The Bridging Function of an Apparently Nonbridging Ligand: Dinuclear Rhodium Complexes with Rh(μ-SbR$_3$)Rh as a Molecular Unit

Peter Schwab, Justin Wolf, Norbert Mahr, Paul Steinert, Ulrich Herber, and Helmut Werner*[a]

Dedicated to Professor Marianne Baudler on the occasion of her 80th birthday

Abstract: Novel dinuclear rhodium complexes of the general composition [$Rh_2Cl_2(\mu\text{-}CRR')_2(\mu\text{-}SbiPr_3)$] (**4**–**6**) were prepared by thermolysis of the mononuclear precursors *trans*-[RhCl(=CRR′)(Sb*i*Pr$_3$)$_2$] in excellent yield. The X-ray crystal structure analysis of **4** (R = R′ = Ph) confirms the symmetrical bridging position of the stibane ligand. Related compounds [$Rh_2Cl_2(\mu\text{-}CPh_2)(\mu\text{-}CRR')(\mu\text{-}SbiPr_3)$] (**7**, **8**) with two different carbene units were obtained either from *trans*-[RhCl(=CPh$_2$)(Sb*i*Pr$_3$)$_2$] (**1**) and RR′CN$_2$ or by a conproportionation of **4** and **5** (R = R′ = *p*-Tol) or **4** and **6** (R = Ph, R′ = *p*-Tol), respectively. While CO reacts with **4** to give the polymeric product [{RhCl(CPh$_2$)(CO)}$_n$] (**9**), *tert*-butyl isocyanide replaces the bridging stibane and yields [$Rh_2Cl_2(\mu\text{-}CPh_2)_2(\mu\text{-}CNtBu)$] (**10**). The reaction of **4** with tertiary phosphanes PR$_3$ leads to complete bridge cleavage and affords the mononuclear compounds *trans*-[RhCl(=CPh$_2$)(PR$_3$)$_2$] (**11**–**15**). In contrast, treatment of **4** with SbMe$_3$ and SbEt$_3$ yields the related triply bridged complexes [$Rh_2Cl_2(\mu\text{-}CPh_2)_2(\mu\text{-}SbR_3)$] (**16**, **17**) by substitution of Sb*i*Pr$_3$ for the smaller stibanes. The displacement of the chloro ligands in **4**–**6** and **10** by η^5-cyclopentadienyl gives the dinuclear complexes [$(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CRR')_2$] (**18**–**20**) and [$(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CPh_2)_2(\mu\text{-}CNtBu)$] (**21**), of which **18** (R = R′ = Ph) was characterized crystallographically.

Keywords: antimony · carbene complexes · cyclopentadienyl complexes · diazo compounds · rhodium

Introduction

Lewis bases of the general composition ER$_3$, where E is phosphorus, arsenic, or antimony and R an alkyl or aryl group, have widely been used as ligands in transition metal chemistry.[1] With regard to the coordination capabilities of ER$_3$ the common rule (discussed in textbooks,[2] monographs,[3] and reviews[4]) is that the metal–ligand bond strength decreases along the series M–PR$_3$ > M–AsR$_3$ > M–SbR$_3$, and that in contrast to CO or isocyanides tertiary phosphanes, arsanes, and stibanes behave only as terminal but not bridging units.[5]

We have found that this rule has to be revised with regard to trialkylstibanes. In the continuation of our studies on the reactivity of square-planar carbenerhodium(I) compounds *trans*-[RhCl(=CRR′)(L)$_2$],[6] we observed—absolutely unexpectedly—that the bis(stibane) derivatives *trans*-[RhCl(=CRR′)(Sb*i*Pr$_3$)$_2$] generate dinuclear rhodium(I) complexes with Rh(μ-Sb*i*Pr$_3$)Rh as a molecular fragment upon heating.[7] Herein we describe in detail the preparation, molecular structure, and reactivity of these new rhodium compounds with bridging stibane ligands and also give an outlook of the direction this chemistry could be extended. Some preliminary results have already been communicated.[7a]

Results and Discussion

Synthesis and structure of the stibane-bridged complexes: The starting materials **1**–**3**, which have been prepared from *trans*-[RhCl(C$_2$H$_4$)(Sb*i*Pr$_3$)$_2$] and diaryldiazomethanes,[6] react on warming in benzene to give, after chromatographic workup, the dinuclear complexes **4**–**6** in about 80% yield (Scheme 1). Under the same conditions, the bis(phosphane) derivatives *trans*-[RhCl(=CRR′)(PX$_3$)$_2$] (X$_3$ = *i*Pr$_3$, *i*Pr$_2$Ph, Ph$_3$) are quite inert and, even after stirring a solution of these compounds in benzene for two days, the starting material is recovered unchanged. Since during the thermolysis of **1**–**3** the formation of free triisopropylstibane was observed, we thought originally that one Sb*i*Pr$_3$ ligand from the precursors **1**–**3** had been

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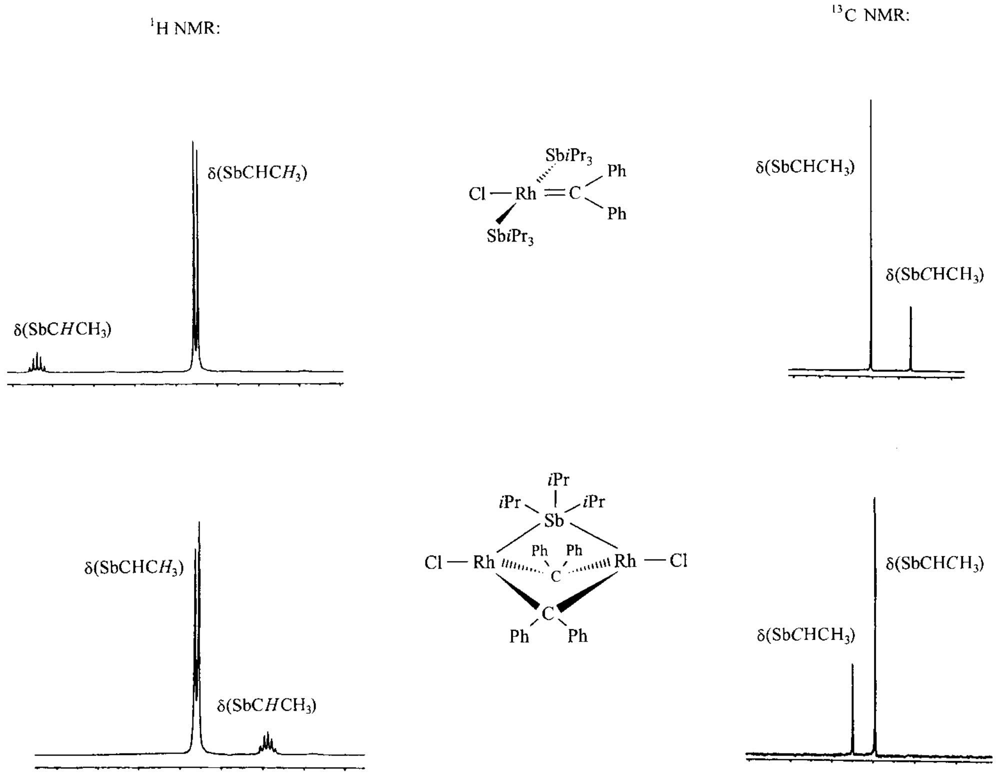
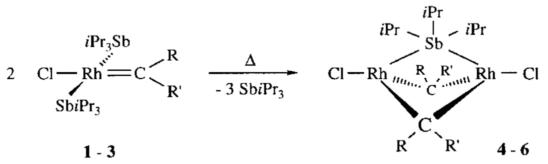


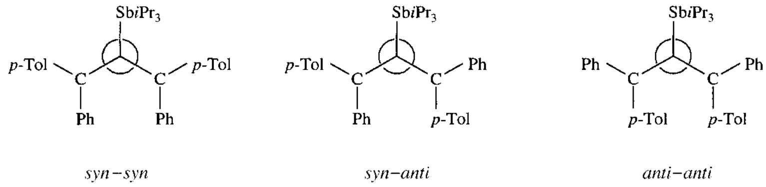
Figure 1. Chemical shifts of the signals for the protons and carbon nuclei of the isopropyl groups in the NMR spectra of compounds **1** and **4** (in C_6D_6).



