Substitution and Oxidative Addition Reactions of the Monoolefin Complex Rh(acac)(cyclooctene)(PCy_3) Including the X-ray Structure Analyses of Rh(acac)(PCy_3)$_2$ and [Rh(acac){(*E*)-CH=CHCy}(PCy_3)$_2$]BF_4

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The olefin complex Rh(acac)(cyclooctene)(PCy_3) (**2**), which is formed from Rh(acac)(cyclooctene)$_2$ (**1**) and PCy_3 in nearly quantitative yield, reacts with CO and alkynes RC≡CR by ligand displacement to give Rh(acac)(CO)(PCy_3) (**3**) and Rh(acac)(η^2-RC≡CR)(PCy_3) [R = CO_2Me (**4**), Ph (**5**)], respectively. The bis(phosphine) compound Rh(acac)(PCy_3)$_2$ (**6**) cannot be prepared directly from **2** and excess PCy_3 but via Rh(acac)(η^2-HC≡CCO_2Me)(PCy_3) (**7**) as intermediate. The X-ray crystal structure analysis of **6** reveals that the rhodium is coordinated in a distorted square-planar manner with O−Rh−O and P−Rh−P bond angles of 85.9(1) and 105.63(4)°. Compound **2** reacts with H_2 in the presence of PCy_3 to yield Rh(acac)H_2(PCy_3)$_2$ (**8**) and with HC≡CR/PCy_3 to give Rh(acac)H(C≡CR)(PCy_3)$_2$ [R = Ph (**9**), Cy (**10**), $SiMe_3$ (**11**)]. On treatment of **10** and **11** with HBF_4·OEt_2, the cationic alkenylrhodium(III) derivatives [Rh(acac){(*E*)-CH=CHCy}(PCy_3)$_2$]BF_4 (**12**) and [Rh(acac)(CH=CH_2)(PCy_3)$_2$]BF_4 (**13**) are obtained. Labeling experiments using DBF_4·OEt_2 illustrate that the deuterium is found at the β-C carbon atom of the alkenyl ligand. Both **12** and [Rh(acac){(*E*)-CH=CDCy}(PCy_3)$_2$]BF_4 (**12**-d_1) react with NEt_3 to regenerate **10**. The structure of **12** was determined by X-ray analysis. The coordination geometry around the metal center can be rationalized as a square pyramid with the alkenyl group in the apical position.

Introduction

In the search for transition-metal complexes which are catalytically active in the hydrogenation, hydrosilylation, and hydrostannylation of unsaturated organic substrates, we have recently reported on the reactivity of the (acetylacetonato)iridium compound Ir(acac)(cyclooctene)(PCy_3),[1] which is formed by ligand displacement from Ir(acac)(cyclooctene)$_2$ and PCy_3.[2] The cyclooctene compound Ir(acac)(cyclooctene)(PCy_3) not only reacts with silanes $HSiR_3$ to give Ir(acac)H(SiR_3)(PCy_3) and with $HSnPh_3$ to afford Ir(acac)H($SnPh_3$)(PCy_3) but in the presence of 3 equiv of phenylacetylene also to yield an unusual chelated alkynyl(alkenyl)iridium(III) complex which is a result of the oxidative addition of the HC≡ bond of an alkyne, the insertion of a second alkyne into an Ir−C[3](acac) bond, and the subsequent insertion of a third alkyne into the Ir−H bond initially formed.[1] Moreover, the five-coordinate hydrido−silyl derivative Ir(acac)H($SiEt_3$)(PCy_3) not only adds one molecule of hydrogen to give the trihydrido compound Ir(acac)H_3($SiEt_3$)(PCy_3) but is also an active catalyst for the addition of $HSiR_3$ to phenylacetylene.[1]

As a continuation of this work, we became interested to find out whether the rhodium complex Rh(acac)(cyclooctene)(PCy_3) behaves similarly to its iridium counterpart and whether it can also be used as starting material for the preparation of the more nucleophilic bis(phosphine)metal derivative Rh(acac)(PCy_3)$_2$. One of us has recently shown that the acetato compound Rh(η^2-O_2CMe)(P^iPr_3)$_2$ which is monomeric[3] and thus probably structurally related to the desired acetylacetonato species Rh(acac)(PCy_3)$_2$ is an excellent precursor both for the preparation of alkyne and vinylidenerhodium complexes[4] and also for the stepwise trimerization of a terminal alkyne; the latter reaction does not lead to a benzene but selectively to a hexadienyne derivative.[5]

In this paper we report on the synthesis of Rh(acac)(cyclooctene)(PCy_3) and Rh(acac)(PCy_3)$_2$, as well as on substitution and oxidative addition reactions of the monoolefin complex. In addition, we illustrate the completely different behavior of the bis(phosphine) complex Rh(acac)(PCy_3)$_2$ when compared with the carboxylato derivatives Rh(η^2-O_2CR)(P^iPr_3)$_2$ (R = CH_3, CF_3) toward molecular hydrogen and terminal alkynes which is probably due to the rigidity of the Rh(acac) ring system.

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(1) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Rodríguez, L.; *Organometallics* **1996**, *15*, 823.
(2) Esteruelas, M. A.; Lahoz, F. J.; Oñate, E.; Oro, L. A.; Rodríguez, L.; *Organometallics* **1995**, *14*, 263.
(3) Werner, H.; Schäfer, M.; Nürnberg, O.; Wolf, J. *Chem. Ber.* **1994**, *127*, 27.
(4) Schäfer, M.; Wolf, J.; Werner, H. *J. Organomet. Chem.* **1995**, *485*, 85.
(5) Werner, H.; Schäfer, M.; Wolf, J.; Peters, K.; von Schnering, H. G. *Angew. Chem.* **1995**, *107*, 213; *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 191.

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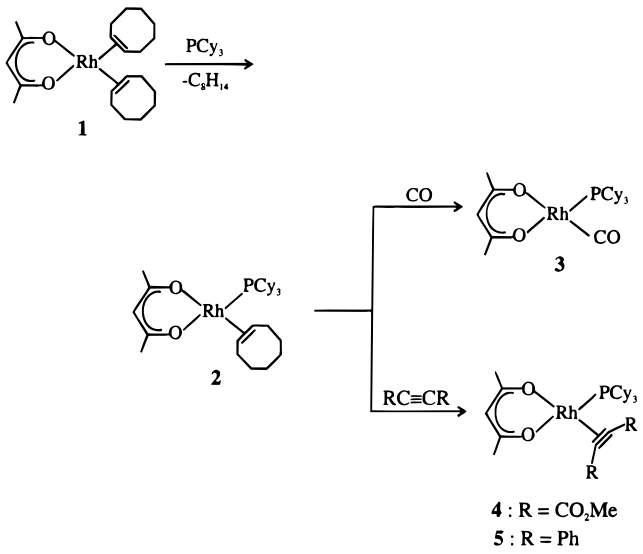
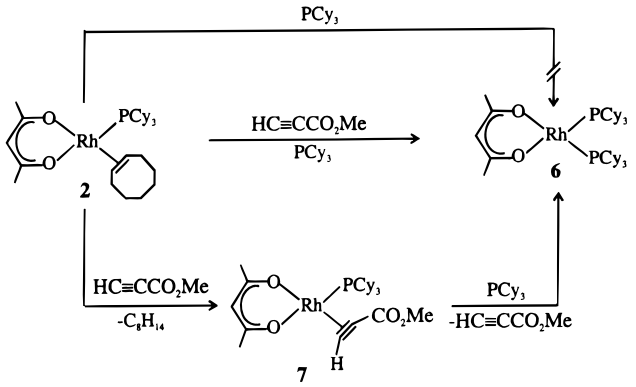
Scheme 1



Scheme 2

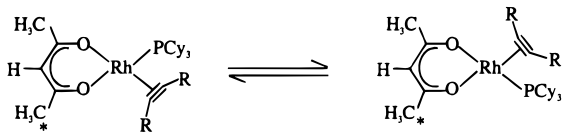


Results and Discussion

1. Synthesis and Characterization of Rh(acac)(cyclooctene)(PCy_3) and Rh(acac)(PCy_3)$_2$. On treatment with PCy_3, the bis(cyclooctene)rhodium complex **1** (Scheme 1) affords the phosphine derivative Rh(acac)(cyclooctene)(PCy_3) (**2**) in 95% yield. The reaction proceeds at room temperature and does not lead to displacement of the second olefin even if excess phosphine is used. The complex **2**, which is a yellow solid, is relative stable under argon at −20 °C. The cyclooctene ligand of **2** is easily displaced by strong π-acceptor ligands such as carbon monoxide, acetylenedicarboxylic dimethyl ester and diphenylacetylene. By passage of a slow stream of carbon monoxide through a toluene solution of **2**, the carbonyl complex Rh(acac)(CO)(PCy_3) (**3**) is formed. Similarly, treatment of hexane solutions of **2** with the stoichiometric amount of acetylenedicarboxylic dimethyl ester and diphenylacetylene affords Rh(acac)(η^2-RC≡CR)(PCy_3) [R = CO_2Me (**4**), Ph (**5**)] as orange (**4**) or yellow (**5**) solids in good yield [89% (**4**), 86% (**5**)].

