Synthesis of ruthenium phenylindenylidene, carbyne, allenylidene and vinylmethylidene complexes from (PPh₃)₃₋₄RuCl₂: A mechanistic and structural investigation

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Abstract

The reaction of (Ph₃P)₃RuCl₂ with 1,1-diphenyl-2-propyn-1-ol was investigated in various solvents. The reaction in thf under reflux is reported to produce the (PPh₃)₂Cl₂Ru(3-phenylindenylidene) complex (**3**) which has undergone rearrangement of the allenylidene C₃-spine. We have improved the reliability of the reported synthesis by adding acetyl chloride which converts the formed water of the reaction and thus increases the acidity of the reaction solution. Without the additive, we observed the exclusive formation of an intermediate of the transformation and identified it as dinuclear (PPh₃)₂ClRu(μ-Cl)₃(PPh₃)₂Ru=C=C=CPh₂ complex (**5**). The reaction of (Ph₃P)₃₋₄RuCl₂ with 1,1-diphenyl-2-propyn-1-ol in CH₂Cl₂ or C₂H₄Cl₂ under reflux in the presence of excess conc. aqueous HCl afforded the new, neutral (PPh₃)₂Cl₃Ru≡C–CH=CPh₂ carbyne complex (**7**), an HCl adduct of previously elusive (PPh₃)₂Cl₂Ru=C=C=CPh₂ complex **6** in high yields. In contrast to the formation of complex **3**, the reaction in a non-coordinating solvent did not afford the rearrangement of the allenylidene C₃-spine. Complex **7** was converted into complex **3** in thf under reflux under loss of a molecule HCl. Complex **7** was converted with triethylamine under loss of HCl to complex **6**. Pentacoordinate complex **6** was crystallized in the presence of O-donor ligands (EtOH, MeOH and H₂O) to give hexacoordinate (PPh₃)₂Cl₂(ROH)Ru=C=C=CPh₂ (R = H, CH₃, C₂H₅) complexes (**9**)–(**11**) with the O-donor coordinating in *trans*-position to the allenylidene moiety. The reaction of complex **7** with 2 equiv. of 4-(*N,N*-dimethylamino)pyridine (DMAP) gave hexacoordinate (PPh₃)₂Cl₂(DMAP)Ru=C=C=CPh₂ complex (**12**) with one molecule DMAP also coordinating in *trans*-position to the allenylidene group. Methanol and acetic acid in the absence of strong bases afforded the Fischer-carbene complexes (PPh₃)₂Cl₂Ru=C(OCH₃)–CH=CPh₂ (**14**) and (PPh₃)₂Cl₂Ru=C(OAc)–CH=CPh₂ (**15**) where the nucleophile added to the α-carbon atom. The structures of complexes **5**, **7**, **9–11**, **14**, and **15** were solved via X-ray crystallography.
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1. Introduction

Olefin metathesis has become a valuable synthetic tool in organic [1–5] and polymer chemistry [6–11]. In particular Ru-based catalysts have proven to be highly applicable in homogeneous solution due to their high tolerance towards functional groups, moisture and air [12]. Whereas several different synthetic strategies had been developed to access such 16-electron Ru–carbene complexes over the past decade, including metathesis-active vinylidene [13], allenylidene [14] and vinylmethylidene complexes [15], today Ru–benzylidene complexes such as Grubbs' catalyst **1** (Fig. 1) and its NHC-ligated counterparts [16–19] are the most prominent representatives of this class of compounds. They are studied to the greatest detail [20,21], are commercially available, and
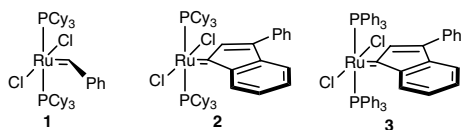
Fig. 1. Structures of commercially available catalysts **1** and **2** and catalyst precursor **3**.

still are most widely used for many applications. Ruthenium–3-phenylindenylidene complex **2** (Fig. 1) and its NHC-ligated derivatives also have been produced in a large variety [21–24]. Their attraction lies in the improved thermal stability profile [23] paired with catalytic activity reported to rival, and in some instances surpass their benzylidene counterparts, in particular for use in Ring Closing Metathesis (RCM) reactions [24]. Complex **2** is also commercially available.

