DALTON
FULL PAPER

A series of ruthenium(II) complexes containing the bulky, functionalized trialkylphosphines tBu$_2$PCH$_2$XC$_6$H$_5$ as ligands

Stefan Jung, Kerstin Ilg, Carsten D. Brandt, Justin Wolf and Helmut Werner*

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany. E-mail: helmut.werner@mail.uni-wuerzburg.de

Received 13th July 2001, Accepted 30th November 2001
First published as an Advance Article on the web 19th December 2001

The monomeric ruthenium(II) complexes [(η^6-C$_6$H$_5$XCH$_2$PtBu$_2$-κ-*P*)RuCl$_2$] **3**, **4** were prepared either on a reductive route from RuCl$_3$·3H$_2$O and tBu$_2$PCH$_2$XPh (X = CH$_2$ **1**, OCH$_2$ **2**) or by ligand replacement reactions from [(*p*-cym)RuCl$_2$]$_2$ and the phosphine *via* the *p*-cymene compounds [(*p*-cym)(C$_6$H$_5$XCH$_2$PtBu$_2$-κ-*P*)RuCl$_2$] **6**, **7** as intermediates. Abstraction of one chloro ligand from **3** with AgPF$_6$ led to the formation of the dinuclear complex [{(η^6-C$_6$H$_5$CH$_2$CH$_2$PtBu$_2$-κ-*P*)RuCl}$_2$](PF$_6$)$_2$ **8**, which reacts with acetone, CH$_3$CN and PMe$_3$ by bridge cleavage to afford the mononuclear compounds [(η^6-C$_6$H$_5$CH$_2$CH$_2$PtBu$_2$-κ-*P*)RuCl(L)]PF$_6$ **9**, **10**, **12**. Both **10** and **11** (the latter containing **2** as chelating ligand) were also obtained from **3**, **4** and AgPF$_6$ in the presence of acetonitrile. Hydridoruthenium(II) complexes [(η^6-C$_6$H$_5$XCH$_2$PtBu$_2$-κ-*P*)RuHCl] **13**, **14**, [RuHCl(H$_2$)(L)$_2$] **15** (L = **1**), **16** (L = **2**) and [RuHCl(CO)(**2**)$_2$] **17** could be prepared from RuCl$_3$·3H$_2$O and **1** or **2** in the presence of NEt$_3$ under reductive conditions. Insertion, substitution and addition reactions of compound **17** led to the formation of [Ru(CH=CH$_2$)Cl(CO)(**2**)$_2$] **18**, [RuHF(CO)(**2**)$_2$] **19**, and [RuHCl(CO)$_2$(**2**)$_2$] **20**, respectively. The cationic allenylidene complexes [(η^6-C$_6$H$_5$XCH$_2$PtBu$_2$-κ-*P*)RuCl(=C=C=CPh$_2$)]A **22a**,**b** (X = CH$_2$; A = BF$_4$, PF$_6$) and **23** (X = OCH$_2$; A = PF$_6$) were prepared from **3**, **4** or **13**, HC≡CC(OH)Ph$_2$ and either one equiv. of AgPF$_6$ or an equivalent amount of HBF$_4$ in diethyl ether. Treatment of **15** and **16** with acetylene afforded the five-coordinate vinylideneruthenium(II) compounds [RuHCl(=C=CH$_2$)(L)$_2$] **24**, **25** which in the presence of HBF$_4$ are highly efficient catalysts for the Ring Opening Metathesis Polymerization (ROMP) of cyclooctene. The molecular structures of **10** and **17** were determined crystallographically.

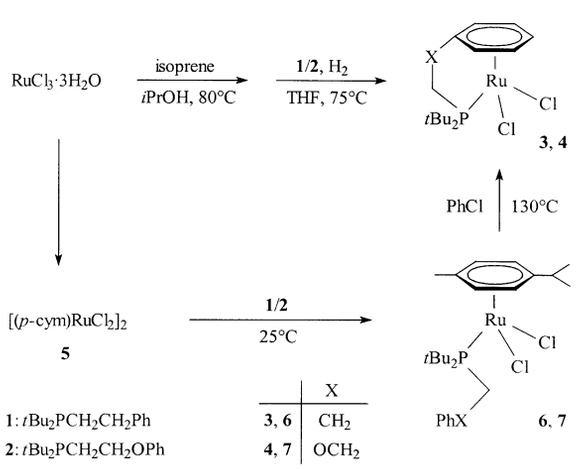
Carbeneruthenium(II) complexes of the general composition [RuCl$_2$(=CHR)(PCy$_3$)(L)], where L is PCy$_3$ or an Arduengo carbene, are at present the most frequently used catalysts for olefin metathesis.[1] Numerous attempts have been made to modify the coordination sphere of the metal in these five-coordinate molecules with the hope to find an even better application profile.[2] Taking into consideration that the majority of carbeneruthenium(II) compounds described to date have a 16-electron count, it was rather surprising when Dixneuf and Fürstner recently reported that the cationic 18-electron complex [(*p*-cym)RuCl(=C=C=CPh$_2$)(PCy$_3$)]$^+$ catalyzes, although at higher temperatures, the ring-closure of α,ω dienes.[3] Although the nature of the catalytically active species remains open to speculation, it was convincingly shown that ruthenium allenylidenes of the type [(η^6-arene)RuCl(=C=C=CR′$_2$)(PR$_3$)]$^+$X$^-$ are excellent catalysts for ring-closing olefin metathesis reactions (RCM).[4]

At the time when the first paper by Dixneuf, Fürstner *et al.* appeared,[3] we had begun to study the coordinating capabilities of bulky trialkylphosphines having a phenyl group in one of the alkyl side-chains. After we prepared a variety of cationic half-sandwich-type rhodium complexes with R$_2$P(CH$_2$)$_n$Ph (n = 2, 3) and R$_2$P(CH$_2$)$_2$OPh (R = *i*Pr, *t*Bu) as ligands and, in the context of these studies, also found that these new phosphines can bind to rhodium in different modes,[5] we became interested to find out how the same phosphines behave toward other transition-metals. In this article we report the synthesis of a series of neutral and cationic ruthenium(II) complexes in which the bulky phosphines tBu$_2$P(CH$_2$)$_2$Ph **1** and tBu$_2$P(CH$_2$)$_2$OPh **2** are coordinated either *via* the six-membered ring *and* the phosphorus atom or *only via* the P-donor to the metal centre. A preliminary account of these results has already been given.[6]

Results and discussion

Half-sandwich-type complexes with tBu$_2$PCH$_2$XPh as ligands

Recently, we reported that the hydrido(dihydrogen) complex [RuHCl(H$_2$)(PCy$_3$)$_2$],[7] being a convenient starting material for the preparation of the Grubbs carbenes [RuCl$_2$(=CHR)-(PCy$_3$)$_2$],[8] can be obtained in a one-pot synthesis from readily available RuCl$_3$·3H$_2$O.[9] Following these studies, we similarly treated RuCl$_3$·3H$_2$O with the functionalized phosphines **1** and **2** but instead of the anticipated compounds [RuHCl(H$_2$)(L)$_2$] (L = **1**, **2**) generated the half-sandwich-type complexes **3** and **4** (Scheme 1) as the dominating species. Since we failed to separate these compounds from some unidentified by-products, we



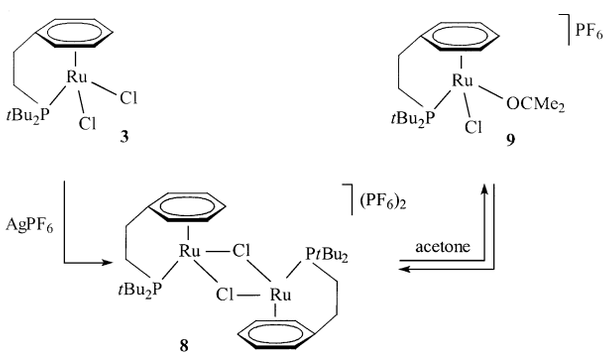
Scheme 1

 DOI: 10.1039/b106243n

looked for a second synthetic route and found that the method developed by Smith and Wright[10] for [{η⁶-$C_6H_5(CH_2)_3PPh_2$-κ-*P*}$RuCl_2$] can also be applied for the preparation of pure samples of **3** and **4**. The first step of this procedure consists of the conversion of the dimeric starting material **5** to the monomeric (*p*-cymene)ruthenium complexes **6** and **7** which upon heating in chlorobenzene at 130 °C for 18 h afford the target molecules **3** and **4** in nearly quantitative yields. Like other compounds of the general composition [(*p*-cym)$RuCl_2(PR_3)$],[11] the intermediates **6** and **7** are air-stable microcrystalline solids which are readily soluble in polar solvents such as acetone or dichloromethane.

The clean intramolecular substitution reaction of **3** and **4** to give **6** and **7** deserves a comment insofar as the previously described complexes [{η⁶-1,2-$C_6H_4(CH_2OH)CH_2CH_2PPh_2$-κ-*P*}$RuCl_2$][12] and [{η⁶-$C_6H_5(CH_2)_3PPh_2$-κ-*P*}$RuCl_2$][10] were obtained from the corresponding *p*-cymene precursors in only small to moderate yields. Based on our experience with arene-ruthenium(II) compounds with sterically demanding non-chelating phosphine ligands,[13] we assume that the bulkiness of the *tert*-butyl substituents at phosphorus facilitates the displacement of the *p*-cymene unit and also hinders side-reactions such as the *inter*molecular attack of the phenyl ring of a second molecule of **6** or **7** to the ruthenium centre. Regarding the spectroscopic data of **3** and **4**, a typical feature is that the resonances of the carbon atoms of the C_6H_5 fragment are significantly shifted to higher fields compared with the intermediates **6** and **7**.

The half-sandwich-type compound **3** reacts with one equiv. of $AgPF_6$ in acetone to give an orange–yellow solution from which, upon addition of pentane, orange–yellow crystals precipitated. In contrast to what we expected, the isolated product is not the monomeric solvento complex [(η⁶-$C_6H_5CH_2CH_2P$-*t*Bu_2-κ-*P*)RuCl(acetone)]PF_6 but the PF_6-salt of the dicationic species **8** (Scheme 2). The composition of **8** was confirmed both



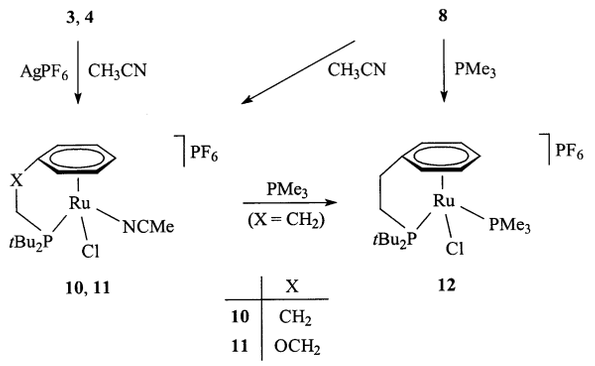
Scheme 2

by elemental analysis and conductivity measurements. In acetone-d_6 as solvent, the chloro bridges of **8** are split and the mononuclear complex **9** is formed. The reaction is completely reversible since after removal of the solvent the dinuclear precursor **8** is regenerated quantitatively.

In contrast to **9**, the corresponding acetonitrileruthenium(II) derivatives **10** and **11** are significantly more stable and can be prepared either from **3** or **4** and $AgPF_6$ in CH_2Cl_2–CH_3CN or, for *t*$Bu_2PCH_2CH_2Ph$ as the ligand, from **8** and acetonitrile (Scheme 3). Treatment of **10** with an equimolar amount of PMe_3 leads to a ligand exchange and the formation of **12**. This cationic trimethylphosphineruthenium(II) complex is also accessible from **8** and PMe_3. Compounds **10** and **11** as well as **12** are yellow microcrystalline solids which are readily soluble in polar organic solvents and, in nitromethane, possess the conductivity of 1 : 1 electrolytes.[14] The ^{1}H NMR spectra of **10**–**12** display five resonances for the C_6H_5 ring protons and the ^{13}C NMR spectra six signals for the corresponding ring carbon

Table 1 Selected bond lengths (Å) and angles (°) for compound **10**

Ru–P1	2.3976(13)	Ru–C3	2.209(5)
Ru–Cl	2.4201(13)	Ru–C4	2.270(5)
Ru–N	2.050(4)	Ru–C5	2.265(5)
Ru–C1	2.163(5)	Ru–C6	2.183(5)
Ru–C2	2.196(5)	N–C10	1.146(6)
P1–Ru–Cl	93.98(5)	Ru–P1–C20	118.47(16)
Cl–Ru–N	85.26(12)	Ru–P1–C21	114.72(17)
P1–Ru–N	94.38(12)	Ru–N–C10	176.3(4)
Ru–P1–C8	102.28(17)	N–C10–C11	176.5(5)



Scheme 3

atoms indicating that, in agreement with the presence of a chiral centre in the cations, all the CH units of the phenyl groups are stereochemically different. The ^{31}P NMR spectrum of **12** displays two doublet resonances at δ 89.2 and −7.5 with a ^{31}P–^{31}P coupling constant of 48.0 Hz.

