A New Family of Carbenerhodium(I) Complexes: Ligand Variation as the Key to Success

Helmut Werner,* Peter Schwab, Elke Bleuel, Norbert Mahr, Paul Steinert, and Justin Wolf

Dedicated to Professor Roald Hoffmann on the occasion of his 60th birthday

Abstract: A synthetic methodology to obtain square-planar carbenerhodium(I) complexes of the general composition *trans*-[RhCl(=CRR′)(L)$_2$] where L is a tertiary phosphane, arsane, or stibane has been developed. The starting material *trans*-[RhCl(C_2H_4)(Sb*i*Pr$_3$)$_2$] (**3**) reacts with diazoalkanes RR′CN_2 [RR′ = Ph_2, Ph(C_6H_4X), (C_6H_4X)$_2$, Ph(CF_3), $C_{12}H_8$] under mild conditions to give the compounds *trans*-[RhCl(=CRR′)(Sb*i*Pr$_3$)$_2$] (**4**–**11**) almost quantitatively. On treatment of **3** with EtO_2CCHN_2 and PhC(N_2)C(O)R, the olefinrhodium and diazoalkanerhodium compounds *trans*-[RhCl{(*E*)-$C_2H_2(CO_2Et)_2$}(Sb*i*Pr$_3$)$_2$] (**12**) and *trans*-[RhCl{N_2C(R)C(O)Ph}(Sb*i*Pr$_3$)$_2$] (**13**, **14**) are obtained instead of carbene complexes. Displacement of the Sb*i*Pr$_3$ ligands in **4** (R = R′ = Ph) by P*i*Pr$_3$, P*i*Pr$_2$Ph, P*i*PrPh$_2$, PPh_3, PPh_2Me, As*i*Pr$_3$, and $SbEt_3$ leads to the corresponding carbene complexes *trans*-[RhCl(=CPh_2)(L)$_2$] (**15**–**21**) in high yields. The results of the X-ray crystal structure analyses of **4** and **15** (L = P*i*Pr$_3$) illustrate that the different donor–acceptor properties of Sb*i*Pr$_3$ and P*i*Pr$_3$ have little influence on the Rh–C bond length. The reactions of **4** and **15** with CO and CN*t*Bu afford, by metal-assisted C–C coupling, diphenylketene $Ph_2C{=}C{=}O$ (**23**) and the corresponding imine $Ph_2C{=}C{=}N$*t*Bu (**26**). On treatment of **4** and **15** with ethene, however, two different olefinic products, 3,3-diphenyl-1-propene (**31**) and 1,1-diphenyl-1-propene (**32**), are formed. Compound **15** reacts with KBr, NaOPh, and NaC_5H_5 by substitution of the chloride to give *trans*-[RhBr(=CPh_2)(P*i*Pr$_3$)$_2$] (**33**), *trans*-[Rh(OPh)(=CPh_2)(P*i*Pr$_3$)$_2$] (**34**) and [C_5H_5Rh(=CPh_2)(P*i*Pr$_3$)] (**35**), and with HCl by oxidative addition to yield [$RhCl_2(CHPh_2)$(P*i*Pr$_3$)$_2$] (**36**).

Keywords
carbene complexes · C–C coupling · diazo compounds · ligand effects · rhodium

Introduction

During the last decade, the chemistry of square-planar vinylidene- and allenylidene-rhodium(I) complexes of type **B** and **C** (Figure 1) has been studied quite extensively in our laboratory.[1] These compounds are not only interesting as far as their preparation and structure is concerned but, even more remarkably, as they offer the chance to perform novel metal-assisted C–C coupling reactions.[2, 3] Following this strategy it has been possible to convert two terminal alkyne molecules to either enynes or butatrienes via alkynyl(vinylidene)rhodium(I) complexes as intermediates,[2a] and also to prepare allene derivatives such as $CH_2{=}CHCH{=}C{=}CPh_2$ or *i*Pr_3PCHC(Ph)=C=C=CPh_2,[3b] which are frequently inaccessible by other synthetic routes.

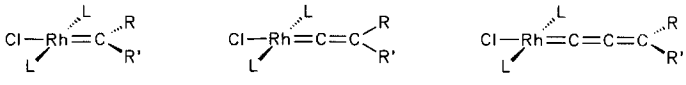

Figure 1. A series of square-planar rhodium(I) complexes containing rhodium–carbon double bonds.

After we found out about the promising aspects of the chemistry of compounds **B** and **C**, we set out to prepare the corresponding carbenerhodium(I) complexes **A** representing the missing link in the series of Rh–C double-bond systems **A**–**B**–**C** (Figure 1). Although our first attempts failed, they had an exciting outcome insofar as they showed that the ethene compound **1** (obtained from [{RhCl(P*i*Pr$_3$)$_2$}$_2$] and CH_2N_2 or, more conveniently, from [{RhCl(P*i*Pr$_3$)$_2$}$_2$] and C_2H_4) as well as the diazoalkane complex **2** (obtained from [{RhCl(P*i*Pr$_3$)$_2$}$_2$] and Ph_2CN_2), in the presence of excess C_2H_4 and Ph_2CN_2, can initiate a catalytic cycle. This leads, very surprisingly, not to the formation of 1,1-diphenylcyclopropane,[4] but exclusively to the isomeric 1,1-diphenyl-1-propene. To explain the mechanism of this unusual and unexpected C–C coupling reaction, we as-

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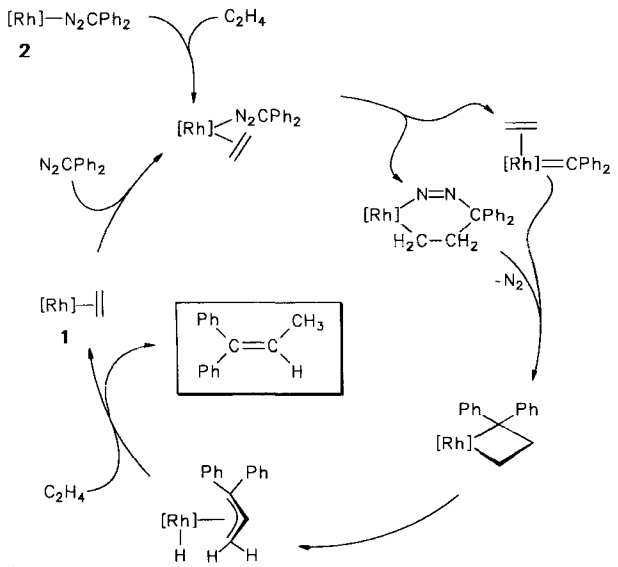
sumed that in the initial step both substrates, the olefin and the diazoalkane, are coordinated to the metal and subsequently either an RhN_2C_3 six-membered ring or a carbene(olefin)-rhodium(I) complex is formed (Scheme 1). From both species, a



Scheme 1. Catalytic cycle, initiated by **1** or **2** ([Rh] = $RhCl(PiPr_3)_2$), leading to the formation of 1,1-diphenyl-1-propene from excess C_2H_4 and Ph_2CN_2.

metallacyclobutane derivative could be generated and leads, via a π-allyl(hydrido) compound as intermediate, to the olefinic product.[5] Since, based on more recent studies,[6] we equally came to the conclusion that rhodium carbenes might be involved in the synthesis of the trisubstituted olefin, the challenge remained to prepare complexes of type **A** and to study their reactivity.

In this paper we report that by a variation of the ligand L it is possible to synthesize square-planar carbenerhodium(I) compounds with various substituents at the carbene carbon atom. Moreover, we illustrate that complexes of type **A** not only readily undergo substitution reactions, in which the Rh=CRR′ unit remains unchanged, but also react with ethene to give, depending on the ligand L, two different olefinic products. Some of these results have already been communicated.[7]

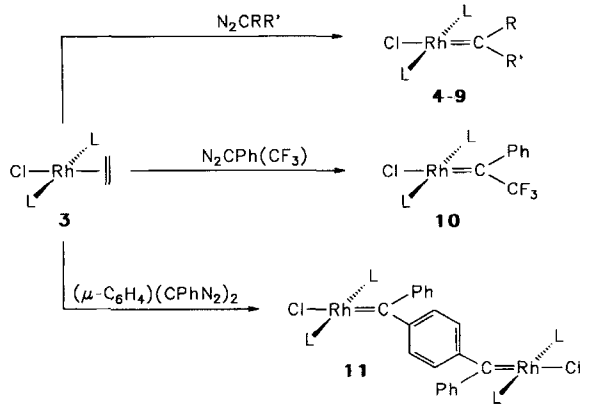
Results and Discussion

Preparation of *trans*-[RhCl(=CRR′)(Sb*i*Pr$_3$)$_2$] from the ethene-rhodium precursor: The route to prepare carbenerhodium(I) complexes of the general composition *trans*-[RhCl(=CRR′)(L)$_2$] was developed stepwise. The observation that compounds such as **2**[5] or *trans*-[RhCl{$N_2C(C_{12}H_8)$}($PiPr_3$)$_2$],[8] either on heating or on photolysis, react to give the dinitrogenrhodium derivative *trans*-[RhCl(N_2)($PiPr_3$)$_2$] instead of the desired metal carbenes, led us to conclude that it is the steric protection of the metal by the triisopropylphosphane ligands which hinders the formation of the rhodium–carbene bond. Therefore, $PiPr_3$ was first replaced by $AsiPr_3$ as the ligand L. The result, however, was disappointing. On treatment of *trans*-[RhCl(C_2H_4)($AsiPr_3$)$_2$] with Ph_2CN_2, the complex *trans*-[RhCl(N_2CPh_2)($AsiPr_3$)$_2$] was formed which, like the phosphane analogue **2**, reacted under UV irradiation to give *trans*-[RhCl(N_2)($AsiPr_3$)$_2$] but not *trans*-[RhCl(=CPh_2)($AsiPr_3$)$_2$].[9]

To go one step further from $AsiPr_3$ to $SbiPr_3$ was the key to success. Treatment of a solution of *trans*-[RhCl(C_2H_4)($SbiPr_3$)$_2$] (**3**) in pentane with Ph_2CN_2 at −78 °C, followed by evaporation of the solvent and warming the residue to room temperature led to an evolution of gas and a characteristic change of color from red-brown to brownish green. Extraction of the residue with pentane and recrystallization from acetone gave green crystals of *trans*-[RhCl(=CPh_2)($SbiPr_3$)$_2$] (**4**) in more than 80% yield (Scheme 2). The solid is only moderately air-sensitive and can be stored under argon at −20 °C, but decomposes in solution within a few hours. Other diaryldiazomethanes RR′CN_2 behave similarly to Ph_2CN_2 toward **3** and afford the corresponding carbenerhodium(I) complexes **5**–**9** in nearly quantitative yield (Scheme 2). The rate of the displacement of the ethene by the