The synthetic access to complex **2** is reported to be straightforward from non-hazardous starting materials [22]. The precursor complex **3** with two PPh$_3$ ligands was obtained from the reaction of $(Ph_3P)_{3-4}RuCl_2$ and 1,1-diphenyl-2-propyn-1-ol in refluxing thf under elimination of water and then converted with PCy$_3$. Instead of the originally proposed allenylidene complex [22], the C$_3$-spine undergoes, presumably acid induced, rearrangement involving one of the phenyl groups to form the 3-phenylindenylidene complex **3** (Fig. 1) [23]. Complex **3**, while lowly metathesis active by itself, is highly useful. In solid, dry form, it is highly stable, can be stored for months in air without noticeable decomposition in contrast to Grubbs' $(PPh_3)_2Cl_2Ru$=CHPh complex, precursor to the family of Grubbs' catalysts. This stability makes complex **3** an ideal precursor to access an array of differently substituted olefin metathesis catalysts. In our experience however, the reported synthetic procedure lacked reliability. Often, the same synthetic procedure (sometimes from the same batch of starting materials) would occasionally afford complex **3** but more often it would afford an unidentified dimeric species containing four different kinds of phosphine ligands as major product. To date, no reliable synthesis for complex **3** has been reported and the nature of dimeric species has not been identified. Also, despite the proposed mechanisms for the formation of complex **3**, no intermediate of the reaction has been isolated and characterized. We now wish to report an improved, reliable and high-yielding synthetic procedure for complex **3**, and the synthesis and characterization of two intermediates of the formation reaction, a dimeric allenylidene and a carbyne complex. Furthermore, we wish to report transformations of the carbyne complex to afford allenylidene and vinylmethylidene complexes which also were isolated and characterized.

2. Results and discussion

2.1. Complex syntheses

Following the procedure of Hill et al. [22], we reacted $(PPh_3)_{3-4}RuCl_2$ (**4**) [26] with 1,1-diphenyl-2-propyn-1-ol

in thf under reflux to obtain complex **3**. The modified work-up protocol [27] required the removal of all solvent and a thorough wash of the residue with diethyl ether. Although, we were occasionally successful following this procedure, we had not once obtained complex **3** in recent years in spite of closely following this protocol. Instead we isolated a new ruthenium complex on these occasions, each time in very high yield. We have identified this compound via NMR-spectroscopy and single crystal X-ray diffraction (Fig. 2) as a non-symmetric binuclear complex **5** with two hexacoordinate ruthenium centers which are μ-Cl$_3$-bridged across an octahedral face. Both ruthenium centers are additionally coordinated by two PPh$_3$ ligands, one ruthenium atom bears another terminal chloro ligand, the other a diphenylallenylidene moiety. The complex could be easily formed upon the reaction of the starting complex **4** and complex **6** (supposedly the initial product of the addition of 1,1-diphenyl-2-propyn-1-ol to complex **4**) and could represent an early intermediate of the formation of complex **3** (Scheme 1). A similar non-symmetric dimeric complex bearing one vinylmethylidene group has been identified as an intermediate of the thermal degradation of the corresponding $(PPh_3)_2Cl_2Ru$(alkylidene) complex [28]. Cationic, $(\mu$-Cl$)_3$-bridged Ru$_2$(allenylidene)$_2$ complexes have also been reported before [22b,29]. Several dinuclear, $(\mu$-Cl$)_2$-bridged ruthenium carbene complexes have been identified as very effective olefin metathesis initiators [30]. The ^{31}P NMR spectrum in d_6-benzene exhibits the presence of four different phosphorus atoms with the signals ($\delta = 37.0$ ppm, 40.8 ppm, 48.9 ppm and 51.4 ppm) split in four duplets $[^2J(^{31}P^{31}P) = 26.6$ Hz and 37.8 Hz] of equal intensity caused by two separate Ru(PPh$_3$)$_2$ units in the molecule. X-ray quality crystals were obtained by vapor diffusion of diethyl ether into a solution of complex **5** in CH$_2$Cl$_2$ which contained 4 equivalent of PPh$_3$.

