were taken from experimentally determined structures.[19] In the $Fe(CO)_2L$ fragment, the ligand–Fe–ligand angle was 90°. The plane of butadiene or the enone was 1.70 Å above the iron atom. Other distances used were the following (Å): Fe–C = 1.76; Fe–P = 2.23; C–O = 1.15; P–H = 1.42; P–O = 1.55; O–H = 1.00; C–C(diene) = 1.418; C–C(phenyl) = 1.39; C–H = 1.08 Å.

The parameters used for the calculations were the standard ones for C, H, O, and P and those reported on Table III for the iron atom.

Synthesis of Alkynylrhodium Complexes Containing a Rhodium–Mercury Bond and of the Vinyl Complex $[C_5H_5Rh(CH{=}CHPh)(P\text{-}i\text{-}Pr_3)SnCl_3]$ from Vinylidenerhodium Precursors[1]

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The reaction of $[C_5H_5Rh({=}C{=}CHR)(P\text{-}i\text{-}Pr_3)]$ (**1**–**3**) with $HgCl_2$, HgI_2, and CH_3HgI in presence of triethylamine produces the alkynylrhodium complexes $[C_5H_5RhHgX(C{\equiv}CR)(P\text{-}i\text{-}Pr_3)]$ (**4**, **6**–**11**) in excellent yield. They have been characterized by ^1H, ^{13}C, ^{31}P, and ^{199}Hg NMR spectroscopy. Treatment of **1** (R = Ph) with $SnCl_2{\cdot}2H_2O$ gives the vinylrhodium compound $[C_5H_5Rh(CH{=}CHPh)(P\text{-}i\text{-}Pr_3)SnCl_3]$ (**12**) probably via primary protonation at the metal atom. Complex **12** is also obtained from $[C_5H_5Rh(CH{=}CHPh)(P\text{-}i\text{-}Pr_3)Cl]$ and $SnCl_2{\cdot}2H_2O$ by insertion of tin dichloride into the Rh–Cl bond.

Introduction

The vinylidenerhodium complexes $C_5H_5Rh({=}C{=}CHR)(PR'_3)$ belong to the family of half-sandwich type compounds C_5H_5MLL', which provided that at least one of the ligands L and L′ possesses good donor properties are strong nucleophiles, i.e., metal bases.[2,3] Recently, we have already demonstrated that the vinylidene compounds $C_5H_5Rh({=}C{=}CHR)(P\text{-}i\text{-}Pr_3)$ (R = H, Me, *t*-Bu, Ph) react with Brønsted acids HX to form substituted vinylrhodium complexes $C_5H_5Rh(CH{=}CHR)(P\text{-}i\text{-}Pr_3)X$ (X = Cl, I, CF_3CO_2) probably via attack of the acid at the metal center.[1,4] Other electrophiles such as diazomethane, sulfur, selenium, tellurium, CuCl, $[Fe(CO)_4]$, etc., behave similarly.[1,5-7]

Owing to our long-standing interest in using the rhodium derivatives C_5H_5RhLL' also as starting materials for the preparation of metal–metal bonded complexes,[8] we became interested in exploring the reactivity of $C_5H_5Rh({=}C{=}CHR)(P\text{-}i\text{-}Pr_3)$ toward mercury dihalides and related species. We note that the first evidence for the interaction between a half-sandwich complex $C_5H_5ML_2$ and an electrophile came from the work by Kemmitt et al.,[9] who showed that on treatment of $C_5H_5Co(CO)_2$ with HgX_2 (X = Cl, Br, I) 1:1 adducts are formed. It was proved by the X-ray structural analysis of $[C_5H_5Co(CO)_2HgCl_2]$ that these nonionic substances contain a direct metal–metal bond.[10] Analogous 1:1 adducts have also been obtained from $C_5H_5Rh(CO)_2$ or $C_5H_5M(diene)$ (M = Co, Rh; diene = norbornadiene, cycloocta-1,5-diene) and $HgCl_2$,[9,11] as well as from $C_5H_5RhL_2$ (L = PMe_3, PMe_2Ph, PEt_3) and $AlMe_3$.[12]

We report in this paper that a similar interaction probably takes place between $C_5H_5Rh({=}C{=}CHR)(P\text{-}i\text{-}Pr_3)$ and HgX_2 or CH_3HgI, respectively. The electrophilic addition is rapidly followed by HX elimination, which results in the formation of novel alkynylrhodium complexes having a Rh–Hg bond.

