Vinylidene Transition-Metal Complexes, XXXI[1]

Stannylalkynes as Starting Materials for the Synthesis of Vinylidene Rhodium Complexes and of Heterodimetallic Compounds Containing a Rh–Hg or Rh–Sn Bond

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Reaction of $[RhCl(PiPr_3)_2]_n$ (**1**) with stannylalkynes $RC{\equiv}CSnPh_3$ [R = H, Me, Ph, CH_2OH, CH_2OMe, CMe_2OH, CH(Me)OH, CH(Ph)OH, $SiMe_3$, $SnPh_3$] gives the vinylidenerhodium(I) complexes *trans*-$[RhCl(=C=C(SnPh_3)R)(PiPr_3)_2]$ (**2a–j**) in good to excellent yields. These compounds react with protic acids to give *trans*-$[RhCl(=C=CHR)(PiPr_3)_2]$ and, for R = CH(Ph)OH, to give the allenylidene complex *trans*-$[RhCl(=C=C=CHPh)(PiPr_3)_2]$ (**5**). On treatment of **2b–j** with PhHgCl, the heterodimetallic compounds $[Rh(C{\equiv}CR)(HgPh)Cl(PiPr_3)_2]$ (**6a–i**) are formed. The bis(alkynyl)rhodium(III) complexes $[RhH(C{\equiv}CSiMe_3)(C{\equiv}CSnPh_3)(py)(PiPr_3)_2]$ (**9**) and $[Rh(C{\equiv}CSiMe_3)(C{\equiv}CCH_2OMe)(SnPh_3)(PiPr_3)_2]$ (**10**) are prepared from *trans*-$[Rh(C{\equiv}CSiMe_3)(L)(PiPr_3)_2]$ (**7**, **8**, L = py, C_2H_4) and $HC{\equiv}CSnPh_3$ or $Ph_3SnC{\equiv}CCH_2OMe$, respectively. The crystal and molecular structures of *trans*-$[RhCl(=C=C(SnPh_3)CH_2OMe)(PiPr_3)_2]$ (**2e**) and $[Rh(C{\equiv}CCH_2OMe)(HgPh)Cl(PiPr_3)_2]$ (**6d**) have been determined.

Currently, there is much interest in the chemistry of vinylidene transition-metal complexes[2], which are key species in the transformation of two-carbon ligands and play an important role in organometallic as well as in organic synthesis[3]. After we had discovered that not only terminal alkynes $HC{\equiv}CR$ but also trimethylsilyl and triphenylsilyl derivatives, $RC{\equiv}CSiMe_3$ and $RC{\equiv}CSiPh_3$, can be converted in the coordination sphere of rhodium to the corresponding vinylidenes $:C=C(R)SiR'_3$[4], we set out to investigate whether a similar rearrangement proceeds with stannyl-substituted acetylenes, too. We expected that due to the decrease in bond strength along the series C–Si > C-Ge > C-Sn[5] a 1,2-SnR_3 shift should be less activated than a 1,2-SiR_3 shift. However, due to the reduced bond strength and the higher electrophilicity of tetravalent tin, an increased tendency to undergo side reactions was also expected. In this context, we note that Lewis et al.[6] have recently shown that mono-, oligo-, and polymeric alkynylrhodium(III) complexes are obtained on treatment of $[Rh(PMe_3)_4]Cl$ with SnR_3-substituted alkynes, one of the driving forces in these processes being the formation of R_3SnCl.

In the present paper we report that with $[RhCl(PiPr_3)_2]_n$ (**1**) and $RC{\equiv}CSnPh_3$ as starting materials square-planar vinylidenerhodium(I) complexes bearing a $SnPh_3$ group at the β-carbon atom of the vinylidene ligand can be prepared. They readily react not only with proton sources by C–Sn bond cleavage but also with PhHgCl to give a novel type of Rh–Hg dimetallic products.

Vinylidenerhodium Complexes from $RC{\equiv}CSnPh_3$

Since we had found that trimethylsilyl-substituted alkynes are more reactive toward **1** than the $SiPh_3$-substituted analogues[4], we began our studies with alkynes $RC{\equiv}CSnMe_3$ (R = H, *t*Bu, Ph, CO_2Me) as substrates. However all attempts to coordinate these alkynes to the $[RhCl(PiPr_3)_2]$ unit or to form via the intermediate *trans*-$[RhCl(RC{\equiv}CSnMe_3)(PiPr_3)_2]$ the corresponding vinylidene rhodium complexes were unsuccessful. In most cases the well-known $SnMe_3$-free compounds *trans*-$[RhCl(=C=CHR)(PiPr_3)_2]$[7] were obtained, possibly formed upon protonation of the expected products *trans*-$[RhCl(=C=C(SnMe_3)R)(PiPr_3)_2]$ by solvent impurities.

A clean reaction occurs by adding triphenylstannyl-substituted alkynes $RC{\equiv}CSnPh_3$ (R = H, Me, Ph) to a solution of **1** in THF at −50 to −78°C. After slow warming to room temperature, red to violet microcrystalline solids are isolated which according to the spectroscopic data are not the alkyne but the isomeric vinylidene complexes **2a–c**. Diagnostic, in particular[2a], are the two signals at low field in the ^{13}C-NMR spectra in the range of δ = 270–290 and 80–110 which are both split into doublets of triplets due to Rh–C and P–C coupling. The absence of a C≡C stretching frequency in the IR spectra at about 1800–1850 cm^{-1} further supports the proposed coordination of a vinylidene instead of an alkyne ligand.

$[RhCl(PiPr_3)_2]_n$ **1**

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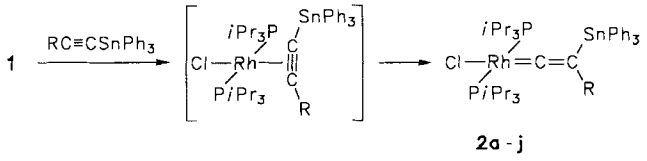


2a - j

R = H (**2a**), CH_3 (**2b**), Ph (**2c**), CH_2OH (**2d**), CH_2OMe (**2e**), CMe_2OH (**2f**), CH(Me)OH (**2g**), CH(Ph)OH (**2h**), $SiMe_3$ (**2i**), $SnPh_3$ (**2j**)

Other alkynes of the general type $RC{\equiv}CSnPh_3$ bearing an OH or OMe functionality in the group R behave similarly toward **1** as the above-mentioned derivatives with R = H, Me, Ph. The main reason for us to use these substrates was our recent finding that (vinylvinylidene)- and allenylidenerhodium complexes *trans*-[RhCl(=C=CH−CR=CH_2)($PiPr_3$)$_2$] and *trans*-[RhCl(=C=C=CRR')($PiPr_3$)$_2$] may be prepared from *trans*-[RhCl(=C=CH−CRR'OH)($PiPr_3$)$_2$] as starting materials[8]. Compound **1** reacts with $RC{\equiv}CSnPh_3$ (R = CH_2OH, CH_2OMe, CMe_2OH, CHMeOH, CHPhOH) at ambient temperature to give the substituted vinylidenerhodium complexes **2d**−**h** in 70−90% yield. The stannyl/silyl- and the bis(stannyl)alkynes $Me_3SiC{\equiv}CSnPh_3$ and $Ph_3SnC{\equiv}CSnPh_3$ behave analogously and upon reaction with **1** afford the complexes **2i** and **2j**. These two compounds as well as the other $SnPh_3$-substituted vinylidenerhodium complexes **2a**−**h** are deeply colored solids which are fairly air-stable but slowly decompose in solution. In all cases, the composition has been confirmed by elemental analyses. With regard to the spectroscopic data of **2g** and **2h**, it is worth mentioning that in the ^{1}H-NMR spectra for the protons of the diastereotopic phosphane CH_3 groups four signals instead of two (as for **2b**−**f**) are observed which is a consequence of the chirality at the γ-carbon atom of the vinylidene ligand. The ^{31}P-NMR data of **2g** and **2h** also support this notion.

Molecular Structure of Compound 2e

The result of the X-ray structure analysis of **2e** is shown in Figure 1. The coordination geometry around the metal center is square-planar with the two phosphane ligands in *trans* position. The Rh−C(1)−C(2) unit is nearly linear with Rh−C(1) and C(1)-C(2) distances corresponding to those of other vinylidenerhodium(I) complexes[4c,7a,8a]. The planes [Rh,Cl,P(1),P(2),C(1)] and [C(1),C(2),C(3),Sn] are perpendicular to each other, a fact which supports the description of the compounds of the general type *trans*-[RhX(=C=CRR')(PR_3)$_2$] as "metalla-allenes"[2d]. The Sn−C bond lengths and the C−Sn−C bond angles are almost identical with those found in $SnPh_4$[9].

