*H*CH_3), 1.85 (br, 6H, CH_3 of acac), 1.44 (dvt, 18H, *N* = 13.7 Hz, J_{HH} = 6.5 Hz, PCHCH_3), 1.42 (dvt, 18H, *N* = 13.7 Hz, J_{HH} = 6.4 Hz, PCHCH_3). ^1H NMR (300 MHz, CD_2Cl_2, 233 K): δ 1.70 (s, 6H, CH_3 of acac). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 233 K): δ 41.1 (d, J_{RhP} = 135.7 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 233 K): δ 189.6 (s, RhCH=*C*=C), 185.8 (s, *C*O of acac), 137.1 (s, $C_{ipso-Ph}$), 128.7 (s, C_{o-Ph}), 128.6 (s, C_{m-Ph}), 128.2 (s, C_{p-Ph}), 119.0 (s, RhCH=C=*C*), 100.2 (s, *C*H of acac), 67.1 (dt, J_{RhC} = 35.5 Hz, J_{PC} = 8.3 Hz, Rh*C*H=C=C), 26.8 (s, *C*H_3 of acac), 26.1 (m, P*C*HCH_3), 20.7 and 19.8 (both s, PCH*C*H_3).

Preparation of [Rh(acac){η^2-CH(P*i*Pr_3)=C=CPh_2}-(P*i*Pr_3)]BF_4 (11). A solution of **10** (200.1 mg, 0.25 mmol) in 10 mL of dichloromethane was stirred for 30 min at 35 °C. Then the solvent was removed *in vacuo*, and the addition of diethyl ether caused the precipitation of a orange-yellow solid. The solid was decanted and washed with diethyl ether. Yield: 180 mg (90%). Anal. Calcd for $C_{38}H_{60}BF_4O_2P_2Rh$: C, 57.01; H, 7.55. Found: C, 56.74; H, 7.31. IR (KBr, cm^{-1}): $\nu(CO)_{acac}$ 1575 and 1520, $\nu(BF_4)$ 1053. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.50−7.11 (m, 10H, Ph), 5.78 (s, 1H, C*H* of acac), 2.46 (m, 3H, PC*H*CH_3), 2.32 (ddd, 1H, J_{PH} = 9.0 Hz, J_{RhH} = 3.0 Hz, $J_{P'H}$ = 2.1 Hz, C*H*(P*i*Pr_3)), 2.15 (m, 3H, PC*H*CH_3), 2.05 (br, 6H, CH_3 of acac), 1.18 (dd, 9H, J_{PH} = 14.4 Hz, J_{HH} = 7.2 Hz, PCHCH_3), 1.18 (dd, 9H, J_{PH} = 13.8 Hz, J_{HH} = 7.2 Hz, PCHCH_3), 1.14 (dd, 9H, J_{PH} = 12.3 Hz, J_{HH} = 7.5 Hz, PCHCH_3), 1.06 (dd, 9H, J_{PH} = 13.8 Hz, J_{HH} = 7.2 Hz, PCHCH_3). ^1H NMR (300 MHz, CD_2Cl_2, 213 K): δ 2.04 and 1.98 (both s, 6H, CH_3 of acac). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 54.6 (d, $^1J_{RhP}$ = 158.8 Hz, Rh(*P*iPr_3)), 50.8 (d, $^2J_{RhP}$ = 6.2 Hz, CH(*P*iPr_3)). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 187.7 and 186.9 (both br, *C*O of acac), 162.2 (ddd, J_{RhC} = 25.2 Hz, J_{PC} = 6.1 Hz, CH(P*i*Pr_3)=*C*=C), 141.3 and 140.8 (both s, $C_{ipso-Ph}$), 132.8 (d, J_{RhC} = 5.8 Hz, CH-(P*i*Pr_3)=C=*C*), 130.5, 129.3, 128.8, 128.5, 128.3, and 127.9 (all s, $C_{o,m,p-Ph}$), 101.0 (s, *C*H of acac), 27.4 and 27.0 (both br, *C*H_3 of acac), 22.8 (d, J_{PC} = 40.5 Hz, P*C*HCH_3), 22.4 (d, J_{PC} = 24.2 Hz, P*C*HCH_3), 19.6 and 19.3 (both s, PCH*C*H_3), 18.5, 17.9, and 17.8 (all d, J_{PC} = 3.8 Hz, PCH*C*H_3), −1.7 (ddd, J_{PC} = 56.5 Hz, J_{RhC} = 14.0 Hz, $J_{P'C}$ = 2.9 Hz, *C*H(P*i*Pr_3)=C=C). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 233 K): δ 187.5 and 186.5 (both s, *C*O of acac), 27.2 (d, J_{PC} = 4.8 Hz, *C*H_3 of acac), 26.7 (s, *C*H_3 of acac).