Results

Reaction of **1** with $HgCl_2$ in benzene or THF leads spontaneously to the formation of a deeply colored solution from which approximately equal amounts of **4** and **5** can be isolated (Scheme I). If the benzene solution of **1** is first treated with excess triethylamine and then with $HgCl_2$, the alkynyl complex **4** is obtained in virtually quantitative yield. The amine method also works with **2** and **3** as starting materials and $HgCl_2$, HgI_2, and CH_3HgI as substrates to give **6**–**11** again nearly quantitatively. The Rh–Hg compounds are orange to red–brown microcrystalline solids that for short times can be handled in air. The solubility in ether and hydrocarbon solvents increases in the order R = Ph < Me < *t*-Bu and also from the mercury chlorides to the iodides. Only the complex **11**, which is

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[1] Part X of the series Vinylidene Transition-Metal Complexes. For part IX, see: Werner, H.; Brekau, U. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1989**, *44B*, 1438.

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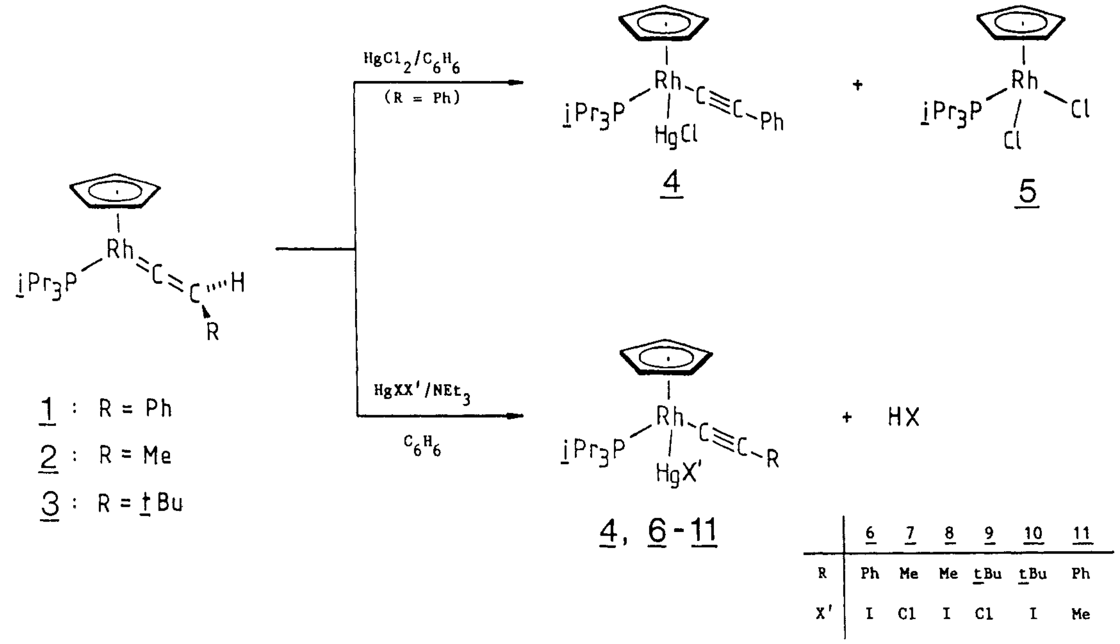
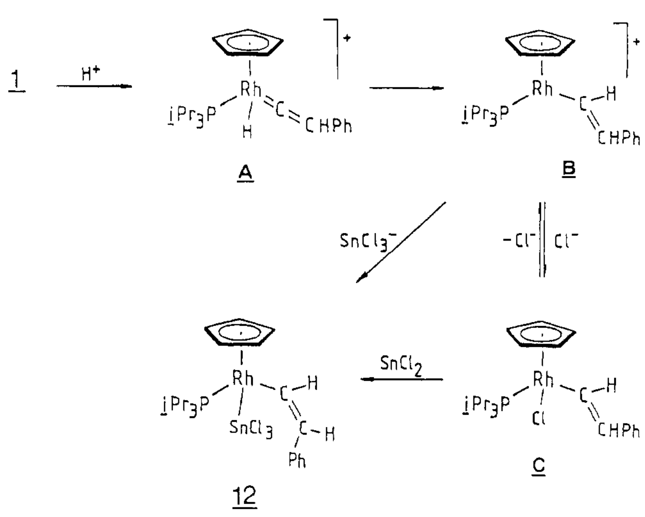
Scheme I