Due to the coordinative saturation of the ruthenium center not bearing a carbene, further reaction to complete the formation of complex **3** only can occur by dissociation of the dimeric complex. Considering three bridging μ-Cl
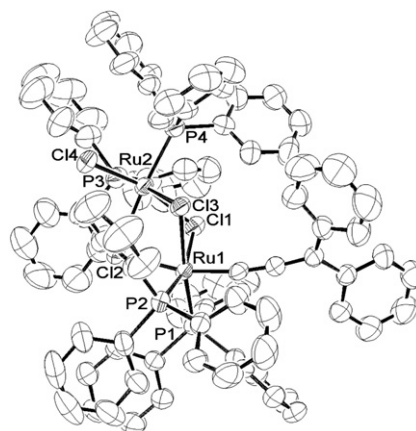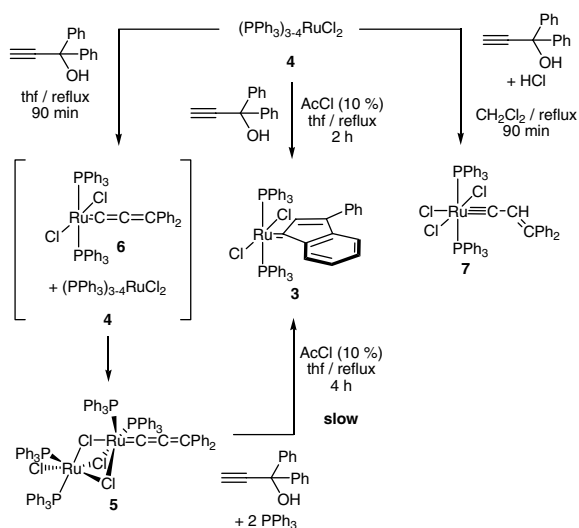

Fig. 2. ORTEP diagram of $(PPh_3)_2ClRu(\mu$-Cl$)_3Ru(PPh_3)_2$=C=C=CPh$_2$ (**5**) (hydrogen atoms omitted for clarity).

Scheme 1. Conversion of complex **4** with 1,1-diphenyl-2-propyn-1-ol under various reaction conditions.

ligands, this may be a very slow process and one reason for the near-exclusive formation of complex **5** under literature conditions [22,27]. In those experiments even extended reaction times up to 12 h did not afford the desired complex **3** as determined by ^{31}P NMR spectroscopy of aliquots. Instead unidentified decomposition products were formed in small amounts alongside complex **5**. Therefore, a successful synthesis of complex **3** requires either avoiding the formation of complex **5** or applying conditions which favor its dissociation. A solvent change to refluxing CH_2Cl_2, generally a very good solvent for ruthenium carbene complexes, also yielded the dinuclear complex **5** as the major product which was isolated in 79% yield from the reaction, however without noticeable formation of complex **3** according to the ^{31}P NMR spectrum of the crude product. We tested adding bases such as triethylamine or pyridine (to prevent the formation of dinuclear species **5**) and acids such as acetyl chloride to facilitate the conversion into complex **3** in thf under reflux. Whereas the added bases did yield mixtures of unidentified products, addition of acetyl chloride indeed dramatically improved the conversion and we were able to isolate complex **3** in high yields. In fact, acid-catalyzed rearrangement of allenylidene to phenylindenylidene moieties has been extensively studied with 18-electron (*p*-cymene)Ru complexes [31]. It is likely that the rearrangement of the C_3-spine is also acid-catalyzed to form 16-electron complex **3**. Formation of complex **3** as the sole product after work-up was accomplished when a catalytic amount of acetyl chloride (0.1 equiv. in respect to propynol) used with a reaction time of 90 min in refluxing thf (Scheme 1). Upon reaction with water (residual moisture in thf and water formed from the reaction) and/or the propynol, the acetyl chloride will provide HCl and some amounts of acetic acid. The reaction also yields complex **3** using an excess of acetyl chloride (2 equiv. in respect to propynol). It seems likely, that the

HCl produced during the reaction is one key to the formation of the 3-phenylindenylidene carbene. Previous successful syntheses of complex **3** [22–25] may have benefited from impurities of the acidic $HPPh_3^+$ cation, a byproduct of the synthesis of starting material **4** [26]. However, upon thorough washing during filtration of precursor **4**, the catalytic amounts acid may be removed sufficiently and the synthesis would not yield the desired complex according to the standard protocol [22,27].

