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A series of triisopropylstibine ruthenium and osmium complexes including the X-ray crystal structure of [RuCl$_2$(CO)(Sb*i*Pr$_3$)$_3$] and [RuCl$_2$(=C=C=CPh$_2$)(CO)(Sb*i*Pr$_3$)$_2$][1]

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Abstract

With [(*p*-cym)RuCl$_2$]$_2$ (**1**) as the starting material, the halfsandwich-type complexes [(*p*-cym)RuCl$_2$(Sb*i*Pr$_3$)] (**2**) and [(*p*-cym)RuCl(Sb*i*Pr$_3$)$_2$]PF$_6$ (**3**) were prepared. Treatment of RuCl$_3$·3H$_2$O in ethanol gave, after addition of Sb*i*Pr$_3$, the monocarbonyl compound [RuCl$_2$(CO)(Sb*i*Pr$_3$)$_3$] (**4**), which reacted with CO by ligand exchange to yield [RuCl$_2$(CO)$_2$(Sb*i*Pr$_3$)$_2$] (**5**). The reaction of RuCl$_3$·3H$_2$O in ethanol, in the presence of Na$_2$CO$_3$, afforded the chloro(hydrido) derivative [RuHCl(CO)(Sb*i*Pr$_3$)$_3$] (**6**). Analogously, using OsCl$_3$·3H$_2$O as the starting material, the chloro(hydrido)osmium complex [OsHCl(CO)(Sb*i*Pr$_3$)$_3$] (**8**) was prepared. The reactions of **8** with C$_2$H$_4$, C$_2$(CO$_2$Me)$_2$ and NaBH$_4$ led to the formation of compounds **9**, **10** and **11**, which all contain the Os(Sb*i*Pr$_3$)$_2$ unit as a building block. While treatment of **6** with C$_2$(CO$_2$Me)$_2$ yielded the substitution product [RuHCl(CO)(MeO$_2$CC≡CCO$_2$Me)(Sb*i*Pr$_3$)$_2$] (**14**), the corresponding reaction of **6** with HC≡CPh and HC≡CCPh$_2$OH afforded the alkynyl and allenylidene ruthenium(II) complexes [RuCl(C≡CPh)(CO)(Sb*i*Pr$_3$)$_3$] (**16**) and [RuCl$_2$(=C=C=CPh$_2$)(CO)(Sb*i*Pr$_3$)$_2$] (**17**), respectively. Compounds **4** and **17** were characterized by X-ray crystal structure analysis. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Ruthenium; Osmium; Stibine complexes; Reactions with alkenes and alkynes

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1. Introduction

After we discovered that low-valent rhodium [1] and iridium [2] complexes with Sb*i*Pr$_3$ as ligand are considerably more reactive than their P*i*Pr$_3$ counterparts, we became interested in preparing ruthenium(II) compounds of the general composition [RuCl$_2$(Sb*i*Pr$_3$)$_n$]. While the complexes [RuCl$_2$(SbPh$_3$)$_4$] and [RuCl$_2$(SbMe$_2$Ph)$_4$] were known [3], there was no report in the literature about related trialkylstibine ruthenium(II) derivatives [4]. When we attempted to obtain [RuCl$_2$(Sb*i*Pr$_3$)$_3$] or [RuCl$_2$(Sb*i*Pr$_3$)$_4$] from the polymeric [RuCl$_2$(C$_8$H$_{12}$)]$_n$ and Sb*i*Pr$_3$ in the presence of H$_2$, we isolated the dihydrido(dihydrogen) complex [RuH$_2$(H$_2$)(Sb*i*Pr$_3$)$_3$] in excellent yield [5]. This species reacted with propene to give a bis(allyl)ruthenium(II), and with butadiene to afford a bis(butadiene)ruthenium(0) derivative [5].

The work presented in this paper is not only an extension of our recent investigations but reveals that even RuCl$_3$·3H$_2$O as well as OsCl$_3$·3H$_2$O can be used as starting materials for the synthesis of triisopropylstibine ruthenium and osmium complexes. Moreover, it illustrates that with Ru(Sb*i*Pr$_3$)$_2$ as a molecular building block, an allenylidene unit: C=C=CPh$_2$ can be generated at ruthenium as the metal center also.

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[1] Dedicated to Professor M.I. Bruce on the occasion of his 60th birthday.

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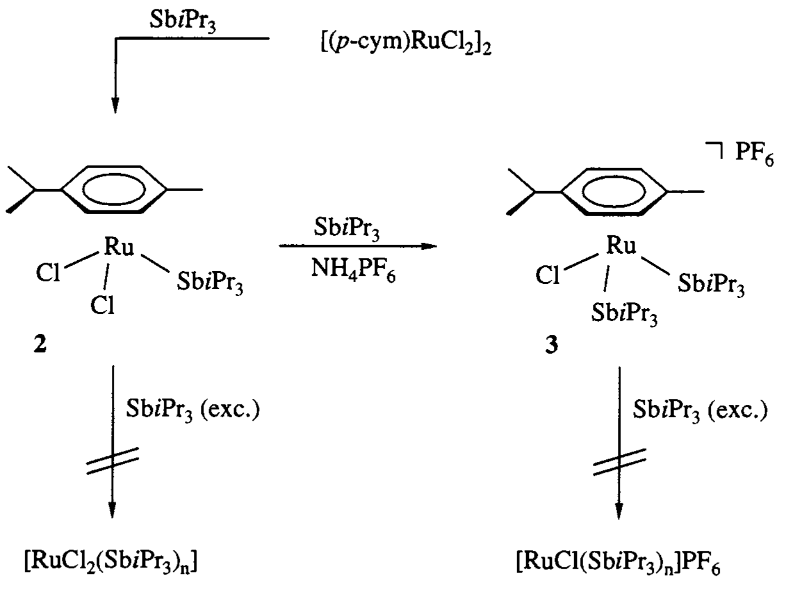


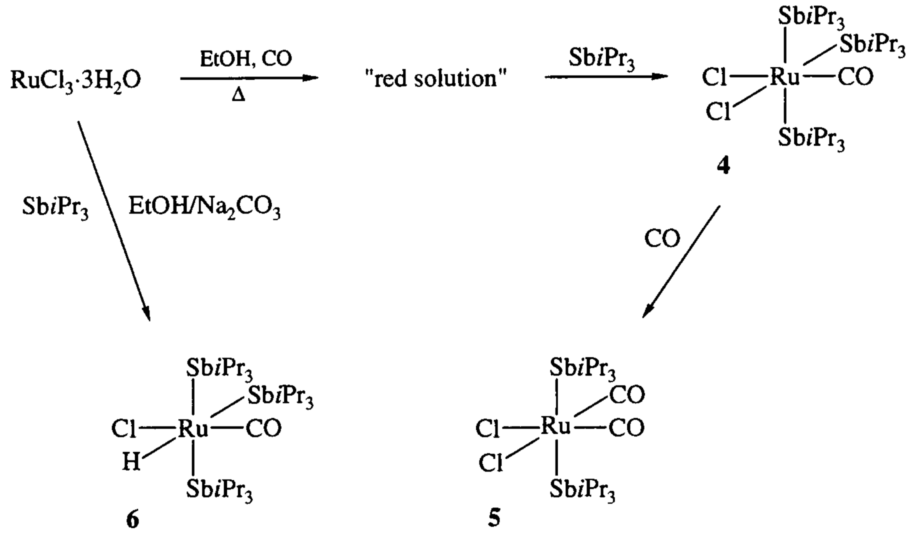
Scheme 1.

