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Acetato and acetylacetonato ruthenium(II) complexes containing $SbPr^i_3$, PPr^i_3 and PCy_3 as ligands‡

Claus Grünwald, Matthias Laubender, Justin Wolf and Helmut Werner *,†

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

The triply bridged binuclear ruthenium complex $[\{Ru(\eta^1\text{-}O_2CMe)(SbPr^i_3)_2\}_2(\mu\text{-}O_2CMe)_2(\mu\text{-}OH_2)]$ **2** was prepared from $[Ru(\eta^3\text{-}C_3H_5)_2(SbPr^i_3)_2]$ **1** and $MeCO_2H$ in the presence of water. Its molecular structure was determined by X-ray crystallography. The bis(acetylacetonato) complex $[Ru(acac)_2(SbPr^i_3)_2]$ **3**, obtained either from **1** or from $[Ru(acac)_3]$, is a suitable starting material for the preparation of monosubstituted derivatives $[Ru(acac)_2(SbPr^i_3)L]$ (L = PCy_3 **4**, PPr^i_3 **5**, C_2H_4 **7** or C=CHPh **8**) as well as of $[Ru(acac)_2(PPr^i_3)_2]$ **6**. Ligand-displacement reactions of **6** with PhC≡CR (R = H or $SiMe_3$) and $HC{\equiv}CCPh_2(O_2CMe)$ led to the vinylidene- and allenylidene-ruthenium complexes $[Ru(acac)_2(PPr^i_3)L]$ [L = C=CHPh **9**, $C{=}C(SiMe_3)Ph$ **10** or $C{=}C{=}CPh_2$ **11**], respectively. Treatment of **2** with PCy_3 and PPr^i_3 gave the compounds $[Ru(O_2CMe)_2(PR_3)_2]$ (R = Cy or PPr^i_3), of which the first smoothly reacted with HC≡CR to yield $[Ru(\eta^2\text{-}O_2CMe)(\eta^1\text{-}O_2CMe)(=C=CHR)(PCy_3)_2]$ (R = Ph or CO_2Me).

In the course of our investigations aimed at preparing square-planar rhodium complexes of the general composition *trans*-[RhCl(=CRR′)L_2], we recently found that the replacement of trialkylphosphines by trialkylstibines leads to a significant difference in the reactivity of the respective starting materials. While the phosphine complex *trans*-$[RhCl(C_2H_4)(PPr^i_3)_2]$ reacts with Ph_2CN_2 by simple ligand exchange to give *trans*-$[RhCl(N_2CPh_2)(PPr^i_3)_2]$, the corresponding stibine derivative *trans*-$[RhCl(C_2H_4)(SbPr^i_3)_2]$ affords the carbene compound *trans*-$[RhCl(=CPh_2)(SbPr^i_3)_2]$ almost quantitatively.[2] This striking difference, with its favorable consequences,[3] initiated our attempts to develop also synthetic pathways to other stibine transition-metal complexes in which the metal centre should have either a 16- or an 18-electron configuration. With iridium, this goal had recently been achieved.[4] As far as ruthenium was concerned, we found not only a preparative route to hydrido and dihydrogen complexes such as $[RuH(Cl)(H_2)(SbPr^i_3)_3]$ and $[RuH_2(H_2)(SbPr^i_3)_3]$,[5] but also discovered that in contrast to PPr^i_3 the corresponding triisopropylstibine reacted with $[\{Ru(\eta^5\text{-}C_5Me_5)(\mu_3\text{-}Cl)\}_4]$ to give $[Ru(\eta^5\text{-}C_5Me_5)Cl(SbPr^i_3)]$ as well as the unsymmetrical binuclear species $[(\eta^5\text{-}C_5Me_5)(Pr^i_3Sb)Ru(\mu\text{-}Cl)_2Ru(\eta^5\text{-}C_5Me_5)]$.[6]

This result together with the isolation and structural characterisation of the 17-electron complex $[Ru(\eta^5\text{-}C_5Me_5)Cl_2(SbPr^i_3)]$ prompted us further to extend the triisopropylstibineruthenium chemistry with the special impetus to include also acetate and acetylacetonate as coligands. In this paper we describe the synthesis of corresponding ruthenium(II) compounds with $Ru(SbPr^i_3)_2$ as a building block and show how easily they undergo ligand-exchange processes to afford triisopropyl- and tricyclohexyl-phosphine ruthenium complexes.

Results and Discussion

An unexpected binuclear $Ru_2(\mu\text{-}OH_2)$ complex

After we had shown that the π-allyl compound $[Ru(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_3H_5)(PPh_3)]$ reacts with carboxylic acids RCO_2H by elimination of propene to yield $[Ru(\eta^5\text{-}C_5H_5)(\eta^2\text{-}O_2CR)(PPh_3)]$,[7] we attempted to use this methodology to prepare also complexes of the type $[Ru(\eta^2\text{-}O_2CR)_2(SbPr^i_3)_2]$. The respective starting material $[Ru(\eta^3\text{-}C_3H_5)_2(SbPr^i_3)_2]$ **1**, which is obtained on treatment of $[RuH_2(H_2)(SbPr^i_3)_3]$ with propene,[5] reacts with CF_3CO_2H in CH_2Cl_2 almost instantaneously to give a mixture of products which could not be separated by fractional crystallisation or column chromatography. The analogous reaction of **1** with $MeCO_2H$ in acetone proceeds somewhat more slowly and finally affords an orange solid, the elemental analysis of which corresponds to $[Ru_2(O_2CMe)_4(SbPr^i_3)_4(OH_2)]$ **2**. We assume that the source of the water ligand is the acetic acid which usually contains 1–2% of water. The presence of a coordinated water molecule is clearly confirmed by the ^1H NMR spectrum which displays a singlet with the relative intensity of two protons at δ 15.35. After addition of D_2O to the solution of **2** this signal disappears and a new broad resonance is observed at δ 5.62. A similar observation was made by Singleton and co-workers[8] who prepared the complexes $[\{Ru(\eta^1\text{-}O_2CR)(\eta^4\text{-}C_8H_{12})\}_2(\mu\text{-}O_2CR)_2(\mu\text{-}OH_2)]$ (R = CF_3, CCl_3 or CH_2Cl), which are structurally related to **2**, by a similar route. As far as the NMR data of **2** are concerned, other characteristic features are the two sets of signals for the protons and the carbon atoms of the CO_2Me groups in the ^1H and ^{13}C NMR spectra and the four resonances (again both in the ^1H and ^{13}C NMR spectra) for the $CHCH_3$ and the $CHCH_3$ nuclei. The latter observation indicates that the two stibine ligands on each metal centre are not equivalent.

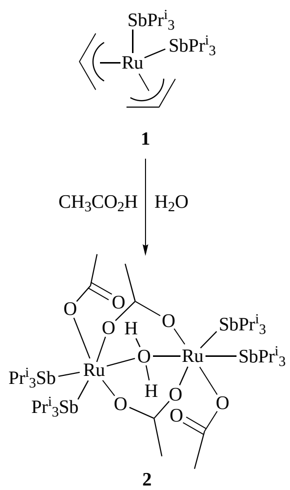
To confirm the structural proposal for complex **2** shown in Scheme 1, a single-crystal X-ray diffraction study was carried out. The ORTEP[9] plot (Fig.1) reveals that the ligand geometry around each metal centre is distorted octahedral with the two antimony atoms in *cis* position. The two $Ru(\eta^1\text{-}O_2CMe)(SbPr^i_3)_2$ units are bridged by two acetate ligands and the water molecule which is probably connected *via* hydrogen bonds to the carbonyl oxygen atoms O(7) and O(9). Indicative of this are the relatively short oxygen–oxygen distances O(1)···O(7) [2.493(2) Å] and O(1)···O(9) [2.503(2) Å], which are comparable to those of $[\{Ru(\eta^1\text{-}O_2CCF_3)(\eta^4\text{-}C_8H_{12})\}_2(\mu\text{-}O_2CCF_3)_2(\mu\text{-}OH_2)]$.[8] The bond lengths between the ruthenium atoms and the central oxygen atom O(1) are also quite similar to those of the Singleton compound[8] and the related phosphine complex $[\{Ru(\eta^1\text{-}O_2CCF_3)[P(C_6H_{11})_2(C_6H_9)]\}_2(\mu\text{-}O_2CCF_3)_2(\mu\text{-}OH_2)]$ which was obtained by Chaudret and co-workers[10] on treatment of $[RuH_2(O_2CCF_3)_2(PCy_3)_2]$ with cyclooctene in the presence of traces of water.