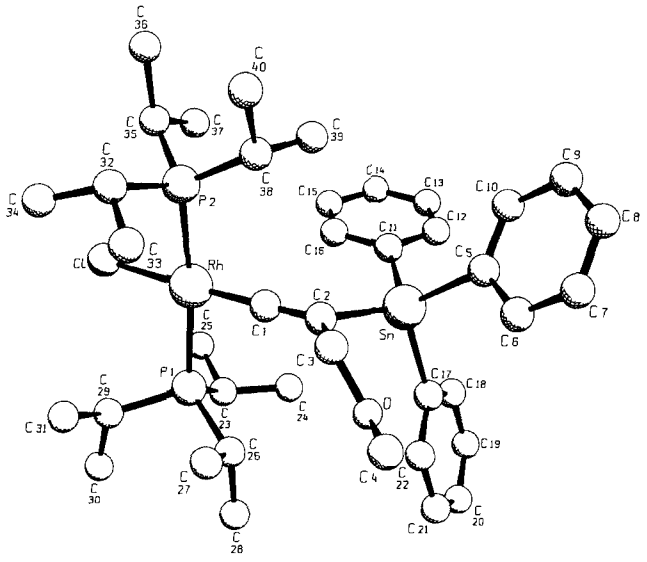


Figure 1. Molecular structure (SCHAKAL drawing) of complex **2e**; selected bond lengths [Å] and angles [°]: Rh−Cl 2.384(1), Rh−P(1) 2.354(1), Rh−P(2) 2.359(1), Rh−C(1) 1.816(4), C(1)−C(2) 1.259(6), C(2)−C(3) 1.547(6), Sn−C(2) 2.143(5), Sn−C(5) 2.145(5), Sn−C(11) 2.128(4), Sn−C(17) 2.147(5); Cl−Rh−P(1) 90.50(5), Cl−Rh−P(2) 89.53(5), P(1)−Rh−C(1) 90.3(1), P(2)−Rh−C(1) 90.2(1), P(1)−Rh−P(2) 170.31(4), Cl−Rh−C(1) 176.3(1), Rh−C(1)−C(2) 176.6(4), C(1)−C(2)−C(3) 122.1(4), C(1)−C(2)−Sn 122.4(4), Sn−C(2)−C(3) 115.5(3), C(2)−C(3)−O 108.0(4), C(2)−Sn−C(5) 105.5(2), C(2)−Sn−C(11) 113.7(2), C(2)−Sn−C(17) 110.8(2)

Studies on the Reactivity of Complexes 2a−j

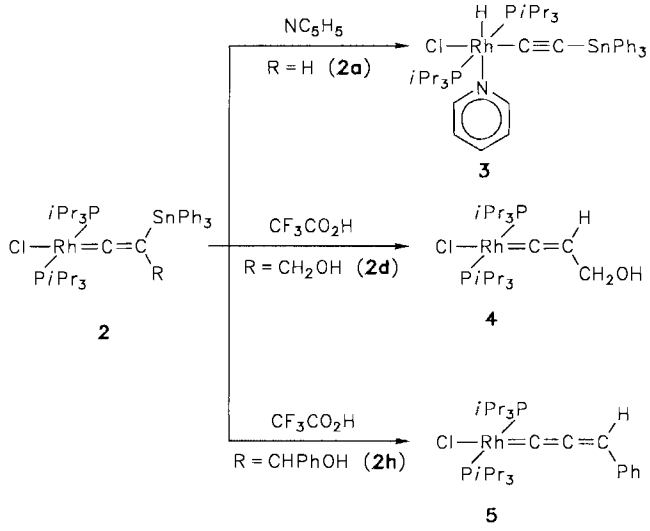
Since we had found[8a] that vinylidenerhodium complexes of the general type *trans*-[RhCl(=C=CHR)($PiPr_3$)$_2$] react with pyridine undergoing a 1,3-H shift to give the octahedral compounds [RhH(C≡CR)Cl(py)($PiPr_3$)$_2$], we were interested to find out whether upon treatment of the complexes **2b** and **2c** with pyridine a similar 1,3-$SnPh_3$ shift would occur. However, both compounds are inert toward NC_5H_5. A slow reaction takes place between **2a** and pyridine, but the only product which could be characterized by ^{1}H- and ^{31}P-NMR spectroscopy is the hydrido complex [RhH(C≡$CSnPh_3$)Cl(py)($PiPr_3$)$_2$] (**3**). Obviously, a 1,3-H shift is kinetically favored over a 1,3-$SnPh_3$ shift and thus the formation of an alkynyl(triphenylstannyl)rhodium(III) derivative seems to be hindered on this route.

Attempts to use compound **2d**, bearing a CH_2OH group at the β-carbon atom of the vinylidene ligand, as starting material for the synthesis of the as yet unknown parent allenylidenerhodium(I) complex *trans*-[RhCl(=C=C=CH_2)($PiPr_3$)$_2$] failed. The reaction of **2d** with CF_3CO_2H yields by cleavage of the C−$SnPh_3$ bond the vinylidenerhodium derivative **4** which was originally prepared from **1** and $HC{\equiv}CCH_2OH$[8b]. Treatment of compound **2h** with CF_3CO_2H leads to the allenylidene complex **5**[8c], presumably via *trans*-[RhCl(=C=CHCH(Ph)OH)($PiPr_3$)$_2$] as intermediate. Even though it is conceivable that upon attack of HX at a OH-functionalized vinylidenemetal complex such as **2d** or **2h** the elimination of water should be possible, the formation of Ph_3SnX appears to control the reaction pathway to give **4** and **5**, respectively.

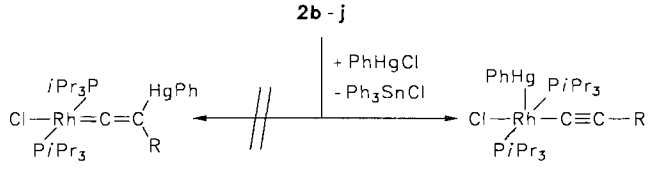
The preferred formation of Ph_3SnCl might be, however, the driving force for the clean reaction which takes place between the compounds **2b**−**j** and PhHgCl. The addition of an equimolar amount of the organomercury derivative to a solution of **2b**−**j** in toluene leads to a spontaneous

Table 1. Data of the X-ray structure analyses of **2e** and **6d**

Compound	**2e**	**6d**
Formula	$C_{40}H_{62}ClOP_2RhSn$	$C_{28}H_{52}ClHgOP_2Rh$
M	877.95	805.62
Crystal system	monoclinic	monoclinic
Space group [#]	$P2_1/n$ [1014]	$P2_1/c$ [14]
a [Å]	12.026(3)	17.212(6)
b [Å]	19.895(3)	16.801(2)
c [Å]	18.381(5)	11.314(3)
β [°]	102.30(1)	99.18(1)
Z	4	4
V [Å^3]	4297(1)	3230.1(1)
d_{calcd} [g/cm^3]	1.3511	1.657
F(000)	1808.0	1600.0
μ (Mo K_α) [cm^{-1}]	11.2	63.2
Radiation (graphite monochromated)	Mo-K_α (0.70930 Å)	Mo-K_α (0.70930 Å)
T [K]	293	223
Scan method	ω/2θ	ω/2θ
2θ (max) [°]	44	50
h, k, l range	12, 21, ±19	20, 19, ±13
Measured reflections	5767	6215
Unique reflections	5460	5900
Observed reflections ($F_o>3\sigma(F_o)$)	3719	4130
Refined parameters	415	307
R	0.040	0.038
R_w	0.043	0.041
reflection/param ratio	8.96	13.45
residual electron density [e/Å^3]	+0.812/-0.976	+3.06/-1.321

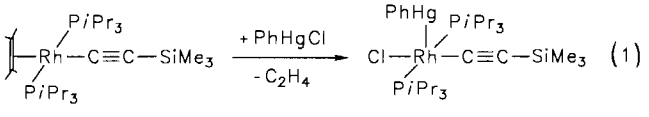


color change from violet to orange and, after removal of the solvent, orange air-stable solids are isolated in nearly quantitative yield. Whereas the elemental analyses of **6a–i** would be in agreement with the expected composition *trans*-[RhCl(=C=C(HgPh)R)(P*i*Pr$_3$)$_2$], the IR spectra indicate that an alkynyl instead of a vinylidene ligand is coordinated to rhodium. The structures thus proposed for the complexes **6a–i** are additionally supported by the NMR data. The ^{13}C-NMR spectra display two signals at δ = 90–120 but show no resonance in the region at δ = 260–290 that would be most typical of a vinylidene α-carbon atom. Another characteristic feature is the splitting of the signal of the *ipso*-carbon atom of the HgC_6H_5 group, which is a doublet of triplets, due to Rh-C and P-C coupling. This observation as well as the appearance of ^{199}Hg satellites in the ^{31}P-NMR spectra of **6a–i** are fully consistent with the presence of a direct Rh–Hg bond.



R = CH_3 (**6a**), Ph (**6b**), CH_2OH (**6c**), CH_2OMe (**6d**), CMe_2OH (**6e**), CH(Me)OH (**6f**), CH(Ph)OH (**6g**), $SiMe_3$ (**6h**), $SnPh_3$ (**6i**)

The question of whether rhodium has the oxidation state +I or +III in the compounds **6a–i** is not easy to answer. If one assumes that the well-known anion [RhCl(C≡CR)(P*i*Pr$_3$)$_2$]$^-$[10] displaces the chloro ligand in PhHgCl to form the dimetallic product [RhCl(C≡CR)(HgPh)(P*i*Pr$_3$)$_2$], then the oxidation state of Rh would not change and should remain +I. If, however, the compounds **6a–i** are considered as close analogues of the alkynyl(hydrido) complexes [RhH(C≡CR)Cl(P*i*Pr$_3$)$_2$][4b,8a,b,11], then the oxidation state of Rh should be +III. Supporting arguments for the second possibility are first the synthesis of **6h** from **7** and PhHgCl (eq. 1), which could be regarded as an oxidative addition reaction of the organomercurial to the three-coordinate fragment [Rh(C≡CSiMe$_3$)(P*i*Pr$_3$)$_2$], and secondly the size of the Rh-P coupling constant of about 100 Hz that is equally typical of related five-coordinate bis(phosphane)rhodium(III) derivatives[4b,c].



With regard to the reactivity of the Rh–Hg dimetallic compounds it should be mentioned that we did not succeed in obtaining stable 1:1 adducts of **6d** with pyridine or CO. We also failed to observe a controlled thermally or photochemically induced abstraction of mercury from **6a** or **6b** which would lead to the five-coodinate rhodium(III) derivative [Rh(C≡CR)(C$_6$H$_5$)Cl(P*i*Pr$_3$)$_2$]. With other compounds that contain a M–Hg bond this process is known and has been used for the formation of complexes containing a metal-carbon bond[12,13].

Molecular Structure of Compound 6d

The result of the X-ray structure analysis of **6d** is shown in Figure 2. As it has been proposed on the basis of the spectroscopic data, the rhodium atom is coordinated in a square-pyramidal fashion with the HgC_6H_5 fragment in the apical position. The basal plane consists of the two *trans*-oriented P atoms, the alkynyl and the chloro ligand, which are also *trans* to each other. The Cl–Rh–C(1) unit is almost linear [angle 179.0(1)°] and the P(1)–Rh–P(2) unit only slightly bent [angle 172.55(4)°] toward the sixth (free) coordination site. We note that the Rh–C(1) and C(1)–C(2) bond lengths are very similar to those in other alkynylrhodium complexes, independent of whether these are five- or six-coordinate[4b,8a,14].