	6	7	8	9	10	11
R	Ph	Me	Me	tBu	tBu	Ph
X'	I	Cl	I	Cl	I	Me

Scheme II

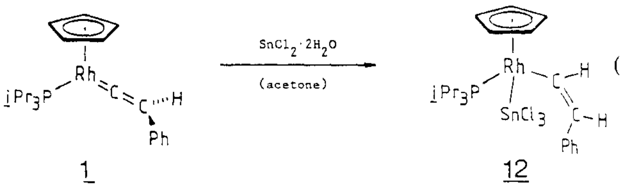


easily soluble even in pentane, turns out to be quite labile, and thus no satisfactory elemental analysis could be obtained.

From the structural features of 4 and 6–11 the presence of the alkynyl ligand is clearly indicated in the IR by the intense C≡C stretching frequency at ca. 2100 cm^{-1}. The fact that the rhodium center possesses four different ligands and thus the complexes are chiral is confirmed by the ^1H and ^{13}C NMR spectra in which *two* signals are observed for the methyl protons and CH_3 carbon atoms of the triisopropylphosphine ligand. The signals of the α and β carbon atoms of the alkynyl group appear at ca. 60–80 and 100–120 ppm showing, as expected, significantly different P–C and Rh–C coupling constants. Similar chemical shifts have been observed by Marder et al. for the alkynyl carbon atoms of *cis*-$[RhH(C{\equiv}CCH_2CH_2OH)(PMe_3)_4]Cl$.[13]

As mercury has an isotope (^{199}Hg) possessing a nuclear spin of $^1/_2$, in both the ^1H NMR (of 4 and 7) and ^{31}P NMR spectra (of 4, 7, 9, and 11) Hg–H and Hg–P coupling is observed. The ^2J(HgP) coupling constants of 310–780 Hz are in good agreement with values found in other Rh–Hg complexes.[14] The ^{199}Hg NMR spectrum of 4 shows a doublet-of-doublets at δ −1076.4 with ^1J(HgRh) and ^1J(HgP) of 738 Hz.

The reactivity of 1 toward tin dichloride (used as the hydrate) was also investigated. Most recently, Chan and Marder reported that $SnCl_2$ reacts both with $RhCl(PMe_3)_3$ and $IrCl(PMe_3)_3(C_8H_{14})$ to form 1:2 adducts $Cl_2Sn[MCl(PMe_3)_3]_2$ (M = Rh, Ir) in which direct tin–rhodium and tin–iridium bonds are present.[15] The hope that $SnCl_2$ may behave similarly toward the rhodium(I) vinylidene complex 1 was not fulfilled. Irrespective of whether the two compounds were reacted in a 1:1 ratio or whether an excess of the Lewis acidic tin dichloride was used, the only product obtained in the reaction was the vinyl derivative 12 (see eq 1). It forms orange moderately air-stable crystals that are soluble in polar solvents such as chloroform, dichloromethane, THF, and acetone.



(1)

The proposed structure of the new Rh–Sn complex 12 is clearly supported by the spectroscopic data. The signals of the two alkenyl protons appear in the ^1H NMR spectrum at δ 6.31 and 7.51, thus showing similar chemical shifts as in the recently prepared complex $C_5H_5Rh(CH{=}CHPh)(P\text{-}i\text{-}Pr_3)(OCOCF_3)$.[4] The H–H coupling constant of ca. 10 Hz is indicative of a *Z* configuration at the C=C double bond.[16] In the ^{13}C NMR spectrum, the α and β carbon atoms of the vinyl ligand resonate at ca. 120 and 143 ppm, the signal of C_α showing the expected Rh–C and