† E-Mail: helmut.werner@mail.uni-wuerzburg.de
‡ Vinylidene transition-metal complexes. Part 4.[1]

Since the oxidation state of ruthenium in complex **2** is +II, it is not to be expected that there is a metal–metal bonding interaction between Ru(1) and Ru(2). The distance between these atoms is 3.740(2) Å and thus almost identical to the Ru···Ru distance in [{Ru(η^1-O_2CCF_3)(η^4-C_8H_{12})}$_2$(μ-O_2CCF_3)$_2$(μ-OH_2)] [3.733(1) Å].[8] The Ru–Sb bond lengths in **2** lie between 2.558(2) and 2.594(2) Å and are quite similar to those in **1** [2.610(4) Å][5] and [$RuCl_2$(CO)($SbPr^i_3$)$_3$] (average 2.633 Å)[11] as well as in the triphenylstibine derivative [$RuCl_2$($SbPh_3$)$_4$] (average 2.629 Å).[12] The bond angles Sb(1)–Ru(1)–Sb(2) [101.36(5)°] and Sb(3)–Ru(2)–Sb(4) [97.80(5)°] are somewhat larger than anticipated for an octahedral geometry which could be due to the bulkiness of the $SbPr^i_3$ ligands.

Bis(acetylacetonato)ruthenium(II) compounds with $SbPr^i_3$ and PPr^i_3 as coligands

In contrast to the reaction of complex **1** with acetic acid which led to the formation of the binuclear compound **2**, treatment of **1** with acetylacetone in benzene at 80 °C gave the mononuclear complex [Ru(acac)$_2$($SbPr^i_3$)$_2$] **3** in 60% yield. An alternative procedure for the preparation of **3** consists in the reduction of [Ru(acac)$_3$] with zinc amalgam in the presence of triisopropylstibine and a small amount of water and affords **3** almost quantitatively. Bennett *et al.*[13] developed this route and by using cyclooctatetraene instead of $SbPr^i_3$ obtained the olefin complex [Ru(acac)$_2$(η^4-C_8H_8)] in excellent yield.



Scheme 1

Compound **3** is an orange-red solid, which is readily soluble in hexane and benzene but less so in more polar solvents such as methanol. The ^{1}H NMR spectrum displays two signals for the CH_3 protons of the acac ligands at δ 1.96 and 1.71 as well as two resonances for the SbCHCH_3 protons at δ 1.42 and 1.41, respectively. In the ^{13}C NMR spectrum also a double set of signals for the *C*(O)CH_3, C(O)*C*H_3 and SbCH*C*H_3 carbon atoms is observed. These results, together with the appearance of two OCO stretching frequencies in the IR spectrum at 1570 and 1510 cm^{-1},[14] clearly indicate that in **3** both the acac and the $SbPr^i_3$ ligands are *cis* disposed. It seems that the *cis* configuration is in general thermodynamically preferred. This is convincingly illustrated by the work of Bennett and co-workers[15]

Table 1 Selected bond lengths (Å) and angles (°) for complex **2**

Ru(1)–O(1)	2.158(7)	Ru(2)–O(1)	2.160(7)
Ru(1)–O(2)	2.152(8)	Ru(2)–O(3)	2.079(8)
Ru(1)–O(4)	2.087(8)	Ru(2)–O(5)	2.147(9)
Ru(1)–O(6)	2.097(8)	Ru(2)–O(8)	2.103(8)
Ru(1)–Sb(1)	2.583(2)	Ru(2)–Sb(3)	2.558(2)
Ru(1)–Sb(2)	2.594(2)	Ru(2)–Sb(4)	2.572(1)
O(1)–Ru(1)–O(2)	88.1(3)	O(1)–Ru(2)–O(3)	91.0(3)
O(1)–Ru(1)–O(4)	88.9(3)	O(1)–Ru(2)–O(5)	85.4(3)
O(1)–Ru(1)–O(6)	91.7(3)	O(1)–Ru(2)–O(8)	92.0(3)
O(2)–Ru(1)–O(4)	93.7(3)	O(3)–Ru(2)–O(5)	94.7(3)
O(2)–Ru(1)–O(6)	85.2(3)	O(3)–Ru(2)–O(8)	176.3(3)
O(4)–Ru(1)–O(6)	178.7(3)	O(5)–Ru(2)–O(8)	83.5(3)
O(1)–Ru(1)–Sb(1)	91.5(2)	O(1)–Ru(2)–Sb(3)	94.6(2)
O(1)–Ru(1)–Sb(2)	167.1(2)	O(1)–Ru(2)–Sb(4)	167.6(2)
O(2)–Ru(1)–Sb(1)	178.7(2)	O(3)–Ru(2)–Sb(3)	89.8(2)
O(2)–Ru(1)–Sb(2)	79.0(2)	O(3)–Ru(2)–Sb(4)	89.2(2)
O(4)–Ru(1)–Sb(1)	87.6(2)	O(5)–Ru(2)–Sb(3)	175.5(2)
O(4)–Ru(1)–Sb(2)	91.0(2)	O(5)–Ru(2)–Sb(4)	82.2(2)
O(6)–Ru(1)–Sb(1)	93.5(2)	O(8)–Ru(2)–Sb(3)	92.0(2)
O(6)–Ru(1)–Sb(2)	88.2(2)	O(8)–Ru(2)–Sb(4)	87.4(2)
Sb(1)–Ru(1)–Sb(2)	101.36(5)	Sb(3)–Ru(2)–Sb(4)	97.80(5)
Ru(1)–O(1)–Ru(2)	120.0(3)		

