Vinylidene Transition-Metal Complexes, 48[+]
A Novel Route to Cationic Four-Coordinate Rhodium(I) Complexes with Rh=C Bonds

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Dedicated to Professor Michael F. Lappert on the occasion of his 70th birthday

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The complex $[Rh(acetone)_2(C_8H_{14})_2]PF_6$ (**2**), which is prepared from $[RhCl(C_8H_{14})_2]_2$ and $AgPF_6$ in acetone, reacts with P*i*Pr$_3$ to afford the PF_6 salt **3** of the cation $[Rh(acetone)_2(PiPr_3)_2]^+$ containing the ketone and phosphane ligands in *cis* dispositions. Treatment of **3** with MeC≡CPh leads to the displacement of one acetone ligand and the formation of the corresponding π-alkyne complex **4**. In contrast, from **3** and terminal alkynes such as HC≡CC_6H_4–4-Me or HC≡CCPh_2OH the cationic vinylidenerhodium(I) compounds **5** and **6** are obtained. The latter, with C=CHCPh_2OH as the ligand, is rather labile and even at room temperature eliminates water to give the cationic four-coordinate rhodium allenylidene **7**. The molecular structure of this compound has been determined by X-ray crystallography. In the presence of pyridine or ammonia, the acetone ligand of **5** and **7** is readily displaced and the substitution products **8**–**10** are formed almost quantitatively. Anions such as acetate or hydroxide also displace the ketone unit of **7** and yield the neutral allenylidenerhodium(I) complexes *trans*-$[RhX(=C=C=CPh_2)(PiPr_3)_2]$ with X = OAc (**11**) and OH (**12**).

Following the synthesis of the first square-planar allenylidenerhodium(I) complex *trans*-[RhCl(=C=C=CPh_2)(P*i*Pr$_3$)$_2$],[1] we have recently shown that rhodium allenylidenes of this particular type are useful tools for the generation of metal bound species that are hardly accessible by other preparative routes.[2] After having characterized a series of compounds of the general composition *trans*-[RhX(=C=C=CRR′)(P*i*Pr$_3$)$_2$] (X = Cl, I, CN, OH, OPh, OAc, OTos),[3] we became interested to find out whether also four-coordinate *cationic* allenylidenerhodium(I) complexes $[Rh(L)(=C=C=CRR')(PiPr_3)_2]^+$ (L = two-electron donor ligand) can be obtained. Recent attempts from our laboratory with the aim to prepare the cation *trans*-$[Rh(=C=C=CPh_2)_2(PiPr_3)_2]^+$ unexpectedly led, via a novel C–C coupling, to the formation of two isomeric hexapentaenerhodium(I) compounds of which the isomer having the polyene coordinated in an unsymmetrical fashion is the thermodynamically more stable.[4] However, after we found that carbonyl-, ethene- and even vinylidenerhodium derivatives such as *trans*-$[Rh(py)(L)(PiPr_3)_2]^+$ and *trans*-$[Rh(NH_3)(L)(PiPr_3)_2]^+$ (L = CO, C_2H_4, C=CHR) are accessible and, with BF_4^- or PF_6^- as counterion, stable under ambient conditions,[5] we felt encouraged to prepare also the corresponding species with L = C=C=CRR′.

In this paper we report the synthesis of complexes *trans*-$[Rh(L')(=C=C=CPh_2)(PiPr_3)_2]PF_6$, the first X-ray crystal structure analysis of a *cationic* rhodium compound with Rh=C=C=CPh_2 as a molecular unit, and an alternative preparative route to neutral species with X^- instead of L′ as ligands coordinated to rhodium(I).

Precursors of the General Composition *cis*-$[Rh(acetone)_2(L)_2]^+$

The procedure which we recently used for the synthesis of the above-mentioned compounds *trans*-[Rh(py)(L)-(P*i*Pr$_3$)$_2$]X with L = CO, C_2H_4 and C=CHR[5] turned out to be not the method of choice for L = C=C=CPh_2. Treatment of the mixture of $[Rh(\eta^3\text{-}C_3H_5)(PiPr_3)_2]$ and $[pyH]BF_4$ with the propargylic alcohol HC≡CCPh_2OH in acetone at room temperature led, within a short period of time, to the formation of a deep red solution from which a red, moderately air-sensitive solid was obtained after removal of the solvent. According to the NMR spectra it consisted mainly of our target, the allenylidene complex *trans*-$[Rh(py)(=C=C=CPh_2)(PiPr_3)_2]BF_4$ but also contained some impurities. Despite several attempts these could not be completely separated from the dominating species.

Therefore, we developed an alternative route to the cations $[Rh(L')(=C=C=CPh_2)(PiPr_3)_2]^+$ by using the dimeric bis(cyclooctene)rhodium(I) complex **1** as the starting material. If a suspension of **1** in acetone is treated with a solution of $AgPF_6$ in the same solvent at 0°C, a brownish yellow solution is formed from which the PF_6 salt **2** can be isolated in 74% yield. The yellow microcrystalline solid

[+] Part 47: J. Wolf, W. Stüer, C. Grünwald, O. Gevert, M. Laubender, H. Werner, *Eur. J. Inorg. Chem.* **1998**, 1827–1834.

