FULL PAPER

Dalton
www.rsc.org/dalton

Preparation of hydrido(vinylidene)ruthenium(II) complexes and a one-pot synthesis of Grubbs-type ruthenium carbenes†

Wolfram Stüer, Birgit Weberndörfer, Justin Wolf and Helmut Werner*

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

Received 17th February 2005, Accepted 24th March 2005
First published as an Advance Article on the web 13th April 2005

Treatment of the hydrido(dihydrogen) compound $[RuHCl(H_2)(PCy_3)_2]$ **1** with alkynes RC≡CH (R = H, Ph) afforded the hydrido(vinylidene) complexes $[RuHCl(=C=CHR)(PCy_3)_2]$ **2**, **3** which react with HCl or $[HPCy_3]Cl$ to give the corresponding Grubbs-type ruthenium carbenes $[RuCl_2(=CHCH_2R)(PCy_3)_2]$ **4**, **5**. The reaction of **2** (R = H) with DCl, or D_2O in the presence of chloride sources, led to the formation of $[RuCl_2(=CHCH_2D)(PCy_3)_2]$ **4**-d_1. Based on these observations, a one-pot synthesis of compounds **4** and **5** was developed using $RuCl_3 \cdot 3H_2O$ as the starting material. The hydrido(vinylidene) derivative **2** reacted with CF_3CO_2H and HCN at low temperatures to yield the carbene complexes $[RuCl(X)(=CHCH_3)(PCy_3)_2]$ **6**, **7**, of which **7** (X = CN) was characterized crystallographically. Salt metathesis of **2** with CF_3CO_2K and KI led to the formation of $[RuH(X)(=C=CH_2)(PCy_3)_2]$ **8**, **9**. The bis(trifluoracetato) and the diiodo compounds $[RuX_2(=CHCH_3)(PCy_3)_2]$ **10**, **11** as well as the new phosphine $P(thp)_3$ **12** (thp = 4-tetrahydropyranyl) and the corresponding complex $[RuCl_2(=CHCH_3)\{P(thp)_3\}_2]$ **14** were also prepared. The catalytic activity of the ruthenium carbenes **4**–**7**, **10**, **11** and **14** in the olefin cross-metathesis of cyclopentene and allyl alcohol was investigated.

Introduction

In the context of our investigations on the chemistry of ruthenium complexes containing $Ru(PiPr_3)_2$ as the building block, we recently reported the preparation and molecular structure of the six-coordinate ruthenium(IV) compound $[RuH_2Cl_2(PiPr_3)_2]$ which was formed from $[RuCl_2(C_8H_{12})]_n$ and $PiPr_3$ in 2-butanol under a hydrogen atmosphere *via* the hydrido(dihydrogen) complex $[RuHCl(H_2)(PiPr_3)_2]$ as an intermediate.[1,2] The reaction of $[RuH_2Cl_2(PiPr_3)_2]$ with a two-fold excess of phenylacetylene gave the expected vinylidene compound $[RuCl_2(=C=CHPh)(PiPr_3)_2]$ but, quite surprisingly, under the chosen conditions small amounts of the ruthenium carbene $[RuCl_2(=CHCH_2Ph)(PiPr_3)_2]$ were equally obtained. Since this complex can be considered as a near relative of the Grubbs-type catalyst $[RuCl_2(=CHPh)(PCy_3)_2]$,[3,4] we were prompted to find out whether ruthenium carbenes of the general composition $[RuCl_2(=CHR)(PCy_3)_2]$ would be accessible from $[RuCl_2(C_8H_{12})]_n$ or, even more simply, from $RuCl_3 \cdot 3H_2O$ as the starting material.

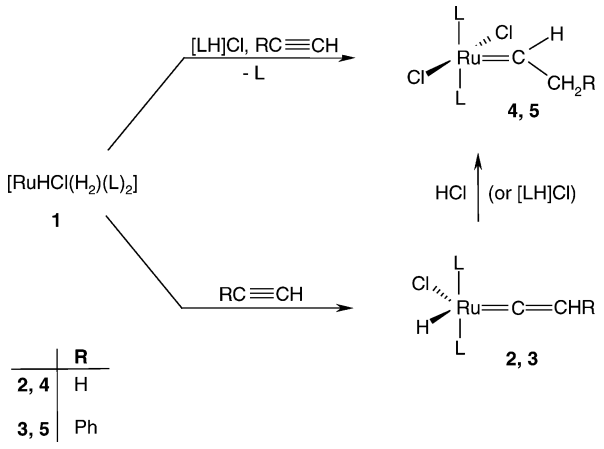
The present paper reports two versions of a one-pot synthesis of the carbene complexes $[RuCl_2(=CHR)(PCy_3)_2]$ (R = CH_3, CH_2Ph) from $RuCl_3 \cdot 3H_2O$ as the precursor, the preparation of the hydrido(vinylidene) ruthenium(II) compounds $[RuHCl(=C=CHR')(PCy_3)_2]$ (R′ = H, Ph) which are intermediates in the generation of the respective carbenes, and the conversion of both the carbenes $[RuCl_2(=CHR)(PCy_3)_2]$ and the vinylidene $[RuHCl(=C=CH_2)(PCy_3)_2]$ into derivatives having iodide or trifluoroacetate instead of chloride as ligands. The preparation of the new phosphine $P(thp)_3$ (thp = 4-tetrahydropyranyl) and its ruthenium complex $[RuCl_2(=CHCH_3)\{P(thp)_3\}_2]$ as well as the catalytic activity of various ruthenium carbenes in the olefin cross-metathesis of cyclopentene and allyl alcohol is also described. Some preliminary results of this work have already been communicated.[5]

† Dedicated to Professor Henri Brunner on the occasion of his 70th birthday, in honour of his pioneering work in metal-chirality and catalysis.

Results and discussion

Preparation and reactivity of five-coordinate hydrido(vinylidene) ruthenium complexes

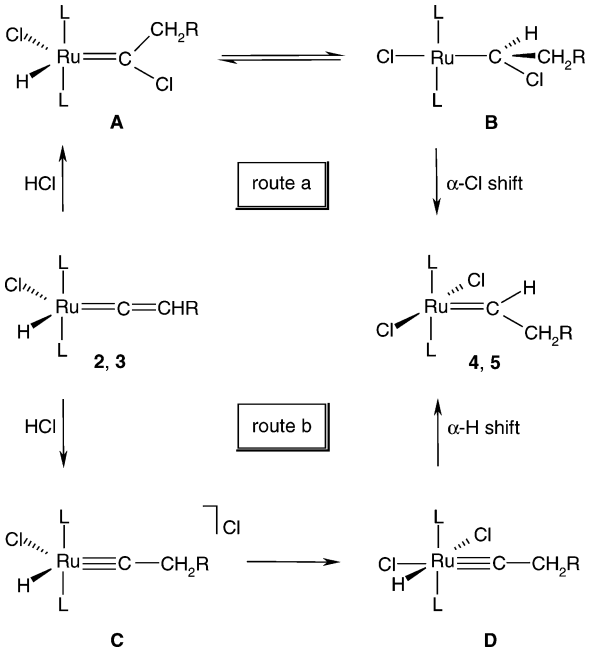
By attempting to develope a synthetic route to ruthenium carbenes $[RuCl_2(=CHR)(PCy_3)_2]$ without using $[RuCl_2(PPh_3)_3]$ as the precursor, both we and the Grubbs group found that the probably polymeric cyclooctadiene derivative $[RuCl_2(C_8H_{12})]_n$ reacts in a suspension of 2-butanol with PCy_3 under a hydrogen atmosphere to give nearly quantitatively the hydrido(dihydrogen) complex $[RuHCl(H_2)(PCy_3)_2]$ **1**.[2,6] Treatment of this compound, which was first prepared by Chaudret and co-workers from $[Ru(\eta^4\text{-}C_8H_{12})(\eta^6\text{-}C_8H_{10})]$,[7] with acetylene in CH_2Cl_2 at low temperatures affords the hydrido(vinylidene) complex **2** in 94% yield (Scheme 1). The reaction has to be stopped after *ca.* 10 seconds, since compound **2** reacts quickly with an excess of C_2H_2 to form some oily ill-defined by-products. Phenylacetylene behaves similarly as C_2H_2 and with **1** gives the phenylvinylidene complex **3**.



Scheme 1 (L = PCy_3).

The hydrido(vinylidene) compounds **2** and **3** are air-sensitive solids, which are quite labile and, even if they are stored at

DOI: 10.1039/b502440d



Scheme 2 (L = PCy_3; R = H, Ph).