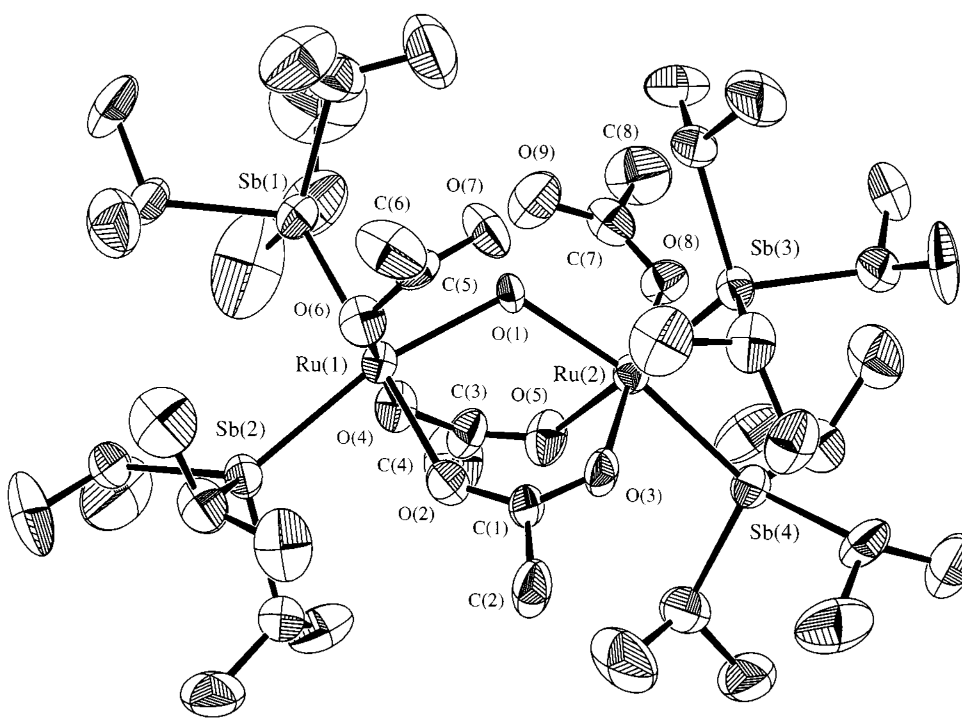
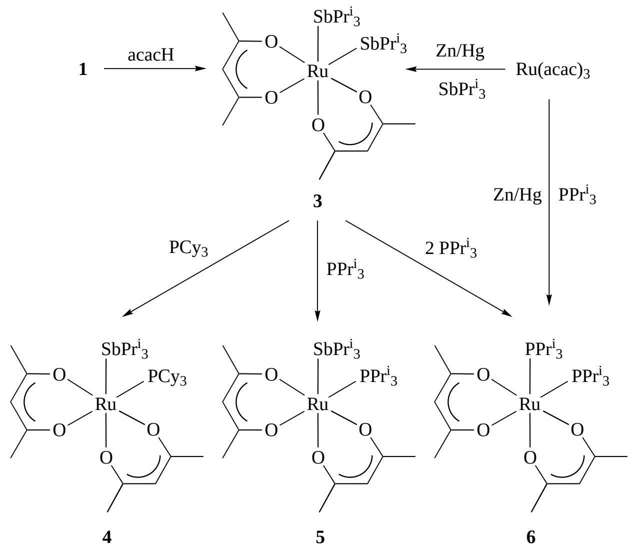
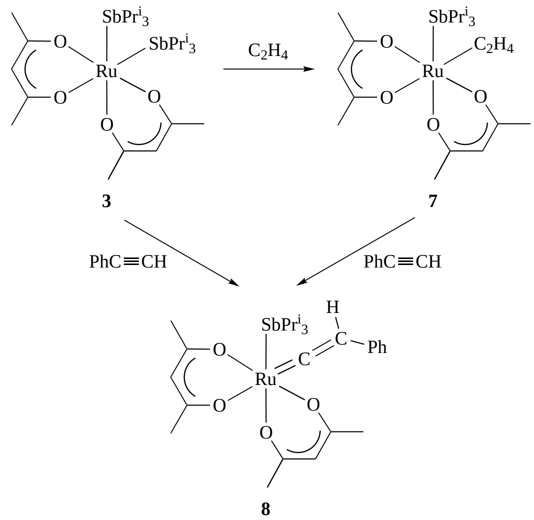


Fig. 1 Molecular structure of complex **2**



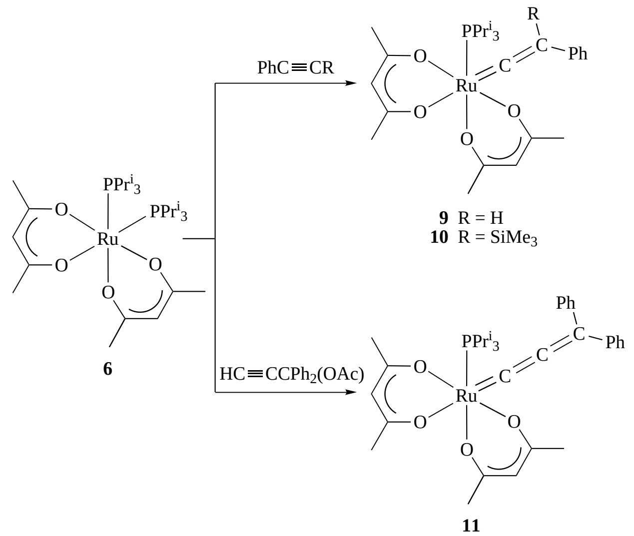
Scheme 2



Scheme 3

which shows that in refluxing toluene *trans*-[Ru(acac)$_2$(PPh$_3$)$_2$] rearranges irreversibly to the *cis* isomer.

The triisopropylstibine ligands of complex **3** are only weakly bonded and can easily be replaced even by bulky tertiary phosphines. Therefore, on treatment of **3** with an equimolar amount of PCy$_3$ or PPr$^i_3$ in benzene at 80 °C, the mixed phosphine–stibine complexes **4** and **5** (Scheme 2) were formed. If in the case of PPr$^i_3$ an excess of the phosphine was used, the bis(phosphine) derivative **6** was obtained in excellent yield. It had also been prepared by the Bennett group from [Ru(acac)$_2$(C$_8$H$_{14}$)$_2$] and PPr$^i_3$.[15] Compounds **4**, **5** and **6** are orange, only moderately air-sensitive solids, which are thermally stable to 60–70 °C. In contrast to **3** (and also to **6**), the ^{1}H NMR spectra of the more unsymmetrical complexes **4** and **5** display two signals for the CH and four signals for the CH$_3$ protons of the acac ligands. Consistent with this, in the ^{13}C NMR spectra of **4** and **5** two resonances for the CH, four resonances for the CH$_3$ and also four resonances for the CO carbon atoms of the chelate rings are observed. Similar sets of signals (with minor differences in the chemical shift) likewise appear in the ^{1}H and ^{13}C NMR spectra of the ethene and vinylidene complexes **7** and **8**, the formation of which is shown in Scheme 3. Compound **7** is rather labile and slowly decomposes in the absence of an ethene atmosphere. Since the ^{1}H NMR spectrum of **7** displays only two symmetrically arranged multiplets for the C$_2$H$_4$ protons, it can be assumed that the rotation of the ethene ligand around the Ru–C$_2$H$_4$ axis is fast on the NMR time-scale.



Scheme 4

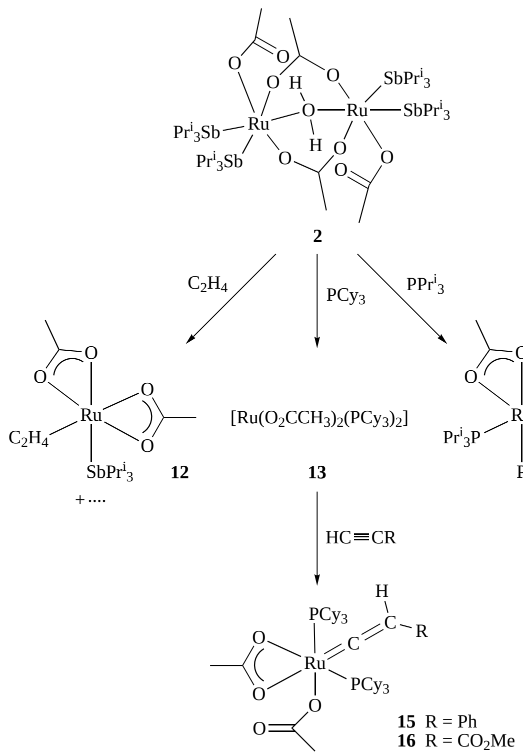
The vinylidene complex **8** was obtained either from **3** or **7** and phenylacetylene in refluxing benzene. Under the reaction conditions also some side-products were formed which could not be completely separated from **8**. In the course of our attempts to purify **8** by fractional crystallisation or column chromatography, we observed that a slow decomposition occurs which could be due to the lability of the Ru–SbPr$^i_3$ bond.