	R	R′
4	Ph	Ph
5	p-C_6H_4Me	p-C_6H_4Me
6	Ph	o-C_6H_4Me

	R	R′
7	Ph	p-C_6H_4Me
8	$C_{12}H_8$	
9	p-C_6H_4OMe	p-C_6H_4OMe



Scheme 2. L = $SbiPr_3$.

carbene ligand depends crucially on the substituent X of the aryl group(s). Ph_2CN_2, Ph(*p*-C_6H_4Me)CN_2, and ($C_{12}H_8$)CN_2 react somewhat faster than Ph(*o*-C_6H_4Me)CN_2 and the latter more rapidly than (*p*-C_6H_4Me)$_2CN_2$ and (*p*-C_6H_4OMe)$_2CN_2$. Like **4**, the analogous compounds **5**–**9** are also green to brown solids, the composition of which has been determined by elemental analysis and spectroscopic techniques. As far as the NMR data are concerned, the most typical feature is the low-field resonance for the carbene carbon atom in the ^{13}C NMR spectra which appears at $\delta \approx 300-315$. The shift to lower fields is more pronounced in this case than for the corresponding carbenerhodium(I) complexes of the Lappert type.[10]

In contrast to CH_2N_2, $PhCHN_2$, and Ph(CH_3)CN_2, which do not react with **3** even at −78 °C to give stable rhodium-containing products, Ph(CF_3)CN_2 and (μ-*p*-C_6H_4)[C(Ph)N_2]$_2$ reacted with **3** to produce the mononuclear complex **10** and the binuclear compound **11** (Scheme 2), respectively. A very selec-

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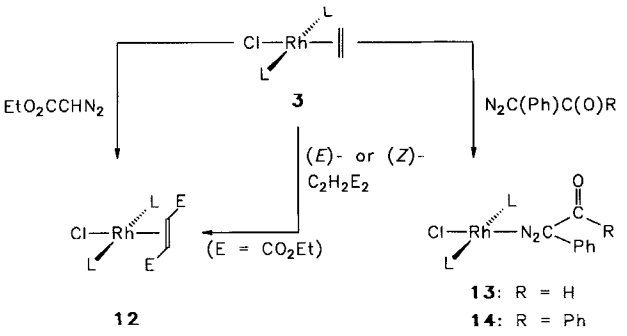
tive reaction takes place between **3** and two equivalents of ethyl diazoacetate. The elemental analysis of the red crystals, which are isolated in 94% yield, reveals, however, that the olefinrhodium(I) complex **12** (Scheme 3) is formed instead of a carbene

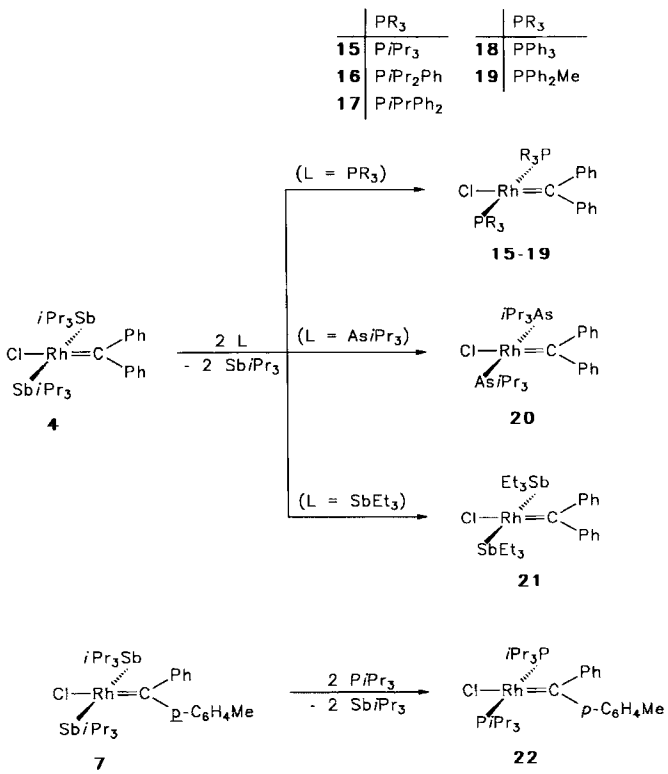


Scheme 3. L = Sb*i*Pr$_3$.

derivative. With regard to the mechanism of this reaction, we assume that in the initial step the expected carbene species *trans*-[RhCl(=CHCO$_2$Et)(Sb*i*Pr$_3$)$_2$] is generated, which rapidly reacts with a second molecule of (EtO$_2$C)CHN$_2$, possibly through a [3+2] cycloaddition of the diazoalkane to the Rh=C bond followed by elimination of N$_2$, to yield the product. Compound **12** is also obtained from **3** and diethyl fumarate or diethyl maleate by displacement of the weakly bound ethene. In agreement with the structural proposal, the ^{1}H NMR spectrum of **12** displays one doublet for the olefinic CH protons at $\delta = 4.50$ and the ^{13}C NMR spectrum a doublet for the corresponding carbon atoms at $\delta = 32.1$. The expected diastereotopic behavior of the CH$_3$ groups of the stibane ligands is indicated by the appearance of two singlets in the ^{13}C NMR spectrum at $\delta = 22.4$ and 22.1.

Compound **3** also reacts quite rapidly with benzoyldiazomethane and PhC(O)C(Ph)N$_2$ (azibenzil) to give the diazoalkanerhodium(I) complexes **13** and **14** (Scheme 3). The behavior of **3** is thus completely similar to that of the related bis(arsane) compounds *trans*-[RhCl(C$_2$H$_4$)(L)$_2$] (L = As*i*Pr$_3$, *i*Pr$_2$AsCH$_2$CH$_2$OMe), which upon treatment with PhC(O)C(R)N$_2$ also bind the intact benzoyldiazomethane unit.[11, 12] According to the spectroscopic data of **13** and **14**, which are slightly air-sensitive red solids, we assume that the diazoalkane moiety is bonded "end-on" via nitrogen to the rhodium center. Diagnostic for this type of coordination is a N–N stretching frequency in the IR spectrum at ca. 1935 cm^{-1} and a signal in the ^{13}C NMR spectrum for the N$_2$*C* carbon atom at $\delta = 117.3$ (**13**) or 99.7 (**14**). In spite of the fact that both compounds are thermally not very stable and decompose at 36 °C (**13**) or 44 °C (**14**), the attempts to transform them to the corresponding carbene complexes *trans*-[RhCl{=C(R)C(O)Ph}(Sb*i*Pr$_3$)$_2$] remained unsuccessful.

Two routes for ligand displacement reactions of *trans*-[RhCl(=CRR')(Sb*i*Pr$_3$)$_2$]: After we found that it is extremely difficult to substitute the P*i*Pr$_3$ ligands in compounds of type **B** or **C** (see Figure 1) by other two-electron donor groups,[11] the observation that bis(stibane) complexes such as **4** or **7** easily undergo ligand displacement reactions was a real surprise. Treatment of a solution of **4** in pentane with two equivalents of triisopropylphosphane at room temperature led to an exchange of Sb*i*Pr$_3$ by P*i*Pr$_3$ and to the formation of the original synthetic target, the carbene complex **15** (type **A** in Figure 1), in virtually quantitative yield. Analogous substitution reactions of **4** occurred with P*i*Pr$_2$Ph, P*i*PrPh$_2$, PPh$_3$, and PPh$_2$Me (Scheme 4), and

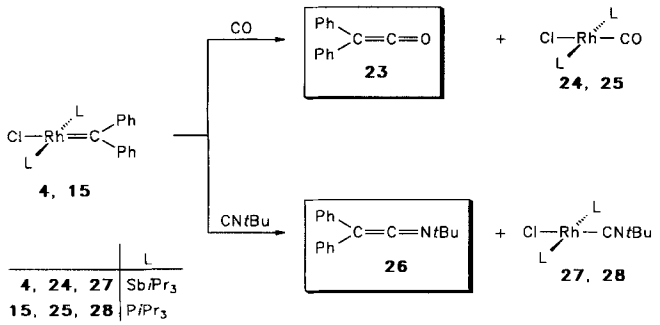


Scheme 4.

also of **7** with P*i*Pr$_3$, to give compounds **16**–**19** and **22**, respectively, in excellent yield. The carbenebis(phosphane)rhodium(I) complexes **15**–**19** are green or green-yellow solids, which are considerably more stable than the bis(stibane) derivatives both in the solid state and in solution (toluene, hexane). The ^{13}C NMR spectra of **15**–**19** and **22** display a low-field signal for the carbene carbon atom at $\delta \approx 310$–340, which is split into a doublet of triplets due to Rh–C and P–C coupling.

Not only tertiary phosphanes but also triisopropylarsane and even triethylstibane are able to displace the Sb*i*Pr$_3$ ligands of **4** giving the structurally related compounds **20** and **21**, respectively. While the properties of **20** are similar to those of the bis(triisopropylphosphane) analogue **15**, the bis(triethylstibane) complex **21** is rather labile and produces, *inter alia*, the dinuclear compound [Rh$_2$Cl$_2$(μ-CPh$_2$)$_2$(μ-SbEt$_3$)].[13] The chemistry of this new type of dinuclear bridging species will be described elsewhere.