The molecular structure of compound **10** was confirmed by a single-crystal X-ray diffraction study. The ORTEP[15] plot (Fig. 1) illustrates the three-legged piano-stool configuration of

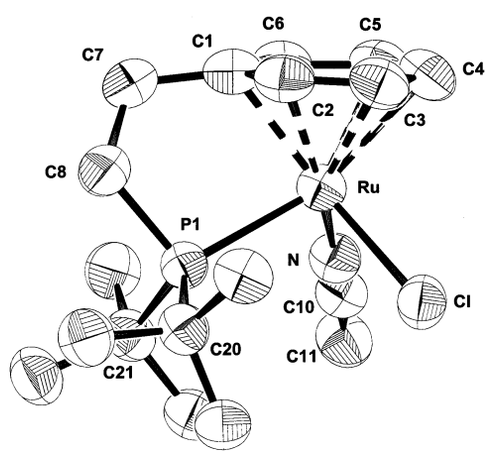


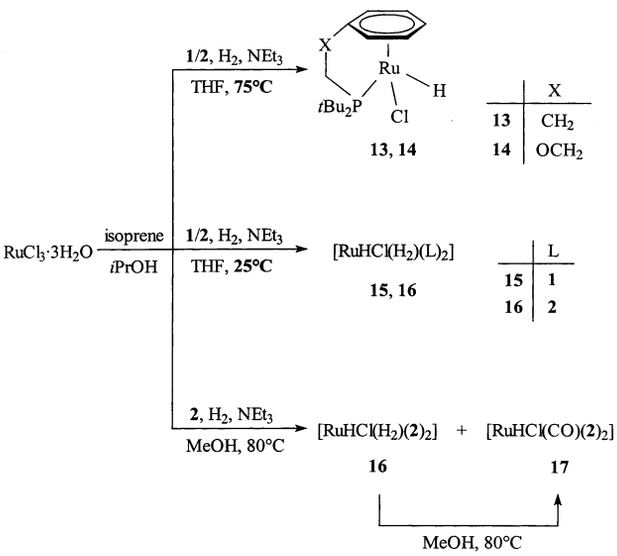
Fig. 1 Molecular structure of **10**.

the cation as well as the chelating bonding mode of the functionalized phosphine. The bond lengths between the metal and the ring carbon atoms differ between 2.163(5) and 2.270(5) Å, the longest distances (Ru–C4 and Ru–C5) being found *trans* to the phosphorus atom. In contrast to the cationic rhodium complex [(η⁶-$C_6H_5CH_2CH_2Pi Pr_2$-κ-*P*)$Rh(C_8H_{14})$]$^+$,[5] the phenyl ring is nearly planar and does not show a boat conformation. The bond angles P1–Ru–Cl, P1–Ru–N and N–Ru–Cl (see Table 1) are near to 90° which is in agreement with the pseudo-octahedral geometry of the molecule.

Hydridoruthenium(II) complexes with *t*Bu_2PCH_2XPh as ligands

Ruthenium(II) complexes with one hydride and the functionalized phosphine **1** or **2** either as chelating or merely *P*-bonded

ligand are also accessible from $RuCl_3 \cdot 3H_2O$ as the starting material. The procedure to prepare the chloro(hydrido) compounds **13** and **14** (Scheme 4) is different to that for the dichloro



Scheme 4

derivatives **3** and **4** only insofar as the *in situ* generated intermediate $[(\eta^3{:}\eta^3\text{-}C_{10}H_{16})RuCl_2]_2$ [16] is treated with the phosphine in methanol or boiling THF under a hydrogen atmosphere *in the presence of one equiv. of* NEt_3. In both cases, the yield of the chelate complexes is nearly quantitative. Compound **14**, which like **13** is a yellow air-sensitive solid, is somewhat less stable than the non-oxygen containing counterpart **13** and decomposes quite rapidly in benzene. The ^{1}H NMR spectra of **13** and **14** display a high-field resonance at around δ −7.5 which is split into a doublet due to ^{31}P–^{1}H coupling.

If the above-mentioned intermediate $[(\eta^3{:}\eta^3\text{-}C_{10}H_{16})RuCl_2]_2$ reacts with **1** or **2** and NEt_3 in THF under H_2 at room temperature for 1 h instead of 80 °C for 24 h, the five-coordinate hydrido(dihydrogen)ruthenium(II) complexes **15** and **16** are produced in moderate to good yields. By treating the intermediate with **2** in methanol a mixture of **16** and **17** is generated. If this mixture is stirred at 80 °C for 6 h, *in the absence of* H_2, the hydrido(carbonyl) compound **17** is formed exclusively. In contrast to **17**, the hydrido(dihydrogen) complexes **15** and **16** are low-melting solids which are considerably more air-sensitive than the corresponding chelate compounds **13** and **14**. The most characteristic spectroscopic feature of **15** and **16** is the broadened signal for the protons of the $RuH(H_2)$ fragment at δ −16.53 (**15**) and −16.63 (**16**) in the ^{1}H NMR spectra, the chemical shift being similar to that of the analogue $[RuHCl(H_2)(PCy_3)_2]$ (δ −16.8).[7] The presence of one resonance in the ^{31}P NMR spectra of **15** and **16** (as well as of **17**) indicates that the two phosphorus atoms are *trans* disposed.

The result of the X-ray crystal structure analysis of **17** is shown in Fig. 2. Although the position of the hydrido ligand could not be exactly located, the coordination geometry around the ruthenium centre is best described as a distorted square-pyramid with the hydride in the apical position. While the P1–Ru–P2 axis is almost linear (see Table 2), the bond angle Cl–Ru–C1 (157.26(19)°) deviates significantly from the ideal value of 180° which is possibly due to steric hindrance between the sterically demanding substituents at the phosphorus atoms and the carbonyl and the chloro ligands. For the related hydrido-ruthenium(II) complex $[RuHCl(CO)(P\textit{i}Pr_3)_2]$ with the less bulky triisopropylphosphine,[17] the bond angle P–Ru–P is 177.3(2)°.[18] While the distances Ru–P1, Ru–P2 and Ru–Cl of **17** and $[RuHCl(CO)(P\textit{i}Pr_3)_2]$ are nearly identical, the bond length

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

Ru–C1	1.825(7)	Ru–Cl	2.4187(18)
Ru–Pl	2.3959(14)	C1–O3	1.140(9)
Ru–P2	2.4021(14)		
P1–Ru–P2	176.66(5)	P2–Ru–Cl	91.61(6)
P1–Ru–C1	88.55(17)	Ru–C1–O3	178.1(6)
P1–Ru–Cl	91.16(6)	C1–Ru–Cl	157.26(19)
P2–Ru–C1	89.62(17)		

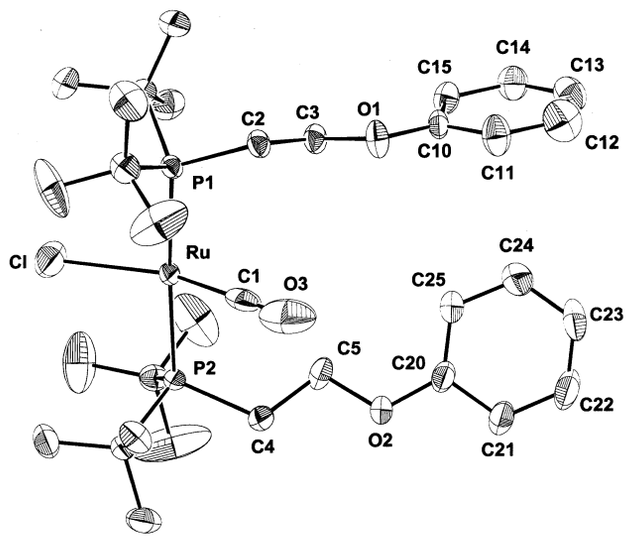
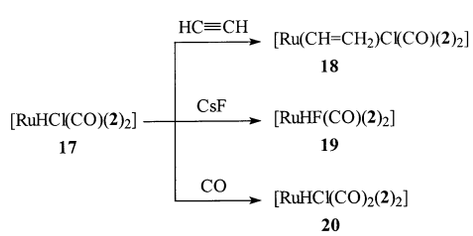


Fig. 2 Molecular structure of **17**.

Ru–C1 of **17** is *ca.* 0.07 Å longer than that of the bis(triisopropylphosphine) compound. We assume that this increase is due to the non-linearity of the Cl–Ru–C1 unit.

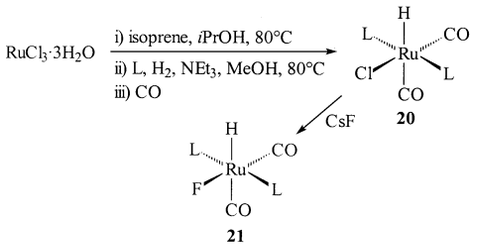
Compound **17** does not only react with acetylene and CsF by, respectively, insertion and substitution but owing to the presence of a coordinatively unsaturated metal centre also with CO to give the 18-electron complex **20** (Scheme 5). The products of



Scheme 5

the reactions of **17** with C_2H_2 and CsF are the five-coordinate vinyl- and fluoro-(hydrido)ruthenium(II) compounds **18** and **19** which presumably possess a similar structure to that of the starting material **17**. We note that the bis(triisopropylphosphine) complexes $[MHCl(CO)(P\textit{i}Pr_3)_2]$ (M = Ru, Os) equally react with acetylene and phenylacetylene by insertion into the M–H bond to yield the corresponding vinyl-ruthenium(II) and -osmium(II) derivatives.[19]

The coordinatively saturated dicarbonyl compound **20** is not only accessible from **17** and CO but also directly in a one-pot synthesis from $RuCl_3 \cdot 3H_2O$ probably *via* $[(\eta^3{:}\eta^3\text{-}C_{10}H_{16})RuCl_2]_2$ and **15** as intermediates (Scheme 6). In contrast to **17**, the 18-electron complex **20** is completely inert towards terminal alkynes. The reaction of **20** with CsF in acetone leads to the formation of the substitution product **21**, being in analogy to **20** thermally much more stable than the monocarbonyl compound **19**. Since the ^{13}C NMR spectra of both **20** and **21** display two resonances at δ 201.1, 200.1 (**20**) and δ 203.1, 200.1 (**21**), we conclude that the two CO ligands are not *trans* but *cis* disposed.



Scheme 6 (L = **2**).

The assumption that one carbonyl is *trans* to hydride is further supported by the chemical shift of the signal for the RuH proton at δ −5.51 (**20**) and −4.31 (**21**), which appears upfield by *ca.* 20 ppm compared to the five-coordinate counterparts where the position *trans* to hydride is unoccupied. The IR spectra of **20** and **21** also show two bands in the metal-carbonyl region indicating that the two CO groups are stereochemically inequivalent.

