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Synthesis and reactivity of cationic vinylidene and allenylidene ruthenium(II) complexes containing the phosphinoether $Pr^i_2PCH_2CH_2OMe$ as chelating ligand †

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An efficient method for the preparation of the chelate complex $[RuCl_2(\kappa^2P,O\text{-}Pr^i_2PCH_2CH_2OMe)_2]$ **2**, using $[\{RuCl_2(C_8H_{12})\}_n]$ **1** as starting material, has been developed. Compound **2** reacts with terminal alkynes HC≡CR (R = Ph, C_6H_4Me-*p* or $C_6H_4C{\equiv}CH$-*m*) in the presence of $Ag(O_3SCF_3)$ to give the octahedral cationic vinylidene complexes $[RuCl(=C=CHR)(\kappa^2P,O\text{-}Pr^i_2PCH_2CH_2OMe)_2][O_3SCF_3]$ **4–6** in 70–80% yield. The parent derivative **3** (R = H) has been prepared analogously but is stable only under an acetylene atmosphere. Crystal structural analysis of **4** (R = Ph) confirms a *cis* arrangement of the chloro and vinylidene ligands. Treatment of **4** with basic Al_2O_3 produces, by deprotonation, a mixture of two isomers $[RuCl(C{\equiv}CPh)(\kappa^2P,O\text{-}Pr^i_2PCH_2CH_2OMe)_2]$ **7**, **8** with the alkynyl and chloro ligands in either *cis* or *trans* disposition. Compounds **7**, **8** easily react by partial cleavage of the chelate bonds to give the corresponding dicarbonyl derivatives $[RuCl(C{\equiv}CPh)(CO)_2(\kappa P\text{-}Pr^i_2PCH_2CH_2OMe)_2]$ **9**, **10**. The isomeric mixture can be completely converted into the thermodynamically preferred species **9** with the two CO and the alkynyl and chloro ligands *cis* disposed. The neutral vinylidene complexes $[RuX_2(=C=CHPh)(\kappa P\text{-}Pr^i_2PCH_2CH_2OMe)(\kappa^2P,O\text{-}Pr^i_2PCH_2CH_2OMe)]$ (X = CN, I or Br) were obtained from **4** and KCN, NaI and LiBr, respectively. The reaction of **2** with propargylic alcohols HC≡CCR(Ph)OH in the presence of $Ag(O_3SCF_3)$, followed by treatment with acidic Al_2O_3, afforded the cationic allenylidene compounds $[RuCl\{=C=C=C(Ph)R\}(\kappa^2P,O\text{-}Pr^i_2PCH_2CH_2OMe)_2][O_3SCF_3]$ (R = Ph or C_6H_4Me-*o*) in moderate yields. The crystal structure where R = Ph has been determined and reveals an almost linear Ru=C=C=C chain with one of the methoxy groups *trans* to the allenylidene ligand. While the R = C_6H_4Me-*o* derivative reacts with CO to give the cationic carbonyl compound $[RuCl(CO)(\kappa^2P,O\text{-}Pr^i_2PCH_2CH_2OMe)_2][O_3SCF_3]$, the reaction of **4** with CO gives a mixture of this complex, **9**/**10**, and *trans*,*trans*,*trans*-$[RuCl_2(CO)_2(\kappa P\text{-}Pr^i_2PCH_2CH_2OMe)_2]$. The latter is formed quantitatively from **2** and carbon monoxide.

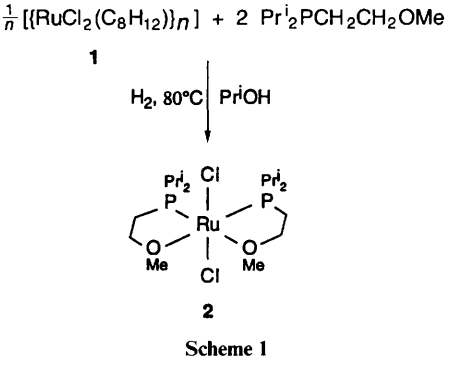
Recently, we have been interested in the synthesis and reactivity of transition-metal complexes containing phosphino-ethers, -amines and -esters as ligands. The characteristic feature of these ligands is that they behave as hemilabile chelating units and even under mild conditions are able to create a free coordination site to which a reactive substrate can be added. When this substrate was a terminal alkyne we could prepare a variety of neutral vinylidenemetal compounds with rhodium(I) [2] and iridium(I) [3] as well as with ruthenium(II) [4] and osmium(II).[5]

As a continuation of this work we describe in this paper the preparation of a variety of *cationic* vinylidene and allenylidene ruthenium complexes with the bulky phosphinoether Pr^i_2P-CH_2CH_2OMe as a supporting ligand. A new and highly efficient method for the synthesis of the starting material $[RuCl_2(\kappa^2P,O\text{-}Pr^i_2PCH_2CH_2OMe)_2]$ **2** is also reported.

Results and Discussion

A new route to the chelate complex 2

While we had used in our initial studies either $RuCl_3$(aq) or $[RuCl_2(PPh_3)_3]$ as starting material for the preparation of **2**,[4a] we discovered more recently that the polymeric cyclooctadiene derivative $[\{RuCl_2(C_8H_{12})\}_n]$ **1** is a more appropriate precursor. Treatment of a suspension of **1** in Pr^iOH with 2 equivalents of the bifunctional phosphine $Pr^i_2PCH_2CH_2OMe$ under hydrogen for 1 h at 80 °C leads to a red solution from which the chelate complex **2** (Scheme 1) can be isolated as a bright red solid in 75% yield. It should be mentioned that in the absence of hydrogen the reaction is considerably slower, requiring 12 h to be completed. In contrast to **1** the related iridium compound $[\{IrCl(C_8H_{14})_2\}_2]$ reacts with $Pr^i_2PCH_2$-CH_2OMe, even at room temperature, not to afford the expected chelate complex $[\{IrCl(\kappa^2P,O\text{-}Pr^i_2PCH_2CH_2OMe)\}_2]$ or $[Ir(\kappa^2P,O\text{-}Pr^i_2PCH_2CH_2OMe)_2]Cl$ but to give the C–H activation product $[IrCl(H)(\kappa^2P,C\text{-}CH_2OCH_2CH_2PPr^i_2)(\kappa^2P,O\text{-}Pr^i_2PCH_2CH_2OMe)]$ instead.[3c]



Scheme 1

Preparation of cationic vinylidene ruthenium(II) complexes

At room temperature and in the absence of UV light compound **2** is rather inert toward alk-1-ynes.[4a] However, in the presence of silver triflate $Ag(O_3SCF_3)$ it smoothly reacts with HC≡CR (R = H, Ph, C_6H_4Me-*p* or $C_6H_4C{\equiv}CH$-*m*) to give the triflates

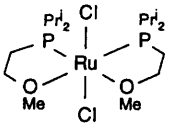
† Vinylidene Transition-metal Complexes. Part 39.[1]

of the cationic vinylideneruthenium(II) complexes **4**–**6** in 70–80% yield (Scheme 2). The parent derivative **3** is stable only under an acetylene atmosphere and cannot be isolated as a solid. It was therefore characterized by ^{1}H and ^{31}P NMR spectroscopy. The most typical feature of the ^{1}H NMR spectrum of **3** is the triplet for the $=CH_2$ protons at δ 3.69 which, according to the cationic nature of the species, appears at lower field if compared with that of the neutral compound $[RuCl_2(=C=CH_2)(\kappa P\text{-}Pr^i{}_2PCH_2CO_2Me)(\kappa^2 P,O\text{-}Pr^i{}_2PCH_2CO_2Me)]$.[4b]

The analogous complexes **4**–**6**, isolated as orange, only slightly air-sensitive solids, are significantly more stable than **3**. The proposed structure with the *cis* disposed $PPr^i{}_2$ groups is supported by the ^{31}P NMR spectra which at room temperature display typical AB patterns and show two doublets with a small P–P coupling constant of about 25 Hz. In contrast to the neutral ruthenium vinylidenes $[RuCl_2(=C=CHR)(\kappa P\text{-}Pr^i{}_2PY)(\kappa^2 P,O\text{-}Pr^i{}_2PY)]$ (Y = CH_2CH_2OMe, CH_2CO_2Me, or CH_2CO_2Et),[4] the cationic complexes **4**–**6** are not fluxional on the NMR time-scale. Further characteristic features are the triplet resonance for the $=CHR$ proton in the ^{1}H NMR spectra at *ca.* δ 5 and the low-field signals in the ^{13}C NMR spectra at δ 355–360 and 117 which, in agreement with DEPT (distortionless enhancement of polarization transfer) measurements, are assigned to the α- and β-C carbon atoms of the vinylidene unit.

