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Reductive elimination of the alkenyl fragment and a phosphine ligand from [Rh(acac){(*E*)-CH=CHR}(PCy_3)$_2$]BF_4 (R = Cy, Ph, H): preparation of [(E)-RHC=CHPCy_3]BF_4 from alkynes

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Abstract

In dichloromethane under reflux, the five-coordinate alkenyl complexes [Rh(acac){(E)-CH=CHR}(PCy_3)$_2$]BF_4 [R = Cy (**1**), Ph (**2**), H (**3**)] evolve into the alkenylphosphonium derivatives [Rh(acac){η^2-(*E*)-CH(PCy_3)=CHR}(PCy_3)]BF_4 [R = Cy (**4**), Ph (**5**), H(**6**)], by reductive elimination reactions involving the one-electron alkenyl fragments and one of the two-electron phosphine ligands of **1**–**3**. Complexes **4**–**6** react with carbon monoxide to afford Rh(acac)(CO)(PCy_3) and [(*E*)-RHC=CHPCy_3]BF_4 [R = Cy (**8**), Ph (**9**), H (**10**)]. In addition, we describe a new route for the preparation of alkenylphophonium salts starting from terminal alkynes, PCy_3 and HBF_4, and using the Rh(acac)(PCy_3) unit as a template.

Keywords: Reductive elimination; Alkenyl fragment; Phosphine

1. Introduction

Alkenylphosphonium salts play a main role in organic synthesis as intermediates reagents in processes such as ring formation by Michael–Wittig, Michael-nucleophilic displacement and Diels–Alder sequences; phosphonioethylation; two-carbon chain-linking and alkenation [1–17].

We have recently shown that the protonation of the hydrido–alkynyl complexes Rh(acac){C≡CC(OH)Ph_2}-H(PR_3)$_2$ with HBF_4 leads to the allenyl derivatives [Rh(acac){CH=C=CPh_2}(PR_3)$_2$]BF_4 (PR_3 = PCy_3, P*i*P-r$_3$), which evolve at room temperature (r.t.) into the square-planar rhodium(I) complexes [Rh(acac){η^2-CH(PR_3)=C=CPh_2}(PR_3)]BF_4. The allenylphosphonium ligand can be displaced from these compounds by carbon monoxide to afford Rh(acac)(CO)(PR_3) and [Ph_2C=C=CHPR_3]BF_4 (PR_3 = PCy_3, P*i*Pr$_3$). The formation of the square-planar allenylphosphonium complexes [Rh(acac){η^2-CH(PR_3)=C=CPh_2}(PR_3)]BF_4 from the corresponding five-coordinate rhodium(III) allenyl precursors is a result of intramolecular reductive eliminations involving the one-electron allenyl fragment and the two-electron phosphine ligands [18]. These type of reductive elimination reactions are uncommon, and previously they had been observed by Rubinskaya and co-workers [19] and Guerchais and co-workers [20] in neutral palladium and tungsten complexes, respectively.

Two years ago we reported the synthesis of the five-coordinate alkenyl complexes [Rh(acac){(*E*)-CH=CHR}-(PCy_3)$_2$]BF_4 (R = Cy, H) which, in contrast to the allenyl species [Rh(acac){CH=C=CPh_2}-(PR_3)$_2$]BF_4, are stable at r.t. [21]. In this paper we show that this type of reductive elimination not only occurs in five-coordinate allenyl rhodium(III) complexes but also in

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five-coordinate alkenyl rhodium(III) compounds. In addition, we describe a new route for the preparation of alkenylphosphonium salts starting from terminal alkynes and using the Rh(acac)(PCy_3) unit as a template.