−20 °C under argon, decompose in 4–6 days. Thus, they are significantly less stable than the triisopropylphosphine counterparts [RuHCl(=C=CHR)(P*i*Pr$_3$)$_2$].[2] The ^{13}C NMR spectra of **2** and **3** display in the low-field region the typical signals for the α- and β-carbon atoms of the vinylidene ligand at δ 326.2 and 86.6 (for **2**) and δ 329.1 and 109.1 (for **3**), which are all split into triplets due to P–C coupling. In the ^{1}H NMR spectra the hydride resonance also appears as a triplet at δ −16.17 (for **2**) and δ −12.88 (for **3**). The chemical shifts are rather similar to those of the related complexes [RuHCl(=C=CHR)(P*i*Pr$_3$)$_2$] (R = H, Ph) and [RuHCl(=C=CHR)(P*t*Bu$_2$Me)$_2$] (R = $SiMe_3$, Ph), the latter of which were recently prepared by Caulton and co-workers and, according to ab initio DFT calculations, should possess a distorted trigonal-bipyramidal coordination sphere with the phosphine ligands in the apical positions.[8]

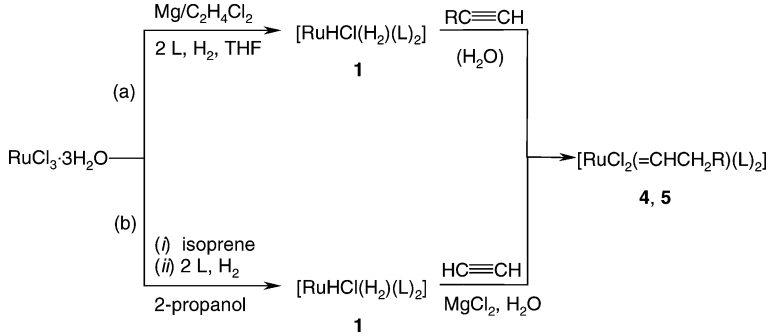
If the hydrido(vinylidene) compounds **2** and **3** are dissolved in acetone or CH_2Cl_2 and then treated with an aqueous solution of HCl, a quick change of colour from brown or green to violet occurs and the Grubbs-type carbene complexes **4** and **5** are formed in virtually quantitative yield. Instead of HCl the phosphonium salt [HPCy$_3$]Cl, in dichloromethane as solvent, can also be used. Moreover, **4** and **5** can be directly obtained by treatment of **1** with acetylene or phenylacetylene in the presence of one equivalent of [HPCy$_3$]Cl (see Scheme 1). While compound **4** was known, being first prepared by Grubbs and co-workers from [RuCl$_2$(=CHPh)(PCy$_3$)$_2$] and propene,[3] the benzylcarbene complex **5** has not been described as yet. Typical spectroscopic features of **5** are the ^{1}H NMR resonance for the Ru=CH proton at δ 19.40 and the ^{13}C NMR signal for the carbene carbon atom at δ 316.5, both appearing as triplets. The ^{31}P NMR spectrum of **5** displays a single resonance at δ 34.6, thus indicating that the phosphine ligands are *trans* disposed.

To explain the mechanism of the reaction of **2** or **3** with HCl, we assume that in the initial step HCl attacks the C=C double bond of the vinylidene ligand to generate intermediate **A** (see Scheme 2, route a) which is converted to the 14-electron species **B** by insertion of the carbene ligand into the Ru–H bond. From **B** the target complex **4** or **5** could be generated by an α-Cl shift from carbon to the metal. Although the formation of α-chloroalkyl ruthenium(II) compounds (corresponding to **B**) as short-lived intermediates has also been proposed by Grubbs and co-workers in the preparation of the carbene complexes [RuCl$_2$(=CHCH$_2$R)(PCy$_3$)$_2$] (R = H, Me) from **1** and vinyl chlorides RCH=CHCl,[6] an alternative mechanism for the conversion of **2**, **3** to **4**, **5** should not be excluded. By taking some recent observations from our laboratory into account,[9] it is also conceivable that HCl reacts initially with the hydrido(vinylidene) compounds to give the cationic ruthenium carbyne [RuHCl(≡CCH$_2$R)(PCy$_3$)$_2$]Cl **C** (see Scheme 2, route b). After addition of the chloride ion to the metal centre of **C**, the hexa-coordinate intermediate **D** would be formed which in the final step could generate the five-coordinate ruthenium carbene *via* an α-H shift. The result that the monodeuterated derivative [RuCl$_2$(=CHCH$_2$D)(PCy$_3$)$_2$] **4**-d$_1$ (characterized by ^{1}H and ^{2}D NMR spectroscopy) is obtained exclusively from **2** and DCl in benzene/D_2O seems to be in agreement with either mechanistic scheme.

One-pot synthesis of the Grubbs-type ruthenium carbenes

After we found that the relatively weak acid [HPCy$_3$]Cl is sufficient as a source of HCl for the conversion of **2** and **3** to the carbene complexes **4** and **5**, we also attempted to find out whether the first step of the reaction is a nucleophilic attack of the chloride at the α-C atom of the vinylidene ligand or at the metal centre. We therefore investigated the reactions of compound **2** with [Ph$_3$PNPPh$_3$]Cl ([PNP]Cl) and $MgCl_2$ in THF. Whereas in the first case no reaction occurred, with $MgCl_2$ small amounts of **4** were formed. The assumption, that the residual content of water in the $MgCl_2$ or in the solvent is responsible for this process, was confirmed by addition of extra water to the reaction mixture of **2** and $MgCl_2$, which led to complete conversion of **2** to the carbene complex **4** within seconds. In contrast, the reaction of **2** with [PNP]Cl and H_2O is significantly slower and only completed after about 5 h. The active role of $MgCl_2$ in the formation of **4** is also supported by the fact that in the presence of $MgCl_2$, but not of [PNP]Cl, acetylene can serve as a proton source instead of water.

By taking these results into consideration, we concluded that **1**, acetylene, $MgCl_2$ and H_2O should give the carbene complex **4** *via* the intermediate formation of **2**. This conclusion led us to develop the first one-pot synthesis of **4** (method (a), Scheme 3).[5] Commercially available $RuCl_3 \cdot 3H_2O$ in THF was reduced in the presence of PCy_3 with Mg/1,2-$C_2H_4Cl_2$ under a hydrogen



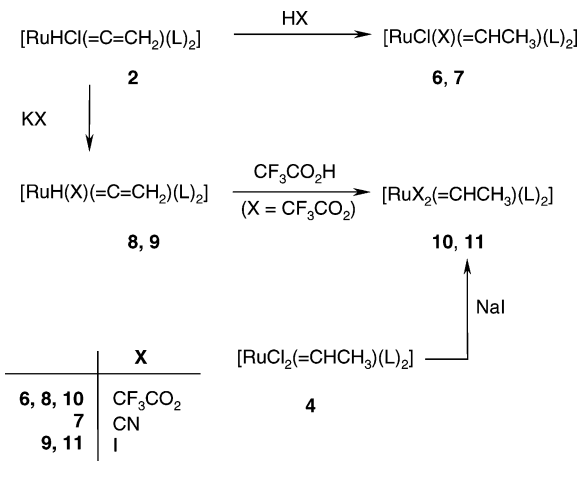
Scheme 3 (L = PCy_3; R = H, Ph).

atmosphere at 60–85 °C to compound **1**. The activation of magnesium with 1,2-dichloroethane serves not only to accelerate the reduction, but also to increase the concentration of $MgCl_2$. After the reaction mixture was cooled to −40 °C, acetylene (about two equivalents) was introduced along with a small excess of water. While warming the solution to room temperature, the carbene complex **4** is formed and, after removal of the solvent *in vacuo* and extraction of the residue with pentane, isolated in about 75% yield. In a similar manner, by using phenylacetylene as the source for the carbene ligand, compound **5** was obtained. In this case we observed that under the reaction conditions the intermediate **1** reacts with phenylacetylene by substitution of H_2. Therefore, in contrast to the formation of **4**, only one equivalent of the alkyne is needed for the preparation of **5**. Both **4** and **5** show nearly the same activity as the standard Grubbs catalyst $[RuCl_2(=CHPh)(PCy_3)_2]$ in olefin metathesis (ROMP and RCM) and in the meantime have been prepared in an industrial research laboratory in 100 g quantities.[10]

More recently, the preparative route to give **4** and **5** was even more simplified. Instead of using Mg/1,2-$C_2H_4Cl_2$ and THF as solvent, we used isoprene and 2-propanol as reagents to convert $RuCl_3 \cdot 3H_2O$ into a more reactive intermediate. This intermediate probably is the dinuclear compound $[RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})]_2$, which was first reported by Porri *et al.*[11,12] and was shown, in independent studies by us, that it reacts with PCy_3 in 2-propanol under a hydrogen atmosphere to give the hydrido(dihydrogen) complex **1** in nearly quantitative yield.[13] By taking into account that treatment of **1** with acetylene, a proton and a chloride source furnishes the ruthenium carbene **4**, we prepared this compound along method (b) in Scheme 3. The main and important advantage is that instead of a *ca.* 4-fold excess of PCy_3 (as used for method a) only two equivalents of the phosphine are needed to achieve an 80% yield of the carbene complex **4**. The ^{1}H NMR spectrum of the crude reaction product indicated that besides **4** small amounts (*ca.* 3–5%) of the vinyl ruthenium derivative $[RuCl(CH{=}CH_2)(CO)(PCy_3)_2]$[14] were also formed but could be separated by washing the product several times with methanol.