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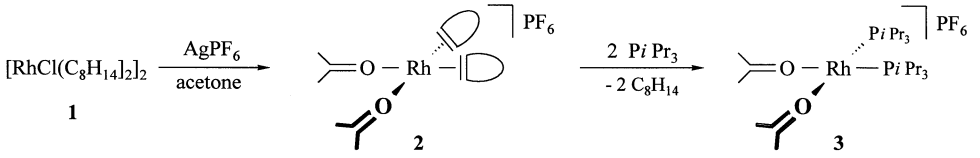
(which decomposes at 58°C) has been characterized by elemental analysis, conductivity measurements and spectroscopic techniques. Although the ^{1}H-NMR data cannot decide whether the structure proposed in Scheme 1 is correct, in analogy to the related cation $[Rh(acetone)_2(C_8H_{12})]^+$ the *cis* arrangement of the acetone ligands seems most likely.[6] the ^{13}C-NMR spectrum at δ = 75.0 (≡CPh) and 64.5 (≡CMe) and also the IR band at 1885 cm^{-1} assigned to ν(C≡C). The Rh−P coupling of the single ^{31}P-NMR resonance of **4** (116.3 Hz) is considerably smaller than that of **3** (204.9 Hz) which also supports the *trans* position of the two P*i*Pr$_3$ groups.



Scheme 1

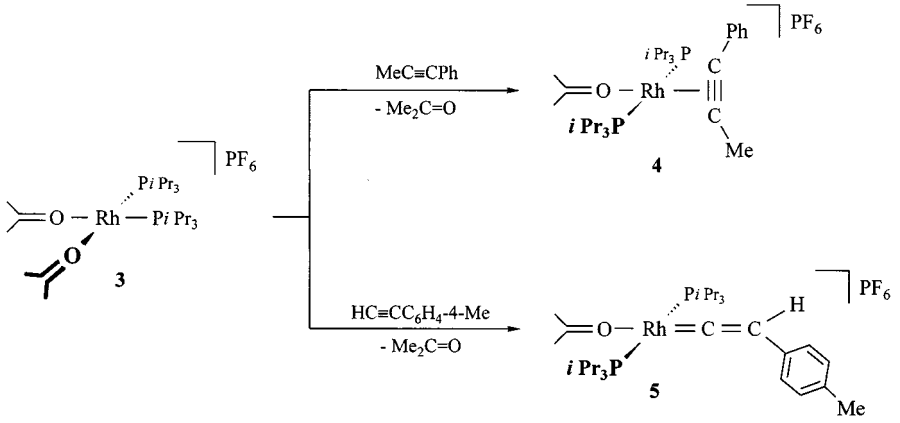
After the isolation of the cationic compound **2** the interesting question arose whether the acetone or the cyclooctene ligands are more weakly bound to the metal center. The experiment revealed that upon treatment of a suspension of **2** in ether/acetone with two equivalents of P*i*Pr$_3$ the olefinic groups are preferentially displaced. Upon recrystallization from acetone/diethyl ether the bis(phosphane) complex **3** was isolated as a violet air-sensitive solid in 98% yield. The ^{31}P-NMR spectrum of **3** displays a doublet at δ = 60.3 with a large Rh−P coupling that is typical for a *cis*-disposed $[Rh(PiPr_3)_2]$ unit.[7]

Cationic Complexes with Rh=C Bonds

The bis(acetone)rhodium(I) complex **3** proved to be an ideal precursor for the preparation of cationic vinylidene and allenylidene rhodium(I) derivatives. In order to test whether one of the metal bound ketones can be selectively replaced by an alkyne ligand, we first carried out the reaction of **3** with MeC≡CPh. It leads to the alkyne complex **4** (Scheme 2) as an orange air-sensitive solid in 75% yield. In contrast to **3**, the ^{1}H-NMR spectrum of **4** displays two resonances for the CH_3 protons of the isopropyl moieties, the virtual coupling of both points to a *trans* arrangement of the phosphane ligands.[8] Typical features of the π-bonded unsymmetrical alkyne unit are the two signals in

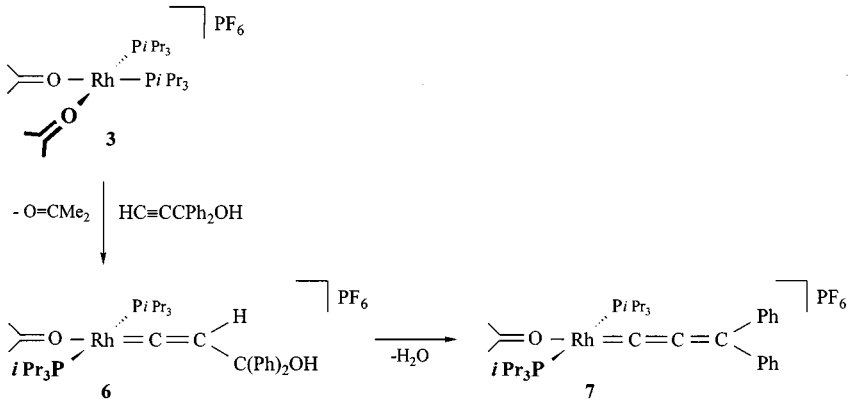
Treatment of compound **3** with HC≡CC_6H_4−4-Me as a representative of a *terminal* acetylene derivative affords instead of an alkyne complex the vinylidene isomer **5** almost quantitatively. If the 1-alkyne is added to a solution of **3** in diethyl ether/acetone at −78°C, a rapid change of color from violet to orange takes place indicating (see: compound **4** is orange) that in the initial step the cation $[Rh(O{=}CMe_2)(HC{\equiv}CR)(PiPr_3)_2]^+$ (R = *p*-tolyl) is probably formed. However, even at −78°C after a few minutes the color of the solution changes again to violet and a violet solid precipitates. Upon warming to room temperature, removal of the solvent and recrystallization of the residue from acetone/diethyl ether the product was obtained in 95% yield. In agreement with the spectroscopic data of other vinylidenerhodium(I) complexes,[5][9][10] the ^{13}C-NMR spectrum of **5** displays two signals (both doublets of triplets) in the low-field region at δ = 309.3 and 113.3 which are assigned to the α- and β-carbon atoms of the vinylidene ligand, respectively.