1-3 **4-6**

	R	R'
1, 4	Ph	Ph
2, 5	*p*-Tol	*p*-Tol
3, 6	Ph	*p*-Tol

Scheme 1.



syn–syn *syn–anti* *anti–anti*

Figure 2. Newman projections of the configurational isomers of compound **6** viewed along the Cl-Rh-Rh-Cl axis.

eliminated and two of the resulting 14-electron species [RhCl(=CRR′)(Sb*i*Pr$_3$)] had formed a dimer with either chloro or diarylcarbene bridges. Although this does not occur, it is nevertheless conceivable that the supposed dimer [{RhCl(=CRR′)(Sb*i*Pr$_3$)}$_2$] with two bridging carbene ligands is generated as an intermediate which on subsequent loss of one stibane affords the final product.

The dinuclear compounds **4–6**, the composition of which was confirmed by elemental analysis, are red crystalline solids that are readily soluble in benzene, toluene, and dichloromethane. Most remarkably, they decompose only above 180 °C. The spectroscopic data of **4–6** differ significantly from those of the precursors **1–3** insofar as in the ^{1}H NMR spectra the signal of the SbC*H* protons appears at *higher* field relative to that of the SbCHC*H*$_3$ protons, while in the ^{13}C NMR spectra the SbCH resonance is observed at *lower* field than that of the SbCHCH$_3$ carbon atoms (Figure 1). Another characteristic feature is that in contrast to **1**, in compound **4** the phenyl groups are spectroscopically inequivalent which is illustrated in particular by the double set of signals for the C_6H_5 carbon nuclei. Regarding the less symmetrical complex **6**, the ^{13}C NMR spectrum reveals that all three possible isomers *syn–syn*, *syn–anti*, and *anti–anti* (Figure 2) with different orientations of the aryl groups are present. Based on the observation that upon stirring a solution of **6** in C_6D_6 for 12 h the intensity of the resonances for the carbene carbon atoms of the three isomers at $\delta = 188.0$, 187.9, and 187.8 remain unchanged, we conclude that under the conditions the isomeric mixture is already at equilibrium.

The X-ray crystal structure analysis of **4** (Figure 3) confirms the hitherto unknown capability of trialkylstibanes to behave as bridging ligands and to form two metal–antimony bonds. Quite surprisingly, there is almost no influence of the bridging function of the stibane on the Sb–C bond lengths and, despite the increase of the coordination number of antimony to five, on the C-Sb-C bond angles (cf. C14-Sb-C16 98.3(1)° in **4** and 100.2° (average value) in **1**). The Rh–Rh distance in **4** (2.5349(5) Å) is relatively short and indicative of a direct metal–metal interaction. Equally short Rh–Rh bond lengths have been found in other carbene-bridged dirhodium complexes of the type [Rh$_2$Cl$_2$(py)$_2$(μ-CPh$_2$)$_2$(μ-CO)][8] and

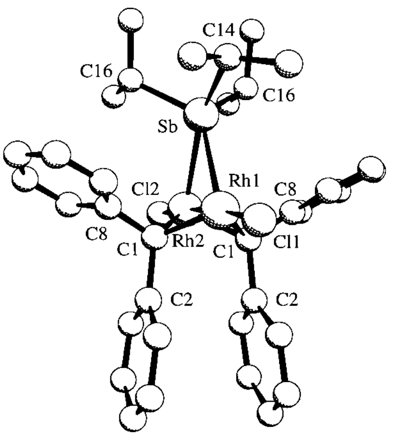
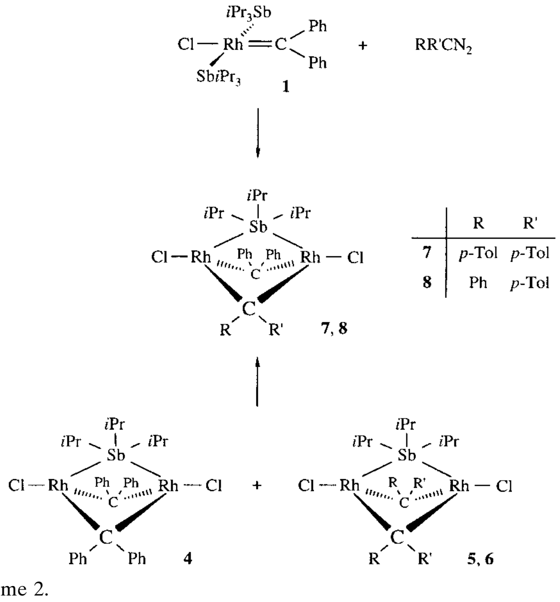


Figure 3. Molecular structure of **4**. Principal bond lengths [Å] and angles [°] (with estimated standard deviations in parathenses): Rh1–Rh2 2.5349(5), Rh1–Sb 2.6868(5), Rh2–Sb 2.6695(5), Rh1–Cl1 2.300(1), Rh–Cl2 2.294(1), Rh1–C1 2.000(3), Rh2–C1 2.007(3), C1–C2 1.504(4), C1–C8 1.507(5); Rh1-Sb-Rh2 56.49(1), Sb-Rh1-Rh2 61.41(1), Sb-Rh2-Rh1 62.10(1), Sb-Rh1-C1 90.24(9), Sb-Rh2-C1 90.59(9), Rh1-Rh2-Cl2 176.35(4), Rh2-Rh1-Cl1 175.45(4), C1-Rh1-C1 87.7(2), C1-Rh2-C1 87.3(2), Rh1-C1-Rh2 78.5(1), Rh1-Rh2-C1 50.63(9), Rh2-Rh1-C1 50.9(1), Rh1-C1-C2 115.5(2), Rh1-C1-C8 114.8(2), Rh2-C1-C2 114.5(2), Rh2-C1-C8 118.4(2), C2-C1-C8 111.5(3), C14-Sb-C16 98.3(1).

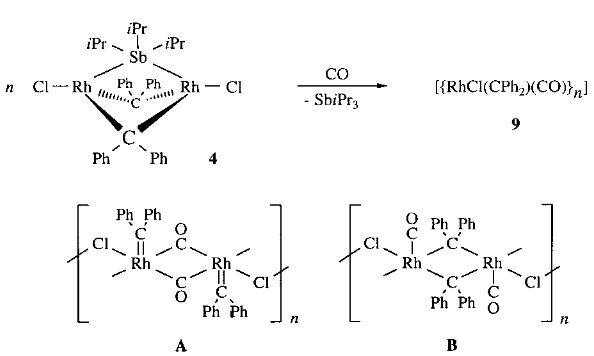


Scheme 2.

$[(C_5H_5)_2Rh_2(\mu\text{-}CPh_2)_2(\mu\text{-}CO)]$.[9] Noteworthy are the significant larger Rh–Sb distances in **4** (2.6868(5) and 2.6695(5) Å) if compared with those in **1** (2.5843(5) and 2.5633(5) Å),[6] which is in agreement with the bridging position of the stibane ligand. Although the Rh–$C_{carbene}$ bond lengths in **4** are also elongated (by ca. 0.14 Å) compared with those in **1**, they are nevertheless considerably shorter than in $[(C_5H_5)_2Rh_2(\mu\text{-}CPh_2)_2(\mu\text{-}CO)]$ (2.094(6) Å)[9] and $[\{(dppe)RhCl\}_2(\mu\text{-}Cl)_2(\mu\text{-}CH_2)]$ (2.057(3) Å; dppe = 1,2-bis(diphenylphosphanyl)ethane).[10] The arrangement of the Cl-Rh-Rh-Cl moiety is nearly linear, the somewhat slight bending away from the antimony atom being possibly due to the steric repulsion between the chloro ligands and the bulky isopropyl groups. The Rh–Cl distances in **4** (2.300(1) and 2.294(1) Å) are significantly shorter than the Rh–Cl distance in **1** (2.452(1) Å),[6] which could be due to the reduced *trans* influence of the bridging units compared to the terminal carbene ligand in **1**.