Ligand displacement reactions of five-coordinate carbene and vinylidene ruthenium(II) complexes

In order to possibly find an even better application profile for the ruthenium(II) carbenes in olefin metathesis, we also exchanged one or both of the chloride ligands in compound **4** for other anions. Treatment of a solution of the hydrido(vinylidene) complex **2** in dichloromethane with an equimolar amount of CF_3CO_2H at −78 °C led to a quick change of colour from brown to dark red and gave, owing to the NMR data, the mixed chloro(trifluoracetato) derivative **6** as the sole reaction product (Scheme 4). If the solution is warmed to room temperature, compound **6** is partly converted to the dichloro carbene **4** without observing the formation of the bis(trifluoracetato) complex **10**. Thus, for the catalytic studies discussed below, solutions with the *in-situ* generated compound **6** have been used. The reaction of **2** with gaseous HCN in THF at −78 °C gave the chloro(cyano) complex **7**, which was isolated as an orange, moderately air-sensitive solid in 86% yield. The ^{1}H NMR spectra of **6** and **7** display for the Ru=CH proton a low-field resonance at δ 19.85 (for **6**) and δ 18.25 (for **7**) being split into a quartet due to ^3J(H,H) coupling. We note that the only other ruthenium carbene of the general composition $[RuCl(X)(=CHR)(PCy_3)_2]$ is the compound $[RuCl(O_2CCF_3)(=CHCH{=}CPh_2)(PCy_3)_2]$, which was mentioned in a patent without giving details about the stability, spectroscopic data, *etc.*[15] Attempts to obtain the chloro(fluoro) complex $[RuCl(F)(=CHCH_3)(PCy_3)_2]$ from **2** and hydrogen fluoride failed.



Scheme 4 (L = PCy_3).

The result of the X-ray crystal structure analysis of **7** is shown in Fig. 1. The molecular diagram illustrates that the coordination geometry around the metal center corresponds to that of a distorted square pyramid with the carbene ligand in the apical position. The two phosphines and the cyano and the chloro ligand are *trans*-disposed. The P(1)-Ru–P(2) axis is significantly bent (161.0(1)°) with the phosphorus atoms pointing away from the carbene unit. The distance Ru–C(2) of 1.810(6) Å (Table 1) is virtually identical to that in the complex $[RuCl_2(=CHCH_2Ph)(P\textit{i}Pr_3)_2]$ (1.813(5) Å)[1] but slightly shorter than in the Grubbs compound $[RuCl_2(=CH\text{-}\textit{p}\text{-}C_6H_4Cl)(PCy_3)_2]$ (1.839(3) Å).[3] Although the cyano and the chloro ligand are disordered, the Ru–Cl bond length in **7** is significantly longer (*ca.* 0.1 Å) than the bond lengths in $[RuCl_2(=CHCH_2Ph)(P\textit{i}Pr_3)_2]$ and $[RuCl_2(=CH\text{-}\textit{p}\text{-}C_6H_4Cl)(PCy_3)_2]$, probably due to the *trans* influence of the cyanide.

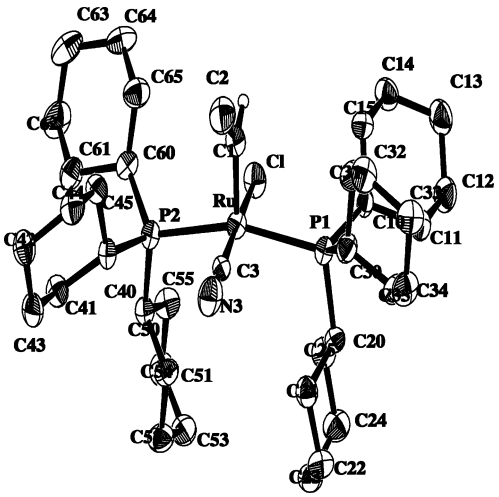


Fig. 1 An ORTEP plot of compound **7**.[32]

The hydrido(vinylidene) complexes **8** and **9** were prepared in good yields by salt metathesis of **2** with CF_3CO_2K and KI, respectively. The iodo derivative **9** is even more labile than the

Table 1 Selected bond lengths (Å) and angles (°) for compound **7**[a]

Ru–C(1)	1.810(6)	Ru–Cl	2.471(3)
Ru–P(1)	2.407(2)	Ru–C(3)	1.92(1)
Ru–P(2)	2.420(2)		
Ru–C(1)–C(2)	132.7(5)	Ru–C(3)–N(3)	175.9(9)
P(1)–Ru–P(2)	161.0(1)	C(1)–Ru–P(1)	98.6(2)
C(1)–Ru–P(2)	100.4(2)	C(1)–Ru–C(3)	92.6(4)
C(1)–Ru–Cl	92.9(2)	C(3)–Ru–Cl	174.4(3)

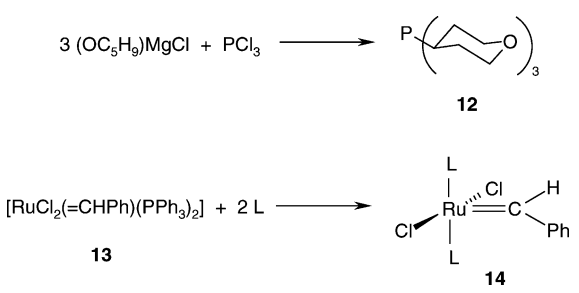
[a] The chloro and the cyano ligands are disordered and lie in two domains with an occupancy factor of 71 : 29. Distances and angles are given only for the molecule in the higher occupied domain.

chloro analogue **2** and thus has been characterized by low-temperature NMR spectroscopy. Diagnostic features for both **8** and **9** are the high-field resonance for the hydride ligand in the ^{1}H NMR spectra at δ −13.16 (for **8**) and δ −10.10 (for **9**) and the low-field signal for the carbene carbon atom in the ^{13}C NMR spectra at δ 332.9 (for **8**) and δ 325.3 (for **9**). The IR spectrum of **8** shows two bands for the asymmetric and symmetric OCO stretching modes at 1604 and 1447 cm^{-1}, which in agreement with reference data[16] suggests a chelating coordination of the trifluoracetate unit.

In analogy to the conversion of **2** to **6**, compound **8** also reacts with CF_3CO_2H to give the bis(trifluoracetato) complex **10** in 94% yield. Owing to the lability of hydrido(iodo) derivative **9**, the diiodide **11** is preferentially prepared from **4** and NaI in THF. Both **10** and **11** are lightly coloured, practically air-stable solids which have been characterized by elemental analysis and spectroscopic techniques. They can be stored under argon at −20 °C for weeks without decomposition. In solutions of benzene or dichloromethane, compound **11** is more labile than the bis(trifluoroacetate) **10**, thus reflecting the same order of stability as observed for **8** and **9**. The CF_3CO_2 ligands in **10** are probably coordinated in a monodentate fashion, as is indicated by the relatively large difference (236 cm^{-1}) in the wave numbers of the asymmetric and symmetric OCO stretching modes.[16] We note that a relative of **10** having the composition $[Ru(CF_3CO_2)_2(=CHCH=CPh_2)(PPh_3)_2]$ was reported by Grubbs and co-workers and prepared from $[RuCl_2(=CHCH=CPh_2)(PPh_3)_2]$ and CF_3CO_2Ag.[17]

A new sterically demanding tertiary phosphine

In the search for analogues of the standard Grubbs-type catalyst $[RuCl_2(=CHPh)(PCy_3)_2]$ containing ligands comparable in size with PCy_3, the related phosphine P(thp)$_3$ **12** (thp = 4-tetrahydropyranyl) has been prepared from PCl_3 and (thp)MgCl (Scheme 5). The synthesis of the Grignard reagent is a little tricky and needs both diethyl ether and THF as solvents. The subsequent reaction of (thp)MgCl with PCl_3 is performed in toluene at −25 °C and, after separation of $MgCl_2$ and recrystallization of the crude product from acetone, the phosphine **12** is obtained analytically pure as a white solid in 53% yield. The ^{1}H NMR spectrum of **12** displays, besides the resonance for the PCH proton, four signals for the CH_2 protons, two of which corresponding to the methylene protons in the axial (H_a) and two to the methylene protons in the equatorial positions (H_e). Since the spectrum does not change upon increasing the temperature to 80 °C, we conclude that in the range between 20 °C and 80 °C no inversion of the tetrahydropyranyl rings occurs. The phosphorus atom of **12** probably occupies an equatorial position at the six-membered rings, similarly as found for $CyPH_2$[18] or $CyPMe_2$[19] and postulated for PCy_3.[20] This proposed stereochemistry is supported by the size of one of the ^3J(H,H) coupling constants for the signal of the PCH proton in the ^{31}P-decoupled ^{1}H NMR spectrum of **12**, which is 12 Hz and thus in agreement with an axial-axial arrangement of the respective protons.[21]



Scheme 5 (L = P(thp)$_3$ **12**).