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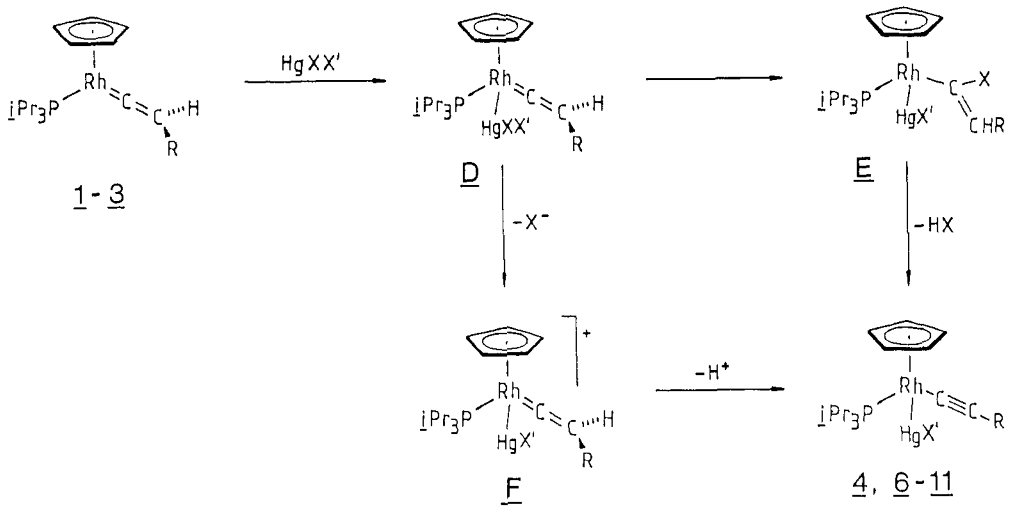
Scheme III



P–C coupling. The presence of a Rh–$SnCl_3$ linkage in **12** is particularly supported by the ^{31}P NMR spectrum, which in addition to the doublet at 62.8 ppm shows tin satellites. The size of $J(^{119}SnP)$ and $J(^{117}SnP)$ are in fully agreement with a tin–phosphorous coupling via one metal atom.[17]

The proposed mechanism for the reaction of **1** and $SnCl_2 \cdot 2H_2O$ is outlined in Scheme II. As it is well-known that solutions of $SnCl_2 \cdot 2H_2O$ in acetone contain not only solvated $SnCl_2$ units and hydroxytin cations but also $SnCl_3^-$, chloride ions, and protons,[18] we assume that after primary protonation of **1** the solvated vinylrhodium species B is formed. This idea is supported by the observation that in presence of NEt_3 no reaction between **1** and $SnCl_2 \cdot 2H_2O$ occurs. Intermediate B may then react either with $SnCl_3^-$ or with Cl^- and $SnCl_2$ in two consecutive steps to give the Rh–$SnCl_3$ complex. There is good evidence for the second alternative as **12** can be prepared not only as shown in eq 1 but also from $C_5H_5Rh(CH{=}CHPh)(P\text{-}i\text{-}Pr_3)Cl$ and $SnCl_2 \cdot 2H_2O$ by insertion of tin dichloride into the Rh–Cl bond.

Discussion

The unexpected formation of the *alkynyl*rhodium complexes **4** and **6–11** from the vinylidene precursors and the mercury halides deserves some comments. As pointed out in the Introduction, we had expected that the starting materials **1–3** on treatment with HgXX′ would give 1:1 adducts analogous to those that had been obtained from $C_5H_5Rh(CO)_2$ or $C_5H_5Rh(diene)$ and $HgCl_2$, respectively.[9,11] Instead, HX′ is eliminated, and products containing a Rh–HgX linkage are formed. Owing to the general behavior of the vinylidene complexes **1–3** toward electrophiles, we assume that also mercury(II) dihalides first attack the rhodium to give an intermediate D, which by 1–3 halide shift rearranges to form the vinyl derivative E (Scheme III). Finally, reaction of this species with base (NEt_3) generates the product. A second mechanism (also shown in Scheme III) includes a dissociation of the adduct D to give the intermediate F, from which by deprotonation the alkynyl complex is obtained. There is precedent both for the dissociation of molecular compounds such as $[C_5H_5M(CO)_2HgCl_2]$ (M = Co, Rh) in acetone solution to give $[C_5H_5M(CO)_2HgCl]^+$ and Cl^-,[9,11] as well as for the acid behavior of cationic vinylidenemetal complexes containing $C_5H_5(PR_3)M$ and $C_6H_6(PR_3)M$ units.[19,20] It thus seems that the route to **4** and **6–11** via D and F is a reasonable alternative.