Allenylidene and vinylidene complexes with tBu$_2$PCH$_2$XPh as ligands

Similarly to **20**, the chloro(hydrido) compound **13** having also an 18-electron configuration is inert towards acetylene and HC≡CC(OH)Ph$_2$. If, however, the reaction of **13** with the substituted propargylic alcohol is carried out in the presence of an equimolar amount of HBF_4 in diethyl ether, the cationic allenylidene complex **22a** is obtained in practically quantitative yield. Treatment of the dichloro derivative **3** with HC≡CC(OH)Ph$_2$ and one equiv. of $AgPF_6$ in acetone affords the corresponding PF_6 salt **22b** (Scheme 7). The preparation of the related complex **23** with tBu$_2$PCH$_2$CH$_2$OPh as ligand proceeds on the same route. **22a**,**b** as well as **23** are violet, rather air-sensitive solids which in nitromethane show the conductivity of 1 : 1 electrolytes. Typical spectroscopic features of the allenylideneruthenium cations are the strong C=C=C stretching mode at *ca.* 1970 cm^{-1} in the IR spectra and, in the ^{13}C NMR spectrum of **22b**, the three low-field resonances at around δ 285.2, 178.5 and 172.0, the latter being assigned to the α-, β- and γ-carbon atoms of the C_3Ph_2 moiety.[20] It should be mentioned that recently the groups of Fürstner and Dixneuf prepared not only a series of areneruthenium(II) complexes [(η^6-arene)-RuCl(PR$_3$)(=C=C=CR′$_2$)]PF$_6$ but also the chelate compound [{η^6-C$_6$H$_5$(CH$_2$)$_3$PCy$_2$-κ-*P*}RuCl(=C=C=CPh$_2$)](O$_3$SCF$_3$) which is a close relative of **23**.[3,4,21]

Following the observation that the hydrido(dihydrogen)-ruthenium complexes [RuHCl(H$_2$)(P*i*Pr$_3$)$_2$] and [RuHCl(H$_2$)-(PCy$_3$)$_2$] react with acetylene to give the five-coordinate hydrido-(vinylidene) derivatives [RuHCl(=C=CH$_2$)(PR$_3$)$_2$] (R = *i*Pr, Cy),[22] we were prompted to study also the reactivity of compounds **15** and **16** towards C_2H_2. Passing a slow stream of acetylene through a solution of the starting material in dichloromethane at −78 °C affords indeed the anticipated vinylidene complexes **24** and **25** in *ca.* 90–95% yield (Scheme 8). The orange–brown or light brown solids are quite air-sensitive and decompose already at 58 °C. The ^{13}C NMR spectra of both **24** and **25** display in the low-field region the typical resonances for the α- and β-carbon atoms of the vinylidene ligand at δ 326.5 and 87.9 (for **24**) and δ 328.1 and 90.0 (for **25**) which are split into triplets due to ^{13}C–^{31}P coupling. In the ^{1}H NMR spectra the signal for the RuH proton also appears as a triplet at δ −15.80 (for **24**) and δ −14.85 (for **25**). With regard to the structure of **24** and **25**, we note that recently Olivan, Eisenstein and Caulton reported the preparation of the compound [RuHCl(=C=CHR)-(PtBu$_2$Me)$_2$] (R = Ph, SiMe$_3$) which according to *ab initio* DFT calculations possess instead of a square-pyramidal a distorted trigonal-bipyramidal geometry with the two phosphines in the apical positions.[23]

The reactions of both **24** and **25** with an ethereal solution of HBF_4 at room temperature leads to a mixture of products in which, after removal of the solvent, only the phosphonium salt [HPtBu$_2$CH$_2$XPh]BF$_4$ could be unambiguously identified.[5] However, if a solution of HBF_4 in ether is added to a solution of **24** in CD_2Cl_2 at −78 °C, the ^{1}H NMR spectrum indicates the formation of the carbyneruthenium cation **26** (see Scheme 8). Owing to the chemical shift of the hydride signal at δ −7.63, which is quite similar to that of the pseudo-octahedral complexes **13** and **14**, we assume that the cation **26** has an 18-electron configuration with a solvent molecule coordinated *trans* to the carbyne moiety. An analogous structure has been proposed for the related cation [RuHCl(≡CCH$_3$)(OEt$_2$)(PCy$_3$)$_2$]$^+$ which is a good catalyst both for the Ring Opening Metathesis Polymerization (ROMP) of cyclooctene as well as for the cross-olefin metathesis of cyclopentene with methylacrylate.[22]

The *in situ* generated cations [RuHCl(≡CCH$_3$)(OEt$_2$)(*t*Bu$_2$-PCH$_2$XPh)$_2$]$^+$ (X = CH$_2$, OCH$_2$) also catalyze the ROMP of cyclooctene. As shown in Fig. 3, the rate of formation of the

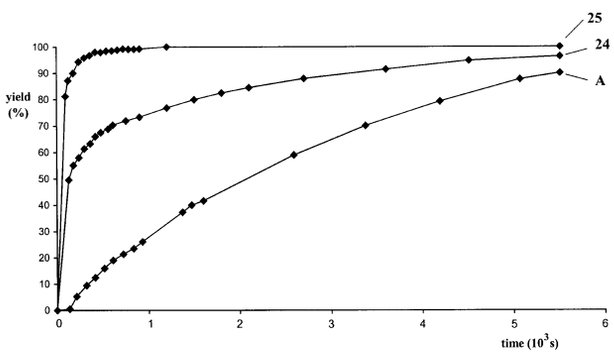
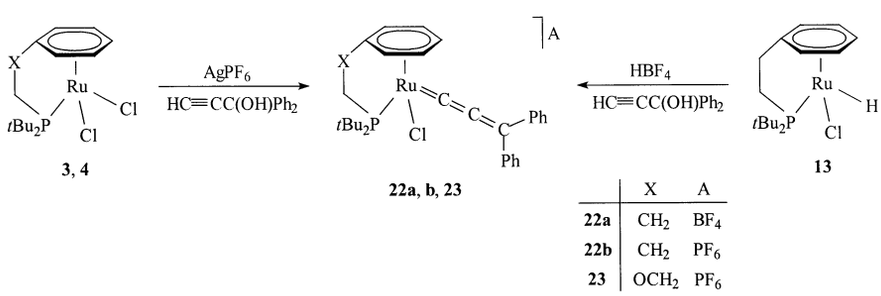


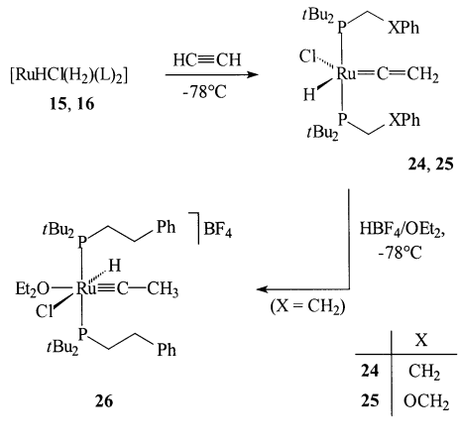
Fig. 3 ROMP of cyclooctene using **24**, **25** (both in the presence of 4 μmol HBF_4) and [RuCl$_2$(=CHPh)(PCy$_3$)$_2$] (**A**) as catalysts. Conditions: 21 °C, 81.4 μl (625 μmol) C_8H_{14}, 0.5 μmol ruthenium compound, CD_2Cl_2–OEt_2 as solvent. Yield of polymer determined by ^{1}H NMR spectroscopy.

polymer is significantly higher than by using the well-known Grubbs carbene [RuCl$_2$(=CHPh)(PCy$_3$)$_2$] as the catalyst. Under identical conditions (CD_2Cl_2, 21 °C, ratio cyclooctene to ruthenium complex = 1250 : 1), the polymerization of C_8H_{14} with the mixture of **25**/HBF_4 as catalyst is finished after *ca.* 8



	X	A
22a	CH_2	BF_4
22b	CH_2	PF_6
23	OCH_2	PF_6

Scheme 7



Scheme 8

min whereas with the carbene compound in the same period of time only *ca.* 15% of the olefin is polymerized. A reasonable explanation for the remarkable difference in rate is that the dissociation of one phosphine ligand, being the rate-determining step in the catalysis with $[RuCl_2(=CHPh)(PCy_3)_2]$,[24] proceeds much faster in the case of the carbyneruthenium cations which in general are considerably more labile than the neutral ruthenium carbenes.

In summary, the work presented in this paper has shown that the functionalized phosphines **1** and **2** having two bulky *tert*-butyl groups at the phosphorus atom coordinate either as chelating 8-electron or *P*-bonded 2-electron donor ligands to ruthenium(II) as the metal centre. By using the readily available $RuCl_3 \cdot 3H_2O$ as the starting material it is possible not only to prepare the chelate complexes $[(\eta^6\text{-}C_6H_5XCH_2P\textit{t}Bu_2\text{-}\kappa\text{-}\textit{P})RuCl_2]$ **3**, **4** and $[(\eta^6\text{-}C_6H_5XCH_2P\textit{t}Bu_2\text{-}\kappa\text{-}\textit{P})RuHCl]$ **13**, **14** but also a series of five-coordinate hydridoruthenium(II) compounds $[RuHCl(L')(L)_2]$ of which that with L′ = CO and L = **2** smoothly undergoes insertion, substitution and addition reactions with appropriate nucleophilic substrates. Cationic allenylidene complexes with **1** or **2** as chelating ligands are accessible both from **3**, **4** and from **13**, while neutral vinylideneruthenium(II) compounds $[RuHCl(=C=CH_2)(L)_2]$ **24**, **25** can be prepared from the hydrido(dihydrogen) derivatives $[RuHCl(H_2)(L)_2]$ **15**, **16** by treatment with acetylene. In the presence of HBF_4, the vinylidene complexes are excellent catalysts for ROMP of cyclooctene being even more efficient than the Grubbs carbene.

Experimental

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The starting materials $\textit{t}Bu_2P(CH_2)_2Ph$ **1**,[5] $\textit{t}Bu_2P(CH_2)_2OPh$ **2**,[5] and $[(\eta^6\text{-}MeC_6H_4CHMe_2)RuCl_2]_2$ **5**,[25] were prepared as described in the literature. The propargylic alcohol $HC{\equiv}CC(OH)Ph_2$ was a commercial product from Aldrich. NMR spectra were recorded at room temperature on Bruker AC 200, Bruker DRX 300 and Bruker AMX 400 instruments, IR spectra on a Perkin-Elmer 1420 or an IFS 25 FT-IR infrared spectrometer, and mass spectra (EI MS, FAB MS) on a Finnigan 90 MAT spectrometer. Melting points were measured by DTA, and molar conductivities, Λ, were determined in CH_3NO_2. Abbreviations used: s, singlet; d, doublet; t, triplet; vt, virtual triplet; m, multiplet; br, broadened signal; coupling constants J and N in Hz; $N = {}^3J(PH) + {}^5J(PH)$ or ${}^2J(PC) + {}^4J(PC)$.

Preparations

$[(\eta^6\text{-}C_6H_5CH_2CH_2P\textit{t}Bu_2\text{-}\kappa\text{-}\textit{P})RuCl_2]$ 3. *Method A.* A solution of $RuCl_3 \cdot 3H_2O$ (222 mg, 0.85 mmol) in isopropanol (12 cm^3) was treated with isoprene (2 cm^3, 0.02 mol) and stirred for 6 h at 80 °C. A change of colour from dark green to red–brown occurred. After cooling to room temperature the solvent was evaporated *in vacuo*, the remaining light brown solid was repeatedly washed with pentane, and dried *in vacuo*. The solid (320 mg) was dissolved in THF (20 cm^3), the solution was treated with **1** (638 mg, 2.55 mmol), and the reaction mixture was stirred under a H_2 atmosphere for 3 h at 70 °C. During that time a gradual change of colour from brown to orange–brown took place and an orange solid precipitated. The solvent was removed *in vacuo*, the residue was washed four-times with 8 cm^3 portions of ether, and dried *in vacuo*; yield 342 mg (95%).

Method B. A solution of compound **6** (355 mg, 0.64 mmol) in chlorobenzene (25 cm^3) was heated for 18 h at 130 °C. After cooling to room temperature, the solution was concentrated to *ca.* 2 cm^3 *in vacuo* and stored for 2 h. An orange solid precipitated, which was separated from the mother liquor, washed twice with 10 cm^3 portions of ether and dried *in vacuo*; yield 267 mg (98%); mp 188 °C (decomp.) (Found: C, 45.39; H, 6.59. $C_{16}H_{27}Cl_2PRu$ requires: C, 45.50; H, 6.44%). NMR (CD_2Cl_2): δ_H (400 MHz) 6.08 (1 H, m, *para*-H of C_6H_5), 5.77, 5.15 (2 H each, both m, C_6H_5), 2.96 (2 H, m, CH_2Ph), 2.66 (2 H, m, PCH_2), 1.40 [18 H, d, J(P,H) 13.2, $PCCH_3$]; δ_C (100.6 MHz) 110.7 [d, J(P,C) 4.8, *ipso*-C of C_6H_5], 96.5 [d, J(P,C) 2.9, C_6H_5], 90.3 [d, J(P,C) 13.5, C_6H_5], 77.5 (s, C_6H_5), 37.9 [d, J(P,C) 11.4, $PCCH_3$], 35.2 [d, J(P,C) 22.9, PCH_2], 32.0 [d, J(P,C) 3.8, CH_2Ph], 29.7 (s, $PCCH_3$); δ_P (162.0 MHz) 85.8 (s). EI MS (70 eV): m/z 422 (M^+, 16.7), 387 ($M^+ - Cl$, 16.3), 352 ($M^+ - 2$ Cl, 4.3%).