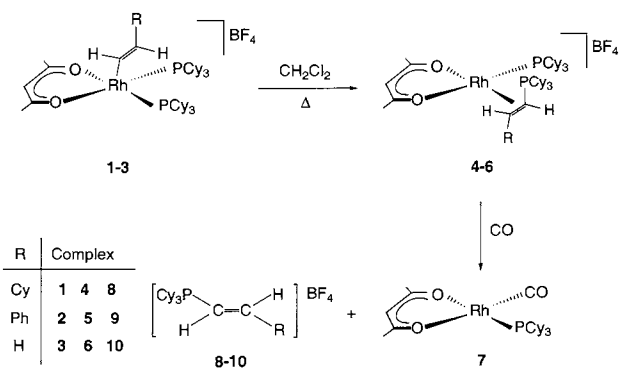
2. Results and discussion

Although the alkenyl complexes [Rh(acac){(*E*)-CH=CHR}(PCy_3)$_2$]BF_4 [R = Cy (**1**), Ph (**2**), H (**3**)] are stable in dichloromethane at r.t., under reflux they undergo the intramolecular reductive elimination of the corresponding alkenylphosphonium ligand to afford the rhodium(I) derivatives [Rh(acac){η^2-(*E*)-CH(PCy_3)=CHR}(PCy_3)]BF_4 [R = Cy (**4**), Ph (**5**), H (**6**)], which were isolated as orange–yellow solids (Scheme 1).

Complexes **4**–**6** were characterized by elemental analysis, IR and ^{1}H-, ^{31}P- and ^{13}C-NMR spectroscopies. Complex **4** was further characterized by an X-ray crystallographic study. A view of the molecular geometry is shown in Fig. 1.

The coordination geometry around the rhodium center is square planar, with the β-diketonato ligand acting with a bite angle of 87.6(1)° (Table 1). Although we find the two olefinic carbons statically disordered, we can confirm, without any doubt, that the alkenylphosphonium ligand has a *trans* stereochemistry at the C=C double bond. Olefinic carbons, C(1) and C(2), of the alkenylphosphonium ligand were modelled using two geometrically restrained moieties.

The *trans* stereochemistry at the C=C double bond of the alkenylphosphonium ligands is also supported by the ^{1}H-NMR spectra of **4**–**6**, which shows a H–H coupling constant of 13.5 Hz in the three cases. In the ^{13}C{^{1}H}-NMR spectra, the resonances due to the sp^2-carbon atoms of alkenylphosphonium ligands appear between 76 and 62 ppm (=CHR) and at about 17 ppm (=CHPCy_3). The first as doublets with C–P coupling constants between 15 and 18 Hz, and the second as doublet of doublet of doublets with C–P coupling



Scheme 1.

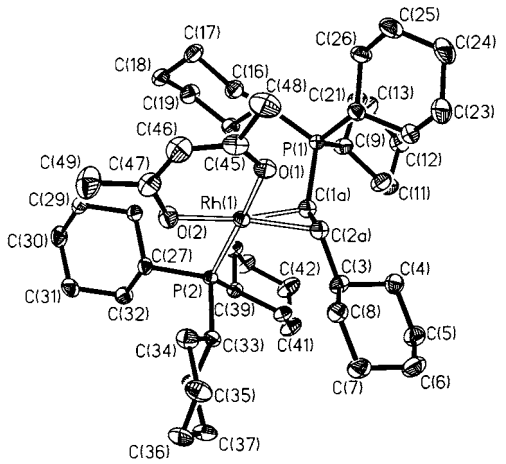


Fig. 1. Molecular representation for the cationic complex [Rh(acac){η^2-(*E*)-CH(PCy_3)=CHCy}(PCy_3)]BF_4 (**4**). Only one group of atoms has been drawn for the disordered olefinic carbon atoms.

constants between 55 and 58 Hz (Cy_3P–C=) and about 3 Hz (Cy_3P–Rh), and C–Rh coupling constants between 16 and 19 Hz. The ^{31}P{^{1}H}-NMR spectra of **4**–**6** show two doublets. Those corresponding to the tricyclohexylphosphine coordinated to the rhodium atom appear between 37 and 47 ppm and show P–Rh coupling constants of about 170 Hz, while the tricyclohexylphosphine groups bonded to the =CH carbon atoms are observed between 33 and 36 ppm and show P–Rh coupling constants of about 6 Hz.

The alkenylphosphonium ligands of **4**–**6** can be displaced by carbon monoxide to afford Rh(acac)(CO)(PCy_3) and the alkenylphosphonium salts [(*E*)-RHC=CHPCy_3]BF_4 [R = Cy (**8**), Ph (**9**), H (**10**)], which were isolated as white solids.

The spectroscopic data of **8**–**10** agree well with those previously reported by Freeman, Schweizer and coworkers [22,23] for related compounds. In the ^{1}H-NMR spectra the vinylic hydrogen resonances appear between 7 and 5 ppm, while in the ^{13}C{^{1}H}-NMR spectra the sp^2-carbon resonances are observed between 100 and 115 ppm (=CHP) and between 166 and 143 ppm (=CHR). The ^{31}P{^{1}H}-NMR spectra shows singlets at about 27 ppm.

