Five- and Six-Coordinate Bis(alkynyl)rhodium(III) Complexes Containing a Rh−SnPh$_3$ Bond

Helmut Werner,* Olaf Gevert, and Pierre Haquette

Institut für Anorganische Chemie der Universität Würzburg,
Am Hubland, D-97074 Würzburg, Germany

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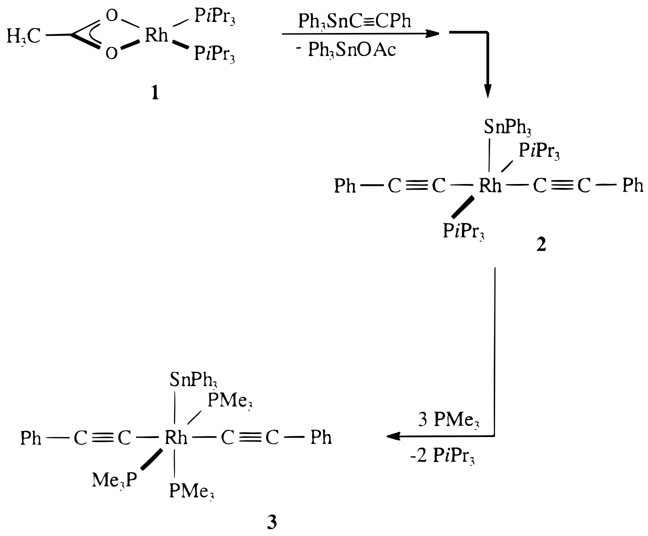
Summary: The reaction of $[Rh(\eta^2\text{-}O_2CMe)(PiPr_3)_2]$ (**1**) *with* $Ph_3SnC{\equiv}CPh$ *afforded, by elimination of* Ph_3SnOAc*, the five-coordinate complex* $[Rh(C{\equiv}CPh)_2(SnPh_3)(PiPr_3)_2]$ (**2**) *in 75% yield. Treatment of* **2** *with excess* PMe_3 *gave the octahedral compound mer,trans-*$[Rh(C{\equiv}CPh)_2(SnPh_3)(PMe_3)_3]$ (**3**)*, the molecular structure of which has been determined. Compound* **2** *reacted with an equimolar amount of iodine to yield the rhodium(I) diyne complex trans-*$[RhI(\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)(PiPr_3)_2]$ (**4**)*, which could also be obtained from* $[RhCl(PiPr_3)_2]_2$*, 1,4-diphenylbutadiyne, and NaI. The X-ray crystal structure analysis of* **4** *confirmed the square-planar geometry around the rhodium center and the coordination of a bent,* η^2*-coordinated diyne ligand.*

Recently, we reported that the monomeric (acetato)rhodium(I) compound $[Rh(\eta^2\text{-}O_2CMe)(PiPr_3)_2]$ (**1**) reacts with terminal alkynes HC≡CR to give, via the alkyne-rhodium(I) derivatives *trans*-$[Rh(\eta^1\text{-}O_2CMe)(HC{\equiv}CR)(PiPr_3)_2]$ as intermediates, the octahedral alkynylhydridorhodium(III) complexes $[Rh(\eta^2\text{-}O_2CMe)H(C{\equiv}CR)(PiPr_3)_2]$ in excellent yield.[1] These compounds not only rearrange, upon UV irradiation or heating, to the isomeric vinylidene species *trans*-$[Rh(\eta^1\text{-}O_2CMe)({=}C{=}CHR)(PiPr_3)_2]$[1] but also undergo insertion reactions with HC≡CR to finally give, after intramolecular C−C coupling, rhodium hexadienynes.[2]

Since the terminal alkynes HC≡CR and triphenylstannyl-substituted alkynes $Ph_3SnC{\equiv}CR$ behave similarly toward the chlororhodium(I) compound $[RhCl(PiPr_3)_2]_2$,[3] we considered the reaction of **1** with $Ph_3SnC{\equiv}CR$ as a possible route to obtain octahedral rhodium(III) complexes with a Rh−SnPh$_3$ bond. We note that, previously, Lewis et al. prepared the compound *mer,trans*-$[Rh(C{\equiv}CPh)_2(SnMe_3)(PMe_3)_3]$ by oxidative addition of $Me_3SnC{\equiv}CPh$ to $[Rh(PMe_3)_4]Cl$. They had also used this latter species, reacting it with $Me_3SnC{\equiv}CR'C{\equiv}CSnMe_3$ (R′ = *p*-$C_6H_4C_6H_4$-*p*), in the synthesis of oligomers containing Rh−C≡CR′C≡C−Rh bridging units.[4]