$[(\eta^6\text{-}C_6H_5OCH_2CH_2P\textit{t}Bu_2\text{-}\kappa\text{-}\textit{P})RuCl_2]$ 4. *Method A.* This compound was prepared as described for **3**, from $RuCl_3 \cdot 3H_2O$ (126 mg, 0.48 mmol) and isoprene (1.5 cm^3, 15.0 mmol) in isopropanol (6 cm^3). The light brown solid (180 mg) was dissolved in THF (20 cm^3), treated with **2** (321 mg, 1.21 mmol) and the reaction mixture was stirred under a H_2 atmosphere for 16 h at 70 °C. After cooling to room temperature, the solvent was removed *in vacuo*, the orange residue was repeatedly washed with ether, and dried *in vacuo*; yield 107 mg (51%).

Method B. The procedure was analogous to that described for **3**, using **7** (246 mg, 0.43 mmol) as starting material. Orange solid: yield 165 mg (88%); mp 168 °C (decomp.) (Found: C, 43.33; H, 6.41. $C_{16}H_{27}Cl_2OPRu$ requires: C, 43.84; H, 6.21%). NMR (CD_2Cl_2): δ_H (400 MHz) 6.01 (1 H, m, *para*-H of C_6H_5), 5.88, 5.14 (2 H each, both m, C_6H_5), 4.54 (2 H, m, CH_2OPh), 2.14 (2 H, m, PCH_2), 1.39 [18 H, d, J(P,H) 13.2, $PCCH_3$]; δ_C (100.6 MHz) 124.6 (s, *ipso*-C of C_6H_5), 98.7 [d, J(P,C) 2.0, C_6H_5], 88.8 [d, J(P,C) 13.2, C_6H_5], 70.0 (s, C_6H_5), 69.9 (s, CH_2OPh), 38.1 [d, J(P,C) 14.2, $PCCH_3$], 30.3 [d, J(P,C) 2.0, $PCCH_3$], 16.2 [d, J(P,C) 17.3, PCH_2]; δ_P (162.0 MHz) 37.0 (s). EI MS (70 eV): m/z 438 (M^+, 1.4), 403 ($M^+ - Cl$, 4.1), 368 ($M^+ - 2$ Cl, 2.0%).

$[(\eta^6\text{-}MeC_6H_4CHMe_2)(C_6H_5CH_2CH_2P\textit{t}Bu_2\text{-}\kappa\text{-}\textit{P})RuCl_2]$ 6. A solution of **5** (500 mg, 0.82 mmol) in CH_2Cl_2 (18 cm^3) was treated with **1** (511 mg, 2.04 mmol) and stirred for 6 h at 30 °C. The solution was filtered and the solvent was evaporated *in vacuo*. The remaining red–brown solid was washed three times with 15 cm^3 portions of pentane, and dried *in vacuo*; yield 819 mg (90%); mp 125 °C (decomp.) (Found: C, 55.63; H, 7.00. $C_{26}H_{41}Cl_2PRu$ requires: C, 56.11; H, 7.42%). NMR (CD_2Cl_2): δ_H (400 MHz) 7.22–7.10 (5 H, m, C_6H_5), 5.68 (4 H, m, C_6H_4), 3.07 (2 H, m, CH_2Ph), 2.85 [1 H, sept, J(H,H) 7.0, $CHCH_3$], 2.13 (3 H, s, $CH_3C_6H_4$), 2.12 (2 H, m, PCH_2), 1.46 [18 H, d, J(P,H) 12.0, $PCCH_3$], 1.32 [6 H, d, J(H,H) 7.0, $CHCH_3$]; δ_C (100.6 MHz) 144.6 [d, J(P,C) 12.2, *ipso*-C of C_6H_5], 128.3, 128.2, 125.6 (all s, C_6H_5), 106.7, 95.6 (both s, *tert*-C of C_6H_4), 88.3 [d, J(P,C) 4.1, C_6H_4], 84.2 [d, J(P,C) 5.1, C_6H_4], 81.2, 80.5 (both s, C_6H_4), 39.1 [d, J(P,C) 12.2, $PCCH_3$], 32.2 (s, CH_2Ph), 31.2 [d, J(P,C) 3.1, $PCCH_3$], 30.7 (s, $CHMe_2$), 25.4 [d, J(P,C) 15.3, PCH_2], 22.5 (s, $CH_3C_6H_4$), 17.8 (s, $CHCH_3$); δ_P (162.0 MHz) 46.1 (s).

[(η⁶-MeC$_6$H$_4$CHMe$_2$)(C$_6$H$_5$OCH$_2$CH$_2$P*t*Bu$_2$-κ-*P*)RuCl$_2$] 7. This compound was prepared as described for **6**, from **5** (306 mg, 0.50 mmol) and **2** (373 mg, 1.40 mmol) in CH_2Cl_2 (18 cm^3); reaction time 3 h. Light brown solid: yield 500 mg (87%); mp 110 °C (decomp.) (Found: C, 54.64; H, 6.72. $C_{26}H_{41}Cl_2OPRu$ requires: C, 54.54; H, 7.22%). NMR (CD_2Cl_2): δ_H (400 MHz) 7.22–6.83 (5 H, m, C_6H_5), 5.74–5.64 (4 H, m, C_6H_4), 4.36 (2 H, m, C*H*$_2$OPh), 2.80 [1 H, sept, *J*(H,H) 7.0, C*H*CH$_3$], 2.21 (2 H, m, PCH$_2$), 2.11 (3 H, s, C*H*$_3$C$_6$H$_4$), 1.44 [18 H, d, *J*(P,H) 12.3, PCCH$_3$], 1.32 [6 H, d, *J*(H,H) 7.0, CHC*H*$_3$]; δ_C (100.6 MHz) 159.0 (s, *ipso*-C of C_6H_5), 129.3, 120.0, 114.6 (all s, C_6H_5), 106.5, 96.3 (both s, *tert*-C of C_6H_4), 88.3, 84.7 [both d, *J*(P,C) 4.1, C_6H_4], 81.2, 80.5 (both s, C_6H_4), 66.5 [d, *J*(P,C) 3.1, *C*H$_2$OPh], 39.1 [d, *J*(P,C) 13.2, P*C*CH$_3$], 30.9 [d, *J*(P,C) 3.1, PC*C*H$_3$], 30.6 (s, *C*HMe$_2$), 22.8 [d, *J*(P,C) 19.3, PCH$_2$], 22.5 (s, *C*H$_3$C$_6$H$_4$), 17.8 (s, CH*C*H$_3$); δ_P (162.0 MHz) 46.9 (s).

[{(η⁶-C$_6$H$_5$CH$_2$CH$_2$P*t*Bu$_2$-κ-*P*)RuCl}$_2$](PF$_6$)$_2$ 8. A suspension of **3** (59 mg, 0.14 mmol) in acetone (8 cm^3) was treated dropwise with a solution of $AgPF_6$ (35 mg, 0.14 mmol) in acetone (5 cm^3). After the reaction mixture was stirred for 75 min at room temperature, an orange–yellow solution resulted from which a white solid precipitated. The solution was filtered and the filtrate was concentrated *in vacuo* to *ca.* 2 cm^3. Addition of pentane (10 cm^3) led to the formation of orange–yellow crystals, which were separated from the mother liquor, washed twice with 5 cm^3 portions of pentane and dried *in vacuo*; yield 46 mg (61%); mp 178 °C (decomp.) (Found: C, 36.68; H, 4.79. $C_{32}H_{54}Cl_2F_{12}P_4Ru_2$ requires: C, 36.13; H, 5.11%). *Λ* 114.6 cm^2 Ω^{-1} mol^{-1}. IR (KBr): *ν*(PF$_6^-$) 835 cm^{-1}. NMR (CD_3NO_2): δ_H (200 MHz) 7.32 (2 H, m, *para*-H of C_6H_5), 6.63, 5.82 (4 H each, both m, C_6H_5), 3.89, 3.39 (4 H each, both m, PC*H*$_2$C*H*$_2$Ph), 2.16–1.72 (36 H, m, PCCH$_3$); δ_P (81.0 MHz) 98.3 (s), −142.9 [sept, *J*(F,P) 706.2, PF$_6^-$].

***In situ* generation of [(η⁶-C$_6$H$_5$CH$_2$CH$_2$P*t*Bu$_2$-κ-*P*)RuCl{O=C(CD$_3$)$_2$}]PF$_6$ 9.** A solution of **8** (45 mg, 0.04 mmol) in acetone-d_6 (0.5 cm^3) was stirred for 3 min at room temperature. The NMR spectra indicated that compound **9** was generated which, however, could not be isolated in an analytically pure state. Careful removal of the solvent led to the re-formation of the starting material. Spectroscopic data for **9**: NMR (acetone-d_6): δ_H(300 MHz): 6.49 (1 H, m, C_6H_5), 6.06, 5.50 (2 H each, both m, C_6H_5), 3.32, 2.89 (2 H each, both m, PC*H*$_2$C*H*$_2$Ph), 1.28 [18 H, d, *J*(P,H) 13.6, PCCH$_3$]; δ_C (75.5 MHz) 210.5 [s, O=*C*(CD$_3$)$_2$], 115.8 (m, *ipso*-C of C_6H_5), 94.6 (s, C_6H_5), 93.1 [d, *J*(P,C) 11.6, C_6H_5], 69.6 (s, C_6H_5), 38.4 [d, *J*(P,C) 12.7, P*C*CH$_3$], 36.1 [d, *J*(P,C) 24.3, PCH$_2$], 33.1 [d, *J*(P,C) 2.9, *C*H$_2$Ph], 31.7 [sept, *J*(D,C) 19.5, O=C(*C*D$_3$)$_2$], 30.3 [d, *J*(P,C) 2.2, PC*C*H$_3$]; δ_P (81.0 MHz) 92.5 (s), −142.7 [sept, *J*(F,P) 706.9, PF$_6^-$].

[(η⁶-C$_6$H$_5$CH$_2$CH$_2$P*t*Bu$_2$-κ-*P*)RuCl(NCMe)]PF$_6$ 10. *Method A.* A solution of **3** (73 mg, 0.17 mmol) in CH_2Cl_2 (10 cm^3) and CH_3CN (5 cm^3) was treated dropwise with a solution of $AgPF_6$ (44 mg, 0.17 mmol) in CH_2Cl_2 (3 cm^3). A gradual change of colour from orange to yellow occurred and a white solid precipitated. After the reaction mixture was stirred for 5 min at room temperature, the solvent was evaporated *in vacuo*, and the residue was extracted twice with 5 cm^3 portions of CH_2Cl_2. The combined extracts were concentrated to *ca.* 1 cm^3 *in vacuo* and after addition of pentane (7 cm^3) a yellow microcrystalline solid precipitated. It was separated from the mother liquor, washed twice with 5 cm^3 portions of ether and dried; yield 73 mg (76%).