Table 1
Selected bond lengths (Å) and angles (°) for the cationic complex [Rh(acac){η^2-(*E*)-CH(PCy_3)=CHCy}(PCy_3)]BF_4 (**4**)

Bond lengths (Å)			
Rh(1)–O(1)	2.078(3)	Rh(1)–P(2)	2.2974(11)
Rh(1)–O(2)	2.052(3)	O(1)–C(45)	1.267(6)
Rh(1)–C(mean)	2.093(4)	O(2)–C(47)	1.277(6)
Bond angles (°)			
P(2)–Rh(1)–O(1)	170.64(9)	O(1)–Rh(1)–O(2)	87.6(1)
P(2)–Rh(1)–O(2)	85.56(10)		

We have previously reported that the addition of one equivalent of terminal alkynes to solutions containing equimolecular amounts of Rh(acac)(η^2-C_8H_{14})(PCy_3) and PCy_3 leads to the hydrido–alkynyl complexes Rh(acac)(C_2R)H(PCy_3)$_2$, which react with HBF_4 to afford complexes **1**–**3**. These reactions together with those shown in Scheme 1 constitute a new synthetic route to easily prepare alkenylphosphonium salts, which involves the formal *cis*-addition of [$HPCy_3$]BF_4 to the carbon–carbon triple bond of terminal alkynes, in the presence of the Rh(acac)(PCy_3) unit. When the intermediate rhodium complexes of the route are not isolated, the alkenylphosphonium salts are obtained in higher yields above 80%, and the rhodium used can also be recovered in a higher yield above 80%.

In conclusion, in dichloromethane under reflux, the five-coordinate alkenyl compounds [Rh(acac){(*E*)-CH=CHR}(PCy_3)$_2$]BF_4 are not stable and evolve by reductive elimination into the alkenylphosphonium derivatives [Rh(acac){η^2-(*E*)-CH(PCy_3)=CHR}(PCy_3)]-BF_4. This unusual reaction allows the preparation of the alkenylphosphonium salts [(*E*)-RHC=CHPCy_3]BF_4 in high yields by formal addition of [$HPCy_3$]BF_4 to terminal alkynes, using the unit Rh(acac)(PCy_3) as a template.

3. 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≡CPh)H(PCy_3)$_2$ and [Rh(acac){(*E*)-CH=CHR}-(PCy_3)$_2$]BF_4 [R = Cy (**1**), H (**3**)] were prepared by a published method [21]. 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. Coupling constants *J* are given in Hertz. Spectra assignment was achieved with the aid of $^1H\{^{31}P\}$, ^{1}H-COSY and ^{13}C-DEPT experiments. C and H analyses were carried out with a Perkin Elmer 2400 CHNS/O microanalyser.

3.1. Preparation of [Rh(acac){(E)-CH=CHPh}-(PCy_3)$_2$]BF_4 (2)

A suspension of Rh(acac)(C≡CPh)H(PCy_3)$_2$ (259.5 mg, 0.30 mmol) in 7 ml of dichloromethane was cooled at −78°C and then a stoichoimetric amount of $HBF_4 \cdot OEt_2$ (44 μl, 0.33 mmol) was added. A change from white to yellow occurred almost instantaneously. The resulting solution was stirring for 30 min at −78°C, and then was carried out to r.t. The solvent was removed in vacuo and the residue was washed with diethyl ether to give a yellow solid. Yield: 206 mg (72%). Anal. Calc. for $C_{49}H_{80}BF_4O_2P_2Rh$: C, 61.76; H, 8.46%. Found: C, 61.41; H, 8.39. IR (KBr, cm^{-1}): $\nu(CO)_{acac}$ 1568 and 1524, $\nu(BF_4)$ 1056. ^{1}H-NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.79 (dt, 1H, $J_{HH} = 12.3$, $J_{PH} = 9.9$, RhC*H*), 7.3–7.1 (m, 5H, Ph), 5.99 (s, 1H, C*H* of acac), 5.49 (dd, 1H, $J_{HH} = 12.3$, $J_{PH} = 1.5$, RhCH=C*H*), 2.5–1.2 (m, 66H, C_6H_{11}), 2.19 (s, 6H, CH_3 of acac). ^{1}H-NMR (300 MHz, CD_2Cl_2, 213 K): δ 2.13 and 2.10 (both s, 6H, CH_3 of acac). $^{31}P\{^1H\}$-NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 31.9 (d, $J_{RhP} = 137.4$). $^{31}P\{^1H\}$-NMR (121.4 MHz, CD_2Cl_2, 213 K): δ 34.3 (dd, $J_{RhP} = 131.2$, $J_{PP} = 27.9$), 22.6 (dd, $J_{RhP} = 143.5$, $J_{PP} = 27.9$). $^{13}C\{^1H\}$-NMR (75.4 MHz, CD_2Cl_2, 213 K): δ 186.0 and 185.5 (both s, *C*O of acac), 134.5 (s, RhCH=*C*H), 129.2 (s, $C_{ipso\text{-}Ph}$), 128.4 (s, $C_{o\text{-}Ph}$), 126.3 (s, $C_{p\text{-}Ph}$), 125.0 (s, $C_{m\text{-}Ph}$), 120.1 (dt, $J_{RhC} = 32.9$ $J_{PC} = 7.9$, Rh*C*H=CH), 100.2 (s, *C*H of acac), signals in the region 37.2–25.6 ppm assigned to PCy_3 and CH_3 of acac are very broad.