The IR spectra of **2**−**5** in Nujol display two strong ν(CO) absorptions between 1590 and 1500 cm^{-1} indicating that the acetylacetonato ligand is coordinated in a η^2-oxygen bonding mode.[6] The π-coordination of the alkyne in **4** and **5** is also supported by the IR spectra of these compounds, in which the C≡C stretching frequency is found at 1890 (**4**) and 1910 (**5**) cm^{-1}, thus shifted 260 (**4**) and 310 (**5**) cm^{-1} to lower wavenumbers if compared with the free alkyne. In agreement with the square-planar coordination of the rhodium atom, at room temperature the ^1H NMR spectra of **2** and **3** display two singlets between 1.91 and 1.61 ppm for the protons of the methyl groups of the acetylacetonato ligand. These spectra are temperature invariant down to −50 °C. However, the ^1H NMR spectra of **4** and **5** are temperature dependent. At room temperature, the methyl protons of the acetylacetonato ligands give only one singlet at 1.86 (**4**) and 1.94 (**5**) ppm, while at −50 °C they display two singlets at 1.91 and 1.80 (**4**) and 2.01 and 1.86 (**5**) ppm, respectively. The $^{13}C\{^1H\}$ NMR spectra of **4** and **5** are also temperature dependent. At room temperature, the spectrum of **4** does not contain resonances due to the methyl and carbonyl carbon atoms of the acetylacetonato ligand. They were located at 188.9, 183.1 (CO) and 28.35 and 26.65 (CH_3) ppm in the spectrum at −50 °C. The spectrum of **5** at room temperature displays two broad resonances due to the carbonyl groups at 187.7 and 183.4 ppm, which are converted into singlets at −50 °C. At this temperature, the spectrum also contains a doublet at 28.15 (J_{P-C} = 4 Hz) and a singlet at 26.95 ppm, assigned to the inequivalent methyl groups. At −50 °C, the spectra of both compounds show only one resonance at 88.55 (**4**) and 86.2 (**5**) for the acetylenic carbon atoms, suggesting that in both compounds the C≡C bond lies perpendicular to the coordination plane of the rhodium as should be expected according to the Dewar−Chatt−Duncanson bonding scheme.

The above mentioned spectroscopic data indicate that complexes **4** and **5** have a rigid structure only at low temperature. At room temperature, a slow (on the NMR time scale) exchange process takes place, which involves the relative positions of the alkyne and phosphine ligands (eq 1).



(1)

Complex **2** does not react with an excess of tricyclohexylphosphine. However, the addition of 1 equiv of methyl propiolate to equimolar amounts of **2** and tricyclohexylphosphine in toluene leads to the formation of the bis(phosphine) derivative Rh(acac)(PCy_3)$_2$ (**6**). The reaction proceeds via the intermediate Rh(acac)(η^2-HC≡CCO_2Me)(PCy_3) (**7**). In fact, the addition of the stoichiometric amount of methyl propiolate to a solution of **2** in hexane affords **7**, which subsequently yields **6** upon the addition of 1 equiv of tricyclohexylphosphine (Scheme 2).

Complex **6** was characterized by elemental analysis, IR and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, and single-crystal X-ray diffraction studies. A view of the molecular geometry is shown in Figure 1, and selected bond distances and angles are listed in Table 1. The coordination geometry around the rhodium center is almost square-planar. The deviations from the best plane are −0.0030(5) (Rh), −0.005(1) (P(1)), 0.016(1) (P(2)), 0.127(3) (O(1)), and −0.064(3) (O(2)) Å. The most noticeable structural feature is the P−Rh−P angle (105.63(4)°),

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

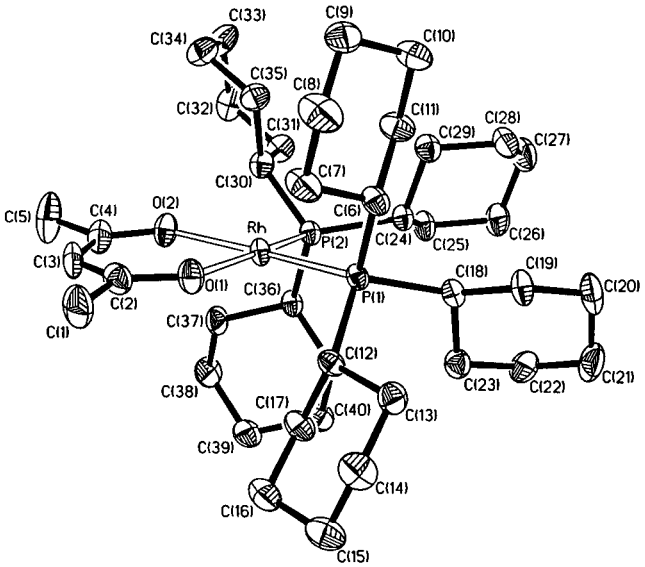


Figure 1. Molecular diagram of complex $Rh(acac)(PCy_3)_2$ (**6**).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Complex $Rh(acac)(PCy_3)_2$ (6)

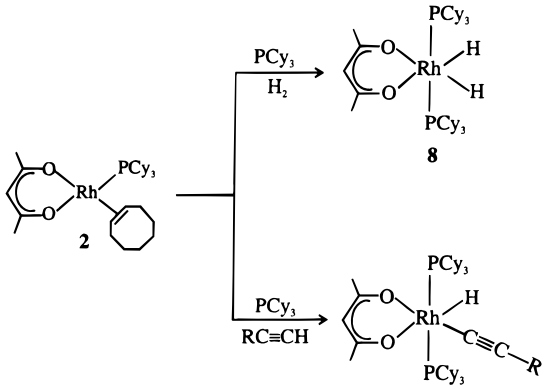
Rh−P(1)	2.252(1)	C(1)−C(2)	1.503(9)
Rh−P(2)	2.260(1)	C(2)−C(3)	1.387(6)
Rh−O(1)	2.089(4)	C(3)−C(4)	1.389(8)
Rh−O(2)	2.083(3)	O(2)−C(4)	1.279(6)
O(1)−C(2)	1.276(6)	C(4)−C(5)	1.508(7)
P(1)−Rh−P(2)	105.63(4)	O(1)−C(2)−C(1)	115.1(4)
P(1)−Rh−O(1)	84.34(8)	O(1)−C(2)−C(3)	125.7(4)
P(1)−Rh−O(2)	169.98(9)	C(1)−C(2)−C(3)	119.3(4)
P(2)−Rh−O(1)	169.26(9)	C(2)−C(3)−C(4)	125.5(4)
P(2)−Rh−O(2)	84.26(9)	C(3)−C(4)−C(5)	120.0(4)
O(1)−Rh−O(2)	85.9(2)	O(2)−C(4)−C(3)	125.7(5)
Rh−O(1)−C(2)	128.4(3)	O(2)−C(4)−C(5)	114.3(5)

which is statistically identical with the P−Rh−P angle of the related complex $Rh(\eta^2\text{-}O_2CCH_3)(P^iPr_3)_2$ (106.00(4)°).[3] These relatively large values can be explained by the fact that for both compounds the two phosphine ligands, *cis* disposed, experience a large steric hindrance, as a result of the large cone angle of the tricyclohexylphosphine and triisopropylphosphine groups. The β-diketonato bite angle O−Rh−O of 85.9(1)° is similar to values found in related chelated rhodium complexes.[7] The Rh−P, Rh−O, C−O, and C−C distances are clearly in the range expected and deserve no further comment.

In agreement with the structure shown in Figure 1, the ^1H NMR spectrum of **6** contains only one singlet at 1.81 ppm for the protons of the methyl groups of the β-diketonate ligand, while the $^{31}P\{^1H\}$ NMR spectrum shows a doublet at 49.9 ppm with a Rh−P coupling constant of 191 Hz.

