The First Triisopropylstibane Ruthenium(II) and Ruthenium(0) Complexes Including the X-ray Crystal Structure of $[Ru(\eta^3\text{-}C_3H_5)_2(Sb\mathit{i}Pr_3)_2]$☆

Helmut Werner*, **Claus Grünwald**, **Matthias Laubender**, and **Olaf Gevert**

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

Received May 23, 1996

Key Words: Ruthenium complexes / Stibane complexes / Dihydrogen complexes / Butadiene complex / π-Allyl complex

The hydridoruthenium(II) complexes $[RuHCl(H_2)(Sb\mathit{i}Pr_3)_3]$ (**2**) and $[RuH_2(H_2)(Sb\mathit{i}Pr_3)_3]$ (**3**), containing dihydrogen as ligand, were prepared from $[RuCl_2(C_8H_{12})]_n$ (**1**) as the starting material. Compound **3** reacts with CO by displacement of H_2 to yield $[RuH_2(CO)(Sb\mathit{i}Pr_3)_3]$ (**4**) and with C_2H_4 to give both $[RuH_2(C_2H_4)_2(Sb\mathit{i}Pr_3)_2]$ (**5**) and $[RuH_2(C_2H_4)(Sb\mathit{i}Pr_3)_3]$ (**6**), the latter as the more stable and isolable product. Treatment of **3** with propene leads to the formation of $[Ru(\eta^3\text{-}C_3H_5)_2(Sb\mathit{i}Pr_3)_2]$ (**7**) while the reaction of **3** with butadiene affords the pentacoordinated ruthenium(0) compound $[Ru(\eta^4\text{-}C_4H_6)_2(Sb\mathit{i}Pr_3)]$ (**8**). The molecular structure of the bis(allyl) complex **7** was determined by X-ray crystallography.

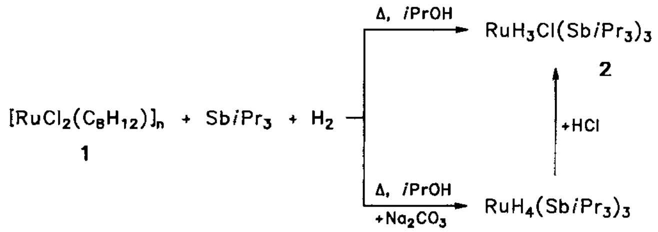
We recently showed that the replacement of triisopropylphosphane by triisopropyl*stibane* as ligand in low-valent rhodium and iridium complexes leads to significant differences in the reactivity of these compounds[1,2]. A striking example is that in contrast to *trans*-$[RhCl(C_2H_4)(P\mathit{i}Pr_3)_2]$ which is not an appropriate starting material for the preparation of carbene–metal derivatives *trans*-$[RhCl({=}CRR')(P\mathit{i}Pr_3)_2]$[3], the corresponding bis(stibane) compound *trans*-$[RhCl(C_2H_4)(Sb\mathit{i}Pr_3)_2]$ reacts quite smoothly with Ph_2CN_2 and other diazoalkanes to give the carbene complexes *trans*-$[RhCl({=}CRR')(Sb\mathit{i}Pr_3)_2]$ almost quantitatively[1a,4]. As far as iridium as the metal center is concerned, an interesting facet is that the reaction of $[IrCl(C_2H_4)_2]_2$ with $P\mathit{i}Pr_3$ yields *trans*-$[IrCl(C_2H_4)(P\mathit{i}Pr_3)_2]$[5] while on treatment of the same dimeric precursor with $Sb\mathit{i}Pr_3$ the pentacoordinated product $[IrCl(C_2H_4)_2(Sb\mathit{i}Pr_3)_2]$ is obtained[2].

These widely unexpected results initiated our attempts to develope also synthetic pathways to ruthenium complexes, either coordinatively saturated or unsaturated, with bulky stibane ligands. In this paper we describe the preparation and characterization of some new mono-, bis-, and tris(triisopropylstibane)ruthenium(II) and -ruthenium(0) derivatives.

