Halfsandwich-Type Triisopropylstibane Ruthenium Complexes with 16-, 17-, and 18-Electron Configurations and an Unsymmetrical Binuclear 18/16-Electron $Ru_2(SbiPr_3)$ Species☆

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The paramagnetic ruthenium complex $[(\eta^5\text{-}C_5Me_5)RuCl_2(SbiPr_3)]$ (**2**), which is prepared from $[(\eta^5\text{-}C_5Me_5)RuCl_2]_n$ (**1**) and $SbiPr_3$, reacts with Mg/Hg in THF to give the coordinatively unsaturated 16-electron species $[(\eta^5\text{-}C_5Me_5)RuCl(SbiPr_3)]$ (**3**). Compound **3** is obtained in much better yield from $[(\eta^5\text{-}C_5Me_5)Ru(\mu_3\text{-}Cl)]_4$ (**4**) and $SbiPr_3$ (molar ratio 1:4). While **3** reacts with CO to give the 18-electron complex $[(\eta^5\text{-}C_5Me_5)RuCl(CO)(SbiPr_3)]$ (**5**), on treatment of **3** with $HC{\equiv}CCO_2Me$ the metallacycle $[(\eta^5\text{-}C_5Me_5)RuCl\{\kappa^2(C,C)\text{-}C(CO_2Me){=}CHC(CO_2Me){=}CH\}(SbiPr_3)]$ (**6**) is obtained. The reaction of **4** with $SbiPr_3$ in the molar ratio of 1:2 affords the binuclear compound $[(\eta^5\text{-}C_5Me_5)(SbiPr_3)Ru(\mu\text{-}Cl)_2Ru(\eta^5\text{-}C_5Me_5)]$ (**7**). The molecular structures of **2** and **7** have been determined by X-ray crystallography.

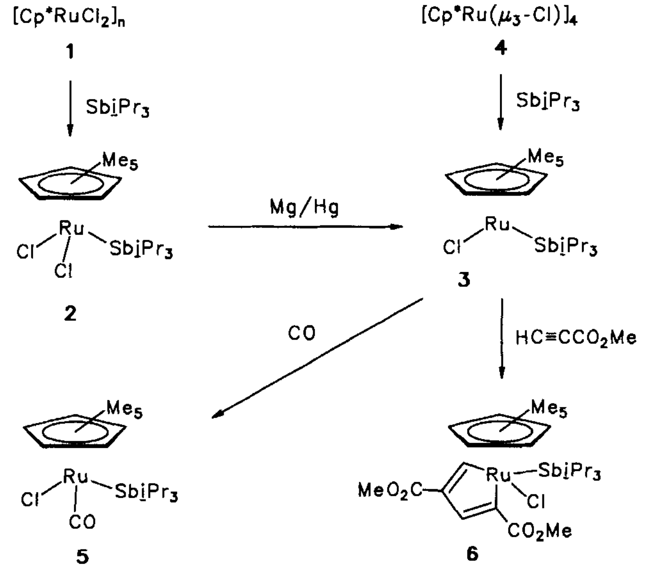
One of the most remarkable features of halfsandwich-type ruthenium complexes containing $\eta^5\text{-}C_5Me_5$ (Cp*) as a ligand is that 16-electron compounds of the general composition $[Cp^*RuCl(PR_3)]$ can be isolated, provided that the phosphane ligand is sufficiently bulky and possesses a cone angle of at least 160°[1-3]. These coordinatively unsaturated Cp*Ru derivatives are quite labile and react, e.g., with PMe_3 or $HC{\equiv}CSiMe_3$ to give products in which the metal centre has an 18-electron configuration[1,4].

Since we showed quite recently that the replacement of $PiPr_3$ by $SbiPr_3$ as a ligand in low-valent rhodium and iridium complexes leads to a significant difference both in the thermodynamic stability and the reactivity of these compounds[5,6], we were interested to find out how triisopropylstibane would behave towards [Cp*RuCl] as a molecular unit. The question was whether $SbiPr_3$ would afford, similarly to $PiPr_3$[1,2] a 16-electron species $[Cp^*RuCl(SbiPr_3)]$ or, due to its smaller cone angle compared with $PiPr_3$[7], would prefer to form an 18-electron complex. The work described in this paper reveals that with $SbiPr_3$ as ligand a 16-electron compound is indeed accessible, and that it can be prepared via two different routes. Moreover, a 17-electron species $[Cp^*RuCl_2(SbiPr_3)]$ can also be isolated, as well as a novel binuclear Cp*Ru complex which has one coordinatively saturated and one coordinatively unsaturated metal centre.