2. Results and discussion

The halfsandwich-type complex $[(p\text{-cym})\text{RuCl}_2(\text{Sb}i\text{Pr}_3)]$ (p-cym $= p\text{-MeC}_6\text{H}_4\text{CHMe}_2$) (**2**), which we considered a useful starting material for the preparation of compounds $[\text{RuCl}_2(\text{Sb}i\text{Pr}_3)_n]$ ($n = 3$ or 4) is obtained from $[(p\text{-cym})\text{RuCl}_2]_2$ and three equivalents of Sb*i*Pr$_3$ in nearly quantitative yield. The subsequent reaction of **2** with triisopropylstibine in the presence of NH_4PF_6 leads to the formation of $[(p\text{-cym})\text{RuCl}(\text{Sb}i\text{Pr}_3)_2]\text{PF}_6$ (**3**) (Scheme 1), which like **2**, is an orange, almost air-stable solid. Both *p*-cymene complexes have been characterized by elemental analysis and spectroscopic techniques. In contrast to **2**, the ^{1}H- and ^{13}C-NMR spectra of **3** display two sets of signals for both the protons and carbon nuclei of the Sb*i*Pr$_3$ ligands, which is due to the diastereotopic character of the isopropyl groups.

Although there is ample precedence for the displacement of the arene ligand in compounds of the general type $[(\text{arene})\text{RuCl}_2(\text{L})]$ by σ- and π-donor ligands [6], our attempts to prepare $[\text{RuCl}_2(\text{Sb}i\text{Pr}_3)_3]$ or $[\text{RuCl}_2(\text{Sb}i\text{Pr}_3)_4]$ from **2** and excess Sb*i*Pr$_3$ failed. Even on prolonged heating in benzene at 80°C or on continuous photolysis, no reaction between the two substrates occurs. The same is true for the cationic derivative **3**, which is also surprisingly inert toward excess triisopropylstibine.

Since further attempts to obtain a compound of the general type $[\text{RuCl}_2(\text{Sb}i\text{Pr}_3)_n]$ by ligand substitution from $[\text{RuCl}_2(\text{SbPh}_3)_4]$ and Sb*i*Pr$_3$ equally failed, we used $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ as the starting material. It was



Scheme 2.

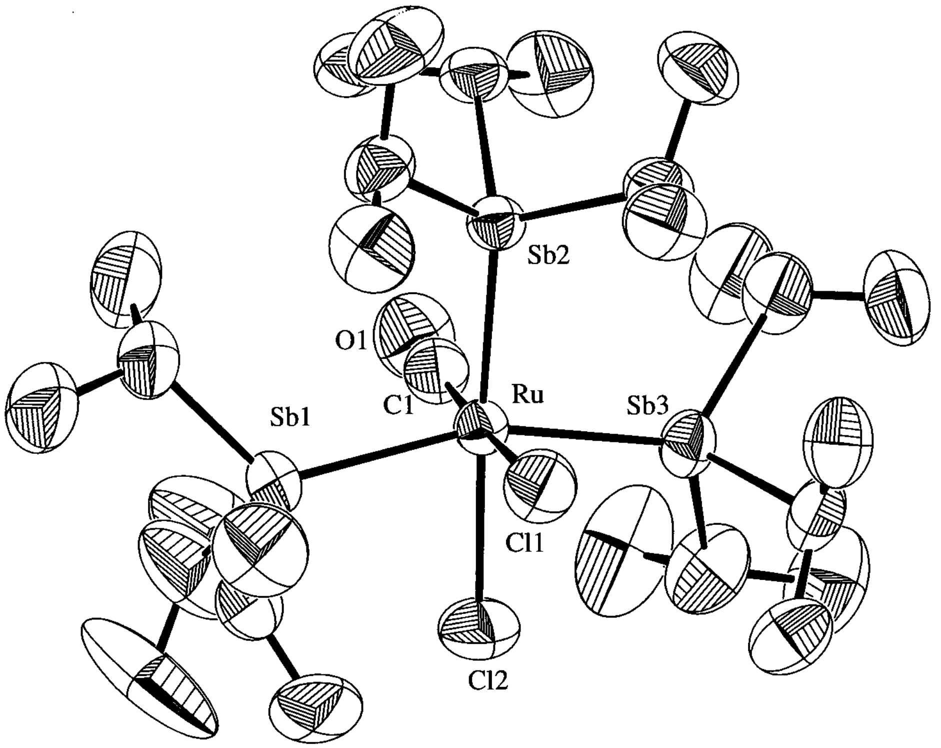


Fig. 1. Molecular structure (ORTEP diagram) of compound **4**.

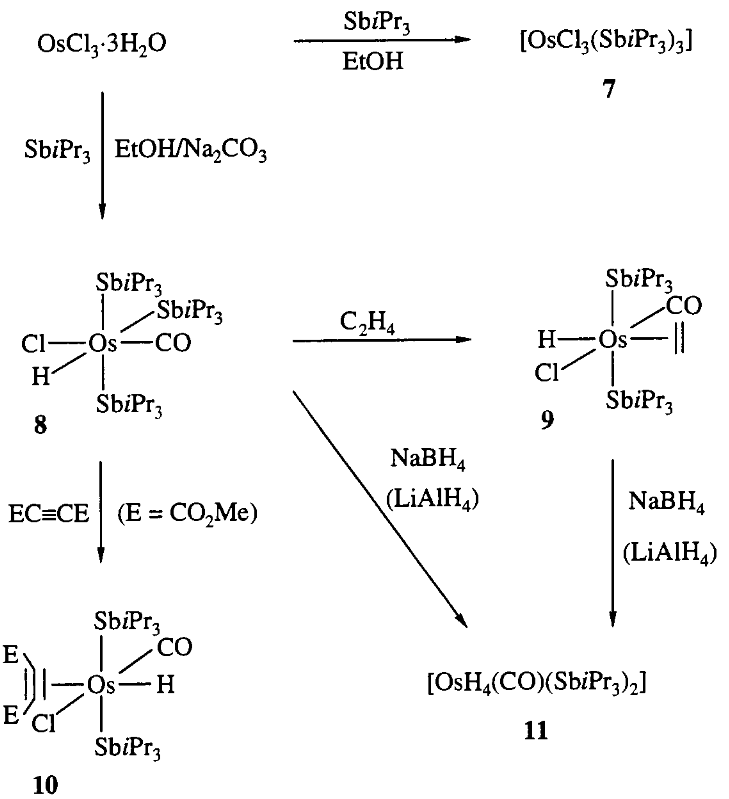
known [7], that upon passing a stream of carbon monoxide through a solution of $RuCl_3 \cdot 3H_2O$ in ethanol a 'red solution' is formed, which reacts with tertiary phosphines or arsines to yield mixed carbonyl(phosphine) or carbonyl(arsine)ruthenium complexes $[RuCl_2(CO)_n(ER_3)_{4-n}]$ ($n = 1$ or 2) [8]. If this 'red solution' is treated with $Sb\textit{i}Pr_3$, a rapid change of color from red to brown occurs and from the mixture of products yellow, air-stable $[RuCl_2(CO)(Sb\textit{i}Pr_3)_3]$ (**4**) (Scheme 2) can be isolated in 40–45% yield. Both the ^1H- and ^{13}C-NMR spectra of **4** confirm that two $Sb\textit{i}Pr_3$ ligands are stereochemically equivalent, while the third is not and thus a meridional configuration of the $Ru(Sb\textit{i}Pr_3)_3$ moiety can be assumed.

Since the spectroscopic data of **4** could not unambigously decide whether the two chloro ligands are *cis* or *trans* disposed, an X-ray crystal structure analysis was carried out. The ORTEP plot reveals (Fig. 1) that the geometry around the ruthenium center is distorted octahedral with two stibine ligands *trans* to each other and the third stibine *trans* to one chloride. The two chlorides are in a *cis* arrangement. The Sb1–Ru–Sb2 axis is significantly bent, which is probably due to the steric requirements of the bulky $Sb\textit{i}Pr_3$ units. Whereas the two Ru–Cl distances (Table 1) are almost identical, the Ru–Sb bond lengths differ slightly, the shortest being *trans* to Cl2. The range of the Ru–Sb distances is very similar to that found in $[Ru(\eta^3\text{-}C_3H_5)_2(Sb\textit{i}Pr_3)_2]$ [5], $[RuCl_2(SbPh_3)_4]$ [9] and in the dinuclear complex $[\{Ru(\eta^1\text{-}O_2CCH_3)(Sb\textit{i}Pr_3)_2\}_2(\mu\text{-}O_2CCH_3)_2(\mu\text{-}H_2O)]$ [10].