"Nonclassical" Tris- and Tetrahydrido Ruthenium(II) Complexes

The polymeric cycloocta-1,5-diene compound $[RuCl_2(C_8H_{12})]_n$ (**1**)[6], which on treatment with triisopropylphosphane in 2-butanol in the presence of H_2 yields the hexacoordinated ruthenium(IV) complex $[RuH_2Cl_2(P\mathit{i}Pr_3)_2]$[7], reacts with $Sb\mathit{i}Pr_3$ under dihydrogen in 2-propanol to give $[RuH_3Cl(Sb\mathit{i}Pr_3)_3]$ (**2**) in low yield. In contrast, the same reaction in the presence of Na_2CO_3 leads nearly quantitatively to the tetrahydrido complex $[RuH_4(Sb\mathit{i}Pr_3)_3]$ (**3**) (Scheme 1). Compound **2** can be obtained in ca. 80% yield by the reaction of a solution of **3** in 2-propanol with aqueous HCl. Both complexes **2** and **3** are yellow, moderately air-stable solids which readily dissolve in hydrocarbon solvents such as benzene and pentane. The ^{1}H-NMR spectra of **2** and **3** at room temperature display only one set of signals for the isopropyl protons and only one resonance for the hydrides at $\delta = -13.74$ (**2**) and -10.66 (**3**), indicating that these molecules are highly fluctional in solution. The NMR data are in good agreement with those of the bis- and tris(phosphane) derivatives $[RuH_3Cl(PR_3)_2]$[8] and $[RuH_4(PR_3)_3]$[9] (R = Cy, *i*Pr) of which the latter are not stable in solution and dissociate to give the corresponding bis(phosphane)ruthenium species.

Scheme 1



Since it had been shown by Chaudret[8] and Crabtree[10] that the tris- as well as the tetrahydrido compounds $[RuH_3Cl(PR_3)_2]$ and $[RuH_4(PR_3)_3]$ are "nonclassical" hydrides and thus should be better formulated as $[RuHCl(H_2)(PR_3)_2]$ and $[RuH_2(H_2)(PR_3)_3]$, respectively, we attempted to find out what the correct structure of **2** and **3** is. The most widely used criterion for differentiating between "classical" and "nonclassical" structures of metal hydrides is the T_1 method which measures the longitudinal relaxation time T_1 of the hydride resonance in the ^{1}H-NMR spectrum at various temperatures[11]. The general rule is that if at 250-MHz the T_1 value at the minimum is smaller