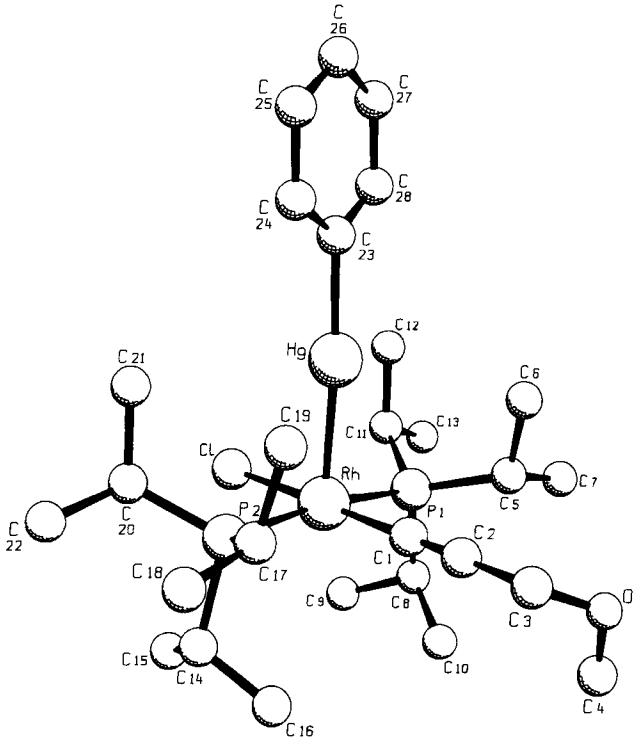
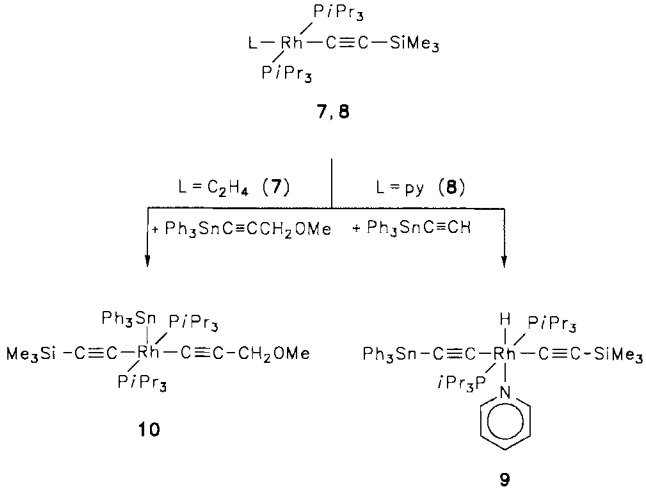


Figure 2. Molecular structure (SCHAKAL drawing) of complex **6d**; selected bond lengths [Å] and angles [°]: Rh–Hg 2.5008(4), Hg–C(23) 2.082(5), Rh–P(1) 2.349(1), Rh–P(2) 2.343(1), Rh–Cl 2.386(1), Rh–C1 1.986(5), C1–C2 1.162(7), C2–C3 1.490(9); Rh–Hg–C(23) 175.5(1), Hg–Rh–Cl 91.28(3), Hg–Rh–P(1) 94.33(3), Hg–Rh–P(2) 92.99(3), Hg–Rh–C(1) 98.5(2), P(1)–Rh–P(2) 172.55(4), Cl–Rh–C(1) 179.0(1), Rh–C(1)–C(2) 177.9(5), C(1)–C(2)–C(3) 178.6(7), Cl–Rh–P(1) 90.63(4), Cl–Rh–P(2) 90.57(4), C(3)–O–C(4) 116.1(1)

The most interesting feature of the structure of **6d**, however, is the short Rh–Hg bond length of 2.5008(4) Å. This distance is significantly shorter than the sum of the covalent radii (2.69 Å) and would be consistent with a postulated d_π-p_π bond[13]. There are other compounds known with a longer Rh–Hg bond ranging from 2.6 to 2.8 Å[15] but because these are all di- and oligomeric or metal clusters, having the HgX_n ligand in a bridging position, a fair comparison is difficult to draw. To our knowledge, **6d** is the first monomeric dimetallic Rh-Hg complex that has been characterized by X-ray diffraction.

Reactions of Alkynylstannanes with Complexes *trans*-[Rh(C≡CSiMe$_3$)(L)(P*i*Pr$_3$)$_2$]

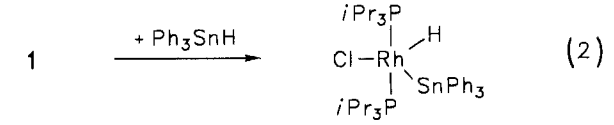
Since we had found that bis(alkynyl)hydridorhodium(III) and alkynyl(vinylidene)rhodium(I) derivatives can be prepared from *trans*-[Rh(C≡CR)(L)(P*i*Pr$_3$)$_2$] (R = alkyl and aryl) and terminal alkynes[16], we were interested whether the recently isolated complexes **7** and **8**[4b] could be used for the same purpose. The first attempt failed. Treatment of a solution of **8** in pentane at −78°C with HC≡CSnMe$_3$ followed by slow warming to room temperature only led to decomposition. In contrast, the reaction of **8** with HC≡CSnPh$_3$ under the same conditions yielded a colorless solid which according to elemental analysis and spectroscopic data is the octahedral complex **9**. It is derived by oxidative addition of the alkynylstannane to the metal center of the square-planar rhodium(I) compound **8** and presumably contains the two alkynyl ligands in *trans* position. The IR spectrum of **9** displays a strong, somewhat broadened band at 2033 cm^{-1}, which is assigned to the asymmetric C≡C stretching mode, as well as a ν(Rh–H) band at 2118 cm^{-1}. Although compound **9** is stable under argon, it decomposes quite rapidly in solution and in this respect resembles the alkynylchlorohydridorhodium(III) derivative **3**.



Whereas treatment of the ethene complex **7** with Ph$_3$SnC≡CMe or Ph$_3$SnC≡CSnPh$_3$ only leads to undefined decomposition products, the reaction of **7** with an equimolar amount of Ph$_3$SnC≡CCH$_2$OMe in THF at −20°C affords the violet compound **10** in 81% yield. Our original assumption that **10** should be either an alkyne or a vinylidene complex with the composition *trans*-[Rh(C≡CSiMe$_3$)(Ph$_3$SnC≡CCH$_2$OMe)(P*i*Pr$_3$)$_2$] or *trans*-[Rh(C≡CSiMe$_3$)(=C=C(SnPh$_3$)CH$_2$OMe)(P*i*Pr$_3$)$_2$], respectively, has not been substantiated by NMR spectroscopy. While the ^{31}P-NMR spectrum shows a broad signal at room temperature, upon cooling to −70°C a sharp doublet at δ = 37.12 is observed with *J*(RhP) = 99.7 Hz which is much smaller than in square-planar alkyne- or vinylidenerhodium(I) complexes containing a linear [Rh(P*i*Pr$_3$)$_2$] unit. Furthermore, the large Sn-P coupling of 93.8 Hz, determined from the $^{117/119}$Sn satellites, is equally inconsistent

with the original assumption and indicates the presence of a direct Rh–Sn bond.

In order to support this proposal, the five-coordinate hydrido(stannyl)rhodium compound **11** has been prepared from **1** and triphenylstannane (see eq. 2). Although it cannot be unambiguously established whether the geometry of **11** corresponds to a trigonal bipyramid or a square-based pyramid, the important point is that the ^{31}P-NMR data are very similar to those of **10**. The Rh-P coupling is 107 Hz and the Sn-P coupling (determined from the satellites) 112 Hz which is of the same order of magnitude as those found for other compounds with a Rh–Sn bond[17–20].



(2)

11

The composition of the Rh–Sn dimetallic complex **10** has been confirmed by elemental analysis. Although the deep color differs from that of **11**, it is in agreement with the properties of other five-coordinate stannylrhodium compounds such as $[Rh(C{\equiv}CPh)_2(SnMe_3)(PPh_3)_2]$[21] and the polymer $[Rh(PPh_3)_2(SnMe_3)(C{\equiv}C\text{-}p\text{-}C_6H_4\text{-}C_6H_4\text{-}p\text{-}C{\equiv}C\text{-})]_n$[22]. As far as the mechanism of formation of **10** is concerned, we assume that in the initial step a displacement of the ethene by the alkyne occurs which is followed by a rearrangement of the supposedly labile intermediate *trans*-$[Rh(C{\equiv}CSiMe_3)(Ph_3SnC{\equiv}CCH_2OMe)(P\mathit{i}Pr_3)_2]$ to give the final product.

Discussion

The work described here has confirmed that not only 1-alkynes HC≡CR and the corresponding $SiMe_3$ and $SiPh_3$ derivatives but also alkynyltriphenylstannanes $Ph_3SnC{\equiv}CR$ can be transformed in the coordination sphere of rhodium to give the isomeric vinylidene $:C{=}C(SnPh_3)R$. Although no intermediates could be detected, it seems most probable that in the first step of the reaction an alkyne complex *trans*-$[RhCl(RC{\equiv}CSnPh_3)(P\mathit{i}Pr_3)_2]$ is formed which quickly rearranges to give the vinylidenerhodium isomer. With regard to the mechanism of the rearrangement we assume that the 1,2-$SnPh_3$ shift proceeds in a concerted way by an initial slippage of the alkyne to an η^1 geometry. On the basis of MO calculations, such a reaction pathway has also been considered as energetically preferred for the 1,2-H shift in the 18-electron system $[C_5H_5Mn(CO)_2(HC{\equiv}CR)]$[23]. The second possibility, namely the stepwise isomerization of *trans*-$[RhCl(RC{\equiv}CSnPh_3)(P\mathit{i}Pr_3)_2]$ via *trans*-$[RhCl(C{\equiv}CR)(SnPh_3)(P\mathit{i}Pr_3)_2]$ to give *trans*-$[RhCl(=C{=}C(SnPh_3)R)(P\mathit{i}Pr_3)_2]$ cannot be excluded although the kinetic stability of compound **10** is to be held against this proposal.