The reaction of **4** with carbon monoxide proceeds quite smoothly and affords the dicarbonyl complex $[RuCl_2(CO)_2(Sb\textit{i}Pr_3)_2]$ (**5**) in excellent yield. Under the conditions used, further displacement of the remaining two stibine ligands by CO does not occur. The behavior of **4** towards CO is thus similar to that of the compounds $[RuCl_2(CO)(AsPh_3)_3]$ [11] and $[RuHCl(CO)(EPh_3)_3]$ (E = P, As) [11,12], which also undergo a single EPh_3/CO exchange. The IR spectrum of **5** displays two CO stretching frequencies at 2040 and 1910 cm^{-1} and this supports the structural proposal for **5** shown in Scheme 2.

Table 1
Selected bond distances (Å) and bond angles (°) of **4** (with estimated S.D. in parentheses)

Ru–Sb1	2.662(1)	Ru–C1	1.89(2)
Ru–Sb2	2.598(1)	Ru–Cl1	2.455(3)
Ru–Sb3	2.639(1)	Ru–Cl2	2.449(3)
Sb1–Ru–Sb2	102.28(3)	Sb2–Ru–Cl2	172.8(1)
Sb1–Ru–C1	91.6(4)	Sb3–Ru–Cl1	90.21(8)
Sb1–Ru–Sb3	160.82(4)	Sb3–Ru–Cl2	82.01(9)
Sb1–Ru–Cl1	89.33(8)	Sb3–Ru–C1	90.3(4)
Sb1–Ru–Cl2	78.82(9)	Cl1–Ru–Cl2	88.0(1)
Sb2–Ru–C1	90.9(4)	Cl1–Ru–C1	175.8(4)
Sb2–Ru–Sb3	96.77(3)	Cl2–Ru–C1	96.2(4)
Sb2–Ru–Cl1	84.91(9)		



Scheme 3.

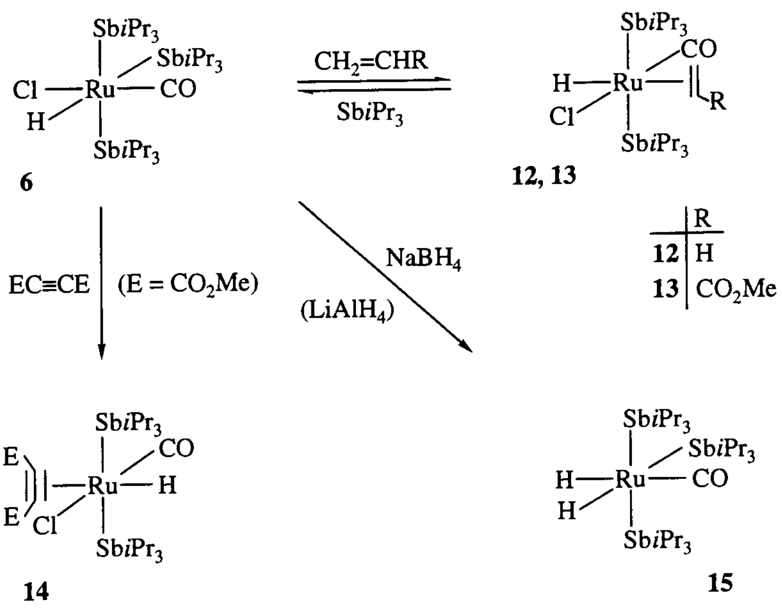
If a solution of $RuCl_3{\cdot}3H_2O$ in ethanol is treated instead of CO with Sb*i*Pr$_3$, small amounts of the chloro(hydrido)ruthenium(II) complex [RuHCl(CO)(Sb*i*Pr$_3$)$_3$] (**6**) are formed. Upon addition of Na_2CO_3 to the reaction mixture, the yield of **6** is substantially increased to ca. 60%. Typical spectroscopic features of **6**, which is a yellow almost air-stable solid, are the hydride signal at δ -8.36 (in C_6D_6) in the ^{1}H-NMR and the strong ν(CO) band at 1900 cm^{-1} in the IR spectrum.

In the same manner, by using $OsCl_3{\cdot}3H_2O$, Sb*i*Pr$_3$ and Na_2CO_3 as the starting materials, the chloro(hydrido)osmium(II) derivative [OsHCl(CO)(Sb*i*Pr$_3$)$_3$] (**8**) has been prepared (Scheme 3). In contrast to **6**, it is a white solid, the spectroscopic data of which are quite similar to those of the ruthenium counterpart. The reaction of $OsCl_3{\cdot}3H_2O$ with Sb*i*Pr$_3$ in refluxing ethanol produces in the absence of Na_2CO_3 a green solid of composition [OsCl$_3$(Sb*i*Pr$_3$)$_3$] (**7**), which is paramagnetic and therefore has been characterized only by elemental analysis. We note that related osmium(III) complexes $[OsCl_3(L)_3]$ with $L = PR_3$, AsR_3 and $SbPh_3$ are already known and have been obtained either from OsO_4/HX or $[OsX_6]^{2-}$ and ligand L [13]. A *mer* configuration of **7** is very likely as the UV/vis spectrum shows three bands at 16.2, 21.0 and 28.6×10^3 cm^{-1} being very similar to those obtained for the comparable complex *mer*-$[OsCl_3(SbPh_3)_3]$ [14].

In compound **6**, one of the Os–Sb bonds is rather labile and thus one of the stibine ligands is easily displaced by ethene or dimethyl acetylenedicarboxylate. Both products [OsHCl(CO)(C_2H_4)(Sb*i*Pr$_3$)$_2$] (**9**) and [OsHCl(CO)($MeO_2CC{\equiv}CCO_2Me$)(Sb*i*Pr$_3$)$_2$] (**10**) are white or yellow, only moderately air-sensitive solids that are soluble in most organic solvents. The NMR patterns for the protons and carbon atoms of the isopropyl groups indicate that in **9** and **10** the two stibine ligands are *trans* disposed. Neither on heating nor on photolysis of **9** and **10** does an insertion of the olefin or the alkyne into the Os–H bond take place.

The tris(stibine) complex **8**, as well as the ethene derivative **9**, react with $NaBH_4$ in ether/methanol or with $LiAlH_4$ in ether at r.t. to give the tetrahydrido compound [OsH$_4$(CO)(Sb*i*Pr$_3$)$_2$] (**11**). The colorless oil did not crystallize even after it was stored for 24 h at -78°C. The ^{1}H-NMR spectrum of **11** displays, besides a doublet for the SbCHC*H*$_3$ and a septett for the SbC*H*CH$_3$ protons, a sharp singlet for the metal-bonded hydrides at δ -10.65. This chemical shift is quite similar to that of the analogous phosphine complex [OsH$_4$(CO)(P*i*Pr$_3$)$_2$] which was prepared from [OsHCl(CO)(P*i*Pr$_3$)$_2$] and $NaBH_4$ [15].

The results describing the reactivity of **6** towards C_2H_4, $CH_2{=}CHCO_2Me$, and $NaBH_4$ (or $LiAlH_4$) are summarized in Scheme 4. Treatment of the starting material with either ethene or methylacrylate leads to



Scheme 4.