The course of the reaction of the bis(acetone)rhodium(I) compound **3** with the propargylic alcohol HC≡CCPh_2OH in diethyl ether/acetone is at least in the initial stage quite similar to that of **3** with HC≡CC_6H_4−4-Me (see Scheme 3). If the solution, after it was stirred at −78°C for 2 min and then warmed to 0°C, was quickly worked up an orange-red solid was isolated which based on the NMR spec-



Scheme 2

tra consists of a mixture of the functionalized vinylidene compound **6** and the allenylidene complex **7**, the first being the dominating species. Attempts to obtain **6** as an analytically pure solid failed since the crude product upon dissolution, e.g., in acetone or dichloromethane smoothly converted completely to **7**. In acetone at room temperature, the formation of **7** is completed in ca. 15 min. Removal of the solvent and recrystallization of the residue from acetone/diethyl ether gave orange crystals which were characterized by elemental analysis, conductivity measurements and spectroscopic means. In contrast to the neutral compounds *trans*-[RhCl{=C=C=C(Ph)R}(P*i*Pr$_3$)$_2$],[1][11] in the ^{13}C-NMR spectrum of **7** the resonances of the α-and β-carbon atoms of the Rh=C=C=C moiety could not be observed, even if a saturated solution of **7** in [D$_6$]acetone was used. The signal of the respective γ-carbon atom appears at δ = 150.8 as a singlet.



Scheme 3

In order to confirm the structure proposed for **7** [which is the first *cationic* allenylidenerhodium(I) complex], an X-ray crystal structure analysis was carried out. The result is shown in Figure 1. The coordination geometry around the rhodium center is almost exactly square-planar with bond angles P1−Rh−P2 and O1−Rh−C1 of 176.78(2)° and 178.67(9)°. The Rh−C1 distance is 1.822(2) Å and thus somewhat shorter than in *trans*-[RhCl{=C=C=C(Ph)C$_6$H$_4$−2-Me}(P*i*Pr$_3$)$_2$] [1.855(5) Å].[11] The shortening is surprising insofar as in *cationic* rhodium(I) species the degree of π-back bonding should be smaller compared to structurally related *neutral* derivatives. The bond length C1−C2 [1.267(3) Å] is slightly longer and the bond length C1−C3 [1.343(3) Å] slightly shorter than in the above-mentioned allenylidene(chloro)rhodium(I) compound [C1−C2 = 1.239(8) Å, C2−C3 = 1.370(9) Å], indicating that for the bonding situation the resonance structure **B** (Figure 2) is less important in the cationic complex than in the neutral analog. The Rh−C−C−C chain is nearly linear, with only a slight bending at the carbon atom C2. The planes of the two phenyl groups are not perpendicular to each other like the aryl rings in *trans*-[RhCl{=C=C=C(Ph)C$_6$H$_4$−2-Me}(P*i*Pr$_3$)$_2$] but form a dihedral angle of 68.31(8)°. The atoms O1, C34, C35 and C36 of the acetone ligand lie in a plane which is orthogonal to the central plane [P1, P2, Rh, O1, C1] and we assume that this minimizes the steric repulsion between the O=CMe$_2$ and the P*i*Pr$_3$ ligands.

Ligand Substitution Reactions of Compounds 5 and 7

The observation that in the starting material **3** one of the ketone ligands could be easily replaced by an alkyne, vinylidene or allenylidene unit, led us to try to substitute also the remaining acetone moiety in the cations *trans*-[Rh(O=CMe$_2$)(L)(P*i*Pr$_3$)$_2$]$^+$ by an olefin, alkyne or even a more typical π-acceptor ligand such as CO. However, all these attempts failed. Nevertheless, the displacement of acetone in the vinylidene and allenylidene complexes **5** and **7** can be achieved with *N-donors* such as pyridine or ammonia under very mild conditions. After workup the substitution products **8**−**10** were isolated in 85−90% yield (Scheme 4). The properties of the pyridine- and ammonia-containing cationic compounds are very similar to those of the acetone derivatives **5** and **7** and thus deserve no further comment. It should be mentioned, however, that since for the preparation of **10** aqueous ammonia was used as the substrate, the C=C=CPh$_2$ ligand is *not* attacked by OH$^-$ or H$_2$O as a nucleophile as was observed with a variety of cationic *six-coordinate* allenylidenemetal complexes.[12] The ^{13}C-NMR spectrum of **9** displays the three expected signals for the α-, β- and γ-carbon atoms of the Rh−C−C−C chain at δ = 270.4, 229.6 and 150.9, of which those at lowest fields (assigned to α-C and β-C) are split into doublets of triplets.

In order to illustrate that the acetone ligand of compound **7** can also be displaced by coordinating anions, the known acetato- and hydroxorhodium(I) derivatives **11** and **12** were prepared by this route (Scheme 5). From **7** as the starting material and with CH$_3$CO$_2$Na or KOH as the substrate, the isolated yield of **11** and **12** is ca. 80%. The neutral allenylidene complex **12** with OH in *trans* position to the C$_3$Ph$_2$ unit was originally prepared from the chloro compound *trans*-[RhCl(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$] and KO*t*Bu in C$_6$H$_6$/*t*BuOH and upon treatment with acetic acid trans-

