The First Peralkylated Phosphino(stibino)methanes and Their Organometallic Rhodium Complexes

Matthias Manger, Justin Wolf, Matthias Laubender, Markus Teichert, Dietmar Stalke, and Helmut Werner*

Dedicated to the memory of Professor Geoffrey Wilkinson

Abstract: The first representatives of phosphino(stibino)methanes $R_2PCH_2SbR'_2$ (**3**–**5**) with bulky alkyl or cycloalkyl groups R and R′ were prepared in two steps from Ph_3SnCH_2I via the isolated stannylated phosphanes $Ph_3SnCH_2PR_2$ (**1**, **2**) as intermediates. X-ray structural analysis of **5** (R = C_6H_{11}, R′ = *t*Bu) reveals that the lone pairs and the substituents R and R′ at phosphorus and antimony and the hydrogen atoms of the CH_2 bridge adopt staggered conformations. Treatment of $[\{C_8H_{12}RhCl\}_2]$ with **3**–**5** affords the neutral compounds $[RhCl(\eta^4\text{-}C_8H_{12})(\kappa\text{-}P\text{-}R_2PCH_2SbR'_2)]$ (**6**–**8**), of which **7** and **8** react with CH_3MgI to give the corresponding methylrhodium derivatives $[RhCH_3(\eta^4\text{-}C_8H_{12})(\kappa\text{-}P\text{-}R_2PCH_2SbR'_2)]$ (**9**, **10**). Cationic complexes $[Rh(\eta^4\text{-}C_8H_{12})(\kappa^2\text{-}P,Sb\text{-}R_2PCH_2SbR'_2)]X$ (X = PF_6: **11a**, **12a**, **13**; X = BPh_4: **11b**, **12b**) containing the phosphino(stibino)methanes as chelating ligands were obtained either from $[\{C_8H_{12}RhCl\}_2]$, $R_2PCH_2SbR'_2$ and MX, or (for **13**) from **8** and $AgPF_6$. Compound **12a** (R = *i*Pr, R′ = *t*Bu) was characterized by X-ray crystallography. The PF_6 salts **11a**, **12a**, and **13** react with CH_2N_2 by insertion of CH_2 into the Rh–Sb bond to yield the complexes **14**–**16**, the first examples of transition-metal compounds with Sb ylides as ligands. Treatment of BPh_4 salts **11b** and **12b** with H_2 gives the half-sandwich-type complexes $[(\eta^6\text{-}C_6H_5BPh_3)Rh(\kappa^2\text{-}P,Sb\text{-}R_2PCH_2SbR'_2)]$ (**17**, **18**), in which the tetraphenylborate is coordinated like a substituted arene to the metal center.

Keywords
antimony · arene complexes · diene complexes · rhodium · ylides

Introduction

Recent work in our laboratory has shown that the replacement of triisopropylphosphane by triisopropylstibane as a ligand leads to remarkable differences in the reactivity of low-valent metal complexes of the iron and cobalt triads.[1–3] While some of these differences are probably steric in nature, they mainly reflect the unequal σ-donor and π-acceptor capabilities of trialkylphosphane and -stibane ligands. In almost all cases studied to date, the M–Sb*i*Pr_3 bond is more labile than its M–P*i*Pr_3 counterpart, and this can be put to advantage for synthetic purposes.[1, 3b, 4] A disadvantage of the stibane–metal complexes, however, is their tendency to decompose under the conditions of subsequent conversions.

In order to combine the favorable aspects of the ligand behavior of bulky trialkylphosphanes on the one hand and of related trialkylstibanes on the other, we set out to prepare mixed P/Sb donor systems. Here we describe the synthesis of peralkylated phosphino(stibino)methanes, the molecular and crystal structure of one representative, and the use of the unsymmetrical ligands to prepare square planar as well as half-sandwich-type organometallic rhodium complexes.

Results and Discussion

Synthesis of the P/Sb donor ligands: The bulky phosphino(stibino)methanes **3**–**5** were prepared by a two-step procedure (Scheme 1). The first step is the metalation of Ph_3SnCH_2I by BuLi in toluene/hexane at low temperature, which, in the presence of TMEDA (tetramethylethylenediamine), probably yields solvated Ph_3SnCH_2Li. This in situ generated intermediate reacts with R_2PCl at −90 to −80 °C to give a clear solution from which, upon warming to room temperature and addition of water, an oily air-sensitive product is obtained. Chromatographic workup for R = cyclohexyl (Cy) affords white crystals (**1**) and for R = *i*Pr a colorless liquid (**2**), both in 85–90% yield. Following a similar route, Kauffmann and Kriegesmann prepared the stannylated arsanes $R_3SnCH_2AsPh_2$ (R = Me, Ph) from R_3SnCH_2I, BuLi, and Ph_2AsCl. Since they did not use any stabilizing agent such as TMEDA for the lithiated intermediate, we assume that the yield was rather low (35%) because of sever-

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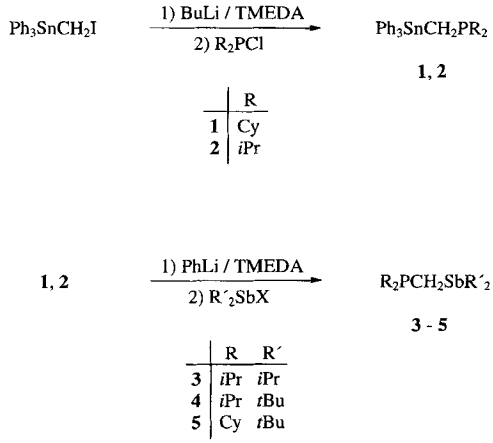


Scheme 1. Two-step procedure for the preparation of phosphino(stibino)methanes **3**–**5**.

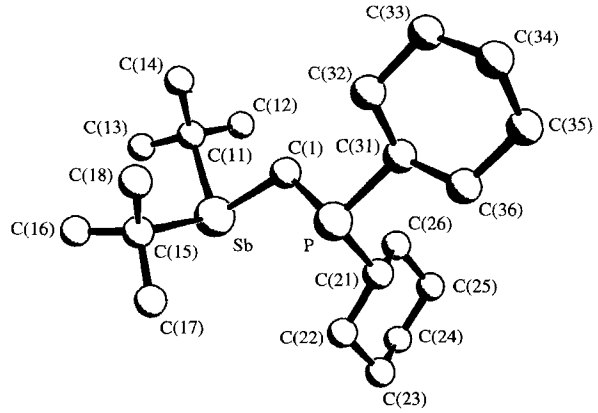


Figure 1. Molecular structure of **5**. Principal bond lengths [Å] and angles [°] with estimated standard deviations in parentheses: P–C(1) 1.842(2), Sb–C(1) 2.175(2), P–C(21) 1.864(2), P–C(31) 1.870(2), Sb–C(11) 2.223(2), Sb–C(15) 2.218(2); P-C(1)-Sb 119.17(8), C(21)-P-C(31) 101.89(6), C(1)-P-C(21) 104.35(7), C(1)-P-C(31) 98.87(7), C(11)-Sb-C(15) 105.31(6), C(1)-Sb-C(11) 93.74(6), C(1)-Sb-C(15) 98.03(6).

al side reactions.[5] The only other stannylated alkylphosphane $R_3SnCH_2PR'_2$ besides **1** and **2** is, to the best of our knowledge, $Et_3SnCH_2PH_2$, but this compound was prepared from $Et_3SnCH_2P(O)(OR)H$ and $LiAlH_4$ and not via Et_3SnCH_2Li as an intermediate.[6]

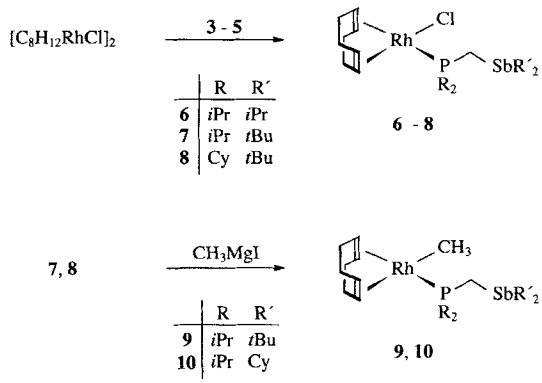
The new phosphanes **1** and **2** are thermally quite stable and soluble in most organic solvents. The ^{13}C NMR spectra of **1** and **2** display two doublets for the diastereotopic carbon atoms $PCHCH_2$ (R = Cy) and $PCHCH_3$ (R = *i*Pr), the chemical shifts and P–C coupling constants of which are similar to those of the chlorophosphanes R_2PCl. The signal of the bridging CH_2 carbon atom appears at $\delta = 2.0$ (for **1**) and $\delta = 1.5$ (for **2**) and is also split into a doublet [J(P,C) = 41–42 Hz].

The second step of the synthesis of **3**–**5** is the transmetalation of **1** or **2** with PhLi, which proceeds smoothly in ether/cyclohexane at room temperature. Besides $SnPh_4$, the corresponding lithiated phosphane R_2PCH_2Li is formed, which reacts with iPr_2SbBr or tBu_2SbCl in the presence of TMEDA at low temperature to give, after chromatographic workup, **3** and **4** as colorless liquids and **5** as a white solid in 75–85% yield. The phosphino(stibino)methanes **3**–**5** are thermally less stable than the precursors **1** and **2** and air- as well as light-sensitive. Under argon at −20 °C, they can be stored for weeks without decomposition. The ^1H, ^{13}C, and ^{31}P NMR data are in full agreement with the proposed structure and deserve no further comment.

The molecular structure of **5** is shown in Figure 1. In analogy to $Ph_2PCH_2PPh_2$ (dppm)[7] and the corresponding cyclohexyl derivative $Cy_2PCH_2PCy_2$,[8] the molecule of **5** has no crystallographic symmetry. The lone pairs at the phosphorus and the antimony atoms are on different sides of the plane formed by these atoms together with the carbon atom of the bridging methylene unit. The relative orientation of the PCy_2 and $SbtBu_2$ moieties at the CH_2 group is such that the lone pairs and the substituents Cy or *t*Bu and the hydrogen atoms of the methylene bridge adopt staggered conformations. The most noteworthy structural detail is the bond angle P-C(1)-Sb of 119.17(8)° which is almost identical to the bond angle P-C-P of $Cy_2PCH_2PCy_2$ [120.5(1)°],[8] but significantly larger than that of dppm [106.2(3)°].[7] In contrast to this, the bond length P–C(1) of **5** [1.842(2) Å] is virtually the same as in dppm [1.848(5) Å][7] and differs only slightly from that in $Cy_2PCH_2PCy_2$ [1.858 Å].[8]

The distance Sb–C(1) [2.175(2) Å] of **5**, however, is somewhat shorter than the distances between Sb and the quarternary carbon atoms C(11) and C(15) [2.223(2) and 2.218(2) Å], which is probably due to the steric bulk and the resulting repulsion of the *tert*-butyl groups.