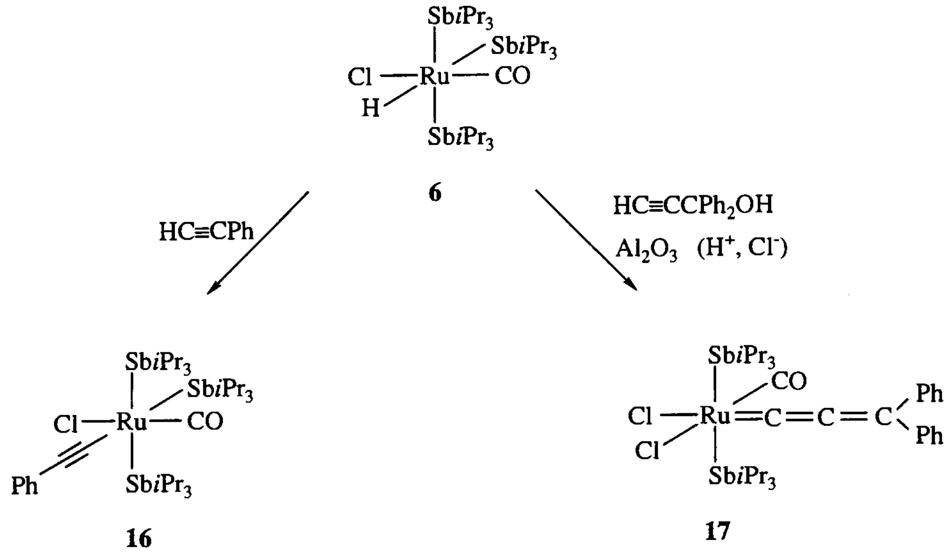
the displacement of one stibine ligand and to the formation of the olefin complexes **12** and **13**, which however are only stable in the presence of excess C_2H_4 or $CH_2{=}CHCO_2Me$, respectively. If the reaction mixtures containing **12** and **13** are worked up by removing all volatile substances in vacuo, the chloro(hydrido) complex **6** is reformed. The spectroscopic data of the ethene derivative are very similar to those of the osmium compound **9**, which suggests that the in situ generated product **12** contains the hydrido and the ethene ligands in *trans* disposition. Since the chemical shift of the hydride signal in the ^{1}H-NMR spectrum of **13** (δ -4.74) is almost identical to that of **12** (δ -4.84), we assume that the stereochemistry of both complexes is the same.

In contrast to the olefin compounds **12** and **13**, the related alkyne complex $[RuHCl(CO)(MeO_2CC{\equiv}CCO_2Me)(SbiPr_3)_2]$ (**14**) is quite stable and has been isolated as a red solid in 63% yield. Likewise to the osmium counterpart, the ^{1}H-NMR spectrum of **14** displays a sharp singlet at δ -3.74, which together with the IR spectroscopic data supports the structural proposal. The reaction of **6** with either $NaBH_4$ (in ether/methanol) or $LiAlH_4$ (in ether) affords the dihydrido complex $[RuH_2(CO)(SbiPr_3)_3]$ (**15**), which was recently prepared in our laboratory from $[RuH_2(H_2)(SbiPr_3)_3]$ and CO [5]. Even if we changed the reaction conditions, the formation of a tetrahydrido or dihydrido(dihydrogen) derivative analogous to **11** could not be observed.

Whereas dimethyl acetylenedicarboxylate reacts with **6** by displacement of a stibine ligand, phenylacetylene behaves differently and upon treatment with **6** undergoes a hydride substitution reaction to give $[RuCl(C{\equiv}CPh)(CO)(SbiPr_3)_3]$ (**16**) (Scheme 5). We assume that in the initial step, an insertion of the alkyne into the Ru–H bond takes place and a vinyl derivative is formed as an intermediate. This could then react with a second molecule of $PhC{\equiv}CH$ to yield **16** and styrene, the latter has been detected by NMR spectroscopy.

The alkynyl complex **16** is quite stable and for a short period of time can be even handled on air. However, in THF or benzene solution, it slowly decomposes. As far as the NMR data of **16** are concerned, the chemical shift and the coupling constants of the signals of the isopropyl protons and carbon nuclei are very similar to those of **4**, and therefore, a meridional arrangement of the three stibine ligands can be proposed. The ^{13}C-NMR spectrum of **16** displays two singlets for the alkynyl carbon atoms at δ 118.6 and 101.6, the values being in agreement to those of the corresponding bisphosphine ruthenium derivative $[Ru(\eta^2\text{-}O_2CCH_3)(C{\equiv}CPh)(CO)(PPh_3)_2]$ [16].

The synthesis of the allenylidene complex $[RuCl_2({=}C{=}C{=}CPh_2)(CO)(SbiPr_3)_2]$ (**17**) follows earlier work by Selegue [17] and, for non-Cp containing rhodium and ruthenium compounds, by some of us [18]. Treatment of **6** in benzene with an excess of the propargylic alcohol $HC{\equiv}CCPh_2OH$ affords a red solution in which the olefin $CH_2{=}CHCPh_2OH$ can be detected by ^{1}H-NMR spectroscopy. Since this observation is in agreement with that made during the preparation of **16** (where styrene is formed as the by-product), we assume that in the initial step of the reaction of **6** with $HC{\equiv}CCPh_2OH$ the functionalized alkynyl complex $[RuCl(C{\equiv}CCPh_2OH)(CO)(SbiPr_3)_3]$ is formed. Passing a benzene solution of the crude reaction product over acidic Al_2O_3 (which always contains chloride ions)



Scheme 5.

finally gives the allenylidene compound **17** in moderate yield. In order to rationalize the formation of **17**, we believe that by attack of H_3O^+ to the OH group of the supposed $RuC{\equiv}CCPh_2OH$ unit a cationic allenylidene ruthenium species is generated as an intermediate, which on substitution of Sb*i*Pr$_3$ by Cl^-, forms **17**. Characteristic features for **17** are the strong C=C=C stretch in the IR spectrum at 1960 cm^{-1} and the three low-field signals for the allenylidene carbon atoms at δ 299.7, 210.2 and 149.1 in the ^{13}C-NMR spectrum. The chemical shift of the resonance for the Ru=C nuclei (δ 299.7) is very similar to that of the structurally related bis(phosphine) complex $[RuCl_2(=C=C=CPh_2)\{\kappa^1(P)$-$i$$Pr_2PCH_2CO_2Me\}\{\kappa^2(P,O)$-$i$$Pr_2PCH_2C(O)OMe\}]$ (δ 306.2) ([18]c).

The structural proposal for **17** has been confirmed by an X-ray crystal structure analysis. As it is shown in Fig. 2, the metal center is octahedrally coordinated with the two stibine ligands *trans* disposed. Both the CO and the allenylidene unit are *trans* to chloride, the distance Ru–Cl1 being somewhat longer than Ru–Cl2 (Table 2). The bond length Ru–Cl is comparable with that of $[RuCl_2(=C=C=CPh_2)\{\kappa^1(P)$-$i$$Pr_2PCH_2CO_2Me\}\{\kappa^2(P,O)$-$i$$Pr_2PCH_2C(O)OMe\}]$ (1.84(1) Å) ([18]c). The two carbon–carbon distances in the Ru=C=C=C chain of **17** are also quite similar to those found in $[RuCl_2(=C=C=CPh_2)\{\kappa^1(P)$ - $i$$Pr_2PCH_2CO_2Me\}\{\kappa^2(P,O)$-$i$$Pr_2PCH_2C(O)OMe\}]$ and other transition metal allenylidene complexes [18,19]. This implies that besides the usual bonding formulation a second resonance structure, corresponding to a zwitterionic species has to be taken into consideration. The Sb–Ru–Sb axis of **17** is almost exactly linear as is the Ru=C=C=C chain. It should be noted that the distances between ruthenium and the carbon atom of CO and the α-carbon atom of the allenylidene ligand are virtually identical, which indicates that in agreement with theoretical calculations [20] the π-acceptor character of unsaturated carbenes such as vinylidenes or allenylidenes and of CO is nearly the same.

3. Experimental

All experiments were carried out under an atmosphere of argon by using Schlenk techniques. The starting materials **1** [21] and Sb*i*Pr3 ([1]d, [22]) were prepared by published methods. IR: Perkin-Elmer 1320, UV/vis: Hitachi U-2000, NMR: Bruker AC 200 and AMX 400. Melting and decomposition points were determined by DTA.