The reaction of the starting material **1** with an equimolar amount of $Ph_3SnC{\equiv}CPh$ in pentane led to a smooth change of color from red to violet. The ^{31}P NMR spectrum of the reaction mixture showed, however, that only 50% of the starting material had been consumed. We therefore concluded that the expected octahedral product $[Rh(\eta^2\text{-}O_2CMe)(SnPh_3)(C{\equiv}CPh)(PiPr_3)_2]$ had not been formed. If 2 equiv of the Ph_3Sn-substituted alkyne was used, a complete conversion of **1** to a dark violet compound occurred. Both the elemental analysis and the spectroscopic data indicated that the five-coordinate bis(alkynyl)rhodium(III) complex $[Rh(C{\equiv}CPh)_2(SnPh_3)(PiPr_3)_2]$ (**2**) was generated. The ^{31}P NMR spectrum of **2** (in C_6D_6) displays one doublet at 37.3 ppm with a Rh−P coupling of 98.9 Hz, which is much smaller than for a $Rh(PiPr_3)_2$ species having the two phosphine ligands in a *cis* disposition.[5] Moreover, the observation of tin satellites in the ^{31}P NMR spectrum with a Sn−P coupling of 94.5 Hz indicates that a Rh−SnPh$_3$ bond should be present. Related to the proposed square-pyramidal geometry of **2** (see Scheme 1) is the molecular structure of the bis(alkynyl) hydrido compound $[RhH(C{\equiv}CR)_2(PiPr_3)_2]$ (R = $CiPr_2OH$), which has been prepared on treatment of $[Rh(\eta^3\text{-}CH_2Ph)(PiPr_3)_2]$ with $HC{\equiv}CCiPr_2OH$ and characterized by X-ray crystallography.[6] A similar five-coordinate complex of composition $[Rh(C{\equiv}CPh)_2(SnMe_3)(PPh_3)_2]$ was obtained by Lappert et al. from $[RhCl(PPh_3)_3]$ and $Me_3SnC{\equiv}CPh$.[7]

Scheme 1



With regard to the mechanism of formation of **2** we assume that, in analogy with the preparation of *trans*-$[Rh(\eta^1\text{-}O_2CMe)(HC{\equiv}CR)(PiPr_3)_2]$ from **1** and HC≡CR,[1] the square-planar alkyne complex *trans*-$[Rh(\eta^1\text{-}O_2CMe)(Ph_3SnC{\equiv}CPh)(PiPr_3)_2]$ is formed initially. This species possibly reacts with a second molecule of $Ph_3SnC{\equiv}CPh$

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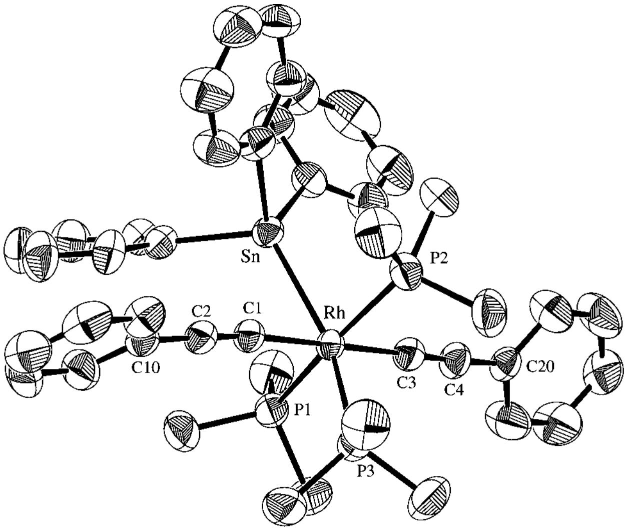
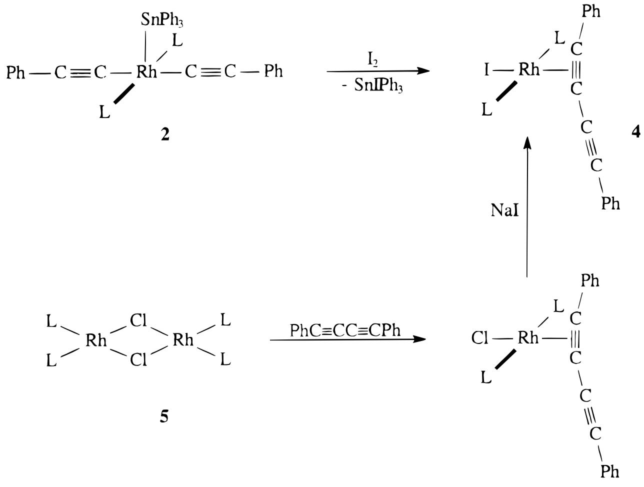