Cyclooctadienerhodium(I) complexes with phosphino(stibino)-methanes as ligands: The reactions of $[\{C_8H_{12}RhCl\}_2]$ with the phosphino(stibino)methanes **3**–**5** in hexane at room temperature involve a facile cleavage of the chloro bridges by the P-donor site of the substrate but not the replacement of the cyclooctadiene or the chloro ligands. The neutral compounds **6**–**8** (Scheme 2), which are isolated in nearly quantitative yield, form



Scheme 2. Reaction of $[\{C_8H_{12}RhCl\}_2]$ with phosphino(stibino)methanes **3**–**5** involves cleavage of the chloro bridges by the P-donor site to give compounds **6**–**8**. Treatment of **7** or **8** with CH_3MgI displaces the chloro ligand completely to form methylrhodium derivatives **9** and **10**.

yellow, moderately air-stable solids that decompose between 55 °C and 80 °C. The analytical and spectroscopic data leaves no doubt that they are monomeric in nature and thus structurally related to complexes of the general composition $[RhCl(\eta^4\text{-}C_8H_{12})(PR_3)]$.[9] The ^1H and ^{13}C NMR spectra of **6**–**8** display two sets of signals for the protons and the carbon atoms of the -CH=CH- double bonds of the cyclooctadiene unit; this is in

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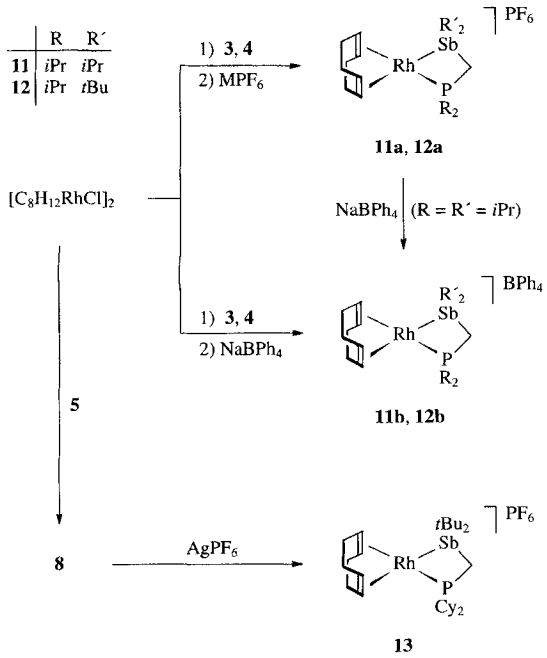
agreement with the different *trans* influence of the chloro and P-donor ligands. A typical feature of the ^{13}C NMR spectra of **7** and **8** is that only the signal of the $=CH_B$ carbon atoms (for assignment H_A and H_B see Experimental Section), which are adjacent to phosphorus, shows a significant $^{103}Rh-^{13}C$ coupling of 14 Hz. Owing to the coordination of the phosphino(stibino)methanes, the signal of the bridging PCH_2Sb carbon atom in the spectra of **6**–**8** exhibits an upfield shift of about 4 ppm compared to **3**–**5**, while at the same time the $^1J(P,C)$ coupling constant decreases from ca. 37 Hz to 8–10 Hz.

On treatment of **7** or **8** with CH_3MgI in ether/pentane at −25 °C, the chloro ligand is readily displaced and the methylrhodium derivatives **9** and **10** are formed in excellent yield. Both compounds are orange-yellow, relatively low-melting solids, which were characterized by elemental analysis and spectroscopic techniques. The ^1H as well as the ^{13}C NMR spectra of **9** and **10** display a doublet of doublets at $\delta = 0.3-0.4$ (^1H) and $\delta = 4.6-4.8$ (^{13}C), each of which is assigned to the protons and the carbon atom of the metal-bonded CH_3 group.

The reactions of $[\{C_8H_{12}RhCl\}_2]$ with **3** or **4** in the presence of $AgPF_6$ or KPF_6 afford the cationic complexes **11a** and **12a** (Scheme 3) in 60–80% yield. The related compound **13** with the phosphino(stibino)methane **5** as ligand is accessible, in the absence of light, from **8** and an equimolar amount of $AgPF_6$ in CH_2Cl_2. If $NaBPh_4$ is used as an additional substrate for the reaction of $[\{C_8H_{12}RhCl\}_2]$ with **3** or **4** instead of a PF_6 salt, the corresponding compounds **11b** and **12b** are obtained. The easy formation of **11a,b**, **12a,b**, and **13** is noteworthy since related chelate complexes of the general composition $[Rh(\eta^4\text{-}C_8H_{12})(\kappa^2\text{-}P,P\text{-}R_2PCH_2PR_2)]X$ do not exist. For R = Ph, such a species is presumably generated as an intermediate on treatment of $[\{C_8H_{12}RhCl\}_2]$ with dppm but it reacts quite rapidly with a second molecule of bis(diphenylphosphino)methane to give $[Rh(dppm)_2]Cl$ as the final product.[10] Compounds **11a**, **12a**, and **13** are deep red, **11b** and **12b** orange-yellow solids that are almost air-stable and readily soluble in CH_2Cl_2, $CHCl_3$, and THF. They slowly decompose in acetone. The most significant difference between the spectroscopic data of **11**–**13** and those of **6**–**8** is the downfield shift of the signals of the protons H_B and PCH_2Sb by ca. 1.3–1.4 ppm in the ^1H NMR, the shift to lower fields of the signals of the corresponding carbon atoms $=CH_B$ and PCH_2Sb by ca. 20 and 10 ppm in the ^{13}C NMR, and the highfield shift of the signal of the PR_2 phosphorus atom by ca. 25 ppm in the ^{31}P NMR spectra. Moreover, the $^{103}Rh-^{31}P$ coupling constant of the PR_2 resonance is reduced from ca. 145 Hz for the neutral compounds **6**–**8** to ca. 125 Hz for the chelate complexes **11a,b**, **12a,b**, and **13**.

In order to obtain information about the detailed structural aspects of a transition-metal complex containing a phosphino(stibino)methane as a chelating ligand, an X-ray crystal structural investigation of **12a** was carried out. The SCHAKAL diagram (Figure 2) reveals that the coordination geometry around the rhodium center is square planar with the C(1)–C(2) double bond of the cyclooctadiene *trans* to phosphorus and the C(5)–C(6) double bond *trans* to antimony. The most notable features are that 1) the four-membered ring RhPCSb is exactly planar and 2) the bond angle P-C(9)-Sb [96.6(2)°] is significantly smaller than in the uncoordinated molecule **5** [119.17(8)°]. The P(1)-Rh-Sb bite angle [74.88(3)°] is also quite small and comparable to the P-Rh-P bite angle of neutral rhodium(I) complexes with $tBu_2PCH_2PtBu_2$ as chelating unit.[11] The Rh–P(1) bond length of **12a** [2.317(1) Å] is almost identical to that of cationic square planar cyclooctadienerhodium(I) complexes with bidentate phosphanes as ligands.[12] The distances Rh–C(5) and Rh–C(6) are shorter by ca. 0.04–0.05 Å than the



Scheme 3. Reactions of $[\{C_8H_{12}RhCl\}_2]$ with **3**, **4**, and **5** in the presence of $AgPF_6$ or KPF_6. **3** and **4** afford cationic complexes **11a** and **12a**. If $NaBPh_4$ is used for the reaction instead of a PF_6 salt, compounds **11b** and **12b** are obtained. The related compound **13** is obtained from **5** with $AgPF_6$ in CH_2Cl_2.

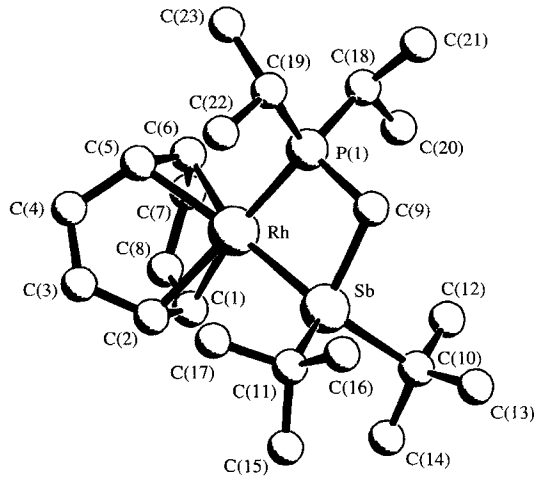


Figure 2. Molecular structure of **12a**. Principal bond lengths [Å] and angles [°] with estimated standard deviations in parentheses: Rh–P(1) 2.317(1), Rh–Sb 2.5876(5), P(1)–C(9) 1.836(4), Sb–C(9) 2.158(4), Rh–C(1) 2.253(5), Rh–C(2) 2.225(5), Rh–C(5) 2.194(5), Rh–C(6) 2.186(5), C(1)–C(2) 1.327(8), C(5)–C(6) 1.367(8), P(1)–C(18) 1.847(4), P(1)–C(19) 1.843(4), Sb–C(10) 2.201(4), Sb–C(11) 2.198(4); P(1)-Rh-Sb 74.88(3), P(1)-C(9)-Sb 96.6(2), C(9)-P(1)-Rh 102.51(14), C(9)-Sb-Rh 86.04(11), C(1)-Rh-C(2) 34.5(2), C(5)-Rh-C(6) 36.4(2), C(10)-Sb-C(11) 109.1(2), C(18)-P(1)-C(19) 103.8(2).