Molecular structure of compound 4

A single-crystal X-ray diffraction study of compound **4** confirms the structural proposal shown in Scheme 2. The ORTEP[6] plot (Fig. 1) reveals that the ligand geometry around the metal centre is distorted octahedral with the two phosphorus atoms in *cis* position. The two phosphinoether ligands are co-ordinated in a κ^2 mode forming two five-membered chelate rings with the ruthenium atom. The relatively small bond angles O(1)–Ru–P(1) [82.92(7)°] and O(2)–Ru–P(2) [80.67(7)°] (Table 1) are probably due to the ring strain in the $RuPC_2O$ chelating system. The Ru–C(1)–C(2) unit is not exactly linear [170.9(3)°] with a Ru–C(1) distance [1.790(3) Å] that is certainly one of the shortest ruthenium–vinylidene carbon bond lengths reported to date.[4,7,8] In the cationic ruthenium complex $[Ru(C_5Me_5)(=C=CHPh)(PMe_2Ph)_2]^+$, which also contains C=CHPh as ligand, the corresponding Ru–C distance is 1.76(1) Å.[9] The Ru–P bond lengths in **4** are in the range found for vinylidene compounds with *cis* P–Ru–P arrangements[8,9] and deserve no further comment.



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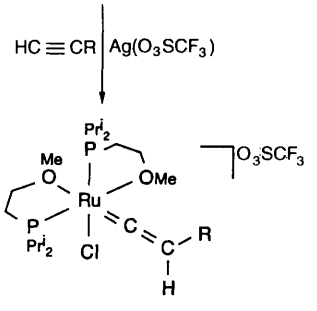


R = H (**3**), Ph (**4**), C_6H_4Me-*p* (**5**), $C_6H_4C\equiv CH$-*m* (**6**)

Scheme 2

Preparation of alkynylruthenium(II) derivatives

The acidic nature of the vinylidene proton in compound **4** becomes immediately evident upon treatment with basic alumina. At room temperature in dichloromethane–acetone a virtually spontaneous reaction occurs which affords a mixture of the two isomers **7** and **8** (Scheme 3). The same isomeric mixture of **7** and **8** is also obtained on treatment of **4** with a stoichiometric amount of Li(C≡CPh) in tetrahydrofuran (thf) at 0 °C. Attempts to separate the two isomers by column chromatography or fractional crystallization failed.

The composition of the mixture of isomers **7** and **8** as determined by ^{1}H and ^{31}P NMR spectroscopy is 2:1. Since the ^{31}P NMR spectrum in $[^2H_8]$toluene at −80 °C displays for the major isomer two well separated doublets which show a small P–P coupling of 32 Hz, we assume that **7** has the two phosphorus atoms in *cis* position. For the minor isomer **8** the spectrum shows only one signal for the two phosphorus atoms and thus, provided that the chloro and alkynyl ligands are *trans* to each other, two configurations, *cis*- and *trans*-P,P, seem to be possible. Owing to the X-ray structural analysis of

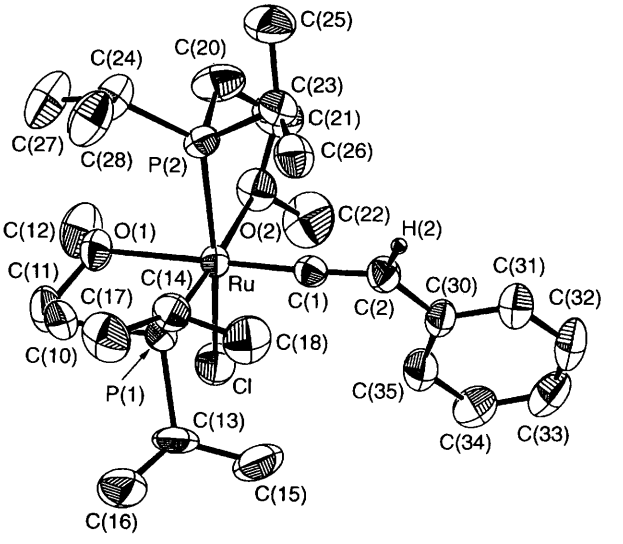
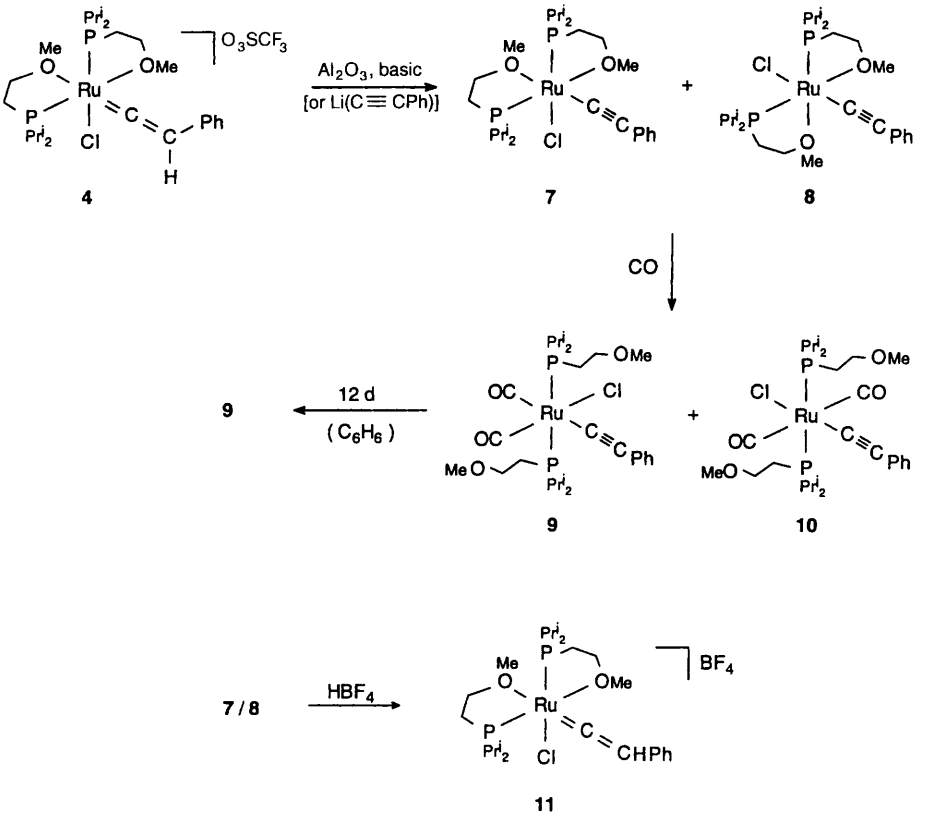


Fig. 1 Molecular structure of **4**

Table 1 Selected bond lengths (Å) and angles (°) for complex **4**

Ru–C(1)	1.790(3)	P(1)–C(10)	1.836(4)
C(1)–C(2)	1.313(5)	C(10)–C(11)	1.504(6)
C(2)–C(30)	1.467(5)	O(1)–C(11)	1.450(5)
Ru–O(1)	2.236(2)	O(1)–C(12)	1.437(5)
Ru–O(2)	2.286(2)	P(2)–C(20)	1.834(4)
Ru–P(1)	2.272(1)	C(20)–C(21)	1.478(6)
Ru–P(2)	2.368(1)	O(2)–C(21)	1.434(5)
Ru–Cl	2.408(1)	O(2)–C(22)	1.434(5)
C(1)–Ru–O(1)	179.2(1)	P(2)–Ru–Cl	162.76(4)
C(1)–Ru–P(1)	97.5(1)	C(10)–P(1)–Ru	100.7(1)
C(1)–Ru–O(2)	88.8(1)	C(11)–C(10)–P(1)	112.2(3)
C(1)–Ru–P(2)	92.8(1)	O(1)–C(11)–C(10)	107.9(3)
C(1)–Ru–Cl	97.5(1)	C(11)–O(1)–Ru	114.2(2)
O(1)–Ru–P(1)	82.92(7)	C(12)–O(1)–C(11)	112.1(3)
O(1)–Ru–P(2)	87.72(7)	C(20)–P(2)–Ru	99.1(2)
O(1)–Ru–O(2)	90.77(9)	C(21)–C(20)–P(2)	112.5(3)
O(1)–Ru–Cl	81.90(7)	C(2)–C(21)–C(20)	108.0(4)
O(2)–Ru–P(2)	80.67(7)	C(21)–O(2)–Ru	114.7(2)
O(2)–Ru–Cl	85.72(8)	C(22)–O(2)–C(21)	110.2(3)
P(1)–Ru–P(2)	101.19(4)	C(2)–C(1)–Ru	170.9(3)
P(1)–Ru–O(2)	173.31(7)	C(1)–C(2)–C(30)	128.0(4)
P(1)–Ru–Cl	91.19(4)		