Reaction of 11 with CO. A stream of CO was passed through a solution of compound **11** (200.1 mg, 0.25 mmol) in 10 mL of dichloromethane for 5 min. A change from yellow to light yellow occurred almost instantaneously. Then the solvent was removed *in vacuo*, and the addition of pentane caused the precipitation of a white solid, which was washed with pentane. The pentane solution was concentrated *in vacuo* to produce a residue, which was identified as Rh(acac)-(CO)(P*i*Pr_3) (**12**). The white solid was identified as [Ph_2C=C=CHP*i*Pr_3]BF_4 (**13**). Spectroscopic data for **12** are as follows: ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 5.45 (s, 1H, C*H* of acac), 2.37 (m, 3H, PC*H*CH_3), 2.03 and 1.85 (both s, 3H, CH_3 of acac), 1.31 (dd, 18H, J_{PH} = 14.1 Hz, J_{HH} = 7.2 Hz, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 70.6 (d, J_{RhP} = 167.0 Hz). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 191.7 (dd, J_{RhC} = 77.4 Hz, J_{PC} = 23.0 Hz, Rh*C*O), 188.1 and 185.4 (both s, *C*O of acac), 100.5 (s, *C*H of acac), 27.9 (d, J_{PC} = 5.3 Hz, CH_3 of acac), 27.2 (s, *C*H_3 of acac), 24.5 (d, J_{PC} = 25.6 Hz, P*C*HCH_3), 19.9 (s, PCH*C*H_3). Data for **13** are as follows: yield: 74 mg (68%). Anal. Calcd for $C_{24}H_{32}BF_4P$: C, 65.77; H, 7.36. Found: C, 65.44; H, 6.95. IR (KBr, cm^{-1}): ν(C=C=C) 1932, $\nu(BF_4)$ 1054. ^1H NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.45−7.31 (m, 10H, Ph), 6.21 (d, J_{PH} = 7.8 Hz, C*H*P*i*Pr_3), 2.80 (m, 3H, PC*H*CH_3), 1.37 (dd, 18H, J_{PH} = 16.8 Hz, J_{HH} = 7.2 Hz, PCHCH_3). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 40.8 (s). $^{13}C\{^1H\}$ NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 217.0 (d, J_{PC} = 3.2 Hz, C=*C*=CH), 132.5 (d, J_{PC} = 5.6 Hz, $C_{ipso-Ph}$), 129.6 and 128.9 (both s, $C_{o,m,p-Ph}$), 114.6 (d, J_{PC} = 12.9 Hz, *C*=C=CH), 72.8 (d, J_{PC} = 79.7 Hz, C=C=*C*H), 22.2 (d, J_{PC} = 42.9 Hz, P*C*HCH_3), 16.7 (s, PCH*C*H_3).