Figure 1. Molecular structure (ORTEP drawing) of **3**. The compound crystallizes with one molecule of CH_2Cl_2, which, like the hydrogen atoms, is omitted for clarity.

Table 1. Selected Bond Distances and Angles with Esd's for Compound 3

	Bond Distances (Å)		
Rh−Sn	2.640(2)	Rh−C3	2.038(7)
Rh−P1	2.325(3)	C1−C2	1.207(6)
Rh−P2	2.320(4)	C3−C4	1.208(6)
Rh−P3	2.369(2)	C2−C10	1.436(7)
Rh−C1	2.028(7)	C4−C20	1.437(7)
	Bond Angles (deg)		
C1−Rh−C3	177.5(2)	P1−Rh−Sn	88.6(1)
C1−Rh−P1	95.4(2)	P2−Rh−P3	93.8(1)
C1−Rh−P2	98.2(2)	P2−Rh−Sn	88.2(1)
C1−Rh−P3	82.2(1)	P3−Rh−Sn	160.31(6)
C1−Rh−Sn	78.1(2)	Rh−C1−C2	173.9(3)
C3−Rh−P1	82.4(2)	Rh−C3−C4	178.4(4)
C3−Rh−P2	84.0(2)	Rh−Sn−C40	117.0(1)
C3−Rh−P3	99.0(1)	Rh−Sn−C50	119.2(2)
C3−Rh−Sn	100.7(2)	Rh−Sn−C60	117.3(1)
P1−Rh−P2	165.16(6)	C1−C2−C10	178.2(5)
P1−Rh−P3	94.09(7)	C3−C4−C20	175.0(4)

Scheme 2[a]



[a] L = P*i*Pr$_3$.

Table 2. Selected Bond Distances and Angles with Esd's for Compound 4

	Bond Distances (Å)		
Rh−C1	2.034(3)	C1−C2	1.259(5)
Rh−C2	2.124(3)	C2−C3	1.380(5)
Rh−P1	2.381(3)	C3−C4	1.198(5)
Rh−P2	2.378(3)	C1−C40	1.448(5)
Rh−I	2.673(1)	C4−C30	1.430(5)
	Bond Angles (deg)		
C1−Rh−C2	35.2(1)	P2−Rh−I	90.29(4)
C1−Rh−P1	92.7(1)	Rh−C1−C2	76.3(2)
C1−Rh−P2	92.6(1)	Rh−C1−C40	134.5(3)
C1−Rh−I	147.8(1)	Rh−C2−C1	68.5(2)
C2−Rh−P1	89.1(1)	Rh−C2−C3	132.9(2)
C2−Rh−P2	89.1(1)	C1−C2−C3	158.5(3)
C2−Rh−I	177.0(1)	C2−C3−C4	173.9(4)
P1−Rh−P2	168.21(4)	C2−C1−C40	149.1(4)
P1−Rh−I	90.90(4)	C3−C4−C30	175.7(4)

either by elimination of Ph_3SnOAc to afford *trans*-[Rh(C≡CPh)(Ph_3SnC≡CPh)(P*i*Pr$_3$)$_2$] or by oxidative addition to give [Rh(η^1-O_2CMe)($SnPh_3$)(C≡CPh)(Ph_3SnC≡CPh)(P*i*Pr$_3$)$_2$]. While the first could rearrange to **2**, the latter could eliminate Ph_3SnOAc to generate the five-coordinate complex **2**. Triphenylstannyl acetate was isolated as a byproduct from the reaction of **1** and Ph_3SnC≡CPh.