Method B. A solution of **8** (32 mg, 0.03 mmol) in acetone (5 cm^3) was treated with acetonitrile (6.3 μl, 0.12 mmol) and stirred for 3 min at room temperature. After pentane (15 cm^3) was added, a yellow solid precipitated, which was separated from the mother liquor, washed twice with 5 cm^3 portions of pentane and dried *in vacuo*; yield 33 mg (96%); mp 191 °C (decomp.) (Found: C, 38.08; H, 5.16; N, 2.62. $C_{18}H_{30}ClF_6NP_2Ru$ requires: C, 37.74; H, 5.28; N, 2.44%). *Λ* 96.3 cm^2 Ω^{-1} mol^{-1}. IR (KBr): *ν*(CN) 2328, *ν*(PF$_6^-$) 843 cm^{-1}. NMR (CD_2Cl_2): δ_H (300 MHz) 6.38, 6.29, 5.95, 5.57, 5.34 (1 H each, all m, C_6H_5), 3.17–2.82, 2.70–2.58 (2 H each, all m, PC*H*$_2$-C*H*$_2$Ph), 2.53 (3 H, s, CH_3CN), 1.41 [9 H, d, *J*(P,H) 14.2, PCCH$_3$], 1.34 [9 H, d, *J*(P,H) 13.6, PCCH$_3$]; δ_C (75.5 MHz) 128.6 (s, CN), 116.0 [d, *J*(P,C) 5.1, *ipso*-C of C_6H_5], 98.1 [d, *J*(P,C) 1.5, C_6H_5], 97.1 [d, *J*(P,C) 3.6, C_6H_5], 92.3 [d, *J*(P,C) 10.5, C_6H_5], 80.3, 78.4 (both s, C_6H_5), 38.8 [d, *J*(P,C) 14.5, P*C*CH$_3$], 36.4 [d, *J*(P,C) 12.4, P*C*CH$_3$], 35.8 [d, *J*(P,C) 24.3, PCH$_2$], 31.9 [d, *J*(P,C) 2.2, *C*H$_2$Ph], 29.6 [d, *J*(P,C) 1.5, PC*C*H$_3$], 29.4 [d, *J*(P,C) 3.3, PC*C*H$_3$], 4.5 (s, *C*H$_3$CN); δ_P (81.0 MHz) 97.0 (s), −143.9 [sept, *J*(F,P) 711.2, PF$_6^-$]. FAB MS (70 eV): *m*/*z* 573 (M$^+$, 0.04), 428 (M$^+$ − PF$_6$, 0.1), 387 (M$^+$ − PF$_6$ − MeCN, 2.3), 352 (M$^+$ − Cl − PF$_6$ − MeCN, 0.3%).

[(η⁶-C$_6$H$_5$OCH$_2$CH$_2$P*t*Bu$_2$-κ-*P*)RuCl(NCMe)]PF$_6$ 11. This compound was prepared as described for **10**, *Method A*, from **4** (75 mg, 0.17 mmol) in CH_2Cl_2–CH_3CN (2 : 1, 15 cm^3) and $AgPF_6$ (44 mg, 0.17 mmol) in CH_2Cl_2 (3 cm^3); reaction time 50 min. Yellow solid: yield 82 mg (82%); mp 156 °C (decomp.) (Found: C, 36.89; H, 5.01; N, 2.46. $C_{18}H_{30}ClF_6NOP_2Ru$ requires: C, 36.71; H, 5.13; N, 2.38%). *Λ* 91.6 cm^2 Ω^{-1} mol^{-1}. IR (KBr): *ν*(CN) 2325, *ν*(PF$_6^-$) 837 cm^{-1}. NMR (CD_2Cl_2): δ_H (400 MHz) 6.30, 6.14, 6.02, 5.33, 5.16 (1 H each, all m, C_6H_5), 4.75–4.52 (2 H, m, C*H*$_2$OPh), 2.45 (3 H, s, CH_3CN), 2.27–2.04 (2 H, m, PCH$_2$), 1.34 [9 H, d, *J*(P,H) 14.1, PCCH$_3$], 1.26 [9 H, d, *J*(P,H) 13.5, PCCH$_3$]; δ_C (100.6 MHz) 129.4 (s, CN), 128.0 (s, *ipso*-C of C_6H_5), 101.5, 98.9 (both s, C_6H_5), 89.1 [d, *J*(P,C) 11.2, C_6H_5], 71.3, 70.7 (both s, C_6H_5), 69.4 (s, *C*H$_2$OPh), 38.8 [d, *J*(P,C) 16.3, P*C*CH$_3$], 36.1 [d, *J*(P,C) 14.2, P*C*CH$_3$], 30.7, 29.6 (both s, PC*C*H$_3$), 15.8 [d, *J*(P,C) 19.3, PCH$_2$], 4.6 (s, *C*H$_3$CN); δ_P (162.0 MHz) 48.6 (s), −144.3 [sept, *J*(F,P) 713.2, PF$_6^-$].

[(η⁶-C$_6$H$_5$CH$_2$CH$_2$P*t*Bu$_2$-κ-*P*)RuCl(PMe$_3$)]PF$_6$ 12. *Method A.* A solution of **10** (92 mg, 0.16 mmol) in CH_2Cl_2 (8 cm^3) was treated with PMe_3 (16.3 μl, 0.16 mmol) and stirred for 30 min at room temperature. After removal of the solvent, the remaining yellow solid was washed three times with 4 cm^3 portions of pentane, and dried *in vacuo*; yield 73 mg (75%).

Method B. A solution of **8** (74 mg, 0.07 mmol) in acetone (10 cm^3) was treated with PMe_3 (16.3 μl, 0.16 mmol) and, after it was stirred for 3 min at room temperature, pentane (15 cm^3) was added. A yellow solid precipitated, which was washed twice with 5 cm^3 portions of pentane, and dried *in vacuo*; yield 73 mg (86%); mp 146 °C (decomp.) (Found: C, 36.81; H, 5.90. $C_{19}H_{36}ClF_6P_3Ru$ requires: C, 37.54; H, 5.97%). *Λ* 68.0 cm^2 Ω^{-1} mol^{-1}. IR (KBr): *ν*(PF$_6^-$) 839 cm^{-1}. NMR (CD_2Cl_2): δ_H (400 MHz) 6.17, 6.09, 5.99, 5.79, 5.16 (1 H each, all m, C_6H_5), 3.25–3.02, 2.82–2.61 (2 H each, both m, PC*H*$_2$C*H*$_2$Ph), 1.78 [9 H, d, *J*(P,H) 10.2, PCH$_3$], 1.40 [9 H, d, *J*(P,H) 14.1, PCCH$_3$], 1.29 [9 H, d, *J*(P,H) 13.5, PCCH$_3$]; δ_C (100.6 MHz) 123.8 (m, *ipso*-C of C_6H_5), 104.7 (m, C_6H_5), 89.9 [d, *J*(P,C) 11.2, C_6H_5], 89.4 (s, C_6H_5), 88.4 [d, *J*(P,C) 10.2, C_6H_5], 80.0 (s, C_6H_5), 39.1 [d, *J*(P,C) 24.4, PCH$_2$], 37.3, 37.2 [both d, *J*(P,C) 13.2, P*C*CH$_3$], 31.0 (s, *C*H$_2$Ph), 30.7 [d, *J*(P,C) 4.1, PC*C*H$_3$], 29.2 (br s, PC*C*H$_3$), 20.6 [d, *J*(P,C) 34.6, PCH$_3$]; δ_P(162.0 MHz) 89.2 [d, *J*(P,P) 48.0, P*t*Bu$_2$], −7.5 [d, *J*(P,P) 48.0, PMe$_3$], −144.3 [sept, *J*(F,P) 709.5, PF$_6^-$]. FAB MS (70 eV): *m*/*z* 463 (M$^+$ − PF$_6$, 11.7), 428 (M$^+$ − PF$_6$ − Cl, 1.7), 387 (M$^+$ − PF$_6$ − PMe$_3$, 3.4%).

[(η⁶-C$_6$H$_5$CH$_2$CH$_2$P*t*Bu$_2$-κ-*P*)RuHCl] 13. A solution of $RuCl_3 \cdot 3H_2O$ (160 mg, 0.61 mmol) in isopropanol (8 cm^3) was treated with isoprene (2 cm^3, 0.02 mol) and stirred for 6 h at 80 °C. A change of colour from dark green to red–brown occurred. After cooling to room temperature the solvent was evaporated *in vacuo*, the remaining light brown solid was repeatedly washed with pentane, and dried *in vacuo*. The solid (229 mg) was dissolved in THF (15 cm^3), the solution was

treated with **1** (456 mg, 1.82 mmol) and NEt_3 (85 μl, 0.61 mmol), and the reaction mixture was stirred under a H_2 atmosphere for 24 h at 75 °C. During that time a gradual change of colour from brown to brown–yellow occurred. The solvent was evaporated *in vacuo*, and the residue was extracted with benzene (20 cm^3). After the extract was brought to dryness *in vacuo*, the remaining yellow solid was washed three times with 5 cm^3 portions of pentane, and dried *in vacuo*; yield 207 mg (87%). Compound **13** could also be obtained by using methanol instead of THF as solvent. In this case the time of reaction is 20 min; yield 95%; mp 66 °C (decomp.) (Found: C, 49.80, H, 6.89. $C_{16}H_{28}ClPRu$ requires: C, 49.54; H, 7.27%). IR (KBr): *ν*(RuH) 1990 cm^{-1}. NMR (CD_2Cl_2): δ_H (400 MHz) 6.31, 6.20, 5.70, 5.15, 4.30 (1 H each, all m, C_6H_5), 2.78–2.44 (4 H, m, PCH_2CH_2Ph), 1.44, 1.23 [9 H each, both d, *J*(P,H), 13.1, $PCCH_3$], −7.52 [1 H, d, *J*(P,H) 39.2, RuH]; δ_C (100.6 MHz) 128.3 (s, *ipso*-C of C_6H_5), 100.0, 98.1 (both s, C_6H_5), 89.3 [d, *J*(P,C) 11.2 Hz, C_6H_5], 87.9 [d, *J*(P,C) 6.1, C_6H_5], 69.9 (s, C_6H_5), 36.1 [d, *J*(P,C) 22.4, PCH_2], 36.0 [d, *J*(P,C) 13.2, $PCCH_3$], 34.9 [d, *J*(P,C) 19.3, $PCCH_3$], 31.4 [d, *J*(P,C) 5.1, CH_2Ph], 30.0, 28.6 [both d, *J*(P,C) 3.1, $PCCH_3$]; δ_P (162.0 MHz) 111.8 (s).

[(η⁶-$C_6H_5OCH_2CH_2PtBu_2$-κ-*P*)RuHCl] 14. This compound was prepared as described for **13**, from $RuCl_3 \cdot 3H_2O$ (180 mg, 0.69 mmol), isoprene (2 cm^3, 0.02 mol), phosphine **2** (460 mg, 1.73 mmol), NEt_3 (96 μl, 0.69 mmol) and H_2 (1 bar). The remaining residue was extracted with hexane–CH_2Cl_2 (5 : 1, 20 cm^3) to give a yellow solid; yield 167 mg (59%); mp 46 °C (decomp.) (Found C, 48.25; H, 7.17. $C_{16}H_{28}ClOPRu$ requires: C, 47.58; H, 6.99%). IR (KBr): *ν*(RuH) 2017 cm^{-1}. NMR (CD_2Cl_2): δ_H (300 MHz) 6.47, 6.31, 5.63, 4.95 (1 H each, all m, C_6H_5), 4.28–4.13 (3 H, m, C_6H_5 and CH_2OPh), 1.70 (2 H, m, PCH_2), 1.45 [9 H, d, *J*(P,H) 13.2, $PCCH_3$], 1.25 [9 H, d, *J*(P,H) 12.9, $PCCH_3$], −7.37 [1 H, d, *J*(P,H) 37.0, RuH]; δ_C (75.5 MHz) 114.6 (s, *ipso*-C of C_6H_5), 100.3, 94.1 (both s, C_6H_5), 89.2 [d, *J*(P,C) 4.7, C_6H_5], 86.8 [d, *J*(P,C) 10.5, C_6H_5], 69.1 (s, C_6H_5), 67.8 (s, CH_2OPh), 35.5 [d, *J*(P,C) 22.9, $PCCH_3$], 35.1 [d, *J*(P,C) 14.5, $PCCH_3$], 29.9 [d, *J*(P,C) 3.6, $PCCH_3$], 27.5 [d, *J*(P,C) 2.5, $PCCH_3$], 15.8 [d, *J*(P,C) 20.7, PCH_2]; δ_P (81.0 MHz) 62.6 (s).