It should be noted that the reaction of complex **5** with 1 equiv. 1,1-diphenyl-2-propyn-1-ol, 2 equiv. PPh_3 and 0.1 equiv. of acetyl chloride in refluxing thf also forms the desired complex **3** (Scheme 1), however, the reaction is slow and the conversion does not go to completion (approx. 50% of **5** are converted into **3** after 4 h). Moreover, the long reaction times additionally afford thermal degradation products which are apparent in the ^{31}P NMR spectrum of the crude product. It appears likely, that the dimeric structure of complex **5** needs to be dissociated into complexes **4** and **6** in order to successfully form complex **3**, and this may be the slow step of this conversion. Therefore, complex **5** may be one, but rather likely a minor intermediate formed during the synthesis of complex **3**. The acidic conditions appear to favor a second reaction pathway which does not include the dimeric complex **5** (*vide infra*).

We also have attempted the conversion of complex **4** with 1,1-diphenyl-2-propyn-1-ol in refluxing CH_2Cl_2, which is a very good solvent for the starting complex **4** and inert against concentrated acid. When we used a catalytic amount of HCl refluxing for 16 h, a mixture of various compounds was produced, among those trace amounts (<10%) of complex **5** were identified via ^{31}P NMR spectroscopy. The use of excess HCl (with respect to starter complex **4**) in refluxing CH_2Cl_2 for 90 min however, yielded the new carbyne complex **7** as yellow powder in high yields (Scheme 1), which precipitated upon addition of 2-propanol, and was obtained as the sole isolated Ru-compound after filtration. Complex **7** obviously had been derived from the allenylidene complex **6** where one molecule HCl has added in 1,3-fashion across the Ru=C=C=C spine. A reminiscent cationic ruthenium monohydride complex with a carbyne moiety has been reported by Werner et al. [32], produced by the addition of acid to vinylidene complexes. The structure of complex **7** was confirmed via NMR spectroscopy and X-ray diffraction (Fig. 3). The ^{31}P NMR (CD_2Cl_2) exhibited one signal at 13.6 ppm (s). The ^{1}H NMR (CD_2Cl_2) signal for $C_\beta H$ atom is significantly shifted from the residual sp^2CH atoms with a resonance at 5.67 ppm and displays coupling to the phosphorus atoms [t, $^4J(^{31}P^1H) = 2.4$ Hz]. The observed coupling constant indicates that phosphine dissociation is slow on the NMR time scale. X-ray quality crystals were obtained by slow layer-diffusion of 2-propanol into a solution of complex **7** in CH_2Cl_2 which contained 4 equiv. of PPh_3.

Protonation of the C_β atom to form carbyne complexes was reported for Re, Ru and Ir vinylidene complexes using
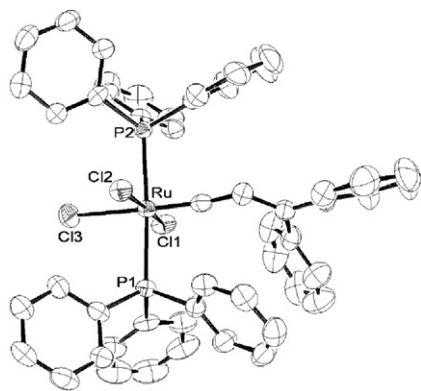
Fig. 3. ORTEP diagram of $(PPh_3)_2Cl_3Ru\equiv C–CH=CPh_2$ (**7**) (hydrogen atoms omitted for clarity).

non-coordinating acids [33,34]. Also the addition of non-nucleophilic acid converted Ru [35,36] and Ir [37] allenylidene complexes into vinylcarbyne complexes. The formation of a dicationic carbyne complex from a diphenylallenylidene moiety was also observed by Dixneuf et al. via ^{31}P NMR spectroscopy when converting a 18-electron (p-cymene)Ru diphenylallenylidene complex into the phenylindenylidene analogue with triflic acid at low temperatures [31]. Hence, it appears likely that complex **7** represents an intermediate of the formation of complex **3**, very likely one intermediate of the major reaction pathway. In refluxing CH_2Cl_2 complex **7** could not be converted into complex **3**. In contrast, when complex **7** is heated under reflux in thf in the presence of 2 equiv. of PPh_3 for 90 min, the rearrangement of the C_3-spine with subsequent dehydrohalogenation is accomplished quantitatively and complex **3** is obtained in high yields (Scheme 2). In this transformation, additional PPh_3 is needed as it limits thermal decomposi-

tion of the product and/or the intermediates. Such decomposition is observed when the reaction is conducted without it via ^{31}P NMR spectroscopy. It should be noted that thermal degradation is intimately linked to the rate of phosphine dissociation in 16-electron carbene complexes and additional phosphine reduces this rate [20,21]. Additionally, the extra phosphine also serves as oxygen sponge to prevent oxidative decomposition. The catalytic effect of ruthenium complexes of the oxidation of phosphines with molecular oxygen was observed previously [38]. The reaction actually was carried out in a closed vessel under non-inert conditions with a sufficient excess of phosphine. Upon work-up, the complex was separated from the excess phosphine and Ph_3PO via filtration of the slurry in 2-propanol.