Mononuclear Complexes with $[Cp^*Ru(SbiPr_3)]$ as a Molecular Unit

The two routes known for the synthesis of $[Cp^*RuCl(PiPr_3)]$[1,2] can also be applied to $[Cp^*RuCl(SbiPr_3)]$ (**3**). Treatment of a solution of $[Cp^*RuCl_2]_n$ (**1**) with an equimolar (for $n = 1$) amount of $SbiPr_3$ causes a gradual change of color from red-brown to red-orange and leads, after removal of the solvent and addition of pentane, to the isolation of $[Cp^*RuCl_2(SbiPr_3)]$ (**2**) in 84% yield. The ^1H-NMR spectrum (in C_6D_6) of the orange-red, moderately air-sensitive compound displays at room temperature three broad signals at $\delta = 26.8$, 14.2, and 5.7 which, by increasing or decreasing the temperature, are considerably shifted to higher or lower fields. The ESR spectrum of **2** (in THF) shows, similarly to $[Cp^*RuCl_2(PiPr_3)]$[2], one broad signal at $g = 2.06$, which is consistent with the presence of one single unpaired electron in the molecule. The conclusion is that **2** can be formulated as a monomeric 17-electron species with ruthenium in the oxidation state +III.

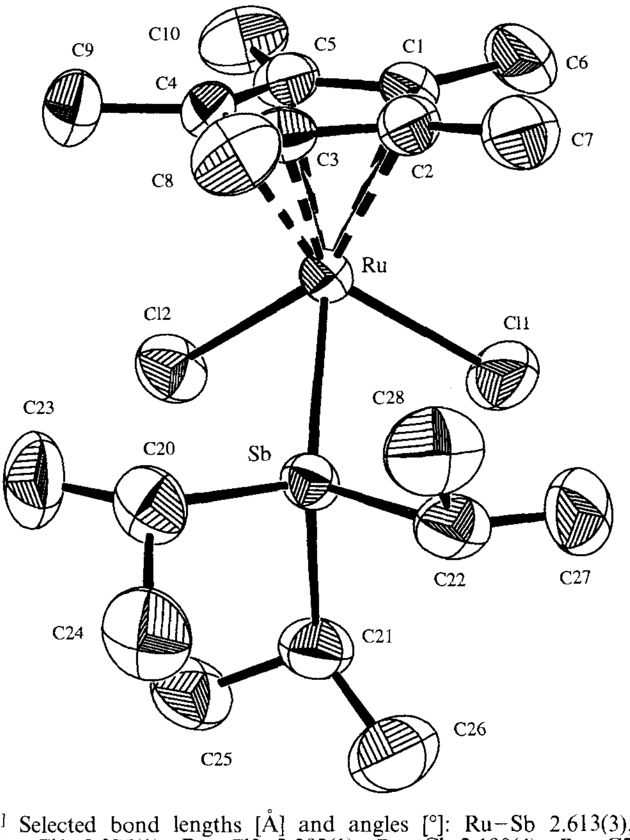
Scheme 1



$(Cp^* = \eta^5\text{-}C_5Me_5)$

The result of an X-ray structural analysis of **2** is shown in Figure 1. The ORTEP plot reveals that the molecule has the expected piano-stool configuration with Sb–Ru–Cl and Cl–Ru–Cl angles between 82.74(4) and 99.33(6)°. The Ru–Cl bond lengths [2.375(1) and 2.392(1) Å] are almost identical to the Ru–Cl distance in the 16-electron species [Cp*RuCl(P*i*Pr$_3$)] [2.365(2) Å][1]; they are, however, significantly shorter than in the coordinatively and electronically saturated complex [Cp*RuCl(PPh$_3$)$_2$] [2.453(2) Å][8]. The Ru–Sb distance [2.613(3) Å] in **2** is the same as that found in [Ru(η^3-C$_3$H$_5$)$_2$(Sb*i*Pr$_3$)$_2$] [2.610(4) Å][9] and also quite similar to the bond lengths in the tris- and tetrakis(stibane)ruthenium(II) derivatives [RuCl$_2$(CO)(Sb*i*Pr$_3$)$_3$] [2.596(1)–2.666(1) Å][10] and *trans*-[RuCl$_2$(SbPh$_3$)$_4$] [2.625(1)–2.632(1) Å][11]. In spite of the different σ- and π-bonding capabilities of the Sb*i*Pr$_3$ and chloro ligands, the Cp* ring of **2** is symmetrically coordinated, the difference in the Ru–C(1–5) distances being less than 0.042 Å.

Figure 1. Molecular structure (ORTEP plot) of **2**[a]



[a] Selected bond lengths [Å] and angles [°]: Ru–Sb 2.613(3), Ru–Cl1 2.375(1), Ru–Cl2 2.392(1), Ru–C1 2.190(4), Ru–C2 2.178(5), Ru–C3 2.220(5), Ru–C4 2.216(4), Ru–C5 2.216(4); Sb–Ru–Cl1 82.74(4), Sb–Ru–Cl2 84.46(4), Cl1–Ru–Cl2 99.33(6).

Whilst treatment of **2** with Zn or Zn/Hg affords a mixture of products, the reduction of **2** with magnesium amalgam in THF gives the monochlororuthenium(II) derivative [Cp*RuCl(Sb*i*Pr$_3$)] (**3**) in modest yield. A more favorable method of synthesis is the reaction of the tetramer [Cp*Ru(μ_3-Cl)]$_4$ (**4**) with Sb*i*Pr$_3$ in the molar ratio of 1:4 (Scheme 1), which leads to the formation of **3** in 63% yield. As the ^{1}H-NMR data and molecular weight measurements indicate, the brownish-yellow air-sensitive stibane complex **3**, like the phosphane analogue [Cp*RuCl(P*i*Pr$_3$)][1,2], is monomeric in solution, and thus contains a coordinatively unsaturated metal centre.

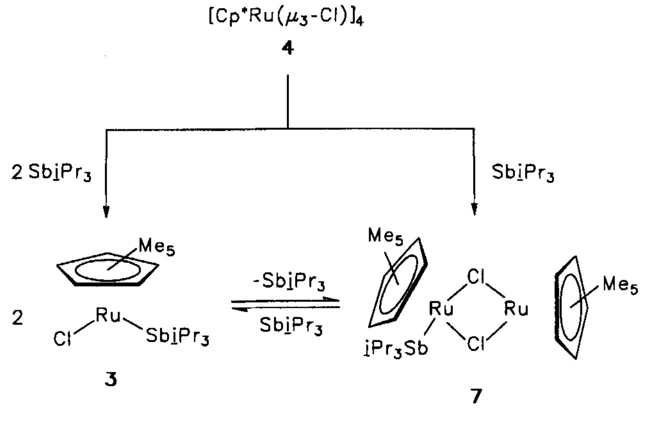
Therefore, it is not surprising that **3** reacts quite rapidly with CO to give the 18-electron compound [Cp*RuCl(CO)(Sb*i*Pr$_3$)] (**5**) in good yield. Complex **5** is an orange, almost air-stable solid showing a single ν(CO) band at 1910 cm^{-1} in the IR spectrum. The ^{13}C-NMR spectrum of **5** displays besides the signals for the CO, C$_5$Me$_5$, and SbCH carbon nuclei, *two* singlets for the diastereotopic carbon atoms of the methyl groups of the stibane ligand, which is in agreement with the chirality of the molecule.