Significantly more stable vinylidene ruthenium(II) derivatives of the general composition [Ru(acac)$_2${=C=C(R)Ph}(PPr$^i_3$)] **9**, **10** were prepared on treatment of **6** with PhC≡CH or PhC≡C-SiMe$_3$, respectively (Scheme 4). Although we failed (by NMR spectroscopy) to detect the supposed intermediates [Ru(acac)$_2$(η^2-PhC≡CR)(PPr$^i_3$)], we nevertheless assume that these π-alkyne compounds are initially formed but rapidly rearrange to the more stable vinylidene isomers.[16] Compounds **9** and **10** are orange-brown or orange, almost air-stable solids which are readily soluble in common organic solvents and were recrystallised from pentane. Typical features of the spectroscopic data are the low-field signals in the ^{13}C NMR spectra at δ 338–358 and 113–114, assigned to the α- and β-C atoms of the Ru=C=C(R)Ph unit, and for **9** the doublet resonance for the =C*H*Ph proton in the ^{1}H NMR spectrum at δ 5.24.

The Selegue method,[17] which we had already used for the synthesis of various allenylidene rhodium,[18] iridium,[19] and ruthenium complexes,[20] can also be applied to prepare [Ru(acac)$_2$(=C=C=CPh$_2$)(PPr$^i_3$)] **11**. Treatment of a solution of compound **6** in benzene with the propargylic ester HC≡CCPh$_2$(O$_2$CMe) under reflux conditions led to the formation of a mixture of products, from which **11** was separated by column chromatography. After recrystallisation from pentane, red air-stable crystals of **11** were isolated in *ca*. 60% yield. In agreement with the structural proposal, the ^{1}H NMR spectrum displays two signals for the CH and four resonances for the CH$_3$ protons of the two *cis* disposed acac ligands. In the ^{13}C NMR spectrum three signals appear in the low-field region at δ 292.0, 239.2 and 143.1 which according to the size of the P–C coupling constants are assigned to the α-, β- and γ-C atoms of the allenylidene ligand. The presence of this ligand is also strongly supported by the IR spectrum which shows a characteristic C=C=C stretching frequency at 1890 cm^{-1}.

Preparation of mononuclear bis(acetato)ruthenium(II) complexes

After we learnt that the triisopropylstibine ligands in compound **3** were smoothly replaced by PCy$_3$, PPr$^i_3$ and even by ethene (see Schemes 2 and 3), we became interested to find out whether the binuclear complex **2**, which contains two Ru(Sb-Pr$^i_3$)$_2$ units, could also be used as starting material for similar ligand-substitution processes. It was known that the cycloocta-



Scheme 5

diene derivative [{Ru(η^1-O_2CCF_3)(η^4-C_8H_{12})}$_2$(μ-O_2CCF_3)$_2$-(μ-OH_2)][8] as well as the water-free binuclear compound [{Ru-(μ-O_2CCF_3)$_2$(η^4-C_8H_{12})}$_2$][21] react with mono- and bi-dentate phosphines to give mononuclear substitution products.

If a stream of ethene was passed through a solution of complex **2** in C_6D_6 at room temperature and the solution was then heated at 60 °C, a slow reaction took place which was monitored by ^{1}H NMR spectroscopy. After most of the starting material was consumed, the NMR spectrum displayed a set of resonances which indicated the formation of the olefin complex [Ru(η^2-O_2CMe)$_2$(C_2H_4)($SbPr^i_3$)] **12**. Besides this compound, also small quantities of unidentified by-products were formed. From the observations made during the attempts to purify **12**, we conclude that this ethene–stibine complex is as labile as the related acac derivative **8**.

The reactions of compound **2** with PCy_3 or PPr^i_3 in dichloromethane at room temperature also proceeded smoothly and gave the bis(phosphine) complexes **13** and **14** in good yield. Owing to the similar solubilities, it was very difficult to separate compound **14** from the displaced triisopropylstibine. When we tried to use chromatographic techniques the bis(acetato) complex decomposed. If we take the spectroscopic data of **14** into account, there is, however, no doubt that the structure shown in Scheme 5 is correct. There are two doublet-of-doublet resonances for the CHCH_3 protons of the phosphine ligands which confirm that these ligands, as in compound **6**, are *cis* disposed.

With regard to the bis(tricyclohexylphosphine) complex **13**, which was isolated as a light red, moderately air-sensitive solid, it is much more difficult to make a convincing structural proposal. In contrast to **14**, the ^{31}P NMR spectrum of which displays a sharp singlet at δ 60.6 both at −20 °C and at room temperature, the spectrum of **13** shows only a broad signal (δ *ca.* 50) at 25 °C. At low temperatures this signal broadens but even at −80 °C no separated lines are observed. By heating the solution of **13** (in C_6D_6) slowly the linewidth of the ^{31}P NMR resonance decreases and at 60 °C a sharp signal appears. Therefore, although we do not know the mechanism of the dynamic process, the molecule definitely has a non-rigid structure in solution at room temperature. This is really surprising insofar as the analogous complex [Ru(η^2-O_2CCF_3)$_2$(PCy_3)$_2$][10] and also some related compounds of the general composition [Ru(η^2-O_2CR)$_2L_2$][22] show no fluxional behaviour in solution. The IR spectrum of **13** displays two OCO stretching frequencies at 1490 and 1420 cm^{-1} which would be consistent with the co-ordination of two bidentate acetato groups at ruthenium.

Despite the uncertainty about the structure of **13**, this compound reacted cleanly with HC≡CPh and HC≡CCO$_2$Me to give [Ru(η^2-O_2CMe)(η^1-O_2CMe)(=C=CHR)(PCy_3)$_2$] **15**, **16** as yellow, almost air-stable solids in about 60% isolated yield. The ^{1}H and in particular the ^{13}C NMR spectra of both compounds confirm that during the reaction a rearrangement of the terminal alkyne to the vinylidene isomers took place in the co-ordination sphere. The most characteristic spectroscopic features are the triplet resonance for the α-C atom of the Ru=C=CHR unit at δ 353.1 (**15**) and 341.8 (**16**) in the ^{13}C NMR and the signal of the =C*H*R proton at δ 5.51 (**15**) and 5.10 (**16**) in the ^{1}H NMR spectra.

However, in addition to these data the NMR spectra of the vinylidene complexes **15** and **16** also illustrate that they, like the starting material **13**, possess a fluxional structure in solution. At 25 °C the ^{31}P NMR spectra display instead of the expected AB pattern a single resonance at δ 20.0 (**15**) and 21.4 (**16**) which broadens at lower temperatures. A similar observation is made regarding the signal of the *C*O$_2$CH$_3$ carbon atoms in the ^{13}C NMR spectra. In both cases coalescence occurs below −70 °C (in $CDCl_3$). This finding is in contrast to the results reported by Robinson and co-workers,[23] who found by variable-temperature NMR measurements that the two dynamic processes which could be detected for the carbonyl ruthenium derivatives [Ru(η^2-O_2CR)(η^1-O_2CR)(CO)(PPh_3)$_2$] leading to the equivalence of the acetato as well as of the phosphine ligands were already frozen out at −33 °C.