The reactivity difference between thf in contrast to the non-coordinating solvent CH_2Cl_2 seems likely to be due to an intermediate formation of a cationic carbyne species **8a** (Scheme 3) where the chloro ligand in trans-position to the carbyne group is replaced by a thf ligand. It is likely that the α-carbon atom in complex **8a** possesses elevated electrophilicity and therefore, is activated towards internal nucleophilic attack by one of the benzene rings attached to $C_γ$ to form the 3-phenylindenylidene moiety.

The reversible abstraction of HCl makes complex **7** reactive towards bases and various nucleophiles. In fact, complex **7** was used to provide the catalytic amount acid needed for the formation of complex **3** from precursor **4** and 1,1-diphenyl-2-propyn-1-ol. The reaction using 10% complex **7** exclusively yields complex **3** under standard conditions (thf reflux, 2 h) in 90% yield. The reaction of complex **7** with triethylamine as a weakly coordinating base afforded the abstraction of a molecule HCl resulting in the formation of deep-red 16-electron allenylidene complex **6** (Scheme 2). The reaction was performed in methanol with an excess triethylamine under sonication (15 min). The product was filtered, washed and dried under vacuum. However, crystallization attempts for complex **6** by slow diffusion of 2-propanol into a saturated CH_2Cl_2 solution did not afford suitable crystals for X-ray analysis. Even more surprising, crystallization attempts using vapor diffusion of diethyl ether into a saturated CH_2Cl_2 solution afforded suitable crystals for X-ray analysis, however complex **9**
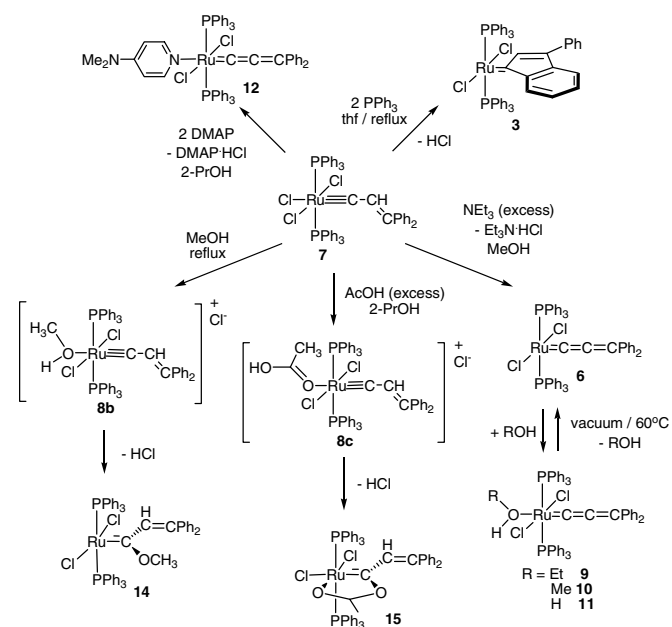
Scheme 2. Conversion of carbyne complex **7** to give 3-phenylindenylidene, allenylidene, and vinylmethylidene complexes.
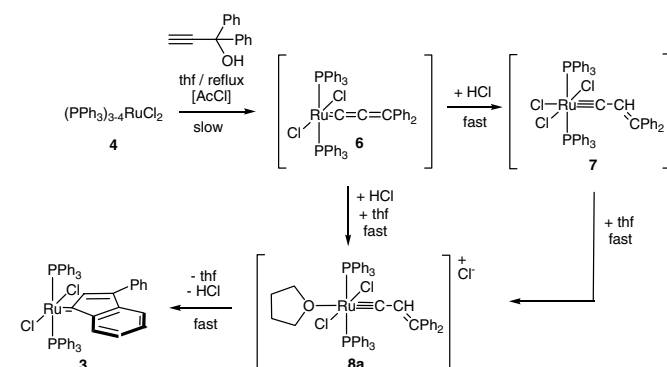
Scheme 3. Proposed mechanism for the formation of complex **3**.