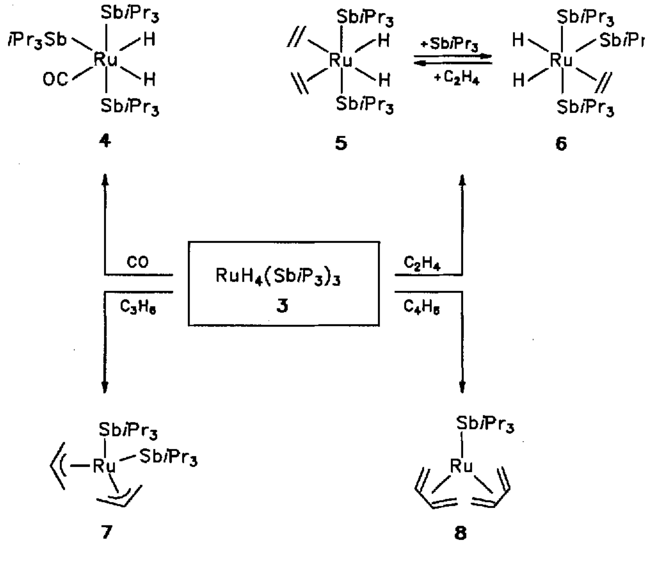
0009–2940/96/1010–1191 $ 15.00+.25/0

than 80 ms, the polyhydrido compound has a "nonclassical" structure (i.e. it contains a side-on bonded H_2 ligand), and if T_1 (min) is larger than 150 ms, a "classical" structure with covalently bonded hydrido ligands can be assumed. For complex **2** we found in $[D_8]$toluene the value T_1 (min) = 63 ms at −41 °C and 400 MHz (corresponding to 39 ms at 250 MHz), from which we consider that in analogy to the phosphane derivatives $[RuHCl(H_2)(PCy_3)_2]$[8] and $[RuHCl(H_2)(CO)(P\mathit{i}Pr_3)_2]$[12] the correct formulation is $[RuHCl(H_2)(Sb\mathit{i}Pr_3)_3]$. In the case of the RuH_4 compound **3**, it was (in $[D_8]$toluene at 400 MHz) not possible to accurately measure the intrinsic minimum T_1 of the system. Since we determined, however, at −71 °C a T_1 value of 84 ms (corresponding to 52 ms at 250 MHz), we assume that **3** like the analogous complex $[RuH_2(H_2)(PPh_3)_3]$[11] possesses the "nonclassical" structure $[RuH_2(H_2)(Sb\mathit{i}Pr_3)_3]$. In contrast to $[RuH_2(H_2)(P\mathit{i}Pr_3)_3]$[8c], the tris(stibane) compound **3** is stable in solution which we explain by a decrease in steric hindrance along the series $[MX_m(PR_3)_n] > [MX_m(AsR_3)_n] > [MX_m(SbR_3)_n]$[13].

Ligand Displacement Reactions of Compound 3

The extensive chemistry, which has been developed with the tris(triphenylphosphane)ruthenium(II) complex $[RuH_2(H_2)(PPh_3)_3]$ as starting material[14], prompted us to investigate also the reactivity of the new polyhydrido compound **3** toward various substrates. In agreement with the assumption that the dihydrogen ligand is only weakly bound, **3** reacts quite smoothly with CO to give the carbonyl complex $[RuH_2(CO)(Sb\mathit{i}Pr_3)_3]$ (**4**) in about 75% yield. While the ^1H-NMR spectrum of **4** in $[D_8]$toluene at room temperature displays rather broad signals, indicating a fluctional behavior under these conditions, upon cooling to −40 °C sharp resonances for the isopropyl as well as for the hydrido protons are observed. The appearance of two signals in the high-field region at $\delta = -10.62$ and -12.71 supports the structural proposal in Scheme 2 with a *mer* arrangement of the stibane ligands and *cis-disposed* hydrides in the octahedral coordination sphere.

Scheme 2

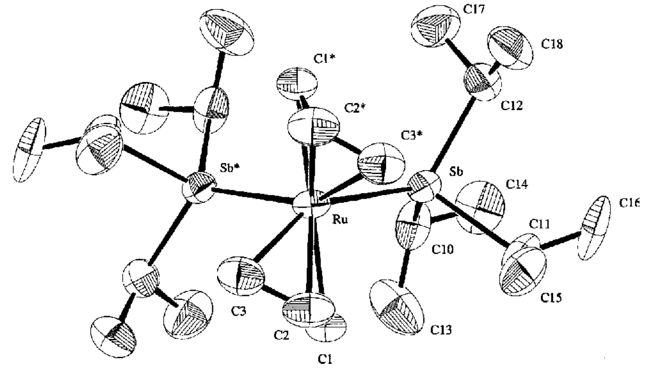


The reaction of **3** with C_2H_4 in benzene under an ethene pressure of 1.0−1.5 bar leads to two products $[RuH_2(C_2H_4)_2(Sb\mathit{i}Pr_3)_2]$ (**5**) and $[RuH_2(C_2H_4)(Sb\mathit{i}Pr_3)_3]$ (**6**) of which the first could only be characterized by ^1H-NMR spectroscopy. If the ethene atmosphere is replaced by argon and the solvent removed in vacuo, complex **6** is isolated as the sole product. The conclusion is that in solution, in the presence of an excess of C_2H_4, an equilibrium between **5** and **6** exists which, after removal of excess ethene, is completely shifted to the side of the monoolefin derivative. The ^1H-NMR spectrum of **6**, in analogy to that of **4**, shows two hydride signals at $\delta = -12.02$ and -17.72 and thus a similar structure for both the carbonyl- and the etheneruthenium(II) compounds can be assumed.

Treatment of **3** with propene does not afford an olefin complex but instead gives the bis(allyl) compound $[Ru(\eta^3\text{-}C_3H_5)_2(Sb\mathit{i}Pr_3)_2]$ (**7**) in excellent yield. According to the ^1H- and ^{13}C-NMR data there is no doubt that the two allyl ligands of **7** are symmetrically π-bonded as found in the bis(phosphane) derivative $[Ru(\eta^3\text{-}C_3H_5)_2(PPh_3)_2]$[14c,15].