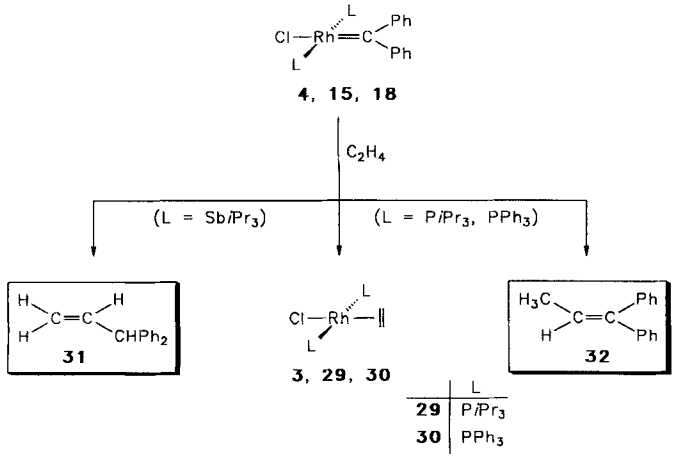
The reactions of **4** with carbon monoxide and *tert*-butylisocyanide did not lead to a displacement of the stibane ligands but took a different course. Instead of a carbene complex of the general composition *trans*-[RhCl(=CPh$_2$)(L)$_2$] (L = CO, CN*t*Bu), the compounds *trans*-[RhCl(L)(Sb*i*Pr$_3$)$_2$] (**24**, **27**) were formed (Scheme 5). The bis(triisopropylphosphane) complex **15** behaves quite similarly to **4**, and on treatment with CO or CN*t*Bu afforded the monocarbonyl and the monoisocyanide



Scheme 5.

compounds *trans*-[RhCl(L)($P i Pr_3$)$_2$] (**25**, **28**) in almost quantitative yield (Scheme 5). As the organic products, diphenylketene **23** and *N-tert*-butylketenimine **26** were obtained. They were separated from the metal-containing components by column chromatography and identified by their IR and ^{13}C NMR spectra. Since tetraphenylethene, which is produced from CPh_2 generated in situ,[14] could not be detected as a by-product in the reactions of **4** and **15** with CO and CN*t*Bu, we assume that both the ketene **23** and the corresponding ketenimine **26** are formed by C–C coupling in the coordination sphere of rhodium. In this context it should be mentioned that the reaction of $Ni(CO)_4$ with Ph_2CN_2 also yields diphenylketene, possibly via a carbene(carbonyl)nickel complex as an intermediate.[15]

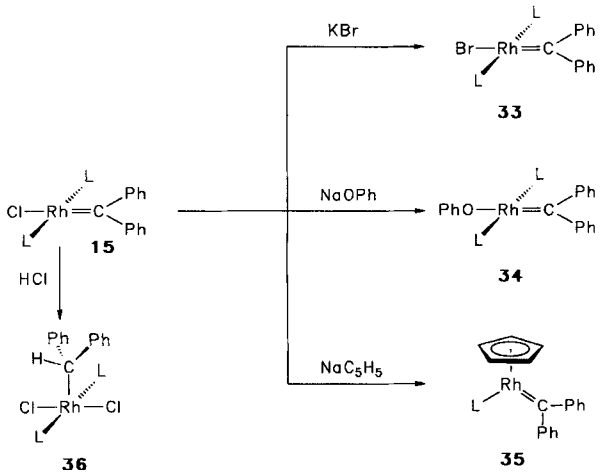
The diphenylcarbene complexes **4**, **15**, and **18** also reacted with ethene to give two different olefinic products, depending on the ligand L of the starting material (Scheme 6). On treatment



Scheme 6.

with ethene, compound **4** (L = $Sb i Pr_3$) afforded the terminal olefin $CH_2{=}CHCHPh_2$ (**31**) in addition to the ethenerhodium(I) derivative **3**; in contrast, complexes **15** and **18** (L = $P i Pr_3$ and PPh_3, respectively) gave the isomeric species $CH_3CH{=}CPh_2$ (**32**), besides **29** and **30**. Since the latter olefin is the product of the *catalytic* reaction of ethene and diphenyldiazomethane (see Scheme 1), the assumption that a carbene(ethene)rhodium compound is involved in the catalytic cycle[5] seems to be reasonable. Another isomer of **31** and **32**, namely 1,1-diphenylcyclopropane, which would be formed from C_2H_4 and Ph_2CN_2 in the presence of rhodium(II) complexes such as $Rh_2(OAc)_4$,[4] could not be detected either in the reaction of **4** and of **15** or **18** with ethene.

Substitution and addition reactions of *trans*-[RhCl(=CPh$_2$)-($P i Pr_3$)$_2$]: In order to find out whether, instead of the neutral ligands L, also the chloride in the carbene complexes of type **A** (Figure 1) could be replaced, compound **15** was treated with potassium halides, NaOPh, and NaC_5H_5. Whilst **15** was inert toward KF and smoothly decomposed in the presence of KI, the reaction with KBr in pentane (i.e., in heterogeneous phase) led to the formation of the bromo(carbene)rhodium(I) complex *trans*-[RhBr(=CPh_2)($P i Pr_3$)$_2$] (**33**) in quantitative yield (Scheme 7).



Scheme 7. L = $P i Pr_3$.

Under similar conditions (pentane:acetone = 40:1), the phenolato derivative *trans*-[Rh(OPh)(=CPh_2)($P i Pr_3$)$_2$] (**34**) was obtained. The spectroscopic data of **33** and **34** (the bromo compound **33** in solution is somewhat more labile than the starting material **15**) are analogous to those of **15** and thus confirm that the phosphane ligands are *trans* disposed. In the ^{13}C NMR spectrum of **34** there is a small shift (by 4–5 ppm) of the signal of the carbene carbon atom to higher field compared with **15** and **33**, which is probably due to the coordination of the stronger π-donor ligand OPh^- *trans* to the carbene unit.

The cyclopentadienyl complex [C_5H_5Rh(=CPh_2)($P i Pr_3$)] (**35**) was prepared from **15** and NaC_5H_5 in THF. It is a blue-violet, almost air-stable solid, which completes the series of halfsandwich-type compounds [$C_5H_5Rh\{{=}C(=C)_nRR'\}(P i Pr_3)$] with $n = 0$, 1 and 2. We note that while **35** and [C_5H_5Rh-(=C=C=CPh_2)($P i Pr_3$)][3b] are accessible from the square-planar precursors *trans*-[RhCl{=C(=C)$_n$$Ph_2$}($P i Pr_3$)$_2$] and NaC_5H_5, the preferred method of synthesis for the vinylidene derivatives [C_5H_5Rh(=C=CHR)($P i Pr_3$)] is the reaction of the rhodium(III) complexes [RhH(C≡CR)Cl(py)($P i Pr_3$)$_2$] with NaC_5H_5.[16] A compound of composition [$C_5H_5Rh\{{=}C(NMe\text{-}CH_2CH_2NMe)\}(CO)$], which is related in structure to **35**, has been prepared by Macomber and Rogers from [$C_5H_5Rh(CO)_2$] and bis(1,3-dimethylimidazolidin-2-ylidene).[17]

The carbene complex **15** and the corresponding vinylidene derivative *trans*-[RhCl(=C=CH_2)($P i Pr_3$)$_2$] behave similarly to-

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wards HCl in benzene or pentane. In both cases, addition of the electrophilic substrate to the Rh=C double bond takes place and the five-coordinate compounds $[RhCl_2(CHPh_2)(PiPr_3)_2]$ (**36**) and $[RhCl_2(CH{=}CH_2)(PiPr_3)_2]$[18] are formed. Complex **36** is a red solid, which is readily soluble in benzene, ether, or acetone, but decomposes almost instantaneously in chlorinated solvents. Although the NMR spectroscopic data of **36** (in particular the Rh–P coupling constant of the signal in the ^{31}P NMR spectrum) are consistent with the assumption that the phosphane ligands are *trans* disposed, they are not conclusive as to whether the molecule has a trigonal-bipyramidal or a square-pyramidal configuration. The closest analogue of **36** that we are aware of is the five-coordinate dichlorohydridorhodium(III) complex $[RhHCl_2(PiPr_3)_2]$, for which a square-pyramidal structure with the hydride in the apical position and the phosphanes and chlorides in the basal plane *trans* to each other has been determined by X-ray crystallography.[19] Based on this result, the structural proposal for **36** shown in Scheme 7 seems to be reasonable.

The molecular structure of compounds 4 and 15: The single-crystal X-ray diffraction studies of the two diphenylcarbene complexes **4** (Figure 2) and **15** (Figure 3) confirm the square-planar

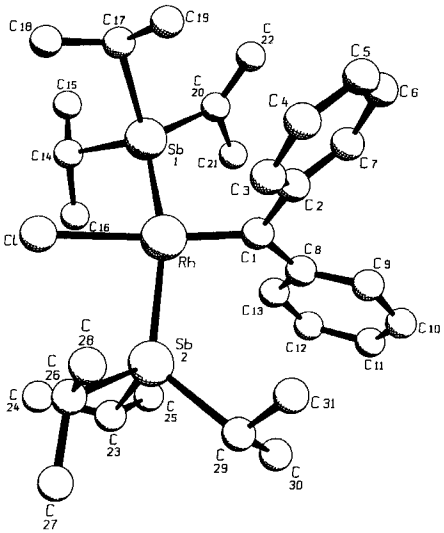

Figure 2. Molecular structure of **4**. Principal bond lengths [Å] and angles [°], with estimated standard deviations in parentheses: Rh–Cl 2.452(1), Rh–Sb1 2.5843(5), Rh–Sb2 2.5633(5), Rh–C1 1.863(4), C1–C2 1.489(6), C1–C8 1.497(6); Sb1-Rh-Sb2 155.48(2), Sb1-Rh-Cl 84.15(3), Sb1-Rh-C1 96.8(1), Sb2-Rh-Cl 84.75(3), Sb2-Rh-C1 97.6(1), Cl-Rh-C1 171.0(1), Rh-C1-C2 115.7(3), Rh-C1-C8 127.6(3), C2-C1-C8 116.6(4).

geometry with *trans*-disposed $SbiPr_3$ and $PiPr_3$ ligands. Both the Sb1-Rh-Sb2 and P1-Rh-P2 axes are somewhat bent, with the corresponding angle in **4** [155.48(2)°] deviating more markedly from the ideal value of 180° than in **15** [161.55(3)°]. The repulsive forces between the isopropyl and the phenyl groups of the $EiPr_3$ and CPh_2 ligands are probably responsible for this bending. We assume that steric effects also explain why the dihedral angle between the planes Rh/Cl/E1/E2 (E = P or Sb) and C1/C2/C8 is not 0° (as expected by bonding considerations) but 72.4(4)° in **4** and 69.5(2)° in **15**.

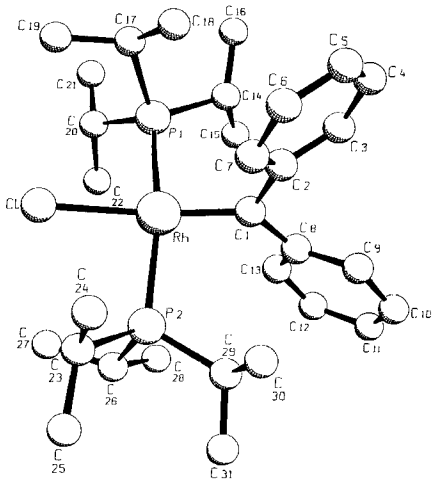

Figure 3. Molecular structure of **15**. Principal bond lengths [Å] and angles [°], with estimated standard deviations in parentheses: Rh–Cl 2.441(1), Rh–P1 2.396(1), Rh–P2 2.372(1), Rh–C1 1.876(3), C1–C2 1.498(5), C1–C8 1.476(4); P1-Rh-P2 161.55(3), P1-Rh-Cl 86.59(3), P1-Rh-C1 95.1(1), P2-Rh-Cl 86.53(3), P2-Rh-C1 95.6(1), Cl-Rh-C1 166.24(9), Rh-C1-C2 116.4(2), Rh-C1-C8 128.5(3), C2-C1-C8 115.0(3).