The ruthenium carbene **14** with two P(thp)$_3$ ligands has been prepared in excellent yield from the well-known starting material **13**, following the standard methodology.[3] Compound **14** is a purple, only slightly air-sensitive solid that dissolves readily in dichloromethane but is nearly insoluble in benzene and other hydrocarbons. The ^{31}P NMR spectrum of **14** (in CD_2Cl_2) shows a single resonance with a chemical shift (δ 30.7), that is almost identical to that of $[RuCl_2(=CHPh)(PCy_3)_2]$ **15** (δ 30.63).[3] In the ^{1}H NMR spectrum of **14**, the Ru=CH proton resonates as a singlet at δ 20.02, whereas the signal for the carbene carbon atom appears in the ^{13}C NMR spectrum as a triplet at δ 299.3. VT NMR measurements in a mixture of C_6D_6 and $CDCl_3$ as the solvent indicate no dynamic behaviour of the P(thp)$_3$ ligands in **14** on the NMR timescale, which supports the data obtained for the free phosphine.

Ruthenium carbenes as catalysts for the cross-olefin metathesis of cyclopentene with allyl alcohol

Recently we reported that treatment of the Grubbs compound **15** with an excess of allyl alcohol generates the expected (hydroxymethyl)carbene derivative $[RuCl_2(=CHCH_2OH)(PCy_3)_2]$ which, however, is unstable in solution and decomposes to give the carbonyl complex $[RuCl_2(CO)(PCy_3)_2]$.[22] This smooth decomposition probably explains why in the catalytic cross-olefin metathesis of cyclopentene with CH_2=$CHCH_2OH$, leading to a mixture of unsaturated alcohols $CH_2(CHCH_2CH_2CH_2CH)_nCHCH_2OH$ with n = 1, 2 and 3 in the ratio of 8 : 4 : 1, a fairly rapid de-activation of catalyst 15 occurs.[23]

Taking into consideration that the before-mentioned alcohols, particularly those with n = 2 (C_{13}) and 3 (C_{18}), are widely used in the fine-chemical industry, we attempted to get some more information how the catalytic activity of the ruthenium carbenes $[RuX_2(=CHR)(PR'_3)_2]$ in the cross-olefin metathesis of cyclopentene with allyl alcohol depends on the anionic ligand X, the substituent R and the type of the phosphine. For this purpose a mixture of cyclopentene (10 cm^3) and allyl alcohol (2.5 cm^3) was treated with a catalytic amount (0.02–0.05 mol%) of the carbene complex and, after it was stirred for 3 h at room temperature, the product mixture was studied by GC/MS (see Table 2). In another experiment, the conversion of the starting materials C_5H_8 and C_3H_5OH to the higher unsaturated alcohols with compound **4** as the catalyst was followed at particular time intervals (see Table 3). The results of these studies can be summarized as follows:

(i) By comparing the carbene complexes **4** and **5** with the standard catalyst **15**, it is quite obvious that the substituent R of the carbene ligand has nearly no influence on the course of the reaction. This is consistent with the proposal,[3] that the starting material reacts in the initial step with an olefin CH_2=CHR'

Table 2 Ratio of unsaturated alcohols $CH_2(CHCH_2CH_2CH_2CH)_n$-$CHCH_2OH$ with n = 1 (C_8), 2 (C_{13}) and 3 (C_{18}) formed in the cross-olefin metathesis of cyclopentene with allyl alcohol and ruthenium carbenes as catalysts[a]

Catalyst	Ratio C_8 : C_{13} : C_{18}
$[RuCl_2(=CHPh)(PCy_3)_2]$ **15**	1.5 : 1 : 0.6
$[RuCl_2(=CHCH_3)(PCy_3)_2]$ **4**	1.4 : 1 : 0.7
$[RuCl_2(=CHCH_2Ph)(PCy_3)_2]$ **5**	1.5 : 1 : 0.7
$[RuCl(O_2CCF_3)(=CHCH_3)(PCy_3)_2]$ **6**	Only traces of metathesis products
$[RuCl(CN)(=CHCH_3)(PCy_3)_2]$ **7**	Only traces of metathesis products
$[Ru(O_2CCF_3)_2(=CHCH_3)(PCy_3)_2]$ **10**	No metathesis products
$[RuI_2(=CHCH_3)(PCy_3)_2]$ **11**	Only traces of metathesis products
$[RuCl_2(=CHPh)\{P(thp)_3\}_2]$ **14**	10 : 1 : 0.2
$[RuCl_2(=CHCH_3)\{P(Coc)_3\}_2]$ **16**	2 : 1 : 0.3

[a] *Conditions*: Starting materials, cyclopentene (10 cm^3) and allyl alcohol (2.5 cm^3); amount of catalyst, 0.02 mol% (for **4**, **5**, **7**, **15**), 0.03 mol% (for **8**, **11**, **14**, **16**) and 0.05 mol% (for **10**); time of reaction 4 h at room temperature.

Table 3 Ratio of unsaturated alcohols $CH_2(CHCH_2CH_2CH_2CH)_nCHCH_2OH$ with $n = 1$ (C_8), 2 (C_{13}), 3 (C_{18}) and 4 (C_{23}) formed in the cross-olefin metathesis of cyclopentene with allyl alcohol and **4** as catalyst, depending on the time of the reaction[a]

Time/min	Conversion of C_5H_8 (%)	Conversion of C_3H_5OH (%)	C_8 (%)	C_{13} (%)	C_{18} (%)	C_{23} (%)
2.5	11.9	26.1	56.7	31.3	11.9	0
5.0	21.9	45.8	55.6	30.6	12.1	1.6
10.0	29.7	66.1	46.0	31.0	17.2	5.8
20.0	47.1	74.0	46.1	31.0	18.7	4.2
45	52.0	76.8	43.9	30.6	18.8	6.7
90	56.9	78.5	42.7	30.3	18.4	8.6
1080	58.3	79.9	40.7	30.4	19.8	9.2
90[b]	91.0	96.0	26.7	27.2	29.6	16.4

[a] *Conditions*: Starting materials, cyclopentene (15 cm^3), allyl alcohol (4 cm^3) and **4** (39.5 mg, 0.05 mmol); room temperature. [b] After 1080 min a second portion of **4** (39.5 mg, 0.05 mmol) was added to the mixture and 90 min later the ratio of products was determined.

to generate the methylene compound $[RuCl_2(=CH_2)(PCy_3)_2]$, which subsequently forms the catalytically active species *via* a dissociative mechanism.[24]

(ii) Regarding the anionic ligands, two chlorides are the best. Even compounds **6** and **7**, in which only one chloro ligand of **4** is displaced by trifluoracetate or cyanide, are much less active than **4**. There is a significant difference between **4** and **11**, the latter containing two iodo instead of two chloro ligands. This observation is in agreement with results from the Grubbs group,[24,25] who found that the catalytic activity of both **15** and $[RuCl_2(=CHPh)(NHC)(PCy_3)]$ (NCH = N-heterocyclic carbene) in olefin metathesis and ROMP of cyclooctadiene decreases if the chlorides are displaced for iodides. The bis(trifluoracetate) **10** is completely inactive in the cross-olefin metathesis of cyclopentene with $CH_2{=}CHCH_2OH$. This is surprising insofar as it was recently reported that replacing chloride for trifluoracetate in a Grubbs–Hoveyda-type ruthenium catalyst allows the living and stereoselective cyclopolymerization of diethyldipropargyl malonate (DEDPM) being not possible with the dichloro analogue.[26]

(iii) The type of the phosphine influences to some extend the ratio of the unsaturated C_8, C_{13} and C_{18} alcohols formed from C_5H_8 and C_3H_5OH. While substitution of PCy_3 for $P(Coc)_3$ (Coc = cyclooctyl) only slightly increases the fraction of C_8 at the expense of C_{18}, the use of $P(thp)_3$ instead of PCy_3 leads predominantly to the formation of the shorter C_8 alcohol. It is conceivable that electronic effects are responsible for the difference in activity between compounds **4** and **14**.[27] However, it is important to note that the overall activity of **14** and $[RuCl_2(=CHMe)\{P(Coc)_3\}_2]$ **16**, for example in ROMP of *cis*-cyclooctene and dicyclopentadiene, is significantly less than that of the PCy_3 counterpart **15**.[28]