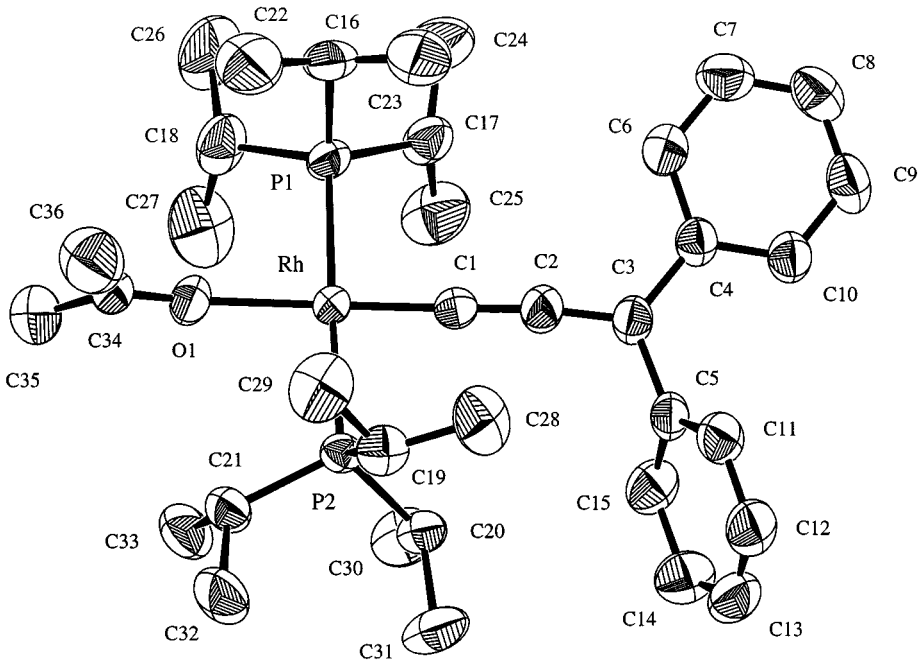


Figure 1. Molecular structure (ORTEP plot) of the cation of compound **7**; the hydrogen atoms are omitted for clarity; selected bond lengths (Å) and angles [°]: Rh−P1 2.3557(6), Rh−P2 2.3513(6), Rh−O1 2.078(2), Rh−C1 1.822(2), C1−C2 1.267(3), C2−C3 1.343(3), C3−C4 1.472(3), C3−C5 1.491(3), O1−C34 1.216(3); P1−Rh−P2 176.78(2), P1−Rh−O1 90.08(5), P1−Rh−C1 90.11(6), P2−Rh−O1 92.41(5), P2−Rh−C1 87.45(6), O1−Rh−C1 178.67(9), Rh−C1−C2 178.1(2), C1−C2−C3 172.6(2), C2−C3−C4 122.8(2), C2−C3−C5 118.2(2), O1−C34−C35 119.1(3), O1−C34−C36 122.4(3)

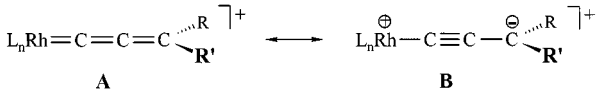
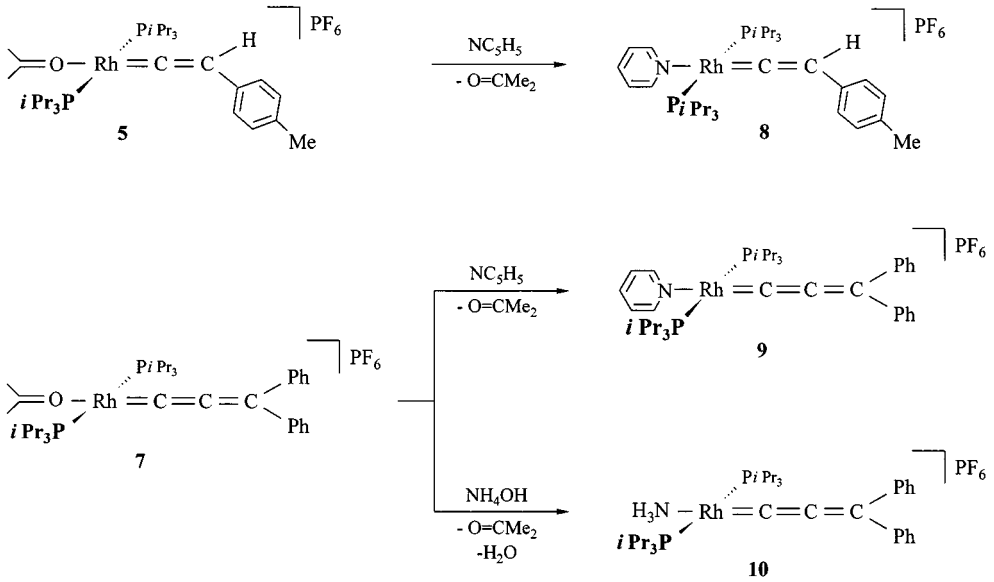


Figure 2. Resonance structures for allenylidenemetal complexes

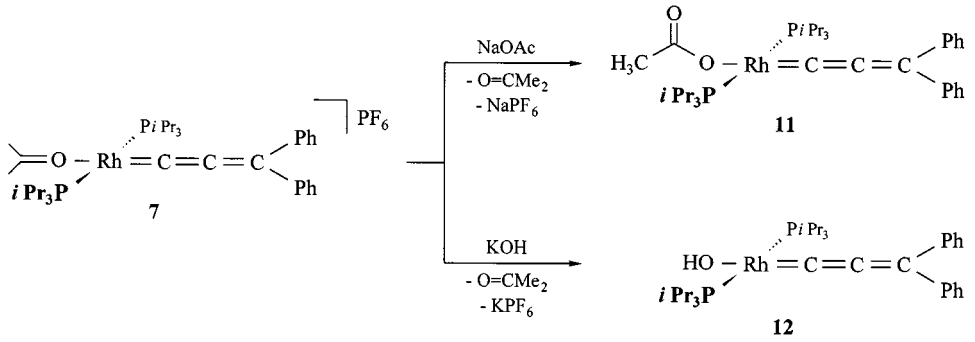
formed to the acetato derivative.[2b][3] Some exploratory studies indicate that it is possible to substitute the acetone ligand of **7** also by C-nucleophiles such as $CH(CN)_2^-$ or CN^- and thus the reaction of **7** with X^- could be an alternative route for the preparation of allenylidenerhodium(I) complexes of the general composition *trans*-[RhX(=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$].