By taking the similarity of the π-acceptor properties of CO and C=CH$_2$ into consideration,[24] it is conceivable that an analogous intramolecular rearrangement also occurs for the vinylidene complexes **15** and **16**. The ^{1}H NMR spectra of both compounds display at 25 °C a relatively sharp singlet at δ 1.98 for the CO_2CH_3 protons, which by lowering the temperature first broadens and then splits into two resonances of equal intensity at δ 2.11 and 1.88. The coalescence temperature could not be exactly determined since in the respective region (between δ 1.1 and 2.1) the broad multiplet of the C_6H_{11} protons appears. The conclusion which we draw from these observations, that in the rigid molecules one acetate ligand is bi- and the other mono-dentate, is strongly supported by the IR spectra of **15** and **16** in which the asymmetric and symmetric ν(OCO) bands for the monodentate O_2CCH_3 group are observed at 1630 and 1300 cm^{-1} (for **15**) and at 1640 and 1305 cm^{-1} (for **16**). The corresponding frequencies for the bidentate O_2CMe ligand appear at 1440 and 1365 cm^{-1} (for **15**) and at 1440 and 1360 cm^{-1} (for **16**). Similar values were found for the related carbonyl derivatives [Ru(O_2CR')$_2$(CO)(PR_3)$_2$] which also contain two differently co-ordinated carboxylate ligands.[23, 25]

Conclusion

Despite the extensive work by Levason[26] and others on triarylstibine metal compounds, the chemistry of corresponding trialkylstibine complexes is still in its infancy. So far as ruthenium is concerned, the work reported here illustrates that mono- and bi-nuclear compounds with Ru($SbPr^i_3$)$_2$ as a building block and acetate or acetylacetonate as coligands are not only accessible but can also be used as starting materials for other octahedral ruthenium(II) complexes. The studies concerning the reactivity of the parent compounds **2** and **3** confirm that the Ru–$SbPr^i_3$ bonds in these molecules are quite labile and that at least one of the stibine ligands is easily replaced by tertiary phosphines as well as by weaker donors such as ethene or terminal alkynes, respectively. Most recently, the different thermodynamic (and in most cases also kinetic) stability of related complexes [M(PPr^i_3)$_2L_n$] and [M($SbPr^i_3$)$_2L_n$] (M = d^6 or d^8 metal center) has prompted us to prepare mixed-donor molecules such as $R_2PCH_2SbR'_2$ and $R_2PCH_2AsR'_2$ and to use them as hemilabile chelating ligands in rhodium chemistry.[27] Work with ruthenium(II) is in progress and will be reported in due course.

Experimental

All reactions were carried out under an atmosphere of argon by Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting materials **1**,[5] $SbPr^i_3$,[28] and [Ru(acac)$_3$][29] were prepared by published methods. The phosphines and the alkynes were commercial products from Strem and Aldrich. The NMR spectra were recorded on Bruker AC 200 and AMX 400 instruments and the IR spectra on a Perkin-Elmer 1420 spectrometer. Some of the ^{13}C NMR signals were assigned by DEPT experiments [vt = virtual triplet; $N = {}^3J(PH) + {}^5J(PH)$ or $^1J(PC) + {}^3J(PC)$, respectively].

Preparations

[{Ru(η^1-O$_2$CMe)(SbPr$^i_3$)$_2$}$_2$(μ-O$_2$CMe)$_2$(μ-H$_2$O)] 2. A suspension of compound **1** (0.528 g, 0.77 mmol) in acetone (10 cm^3) was treated with 98% acetic acid (0.175 cm^3, 3.10 mmol) at room temperature. After the reaction mixture was stirred for *ca*. 5 min a clear red solution was formed from which after *ca*. 30 min an orange solid precipitated. The solution was stored for 1 h, the mother-liquor removed by decantation, and the remaining solid washed twice with cold acetone (0 °C, 3 cm^3): yield 0.325 g (58%); m.p. 112 °C (decomp.) (Found: C, 36.10; H, 6.57. $C_{44}H_{98}O_9Ru_2Sb_4$ requires C, 36.19; H, 6.76%). IR (KBr): ν(OCO) 1587 and 1400 cm^{-1}. NMR (C_6D_6): δ_H(400 MHz) 15.35 (2 H, s, OH$_2$), 2.69, 2.48 [12 H, both sept, *J*(HH) 7.4, C*H*CH$_3$], 2.06, 1.79 (12 H, both s, CO$_2$CH$_3$), 1.57, 1.48, 1.45, 1.42 [72 H, all d, *J*(HH) 7.4 Hz, CHC*H*$_3$]; δ_C(100.6 MHz) 186.5, 182.2 (both s, *C*O$_2$CH$_3$), 24.8, 23.8 (both s, CO$_2$*C*H$_3$), 22.0, 21.8, 21.6, 21.5 (all s, CH*C*H$_3$), 19.0, 17.3 (both s, *C*HCH$_3$).

[Ru(acac)$_2$(SbPr$^i_3$)$_2$] 3. A solution of compound **1** (0.184 g, 0.27 mmol) in benzene (10 cm^3) was treated with acetylacetone (0.061 cm^3, 0.59 mmol) and stirred at reflux for 1 h. A change from yellow to red occurred. After the solution was cooled to room temperature, the solvent was removed *in vacuo* and the oily residue treated with methanol (3 cm^3). Orange crystals precipitated, which were washed with small portions of methanol and diethyl ether: yield 0.130 g (60%); m.p. 72 °C (decomp.) (Found: C, 41.69; H, 6.87. $C_{28}H_{56}O_4RuSb_2$ requires C, 41.97; H, 7.04%). IR (KBr): ν(acac) 1570 and 1510 cm^{-1}. NMR (C_6D_6): δ_H(400 MHz) 5.34 [2 H, s, CHC(O)], 2.20 [6 H, sept, *J*(HH) 7.2, C*H*CH$_3$], 1.96, 1.71 [12 H, both s, C(O)CH$_3$], 1.42, 1.41 [36 H, both d, *J*(HH) 7.2 Hz, CHC*H*$_3$]; δ_C(100.6 MHz) 184.9, 182.2 [both s, *C*(O)CH$_3$], 98.2 [s, *C*HC(O)], 28.1, 27.3 [both s, C(O)*C*H$_3$], 21.8, 21.7 (both s, CH*C*H$_3$) and 18.1 (s, *C*HCH$_3$).

Alternatively, a solution of [Ru(acac)$_3$] (1.01 g, 2.51 mmol) in thf (50 cm^3) was treated stepwise with $SbPr^i_3$ (1.30 cm^3, 6.28 mmol) and then with an excess of Zn/Hg (2–3% Zn, 15 g). A rapid change from red to brown took place. After water (1 cm^3) was added, the reaction mixture was stirred at reflux for 2 h. The mixture then changed from brown to red. It was cooled to room temperature, then filtered over Celite and the filtrate worked up as described above: yield 1.72 g (86%).

[Ru(acac)$_2$(SbPr$^i_3$)(PCy$_3$)] 4. A solution of complex **3** (0.236 g, 0.29 mmol) in benzene (15 cm^3) was treated with PCy$_3$ (0.081 g, 0.29 mmol) and then stirred at reflux for 1 h. After the solution was cooled to room temperature, the solvent was removed *in vacuo* and the oily residue treated with methanol (3 cm^3). Orange crystals precipitated, which were washed with small portions of methanol and ether: yield 0.193 (80%); m.p. 73 °C (decomp.) (Found: C, 53.73; H, 8.13. $C_{37}H_{68}O_4PRuSb$ requires C, 53.50; H, 8.25%). IR (KBr): ν(acac) 1590 and 1520 cm^{-1}. NMR (C_6D_6): δ_H(400 MHz) 5.36, 5.31 [2 H, both s, CHC(O)], 2.43–1.24 (33 H, m, C$_6$H$_{11}$), 2.27 [3 H, sept, *J*(HH) 7.2, C*H*CH$_3$], 2.02, 1.91, 1.80, 1.77 [12 H, all s, C(O)CH$_3$], 1.44, 1.40 [18 H, both d, *J*(HH) 7.2 Hz, CHC*H*$_3$]; δ_C(100.6 MHz) 186.6, 186.4, 184.1, 183.5 [all s, *C*(O)CH$_3$], 100.0, 99.7 [both s, *C*H(CO)], 38.7 [d, *J*(PC) 17.1, *ipso*-C of C$_6$H$_{11}$], 30.0, 29.5 (both s, *m*-C of C$_6$H$_{11}$), 28.8 [d, *J*(PC) 8.8, *o*-C of C$_6$H$_{11}$], 28.7 [d, *J*(PC) 9.8 Hz, *o*-C of C$_6$H$_{11}$], 28.1, 28.0, 27.8, 27.5 [all s, C(O)*C*H$_3$], 27.4 (s, *p*-C of C$_6$H$_{11}$), 21.8, 21.7 (both s, CH*C*H$_3$) and 18.0 (s, *C*HCH$_3$); δ_P(162.0 MHz) 55.4 (s).