(iv) The relative amount of the C_8, C_{13}, C_{18} and C_{23} alcohols, formed from cyclopentene and allyl alcohol with compound **4** as the catalyst, depends on the time of the reaction. Whereas after 2.5 min 56.7% of the mixture of products consists of C_8 and only 11.9% of C_{18}, after 90 min the mixture contains 42.7% of C_8 and 18.4% of C_{18} plus 8.6% of C_{23}. The relative amount of C_{13} remains nearly constant. After *ca.* 20 min, the rate of the reaction decreases considerably, which is probably due to the de-activation of the catalyst by allyl alcohol. At the same time, a change of colour from violet to yellow can be observed. Subsequent addition of 0.05 mol% of **4** re-activates the olefinic substrates and finally leads to a nearly quantitative consumption of cyclopentene and allyl alcohol. Since for the reaction a molar ratio of $C_5H_8 : C_3H_5OH = 2.9 : 1$ was used and part of the allyl alcohol reacted with the catalyst, it is understandable that with increasing time the relative amount of the C_{18} and C_{23} alcohols increases.

Conclusion

The results presented in this paper have shown that Grubbs-type ruthenium carbenes can be prepared directly from $RuCl_3{\cdot}3H_2O$ as the starting material. The two versions of the one-pot synthesis not only avoid rather expensive starting materials such as $[RuCl_2(PPh_3)_3]$[3] or $[RuH_2(H_2)_2(PCy_3)_2]$[29] but also uses 1-alkynes instead of diazoalkanes, vinyl chlorides or propargylic chlorides as carbene sources. A crucial intermediate in the formation of the ruthenium carbenes **4** and **5** from $RuCl_3{\cdot}3H_2O$ is the hydrido(dihydrogen) compound **1**, which reacts with alkynes RC≡CH to give the hydrido(vinylidene) complexes **2** and **3** by displacement of the dihydrogen ligand. The conversion of **2** and **3** to the five-coordinate carbene ruthenium derivatives **4** and **5** by treatment with aqueous HCl proceeds under mild conditions and affords the products in nearly quantitative yields. While the carbene complexes **4** and **5** display high catalytic activity in ROMP of cycloolefins, comparable to that of the Grubbs compound **15**, they are (also similarly to **15**) relatively poor catalysts in the olefin cross-metathesis of cyclopentene and allyl alcohol to give higher unsaturated C_8, C_{13} and C_{18} alcohols. Displacing one or two of the chloro ligands in **4** by cyanide, iodide or trifluoracetate decreases the catalytic activity of the respective ruthenium carbenes as does the substitution of the PCy_3 units in **4** by the sterically related tris(4-tetrahydropyranyl)phosphine **12**, first prepared in this work. Thus it remains a challenge to find a catalyst that not only effectively catalyzes the conversion of cycloolefins and C_3H_5OH to the required long-chain unsaturated alcohols but also being stable under the reaction conditions.

Experimental

All experiments were carried out under an atmosphere of argon by Schlenk techniques. The starting materials $[RuHCl(H_2)(PCy_3)_2]$ **1**,[13] $[RuCl_2(=CHPh)(PPh_3)_2]$ **13**,[3] $[RuCl_2(=CHPh)(PCy_3)_2]$ **15**,[3] and $[RuCl_2(=CHMe)\{P(Coc)_3\}_2]$ **16**,[27] were prepared as described in the literature. NMR spectra were recorded, if not otherwise stated, at room temperature on Bruker AC 200 and Bruker AMX 400 instruments, and IR spectra on a Perkin-Elmer 1420 or an IFS 25 FT-IR infrared spectrometer. Melting points were measured by DTA. Abbreviations used: s, singlet; d, doublet; t, triplet; q, quartet; vt, virtual triplet; m, multiplet; br, broadened signal; coupling constants J and N in Hz; $N = {}^2J(PC) + {}^4J(PC)$.

Preparations

$[RuHCl(=C=CH_2)(PCy_3)_2]$ 2. A stream of acetylene was passed for *ca.* 10 s through a solution of **1** (102 mg, 0.15 mmol) in CH_2Cl_2 (5 cm^3) at −78 °C. A change of colour from orange-yellow to brown occurred. The solvent was evaporated in *vacuo*, the remaining brown solid was washed twice with 3 cm^3 portions of pentane (−20 °C), and dried *in vacuo*; yield 99 mg (94%); mp 109 °C (decomp.) (Found: C, 62.76; H, 9.32. $C_{38}H_{69}ClP_2Ru$ requires: C, 63.00; H, 9.60%). IR (KBr): ν(C=C) 2065, ν(RuH) 1905 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 2.70 [2 H, t, J(P,H) 3.0, C=CH_2], 2.61, 2.13, 1.65, 1.20 (66 H, all m, C_6H_{11}), −16.17

[1 H, t, J(P,H) 18.0, RuH]; δ_C (100.6 MHz) 326.2 [t, J(P,C) 15.0, C=CH_2], 86.6 [t, J(P,C) 4.0, C=CH_2], 34.4, 31.0, 30.7, 27.1 (all s, C_6H_{11}), 28.2, 28.0 (both vt, N 10.0, C_6H_{11}); δ_P (162.0 MHz) 41.5 (s).

[RuHCl(=C=CHPh)(PCy_3)$_2$] 3. A solution of **1** (96 mg, 0.14 mmol) in CH_2Cl_2 (10 cm^3) was treated with phenylacetylene (0.028 cm^3, 0.27 mmol) at −78 °C. After the solution was warmed to room temperature, it was concentrated to *ca.* 1 cm^3 *in vacuo*. Addition of pentane (10 cm^3) led to the precipitation of a green solid, which was separated from the mother-liquor, washed three times with 5 cm^3 portions of pentane and dried; yield 80 mg (73%); mp 46 °C (decomp.) (Found: C, 65.77; H, 8.70. $C_{44}H_{73}ClP_2Ru$ requires: C, 66.02; H, 9.19%). IR (KBr): ν(C=C) 2065, ν(RuH) 1900 cm^{-1}. NMR (C_6D_6): δ_H (200 MHz) 7.05 (5 H, br m, C_6H_5), 4.41 (1 H, br s, =CHPh), 2.50–1.10 (66 H, br m, C_6H_{11}), −12.88 [1 H, t, J(P,H) 17.4, RuH]; δ_C (100.6 MHz) 329.1 [t, J(P,C) 12.0, C=CHPh], 133.9, 128.6, 123.7, 123.4 (all s, C_6H_5), 109.1 [t, J(P,C) 4.0, C=CHPh], 35.2 (vt, N 19.0, C1 of C_6H_{11}), 31.0, 30.6 (both s, C_6H_{11}), 28.1, 27.9 (both vt, N 10.0, C_6H_{11}), 26.9 (s, C_6H_{11}); δ_P (162.0 MHz) 41.3 (s).

[$RuCl_2$(=$CHCH_3$)(PCy_3)$_2$] 4. A suspension of **2** (56 mg, 0.08 mmol) in acetone (2 cm^3) was treated with a 2 M solution of HCl in water (0.05 cm^3, 0.10 mmol) at room temperature. The mixture was stirred for *ca.* 1 min and then a light-violet solid began to precipitate. After 10 min the precipitate was filtered, washed twice with 5 cm^3 portions of acetone, and dried *in vacuo*; yield 52 mg (89%). Alternatively, compound **4** can also be prepared in virtually quantitative yield from **2** (30 mg, 0.04 mmol) and an excess of [$HPCy_3$]Cl (*ca.* 50 mg) in 1 cm^3 of dichloromethane. The product was characterized by comparison of the ^{1}H and ^{13}C NMR data with those reported in the literature.[3]

[$RuCl_2$(=$CHCH_2D$)(PCy_3)$_2$] 4-d_1. A solution of **2** (50 mg, 0.07 mmol) in benzene (3 cm^3) was treated with a 37% solution of DCl in D_2O (0.06 cm^3, 0.07 mmol) and stirred for 5 min at room temperature. A change of colour from brown to violet occurred. The solvent was evaporated *in vacuo*, the residue was washed twice with 3 cm^3 portions of acetone, and dried *in vacuo*; yield 50 mg (94%). NMR (C_6H_6): δ_D (61.4 MHz) 2.62 (br s, =CHCH_2D). NMR (C_6D_6): δ_H (200 MHz) 19.67 (1 H, br s, Ru=CH), 2.78 (6 H, m, C_6H_{11}), 2.63, 2.62 (2 H, both m, =CHCH_2D), 2.20–2.01, 1.75–1.67, 1.45–1.35, 1.26–1.23 (60 H, all m, C_6H_{11}); δ_P (162.0 MHz) 35.4 (s).