The result of the X-ray crystal structural analysis of **7** is shown in Figure 1. The ORTEP plot reveals that the geometry around the metal center is distorted tetrahedral with the antimony and the central carbon atoms (C2, C2*) of the C_3 units at the corners of the polyhedron. The ruthenium atom lies on a crystallographic center of symmetry and, therefore, only eight halves of the molecule are found in the unit cell. The angles Sb−Ru−Sb* and C2−Ru−C2* are 101.6(2)° and 103.5(4)°, respectively. The bond length Ru−C2 [2.131(6) Å] is significantly shorter than the Ru−C distances [2.231(7) and 2.215(8) Å] to the terminal carbon atoms of the allyl groups. As mentioned above, a similar bonding mode exists in the triphenylphosphane complex $[Ru(\eta^3\text{-}C_3H_5)_2(PPh_3)_2]$[15]. The Ru−Sb bond length in **7** [2.610(4) Å] is similar to the Ru−Sb distances in the carbonyl compound $[RuCl_2(CO)(Sb\mathit{i}Pr_3)_3]$ (average value 2.633 Å)[16] as well as in the triphenylstibane derivative *trans*-$[RuCl_2(SbPh_3)_4]$ (average value 2.629 Å)[17].

Figure 1. Molecular structure (ORTEP plot) of 7



Selected bond lengths [Å] and angles [°]: Ru−Sb 2.610(4), Ru−C1 2.231(7), Ru−C2 2.131(6), Ru−C3 2.215(8), C1−C2 1.40(1), C2−C3 1.40(1); Ru−Sb−C10 118.5(2), Ru−Sb−C11 113.9(3), Ru−Sb−C12 125.2(2), C1−Ru−C2 37.3(3), C1−Ru−C3 65.7(3), C2−Ru−C3 37.3(3), Ru−C1−C2 67.4(3), Ru−C2−C1 75.2(4), Ru−C2−C3 74.7(4), Ru−C3−C2 68.1(4), C1−C2−C3 119.5(8), C2−Ru−C2* 103.5(4), Sb−Ru−Sb* 101.6(2).

In contrast to the reaction of **3** with propene which leads to **7**, i.e., to a ruthenium(II) compound, treatment of **3** with butadiene yields the ruthenium(0) complex [Ru(η^4-C_4H_6)$_2$(Sb*i*Pr$_3$)] (**8**). The starting material therefore behaves analogous to the triphenylphosphane derivative [$RuH_2(H_2)(PPh_3)_3$] which with butadiene reacts stepwise to give first [Ru(η^4-C_4H_6)(PPh_3)$_3$] and then [Ru(η^4-C_4H_6)$_2$(PPh_3)][14b,c]. The ^{1}H-NMR spectrum of **8** displays for the butadiene protons three distinct signals at δ = 4.10, 1.67, and 0.03 which are of equal intensity and correspond to an AA'BB'CC' pattern. In the ^{13}C-NMR spectrum of **8** two resonances at δ = 72.7 and 28.1 for the "inner" and the "outer" carbon atoms of the two C_4H_6 ligands are observed, the position of which is similar to those of other η^4-butadiene ruthenium(0) complexes[18].

In conclusion, the results summarized in Scheme 2 illustrate that the reactions of the tris(triisopropylstibane) derivative **3** with ethene, propene, and butadiene lead to different types of products. We assume that also during the generation of **7** and **8**, dihydridoruthenium(II) species are formed as intermediates. However, these are probably very labile and on treatment with an excess of propene or butadiene, by further hydrogenation and dehydrogenation steps, afford the final products. We are presently attempting to prepare dihydridoruthenium(II) complexes with chelating stibane ligands which if used as catalysts for hydrogenation or hydroformylation reactions could be more reactive than the corresponding phosphane species.

This work was supported by the Deutsche Forschungsgemeinschaft (SFB 347) and the *Fonds der Chemischen Industrie*. We are also grateful to Mrs. *R. Schedl* and to Mr. *C. P. Kneis* for performing the elemental analyses and DTA measurements, to Dr. *W. Buchner* for determining the T_1 values, and to the *Degussa AG* for generous gifts of chemicals.