3.1. Preparation of [(p-cym)RuCl$_2$(SbiPr$_3$)] (2)

A solution of 423 mg (0.69 mmol) of **1** in 30 ml of CH_2Cl_2 was treated with 430 µl (2.08 mmol) of Sb*i*Pr$_3$ and stirred for 2 h at r.t. The solution was filtered and the filtrate was brought to dryness in vacuo. After the oily residue was layered with 10 ml of pentane, an orange solid was formed; this was filtered and dried in vacuo. Yield 715 mg (93%); m.p. 90°C (decomp.). Anal. Found: C, 40.90; H, 6.11. $C_{15}H_{32}Cl_2RuSb$ calc.: C, 40.96; H, 6.33. ^1H-NMR (400 MHz, C_6D_6): δ 5.49, 5.38 (both d; $J(HH) = 5.6$ Hz; 4H; C_6H_4), 2.98 (sept; $J(HH) = 7.2$ Hz; 1H; $CHCH_3$ of *p*-cym), 2.41 (sept; $J(HH) = 7.6$ Hz; 3H; $SbCHCH_3$), 1.91 (s; 3H; $C_6H_4CH_3$), 1.34 (d; $J(HH) = 7.6$ Hz; 18H; $SbCHCH_3$), 1.17 (d; $J(HH) = 7.2$ Hz; 6H; $CHCH_3$ of *p*-cym). ^{13}C-NMR (100.6 MHz, C_6D_6): δ 105.2, 92.8 (both s; CCH_3 and $CCHCH_3$ of *p*-cym), 85.0, 80.9 (both s; CH of C_6H_4), 31.0 (s; $CHCH_3$ of *p*-cym), 22.5 (s; $CHCH_3$ of

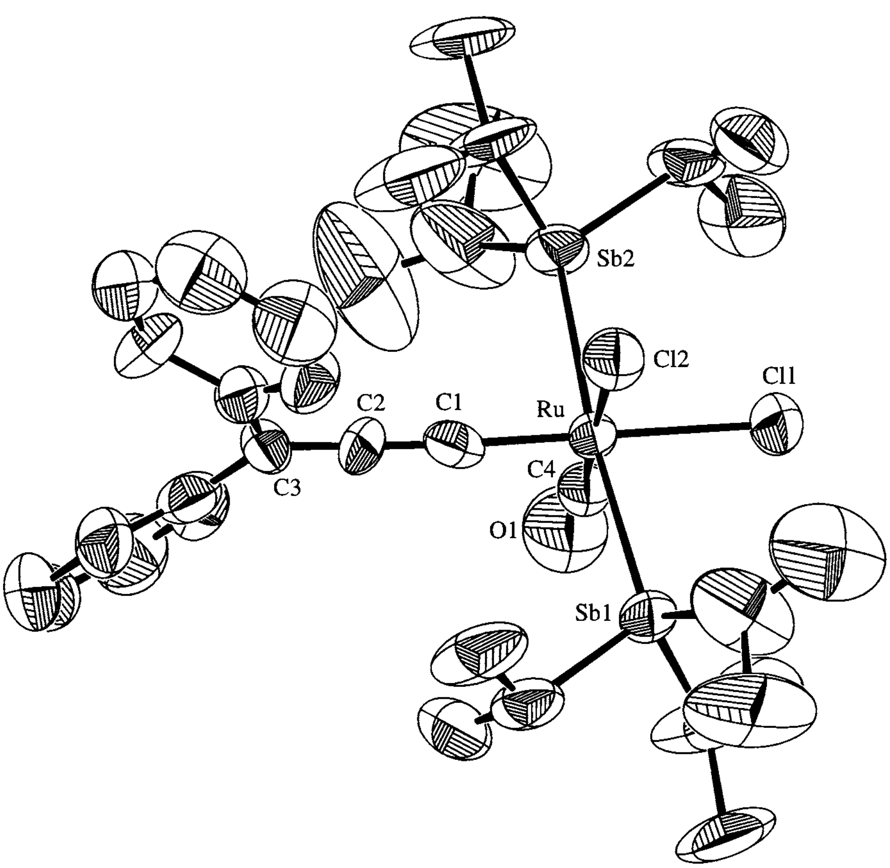


Fig. 2. Molecular structure (ORTEP diagram) of compound **17**.

p-cym), 22.0 (s; SbCH*C*H$_3$), 20.3 (s; Sb*C*HCH$_3$), 18.4 (s; C$_6$H$_4$*C*H$_3$).

3.2. Preparation of [(p-cym)RuCl(SbiPr$_3$)$_2$]PF$_6$ (3)

A solution of 346 mg (0.62 mmol) of **2** in 30 ml of methanol was treated with 650 µl (3.14 mmol) of Sb*i*Pr$_3$ and 172 mg (1.05 mmol) of NH$_4$PF$_6$ and stirred for 2 h at r.t. The solvent was removed, the residue was dissolved in 30 ml of CH$_2$Cl$_2$ and the solution was filtered with Celite. The filtrate was concentrated to ca. 1 ml in vacuo and after 10 ml of pentane were added, an orange solid precipitated; it was separated from the mother liquor and dried in vacuo. Yield 503 mg (88%); m.p. 80°C (decomp.). Anal. Found: C, 36.15; H, 5.78. C$_{28}$H$_{56}$ClF$_6$PRuSb$_2$ calc.: C, 36.65; H, 6.15. ^{1}H-NMR (400 MHz, CDCl$_3$): δ 6.30, 5.98 (both d; J(HH) = 6.0 Hz; 4H; C$_6$H$_4$), 2.61 (sept; J(HH) = 7.6 Hz; 6H; SbC*H*CH$_3$), 2.56 (sept; J(HH) = 7.2 Hz; 1H; C*H*CH$_3$ of *p*-cym), 2.04 (s; 3H; C$_6$H$_4$C*H*$_3$), 1.47, 1.44 (both d; J(HH) = 7.6 Hz; 36H; SbCHC*H*$_3$), 1.25 (d; J(HH) = 7.2 Hz; 6H; CHC*H*$_3$ of *p*-cym). ^{13}C-NMR (100.6 MHz, CDCl$_3$): δ 109.0, 96.5 (both s; *C*CH$_3$ and *C*CHCH$_3$ of *p*-cym), 85.3, 80.2 (both s; CH of C$_6$H$_4$), 31.1 (s; *C*HCH$_3$ of *p*-cym), 22.7 (s; Sb*C*HCH$_3$), 22.3, 21.9 (both s; SbCH*C*H$_3$), 21.8 (s; CH*C*H$_3$ of *p*-cym), 19.8 (s; C$_6$H$_4$*C*H$_3$). ^{31}P-NMR (162.0 MHz, CDCl$_3$): δ −144.1 (sept; J(PF) = 712.8 Hz; PF$_6$).