Studies concerned to the ability of the starting material **1** to undergo C–C coupling reactions with various substrates offered an alternative route to dinuclear rhodium complexes with a bridging stibane ligand. While attempts to connect the CPh_2 unit of compound **1** with CH_2 or $CH(CO_2Et)$ by using CH_2N_2 or $CH(CO_2Et)N_2$ as a carbene source did not generate the corresponding olefin but gave a mixture of products (which were not exactly identified), treatment of **1** with $(p\text{-}Tol)_2CN_2$ or $Ph(p\text{-}Tol)CN_2$ led under the same conditions (diethyl ether, 25 °C) to the formation of the more unsymmetrical dirhodium complexes **7** and **8** in about 75% yield (Scheme 2). Compounds **7** and **8** are also accessible by conproportionation of equimolar amounts of **4** and **5** or **4** and **6**, respectively. Although the structure and bonding of the starting materials **4**–**6** is probably very similar, it is quite remarkable that after stirring a solution, for example, of **4** and **5** in diethyl ether for 5 h at room temperature instead of an equilibrium mixture of **4**, **5**, and **7** in the ratio of 1:1:2 the less symmetrical product **7** is obtained nearly quantitatively. Moreover, we note that in contrast to **1** the dinuclear complex **4** is inert toward $(p\text{-}Tol)_2CN_2$ and does not form either **5** or one of the olefins $R_2C{=}CR'_2$ (R, R′ = Ph, *p*-Tol).

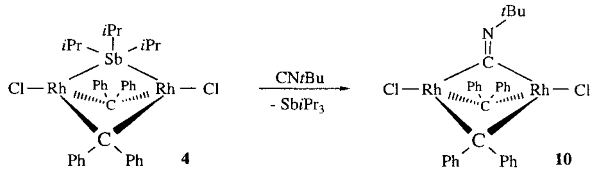
Reactions of the stibane-bridged complex 4 with Lewis bases: Taking into consideration that **4** is a 26-electron compound and appears to be not only electronically but also coordinatively unsaturated, we anticipated a pronounced reactivity of the stibane-bridged dirhodium complex toward Lewis bases. This has been confirmed by a variety of experiments. Whereas **4** is inert toward ethene, phenylacetylene, and 2-butyne even under UV irradiation, it reacts with CO in benzene at room temperature to afford a brick-red solid that is practically insoluble in all common organic solvents. Since the elemental analysis is consistent with the composition $[\{RhCl(CPh_2)(CO)\}_n]$ (**9**) we assume that the (presumably polymeric) product is identical to that obtained by Sonogashira et al. from $[\{RhCl(CO)_2\}_2]$ and diphenylketene.[11] While these authors proposed for **9** a structure like **A**, we think that a structure like **B** (see Scheme 3) is also conceivable. The reason why in contrast to **4** the analogous bridged carbonyl



Scheme 3.

complex is not monomeric could be that the steric repulsion between the bulky triisopropylstibane and the four bridging chloride ions (in the polymeric structure) prevents the formation of a polymer. An argument in favor of structure **B** is that the compound reacts with NaC_5H_5 to give $[(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CPh_2)_2(\mu\text{-}CO)]$ and with pyridine to afford $[Rh_2Cl_2(py)_2(\mu\text{-}CPh_2)_2(\mu\text{-}CO)]$.[8]

Treatment of **4** with an equimolar amount of CN*t*Bu yields the isocyanide complex **10** (Scheme 4), the proposed composition of which is supported by the elemental analysis and the mass spectrum. Similarly to the CO derivative **9**, the isocyanide-bridged compound **10** is also thermally quite stable, but in contrast to **9** moderately soluble in common organic solvents. In the IR spectrum of **10**, the CN stretching mode is observed at relatively high wavenumbers indicating that the C–N linkage possibly exhibits some triple-bond character. Although we are not sure that the isocyanide ligand is in a bridging position, we consider this as most likely regarding the structure of the substitution product **21** which is discussed below.

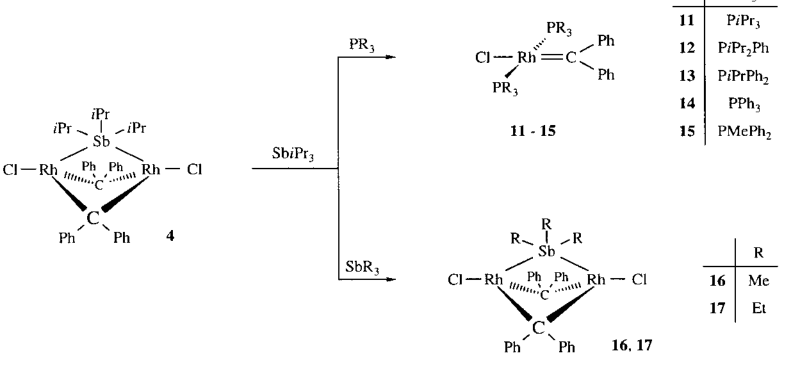


Scheme 4.

Attempts to replace the stibane ligand in **4** by a bridging P*i*Pr$_3$ unit failed. Compound **4** reacts with one equivalent of triisopropylphosphane to give the carbenerhodium(I) complex **11** in about 25% yield. With four equivalents of P*i*Pr$_3$, the mononuclear product is obtained almost quantitatively. Other tertiary phosphanes such as P*i*Pr$_2$Ph, P*i*PrPh$_2$, PPh$_3$, and PMePh$_2$ behave similarly (Scheme 5). The resulting four-coordinate rhodium(I) compounds **12**–**15** (which in each case are exclusively formed) were already known and had originally been prepared from **1** and the corresponding phosphane by ligand exchange.[6b] Although we did not succeed by using variable-temperature NMR spectroscopy to detect a phosphane-bridged intermediate in the reaction of **4** with P*i*Pr$_3$ or the less bulky PPh$_3$, the existence of a species of this type should not be excluded. Theoretical work (based on geometrical optimisations with the ZINDO method)[12] at least indicate that a molecule like $[Rh_2Cl_2(\mu\text{-}CPh_2)_2(\mu\text{-}PiPr_3)]$ should be stable and could be structurally related to the stibane-bridged complex **4**.[13] In this context we note that some years ago van Leeuwen and co-workers reported the synthesis and structural characterization of a palladium(I) dimer with 1,3-bis(diphenylphosphino)propane as ligand in which one phosphorus atom occupies an asymmetrical bridging position.[14]

Under the same conditions under which the mononuclear compounds **11**–**15** are formed from **4** and PR$_3$, the stibane-bridged complex **4** is completely inert toward As*i*Pr$_3$. However, the Sb*i*Pr$_3$ ligand of **4** can be replaced by SbMe$_3$ or SbEt$_3$ without destroying the $Cl_2Rh_2(\mu\text{-}CPh_2)_2$ part of the molecule. The reactions of **4** with the smaller stibanes proceed relatively fast in benzene at room temperature and give the dinuclear complexes **16** and **17** (see Scheme 5) as red, moderately air-stable solids in about 90% yield. It is worth mentioning that the SbMe$_3$-bridged compound **16** is thermally even more stable than the Sb*i*Pr$_3$ counterpart and decomposes at 242 °C! The above-mentioned theoretical work supports the assumption that the surprising stability of the novel dirhodium species **4**–**8** and **16**, **17** might be due to the presence of the aryl groups at the bridging carbene ligands which could interact through π donation with the electronically unsaturated metal centers.[13]