The course of the reaction of the stannyl-substituted vinylidene complexes with PhHgCl also deserves some comments. As it has already been mentioned, according to the reactivity of compounds **2a–h** toward acidic substrates, we originally expected a replacement of the $SnPh_3$ by the HgPh group at the β-carbon atom of the vinylidene unit. Although this mechanistic pathway is still conceivable, the better alternative seems to be an attack of the electrophilic organomercury halide on the electron-rich metal center. It is well-known[24] that half-sandwich-type rhodium(I) complexes such as $[C_5H_5Rh(CO)_2]$ or $[C_5H_5Rh(dien)]$ give 1:1 adducts with HgX_2, and a similar adduct may also be formed from **2b–j** and PhHgCl. A subsequent shift of the chloride from mercury to the vinylidene α-carbon may generate a vinylrhodium intermediate (containing a $Rh{-}CCl{=}C(SnPh)_3R$ linkage) which by Ph_3SnCl abstraction would finally give the Rh–Hg product. We note in this context that vinylidenerhodium(I) complexes of the general composition $[C_5H_5Rh(=C{=}CHR)(P\mathit{i}Pr_3)]$ also react with mercury halides HgXX′ to afford after elimination of HX piano-stool-type compounds $[C_5H_5Rh(C{\equiv}CR)(HgX')(P\mathit{i}Pr_3)]$[20].

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Experimental

All experiments were carried out under argon with the Schlenk-tube technique. The starting materials $[RhCl(P\mathit{i}Pr_3)_2]_n$ (**1**)[25], $Me_3SnC{\equiv}CR$[26], $Ph_3SnC{\equiv}CR$[26d,27], $Ph_3SnC{\equiv}CSnPh_3$[26d,28], *trans*-$[Rh(C{\equiv}CSiMe_3)(C_2H_4)(P\mathit{i}Pr_3)_2]$ (**7**)[4b], and *trans*-$[Rh(C{\equiv}CSiMe_3)(py)(P\mathit{i}Pr_3)_2]$ (**8**)[4b] were prepared by published procedures. – Melting points: measured by DTA. – IR: Perkin-Elmer 1420. – ^{1}H NMR: Jeol FX 90 Q, Bruker AC 200, Bruker AMX 400, vt = virtual triplet.

1. *Reaction of* $[RhCl(P\mathit{i}Pr_3)_2]_n$ (**1**) *with* $Me_3SnC{\equiv}CR$: A solution of 100 mg (0.22 mmol for n = 1) of **1** in 10 ml of hexane was treated at −30°C with an equimolar amount of the alkyne $Me_3SnC{\equiv}CR$ (R = H, *t*Bu, Ph, CO_2Me). A gradual change of color from red to red-violet occurred. After the solution had been concentrated in vacuo to ca. 1 ml and then stored at −78°C, violet crystals precipitated which, by comparison with an authentic sample, were identified as *trans*-$[RhCl(=C{=}CHR)(P\mathit{i}Pr_3)_2]$[7a,b]. Yield 50–70%.

2. *trans-*$[RhCl(=C{=}C(SnPh_3)H)(P\mathit{i}Pr_3)_2]$ (**2a**): A solution of 80 mg (0.17 mmol for n = 1) of **1** in 3 ml of THF was treated at −78°C with 70 mg (0.19 mmol) of $Ph_3SnC{\equiv}CH$. After the solution had been stirred for 20 min the solvent was removed, the residue was dissolved in 2 ml of ether, and 5 ml of pentane was added to the ethereal solution. A red solid precipitated which was filtered off, washed with small amounts of pentane, and dried in vacuo; yield 119 mg (82%), m.p. 106°C (dec.). – IR (KBr): ν(C=C) = 1634 cm^{-1}. – ^{1}H NMR (90 MHz, C_6D_6): δ = 7.63–7.06 (m, 15H, C_6H_5), 2.81 (m, 6H, PC*H*CH$_3$), 1.27 [dvt, N = 13.4, J(HH) = 6.9 Hz, 36H, PCHC*H*$_3$], −0.09 [dt, J(RhH) = 1.2, J(PH) = 2.9 Hz, 1H, H]. – ^{13}C NMR (50.3 MHz, C_6D_6): δ = 271.27 [dt, J(RhC) = 58.4, J(PC) = 15.6 Hz, Rh=*C*=C], 138.61, 137.15, 129.47, 128.86 (all s, C_6H_5), 82.18 [dt, J(RhC) = 19.1, J(PC) = 5.7 Hz, Rh=C=*C*], 23.82 [vt, N = 19.8 Hz, P*C*HCH$_3$], 20.39 (s, PCH*C*H$_3$). – ^{31}P NMR (81.0 MHz, C_6D_6): δ = 42.57 [d, J(RhP) = 136.3,

J(SnP) = 16.1 Hz]. – $C_{38}H_{58}ClP_2RhSn$ (833.9): calcd. C 54.73, H 7.01; found C 55.06; H 6.56.

3. *trans-[RhCl(=C=C(SnPh$_3$)CH$_3$)(PiPr$_3$)$_2$]* (**2b**): A solution of 120 mg (0.26 mmol for n = 1) of **1** in 5 ml of THF was treated at −78°C with 106 mg (0.27 mmol) of $Ph_3SnC{\equiv}CCH_3$ and during 30 min slowly warmed to room temp. A change of color from red to violet occurred. The solution was concentrated to ca. 1 ml in vacuo, and the concentrate was extracted three times with 5 ml of pentane each. The combined extracts were brought to dryness in vacuo, and the residue was dissolved in 2 ml THF/ether (1:1). After the solution had been stored at −40°C a violet microcrystalline powder was obtained; yield 156 mg (70%); m.p. 102°C (dec.). – IR (CH_2Cl_2): ν(C=C) = 1670 cm^{-1}. – ^{1}H NMR (90 MHz, C_6D_6): δ = 7.71−7.27 (m, 15H, C_6H_5), 2.74 (m, 6H, PC*H*CH$_3$), 2.14 [dt, J(RhH) = 0.6, J(PH) = 2.1, J(SnH) = 48.8 Hz, 3H, =CCH$_3$], 1.32 [dvt, N = 12.9, J(HH) = 6.9 Hz, 18H, PCHC*H*$_3$], 1.19 [dvt, N = 13.0, J(HH) = 7.0 Hz, 18H, PCHC*H*$_3$]. – ^{13}C NMR (100.6 MHz, C_6D_6): δ = 292.22 [dt, J(RhC) = 62.1, J(PC) = 15.5 Hz, Rh=*C*=C], 138.47, 137.66, 129.45, 128.74 (all s, C_6H_5), 98.84 [dt, J(RhC) = 15.8, J(PC) = 6.4 Hz, Rh=C=*C*], 24.07 [vt, N = 19.1 Hz, P*C*HCH$_3$], 20.65, 20.19 (both s, PCH*C*H$_3$), 3.78 (s, =C*C*H$_3$). – ^{31}P NMR (36.2 MHz, C_6D_6): δ = 40.87 [d, J(RhP) = 134.8 Hz]. – $C_{39}H_{60}ClP_2RhSn$ (847.9): calcd. C 55.25, H 7.13; found C 55.48, H 7.61.

4. *trans-[RhCl(=C=C(SnPh$_3$)C$_6$H$_5$)(PiPr$_3$)$_2$]* (**2c**): A solution of 130 mg (0.28 mmol for n = 1) of **1** in 5 ml of THF was treated at −50°C with 128 mg (0.28 mmol) of $Ph_3SnC{\equiv}CC_6H_5$. With continuous stirring the solution was warmed to room temp., and then the solvent was removed. The oily residue was dissolved in 5 ml of pentane, the solution was filtered, and the filtrate was concentrated to ca. 2 ml in vacuo. After the concentrate had been cooled to −78°C, violet crystals precipitated which were filtered off, washed with small amounts of pentane and dried in vacuo; yield 142 mg (55%), m.p. 114°C (dec.). – IR (KBr): ν(C=C) = 1630 cm^{-1}. – ^{1}H NMR (200 MHz, C_6D_6): δ = 7.82−7.14 (m, 20H, C_6H_5), 2.74 (m, 6H, PC*H*CH$_3$), 1.33 [dvt, N = 13.6, J(HH) = 6.9 Hz, 18H, PCHC*H*$_3$], 1.19 [dvt, N = 13.4, J(HH) = 6.8 Hz, 18H, PCHC*H*$_3$]. – ^{13}C NMR (50.3 MHz, C_6D_6): δ = 295.14 [dt, J(RhC) = 60.1, J(PC) = 16.2 Hz, Rh=*C*=C], 138.18, 136.88, 136.67, 135.37, 129.95, 129.78, 125.70 (all s, C_6H_5), 112.13 [dt, J(RhC) = 14.8, J(PC) = 6.2 Hz, Rh=C=*C*], 24.68 [vt, N = 19.8 Hz, P*C*HCH$_3$], 20.79, 20.40 (both s, PCH*C*H$_3$). – ^{31}P NMR (36.2 MHz, C_6D_6): δ = 40.80 [d, J(RhP) = 137.7 Hz]. – $C_{44}H_{62}ClP_2RhSn$ (910.0): calcd. C 58.08, H 6.87; found C 58.40, H 7.21.