One-pot synthesis of compound 4.

Method a. Finely divided Mg (10 g, 0.412 mol) in THF (500 cm^3) was activated with 1,2-dichloroethane (10 cm^3) and first PCy_3 (36 g, 0.161 mol) and then $RuCl_3 \cdot 3H_2O$ (10 g, 38.3 mmol) were added. The mixture was warmed under an atmosphere of hydrogen and vigorously stirred for 2 h at 65 °C and subsequently for 2 h at 85 °C. A red solution was formed and an orange solid precipitated. The mixture was cooled to −40 °C, and acetylene (1900 cm^3, *ca.* 79 mmol) was introduced by a gas burette. After the solution was stirred for 5 min at −40 °C, water (2.5 cm^3, 0.139 mol) was added. The reaction mixture was warmed to room temperature and the volatiles were removed *in vacuo*. The residue was transferred to a Soxhlet apparatus and extracted with pentane (800 cm^3) for 20 h. After the solvent was evaporated *in vacuo*, a light-violet solid was isolated, which was washed four times with 20 cm^3 portions of pentane, and dried *in vacuo*; yield 22.1 g (76%).

Method b. A suspension of $RuCl_3 \cdot 3H_2O$ (1.09 g, 3.95 mmol) and Na_2CO_3 (210 mg, 1.98 mmol) in degassed 2-propanol (150 cm^3) was treated with isoprene (4 cm^3, 40.0 mmol) and stirred for 4 h at 85 °C. A stepwise change of colour from red to dark brown and finally to orange-red occurred. After the suspension was cooled to room temperature, most of the solvent (*ca.* 125 cm^3) and the excess of isoprene were removed *in vacuo*. The remaining suspension was treated with NEt_3 (2 cm^3, 14.35 mmol), stirred for 5 min, and then PCy_3 (2.24 g, 8.0 mol) was added. The suspension was stirred for 10 min, the argon atmosphere was replaced by hydrogen, and the mixture was vigorously stirred for 45 min at 70 °C. An orange–yellow suspension was formed, which was cooled to room temperature under the H_2 atmosphere. After $MgCl_2 \cdot 6H_2O$ (1.60 g, 7.87 mmol) was added, a steady stream of acetylene (220 cm^3, *ca.* 4.6 mmol) was passed through the suspension for 90 min. The suspension was stirred for 10 min, the small excess of acetylene was evaporated *in vacuo*, and the mixture was poured into water (200 cm^3). A slightly exothermic reaction was observed. The light-violet precipitate was filtered, washed four times with 50 cm^3 portions of methanol, and dried *in vacuo*; yield 2.4 g (80%); mp 116 °C (decomp.) (Found: C, 59.77; H, 8.90; Ru, 13.63. $C_{38}H_{70}Cl_2P_2Ru$ requires: C, 59.98; H, 9.27; Ru, 13.28%).

One-pot synthesis of [$RuCl_2$(=$CHCH_2Ph$)(PCy_3)$_2$] 5. This compound was prepared as described for **4**, using method a, from $RuCl_3 \cdot 3H_2O$ (0.50 g, 1.91 mmol), Mg (0.50 g, 20.6 mmol), 1,2-$C_2H_4Cl_2$ (0.5 cm^3) and PCy_3 (2.31 g, 8.20 mmol). After the reaction mixture was cooled to −40 °C, phenylacetylene (0.22 cm^3, 1.91 mmol) was added dropwise, which led to a vigorous evolution of gas. The suspension was stirred for 20 min at −40 °C, and after it was warmed to 0 °C, water (0.13 cm^3, 7.20 mmol) was added. The suspension was warmed to room temperature, stirred for 10 min, and then the solvent was evaporated in *vacuo*. The residue was extracted with toluene (60 cm^3), and the extract was brought to dryness *in vacuo*. The remaining purple solid was washed four times with 10 cm^3 portions of pentane, twice with 40 cm^3 portions of methanol and dried; yield 1.24 g (78%); mp 136 °C (decomp.) (Found: C, 63.23; H, 8.72. $C_{44}H_{74}Cl_2P_2Ru$ requires: C, 63.14; H, 8.91%). NMR ($CDCl_3$): δ_H (400 MHz) 19.40 [1 H, t, J(H,H) 5.1, =CHCH$_2$Ph], 7.21 (5 H, m, C_6H_5), 3.98 [2 H, d, J(H,H) 5.1, =CHCH_2Ph], 2.45 (6 H, m, C_6H_{11}), 1.79–1.63, 1.47–1.39, 1.23–1.12 (60 H, all m, C_6H_{11}); δ_C (100.6 MHz) 316.5 [t, J(P,C) 7.4, Ru=C], 138.9, 128.3, 128.2, 126.3 (all s, C_6H_5), 64.5 (s, CH$_2$Ph), 32.0 (vt, N 18.4, C1 of C_6H_{11}), 27.6 (vt, N 10.1, C_6H_{11}), 29.4, 26.3 (both s, C_6H_{11}); δ_P (162.0 MHz) 34.6 (s).

Generation of compound 5 from 3. A solution of **3** (30 mg, 0.04 mmol) in C_6D_6 (1 cm^3) was treated in an NMR tube with a 0.27 M solution of HCl in C_6D_6 (0.22 cm^3, 0.06 mmol). A change of colour from green to violet occurred. The ^{1}H and ^{31}P spectra revealed that a quantitative conversion of **3** to **5** took place. In an analogous experiment, a solution of **3** (30 mg, 0.04 mmol) in CD_2Cl_2 (1 cm^3) was treated with an excess of [$HPCy_3$]Cl (*ca.* 50 mg) and stirred for 15 min. Also under these conditions, a quantitative formation of **5** was observed.

[$RuCl(O_2CCF_3)$(=$CHCH_3$)(PCy_3)$_2$] 6. A solution of **2** (116 mg, 0.16 mmol) in CH_2Cl_2 (5 cm^3) was treated with trifluoroacetic acid (0.012 cm^3, 0.16 mmol) at −78 °C. A change of colour from brown to dark red occurred. Since after warming the solution to room temperature a smooth decomposition of **6** was observed, the product was characterized spectroscopically. NMR (CD_2Cl_2, −20 °C): δ_H (200 MHz) 19.85 [1 H, q, J(H,H) 5.5, Ru=CH], 2.61 [3 H, d, J(H,H) 5.5, =CHCH_3], 2.16 (6 H, br m, C_6H_{11}), 1.91–1.49, 1.25–1.22 (60 H, both m, C_6H_{11}); δ_F (188.0 MHz) −75.8 (s); δ_P (81.0 MHz) 36.8 (s).

[RuCl(CN)(=$CHCH_3$)(PCy_3)$_2$] 7. A slow stream of HCN was passed for *ca.* 15 s through a solution of **2** (204 mg, 0.28 mmol) in THF (6 cm^3) at −78 °C. A stepwise change of colour from brown to red and then from red to orange–brown occurred. After the solution was warmed to room temperature, it was concentrated to *ca.* 1 cm^3 *in vacuo*. Addition of pentane (4 cm^3) led to the precipitation of an orange solid, which was separated from the mother-liquor, washed three times with 5 cm^3 portions of pentane and dried; yield 183 mg (86%); mp 123 °C (decomp.) (Found: C, 62.02; H, 9.08; N, 1.73. $C_{39}H_{70}ClNP_2Ru$ requires: C, 62.34; H, 9.39; N, 1.86%). IR (KBr):

ν(CN) 2073 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 18.25 [1 H, q, J(H,H) 5.6, Ru=CH], 2.73 (6 H, m, C_6H_{11}), 2.66 [3 H, d, J(H,H) 5.6, =CHCH_3], 1.87–1.62, 1.31–1.21, 1.08–1.01 (60 H, all m, C_6H_{11}); δ_C (100.6 MHz) 322.1 [t, J(P,C) 6.0, Ru=CH], 49.4 (s, =CHCH$_3$), 34.1 (vt, N 19.8, C1 of C_6H_{11}), 30.1, 29.7, 26.7 (all s, C_6H_{11}), 27.9 (m, C_6H_{11}), signal of CN carbon atom not observed; δ_P (162.0 MHz) 42.3 (s).