The Rh–C1 bond lengths in **4** [1.863(4) Å] and **15** [1.876(3) Å] are surprisingly short and are, to the best of our knowledge, the shortest Rh–C(carbene) distances ever found. In the structurally related compounds, studied by Lappert et al., the Rh–C bond length is 1.92(3) Å in *trans*-$[RhCl\{=C(NMeCH_2CH(CH_2iPr)NMe)\}(PPh_3)_2]$[10b] and 2.006(25) Å in *trans*-$[Rh\{N=C(CF_3)_2\}\{=C(NMeCH_2CH_2NMe)\}(PPh_3)_2]$.[20]

However, the most interesting aspect is that if the three types of square-planar complexes **A**, **B**, and **C**, shown in Figure 1, are compared, the shortest Rh–C distance is found for the vinylidene compounds *trans*-$[RhCl(=C=CRR')(PiPr_3)_2]$.[21] The order of decreasing Rh–C bond length is $\mathbf{A} \geq \mathbf{C} > \mathbf{B}$, which is in agreement with theoretical studies predicting that the highest degree of metal-to-carbon back-bonding should be expected for :C=CRR′ as the carbon-bonded unit.[22]

Conclusion

The present investigations have shown that the diazoalkane method, initially used by Herrmann[23] and Roper[24] and more recently by Grubbs[25] for the synthesis of carbene–metal complexes, can also be applied to the preparation of corresponding rhodium(I) derivatives. The compounds **4**–**11** and **15**–**22** are the first rhodium(I) complexes carrying a carbene ligand that is not stabilized by linkage to a hetero atom like O, S, or N.[26] From the preparative point of view, it is most remarkable that not only the primary reaction products **4**–**11** but also the subsequently formed compounds **15**–**20** and **22** are isolated in excellent, sometimes quantitative yields. Moreover, the ligand displacement reactions of **4** and **7** leading to **15**–**20** and **22** illustrate that the attack of nucleophilic substrates such as PR_3 or AsR_3 is preferentially directed to the metal and not to the carbene carbon atom as is found in Fischer-type carbene complexes.[27] The behavior of CO and CN*t*Bu seems to be exceptional since these Lewis bases displace the carbene unit instead of the $SbiPr_3$ or $PiPr_3$ ligands of **4** and **15**, thereby generating the C–C coupling products $Ph_2C{=}C{=}O$ and $Ph_2C{=}C{=}NtBu$, respectively.

The fact that the use of $SbiPr_3$ as ligand in the starting material opened the gate to a new family of carbenerhodium complexes of the general composition *trans*-[RhCl(=CRR')$(L)_2$] deserves a further comment. Although we had already prepared **3**, **24**, **27**, and some other mono- and bis(triisopropylstibane)-rhodium derivatives,[28, 29] trialkylstibane compounds of the late (electron-rich) transition metals are quite rare.[30] There is a general belief that trialkylstibanes are weaker σ donors than the corresponding trialkylphosphanes and -arsanes, and that also the π-acceptor properties are considerably reduced along the series $PR_3 > AsR_3 > SbR_3$.[31] Both arguments have been used to explain the problems associated with the synthesis of trialkylstibanemetal complexes although caution should be applied.

Recent work from our laboratory has shown that not only rhodium but also various iridium[32] and ruthenium compounds[33] containing $SbiPr_3$ and $SbMe_3$ as ligands can be prepared; for M = Ru there are even examples that are coordinatively and electronically unsaturated. We are presently trying to use the advantage of $SbiPr_3$ and other trialkylstibanes as ligands also in halfsandwich-type rhodium complexes and will report these results in due course.

Experimental Section

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **3**,[9] $AsiPr_3$,[34] $SbEt_3$,[35] CH_2N_2, and its derivatives[36] were prepared as described in the literature. NMR spectra were recorded at room temperature on Bruker AC200 and Bruker AMX400 instruments, and IR spectra on a Perkin-Elmer 1420 infrared spectrometer. Melting points were measured by DTA. Abbreviations used: s, singlet; d, doublet; t, triplet; vt, virtual triplet; sept, septet; m, multiplet; br, broadened signal; $N = {}^3J(PH) + {}^5J(PH)$ or ${}^1J(PC) + {}^3J(PC)$.

***trans*-[RhCl(=CPh$_2$)(Sb*i*Pr$_3$)$_2$] (4)**: A solution of **3** (808 mg, 1.21 mmol) in pentane (3 mL) was treated at $-78\,^\circ C$ with a solution of Ph_2CN_2 (470 mg, 2.42 mmol) in pentane (3 mL). Under continuous stirring and warming to room temperature, the solvent was removed in vacuo. An evolution of gas was observed. After the remaining residue had been stored for ca. 1.5 h under vacuo, a brownish green solid was formed. It was washed twice with 2 mL portions of methanol ($0\,^\circ C$) and then extracted with pentane (30 mL). The extract was brought to dryness in vacuo, and the residue recrystallized from acetone (15 mL). Upon storing at $-78\,^\circ C$ for 24 h, dark green crystals were formed which were separated from the mother liquor, washed with small quantities of acetone ($-20\,^\circ C$), and dried; yield 859 mg (88%); m.p. $61\,^\circ C$ (decomp.); ^1H NMR (C_6D_6, 200 Mz): $\delta = 8.03$ (m, 4H, *ortho*-H of C_6H_5), 7.24 (m, 2H, *para*-H of C_6H_5), 7.00 (m, 4H, *meta*-H of C_6H_5), 2.08 [sept, $J(H,H) = 7.3$ Hz, 6H, $SbCHCH_3$], 1.31 [d, $J(H,H) = 7.3$ Hz, 36H, $SbCHCH_3$]; ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 316.2$ [d, $J(Rh,C) = 29.1$ Hz, Rh=C], 160.1 (s, *ipso*-C of C_6H_5), 129.7, 129.1, 123.7 (all s, C_6H_5),21.9 (s, $SbCHCH_3$), 19.1 [d, $J(Rh,C) = 3.4$ Hz, $SbCHCH_3$]; $C_{31}H_{52}ClRhSb_2$ (806.6): calcd C 46.16, H 6.50, Rh 12.76; found C 46.37, H 6.76, Rh 12.86.

***trans*-[RhCl{=C(*p*-C$_6$H$_4$Me)$_2$}(Sb*i*Pr$_3$)$_2$] (5)** was prepared as described for **4**, from **3** (79 mg, 0.12 mmol) and a solution of $(p\text{-}C_6H_4Me)_2CN_2$ (53 mg, 0.24 mmol) in ether (3 mL); yield 92 mg (94%). Brownish green crystals; m.p. $55\,^\circ C$ (decomp.); ^1H NMR (C_6D_6, 200 MHz): $\delta = 8.05$ (m, 4H, *ortho*-H of C_6H_4Me), 6.83 (m, *meta*-H of C_6H_4Me), 2.12 [sept, $J(H,H) = 7.3$ Hz, 6H, $SbCHCH_3$], 1.80 (s, 6H, $C_6H_4CH_3$), 1.35 [d, $J(H,H) = 7.3$ Hz, 36H,$SbCHCH_3$]; ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 316.6$ [d, $J(Rh,C) = 28.0$ Hz, Rh=C], 157.8 (s, *ipso*-C of C_6H_4Me), 131.9, 129.0, 125.5 (all s, $C_6H_4CH_3$), 22.6 (s, $C_6H_4CH_3$), 22.2 (s, $SbCHCH_3$), 19.1 [d, $J(Rh,C) = 3.7$ Hz, $SbCHCH_3$]; $C_{33}H_{56}ClRhSb_2$ (834.7): calcd C 47.49, H 6.76; found C 47.63, H 6.67.

***trans*-[RhCl{=C(*o*-C$_6$H$_4$Me)Ph}(Sb*i*Pr$_3$)$_2$] (6)** was prepared as described for **4**, from **3** (92 mg, 0.14 mmol) and a solution of $(o\text{-}C_6H_4Me)PhCN_2$ (57 mg, 0.28 mmol) in pentane (3 mL); yield 105 mg (93%). Dark green crystals; m.p. $28\,^\circ C$ (decomp.); ^1H NMR (C_6D_6, 200 MHz): $\delta = 7.87$ (m, 3H, *ortho*-H of C_6H_5 and C_6H_4), 7.00 (m, 6H, *meta*- and *para*-H of C_6H_5 and C_6H_4), 2.07 (s, 3H, $C_6H_4CH_3$), 2.03 [sept, $J(H,H) = 7.3$ Hz, 6H, $SbCHCH_3$], 1.31 [d, $J(H,H) = 7.3$ Hz, 36H, $SbCHCH_3$]; ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 298.1$ [d, $J(Rh,C) = 31.0$ Hz, Rh=C], 163.8 and 161.3 (both s, *ipso*-C of C_6H_5 and C_6H_4), 141.6, 131.9, 130.8, 130.3, 130.1, 126.8, 126.5, 126.3 (all s, C_6H_5 and C_6H_4), 22.5 (s, $C_6H_4CH_3$), 22.1 (s, $SbCHCH_3$), 18.7 [d, $J(Rh,C) = 3.6$ Hz, $SbCHCH_3$]; $C_{32}H_{54}ClRhSb_2$ (820.6): calcd C 46.84, H 6.63; found C 46.97, H 6.47.

***trans*-[RhCl{=C(*p*-C$_6$H$_4$Me)Ph}(Sb*i*Pr$_3$)$_2$] (7)** was prepared as described for **4**, from **3** (92 mg, 0.14 mmol) and a solution of $(p\text{-}C_6H_4Me)PhCN_2$ (57 mg, 0.28 mmol) in pentane (3 mL); yield 104 mg (92%). Olive green crystals; m.p. $46\,^\circ C$ (decomp.); ^1H NMR (C_6D_6, 200 MHz): $\delta = 8.03$ (m, 4H, *ortho*-H of C_6H_5 and C_6H_4), 7.05 (m, 5H, *meta*- and *para*-H of C_6H_5, *meta*-H of C_6H_4), 2.09 [sept, $J(H,H) = 7.3$ Hz, 6H, $SbCHCH_3$], 1.77 (s, 3H, $C_6H_4CH_3$), 1.32 [d, $J(H,H) = 7.3$ Hz, 36H, $SbCHCH_3$]; ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 316.4$ [d, $J(Rh,C) = 28.9$ Hz, Rh=C], 159.9 and 157.9 (both s, *ipso*-C of C_6H_5 and C_6H_4), 131.9, 130.5, 130.1, 128.8, 128.3, 128.1 (all s, C_6H_5 and C_6H_4), 22.6 (s, $C_6H_4CH_3$), 22.2 (s, $SbCHCH_3$), 19.1 [d, $J(Rh,C) = 3.6$ Hz, $SbCHCH_3$]; $C_{32}H_{54}ClRhSb_2$ (820.6): calcd C 46.84, H 6.63; found C 46.97, H 6.69.