The final question remains as to what the oxidation number of rhodium in the alkynyl compounds **4** and **6–11** is. If mercury has the oxidation state +II (which would be expected), the $[C_5H_5(P\text{-}i\text{-}Pr_3)RhC{\equiv}CR]$ fragment formally is an anion, and thus we have rhodium(I). Consequently, the metal–metal bond in **4** and **6–11** is a donor bond from rhodium to mercury, similarly to that in $[C_5H_5Rh(CO)_2HgCl_2]$. As on the other hand the piano stool geometry is typical for rhodium(III) complexes, the HgX fragment may be formally considered as an anion, and in such a species the mercury should be in the oxidation state zero. Even if we would have a ^{103}Rh NMR spectrum of one of the title compounds, we doubt that the chemical shift would provide a clear answer on the aforementioned question because the polarity of the Rh–HgX bond in **4** and **6–11** is certainly less than in the related alkynyl hydrido complex $C_5H_5RhH(C{\equiv}CPh)(P\text{-}i\text{-}Pr_3)$.[21] The interesting problem of whether this hydrido compound and the corresponding title complexes $C_5H_5RhHgX(C{\equiv}CPh)(P\text{-}i\text{-}Pr_3)$ are real relatives as far as the reactivity is concerned will be further investigated.

Experimental Section

All reactions were carried out under an atmosphere of argon by using Schlenk tube techniques. The starting vinylidene complexes **1–3** were prepared as described in the literature.[1,21] IR spectra were recorded on a Perkin-Elmer 457, and NMR spectra on a Jeol FX 90 Q and a Bruker AC 200 spectrometer. Melting points were determined by differential thermal analysis.

Reaction of $C_5H_5Rh({=}C{=}CHPh)(P\text{-}i\text{-}Pr_3)$ (1) with $HgCl_2$ in Benzene. A solution of **1** (110 mg, 0.23 mmol) in 5 mL of benzene was treated with $HgCl_2$ (75 mg, 0.28 mmol) and stirred for 5 min at room temperature. The ^1H NMR spectrum of the reaction solution showed the presence of about equal amounts of $C_5H_5Rh(HgCl)(C{\equiv}CPh)(P\text{-}i\text{-}Pr_3)$ (**4**) and $C_5H_5Rh(P\text{-}i\text{-}Pr_3)Cl_2$

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(5).[22] The solvent was removed in vacuo, and the solid residue was extracted with CH_2Cl_2. The dichloromethane solution was concentrated to ca. 2 mL and chromatographed on Al_2O_3 (neutral, activity grade V, length of column 10 cm) with CH_2Cl_2. After the eluant solvent was removed, the residue was recrystallized from THF/OEt_2 to give small orange crystals. They were characterized as 4 by the IR and NMR spectra (see below), yield 70 mg (41%).

General Procedure for the Synthesis of $C_5H_5Rh(HgX')(C\equiv CR)(P$-*i*-$Pr_3)$ (4, 6-11). A solution of 1, 2, or 3 (0.4 mmol) in 5 mL of benzene was treated first with 0.6 mL of NEt_3 and then with HgXX′ (0.4 mmol). After the reaction mixture was stirred for 5 min at room temperature, the solvent was removed in vacuo. The remaining solid was dissolved in 3 mL of CH_2Cl_2, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, length of column 5 cm) with CH_2Cl_2. The eluant solvent was removed, and the residue was recrystallized from THF/OEt_2 (for 4, 6, 7), Et_2O/pentane (8-10), or pentane (11). Orange (4, 7, 9) or red-brown (6, 8, 10, 11) moderately air-stable crystalline solids were obtained.

4: yield 250 mg (94%); mp 165 °C (dec). Anal. Calcd for $C_{22}H_{31}ClHgPRh$: C, 39.71; H, 4.70; Rh, 15.46. Found: C, 39.21; H, 4.56; Rh, 15.53. IR (KBr): ν(C≡C) 2097 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.11 (m), C_6H_5; δ 5.47 (d), *J*(PH) = 1.6 Hz, *J*(HgH) = 25.3 Hz (from satellites), C_5H_5; δ 2.42 (m), PCH; δ 1.35 (dd), *J*(PH) = 15.0 Hz, *J*(HH) = 7.1 Hz, and δ 1.26(dd), *J*(PH) = 14.0, *J*(HH) = 7.1 Hz, both PCHC*H*$_3$. ^{13}C NMR (90 MHz, $CDCl_3$): δ 130.74 (s), 127.92 (s), 127.62 (s), 124.63 (s), all C_6H_5; δ 110.35 (dd), *J*(RhC) = 10.8, *J*(PC) = 1.9 Hz, C≡*C*Ph; δ 85.41 (dd), *J*(RhC) = *J*(PC) = 2.9 Hz, *J*(HgC) = 21.2 Hz (from satellites), C_5H_5; δ 81.60 (dd), *J*(RhC) = 51.3 Hz; *J*(PC) = 24.9 Hz, *C*≡CPh; δ 27.66 (d), *J*(PC) = 24.4 Hz, *J*(HgC) = 21.2 Hz (from satellites), PCH; δ 20.66 (s) and 19.83 (s), both PCH*C*H$_3$. ^{31}P NMR (90 MHz, $CDCl_3$): δ 78.45(d), *J*(RhP) 137.7 Hz, *J*(HgP) = 741.5 Hz (from satellites). ^{199}Hg NMR (90 MHz, $CDCl_3$): δ −1076.4(dd), *J*(HgP) = *J*(HgRh) = 738.4 Hz.