Since we failed to obtain single crystals of **2**, some subsequent reactions of the new compound were investigated. On treatment of a solution of **2** in pentane with excess PMe_3, a change of color from violet to light yellow was observed and a colorless solid slowly precipitated. This solid, which after removal of the solvent was isolated in 77% yield, proved to be only slightly soluble in most organic solvents. As the elemental analysis showed (and the X-ray structural analysis confirmed), the tris(trimethylphosphine) complex *mer,trans*-[Rh(C≡CPh)$_2$($SnPh_3$)(PMe_3)$_3$] (**3**) was formed. The ^{31}P NMR spectrum of **3** (in C_6D_6) displays two signals at −10.1 and −20.6 ppm, the first of which is split into a doublet of triplets with *J*(RhP) = 88.6 Hz and the second into a doublet of doublets with *J*(RhP) = 85.7 Hz. Due to the splitting pattern and the difference in intensity, we assign the first signal to a PMe_3 ligand *trans* to the $SnPh_3$ group and the second to the two other PMe_3 ligands being in *trans* disposition. In agreement with these data, the ^1H NMR spectrum of **3** displays two resonances for the PMe_3 protons at 1.79 and 1.63 ppm with an intensity ratio of 1:2.

The result of the X-ray crystal structure analysis of **3** is shown in Figure 1. As has been expected from the NMR spectroscopic data, the molecular structure corresponds to an octahedron with two phosphine and two alkynyl ligands *trans* to each other. However, while the C−C−Rh−C−C chain is almost linear, the angle P1−Rh−P2 deviates significantly from the ideal value of 180°. Moreover, the Sn−Rh−P3 axis is also slightly bent, with the remarkable feature that both the $SnPh_3$ and the PMe_3 groups are turned toward the same alkynyl unit. For both types of bending the different size of the ligands probably play an important role. The Rh−Sn bond length is 2.640(2) Å (Table 1) and thus is almost identical with the distance between the metal and the $SnPh_3$ ligand in [Ir($SnPh_3$)(CO)$_3$(PCy_3)] (Ir−Sn = 2.6610(3) Å),[8] [PtH($SnPh_3$)(PCy_3)$_2$] (Pt-Sn = 2.6539(6) Å),[9] and [Rh(acac){(*E*)-CH=CHC(OH)(CH_2)$_4$$CH_2$}($SnPh_3$)($PCy_3$)].[10] In agreement with the different *trans* influences of the $SnPh_3$ and PMe_3 groups, the bonds Rh−P1 and Rh−P2 in compound **2** are somewhat

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Table 3. Crystallographic Data for $3\cdot CH_2Cl_2$ and 4

formula	$C_{44}H_{54}Cl_2P_3RhSn$ (**3**·CH_2Cl_2)	$C_{34}H_{52}IP_2Rh$ (**4**)
fw	968.28	752.51
cryst size, mm^3	0.45 × 0.30 × 0.20	0.45 × 0.30 × 0.25
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
cell dimens determn	25 rflns, 10° < θ < 15°	25 rflns, 10° < θ < 15°
a, Å	9.783(3)	12.719(9)
b, Å	19.220(6)	12.474(4)
c, Å	24.25(8)	24.50(4)
β, deg	98.5(2)	93.05(4)
V, Å^3	4510(9)	3565(7)
Z	4	4
d_{calcd}, g cm^{-3}	1.426	1.402
diffractometer	Enraf-Nonius CAD4	
radiation (λ, Å)	Mo Kα (0.709 30)	
filter factor (Zr filter)	15.4	15.4
temp, °C	+20(2)	+20(2)
μ, mm^{-1}	1.172	1.440
scan method	ω/θ	ω/θ
2θ(max), deg	46	48
total no. of rflns scanned	5937	6517
no. of unique rflns	5511 (R(int) = 0.0084)	6220 (R(int) = 0.0152)
no. of obsd rflns ($I > 2(I)$)	4889	4966
no. of rflns used for refinement	5510	6219
no. of params refined	469	355
final R indices ($I > 2(I)$)	R1 = 0.0290[a] wR2 = 0.0725	R1 = 0.0293[a] wR2 = 0.0631
R indices (all data)	R1 = 0.0349 wR2 = 0.0788[b]	R1 = 0.0428 wR2 = 0.0710[b]
rfln: param ratio	11.75	17.5
resid electron density, e Å^{-3}	+0.413/−0.542	+0.501/−0.515