Table 2
Selected bond distances (Å) and bond angles (°) of **17** (with estimated S.D. in parentheses)

Ru–Sb1	2.680(2)	Ru–C1	1.88(2)
Ru–Sb2	2.679(2)	Ru–C4	1.88(4)
Ru–Cl1	2.469(5)	C1–C2	1.24(2)
Ru–Cl2	2.41(2)	C2–C3	1.34(2)
Sb1–Ru–Sb2	174.31(7)	Sb2–Ru–C4	89(1)
Sb1–Ru–C1	98.8(5)	C1–Ru–Cl1	178.6(6)
Sb1–Ru–Cl1	80.6(1)	C1–Ru–Cl2	90.1(7)
Sb1–Ru–Cl2	89.4(3)	Cl1–Ru–Cl2	88.7(5)
Sb1–Ru–C4	92(1)	Cl1–Ru–C4	88(1)
Sb2–Ru–C1	86.8(5)	Cl2–Ru–C4	176(1)
Sb2–Ru–Cl1	93.8(1)	Ru–C1–C2	177(2)
Sb2–Ru–Cl2	89.4(3)	C1–C2–C3	174(2)

3.3. Preparation of cis,mer-[RuCl$_2$(CO)(SbiPr$_3$)$_3$] (4)

A slow stream of CO was passed through a solution of 438 mg (1.68 mmol) of RuCl$_3$·3H$_2$O in 35 ml of ethanol for 30 min at 80°C. After cooling to r.t., the solution was treated with 1.04 ml (5.02 mmol) of Sb*i*Pr$_3$ which led to an instantaneous change of color from red to brown. The solution was stirred for 2 h and then concentrated to ca. 10 ml in vacuo. After it was stored for 3 h at 25°C, a yellow solid precipitated which was filtered, washed twice with 5-ml portions of methanol and dried in vacuo. Yield 665 mg (42%); m.p. 66°C (decomp.). Anal. Found: C, 34.99; H, 6.91. $C_{28}H_{63}Cl_2ORuSb_3$ calc.: C, 35.29; H, 6.66. IR (C_6H_6): ν(CO) 1905 cm^{-1}. ^{1}H-NMR (200 MHz, C_6D_6): δ 2.62 (sept; J(HH) = 7.3 Hz; 6H; SbC*H*CH$_3$), 2.16 (sept; J(HH) = 7.3 Hz; 3H; SbC*H*CH$_3$), 1.58, 1.57, 1.41 (all d; J(HH) = 7.3 Hz; 54H; SbCHC*H*$_3$). ^{13}C-NMR (50.3 MHz, C_6D_6): δ 200.8 (s; CO), 24.4, 22.6, 22.4 (all s; SbCH*C*H$_3$), 22.3, 22.2 (both s; Sb*C*HCH$_3$).

3.4. Preparation of *cis,cis,trans*-[RuCl$_2$(CO)$_2$(SbiPr$_3$)$_2$] (**5**)

A slow stream of CO was passed through a solution of 273 mg (0.30 mmol) of **4** for 5 min at r.t. After the solution was stirred for 20 min, the solvent was removed and the residue was layered with 3 ml of methanol (0°C). A yellow solid precipitated, which was filtered, washed twice with 3-ml portions of methanol (0°C) and dried in vacuo. Yield 204 mg (76%); m.p. 63°C (decomp.). Anal. Found: C, 32.82; H, 5.85. $C_{20}H_{42}Cl_2O_2RuSb_2$ calc.: C, 32.91; H, 5.80. IR (C_6H_6): ν(CO) 2040, 1960 cm^{-1}. ^{1}H-NMR (200 MHz, C_6D_6): δ 2.60 (sept; J(HH) = 7.3 Hz; 6H; SbC*H*CH$_3$), 1.39 (d; J(HH) = 7.3 Hz; 36H; SbCHC*H*$_3$).

3.5. Preparation of [RuHCl(CO)(SbiPr$_3$)$_3$] (**6**)

A solution of 1.06 g (4.04 mmol) of $RuCl_3 \cdot 3H_2O$ and 5.0 ml (24.15 mmol) of Sb*i*Pr$_3$ in 60 ml of ethanol was heated under reflux for 1 h and then treated with an excess (ca. 3 g) of Na_2CO_3. A change of color from brown to yellow occurred. The solution was continuously refluxed for 5 h and then cooled to r.t. The solvent was removed, the residue was extracted three times with 20-ml portions of pentane and the combined extracts were brought to dryness in vacuo. After the oily residue was layered with 10 ml of methanol, a yellow solid precipitated, which was filtered, washed twice with 5-ml portions of methanol (0°C) and dried in vacuo. Yield 2.30 g (62%); m.p. 55°C (decomp.). Anal. Found: C, 36.17; H, 6.95; Sb, 39.00. $C_{28}H_{64}ClORuSb_3$ calc.: C, 36.61; H, 7.02; Sb, 39.76. IR (hexane): ν(CO) 1900 cm^{-1}. ^{1}H-NMR (400 MHz, C_6D_6): δ 2.37 (sept; J(HH) = 7.3 Hz; 6H; SbC*H*CH$_3$), 2.26 (sept; J(HH) = 7.3 Hz; 3H; SbC*H*CH$_3$), 1.51, 1.50, 1.44 (all d; J(HH) = 7.3 Hz; 54H; SbCHC*H*$_3$), −8.36 (s; 1H; RuH). ^{13}C-NMR (100.6 MHz, C_6D_6): δ 201.5 (s; CO), 22.1, 21.8, 21.7 (all s; SbCH*C*H$_3$), 21.5, 20.3 (both s; Sb*C*HCH$_3$).

3.6. Preparation of [OsCl$_3$(SbiPr$_3$)$_3$] (**7**)

A solution of 123 mg (0.36 mmol) of $OsCl_3 \cdot 3H_2O$ in 15 ml of ethanol was treated with 450 µl (2.17 mmol) of Sb*i*Pr$_3$ and heated under reflux for 1 h. A smooth change of color from brown to green occurred. After the solution was brought to r.t., it was concentrated to ca. 5 ml in vacuo. A green solid precipitated which was filtered, washed with small portions of methanol and dried in vacuo. Yield 275 mg (73%); m.p. 78°C (decomp.). Anal. Found: C, 30.66; H, 6.26; Sb, 34.37. $C_{27}H_{63}Cl_3OsSb_3$ calc.: C, 30.90; H, 6.50; Sb, 34.80. UV/vis (CH_2Cl_2): 16.2, 21.0 and 28.6 × 10^3 cm^{-1}.

3.7. Preparation of [OsHCl(CO)(SbiPr$_3$)$_3$] (**8**)

A solution of 386 mg (1.10 mmol) of $OsCl_3 \cdot 3H_2O$ and 1.4 ml (6.76 mmol) of Sb*i*Pr$_3$ in 25 ml of ethanol was heated under reflux for 1 h. A smooth change of color from brown to green occurred. After the solution was brought to r.t., an excess of Na_2CO_3 (ca. 1 g) was added and the reaction mixture was again refluxed for 2 h. During this process, the solution became colorless. After cooling to r.t., the solvent was removed and the remaining residue was extracted twice with 20-ml portions of pentane. The combined extracts were brought to dryness in vacuo and the oily residue was treated with 10 ml of methanol. A colorless solid precipitated which was separated from the mother liquor, washed twice with small portions of methanol (0°C) and dried in vacuo. Yield 789 mg (71%); m.p. 103°C (decomp.). Anal. Found: C, 33.47; H, 6.14; Sb, 36.25. $C_{28}H_{64}ClOOsSb_3$ calc.: C, 33.37; H, 6.40; Sb, 37.02. IR (C_6H_6): ν(CO) 1875 cm^{-1}. ^{1}H-NMR (200 MHz, C_6D_6): δ 2.42 (sept; J(HH) = 7.3 Hz; 6H; SbC*H*CH$_3$), 2.30 (sept; J(HH) = 7.3 Hz; 3H; SbC*H*CH$_3$), 1.52, 1.48, 1.43 (all d; J(HH) = 7.3 Hz; 54H; SbCHC*H*$_3$), −9.21 (s; 1H; OsH). ^{13}C-NMR (50.3 MHz, C_6D_6): δ 178.1 (s; CO), 22.7, 22.6, 21.9 (all s; SbCH*C*H$_3$), 21.8, 20.1 (both s; Sb*C*HCH$_3$).

3.8. Preparation of [OsHCl(CO)(C$_2$H$_4$)(SbiPr$_3$)$_2$] (**9**)

A slow stream of ethene was passed through a solution of 621 mg (0.62 mmol) of **8** in 15 ml of benzene for 1 min at r.t. After the solution was stirred for 1 h, the solvent was removed and the oily residue was treated with 5 ml of methanol. A colorless solid precipitated was separated from the mother liquor, washed twice with small portions of methanol (0°C) and dried in vacuo. Yield 427 mg (88%); m.p. 92°C (decomp.). Anal. Found: C, 32.44; H, 5.85. $C_{21}H_{47}ClOOsSb_2$ calc.: C, 32.14; H, 6.04. IR (C_6H_6): ν(CO) 1895 cm^{-1}. ^{1}H-NMR (200 MHz, C_6D_6): δ 2.85 (br s; 4H; C_2H_4), 2.41 (sept; J(HH) = 7.3 Hz; 6H; SbC*H*CH$_3$), 1.37, 1.32 (both d; J(HH) = 7.3 Hz; 36H; SbCHC*H*$_3$), −4.91 (s; 1H;

OsH). ^{13}C-NMR (50.3 MHz, C_6D_6): δ 175.2 (s; CO), 28.9 (s; C_2H_4), 21.3, 21.2 (both s; SbCH*C*H$_3$), 18.4 (s; Sb*C*HCH$_3$).