[Ru(acac)$_2$(SbPr$^i_3$)(PPr$^i_3$)] 5. This compound was prepared as described for **4**, using **3** (0.235 g, 0.29 mmol) and PPr^i_3 (0.056 cm^3, 0.29 mmol) as starting materials. Orange solid: yield 0.153 g (74%); m.p. 60 °C (decomp.) (Found: C, 46.96; H, 8.31. $C_{28}H_{56}O_4PRuSb$ requires C, 47.33; H, 7.94%). IR (KBr): ν(acac) 1580 and 1510 cm^{-1}. NMR (C_6D_6): δ_H(400 MHz) 5.37, 5.28 [2 H, both s, CHC(O)], 2.42 (3 H, m, PC*H*CH$_3$), 2.21 [3 H, sept, *J*(HH) 7.6 Hz, SbC*H*CH$_3$], 2.01, 1.85 [6 H, both s, C(O)CH$_3$], 1.77 [6 H, two overlapping s, C(O)CH$_3$], 1.40, 1.36 [18 H, both d, *J*(HH) 7.6, SbCHC*H*$_3$], 1.30 [9 H, dd, *J*(PH) 11.6, *J*(HH) 7.2 Hz, PCHC*H*$_3$], second signal for PCHC*H*$_3$ protons overlaps with signals at δ 1.40 and 1.36; δ_C(100.6 MHz) 186.8, 186.5, 184.1, 183.6 [all s, *C*(O)CH$_3$], 100.0, 99.5 [both s, *C*HC(O)], 28.7 [d, *J*(PC) 18.1 Hz, P*C*HCH$_3$], 27.9, 27.8, 27.6, 27.5 [all s, C(O)*C*H$_3$], 21.7, 21.6 (both s, SbCH*C*H$_3$), 20.0, 19.7 (both s, PCH*C*H$_3$) and 18.2 (s, Sb*C*HCH$_3$); δ_P(162.0 MHz) 65.5 (s).

[Ru(acac)$_2$(PPr$^i_3$)$_2$] 6. A solution of complex **3** (0.256 g, 0.32 mmol) in benzene (10 cm^3) was treated with PPr^i_3 (0.150 cm^3, 0.79 mmol) and then stirred at reflux for 1 h. The reaction mixture was worked up as described for compound **5**. Orange solid: yield 0.153 g (77%); m.p. 70 °C (decomp.) (Found: C, 54.10; H, 8.76. $C_{28}H_{56}O_4P_2Ru$ requires C, 54.26; H, 9.11%). IR (KBr): ν(acac) 1570 and 1505 cm^{-1}. NMR (C_6D_6): δ_H(400 MHz) 5.31 [2H, s, CHC(O)], 2.46 (6 H, m, C*H*CH$_3$), 1.92, 1.79 [12 H, both s, C(O)CH$_3$], 1.38, 1.26 [36 H, both dd, *J*(PH) 11.0, *J*(HH) 7.3 Hz, CHC*H*$_3$]; δ_C(100.6 MHz) 186.8, 183.7 [both s, *C*(O)CH$_3$], 99.8 [s, *C*HC(O)], 27.9, 27.7 [both s, C(O)*C*H$_3$], 27.6 [t, *J*(PC) 7.5 Hz, *C*HCH$_3$], 20.1, 20.0 (both s, CH*C*H$_3$); δ_P(162.0 MHz) 47.4 (s).

Alternatively, compound **6** was also prepared as described for **3**, using [Ru(acac)$_3$] (0.232 g, 0.58 mmol), PPr^i_3 (0.275 cm^3, 1.44 mmol) and an excess of Zn/Hg as starting materials; yield 0.297 g (83%).

[Ru(acac)$_2$(C$_2$H$_4$)(SbPr$^i_3$)] 7. A stream of ethene was passed through a solution of complex **3** (0.134 g, 0.17 mmol) in benzene (10 cm^3) at room temperature. Upon stirring the solution at reflux for 1 h, a smooth change from red to yellow occurred. The solution was cooled to room temperature and the solvent removed *in vacuo*. The oily residue was dissolved in hexane (1 cm^3) and the solution chromatographed on Al$_2$O$_3$ (neutral, activity grade V, column length 5 cm). With hexane a yellow fraction was eluted from which after removal of the solvent a yellow oil was obtained. The compound did not crystallise even when stored for 24 h at −20 °C; yield *ca*. 0.070 g (71%). NMR (C_6D_6): δ_H(400 MHz) 5.32, 5.25 [2 H, both s, CHC(O)], 4.15, 3.81 (4 H, both m, C$_2$H$_4$), 2.16 [3 H, sept, *J*(HH) 7.2, C*H*CH$_3$], 2.05, 2.00, 1.67, 1.63 [12 H, all s, C(O)CH$_3$], 1.30, 1.25 [18 H, both d, *J*(HH) 7.2 Hz, CHC*H*$_3$]; δ_C(100.6 MHz) 188.6, 185.9, 184.8, 184.6 [all s, *C*(O)CH$_3$], 99.7, 98.2 [both s, *C*HC(O)], 55.3 (s, C$_2$H$_4$), 28.1, 27.8, 27.7, 27.1 [all s, C(O)*C*H$_3$], 21.5, 21.2 (both s, CH*C*H$_3$) and 16.9 (s, *C*HCH$_3$).

[Ru(acac)$_2$(=C=CHPh)(SbPr$^i_3$)] 8. A solution of complex **3** (0.291 g, 0.36 mmol) in benzene (10 cm^3) was treated with phenylacetylene (0.052 cm^3, 0.47 mmol) and stirred at reflux for 1 h. After the solution was cooled to room temperature, the solvent was removed *in vacuo*. The oily residue was dissolved in hexane (1 cm^3) and the solution chromatographed on Al_2O_3 (neutral, activity grade V, column length 5 cm). With hexane a brown fraction was eluted from which after removal of the solvent a brown oil was obtained. The compound did not crystallise even when stored for 24 h at −20 °C; yield *ca.* 0.150 g (64%). NMR (C_6D_6): δ_H(400 MHz) 7.34–6.86 (5 H, m, C_6H_5), 5.40, 5.29, 5.16 [3 H, all s, CHC(O) and =C*H*Ph], 2.12 [3 H, sept, *J*(HH) 7.2 Hz, C*H*CH_3], 2.02, 1.85, 1.81, 1.78 [12 H, all s, C(O)CH_3], 1.30, 1.28 [18 H, both d, *J*(HH) 7.2 Hz, CHC*H*$_3$]; δ_C(100.6 MHz) 354.6 (s, =C=), 189.0, 188.8, 187.5, 185.4 [all s, *C*(O)CH_3], 133.6, 128.6, 125.3, 124.2 (all s, C_6H_5), 116.8 (s, =*C*HPh), 99.8, 99.1 [both s, *C*HC(O)], 28.0, 27.9, 27.8, 26.6 [all s, C(O)*C*H_3], 21.2, 21.1 (both s, CH*C*H_3) and 17.4 (s, CH*C*H_3).

Alternatively, compound **8** was also prepared on treatment of a solution of **7** (*ca.* 0.174 g, 0.30 mmol) in benzene (10 cm^3) with phenylacetylene (0.038 cm^3, 0.35 mmol). After the solution was stirred at reflux for 1 h, it was worked up as described above to give a brown oil; yield *ca.* 0.130 g (66%).