Scheme 3

$[RuCl_2(\kappa^2P,O\text{-}Ph_2PCH_2CH_2OMe)_2]$, which proved that in the basal plane of the octahedron both the phosphorus and the oxygen atoms are *cis* disposed,[10] and by comparison with the NMR data for **2**,[4a] we favour a similar ligand arrangement for compound **8** (see Scheme 3). In agreement with the structural proposal for both isomers, the ^1H NMR spectrum of the mixture displays two signals at δ 4.06 and 3.16 for the protons of the inequivalent OCH_3 groups of **7** and one resonance at δ 3.55 for the OCH_3 protons of **8**. The IR spectrum of the solid shows two ν(C≡C) bands at 2000 and 2050 cm^{-1}, respectively. We note that in contrast to **7/8** in two related alkynyl(chloro)-ruthenium(II) complexes, $[RuCl(C{\equiv}CPh)(dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$) and $[RuCl(C{\equiv}CPh)(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) a *trans* position of Cl and C≡CPh is preferred.[11,12]

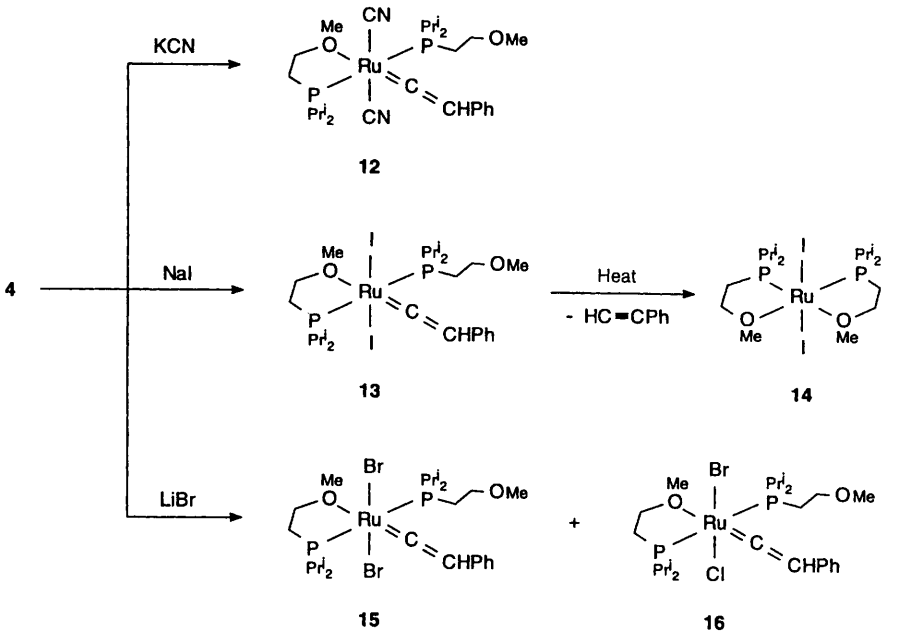
The hemilabile character of the *P,O*-chelating ligands in isomers **7/8** is illustrated by the reaction with carbon monoxide (Scheme 3). Under mild conditions (benzene, room temperature) a partial cleavage of the chelate bonds occurs which gives the corresponding alkynyl dicarbonyl derivatives **9/10** in moderate yield. The isomeric mixture of **9/10** can be completely converted into the thermodynamically preferred compound **9**, if a solution of **9/10** in benzene is stirred for 12 d at 25 °C. Based on the observation of *two* co-stretching frequencies at 2020 and 1960 cm^{-1} in the IR spectrum of **9**, and the *two* signals for the CO carbon atoms at δ 197.9 and 197.2 in the ^{13}C NMR spectrum, we assume that the carbonyl ligands are *cis* disposed, one *trans* to Cl and the other *trans* to C_2Ph. The appearance of one resonance in the ^{31}P NMR spectrum of **9** for the two phosphorus atoms, which is consistent with a *trans* P–Ru–P arrangement, supports the structural proposal. The IR spectrum of the isomer **10** shows only one ν(CO) band thus confirming the *trans* geometry of the $Ru(CO)_2$ unit. With regard to the reactivity of unsymmetrical five-membered $RuPC_2O$ chelate rings, it should be mentioned that the tendency to cleave the Ru–O bond generally depends on the bonding capability of the oxygen-donor moiety. While not only **7** and **8** but also **2** and $[RuCl_2(\kappa^2P,O\text{-}Ph_2PCH_2CH_2OMe)_2]$ react with CO to give the corresponding dicarbonyl derivatives,[4a,13] the phosphinoester complex $[RuCl_2(\kappa^2P,O\text{-}Pr^i_2PCH_2CO_2Me)_2]$ on treatment with carbon monoxide exclusively yields the monocarbonyl compound $[RuCl_2(CO)(\kappa P\text{-}Pr^i_2PCH_2CO_2Me)(\kappa^2P,O\text{-}Pr^i_2PCH_2CO_2Me)]$.[4b]

The reaction of compound **4** with base to give **7/8** is reversible. If a solution of the two isomers in thf is treated with $HBF_4{\cdot}OEt_2$ immediately a change from yellow to orange takes place and after partial removal of the solvent an orange solid **11** (Scheme 3) can be isolated. It has been identified by comparison of the ^1H and ^{31}P NMR spectroscopic data with those of the corresponding triflate **4**.

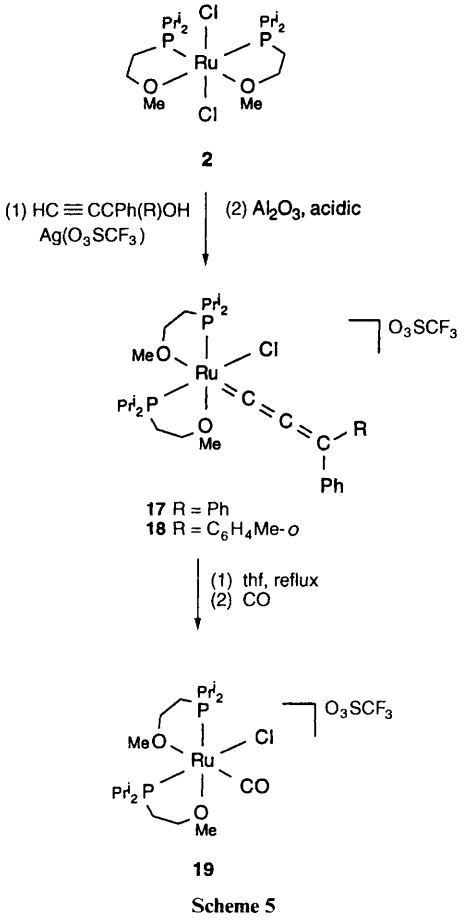
The results of ligand-displacement reactions of compound **4** are summarized in Scheme 4. Lithium bromide and NaI as well as KCN react with **4** in methanol or dichloromethane by substitution of the chloride and partial opening of one of the chelate bonds to give the neutral vinylideneruthenium complexes **12**, **13** and **15** in good yield. Although a six-fold excess of LiBr was used, the isolated product contains beside the dibromo derivative **15** the mixed bromo(chloro)ruthenium(II) compound **16** as a minor component (≈20%). Attempts to separate the two complexes failed. If the reaction mixture generated from **4** and NaI in methanol, containing **13** as the main species, is further heated under reflux for 3 h, phenylacetylene is eliminated and the diiodo complex **14** is formed. As expected, the ^1H and ^{31}P NMR spectroscopic data for **14** are almost identical to those of the dichloro derivative **2**.

Cationic allenylidene ruthenium complexes

The method first employed by Selegue[14] and, in ruthenium chemistry, subsequently used by Dixneuf and others[15] to prepare complexes with Ru=C=C=CRR′ as a molecular unit, can also be applied to the synthesis of **17** and **18** (Scheme 5). While compound **2** is inert toward HC≡CCPh(R)OH (R = Ph