Concluding Remarks

The present investigation has shown that in addition to the well-known neutral rhodium allenylidenes *trans*-[RhX(=C=C=CRR′)(P*i*Pr$_3$)$_2$] structurally related *cationic* complexes *trans*-[Rh(=C=C=CPh$_2$)(L)(P*i*Pr$_3$)$_2$]$^+$ with L = acetone, pyridine or ammonia are also accessible. The



Scheme 4



Scheme 5

method of choice for preparing these compounds (as the PF_6 salts) is the "alkynol route", which was developed by Selegue[13] and later used by us[3][14] and several other groups as well.[15][16] The most remarkable feature is that the starting material **3** (which despite the lability of the acetone-metal bonds has been isolated and fully characterized) reacts with terminal alkynes HC≡CR, including the propargylic alcohol $HC{\equiv}CCPh_2OH$, almost instantaneously to give cationic vinylidene compounds with Rh=C=CHR as the central unit. Since all attempts to detect the corresponding *alkyne*rhodium(I) derivatives assumed to be formed in the initial step failed, we conclude that the metal-assisted isomerization of HC≡CR to C=CHR takes place considerably *faster* in the coordination sphere of a four-coordinate *cationic* than of a related *neutral* d^8 metal center. With regard to the subsequent conversion of the Rh=C=$CHCPh_2OH$ to the Rh=C=C=CPh_2 unit we note that in the case of the *cationic* species the elimination of water also occurs much more readily than for the analogous neutral derivative and that neither the presence of Al_2O_3 nor of Brønsted acids HX is necessary for this process.

Experimental Section

General: All operations were carried out under argon using Schlenk techniques. The starting material $[RhCl(C_8H_{14})_2]_2$ (**1**)[17] and the propargylic alcohol $HC{\equiv}CCPh_2OH$[18] were prepared as described in the literature. The other alkynes were commercial products from ABCR and Aldrich. − IR: Perkin-Elmer 1420. − NMR: Bruker AC 200 and AMX 400 [dvt = doublet of virtual triplets; $N = {}^3J(PH) + {}^5J(PH)$ or ${}^2J(PC) + {}^4J(PC)$, respectively]. − Conductivity measurements in nitromethane with a Schott Konduktometer CG 851. − Melting and decomposition points determined by DTA.

1. Preparation of *cis*-[Rh(O=CMe_2)$_2$(C_8H_{14})$_2$]PF_6 (2): A suspension of 404 mg (0.56 mmol) of **1** in 30 mL of acetone was treated dropwise at 0°C with a solution of 276 mg (1.09 mmol) of $AgPF_6$ in 2 mL of acetone. Under continuous stirring the reaction mixture was slowly warmed to room temp. (ca. 20 min) and after it was stored for 1 h the solution was filtered. The filtrate was concentrated to ca. 5 mL in vacuo and 20 mL of diethyl ether was added. A yellow microcrystalline solid precipitated which was separated from the mother liquor, washed three times with 2-mL portions of diethyl ether and dried; yield 471 mg (74%); dec. temp. 58°C; Λ = 80 $cm^2\Omega^{-1}mol^{-1}$. − ^1H NMR (200 MHz, CD_3NO_2): δ = 2.97 (m, 4 H, =CH of C_8H_{14}), 2.42 (s, 12 H, O=CMe_2), 2.25, 1.62, 1.42 (all m, 24 H, CH_2 of C_8H_{14}). − $C_{22}H_{40}F_6O_2PRh$ (584.4): calcd. C 45.21, H 6.90; found C 44.98, H 6.61.

2. Preparation of *cis*-[Rh(O=CMe_2)$_2$($PiPr_3$)$_2$]PF_6 (3): A suspension of 90 mg (0.15 mmol) of **2** in 10 mL of diethyl ether/acetone (9:1) was treated at −78°C with 62 μL (0.31 mmol) of P*i*Pr_3. Under continuous stirring the reaction mixture was slowly warmed to room temp. (ca. 30 min) which led to a change of color from yellow to dark violet. Moreover, a small amount of a violet solid precipitated. The solution was concentrated to ca. 1 mL in vacuo and then 10 mL of diethyl ether was added. After the mixture was stored for 2 h, the violet precipitate was separated from the mother liquor, washed three times with 2-mL portions of diethyl ether and dried; yield 103 mg (98%); dec. temp. 83°C; Λ = 110 $cm^2\Omega^{-1}mol^{-1}$. − IR (CH_2Cl_2): $\tilde{\nu}$ = 1705, 1653 cm^{-1} (C=O). − ^1H NMR (200 MHz, $(CD_3)_2CO$): δ = 2.08 (s, 12 H, O=CMe_2), 2.03 (m, 6 H, PC*H*CH_3), 1.40 [dd, J(PH) = 13.1, J(HH) = 7.3 Hz, 36 H, PCHC*H*$_3$]. − ^{31}P NMR (81.0 MHz, $(CD_3)_2CO$): δ = 60.3 [d, J(RhP) = 204.9 Hz]. − $C_{24}H_{54}F_6O_2P_3Rh$ (684.5): calcd. C 42.11, H 7.95; found C 42.62, H 7.84.