Complex **7** was isolated as a yellow solid in 68% yield. In the IR spectrum in Nujol the most noticeable absorption is that of the C≡C bond stretch, which appears at 1810 cm^{-1}, i.e., shifted by 311 cm^{-1} when compared with the free alkyne (2121 cm^{-1}). Similarly to the ^1H NMR spectra of **4** and **5**, the ^1H NMR spectrum of **7** is temperature dependent. At room temperature, the spectrum shows only one singlet at 1.80 ppm for the methyl protons of the acetylacetonato ligand, while at −50 °C two singlets at 1.88 and 1.75 ppm are observed, in agreement with the square-planar structure proposed in Scheme 2. In addition, a doublet at 5.63 ppm with a Rh−H coupling constant of 3 Hz is assigned to the ≡C*H* proton. The temperature behavior of the $^{13}C\{^1H\}$ NMR spectrum of **7** is similar to that of **5**. At room temperature, the spectrum shows two broad resonances centered at 188.5 and 182.8 ppm and a singlet at 27.15 ppm, which are assigned to the carbonyl and methyl carbons of the acetylacetonato ligand. At −50 °C, the broad resonances are converted into singlets, while the singlet at 27.15 ppm is split into a singlet at 27.9 ppm and a doublet at 26.9 ppm with a P−C coupling constant of 5 Hz. At room temperature, the signals of the acetylenic carbon atoms of the π-alkyne ligand appear at 93.8 and 76.0 ppm as doublet-of-doublets with Rh−C coupling constants of 17 and 19 Hz and a P−C coupling constant of 5 Hz. At −50 °C, these carbon atoms display broad resonances at 95.5 and 76.9 ppm.

Scheme 3



9 : R = Ph
10 : R = Cy
11 : R = $SiMe_3$

2. Oxidative Addition Reactions of Complex 2. While complex **6** does not react with tricyclohexylphosphine or molecular hydrogen individually, the dihydrido compound $Rh(acac)H_2(PCy_3)_2$ (**8**) is easily formed by passing a slow stream of molecular hydrogen through a toluene solution of **2** in the presence of a stoichiometric amount of tricyclohexylphosphine. Similarly, the addition of 1 equiv of phenylacetylene, cyclohexylacetylene, or (trimethylsilyl)acetylene to equimolecular amounts of **2** and tricyclohexylphosphine in solution leads to the hydrido−alkynyl complexes $Rh(acac)H(C_2R)(PCy_3)_2$ [R = Ph (**9**), Cy (**10**), $SiMe_3$ (**11**); see Scheme 3]. The behavior of **6** toward molecular hydrogen and terminal alkynes is in contrast with that previously observed for $Rh(\eta^2\text{-}O_2CR)(P^iPr_3)_2$, which on treatment with molecular hydrogen and terminal alkynes affords $Rh(\eta^2\text{-}O_2CR)H_2(P^iPr_3)_2$ and $Rh(\eta^2\text{-}O_2CR)H(C_2R')(P^iPr_3)_2$ (R = CH_3, CF_3), respectively.[4]

Recently, we have reported on the synthesis of the iridium(III) complexes $Ir(acac)H_2(PCy_3)_2$ and $Ir(acac)H(C_2R)(PCy_3)_2$ (R = Ph, Cy, $SiMe_3$), which were obtained on reaction of $Ir(acac)(cyclooctene)(PCy_3)$ with HX (X = H, C_2R) in the presence of an excess of phosphine. These reactions probably occur by the oxidative addition of HX to the bis(phosphine) intermediate $Ir(C^3\text{-acac})(cyclooctene)(PCy_3)_2$, which is formed by reaction of Ir-

(7) (a) Leipoldt, J. G.; Lamprecht, G. J.; Van Zyl, G. J. *Inorg. Chim. Acta* **1985**, *96*, L31. (b) Van Zyl, G. J.; Lamprecht, G. J.; Leipoldt, J. G. *Inorg. Chim. Acta* **1985**, *102*, L1. (c) Duan, Z.; Hampden-Smith, M. J.; Duesler, E. N.; Rheingold, A. L. *Polyhedron* **1994**, *13*, 609.

(acac)(cyclooctene)(PCy_3) with phosphine.[1] A similar reaction pathway for the formation of **8**−**11** does not seem likely, given that the bis(phosphine) complex **6** does not undergo oxidative addition reactions, most probably as a result of the steric hindrance imposed by the tricyclohexylphosphine groups and of the stability of the Rh(acac) chelate ring system. In this context, it should be mentioned that the η^2-O_2(acac) → η^1-C^3(acac) conversion is known for iridium(I),[6] whereas it has no precedent for rhodium(I). Hence, it can be proposed that in the presence of the HX substrates **2** is in equilibrium with undetectable concentrations of the five-coordinate Rh(acac)H(X)(PCy_3) species, and thus the addition of phosphine could shift the equilibrium toward the rhodium(III) complexes by coordination, generating in this way **8**−**11**. The stability of the Rh(acac) ring system also seems to be responsible for the different behavior of **6** when compared with that of the carboxylato complexes Rh(η^2-O_2CR)(P^iPr_3)$_2$ (R = CH_3, CF_3).

The formation of the five-coordinate rhodium(III) intermediates Rh(acac)H(C_2R)(PCy_3) most probably involves the generation of labile species related to **7**, Rh(acac)(η^2-HC≡CR)(PCy_3), which evolve by carbon−hydrogen activation of the H−C(sp) bond of the π-alkyne ligands. The high stability of **7** toward the C−H activation of the H−C(sp) bond of the coordinated methyl propiolate is not surprising. We note in this context that the complexes Rh{η^1-OC(O)CF_3}(η^2-HC≡CR)(P^iPr_3)$_2$ (R = H, Ph) afford the corresponding six-coordinate hydrido−alkynyl RhH(η^2-O_2CCF_3)(C_2R)(P^iPr_3)$_2$ derivatives in benzene at room temperature, whereas the compound Rh{η^1-OC(O)CF_3}(η^2-HC≡CCO_2Me)(P^iPr_3)$_2$ is stable under the same conditions.[4]

Complex **8** was isolated as a white, air-stable solid in 67% yield. In agreement with the *cis* disposition of the hydrido ligands, the IR spectrum in Nujol displays two strong absorptions at 2120 and 2085 cm^{-1} assigned to the Ir−H stretches, while in the ^{1}H NMR spectrum the hydride resonance appears at −22.18 ppm as a doublet-of-triplets with Rh−H and P−H coupling constants of 20 and 16 Hz, respectively. The $^{31}P\{^1H\}$ NMR spectrum contains a doublet at 15.8 ppm with a Rh−P coupling constant of 117 Hz, indicating that the phosphine ligands are equivalent and mutually *trans* disposed. Under off-resonance conditions the doublet is split into a doublet-of-triplets due to P−H coupling.

Complexes **9**−**11** were isolated as white or pale yellow solids by addition of methanol. Although the reactions shown in Scheme 2 spectroscopically proceed nearly quantitatively, the products were obtained in 45−50% yield as a result of their moderate solubility in the alcohol. The most noticeable features in the IR spectra of **9**−**11** (in Nujol) are the two bands between 2155 and 2042 cm^{-1}, which were assigned to the ν(Ir−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 signal of the α-C carbon atom appears at about 103 ppm as doublet-of-triplets with Rh−C and P−C coupling constants between 48 and 40 Hz and 18 and 16 Hz, respectively, while the β-C carbon atom gives rise to a doublet at about 107 ppm with a Rh−C coupling constant of 10 Hz. In the ^{1}H NMR spectra, the hydrido ligands display doublet-of-triplets between −19.33 and −18.79 ppm with Rh−H and P−H coupling constants of about 18 and 13 Hz, respectively.

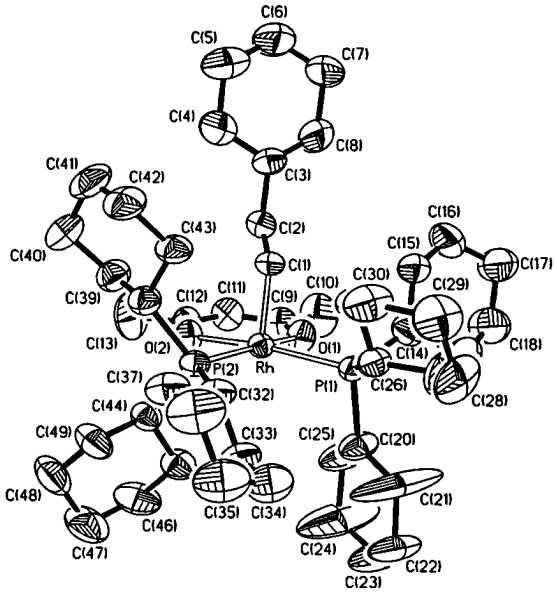
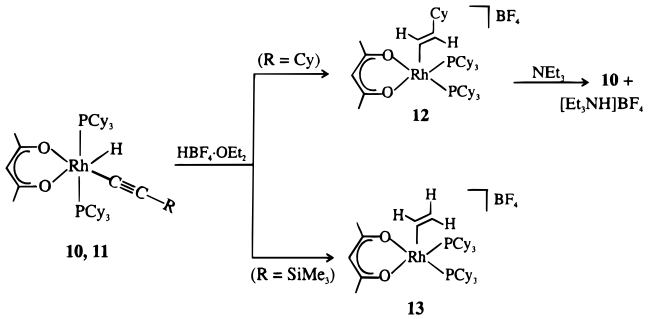


Figure 2. Molecular diagram of complex [Rh(acac){(*E*)-CH=CHCy}(PCy_3)$_2$]BF_4 (**12**).