3.2. Preparation of [Rh(acac){η²-(E)-CH(PCy₃)=CHCy}(PCy₃)]BF₄ (4)

A yellow solution of **1** (201.0 mg, 0.21 mmol) in 10 ml of dichloromethane was stirred under reflux for 10 h. The resulting orange solution was cooled and filtered through Kieselguhr, and the filtrate was concentrated to ca. 0.1 ml in vacuo; addition of diethyl ether caused the precipitation of an orange–yellow solid. The solid was decanted and washed with diethyl ether. Yield: 153 mg (76%). Anal. Calc. for $C_{49}H_{86}BF_4O_2P_2Rh$: C, 61.38; H, 9.04%. Found: C, 60.95; H, 9.12. IR (KBr, cm^{-1}): $\nu(CO)_{acac}$ 1582 and 1520, $\nu(BF_4)$ 1056. ^{1}H-NMR (300 MHz, CD_2Cl_2, 293 K): δ 5.50 (s, 1H, C*H* of acac), 3.70 (ddd, 1H, $J_{HH} = J_{PH} = 13.5$, $J_{HH'} = 6.7$, =C*H*Cy), 2.7–1.4 (m, 77H, C_6H_{11}), 2.01 and 1.94 (both s, 6H, CH_3 of acac), signal of C*H*(PCy_3) is localized in the ^{1}H-COSY spectrum at 1.36 ppm. $^{31}P\{^1H\}$-NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 37.8 (d, $J_{RhP} = 170.3$, Rh(*P*Cy_3)), 33.7 (d, $^2J_{RhP} = 7.0$, CH(*P*Cy_3)). $^{13}C\{^1H\}$-NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 186.8 and 185.7 (both s, *C*O of acac), 100.3 (s, *C*H of acac), 75.1 (d, $^2J_{PC} = 18.0$, =*C*HCy), 45.8 (d, $^3J_{PC} = 5.1$, *C*H of Cy), 36.7, 33.2, 31.0 and 29.9 (all s, *C*H_2 of Cy), 34.4 and 32.5 (both br, *C*H of PCy_3), 33.7 (d, $J_{PC} = 40.0$, *C*H of PCy_3), 30.2, 30.1, 28.7, 28.6, 28.34, 28.25, 28.2, 28.1, 27.6, 27.4, 27.3, 27.1, 27.0, 26.9, 26.7, 26.3, 26.2 and 25.8 (all s, *C*H_2 of PCy_3), 28.0 (d, $J_{PC} = 5.9$, *C*H_3 of acac), 26.6 (s, *C*H_3 of acac), 16.6 (ddd, $J_{PC} = 55.7$, $J_{RhC} = 16.1$, $^2J_{P'C} = 2.7$, *C*H(PCy_3)).