3. Preparation of *trans*-[Rh(O=CMe_2)(MeC≡CPh)($PiPr_3$)$_2$]PF_6 (4): A suspension of 103 mg (0.15 mmol) of **3** in 10 mL of diethyl ether/acetone (9:1) was treated at −78°C with 19 μL (0.15 mmol) of MeC≡CPh. After the reaction mixture was slowly warmed to room temp. (ca. 30 min), it was worked up analogously as described for **3**. Orange microcrystalline solid; yield 84 mg (75%); dec. temp. 44°C; Λ = 77 $cm^2\Omega^{-1}mol^{-1}$. − IR (CH_2Cl_2): $\tilde{\nu}$ = 1885 (C≡C), 1707 cm^{-1} (C=O). − ^1H NMR (400 MHz, $(CD_3)_2CO$): δ = 7.68 (m, 5 H, C_6H_5), 2.50 (br. s, 3 H, ≡CMe), 2.08 (s, 6 H, O=CMe_2), 1.94 (m, 6 H, PC*H*CH_3), 1.37 [dvt, N = 13.5, J(HH) = 7.0 Hz, 18 H, PCHC*H*$_3$], 1.12 [dvt, N = 13.1, J(HH) = 6.8 Hz, 18 H, PCHC*H*$_3$]. − ^{13}C NMR (100.6 MHz, $(CD_3)_2CO$): δ = 206.2 (s, O=*C*Me_2), 130.9, 129.1, 128.8, 127.7 (all s, C_6H_5), 75.0 (br. m, ≡*C*Ph), 64.5 (br. m, ≡*C*Me), 30.4 (s, O=C*C*H_3), 23.5 (vt, N = 17.7 Hz, P*C*HCH_3), 20.8, 19.6 (both s, PCH*C*H_3), 13.2 (s, ≡C*C*H_3). − ^{31}P NMR (81.0 MHz, $(CD_3)_2CO$): δ = 33.9 [d, J(RhP) = 116.3 Hz]. − $C_{30}H_{56}F_6OP_3Rh$ (742.6): calcd. C 48.52, H 7.60; found C 48.42, H 7.33.

4. Preparation of *trans*-[Rh(O=CMe_2)(=C=CHC_6H_4−4-Me)($PiPr_3$)$_2$]PF_6 (5): A suspension of 103 mg (0.15 mmol) of **3** in 10 mL of diethyl ether/acetone (9:1) was treated at −78°C with 19 μL (0.15 mmol) of $HC{\equiv}CC_6H_4$−4-Me. A rapid change of color from violet to orange occurred which after ca. 5 min was followed by a reverse change of color from orange to violet. Upon continuous stirring a violet solid precipitated. The reaction mixture was slowly warmed to room temp. (ca. 30 min), and after it was stirred for 8 h the solvent was removed in vacuo. The residue was dissolved in 1 mL of acetone and 20 mL of diethyl ether was added to the

solution. Violet crystals were formed which were washed three times with 2-mL portions of diethyl ether and dried; yield 106 mg (95%); dec. temp. 98°C; Λ = 92 $cm^2\Omega^{-1}mol^{-1}$. – ^1H NMR [400 MHz, $(CD_3)_2CO$]: δ = 6.65 (m, 4 H, C_6H_4), 2.46 (m, 6 H, PC*H*CH_3), 2.30 (s, 3 H, C_6H_4C*H*$_3$), 2.08 (s, 6 H, O=CMe_2), 1.38 [dvt, *N* = 14.0, *J*(HH) = 7.0 Hz, 36 H, PCHC*H*$_3$]; signal of =CH proton probably covered by signal of PCHC*H*$_3$ protons. – ^{13}C NMR [100.6 MHz, $(CD_3)_2CO$]: δ = 309.3 [dt, *J*(RhC) = 61.4, *J*(PC) = 17.6 Hz, Rh=C], 206.3 (s, O=*C*Me_2), 136.2, 129.8, 126.8, 120.6 (all s, C_6H_4), 113.3 [dt, *J*(RhC) = 16.1, *J*(PC) = 6.0 Hz, =CH], 30.3 (s, O=C*C*H_3), 24.3 (vt, *N* = 20.9 Hz, P*C*HCH_3), 20.8 (s, C_6H_4*C*H_3), 20.1 (s, PCH*C*H_3). – ^{31}P NMR (162.0 MHz, $(CD_3)_2CO$): δ = 42.5 [d, *J*(RhP) = 135.1 Hz]. – $C_{30}H_{56}F_6OP_3Rh$ (742.6): calcd. C 48.52, H 7.60; found C 48.56, H 7.62.

5. Generation of *trans*-[Rh(O=CMe_2)(=C=CHCPh_2OH)-($PiPr_3$)$_2$]PF_6 (6): A suspension of 103 mg (0.15 mmol) of **3** in 10 mL of diethyl ether/acetone (9:1) was treated at −78°C with 31 mg (0.15 mmol) of HC≡CCPh_2OH. A rapid change of color from violet to orange occurred. After the solution was stirred for 2 min and then warmed to 0°C, it was concentrated to ca. 1 mL in vacuo. Upon dropwise addition of diethyl ether and subsequently of pentane (ca. 10 mL) an orange-red solid precipitated which was separated from the mother liquor, washed three times with 2-mL portions of diethyl ether, then with 2 mL of pentane, and dried. The ^1H- and ^{31}P-NMR spectra revealed that besides **6** also compound **7** was formed. – IR (CH_2Cl_2): $\tilde{\nu}$ = 3410 (OH), 1642 cm^{-1} (C=C). – ^1H NMR [400 MHz, $(CD_3)_2CO$]: δ = 7.57 (m, 10 H, C_6H_5), 3.05 (br. s, 1 H, OH), 2.41 (m, 6 H, PC*H*CH_3), 2.08 (s, 6 H, O=CMe_2), 1.30 [dvt, *N* = 13.9, *J*(HH) = 6.8 Hz, 36 H, PCHC*H*$_3$]; signal of =CH proton probably covered by signal of PCHC*H*$_3$ protons. – ^{13}C NMR [100.6 MHz, $(CD_3)_2CO$]: δ = 206.3 (s, O=*C*Me_2), 130.2, 128.4, 125.9 (all s, C_6H_5), 117.8 [dt, *J*(RhC) = 17.1, *J*(PC) = 6.0 Hz, =CH], 72.0 (s, *C*Ph_2OH), 30.2 (s, O=C*C*H_3), 23.9 (vt, *N* = 20.7 Hz, P*C*HCH_3), 19.8 (s, PCH*C*H_3); signal of Rh=C not exactly located. – ^{31}P NMR [162.0 MHz, $(CD_3)_2CO$]: δ = 42.3 [d, *J*(RhP) = 135.9 Hz].