3.9. Preparation of [OsHCl(CO)(MeO$_2$CC≡CCO$_2$Me)(Sb*i*Pr$_3$)$_2$] (**10**)

A solution of 147 mg (0.15 mmol) of **8** and 35 μl (0.28 mmol) of $C_2(CO_2Me)_2$ in 10 ml of benzene was stirred for 4 h at r.t. The solvent was removed in vacuo and the oily residue was treated with 3 ml of methanol. A yellow solid precipitated which was filtered, washed with small portions of methanol (0°C) and dried in vacuo. Yield 97 mg (72%); m.p. 70°C (decomp.). Anal. Found: C, 34.06; H, 5.74. $C_{25}H_{49}ClO_5OsSb_2$ calc.: C, 33.41; H, 5.49. IR (C_6H_6): ν(CO) 1925, ν(CO_2) 1700 cm^{-1}. ^{1}H-NMR (400 MHz, C_6D_6): δ 3.51 (s; 6H; OCH$_3$), 2.75 (sept; *J*(HH) = 7.4 Hz; 6H; SbC*H*CH$_3$), 1.41, 1.39 (both d; *J*(HH) = 7.4 Hz; 36H; SbCHC*H*$_3$), − 3.92 (s; 1H; OsH). ^{13}C-NMR (100.6 MHz, C_6D_6): δ 175.9 (s; CO), 156.6 (s; *C*O$_2$CH$_3$), 100.4 (s; C≡C), 51.1 (s; CO$_2$*C*H$_3$), 21.9, 21.4 (both s; SbCH*C*H$_3$), 20.2 (s; Sb*C*HCH$_3$).

3.10. Reaction of **8** and **9** with NaBH$_4$ or LiAlH$_4$

A solution of either 112 mg (0.11 mmol) of **8** or 113 mg (0.14 mmol) of **9** in 15 ml of diethylether was treated with an excess (ca. 300 mg) of NaBH$_4$ and 2 ml of methanol. The solution was stirred for 4 h at 60°C and then cooled to r.t. The solvent was removed, the residue was extracted twice with 15-ml portions of pentane and the combined extracts were brought to dryness in vacuo. A colorless oil was isolated, which besides small amounts of impurities, contained the tetrahydrido complex [OsH$_4$(CO)(Sb*i*Pr$_3$)$_2$] (**11**) as the main product. An alternative procedure to generate **11** is treating a solution of 117 mg (0.12 mmol) of **8** or 101 mg (0.13 mmol) of **9** in 15 ml of diethylether with an excess (ca. 200 mg) of LiAlH$_4$. The reaction mixture was worked up as described above. On both routes the yield of **11** is 85–90%. Spectroscopic data of **11**: IR (C_6H_6): ν(CO) 1935 cm^{-1}. ^{1}H-NMR (400 MHz, C_6D_6): δ 1.85 (sept; *J*(HH) = 7.2 Hz; 6H; SbC*H*CH$_3$), 1.22 (d; *J*(HH) = 7.2 Hz; 36H; SbCHC*H*$_3$), − 10.65 (s; 4H; OsH). ^{13}C-NMR (100.6 MHz, C_6D_6): δ 182.9 (s; CO), 20.9 (s; SbCH*C*H$_3$), 18.3 (s; Sb*C*HCH$_3$).

3.11. Reaction of **6** with olefins CH$_2$=CHR (R = H, CO$_2$Me)

(a) A slow stream of ethene was passed through a solution of 167 mg (0.18 mmol) of **6** in 10 ml of benzene for 5 min at r.t. The ^{1}H-NMR spectrum of the solution indicated that the ethene complex [RuHCl(CO)(C_2H_4)(Sb*i*Pr$_3$)$_2$] (**12**) was formed. After the solvent was removed in vacuo and the residue treated with methanol, a yellow solid was isolated, which due to the ^{1}H-NMR spectrum was the starting material **6**. ^{1}H-NMR data (200 MHz, C_6D_6) of **12**: δ 3.48 (s; 4H; C_2H_4), 2.38 (sept; *J*(HH) = 7.3 Hz; 6H; SbC*H*CH$_3$), 1.40, 1.36 (both d; *J*(HH) = 7.3 Hz; 36H; SbCHC*H*$_3$), − 4.84 (s; 1H; RuH).

(b) A solution of 111 mg (0.12 mmol) of **6** in 10 ml of benzene was treated with 33 μl (0.31 mmol) of methylacrylate and stirred for 5 min at r.t. The ^{1}H-NMR spectrum of the solution indicated that the olefin complex [RuHCl(CO)(CH$_2$=CHCO$_2$Me)(Sb*i*Pr$_3$)$_2$] (**13**) was formed. Attempts to isolate **13** led to the reformation of the starting material **6**. ^{1}H-NMR data (200 MHz, C_6D_6) of **13**: δ 4.40 (dd; *J*(HH) = 11.0 and 8.5 Hz; 1H; =C*H*CO$_2$Me), 4.13 (d; *J*(HH) = 11.0 Hz; 1H of CH$_2$), 3.41 (s; 3H; OCH$_3$), 2.74, 2.36 (both sept; *J*(HH) = 7.3 Hz; 6H; SbC*H*CH$_3$), 1.48, 1.38, 1.33, 1.32 (all d; *J*(HH) = 7.3 Hz; 36H; SbCHC*H*$_3$), − 4.74 (s; 1H; RuH), signal of one proton of the CH$_2$ unit of **13** covered by CH$_2$ signal of free CH$_2$=CHCO$_2$Me.

3.12. Preparation of [RuHCl(CO)(MeO$_2$CC≡CCO$_2$Me)(SbiPr$_3$)$_2$] (**14**)

A solution of 156 mg (0.17 mmol) of **6** in 10 ml of benzene was treated with 63 μl (0.51 mmol) of $C_2(CO_2Me)_2$ at r.t. A rapid change of color from yellow to red occurred. After the reaction mixture was stirred for 30 min, the solvent was removed and the oily residue treated with 3 ml of methanol. A red solid precipitated, which was separated from the mother liquor, washed twice with small portions of methanol (0°C) and dried in vacuo. Yield 87 mg (63%); m.p. 87°C (decomp.). Anal. Found: C, 37.40; H, 5.99. $C_{25}H_{49}ClO_5RuSb_2$ calc.: C, 37.09; H, 6.10. IR (THF): ν(CO) 1955, ν(CO_2) 1705 cm^{-1}. ^{1}H-NMR (200 MHz, C_6D_6): δ 3.48 (s; 6H; OCH$_3$), 2.71 (sept; *J*(HH) = 7.9 Hz; 6H; SbC*H*CH$_3$), 1.43, 1.42 (both d; *J*(HH) = 7.9 Hz; 36H; SbCHC*H*$_3$), − 3.74 (s; 1H; RuH).