[a] Conventional R factor: $R1 = \sum|F_o - F_c|/\sum F_o$ (for $F_o > 4\sigma(F_o)$). [b] Weighted R factor: $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, with $w^{-1} = \sigma^2(F_o)^2 + 0.0267P^2 + 3.4808P$ (**3**) and $w^{-1} = \sigma^2(F_o)^2 + 0.0404P^2 + 5.4926P$ (**4**), where $P = (F_o^2 + 2F_c^2)/3$.

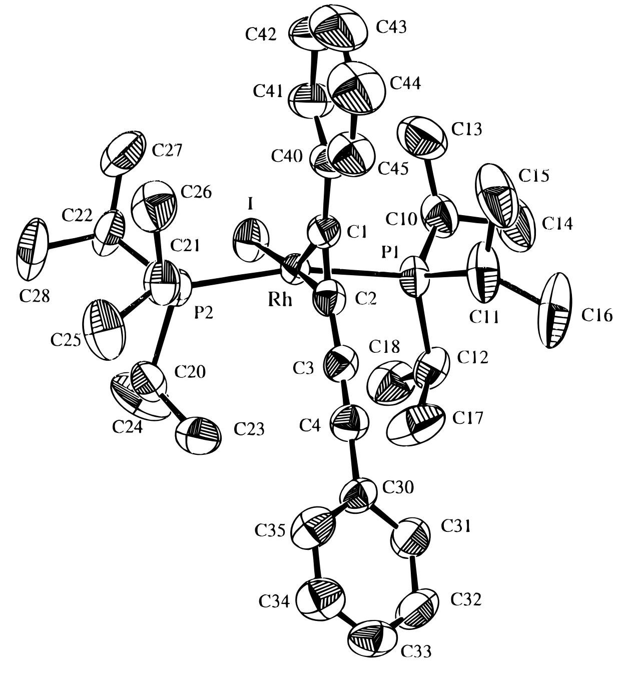

Figure 2. Molecular structure (ORTEP drawing) of **4**. The hydrogen atoms are omitted for clarity.

shorter than the bond between Rh and P3. A completely similar situation has been found by Marder et al. for $[RhH(C{\equiv}CPh)_2(PMe_3)_3]$.[11]

The attempt to cleave the Rh−SnPh$_3$ bond in **2** by iodine led to a surprising result. Instead of the expected five-coordinate bis(alkynyl)iodorhodium(III) compound $[RhI(C{\equiv}CPh)_2(P\textit{i}Pr_3)_2]$, the square-planar rhodium(I) diyne complex *trans*-$[RhI(\eta^2\text{-}PhC{\equiv}CC{\equiv}CPh)(P\textit{i}Pr_3)_2]$ (**4**) was obtained. The latter could also be prepared in two steps by reacting the dimer $[RhCl(P\textit{i}Pr_3)_2]_2$ (**5**)[12] with 1,4-diphenylbutadiyne and NaI (Scheme 2). Compound **4** is an analogue of *trans*-$[RhCl(\eta^2\text{-}Me_3SiC{\equiv}CC{\equiv}CSiMe_3)(P\textit{i}Pr_3)_2]$, which has been synthesized from **5** and the corresponding diyne.[13]