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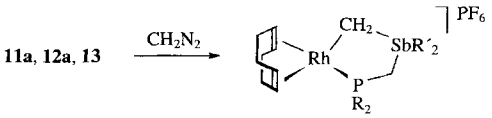
distances Rh–C(1) and Rh–C(2), which we attribute to the stronger *trans* influence of the PR_2 compared to the SbR'_2 moiety. The Rh–Sb bond length of **12a** [2.5876(5) Å] is virtually the same as the Rh–Sb distances of *trans*-$[RhCl(=CPh_2)(SbiPr_3)_2]$[1b] and *mer*-$[RhCl_2(C_6H_5)(SbPh_3)_3]$,[13] although in the latter compound the oxidation state of rhodium is + III and the ligand is a triaryl- and not a trialkylstibane.

Studies on the reactivity of the chelate complexes 11–13: The reactions of the compounds **11a**, **12a**, and **13** with diazomethane led to a surprising result. Since we considered the phosphino(stibino)methanes as hemilabile chelating systems, we had expected that on treatment of the cations $[Rh(\eta^4\text{-}C_8H_{12})(\kappa^2\text{-}P,Sb\text{-}R_2PCH_2SbR'_2)]^+$ with CH_2N_2 a cleavage of the supposedly labile Rh–Sb bond would take place and a carbenerhodium complex containing the phosphino(stibino)methane as a monodentate P-bonded ligand would be formed. The elemental analyses of the products obtained upon addition of diazomethane to a solution of **11a**, **12a**, or **13** in THF/ether at −30 °C and subsequent workup were indeed in agreement with those of 1:1 adducts of the starting materials with CH_2. The NMR spectroscopic data revealed, however, that the new crystalline, almost air-stable compounds do not contain a $Rh{=}CH_2$ bond. Instead of a signal for the CH_2 carbon atom at low field (which has been observed at $\delta = 315\text{–}260$ for square planar and half-sandwich-type diphenylcarbenerhodium(I) complexes[1b, 14]), the ^{13}C NMR spectra of **14–16** (Scheme 4) display a resonance at $\delta = 2.5\text{–}2.9$, which is split



	R	R′
14	*i*Pr	*i*Pr
15	*i*Pr	*t*Bu
16	Cy	*t*Bu

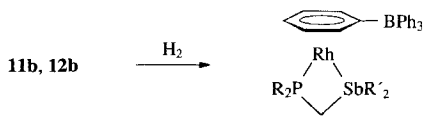
14 - 16

Scheme 4. The products **14**, **15**, and **16** obtained from diazomethane and **11a**, **12a**, or **13** are equivalent to 1:1 adducts of the starting materials with CH_2.

into a doublet of doublets owing to Rh,C and P,C coupling. Since the large value of the coupling constant $J(Rh,C) = 31$ Hz indicates that the CH_2 group is linked to rhodium, we assume that a five-membered RhCSbCP ring is formed by insertion of the methylene unit into the Rh–Sb bond. In the ^1H NMR spectra of **14–16**, the signals for the protons of the metal-bonded CH_2 group appear at $\delta \approx 1.0$ and thus at somewhat lower field than for neutral rhodium(I) compounds with CH_2PiPr_3 as ligand.[15] The chemical shift of the resonances of the protons and the carbon atoms of the C_8H_{12} ligand and the $R_2PCH_2SbR'_2$ fragment of **14–16** are not significantly different to those of the precursors **11a**, **12a**, and **13**; this backs up the structural proposal shown in Scheme 4.

With regard to the mechanism of formation of the chelate complexes **14–16** we consider two possibilities as most likely. Taking the supposed lability of the Rh–Sb linkage into consideration, the attacking diazomethane could replace the SbR'_2 unit and generate a four-coordinate intermediate in which either CH_2N_2 or CH_2 would be bonded to rhodium. However, since the metal center in the compounds **14–16** has a 16-electron configuration, the alternative could be the formation of a five-coordinate species, in which CH_2N_2 or CH_2 would probably occupy the apical position of a square pyramid. Upon elimination of N_2 (if this is not already lost in the initial step) and attack of the Sb donor at the CH_2 carbon atom the five-membered ring $RhCH_2Sb(R')_2CH_2PR_2$ containing two unequal methylene units would be formed. The driving force for this ring expansion is probably the decrease of strain on going from the four-membered chelate rings of **11a**, **12a**, and **13** to the five-membered rings of **14–16**. A similar heterocyclic system $RhCH_2P(Ph)_2CH_2PPh_2$ is part of the rhodium(III) complex $[C_5Me_5RhI\{\kappa^2\text{-}C,P\text{-}CH_2P(Ph)_2CH_2PPh_2\}]I$, which has been prepared from $[C_5Me_5RhCH_2I(CO)I]$ and dppm.[16]

Attempts to displace the cyclooctadiene ligand of **11b** and **12b** by H_2 and to obtain a (presumably catalytically active) dihydridorhodium(III) cation led to the neutral half-sandwich-type compounds **17** and **18** (Scheme 5) in 70–80% yield. The



	R	R′
17	*i*Pr	*i*Pr
18	*i*Pr	*t*Bu

17, 18

Scheme 5. Neutral half-sandwich-type compounds **17** and **18** obtained from attempts to displace the cyclooctadiene ligand of **11b** or **12b** with H_2.

postulated dihydridorhodium(III) species is possibly formed and responsible for the hydrogenation of cyclooctadiene to give cyclooctane. The red, only moderately air-sensitive solids **17** and **18** are readily soluble in acetone, THF and CH_2Cl_2, but insoluble in ether and hexane. Related complexes of the general composition $[(\eta^6\text{-}C_6H_5BPh_3)RhL_2]$ with $L = P(OR)_3$[17] and $L_2 = R_2PCH_2CH_2PR_2$,[18] or $R_2P(CH_2)_4PR_2$[19] have been reported, while those with $L_2 = R_2PCH_2PR_2$, $R_2AsCH_2AsR_2$, or $R_2SbCH_2SbR_2$ are unknown. The ^1H and ^{13}C NMR data of **17** and **18** clearly indicate that one of the phenyl rings of the BPh_4 anion is coordinated to rhodium, in analogy to the complexes mentioned above. Compared with those for **11b** and **12b**, the signal of the ^{31}P nuclei in the ^{31}P NMR spectra of **17** and **18** is shifted significantly to lower fields, whereas the $^{103}Rh\text{–}^{31}P$ coupling constant increases from ca. 125 to 166–170 Hz. A similar value is found for the cyclopentadienyl compound $[C_5H_5Rh(\kappa^2\text{-}P,P\text{-}Ph_2PCH_2PPh_2)]$, which is formed from $[C_5H_5Rh(PMe_3)(\kappa\text{-}P\text{-}Ph_2PCH_2PPh_2)]$ by elimination of PMe_3.[20]

Conclusions

The work presented in this paper has shown that phosphino(stibino)methanes $R_2PCH_2SbR'_2$ with bulky alkyl or cycloalkyl groups R and R′ are accessible in two steps from Ph_3SnCH_2I via stannylated phosphanes $Ph_3SnCH_2PR_2$ as intermediates. In order to avoid side reactions, it is important to work at low temperatures and to use TMEDA as a supporting reagent both

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for the lithiation of Ph_3SnCH_2I and for the transmetalation of $Ph_3SnCH_2PR_2$ with PhLi. The closest analogy to the synthetic route which we used is probably that reported by Kauffmann et al., who prepared (in 20% yield) the tetraphenyl derivative $Ph_2PCH_2SbPh_2$ from $(Ph_2Sb)_2CH_2$, PhLi, and Ph_2PCl via Ph_2SbCH_2Li as an intermediate.[21]

The investigations intended to prepare rhodium complexes of the new phosphino(stibino)methanes reveal that **3**–**5** behave as monodentate (P-bonded) as well as bidentate ligands. The most remarkable feature is that on treatment of the cationic chelate compounds $[Rh(\eta^4\text{-}C_8H_{12})(\kappa^2\text{-}P,Sb\text{-}R_2PCH_2SbR'_2)]^+$ with diazomethane an insertion of CH_2 into the Rh–Sb bond takes place, supporting the assumption that in a $M(\kappa^2\text{-}R_2P\text{-}X\text{-}SbR'_2)$ chelate the M–Sb linkage is more labile than the M–P counterpart. The cationic species **14**–**16**, formed by CH_2 insertion, are to the best of our knowledge the first transition-metal complexes containing a methylenestiborane (Sb ylide) as ligand.[22] In this context it is worth mentioning that the reaction of $[Cr(CO)_5\{\kappa\text{-}C\text{-}CH_2S(O)Me_2\}]$ with $Ph_2PCH_2SbPh_2$ leads exclusively to the formation of $[Cr(CO)_4(\kappa^2\text{-}C,Sb\text{-}CH_2PPh_2\text{-}CH_2SbPh_2)]$ but not to that of the *C*,*P*-bonded isomer.[23] Finally, we note that although a huge number of metal compounds with methylenephosphoranes (P ylides) are known,[22] there is only one (a dinuclear platinum complex) which has been prepared by insertion of CH_2 into a $M\text{–}PR_3$ bond.[24]

Experimental Section

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The starting materials Ph_3SnCH_2I,[25] R_2PCl,[26] R_2SbX,[27] and $[\{C_8H_{12}RhCl\}_2]$[28] were prepared as described in the literature. TMEDA (tetramethylethylenediamine) was a commercial product from Fluka. It was dried over CaH_2 and distilled before use. NMR spectra were recorded at room temperature on Bruker AC200 and Bruker AMX400 instruments. Abbreviations used: s, singlet; d, doublet; q, quartet; sept, septet; m, multiplet; br, broadened signal. Melting points were measured by DTA. For the assignment of H_A and H_B see procedure for the preparation of compound **6**.