[Ru(acac)$_2$(=C=CHPh)(PPr$^i_3$)] 9. A solution of complex **6** (0.152 g, 0.25 mmol) in benzene (10 cm^3) was treated with phenylacetylene (0.030 cm^3, 0.27 mmol) and stirred at reflux for 1 h. After the solution was cooled to room temperature, the solvent was removed *in vacuo*. The brown oily residue was dissolved in hexane (1 cm^3) and the solution chromatographed on Al_2O_3 (neutral, activity grade V, column length 5 cm). With hexane, first a yellow fraction was obtained which was discarded. Subsequently, with ether a red fraction was eluted which was brought to dryness *in vacuo*. The oily residue was dissolved in pentane (3 cm^3) and after the solution was stored at −78 °C for 12 h a brown solid was isolated: yield 0.078 g (56%); m.p. 116 °C (decomp.) (Found: C, 57.43; H, 7.18. $C_{27}H_{41}O_4PRu$ requires C, 57.74; H, 7.36%). IR (KBr): ν(acac) 1585 and 1510 cm^{-1}. NMR (C_6D_6): δ_H(400 MHz) 7.27–6.88 (5 H, m, C_6H_5), 5.40, 5.20 [2 H, both s, CHC(O)], 5.24 [1H, d, *J*(PH) 3.6, =C*H*Ph], 2.39 (3 H, m, C*H*CH_3), 1.97, 1.88, 1.86, 1.78 [12 H, all s, C(O)CH_3], 1.22, 1.16 [18 H, both dd, *J*(PH) 12.8, *J*(HH) 7.2 Hz, CHC*H*$_3$]; δ_C(100.6 MHz) 358.8 [d, *J*(PC) 20.1 Hz, =C=], 189.5, 188.4, 187.4, 184.5 [all s, *C*(O)CH_3], 133.8, 128.6, 125.5, 124.2 (all s, C_6H_5), 114.2 [d, *J*(PC) 1.3, =*C*HPh], 99.9, 99.2 [both s, *C*HC(O)], 28.1, 27.9, 27.8, 26.9 [all s, C(O)*C*H_3], 24.3 [d, *J*(PC) 22.6 Hz, *C*HCH_3], 19.1, 18.8 (both s, CH*C*H_3); δ_P(162.0 MHz) 53.8 (s).

[Ru(acac)$_2${=C=C(SiMe$_3$)Ph}(PPr$^i_3$)] 10. This compound was prepared as described for **9**, using **6** (0.214 g, 0.35 mmol) and PhC≡CSiMe$_3$ (0.102 cm^3, 0.52 mmol) as starting materials. Orange solid: yield 0.132 g (60%); m.p. 74 °C (decomp.) (Found: C, 56.51; H, 7.47. $C_{30}H_{49}O_4PRuSi$ requires C, 56.85; H, 7.79%). IR (KBr): ν(acac) 1575 and 1505 cm^{-1}. NMR (C_6D_6): δ_H(400 MHz) 7.44–6.99 (5 H, m, C_6H_5), 5.37, 5.32 [2 H, both s, CHC(O)], 2.37 (3 H, m, C*H*CH_3), 1.94, 1.93, 1.87, 1.85 [12 H, all s, C(O)CH_3], 1.21, 1.08 [18 H, both dd, *J*(PH) 12.8, *J*(HH) 7.2 Hz, CHC*H*$_3$] and 0.42 (9 H, s, SiMe$_3$); δ_C(100.6 MHz) 338.9 [d, *J*(PC) 19.1 =C=], 188.3, 188.1, 187.1, 185.0 [all s, *C*(O)CH_3], 134.1, 130.4, 128.5, 124.8 (all s, C_6H_5), 113.1 [s, =*C*(SiMe$_3$)Ph], 99.8, 99.3 [both s, *C*HC(O)], 28.1, 28.0, 27.9, 27.1 [all s, C(O)*C*H_3], 25.1 [d, *J*(PC) 22.2 Hz, *C*HCH_3], 19.2, 18.8 (both s, CH*C*H_3) and 1.2 (s, SiMe$_3$); δ_P(162.0 MHz) 55.3 (s).

[Ru(acac)$_2$(=C=C=CPh$_2$)(PPr$^i_3$)] 11. A solution of complex **6** (0.184 g, 0.30 mmol) in benzene (10 cm^3) was treated with HC≡CCPh$_2$(O$_2$CMe) (0.082 g, 0.33 mmol) and stirred at reflux for 30 min. After the solution was cooled to room temperature, the solvent was removed *in vacuo*. The oily residue was dissolved in hexane (1 cm^3) and the solution chromatographed on Al_2O_3 (neutral, activity grade V, column length 5 cm). With hexane, first a yellow fraction was obtained which was discarded. Subsequently, with ether a red fraction was eluted from which, after removal of the solvent and recrystallisation of the residue from pentane (3 cm^3) at −78 °C, deep red crystals were obtained: yield 0.113 g (58%), m.p. 66 °C (decomp.) (Found: C, 63.09; H, 6.89. $C_{34}H_{45}O_4PRu$ requires C, 62.85; H, 6.98%). IR (C_6H_6): ν(C=C=C) 1890, ν(acac) 1585 and 1510 cm^{-1}. NMR (C_6D_6): δ_H(400 MHz) 7.99–7.01 (10 H, m, C_6H_5), 5.45, 5.13 [2 H, both s, CHC(O)], 2.46 (3 H, m, C*H*CH_3), 2.13, 1.98, 1.84, 1.76 [12 H, all s, C(O)CH_3], 1.24, 1.21 [18 H, both dd, *J*(PH) 12.8, *J*(HH) 7.2 Hz, CHC*H*$_3$]; δ_C(100.6 MHz) 292.0 [d, *J*(PC) 22.1, Ru=C], 239.2 [d, *J*(PC) 2.0, Ru=C=*C*], 189.0, 188.3, 186.9, 184.5 [all s, *C*(O)CH_3], 148.7 (s, *ipso*-C of C_6H_5), 143.1 (s, =*C*Ph$_2$), 129.2, 128.1, 127.1 (all s, C_6H_5), 99.3, 98.4 [both s, *C*HC(O)], 28.0, 27.9, 27.8, 26.8 [all s, C(O)*C*H_3], 24.0 [d, *J*(PC) 21.9 Hz, *C*HCH_3], 19.1, 18.8 (both s, CH*C*H_3); δ_P(162.0 MHz) 51.2 (s).

Reaction of complex 2 with C_2H_4. A stream of ethene was passed through a solution of complex **2** (0.019 g, 0.013 mmol) in C_6D_6 (0.5 cm^3) which was kept in an NMR tube. After the solution was warmed at 60 °C for 1 h the ^{1}H NMR spectrum indicated the formation of [Ru(η^2-O$_2$CCH$_3$)$_2$(C$_2$H$_4$)(SbPr$^i_3$)] **12**; δ_H(200 MHz) 4.32, 4.12 (4 H, both m, C_2H_4), 2.42 [3 H, sept, *J*(HH) 7.8, C*H*CH_3], 1.88, 1.65 (6 H, both s, O$_2$CCH$_3$), 1.29, 1.25 [18 H, both d, *J*(HH) 7.8 Hz, CHC*H*$_3$]. Besides compound **12**, small amounts of unidentified products were also formed.