Scheme 4



The presence of only one hydrido ligand in these compounds was inferred from the $^{31}P\{^1H\}$ NMR spectra which contain doublets between 38 and 35 ppm (J_{Rh-P} ≅ 103 Hz), in agreement with the mutually *trans* disposition of the phosphine ligands. Under off-resonance conditions these signals split into doublets-of-doublets due to P−H coupling.

Protonation of 10 and 11. Treatment of complex **10** with a stoichiometric amount of HBF_4·OEt_2 in diethyl ether leads to the precipitation of a yellow solid, which was characterized as the five-coordinate alkenyl complex [Rh(acac){(*E*)-CH=CHCy}(PCy_3)$_2$]BF_4 (**12**, Scheme 4) by elemental analysis, IR and ^{1}H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy, and an X-ray diffraction study. The molecular structure is presented in Figure 2, while selected bond distances and angles are listed in Table 2. The most remarkable features of the structure are the square-pyramidal coordination of the metal with the alkenyl group located at the apex and the *trans* position of the two substituents C_6H_{11} and Rh-(acac)(PCy_3)$_2$ at the C=C double bond. The four atoms O(1), O(2), P(1), and P(2) forming the base of the pyramid are approximately in one plane, while the rhodium atom is located 0.1384(8) Å above this plane toward the apical position. As a result of the large steric hindrance experienced by the two *cis* disposed phosphine ligands, the P−Rh−P angle (105.3(1)°) strongly deviates from the ideal value of 90°. The acetylacetonato bite angle O−Rh−O (87.3(2)°) is similar to that found in **6**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for the Cation of Complex [Rh(acac){(*E*)-CH=CHCy}(PCy_3)$_2$]BF_4 (12)

Rh−P(1)	2.336(3)	O(1)−C(9)	1.27(1)
Rh−P(2)	2.357(3)	C(9)−C(10)	1.49(2)
Rh−O(1)	2.049(8)	C(9)−C(11)	1.39(2)
Rh−O(2)	2.054(7)	C(11)−C(12)	1.37(2)
Rh−C(1)	1.98(1)	O(2)−C(12)	1.27(1)
C(1)−C(2)	1.29(2)	C(12)−C(13)	1.49(2)
C(2)−C(3)	1.54(2)		
P(1)−Rh−P(2)	105.3(1)	Rh−C(1)−C(2)	124.2(9)
P(1)−Rh−O(1)	84.4(3)	C(1)−C(2)−C(3)	121(1)
P(1)−Rh−O(2)	168.6(2)	Rh−O(1)−C(9)	127.5(7)
P(1)−Rh−C(1)	92.2(2)	O(1)−C(9)−C(10)	116(1)
P(2)−Rh−O(1)	168.4(3)	O(1)−C(9)−C(11)	126(1)
P(2)−Rh−O(2)	82.1(2)	C(10)−C(9)−C(11)	118(1)
P(2)−Rh−C(1)	93.7(3)	C(9)−C(11)−C(12)	124(1)
O(1)−Rh−O(2)	87.3(2)	C(11)−C(12)−C(13)	119(1)
O(1)−Rh−C(1)	92.3(5)	O(2)−C(12)−C(11)	127(1)
O(2)−Rh−C(1)	96.0(4)	O(2)−C(12)−C(13)	114(1)

The Rh−C(1) distance (1.98(1) Å) is shorter than the Rh−C distances found in related six-coordinate alkenylrhodium(III) compounds such as Rh(η^5-C_5Me_5)(2,6-$C_6H_3Me_2$){(*E*)-C(CO_2Me)=CHCO_2Me}(PMe_3) (2.065(3) Å), Rh(η^5-C_5Me_5)(2,6-$C_6H_3Me_2$){(*Z*)-C(CO_2Me)=CHCO_2Me}(PMe_3) (2.056(3) Å),[8] Rh(CPh=CPhCPh=$CHCH_2$)(acac)(PMe_3)$_2$ (2.032(4) Å),[9] Rh(η^5-C_5H_5){(*E*)-CPh=CHPh}{η^1-OC(O)CF_3}(P^iPr_3) (2.189(13) Å), and Rh(η^5-C_5H_5)-{CPh=CH(C_6H_4)}{η^1-OC(O)CF_3}(P^iPr_3) (2.066(7) Å)[10] and statistically identical with those reported for the complexes Rh{C(CH=CHCO_2Me)=CHCO_2Me}(C≡CCO_2-Me)(η^2-O_2CCH_3}(P^iPr_3)$_2$ (2.015(9) Å)[5] and Rh{C(CF_3)=C(CF_3)CH_2CH_2}(acac)(py)$_2$ (2.020(7) Å).[11] The C(1)−C(2) bond length (1.29(2) Å) is similar to that found in the above-mentioned compounds, and it agrees well with average carbon−carbon bond distances for a C(sp^2)−C(sp^2) double bond (1.32(1) Å).[12]

In agreement with the structure shown in Figure 2, the IR spectrum of **12** in Nujol shows two strong ν(CO) absorptions at 1570 and 1530 cm^{-1}, due to the carbonyl groups of the β-diketonato ligand. The ^{1}H NMR spectrum, which is not temperature dependent, contains only one singlet for the methyl protons of the acac unit at 2.11 ppm, while the vinylic protons of the alkenyl ligand are located at 6.50 (RhC*H*=) and 4.25 (=C*H*Cy) ppm. In agreement with the *E*-stereochemistry, the H−H coupling constant is 10 Hz.[13] In the ^{13}C{^{1}H} NMR spectrum, the most noticeable resonances are those corresponding to the C(sp^2) carbon atoms of the unsaturated η^1-carbon ligand. The resonance of the α-C carbon atom is observed at 111.6 ppm as a doublet-of-triplets with Rh−C and P−C coupling constants of 35 and 9 Hz, respectively, while the resonance of the β-C carbon atom appears at 135.6 ppm as a singlet. The ^{31}P{^{1}H} NMR spectrum shows a doublet at 28.7 ppm with a Rh−P coupling constant of 132 Hz.

In general the coordination of an acetylide anion to a transition metal center transfers the nucleophilicity from the α-C to the β-C carbon atom.[14] Thus, at first glance, complex **10** has three nucleophilic centers, namely the metal, the hydrido ligand, and the β-C carbon atom of the alkynyl group. Therefore, the initial electrophilic attack of the proton, which subsequently affords the alkenyl derivative **12**, could occur by the reaction pathways shown in Scheme 5. According to pathway **a**, the protonation takes place at the metal center to yield a dihydrido−alkynyl intermediate, which could afford a hydrido−π-alkyne species by intramolecular reductive elimination. The subsequent insertion of the π-alkyne ligand into the Rh−H bond should lead to **12**. According to pathway **b**, the initial formation of an alkynyl dihydrogen intermediate is followed by the electrophilic attack of the acidic proton of the dihydrogen ligand at the β-C carbon atom of the alkynyl group. Migratory insertion of the resulting vinylidene group into the Rh−H bond could also give **12**. A similar mechanism has been proposed for the formation of Os{(*E*)-CH=CHCy}Cl(CO)($PiPr_3$)$_2$ from OsHCl(CO)($PiPr_3$)$_2$ and cyclohexylacetylene.[16] Pathway **c** suggests that the protonation directly occurs at the β-C carbon atom of the alkynyl group.[17] As discussed for route **b**, the subsequent migratory insertion of the vinylidene ligand into the metal−hydride bond would lead to **12**.

If the reaction of **10** with HBF_4 to give **12** goes via pathway **a** or **b**, treatment of **10** with DBF_4 should result in an approximate 1:1 distribution of the deuterium at the α-C and β-C carbon atoms of the alkenyl ligand. However, the addition of a stoichiometric amount of DBF_4 to a suspension of **10** in diethyl ether leads almost exclusively to **12**-d_1 with the deuterium atom located on the β-C carbon atom of the alkenyl ligand. This has been confirmed by the ^{2}H NMR spectrum which shows only one resonance at 4.33 ppm. According to this observation there is no doubt that the reaction of **10** with HBF_4 occurs along pathway **c**. The reaction is reversible, and thus, on treatment of **12**-d_1 with a stoichiometric amount of triethylamine, complex **10** is regenerated. The conclusion is that the pK_a of the alkenyl ligand is lower than the pK_a of $HNEt_3^+$.