Scheme 4



Scheme 5

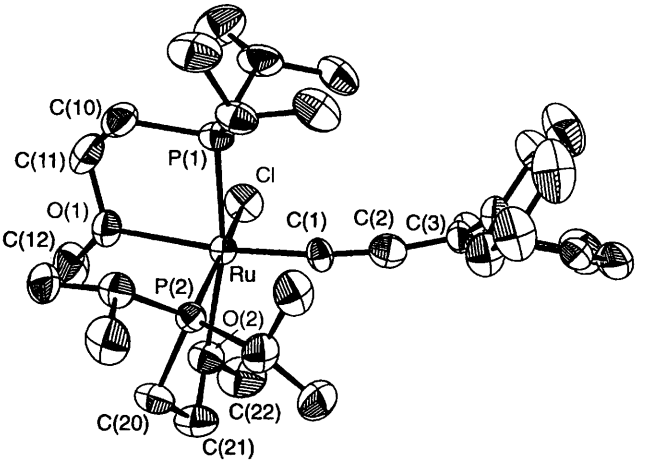


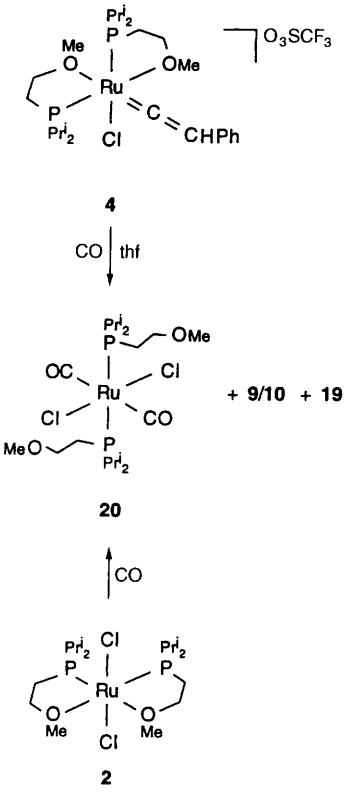
Fig. 2 Molecular structure of **17**

or C_6H_4Me-*o*), it slowly reacts in thf with these propargylic alcohols in the presence of silver triflate in the dark to give an orange-brown solution which possibly contains a CPh(R)OH-substituted vinylidene ruthenium intermediate.[16] If this solution is chromatographed on acidic alumina a red fraction is eluted from which the allenylidene complexes **17** and **18** are isolated in 30–40% yield. We assume that in contrast to the reaction of **2** with HC≡CR (Scheme 2) which affords the vinylidene complexes **4**–**6** almost quantitatively, on treatment of **2** with HC≡CCPh(R)OH and $Ag(O_3SCF_3)$ some unknown side reactions occur, thus lowering the yield of **17** and **18**. Both allenylidene complexes are red solids which are only moderately air-sensitive and readily soluble in polar organic solvents. Regarding the spectroscopic data for **17** and **18**, the most characteristic features are the strong C=C=C stretching frequency in the IR spectra at 1930 cm^{-1} and the three low-field resonances in the ^{13}C NMR spectra at δ 305–308, 220–222 and 155 which by comparison[7] are assigned to the carbon atoms of the allenylidene unit. Since the ^{31}P NMR spectra of **17** and **18** display two doublets representing an AB spin pattern, there is no doubt that the two Pr^i_2P groups are *cis* to each other.

The molecular structure of the cationic complex **17** is shown in Fig. 2. The configuration around ruthenium corresponds to a slightly distorted octahedron and is analogous to that of the vinylidene compound **4**. The angles of the *trans* arranged units C(1)–Ru–O(1), P(1)–Ru–O(2) and P(2)–Ru–Cl are 172.1(2), 168.4(1) and 166.52(5)°, respectively. The distance Ru–C(1) [1.829(6) Å] is almost the same as in the structurally related, neutral allenylidenedichlororuthenium derivative $[RuCl_2(=C=C=CPh_2)(\kappa P\text{-}Pr^i_2PCH_2CO_2Me)(\kappa^2 P,O\text{-}Pr^i_2PCH_2CO_2Me)]$ [1.84(1) Å][4b] and somewhat shorter than in cationic complexes containing a *trans* ClRu=C=C=CRR′ fragment.[17] The two carbon–carbon bond lengths in the Ru=C=C=C chain (Table 2) are quite similar to those found in $[Ru(C_5H_5)(=C=C=CPh_2)(PMe_3)_2]^+$[14] as well as in other metal allenyl-

Table 2 Selected bond lengths (Å) and angles (°) for complex **17**

Ru–C(1)	1.829(6)	Ru–Cl	2.434(2)
C(1)–C(2)	1.259(9)	P(1)–C(10)	1.825(7)
C(2)–C(3)	1.352(9)	C(10)–C(11)	1.511(9)
C(3)–C(30)	1.484(8)	O(1)–C(11)	1.437(7)
C(3)–C(40)	1.466(8)	O(1)–C(12)	1.448(7)
Ru–O(1)	2.252(4)	P(2)–C(20)	1.828(6)
Ru–O(2)	2.232(4)	C(20)–C(21)	1.506(8)
Ru–P(1)	2.282(2)	O(2)–C(21)	1.432(7)
Ru–P(2)	2.336(2)	O(2)–C(22)	1.454(7)
C(1)–Ru–O(1)	172.1(2)	C(10)–P(1)–Ru	100.5(2)
C(1)–Ru–P(1)	91.8(2)	C(11)–C(10)–P(1)	112.2(4)
C(1)–Ru–O(2)	99.8(2)	O(1)–C(11)–C(10)	108.6(5)
C(1)–Ru–P(2)	94.9(2)	C(11)–O(1)–Ru	113.9(4)
C(1)–Ru–Cl	91.3(2)	C(12)–O(1)–C(11)	111.1(5)
O(1)–Ru–P(1)	82.8(1)	C(20)–P(2)–Ru	100.0(2)
O(1)–Ru–P(2)	91.7(2)	C(21)–C(20)–P(2)	112.9(4)
O(1)–Ru–O(2)	85.6(2)	O(2)–C(21)–C(20)	108.5(5)
O(1)–Ru–Cl	83.2(1)	C(21)–O(2)–Ru	119.3(3)
O(2)–Ru–P(2)	80.8(1)	C(22)–O(2)–C(21)	110.3(5)
O(2)–Ru–Cl	86.3(1)	C(2)–C(1)–Ru	170.9(4)
P(1)–Ru–P(2)	99.54(5)	C(1)–C(2)–C(3)	171.8(6)
P(1)–Ru–O(2)	168.4(1)	C(2)–C(3)–C(30)	119.4(5)
P(1)–Ru–Cl	92.20(5)	C(2)–C(3)–C(40)	120.8(5)
P(2)–Ru–Cl	166.52(5)	C(30)–C(3)–C(40)	119.8(5)



Scheme 6

idenes[17,18] and indicate that, besides the usual bonding formulation M=C=C=CRR′, a second zwitterionic resonance structure M–C≡C–CRR′ with a positive charge at the metal and a negative charge at the γ-carbon atom has to be taken into consideration.

If the allenylidene complexes **17** and **18** are heated in thf under reflux and then treated with CO the cationic monocarbonylruthenium(II) compound **19** is formed in excellent yield. The 'fate' of the allenylidene fragment is unknown. We have recently found that in the co-ordination sphere of rhodium(I) two C_3 units can be coupled together to give a hexapentaene ligand,[19] but we failed to detect such a species in the reaction mixture obtained from **17** (or **18**), thf and CO.

Finally, also the reaction of the cationic vinylidene complex **4** with CO was investigated (Scheme 6). Under mild conditions (thf, 25 °C) phenylacetylene is eliminated and a mixture of **19**, the alkynylruthenium(II) derivatives **9**, **10** (see Scheme 3) and the dicarbonyl dichloro compound **20** is formed. Complex **20** is prepared as the sole product if CO is passed through a solution of **2** in CH_2Cl_2 at room temperature. We note that under different conditions, in toluene as solvent, from **2** and CO instead of the *trans,trans,trans* isomer **20** the corresponding *cis,cis,trans* isomer (having only the Pr^i_2P groups in *trans* disposition) has been obtained.[4a]

Experimental

All reactions were carried out under an atmosphere of argon by using Schlenk-tube techniques. Solvents were dried by the usual procedures and distilled under argon prior to use. The starting materials $[\{RuCl_2(C_8H_{12})\}_n]$,[20] $Pr^i_2PCH_2CH_2OMe$,[2a] and HC≡CCPh(R)OH (R = Ph or C_6H_4Me-*o*)[21] were prepared by published methods. The alkynes HC≡CR (R = H, Ph, C_6H_4Me-*p* or $C_6H_4C{\equiv}CH$-*m*) were commercial products from Aldrich and ABCR. The NMR spectra were recorded on Bruker AC 200 and AMX 400 instruments and the IR spectra on a Perkin-Elmer 1420 spectrometer. 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

[$RuCl_2(\kappa^2P,O\text{-}Pr^i_2PCH_2CH_2OMe)_2$] 2. A suspension of $[\{RuCl_2(C_8H_{12})\}_n]$ (0.140 g, 0.50 mmol of ruthenium) in Pr^iOH (20 cm^3) was treated with $Pr^i_2PCH_2CH_2OMe$ (0.19 cm^3, 1.00 mmol) and stirred under hydrogen for 1 h at 80 °C. During this time a change from brown to dark red was observed. Upon cooling to room temperature the solvent was removed *in vacuo*, and the residue treated with pentane (10 cm^3) to give a bright red microcrystalline solid, which was filtered off, washed repeatedly with pentane and dried *in vacuo*: yield 0.197 g (75%). The compound was identified by its ^1H and ^{31}P NMR spectra.[4a]