In contrast to the "pseudo-16-electron" complex [Cp*RuCl{κ^2(*P*,*O*)-*i*Pr$_2$PCH$_2$CO$_2$Me}], which reacts with methylpropiolate to give the vinylideneruthenium(II) species [Cp*RuCl(=C=CHCO$_2$Me){κ(*P*)-*i*Pr$_2$PCH$_2$CO$_2$Me}][12], the reaction of **3** with HC≡CCO$_2$Me affords a 70% yield of the ruthenacyclopentadiene [Cp*RuCl{κ^2(C,C)-C(CO$_2$Me)=CHC(CO$_2$Me)=CH}(Sb*i*Pr$_3$)] (**6**) rather than [Cp*RuCl(=C=CHCO$_2$Me)(Sb*i*Pr$_3$)]. Compound **6** is related to cobalt complexes of the general composition [C$_5$H$_5$Co{κ^2(*C*,*C*)-CR=CR'–CR=CR'}(L)] (L = CO, PPh$_3$ etc.) which are also formed by alkyne-alkyne coupling from [C$_5$H$_5$Co(L)$_2$] as the precursor[13]. It should be mentioned that the phosphane derivative [Cp*RuCl(P*i*Pr$_3$)] reacts with acetylene to yield the *binuclear* ruthenacyclopentadiene [Cp*RuCl$_2${κ^2(*C*,*C*)-μ-C$_4$H$_4$}RuCp*], in which the five-membered metallacycle behaves as a bridging ligand[1b]. The most typical features of the NMR data of **6** are the two doublets for the CH protons of the RuC$_4$ ring at rather low field (δ = 9.23 and 7.70) in the ^{1}H-NMR spectrum and the four signals for the four different carbon atoms of the metallacycle at δ = 188.4, 179.6 (α-C), and δ = 147.4 and 140.2 (β-C) in the ^{13}C-NMR spectrum, respectively. The ^{13}C-NMR spectrum of the electronically unsaturated ruthenacyclopentadiene [C$_5$H$_5$RuBr{κ^2(*C*,*C*)-CPhCH=CHCPh}] shows one resonance for the *C*Ph carbon atoms at δ = 271.1 and one for the *C*H carbon atoms at δ = 156.0, which is consistent with a bis(carbenoid)-type resonance structure of the metallacycle[14].

The Preparation and Structure of the Binuclear Complex [Cp*(Sb*i*Pr$_3$)Ru(μ-Cl)$_2$RuCp*]

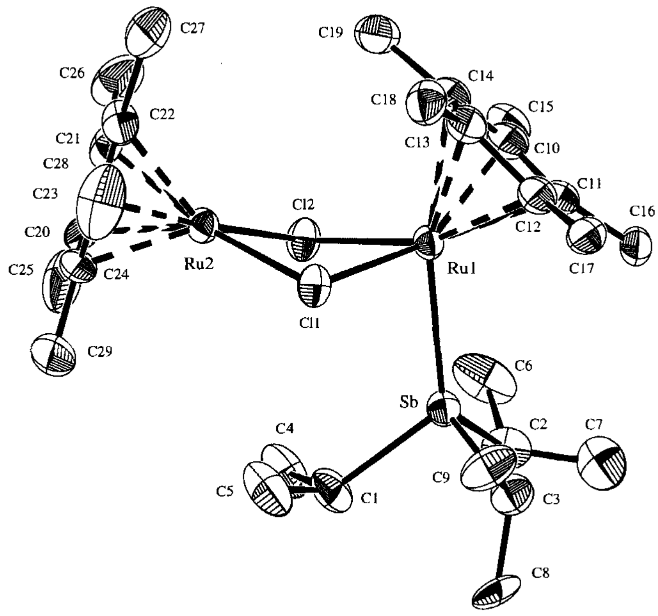
The observation made by Chaudret (and independently by Koelle et al. for the η^5-C$_5$Me$_4$Et derivative)[15] that the tetrameric compound **4** can be converted to binuclear complexes [Cp*(L)Ru(μ_2-Cl)]$_2$ under certain conditions and by using "flat" ligands such as pyridine[16], prompted us to study the reaction of **4** with Sb*i*Pr$_3$ in a molar ratio of less than 1:4. Thus, if a solution of **4** in benzene is treated with *two* equivalents of the stibane at room temperature, the orange compound **7** is formed which, according to the elemental analysis, contains one Sb*i*Pr$_3$ for every two Cp*RuCl fragments. The ^{1}H-NMR spectrum of **7** (in C$_6$D$_6$) displays, besides the resonances for the protons of the isopropyl groups, two singlets at δ = 1.61 and 1.38 which can be assigned to the CH$_3$ protons of the two differently coordinated C_5Me_5 units. The new complex **7** is also obtained by storing a solution of **3** in acetone for 12 h at $-20\,^{\circ}C$ and can be reconverted to **3** by addition of one equivalent of the stibane (Scheme 2).