5. *trans-[RhCl(=C=C(SnPh$_3$)CH$_2$OH)(PiPr$_3$)$_2$]* (**2d**): A solution of 201 mg (0.44 mmol for n = 1) of **1** in 10 ml of THF was treated with 177 mg (0.44 mmol) of $Ph_3SnC{\equiv}CCH_2OH$ at room temp. After the solution had been stirred for 20 min the solvent was removed, and the oily residue was dissolved in 5 ml of ether. Pentane was added to the ethereal solution until a precipitate had formed. The violet solid was filtered off, washed with 2 ml of pentane and ether and dried in vacuo; yield 291 mg (77%), m.p. 99°C. – IR (KBr): ν(OH) = 3420, ν(C=C) = 1660 cm^{-1}. – ^{1}H NMR (200 MHz, C_6D_6): δ = 7.93−7.17 (m, 15H, C_6H_5), 4.53 [s, J(SnH) = 57.4 Hz, 2H, C*H*$_2$OH], 2.76 (m, 6H, PC*H*CH$_3$), 1.34 [dvt, N = 13.5, J(HH) = 6.9 Hz, 18H, PCHC*H*$_3$], 1.20 [dvt, N = 13.3, J(HH) = 6.8 Hz, 18H, PCHC*H*$_3$], signal of OH not exactly located. – ^{13}C NMR (50.3 MHz, C_6D_6): δ = 266.02 [dt, J(RhC) = 60.0, J(PC) = 15.3 Hz, Rh=*C*=C], 138.97, 138.09, 129.73, 129.07 (all s, C_6H_5), 102.51 [dt, J(RhC) = 17.6, J(PC) = 5.3 Hz, Rh=C=*C*], 50.13 (s, CH_2OH), 24.38 [vt, N = 20.5 Hz, P*C*HCH$_3$], 20.91, 20.51 (both s, PCH*C*H$_3$). – ^{31}P NMR (81.0 MHz, C_6D_6): δ = 42.22 [d, J(RhP) = 135.2, J(SnP) = 17.6 Hz]. – $C_{39}H_{60}ClOP_2RhSn$ (863.9): calcd. C 54.22, H 7.00; found C 54.22, H 7.39.

6. *trans-[RhCl(=C=C(SnPh$_3$)CH$_2$OMe)(PiPr$_3$)$_2$]* (**2e**): A solution of 130 mg (0.28 mmol for n = 1) of **1** in 5 ml THF was treated with 130 mg (0.31 mmol) of $Ph_3SnC{\equiv}CCH_2OMe$ at room temp. Almost spontaneously a color change from red to dark-violet occurred. The solvent was removed, the oily residue was dissolved in 2 ml of ether, and 10 ml of pentane was added to the etheral solution. After the solution had been stored at 0°C, violet crystals precipitated which were collected by filtration, washed with small amounts of pentane (0°C) and dried in vacuo; yield 199 mg (80%), m.p. 110°C (dec.). – IR (KBr): ν(C=C) = 1680 cm^{-1}. – ^{1}H NMR (200 MHz, C_6D_6): δ = 7.91−7.18 (m, 15H, C_6H_5), 4.36 [s, J(SnH) = 56.2 Hz, 2H, C*H*$_2$OCH$_3$], 2.78 (m, 6H, PC*H*CH$_3$), 2.75 (s, 3H, CH$_2$OC*H*$_3$), 1.35 [dvt, N = 13.5, J(HH) = 6.8 Hz, 18H, PCHC*H*$_3$], 1.22 [dvt, N = 13.4, J(HH) = 6.8 Hz, 18H, PCHC*H*$_3$]. – ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ = 265.47 [dt, J(RhC) = 59.2, J(PC) = 15.3 Hz, Rh=*C*=C], 139.23, 138.13, 129.52, 128.88, (all s, C_6H_5), 100.73 [dt, J(RhC) = 17.8, J(PC) = 5.4 Hz, Rh=C=*C*], 59.77 (s, *C*H$_2$OCH$_3$), 57.99 (s, CH$_2$O*C*H$_3$), 24.36 [vt, N = 19.7 Hz, P*C*HCH$_3$], 20.86, 20.48 (both s, PCH*C*H$_3$). – ^{31}P NMR (81.0 MHz, C_6D_6): δ = 42.44 [d, J(RhP) = 135.9, J(SnP) = 18.2 Hz]. – $C_{40}H_{62}ClOP_2RhSn$ (877.9): calcd. C 54.72, H 7.12, Rh 11.72, Sn 13.52; found C 54.92, H 7.16, Rh 11.45, Sn 13.70.

7. *trans-[RhCl(=C=C(SnPh$_3$)CMe$_2$OH)(PiPr$_3$)$_2$]* (**2f**): A solution of 100 mg (0.22 mmol for n = 1) of **1** in 10 ml of THF was treated at −78°C with 94 mg (0.22 mmol) of $Ph_3SnC{\equiv}CCMe_2OH$ and then slowly warmed to room temp. A change of color from red to dark-blue occurred. The solvent was removed, the residue was dissolved in 2 ml of ether (0°C), and pentane was added to the solution until a precipitate could be observed. After storage at 0°C for 12 h, the dark microcrystalline solid was collected by filtration, washed twice with 4 ml of pentane/ether (0°C) and dried in vacuo; yield 171 mg (88%), m.p. 94°C. – IR (CH_2Cl_2): ν(OH) = 3390, ν(C=C) = 1635 cm^{-1}. – ^{1}H NMR (200 MHz, C_6D_6): δ = 8.09−7.05 (m, 15H, C_6H_5), 2.83 (m, 6H, PC*H*CH$_3$), 1.34 [s, 6H, C(C*H*$_3$)$_2$OH], 1.30 [dvt, N = 13.5, J(HH) = 7.0 Hz, 18H, PCHC*H*$_3$], 1.20 [dvt, N = 13.3, J(HH) = 6.8 Hz, 18H, PCHC*H*$_3$], signal of OH not exactly located. – ^{13}C NMR (50.3 MHz, C_6D_6): δ = 262.94 [dt, J(RhC) = 60.6, J(PC) = 14.5 Hz, Rh=*C*=C], 140.12, 138.39, 130.14, 129.57 (all s, C_6H_5), 117.45 [dt, J(RhC) = 16.5, J(PC) = 5.3 Hz, Rh=C=*C*], 65.61 [s, *C*(CH$_3$)$_2$OH], 34.37 [s, C(*C*H$_3$)$_2$OH], 25.50 (vt, N = 19.7 Hz, P*C*HCH$_3$), 22.38, 21.65 (both s, PCH*C*H$_3$). – ^{31}P NMR (81.0 MHz, C_6D_6): δ = 39.40 [d, J(RhP) = 136.3, J(SnP) = 19.5 Hz]. – $C_{41}H_{64}ClOP_2RhSn$ (891.95): calcd. C 55.21, H 7.23; found C 55.65, H 7.07.

8. *trans-[RhCl(=C=C(SnPh$_3$)CH(CH$_3$)OH)(PiPr$_3$)$_2$]* (**2g**): A solution of 116 mg (0.25 mmol for n = 1) of **1** in 5 ml of THF was treated at −78°C with 106 mg (0.25 mmol) of $Ph_3SnC{\equiv}CCH(CH_3)OH$ and then slowly warmed to room temp. The solvent was removed, the oily residue was extracted three times with 10 ml of pentane each, and the combined extracts were concentrated to ca. 5 ml in vacuo. After the concentrate had been stored at −78°C, red crystals precipitated which were collected by filtration, washed with small amounts of pentane (0°C) and dried in vacuo; yield 188 mg (85%), m.p. 104°C (dec.). – IR (KBr): ν(OH) = 3400, ν(C=C) = 1645 cm^{-1}. – ^{1}H NMR (400 MHz, C_6D_6): δ = 8.06−7.10 (m, 15H, C_6H_5), 5.08, 5.06 [both q, J(HH) = 5.1, J(SnH) = 54.8 Hz, 1H, C*H*(CH$_3$)OH], 2.85, 2.78 (both m, 6H, PC*H*CH$_3$), 1.46, 1.45 [both s, br, 3H, CH(C*H*$_3$)OH],

1.36, 1.34 [both dvt, N = 13.6, J(HH) = 7.5 Hz, 18H, PCHCH_3], 1.24, 1.20 [both dvt, N = 13.6, J(HH) = 7.2 Hz, 18H, PCHCH_3], Signal of OH not exactly located. – ^{13}C NMR (100.6 MHz, C_6D_6): δ = 264.59 [dt, J(RhC) = 58.8, J(PC) = 14.2 Hz, Rh=*C*=C], 138.16, 137.28, 129.12, 128.53 (all s, C_6H_5), 109.06 [dt, J(RhC) = 17.8, J(PC) = 4.9 Hz, Rh=C=*C*], 57.17 [s, *C*H(CH$_3$)OH], 27.59 [s, CH(*C*H$_3$)OH], 24.18 [dd, ^1J(PC) = 11.5, ^3J(PC) = 7.9 Hz, P*C*HCH$_3$], 23.87 [dd, ^1J(PC) = 11.5, ^3J(PC) = 7.5 Hz, P*C*HCH$_3$], 20.72, 20.26, 20.16 (all s, PCH*C*H$_3$). – ^{31}P NMR (162.0 MHz, C_6D_6): δ = 40.81, 40.74 [both d, J(RhP) = 135.8 Hz, J(PP) not resolved]. – $C_{40}H_{62}ClOP_2RhSn$ (877.9): calcd. C 54.72, H 7.12; found C 54.42, H 6.91.

9. *trans-[RhCl(=C=C(SnPh$_3$)CH(Ph)OH)(PiPr$_3$)$_2$]* (**2h**): Analogously as described for **2g** by using 125 mg (0.27 mmol for n = 1) of **1** and 131 mg (0.27 mmol) of Ph$_3$SnC≡CCH(Ph)OH as starting materials; red microcrystalline solid, yield 175 mg (68%), m.p. 100°C. – IR (KBr): ν(OH) = 3380, ν(C=C) = 1665 cm^{-1}. – ^{1}H NMR (400 MHz, C_6D_6): δ = 8.04–6.91 (m, 20H, C_6H_5), 6.06 [s, J(SnH) = 44.9 Hz, 1H, C*H*(Ph)OH], 2.85, 2.49 (both m, 6H, PC*H*CH$_3$), 1.75 [s, 1H, CH(Ph)O*H*], 1.40, 1.21 [both dvt, N = 12.2, J(HH) = 7.0 Hz, 18H, PCHCH_3], 1.16, 1.11 [both dvt, N = 13.8, J(HH) = 7.0 Hz, 18H, PCHCH_3]. – ^{13}C NMR (100.6 MHz, C_6D_6): δ = 263.07 [dt, J(RhC) = 60.5, J(PC) = 19.8 Hz, Rh=*C*=C], 141.37, 138.44, 137.06, 129.29, 128.88, 128.39, 127.86, 127.02 (all s, C_6H_5), 110.11 [dt, J(RhC) = 17.8, J(PC) = 4.9 Hz, Rh=C=*C*], 62.19 [s, *C*H(Ph)OH], 24.09, 23.61 [both dd, ^1J(PC) = 11.4, ^3J(PC) = 7.6 Hz, P*C*HCH$_3$], 20.72, 20.19, 20.11 (all s, PCH*C*H$_3$). – ^{31}P NMR (162.0 MHz, C_6D_6): δ = 40.87, 40.74 [both d, J(RhP) = 134.9 Hz, J(PP) not resolved]. – $C_{45}H_{64}ClOP_2RhSn$ (940.0). calcd. C 57.50, H 6.86; found C 56.93, H 6.99.