$Ph_3SnCH_2PCy_2$ (1): A solution of Ph_3SnCH_2I (4.03 g, 8.21 mmol) in 70 mL of toluene was treated dropwise at −55 °C (over ca. 10 min) with a 2.72 M solution of BuLi (3.00 mL, 8.20 mmol) in hexane. The solution was stirred for 20 min and then TMEDA (2.46 mL, 16.42 mmol) was added. After the reaction mixture had been cooled to −90 °C, it was treated with Cy_2PCl (1.79 mL, 8.04 mmol), then warmed to −80 °C and stirred for 30 min. The solution was slowly brought to room temperature and treated with 20 mL of water. The organic phase was separated, washed twice with 10 mL portions of water, carefully dried with Na_2SO_4 and then filtered. The filtrate was brought to dryness in vacuo, the oily residue was dissolved in 10 mL of pentane, and the solution was chromatographed on Al_2O_3 (basic, activity grade III, column height 5 cm). A colorless fraction was eluted with pentane, and concentrated to ca. 5 mL in vacuo. Upon storing of the solution at −35 °C for 18 h, white crystals precipitated, which were separated from the mother liquor, washed twice with 5 mL portions of pentane (−40 °C) and dried; yield 3.80 g (85%); m.p. 87 °C; ^{1}H NMR (200 MHz, C_6D_6): δ = 7.68 (m, 6H, *ortho*-H of C_6H_5), 7.15 (m, 9H, *meta*-H and *para*-H of C_6H_5), 1.71–1.30, 1.13 (both br m, 22H, PCH and CH_2 of C_6H_{11}), 1.39 [d, J(P,H) = 0.8 Hz, 2H, PCH_2Sn]; ^{13}C NMR (50.3 MHz, C_6D_6): δ = 139.7 [d, J(P,C) = 2.0 Hz, *ipso*-C of C_6H_5], 137.6 [d, J(P,C) = 1.4, $J(^{119/117}Sn,C)$ = 35.8 Hz, *ortho*-C of C_6H_5], 129.2 [s, $J(^{119/117}Sn,C)$ = 11.3 Hz, *meta*-C of C_6H_5], 128.8 (s, *para*-C of C_6H_5), 36.2 [d, J(P,C) = 16.9 Hz, PCH], 30.3 [d, J(P,C) = 12.7 Hz, $PCHCH_2$], 29.9 [d, J(P,C) = 11.6 Hz, $PCHCH_2$], 27.7, 27.5 [both d, J(P,C) = 9.5 Hz, CH_2 of C_6H_{11}], 26.7 (s, CH_2 of C_6H_{11}), 2.0 [d, J(P,C) = 41.8 Hz, $SnCH_2P$]; ^{31}P NMR (81.0 MHz, $CDCl_3$): δ = −6.7 [s, $J(^{119}Sn,P)$ = 94.5, $J(^{117}Sn,P)$ = 90.1 Hz]; $C_{31}H_{39}PSn$ (561.3): calcd C 66.33, H 7.00; found C 66.28, H 7.01.

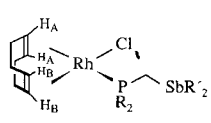
$Ph_3SnCH_2PiPr_2$ (2): This was prepared as described for **1**, from Ph_3SnCH_2I (5.04 g, 10.27 mmol), 3.84 mL of a 2.67 M solution of BuLi (10.27 mmol) in hexane, TMEDA (3.01 mL, 20.53 mmol) and iPr_2PCl (1.63 mL, 10.25 mmol). Colorless liquid (ρ = 1.35); yield 4.39 g (89%); ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.90–7.51 (m, 15H, C_6H_5), 1.90 [d sept, J(P,H) = 2.0, J(H,H) = 7.0 Hz, 2H, $PCHCH_3$], 1.66 [br s, $J(^{119/117}Sn,H)$ = 34.6 Hz, 2H, PCH_2Sn], 1.25 [dd, J(P,H) = 12.5, J(H,H) = 7.0 Hz, 12H, $PCHCH_3$]; ^{13}C NMR (50.3 MHz, C_6D_6): δ = 138.9 [d, J(P,C) = 1.9 Hz, *ipso*-C of C_6H_5], 136.9 [s, $J(^{119/117}Sn,C)$ = 32.4 Hz, *ortho*-C of C_6H_5], 128.7 (s, *para*-C of C_6H_5), 128.3 (s, *meta*-C of C_6H_5), 25.4 [d, J(P,C) = 14.8 Hz, $PCHCH_3$], 19.3 and 19.1 [both d, J(P,C) = 13.0 Hz, $PCHCH_3$], 1.5 [d, J(P,C) = 41.2 Hz, $SnCH_2P$]; ^{31}P NMR (81.0 MHz, $CDCl_3$): δ = −0.02 [s, $J(^{119/117}Sn,P)$ = 110.0 Hz]; $C_{25}H_{31}PSn$ (481.2): calcd C 62.40, H 6.49; found C 62.40, H 6.33.

***i*Pr$_2$PCH$_2$Sb*i*Pr$_2$ (3)**: A solution of **2** (3.32 g, 6.90 mmol) in 60 mL of ether was treated with a 1.72 M solution of PhLi (4.00 mL, 6.88 mmol) in cyclohexane/ether (1:1) and stirred for 6 h at room temperature. A white solid precipitated during the reaction. The reaction mixture was cooled to −70 °C, and then TMEDA (1.05 mL, 6.90 mmol) and subsequently a solution of iPr_2SbBr (1.97 g, 6.84 mmol) in 4 mL of hexane were added. After the solution had been stirred at −70 °C for 30 min, it was slowly warmed to room temperature. The solvent was removed, the residue was extracted with 40 mL of hexane, and the extract was brought to dryness in vacuo. The remaining oily product was suspended in 3 mL of pentane, and the suspension was chromatographed on Al_2O_3 (basic, activity grade I, column height 8 cm). A colorless fraction was eluted with pentane; upon removal of the solvent a colorless liquid was obtained from this (ρ = 1.16); yield 1.87 g (81%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.83 [sept, J(H,H) = 7.2 Hz, 2H, $SbCHCH_3$], 1.71 [d sept, J(P,H) = 2.0, J(H,H) = 7.2 Hz, 2H, $PCHCH_3$], 1.30, 1.28 [both d, J(H,H) = 7.2 Hz, 6H each, $SbCHCH_3$], 1.24 (s, 2H, PCH_2Sb), 1.08 [dd, J(P,H) = 12.8, J(H,H) = 7.2 Hz, 6H, $PCHCH_3$], 1.08 [dd, J(P,H) = 12.0, J(H,H) = 7.2 Hz, 6H, $PCHCH_3$]; ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 25.0 [d, J(P,C) = 14.3 Hz, $PCHCH_3$], 22.0, 21.6 (both s, $SbCHCH_3$), 19.8 [d, J(P,C) = 14.8 Hz, $PCHCH_3$], 19.1 [d, J(P,C) = 10.2 Hz, $PCHCH_3$], 18.2 [d, J(P,C) = 5.6 Hz, $SbCHCH_3$], 2.5 [d, J(P,C) = 36.5 Hz, PCH_2Sb]; ^{31}P NMR (81.0 MHz, $CDCl_3$): δ = 1.5 (s); $C_{13}H_{30}PSb$ (339.1): calcd C 46.05, H 8.92; found C 46.48, H 9.15.

***i*Pr$_2$PCH$_2$Sb*t*Bu$_2$ (4)**: This was prepared as described for **3**, from **2** (6.78 g, 14.08 mmol), a solution of PhLi (1.68 M, 8.30 mL, 14.00 mmol) in cyclohexane/ether (1:1), TMEDA (2.13 mL, 14.10 mmol) and tBu_2SbCl (3.77 g, 13.90 mmol). Colorless liquid (ρ = 1.16); yield 4.70 g (85%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.66 [d sept, J(P,H) = 2.0, J(H,H) = 7.2 Hz, 2H, $PCHCH_3$], 1.22 (br s, 2H, PCH_2Sb), 1.17 (s, 18H, $SbCCH_3$), 1.03 [dd, J(P,H) = 11.6, J(H,H) = 7.2 Hz, 6H, $PCHCH_3$], 1.02 [dd, J(P,H) = 13.2, J(H,H) = 7.2 Hz, 6H, $PCHCH_3$]; ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 31.0 [d, J(P,C) = 0.9 Hz, $SbCCH_3$], 28.0 [d, J(P,C) = 4.6 Hz, $SbCCH_3$], 25.1 [d, J(P,C) = 14.9 Hz, $PCHCH_3$], 19.8 [d, J(P,C) = 13.7 Hz, $PCHCH_3$], 19.2 [d, J(P,C) = 10.7 Hz, $PCHCH_3$], 4.7 [d, J(P,C) = 37.5 Hz, PCH_2Sb]; ^{31}P NMR (81.0 MHz, $CDCl_3$): δ = 1.55 (s); $C_{15}H_{34}PSb$ (367.2): calcd C 49.06, H 9.33; found C 49.09, H 9.64.

Cy$_2$PCH$_2$Sb*t*Bu$_2$ (5): This was prepared as described for **3**, from **1** (1.77 g, 3.15 mmol), PhLi (1.67 M, 1.86 mL, 3.11 mmol) in cyclohexane/ether (1:1), TMEDA (470 µL, 3.11 mmol) and tBu_2SbCl (0.82 g, 3.00 mmol). Recrystallization from ethanol/hexane (4:1) at −25 °C gave colorless crystals; yield 0.98 g (73%); m.p. 37 °C; ^{1}H NMR (200 MHz, C_6D_6): δ = 1.76–1.55 (br m, 10H, CH and CH_2 of C_6H_{11}), 1.28 (br m, 14H, CH_2 of C_6H_{11} and PCH_2Sb), 1.24 (s, 18H, $SbCCH_3$); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 35.5 [d, J(P,C) = 14.8 Hz, PCH], 31.2 (br s, $SbCCH_3$), 30.2 [d, J(P,C) = 12.9 Hz, $PCHCH_2$], 29.5 [d, J(P,C) = 9.2 Hz, $PCHCH_2$], 28.4 [d, J(P,C) = 4.6 Hz, $SbCCH_3$], 27.5 [d, J(P,C) = 3.7 Hz, CH_2 of C_6H_{11}], 27.3, 26.6 (both s, CH_2 of C_6H_{11}), 4.5 [d, J(P,C) = 36.5 Hz, PCH_2Sb]; ^{31}P NMR (81.0 MHz, $CDCl_3$): δ = −5.8 (s); $C_{21}H_{42}PSb$ (447.3): calcd C 56.39, H 9.46; found C 55.89, H 9.57.