Reaction of complex 2 with acetylene and $Ag(O_3SCF_3)$. Compound **2** (0.100 g, 0.19 mmol) was dissolved in $(CD_3)_2CO$ (0.8 cm^3) degassed under argon and transferred into an NMR tube. A stream of acetylene was passed through the solution for 5 min, and $Ag(O_3SCF_3)$ (0.049 g, 0.19 mmol) was added. After 15 min at room temperature the ^1H and ^{31}P NMR spectra showed the formation of $[RuCl(=C{=}CH_2)(\kappa^2P,O\text{-}Pr^i_2PCH_2CH_2OMe)_2][O_3SCF_3]$ **3**. In the absence of an acetylene atmosphere **3** decomposes, therefore we were unable to isolate it as a solid. NMR [$(CD_3)_2CO$]: δ_H(200 MHz) 4.20, 4.12, 3.87, 3.70 (1 H each, all m, CH_2OCH_3), 3.69 [2 H, t, J(PH) 2.9, $=CH_2$], 3.75, 3.41 (3 H each, both s, OCH_3), 2.84, 2.63 (1 H each, both m, $PCHCH_3$ and PCH_2), 2.36 (2 H, m, $PCHCH_3$ and PCH_2), 2.30, 2.00 (signals partially covered by acetone resonance, m, $PCHCH_3$ and PCH_2), 1.90 (signal partially covered by acetylene resonance, m, $PCHCH_3$ and PCH_2) and 1.45–1.05 (24 H, m, $PCHCH_3$); δ_P(81 MHz) 69.8, 58.9 [both d, AB spin system, J(PP) 26.1 Hz]; δ_F(188.3 MHz) −78.6 (s).

[RuCl(=C=CHPh)($\kappa^2P,O\text{-}Pr^i_2PCH_2CH_2OMe)_2$][$O_3SCF_3$] 4. To a solution of compound **2** (0.262 g, 0.50 mmol) in acetone (10 cm^3) were added HC≡CPh (0.3 cm^3, 2.50 mmol) and $Ag(O_3SCF_3)$ (0.128 g, 0.50 mmol). After stirring for 2 h in the dark the precipitate (AgCl) was filtered off through Kieselgur and the filtrate concentrated to *ca.* 0.5 cm^3. The precipitate was washed with diethyl ether to give an orange microcrystalline solid: yield 0.285 g (77%) (Found: C, 43.75; H, 6.25; S, 4.35. $C_{27}H_{48}ClF_3O_5P_2RuS$ requires C, 43.8; H, 6.55; S, 4.35%). IR (KBr): ν(C=C) 1610 and 1580 cm^{-1}. NMR ($CDCl_3$): δ_H(400 MHz) 7.3–7.0 (5 H, m, C_6H_5), 4.99 [1 H, t, J(PH) 3.4, =CH],

4.19, 4.12, 3.98, 3.73 (1 H each, all m, CH_2OCH_3), 3.84, 3.67 (3 H each, both s, OCH_3), 2.89, 2.56 (1 H each, both m, PC*H*CH_3 and PCH_2), 2.36, 2.29 (2 H each, both m, PC*H*CH_3 and PCH_2), 2.06, 1.97 (1 H each, both m, PC*H*CH_3 and PCH_2) and 1.5–1.2 (24 H, m, PCHC*H*$_3$); δ_C(100.6 MHz) 357.1 [dd, *J*(PC) 17.8, *J*(P′C) 15.3, Ru=C], 128.6, 128.4, 126.2 (all s, C_6H_5), 120.8 [q, *J*(CF) 321.0, CF_3SO_3], 117.4 (s, =CH), 72.4, 71.2 (both s, CH_2OCH_3), 62.8, 61.3 (both s, OCH_3), 36.9, 28.8 and 26.0 [all d, *J*(PC) 30.0, PCHCH$_3$], 25.1 [d, *J*(PC) 20.0, PCH_2 and PCHCH$_3$], 23.1 [d, *J*(PC) 20.0, PCH_2], 19.8, 19.5, 19.43, 19.41, 19.37, 19.24, 19.22, 18.87 (all s, PCH*C*H$_3$); δ_P(162 MHz) 67.8, 56.1 [both d, AB spin system, *J*(PP) 24.4 Hz]; δ_F(376.5 MHz) −78.6 (s).

[RuCl(=C=CHC$_6$H$_4$Me-*p*)(κ^2*P*,*O*-Pr$^i_2$PCH$_2$CH$_2$OMe)$_2$][O$_3$SCF$_3$] 5. This compound was prepared as described for **4**, using **2** (0.262 g, 0.50 mmol) and HC≡C(C_6H_4Me-*p*) (0.32 cm^3, 2.50 mmol) as starting materials. Orange solid: yield 0.301 g (80%) (Found: C, 44.55; H, 6.8; S, 4.15. $C_{28}H_{50}ClF_3O_5P_2RuS$ requires C, 44.6; H, 6.7; S, 4.25%). IR (KBr): ν(C=C) 1610 and 1580 cm^{-1}. NMR ($CDCl_3$): δ_H(400 MHz) 7.11 (4 H, m, C_6H_4), 4.98 [1 H, t, *J*(PH) 3.4, =CH], 4.19, 4.11, 3.98, 3.74 (1 H each, all m, CH_2OCH_3), 3.80, 3.64 (3 H each, both s, OCH_3), 2.83, 2.52 (1 H each, both m, PC*H*CH_3 and PCH_2), 2.47, 2.24 (2 H each, both m, PC*H*CH_3 and PCH_2), 2.31 (3 H, s, $C_6H_4CH_3$), 2.02, 1.93 (1 H each, both m, PC*H*CH_3 and PCH_2) and 1.5–1.3 (24 H, m, PCHC*H*$_3$); δ_C(100.6 MHz) 358.9 [dd, *J*(PC) 18.4, *J*(P′C) 15.7, Ru=C], 136.0, 129.4, 126.2, 124.7 (all s, C_6H_4), 120.9 [q, *J*(CF) 321.0, CF_3SO_3], 117.3 (s, =CH), 72.4, 71.2 (both s, CH_2OCH_3), 62.9, 61.3 (both s, OCH_3), 37.0 [d, *J*(PC) 30.3, PCHCH$_3$], 28.8 [d, *J*(PC) 25.8, PCHCH$_3$], 26.1 [d, *J*(PC) 28.5, PCHCH$_3$], 25.2 [d, *J*(PC) 19.0, PCH_2 and PCHCH$_3$], 23.1 [d, *J*(PC) 23.9, PCH_2], 21.0 (s, $C_6H_4CH_3$), 19.9, 19.5, 19.47, 19.42, 19.37, 18.94, 18.89, 18.81 (all s, PCH*C*H$_3$); δ_P(162 MHz) 67.9, 56.4 [both d, AB spin system, *J*(PP) 24.6 Hz]; δ_F(376.5 MHz) −78.6 (s).

[RuCl(=C=CHC$_6$H$_4$C≡CH-*m*)(κ^2*P*,*O*-Pr$^i_2$PCH$_2$CH$_2$OMe)$_2$][O$_3$SCF$_3$] 6. This compound was prepared as described for **4**, using **2** (0.262 g, 0.50 mmol) and $C_6H_4(C{\equiv}CH)_2$-*m* (0.252 g, 2.00 mmol) as starting materials, the reaction time being only 20 min. Orange solid: yield 0.263 g (69%) (Found: C, 45.35; H, 6.45; S, 4.0. $C_{29}H_{48}ClF_3O_5P_2RuS$ requires C, 45.6; H, 6.35; S, 4.2%). IR (KBr): ν(≡CH) 3200, ν(C≡C) 2080, ν(C=C) 1620 and 1575 cm^{-1}. NMR: δ_H(400 MHz, CD_2Cl_2) 7.41–7.18 (4 H, m, C_6H_4), 5.06 [1 H, t, *J*(PH) 3.4, =CH], 4.18, 4.11, 4.05, 3.81 (1 H each, all m, CH_2OCH_3), 3.84, 3.64 (3 H each, both s, OCH_3), 3.13 (1 H, s, ≡CH), 2.87, 2.49, 2.41, 2.22, 2.02, 1.90 (1 H each, all m, PC*H*CH_3 and PCH_2), 2.34 (2 H, m, PC*H*CH_3 and PCH_2) and 1.5–1.25 (24 H, m, PCHC*H*$_3$); δ_C(100.6 MHz, CD_2Cl_2) 356.2 [dd, *J*(PC) 18.1, *J*(P′C) 16.1, Ru=C], 130.2, 129.8, 129.5, 129.1, 127.6, 122.5 (all s, C_6H_4), 121.5 [q, *J*(CF) 320.9, CF_3SO_3], 117.2 (s, =CH), 83.7 and 77.5 (both s, *C*≡CH and C≡*C*H), 72.9, 71.7 (both s, CH_2OCH_3), 63.1, 61.7 (both s, OCH_3), 37.1 [d, *J*(PC) 30.4, PCHCH$_3$], 29.5 [d, *J*(PC) 26.7, PCHCH$_3$], 26.7 [d, *J*(PC) 28.3, PCHCH$_3$], 25.7 [d, *J*(PC) 19.4, PCH_2 and PCHCH$_3$], 23.1 [d, *J*(PC) 24.0, PCH_2], 19.9, 19.5, 19.47, 19.44, 19.30, 19.28, 19.01, 18.91 (all s, PCH*C*H$_3$); δ_P(162 MHz, CD_2Cl_2) 67.9, 56.3 [both d, AB spin system, *J*(PP) 24.1 Hz]; δ_F(376.5 MHz, $CDCl_3$) −78.6 (s).