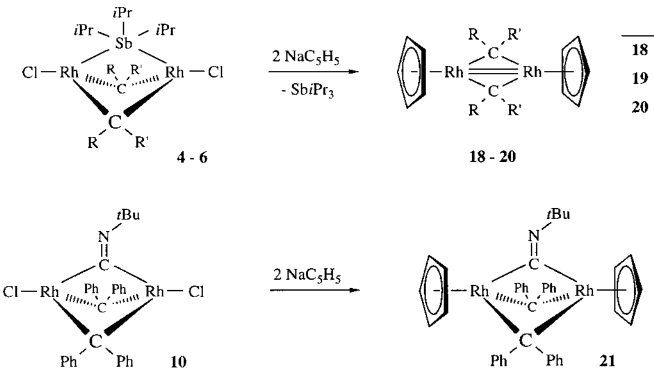
Doubly and triply bridged rhodium complexes with two (η^5-C$_5$H$_5$)Rh units: Both the stibane-bridged compounds **4**–**6** and the isocyanide-bridged analogue **10** react with NaC_5H_5 in THF by substitution of the chloro ligands for cyclopentadienyl. After removal of the solvent and chromatographic workup of the reaction mixtures the dinuclear complexes **18**–**21** (Scheme 6) were isolated as violet solids in good (**18**–**20**) to moderate (**21**) yields. The elemental analyses, the mass and the NMR spectra confirm that while upon treatment of **4**–**6** with NaC_5H_5 the stibane ligand is eliminated, in the corresponding reaction of **10** the isocyanide bridge is preserved. This different behavior points to a lower thermodynamic stability of the Rh(μ-Sb*i*Pr$_3$)Rh compared with the Rh(μ-CN*t*Bu)Rh unit. Attempts to generate the dinuclear complex $[(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CPh_2)_2(\mu\text{-}SbiPr_3)]$ by addition of triisopropylstibane to **18** failed. Compound **18** is known and has previously been prepared by abstraction of CO from the carbonyl-bridged species $[(\eta^5\text{-}C_5H_5)_2Rh_2(\mu\text{-}CPh_2)_2(\mu\text{-}CO)]$.[8, 9, 11] Regarding the NMR data of **18**–**20**, a typical feature is that the $^{13}C-^{103}Rh$ coupling constant of the triplet resonance for the *C*R$_2$ carbon atoms is significantly larger (ca. 42–43 Hz) than in the case of the stibane-containing precursors **4**–**6** (ca. 26 Hz). The corresponding value of $^1J(^{13}C,^{103}Rh)$ for **21** is 24.8 Hz indicating that the coupling constant de-



	PR$_3$
11	P*i*Pr$_3$
12	P*i*Pr$_2$Ph
13	P*i*PrPh$_2$
14	PPh$_3$
15	PMePh$_2$

	R
16	Me
17	Et

Scheme 5.



4 - 6 **18 - 20** **10** **21**

	R	R'
18	Ph	Ph
19	*p*-Tol	*p*-Tol
20	Ph	*p*-Tol

Scheme 6.

creases by expanding the doubly bridged to a triply bridged system.

The result of the X-ray crystal structure analysis of **18** is shown in Figure 4. The asymmetric unit contains besides the *unsymmetrical* dimer (drawn in the molecular diagram) two halves of two *symmetrical* dimers which possess a center of inversion at the midpoint of the Rh–Rh axis.[15] The distance Rh1–Rh2 of 2.4778(16) Å is even shorter (by ca. 0.1 Å) than in the doubly CO-bridged dimer $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CO})_2]$,[16] for which a double bond between the two metal centers has been postulated. The planes of the two cyclopentadienyl rings are parallel to each other and lie perpendicular to the plane formed by the rhodium and the carbene carbon atoms. The dihedral angles are 89.0(4)° and 89.5(3)°, respectively. Like in the CO-bridged dimer $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CO})_2]$, the two five-membered rings occupy a staggered conformation. The averaged bond length between the metal and the carbene carbon atoms is 2.040 Å and thus somewhat shorter than the $\text{Rh–C}_{\text{carbene}}$ distances in the triply bridged compounds $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Rh}_2(\mu\text{-CPh}_2)_2(\mu\text{-CO})]$[9] and $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Rh}_2(\mu\text{-CO})_2(\mu\text{-CC}_4\text{Br}_4)]$.[17] The phenyl rings of the bridging carbene ligands in **18** are twisted forming dihedral angles of 51.1(4)° (between the planes (C2–C7) and (C8–C14)) and 66.7(4)° (between the planes (C15–C20) and (C21–C26)), respectively.

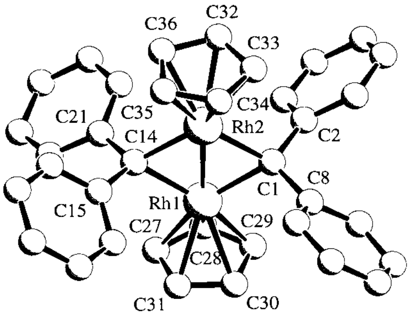


Figure 4. Molecular structure of **18**. Principal bond lengths [Å] and angles [°] (with estimated standard deviations in parathenses; values only for the unsymmetrical dimer): Rh1–Rh2 2.4778(16), Rh1–C1 2.040(10), Rh1–C14 2.040(10), Rh2–C1 2.045(10), Rh2–C14 2.037(10), Rh1–C27 2.267(12), Rh1–C28 2.245(11), Rh1–C29 2.237(12), Rh1–C30 2.224(12), Rh1–C31 2.219(12), Rh2–C32 2.246(13), Rh2–C33 2.253(12), Rh2–C34 2.247(12), Rh2–C35 2.220(13), Rh2–C36 2.215(13); C1-Rh1-C14 105.2(4), C1-Rh2-C14 105.1(4), Rh1-C1-Rh2 74.7(3), Rh1-C14-Rh2 74.8(3), C2-C1-C8 113.8(9), C15-C14-C21 114.6(8).

Conclusion

The present investigations have shown that in contrast to former belief trialkylstibanes can behave not only as terminal but also as *bridging* ligands. The series of dinuclear compounds with Sb-containing species—Sb, SbX, SbX_2, and SbX_3—in bridging position is now complete.[18] Besides the fact that complexes of the general composition $[\text{Rh}_2\text{Cl}_2(\mu\text{-CRR}')_2(\mu\text{-SbX}_3)]$ (X = Me, Et, *i*Pr) exist, the interesting facet is that these dinuclear molecules are remarkably stable, in most cases decomposing at temperatures around 190 °C or even above. It is conceivable that the thermal stability is at least partly due to the presence of two aryl substituents at the bridging carbene carbon atoms which might interact with the electronically unsaturated metal centers.

However, the novel stibane-bridged dirhodium complexes are not only exceptional from a structural point of view but also with respect to their reactivity toward Lewis bases. By using compound **4** as an example, we found that the bridging Sb*i*Pr$_3$ ligand can be substituted by CN*t*Bu and—most noteworthy—also by SbMe_3 and SbEt_3 without changing the $\text{Cl}_2\text{Rh}_2(\mu\text{-CPh}_2)_2$ part of the molecule. A similar reaction between **4** and tertiary phosphanes does not occur which could be due to the stronger σ-donating capabilities of PR_3 compared to those of SbR_3. Treatment of **4** with NaC_5H_5 does not lead to the known mononuclear half-sandwich-type complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Rh}(=\text{CPh}_2)(\text{Sb}i\text{Pr}_3)]$[19] but affords the doubly carbene-bridged dimer **18**, the structure of which was determined crystallographically. With regard to future studies, it would be interesting to find out whether compounds such as **4-8**, **10**, **16**, **17**, or **21** with $\text{Rh}(\mu\text{-CRR}')_2\text{Rh}$ (R and R′ = aryl) as the core fragment possess a similar reactivity to the dinuclear $\text{Rh}(\mu\text{-CHR})_2\text{Rh}$ complexes discovered and thoroughly investigated by Maitlis et al.[20] in which, however, the oxidation state of rhodium is +II instead of +I as in all the Rh_2 species described in this work.

Experimental Section

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The starting materials **1–3** were prepared as described in the literature.[6] NMR spectra were recorded at room temperature on Jeol FX 90Q, Bruker AC 200 and Bruker AMX 400 instruments, IR spectra on a Perkin-Elmer 1420 or an IFS 25 FT-IR infrared spectrometer, and mass spectra on a Varian CH7 MAT or a Finnigan 90 MAT instrument. Melting points were measured by differential thermal analysis (DTA). Abbreviations used: s, singlet; d, doublet; t, triplet; sept, septet; m, multiplet; v, virtual coupling; br, broadened signal.