6. Preparation of *trans*-[Rh(O=CMe_2)(=C=C=CPh_2)($PiPr_3$)$_2$]PF_6 (7): A suspension of 103 mg (0.15 mmol) of **3** in 10 mL of diethyl ether/acetone (9:1) was treated at −78°C with 31 mg (0.15 mmol) of HC≡CCPh_2OH, and upon warming to room temp. was stirred for 15 h. The solvent was removed, the residue was dissolved in 1 mL of acetone and the solution was layered with 20 mL of diethyl ether. Orange crystals were formed which were separated from the mother liquor, washed three times with 2-mL portions of diethyl ether, once with 2 mL of pentane, and dried; yield 93 mg (76%); dec. temp. 62°C; Λ = 87 $cm^2\Omega^{-1}mol^{-1}$. – IR (KBr): $\tilde{\nu}$ = 1873 cm^{-1} (C=C=C). – ^1H NMR [400 MHz, $(CD_3)_2CO$]: δ = 7.73 (m, 10 H, C_6H_5), 2.49 (m, 6 H, PC*H*CH_3), 2.18 (s, 6 H, O=CMe_2), 1.41 [dvt, *N* = 13.8, *J*(HH) = 7.1 Hz, 36 H, PCHC*H*$_3$]. – ^{13}C NMR [100.6 MHz, $(CD_3)_2CO$]: δ = 206.3 (s, O=*C*Me_2), 150.8 (s, Rh=C=C=*C*), 130.5, 130.3, 126.5 (all s, C_6H_5), 30.2 (s, O=C*C*H_3), 24.8 (vt, *N* = 20.6, P*C*HCH_3), 20.0 (s, PCH*C*H_3); signals of α- and β-carbon atoms of Rh=C=C=C unit not exactly located. – ^{31}P NMR [162.0 MHz, $(CD_3)_2CO$]: δ = 41.8 [d, *J*(RhP) = 132.7 Hz]. – $C_{36}H_{58}F_6OP_3Rh$ (816.7): calcd. C 52.94, H 7.16, Rh 12.60; found C 52.51, H 6.87, Rh 13.00.

7. Preparation of *trans*-[Rh(=C=CHC$_6$H$_4$−4-Me)(py)($PiPr_3$)$_2$]PF_6 (8): A suspension of 111 mg (0.15 mmol) of **5** in 10 mL of diethyl ether was treated at −78°C with an excess (ca. 0.5 mL) of pyridine which led to the precipitation of a red-violet solid. After the reaction mixture was warmed under continuous stirring to room temp. (ca. 30 min), it was stored for 1 h. The red-violet solid was separated from the mother liquor, washed three times with 2-mL portions of diethyl ether and dried; yield 86 mg (91%); dec. temp. 96°C. – ^1H NMR (200 MHz, CD_3NO_2): δ = 8.03 (m, 5 H, NC_5H_5), 6.63 (m, 4 H, C_6H_4), 2.42 (m, 6 H, PC*H*CH_3), 2.28 (s, 3 H, C_6H_4C*H*$_3$), 1.39 [dvt, *N* = 14.0, *J*(HH) = 7.0 Hz, 36 H, PCHC*H*$_3$]; signal of =CH proton probably covered by signal of PCHC*H*$_3$ protons. – ^{13}C NMR (50.3 MHz, CD_3NO_2): δ = 309.2 [dt, *J*(RhC) = 61.2, *J*(PC) = 17.4 Hz, Rh=C], 151.8, 140.5, 136.2, 129.7, 127.3, 126.8, 121.5 (all s, NC_5H_5 and C_6H_4), 114.3 [dt, *J*(RhC) = 16.0, *J*(PC) = 6.1 Hz, =CH], 24.6 (vt, *N* = 20.9 Hz, P*C*HCH_3), 21.1 (s, C_6H_4*C*H_3), 20.1 (s, PCH*C*H_3). – ^{31}P NMR [162.0 MHz, $(CD_3)_2CO$]: δ = 40.3 [d, *J*(RhP) = 134.9 Hz]. $C_{32}H_{55}F_6NP_3Rh$ (763.6): calcd. C 50.33, H 7.62, N 1.83; found C 49.56, H 7.62, N 1.50.

8. Preparation of *trans*-[Rh(=C=C=CPh_2)(py)($PiPr_3$)$_2$]PF_6 (9): Analogously as described for **8**, by using 123 mg (0.15 mmol) of **7** and ca. 0.5 mL of pyridine as starting materials. Red-violet solid; yield 109 mg (87%); dec. temp. 98°C. – IR (CH_2Cl_2): $\tilde{\nu}$ = 1916 cm^{-1} (C=C=C). – ^1H NMR (400 MHz, CD_3NO_2): δ = 8.38, 7.48, 7.27 (all m, 5 H, NC_5H_5), 7.92, 7.59, 7.37 (all m, 10 H, C_6H_5), 2.16 (m, 6 H, PC*H*CH_3), 1.24 [dvt, *N* = 13.7, *J*(HH) = 6.6 Hz, 36 H, PCHC*H*$_3$]. – ^{13}C NMR (100.6 MHz, CD_3NO_2): δ = 270.4 [dt, *J*(RhC) = 56.0, *J*(PC) = 19.0 Hz, Rh=C], 229.6 [dt, *J*(RhC) = 15.0, *J*(PC) = 9.0 Hz, Rh=C=*C*], 153.2, 140.3, 131.1, 129.7, 128.1, 127.3, 126.5 (all s, NC_5H_5 and C_6H_5), 150.9 (s, =*C*Ph_2), 26.4 (vt, *N* = 20.0 Hz, P*C*HCH_3), 20.5 (s, PCH*C*H_3). – ^{31}P NMR (162.0 MHz, CD_3NO_2): δ = 38.2 [d, *J*(RhP) = 134.0 Hz]. – $C_{38}H_{57}F_6NP_3Rh$ (837.7): calcd. C 54.99, H 6.86, N 1.67; found C 54.87, H 7.20, N 1.79.