[RuCl(C≡CPh)(κ^2*P*,*O*-Pr$^i_2$PCH$_2$CH$_2$OMe)$_2$] 7 and 8. A solution of compound **4** (0.148 g, 0.20 mmol) in dichloromethane (1 cm^3) was chromatographed on Al_2O_3 (basic, activity grade III, column length 5 cm). With acetone a yellow fraction was eluted which was brought to dryness *in vacuo*. The residue was treated with hexane and the solution cooled to −78 °C to give a yellow solid which consists of the two isomers, **7** and **8**, in the ratio 2:1; yield 0.094 g (80%) (Found: C, 52.65; H, 7.85. $C_{26}H_{47}ClO_2P_2Ru$ requires C, 52.9; H, 8.05%). Compound **7**: IR (KBr) ν(C≡C) 2000 cm^{-1}. NMR ($C_6D_5CD_3$): δ_H(400 MHz, −80 °C) 7.61–7.15 (5 H, m, C_6H_5), 3.51, 3.26, 2.96, 2.58 (1 H each, all m, CH_2OCH_3), 4.06, 3.16 (3 H each, both s, OCH_3), 1.99, 1.84, 1.73, 0.91 (1 H each, all m, PC*H*CH_3 and PCH_2), 1.49, 0.77 (2 H each, both m, PC*H*CH_3 and PCH_2) and 1.30–1.25 (24 H, m, PCHC*H*$_3$); δ_P(162 MHz, −80 °C) 84.3, 64.9 [both d, AB spin system, *J*(PP) 32.1 Hz]. Compound **8**: IR (KBr) ν(C≡C) 2050 cm^{-1}. NMR ($C_6D_5CD_3$): δ_H(400 MHz, −80 °C) 7.61–7.15 (5 H, m, C_6H_5), 3.69 (4 H, m, CH_2OCH_3), 3.55 (6 H, s, OCH_3), 2.89, 2.80 (4 H each, both m, PC*H*CH_3 and PCH_2) and 1.30–1.25 (24 H, m, PCHC*H*$_3$); δ_P(162 MHz, −80 °C) 79.8 (s).

Alternatively, a solution of compound **4** (0.111 g, 0.15 mmol) in tetrahydrofuran (4 cm^3) was cooled at 0 °C and then a stoichiometric amount of Li(C≡CPh) (0.016 g, 0.15 mmol) in tetrahydrofuran (3 cm^3) was added dropwise (8 min). After stirring for 30 min the solution changed from orange to pale yellow. The cooling bath was removed and the solution brought to dryness *in vacuo*. The oily residue was extracted with hexane and the resulting solution concentrated to *ca.* 2 cm^3 *in vacuo*. Upon cooling to −78 °C after some hours a yellow solid formed: yield 0.027 g (31%).

Reaction of complexes 7/8 with CO. In an NMR tube complexes **7**/**8** (0.118 g, 0.20 mmol) were dissolved in C_6D_6 (0.8 cm^3). A stream of CO was passed through the solution for 30 min. The ^{1}H and ^{31}P NMR spectra showed the formation of **9** and **10** in the ratio of 3:2. After 12 d at room temperature the NMR spectra showed only the isomer **9**. The yellow solution was then transferred to a Schlenk tube and brought to dryness *in vacuo*. The oily residue was treated with hexane to give **9** as a yellow microcrystalline solid: yield 0.052 g (40%) (Found: C, 52.35; H, 7.75. $C_{28}H_{47}ClO_4P_2Ru$ requires C, 52.05; H, 7.35%). IR (KBr): ν(C≡C) 2100, ν(RuCO) 2020, 1960 cm^{-1}. NMR (C_6D_6): δ_H(400 MHz) 7.55–6.96 (5 H, m, C_6H_5), 3.75 (4 H, m, CH_2OCH_3), 3.06 (6 H, s, OCH_3), 2.81 (4 H, m, PC*H*CH_3), 2.55, 2.45 (2 H each, both m, PCH_2), 1.32 [12 H, dvt, *N* 15.0, *J*(HH) 7.1, PCHC*H*$_3$] and 1.16 [12 H, dvt, *N* 14.1, *J*(HH) 7.1, PCHC*H*$_3$]; δ_C(100.6 MHz) 197.9 [t, *J*(PC) 10.9, RuCO], 197.2 [t, *J*(PC) 9.2, RuCO], 131.0, 129.0, 128.4, 125.6 (all s, C_6H_5), 112.6 (s, ≡*C*Ph), 111.9 [t, *J*(PC) 18.0, RuC≡CPh], 69.0 (s, CH_2OCH_3), 58.0 (s, OCH_3), 25.9 (vt, *N* 24.7, PCH_2), 25.3 (vt, *N* 24.0, PCHCH$_3$), 23.5 (vt, *N* 24.0, PCHCH$_3$), 18.8, 18.6 (both s, PCH*C*H$_3$); δ_P(162 MHz) 34.4 (s). Spectroscopic data for **10**: IR (KBr) ν(C≡C) 2040, ν(RuCO) 1980 cm^{-1}; NMR (C_6D_6): δ_H(400 MHz) 7.55–6.96 (5 H, m, C_6H_5), 2.69 (4 H, m, CH_2OCH_3), 3.08 (6 H, s, OCH_3), 2.81 (4 H, m, PC*H*CH_3), 2.55, 2.45 (2 H each, both m, PCH_2), 1.32 [12 H, dvt, *N* 15.0, *J*(HH) 7.1, PCHC*H*$_3$] and 1.16 [12 H, dvt, *N* 14.1, *J*(HH) 7.1 Hz, PCHC*H*$_3$]; δ_P(162 MHz) 34.7 (s).

[RuCl(=C=CHPh)(κ^2*P*,*O*-Pr$^i_2$PCH$_2$CH$_2$OMe)$_2$][BF$_4$] 11. A solution of complexes **7**/**8** (0.088 g, 0.15 mmol) in tetrahydrofuran (5 cm^3) was treated with $HBF_4{\cdot}OEt_2$ (26 μl, 0.16 mmol). A change from yellow to orange occurred almost instantaneously. The solution was concentrated to *ca.* 0.5 cm^3 *in vacuo*, and on addition of ether an orange precipitate was formed. It was filtered off and spectroscopically identified as **11** by comparing with the data for **4**.

[Ru(CN)$_2$(=C=CHPh)(κ^2*P*,*O*-Pr$^i_2$PCH$_2$CH$_2$OMe)$_2$] 12. A solution of compound **4** (0.370 g, 0.50 mmol) in methanol (10 cm^3) was treated with KCN (0.065 g, 1.00 mmol). Upon stirring for 12 h the solvent was removed *in vacuo*. After recrystallization from dichloromethane–hexane an orange-yellow solid was obtained: yield 0.20 g (67%) (Found: C, 55.7; H, 7.65; N, 4.75. $C_{28}H_{48}N_2O_2P_2Ru$ requires C, 55.35; H, 7.95; N, 4.6%). IR (KBr): ν(CN) 2040, ν(C=C) 1620 and 1585 cm^{-1}. NMR: δ_H(200 MHz, $CDCl_3$) 7.20–6.97 (5 H, m, C_6H_5), 4.73 [1 H, t, *J*(PH), 3.6, =CH], 3.67 (4 H, m, CH_2OCH_3), 3.18 (6 H,

s, OCH_3), 2.70 (4 H, m, PC*H*CH_3), 2.23 (4 H, m, PCH_2), 1.38, 1.31 [12 H each, both dvt, *N* 9.1, *J*(HH) 5.1, PCHC*H*$_3$]; δ_C(100.6 MHz, $CDCl_3$) 356.6 [dd, *J*(PC) = *J*(P′C) 14.8, Ru=C], 141.3 [dd, *J*(PC) = *J*(P′C) 13.0, CN], 129.7, 128.5, 125.4, 124.9 (all s, C_6H_5), 109.0 [dd, *J*(PC) = *J*(P′C) 4.0, =CH], 67.9 (s, *C*H_2OCH_3), 58.3 (s, OCH_3), 26.0 (vt, *N* 23.4, P*C*HCH$_3$), 22.7 (vt, *N* 20.9, PCH_2), 19.2, 19.0 (both s, PCH*C*H$_3$); δ_P(162 MHz, CD_2Cl_2, −70 °C) 44.9, 27.2 [both d, AB spin system, *J*(PP) 272.7 Hz].