Scheme 2



(Cp* = η^5-C_5Me_5)

Figure 2. Molecular structure (ORTEP plot) of **7**[a]



[a] Selected bond lengths [Å] and angles [°]: Ru1–Sb 2.656(7), Ru1–Cl1 2.504(7), Ru1–Cl2 2.506(5), Ru2–Cl1 2.427(4), Ru2–Cl2 2.40(1), Ru1–Ru2 3.524(2), Ru1–C10 2.162(8), Ru1–C11 2.159(8), Ru1–C12 2.168(9), Ru1–C13 2.17(1), Ru1–C14 2.174(8), Ru2–C20 2.09(2), Ru2–C21 2.12(2), Ru2–C22 2.10(2), Ru2–C23 2.13(2), Ru2–C24 2.09(2); Sb–Ru1–Cl1 88.2(3), Sb–Ru1–Cl2 85.6(2), Cl1–Ru1–Cl2 82.4(3), Cl1–Ru2–Cl2 86.2(2), Ru1–Cl1–Ru2 91.2(2), Ru1–Cl2–Ru2 91.7(3).

An ORTEP drawing of the structure of **7** is shown in Figure 2. The molecule contains a central unsymmetrical Ru_2Cl_2 fragment which, in contrast to $[(\eta^5\text{-}C_5Me_4Et)(C_2H_4)Ru(\mu\text{-}Cl)]_2$[15] and $[Cp^*(Cl)Ru(\mu\text{-}Cl)]_2$[17], is not planar. The dihedral angle between the planes [Ru1,Cl1,Cl2] and [Ru2,Cl1,Cl2] is 29.9(4)°. The bond lengths of the bridging chlorides to the electronically saturated metal centre Ru1 are significantly longer [2.504(7) and 2.506(5) Å] than those of Ru2 [2.427(4) and 2.40(1) Å] which has only a 16-electron configuration. It is worth mentioning that the distances Ru2–Cl1 and Ru2–Cl2 are almost the same as those in the 17-electron species **2** (see Figure 1), while the bond lengths Ru1–Cl1 and Ru1–Cl2 are almost identical to those in the tetramer **4** [2.513(3)–2.537(3) Å][18]. An analogous situation to that found in **7** exists in the binuclear copper(I) complex $[(PPh_3)_2Cu(\mu\text{-}Br)_2Cu(PPh_3)]$, which also contains an unsymmetrical M_2X_2 core in which one copper has an 18-electron and the other a 16-electron configuration[19]. The bond length Ru1–Sb in **7** is 2.656(7) Å and is therefore similar to the Ru–Sb distance in the mononuclear compound **2**.

Conclusion

The work described in this paper has shown that there are similarities as well as differences in the behavior of $PiPr_3$ and $SbiPr_3$ toward starting materials containing Cp*RuCl as a molecular unit. The oligomeric (possibly polymeric) ruthenium(III) complex $[Cp^*RuCl_2]_n$ (**1**) reacts with both triisopropylphosphane and -stibane to generate a paramagnetic 17-electron compound $[Cp^*RuCl_2(EiPr_3)]$ (E = P[2], Sb), which upon reduction with Zn or Mg/Hg yields the 16-electron species $[Cp^*RuCl(EiPr_3)]$. The tetramer $[Cp^*Ru(\mu_3\text{-}Cl)]_4$ (**4**), however, behaves somewhat differently towards $PiPr_3$ and $SbiPr_3$. Whereas the reaction of **4** with the phosphane gives only the mononuclear complex $[Cp^*RuCl(PiPr_3)]$, the corresponding stibane derivative **3** as well as the unsymmetrical binuclear compound **7** can be obtained upon treatment of **4** with $SbiPr_3$. The reactivity of the coordinatively unsaturated species $[Cp^*RuCl(PiPr_3)]$ and **3** towards terminal alkynes also differs in some respects. In contrast to the phosphane complex, which in the presence of HC≡CH yields the binuclear ruthenacyclopentadiene $[Cp^*RuCl_2\{\kappa^2(C,C)\text{-}\mu\text{-}C_4H_4\}RuCp^*]$[1b], the stibane analogue **3** reacts with $HC{\equiv}CCO_2Me$ to give the mononuclear metallacycle **6**. Finally, it should be noted that in spite of recent progress made in this field[5,6,9] tri*alkyl*stibane compounds of the late (electron-rich) transition metals are still quite rare[20]. Moreover, the species **2**, **3** and **5**, **6** are the first halfsandwich-type ruthenium complexes with SbR_3.