***trans*-[RhCl{=C(C$_{12}$H$_8$)}(Sb*i*Pr$_3$)$_2$] (8)**: A solution of **3** (67 mg, 0.10 mmol) in pentane (10 mL) was treated at $-78\,^\circ C$ with a solution of 9-diazofluorene (40 mg, 0.20 mmol) in ether (5 mL). An almost instantaneous change of color from red-violet to brown occurred. The reaction mixture was warmed up to room temperature and under reduced pressure (ca. 10^{-2} Torr) stirred for 30 min. The suspension (already containing a brown solid) was concentrated to ca. 5 mL in vacuo, and then kept for 1 h at room temperature. The brown precipitate was separated from the mother liquor, washed three times with 3 mL portions of pentane, and dissolved in ether (3 mL). After the solution had been stored at $-78\,^\circ C$, brown crystals were formed, which were washed with pentane ($0\,^\circ C$) and dried; yield 76 mg (94%); m.p. $55\,^\circ C$ (decomp.); ^1H NMR (C_6D_6, 200 MHz): $\delta = 8.52$ (m, 2H, *ortho*-H of $C_{12}H_8$), 7.35 (m, 2H, $C_{12}H_8$), 6.98 (m, 4H, $C_{12}H_8$), 2.11 [sept, $J(H,H) = 7.3$ Hz, 6H, $SbCHCH_3$], 1.27 [d, $J(H,H) = 7.3$ Hz, 36H, $SbCHCH_3$]; ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 309.3$ [d, $J(Rh,C) = 29.0$ Hz, Rh=C], 151.7 and 151.6 (both s, *ipso*-C of $C_{12}H_8$), 141.8, 138.7, 136.3, 133.0, 130.1, 129.3, 128.9, 127.1, 120.2, 119.8 (all s, $C_{12}H_8$), 22.1 (s, $SbCHCH_3$), 20.2 [d, $J(Rh,C) = 3.4$ Hz, $SbCHCH_3$]; $C_{31}H_{50}ClRhSb_2$ (804.6): calcd C 46.27, H 6.26; found C 46.31, H 6.13.

***trans*-[RhCl{=C(*p*-C$_6$H$_4$OMe)$_2$}(Sb*i*Pr$_3$)$_2$] (9)** was prepared as described for **4**, from **3** (71 mg, 0.11 mmol) and a solution of di(*p*-anisyl)diazomethane (54 mg, 0.22 mmol) in ether (4 mL); yield 76 mg (83%). Brownish green crystals; m.p. $39\,^\circ C$ (decomp.); ^1H NMR (C_6D_6, 400 MHz): $\delta = 7.84$ (m, 4H, *ortho*-H of C_6H_4), 6.68 (m, 4H, *meta*-H of C_6H_4), 3.25 (s, 6H, OCH_3), 2.49 [sept, $J(H,H) = 7.3$ Hz, 6H, $SbCHCH_3$], 1.31 [d, $J(H,H) = 7.3$ Hz, 36H, $SbCHCH_3$]; ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta = 317.0$ [d, $J(Rh,C) = 33.7$ Hz, Rh=C], 161.3 (s, *ipso*-C of C_6H_4), 131.6 and 127.9 (both s, *ortho*- and *meta*-C of C_6H_4), 113.4 (s, *para*-C of C_6H_4), 54.7 (s, $C_6H_4OCH_3$), 21.8 (s, $SbCHCH_3$), 20.1 (s, $SbCHCH_3$); $C_{33}H_{56}ClO_2RhSb_2$ (866.7): calcd C 45.73, H 6.51; found C 46.03, H 6.47.

***trans*-[RhCl{=C(CF$_3$)Ph}(Sb*i*Pr$_3$)$_2$] (10)**: A solution of **3** (83 mg, 0.12 mmol) in pentane (10 mL) was treated at $-78\,^\circ C$ with a 0.85M solution of $(CF_3)PhCN_2$ (146 µL, 0.24 mmol) in ether (3 mL). An almost instantaneous change of color from red to brownish green occurred. The solvent was removed in vacuo, and the residue was washed twice with 1 mL portions of methanol ($-20\,^\circ C$) and dissolved in pentane (2 mL). After the solution had been stored at $-78\,^\circ C$, brown crystals precipitated, which were washed with pentane ($-20\,^\circ C$) and dried; yield 90 mg (91%); m.p. $43\,^\circ C$ (decomp.); ^1H NMR (C_6D_6, 200 MHz): $\delta = 7.35$ (m, 2H, *ortho*-H of C_6H_5), 7.21 (m, 2H, *meta*-H of C_6H_5), 6.75 (m, 1H, *para*-H of C_6H_5), 2.14 [sept, $J(H,H) = 7.3$ Hz, 6H, $SbCHCH_3$], 1.33 [d, $J(H,H) = 7.3$ Hz, 36H, $SbCHCH_3$]; ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta = 293.6$ [dq, $J(Rh,C) = 17.4$, $J(F,C) = 14.6$ Hz, Rh=C], 155.7 (s, *ipso*-C of C_6H_5), 131.4, 129.9, 128.8 (all s, C_6H_5), 127.7 [q, $J(F,C) = 259.8$ Hz, CF_3], 21.9 (s, $SbCHCH_3$), 19.7 (s,

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$SbCHCH_3$); ^{19}F NMR (C_6D_6, 188.3 MHz): $\delta = -57.2$ (s, CF_3); $C_{26}H_{47}ClF_3RhSb_2$ (798.5): calcd C 39.11, H 5.93; found C 38.83, H 6.09.

***trans,trans*-[(Sb*i*Pr$_3$)$_2$ClRh{=CPh(*p*-C$_6$H$_4$)C(Ph)=}RhCl(Sb*i*Pr$_3$)$_2$] (11)**: A solution of **3** (120 mg, 0.18 mmol) in toluene (10 mL) was treated at $-78\,^\circ C$ with a solution of *p*-$C_6H_4[C(Ph)N_2]_2$ (112 mg, 0.36 mmol) in toluene (3 mL). A smooth change of color from red to brown occurred. The reaction mixture was warmed to room temperature and under reduced pressure (ca. 10^{-2} Torr) stirred for 45 min. The solvent was removed in vacuo, the remaining brownish green solid was washed three times with 5 mL portions of pentane ($20\,^\circ C$) and dried; yield 125 mg (91%); m.p. $64\,^\circ C$ (decomp.); ^1H NMR (C_6D_6, 200 MHz): $\delta = 8.04$, 7.63, 6.87 (all m, 14H, C_6H_5 and C_6H_4), 2.12 [sept, $J(H,H) = 7.6$ Hz, 12H, $SbCHCH_3$], 1.34 [d, $J(H,H) = 7.6$ Hz, 72H, $SbCHCH_3$]; ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 315.1$ [d, $J(Rh,C) = 31.2$ Hz, Rh=C], 160.2 and 160.1 (both s, *ipso*-C of C_6H_5 and C_6H_4), 131.8, 130.2, 129.3, 127.8, 124.7 (all s, C_6H_5 and C_6H_4), 22.2 (s, $SbCHCH_3$), 19.2 [d, $J(Rh,C) = 3.8$ Hz, $SbCHCH_3$]; $C_{56}H_{98}Cl_2Rh_2Sb_4$ (1535.1): calcd C 43.82, H 6.43; found C 43.86, H 6.37.

***trans*-[RhCl{(*E*)-C$_2$H$_2$(CO$_2$Et)$_2$}(Sb*i*Pr$_3$)$_2$] (12)**: a) A solution of **3** (85 mg, 0.13 mmol) in pentane (10 mL) was treated at $-78\,^\circ C$ with ethyl diazoacetate (27 μL, 0.26 mmol). A gradual change of color from orange to red occurred. The reaction mixture was warmed to room temperature and under reduced pressure (ca. 10^{-2} Torr) stirred for 15 min. The solvent was removed in vacuo, and the residue was washed twice with 1 mL portions of pentane ($-20\,^\circ C$) and then dissolved in pentane (3 mL) at $20\,^\circ C$. After the solution had been stored for 12 h at $-78\,^\circ C$, deep red crystals precipitated, which were washed with pentane ($0\,^\circ C$) and dried; yield 97 mg (94%).

b) A solution of **3** (132 mg, 0.20 mmol) in pentane (15 mL) was treated at $-78\,^\circ C$ with diethyl malonate (32 μL, 0.20 mmol) or diethyl fumarate (33 μL, 0.20 mmol). An instantaneous change of color from orange to red occurred. After the reaction mixture had been warmed to room temperature, the solvent was removed in vacuo, and the residue was worked up as described for a); yield 146 mg (90%); m.p. $99\,^\circ C$ (decomp.); IR (KBr): $\tilde{\nu} = 1694\ cm^{-1}$ (C=O); ^1H NMR (C_6D_6, 200 MHz): $\delta = 4.50$ [d, $J(Rh,H) = 2.0$ Hz, 2H, CH=CH], 4.04 and 3.95 [both dq, $^2J(H,H) = 10.8$, $^3J(H,H) = 7.2$ Hz, CH_2CH_3], 2.55 [sept, $J(H,H) = 7.4$ Hz, 6H, $SbCHCH_3$], 1.56 [d, $J(H,H) = 7.4$ Hz, 36H, $SbCHCH_3$], 1.07 [t, $J(H,H) = 7.2$ Hz, 6H, CH_2CH_3]; ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 174.4$ [d, $J(Rh,C) = 2.2$ Hz, CO_2], 60.2 (s, CH_2CH_3), 32.1 [d, $J(Rh,C) = 13.4$ Hz, CH=CH], 22.4 and 22.1 (both s, $SbCHCH_3$), 20.1 (s, CH_2CH_3), 14.3 (s, $SbCHCH_3$); $C_{26}H_{54}ClO_4RhSb_2$ (812.6): calcd C 38.43, H 6.70; found C 38.40, H 6.96.