The X-ray crystal structure analysis of **4** revealed (see Figure 2) that the coordination geometry around the rhodium center is square-planar with the two phosphine ligands *trans*-disposed. The distances Rh−C1 and Rh−C2 are 2.034(3) and 2.124(3) Å and are therefore quite similar to those in *trans*-$[RhCl(\eta^2\text{-}Me_3SiC{\equiv}CC{\equiv}CSiMe_3)(P\textit{i}Pr_3)_2]$[13] and $[Rh(CO)(P\textit{i}Pr_3)_2\text{-}(\eta^1{:}\eta^2\text{-}C{\equiv}CC{\equiv}CPh)RhCl(P\textit{i}Pr_3)_2]$.[14] As in the dinuclear complex, the halide−Rh−C2 axis in **4** is almost exactly linear, which is in contrast to the situation for $[RhCl(\eta^2\text{-}Me_3SiC{\equiv}CC{\equiv}CSiMe_3)(P\textit{i}Pr_3)_2]$, in which the angle Cl−Rh−C1 (and not Cl−Rh−C2) is 173.8(5)°. The C1−C2 bond in **4** (Table 2) is 1.259(5) Å and thus is elongated by ca. 0.06 Å compared to C3−C4.

Studies concerning the reactivity of the five- and six-coordinate compounds **2** and **3** are underway. We are particularly interested to find out whether on treatment of **2** with RHgCl a displacement of SnPh$_3$ by HgR occurs and whether heterodimetallic complexes with a Rh−Hg bond, similar to those obtained from the rhodium vinylidenes *trans*-$[RhCl\{{=}C{=}C(SnPh_3)R\}(P\textit{i}Pr_3)_2]$ and PhHgCl,[3] would be formed.

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Experimental Section

All experiments were carried out under an atmosphere of argon by using Schlenk techniques. The starting materials **1**,[15] **5**,[12a] and $Ph_3SnC{\equiv}CPh$[16] were prepared as described in the literature. 1,4-Diphenylbutadiyne was a commercial product from Aldrich. Melting points were determined by DTA. IR spectra were measured with Perkin-Elmer 1420 and NMR spectra with Bruker AC 200 and AMX 400 instruments.

Preparation of [Rh(C≡CPh)$_2$(SnPh$_3$)(P*i*Pr$_3$)$_2$] (2). A solution of **1** (145 mg, 0.30 mmol) in 10 mL of pentane was treated with $Ph_3SnC{\equiv}CPh$ (284 mg, 0.63 mmol) and stirred for 30 min at room temperature. A change of color from red to deep violet occurred. The solvent was removed, the residue was dissolved in 1 mL of benzene, and the solution was chromatographed on Al_2O_3 (neutral, activity V, length of column 7 cm). With pentane, a violet fraction was eluted, after removal of the solvent from this fraction a deep violet solid was isolated: yield 220 mg (75%); mp 104 °C dec. Anal. Calcd for $C_{52}H_{67}P_2RhSn$: C, 64.02; H, 6.92. Found: C, 63.88; H, 7.02. IR (KBr): ν(C≡C) 2060 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 8.09−7.18 (m, 25H, C_6H_5), 2.85 (m, 6H, PC*H*CH$_3$), 1.29 (dvt, N = 13.5 Hz, J(HH) = 7.0 Hz, 36H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 146.1, 138.9, 131.1, 129.8, 129.0, 128.2, 127.7, 125.8 (all s, C_6H_5), 26.0 (vt, N = 20.3 Hz, P*C*HCH$_3$), 21.3 (s, PCH*C*H$_3$), signals of alkynyl carbon atoms not exactly located. ^{31}P NMR (162.0 MHz, C_6D_6): δ 37.3 (d, J(RhP) = 98.9, J(SnP) = 94.5 Hz).

Preparation of [Rh(C≡CPh)$_2$(SnPh$_3$)(PMe$_3$)$_3$] (3). A solution of **2** (130 mg, 0.13 mmol) in 5 mL of acetone was treated with excess PMe$_3$ (ca. 0.1 mL) and stirred for 2 h at room temperature. During the reaction, a white solid slowly precipitated. The solvent and the volatile substances were removed in vacuo (ca. 10^{-4} Torr), and the white residue was washed three times with 3 mL portions of acetone and dried: yield 89 mg (77%); mp 60 °C dec. Anal. Calcd for $C_{43}H_{52}P_3RhSn$: C, 58.46; H, 5.93. Found: C, 58.58; H, 5.72. IR (KBr): ν(C≡C) 2030 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 8.30−7.37 (m, 25H, C_6H_5), 1.79 (d, J(PH) = 7.3 Hz, 9H, PCH$_3$), 1.63 (s, br, 18 H, PCH$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ −10.1 (dt, J(RhP) = 88.6, J(PP) = 33.4 Hz, PMe$_3$ *trans* to SnPh$_3$), −20.6 (dd, J(RhP) = 85.7, J(PP) = 33.4 Hz, PMe$_3$ *cis* to SnPh$_3$).