10. *trans-[RhCl(=C=C(SnPh$_3$)SiMe$_3$)(PiPr$_3$)$_2$]* (**2i**): A solution of 135 mg (0.29 mmol for n = 1) of **1** in 10 ml of THF was treated at –40°C with 135 mg (0.30 mmol) of Ph$_3$SnC≡CSiMe$_3$. The solution was warmed to room temp., stirred for 30 min, and then brought to dryness in vacuo. The residue was extracted with 5 ml of pentane, the extract was concentrated to ca. 2 ml, and the concentrate was stored at –78°C. Red crystals precipitated which were collected by filtration, washed with small amounts of pentane (0°C) and dried in vacuo, yield 214 mg (80%), m.p. 58°C (dec.). – IR (hexane): ν(C=C) = 1638 cm^{-1}. – ^{1}H NMR (200 MHz, C_6D_6): δ = 7.54–7.05 (m, 15H, C_6H_5), 2.76 (m, 6H, PC*H*CH$_3$), 1.35 [dvt, N = 13.4, J(HH) = 6.8 Hz, 18H, PCHCH_3], 1.20 [dvt, N = 13.2, J(HH) = 6.7 Hz, 18H, PCHCH_3], 0.13 (s, 9H, SiCH$_3$). – ^{13}C NMR (100.6 MHz, C_6D_6): δ = 259.82 [dt, J(RhC) = 63.8, J(PC) = 14.0 Hz, Rh=*C*=C], 139.72, 138.16, 129.43, 128.65 (all s, *C*$_6$H$_5$), 86.50 [dt, J(RhC) = 16.8, J(PC) = 3.9 Hz, Rh=C=*C*], 24.31 (vt, N = 18.8 Hz, P*C*HCH$_3$), 21.08, 20.44 (both s, PCH*C*H$_3$), 3.24 (s, SiCH$_3$). – ^{3}P NMR (81.0 MHz, C_6D_6): δ = 41.50 [d, J(RhP) = 136.6 Hz]. – $C_{41}H_{66}ClP_2RhSiSn$ (906.1): calcd. C 54.35, H 7.34; found C 54.97, H 7.81.

11. *trans-[RhCl(=C=C(SnPh$_3$)$_2$)(PiPr$_3$)$_2$]* (**2j**): A solution of 125 mg (0.27 mmol for n = 1) of **1** in 10 ml of THF was treated at –40°C with 210 mg (0.29 mmol) of Ph$_3$SnC≡CSnPh$_3$. The solution was slowly warmed to room temp., and after 30 min the solvent was removed. The residue was dissolved in 3 ml of ether (0°C), and 30 ml of pentane was added to the obtained solution. A light-red crystalline solid precipitated which was collected by filtration, washed twice with 2 ml of pentane each, and dried in vacuo, yield 264 mg (82%), m.p. 83°C (dec.). – IR (KBr): ν(C=C) = 1640 cm^{-1}. – ^{1}H NMR (200 MHz, C_6D_6): δ = 7.78– 7.10 (m, 30H, C_6H_5), 2.77 (m, 6H, PC*H*CH$_3$), 1.31 [dvt, N = 13.4, J(HH) = 6.9 Hz, 36H, PCHCH_3]. – ^{13}C NMR (50.3 MHz, [D$_8$]THF): δ = 273.39 [dt, J(RhC) = 58.0, J(PC) = 15.5 Hz, Rh=*C*=C], 138.73, 138.33, 131.19, 130.34 (all s, C_6H_5), 83.92 [dt, J(RhC) = 18.8, J(PC) = 5.2 Hz, Rh=C=*C*], 24.45 (vt, N = 19.1 Hz, P*C*HCH$_3$), 21.79 (s, PCH*C*H$_3$). – ^{31}P NMR (81.0 MHz, C_6D_6): δ = 40.64 [d, J(RhP) = 135.2, J(SnP) = 16.2 Hz]. – $C_{56}H_{72}ClP_2RhSn_2$ (1182.9): calcd. C 56.86, H 6.14, Rh 8.70, Sn 20.07; found C 57.01, H 6.30, Rh 8.53, Sn 20.35.

12. *Reaction of Complex* **2a** *with Pyridine:* A solution of 45 mg (0.05 mmol) of **2a** in 0.5 ml of benzene was treated in an NMR tube with 10 µl of pyridine. After 1 h the formation of [RhH(C≡CSnPh$_3$)Cl(py)(P*i*Pr$_3$)$_2$] (**3**) was detected by ^{1}H-NMR spectroscopy. The ratio of **2a**:**3** was approximately 4:1. The addition of excess pyridine as well as longer reaction times led to increasing decomposition. – **3**: ^{1}H NMR (90 MHz, C_6D_6): δ = 7.97–7.15 (m, 15H, C_6H_5), 7.02–6.62 (m, 5H, C_5H_5N), 2.85 (m, 6H, PC*H*CH$_3$), 1.13 [dvt, N = 13.4, J(HH) = 6.8 Hz, 36H, PCHCH_3], –17.12 [dt, J(RhH) = 13.6, J(PH) = 13.4 Hz, 1H, RhH]. – ^{31}P NMR (36.2 MHz, C_6D_6): δ = 37.66 [d, J(RhP) = 98.8 Hz, dd in off-resonance].

13. *Reaction of Complex* **2d** *with CF$_3$CO$_2$H:* A solution of 70 mg (0.08 mmol) of **2d** in 5 ml of benzene was treated with 7 µl (0.09 mmol) of CF$_3$CO$_2$H which led to a spontaneous change of color from violet to green. After the solvent had been removed the residue was dissolved in 5 ml of pentane. The solution was filtered, and the filtrate was stored at –78°C. Green crystals precipitated which were identified by ^{1}H-NMR spectroscopy as *trans*-[RhCl(=C=CHCH$_2$OH)(P*i*Pr$_3$)$_2$] (**4**)[8a]; yield 29 mg (72%).

14. *Reaction of Complex* **2h** *with CF$_3$CO$_2$H:* Analogously as described for the reaction of **2d** by using 107 mg (0.11 mmol) of **2h** and 9 µl (0.11 mmol) of CF$_3$CO$_2$H as starting materials. The yellow crystals obtained were identified by ^{1}H-NMR spectroscopy as *trans*-[RhCl(=C=C=CHPh)(P*i*Pr$_3$)$_2$] (**5**)[8c]: yield 32 mg (49%).

15. *[Rh(C≡CCH$_3$)Cl(HgPh)(PiPr$_3$)$_2$]* (**6a**): A solution of 108 mg (0.13 mmol) of **2b** in 10 ml of toluene was treated with 42 mg (0.13 mmol) of PhHgCl and stirred for 30 min at room temp. During that time, a change of color from violet to orange-red occurred. The solvent was removed in vacuo, the oily residue was dissolved in 2 ml of benzene, and pentane was added to the solution until a white solid precipitated. The solution was filtered, the residue washed with benzene/pentane (1:2), and the filtrate was concentrated in vacuo to ca. 1 ml. After 20 ml of pentane had been added to the concentrate, an orange-red crystalline powder formed which was collected by filtration, repeatedly washed with pentane and dried in vacuo, yield 94 mg (95%), m.p. 100°C (dec.). – IR (KBr): ν(C≡C) = 2090 cm^{-1}. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.53–6.90 (m, 5H, C_6H_5), 2.85 (m, 6H, PC*H*CH$_3$), 1.63 [t, J(PH) = 1.5 Hz, 3H, ≡CCH$_3$], 1.38 [dvt, N = 14.0, J(HH) = 7.0 Hz, 18H, PCHCH_3], 1.36 [dvt, N = 13.3, J(HH) = 6.8 Hz, 18H, PCHCH_3]. – ^{31}P NMR (81.0 MHz, $CDCl_3$): δ = 46.58 [d, J(RhP) = 101.7, J(HgP) = 144.2 Hz]. – $C_{27}H_{50}ClHgP_2Rh$ (775.6): calcd. C 41.81, H 6.50; found C 42.18, H 6.50.

16. *[Rh(C≡CPh)Cl(HgPh)(PiPr$_3$)$_2$]* (**6b**): – a) Analogously as described for **6a** by using 115 mg (0.13 mmol) of **2c** and 42 mg (0.13 mmol) of PhHgCl. An orange-red solid was obtained; yield 101 mg (95%). – b) A solution of 200 mg (0.44 mmol for n = 1) of **1** in 10 ml of THF was treated at –78°C with 200 mg (0.44 mmol) of Ph$_3$SnC≡CPh and warmed to room temp. with stirring over a period of 30 min. The solvent was removed, the residue was dissolved in 10 ml of toluene and the solution treated with 137 mg (0.44 mmol) of PhHgCl. The workup procedure was the same as described for a); yield 313 mg (86%), m.p. 92°C (dec.). – IR (KBr): ν(C≡C) = 2077 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ =

7.60–6.88 (m, 10H, C_6H_5), 2.93 (m, 6H, PC*H*CH_3), 1.40 [dvt, N = 13.7, J(HH) = 6.8 Hz, 18H, PCHC*H*$_3$], 1.38 [dvt, N = 13.3, J(HH) = 6.7 Hz, 18H, PCHC*H*$_3$]. – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 155.56 [dt, J(RhC) = 13.1, J(PC) = 1.7 Hz, *ipso*-C of HgC_6H_5], 137.59, 134.33, 129.72, 128.06, 128.04, 127.76, 124.42 (all s, C_6H_5), 115.30 [dt, J(RhC) = 13.2, J(PC) = 1.8 Hz, Rh–C≡*C*], 102.30 [dt, J(RhC) = 47.2, J(PC) = 15.6 Hz, Rh–*C*≡C], 23.02 (vt, N = 20.8 Hz, P*C*HCH$_3$), 20.76, 20.33 (both s, PCH*C*H$_3$). – ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 46.45 [d, J(RhP) = 100.8, J(HgP) = 138.8 Hz]. – $C_{32}H_{52}ClHgP_2Rh$ (837.7): calcd. C 45.88, H 6.26; found C 45.81, H 5.81.