9. Preparation of *trans*-[Rh(=C=C=CPh_2)(NH_3)($PiPr_3$)$_2$]PF_6 (10): A solution of 123 mg (0.15 mmol) of **7** in 10 mL of CH_2Cl_2 was treated at −20°C with 2.8 mL of a 0.55 M solution of NH_4OH (0.15 mmol) in water. The solution was slowly warmed to room temp. and, after it was continuously stirred for 1 h, concentrated to ca. 1 mL in vacuo. The solution was then layered with 10 mL of diethyl ether and upon storing for 6 h at room temp. red crystals were formed. The crystals were separated from the mother liquor, washed three times with 2-mL portions of diethyl ether and pentane and dried; yield 116 mg (85%); dec. temp. 134°C. – IR (CH_2Cl_2): $\tilde{\nu}$ = 1905 cm^{-1} (C=C=C). – ^1H NMR (400 MHz, CD_3NO_2): δ = 7.89, 7.31 (both m, 10 H, C_6H_5), 2.52 (m, 6 H, PC*H*CH_3), 1.32 [dvt, *N* = 13.4, *J*(HH) = 6.7 Hz, 36 H, PCHC*H*$_3$]. – ^{13}C NMR (100.6 MHz, CD_3NO_2): δ = 269.1 (br. m, Rh=C), 230.5 [dt, *J*(RhC) = 19.0 *J*(PC) = 7.0 Hz, Rh=C=*C*], 151.8 (s, =*C*Ph_2), 152.4, 130.7, 130.1, 127.0 (all s, C_6H_5), 25.5 (vt, *N* = 20.0 Hz, P*C*HCH_3), 20.4 (s, PCH*C*H_3). – ^{31}P NMR (162.0 MHz, CD_3NO_2): δ = 41.6 [*J*(RhP) = 131.0 Hz]. – $C_{33}H_{55}F_6NP_3Rh$ (775.6): calcd. C 51.10, H 7.15, N 1.81; found C 50.87, H 7.12, N 1.78.

10. Preparation of *trans*-[Rh(OAc)(=C=C=CPh_2)($PiPr_3$)$_2$] (11): A suspension of 123 mg (0.15 mmol) of **7** in 10 mL of diethyl ether/acetone (9:1) was treated at −78°C with 12 mg (0.15 mmol) of sodium acetate. A rapid change of color from deep orange to green occurred. Under continuous stirring the reaction mixture was warmed to room temp. and then brought to dryness in vacuo. The residue was extracted with 20 mL of diethyl ether, and the solvent was removed from the extract. The residue was dissolved in 2 mL of acetone and the solution was stored at −20°C for 8 h. Green crystals were formed which were separated from the mother liqour, washed three times with 2-mL portions of acetone (−20°C) and dried; yield 82 mg (81%). Compound **11** was identified by comparison of the IR and NMR data with those of an authentic sample.[2b][19]

11. Preparation of *trans*-[Rh(OH)(=C=C=CPh$_2$)(PiPr$_3$)$_2$] (12): Analogously as described for **11**, by using 123 mg (0.15 mmol) of **7** and 8 mg (0.15 mmol) of KOH as starting materials. Green solid; yield 76 mg (79%). Compound **12** was identified by comparison of the IR and NMR data with those of an authentic sample.[2b][19]

12. Determination of the X-ray Crystal Structure of 7:[20] Single crystals were grown from acetone/diethyl ether at room temp. Crystal data (from 23 reflections, $10° < \Theta < 13°$): triclinic; space group P-1 (No. 2); a = 9.074(6), b = 14.42(1), c = 16.16(1) Å, α = 85.50(5), β = 87.16(5), γ = 77.61(5)°; V = 2057(3) Å^3, Z = 2; $d_{calcd.}$ = 1.32 gcm^{-3}; μ(Mo-K_α) = 5.7 cm^{-1}; crystal size 0.15 × 0.15 × 0.40 mm; Enraf-Nonius CAD-4 diffractometer, Mo-K_α radiation (λ = 0.71073 Å), graphite monochromator, zirconium filter (factor 16.4); T = 293(1) K; ω/Θ-scan, max. 2Θ = 48°; 6904 reflections measured, 6442 independent ($R_{int.}$ = 0.0091), 5779 with $F_o > 2\sigma(F_o)$. Intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction (Ψ-scan method) was applied (min. transmission 96.1%). The structure was solved by direct methods (SHELXS-86).[21] Atomic coordinates and the anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least squares on F^2 (SHELXS-93).[22] The PF_6^- anion is disordered. The positions of 18 fluorine atoms (3 × 6) could be located around the central phosphorus atom P3 and refined anisotropically with a weighting factor of 1/3. The positions of all hydrogen atoms could be located in a final difference Fourier synthesis and refined isotropically. Conventional R = 0.0216 [for 5779 reflections with $F_o > 2\sigma(F_o)$], and weighted wR_2 = 0.0612 for all 6442 located reflections; reflection/parameter ratio 10.1; residual electron density +0.20/-0.27 eÅ^{-3}.

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