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Experimental Section

All operations were carried out under argon in carefully dried solvents. The starting materials **1**[21], **4**[22], and $SbiPr_3$[23] were prepared by known methods. – IR: Perkin-Elmer 1420. – NMR:

Bruker AC 200 and AMX 400. – ESR: Bruker ESP 300. – Melting points were determined by DTA.

1. Preparation of [(η^5-C_5Me_5)$RuCl_2$($SbiPr_3$)] (**2**): To a solution of 98 mg (0.32 mmol for $n = 1$) of **1** in 5 ml of CH_2Cl_2, 66 µl (0.32 mmol) of Sb*i*Pr$_3$ was added dropwise and the mixture was stirred for 10 min at room temp. The solvent was then removed in vacuo, and the residue was treated with 3 ml of pentane to give an orange microcrystalline solid; yield 150 mg (84%), m.p. 64 °C (dec.). – ^1H NMR (200 MHz, C_6D_6): $\delta = 26.8, 14.2, 5.7$ (all s, br). – ESR (9.76 GHz, THF, 293 K): $g = 2.06$ (s, br). – $C_{19}H_{36}Cl_2RuSb$ (558.2): calcd. C 40.88, H 6.50; found C 40.50, H 6.38.

2. Preparation of [(η^5-C_5Me_5)RuCl($SbiPr_3$)] (**3**): (a) A solution of 80 mg (0.15 mmol) of **2** in 10 ml of THF was treated with Mg/Hg (2.0 g Hg, 9.97 mmol; 30 mg Mg, 1.23 mmol) and stirred for 1 h at room temp. The solution was then filtered and the filtrate was concentrated in vacuo. The residue was extracted with 10 ml of benzene, and the extract was filtered. After removal of the solvent, the residue was treated with 1 ml of pentane (–78 °C) to give a brownish-yellow microcrystalline solid; yield 22 mg (29%). – (b) To a solution of 163 mg (0.15 mmol) of **4** in 10 ml of benzene, 123 µl (0.60 mmol) of Sb*i*Pr$_3$ was added dropwise and the mixture was stirred for 5 min at room temp. The solvent was then removed in vacuo, and the residue was worked-up as described for a); yield 197 mg (63%). – (c) To a solution of 70 mg (0.09 mmol) of **5** in 10 ml of benzene, 18 µl (0.09 mmol) of Sb*i*Pr$_3$ was added dropwise and the mixture was stirred for 5 min at room temp. The solvent was then removed in vacuo, and the residue was worked-up as described for a); yield 76 mg (82%); m.p. 58 °C (dec.). – ^1H NMR (200 MHz, C_6D_6): $\delta = 1.93$ (m, br, SbC*H*CH$_3$), 1.62, 1.30 (both s, br, C_5Me_5 and SbCHC*H*$_3$). – $C_{19}H_{36}ClRuSb$ (522.8): calcd. C 43.65, H 6.94; found C 43.57, H 6.96; mol. mass 480 (osmometric in CH_2Cl_2).