$[\text{Rh}_2\text{Cl}_2(\mu\text{-CPh}_2)_2(\mu\text{-Sb}i\text{Pr}_3)]$ (4): A solution of **1** (98 mg, 0.12 mmol) in benzene (10 mL) was stirred for 4 h at 60 °C. A slow change of color from green to red occurred. After the solution was cooled to room temperature, the solvent was removed in vacuo, the oily residue was dissolved in pentane (3 mL), and the red-brown suspension was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 3 cm). With hexane, a brown fraction was eluted which was withdrawn. With benzene, a deep red fraction was eluted which was evaporated to dryness in vacuo. The remaining red solid was washed three times with pentane (10 mL each) and then recrystallized from acetone (5 mL) at −78 °C; yield 42 mg (81 %); m.p. 190 °C (decomp); MS (70 eV): m/z: 817 [$M^+ - C_3H_7$], 332 [$C_2Ph_4^+$], 304 [$ClRhCPh_2^+$], 251 [$SbiPr_3^+$], 138 [$RhCl^+$]; ^{1}H NMR (C_6D_6, 400 MHz): $\delta = 7.72$, 7.55 (both m, 8H; *ortho*-H of C_6H_5), 6.70, 6.65 (both m, 8H; *meta*-H of C_6H_5), 6.58 (m, 4H; *para*-H of C_6H_5), 1.12 (d, J(H,H) = 7.2 Hz, 18H; $SbCHCH_3$), 0.79 (sept, J(H,H) = 7.2 Hz, 3H; $SbCHCH_3$); ^{13}C NMR (C_6D_6, 100.6 MHz): d = 187.0 (t, J(Rh,C) = 26.3 Hz; RhCRh), 155.2, 152.0 (both s; *ipso*-C of C_6H_5), 128.6, 127.6, 127.3, 127.1, 123.8 (all s; C_6H_5), 23.0 (s; $SbCHCH_3$), 21.9 (s; $SbCHCH_3$); elemental analysis for $C_{35}H_{41}Cl_2Rh_2Sb$ (860.2) : calcd: C 48.87, H 4.80, Rh 23.93, Sb 14.15; found: C 49.09, H 5.02, Rh 23.95, Sb 14.21.

[$Rh_2Cl_2\{\mu$-$C(p$-$Tol)_2\}_2(\mu$-$SbiPr_3)$] (5): Compound **5** was prepared as described for **4**, from **2** (103 mg, 0.12 mmol) in benzene (10 mL) at 60 °C (5 h); yield 42 mg (77 %); m.p. 190 °C (decomp); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.13$, 7.02 (both m, 8H; *ortho*-H of C_6H_4), 6.86, 6.50 (both m, 8H; *meta*-H of C_6H_4), 3.13, 2.01 (both s, 12H; p-$C_6H_4CH_3$), 1.20 (d, J(H,H) = 6.9 Hz, 18H; $SbCHCH_3$), 1.00 (sept, J(H,H) = 7.2 Hz, 3H; $SbCHCH_3$); ^{13}C NMR ($CDCl_3$, 50.3 MHz): $\delta = 188.3$ (t, J(Rh,C) = 26.2 Hz; RhCRh), 151.6, 148.8 (both s, *ipso*-C of C_6H_4), 137.4, 136.4 (both s; *para*-C of C_6H_4), 128.9, 127.7, 126.7, 122.9 (all s; *ortho*- and *meta*-C of C_6H_4), 23.0 (s; $SbCHCH_3$), 21.9 (s; $SbCHCH_3$), 21.0 (s, $C_6H_4CH_3$); elemental analysis for $C_{39}H_{49}Cl_2Rh_2Sb$ (916.3) : calcd: C 51.12, H 5.39, Rh 22.46; found: C 51.01, H 5.31, Rh 22.48.

[$Rh_2Cl_2\{\mu$-$CPh(p$-$Tol)\}_2(\mu$-$SbiPr_3)$] (6): Compound **6** was prepared as described for **4**, from **3** (108 mg, 0.13 mmol) in benzene (10 mL) at 60 °C (5 h); yield 46 mg (78 %); m.p. 178 °C (decomp); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.34$–6.49 (m, 18H; C_6H_5 and C_6H_4), 2.16, 2.05 (both s, 6H; $C_6H_4CH_3$), 1.23 (d, J(H,H) = 6.4 Hz, 18H; $SbCHCH_3$), 0.97 (sept, J(H,H) = 6.4 Hz, 3H; $SbCHCH_3$); ^{13}C NMR ($CDCl_3$, 50.3 MHz): $\delta =$ 188.0, 187.8 (both t, J(Rh,C) = 25.6 Hz; RhCRh), 154.3, 151.7, 151.5, 151.4, 148.5, 146.1 (all s; *ipso*-C of C_6H_5 and C_6H_4), 137.5, 136.7 (both s; *para*-C of C_6H_4), 128.9, 128.4, 128.3, 127.8, 127.3, 127.1, 126.8, 125.8, 123.0 (all s; C_6H_5 and $C_6H_4CH_3$), 23.1 (s; $SbCHCH_3$), 21.9 (s; $SbCHCH_3$), 21.0 (s; $C_6H_4CH_3$); elemental analysis for $C_{37}H_{45}Cl_2Rh_2Sb$ (888.2) : calcd: C 50.03, H 5.11; found: C 49.84, H 5.06.

[$Rh_2Cl_2(\mu$-$CPh_2)\{\mu$-$C(p$-$Tol)_2\}(\mu$-$SbiPr_3)$] (7): a) A solution of **1** (81 mg, 0.10 mmol) in diethyl ether (10 mL) was treated with a solution of (p-Tol)$_2CN_2$ (22 mg, 0.10 mmol) in diethyl ether (5 mL) and stirred for 3 h at room temperature. The solvent was removed in vacuo, the remaining red solid was washed three times with pentane (3 mL each) and dried; yield 34 mg (76 %). b) A solution of **4** (47 mg, 0.06 mmol) and **5** (49 mg, 0.06 mmol) in benzene (10 mL) was stirred for 5 h at room temperature and then worked up as described for a); yield 93 mg (96 %); m.p. 183 °C (decomp); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.34$–7.02, 6.89, 6.75, 6.53 (all m 18H; C_6H_5 and C_6H_4), 2.15, 2.04 (both s, 6H; $C_6H_4CH_3$), 1.23 (d, J(H,H) = 6.9 Hz, 18H; $SbCHCH_3$), 0.98 (sept, J(H,H) = 6.9 Hz, 3H; $SbCHCH_3$); ^{13}C NMR ($CDCl_3$, 50.3 MHz): $\delta = 188.3$, 187.5 (both t, J(Rh,C) = 26.5 Hz; RhCRh), 154.2, 151.6, 151.2, 148.8 (all s; *ipso*-C of C_6H_5 and C_6H_4), 137.4, 136.4 (both s; *para*-C of C_6H_4), 128.9, 128.4, 127.7, 127.4, 127.2, 126.9, 126.8, 126.7, 123.1, 122.9 (all s; C_6H_5 and C_6H_4), 23.2, 23.0 (both s; $C_6H_4CH_3$), 21.9 (s; $SbCHCH_3$), 21.0 (s; $SbCHCH_3$); elemental analysis for $C_{37}H_{45}Cl_2Rh_2Sb$ (888.2) : calcd: C 50.03, H 5.11, Rh 23.17; found: C 50.07, H 5.08, Rh 23.21.