[($C_6H_5CH_2CH_2PtBu_2$-κ-*P*)$_2$RuHCl(H_2)] 15. The generation of the intermediate, from $RuCl_3 \cdot 3H_2O$ (58 mg, 0.22 mmol) and isoprene (1 cm^3, 0.01 mol) in isopropanol (5 cm^3) at 80 °C was carried out analogously to **13**. The subsequent reaction of the residue (84 mg) with **1** (168 mg, 0.67 mmol) and NEt_3 (31 μl, 0.22 mmol) in THF (10 cm^3) under a H_2 atmosphere (1 bar) took place at room temperature. After stirring the reaction mixture for 60 min, an orange–brown suspension was obtained, from which the solvent was evaporated *in vacuo*. The remaining residue was extracted with pentane (25 cm^3), the extract was brought to dryness *in vacuo*, and the oily residue was treated with methanol (1 cm^3). An orange–yellow solid was formed, which was filtered, washed twice with 2 cm^3 portions of methanol, and dried *in vacuo*; yield 64 mg (45%); mp 25 °C (decomp.) (Found: C, 59.91; H, 8.58. $C_{32}H_{57}ClP_2Ru$ requires: C, 60.03; H, 8.97%). NMR (CD_2Cl_2): δ_H (300 MHz) 7.40–7.16 (10 H, m, C_6H_5), 3.06, 2.18 (4 H each, both m, PCH_2CH_2Ph), 1.31 (36 H, vt, *N* 12.3, $PCCH_3$), −16.53 [3 H, br s, RuH(H_2)]; δ_C (50.3 MHz) 144.3 (vt, *N* 12.9, *ipso*-C of C_6H_5), 128.4, 128.3, 125.8 (all s, C_6H_5), 35.1 (vt, *N* 14.8, $PCCH_3$), 33.6 (s, CH_2Ph), 30.4 (s, $PCCH_3$), 25.4 (vt, *N* 12.9, PCH_2); δ_P (81.0 MHz) 69.3 (s).

[($C_6H_5OCH_2CH_2PtBu_2$-κ-*P*)$_2$RuHCl(H_2)] 16. This compound was prepared as described for **15**, from $RuCl_3 \cdot 3H_2O$ (88 mg, 0.34 mmol), isoprene (2 cm^3, 0.02 mol), phosphine **2** (270 mg, 1.01 mmol), NEt_3 (47 μl, 0.34 mmol) and H_2 (1 bar). Orange solid: yield 124 mg (53%); mp 22 °C (decomp.) (Found: C, 56.91; H, 8.08. $C_{32}H_{57}ClO_2P_2Ru$ requires: C, 57.17; H, 8.54%). NMR (CD_2Cl_2): δ_H (300 MHz) 7.30–6.89 (10 H, m, C_6H_5), 4.43 (4 H, m, CH_2OPh), 2.38 (4 H, m, PCH_2), 1.28 (36 H, vt, *N* 12.3, $PCCH_3$), −16.63 [3 H, br s, RuH(H_2)]; δ_C (50.3 MHz) 158.9 (s, *ipso*-C of C_6H_5), 129.5, 120.5, 114.7 (all s, C_6H_5), 66.8 (s, CH_2OPh), 35.2 (vt, *N* 16.6, $PCCH_3$), 30.2 (vt, *N* 5.5, $PCCH_3$), 22.0 (s, PCH_2); δ_P (81.0 MHz) 67.2 (s).

[($C_6H_5OCH_2CH_2PtBu_2$-κ-*P*)$_2$RuHCl(CO)] 17. The generation of the intermediate, from $RuCl_3 \cdot 3H_2O$ (196 mg, 0.75 mmol) and isoprene (4 cm^3, 0.04 mol) in isopropanol (10 cm^3) at 80 °C was carried out analogously as described for **13**. The subsequent reaction of the residue (282 mg) with **2** (599 mg, 2.25 mmol) and NEt_3 (0.1 cm^3, 0.75 mmol) in THF (10 cm^3) under a H_2 atmosphere (1 bar) took place at 80 °C for 16 h. After the reaction mixture was cooled to room temperature, the ^{31}P NMR spectrum of the solution indicated that a mixture of **16** (*ca.* 40%) and **17** (*ca.* 60%) was formed. Therefore, the reaction mixture was stirred again at 80 °C for 6 h but under an argon atmosphere. An orange–yellow solution was obtained, which after cooling was concentrated to *ca.* 2 cm^3 *in vacuo*. A yellow solid precipitated, which was filtered, washed twice with 2 cm^3 portions of methanol, and dried *in vacuo*; yield 494 mg (95%); mp 36 °C (decomp.) (Found: C, 56.46; H, 8.05. $C_{33}H_{55}ClO_3P_2Ru$ requires: C, 56.76; H, 7.94%). IR (KBr): *ν*(RuH) 2108, *ν*(CO) 1906 cm^{-1}. NMR (CD_2Cl_2): δ_H (400 MHz) 7.25–6.87 (10 H, m, C_6H_5), 4.41, 4.26 (2 H each, both m, CH_2OPh), 2.90, 2.41 (2 H each, both m, PCH_2), 1.42, 1.40 (18 H each, both vt, *N* 12.8, $PCCH_3$), −25.15 [1 H, t, *J*(P,H) 18.4, RuH]; δ_C (100.6 MHz) 202.4 [t, *J*(P,C) 13.8, CO], 158.8 (s, *ipso*-C of C_6H_5), 129.5, 120.7, 114.6 (all s, C_6H_5), 66.2 (vt, *N* 8.6, CH_2OPh), 36.7 (vt, *N* 15.3, $PCCH_3$), 35.6 (vt, *N* 17.2, $PCCH_3$), 30.8, 30.5 (both br s, $PCCH_3$), 21.4 (vt, *N* 18.2, PCH_2); δ_P (162.0 MHz) 59.0 (s).

[($C_6H_5OCH_2CH_2PtBu_2$-κ-*P*)$_2$Ru(CH=CH_2)Cl(CO)] 18. A slow stream of acetylene was passed for 60 s through a solution of **17** (60 mg, 0.09 mmol) in CH_2Cl_2 (6 cm^3) at room temperature. The solution was then stirred for 3 min, the solvent was removed *in vacuo*, and pentane (2 cm^3) was added to the oily residue. After storing for 6 h, an orange solid was obtained which was washed twice with 2 cm^3 portions of pentane, and dried *in vacuo*; yield 55 mg (88%); mp 66 °C (decomp.) (Found: C, 57.91; H, 7.72. $C_{35}H_{57}ClO_3P_2Ru$ requires: C, 58.04; H, 7.93%). IR (KBr): *ν*(CO) 1913, *ν*(C=C) 1599 cm^{-1}. NMR (CD_2Cl_2): δ_H (200 MHz) 7.83 [1 H, br d, *J*(H,H) 13.0, RuCH], 7.27–6.92 (10 H, m, C_6H_5), 5.22 (1 H, br m, *cis*-H of CH=CH_2), 4.82 [1 H, br d, *J*(H,H) 13.0, *trans*-H of CH=CH_2], 4.55 (4 H, m, CH_2OPh), 2.82, 2.63 (2 H each, both m, PCH_2), 1.25, 1.21 (18 H each, both vt, *N* 12.2, $PCCH_3$); δ_C (50.3 MHz) 180.9 (br m, CO), 158.9 (s, *ipso*-C of C_6H_5), 151.8 (br m, RuCH), 129.5 (s, C_6H_5), 122.0 (s, CH=CH_2), 120.6, 114.6 (both s, C_6H_5), 64.6 (s, CH_2OPh), 37.8, 37.7 (both vt, *N* 13.1, $PCCH_3$), 31.0, 30.4 (both s, $PCCH_3$), 22.9 (vt, *N* 15.3, PCH_2); δ_P (81.0 MHz) 40.1 (s). FAB MS (70 eV): *m*/*z* 724 (M^+, 0.4), 689 (M^+ − Cl, 0.4%).

[($C_6H_5OCH_2CH_2PtBu_2$-κ-*P*)$_2$RuHF(CO)] 19. A solution of **17** (102 mg, 0.15 mmol) in acetone (10 cm^3) was treated with CsF (130 mg, 0.86 mmol) and stirred for 24 h at room temperature. The solvent was removed *in vacuo*, and the residue was extracted twice with 5 cm^3 portions of pentane. The combined extracts were brought to dryness *in vacuo*, and the pale-yellow residue was recrystallized from pentane (2 cm^3) at −60 °C; yield 61 mg (60%). (Found: C, 56.79; H, 7.72. $C_{33}H_{55}FO_3P_2Ru$ requires: C, 58.13; H, 8.13%). IR (KBr): *ν*(RuH) 2102, *ν*(CO) 1898 cm^{-1}. NMR (CD_2Cl_2): δ_H (200 MHz) 7.21–6.86 (10 H, m, C_6H_5), 4.48, 4.30 (2 H each, both m, CH_2OPh), 2.58, 2.27 (2 H each, both m, PCH_2), 1.39, 1.38 (18 H each, both vt, *N* 13.0, $PCCH_3$), −24.20 [1 H, dt, *J*(F,H) 2.2, *J*(P,H) 18.0, RuH]; δ_C (100.6 MHz) 205.5 (m, CO), 158.8 (s, *ipso*-C of C_6H_5), 129.5, 120.6, 114.6 (all s, C_6H_5), 66.2 [dvt, *N* 8.6, *J*(F,C) 4.3, CH_2OPh], 36.2 (vt, *N* 15.3, $PCCH_3$), 35.1 (vt, *N* 17.2, $PCCH_3$), 30.2 (br s, $PCCH_3$), 30.0 (vt, *N* 4.8, $PCCH_3$), 21.1 (vt, *N* 16.2, PCH_2);

δ_P (81.0 MHz) 62.1 [d, *J*(F,P) 21.8]; δ_F (188.3 MHz) −203.0 [t, *J*(P,F) 21.8 Hz].

[($C_6H_5OCH_2CH_2PtBu_2$-κ-*P*)$_2$RuHCl(CO)$_2$] 20. *Method A.* A slow stream of CO was passed for 60 s through a suspension of **17** (51 mg, 0.07 mmol) in hexane (5 cm^3) at room temperature. A colourless solution was formed, of which the solvent was removed *in vacuo*. The off-white residue was washed twice with 2 cm^3 portions of pentane, and dried *in vacuo*; yield 50 mg (95%).

Method B. The generation of the intermediate, from $RuCl_3 \cdot 3H_2O$ (47 mg, 0.18 mmol) and isoprene (1 cm^3, 0.01 mol) in isopropanol (5 cm^3) at 80 °C was carried out analogously to **13**. The subsequent reaction of the residue (69 mg) with **2** (146 mg, 0.55 mmol) and NEt_3 (26 μl, 0.18 mmol) in methanol (10 cm^3) under a H_2 atmosphere (1 bar) took place at 70 °C for 30 min. After the reaction mixture was cooled to room temperature, a slow stream of CO was passed through the solution for 45 s. A change of colour from orange–yellow to pale yellow was observed. The solution was concentrated to *ca.* 2 cm^3 *in vacuo*, which led to the precipitation of an off-white solid. It was filtered, washed three times with 3 cm^3 portions of methanol, and dried *in vacuo*; yield 75 mg (56%); mp 110 °C (decomp.) (Found: C, 55.77; H, 7.33. $C_{34}H_{55}ClO_4P_2Ru$ requires: C, 56.22; H, 7.63%). IR (KBr): *ν*(RuH) 2041, *ν*(CO) 1965, 1925 cm^{-1}. NMR (CD_2Cl_2): δ_H (400 MHz) 7.28–6.92 (10 H, m, C_6H_5), 4.53, 4.39 (2 H each, both m, C*H*$_2$OPh), 2.78, 2.49 (2 H each, both m, PCH_2), 1.48 (36 H, vt, *N* 11.4, $PCCH_3$), −5.51 [1 H, t, *J*(P,H) 19.7, RuH]; δ_C (100.6 MHz) 201.1 [t, *J*(P,C) 13.4, CO], 200.1 [t, *J*(P,C) 6.2, CO], 158.8 (s, *ipso*-C of C_6H_5), 129.5, 120.7, 114.6 (all s, C_6H_5), 65.7 (vt, *N* 5.7, *C*H$_2$OPh), 37.1 (vt, *N* 20.0, P*C*CH$_3$), 36.9 (vt, *N* 16.2, P*C*CH$_3$), 30.6, 29.9 (both s, PC*C*H$_3$), 21.3 (vt, *N* 19.1, PCH_2); δ_P (162.0 MHz) 65.8 (s).