3. Preparation of [(η^5-C_5Me_5)RuCl(CO)($SbiPr_3$)] (**5**): A stream of CO was passed for 1 min through a solution of 86 mg (0.16 mmol) of **3** in 2 ml of CH_2Cl_2 at room temp. The solvent was removed in vacuo, and the residue was treated with 3 ml of pentane to give an orange microcrystalline solid; yield 69 mg (76%), m.p. 95 °C (dec.). – IR (C_6H_6): $\tilde{\nu} = 1910\ cm^{-1}$ [ν(C≡O)]. – ^1H NMR (400 MHz, C_6D_6): $\delta = 2.03$ (m, 3H, SbC*H*CH$_3$), 1.51 (s, 15H, C_5Me_5), 1.24 [d, *J*(HH) = 7.2 Hz, 9H, SbCHC*H*$_3$), 1.15 [d, *J*(HH) = 7.6 Hz, 9H, SbCHC*H*$_3$]. – ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 207.0$ (s, CO), 92.8 (s, *C*$_5$Me$_5$), 22.5, 22.3 (both s, SbCH*C*H$_3$), 17.7 (s, Sb*C*HCH$_3$), 9.5 (s, C$_5$*Me*$_5$). – $C_{20}H_{36}ClORuSb$ (550.8): calcd. C 43.62, H 6.59; found C 43.10, H 6.00.

4. Preparation of [(η^5-C_5Me_5)RuCl{κ^2(C,C)-C(CO_2Me)=CHC(CO_2Me)=CH}($SbiPr_3$)] (**6**): A solution of 150 mg (0.28 mmol) of **3** in 5 ml of CH_2Cl_2 was treated with 120 µl (1.40 mmol) of HC≡CCO$_2$Me and the mixture was stirred for 5 min at room temp. The solution was concentrated to ca. 1 ml in vacuo, and then chromatographed on Al_2O_3 (neutral, activity gradce V, length of column 7 cm). With CH_2Cl_2, an orange fraction was eluted, from which the solvent was removed. The residue was treated with 5 ml of pentane to give an orange microcrystalline solid; yield 96 mg (70%), m.p. 98 °C (dec.). – IR (C_6H_6): $\tilde{\nu} = 1685\ cm^{-1}$ [ν(C=O)]. – ^1H NMR (400 MHz, C_6D_6): $\delta = 9.23$ [d, *J*(HH) = 3.3 Hz, 1H, RuCH], 7.70 [d, *J*(HH) = 3.3 Hz, 1H, RuC(CO$_2$CH$_3$)C*H*], 3.66, 3.57 (both s, 3H each, CO$_2$CH$_3$), 2.44 (sept, *J*(HH) = 7.4 Hz, 3H, SbC*H*CH$_3$), 1.40 (s, 15H, C_5Me_5), 1.29 [d, *J*(HH) = 7.4 Hz, 9H, SbCHC*H*$_3$), 1.25 [d, *J*(HH) = 7.4 Hz, 9H, SbCHC*H*$_3$]. – ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 188.4$ [s, Ru*C*(CO$_2$CH$_3$)], 179.6 (s, RuCH), 175.9, 162.3 (both s, *C*O$_2$CH$_3$), 147.4 [s, RuCH*C*(CO$_2$CH$_3$)], 140.2 [s, RuC(CO$_2$CH$_3$)*C*H], 102.9 (s, *C*$_5$Me$_5$), 50.7, 50.1 (both s, CO$_2$*C*H$_3$), 22.5, 22.0 (both s, SbCH*C*H$_3$), 19.1 (s, Sb*C*HCH$_3$), 9.8 (s, C$_5$*Me*$_5$). – $C_{27}H_{44}ClO_4RuSb$ (690.9): calcd. C 46.94, H 6.42; found C 47.50, H 6.70.

5. Preparation of [(η^5-C_5Me_5)($SbiPr_3$)Ru(μ-Cl)$_2$Ru(η^5-C_5Me_5)] (**7**): (a) A solution of 133 mg (0.25 mmol) of **3** in 4 ml of acetone was cooled to –20 °C. After ca. 12 h orange crystals precipitated, which were filtered off, washed with 2 ml of pentane and dried in vacuo; yield 57 mg (56%). – (b) To a solution of 70 mg (0.06 mmol) of **4** in 10 ml of benzene, 26 µl (0.13 mmol) of Sb*i*Pr$_3$ was added dropwise and the mixture was stirred for 5 min at room temp. The solvent was then removed in vacuo, and the residue was treated with 1 ml of pentane (–30 °C) to give an orange microcrystalline solid; yield 85 mg (89%), m.p. 75 °C (dec.). – ^1H NMR (200 MHz, C_6D_6): $\delta = 2.03$ [sept, *J*(HH) = 6.9 Hz, 3H, SbC*H*CH$_3$], 1.61 (s, 15H, C_5Me_5), 1.38 (s, br, 15H, C_5Me_5), 1.37 [d, *J*(HH) = 6.9 Hz, 18H, SbCHC*H*$_3$]. – $C_{29}H_{51}Cl_2Ru_2Sb$ (794.5): calcd. C 43.84, H 6.47; found C 43.02, H 6.98.