3.13. Reaction of **6** with NaBH$_4$ or LiAlH$_4$

A solution of 117 mg (0.13 mmol) of **6** in 15 ml of diethylether was treated with an excess (ca. 300 mg) of NaBH$_4$ and 3 ml of methanol and stirred for 3 h at r.t. The solvent was removed and the residue was extracted twice with 15 ml of pentane. The combined extracts were brought to dryness in vacuo and after the oily residue was treated with 3 ml of methanol, a colorless solid was isolated. The ^{1}H-NMR spectrum revealed that besides small amounts of impurities, the dihydrido complex [RuH$_2$(CO)(Sb*i*Pr$_3$)$_3$] (**15**) was formed. It was identified by comparison of the NMR data with those of an authentic sample [5]. An alternative procedure to generate **15** is treating a solution of 124 mg (0.13 mmol) of **6** in 15 ml of diethylether with an excess (ca. 200 mg) of $LiAlH_4$. After the reaction mixture was worked up as described above, the formation of **15** was confirmed by NMR spectroscopy.

3.14. Preparation of [RuCl(C≡CPh)(CO)(SbiPr$_3$)$_3$] (16)

A solution of 213 mg (0.23 mmol) of **6** in 10 ml of benzene was treated with 84 μl (0.76 mmol) of phenylacetylene and stirred for 30 min at r.t. A smooth change of color from yellow to red occurred. The solvent was removed in vacuo and the oily residue treated with 3 ml of pentane. A yellow solid precipitated, which was separated from the mother liquor, washed with 3 ml of pentane (0°C) and dried in vacuo. Yield 134 mg (57%); m.p. 52°C (decomp.). Anal. Found: C, 43.00; H, 6.98. $C_{36}H_{68}ClORuSb_3$ calc.: C, 42.45; H, 6.73. IR (THF): ν(C≡C) 2100, ν(CO) 1920 cm^{-1}. ^{1}H-NMR (200 MHz, C_6D_6): δ 7.59–6.91 (m; 5H; C_6H_5), 2.62 (sept; J(HH) = 7.3 Hz; 6H; SbCHCH$_3$), 2.23 (sept; J(HH) = 7.3 Hz; 3H; SbCHCH$_3$), 1.58, 1.57, 1.49 (all d; J(HH) = 7.3 Hz; 54H; SbCHCH_3). ^{13}C-NMR (50.3 MHz, C_6D_6): δ 201.1 (s; CO), 131.5, 130.3, 129.9, 125.6 (all s; C_6H_5), 118.6 (s; C≡CPh), 101.6 (C≡CPh), 23.8, 23.6, 23.1 (all s; SbCHCH$_3$), 22.9, 22.8 (both s; SbCHCH$_3$).

3.15. Preparation of [RuCl$_2$(=C=C=CPh$_2$)(CO)(SbiPr$_3$)$_2$] (17)

A solution of 136 mg (0.15 mmol) of **6** in 10 ml of benzene was treated with 0.95 ml (0.38 mmol) of a 0.4 M solution of HC≡CCPh$_2$OH in toluene and stirred for 1 h at r.t. A change of color from yellow to red occurred. The solvent was removed, the residue was dissolved in 2 ml of benzene and the solution was chromatographed on Al_2O_3 (acidic, activity grade I, length of column 7 cm). With benzene, a yellow fraction was eluted that contained a mixture of products and was discarded. A red fraction was eluted with diethylether, which was brought to dryness in vacuo. The residue was extracted with 30 ml of pentane, the extract was concentrated to ca. 10 ml and then stored for 12 h at −78°C. A red solid precipitated, which was filtered, washed with small portions of pentane (−20°C) and dried in vacuo. Yield 46 mg (34%); m.p. 56°C (decomp.). Anal. Found: C, 45.61; H, 6.13. $C_{34}H_{52}Cl_2ORuSb_2$ calc.: C, 45.77; H, 5.87. IR (THF): ν(C=C=C) 1960, ν(CO) 1920 cm^{-1}. ^{1}H-NMR (200 MHz, C_6D_6): δ 8.06–7.02 (m; 10H; C_6H_5), 2.54 (sept; J(HH) = 7.3 Hz; 6H; SbCHCH$_3$), 1.44, 1.35 (both d; J(HH) = 7.3 Hz; 36H; SbCHCH_3). ^{13}C-NMR (50.3 MHz, C_6D_6): δ 299.7 (s; Ru=C), 210.2 (s; Ru=C=C), 197.3 (s; CO), 149.1 (s; CPh$_2$), 143.2 (s; *ipso*-C of C_6H_5), 131.3, 130.8, 127.5 (all s; C_6H_5), 21.8, 21.5 (both s; SbCHCH$_3$), 21.0 (s; SbCHCH$_3$).

3.16. Crystal structure analysis of 4

Single crystals were grown from ethanol. Crystal data (from 25 reflections with $11° < \Theta < 14°$): orthorhombic, space group $Pna2_1$ (no. 33), $a = 23.159(3)$, $b = 10.314(3)$, $c = 16.134(3)$ Å, $V = 3854(1)$ Å^3; $Z = 4$, $D_{calc.} = 1.641$ g cm^{-3}, $\mu = 2.632$ mm^{-1}. Crystal size $0.35 \times 0.25 \times 0.25$ mm^3. Enraf Nonius CAD4 diffractometer, Mo–K$_\alpha$ radiation (0.71073 Å), graphite monochromator, $T = 293(2)$ K, ω/Θ scan, max. $2\Theta = 56°$; 5521 reflections scanned, 4805 reflections independent, 4804 included in dataset; intensity data corrected for Lorentz and polarization effects, empirical absorption correction applied (Ψ-scans, minimum transmission 92.35%). The structure was solved by direct methods (SHELXS-86); atomic coordinates were refined by full-matrix least-squares against F_o^2 (334 parameters, SHELXL-93). The positions of the hydrogen atoms were calculated according to ideal geometry (distance C–H 0.95 Å). $R_1 = 0.0355$, $wR_2 = 0.0682$ for 3779 observed reflections [$I > 2\sigma(I)$], $R_1 = 0.0710$, $wR_2 = 0.0874$ for all 4804 data reflections; reflex to parameter ratio 14.4; residual electron density $+1.092/-0.622$ eÅ^{-3}.

3.17. Crystal structure analysis of 17

Single crystals were grown from cyclohexane. Crystal data (from 25 reflections with $11° < \Theta < 14°$): triclinic, space group $P\bar{1}$ (no. 2), $a = 8.966(3)$, $b = 13.134(4)$, $c = 19.412(3)$ Å, $\alpha = 75.52(2)°$, $\beta = 79.94(2)°$, $\gamma = 74.25(2)°$, $V = 2087.6(9)$ Å^3; $Z = 2$, $D_{calc} = 1.42$ g cm^{-3}, $\mu = 1.771$ mm^{-1}. Crystal size $0.1 \times 0.1 \times 0.15$ mm^3. Enraf Nonius CAD4 diffractometer, Mo–K$_\alpha$ radiation (0.71073 Å), graphite monochromator, $T = 293$ K, ϖ/Θ-scan, max. $2\Theta = 48°$; 6098 reflections scanned, 5623 reflections independent and included in dataset; intensity data corrected for Lorentz and polarization effects, empirical absorption correction applied, minimum transmission 80.8%. The structure was solved by direct methods (SHELXS-86); atomic coordinates were refined by full-matrix least-squares against F_o^2 (371 parameters, SHELXL-93). The positions of the hydrogen atoms were calculated according to ideal geometry (distance C–H 0.95 Å). The chlorine atom Cl2 and the *trans* disposed carbonyl ligand were found to be disordered. The alternative positions were refined isotropically with occupation factors of 0.6:0.4 for Cl2 and 0.6:0.2:0.2 for C4 and O. The unit cell contains one solvent molecule (methylcyclohexane) which could not be refined due to multidisordering. The five highest peaks of the final difference Fourier synthesis are located near to this solvent molecule. $R = 0.0749$, $Rw = 0.2022$ for 2876 reflections [$I > 2\sigma(I)$]; $R = 0.1848$, $Rw = 0.2629$ for all data reflections; reflex:parameter ratio 15.16; residual electron density $+1.439/-1.400$

e Å^{-3}. Detailed crystallographic data (excluding structure factors) for the structure of **4** and **17** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 101236. Copies of the data can be obtained free of charge on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (email: deposit@chemcrys.cam.ac.uk).

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