Experimental

All operations were carried out under argon with the Schlenk-tube technique. The starting materials **1**[6] and Sb*i*Pr$_3$[19] were prepared as described in the literature. – IR: Perkin-Elmer 1420. – NMR: Bruker AC 200 and AMX 400.

1. *Preparation of [RuHCl(H_2)(SbiPr$_3$)$_3$]* (**2**): A suspension of 363 mg (1.29 mmol for n = 1) of **1** in 60 ml of 2-propanol was treated with 1.10 ml (5.31 mmol) of Sb*i*Pr$_3$ and an excess (ca. 4 g) of Na_2CO_3 and stirred under hydrogen (1.0–1.5 bar) for 4 h at 80°C. Upon cooling to room temp., the solution was filtered through Celite and 26 ml of a 0.1 N aqueous solution of HCl was added to the filtrate. A rapid evolution of gas took place, and after this was finished, the solution was concentrated to ca. 20 ml in vacuo. A yellow microcrystalline solid precipitated which was filtered off, washed with 10 ml of methanol (0°C) and dried; yield 892 mg (78%), m.p. 52°C (dec.). – ^{1}H NMR (C_6D_6, 25°C, 400 MHz): δ = 2.16 [sept, *J*(HH) = 7.4 Hz, 9H, C*H*CH$_3$], 1.42 [d, *J*(HH) = 7.4 Hz, 54H, CHC*H*$_3$], –13.74 (s, 3H, RuH). – ^{13}C NMR (C_6D_6, 25°C, 100.6 MHz): δ = 21.9 (s, CH*C*H$_3$), 19.9 (s, *C*HCH$_3$). – $C_{27}H_{66}ClRuSb_3$ (892.6): calcd. C 36.33, H 7.45, Sb 40.92; found C 36.02, H 7.42, Sb 41.80.

2. *Preparation of [RuH$_2$(H_2)(SbiPr$_3$)$_3$]* (**3**): A suspension of 421 mg (1.50 mmol for n = 1) of **1** in 60 ml of 2-propanol was treated with 1.25 ml (6.23 mmol) of Sb*i*Pr$_3$ and an excess (ca. 4 g) of Na_2CO_3 and stirred under hydrogen (1.0–1.5 bar) for 4 h at 80°C. Upon cooling to room temp., the solvent was removed, and the residue was extracted 4 times with 20-ml portions of pentane. The combined extracts were concentrated in vacuo, and the brown oily residue was crystallized by stirring with 10 ml of methanol. The yellow solid was filtered off, washed with 5 ml of methanol (–78°C) and dried; yield 1.12 g (87%), m.p. 147°C (dec.). – ^{1}H NMR (C_6D_6, 25°C, 200 MHz): δ = 1.81 [sept, *J*(HH) = 7.3 Hz, 9H, C*H*CH$_3$], 1.31 [d, *J*(HH) = 7.3 Hz, 54H, CHC*H*$_3$], –10.66 (s, 4H, RuH). – ^{13}C NMR (C_6D_6, 25°C, 50.3 MHz): δ = 21.3 (s, CH*C*H$_3$), 19.0 (s, *C*HCH$_3$). – $C_{27}H_{67}RuSb_3$ (858.1): calcd. C 37.79, H 7.87; found C 37.65, H 7.76.

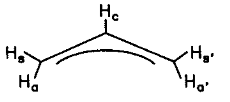
3. *Preparation of [RuH$_2$(CO)(SbiPr$_3$)$_3$]* (**4**): A slow stream of CO was passed through a solution of 164 mg (0.19 mmol) of **3** in 10 ml of benzene at room temp. Upon heating at 80°C for 45 min and then cooling to 25°C, the solvent was removed in vacuo, and the residue was recrystallized from 3 ml of methanol to give white crystals; yield 123 mg (73%), m.p. 86°C (dec.). – IR (C_6H_6): $\tilde{\nu}$ = 1900 cm^{-1} [ν(CO)]. – ^{1}H NMR ($C_6D_5CD_3$, –40°C, 400 MHz): δ = 1.86 [sept, *J*(HH) = 7.1 Hz, 6H, C*H*CH$_3$], 1.73 [sept, *J*(HH) = 7.2 Hz, 3H, C*H*CH$_3$], 1.32, 1.31 [both d, *J*(HH) = 7.1 Hz, 36H, CHC*H*$_3$], 1.27 [d, *J*(HH) = 7.2 Hz, 18H, CHC*H*$_3$], –10.62, –12.71 [both d, *J*(HH) = 7.0 Hz, 2H, RuH]. – ^{13}C NMR (C_6D_6, 25°C, 100.6 MHz): δ = 209.0 (s, CO), 21.6, 21.4, 21.2 (all s, CH*C*H$_3$), 20.5, 20.0 (both s, *C*HCH$_3$). – $C_{28}H_{65}ORuSb_3$ (884.1): calcd. C 38.04, H 7.41; found C 37.84, H 7.39.