$[RhCl(\eta^4\text{-}C_8H_{12})(\kappa\text{-}P\text{-}iPr_2PCH_2SbiPr_2)]$ (6): A suspension of $[\{C_8H_{12}RhCl\}_2]$ (94 mg, 0.19 mmol) in 3 mL of hexane was treated with a solution of **3** (130 mg, 0.38 mmol) in 3 mL of hexane and stirred for 10 min at room temperature. The solvent was removed, the oily residue was dissolved in



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1.5 mL of acetone, and the solution was stored at −78 °C. Small yellow crystals precipitated, which were separated from the mother liquor, washed with 1 mL of acetone (−40 °C) and dried; yield 195 mg (88%); m.p. 80 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6): δ = 5.54 (brs, 2H, H_A), 3.65 (brs, 2H, H_B), 2.38 (m, 2H, PC*H*CH$_3$), 2.19 (brm, 4H, CH_2 of C_8H_{12}), 1.83 (m, 2H, SbC*H*CH$_3$), 1.75 (m, 4H, CH_2 of C_8H_{12}), 1.38 [brd, J(P,H) = 6.8 Hz, 2H, PCH_2Sb], 1.31 [dd, J(P,H) = 14.6, J(H,H) = 7.0 Hz, 6H, PCHC*H*$_3$], 1.26, 1.24 [both d, J(H,H) = 7.2 Hz, 6H each, SbCHC*H*$_3$], 1.18 [dd, J(P,H) = 13.8, J(H,H) = 7.0 Hz, 6H, PCHC*H*$_3$]; ^{13}C NMR (100.6 MHz, C_6D_6): δ = 103.1 (brm, =CH_A), 67.8 (brm, =CH_B), 33.6, 28.8 (both brs, CH_2 of C_8H_{12}), 26.3 [d, J(P,C) = 21.3 Hz, PC*H*CH$_3$], 22.3, 2.0 (both s, SbCH*C*H$_3$), 20.0 [d, J(P,C) = 2.2 Hz, PCH*C*H$_3$], 19.5 (s, PCH*C*H$_3$), 19.1 (brs, Sb*C*HCH$_3$), −0.14 [d, J(P,C) = 10.2 Hz, PCH_2Sb]; ^{31}P NMR (162.0 MHz, C_6D_6): δ = 34.7 [d, J(Rh,P) = 144.2 Hz]; $C_{21}H_{42}$ClPRhSb (585.6): calcd C 43.09, H 7.23; found C 43.03, H 7.25.

[RhCl(η^4-C_8H_{12})(κ-*P*-*i*Pr$_2$PCH$_2$Sb*t*Bu$_2$)] (7): This was prepared as described for **6**, from [{C_8H_{12}RhCl}$_2$] (148 mg, 0.30 mmol) and **4** (220 mg, 0.60 mmol). Yellow microcrystalline solid; yield 312 mg (86%); m.p. 55 °C (decomp.); ^{1}H NMR (400 MHz, C_6D_6): δ = 5.64 (brs, 2H, H_A), 3.68 (brs, 2H, H_B), 2.58 (m, 2H, PC*H*CH$_3$), 2.30 (brm, 4H, CH_2 of C_8H_{12}), 1.73 (brm, 4H, CH_2 of C_8H_{12}), 1.44 [dd, J(P,H) = 14.8, J(H,H) = 7.2 Hz, 6H, PCHC*H*$_3$], 1.39 [d, J(P,H) = 7.2 Hz, 2H, PCH_2Sb], 1.31 [dd, J(P,H) = 14.4, J(H,H) = 6.8 Hz, 6H, PCHC*H*$_3$], 1.19 (s, 18H, SbCCH$_3$); ^{13}C NMR (50.3 MHz, C_6D_6): δ = 103.1 (brm, =CH_A), 67.7 [d, J(Rh,C) = 14.1 Hz, =CH_B], 33.6 (brs, CH_2 of C_8H_{12}), 31.4 (s, SbC*C*H$_3$), 29.6 [d, J(P,C) = 2.3 Hz, Sb*C*CH$_3$], 28.7 (brs, CH_2 of C_8H_{12}), 27.0 [d, J(P,C) = 21.7 Hz, P*C*HCH$_3$], 20.4 (s, PCH*C*H$_3$), 19.8 [d, J(P,C) = 2.8 Hz, PCH*C*H$_3$], 0.7 [d, J(P,C) = 8.0 Hz, PCH_2Sb]; ^{31}P NMR (162.0 MHz, C_6D_6): δ = 36.0 [d, J(Rh,P) = 145.3 Hz]; $C_{23}H_{46}$ClPRhSb (613.7): calcd C 45.01, H 7.55; found C 44.68, H 7.76.

[RhCl(η^4-C_8H_{12})(κ-*P*-Cy$_2$PCH$_2$Sb*t*Bu$_2$)] (8): This was prepared as described for **6**, from [{C_8H_{12}RhCl}$_2$] (49 mg, 0.10 mmol) and **5** (90 mg, 0.20 mmol). Yellow microcrystalline solid; yield 113 mg (81%); m.p. 64 °C (decomp.); ^{1}H NMR (200 MHz, C_6D_6): δ = 5.61 (brs, 2H, H_A), 3.68 (brs, 2H, H_B), 2.54–1.52 (brm, 18H, C_6H_{11} and CH_2 of C_8H_{12}), 1.39 [d, J(P,H) = 7.0 Hz, 2H, PCH_2Sb], 1.21 (s, 18H, SbCCH$_3$), 1.35–1.01 (brm, 12H, CH_2 of C_6H_{11}); ^{13}C NMR (50.3 MHz, C_6D_6): δ = 102.8 (brm, =CH_A), 67.8 [d, J(Rh,C) = 14.1 Hz, =CH_B], 37.2 [d, J(P,C) = 21.7 Hz, P*C*HCH$_2$], 33.6 (brm, CH_2 of C_8H_{12}), 31.5 (s, SbC*C*H$_3$), 30.0 (s, Sb*C*CH$_3$), 30.9, 29.7, 28.8 (all brs, CH_2 of C_8H_{12} and CH_2 of C_6H_{11}), 27.6 [d, J(P,C) = 11.8 Hz, PCH*C*H$_2$], 27.2 [d, J(P,C) = 9.9 Hz, PCH*C*H$_2$], 26.6 (s, CH_2 of C_6H_{11}), 0.5 [brd, J(P,C) = 8.4 Hz, PCH_2Sb]; ^{31}P NMR (81.0 MHz, C_6D_6): δ = 29.4 [d, J(Rh,P) = 143.9 Hz]; $C_{29}H_{54}$ClPRhSb (693.8): calcd C 50.20, H 7.85; found C 49.85, H 7.77.

[RhCH$_3$(η^4-C_8H_{12})(κ-*P*-*i*Pr$_2$PCH$_2$Sb*t*Bu$_2$)] (9): A solution of **7** (107 mg, 0.17 mmol) in 6 mL of ether/pentane (1:1) was treated at −25 °C with a 2.52 M solution of CH_3MgI (76 µL, 0.19 mmol) in ether. After the reaction mixture had been stirred for 15 min, it was warmed to room temperature. The solvent was removed, the residue was extracted with 15 mL of pentane, and the extract dried in vacuo. The residue was dissolved in 2 mL of acetone, and the solution was stored at −78 °C. After 18 h an orange-yellow solid was obtained, which was separated from the mother liquor, washed twice with 0.5 mL portions of acetone (−40 °C) and dried; yield 76 mg (75%); m.p. 46 °C (decomp.); ^{1}H NMR (200 MHz, C_6D_6): δ = 4.84 (m, 2H, H_A), 4.22 (brs, 2H, H_B), 2.24 (brm, 6H, PC*H*CH$_3$ and CH_2 of C_8H_{12}), 2.02 (m, 4H, CH_2 of C_8H_{12}), 1.54 [dd, J(Rh,H) = 0.9, J(P,H) = 6.7 Hz, 2H, PCH_2Sb], 1.27 [dd, J(P,H) = 13.7, J(H,H) = 7.0 Hz, 6H, PCHC*H*$_3$], 1.22 [dd, J(P,H) = 13.7, J(H,H) = 7.2 Hz, 6H, PCHC*H*$_3$], 1.22 (s, 18H, SbCCH$_3$), 0.31 [dd, J(Rh,H) = 1.6, J(P,H) = 4.8 Hz, 3H, Rh CH$_3$]; ^{13}C NMR (50.3 MHz, C_6D_6): δ = 92.1 [dd, J(Rh,C) = 12.0, J(P,C) = 9.2 Hz, =CH_A], 78.2 [d, J(Rh,C) = 7.6 Hz, =CH_B], 32.2 [d, J(Rh,C) = 2.1 Hz, CH_2 of C_8H_{12}], 31.6 (s, SbC*C*H$_3$), 31.0 (brs, CH_2 of C_8H_{12}), 29.2 [d, J(P,C) = 2.6 Hz, Sb*C*CH$_3$], 26.9 [dd, J(Rh,C) = 1.6, J(P,C) = 18.0 Hz, P*C*HCH$_3$], 20.6 [d, J(P,C) = 2.1 Hz, PCH*C*H$_3$], 19.7 [d, J(P,C) = 3.5 Hz, PCH*C*H$_3$], 4.8 [dd, J(Rh,C) = 25.1, J(P,C) = 11.7 Hz, Rh–CH$_3$], 3.7 [d, J(P,C) = 3.0 Hz, PCH_2Sb]; ^{31}P NMR (81.0 MHz, C_6D_6): δ = 34.5 [d, J(Rh,P) = 170.8 Hz]; $C_{24}H_{49}$PRhSb (593.3): calcd C 48.59, H 8.33; found C 48.28, H 8.49.