[$Rh_2Cl_2(\mu$-$CPh_2)\{\mu$-$CPh(p$-$Tol)\}(\mu$-$SbiPr_3)$] (8): Compound **8** was prepared as described for **7**, either by route a) using a mixture of **1** (76 mg, 0.09 mmol) and Ph(p-Tol)CN_2 (19 mg, 0.09 mmol) as starting materials, or by route b) using a 1:1 mixture of **4** (43 mg, 0.05 mmol) and **6** (44 mg, 0.05 mmol) as starting materials; red solid; yield 28 mg (73 %) by route a) and 83 mg (95 %) by route b); m.p. 196 °C (decomp); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.34$–7.22 (m, 8H; C_6H_5 and C_6H_4), 7.15–6.98 (m, 8H; C_6H_5 and C_6H_4), 6.75 (m, 3H; *para*-H of C_6H_5), 2.15 (s, 3H; $C_6H_4CH_3$), 1.24 (d, J(H,H) = 6.9 Hz, 18H; $SbCHCH_3$), 0.92 (sept, J(H,H) = 6.9 Hz, 3H; $SbCHCH_3$); ^{13}C NMR ($CDCl_3$, 50.3 MHz): $\delta = 187.5$, 186.5 (both t, J(Rh,C) = 26.4 Hz; RhCRh), 154.2, 152.4, 151.2, 146.1 (all s; *ipso*-C of C_6H_5 and C_6H_4), 131.2 (s; *para*-C of C_6H_4), 128.7, 128.5, 127.4, 127.2, 127.0, 126.9, 126.8, 126.2, 126.0, 124.7, 123.1 (all s; C_6H_5 and C_6H_4), 23.2 (s; $SbCHCH_3$), 21.9 (s; $SbCHCH_3$), 14.0 (s; $C_6H_4CH_3$); elemental analysis for $C_{36}H_{43}Cl_2Rh_2Sb$ (874.2) : calcd: C 49.46, H 4.96; found: C 49.33, H 4.62.

[$\{RhCl(CPh_2)(CO)\}_n$] (9): A slow stream of CO was passed through a solution of **4** (63 mg, 0.07 mmol) in benzene (10 mL) for 20 s at room temperature. The solution was stirred for 1 h, which led to the precipitation of a red solid. After 20 min, the mother liquid was decanted, the remaining solid was washed three times with pentane (5 mL each) and dried in vacuo; yield 49 mg (quantitative); m.p. 281 °C (decomp); IR (KBr): $\tilde{\nu} = 1857$ cm^{-1} (CO); elemental analysis for $C_{28}H_{20}Cl_2O_2Rh_2$ (665.2) : calcd: C 50.33, H 3.03; found: C 50.32, H 3.09.

[$Rh_2Cl_2(\mu$-$CPh_2)_2(\mu$-$CNtBu)$] (10): A solution of **4** (71 mg, 0.08 mmol) in benzene (10 mL) was treated with *tert*-butylisocyanide (9 mL, 0.08 mmol) and stirred for 1 h at room temperature. The solvent was removed in vacuo, the remaining orange-red solid was washed three times with acetone and pentane (5 mL each) and dried; yield 56 mg (98 %); m.p. 222 °C (decomp); MS (70 eV): m/z (I_r): 692 [M^+], 609 [$M^+ - CNtBu$], 526 [$M^+ - CPh_2$], 443 [$M^+ - CPh_2 - CNtBu$], 360 [$M^+ - 2\,CPh_2$], 332 [$C_2Ph_4^+$], 304 [$ClRhCPh_2^+$], 276 [$Rh_2Cl_2^+$], 249 [$Ph_2CCNtBu^+$]; IR (KBr): $\tilde{\nu} = 1890$ cm^{-1} (CN); ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 7.34$–6.76 (m, 20H; C_6H_5), 1.54 (s, 9H; CH_3); elemental analysis for $C_{31}H_{29}Cl_2NRh_2$ (692.3) : calcd: C 53.78, H 4.22, N 2.20, Rh 30.94; found: C 53.8, H 4.49, N 1.88, Rh 31.00.

Reaction of [$Rh_2Cl_2(\mu$-$CPh_2)_2(\mu$-$SbiPr_3)$] (4) with $PiPr_3$: A solution of **4** (41 mg, 0.05 mmol) in benzene (10 mL) was treated with $PiPr_3$ (41 µL, 0.20 mmol) and stirred for 30 min at room temperature. A change of color from red to green occured. The solvent was removed in vacuo and the green oily residue was dissolved in C_6D_6 (0.5 mL). The ^{1}H NMR spectrum confirmed that besides $SbiPr_3$ the mononuclear complex *trans*-[$RhCl(=CPh_2)(PiPr_3)_2$] (**11**) was formed[6]; yield virtually quantitative. The reactions of **4** with $PiPr_2Ph$, $PiPrPh_2$, PPh_3 and $PMePh_2$ were carried out analogously, using acetone (10 mL) as solvent. The green oily residue was purified by column chromatography on Al_2O_3 (neutral, activity grade V, height of column 3 cm) with pentane as eluens. The ^{1}H and ^{31}P NMR spectra of the products revealed that in all cases the complexes *trans*-[$RhCl(=CPh_2)(PR_3)_2$] (**12**–**15**) were obtained.[6b]

[$Rh_2Cl_2(\mu$-$CPh_2)_2(\mu$-$SbMe_3)$] (16): A solution of **4** (82 mg, 0.10 mmol) in benzene (10 mL) was treated with $SbMe_3$ (16 mL, 0.10 mmol) and stirred for 30 min at room temperature. The solvent was removed in vacuo, the red-brown residue was suspended in hexane (3 mL) and the suspension was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 3 cm). With hexane, an almost colorless fraction was eluted which contained free $SbiPr_3$ and was withdrawn. With benzene/CH_2Cl_2 (5:1), a deep red fraction was eluted which was evaporated to dryness in vacuo. The remaining red solid was washed three times with pentane (10 mL each) and dried; yield 66 mg (89 %); m.p. 242 °C (decomp); ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.67$ (m, 8H; *ortho*-H of C_6H_5), 7.11 (m, 8H; *meta*-H of C_6H_5), 6.68 (m, 4H; *para*-H of C_6H_5), 0.84 (s, 9H; $SbCH_3$); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 187.4$ (t, J(Rh,C) = 26.1 Hz; RhCRh), 154.1, 152.1 (both s; *ipso*-C of C_6H_5), 128.3, 127.8, 127.0, 126.7, 126.2, 125.2 (all s; C_6H_5), 13.8 (s; $SbCH_3$); elemental analysis for $C_{29}H_{29}Cl_2Rh_2Sb$ (776.0) : calcd: C 44.89, H 3.77; found: C 45.26, H 3.95.

[$Rh_2Cl_2(\mu$-$CPh_2)_2(\mu$-$SbEt_3)$] (17): Compound **17** was prepared as described for **16**, using **4** (73 mg, 0.08 mmol) and $SbEt_3$ (14 mL, 0.09 mmol) as starting materials; deep red solid; yield 57 mg (87 %); m.p. 152 °C (decomp); ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.64$ (m, 8H; *ortho*-H of C_6H_5), 7.11 (m, 8H; *meta*-H of C_6H_5), 6.65 (m, 4H; *para*-H of C_6H_5), 1.48 (q, J(H,H) = 7.8 Hz, 6H; $SbCH_2CH_3$), 0.95 (t, J(H,H) = 7.8 Hz, 9H; $SbCH_2CH_3$); ^{13}C NMR ($CDCl_3$, 100.6 MHz): $\delta = 183.0$ (t, J(Rh,C) = 25.7 Hz; RhCRh), 154.7, 152.7 (both s; *ipso*-C of C_6H_5), 128.3, 127.8, 127.2, 126.9, 126.5, 125.0 (all s; C_6H_5), 12.7 (s; $SbCH_2CH_3$), 10.7 (s; $SbCH_2CH_3$); elemental analysis for $C_{32}H_{35}Cl_2Rh_2Sb$ (818.1) : calcd: C 46.98, H 4.31; found: C 47.11, H 4.09.