Crystal Data for 7. Crystals suitable for the X-ray diffraction study were obtained by slow diffusion of pentane into a saturated solution of **7** in dichloromethane. A summary of crystal and refinement data is reported in Table 3. An unstable yellow irregular block of approximate dimensions 0.67 × 0.65 × 0.15 mm was mounted on a glass fiber at low temperature. A set of randomly searched reflections in the range $20 \le 2\theta \le 36°$ showed strong reflections, from which a group of 48 were carefully centered and used to obtain by least-squares methods the unit cell dimensions. A Siemens-STOE AED four-circle diffractometer was used for data acquisition ($\omega/2\theta$ scans), with graphite-monochromated Mo Kα radiation and 2θ range $3 \le 2\theta \le 45°$ ($-20 \le h \le 19$, $0 \le k \le 15$, $0 \le l \le 27$). A total of 8736 reflections were measured; from 8513 unique reflections (R_{merge} = 0.05), 7601 having $F_o > 0$ were used in the refinement. Three orientation and intensity standards were monitored every 55 min; no significant variation was observed. Reflections were also corrected by a semiempirical method (ψ-scans).[18]

Table 3. Crystal Data and Data Collection and Refinement Data for [Rh(acac){η^2-CH(PCy$_3$)=C=CPh$_2$}(PCy$_3$)]BF$_4$ (7)

Crystal Data	
formula	$C_{56}H_{84}BF_4O_2P_2Rh \cdot 1.55CH_2Cl_2 \cdot 0.25C_5H_{12}$
mol wt	1190.565
color, habit	yellow, irregular block
cryst size, mm	0.67 × 0.65 × 0.15
symmetry	monoclinic
space group	$P2_1/n$ (No. 14)
a, Å	18.700(3)
b, Å	14.041(3)
c, Å	25.701(4)
α, deg	90
β, deg	105.05(2)
γ, deg	90
V, Å^3	6517(2)
Z	4
D_{calc}, g cm^{-3}	1.213
Data Collection and Refinement	
diffractometer	four-circle Siemens-STOE AED
λ(Mo Kα), Å; technique	0.710 73; bisecting geometry
monochromator	graphite oriented
μ, mm^{-1}	0.49
scan type	$\omega/2\theta$
2θ range, deg	$3 \le 2\theta \le 45°$
temp, K	200
no. of data collcd	8736
no. of unique data	8513 ($R_{int} = 0.0508$)
no. of params refined	925
R1[a] ($F^2 > 2\sigma(F^2)$)	0.0638
wR2[b] (all data ($F_o \ge 0$))	0.1677
S[c]	1.070

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] GOF $= S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of observed reflections and p is the number of refined parameters.

The structure was solved by Patterson (rhodium atom) and conventional Fourier techniques. A zone of disordered solvent was found close to the inversion center. This disorder was modeled with seven molecules of CH_2Cl_2 (with two sites for some atoms) and one molecule of pentane with partial occupancy factors. The BF_4^- anion was also observed to be severely disordered. A common B−F unit, and three sites for the other three fluorines, were included in the model established for the anion. The refinement of this group includes restrictions of bond distances, angles, and thermal parameters (SHELX93 facilities).[19] The occupancy factors for the latter disordered groups were estimated on the basis of the thermal parameters and refined (anion) or maintained fixed (solvent) during refinement. Anisotropic thermal parameters were used for all non-hydrogen atoms; and hydrogens, except those bonded to disordered groups, were included in calculated positions[19] riding on carbon atoms with isotropic thermal parameters related to bonded atoms. Final $R(F, I_o > 2.0\sigma(I_o))$ and $R_w(F^2$, all reflections with $F_o > 0)$ values were 0.0638 and 0.1677. All calculations were performed by the SHELXTL (v. 5) system of computer programs.[20]

Kinetic Analysis. The isomerization of complex **10** to **11** was followed quantitatively by ^{1}H NMR spectroscopy in CD_2Cl_2. The decrease of the intensity of the C*H* signal of acac in complex **10** was measured automatically at intervals in a Varian GEMINI 2000 spectrometer. The rate constants and the errors were obtained by fitting the data to an exponential decay function, using the routine programs of the spectrometer. Activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained by a least-squares fit of the Eyring plot. Error analysis assumed a 6.0% error in the rate constant (the maximum value found in the experimental determinations) and 1 K in the temperature. Errors were computed by published methods.[21]

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, distances and angles, and interatomic distances for **7** (15 pages). Ordering information is given on any current masthead page.

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