Preparation of *trans*-[RhI(η^2-Ph*C*≡*C*C≡CPh)(P*i*Pr$_3$)$_2$] (4). (a) A solution of **2** (98 mg, 0.10 mmol) in 6 mL of ether was treated with iodine (25 mg, 0.10 mmol) and stirred for 20 min at room temperature. A change of color from violet to orange-red occurred. The solvent was removed in vacuo, and the deep yellow residue was washed three times with 3 mL portions of acetone (0 °C) and dried: yield 42 mg (55%).

(b) A solution of **5** (123 mg, 0.14 mmol) in 10 mL of pentane was treated with 1,4-diphenylbutadiyne (54 mg, 0.27 mmol) and stirred for 10 min at room temperature. The solvent was removed, and the residue was dissolved in 5 mL of acetone. After an excess of NaI (ca. 1 g) was added to the solution, the reaction mixture was stirred for 16 h at 20 °C, and then the solvent was removed. The residue was extracted with 10 mL of pentane, the extract was brought to dryness in vacuo, and the residue was recrystallized from 2 mL of acetone (−20 °C) to give deep yellow crystals: yield 140 mg (70%); mp 86 °C dec. Anal. Calcd for $C_{34}H_{52}IP_2Rh$: C, 54.27; H, 6.92. Found: C, 54.05; H, 7.03. IR (KBr): ν(C≡C)$_{\text{uncoord}}$ 2140, ν(C≡C)$_{\text{coord}}$ 1840 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ 7.55−6.97 (m, 10H, C_6H_5), 2.69 (m, 6H, PC*H*CH$_3$), 1.38 (dvt, N = 13.7 Hz, J(HH) = 7.0 Hz, 18H, PCHC*H*$_3$), 1.13 (dvt, N = 12.5 Hz, J(HH) = 6.1 Hz, 18H, PCHC*H*$_3$). ^{13}C NMR (100.6 MHz, C_6D_6): δ 131.8, 130.4, 129.5, 128.6, 128.2, 127.8, 125.6, 125.5 (all s, C_6H_5), 96.0 (s, C≡C uncoord), 91.1 (dt, J(RhC) = 19.1, J(PC) = 4.1 Hz, C≡C coord), 63.6 (d, br, J(RhC) = 13.1 Hz, C≡C coord), 24.3 (vt, N = 18.4 Hz, P*C*HCH$_3$), 21.3 (s, PCH*C*H$_3$). ^{31}P NMR (162.0 MHz, C_6D_6): δ 33.4 (d, J(RhP) = 111.5 Hz).

X-ray Structural Analyses of 3 and 4. Single crystals were grown from CH_2Cl_2 (**3**) and acetone (**4**). Crystal data collection parameters are summarized in Table 3. Intensity data were corrected for Lorentz and polarization effects; for **3** a linear decay (loss of gain −6.4%) was taken into consideration, and for **4** an empirical absorption correction (ψ-scans, minimum transmission 93.22%) was applied. The structures were solved by direct methods (SHELXS-86). The positions of the hydrogen atoms were calculated according to ideal geometry (distance of C−H set at 0.95 Å) and were refined by the riding method. Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares on F^2 (SHELXL-93). One molecule of CH_2Cl_2 per asymmetic unit is present in the crystal of **3**, which was refined anisotropically, leading to an angle Cl1−C90−Cl2 of 112.6(5)°. For other details see Table 3.

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Supporting Information Available: Tables of data collection parameters, bond lengths and angles, positional and thermal parameters, and least-squares planes for **3** and **4** (13 pages). Ordering information is given on any current masthead page.

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