6. Determination of the X-ray Crystal Structure of **2**[24]: Single crystals were grown from methanol. Crystal data (from 25 reflections, $4° < \Theta < 21°$): triclinic, space group $P\bar{1}$ (No. 2); $a = 8.4576(9)$, $b = 8.616(1)$, $c = 18.226(3)$ Å, $\alpha = 102.52(1)$, $\beta = 90.69(1)$, $\gamma = 177.93(1)°$, $V = 1135.5(3)$ Å^3, $Z = 2$, $d_{calcd.} = 1.633$ g cm^{-3}, μ(Mo-K_α) = 2.088 mm^{-1}; crystal size 0.25 × 0.30 × 0.36 mm; Enraf-Nonius CAD4 diffractometer, Mo-K_α radiation (0.70930 Å), graphite monochromator, zirconium filter (factor 15.4); $T = 293(2)$ K; ω/Θ scan, max. $2\Theta = 48°$; 3823 reflections measured, 3549 independent reflections, 2751 reflections with $I > 2\sigma(I)$, 3548 independent reflections included in data set. Intensity data were corrected for Lorentz and polarization effects, an empirical absorption correction (Ψ-scan method) was applied (minimum transmission 75.68%). The structure was solved by the direct methods (SHELXS-86). Atomic coordinates and the anisotropic thermal parameters of the non-hydrogen atoms were refined by full matrix least-squares on F^2 {352 parameters, weighting scheme applied in the last cycle: $w = 1/[\sigma^2(F_o^2) + (0.0288 \cdot P)^2 + 0.2569 \cdot P]$ where $P = (F_o^2 + 2F_c^2)/3$, SHELXL-93}. The positions of all hydrogen atoms were found and refined isotropically. Conventional $R = 0.0274$ [for 2751 reflections with $I > 2\sigma(I)$] and weighted $wR2 = 0.0632$ for all 3548 data reflections; reflex/parameter ratio 10.08; residual electron density +0.388/–0.315 eÅ^{-3}.

7. Determination of the X-ray Crystal Structure of **7**[24]: Single crystals were grown at –30 °C from acetone. Crystal data (from 25 reflections, $8° < \Theta < 15°$): orthorhombic, space group *Pbca* (No. 61); $a = 18.369(5)$, $b = 23.871(6)$, $c = 14.86(1)$ Å, $V = 6516(4)$ Å^3, $Z = 8$, $d_{calcd} = 1.620$ g cm^{-3}, μ(Mo-K_α) = 1.172 mm^{-1}; crystal size 0.25 × 0.35 × 0.50 mm; Enraf-Nonius CAD4 diffractometer, Mo-K_α radiation (0.70930 Å), graphite monochromator, zirconium filter (factor 16.4); $T = 173$ K; ω/Θ scan, max. $2\Theta = 46°$; 6032 reflections measured, 3677 independent reflections, 2872 reflections with $I > 2\sigma(I)$, 3677 independent reflections included in data set. Intensity data were corrected for Lorentz and polarization effects, an empirical absorption correction (Ψ-scan method) was applied (minimum transmission 86.3%). The structure was solved by the direct methods (SHELXS-86). Atomic coordinates and the anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least-squares on F^2 {247 parameters, weighting scheme applied in the last cycle: $w = 1/[\sigma^2(F_o^2) + (0.0345 \cdot P)^2 + 156.1142 \cdot P]$ 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 $R = 0.0481$ [for 2872 reflections with $I > 2\sigma(I)$] and weighted $wR2 = 0.1554$ for all 3677 data reflections; reflex/parameter ratio 9.0; residual electron density +1.062/–0.978 eÅ^{-3}.

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[24] 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 numbers CSD-406230 (**2**), CSD-406231 (**7**), the names of the authors, and the journal citation.

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