17. *[Rh(C≡CCH$_2$OH)Cl(HgPh)(PiPr$_3$)$_2$]* (**6c**): Analogously as described for **6a** by using 130 mg (0.15 mmol) of **2d** and 48 mg (0.15 mmol) of PhHgCl as starting materials. Crystallization from toluene/pentane (1:5) gave orange-red crystals; yield 97 mg (81%), m.p. 107°C (dec.). – IR (KBr): ν(OH) = 3440, ν(C≡C) = 2082 cm^{-1}. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.74–6.95 (m, 5H, C_6H_5), 4.14 (s, 2H, C*H*$_2$OH), 3.00 (m, 6H, PC*H*CH$_3$), 2.40 (s, 1H, CH$_2$O*H*), 1.47 [dvt, N = 13.8, J(HH) = 6.9 Hz, 36H, PCHC*H*$_3$]. – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 155.98 [dt, J(RhC) = 13.0, J(PC) = 1.7 Hz, *ipso*-C of C_6H_5], 134.94, 128.81, 127.71 (all s, C_6H_5), 113.10 [dt, J(RhC) = 12.8, J(PC) = 3.3 Hz, Rh–C≡*C*], 95.52 [dt, J(RhC) = 47.5, J(PC) = 16.6 Hz, Rh–*C*≡C], 54.85 (s, CH$_2$OH), 23.53 (vt, N = 19.9 Hz, P*C*HCH$_3$), 21.42, 20.94 (both s, PCH*C*H$_3$). – ^{31}P NMR (81.0 MHz, $CDCl_3$): δ = 46.59 [d, J(RhP) = 101.0, J(HgP) = 140.2 Hz]. – $C_{27}H_{50}ClHgOP_2Rh$ (791.6): calcd. C 40.97, H 6.37, Hg 25.34, Rh 13.00; found C 40.64, H 6.30, Hg 25.80, Rh 13.40.

18. *[Rh(C≡CCH$_2$OMe)Cl(HgPh)(PiPr$_3$)$_2$]* (**6d**): A solution of 80 mg (0.09 mmol) of **2e** in 5 ml of toluene was treated with 31 mg (0.10 mmol) of PhHgCl and stirred for 30 min at room temp. A change of color from violet to orange-red occurred. The solution was concentrated to ca. 1 ml of vacuo, and 5 ml of pentane was added. A white solid precipitated which was collected by filtration and washed with toluene/pentane (1:5). The combined filtrates were brought to dryness in vacuo, the residue was dissolved in 2 ml of toluene/pentane (1:3) and the solution was stored at –78°C. Orange-red crystals formed which were collected by filtration, washed with pentane and dried in vacuo; yield 70 mg (95%), m.p. 92°C. – IR (KBr): ν(C≡C) = 2087 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62–6.96 (m, 5H, C_6H_5), 4.06 (s, br, 2H, C*H*$_2$OCH$_3$) 3.26 (s, br, 3H, CH$_2$OC*H*$_3$), 2.86 (m, 6H, PC*H*CH$_3$), 1.38 [dvt, N = 12.6, J(HH) = 6.9 Hz, 18H, PCHC*H*$_3$], 1.35 [dvt, N = 12.2, J(HH) = 6.6 Hz, 18H, PCHC*H*$_3$]. – ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 156.36 [dt, J(RhC) = 13.2, J(PC) = 1.9 Hz, *ipso*-C of C_6H_5], 134.79, 128.64, 128.51 (all s, C_6H_5), 110.88 [dt, J(RhC) = 12.8, J(PC) = 1.6 Hz, Rh–C≡*C*], 94.84 [dt, J(RhC) = 46.3, J(PC) = 13.8 Hz, Rh–*C*≡C], 63.24 (s, *C*H$_2$OCH$_3$) 56.73 (s, CH$_2$O*C*H$_3$), 23.21 (vt, N = 20.7 Hz, P*C*HCH$_3$), 20.97, 20.23 (both s, PCH*C*H$_3$). – ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 46.57 [d, J(RhP) = 101.4, J(HgP) = 142.7 Hz]. – $C_{28}H_{52}ClHgOP_2Rh$ (805.6): calcd. C 41.75, H 6.51; found C 42.08, H 6.66.

19. *[Rh(C≡CCMe$_2$OH)Cl(HgPh)(PiPr$_3$)$_2$]* (**6e**): Analogously as described for **6a** by using 160 mg (0.18 mmol) of **2f** and 56 mg (0.18 mmol) of PhHgCl as starting materials. Orange-yellow crystals, yield 136 mg (92%), m.p. 127°C. – IR (KBr): ν(OH) = 3430, ν(C≡C) = 2079 cm^{-1}. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.73–6.99 (m, 5H, C_6H_5), 3.04 (m, 6H, PC*H*CH$_3$), 2.40 [s, 1H, C(CH$_3$)$_2$O*H*], 1.48 [dvt, N = 13.5, J(HH) = 7.0 Hz, 36H, PCHC*H*$_3$], 1.41 [s, 6H, C(C*H*$_3$)$_2$OH]. – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 155.95 [dt, J(RhC) = 12.8, J(PC) = 1.8 Hz, *ipso*-C of C_6H_5], 134.92, 129.72, 128.67 (all s, C_6H_5), 119.49 [dt, J(RhC) = 12.9, J(PC) = 1.5 Hz, Rh–C≡*C*], 90.11 [dt, J(RhC) = 47.0, J(PC) = 15.4 Hz, Rh–*C*≡C], 67.64 [s, *C*(CH$_3$)$_2$OH], 32.70 [s, C(*C*H$_3$)$_2$OH], 23.38 (vt, N = 19.9 Hz, P*C*HCH$_3$), 21.26, 20.97 (both s, PCH*C*H$_3$). – ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 46.58 [d, J(RhP) = 101.3, J(HgP) = 140.7 Hz]. – $C_{29}H_{54}ClHgOP_2Rh$ (819.6): calcd. C 42.50, H 6.64, Hg 24.47, Rh 12.55; found C 41.93, H 6.22, Hg 24.65, Rh 12.30.

20. *[Rh(C≡CCH(CH$_3$)OH)Cl(HgPh)(PiPr$_3$)$_2$]* (**6f**): – a) Analogously as described for **6a** by using 98 mg (0.11 mmol) of **2g** and 42 mg (0.13 mmol) of PhHgCl as starting materials. After recrystallization from toluene/pentane (1:10) red crystals were obtained; yield 86 mg (96%). – b) A solution of 120 mg (0.26 mmol for n = 1) of **1** in 10 ml of THF was treated at –40°C with 126 mg (0.30 mmol) of Ph$_3$SnC≡CCH(CH$_3$)OH and warmed to room temp. with stirring over a period of 1 h. The solvent was removed and the residue dissolved in 6 ml of toluene. After 85 mg (0.26 mmol) of PhHgCl had been added, the solution was stirred for 2 h at room temp. The further workup procedure was the same as described for **6a**; yield 152 mg (72%), m.p. 96°C (dec.). – IR (KBr): ν(OH) = 3425, ν(C≡C) = 2080 cm^{-1}. – ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.75–6.98 (m, 5H, C_6H_5), 4.40 [q, J(HH) = 6.2 Hz, 1H, C*H*(CH$_3$)OH], 3.02 (m, 6H, PC*H*CH$_3$), 2.40 [s, br, 3H, CH(C*H*$_3$)OH], 1.48 [dvt, N = 13.9, J(HH) = 7.1 Hz, 18H, PCHC*H*$_3$], 1.47 [dvt, N = 13.0, J(HH) = 6.8 Hz, 18H, PCHC*H*$_3$], signal of OH not exactly located. – ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 156.00 [dt, J(RhC) = 13.3, J(PC) = 1.5 Hz, *ipso*-C of C_6H_5], 134.96, 128.82, 128.72 (all s, C_6H_5), 117.17 [dt, J(RhC) = 12.7, J(PC) = 1.8 Hz, Rh–C≡*C*], 92.93 [dt, J(RhC) = 47.0, J(PC) = 15.7 Hz, Rh–*C*≡C], 61.57 [s, *C*H(CH$_3$)OH], 25.98 [s, CH(*C*H$_3$)OH], 23.49 (vt, N = 20.8 Hz, P*C*HCH$_3$), 21.39, 20.96 (both s, PCH*C*H$_3$). – ^{31}P NMR (162.0 MHz, $CDCl_3$): δ = 46.56 [d, J(RhP) = 100.3, J(HgP) = 141.0 Hz]. – $C_{28}H_{52}ClHgOP_2Rh$ (805.6): calcd. C 41.75, H 6.51; found C 41.60, H 6.19.