[RuH(κ²-O_2CCF_3)(=C=CH_2)(PCy_3)$_2$] 8. A solution of **2** (135 mg, 0.19 mmol) in THF (18 cm^3) was treated with CF_3CO_2K (283 mg, 1.86 mmol) and stirred for 10 min at room temperature. The solvent was evaporated *in vacuo* and the residue was extracted twice with 10 cm^3 portions of toluene. After the combined extracts were brought to dryness *in vacuo*, the remaining brown–yellow solid was washed twice with 3 cm^3 portions of pentane, and dried *in vacuo*; yield 129 mg (86%); mp 44 °C (decomp.) (Found: C, 59.48; H, 8.32. $C_{40}H_{69}F_3O_2P_2Ru$ requires: C, 59.91; H, 8.67%). IR (C_6H_6): ν(C=C) 2067, ν(RuH) 1908, $\nu(OCO)_{asym}$ 1604, $\nu(OCO)_{sym}$ 1447 cm^{-1}. NMR (C_6D_6): δ_H (400 MHz) 2.72 [2 H, t, J(P,H) 3.2, C=CH_2], 2.33 (6 H, m, C_6H_{11}), 2.14–2.05, 1.77–1.62, 1.27–1.22 (60 H, all m, C_6H_{11}), −13.16 [1 H, t, J(P,H) 18.4, RuH]; δ_C (100.6 MHz) 332.9 [t, J(P,C) 14.5, C=CH_2], 163.1 [q, J(F,C) 37.7, CF_3CO_2], 114.8 [q, J(F,C) 287.0, CF_3CO_2], 86.5 [t, J(P,C) 3.2, C=CH_2], 34.4 (vt, N 19.3, C1 of C_6H_{11}), 30.7, 30.0, 27.0 (all s, C_6H_{11}), 28.3, 28.2 (both vt, N 10.0, C_6H_{11}); δ_P (162.0 MHz) 39.2 (s).

[RuHI(=C=CH_2)(PCy_3)$_2$] 9. A solution of **2** (158 mg, 0.22 mmol) in THF (4 cm^3) was treated with an excess of KI (500 mg, 3.0 mmol) and stirred for 20 min at room temperature. The solvent was evaporated *in vacuo* and the oily residue was extracted twice with 5 cm^3 portions of benzene. After the combined extracts were brought to dryness *in vacuo*, the remaining brown solid was washed three times with 5 cm^3 portions of pentane, and dried *in vacuo*; yield 129 mg. The ^1H and ^{31}P NMR spectra revealed that besides compound **2** some by-products were formed, which could not be completely removed by fractional crystallization. Data for **2**: NMR (CD_2Cl_2, −10 °C): δ_H (200 MHz) 2.72 [2 H, t, J(P,H) 3.2, C=CH_2], 2.64, 2.13, 1.93–1.67, 1.28–1.13 (66 H, all m, C_6H_{11}), −10.10 [1 H, t, J(P,H) 17.2, RuH]; δ_C (50.3 MHz) 325.3 [t, J(P,C) 15.0, C=CH_2], 85.6 (br s, C=CH_2), 35.6 (vt, N 20.0, C1 of C_6H_{11}), 30.6, 29.6, 27.6, 27.3, 26.4 (all s, C_6H_{11}); δ_P (162.0 MHz) 39.2 (s).

[Ru(O_2CCF_3)$_2$(=CHCH_3)(PCy_3)$_2$] 10. A solution of **8** (82 mg, 0.10 mmol) in THF (5 cm^3) was treated dropwise at −78 °C with a solution of CF_3CO_2H (0.008 cm^3, 0.10 mmol) in THF (2 cm^3). After the solution was warmed to room temperature, it was stirred for 10 min. The solvent was evaporated *in vacuo*, the light green residue was washed twice with 3 cm^3 portions of methanol, and dried *in vacuo*; yield 105 mg (94%); mp 64 °C (decomp.) (Found: C, 54.85; H, 7.49. $C_{42}H_{70}F_6O_4P_2Ru$ requires: C, 55.07; H, 7.70%). NMR (C_6D_6): δ_H (400 MHz) 20.91 [1 H, q, J(H,H) 5.2, Ru=CH], 2.54 [3 H, d, J(H,H) 5.2, =CHCH_3], 2.05 (6 H, br m, C_6H_{11}), 1.91–1.49, 1.29–1.16 (60 H, both m, C_6H_{11}); δ_C (100.6 MHz) 332.7 [t, J(P,C) 5.0, Ru=CH], 164.4 [q, J(F,C) 36.0, CF_3CO_2], 114.8 [q, J(F,C) 292.0, CF_3CO_2], 43.5 (br s, =CHCH$_3$], 34.4, 29.7 (both br m, C_6H_{11}), 27.6, 26.6 (both s, C_6H_{11}); δ_P (81.0 MHz) 38.3 (s).

[RuI_2(=CHCH_3)(PCy_3)$_2$] 11. A solution of **4** (380 mg, 0.50 mmol) in THF (20 cm^3) was treated with an excess of NaI (3.0 g, 20.0 mmol) and stirred for 30 min at room temperature. The solution was filtered, the solvent of the filtrate was evaporated *in vacuo*, and the residue was extracted three times with 20 cm^3 portions of methanol. The remaining light violet solid was dried *in vacuo*; yield 325 mg (69%); mp 87 °C (decomp.) (Found: C, 48.40; H, 7.55. $C_{38}H_{70}I_2P_2Ru$ requires: C, 48.36; H, 7.48%). NMR (C_6D_6): δ_H (400 MHz) 19.20 [1 H, q, J(H,H) 5.6, Ru=CH], 3.41 (6 H, m, C_6H_{11}), 2.66 [3 H, d, J(H,H) 5.6, =CHCH_3], 2.10–2.03, 1.78–1.55, 1.37–1.16 (60 H, all m, C_6H_{11}); δ_C (100.6 MHz) 58.0 (s, =CHCH_3), 35.8 (vt, N 19.5, C1 of C_6H_{11}), 28.0 (vt, N 10.0, C_6H_{11}), 31.1, 26.9 (both s, C_6H_{11}), signal of Ru=CH carbon atom not observed; δ_P (162.0 MHz) 36.6 (s).

Tris(4-tetrahydropyranyl)phosphine P(thp)$_3$ 12. In a three-necked round-bottom flask equipped with a reflux condenser and a dropping funnel, magnesium filings (1.40 g, 57.6 mmol) were covered with diethyl ether (5 cm^3) and activated by addition with 1,2-$C_2H_4Br_2$ (0.65 cm^3, 7.70 mmol). After addition of a second portion of diethyl ether (30 cm^3), the slurry was treated dropwise with a solution of 4-chlorotetrahydropyran (5.40 cm^3, 49.89 mmol) in diethyl ether (5 cm^3). Parallel to the addition of the solution of 4-OC_5H_9Cl, THF (30 cm^3) was added in several portions to the reaction mixture in order to dissolve the precipitated white solid. The major part of the solvents (*ca.* 65%) was evaporated *in vacuo*, and the remaining suspension was heated for 30 min under reflux. After cooling to room temperature, the solution containing the Grignard reagent was filtered and the filtrate was added dropwise to a solution of PCl_3 (1.31 cm^3, 15.0 mmol) in toluene (30 cm^3) at −25 °C. An off-white solid precipitated. Toluene (20 cm^3) was added, the mixture was warmed to 50 °C and stirred for 10 min at this temperature. The mixture was then cooled to 0 °C and treated with a diluted solution of aqueous HCl (*ca.* 20 cm^3). After the reaction was finished, three phases separated. The upper organic phase was withdrawn, and the two lower aqueous phases were extracted three times with 30 cm^3 portions of diethyl ether. To the aqueous phases diethyl ether (50 cm^3) was added and the mixture was then treated with a concentrated aqueous solution of NH_3 as long as the aqueous phase reached pH 9. The ethereal phase was separated and the aqueous phase was furthermore extracted twice with 10 cm^3 portions of diethyl ether. The combined ethereal solutions were evaporated *in vacuo* to give a white solid, which was recrystallized from acetone; yield 2.28 g (53%), mp 125 °C. (Found: C, 62.67; H, 9.20. $C_{15}H_{27}O_3P$ requires: C, 62.92; H, 9.50%). NMR (C_6D_6): δ_H (400 MHz) 3.86, 3.15 (6 H each, both m, OCH_2), 1.59 (3 H, m, PCH), 1.51, 1.31 (6 H each, both m, PCHCH_2); δ_C (100.6 MHz) 68.7 [d, J(P,C) 9.5, OCH_2], 31.2 [d, J(P,C) 11.7, PCHCH_2], 29.1 [d, J(P,C) 19.2, PCH]; δ_P (162.0 MHz) 5.5 (s).