[($C_6H_5OCH_2CH_2PtBu_2$-κ-*P*)$_2$RuHF(CO)$_2$] 21. A solution of **20** (62 mg, 0.09 mmol) in acetone (8 cm^3) was treated with CsF (100 mg, 0.66 mmol) and stirred for 24 h at room temperature. The solvent was removed *in vacuo*, and the residue was extracted twice with 6 cm^3 portions of pentane. The combined extracts were brought to dryness *in vacuo*, the remaining yellow solid was washed twice with 2 cm^3 portions of pentane (−78 °C) and dried *in vacuo*; yield 55 mg (87%); mp 117 °C (Found: C, 56.96; H, 7.85. $C_{34}H_{55}FO_4P_2Ru$ requires: C, 57.53; H, 7.81%). IR (KBr): *ν*(RuH) 2048, *ν*(CO) 1975, 1910 cm^{-1}. NMR (CD_2Cl_2): δ_H (400 MHz) 7.24–6.88 (10 H, m, C_6H_5), 4.44 (4 H, m, C*H*$_2$OPh), 2.49, 2.40 (2 H each, both m, PCH_2), 1.46 (36 H, vt, *N* 12.2, $PCCH_3$), −4.31 [1 H, dt, *J*(F,H) 7.6, *J*(P,H) 19.8, RuH]; δ_C (100.6 MHz) 203.1 [dt, *J*(F,C) 66.8, *J*(P,C) 11.9, CO], 200.1 [dt, *J*(F,C) 6.7, *J*(P,C) 6.7, CO], 158.8 (s, *ipso*-C of C_6H_5), 129.5, 120.5, 114.5 (all s, C_6H_5), 66.0 [dvt, *N* 7.6, *J*(F,C) 3.8, *C*H$_2$OPh], 36.4, 36.3 (both vt, *N* 18.1, P*C*CH$_3$), 30.3, 29.9 (both s, PC*C*H$_3$), 20.8 [dvt, *N* 18.1, *J*(F,C) 3.8, PCH_2]; δ_P (162.0 MHz) 71.9 [d, *J*(F,P) 20.3]; δ_F (376.5 MHz) −395.2 [t, *J*(P,F) 20.3].

[(η^6-$C_6H_5CH_2CH_2PtBu_2$-κ-*P*)RuCl(=C=C=CPh$_2$)]BF_4 22a. A solution of **13** (127 mg, 0.33 mmol) and 1,1-diphenyl-2-propyn-1-ol (75 mg, 0.36 mmol) in acetone (10 cm^3) was treated dropwise at −78 °C with a solution of HBF_4 in ether (0.2 cm^3, 0.32 mmol). After stirring for 2 min, the reaction mixture was warmed to room temperature, and then the solvent was removed *in vacuo*. A violet solid was obtained, which was washed three times with 5 cm^3 portions of pentane, and dried *in vacuo*; yield 207 mg (94%); mp 68 °C (decomp.) (Found: C, 56.10; H, 6.60. $C_{31}H_{37}BClF_4PRu$ requires: C, 56.08; H, 5.62%). *Λ* (CH_3NO_2) 49.5 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR (KBr): *ν*(C=C=C) 1970, *ν*(BF_4^-) 1056 cm^{-1}.

[(η^6-$C_6H_5CH_2CH_2PtBu_2$-κ-*P*)RuCl(=C=C=CPh$_2$)]PF_6 22b. A suspension of **3** (65 mg, 0.15 mmol) and 1,1-diphenyl-2-propyn-1-ol (42 mg, 0.20 mmol) in acetone (7 cm^3) was treated dropwise with a solution of $AgPF_6$ (39 mg, 0.15 mmol) in acetone (5 cm^3). After the reaction mixture was stirred for 5 min at room temperature, the solution was filtered, and the filtrate was brought to dryness *in vacuo*. The residue was dissolved in CH_2Cl_2 (15 cm^3), and the solution was filtered with Celite. After the solvent was evaporated from the filtrate, the remaining violet solid was repeatedly washed with pentane and dried *in vacuo*; yield 85 mg (80%); mp 94 °C (decomp.) (Found: C, 51.85; H, 5.49. $C_{31}H_{37}ClF_6P_2Ru$ requires: C, 51.56; H, 5.16%). *Λ* (CH_3NO_2) 54.0 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR (KBr): *ν*(C=C=C) 1972, *ν*(PF_6^-) 840 cm^{-1}. NMR (CD_2Cl_2): δ_H (300 MHz) 8.04–7.50 (10 H, m, C_6H_5), 6.89, 6.64, 6.50, 6.08, 5.61 (1 H each, all m, η^6-C_6H_5), 3.27–2.84, 2.31–2.17 (2 H each, both m, PC*H*$_2$-C*H*$_2$Ph), 1.52 [9 H, d, *J*(P,H) 14.3, $PCCH_3$], 1.15 [9 H, d, *J*(P,H) 14.9, $PCCH_3$]; δ_C (75.5 MHz) 285.2 [d, *J*(P,C) 17.1, Ru=C], 178.5, 172.0 (both s, =*C*=*C*Ph$_2$), 142.0 (s, *ipso*-C of C_6H_5), 135.2, 133.9, 129.6 (all s, C_6H_5), 120.5 [d, *J*(P,C) 5.2, *ipso*-C of η^6-C_6H_5], 111.9, 103.7 (both s, η^6-C_6H_5), 101.5 [d, *J*(P,C) 4.7, η^6-C_6H_5], 95.3 [d, *J*(P,C) 8.8, η^6-C_6H_5], 86.8 (s, η^6-C_6H_5), 39.1 [d, *J*(P,C) 14.5, PCH_2], 38.1 [d, *J*(P,C) 10.9, P*C*CH$_3$], 37.8 [d, *J*(P,C) 3.1, P*C*CH$_3$], 32.2 (s, *C*H$_2$Ph), 29.8, 28.9 (both s, PC*C*H$_3$); δ_P (81.0 MHz) 113.6 (s, P*t*Bu$_2$), −143.9 [sept, *J*(F,P) 711.2, PF_6^-].

[(η^6-$C_6H_5OCH_2CH_2PtBu_2$-κ-*P*)RuCl(=C=C=CPh$_2$)]PF_6 23. This compound was prepared as described for **22b**, from **4** (67 mg, 0.15 mmol), 1,1-diphenyl-2-propyn-1-ol (34 mg, 0.16 mmol) and $AgPF_6$ (39 mg, 0.15 mmol) in acetone (12 cm^3). Violet solid: yield 74 mg (67%); mp 66 °C (decomp.) (Found: C, 50.12; H, 5.23. $C_{31}H_{37}ClF_6OP_2Ru$ requires: C, 50.45; H, 5.05%). *Λ* (CH_3NO_2) 64.4 $cm^2\ \Omega^{-1}\ mol^{-1}$. IR (KBr): *ν*(C=C=C) 1970, *ν*(PF_6^-) 841 cm^{-1}. NMR (CD_2Cl_2): 7.81–7.27 (10 H, m, C_6H_5), 6.60, 6.45, 6.09, 6.01, 5.41 (1 H each, all m, η^6-C_6H_5), 4.84–4.49 (2 H, m, C*H*$_2$OPh), 2.39–1.89 (2 H, m, PCH_2), 1.53 [9 H, d, *J*(P,H) 14.2, $PCCH_3$], 1.14 [9 H, d, *J*(P,H) 14.6, $PCCH_3$]; δ_H (81.0 MHz) 64.7 (s, P*t*Bu$_2$), −144.0 [sept, *J*(F,P) 712.0, PF_6^-].

[($C_6H_5CH_2CH_2PtBu_2$-κ-*P*)$_2$RuHCl(=C=CH$_2$)] 24. A slow stream of acetylene was passed for 10 s through a cooled solution (−78 °C) of **15** (54 mg, 0.08 mmol) in CH_2Cl_2 (5 cm^3). A change of colour from orange to red–brown occurred. The solvent was evaporated *in vacuo*, the orange–brown residue was washed twice with 2 cm^3 portions of pentane (0 °C), and dried *in vacuo*; yield 53 mg (95%); mp 58 °C (decomp.) (Found: C, 61.40; H, 8.71. $C_{34}H_{57}ClP_2Ru$ requires: C, 61.48; H. 8.65%). IR (KBr): *ν*(RuH) 2106, *ν*(C=C) 1601 cm^{-1}. NMR (CD_2Cl_2): δ_H (300 MHz) 7.16 (10 H, m, C_6H_5), 3.18, 2.95 (2 H each, both m, PC*H*$_2$C*H*$_2$Ph), 2.63 [2 H, t, *J*(P,H) 3.5, =CH_2], 2.50, 2.13 (2 H each, both m, PC*H*$_2$C*H*$_2$Ph), 1.42, 1.39 (18 H each, both vt, *N* 12.3, $PCCH_3$), −15.80 [1 H, t, *J*(P,H) 18.0, RuH]; δ_C (75.5 MHz) 326.5 [t, *J*(P,C) 15.1, Ru=C], 142.7 (vt, *N* 13.0, *ipso*-C of C_6H_5), 127.7, 127.4, 125.2 (all s, C_6H_5), 87.9 [t, *J*(P,C) 3.4, =CH_2], 36.9 (vt, *N* 13.5, P*C*CH$_3$), 35.7 (vt, *N* 14.0, P*C*CH$_3$), 32.9 (s, *C*H$_2$Ph), 30.3 (vt, *N* 4.7, PC*C*H$_3$), 29.6 (vt, *N* 4.2, PC*C*H$_3$), 22.4 (vt, *N* 17.7, PCH_2); δ_P (81.0 MHz) 53.7 (s).

[($C_6H_5OCH_2CH_2PtBu_2$-κ-*P*)$_2$RuHCl(=C=CH$_2$)] 25. This compound was prepared as described for **24**, from **16** (109 mg, 0.16 mmol) and acetylene in CH_2Cl_2 (8 cm^3) at −78 °C. Light brown solid: yield 98 mg (88%); mp 58 °C (decomp.) (Found: C, 58.61; H, 8.07. $C_{34}H_{57}ClO_2P_2Ru$ requires: C, 58.65; H, 8.25%). IR (KBr): *ν*(RuH) 2085, *ν*(C=C) 1600 cm^{-1}. NMR (CD_2Cl_2): δ_H (300 MHz) 7.21–6.76 (10 H, m, C_6H_5), 4.31 (4 H, m, C*H*$_2$OPh), 2.64 [2 H, t, *J*(P,H) 3.7, =CH_2], 2.58, 2.31 (2 H each, both m, PCH_2), 1.35, 1.31 (18 H each, both vt, *N* 12.8, $PCCH_3$), −14.85 [1 H, t, *J*(P,H) 18.5, RuH]; δ_C (75.5 MHz) 328.1 [t, *J*(P,C) 15.1, Ru=C], 159.6 (s, *ipso*-C of C_6H_5), 130.2, 121.4, 115.3 (all s, C_6H_5), 90.0 [t, *J*(P,C) 3.9, =CH_2], 67.7 (vt, *N* 8.3, *C*H$_2$OPh], 38.6 (vt, *N* 14.8, P*C*CH$_3$), 37.2 (vt, *N* 15.2,

Table 3 Crystallographic data for **10** and **17**

Formula	$C_{18}H_{30}ClF_6NP_2Ru$ (**10**)	$C_{33}H_{55}ClO_3P_2Ru$ (**17**)
M	572.90	698.26
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	11.204(2)	11.676(2)
b/Å	12.920(3)	12.255(3)
c/Å	15.626(3)	13.537(3)
α/°	90.0	79.57(3)
β/°	90.24(3)	68.26(3)
γ/°	90.0	82.44(3)
V/Å^3	2261.9(8)	1765.1(6)
T/K	173(2)	173(2)
Z	4	2
D_c/g cm^{-3}	1.682	1.314
λ(Mo-Kα)/Å	0.71073	0.71073
μ/mm^{-1}	1.007	0.640
No. of reflections measured	23880	16057
No. of unique reflections	4006	5845
$R1$ [a]	0.0353	0.0509
$wR2$ [b]	0.0968	0.1464
Residual electron density/e Å^{-3}	0.030/−0.029	1.924/−0.567

[a] $R = \Sigma|F_o - F_c|/\Sigma F_o$ [for $I > 2\sigma(I)$] for the number of observed reflections, respectively. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (0.0507P)^2 + 0.0128P]$ (**10**), $[\sigma^2(F_o^2) + (0.1062P)^2 + 0.0000P]$ (**17**), where $P = [F_o^2 + 2F_c^2]/3$; for all data reflections, respectively.