3.3. Preparation of [Rh(acac){η²-(E)-CH(PCy₃)=CHPh}(PCy₃)]BF₄ (5)

This compound was prepared as described for **4**, using **2** (238.2 mg, 0.25 mmol) as starting material:

orange–yellow solid. Yield: 190 mg (80%). Anal. Calc. for $C_{49}H_{80}BF_4O_2P_2Rh$: C, 61.76; H, 8.46%. Found: C, 61.39; H, 8.33. IR (KBr, cm^{-1}): $\nu(CO)_{acac}$ 1572 and 1529, $\nu(BF_4)$ 1054. ^{1}H-NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.5–7.2 (m, 5H, Ph), 5.61 (s, 1H, C*H* of acac), 5.47 (dd, 1H, $J_{HH} = J_{PH} = 13.5$, =C*H*Ph), 2.6–1.2 (m, 66H, C_6H_{11}), 2.12 and 2.03 (both s, 6H, CH_3 of acac), signal of C*H*(PCy_3) is localized in the ^{1}H-COSY spectrum at 2.20 ppm. $^{31}P\{^1H\}$-NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 40.1 (d, $J_{RhP} = 169.3$, Rh(*P*Cy_3)), 33.9 (d, $^2J_{RhP} = 6.2$, CH(*P*Cy_3)). $^{13}C\{^1H\}$-NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 187.4 and 185.6 (both s, *C*O of acac), 141.8 (d, $^3J_{PC} = 6.8$, $C_{ipso\text{-}Ph}$), 129.7 (s, $C_{o,m\text{-}Ph}$), 127.7 (s, $C_{p\text{-}Ph}$), 100.3 (s, *C*H of acac), 62.2 (d, $^2J_{PC} =$ 15.7, =*C*HPh), 34.3 (d, $J_{PC} = 40.3$, *C*H of PCy_3), 33.0 (d, $J_{PC} = 21.6$, *C*H of PCy_3), 30.4, 29.9, 28.6, 28.1, 27.7, 27.5, 27.4, 27.3, 26.7, 26.4 and 25.9 (all s, CH_2 of PCy_3), 28.0 (s, CH_3 of acac), 26.8 (d, $J_{PC} = 6.0$, CH_3 of acac), 16.8 (ddd, $J_{PC} = 58.0$, $J_{RhC} = 18.8$, $^2J_{P'C} = 3.8$, *C*H(PCy_3)).

3.4. Preparation of [Rh(acac){η^2-(E)-CH(PCy_3)=CH_2}(PCy_3)]BF_4 (6)

A yellow solution of **3** (201.6 mg, 0.23 mmol) in 10 ml of dichloromethane was stirred under reflux for 10 h. The resulting dark brown solution was concentrated to dryness, and the oil obtained was cromatographed on Al_2O_3 (neutral, activity grade I, column length 15 cm). With acetone a yellow fraction was eluted from which the solvent was removed in vacuo. The residue was washed with diethyl ether to give compound **6** as a yellow solid: yield: 30 mg (15%). Anal. Calc. for $C_{43}H_{76}BF_4O_2P_2Rh$: C, 58.91; H, 8.74%. Found: C, 58.36; H, 8.51. IR (KBr, cm^{-1}): $\nu(CO)_{acac}$ 1570 and 1524, $\nu(BF_4)$ 1056. ^{1}H-NMR (300 MHz, CD_2Cl_2, 293 K): δ 5.54 (s, 1H, C*H* of acac), 3.30 (dd, 1H, $J_{HH} =$ $J_{PH} = 13.3$, =CH_2), 3.05 (dd, 1H, $J_{PH} = 20.4$, $J_{HH} = 7.5$, =CH_2), 2.5–1.2 (m, 66H, C_6H_{11}), 2.05 and 1.25 (both s, 6H, CH_3 of acac), signal of C*H*(PCy_3) is localized in the ^{1}H-COSY spectrum at 1.75 ppm. $^{31}P\{^1H\}$-NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 44.1 (d, $J_{RhP} = 163.9$, Rh(*P*Cy_3)), 35.6 (d, $^2J_{RhP} = 5.2$, CH(*P*Cy_3)).