[RuI$_2$(=C=CHPh)(κ^2*P*,*O*-Pr$^i_2$PCH$_2$CH$_2$OMe)$_2$] 13. To a solution of compound **4** (0.370 g, 0.50 mmol) in methanol (10 cm^3) was added NaI (0.300 g, 2.00 mmol). After stirring at reflux for 1 h and cooling to room temperature the solvent was removed *in vacuo*. After recrystallization from dichloromethane–hexane a brown solid was obtained: yield 0.201 g (67%) (Found: C, 38.65; H, 5.90. $C_{26}H_{48}I_2O_2P_2Ru$ requires C, 38.6; H, 6.0%). IR (KBr): ν(C=C) 1620 and 1580 cm^{-1}. NMR: δ_H(200 MHz, $CDCl_3$) 7.3–6.8 (5 H, m, C_6H_5), 4.24 [1 H, t, *J*(PH) 3.6, =CH], 3.67 (4 H, m, C*H*$_2$OCH$_3$), 3.26 (4 H, m, PC*H*CH$_3$), 3.18 (6 H, s, OCH_3), 2.26 (4 H, m, PCH_2), 1.35 [12 H, dvt, *N* 13.2, *J*(HH) 6.9, PCHC*H*$_3$], 1.18 [12 H, dvt, *N* 13.5, *J*(HH) 6.6, PCHC*H*$_3$]; δ_P(162 MHz, $C_6D_5CD_3$, −70 °C) 18.9, 15.2 [both d, AB spin system, *J*(PP) 331.0 Hz].

If the reaction mixture described above was refluxed for 3 h red crystals of [RuI$_2$(κ^2*P*,*O*-Pr$^i_2$PCH$_2$CH$_2$OMe)$_2$] **14** were obtained (Found: C, 30.5; H, 6.1. $C_{18}H_{42}I_2O_2P_2Ru$ requires C, 30.55; H, 6.0%). NMR: δ_H(200 MHz, C_6D_6) 3.57 (6 H, s, OCH_3), 3.50 (4 H, m, C*H*$_2$OCH$_3$), 3.14 (4 H, m, PC*H*CH$_3$), 2.24 (4 H, m, PCH_2), 1.30 [12 H, dvt, *N* 14.6, *J*(HH) 6.9, PCHC*H*$_3$] and 1.11 [12 H, dvt, *N* 11.7, *J*(HH) 4.4 Hz, PCHC*H*$_3$]; δ_P(81 MHz, $CDCl_3$) 72.0 (s).

Reaction of complex 4 with LiBr. A solution of complex **4** (0.370 g, 0.50 mmol) in dichloromethane (15 cm^3) was treated with LiBr (0.260 g, 3.00 mmol) and stirred for 26 h at room temperature. After the solvent was removed *in vacuo* a red oil was obtained which contained complexes **15** and **16** in the ratio of 4:1. Complex **15**: NMR δ_H(200 MHz, C_6D_6) 7.3–6.8 (5 H, m, C_6H_5), 4.43 [1 H, t, *J*(PH) 3.8, =CH], 3.73 (4 H, m, C*H*$_2$OCH$_3$), 3.24 (6 H, s, OCH_3), 2.89 (4 H, m, PC*H*CH$_3$), 2.07 (4 H, m, PCH_2), 1.36 [12 H, dvt, *N* 14.2, *J*(HH) 6.9, PCHC*H*$_3$] and 1.23 [12 H, dvt, *N* 13.5, *J*(HH) 6.6, PCHC*H*$_3$]; δ_P(162 MHz, $C_6D_5CD_3$, −70 °C) 24.9, 19.8 [both d, AB spin system, *J*(PP) 344 Hz]. Complex **16**: NMR δ_H(200 MHz, C_6D_6) 7.3–6.8 (5 H, m, C_6H_5), 4.36 [1 H, t, *J*(PH) 3.1, =CH], 3.67 (4 H, m, C*H*$_2$OCH$_3$), 3.26 (4 H, m, PC*H*CH$_3$), 3.26 (6 H, s, OCH_3), 2.26 (4 H, m, PCH_2), 1.35 [12 H, dvt, *N* 13.2, *J*(HH) 6.9, PCHC*H*$_3$)] and 1.18 [12 H, dvt, *N* 13.5, *J*(HH) 6.6, PCHC*H*$_3$]; δ_P(162 MHz, $C_6D_5CD_3$, −70 °C) 25.3, 21.18 [both d, AB spin system, *J*(PP) 348 Hz].

[RuCl(=C=C=CPh$_2$)(κ^2*P*,*O*-Pr$^i_2$PCH$_2$CH$_2$OMe)$_2$][O$_3$SCF$_3$] 17. To a solution of compound **2** (0.262 g, 0.50 mmol) in tetrahydrofuran (10 cm^3) were added HC≡CCPh$_2$OH (0.104 g, 0.50 mmol) and Ag(O$_3$SCF$_3$) (0.128 g, 0.50 mmol). After stirring for 15 h at room temperature in the dark the precipitate formed (AgCl) was filtered off through Kieselgur. The filtrate was concentrated to *ca.* 0.5 cm^3 *in vacuo*, and the solution chromatographed on Al_2O_3 (acidic, activity grade I, column length 5 cm). With dichloromethane–acetone (4:1) a deep red fraction was eluted from which the solvent was removed *in vacuo*. The residue was washed with ether to give a red microcrystalline solid: yield 0.120 g (29%) (Found: C, 49.2; H, 6.4; S, 3.8. $C_{34}H_{52}ClF_3O_5P_2RuS$ requires C, 49.3; H, 6.35; S, 3.85%). IR (KBr): ν(C=C=C) 1930 cm^{-1}. NMR ($CDCl_3$): δ_H(400 MHz) 7.73–7.33 (10 H, m, C_6H_5), 4.28, 4.19, 4.09, 3.68 (1 H each, all m, C*H*$_2$OCH$_3$), 3.81, 3.71 (3 H each, both s, OCH_3), 2.75, 2.44, 2.30, 2.20, 2.13, 2.12, 2.01, 1.80 (1 H each, all m, PC*H*CH$_3$ and PCH_2) and 1.47–0.97 (24 H, m, PCHC*H*$_3$); δ_C(100.6 MHz) 304.6 [dd, *J*(PC) = *J*(P′C) 18.5, Ru=C], 220.3 (s, Ru=C=*C*), 154.6 (s, Ru=C=C=*C*), 145.2, 130.9, 129.5, 129.2 (all s, C_6H_5), 120.9 [q, *J*(CF) 321.0, CF_3SO_3], 72.9, 71.9 (both s, *C*H_2OCH$_3$), 62.0, 61.6 (both s, OCH_3), 36.8 [d, *J*(PC) 29.0, P*C*HCH$_3$], 28.9 [d, *J*(PC) 25.0, P*C*HCH$_3$], 26.5 [d, *J*(PC) 27.0, P*C*HCH$_3$], 25.5 [d, *J*(PC) 23.0, PCH_2], 25.0 [d, *J*(PC) 19.0, P*C*HCH$_3$], 22.0, [d, *J*(PC), 22.0, PCH_2], 20.3, 19.2, 19.1, 19.0, 18.4, 18.1, 17.89, 17.82 (all s, PCH*C*H$_3$); δ_P(162 MHz) 70.3, 54.9 [both d, AB spin system, *J*(PP) 27.0 Hz]; δ_F(376.5 MHz) −78.6 (s).