Under the same experimental conditions as those previously described for the preparation of **12**, the hydrido−alkynyl complex **11** affords [Rh(acac)(CH=CH_2)(PCy_3)$_2$]BF_4 (**13**, Scheme 4). There are precedents for the cleavage of the Si−C bond in related processes. The protonation of the alkynyl complex Rh_2(μ-OOCCH_3)(μ-η^1:η^2-C_2SiMe_3)(CO)$_2$(PCy_3)$_2$ with HBF_4·OEt_2 leads to the vinylidene-bridged rhodium compound [Rh_2(μ-OOCCH_3)-(μ-C=CH_2)(CO)$_2$(PCy_3)$_2$]BF_4.[18] The vinylidene ligand C=CH_2 of the complex [OsI(η^6-C_6H_6)(C=CH_2)(PMe^tBu_2)]-PF_6 is formed on treatment of OsI_2(η^6-C_6H_6)(PMe^tBu_2) with $AgPF_6$ in the presence of (trimethylsilyl)acetylene.[19] With the same alkyne, the iridium complex

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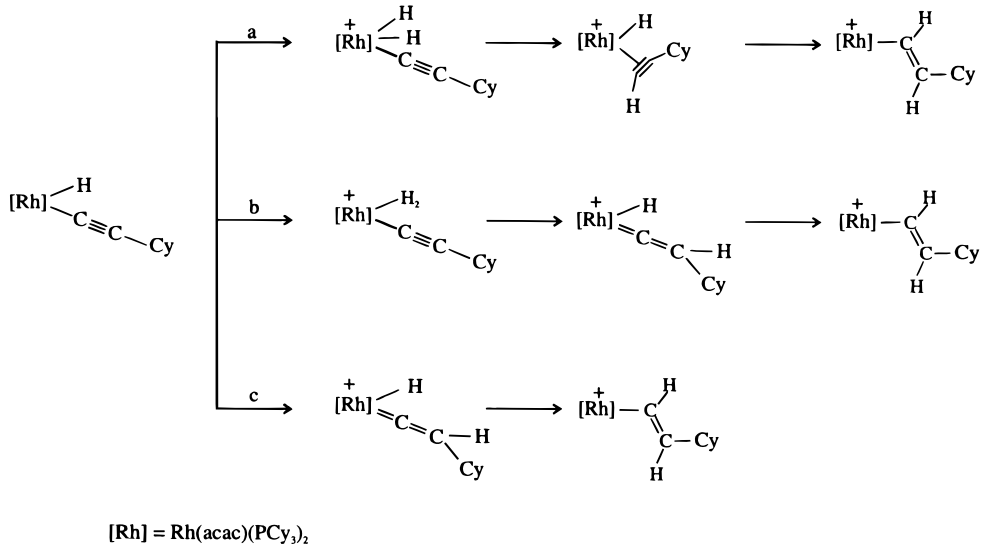
Scheme 5



trans-IrCl(C═CH$_2$)(P^{i}Pr$_3$)$_2$ has been prepared.[20] It has been suggested that these desilylation processes are due to the presence of traces of water in the reaction media acting as an electrophilic reagent.[19,21] We note that, in contrast to compounds containing silylvinylidene ligands, corresponding species with silylalkynyl ligands are quite stable in aqueous media. This is exemplified, i.e., by the preparation of the complex Rh(C≡CSiMe$_3$)(PMe$_3$)$_3$ from *cis*-[RhH(C≡CSiMe$_3$)(PMe$_3$)$_3$]Cl in concentrated aqueous KOH.[22] Therefore, the formation of **13** from the silylalkynyl−hydrido complex **11** is in full agreement with the participation of vinylidenerhodium species (pathway **c**, Scheme 5) as reaction intermediates.

With regard to the structural proposal for complex **13** we note that the IR spectrum in Nujol shows two ν(CO) absorptions at 1573 and 1530 cm^{-1}. The ^{1}H NMR spectrum contains only one singlet for the methyl protons of the β-diketonato ligand at 2.11 ppm, while the signals of the vinyl protons appear at 7.31 (RhC*H*═), 4.38 and 4.22 (═C*H*$_2$) ppm. In the ^{13}C{^{1}H} NMR spectrum, the resonance of the α-C carbon atom is observed at 127.3 ppm as a doublet-of-triplets with Rh−C and P−C coupling constants of 37 and 9 Hz, respectively; the resonance of the β-C carbon atom appears at 117.6 as a singlet. In accordance with the square-pyramidal geometry, proposed in Scheme 4, the ^{31}P{^{1}H} NMR spectrum of **13** displays a doublet at 28.7 ppm with a Rh−P coupling constant of 130 Hz.

Concluding Remarks

The results of this study have revealed that the olefinic unit of Rh(acac)(cyclooctene)(PCy$_3$) can be easily displaced by strong π-acceptor ligands such as carbon monoxide, acetylenedicarboxylic dimethyl ester, and diphenylacetylene. The bis(phosphine) complex Rh(acac)(PCy$_3$)$_2$ is not accessible by direct reaction of Rh(acac)(cyclooctene)(PCy$_3$) and tricyclohexylphosphine. However, it can be prepared from **2** and PCy$_3$ in the presence of methyl propiolate. The reaction involves the displacement of the cyclooctene ligand by the terminal alkyne to give Rh(acac)(η^2-HC≡CCO$_2$Me)(PCy$_3$) and the subsequent sustitution of the π-alkyne by the phosphine.

The X-ray structural characterization of Rh(acac)(PCy$_3$)$_2$ proves the presence of a large P−Rh−P angle (105.63(4)°), probably as a result of the steric hindrance between the two *cis* disposed phosphine ligands. The bis(phosphine) complex does not react with molecular hydrogen and terminal alkynes by oxidative addition. However, the rhodium(III) compounds Rh(acac)H(X)(PCy$_3$)$_2$ (X = H, C≡CPh, C≡CCy, C≡CSiMe$_3$) can be obtained by addition of HX to Rh(acac)(cyclooctene)(PCy$_3$) in the presence of the stoichiometric amount of tricyclohexylphosphine. The protonation of the rhodium(III) hydrido−alkynyl derivatives with HBF$_4$·OEt$_2$ affords the cationic five-coordinate alkenyl complexes [Rh(acac){(*E*)-CH═CHR}(PCy$_3$)$_2$]BF$_4$ (R = Cy, H). These reactions proceed via the initial electrophilic attack of the proton at the β-C carbon atom of the alkynyl ligand. As shown by the X-ray crystal structure analysis of **12**, the coordination geometry around the rhodium atom of these alkenyl compounds can be described as square-pyramidal with the alkenyl group in the apical position.

In conclusion, the monoolefin complex Rh(acac)(cyclooctene)(PCy$_3$) is a useful starting material for the preparation of new organometallic rhodium compounds, including π-alkyne, hydrido−alkynyl, and cationic five-coordinate alkenylmetal derivatives.

Experimental Section

General Considerations. All reactions were carried out under an argon atmosphere using Schlenk tube techniques. Solvents were dried and purified by known procedures and distilled under argon prior to use. The starting complex Rh(acac)(cyclooctene)$_2$ (**1**) was prepared by a published method.[23] Elemental analyses were performed with a Perkin-Elmer 240 XL microanalyzer. NMR spectra were recorded on Varian 200 XL or Varian UNITY 300 instruments. Chemical shifts are expressed in parts per million, downfield from Si(CH$_3$)$_4$ (^{13}C{^{1}H}, ^{1}H) and 85% H$_3$PO$_4$ (^{31}P{^{1}H}). Infrared spectra were obtained from a Perkin-Elmer 783 instrument.

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Preparation of Rh(acac)(cyclooctene)(PCy_3) (2). A solution of **1** (130 mg, 0.31 mmol) in toluene (10 mL) was treated with PCy_3 (86 mg, 0.31 mmol). The resulting solution was stirred for 15 min at room temperature and filtered through Kieselguhr. <ssen>The filtrate was concentrated to ca. 0.1 mL in vacuo; addition of methanol led to the precipitation of a yellow solid. The solvent was decanted, and the residue was washed twice with methanol and then dried in vacuo. Compound **2** was isolated as a yellow solid: yield 173 mg (95%). Anal. Calcd for $C_{31}H_{54}O_2PRh$: C, 62.83; H, 9.18. Found: C, 62.99; H, 9.27. IR (Nujol, cm^{-1}): ν(acac) 1575, 1500. ^1H NMR (300 MHz, C_6D_6, 20 °C, δ): 5.20 (s, 1 H, C*H* of acac); 3.13 (br, 2 H, *H*C=C*H*); 2.60−2.42 (m, 4 H, CHCH_2); 2.02 (m, 4 H, CH_2); 2.2−1.2 (m, 37 H, C_6H_{11} and CH_2); 1.91 and 1.61 (both s, 6 H, CH_3 of acac). $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 47.2 (d, J_{Rh-P} = 183 Hz).