6: yield 285 mg (94%); mp 154 °C. Anal. Calcd for $C_{22}H_{31}HgIPRh$: C, 34.91; H, 4.13; Rh, 13.60. Found: C, 34.63; H, 4.00; Rh, 13.60. IR (KBr): ν(C≡C) 2096 cm^{-1}. ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.24 (m), C_6H_5; δ 5.51 (d), *J*(PH) = 1.2 Hz, C_5H_5; δ 2.49 (m), PCH; δ 1.50 (dd), *J*(PH) = 14.5 Hz, *J*(HH) = 7.1 Hz, and δ 1.34(dd), *J*(PH) = 14.0 Hz, *J*(HH) = 7.1 Hz, both PCHC*H*$_3$. ^{13}C NMR (90 MHz, $CDCl_3$): δ 130.71 (s), 128.03 (s), 127.63 (s), 124.51 (s), all C_6H_5; δ 110.29 (dd), *J*(RhC) = 11.0 Hz, *J*(PC) = 1.2 Hz, C≡*C*Ph; δ 85.24 (dd), *J*(RhC) = *J*(PC) = 2.5 Hz, C_5H_5; δ 27.85(d), *J*(PC) = 23.8 Hz, PCH; δ 20.33 (s) and 19.33 (s), both PCH*C*H$_3$; signal of *C*≡CPh not observed. ^{31}P NMR (90 MHz, $CDCl_3$): δ 77.40 (d), *J*(RhP) = 141.0 Hz.

7: yield 208 mg (86%); mp 135 °C (dec). Anal. Calcd for $C_{17}H_{29}ClHgPRh$: C, 33.84; H, 4.84; Rh, 17.06. Found: C, 33.75; H, 5.12; Rh, 17.30. IR (KBr): ν(C≡C) 2128 cm^{-1}. ^{1}H NMR (90 MHz, C_6D_6): δ 4.85 (d), *J*(PH) = 1.7 Hz, *J*(HgH) = 23.8 Hz (from satellites), C_5H_5; δ 2.08 (dd), *J*(PH) = *J*(RhH) = 1.0 Hz, C_2CH_3; δ 1.98 (m), PCH; δ 1.11 (dd), *J*(PH) = 14.0 Hz, *J*(HH) = 7.0 Hz, and δ 0.96 (dd), *J*(PH) = 13.4 Hz, *J*(HH) = 7.1 Hz, both PCHC*H*$_3$. ^{13}C NMR (90 MHz, $CDCl_3$): δ 102.97 (dd), *J*(RhC) = 11.0 Hz, *J*(PC) = 1.7 Hz, C≡*C*CH$_3$; δ 84.57 (dd), *J*(RhC) = *J*(PC) = 2.7 Hz, C_5H_5; δ 59.48 (dd), *J*(RhC) = 50.8 Hz, *J*(PC) = 24.9 Hz, *C*≡CCH$_3$; δ 27.41 (d), *J*(PC) = 23.9 Hz, PCH; δ 20.07 (s) and 19.77 (s), both PCH*C*H$_3$; δ 6.10 (s), C_2CH_3. ^{31}P NMR (90 MHz, C_6D_6): δ 77.24 (d), *J*(RhP) = 142.9 Hz, *J*(HgP) = 505.3 Hz (from satellites).