3.5. Preparation of [(E)-CyHC=CHPCy_3]BF_4 (8)

A stream of CO was passed through a solution of compound **4** (200.0 mg, 0.21 mmol) in 10 ml of dichloromethane for 2 min. A change from yellow to light yellow occurred almost instantaneously. Then the solvent was removed and the addition of diethyl ether caused the precipitation of a white solid, which was washed with diethyl ether. The ether solution was concentrated in vacuo to produce a residue, which was identified as Rh(acac)(CO)(PCy_3)[5] (**7**). The white solid was identified as **8**. Yield: 92 mg (96%). Anal. Calc. for $C_{26}H_{46}BF_4P$: C, 65.55; H, 9.73%. Found: C, 65.23; H, 9.32. IR (KBr, cm^{-1}): $\nu(BF_4)$ 1053. ^{1}H-NMR (300 MHz, CD_2Cl_2, 293 K): δ 6.67 (ddd, 1H, $J_{HH} = J_{PH} =$ 17.6, $J_{HH'} = 6.5$, C*H*(PCy_3)), 5.54 (dd, 1H, $J_{HH} =$ $J_{PH} = 17.6$, =C*H*Cy), 2.5–1.1 (m, 44H, C_6H_{11}). $^{31}P\{^1H\}$-NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 25.7 (s). $^{13}C\{^1H\}$-NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 166.0 (s, =*C*HCy), 101.5 (d, $J_{PC} = 74.3$, *C*H(PCy_3)), 44.3 (d, $^3J_{PC} = 13.7$, *C*H of Cy), 30.4 (d, $J_{PC} = 43.2$, *C*H of PCy_3), 31.8, 27.0, 26.9, 26.7, 26.1, and 25.8 (all s, CH_2 of Cy and PCy_3).

3.6. Preparation of [(E)-HPhC=CHPCy_3]BF_4 (9)

This compound was prepared as described for **8**, using compound **5** (95.2 mg, 0.10 mmol) as starting material: white solid. Yield: 46 mg (98%). Anal. Calc. for $C_{26}H_{40}BF_4P$: C, 66.39; H, 8.57%. Found: C, 66.55; H, 8.91. IR (KBr, cm^{-1}): $\nu(BF_4)$ 1051. ^{1}H-NMR (300 MHz, CD_2Cl_2, 293 K): δ 7.7–7.5 (m, 5H, Ph), 7.42 (dd, 1H, $J_{HH} = J_{PH} = 17.4$, =C*H*Ph), 6.27 (dd, 1H, $J_{HH} =$ 17.4, $J_{PH} = 15.9$, C*H*(PCy_3)), 2.6–1.3 (m, 33H, C_6H_{11}). $^{31}P\{^1H\}$-NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 28.0 (s). $^{13}C\{^1H\}$-NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 154.2 (s, =*C*HPh), 134.3 (d, $^3J_{PC} = 16.5$, $C_{ipso\text{-}Ph}$), 132.1, 129.4 and 128.7 (all s, $C_{o,\ m,\ p\text{-}Ph}$), 100.8 (d, $J_{PC} = 77.8$, *C*H(PCy_3)), 30.7 (d, $J_{PC} = 43.1$, *C*H of PCy_3), 27.0, 26.91, 26.97, 26.6 and 25.8 (all s, CH_2 of PCy_3).

3.7. Preparation of [(E)-H_2C=CHPCy_3]BF_4 (10)

This compound was prepared as described for **8**, using compound **6** (30.0 mg, 0.036 mmol) as starting material: white solid. Yield: 12 mg (86%). Anal. Calc. for $C_{20}H_{36}BF_4P$: C, 60.92; H, 9.20%. Found: C, 60.85; H, 9.32. IR (KBr, cm^{-1}): $\nu(BF_4)$ 1042. ^{1}H-NMR (300 MHz, CD_2Cl_2, 293 K): δ 6.82 (part A of a ABCX system, 1H, $J_{PH} = 41.7$, =CH_2), 6.53 (part BC of a ABCX system, 2H, $J_{PH} = 19.5$, =CH_2 and C*H*(PCy_3)), 2.7–1.1 (m, 33H, C_6H_{11}). $^{31}P\{^1H\}$-NMR (121.4 MHz, CD_2Cl_2, 293 K): δ 27.2 (s). $^{13}C\{^1H\}$-NMR (75.4 MHz, CD_2Cl_2, 293 K): δ 143.3 (s, =*C*HPh), 115.0 (d, $J_{PC} =$ 69.6, *C*H(PCy_3)), 30.2 (d, $J_{PC} = 42.2$, *C*H of PCy_3), 27.1, 27.0, 26.9, 26.7 and 25.9 (all s, CH_2 PCy_3).