[RuCl{=C=C=CPh(C$_6$H$_4$Me-*o*)}(κ^2*P*,*O*-Pr$^i_2$PCH$_2$CH$_2$OMe)$_2$][O$_3$SCF$_3$] 18. This compound was prepared as described for **17**, using **2** (0.262 g, 0.50 mmol) and HC≡CCPh(C$_6$H$_4$Me-*o*)OH (0.46 cm^3 of a 1.2 mol dm^{-3} solution in toluene) as starting materials. Red solid: yield 0.160 g (38%) (Found: C, 49.85; H, 6.65; S, 3.75. $C_{35}H_{54}ClF_3O_5P_2RuS$ requires C, 49.9; H, 6.5; S, 3.8%). IR (KBr): ν(C=C=C) 1930 cm^{-1}. NMR ($CDCl_3$): δ_H(400 MHz) 7.8–7.15 (9 H, m, C_6H_5 and C_6H_4), 4.26, 4.18, 4.07, 3.67 (1 H each, all m, C*H*$_2$OCH$_3$), 3.78, 3.72 (3 H each, both s, OCH_3), 2.68, 2.44 (1 H each, both m, PC*H*CH$_3$ and PCH_2), 2.18 (4 H, m, PC*H*CH$_3$ and PCH_2), 1.97, 1.74 (1 H each, both m, PC*H*CH$_3$ and PCH_2), 2.09 (3 H, s, $C_6H_4CH_3$) and 1.34–1.02 (24 H, m, PCHC*H*$_3$); δ_C(100.6 MHz) 308.3 [dd, *J*(PC) = *J*(P′C) 18.0 Hz, Ru=C], 222.0 (s, Ru=C=*C*), 155.0 (s, Ru=C=C=*C*), 145.0, 133.0, 130.0, 128.0, 126.0, 125.0 (all s, C_6H_4), 144.0, 131.0, 129.0, 128.6 (all s, C_6H_5), 120.9 [q, *J*(CF) 321.0, CF_3SO_3], 73.0, 71.9 (both s, *C*H_2OCH$_3$), 62.0, 61.6 (both s, OCH_3), 36.5 [d, *J*(PC) 29.0, P*C*HCH$_3$], 28.9 [d, *J*(PC) 25.0, P*C*HCH$_3$], 26.3 [d, *J*(PC) 27.6, P*C*HCH$_3$], 25.4 [d, *J*(PC) 23.0, PCH_2], 25.0 [d, *J*(PC) 19.9 Hz, P*C*HCH$_3$], 22.2 [d, *J*(PC) 23.0, PCH_2], 20.0, 19.8, 19.1, 19.0, 18.7, 18.5, 18.4, 18.2 (all s, $C_6H_4CH_3$ and PCH*C*H$_3$); δ_P(162 MHz) 69.8, 54.6 [both d, AB spin system, *J*(PP) 26.2 Hz]; δ_F(376.5 MHz) −78.6 (s).

[RuCl(CO)(κ^2*P*,*O*-Pr$^i_2$PCH$_2$CH$_2$OMe)$_2$][O$_3$SCF$_3$] 19. A solution of compound **18** (0.101 g, 0.12 mmol) in tetrahydrofuran (10 cm^3) was heated under reflux for 13 h. A change from deep red to orange was observed. After cooling to room temperature a stream of CO was passed through the solution for 15 min. The solvent was then removed and the residue washed with ether to give a light orange microcrystalline solid: yield 0.066 g (80%) (Found: C, 36.0; H, 6.4; S, 4.85. $C_{20}H_{42}ClF_3O_6P_2RuS$ requires C, 36.1; H, 6.35; S, 4.8%). IR (KBr): ν(RuCO) 1960 cm^{-1}. NMR ($CDCl_3$): δ_H(200 MHz) 4.33, 4.22, 3.95, 3.79 (1 H each, all m, C*H*$_2$OCH$_3$), 4.00, 3.55 (3 H each, both s, OCH_3), 2.78 (2 H, m, PC*H*CH$_3$ and PCH_2), 2.39–2.02 (6 H, m, PC*H*CH$_3$ and PCH_2) and 1.6–1.2 (24 H, m, PCHC*H*$_3$); δ_C(50.3 MHz, $CDCl_3$) 200.6 [dd, *J*(PC) 17.8, *J*(P′C) 15.2, RuCO], 119.0 [q, *J*(CF) 320.0, CF_3SO_3], 74.6, 72.5 (both s, *C*H_2OCH$_3$), 63.4, 61.2 (both s, OCH_3), 36.6 [d, *J*(PC) 32.0, P*C*HCH$_3$], 28.2 [d, *J*(PC) 27.0, P*C*HCH$_3$], 26.7 [d, *J*(PC) 29.0, P*C*HCH$_3$], 25.1 [d, *J*(PC) 22.0, PCH_2], 24.6 [d, *J*(PC) 22.0, P*C*HCH$_3$], 21.3 [d, *J*(PC) 23.0, PCH_2], 19.9, 19.6, 19.3, 18.9, 18.8, 18.7, 18.4 (all s, PCH*C*H$_3$); δ_P(81 MHz) 79.4, 59.9 [both d, AB spin system, *J*(PP) 21.8 Hz]; δ_F(188.3 MHz) −78.6 (s). Compound **19** was also obtained in *ca.* 80% yield if instead of **18** the related complex **17** was used as starting material.

***trans*,*trans*,*trans*-[RuCl$_2$(CO)$_2$(κ*P*-Pr$^i_2$PCH$_2$CH$_2$OMe)$_2$] 20.** A stream of CO was passed through a solution of compound **2** (0.105 g, 0.20 mmol) in dichloromethane (10 cm^3) for 30 min at room temperature. The solvent was removed *in vacuo*, and the oily residue treated twice with hexane (5 cm^3) to give a pale yellow microcrystalline solid: yield 0.104 g (90%) (Found: C, 41.35; H, 7.30. $C_{20}H_{42}Cl_2O_4P_2Ru$ requires C, 41.40; H, 7.30%). IR (CH_2Cl_2): ν(RuCO) 1980 cm^{-1}. NMR ($CDCl_3$): δ_H(200 MHz) 3.75 (4 H, m, C*H*$_2$OCH$_3$), 3.35 (6 H, s, OCH_3), 2.61 (4 H, m, PC*H*CH$_3$), 2.47 (4 H, m, PCH_2), 1.41, 1.33 [12 H each, both dvt, *N* 15.3, *J*(HH) 7.7 Hz, PCHC*H*$_3$]; δ_P(81 MHz) 30.5 (s).

Table 3 Crystal data for complexes **4** and **17**[a]

	4	**17**
Formula	$C_{27}H_{48}ClF_3O_5P_2RuS$	$C_{34}H_{52}ClF_3O_5P_2RuS$
M	740.17	828.28
Crystal size/mm	0.23 × 0.30 × 0.45	0.20 × 0.30 × 0.55
Cell dimensions determination (reflections, θ range/°)	25, 10–15	25, 13–15
a/Å	9.158(3)	9.693(3)
b/Å	21.313(4)	23.362(5)
c/Å	17.464(7)	16.920(3)
β/°	102.68(2)	91.300(3)
U/Å^3	3326(2)	3831(2)
D_c/g cm^{-3}	1.478	1.436
μ/mm^{-1}	0.754	0.663
$2\theta_{max}$/°	46	48
Total reflections scanned	5105	5739
No. unique reflections	4607	5405
No. observed reflections [$I > 2\sigma(I)$]	3798	4738
No. reflections used in refinement	4606	5404
R[b]	0.0303	0.0577
$wR2$[c]	0.0789	0.1663
Residual electron density/e Å^{-3}	0.326, −0.272	0.967, −0.989

[a] Details in common: monoclinic; space group $P2_1/n$ (no. 14); $Z = 4$; Enraf-Nonius CAD4 diffractometer, Mo-Kα radiation (λ 0.709 30 Å), graphite monochromator; 20 ± 2 °C; ω–θ scan. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ [for $F_o > 4\sigma(F_o)$]. [c] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$, $w^{-1} = \sigma^2(F_o)^2 + 0.041P^2 + 3.7566P$ (**4**) and $\sigma^2(F_o)^2 + 0.0981P^2 + 11.4222P$ (**17**) where $P = (F_o^2 + 2F_c^2)/3$.

Reaction of complex 4 with CO. A stream of CO was passed through a solution of complex **4** (0.185 g, 0.25 mmol) in tetrahydrofuran (10 cm^3) at room temperature. The reaction was followed by IR and NMR spectroscopy. A mixture consisting of three major products (**9**/**10** and **20**) and small amounts of **19** resulted after 60 min.

Crystallography

Single crystals were grown by diffusion of pentane (in the case of complex **4**) and ether (in the case of **17**) into saturated solutions of the complexes in dichloromethane. They both appear as red prisms. Crystal data collection parameters are summarized in Table 3. Intensity data were corrected for Lorentz and polarization effects. For **17** an empirical absorption correction (ψ scans; minimum transmission 78.4%) was applied. Both structures were solved by direct methods (SHELXS 86).[22] The refinement was performed on a 486 DX4/66 personal computer using SHELXL 93.[23] In complex **4** C(16) was found to be disordered. The two alternative positions C(16) and C(16A) were located and refined anisotropically with an occupation factor of 0.5 for each. The position of the vinylidene hydrogen atom H(2) of **4** was taken from a Fourier-difference synthesis and refined isotropically. The three fluorine atoms F(1)–F(3) of the triflate anion of **17** were found to be disordered. The alternative positions were located and refined anisotropically, using the same thermal parameters for F(1)–F(3) and F(1A)–F(3A) with occupation factors of 0.7:0.3. Furthermore, C(17) was also disordered, and the alternative position C(17A) located and treated in the same way as for the fluorine atoms [occupation factor C(17):C(17A) = 0.64:0.36]. The positions of all other hydrogen atoms were calculated according to ideal geometry and refined by the riding method with the following C–H distances: 0.98 (CH aliphatic), 0.93 (CH aromatic), 0.97 (CH_2) and 0.96 Å (CH_3).

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/20.

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