PC*C*H$_3$), 31.5 (vt, *N* 4.6, PC*C*H$_3$), 30.8 (vt, *N* 4.2, PC*C*H$_3$), 21.8 (vt, *N* 19.0, PCH$_2$); δ_P (81.0 MHz) 50.5 (s).

***In situ* generation of [(C$_6$H$_5$CH$_2$CH$_2$P*t*Bu$_2$-κ-*P*)$_2$RuHCl(≡CCH$_3$)(OEt$_2$)]BF$_4$ 26.** A solution of **24** (40 mg, 0.06 mmol) in CD_2Cl_2 (0.5 cm^3) was treated at −78 °C with a slight excess of a 1.6 M solution of HBF_4 in ether (50 µl, 0.08 mmol). After the solution was warmed to *ca.* 0 °C, the ^{1}H and ^{31}P NMR spectra were measured. NMR (CD_2Cl_2): δ_H (200 MHz) 7.29–6.80 (10 H, m, C_6H_5), 3.06 (4 H, m, C*H*$_2$Ph), 2.64 (3 H, s, Ru≡CCH$_3$), 2.45 (4 H, m, PCH$_2$), 1.46 (36 H, m, PCCH$_3$), −7.63 [1 H, t, *J*(P,H) 15.6, RuH]; δ_P (81.0 MHz) 68.3 (s).

General procedure for studying the catalytic activity for ROMP of the vinylidene and carbene ruthenium complexes

An NMR tube was filled stepwise with cyclooctene (81.4 µl, 625 µmol) and a 1.6 M solution of HBF_4 in diethyl ether (2.5 µl, 4 µmol). To this mixture, a solution of compound **24** or **25** (0.5 µmol) or of the Grubbs carbene [RuCl$_2$(=CHPh)(PCy$_3$)$_2$] (0.5 µmol) in CD_2Cl_2 (0.5 cm^3) was added. The solution was shaken for 10–20 s, and then the increase in concentration of the polymer was followed by ^{1}H NMR spectroscopy. For **24** as the catalyst, the amount of *trans*-olefinic bonds in the polymer was 69%, and for **25** as the catalyst 50%.

Crystallography

Single crystals of **10** were grown from dichloromethane at room temperature, those of **17** from dichloromethane–pentane at −78°C. Crystal data collection parameters are summarized in Table 3. Intensity data were corrected for Lorentz and polarisation effects for **10** and **17**. Data reduction was performed with Stoe IPDS software. An absorption correction could not be applied, and therefore large residual electron densities result. The structures were solved by direct methods (SHELXS-97).[26] For **10** the counterion PF_6 was found disordered (F3–F6) and refined anisotropically without restraints (occupancy factors 69/31); moreover, twin refinement was necessary [BASF = 0.141(1)]. For **17** the hydrido ligand could not be located. Atomic coordinates and anisotropic thermal displacement parameters of the non-hydrogen atoms were refined anisotropically by full-matrix least squares on F^2 (SHELXL-97).[26]

CCDC reference numbers 175267 and 175268.

See http://www.rsc.org/suppdata/dt/b1/b106243n/ for crystallographic data in CIF or other electronic format.

Acknowledgements

We thank the Deutsche Forschungsgemeinschaft (SFB 347) and the Fonds der Chemischen Industrie for financial support, the latter in particular for a Ph. D. grant (to K. I.). We are also grateful to Mrs R. Schedl and Mr C. P. Kneis (DTA measurements and elemental analyses), to Mrs M.-L. Schäfer and Dr W. Buchner (NMR spectra), and to Dr G. Lange and Mr F. Dadrich (mass spectra). The experimental assistance of Mr S. Stellwag is also gratefully acknowledged.

References

1 R. H. Grubbs, S. J. Miller and G. C. Fu, *Acc. Chem. Res.*, 1995, **28**, 446; T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2001, **34**, 18; R. H. Grubbs and S. Chang, *Tetrahedron*, 1998, **54**, 4413; S. K. Armstrong, *J. Chem. Soc., Perkin Trans. 1*, 1998, 371; A. Fürstner, *Top. Organomet. Chem.*, 1998, **1**, 37; A. Fürstner, *Top. Catal.*, 1997, **4**, 285; M. Schuster and S. Blechert, *Angew. Chem.*, 1997, **109**, 2124; M. Schuster and S. Blechert, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2036; K. J. Ivin and J. C. Mol, *Olefin Metatheses and Metatheses Polymerization*, Academic Press, New York, 1997.

2 Representative articles: E. L. Dias and R. H. Grubbs, *Organometallics*, 1998, **17**, 2758; S. Chang, L. Jones, C. Wang, L. M. Henling and R. H. Grubbs, *Organometallics*, 1998, **17**, 3460; M. S. Sanford, L. M. Henling and R. H. Grubbs, *Organometallics*, 1998, **17**, 5384; S. M. Hansen, M. A. O. Volland, F. Rominger, F. Eisenträger and P. Hofmann, *Angew. Chem.*, 1999, **111**, 1360; S. M. Hansen, M. A. O. Volland, F. Rominger, F. Eisenträger and P. Hofmann, *Angew. Chem., Int. Ed.*, 1999, **38**, 1273; S. M. Hansen, F. Rominger, M. Metz and P. Hofmann, *Chem. Eur. J.*, 1999, **5**, 557; T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich and W. A. Herrmann, *Angew. Chem.*, 1999, **111**, 2573; T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich and W. A. Herrmann, *Angew. Chem., Int. Ed.*, 1999, **38**, 2416; T. Weskamp, F. J. Kohl and W. A. Herrmann, *J. Organomet. Chem.*, 1999, **582**, 362; L. Ackermann, A. Fürstner, T. Weskamp, F. J. Kohl and W. A. Herrmann, *Tetrahedron Lett.*, 1999, **40**, 4787; J. S. Kingsbury, J. P. A. Harrity, P. J. Bonitatebus Jr. and A. H. Hoveyda, *J. Am. Chem. Soc.*, 1999, **121**, 791; J. Huang, E. D. Stevens, S. P. Nolan and J. L. Petersen, *J. Am. Chem. Soc.*, 1999, **121**, 2674; J. Huang, H.-J. Schanz, E. D. Stevens and S. P. Nolan, *Organometallics*, 1999, **18**, 5375; M. Scholl, S. Ding, C. W. Lee and R. H. Grubbs, *Org. Lett.*, 1999, **1**, 953; M. S. Sanford, L. M. Henling, M. W. Day and R. H. Grubbs, *Angew. Chem.*, 2000, **112**, 3593; M. S. Sanford, L. M. Henling, M. W. Day and R. H. Grubbs, *Angew. Chem., Int. Ed.*, 2000, **39**, 3451; D. M. Lynn, B. Mohr, R. H. Grubbs, L. M. Henling and M. W. Day, *J. Am. Chem. Soc.*, 2000, **122**, 6601; H. Katayama, H. Urushima and F. Ozawa, *J. Organomet. Chem.*, 2000, **606**, 16; L. Jafarpour and S. P. Nolan, *J. Organomet. Chem.*, 2001, **617–618**, 17.

3 A. Fürstner, M. Picquet, C. Bruneau and P. H. Dixneuf, *Chem. Commun.*, 1998, 1315.
4 A. Fürstner, M. Liebl, C. W. Lehmann, M. Picquet, R. Kunz, C. Bruneau, D. Touchard and P. H. Dixneuf, *Chem. Eur. J.*, 2000, **6**, 1847.
5 H. Werner, G. Canepa, K. Ilg and J. Wolf, *Organometallics*, 2000, **19**, 4756; G. Canepa, C. D. Brandt and H. Werner, *Organometallics*, 2001, **20**, 604.
6 H. Werner, *International Symposium Interactions of π-Systems with Metals*, Heidelberg, Germany, 26–28th April 2001, Abstract p. 12; S. Jung, J. Wolf and H. Werner, *8th E. O. Fischer-Meeting*, Blankensee, Germany, 24–26th May 2001, Abstract p. 7.
7 M. Christ, S. Sabo-Etienne and B. Chaudret, *Organometallics*, 1994, **13**, 3800; T. Burrow, S. Sabo-Etienne and B. Chaudret, *Inorg. Chem.*, 1995, **34**, 2470.
8 T. E. Wilhelm, T. R. Belderrain, S. N. Brown and R. H. Grubbs, *Organometallics*, 1997, **16**, 3867; J. Wolf, W. Stüer, C. Grünwald, H. Werner, P. Schwab and M. Schulz, *Angew. Chem.*, 1998, **110**, 1165; J. Wolf, W. Stüer, C. Grünwald, H. Werner, P. Schwab and M. Schulz, *Angew. Chem., Int. Ed.*, 1998, **37**, 1124.
9 W. Stüer, J. Wolf and H. Werner, unpublished work; see: W. Stüer, Ph. D. Thesis, Universität Würzburg, 1999.
10 P. D. Smith and A. H. Wright, *J. Organomet. Chem.*, 1998, **559**, 141.
11 R. A. Zelonka and M. C. Baird, *Can. J. Chem.*, 1972, **50**, 3063; P. Petrici, S. Bertozzi, R. Lazzaroni, G. Vitulli and M. A. Bennett, *J. Organomet. Chem.*, 1988, **354**, 117; S. A. Serron and S. P. Nolan, *Organometallics*, 1995, **14**, 4611.
12 B. Therrien, T. R. Ward, M. Pilkington, C. Hoffmann, F. Gilardoni and J. Weber, *Organometallics*, 1998, **17**, 330.
13 H. Kletzin and H. Werner, *Angew. Chem.*, 1983, **95**, 916; H. Kletzin and H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 873; H. Werner, H. Kletzin and K. Roder, *J. Organomet. Chem.*, 1988, **355**, 401.
14 For comparison, see: R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 1964, 4587.
15 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
16 L. Porri, M. C. Gallazzi, A. Colombo and G. Allegra, *Tetrahedron Lett.*, 1965, **47**, 4187; D. N. Cox and R. Roulet, *Inorg. Chem.*, 1990, **29**, 1360.
17 M. A. Esteruelas and H. Werner, *J. Organomet. Chem.*, 1986, **303**, 221.
18 D. Huang, W. E. Streib, J. C. Bollinger, K. G. Caulton, R. F. Winter and T. Scheiring, *J. Am. Chem. Soc.*, 1999, **121**, 8087.
19 H. Werner, M. A. Esteruelas and H. Otto, *Organometallics*, 1986, **5**, 2295.
20 Reviews: M. I. Bruce, *Chem. Rev.*, 1991, **91**, 197; M. I. Bruce, *Chem. Rev.*, 1998, **98**, 2797; V. Cadierno, M. P. Gamasa and J. Gimeno, *Eur. J. Inorg. Chem.*, 2001, 571.
21 D. Pilette, K. Ouzzine, H. Le Bozec, P. H. Dixneuf, C. E. F. Rickard and W. R. Roper, *Organometallics*, 1992, **11**, 809; D. Touchard, N. Pirio and P. H. Dixneuf, *Organometallics*, 1995, **14**, 4920.
22 J. Wolf, W. Stüer, C. Grünwald, O. Gevert, M. Laubender and H. Werner, *Eur. J. Inorg. Chem.*, 1827; W. Stüer, J. Wolf, H. Werner, P. Schwab and M. Schulz, *Angew. Chem.*, 1998, **110**, 3603; W. Stüer, J. Wolf, H. Werner, P. Schwab and M. Schulz, *Angew. Chem., Int. Ed.*, 1998, **37**, 3421.
23 M. Olivan, O. Eisenstein and K. G. Caulton, *Organometallics*, 1997, **16**, 2227.
24 E. L. Dias, S. T. Nguyen and R. H. Grubbs, *J. Am. Chem. Soc.*, 1997, **119**, 3887; M. Ulman and R. H. Grubbs, *Organometallics*, 1998, **17**, 2484; O. M. Aaagaard, R. J. Meier and F. Buda, *J. Am. Chem. Soc.*, 1998, **120**, 7174.
25 M. A. Bennett, T.-N. Huang, T. W. Matheson and A. K. Smith, *Inorg. Synth.*, 1982, **21**, 74.
26 G. M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1997; G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.