***trans*-[RhCl{N$_2$CHC(O)Ph}(Sb*i*Pr$_3$)$_2$] (13)**: A solution of **3** (69 mg, 0.10 mmol) in pentane (10 mL) was treated dropwise at $-78\,^\circ C$ with a solution of benzoyldiazomethane (15 mg, 0.10 mmol) in ether (2 mL). An instantaneous change of color from orange-red to deep red occurred. The solvent was removed in vacuo, the oily residue was washed twice with 1 mL portions of methanol ($0\,^\circ C$) and dissolved in pentane (5 mL). After the solution had been stored at $-78\,^\circ C$, dark red crystals precipitated, which were washed twice with 1 mL portions of pentane ($-20\,^\circ C$) and dried; yield 71 mg (88%); m.p. $36\,^\circ C$ (decomp.); IR (C_6H_6): $\tilde{\nu} = 1937$ (N≡N), $1632\ cm^{-1}$ (C=O); ^1H NMR (C_6D_6, 200 MHz): $\delta = 8.15$ (m, 2H, *ortho*-H of C_6H_5), 7.13 (m, 3H, *meta*- and *para*-H of C_6H_5), 5.53 [d, $J(Rh,H) = 2.0$ Hz, 1H, N_2CH], 2.23 [sept, $J(H,H) = 7.4$ Hz, 6H, $SbCHCH_3$], 1.25 [d, $J(H,H) = 7.4$ Hz, 36H, $SbCHCH_3$]; ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 169.9$ [s, $C(O)C_6H_5$], 141.0 (s, *ipso*-C of C_6H_5), 129.7, 126.7, 125.9 (all s, C_6H_5), 117.3 (br s, N_2C), 21.6 (s, $SbCHCH_3$), 20.0 (s, $SbCHCH_3$); $C_{26}H_{48}ClN_2ORhSb_2$ (786.5): calcd C 39.70, H 6.15, N 3.56; found C 39.85, H 5.97, N 3.39.

***trans*-[RhCl{N$_2$CPhC(O)Ph}(Sb*i*Pr$_3$)$_2$] (14)** was prepared as described for **13**, from **3** (71 mg, 0.11 mmol) and azibenzyl (24 mg, 0.11 mmol); yield 85 mg (93%). Dark red solid; m.p. $44\,^\circ C$ (decomp.); IR (C_6H_6): $\tilde{\nu} = 1933$ (N≡N), $1612\ cm^{-1}$ (C=O); ^1H NMR (C_6D_6, 200 MHz): $\delta = 8.10$ (m, 4H, *ortho*-H of C_6H_5), 7.05 (m, 6H, *meta*- and *para*-H of C_6H_5), 2.04 [sept, $J(H,H) = 7.3$ Hz, 6H, $SbCHCH_3$], 1.44 and 1.43 [both d, $J(H,H) = 7.3$ Hz, 18H each, $SbCHCH_3$]; ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 149.2$ [s, $C(O)C_6H_5$], 144.0 and 140.9 (both s, *ipso*-C of C_6H_5), 129.7, 128.7, 128.3, 127.7, 126.3, 123.7 (all s, C_6H_5), 99.7 (br s, N_2C), 21.9 and 21.5 (both s, $SbCHCH_3$), 19.2 (s, $SbCHCH_3$); $C_{32}H_{52}ClN_2ORhSb_2$ (862.6): calcd C 44.56, H 6.08, N 3.25; found C 44.33, H 5.97, N 3.39.

***trans*-[RhCl(=CPh$_2$)(P*i*Pr$_3$)$_2$] (15)**: A solution of **4** (81 mg, 0.10 mmol) in pentane (10 mL) was treated with $PiPr_3$ (41 μL, 0.20 mmol) and stirred for 30 min at room temperature. The solvent was removed in vacuo, and the oily residue was washed twice with 2 mL portions of methanol ($-20\,^\circ C$) and dissolved in pentane (2 mL). The solution was chromatographed an Al_2O_3 (neutral, activity grade V, height of column 4 cm). With hexane, a green fraction was eluted, which was brought to dryness in vacuo. Upon recrystallization from pentane (5 mL) at $-78\,^\circ C$ green crystals were obtained. They were washed with small quantities of pentane ($0\,^\circ C$) and dried; yield 61 mg (98%); m.p. $81\,^\circ C$ (decomp.); ^1H NMR (C_6D_6, 200 Mz): $\delta = 8.03$ (m, 4H, *ortho*-H of C_6H_5), 7.14 (m, 6H, *meta*- and *para*-H of C_6H_5), 2.33 (m, 6H, $PCHCH_3$), 1.18 [d vt, $N = 13.2$, $J(H,H) = 7.1$ Hz, 36H, $PCHCH_3$]; ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 316.1$ [dt, $J(Rh,C) = 36.9$, $J(P,C) = 8.4$ Hz, Rh=C], 160.6 (s, *ipso*-C of C_6H_5), 129.8, 129.1, 127.9 (all s, C_6H_5), 25.3 (vt, $N = 17.4$ Hz, $PCHCH_3$), 20.6 (s, $PCHCH_3$); ^{31}P NMR (C_6D_6, 81.0 MHz): $\delta = 22.9$ [d, $J(Rh,P) = 169.4$ Hz]; $C_{31}H_{52}ClP_2Rh$ (625.1): calcd C 59.57, H 8.39; found C 59.37, H 8.33.

***trans*-[RhCl(=CPh$_2$)(P*i*Pr$_2$Ph)$_2$] (16)** was prepared as described for **15**, from **4** (120 mg, 0.15 mmol) and $PiPr_2Ph$ (58 mg, 0.30 mmol); yield 96 mg (92%). Green solid; m.p. $54\,^\circ C$ (decomp.); ^1H NMR (C_6D_6, 200 MHz): $\delta = 7.24$ (m, 8H, *ortho*-H of C_6H_5 and C_6H_5P), 6.92 (m, 12H, *meta*- and *para*-H of C_6H_5 and C_6H_5P), 2.78 (m, 4H, $PCHCH_3$), 1.63 [d vt, $N = 14.8$, $J(H,H) = 7.4$ Hz, 12H, $PCHCH_3$], 1.00 [d vt, $N = 13.9$, $J(H,H) = 6.9$ Hz, 12H, $PCHCH_3$]; ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta = 318.7$ [dt, $J(Rh,C) = 37.2$, $J(P,C) = 8.3$ Hz, Rh=C], 160.3 (vt, $N = 6.0$ Hz, *ipso*-C of C_6H_5), 134.6 [d vt, $N = 25.7$, $J(Rh,C) = 2.4$ Hz, *ipso*-C of C_6H_5P], 132.7 (vt, $N = 9.1$ Hz, *meta*-C of C_6H_5P), 128.0, 127.8, 127.7, 127.3 (all s, *para*-C of C_6H_5P and *ortho*-, *meta*- and *para*-C of C_6H_5), 127.1 (vt, $N = 7.0$ Hz, *ortho*-C of C_6H_5P), 24.8 (vt, $N = 21.2$ Hz, $PCHCH_3$), 21.2 (s, $PCHCH_3$), 19.3 (s, $PCHCH_3$); ^{31}P NMR (C_6D_6, 162.0 MHz): $\delta = 23.0$ [d, $J(Rh,P) = 174.0$ Hz]; $C_{37}H_{48}ClP_2Rh$ (693.1): calcd C 64.12, H 6.98; found C 63.91, H 7.17.

***trans*-[RhCl(=CPh$_2$)(P*i*PrPh$_2$)$_2$] (17)** was prepared as described for **15**, from **4** (116 mg, 0.14 mmol) and $PiPrPh_2$ (66 mg, 0.29 mmol); yield 103 mg (97%). Green solid; m.p. $100\,^\circ C$ (decomp.); ^1H NMR (C_6D_6, 200 MHz): $\delta = 7.52$ (m, 12H, *ortho*-H of C_6H_5 and C_6H_5P), 7.00 (m, 18H, *meta*- and *para*-H of C_6H_5 and C_6H_5P), 3.23 (m, 2H, $PCHCH_3$), 0.97 [d vt, $N = 15.0$, $J(H,H) = 7.4$ Hz, 12H, $PCHCH_3$]; ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta = 310.6$ [dt, $J(Rh,C) = 36.2$, $J(P,C) = 10.1$ Hz, Rh=C], 159.8 (vt, $N = 6.0$ Hz, *ipso*-C of C_6H_5), 134.6 [vt, $N = 10.1$ Hz, *meta*-C of C_6H_5P), 132.6 (vt, $N = 34.2$ Hz, *ipso*-C of C_6H_5P), 128.8, 128.4, 128.0, 127.9 (all s, *para*-C of C_6H_5P and *ortho*-, *meta*- and *para*-C of C_6H_5), 127.4 (vt, $N = 8.1$ Hz, *ortho*-C of C_6H_5P), 24.8 (vt, $N = 24.2$ Hz, $PCHCH_3$), 18.9 (s, $PCHCH_3$); ^{31}P NMR (C_6D_6, 162.0 MHz): $\delta = 27.6$ [d, $J(Rh,P) = 173.8$ Hz]; $C_{43}H_{44}ClP_2Rh$ (761.1): calcd C 67.86, H 5.83; found C 67.65, H 5.53.

***trans*-[RhCl(=CPh$_2$)(PPh$_3$)$_2$] (18)**: A solution of **4** (79 mg, 0.10 mmol) in pentane (10 mL) was treated dropwise at $-78\,^\circ C$ with a solution of PPh_3 (52 mg, 0.20 mmol) in pentane (2 mL). Upon warming to room temperature, a change of color to green-yellow occurred and a green-yellow solid precipitated. After the reaction mixture had been stirred for 45 min, the solid was separated from the mother liquor, washed twice with 5 mL portions of pentane ($25\,^\circ C$) and twice with 2 mL portions of acetone ($-20\,^\circ C$), and dried; yield 81 mg (98%); m.p. $90\,^\circ C$ (decomp.); ^1H NMR (C_6D_6, 200 MHz): $\delta = 7.81$ (m, 12H, *ortho*-H of C_6H_5P), 7.45 (m, 4H, *ortho*-H of C_6H_5), 6.88 (m, 24H, *meta*- and *para*-H of C_6H_5P and C_6H_5); ^{13}C NMR (CD_2Cl_2, 100.6 MHz): $\delta = 341.2$ [dt, $J(Rh,C) = 41.3$, $J(P,C) = 8.4$ Hz, Rh=C], 157.2 (br s, *ipso*-C of C_6H_5), 135.2 (vt, $N = 12.1$ Hz, *meta*-C of C_6H_5P), 135.0 (vt, $N = 40.3$ Hz, *ipso*-C of C_6H_5P), 129.8, 129.7, 129.1 (all s, *para*-C of C_6H_5P and *ortho*-, *meta*- and *para*-C of C_6H_5), 128.1 (vt, $N = 9.1$ Hz, *ortho*-C of C_6H_5P), 128.0 (s, *para*-C of C_6H_5P); ^{31}P NMR (CD_2Cl_2, 81.0 MHz): $\delta = 19.9$ [d, $J(Rh,P) = 183.1$ Hz]; $C_{49}H_{40}ClP_2Rh$ (829.2): calcd C 70.98, H 4.86; found C 70.81, H 4.69.