Compounds **8**–**10** were also obtained by the following method: solutions of complex Rh(acac)(η^2-C_8H_{14})(PCy_3)[5] (100.8 mg, 0.17 mmol) in toluene were treated with one equivalent of HC≡CR (R = Cy, Ph, or $SiMe_3$) in the presence of equimolecular amounts of PCy_3 (47.7 mg, 0.17 mmol). After stirring at 50°C until white solids precipitated (about 30 min), the solvent was removed and the residues were dissolved in dichloromethane and treated with one equivalent of $HBF_4 \cdot OEt_2$ (26 μl, 0.19 mmol). The solvent was removed and after addition of diethyl ether yellow solids were precipitated, which were washed with diethyl

Table 2
Crystal data and data collection and refinement for [Rh(acac){η^2-(*E*)-CH(PCy_3)=CHCy}(PCy_3)]BF_4 (**4**)

Empirical formula	$C_{449}H_{86}BF_4O_2P_2Rh \cdot CH_2Cl_2$
Molecular weight	1043.76
Color and habit	Orange, prismatic block
Crystal size (mm)	$0.37 \times 0.29 \times 0.26$
Symmetry	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	11.4093(14)
b (Å)	13.0571(17)
c (Å)	18.797(3)
α (°)	96.989(11)
β (°)	94.308(9)
γ (°)	109.110(9)
V (Å^{-3})	2606.5(6)
Z	2
$D_{calc.}$ (g cm^{-3})	1.330
Diffractometer	Siemens-STOE
λ(Mo–K$_\alpha$) (Å); technique	0.71073; bisecting geometry
Monochromator	Graphite oriented
μ (mm^{-1})	0.543
Scan type	$\omega/2\theta$
2θ range (°)	$3 \leq 2\theta \leq 50°$
Temperature (K)	173.0(2)
No. of data collected	11730
No. of unique data	9216
No. of parameters refined	564
wR^a (all data)	0.1526
R^b [observed data, $I > 2\sigma(I)$]	0.0580
Goodness-of-fit[c]	1.058

[a] $wR(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.
[b] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[c] $S = \{\Sigma[\omega(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, where n is the number of reflections and p the number of parameters.

ether. This solid was dissolved in dichoromethane and stirred under reflux for 10 h. Then, a stream of CO was passed through the solutions for 2 min and the solvent was removed, the addition of diethyl ether caused the precipitation of white solids, which were washed with diethyl ether. From the ether solution was isolated the complex Rh(acac)(CO)(PCy_3) (**7**), [21] and the white solids were identified as [(*E*)-RHC=CHPCy_3]BF_4 [R = Cy (**8**), Ph (**9**) or H (**10**)] (yields about 85%).

4. Crystal data for 4

Crystals suitable for the X-ray diffraction study were obtained by slow diffusion of pentane into a saturated solution of **4** in dichloromethane. A summary of crystal and refinement data is reported in Table 2. Data were collected on a Siemens-Stoe diffractometer by using oil-coated rapidly cooled crystal of approximate dimensions $0.37 \times 0.29 \times 0.26$ mm mounted directly from solution. Of a total of 11730 reflections collected by $\omega/2\theta$ scans ($3 \leq 2\theta \leq 50°$), 9216 were unique. Data were corrected for absorption (psi-scan method); minimum and maximum transmission factors, 0.185 and 0.227, respectively. The structure was solved by direct methods [24] and refined by full-matrix least-squares on F^2 [25]. After isotropic refinement, the presence of high electron density residuals in the proximity of the olefinic carbons [C(1) and C(2)] together with the impossibility of a proper refinement of an anisotropic model for these two atoms suggested the presence of a situation of static disorder affecting fundamentally these two carbon atoms. The molecule disorder was carefully stepwise modeled after anisotropic refinement of all non-hydrogen non-disordered atoms. Two different positions were included for each olefinic carbon [C(1a) and C(2a), and C(1b) and C(2b)], and were refined with complementary occupancy factors, a common fixed displacement parameter, and feeble geometric restrains (DFIX commands applied to Rh–C(1)/C(2), P–C(1), C(1)–C(2) and C(2)–C(3) bond distances). Geometric data for these restrains were obtained from a detailed search of related complexes in the CSD file; distances used were 2.11, 1.77, 1.39 and 1.48 Å, respectively (more details in supplementary material). All disordered atoms were refined isotropically and hydrogen atoms were included in calculated positions. A crystallization solvent molecule (dichloromethane) was also detected and included in the refinement. Final agreement factors were R_1 0.0580 [$I = 2\sigma(I)$, 7908 reflections] and wR_2 0.1526 (all data).

5. Supporting information available

A listing of full experimental details of the structure determination, crystal data, atomic coordinates, thermal parameters, bond distances and angles for **4** (CIF format, 15 pages). Ordering information is given on any current masthead page.

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