[$(\eta^5$-$C_5H_5)_2Rh_2(\mu$-$CPh_2)_2$] (18): A solution of **4** (87 mg, 0.10 mmol) in THF (15 mL) was treated with NaC_5H_5 (44 mg, 0.50 mmol) and stirred for 1 h at room temperature. A rapid change of color from red to violet occurred. The solvent was removed in vacuo, the residue was extracted with pentane/benzene (1:1, 15 mL) and the extract was evaporated to dryness in vacuo. The remaining brown-violet solid was dissolved in pentane/diethyl ether (1:1, 5 mL) and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 4 cm). With pentane/diethyl ether (1:1) a violet fraction was eluted, which was brought to dryness in vacuo. The residue was recrystallized from pentane/diethyl ether (1:1) at −20 °C to give violet needles, which were washed with small amounts of pentane (−20 °C) and dried; yield 53 mg (80 %); m.p. 209 °C (decomp); MS (70 eV):

m/*z*: 668 $[M^+]$, 603 $[M^+ - C_5H_5]$, 538 $[M^+ - 2\,C_5H_5]$, 502 $[M^+ - CPh_2]$, 437 $[M^+ - CPh_2 - C_5H_5]$, 372 $[Rh_2CPh_2^+]$, 336 $[Rh_2(C_5H_5)_2^+]$, 334 $[C_5H_5RhCPh_2^+]$, 332 $[C_2Ph_4^+]$, 206 $[Rh_2^+]$, 168 $[RhC_5H_5^+]$; ^{1}H NMR (C_6D_6, 400 MHz): $\delta = 7.60$ (m, 8H; *ortho*-H of C_6H_5), 7.22 (m, 8H; *meta*-H of C_6H_5), 7.01 (m, 4H; *para*-H of C_6H_5), 4.30 (m, 10H; C_5H_5); ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta = 187.9$ (t, J(Rh,C) = 41.7 Hz; RhCRh), 161.7 (s; *ipso*-C of C_6H_5), 131.7, 126.7, 125.0 (all s; C_6H_5), 88.5 (vt, $N = {}^1J(\mathrm{Rh,C}) + {}^3J(\mathrm{Rh,C}) = 2.5$ Hz; C_5H_5); elemental analysis for $C_{36}H_{30}Rh_2$ (668.5) : calcd: C 64.69, H 4.52, Rh 30.79; found: C 64.73, H 4.69, Rh 30.85.

[(η^5-C_5H_5)$_2$Rh$_2${μ-C(*p*-Tol)$_2$}$_2$] (19): Compound **19** was prepared as described for **18**, using **5** (92 mg, 0.10 mmol) and NaC_5H_5 (44 mg, 0.50 mmol) as starting materials; violet solid; yield 56 mg (78%); m.p. 132 °C (decomp); MS (70 eV): *m*/*z*: 724 $[M^+]$, 659 $[M^+ - C_5H_5]$, 594 $[M^+ - 2\,C_5H_5]$, 530 $[M^+ - C(p\text{-Tol})_2]$, 465 $[M^+ - C(p\text{-Tol})_2 - C_5H_5]$, 400 $[Rh_2C(p\text{-Tol})_2^+]$, 336 $[Rh_2(C_5H_5)_2^+]$, 271 $[Rh_2C_5H_5^+]$, 206 $[Rh_2^+]$, 194 $[C_2(p\text{-Tol})_4^+]$; ^{1}H NMR (C_6D_6, 400 MHz): $\delta = 7.61$ (m, 8H; *ortho*-H of C_6H_4), 7.08 (m, 8H; *meta*-H of C_6H_4), 4.39 (m, 10H; C_5H_5), 2.28 (s, 12H; $C_6H_4CH_3$); ^{13}C NMR (C_6D_6, 100.6 MHz): $\delta = 187.8$ (t, J(Rh,C) = 42.8 Hz; RhCRh), 159.5 (s; *ipso*-C of C_6H_4), 134.1 (s; *para*-C of C_6H_4), 131.9, 127.3 (both s; *ortho*- and *meta*-C of C_6H_4), 88.4 (vt, $N = {}^1J(\mathrm{RhC}) + {}^3J(\mathrm{RhC}) = 2.5$ Hz; C_5H_5), 21.0 (s; $C_6H_4CH_3$); elemental analysis for $C_{40}H_{38}Rh_2$ (724.6) : calcd: C 66.31, H 5.29, Rh 28.40; found: C 65.95, H 5.04, Rh 28.44.

[(η^5-C_5H_5)$_2$Rh$_2${μ-CPh(*p*-Tol)}$_2$] (20): Compound **20** was prepared as described for **18**, using **6** (81 mg, 0.09 mmol) and NaC_5H_5 (40 mg, 0.45 mmol) as starting materials; violet solid; yield 50 mg (79%); m.p. 157 °C (decomp); MS (70 eV): *m*/*z*: 696 $[M^+]$, 631 $[M^+ - C_5H_5]$, 566 $[M^+ - 2\,C_5H_5]$, 516 $[M^+ - CPh(p\text{-Tol})]$, 451 $[M^+ - CPh(p\text{-Tol}) - C_5H_5]$, 336 $[Rh_2(C_5H_5)_2^+]$, 206 $[Rh_2^+]$, 180 $[CPh(p\text{-Tol})^+]$; ^{1}H NMR (C_6D_6, 200 MHz): $\delta = 7.69–7.51$ (m, 8H; *ortho*-H of C_6H_5 and C_6H_4), 7.29–6.95 (m, 10H; *meta*-H and *para*-H of C_6H_5 and C_6H_4), 4.33 (m, 10H; C_5H_5), 2.26, 2.09 (both s, 6H; $C_6H_4CH_3$); ^{13}C NMR (C_6D_6, 50.3 MHz): $\delta = 187.9$ (t, J(Rh,C) = 43.5 Hz; RhCRh), 161.9, 159.3 (both s; *ipso*-C of C_6H_5 and C_6H_4), 134.2 (s; *para*-C of C_6H_4), 131.8, 128.6, 128.3, 127.4, 126.6 (all s; C_6H_5 and C_6H_4), 88.4 (vt, $N = {}^1J(\mathrm{Rh,C}) + {}^3J(\mathrm{Rh,C}) = 2.6$ Hz; C_5H_5), 20.7, 20.4 (both s; $C_6H_4CH_3$); elemental analysis for $C_{38}H_{34}Rh_2$ (696.5) : calcd: C 65.53, H 4.92; found: C 65.71, H 5.01.

[(η^5-C_5H_5)$_2$Rh$_2$(μ-CPh$_2$)$_2$(μ-CN*t*Bu)] (21): A suspension of **10** (85 mg, 0.12 mmol) in THF (10 mL) was treated with NaC_5H_5 (53 mg, 0.60 mmol) and stirred for 3 h at room temperature. The solvent was removed, the residue was extracted with hexane/benzene (1:1, 35 mL) and the extract was evaporated to dryness in vacuo. The remaining oily solid was suspended in hexane (5 mL) and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 5 cm). With hexane, a violet fraction was eluted, which was withdrawn. Subsequent elution with benzene gave a dark violet fraction which was brought to dryness in vacuo. The residue was recrystallized from toluene/pentane (1:1, 3 mL) at −78 °C to give dark violet crystals, which were washed three times with pentane (3 mL each) and dried; yield 37 mg (40%); m.p. 137 °C (decomp); MS (70 eV): *m*/*z*: 751 $[M^+]$, 668 $[M^+ - CNtBu]$, 585 $[M^+ - CPh_2]$, 502 $[M^+ - CPh_2 - CNtBu]$, 233 $[Rh(C_5H_5)_2^+]$, 168 $[RhC_5H_5^+]$; IR (KBr): $\nu = 1882$ cm^{-1} (CN); ^{1}H NMR (C_6D_6, 400 MHz): $\delta = 7.25$ (m, 8H; *ortho*-H of C_6H_5), 6.92 (m, 4H; *para*-H of C_6H_5), 6.84 (m, 8H; *meta*-H of C_6H_5), 5.04 (m, 10H; C_5H_5), 1.14 (s, 9H; CH_3); ^{13}C NMR (C_6D_6, 100.6 MHz): d = 164.2, 157.4 (both s; *ipso*-C of C_6H_5), 146.2 (t, J(Rh,C) = 41.3 Hz; Rh*C*(N*t*Bu)Rh), 145.5 (t, J(Rh,C) = 24.8 Hz; Rh*C*Ph$_2$Rh), 131.6, 129.0, 126.6, 126.4, 124.3, 123.8 (all s; C_6H_5), 97.9 (br s; C_5H_5), 58.2 (s; *C*CH$_3$), 30.4 (s; CH_3); elemental analysis for $C_{41}H_{39}NRh_2$ (751.6) : calcd: C 65.52, H 5.23, N 1.86; found: C 65.29, H 4.97, N 1.80.