Preparation of Rh(acac)(CO)(PCy_3) (3). A stream of CO was passed through a solution of **2** (123 mg, 0.21 mmol) in toluene (10 mL) for 15 min. The resulting solution was filtered through Kieselguhr, and the filtrate was concentrated to ca. 0.1 mL in vacuo; addition of hexane led to the precipitation of a yellow solid. The solvent was decanted, and the solid was washed twice with hexane and then dried in vacuo: yield 82 mg (77%). Anal. Calcd for $C_{24}H_{40}O_3PRh$: C, 56.47; H, 7.90. Found: C, 56.36; H, 7.82. IR (Nujol, cm^{-1}): ν(CO) 1945; ν(acac) 1583, 1518. ^1H NMR (300 MHz, C_6D_6, 20 °C, δ): 5.32 (s, 1 H, C*H* of acac); 2.00−1.11 (m, 33 H, C_6H_{11}); 1.78 and 1.66 (both s, 6 H, CH_3 of acac).$^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 59.6 (J_{Rh-P} = 168 Hz).

Preparation of Rh(acac)(η^2-$CH_3O_2CC{\equiv}CCO_2CH_3$)($PCy_3$) (4). A solution of **2** (109 mg, 0.18 mmol) in hexane (15 mL) was treated with $CH_3O_2CC{\equiv}CCO_2CH_3$ (23 μL, 0.18 mmol) whereupon the yellow solution rapidly became orange. After stirring of the solution for 30 min at room temperature, an orange solid was formed. The solvent was decanted, and the solid was washed twice with hexane and dried in vacuo: yield 101 mg (89%). Anal. Calcd for $C_{29}H_{46}O_6PRh$: C, 55.77; H, 7.42. Found: C, 55.48; H, 7.45. IR (Nujol, cm^{-1}): ν(C≡C) 1890; ν(C=O) 1710, 1690, ν(acac) 1590, 1520. ^1H NMR (300 MHz, C_7D_8, 20 °C, δ): 5.41 (s, 1 H, C*H* of acac); 3.79 (s, 6 H, CO_2CH_3); 2.19−1.20 (m, 33 H, C_6H_{11}); 1.86 (s, 6 H, CH_3 of acac). ^1H NMR (300 MHz, C_7D_8, −50 °C, δ): 1.91 and 1.80 (both s, 6 H, CH_3 of acac). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_7D_8, 20 °C, δ): 158.8 (s, CO_2CH_3); 99.8 (s, *C*H of acac); 88.25 (dd, J_{Rh-C} = 19 Hz, J_{P-C} = 6 Hz, *C*≡C); 52.4 (s, CO_2CH_3); 32.15 (d, J_{P-C} = 23 Hz, P*C*HCH$_2$); 29.2 (s, *C*H$_2$); 27.6 (d, J_{P-C} = 11 Hz, PCH*C*H$_2$); 26.4 (s, *C*H$_2$). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_7D_8, −50 °C, δ): 188.9 and 183.1 (both s, *C*O of acac); 88.55 (br *C*≡C); 28.35 (d, J_{P-C} = 6 Hz, *C*H$_3$ of acac); 26.65 (s, *C*H$_3$ of acac). $^{31}P\{^1H\}$ NMR (121.45 MHz, C_7D_8): δ 48.8 (d, J_{Rh-P} = 167 Hz).

Preparation of Rh(acac)(η^2-PhC≡CPh)(PCy_3) (5). The complex was prepared using the procedure described for **4**, starting from **2** (118 mg, 0.20 mmol) and PhC≡CPh (36 mg, 0.20 mmol). Complex **5** was isolated as a yellow solid: yield 114 mg (86%). Anal. Calcd for $C_{37}H_{50}O_2PRh$: C, 67.26; H, 7.63. Found: C, 66.96; H, 8.07. IR (Nujol, cm^{-1}): ν(C≡C) 1910; ν(acac) 1575, 1510. ^1H NMR (300 MHz, $CDCl_3$, 20 °C, δ): 8.05−7.23 (m, 10 H, Ph); 5.40 (s, 1 H, C*H* of acac); 1.94−1.02 (m, 33 H, C_6H_{11}); 1.94 (s, 6 H, CH_3 of acac). ^1H NMR (300 MHz, $CDCl_3$, −50 °C, δ): 2.01 and 1.86 (both s, 6 H, CH_3 of acac). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$, 20 °C, δ): 187.7 and 183.4 (both br, *C*O of acac); 131.3, 130.6, 130.2, 128.2, 127.4, 125.9 (all s, Ph); 99.2 (s, CH of acac); 86.2 (dd, J_{Rh-C} = 17 Hz, J_{P-C} = 4 Hz, *C*≡*C*); 32.6 (d, J_{P-C} = 23 Hz, P*C*HCH$_2$); 29.6 (s, *C*H$_2$); 27.8 (d, J_{P-C} = 10 Hz, PCH*C*H$_2$); 26.8 (s, *C*H$_2$). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$, −50 °C, δ): 86.2 (br, *C*≡*C*); 28.15 (d, J_{P-C} = 4 Hz, CH_3 of acac); 26.95 (s, CH_3 of acac). $^{31}P\{^1H\}$ NMR (121.45 MHz, $CDCl_3$): δ 49.6 (d, J_{Rh-P} = 179 Hz).

Preparation of Rh(acac)(PCy_3)$_2$ (6). This complex can be prepared by two different procedures. (a) A solution of **2** (154 mg, 0.26 mmol) in toluene (10 mL) was treated with PCy_3 (73 mg, 0.26 mmol) and HC≡CCO_2CH_3 (16 μL, 0.26 mmol). The resulting solution was stirred for 45 min at room temperature and then filtered through Kieselguhr. The filtrate was concentrated to ca. 0.1 mL in vacuo, and addition of methanol led to precipitation of an orange solid. The solvent was decanted, and the solid was washed twice with methanol and then dried in vacuo; yield 84 mg (42%). (b) A solution of **7** (125 mg, 0.23 mmol) in toluene (15 mL) was treated with PCy_3 (62 mg, 0.22 mmol). After the mixture was stirred for 45 min at room temperature, the solution was filtered through Kieselguhr. The filtrate was concentrated to ca. 0.1 mL in vacuo, and addition of methanol led to precipitation of an orange solid. The solvent was decanted, and the solid was washed twice with methanol and then dried in vacuo: yield 60 mg (34%). Anal. Calcd for $C_{41}H_{73}O_2P_2Rh$: C, 64.45; H, 9.64. Found: C, 64.89; H, 10.06. IR (Nujol, cm^{-1}): ν(acac) 1593, 1528. ^1H NMR (300 MHz, C_6D_6, 20 °C, δ): 5.04 (s, 1 H, C*H* of acac); 2.20−1.18 (m, 66 H, C_6H_{11}); 1.81 (s, 6 H, CH_3 of acac). $^{31}P\{^1H\}$ NMR (121.45 MHz, C_6D_6): δ 49.9 (J_{Rh-P} = 191 Hz).

Preparation of Rh(acac)(η^2-HC≡CCO_2CH_3)(PCy_3) (7). The complex was prepared using the procedure described for **4**, starting from **2** (111 mg, 0.26 mmol) and HC≡CCO_2CH_3 (16 μL, 0.26 mmol). Complex **7** was isolated as a yellow solid: yield 99 mg (68%). Anal. Calcd for $C_{27}H_{44}O_4PRh$: C, 57.24; H, 7.83. Found: C, 56.87; H, 8.31. IR (Nujol, cm^{-1}): ν(C≡C) 1810; ν(C=O) 1685; ν(acac) 1582, 1514. ^1H NMR (300 MHz, C_7D_8, 20 °C, δ): 5.63 (d, J_{Rh-H} = 3 Hz, ≡C*H*); 5.21 (s, 1 H, C*H* of acac); 3.52 (s, 3 H, CO_2CH_3); 1.94−1.10 (m, 33 H, C_6H_{11}); 1.80 (s, 6 H, CH_3 of acac). ^1H NMR (300 MHz, C_7D_8, −50 °C, δ): 1.88 and 1.75 (both s, 6 H, CH_3 of acac). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_7D_8, 20 °C, δ): 188.5 and 182.8 (both br, *C*O of acac); 158.8 (s, CO_2CH_3); 99.7 (s, *C*H of acac); 93.8 (dd, J_{Rh-C} = 17 Hz, J_{P-C} = 5 Hz, one C of *C*≡C); 76.0 (dd, J_{Rh-C} = 19 Hz, J_{P-C} = 5 Hz, one C of *C*≡C); 51.5 (s, CO_2CH_3); 32.35 (d, J_{P-C} = 23 Hz, P*C*HCH$_2$); 29.9 and 29.6 (both s, *C*H$_2$); 28.65 (d, J_{P-C} = 11 Hz, PCH*C*H$_2$); 27.15 (s, *C*H$_3$ of acac); 26.9 (s, *C*H$_2$). $^{13}C\{^1H\}$ NMR (75.45 MHz, C_7D_8, −60 °C, δ): 188.5 and 182.8 (both s, *C*O of acac); 95.5 (br, one of *C*≡C); 76.9 (br, one of *C*≡C); 27.9 (s, *C*H$_3$ of acac); 26.9 (d, J_{P-C} = 5 Hz, *C*H$_3$ of acac). $^{31}P\{^1H\}$ NMR (121.45 MHz, C_7D_8): δ 50.0 (d, J_{Rh-P} = 172 Hz).