[RhCH$_3$(η^4-C_8H_{12})(κ-*P*-Cy$_2$PCH$_2$Sb*t*Bu$_2$)] (10): This was prepared as described for **9**, from **8** (80 mg, 0.12 mmol) and a solution of CH_3MgI (2.52 M, 50 µL, 0.13 mmol) in ether. Orange-yellow microcrystalline solid; yield 64 mg (82%); m.p. 58 °C (decomp.); ^{1}H NMR (200 MHz, C_6D_6): δ = 4.88 (brm, 2H, H_A), 4.25 (brs, 2H, H_B), 2.35–2.07 (brm, 18H, C_6H_{11} and CH_2 of C_8H_{12}), 1.85–1.55 (brm, 6H, PCH_2Sb and CH_2 of C_8H_{12}), 1.25 (s, 18H, SbCCH$_3$), 1.25 (brm, 12H, CH_2 of C_6H_{11}), 0.40 [dd, J(Rh,H) = 1.7, J(P,H) = 4.7 Hz, 3H, Rh–CH$_3$]; ^{13}C NMR (50.3 MHz, C_6D_6): δ = 91.9 [dd, J(Rh,C) = 12.1, J(P,C) = 9.4 Hz, =CH_A], 78.2 [d, J(Rh,C) = 7.6 Hz, =CH_B], 37.3 [brd, J(P,C) = 16.6 Hz, P*C*HCH$_2$], 32.3 [d, J(Rh,C) = 1.9 Hz, CH_2 of C_8H_{12}], 31.7 (s, SbC*C*H$_3$), 31.0, 30.0 (both m, CH_2 of C_8H_{12} and CH_2 of C_6H_{11}), 29.4 [d, J(P,C) = 2.3 Hz, Sb*C*CH$_3$], 27.8 [d, J(P,C) = 11.1 Hz, PCH*C*H$_2$], 27.4 [d, J(P,C) = 10.6 Hz, PCH*C*H$_2$], 26.8 (s, CH_2 of C_6H_{11}), 4.6 [dd, J(Rh,C) = 25.9, J(P,C) = 11.4 Hz, Rh–CH$_3$], 3.3 [d, J(P,C) = 3.7 Hz, PCH_2Sb]; ^{31}P NMR (81.0 MHz, C_6D_6): δ = 27.3 [d, J(Rh,P) = 168.6 Hz]; $C_{30}H_{57}$PRhSb (673.4): calcd. C 53.51, H 8.53; found C 53.44, H 8.78.

[Rh(η^4-C_8H_{12})(κ^2-*P*,*Sb*-*i*Pr$_2$PCH$_2$Sb*i*Pr$_2$)]PF$_6$ (11a): A solution of [{C_8H_{12}RhCl}$_2$] (54 mg, 0.11 mmol) in 4 mL of CH_2Cl_2 was treated with a solution of **3** (76 mg, 0.22 mmol) in 3 mL of CH_2Cl_2 and stirred for 10 min at room temperature. A gradual change of color from yellow to orange-yellow occurred. A solution of $AgPF_6$ (55 mg, 0.22 mmol) in 4 mL of CH_2Cl_2 was then added dropwise, and the reaction mixture was stirred for 2 h under exclusion of light. An almost colorless solid (AgCl) precipitated. The solution was filtered and the filtrate was brought to dryness in vacuo. The oily residue was dissolved in 1.5 mL of methanol (50 °C), and the solution was stored for 12 h at −25 °C. Red needle-like crystals were obtained, which were washed twice with 5 mL portions of pentane and dried; yield 90 mg (60%); m.p. 107 °C (decomp.); ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 5.63 (brs, 2H, H_A), 5.08 (brs, 2H, H_B), 2.70 [dd, J(Rh,H) = 0.9, J(P,H) = 10.0 Hz, 2H, PCH_2Sb], 2.65 (m, 2H, SbC*H*CH$_3$), 2.32 (brm, 8H, CH_2 of C_8H_{12}), 2.11 (m, 2H, PC*H*CH$_3$), 1.49 [d, J(H,H) = 7.4 Hz, 6H, SbCHC*H*$_3$], 1.48 [d, J(H,H) = 7.2 Hz, 6H, SbCHC*H*$_3$], 1.32 [dd, J(P,H) = 16.8, J(H,H) = 7.2 Hz, 6H, PCHC*H*$_3$], 1.27 [dd, J(P,H) = 15.3, J(H,H) = 7.0 Hz, 6H, PCHC*H*$_3$]; ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ = 99.1 [dd, J(Rh,C) = 9.2, J(P,H) = 6.5 Hz, =CH_A], 88.0 [d, J(Rh,C) = 9.9 Hz, =CH_B], 31.0, 30.2 (both brs, CH_2 of C_8H_{12}), 27.3 [d, J(P,C) = 17.1 Hz, P*C*HCH$_3$], 22.6 (brs, Sb*C*HCH$_3$), 22.5, 22.0 (both s, SbCH*C*H$_3$), 19.0 [d, J(P,C) = 2.0 Hz, PCH*C*H$_3$], 17.6 (s, PCH*C*H$_3$), 13.1 [d, J(P,C) = 14.1 Hz, PCH_2Sb]; ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ = 11.2 [d, J(Rh,P) = 125.0 Hz, *i*Pr$_2$P], −144.0 [sept, J(F,P) = 710.6 Hz, PF_6^-]; $C_{21}H_{42}F_6P_2RhSb$ (695.2): calcd C 36.28, H 6.09, Rh 14.80; found C 36.26, H 5.96, Rh 15.05.

[Rh(η^4-C_8H_{12})(κ^2-*P*,*Sb*-*i*Pr$_2$PCH$_2$Sb*i*Pr$_2$)]BPh$_4$ (11b): a) A solution of **6** (56 mg, 0.10 mmol) in 3 mL of methanol was treated with a solution of $NaBPh_4$ (65 mg, 0.20 mmol) in 4 mL of methanol and stirred for 15 min at room temperature. An orange-yellow solid precipitated, which was separated from the mother liquor, washed with 3 mL of water, 4 mL of methanol, then twice with 5 mL portions of pentane, and dried; yield 37 mg (45%). b) A solution of **11a** (86 mg, 0.10 mmol) in 8 mL of methanol was treated with a solution of $NaBPh_4$ (67 mg, 0.20 mmol) in 5 mL of methanol and stirred for 15 min at room temperature. An orange-yellow precipitate was formed, which was separated from the mother liquor, washed with 2 mL of methanol, then twice with 5 mL portions of pentane, and dried; yield 64 mg (81%); m.p. 96 °C (decomp.); ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 7.36–6.89 (m, 20H, C_6H_5), 5.63 (brs, 2H, H_A), 5.10 (brs, 2H, H_B), 2.66 [d, J(P,H) = 10.1 Hz, 2H, PCH_2Sb], 2.58 (m, 2H, SbC*H*CH$_3$), 2.29 (brm, 8H, CH_2 of C_8H_{12}), 2.11 (m, 2H, PC*H*CH$_3$), 1.50 [d, J(H,H) = 7.2 Hz, 6H, SbCHC*H*$_3$], 1.48 [d, J(H,H) = 7.3 Hz, 6H, SbCHC*H*$_3$], 1.33 [dd, J(P,H) = 16.8, J(H,H) = 7.1 Hz, 6H, PCHC*H*$_3$], 1.27 [dd, J(P,H) = 15.3, J(H,H) = 6.9 Hz, 6H, PCHC*H*$_3$]; ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ = 164.3 [q, J(B,C) = 49.3 Hz, *ipso*-C of C_6H_5], 136.1 (s, *meta*-C of C_6H_5), 125.8 (brs, *ortho*-C of C_6H_5), 121.9 (s, *para*-C of C_6H_5), 99.05 [dd, J(Rh,C) = 9.4, J(P,H) = 6.4 Hz, =CH_A], 88.3 [d, J(Rh,C) = 9.7 Hz, =CH_B], 31.0, 30.2 (both brs, CH_2 of C_8H_{12}), 27.3 [d, J(P,C) = 17.3 Hz, P*C*HCH$_3$], 22.6 (brs, Sb*C*HCH$_3$ and SbCH*C*H$_3$), 22.1 (s, SbCH*C*H$_3$), 19.0 [d, J(P,C) = 3.0 Hz, PCH*C*H$_3$], 17.6 (s, PCH*C*H$_3$), 13.2 [d, J(P,C) = 13.9 Hz, PCH_2Sb]; ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ = 11.4 [d, J(Rh,P) = 125.0 Hz]; $C_{45}H_{62}$BPRhSb (869.4): calcd C 62.17, H 7.19; found C 61.80, H 6.95.

[Rh(η^4-C_8H_{12})(κ^2-*P*,*Sb*-*i*Pr$_2$PCH$_2$Sb*t*Bu$_2$)]PF$_6$ (12a): a) A solution of [{C_8H_{12}RhCl}$_2$] (70 mg, 0.14 mmol) in 5 mL of CH_2Cl_2 was treated with a solution of **4** (105 mg, 0.28 mmol) in 3 mL of CH_2Cl_2 and stirred for 10 min

at room temperature. A gradual change of color from yellow to orange-yellow occurred. To this solution, a solution of KPF_6 (53 mg, 0.28 mmol) in 4 mL of methanol was added. After the reaction mixture had been stirred for 2 h, the solvent was removed, the residue was extracted with 10 mL of CH_2Cl_2, and the extract was brought to dryness in vacuo. Recrystallization of the crude product from methanol (60 °C to −25 °C) gave red needle-like crystals, which were filtered, washed twice with 5 mL portions of pentane and dried: yield 170 mg (82%). b) A solution of $[\{C_8H_{12}RhCl\}_2]$ (141 mg, 0.29 mmol) in 7 mL of CH_2Cl_2 was treated with a solution of **4** (210 mg, 0.58 mmol) in 5 mL of CH_2Cl_2 and stirred for 20 min at room temperature. A solution of $AgPF_6$ (144 mg, 0.57 mmol) in 4 mL of CH_2Cl_2 was then added dropwise, and the resulting reaction mixture was stirred for 1.5 h under exclusion of light. An almost colorless solid (AgCl) was precipitated, which was filtered off, and the filtrate was dried in vacuo. Recrystallization of the residue from methanol as described for a) gave red crystals; yield 326 mg (80%); m.p. 120 °C (decomp.); ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 5.63 (brs, 2H, H_A), 5.11 (brs, 2H, H_B), 2.80 [dd, J(Rh,H) = 0.8, J(P,H) = 10.0 Hz, 2H, PCH_2Sb], 2.32 (brm, 8H, CH_2 of C_8H_{12}), 2.19 (m, 2H, $PCHCH_3$), 1.52 (s, 18H, $SbCCH_3$), 1.35 [dd, J(P,H) = 16.5, J(H,H) = 7.2 Hz, 6H, $PCHCH_3$], 1.30 [dd, J(P,H) = 15.3, J(H,H) = 6.9 Hz, 6H, $PCHCH_3$]; ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ = 98.4 [dd, J(Rh,C) = 9.4, J(P,H) = 6.4 Hz, $=CH_A$], 87.9 [d, J(Rh,C) = 9.7 Hz, $=CH_B$], 38.8 [brd, J(Rh,C) = 1.4 Hz, $SbCCH_3$], 31.9 (s, $SbCCH_3$), 30.9 [d, J(Rh,C) = 2.1 Hz, CH_2 of C_8H_{12}], 30.3 (s, CH_2 of C_8H_{12}), 27.8 [d, J(P,C) = 16.6 Hz, $PCHCH_3$], 19.5 [d, J(P,C) = 2.1 Hz, $PCHCH_3$], 18.2 (s, $PCHCH_3$), 16.3 [d, J(P,C) = 12.5 Hz, PCH_2Sb]; ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ = 8.7 [d, J(Rh,P) = 126.4 Hz, iPr_2P], −144.0 [sept, J(F,P) = 710.6 Hz, PF_6^-]; $C_{23}H_{46}F_6P_2RhSb$ (723.2): calcd C 38.20, H 6.41, Rh 14.23; found C 37.97, H 6.36, Rh 14.31.