[$RuCl_2$(=CHPh){P(thp)$_3$}$_2$] 14. A solution of **13** (350 mg, 0.45 mmol) in CH_2Cl_2 (10 cm^3) was treated with **12** (280 mg, 0.98 mmol) and stirred for 1 h at room temperature. The solvent was evaporated *in vacuo*, the light violet residue was washed three times with 10 cm^3 portions of pentane and dried *in vacuo*; yield 316 mg (85%); mp 165 °C (decomp.) (Found: C, 52.91; H, 7.03. $C_{37}H_{60}Cl_2O_6P_2Ru$ requires: C, 53.23; H, 7.24%). NMR (CD_2Cl_2): δ_H (400 MHz) 20.02 (1 H, s, Ru=CH), 8.45 (1 H, m, C_6H_5), 7.62 (2 H, m, C_6H_5), 7.36 (2 H, m, C_6H_5), 3.91, 3.30 (12 H each, both m, OCH_2), 2.91 (6 H, m, PCH), 1.89, 1.61 (12 H each, both m, PCHCH_2); δ_C (100.6 MHz) 299.3 [t, J(P,C) 9.0, Ru=CH], 153.1, 131.1, 130.8, 129.7 (all s, C_6H_5), 68.9 (vt, N 9.0, OCH_2), 29.7 (s, PCHCH_2), 29.4 (vt, N 18.0, PCH); δ_P (162.0 MHz) 30.7 (s).

Catalytic studies

In a typical experiment, a mixture of cyclopentene and allyl alcohol (for exact amounts see Tables 2 and 3) was stirred at room temperature and treated with 0.02–0.05 mol% of the catalyst. After a given time a small quantity (0.5 cm^3) of the mixture was removed and diethyl ether (0.5 cm^3) was added. A slow stream of CO was then passed through the solution for *ca.* 10 s, which led to the de-activation of the catalyst. The amount and the ratio of the products was then analyzed by GC/MS using a Hewlett Packard GCD instrument.

Crystallography

Single crystals of **7** were grown from a saturated solution in pentane which was slowly cooled from room temperature

to −20 °C; crystal size 0.13 × 0.11 × 0.07 mm, triclinic, space group $P\bar{1}$ (no. 2), a = 10.672(2), b = 11.352(2), c = 19.703(4) Å, α = 86.43(3), β = 76.10(3), γ = 74.81(3)°, V = 2236.1(8) Å^3, Z = 2, D_c = 1.219 g cm^{-3}; max. 2θ = 49.42° [Mo-Kα, λ = 0.71073 Å, graphite monochromator, ω-scan, T = 173(2) K], 26086 reflections scanned, 7178 unique [R_{int} = 0.0881], 4230 observed [$I > 2\sigma(I)$], Lorentz polarization and empirical absorption corrections, Patterson method (SHELXS-97),[30] atomic coordinates and anisotropic thermal displacement parameters of the non-hydrogen atoms refined anisotropically by full-matrix least squares on F^2 (SHELXL-97),[31] carbene hydrogen atom H(1) found in a differential Fourier synthesis and refined isotropically, positions of all other hydrogen atoms calculated according to ideal geometry and refined using the riding method, one molecule of pentane in the asymmetric unit; the chloro and the cyano ligands found to be disordered, they lie in two domains with an occupancy factor of 71 : 29; 464 parameters, reflections/parameter ratio 15.67 : 1, $R1$ = 0.0529, $wR2$ = 0.1168, residual electron density = 0.716/−995 e Å^{-3}.

CCDC reference number 262120.

See http://www.rsc.org/suppdata/dt/b5/b502440d/ 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. We are also grateful to Mrs R. Schedl, Mr C. P. Kneis (DTA measurements and elemental analyses), Mrs M.-L. Schäfer, Dr R. Bertermann (NMR spectra), and Degussa AG and BASF AG for gifts of chemicals. The collaboration with and the support of Prof. M. Röper and his group at BASF AG is also gratefully acknowledged.

References

1 C. Grünwald, O. Gevert, J. Wolf, P. González-Herreo and H. Werner, *Organometallics*, 1996, **15**, 1960.
2 J. Wolf, W. Stüer, C. Grünwald, O. Gevert, M. Laubender and H. Werner, *Eur. J. Inorg. Chem.*, 1998, 1217–1224.
3 P. Schwab, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1996, **118**, 100.
4 Selected overviews: R. H. Grubbs and S. Chang, *Tetrahedron*, 1998, **54**, 4413; T. M. Trnka and R. H. Grubbs, *Acc. Chem. Res.*, 2001, **34**, 18; S. T. Nguyen and T. M. Trnka, in *Handbook of Metathesis*, ed. R. H. Grubbs), Wiley-VCH, Weinheim, 2003, vol. 1, p. 61.
5 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.
6 T. E. Wilhelm, T. R. Belderrain, S. N. Brown and R. H. Grubbs, *Organometallics*, 1997, **16**, 3867.
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 M. Oliván, O. Eisenstein and K. G. Caulton, *Organometallics*, 1997, **16**, 2227.
9 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.
10 W. Stüer, personal communication; see also: J. Wolf, W. Stüer, H. Werner, P. Schwab, M. Schulz (BASF AG), O. Z. 0050/48279, 1997.
11 L. Porri, R. Rossi, P. Deversi and G. Allegra, *Tetrahedron Lett.*, 1965, 4187.
12 An improved synthetic procedure for [$RuCl_2(\eta^3{:}\eta^3\text{-}C_{10}H_{16})$]$_2$ has been reported: D. N. Cox and R. Roulet, *Inorg. Chem.*, 1990, **29**, 1360.
13 H. Werner, W. Stüer, S. Jung, B. Weberndörfer and J. Wolf, *Eur. J. Inorg. Chem.*, 2002, 1076.
14 S. Jung, C. D. Brandt, J. Wolf and H. Werner, *Dalton Trans.*, 2004, 375.
15 R. H. Grubbs, S. T. Nguyen, L. K. Johnson, M. A. Hillmyer and G. Fu (California Institute of Technology, USA), *Int. Pat.*, WO 96/04289, 1996.
16 S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 1973, 1912; G. B. Deacon and R. J. Phillips, *Coord. Chem. Rev.*, 1980, **33**, 227; C. Oldham, in *Comprehensive Coordination Chemistry*, ed. G. Wilkinson, R. D. Gillard and J. A. McCleverty, Pergamon Press, Oxford, 1987, vol. 2, p. 435.
17 Z. Wu, S. T. Nguyen, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1995, **117**, 5503.
18 L. D. Quin and M. D. Gordon, *J. Am. Chem. Soc.*, 1976, **98**, 15.
19 M. D. Gordon and L. D. Quin, *J. Org. Chem.*, 1976, **41**, 1690.
20 J. Schraml, M. Capka and V. Blechta, *Magn. Reson. Chem.*, 1992, **30**, 544.
21 H. Günther, *NMR-Spektroskopie, 3*, Georg Thieme Verlag, Stuttgart, 1992.
22 H. Werner, C. Grünwald, W. Stüer and J. Wolf, *Organometallics*, 2003, **22**, 1558.
23 P. Schwab, A. Höhn and R. A. Paciello (BASF AG), *Ger. Pat.*, O. Z. 0050/47116, 1996; P. Schwab, A. Höhn and R. A. Paciello (BASF AG), *Ger. Pat.*, O. Z. 0050/47400, 1996.
24 E. L. Dias, S. T. Nguyen and R. H. Grubbs, *J. Am. Chem. Soc.*, 1997, **119**, 3887.
25 M. S. Sanford, J. A. Love and R. H. Grubbs, *J. Am. Chem. Soc.*, 2001, **123**, 6543; see also: M. S. Sanford and J. A. Love, in *Handbook of Metathesis*, ed. R. H. Grubbs, Wiley-VCH, Weinheim, 2003, vol. 1, p. 112.
26 J. O. Krause, M. T. Zarka, U. Anders, R. Weberskirch, O. Nuyken and M. R. Buchmeiser, *Angew. Chem.*, 2003, **115**, 6147; J. O. Krause, M. T. Zarka, U. Anders, R. Weberskirch, O. Nuyken and M. R. Buchmeiser, *Angew. Chem., Int. Ed.*, 2003, **42**, 5965.
27 W. Stüer, J. Wolf and H. Werner, *J. Organomet. Chem.*, 2002, **641**, 203.
28 W. Stüer, PhD Thesis, Universität Würzburg, 1999.
29 M. Oliván and K. G. Caulton, *Chem. Commun.*, 1997, 1733.
30 G. M. Sheldrick, *SHELXS-97*, Universität Göttingen, Göttingen, Germany, 1997.
31 G. M. Sheldrick, *SHELXL-97, Programm zur Strukturverfeinerung*, Universität Göttingen, Göttingen, Germany, 1997.
32 M. N. Burnett and C. K. Johnson, *ORTEP3, Report ORNL-6895*, Oak Ridge National Laboratory, Oak Ridge, TN, 1996.