X-ray structure determination of compounds 4 and 18: Single crystals of **4** were grown from a saturated solution in tetrahydrofuran/2-propanol (room temperature), and those of **18** from a saturated solution in tetrahydrofuran/methanol (room temperature). Crystal data collection parameters are summarized in Table 1. Intensity data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied (ϕ-scans). The structures were solved by Direct methods (SHELXS-86 and 97).[21] Atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by the full-matrix least-squares method (program packet SDP (Enraf-Nonius) and SHELXL-97).[22] The positions of all hydrogen atoms were calculated according to ideal geometry (distance C–H 0.95 Å) and used only in structure factor calculation.[23]

Table 1. Crystal structure data of compounds **4** and **18**.

	4	**18**
formula	$C_{35}H_{41}Cl_2Rh_2Sb$	$C_{36}H_{30}Rh_2$
mol. mass	860.18	668.45
crystal size [mm]	0.3 × 0.2 × 0.2	0.13 × 0.18 × 0.30
crystal system	orthorhombic	monoclinic
space group	*Pnma* (no. 62)	$P2_1/n$ (no. 14)
a [Å]	17.730(7)	11.143(9)
b [Å]	13.008(1)	31.86(1)
c [Å]	14.919(1)	15.96(2)
α [°]	90.0	90.0
β [°]	90.0	98.79(4)
γ [°]	90.0	90.0
V [Å^3]	3441.0(7)	5600
Z	4	8
ρ_{calcd} [g cm^{-1}]	1.660	1.78
diffractometer	Enraf-Nonius CAD 4	Enraf-Nonius CAD 4
radiation (graphite-monochromated)	$Mo_{K\alpha}$ (0.71073 Å)	$Mo_{K\alpha}$ (0.71073 Å)
T [K]	293(2)	293(2)
μ [mm^{-1}]	1.90	0.95
transmission min. [%]	95.37	89.0
scan method	ω/θ	ω/θ
2θ (max) [°]	54	47.98
total reflections	4264	8752
unique reflections	4028	8751
observed reflections	2777 $[I > 2\sigma(I)]$	4004 $[I > 2\sigma(I)]$
parameters refined	211	685
R_1	0.027	0.0587
wR_2	0.033	0.1140
reflection/parameter ratio	13.16	13.3
residual electron density [e Å^{-3}]	+0.738/−0.554	+0.665/−0.804

[1] a) L. H. Gade, *Koordinationschemie*, WILEY-VCH, Weinheim, **1998**; b) R. Demuth, F. Kober, *Grundlagen der Komplexchemie*, 2th ed., Salle und Sauerländer, Frankfurt-Aarau, **1992**; c) C. Elschenbroich, A. Salzer, *Organometallics*, VCH, Weinheim, **1992**; d) J. P. Collman, L. S. Hegedus, J. R. Norton, R. G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, **1987**; e) A. Yamamoto, *Organotransition Metal Chemistry*, Wiley, New York, **1986**.

[2] a) A. F. Holleman, E. Wiberg, *Lehrbuch der Anorganischen Chemie*, 101th ed., de Gruyter, Berlin, New York, **1995**, Chap. XIV; b) F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, *Advanced Inorganic Chemistry*, 6th ed., Wiley, New York, **1999**, Chap. 16.4; c) E. Riedel, *Moderne Anorganische Chemie*, de Gruyter, Berlin, New York, **1999**, Chap. 4.3.

[3] a) G. Booth, in *Organic Phosphorus Compounds*, *Vol. 1* (Eds.: G. M. Kosolapoff, L. Maier), Wiley, New York, **1972**, Chap. 3A; b) W. Levason, C. A. McAuliffe, *Phosphine*, *Arsine and Stibine Complexes of the Transition Elements*, Elsevier, Amsterdam, **1979**; c) C. A. McAuliffe, in *Comprehensive Coordination Chemistry*, *Vol. 2* (Eds.: G. Wilkinson, R. D. Gillard, J. A. McCleverty), Pergamon, Oxford, **1987**, pp. 989–1066.

[4] a) O. Stelzer, *Topics Phosphorus Chemistry* **1977**, *9*, 1–229; b) W. Levason, C. A. McAuliffe, *Acc. Chem. Res.* **1978**, *11*, 363–368; c) N. R. Champness, W. Levason, *Coord. Chem. Rev.* **1994**, *133*, 115–217.

[5] There is one Pd_3 complex known in which PF_3 occupies a nearly symmetrical triply bridging position: A. L. Balch, B. J. Davis, M. M. Olmstead, *Inorg. Chem.* **1993**, *32*, 3937–3942.

[6] a) P. Schwab, N. Mahr, J. Wolf, H. Werner, *Angew. Chem.* **1993**, *105*, 1498–1500; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1480–1482; b) H.

Werner, P. Schwab, E. Bleuel, N. Mahr, P. Steinert, J. Wolf, *Chem. Eur. J.* **1997**, *3*, 1375 – 1384.

[7] a) P. Schwab, N. Mahr, J. Wolf, H. Werner, *Angew. Chem.* **1994**, *106*, 82 – 84; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 97 – 99; b) H. Werner, *J. Organomet. Chem.* **1995**, *500*, 331 – 336.

[8] T. Yamamoto, A. R. Garber, J. R. Wilkinson, C. B. Boss, W. E. Streib, L. J. Todd, *J. Chem. Soc.*, *Chem. Commun.* **1974**, 354 – 356.

[9] H. Ueda, Y. Kai, N. Yasuoka, N. Kasai, *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2250 – 2254.

[10] G. E. Ball, W. R. Cullen, M. D. Fryzuk, B. R. James, S. J. Rettig, *Organometallics* **1991**, *10*, 3767 – 3769.

[11] P. Hong, N. Nishii, K. Sonogashira, N. Hagihara, *J. Chem. Soc. Chem. Commun.* **1972**, 993.

[12] W. P. Anderson, W. D. Edwards, M. C. Zerner, *Inorg. Chem.* **1986**, *25*, 2728 – 2732.

[13] A. Muth (Universität Heidelberg), personal communication.

[14] P. H. M. Budzelaar, P. W. N. M. van Leeuwen, C. F. Roobeek, A. G. Orpen, *Organometallics* **1992**, *11*, 23 – 25.

[15] Since both the bond lengths and bond angles of the unsymmetrical and the symmetrical dimer are almost the same, only those of the unsymmetrical dimer will be discussed here.

[16] M. Green, D. R. Hankey, J. A. K. Howard, P. Louca, F. G. A. Stone, *J. Chem. Soc. Chem. Commun.* **1983**, 757 – 758.

[17] W. A. Herrmann, C. Bauer, J. Plank, W. Kalcher, D. Speth, M. L. Ziegler, *Angew. Chem.* **1981**, *93*, 212 – 214; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 193 – 195.

[18] a) U. Weber, L. Zsolnai, G. Huttner, *J. Organomet. Chem.* **1984**, *260*, 281 – 291; b) G. Huttner, U. Weber, B. Sigwarth, O. Scheidsteger, H. Lang, L. Zsolnai, *J. Organomet. Chem.* **1985**, *282*, 331 – 348; c) A. R. Barron, A. H. Cowley, R. A. Jones, C. M. Nunn, D. L. Westmoreland, *Polyhedron* **1988**, *7*, 77 – 78; d) A. L. Balch, V. J. Catalano, M. A. Chatfield, J. K. Nagle, M. M. Olmstead, P. E. Reedy, Jr., *J. Am. Chem. Soc.* **1991**, *113*, 1252 – 1258.

[19] a) P. Schwab, Dissertation, Universität Würzburg, **1994**; b) H. Werner, P. Schwab, E. Bleuel, N. Mahr, B. Windmüller, J. Wolf, *Chem. Eur. J.* **2000**, *6*, 4461 – 4470.

[20] Reviews: a) P. M. Maitlis, *J. Organomet. Chem.* **1995**, *500*, 239 – 249; b) P. M. Maitlis, H. C. Long, R. Quyoum, M. L. Turner, Z.-Q. Wang, *Chem. Commun.* **1996**, 1 – 8.

[21] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467 – 473.

[22] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, **1997**.

[23] Further details on the crystal structure investigation for **4** may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-57659. Crystallographic data (excluding structure factors) for structure **18** reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-147209. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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