4. *Reaction of* **3** *with Ethene:* In an NMR tube, a slow stream of ethene was passed for 1 min through a solution of 20 mg (0.02 mmol) of **3** in 0.5 ml of C_6D_6 at room temp. Upon heating at 70°C for 15 min and then cooling to 25°C, the ^{1}H-NMR spectrum of the solution confirmed the formation of **5**. – ^{1}H NMR (C_6D_6, 25°C, 200 MHz): δ = 2.12 [sept, *J*(HH) = 6.9 Hz, 6H, C*H*CH$_3$], 1.72 (s, 8H, C_2H_4), 1.28 [d, *J*(HH) = 6.9 Hz, 36H, CHC*H*$_3$], –13.33 (s, 2H, RuH).

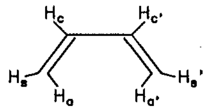
5. *Preparation of [RuH$_2$(C_2H_4)(SbiPr$_3$)$_3$]* (**5**): A slow stream of ethene was passed for 1 min through a solution of 249 mg (0.29 mmol) of **3** in 10 ml of benzene at room temp. Upon heating at 70°C for 15 min and then cooling to 25°C the solvent was removed in vacuo, and the residue was recrystallized from 3 ml of methanol to give yellow crystals; yield 187 mg (73%), m.p. 123°C (dec.). – ^{1}H NMR (C_6D_6, 25°C, 400 MHz): δ = 2.61 (s, 4H, C_2H_4), 2.09 [sept, *J*(HH) = 7.2 Hz, 6H, C*H*CH$_3$], 1.81 [sept, 3H, *J*(HH) = 7.4 Hz, C*H*CH$_3$], 1.36, 1.35 [both d, *J*(HH) = 7.2 Hz, 36H, CHC*H*$_3$], 1.31 [d, *J*(HH) = 7.4 Hz, 18H, CHC*H*$_3$], –12.02, –17.72 [both d, *J*(HH) = 8.0 Hz, 2H, RuH]. – ^{13}C NMR (C_6D_6, 25°C, 100.6 MHz): δ = 22.0, 21.6, 21.5 (all s, CH*C*H$_3$), 20.9, 20.8 (both s, *C*HCH$_3$), 19.68 (s, C_2H_4). – $C_{29}H_{69}RuSb_3$ (884.2): calcd. C 39.39, H 7.87; found C 39.03, H 7.83.

6. *Preparation of [Ru(η^3-C_3H_5)$_2$(SbiPr$_3$)$_2$]* (**7**): A suspension of 411 mg (1.47 mmol for n = 1) of **1** in 60 ml of 2-propanol was treated with 1.20 ml (5.75 mmol) of Sb*i*Pr$_3$ and an excess (ca. 4 g) of Na_2CO_3 and stirred under hydrogen (1.0–1.5 bar) for 4 h at 80°C. Upon cooling to room temp., the solvent was removed, and the residue was extracted with three 20-ml portions of hexane. The combined extracts were concentrated to ca. 30 ml in vacuo, and then a slow stream of propene was passed through the solution for 2 min. The reaction mixture was heated at 70°C for 15 min, and upon cooling to room temp. it was concentrated in vacuo. The oily residue was stirred with 10 ml of methanol to give a yellow crystalline solid; yield 795 mg (80%), m.p. 56°C (dec.). – ^{1}H NMR (C_6D_6, 25°C, 400 MHz): δ = 3.88 (m, 2H, H_c), 2.82 [dd, *J*($H_{s'}$,$H_{a'}$) = 2.4, *J*($H_{s'}$,H_c) = 6.0 Hz, 2H, $H_{s'}$], 1.99 [sept, *J*(HH) =