8: yield 228 mg (82%); mp 108 °C (dec). Anal. Calcd for $C_{17}H_{29}HgIPRh$: C, 29.39; H, 4.21; Rh, 14.81. Found: C, 29.66; H, 3.95; Rh, 14.80. IR (KBr): ν(C≡C) 2127 cm^{-1}. ^{1}H NMR (90 MHz, C_6D_6): δ 4.83 (d), *J*(PH) = 1.2 Hz, C_5H_5; δ 2.08 (dd), *J*(PH) = 1.2 Hz, *J*(RhH) = 0.7 Hz, C_2CH_3; δ 2.03 (m), PCH; δ 1.11 (dd), *J*(PH) = 14.3 Hz, *J*(HH) = 7.0 Hz, and δ 0.96 (dd), *J*(PH) = 13.7 Hz, *J*(HH) = 7.1 Hz, both PCHC*H*$_3$. ^{13}C NMR (90 MHz, $CDCl_3$): δ 102.92 (dd), *J*(RhC) = 10.7 Hz, *J*(PC) = 2.0 Hz, C≡*C*CH$_3$; δ 84.53 (dd); *J*(RhC) = *J*(PC) = 2.7 Hz, C_5H_5; δ 27.72 (d), *J*(PC) = 23.4 Hz, PCH; δ 19.90 (s), PCH*C*H$_3$; δ 6.38 (s), C_2CH_3; signal of *C*≡CCH$_3$ not observed. ^{31}P NMR (90 MHz, C_6D_6): δ 76.71 (d), *J*(RhP) = 141.4 Hz.

9: yield 219 mg (85%); mp 148 °C (dec). Anal. Calcd for $C_{20}H_{35}ClHgPRh$: C, 37.22; H, 5.47; Rh, 15.94; *M*$_r$, 645.42. Found: C, 36.75; H, 5.59, Rh, 15.77; *M*$_r$, 646 (MS). IR (KBr): ν(C≡C) 2103 cm^{-1}. ^{1}H NMR (90 MHz, $CDCl_3$): δ 5.33 (s, br), C_5H_5; δ 2.36 (m), PCH; δ 1.28 (dd), *J*(PH) = 15.4 Hz, *J*(HH) = 7.1 Hz, and δ 1.19 (dd), *J*(PH) = 13.8 Hz, *J*(HH) = 7.2 Hz, both PCHC*H*$_3$; δ 1.05 (s), $C(CH_3)_3$. ^{13}C NMR (90 MHz, C_6D_6): δ 118.13 (dd), *J*(RhC) = 10.5 Hz, *J*(PC) = 2.2 Hz, C≡*C*C$_4$H$_9$; δ 85.15 (dd), *J*(RhC) = 3.9, *J*(PC) = 2.5 Hz, *J*(HgC) = 22.5 Hz (from satellites), C_5H_5; δ 57.45(dd), *J*(RhC) = 50.3 Hz, *J*(PC) = 24.4 Hz, *C*≡CC$_4$H$_9$; δ 32.94 (s), C(*C*H$_3$)$_3$; δ 30.03(s), *C*(CH$_3$)$_3$; δ 27.73 (d), *J*(PC) = 24.2 Hz, PCH; δ 20.76 (s) and 20.11 (s), both PCH*C*H$_3$. ^{31}P NMR (90 MHz, $CDCl_3$): δ 78.20 (d), *J*(RhP) = 141.4 Hz, *J*(HgP) = 777.7 Hz (from satellites).

10: yield 253 mg (86%); mp 135 °C. Anal. Calcd for $C_{20}H_{35}HgIPRh$: C, 32.60; H, 4.79; Rh, 13.97; *M*$_r$, 736.87. Found: C, 32.58; H, 4.74; Rh, 14.14; *M*$_r$, 738 (MS). IR (KBr): ν(C≡C) 2104 cm^{-1}. ^{1}H NMR (90 MHz, C_6D_6): δ 4.72 (d), *J*(PH) = 1.2 Hz, C_5H_5; δ 2.00 (m), PCH; δ 1.31 (s), $C(CH_3)_3$; δ 1.02 (dd), *J*(PH) = 14.5 Hz, *J*(HH) = 7.0 Hz, and 0.89 (dd), *J*(PH) = 13.7 Hz, *J*(HH) = 7.1 Hz, both PCHC*H*$_3$. ^{13}C NMR (90 MHz, C_6D_6): δ 118.70 (dd), *J*(RhC) = 10.7 Hz, *J*(PC) = 2.0 Hz, C≡*C*C$_4$H$_9$; δ 84.95 (dd), *J*(RhC) = *J*(PC) = 2.7 Hz, C_5H_5; δ 33.09 (s), C(*C*H$_3$)$_3$; δ 30.10 (s), *C*(CH$_3$)$_3$; δ 27.96 (d), *J*(PC) = 23.9 Hz, PCH; δ 20.35 (s) and 20.13 (s), both PCH*C*H$_3$; signal of *C*≡CC$_4$H$_9$ not observed. ^{31}P NMR (90 MHz, C_6D_6): δ 75.92 (d), *J*(RhP) = 147.4 Hz.