***trans*-[RhCl(=CPh$_2$)(PPh$_2$Me)$_2$] (19)** was prepared as described for **18**, from **4** (113 mg, 0.14 mmol) and PPh_2Me (48 μL, 0.26 mmol); yield 97 mg (98%). Green-yellow solid; m.p. $70\,^\circ C$ (decomp.); ^1H NMR (C_6D_6, 400 MHz): $\delta = 7.50$ (m, 12H, *ortho*-H of C_6H_5 and C_6H_5P), 6.90 (m, 18H, *meta*- and *para*-H of C_6H_5 and C_6H_5P), 1.88 (br s, 6H, PCH_3); ^{31}P NMR (CD_2Cl_2, 162.0 MHz): $\delta = 1.6$ [d, $J(Rh,P) = 173.8$ Hz]; $C_{39}H_{36}ClP_2Rh$ (705.0): calcd C 66.44, H 5.15; found C 65.91, H 5.27.

trans-**[RhCl(=CPh$_2$)(As*i*Pr$_3$)$_2$] (20)** was prepared as described for **15**, from **4** (91 mg, 0.11 mmol) and As*i*Pr$_3$ (88 μL, 0.44 mmol); reaction time 3 h; yield 68 mg (85%). Green-yellow crystals; m.p. 84 °C (decomp.); ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 8.05 (m, 4H, *ortho*-H of C$_6$H$_5$), 7.24 (m, 2H, *para*-H of C$_6$H$_5$), 6.99 (m, 4H, *meta*-H of C$_6$H$_5$), 2.23 [sept, J(H,H) = 7.3 Hz, 6H, AsC*H*CH$_3$], 1.32 [d, J(H,H) = 7.3 Hz, 36H, AsCHC*H*$_3$]; ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ = 315.9 [d, J(Rh,C) = 31.8 Hz, Rh=C], 160.5 (s, *ipso*-C of C$_6$H$_5$), 130.2, 127.1, 123.9 (all s, C$_6$H$_5$), 26.1 [d, J(Rh,C) = 2.2 Hz, AsCHCH$_3$], 21.9 (s, AsCH*C*H$_3$); C$_{31}$H$_{52}$As$_2$ClRh (713.0): calcd C 52.22, H 7.35; found C 52.53, H 7.39.

trans-**[RhCl(=CPh$_2$)(SbEt$_3$)$_2$] (21)**: A solution of **4** (81 mg, 0.10 mmol) in pentane (10 mL) was treated at −78 °C with SbEt$_3$ (32 μL, 0.20 mmol). The reaction mixture was warmed to room temperature and stirred for 10 min. A change of color from green to red-brown was observed. After the solvent had been removed, the residue was extracted with ether (20 mL), and the extract was brought to dryness in vacuo. A brownish green solid was obtained, which was washed three times with 1 mL portions of pentane (− 20 °C) and dried carefully in vacuo; yield 25 mg (35%); m.p. 59 °C (decomp.); ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 7.81 (m, 4H, *ortho*-H of C$_6$H$_5$), 7.48 (m, 2H, *para*-H of C$_6$H$_5$), 7.27 (m, 4H, *meta*-H of C$_6$H$_5$), 1.55 (m, 18H, A_3B_2 spin system, SbCH$_2$C*H*$_3$), 1.19 (m, 12H, A_3B_2 spin system, SbC*H*$_2$CH$_3$); C$_{25}$H$_{40}$ClRhSb$_2$ (722.5): calcd C 41.56, H 5.58; found C 41.70, H 5.43.

trans-**[RhCl{=C(*p*-C$_6$H$_4$Me)Ph}(P*i*Pr$_3$)$_2$] (22)** was prepared as described for **15**, from **7** (73 mg, 0.09 mmol) and P*i*Pr$_3$ (37 μL, 0.18 mmol); yield 55 mg (96%). Light-green crystals; m.p. 78 °C (decomp.); ^{1}H NMR (C$_6$D$_5$CD$_3$, 200 MHz): δ = 8.01 (m, 4H, *ortho*-H of C$_6$H$_5$ and C$_6$H$_4$), 7.30 (m, 4H, *meta*-H of C$_6$H$_5$ and C$_6$H$_4$), 6.94 (m, 1H, *para*-H of C$_6$H$_5$), 2.33 (m, 6H, PC*H*CH$_3$), 1.78 (s, 3H, C$_6$H$_4$C*H*$_3$), 1.20 and 1.18 [both dvt, N = 13.3, J(H,H) = 7.0 Hz, 18H each, PCHC*H*$_3$]; ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ = 316.6 [dt, J(Rh,C) = 29.2, J(P,C) = 5.1 Hz, Rh=C], 160.2 and 158.5 (both s, *ipso*-C of C$_6$H$_5$ and C$_6$H$_4$), 130.5, 129.2, 129.1, 128.3, 127.7, 127.0 (all s, C$_6$H$_5$ und C$_6$H$_4$), 25.3 (vt, N = 17.6 Hz, PCHCH$_3$), 21.4 (s, C$_6$H$_4$CH$_3$), 20.6 and 20.3 (both s, PCHCH$_3$); ^{31}P NMR (C$_6$D$_5$CD$_3$, 81.0 MHz, 293 K): δ = 28.2 [d, J(Rh,P) = 170.0 Hz]; C$_{32}$H$_{54}$ClP$_2$Rh (693.1): calcd C 60.14, H 8.52; found C 60.07, H 8.47.

Reaction of *trans*-[RhCl(=CPh$_2$)(Sb*i*Pr$_3$)$_2$] (4) with CO: A slow stream of CO was passed through a solution of **4** (81 mg, 0.10 mmol) in pentane (10 mL) for 30 s at room temperature. The solution was then stirred for 1 h. This led to a change of color from green to orange-red. The solvent was removed, the oily residue dissolved in hexane (2 mL), and the solution chromatographed on Al$_2$O$_3$ (neutral, activity grade III, height of column 6 cm). With hexane, a yellow fraction was eluted, which gave a yellow microcrystalline solid upon removal of the solvent. This was identified by ^{1}H and ^{31}P NMR spectroscopy as *trans*-[RhCl(CO)(Sb*i*Pr$_3$)$_2$] (**24**).[9] With hexane/benzene (1:1), a red fraction was eluted, which gave diphenylketene (**23**), identified by IR and ^{13}C NMR spectroscopy;[41] yield 175 mg (90%).

Reaction of *trans*-[RhCl(=CPh$_2$)(P*i*Pr$_3$)$_2$] (15) with CO: This reaction was carried out analogously to that of **4** with CO, with **15** (62 mg, 0.10 mmol) as starting material. The products were identified by IR and NMR spectroscopy as *trans*-[RhCl(CO)(P*i*Pr$_3$)$_2$] (**25**)[38, 42] and **23**; yield virtually quantitative.

Reaction of *trans*-[RhCl(=CPh$_2$)(Sb*i*Pr$_3$)$_2$] (4) with CN*t*Bu: A solution of **4** (82 mg, 0.10 mmol) in pentane (10 mL) was treated with CN*t*Bu (23 μL, 0.20 mmol) at room temperature. After the reaction mixture was stirred for 1 h it was worked up analogously as described for the solution obtained from **4** and CO. The products were identified by IR and NMR spectroscopy as Ph$_2$C=C=NtBu (**26**)[43] and *trans*-[RhCl(CN*t*Bu)(Sb*i*Pr$_3$)$_2$] (**27**);[28] yield virtually quantitative.

Reaction of *trans*-[RhCl(=CPh$_2$)(P*i*Pr$_3$)$_2$] (15) with CN*t*Bu: This reaction was carried out analogously to that of **4** with CN*t*Bu, with **15** (62 mg, 0.10 mmol) and CN*t*Bu (23 μL, 0.20 mmol) as starting materials. After the products had been separated by column chromatography, they were identified as **26**[43] and *trans*-[RhCl(CN*t*Bu)(P*i*Pr$_3$)$_2$] (**28**); yield (of **28**) 46 mg (85%). Data for **28**: Yellow solid; m.p. 102 °C (decomp.); IR (KBr): $\tilde{\nu}$ = 2151, 2056 cm^{-1} (C≡N); ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 2.62 (m, 6H, PC*H*CH$_3$), 1.38 [dvt, N = 13.2, J(H,H) = 7.1 Hz, 36H, PCHC*H*$_3$], 0.99 [s, 9H, C(CH$_3$)$_3$]; ^{31}P NMR (C$_6$D$_6$, 81.0 Hz): δ = 46.8 [d, J(Rh,P) = 129.2 Hz]; C$_{23}$H$_{51}$ClNP$_2$Rh (542.0): calcd C 50.97, H 9.49, N 2.58; found C 51.12, H 9.29, N 2.63.

Reaction of *trans*-[RhCl(=CPh$_2$)(Sb*i*Pr$_3$)$_2$] (4) with ethene: In an NMR tube, a slow stream of ethene was passed through a solution of **4** (40 mg, 0.05 mmol) in C$_6$D$_6$ (0.6 mL). During ca. 3 min, a change of color from green to yellow occurred. The ^{1}H NMR spectrum confirmed that both **3**[9] and 3,3-diphenyl-1-propene (**31**)[37] were formed; yield virtually quantitative.

Reaction of *trans*-[RhCl(=CPh$_2$)(P*i*Pr$_3$)$_2$] (15) with ethene: This reaction was carried out analogously to that described for **4**, with **15** (31 mg, 0.05 mmol) as starting material. The ^{1}H NMR spectrum displayed the signals of both *trans*-[RhCl(C$_2$H$_4$)(P*i*Pr$_3$)$_2$] (**29**)[38] and 1,1-diphenyl-1-propene (**32**);[39] yield virtually quantitative.