[Ru(η^2-O$_2$CMe)$_2$(PCy$_3$)$_2$] 13. A suspension of compound **1** (0.451 g, 0.66 mmol) in acetone (20 cm^3) was treated with 98% acetic acid (0.150 cm^3, 2.65 mmol) at room temperature. After the reaction mixture was stirred for 16 h orange crystals of **2** precipitated. They were separated and the mother-liquor was brought to dryness *in vacuo*. The remaining oily residue together with the crystals was dissolved in dichloromethane (20 cm^3) and PCy$_3$ (0.425 g, 1.52 mmol) added. The solution was stirred for 8 h at room temperature, the solvent removed *in vacuo*, and the oily residue treated with acetone (5 cm^3). Upon storing the mixture at 0 °C for 3 h a red solid was formed which was recrystallised from CH_2Cl_2–acetone (1 : 4, 5 cm^3) to give red crystals: yield 0.371 g (72%), m.p. 70 °C (decomp.) (Found: C, 61.02; H, 8.91. $C_{40}H_{72}O_4P_2Ru$ requires C, 61.59; H, 9.30%). IR (KBr): ν(OCO) 1490 and 1420 cm^{-1}. NMR (C_6D_6): δ_P(81.0 MHz, 60 °C) 50.8 (s).

Reaction of complex 2 with PPr$^i_3$. A solution of complex **2** (0.124 g, 0.085 mmol) in dichloromethane (10 cm^3) was treated with PPr$^i_3$ (0.075 cm^3, 0.39 mmol) and stirred for 8 h at room temperature. After the solvent was removed *in vacuo*, an oily residue was obtained which according to the ^{1}H NMR spectrum contained a mixture of [Ru(η^2-O$_2$CMe)$_2$(PPr$^i_3$)$_2$] **14** and SbPr$^i_3$. Attempts to separate the two products by fractional crystallisation and column chromatography failed. NMR (C_6D_6) of **14**: δ_H(200 MHz) 2.85 (6 H, m, C*H*CH_3), 1.69 (6 H, s, CO$_2$CH$_3$), 1.26 (dd, CHC*H*$_3$; coupling constants not determined due to overlap of the signal with that of SbCHC*H*$_3$) and 1.05 [18H, dd, *J*(PH) 12.1, *J*(HH) 6.8 Hz, CHC*H*$_3$]; δ_P(81.0 MHz) 60.6 (s).

[Ru(η^2-O$_2$CMe)(η^1-O$_2$CMe)(=C=CHPh)(PCy$_3$)$_2$] 15. A solution of complex **13** (0.141 g, 0.18 mmol) in dichloromethane (10 cm^3) was treated with phenylacetylene (0.026 cm^3, 0.24 mmol) and stirred for 10 min at room temperature. After the solvent was removed *in vacuo* the oily residue was treated with pentane (3 cm^3) and the mixture was stored for 3 h at 0 °C. A yellow, only slightly air-sensitive solid was obtained: yield 0.098 g (61%); m.p. 81 °C (decomp.) (Found: C, 65.57; H, 8.42. $C_{48}H_{78}O_4P_2Ru$ requires C, 65.35; H, 8.91%). IR (KBr): ν_{asym}(OCO) 1630, 1440, ν(C=C) 1590, ν_{sym}(OCO) 1365, 1300 cm^{-1}. NMR (CDCl$_3$): δ_H(400 MHz) 7.53–6.87 (5 H, m, C_6H_5), 5.51 [1 H, t, J(PH) 3.2 Hz, =CHPh], 2.04–1.12 (66 H, m, C_6H_{11}) and 1.98 (6 H, s, CO_2CH_3); δ_C(100.6 MHz) 353.1 [t, J(PC) 15.1, =C=], 178.7 (s, br, O_2CCH_3), 134.8, 127.9, 124.5, 122.9 (all s, C_6H_5), 111.8 [t, J(PC) 4.0 Hz, =CHPh], 33.3 (vt, N 16.0, *ipso*-C of C_6H_{11}), 29.1 (s, *m*-C of C_6H_{11}), 28.1 (vt, N 9.8 Hz, *o*-C of C_6H_{11}), 26.5 (s, *p*-C of C_6H_{11}) and 24.0 (s, O_2CCH_3); δ_P(162.0 MHz) 20.0 (s).

[Ru(η^2-O_2CMe)(η^1-O_2CMe)(=C=CHCO$_2$Me)(PCy$_3$)$_2$] 16. This compound was prepared as described for **15**, using **13** (0.118 g, 015 mmol) and methyl propiolate (0.018 cm^3, 0.22 mmol) as starting materials. Yellow solid: yield 0.085 g (65%); m.p. 131 °C (decomp.) (Found: C, 60.67; H, 8.44. $C_{44}H_{76}O_6P_2Ru$ requires C, 61.16; H, 8.86%). IR (KBr): $\nu(CO_2)$ 1680, ν_{asym}(OCO) 1640, 1440, ν(C=C) 1585, ν_{sym}(OCO) 1360, 1305 cm^{-1}. NMR ($CDCl_3$): δ_H(400 MHz) 5.10 [1 H, t, J(PH) 2.8 Hz, =CHCO$_2$CH$_3$], 3.59 (3 H, s, =CHCO$_2$CH_3), 1.98 (6 H, s, O_2CCH_3), 2.13–1.19 (66 H, m, C_6H_{11}); δ_C(100.6 MHz) 341.8 [t, J(PC) 14.1 Hz, =C=], 178.7 (s, br, O_2CCH_3), 169.6 (s, =CHCO$_2$CH$_3$), 104.4 (s, =CHCO$_2$CH$_3$), 50.5 (s, =CHCO$_2$$CH_3$), 33.6 (vt, N 16.0, *ipso*-C of C_6H_{11}), 29.0 (s, *m*-C of C_6H_{11}), 28.0 (vt, N 9.4 Hz, *o*-C of C_6H_{11}), 26.5 (s, *p*-C of C_6H_{11}) and 23.8 (s, O_2CCH_3); δ_P(162.0 MHz) 21.4 (s).

Crystallography

Data for X-ray diffraction analysis of complex **2**: crystals from toluene (−40 °C), $C_{44}H_{98}O_9Ru_2Sb_4$, M = 1460.36, monoclinic, space group $P2_1/c$ (no. 14), a = 20.134(9), b = 14.738(3), c = 20.852(8) Å, β = 106.829(7)°, U = 5923(4) Å^3 (by least-squares refinement on diffractometer angles from 25 centred reflections, 14 < 2θ < 30), T = 293(2) K, graphite monochromated Mo-Kα radiation (λ = 0.710 73 Å), zirkon filter (factor 15.4), Z = 4, D_c = 1.638 g cm^{-3}, F(000) = 2904, red prism with dimensions 0.1 × 0.2 × 0.3 mm, μ(Mo-Kα) = 2.345 mm^{-1}, Lorentz-polarisation and semi-empirical absorption correction based on ψ scans, transmission factors 0.86–1.00; Enraf-Nonius CAD4 diffractometer, ω–θ scans, data collection range 4.0 < 2θ < 46, $+h$, $-k$, $\pm l$, two standard reflections showed no significant variation in intensity; 9463 reflections measured, 8009 unique (R_{int} = 0.0483) of which 8006 were used in all calculations, 4902 observed [$I > 2\sigma(I)$].

Structure solution and refinement. The structure was solved by direct methods and subsequent Fourier-difference techniques, and refined anisotropically, by full-matrix least squares, on F^2 (program SHELXL 93).[30] Hydrogen atoms were included using a riding model. The weighting scheme was $w^{-1} = [\sigma^2(F_o^2) + (0.0262P)^2 + 22.2966P]$, where $3P = F_o^2 + 2F_c^2$; R_1 = 0.0557 and wR_2 = 0.0908 for 4902 observed reflections [$I > 2\sigma(I)$], 0.1131 and 0.1171 for all 8006 reflections, 560 parameters, data to parameter ratio 14.3, goodness of fit = 1.048, residual electron density +0.602, −0.684 e Å^{-3}.

CCDC reference number 186/850.

See http://www.rsc.org/suppdata/dt/1998/833/ for crystallographic files in .cif format.

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