Preparation of Rh(acac)H_2(PCy_3)$_2$ (8). A solution of **1** (105 mg, 0.23 mmol) in toluene (10 mL) was treated with PCy_3 (129 mg, 0.46 mmol), while a slow stream of H_2 was passed through the solution for 30 min at room temperature. The resulting solution was filtered through Kieselguhr, and the filtrate was concentrated to ca. 0.1 mL in vacuo; addition of hexane led to the precipitation of a white solid. The solvent was decanted, and the solid was washed twice with hexane and dried in vacuo: yield 118 mg (67%). Anal. Calcd for $C_{41}H_{75}O_2P_2Rh$: C, 64.38; H, 9.88. Found: C, 64.35; H, 10.64. IR (Nujol, cm^{-1}): ν(Rh−H) 2120, 2085; ν(acac) 1600, 1510. ^1H NMR (300 MHz, C_6D_6, 20 °C, δ): 5.27 (s, 1 H, C*H* of acac); 2.21−1.26 (m, 66 H, C_6H_{11}); 1.93 (s, 6 H, CH_3 of acac); −22.18 (dt, 2 H, J_{Rh-H} = 20 Hz, J_{P-H} = 16 Hz, Rh−H). $^{31}P\{^1H\}$ NMR (80 MHz, C_6D_6): δ 15.8 (d, J_{Rh-P} = 117 Hz).

Preparation of Rh(acac)H(C≡CPh)(PCy_3)$_2$ (9). A solution of **2** (83 mg, 0.14 mmol) in toluene (10 mL) was treated with PCy_3 (40 mg, 0.14 mmol) and PhC≡CH (16 μL, 0.14 mmol). The resulting reaction mixture was stirred for 6 h at room temperature and then filtered through Kieselguhr. The filtrate was concentrated to ca. 0.1 mL in vacuo, and the addition of methanol led to the precipitation of a white solid. The solvent was decanted, and the solid was washed twice with methanol and dried in vacuo: yield 57 mg (47%). Anal. Calcd for $C_{49}H_{79}O_2P_2Rh$: C, 68.04; H, 9.21. Found: C, 67.75; H, 9.66. IR (Nujol, cm^{-1}): ν(Rh−H) 2155; ν(C≡C) 2118; ν(acac) 1600, 1515. ^1H NMR (300 MHz, $CDCl_3$, 20 °C, δ): 9.90−7.45 (m, 5 H, Ph); 5.35 (s, 1 H, C*H* of acac); 2.40−1.20 (m, 66 H, C_6H_{11}); 2.08 and 1.86 (both s, 6 H, CH_3 of acac); −18.79 (dt, 1 H, J_{Rh-H} = 19 Hz, J_{P-H} = 12 Hz, Rh−H). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$, 20 °C, δ): 188.3 and 184.4 (both s, *C*O of acac); 130.7,

Table 3. Crystal Data and Data Collection and Refinement for Rh(acac)(PCy$_3$)$_2$ (6) and [Rh(acac){(*E*)-CH=CHCy)(PCy$_3$)$_2$]BF$_4$ (12)

	6	12
	Crystal Data	
formula	$C_{41}H_{73}O_2P_2Rh$	$C_{49}H_{79}BF_4O_2P_2Rh$
mol wt	762.88	951.84
color and habit	orange, irregular prism	yellow, irregular prism
cryst size, mm	0.41 × 0.32 × 0.31	0.25 × 0.38 × 0.38
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a, Å	10.400(3)	12.463(4)
b, Å	11.593(3)	20.861(4)
c, Å	18.708(6)	21.025(7)
α, deg	83.55(2)	
β, deg	85.08(2)	101.03(2)
γ, deg	65.52(2)	
V, Å^3; *Z*	2037(1), 2	5365, 4
D(calcd), g cm^{-3}	1.24	1.18
temp (K)	173	293
	Data Collection and Refinement	
diffractometer	Siemens-STOE AED-2	Enraf-Nonius CAD-4
λ(Mo Kα) radiation, Å;	0.710 73	0.709 30
technique	bisecting geometry	*κ* geometry
monochomator	graphite oriented	graphite, Zr filter (factor 15.41)
μ, mm^{-1}	0.53	0.42
scan type	*ω*/2*θ*	*ω*/*θ*
2*θ* range, deg	3 ≤ 2*θ* ≤ 50	2 ≤ 2*θ* ≤ 48
no. of data collcd	7569	8383
no. of unique data	7146	7505
no. of obsd data	5390 ($F_o > 4.0\sigma(F_o)$)	5023 ($F_o > 3.0\sigma(F_o)$)
no. of params refined	417	539
R1(**6**, **12**)[a]	0.0462	0.060
w*R2*(**6**),[b] R_w(**12**)[c]	0.1256	0.093

[a] $R1(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2(F^2, \text{all data}) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] $R_w = \sum(w^{1/2}|[F_o - F_c]|)/(\sum w^{1/2}F_o)$.

130.6, 167.7, 123.4 (all s, Ph); 106.25 (d, J_{Rh-C} = 10 Hz, C≡*C*Ph); 103.85 (dt, J_{Rh-C} = 48 Hz, J_{P-C} = 16 Hz, *C*≡CPh); 99.55 (s, *C*H of acac); 33.8 and 33.7 (both d, J_{P-C} = 20 Hz, P*C*HCH$_2$); 29.9 and 29.5 (both s, *C*H$_2$); 28.65 and 28.4 (both d, J_{P-C} = 8 Hz, PCH*C*H$_2$); 27.4 and 27.3 (s, *C*H$_2$); 23.75 (s, *C*H$_3$ of acac). ^{31}P{^{1}H} NMR (80 MHz, C_6D_6): *δ* 38.0 (d, J_{Rh-P} = 103 Hz).

Preparation of Rh(acac)H(C≡CCy)(PCy$_3$)$_2$ (10). The complex was prepared using the procedure described for **9**, starting from **2** (166 mg, 0.28 mmol), PCy$_3$ (78 mg, 0.28 mmol), and CyC≡CH (36 *μ*L, 0.28 mmol). Complex **10** was isolated as a pale yellow solid: yield 115 mg (47%). Anal. Calcd for $C_{49}H_{85}O_2P_2Rh$: C, 67.57; H, 9.84. Found: C, 67.75; H, 10.03. IR (Nujol, cm^{-1}): *ν*(Rh−H) 2140; *ν*(C≡C) 2115; *ν*(acac) 1600, 1515. ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C, *δ*): 5.35 (s, 1 H, C*H* of acac); 2.40−1.20 (m, 77 H, C_6H_{11}); 2.04 and 1.72 (both s, 6 H, C*H*$_3$ of acac); −19.33 (dt, 1 H, J_{Rh-H} = 18 Hz, J_{P-H} = 13 Hz, Rh−H). ^{13}C{^{1}H} NMR (75.45 MHz, $CDCl_3$, 20 °C, *δ*): 187.9 and 184.1 (both s, *C*O of acac); 107.45 (d, J_{Rh-C} = 10 Hz, C≡*C*CCy); 101.85 (dt, J_{Rh-C} = 40 Hz, J_{P-C} = 18 Hz, *C*≡CCy); 99.3 (s, *C*H of acac); 35.0 (s, *C*H$_2$); 33.5 and 33.4 (both d, J_{P-C} = 23 Hz, P*C*HCH$_2$); 29.65 and 29.6 (both s, *C*H$_2$); 26.9 (s, *C*H$_2$); 26.5 (s, *C*H$_3$ of acac); 26.0 (s, *C*H$_2$). ^{31}P{^{1}H} NMR (80 MHz, C_6D_6): *δ* 37.1 (d, J_{Rh-P} = 104 Hz).