Reaction of *trans*-[RhCl(=CPh$_2$)(PPh$_3$)$_2$] (18) with ethene: This reaction was carried out analogously to that described for **4**, with **18** (33 mg, 0.04 mmol) as starting material. The ^{1}H NMR spectrum displayed the signals of both *trans*-[RhCl(C$_2$H$_4$)(PPh$_3$)$_2$] (**30**)[40] and 1,1-diphenyl-1-propene (**32**).[39] The formation of **30** was also confirmed by the ^{31}P NMR spectrum; yield virtually quantitative.

trans-**[RhBr(=CPh$_2$)(P*i*Pr$_3$)$_2$] (33)**: A solution of **15** (100 mg, 0.16 mmol) in pentane (5 mL) was treated with finely divided KBr (1.00 g, 8.40 mmol) and stirred for 48 h at room temperature. The solvent was removed in vacuo, and the residue was extracted with ether (5 mL). After the extract had been brought to dryness, a green solid was obtained. It was washed twice with 1 mL portions of methanol (− 20 °C) and dried; yield 105 mg (98%); m.p. 75 °C (decomp.); ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 8.05 (m, 4H, *ortho*-H of C$_6$H$_5$), 7.13 (m, 6H, *meta*- and *para*-H of C$_6$H$_5$), 2.44 (m, 6H, PC*H*CH$_3$), 1.16 [dvt, N = 13.2, J(H,H) = 6.8 Hz, 36H, PCHC*H*$_3$]; ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ = 317.7 [dt, J(Rh,C) = 39.2, J(P,C) = 7.3 Hz, Rh=C], 160.0 (s, *ipso*-C of C$_6$H$_5$), 128.6, 128.3, 127.9 (all s, *ortho*-, *meta*- and *para*-C of C$_6$H$_5$), 26.0 (vt, N = 17.3 Hz, PCHCH$_3$), 20.7 (s, PCHCH$_3$); ^{31}P NMR (C$_6$D$_6$, 162.0 MHz): δ = 19.8 [d, J(Rh,P) = 169.6 Hz]; C$_{31}$H$_{52}$BrP$_2$Rh (669.5): calcd C 55.61, H 7.83; found C 55.33, H 7.90.

trans-**[Rh(OPh)(=CPh$_2$)(P*i*Pr$_3$)$_2$] (34)**: A solution of **15** (125 mg, 0.20 mmol) in pentane (20 mL) was treated dropwise at − 78 °C with a solution of NaOPh (116 mg, 1.00 mmol) in acetone (0.5 mL). Upon warming to room temperature, a change of color from green to dark red occurred. After the reaction mixture had been stirred for 2 h at ca. 25 °C, the solvent was removed in vacuo. The residue was extracted with pentane (40 mL), and the extract concentrated to ca. 2 mL in vacuo. After the solution had been stored for 48 h at −78 °C, dark red crystals were formed, which were separated from the mother liquor, washed with 1 mL of pentane (− 30 °C) and dried; yield 98 mg (72%); m.p. 58 °C (decomp.); ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 8.05 (m, 4H, *ortho*-H of C$_6$H$_5$), 7.11 (m, 11H, *ortho*-, *meta*- and *para*-H of C$_6$H$_5$O and *meta*- and *para*-H of C$_6$H$_5$), 1.86 (m, 6H, PC*H*CH$_3$), 1.08 [dvt, N = 13.0, J(H,H) = 6.6 Hz, 36H, PCHC*H*$_3$]; ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ = 312.0 [dt, J(Rh,C) = 33.2, J(P,C) = 10.8 Hz, Rh=C], 170.2 (s, *ipso*-C of C$_6$H$_5$O), 160.5 (vt, N = 4.0 Hz, *ipso*-C of C$_6$H$_5$), 128.9, 128.7, 127.9, 127.3, 121.4, 112.7 (all s, *ortho*-, *meta*- and *para*-C of C$_6$H$_5$O and *ortho*-, *meta*- and *para*-C of C$_6$H$_5$), 24.4 (vt, N = 15.1 Hz, PCHCH$_3$), 20.3 (s, PCHCH$_3$); ^{31}P NMR (C$_6$D$_6$, 162.0 MHz): δ = 23.2 [d, J(Rh,P) = 177.0 Hz]; C$_{37}$H$_{57}$OP$_2$Rh (682.7): calcd C 65.09, H 8.42; found C 65.35, H 8.03.

[C$_5$H$_5$Rh(=CPh$_2$)(P*i*Pr$_3$)] (35): A solution of **15** (72 mg, 0.12 mmol) in THF (10 mL) was treated with NaC$_5$H$_5$ (44 mg, 0.50 mmol) and stirred for 30 min at room temperature. A quick change of color from green to deep blue occurred. The solvent was removed in vacuo, and the oily residue extracted with pentane (10 mL). The extract was concentrated to ca. 1 mL, and then the solution was chromatographed on Al$_2$O$_3$ (neutral, activity grade V, height of column 5 cm). With hexane, a blue fraction was eluted, which after removal of the solvent gave a blue-violet solid. This was washed twice with 2 mL portions of methanol (− 30 °C) and recrystallized from pentane (−78 °C); yield 47 mg (82%); m.p. 76 °C (decomp.); MS (70 eV): m/z (I_r) = 494 (30; M^+), 429 (0.3; $M^+ - C_5H_5$), 334 (100; $M^+ - PiPr_3$), 328 (2.4; $M^+ - CPh_2$), 269 (2.9; Rh=CPh$_2^+$), 168 (16; RhC$_5$H$_5^+$); ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 7.43 (m, 4H, *ortho*-H of C$_6$H$_5$), 7.07 (m, 6H, *meta*- and *para*-H of C$_6$H$_5$), 4.98 [dd, J(Rh,H) = J(P,H) = 0.8 Hz, 5H, C$_5$H$_5$], 1.48 [dsept, J(P,H) = 13.1, J(H,H) = 7.1 Hz, 3H, PC*H*CH$_3$], 0.98 [dd, J(P,H) = 13.1, J(H,H) = 7.1 Hz, 18H, PCHC*H*$_3$]; ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ = 261.0 [dd, J(Rh,C) = 50.9, J(P,C) = 17.9 Hz, Rh=C], 143.6 and 141.1 (both s, *ipso*-C of C$_6$H$_5$), 129.0, 128.6, 126.8, 126.6, 125.8, 125.1

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(all s, C_6H_5), 86.1 [dd, $J(Rh,C) = J(P,C) = 2.4$ Hz, C_5H_5], 26.7 [d, $J(P,C) = 18.2$ Hz, $PCHCH_3$], 20.4 (s, $PCHCH_3$); ^{31}P NMR (C_6D_6, 81.0 MHz): $\delta = 58.0$ [d, $J(Rh,P) = 241.2$ Hz]; $C_{27}H_{36}PRh$ (494.5): calcd C 65.59, H 7.34; found C 66.06, H 7.53.

$[RhCl_2(CHPh_2)(PiPr_3)_2]$ (36): A solution of **15** (63 mg, 0.10 mmol) in pentane (10 mL) was treated at −20 °C with a 0.5 M solution of HCl in benzene (200 μL, 0.10 mmol). An almost instantaneous change of color from green to red occurred, and the reaction mixture turned cloudy. The solvent was removed in vacuo, the residue was dissolved in ether (3 mL), and pentane (2 mL) was added. A red solid precipitated, which was separated from the mother liquor, washed three times with 2 mL portions of pentane (−20 °C) and dried; yield 63 mg (95%); m.p. 104 °C (decomp.); ^1H NMR (C_6D_6, 200 MHz): $\delta = 7.73$ (m, 4H, *ortho*-H of C_6H_5), 7.12 (m, 2H, *para*-H of C_6H_5), 6.64 (m, 4H, *meta*-H of C_6H_5), 4.67 (m, 1H, $CHPh_2$), 2.94 and 2.83 (both m, 3H each, $PCHCH_3$), 1.46 and 1.26 [both dvt, $N = 13.8$, $J(H,H) = 6.9$ Hz, 18H each, $PCHCH_3$]; ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 160.2$ and 155.1 (both s, *ipso*-C of C_6H_5), 129.0, 127.5, 127.1, 126.8, 126.1, 123.7 (all s, C_6H_5), 49.0 [dt, $J(Rh,C) = 19.5$, $J(P,C) = 9.8$ Hz, $CHPh_2$], 25.7 (vt, $N = 16.6$ Hz, $PCHCH_3$), 20.3 and 19.9 (both s, $PCHCH_3$); ^{31}P NMR (C_6D_6, 81.0 MHz): $\delta = 68.3$ [d, $J(Rh,P) = 121.1$ Hz]; $C_{31}H_{53}Cl_2P_2Rh$ (661.5): calcd C 56.29, H 8.08; found C 56.13, H 7.97.

X-ray structure determination of compounds 4 and 15: Single crystals of **4** were grown from pentane at −20 °C and those of **15** from hexane at room temperature. Crystal data collection parameters are summarized in Table 1. Intensity data were corrected for Lorentz and polarization effects. The structures were solved by direct methods for **4** and by the Patterson method for **15**. Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by the full-matrix least-squares method (Enraf-Nonius SDP).[44] The positions of the phenyl hydrogen atoms of **15** were taken from a difference Fourier synthesis and refined isotropically. The positions of the other hydrogen atoms of **4** and **15** were calculated according to ideal geometry (distance C–H = 0.95 Å) and used only in structure factor calculation.[45]

Table 1. Crystal structure data of compounds **4** and **15**.

	4	**15**
formula	$C_{31}H_{52}ClRhSb_2$	$C_{31}H_{52}ClP_2Rh$
M_r	806.62	625.06
cryst. size [mm]	0.4 × 0.3 × 0.2	0.25 × 0.33 × 0.48
cryst. system	triclinic	triclinic
space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a [Å]	11.025(2)	10.449(4)
b [Å]	12.348(5)	12.244(4)
c [Å]	14.194(2)	13.972(6)
α [°]	83.18(2)	94.01(3)
β [°]	86.17(1)	92.81(3)
γ [°]	63.11(2)	114.26(2)
V [Å^3]	1711(1)	1620(1)
Z	2	2
ρ_{calcd} [g cm^{-3}]	1.5606	1.28
diffractometer	Enraf-Nonius CAD4	
radiation (graphite-monochromated)	$Mo_{K\alpha}$ (0.70930 Å)	
T [K]	223	293
μ [cm^{-1}]	21.4	7.2
transmission min. [%]	84.11	93.2
scan method	$\omega/2\theta$	ω/θ
2θ (max) [°]	44	48
absorption correction	not applied	not applied
total reflections	4447	5364
unique reflections	4180	4736
observed reflections [a]	3950	4409
parameters refined	316	398
R	0.0285	0.029
R_w	0.0395	0.034
reflections/parameter ratio	12.5	11.08
residual electron density [e Å^{-3}]	+0.58/−0.91	+0.45/−0.31

[a] $[F_o > 3\sigma(F_o)]$.

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