11: yield 243 mg (94%); mp 144 °C. IR (KBr): ν(C≡C) 2080 cm^{-1}. ^{1}H NMR (90 MHz, C_6D_6): δ 7.31 (m), C_6H_5; δ 5.28 (dd), *J*(PH) = 1.5 Hz, *J*(RhH) = 0.3 Hz, C_5H_5; δ 2.19 (m), PCH; δ 1.17 (dd), *J*(PH) = 14.2 Hz, *J*(HH) = 7.1 Hz, and 1.15(dd), *J*(PH) = 13.5 Hz, *J*(HH) = 7.0 Hz, both PCHC*H*$_3$; δ 1.16 (dd), *J*(PH) = 13.4 Hz, *J*(RhH) = 7.3 Hz, HgCH$_3$. ^{13}C NMR (200 MHz, C_6D_6): δ 131.03 (s), 129.45 (s), 129.26 (s), 123.83 (s), all C_6H_5; δ 109.95 (dd), *J*(RhC) = 14.7 Hz, *J*(PC) = 1.0 Hz, C≡*C*Ph; δ 85.69 (s), C_5H_5; δ 27.93 (d), *J*(PC) = 22.9 Hz, PCH; δ 20.43 (s) and 20.25 (s), both PCH*C*H$_3$; δ 19.89 (s), HgCH$_3$; signal of *C*≡CPh not observed. ^{31}P NMR (90 MHz, C_6D_6): δ 75.12 (d), *J*(RhP) = 166.7 Hz, *J*(HgP) = 310.4 Hz (from satellites).

Synthesis of C_5H_5Rh(*Z*-CH=CHPh)(P-*i*-Pr_3)$SnCl_3$ (12). A solution of 1 (186 mg, 0.43 mmol) in 5 mL of acetone was treated with $SnCl_2\cdot 2H_2O$ (100 mg, 0.44 mmol) and stirred for 10 min at room temperature. After removal of the solvent in vacuo, the residue was extracted with CH_2Cl_2, and the dichloromethane solution was brought to dryness. The remaining solid was recrystallized from THF/OEt_2 to give orange moderately air-stable crystals, yield 250 mg (88%); mp 107 °C (dec). Anal. Calcd for $C_{22}H_{33}Cl_3PRhSn$: C, 40.25; H, 5.07; Rh, 15.68. Found: C, 40.52; H, 5.32; Rh, 15.42. ^{1}H NMR (90 MHz, $CDCl_3$): δ 7.51 (d), *J*(HH) = 10.3 Hz, C*H*Ph; δ 7.33 (m), C_6H_5; δ 6.31 (dd), *J*(PH) = 15.2 Hz, *J*(HH) = 10.3 Hz, RhCH; δ 5.17 (d), *J*(SnH) = 20.6 Hz, *J*(PH) = 1.0 Hz, C_5H_5; δ 2.30 (m), PCH; δ 1.32 (dd), *J*(PH) = 14.2 Hz, *J*(HH) = 7.1 Hz, PCHC*H*$_3$. ^{13}C NMR (200 MHz, $CDCl_3$): δ 142.98 (s), *C*HPh; δ 143.95 (s), 128.83 (s), 128.19 (s), 126.25 (s), all C_6H_5; δ 120.17 (dd), *J*(RhC) = 29.7 Hz, *J*(PC) = 13.0 Hz, RhCH; δ 88.88 (s), C_5H_5; δ 27.19 (d), *J*(PC) = 22.4 Hz, PCH; δ 20.21 (s), PCH*C*H$_3$. ^{31}P NMR (90 MHz, $CDCl_3$): δ 62.81 (d), *J*(RhP) = 146.5 Hz.

12 was also obtained from C_5H_5Rh(CH=CHPh)(P-*i*-Pr_3)Cl (60 mg, 0.13 mmol) and $SnCl_2\cdot 2H_2O$ (30 mg, 0.13 mmol) in 1 mL of $CDCl_3$ by treating the reaction mixture for 5 min in an ultrasonic bath. The yield (determined by ^{1}H NMR) was virtually quantitative.

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