$[Rh(\eta^4\text{-}C_8H_{12})(\kappa^2\text{-}P,Sb\text{-}iPr_2PCH_2SbtBu_2)]BPh_4$ (12b): A suspension of $[\{C_8H_{12}RhCl\}_2]$ (82 mg, 0.17 mmol) in 5 mL of methanol was treated with a solution of **4** (123 mg, 0.34 mmol) in 3 mL of methanol. The reaction mixture was stirred at room temperature until a clear orange-red solution was formed. To this solution a solution of $NaBPh_4$ (220 mg, 0.68 mmol) in 4 mL of methanol was added. After the resulting reaction mixture had been stirred for 30 min, an orange-yellow solid precipitated. It was separated from the mother liquor, washed with 5 mL of water, 5 mL of methanol, then twice with 7 mL portions of pentane, and dried; yield 203 mg (68%); m.p. 117 °C (decomp.); ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 7.40–6.89 (m, 20H, C_6H_5), 5.64 (brs, 2H, H_A), 5.11 (brs, 2H, H_B), 2.76 [d, J(P,H) = 9.9 Hz, 2H, PCH_2Sb], 2.29 (brm, 8H, CH_2 of C_8H_{12}), 2.17 (m, 2H, $PCHCH_3$), 1.54 (s, 18H, $SbCCH_3$), 1.36 [dd, J(P,H) = 16.4, J(H,H) = 7.3 Hz, 6H, $PCHCH_3$], 1.31 [dd, J(P,H) = 15.3, J(H,H) = 7.0 Hz, 6H, $PCHCH_3$]; ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ = 164.3 [q, J(B,C) = 49.2 Hz, *ipso*-C of C_6H_5], 136.1 (s, *meta*-C of C_6H_5), 125.8 [q, J(B,C) = 2.8 Hz, *ortho*-C of C_6H_5], 121.9 (s, *para*-C of C_6H_5), 98.5 (brm, $=CH_A$), 88.0 [d, J(Rh,C) = 8.4 Hz, $=CH_B$], 38.9 (s, $SbCCH_3$), 31.9 (s, $SbCCH_3$), 30.9 [d, J(Rh,C) = 1.4 Hz, CH_2 of C_8H_{12}], 30.3 (s, CH_2 of C_8H_{12}), 27.8 [d, J(P,C) = 17.1 Hz, $PCHCH_3$], 19.6 [d, J(P,C) = 2.1 Hz, $PCHCH_3$], 18.3 (s, $PCHCH_3$), 16.1 [d, J(P,C) = 13.4 Hz, PCH_2Sb]; ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ = 8.8 [d, J(Rh,P) = 126.4 Hz]; $C_{47}H_{66}BPRhSb$ (897.5): calcd C 62.90, H 7.41; found C 63.11, H 7.67.

$[Rh(\eta^4\text{-}C_8H_{12})(\kappa^2\text{-}P,Sb\text{-}Cy_2PCH_2SbtBu_2)]PF_6$ (13): A solution of **8** (626 mg, 0.90 mmol) in 5 mL of CH_2Cl_2 was treated with a solution of $AgPF_6$ (223 mg, 0.89 mmol) in 4 mL of CH_2Cl_2 and stirred for 3 h at room temperature under exclusion of light. A change of color from yellow to red occurred and an almost colorless solid (AgCl) precipitated. The solution was filtered and the filtrate was brought to dryness in vacuo. Recrystallization of the oily residue from methanol as described for **12a** gave dark red crystals; yield 542 mg (75%); m.p. 138 °C (decomp.); ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 5.58 (brs, 2H, H_A), 5.09 (brs, 2H, H_B), 2.83 [d, J(P,H) = 10.0 Hz, 2H, PCH_2Sb], 2.35–2.19 (brm, 30H, C_6H_{11} and CH_2 of C_8H_{12}), 1.51 (s, 18H, $SbCCH_3$); ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ = 97.8 [dd, J(Rh,C) = 9.3, J(P,H) = 6.5 Hz, $=CH_A$], 87.8 [d, J(Rh,C) = 9.7 Hz, $=CH_B$], 38.7 [brd, J(Rh,C) = 1.6 Hz, $SbCCH_3$], 37.5 [d, J(P,C) = 16.0 Hz, $PCHCH_2$], 31.8 (s, $SbCCH_3$), 30.8, 30.2 (both s, CH_2 of C_8H_{12}), 29.5, 28.7 (both s, CH_2 of C_6H_{11}), 27.1 [d, J(P,C) = 12.0 Hz, $PCHCH_2$], 26.7 [d, J(P,C) = 10.6 Hz, $PCHCH_2$], 26.0 (s, CH_2 of C_6H_{11}), 16.8 [d, J(P,C) = 13.4 Hz, PCH_2Sb]; ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ = −1.0 [d, J(Rh,P) = 124.3 Hz, Cy_2P], −144.0 [sept, J(F,P) = 711.4 Hz, PF_6^-]; $C_{29}H_{54}F_6P_2RhSb$ (803.4): calcd C 43.36, H 6.77; found C 43.45, H 6.51.

$[Rh(\eta^4\text{-}C_8H_{12})\{\kappa^2\text{-}C,P\text{-}CH_2Sb(iPr)_2CH_2PiPr_2\}]PF_6$ (14): A solution of **11a** (76 mg, 0.11 mmol) in 6 mL of THF was treated at −30 °C with a solution of CH_2N_2 (ca. 0.25 M, 1.20 mL, ca. 0.30 mmol) in ether, which led immediately to evolution of N_2. Under slightly reduced pressure, the solution was slowly warmed to room temperature and stirred for 45 min. The resulting yellow-brown solution was concentrated to 3 mL in vacuo, and then 1 mL of hexane was added. The reaction mixture was stirred at 40 °C until a clear solution was obtained. This solution was layered with 20 mL of hexane and after standing for 18 h at room temperature, yellow needle-like crystals precipitated. They were filtered, washed twice with 5 mL portions of pentane and dried; yield 57 mg (74%); m.p. 74 °C (decomp.); ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 4.99 (brs, 2H, H_A), 4.28 (brs, 2H, H_B), 2.86 (m, 2H, $SbCHCH_3$), 2.24 (brm, 8H, CH_2 of C_8H_{12}), 2.13–1.99 (m, 4H, PCH_2Sb and $PCHCH_3$), 1.59, 1.53 [both d, J(H,H) = 7.3 Hz, 12H, $SbCHCH_3$], 1.25 [dd, J(P,H) = 16.1, J(H,H) = 7.0 Hz, 6H, $PCHCH_3$], 1.21 [dd, J(P,H) = 14.1, J(H,H) = 6.9 Hz, 6H, $PCHCH_3$], 1.05 (brm, 2H, $RhCH_2$); ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ = 98.0 [dd, J(Rh,C) = 11.1, J(P,H) = 7.7 Hz, $=CH_A$], 82.9 [d, J(Rh,C) = 8.6 Hz, $=CH_B$], 31.8 [d, J(Rh,C) = 1.9 Hz, CH_2 of C_8H_{12}], 30.0 (s, CH_2 of C_8H_{12}), 27.1 [d, J(P,C) = 17.8 Hz, $PCHCH_3$], 26.1 [d, J(P,C) = 4.5 Hz, $SbCHCH_3$], 20.9, 20.5 (both s, $SbCHCH_3$), 19.4 [d, J(P,C) = 3.8 Hz, $PCHCH_3$], 17.9 (s, $PCHCH_3$), 6.6 (brm, PCH_2Sb), 2.9 [dd, J(Rh,C) = 30.7, J(P,C) = 7.2 Hz, $RhCH_2$]; ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ = 52.9 [d, J(Rh,P) = 162.0 Hz, iPr_2P], −144.0 [sept, J(F,P) = 711.4 Hz, PF_6^-]; $C_{22}H_{44}F_6P_2RhSb$ (709.2): calcd C 37.26, H 6.25; found C 37.16, H 5.96.

$[Rh(\eta^4\text{-}C_8H_{12})\{\kappa^2\text{-}C,P\text{-}CH_2Sb(tBu)_2CH_2PiPr_2\}]PF_6$ (15): This was prepared as described for **14**, from **12a** (74 mg, 0.10 mmol) and a solution of CH_2N_2 (ca. 0.5 M, 600 μL, ca. 0.30 mmol) in ether. Yellow microcrystalline solid; yield 62 mg (84%); m.p. 70 °C (decomp.); ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 4.95 (brs, 2H, H_A), 4.31 (brs, 2H, H_B), 2.22 (brm, 8H, CH_2 of C_8H_{12}), 2.13–2.04 (brm, 4H, PCH_2Sb and $PCHCH_3$), 1.61 (s, 18H, $SbCCH_3$), 1.25 [dd, J(P,H) = 14.0, J(H,H) = 6.9 Hz, 6H, $PCHCH_3$], 1.25 [dd, J(P,H) = 16.0, J(H,H) = 7.1 Hz, 6H, $PCHCH_3$], 1.05 (brm, 2H, $RhCH_2$); ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ = 97.2 [dd, J(Rh,C) = 11.1, J(P,H) = 8.0 Hz, $=CH_A$], 82.3 [d, J(Rh,C) = 8.6 Hz, $=CH_B$], 42.9 [brd, J(P,C) = 4.1 Hz, $SbCCH_3$], 31.9 (s, CH_2 of C_8H_{12}), 30.4 (s, $SbCCH_3$), 29.9 (s, CH_2 of C_8H_{12}), 27.7 [d, J(P,C) = 17.2 Hz, $PCHCH_3$], 19.5 [d, J(P,C) = 2.9 Hz, $PCHCH_3$], 18.4 (s, $PCHCH_3$), 7.8 (brm, PCH_2Sb), 2.6 [dd, J(Rh,C) = 31.0, J(P,C) = 7.2 Hz, $RhCH_2$]; ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ = 54.6 [d, J(Rh,P) = 162.0 Hz, iPr_2P], −144.0 [sept, J(F,P) = 710.6 Hz, PF_6^-]; $C_{24}H_{48}F_6P_2RhSb$ (737.2): calcd 39.10, H 6.56; found C 38.74, H 6.88.