21. *[Rh(C≡CCH(Ph)OH)Cl(HgPh)(PiPr$_3$)$_2$]* (**6g**): Analogously as described for **6a** by using 80 mg (0.09 mmol) of **2h** and 27 mg (0.09 mmol) of PhHgCl as starting materials. After recrystallization from toluene/pentane (1:10) a red microcrystalline solid was obtained; yield 55 mg (74%), m.p. 81°C (dec.). – IR (KBr): ν(OH) = 3420, ν(C≡C) = 2086 cm^{-1}. – ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–6.95 (m, 10H, C_6H_5), 5.32 [d, J(HH) = 5.2 Hz, 1H, C*H*(Ph)OH], 2.93 (m, 6H, PC*H*CH$_3$), 1.87 [d, J(HH) = 5.2 Hz, 1H, CH(Ph)O*H*], 1.41 [dvt, N = 13.6, J(HH) = 6.9 Hz, 36H, PCHC*H*$_3$].– ^{31}P NMR (81.0 MHz, $CDCl_3$): δ = 46.74 [d, J(RhP) = 100.3, J(HgP) = 140.7 Hz]. – $C_{33}H_{54}ClHgOP_2Rh$ (867.7): calcd. C 45.68, H 6.27; found C 45.13, H 5.64.

22. *[Rh(C≡CSiMe$_3$)Cl(HgPh)(PiPr$_3$)$_2$]* (**6h**): – a) Analogously as described for **6a** by using 107 mg (0.12 mmol) of **2i** and 38 mg (0.12 mmol) of PhHgCl as starting materials. Recrystallization from toluene/pentane (1:4) gave orange-red crystals; yield 93 mg (95%). – b) A solution of 70 mg (0.13 mmol) of **7** in 5 ml toluene was treated at –30°C with 40 mg (0.13 mmol) of PhHgCl. After the solution had been stirred for 30 min, it was worked up as described for **6a**. Recrystallization from toluene/pentane (1:4) gave orange-red crystals; yield 47 mg (44%), m.p. 147°C (dec.). – IR (KBr): $\tilde{\nu}$ (C≡C) = 2008 cm^{-1}. – ^{1}H NMR (200 MHz, C_6D_6): δ = 7.56–7.03 (m, 5H, C_6H_5), 2.91 (m, 6H, PC*H*CH$_3$), 1.38 [dvt, N = 13.6, J(HH) = 7.2 Hz, 18H, PCHC*H*$_3$], 1.34 [dvt, N = 13.2, J(HH) = 6.9 Hz, 18H, PCHC*H*$_3$], 0.19 (s, 9H, SiCH$_3$). – ^{31}P NMR (81.0 MHz, C_6D_6): δ = 46.87 [d, J(RhP) = 101.7, J(HgP) = 139.3 Hz]. – $C_{29}H_{56}ClHgP_2RhSi$ (833.75): calcd. C 41.78, H 6.77; found C 41.69, H 7.08.

23. *[Rh(C≡CSnPh$_3$)Cl(HgPh)(PiPr$_3$)$_2$]* (**6i**): – a) Analogously as described for **6a** by using 115 mg (0.13 mmol) of **2j** and 42 mg

(0.13 mmol) of PhHgCl as starting materials. Recrystallization from benzene/pentane (1:2) gave orange-red crystals; yield 101 mg (72%). – b) A solution of 200 mg (0.44 mmol for $n = 1$) of **1** in 10 ml of THF was treated at −78°C with 320 mg (0.44 mmol) of $Ph_3SnC{\equiv}CSnPh_3$ and warmed to room temp. with stirring over a period of 30 min. The solvent was removed, the residue was dissolved in 10 ml of toluene and the solution treated with 137 mg (0.44 mmol) of PhHgCl. The workup procedure was the same as described for a); yield 313 mg (65%), m.p. 85°C. – IR (KBr): ν(C≡C) = 1980 cm^{-1}. – ^1H NMR (400 MHz, $CDCl_3$): δ = 7.80–6.81 (m, 20H, C_6H_5), 2.95 (m, 6H, PC*H*CH_3), 1.30 [dvt, N = 13.2, J(HH) = 6.7 Hz, 36H, PCHC*H*$_3$]. – ^{31}P NMR (36.2 MHz, C_6D_6): δ = 46.28 [d, J(RhP) = 101.1, J(HgP) = 139.2, J(SnP) = 10.3 Hz]. – $C_{44}H_{62}ClHgP_2RhSn$ (1110.6): calcd. C 47.59, H 5.63; found C 47.29, H 5.84.

24. *[RhH(C≡CSiMe$_3$)(C≡CSnPh$_3$)(py)(PiPr$_3$)$_2$]* (**9**): A solution of 140 mg (0.23 mmol) of **8** in 8 ml of THF was treated at −78°C with 87 mg (0.23 mmol) of $Ph_3SnC{\equiv}CH$ and warmed to room temp. with stirring over a period of 15 min. The solvent was removed, and the residue was extracted three times with 4 ml of ether each. The combined extracts were concentrated to ca. 2 ml, and the concentrate was stored at −78°C. A white crystalline solid precipitated which was collected by filtration, washed with pentane and dried in vacuo; yield 101 mg (44%), m.p. 57°C (dec.). – IR (KBr): ν(RhH) = 2118, ν(C≡C) = 2033 cm^{-1}. – ^1H NMR (200 MHz, C_6D_6): δ = 7.86–7.07 (m, 15H, C_6H_5), 6.88–6.64 (s, 5H, C_5H_5N), 3.03 (m, 6H, PC*H*CH_3), 1.19 [dvt, N = 13.0, J(HH) = 6.4 Hz, 36H, PCHC*H*$_3$], 0.33 (s, 9H, $SiCH_3$), −17.89 [dt, J(RhH) = 17.0, J(PH) = 14.5 Hz, 1H, RhH]. – ^{31}P NMR (81.0 MHz, C_6D_6): δ = 41.65 [d, J(RhP) = 98.1, J(SnP) = 8.8 Hz, dd in off resonance]. – $C_{48}H_{72}NP_2RhSiSn$ (974.7): calcd. C 59.15, H 7.45, N 1.44; found C 58.87, H 6.96, N 1.32.

25. *[Rh(C≡CCH$_2$OMe)(C≡CSiMe$_3$)(SnPh$_3$)(PiPr$_3$)$_2$]* (**10**): A solution of 250 mg (0.46 mmol) of **7** in 10 ml of THF was treated at −20°C with 191 mg (0.46 mmol) of $Ph_3SnC{\equiv}CCH_2OMe$ and stirred for 1 h. A change of color from red to violet occurred. The solvent was removed in vacuo, and the oily residue was dissolved in 5 ml of ether. Pentane was added to the solution until a violet precipitate occurred, which was collected by filtration, washed twice with 3 ml of pentane each, and dried in vacuo; yield 82 mg (81%), m.p. 86°C (dec.). – IR (KBr): $\tilde{\nu}$(C≡C) = 1995 cm^{-1}. – ^1H NMR (200 MHz, C_6D_6): δ = 8.27–7.08 (m, 15H, C_6H_5), 4.45 (s, 2H, CH_2OCH_3), 3.41 (s, 3H, CH_2OCH_3), 2.77 (m, 6H, PC*H*CH_3), 1.19 [dvt, N = 13.6, J(HH) = 6.8 Hz, 36H, PCHC*H*$_3$], 0.43 (s, 9H, $SiCH_3$). – ^{31}P NMR (36.2 MHz, $C_6D_5CD_3$, 203 K): δ = 37.12 [d, J(RhP) = 99.7, J(SnP) = 93.8 Hz]. – $C_{45}H_{71}OP_2RhSiSn$ (939.7): calcd. C 57.52, H 7.62, Rh 10.95, Sn 12.63; found C 57.78, H 7.40, Rh 10.75, Sn 12.70.

26. *[RhHCl(SnPh$_3$)(PiPr$_3$)$_2$]* (**11**): A solution of 50 mg (0.11 mmol for $n = 1$) of **1** in 5 ml of THF was treated at −30°C with 39 mg (0.11 mmol) of Ph_3SnH. A change of color from red to yellow occurred. The solvent was removed in vacuo, the residue was dissolved in 10 ml of pentane, and the solution was filtered. The filtrate was concentrated in vacuo to ca. 3 ml, and the concentrate was stored at −78°C. Orange-yellow crystals precipitated which were collected by filtration, washed twice with 2 ml of pentane, and dried in vacuo; yield 70 mg (79%), m.p. 80°C (dec.). – ^1H NMR (200 MHz, C_6D_6): δ = 8.01–7.04 (m, 15H, C_6H_5), 2.23 (m, 6H, PC*H*CH_3), 1.18 [dvt, N = 13.5, J(HH) = 6.9 Hz, 18H, PCHC*H*$_3$], 1.08 [dvt, N = 13.2, J(HH) = 6.7 Hz, 18H, PCHC*H*$_3$], −17.77 [dt, J(RhH) = 14.2, J(PH) = 13.4 Hz, 1H, RhH]. – ^{31}P NMR (36.2 MHz, C_6D_6): δ = 43.06 [d, J(RhP) = 107.0, J(SnP) = 112.1 Hz, dd in off-resonance]. – $C_{36}H_{58}ClP_2RhSn$ (809.85): calcd. C 53.39, H 7.22; found C 53.23, H 6.83.

27. *Determination and Refinement of the Structures of* **2e** *and* **6d**: The respective space groups and cell constants were determined on an Enraf Nonius CAD4 diffractometer which was subsequently used for the data collection. Cell constants were obtained by a least-squares fit of 23-high-angle reflections using the CAD centering routines and are listed along with other crystallographic data and data collection parameters in Table 1. The crystal stability and orientation was checked by measuring standard reflections every hour. All calculations were performed on a Micro-VAX computer using the program package SDP[29] from Enraf Nonius. Intensity data were corrected for Lorentz and polarization effects. An empirical absorption correction (ψ-scan method) was applied, the transmission for **2e** was 75.85% (max.: 99.89%), for **6d** 50.94% (max.: 99.84%). Both structures were solved by direct methods (SHELXS-86). Atomic coordinates and anisotropic thermal parameters of the nonhydrogen atoms were refined by full-matrix least-squares (unit weights). The positions of all hydrogen atoms were calculated according to ideal geometry (C–H distance 0.95 Å) and were taken for the structure factor calculation. The six highest peaks of the last difference fourier synthesis of **6d** were located near the heavy atoms Rh and Hg. Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-58283, the names of the authors, and the journal citation.

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