Preparation of Rh(acac)H(C≡CSiMe$_3$)(PCy$_3$)$_2$ (11). The complex was prepared using the procedure described for **9**, starting from **2** (142 mg, 0.24 mmol), PCy$_3$ (67 mg, 0.24 mmol), and Me$_3$SiC≡CH (34 *μ*L, 0.24 mmol). Complex **11** was isolated as a white solid: yield 95 mg (46%). Anal. Calcd for $C_{46}H_{83}O_2P_2RhSi$: C, 64.16; H, 9.72. Found: C, 64.52: H; 10.68. IR (Nujol, cm^{-1}): *ν*(Rh−H) 2146; *ν*(C≡C) 2042; *ν*(acac) 1587, 1514. ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C, *δ*): 5.10 (s, 1 H, C*H* of acac); 2.19−1.18 (m, 66 H, C_6H_{11}); 1.84 and 1.69 (both s, 6 H, C*H*$_3$ of acac); 0.20 (s, 9 H, C*H*$_3$Si); −19.19 (dt, 1 H, J_{Rh-H} = 18 Hz, J_{P-H} = 13 Hz, Rh−H). ^{31}P{^{1}H} NMR (80 MHz, $CDCl_3$): *δ* 35.6 (d, J_{Rh-P} = 102 Hz).

Preparation of [Rh(acac){(*E*)-CH=CHCy}(PCy$_3$)$_2$]BF$_4$ (12). A suspension of **10** (100 mg, 0.12 mmol) in diethyl ether (15 mL) was treated with HBF$_4$·OEt$_2$ (16 *μ*L, 0.12 mmol), causing an immediate color change to bright yellow. After the mixture was stirred for 30 min at room temperature, a yellow precipitate formed. The solvent was decanted, and the solid was washed twice with diethyl ether and then dried in vacuo; yield 93 mg (81%). Anal. Calcd for $C_{49}H_{86}BF_4O_2P_2Rh$: C, 61.38; H, 9.04. Found: C, 60.87; H, 9.34. IR (Nujol, cm^{-1}): *ν*(acac) 1570, 1530. ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C, *δ*): 6.50 (dt, 1 H, J_{H-H} = 10 Hz, J_{P-H} = 9Hz, RhC*H*=CHCy); 5.90 (s, 1 H, C*H* of acac); 4.25 (dd, 1 H, J_{H-H} = 10 Hz, J_{Rh-H} = 8 Hz, RhCH=C*H*Cy); 2.59−1.00 (m, 77 H, C_6H_{11}); 2.11 (s, 6 H, C*H*$_3$ of acac). ^{13}C{^{1}H} NMR (75.45 MHz, $CDCl_3$, 20 °C, *δ*): 185.2 (s, *C*O of acac); 135.6 (s, RhCH=*C*HCy); 111.6 (dt, J_{Rh-C} = 35 Hz, J_{P-C} = 9 Hz, Rh*C*H=CHCy); 99.8 (s, *C*H of acac); 35.6 (d, J_{P-C} = 22 Hz, P*C*HCH$_2$); 32.1 (s, Cy); 29.95 and 28.7 (both s, *C*H$_2$); 27.0 and 26.8 (both d, J_{P-C} = 10 Hz, PCH*C*H$_2$); 26.2 (s, *C*H$_2$); 25.6 (s, CH$_3$ of acac); 25.4, 25.2, 24.9 (all s, *C*H$_2$). ^{31}P-{^{1}H} NMR (80 MHz, $CDCl_3$): *δ* 28.7 (d, J_{Rh-P} = 132 Hz).

Preparation of [Rh(acac)(CH=CDCy)(PCy$_3$)$_2$]BF$_4$ (12-*d*$_1$). To prepare a solution of DBF$_4$, 1 mL of D$_2$O was added dropwise to an equal volume of HBF$_4$·OEt$_2$ until effervescence ceased. Addition of the stoichiometric amount of this solution to an ether slurry of **11** proceeded as described above for the preparation of **12**. ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C, *δ*): 6.56 (t, 1 H, J_{P-H} = 10 Hz, RhC*H*=CDCy); 5.90 (s, 1 H, C*H* of acac); 2.59−1.00 (m, 77 H, C_6H_{11}); 2.11 (s, 6 H, C*H*$_3$ of acac). ^{2}H NMR (46.07 MHz, CH_2Cl_2, 20 °C, *δ*): 4.33 (s, RhCH=C*D*Cy). ^{31}P-{^{1}H} NMR (80 MHz, $CDCl_3$): *δ* 28.9 (d, J_{Rh-P} = 132 Hz).

Preparation of [Rh(acac)(CH=CH$_2$)(PCy$_3$)$_2$]BF$_4$ (13). The complex was prepared using the procedure described for **12** starting from **11** (112 mg, 0.13 mmol) and HBF$_4$·OEt$_2$ (18 *μ*L, 0.13 mmol). Compound **13** was isolated as a yellow solid: yield: 87 mg (76%). Anal. Calcd for $C_{43}H_{76}BF_4O_2P_2Rh$: C, 58.91; H, 8.74. Found: C, 58.30; H, 9.03. IR (Nujol, cm^{-1}): *ν*(acac) 1573, 1530. ^{1}H NMR (300 MHz, $CDCl_3$, 20 °C, *δ*): 7.31 (m, RhC*H*=CH$_2$); 5.91 (s, 1 H, C*H* of acac); 4.38 (br, 1H, one H of RhCH=C*H*$_2$ *cis* to Rh); 4.22 (dd, 1 H, J_{H-H} = 12 Hz, J_{Rh-H} = 5 Hz, one H of RhCH=C*H*$_2$ *trans* to Rh); 2.59−1.00 (m, 77

H, C_6H_{11}); 2.11 (s, 6 H, CH_3 of acac). $^{13}C\{^1H\}$ NMR (75.45 MHz, $CDCl_3$, 20 °C, δ): 186.2 (s, *C*O of acac); 127.3 (dt, J_{Rh-C} = 37 Hz, J_{P-C} = 9 Hz, RhCH=CH_2); 117.6 (s, RhCH=CH_2); 100.7 (s, *C*H of acac); 36.3 (d, J_{P-C} = 20 Hz, P*C*HCH$_2$); 30.75 and 29.65 (both s, *C*H$_2$); 27.8 (d, J_{P-C} = 10 Hz, PCH*C*H$_2$); 26.25 (s, CH_3 of acac); 25.9 (s, *C*H$_2$). $^{31}P\{^1H\}$ NMR (80 MHz, $CDCl_3$): δ 28.7 (d, J_{Rh-P} = 130 Hz).

X-ray Structure Analysis of Rh(acac)(PCy$_3$)$_2$ (6). Crystals suitable for an X-ray diffraction experiment were obtained by slow diffusion of hexane into a concentrated solution of **6** in CH_2Cl_2. A summary of crystal data, intensity collection procedure, and refinement data is reported in Table 3. The crystal studied was glued on a glass fiber and mounted on a Siemens AED-2 diffractometer. Cell constants were obtained from the least-squares fit of the setting angles of 65 reflections in the range $20 \leq 2\theta \leq 30°$. The recorded reflections were corrected for Lorentz and polarization effects. Reflections were also corrected for absorption by an empirical method (ψ-scan method).[24]

The structure was solved by Patterson (Rh atom) and conventional Fourier techniques. Refinement was carried out by full-matrix least-squares methods with initial isotropic thermal parameters. Hydrogen atoms were calculated according to the ideal geometry (distance C−H = 0.96 Å) and included in the refinement riding on carbon atoms with a commom isotropic thermal parameter. Anisotropic thermal parameters were used in the last cycles of refinement for all non-hydrogen atoms. All calculations were performed using SHELXTL-PLUS[25] and SHELX-93.[26]

X-ray Structure Analysis of [Rh(acac){(*E*)-CH=CHCy}(PCy$_3$)$_2$]BF$_4$ (12). Crystals suitable for an X-ray diffraction experiment were obtained by slow diffusion of diethyl ether into a concentrated solution of **12** in CH_2Cl_2. A summary of crystal data, intensity collection procedure, and refinement data is reported in Table 3. The crystal studied was glued on a glass fiber and mounted on a Enraf-Nonius CAD-4 diffractometer. Cell constants were obtained from the least-squares fit of the setting angles of 23 reflections in the range $20 \leq 2\theta \leq 26°$. Intensity data were corrected for Lorentz and Polarization effects, and a semiempirical absorption correction (ψ-scan method) was applied.[24] The structure was solved by direct methods (SHELXS-86).[27] Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares methods (unit weights, Enraf-Nonius SDP[28]). The hydrogen atoms were calculated according to the ideal geometry (distance C−H = 0.95 Å) and used only in structure factor calculations. The BF_4 group was found to be disordered over three sites; with equal occupancies the positions were refined independently with isotropic temperature factors.

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Supporting Information Available: Tables of anisotropic thermal parameters, complete atomic coordinates and thermal parameters, experimental details of the X-ray study, bond distances and angles, selected least-squares planes, and interatomic distances (31 pages). Ordering information is given on any current masthead page.

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