$[Rh(\eta^4\text{-}C_8H_{12})\{\kappa^2\text{-}C,P\text{-}CH_2Sb(tBu)_2CH_2PCy_2\}]PF_6$ (16): A solution of **13** (54 mg, 0.07 mmol) in THF (3 mL) was treated at −30 °C with a solution of CH_2N_2 (ca. 0.30 M, 100 μL, ca. 0.30 mmol) in ether, which led immediately to an evolution of gas (N_2). Under slightly reduced pressure, the solution was slowly warmed to room temperature and stirred for 30 min. The resulting yellow solution was brought to dryness in vacuo. The oily residue was washed twice with 10 mL portions of ether, then twice with 5 mL portions of pentane, and dried. Yellow solid; yield 49 mg (86%); m.p. 52 °C (decomp.); ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 4.91 (brs, 2H, H_A), 4.28 (brs, 2H, H_B), 2.21 (brm, 8H, CH_2 of C_8H_{12}), 2.12 [dd, J(Rh,H) = 1.1, J(P,H) = 7.6 Hz, 2H, PCH_2Sb], 2.00–1.32 (m, 22H, C_6H_{11}), 1.60 (s, 18H, $SbCCH_3$), 1.02 (brm, 2H, $RhCH_2$); ^{13}C NMR (50.3 MHz, CD_2Cl_2): δ = 96.8 [dd, J(Rh,C) = 11.1, J(P,C) = 8.0 Hz, $=CH_A$], 82.1 [d, J(Rh,C) = 8.5 Hz, $=CH_B$], 42.7 [d, J(P,C) = 4.1 Hz, $SbCCH_3$], 37.7 [d, J(P,C) = 16.2 Hz, $PCHCH_2$], 31.8 (brs, CH_2 of C_8H_{12}), 30.3 (s, $SbCCH_3$), 30.0 (brs, CH_2 of C_6H_{11}), 28.9 (s, CH_2 of C_8H_{12}), 27.3 [d, J(P,C) = 5.7 Hz, $PCHCH_2$], 27.1 [d, J(P,C) = 4.1 Hz, $PCHCH_2$], 26.3 (s, CH_2 of C_6H_{11}), 8.1 [d, J(P,C) = 3.2 Hz, PCH_2Sb], 2.5 [dd, J(Rh,C) = 30.8, J(P,C) = 6.7 Hz, $RhCH_2$]; ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ = 44.5 [d, J(Rh,P) = 160.6 Hz, Cy_2P], −143.9 [sept, J(F,P) = 711.4 Hz, PF_6^-]; $C_{30}H_{56}F_6P_2RhSb$ (817.4): calcd C 44.08, H 6.91, Rh 12.59; found C 44.31; H 6.49, Rh 12.27.

$[(\eta^6\text{-}C_6H_5BPh_3)Rh(\kappa^2\text{-}P,Sb\text{-}iPr_2PCH_2SbiPr_2)]$ (17): A slow stream of H_2 was passed through a solution of **11b** (100 mg, 0.11 mmol) in 5 mL of CH_2Cl_2 for 30 s. After the solution had been stirred under H_2 for 1.5 h at room temperature, it was concentrated to ca. 2 mL in vacuo and then layered with 15 mL of hexane. Upon storing for 15 h at 20 °C, red crystals precipitated, which were separated from the mother liquor, washed twice with 5 mL portions of pentane, and dried; yield 64 mg (73%); m.p. 108 °C (decomp.); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 7.41–6.98 (all m, 15H, C_6H_5), 6.48

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[brd, J(H,H) = 6.0 Hz, 2H, *ortho*-H of η^6-C_6H_5], 6.12 (m, 1H, *para*-H of η^6-C_6H_5), 6.08 (m, 2H, *meta*-H of η^6-C_6H_5), 2.38 2.30 (m, 4H, PCH_2Sb and $SbCHCH_3$), 1.74 (m, 2H, $PCHCH_3$), 1.27, 1.25 [both d, J(H,H) = 7.8 Hz, 12H, $SbCHCH_3$], 1.12 [dd, J(P,H) = 15.4, J(H,H) = 6.8 Hz, 6H, $PCHCH_3$], 1.08 [dd, J(P,H) = 17.0, J(H,H) = 6.8 Hz, 6H, $PCHCH_3$]; ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 161.1 [q, J(B,C) = 50.3 Hz, *ipso*-C of C_6H_5], 135.9, 126.2, 123.1 (all s, C_6H_5), 103.0, 92.7, 91.8 (all s, η^6-C_6H_5), 28.3 [d, J(P,C) = 20.3 Hz, $PCHCH_3$], 21.9, 21.2 (both s, $SbCHCH_3$), 21.2 [d, J(P,C) = 3.8 Hz, $PCHCH_3$], 18.8 [d, J(P,C) = 3.5 Hz, $PCHCH_3$], 17.9 (s, $SbCHCH_3$), 16.2 [dd, J(Rh,C) = 1.4, J(P,C) = 14.9 Hz, PCH_2Sb], the signal of the *ipso*-C of η^6-C_6H_5 was not exactly located; ^{31}P NMR (162.0 MHz, CD_2Cl_2): δ = 32.8 [d, J(Rh,P) = 166.2 Hz]; $C_{37}H_{50}BPRhSb$ (761.2): calcd C 58.38, H 6.62; found C 58.62, H 7.02.

[(η^6-$C_6H_5BPh_3$)Rh(κ^2-*P,Sb*-*i*Pr_2PCH_2SbtBu$_2$)] (18): This was prepared as described for **17**, from **12b** (192 mg, 0.21 mmol) and H_2. Red microcrystalline solid; yield 132 mg (78%); ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 7.44–6.96 (brm, 15H, C_6H_5), 6.44 [d, J(H,H) = 6.2 Hz, 2H, *ortho*-H of η^6-C_6H_5], 5.95 (m, 3H, *meta*-H and *para*-H of η^6-C_6H_5), 2.46 [brd, J(P,H) = 9.9 Hz, 2H, PCH_2Sb], 1.74 (m, 2H, $PCHCH_3$), 1.38 (s, 18H, $SbCCH_3$), 1.14 [dd, J(P,H) = 15.7, J(H,H) = 7.0 Hz, 6H, $PCHCH_3$], 1.08 [dd, J(P,H) = 16.5, J(H,H) = 7.0 Hz, 6H, $PCHCH_3$]; ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ = 161.1 (brm, *ipso*-C of C_6H_5), 146.9 (brm, *ipso*-C of η^6-C_6H_5), 135.9, 126.2, 123.0 (all s, C_6H_5), 100.8, 95.6, 91.5 (all s, η^6-C_6H_5), 36.2 [d, J(Rh,C) = 3.2 Hz, $SbCCH_3$], 31.2 (s, $SbCCH_3$), 29.1 [d, J(P,C) = 19.9 Hz, $PCHCH_3$], 20.0 [brd, J(P,C) = 14.1 Hz, PCH_2Sb], 19.1 [d, J(P,C) = 1.7 Hz, $PCHCH_3$], 18.6 (s, $PCHCH_3$); ^{31}P NMR (81.0 MHz, CD_2Cl_2): δ = 28.7 [d, J(Rh,P) = 169.3 Hz]; $C_{39}H_{54}BPRhSb$ (789.3): calcd C 59.35, H 6.90, Rh 13.04; found C 58.99, H 6.95, Rh 12.97.

X-ray structure determination of compounds 5 and 12a:[29] Single crystals of **5** were grown by cooling a solution in ethanol/hexane (4:1) (from 50 °C to −25 °C) and those of **12a** by cooling a solution in methanol (from 60 °C to −25 °C). Crystal data for the two structures are presented in Table 1. The

Table 1. Crystal structure data for **5** and **12a**.

Compound	**5**	**12a**
formula	$C_{21}H_{42}PSb$	$C_{23}H_{46}F_6P_2RhSb$
M_r	447.27	723.20
T [K]	193(2)	293(2)
cryst. size [mm]	0.40 × 0.35 × 0.35	0.88 × 0.75 × 0.30
space group	$P\bar{1}$ (no. 2)	*Pbca* (no. 16)
a [pm]	1050.6(1)	1489.2(3)
b [pm]	1165.2(1)	1366.5(3)
c [pm]	1192.7(1)	2970.6(6)
α [°]	61.34(1)	90
β [°]	68.91(1)	90
γ [°]	66.68(1)	90
V [nm^3]	1.1500(2)	6.046(2)
Z	2	8
ρ_c [Mgm^{-3}]	1.292	1.589
μ [mm^{-1}]	1.269	1.593
F(000)	468	2912
2θ range [°]	4–60	5–44
no. meas. reflns	18554	4182
no. unique reflns	6051	3707
no. reflns used	6051	3688
refined parameters	214	338
$R1$ [$I > 2\sigma(I)$] [a]	0.020	0.024
$wR2$ [all data] [b]	0.050	0.111
g1; g2 [c]	0.023; 0.307	0.030; 8.646
resid. elec. ρ [10^{-6} e pm^{-3}]	+0.94/−0.45	+0.45/−0.30

[a] $R1 = \sum||F_o| - |F_c||/S|F_o|$. [b] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [c] $w = 1/[\sigma^2(F_o^2) + (g1 \times P)^2 + g2 \times P]$; $P = (F_o^2 + 2F_c^2)/3$.

data for **5** were collected at low temperature from an oil-coated shock-cooled crystal[30] on a Huber–Stoe–Siemens diffractometer fitted with a Siemens CCD detector. The data for **12a** were collected at room temperature on a Enraf–Nonius CAD4 instrument using monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å). Semiempirical absorption correction was applied.[31] The structures were solved by Patterson or direct methods with SHELXS-86.[32] All structures were refined by full-matrix least-squares procedures on F^2, using SHELXL-96.[33] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions.

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