7.5 Hz, 6H, C*H*CH$_3$], 1.89 [d, J(H$_s$,H$_c$) = 9.6 Hz, 2H, H$_s$], 1.58 [d, J(H$_a$,H$_c$) = 9.0 Hz, 2H, H$_a$], 1.37 (m, 2H, H$_{a'}$), 1.27, 1.23 [both d, J(HH) = 7.5 Hz, 36H, CHC*H*$_3$]. – ^{13}C NMR (C$_6$D$_6$, 25°C, 100.6 MHz): δ = 73.0 [s, *C*H(CH$_2$)$_2$], 25.7, 25.4 [both s, CH(*C*H$_2$)$_2$], 22.3, 21.9 (both s, CH*C*H$_3$), 20.3 (s, *C*HCH$_3$). – $C_{24}H_{52}RuSb_2$ (685.2): calcd. C 42.07, H 7.65; found C 41.73, H 7.35.



7. *Preparation of [Ru(η^4-C$_4$H$_6$)$_2$(SbiPr$_3$)]* (**8**): A slow stream of butadiene was passed through a solution of 163 mg (0.19 mmol) of **3** in 10 ml of benzene at room temp. Upon heating at 70°C for 45 min, the reaction mixture was worked up as described for **5**. White crystals; yield 64 mg (74%), m.p. 70°C (dec.). – ^{1}H NMR (C$_6$D$_6$, 400 MHz): 4.10 (m, 4H, H$_{c,c'}$), 2.12 [sept, J(HH) = 7.4 Hz, 3H, C*H*CH$_3$], 1.67 (m, 4H, H$_{s,s'}$), 1.28 [d, J(HH) = 7.4 Hz, 18H, CHC*H*$_3$], 0.03 (m, 4H, H$_{a,a'}$). – ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ = 72.7 (s, *C*H=CH$_2$), 28.1 (s, CH=*C*H$_2$), 21.8 (s, CH*C*H$_3$), 19.2 (s, *C*HCH$_3$). – $C_{17}H_{33}RuSb$ (460.3): calcd. C 44.36, H 7.23; found C 44.27, H 7.16.



8. *Determination of the X-ray Crystal Structure of* **7**[20]: Single crystals were grown at −10°C from hexane. Crystal data (from 25 reflections, $6° < \Theta < 25°$): monoclinic, space group *C*2/*c* (No. 15); a = 21.05(3), b = 8.90(3), c = 15.46(3) Å, β = 102.98(3)°, V = 2822(12) Å^3, Z = 4 (8/2), d_{calcd} = 1.613 g cm^{-3}, μ(Mo-$K\alpha$) = 2.44 mm^{-1}; crystal size 0.30 × 0.25 × 0.10 mm; Enraf-Nonius CAD4 diffractometer, Mo-$K\alpha$ radiation (0.70930 Å), graphite monochromator, zirconium filter (factor 15.4); T = 293(2) K; ω/Θ scan, max 2Θ = 54°; 4091 reflections measured, 1985 independent reflections, 1567 reflections with $I > 2\sigma(I)$, 1984 independent reflections included in data set. Intensity data were corrected for Lorentz and polarization effects, a linear decay correction (loss of intensity 3.6%) and an empirical absorption correction (Ψ-scan method) were applied (minimum transmission 80%). The structure was solved by the Patterson method (SHELXS-86). Atomic coordinates and the anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares on F^2 {149 parameters, weighting scheme applied in the last cycle: $w = 1/[\sigma^2(F_o^2) + (0.0772 \cdot P)^2 + 16.7651 \cdot P]$ where $P = (F_o^2 + 2F_c^2)/3$, SHELXL-93}. The positions of all hydrogen atoms were calculated according to ideal geometry and were refined by using the riding method. Conventional R = 0.030 [for 1567 reflections with $I > 2\sigma(I)$] and weighted $wR2$ = 0.1014 for all 1984 data reflections; reflection-to-parameter ratio 13.32; residual electron density +0.655/−0.575 eÅ^{-3}.

☆ Dedicated to Professor *Markus Wieber* on the occasion of his 60th birthday.

[1] [1a] P. Schwab, N. Mahr, J. Wolf, H. Werner, *Angew. Chem.* **1993**, *105*, 1498–1500; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1480–1482. – [1b] P. Schwab, N. Mahr, J. Wolf, H. Werner, *Angew. Chem.* **1994**, *106*, 82–84; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 97–99.

[2] H. Werner, D. A. Ortmann, O. Gevert, *Chem. Ber.* **1996**, *129*, 411–417.

[3] J. Wolf, L. Brandt, A. Fries, H. Werner, *Angew. Chem.* **1990**, *102*, 584–586; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 510–512.

[4] Review: H. Werner, *J. Organomet. Chem.* **1995**, *500*, 331–336.

[5] [5a] M. Dziallas, A. Höhn, H. Werner, *J. Organomet. Chem.* **1987**, *330*, 207–219. – [5b] M. Schulz, Dissertation, Universität Würzburg **1991**.

[6] M. O. Albers, E. Singleton, Y. E. Yates, *Inorg. Synth.* **1989**, *26*, 253.

[7] C. Grünwald, O. Gevert, J. Wolf, P. Gonzalez-Herrero, H. Werner, *Organometallics* **1996**, *15*, 1960–1962.

[8] [8a] B. Chaudret, G. Chung, O. Eisenstein, S. A. Jackson, F. J. Lahoz, J. A. Lopez, *J. Am. Chem. Soc.* **1991**, *113*, 2314–2316. – [8b] M. L. Christ, S. Sabo-Etienne, B. Chaudret, *Organometallics* **1994**, *13*, 3800–3804. – [8c] T. Burrow, S. Sabo-Etienne, B. Chaudret, *Inorg. Chem.* **1995**, *24*, 2470–2472.

[9] [9a] B. Chaudret, *J. Organomet. Chem.* **1984**, *268*, C33–C37. – [9b] B. Chaudret, R. Poilblanc, *Organometallics* **1985**, *4*, 1722–1726.

[10] [10a] R. H. Crabtree, D. G. Hamilton, *J. Am. Chem. Soc.* **1986**, *108*, 3124–3125. – [10b] D. G. Hamilton, R. H. Crabtree, *J. Am. Chem. Soc.* **1988**, *110*, 4126–4133.

[11] [11a] R. H. Crabtree, M. Lavin, L. Bonneviot, *J. Am. Chem. Soc.* **1986**, *108*, 4032–4037. – [11b] R. H. Crabtree, D. G. Hamilton, *Adv. Organomet. Chem.* **1988**, *28*, 299–338.

[12] D. G. Gusev, A. B. Vymenits, V. I. Bakhmutov, *Inorg. Chem.* **1992**, *31*, 1–2.

[13] C. A. McAuliffe in *Comprehensive Coordination Chemistry* (Eds.: G. Wilkinson, J. A. McCleverty, R. D. Gillard), vol. 2, Pergamon Press, Oxford, **1987**, p. 989.

[14] [14a] R. O. Harris, N. K. Hota, L. Sadavoy, J. M. C. Yuen, *J. Organomet. Chem.* **1973**, *54*, 259–264. – [14b] D. J. Cole-Hamilton, G. Wilkinson, *J. Chem. Soc., Chem. Commun.* **1977**, 59–60. – [14c] D. J. Cole-Hamilton, G. Wilkinson, *Nouv. J. Chem.* **1977**, 141–155.

[15] A. E. Smith, *Inorg. Chem.* **1972**, *11*, 2306–2310.

[16] C. Grünwald, O. Gevert, unpublished results.

[17] N. R. Champness, W. Levason, M. Webster, *Inorg. Chim. Acta* **1993**, *208*, 189–194.

[18] [18a] C. Bohanna, M. A. Esteruelas, F. J. Lahoz, E. Onate, L. A. Oro, E. Sola, *Organometallics* **1995**, *14*, 4825–4831. – [18b] A. J. Blake, M. A. Halcrow, M. Schröder, *J. Chem. Soc., Dalton Trans.* **1994**, 1631–1639. – [18c] S. Zobl-Ruh, W. v. Philipsborn, *J. Organomet. Chem.* **1977**, *127*, C59–C63.

[19] H. Werner, P. Schwab, N. Mahr, J. Wolf, *Chem. Ber.* **1992**, *125*, 2641–2650.

[20] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-405281, the names of the authors, and the journal citation.

[96108]