was obtained with an additional ethanol molecule coordinating *trans* to the allenylidene moiety instead of complex **6**. The ethanol molecule is likely formed as a result from the hydrolysis of diethyl ether, perhaps catalyzed by complex **6**. Other vapor diffusion crystallization attempts (Et$_2$O into CH$_2$Cl$_2$) in the presence of methanol or water (added in a 1:1 v/v mixture with 2-propanol) also afforded hexacoordinate species, namely complexes **10** and **11** which were analyzed by X-ray diffraction (Figs. 4–6). On the other hand, the use of 2-propanol in these experiments did not yield suitable crystals. Standard drying conditions (2 h vacuum/60 °C) accomplished the complete removal of the *trans*-ligand from all three complexes to afford complex **6**. The coordination of the donor ligands (Scheme 2) can be observed via ^{31}P NMR spectroscopy. The spectrum (d_6-benzene) exhibited one resonance at 30.9 ppm (s) for complex **6**. Addition of excess (>10 equiv.) ethanol, methanol and water to the NMR solution afforded a resonance shift up-field to 27.0 ppm (s, **9**), 27.6 ppm (s, **10**) and 27.5 ppm (s, **11**), respectively. In contrast, the addition of 2-propanol caused a minimal up-field shift to 30.6 ppm. It appears likely that 2-propanol is too bulky to coordinate
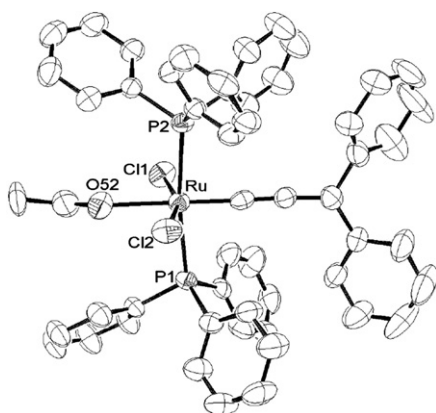

Fig. 4. ORTEP diagram of (EtOH)(PPh$_3$)$_2$Cl$_2$Ru=C=C=CPh$_2$ (**9**) (hydrogen atoms omitted for clarity).
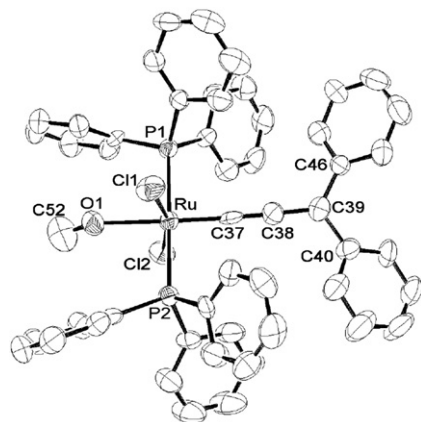
Fig. 5. ORTEP diagram of (MeOH)(PPh$_3$)$_2$Cl$_2$Ru=C=C=CPh$_2$ (**10**) (hydrogen atoms omitted for clarity).
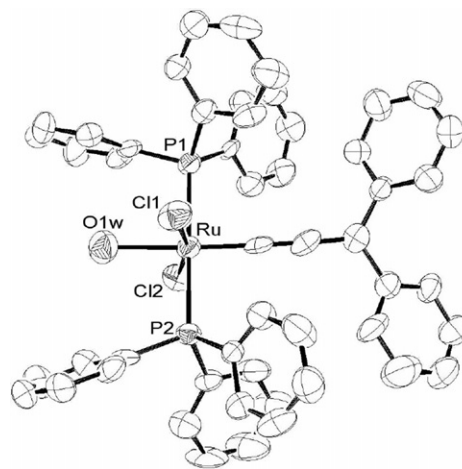
Fig. 6. ORTEP diagram of (H$_2$O)(PPh$_3$)$_2$Cl$_2$Ru=C=C=CPh$_2$ (**11**) (hydrogen atoms omitted for clarity).

to the vacant site in order to form a stable hexacoordinate complex.

Complexes **9**–**11** are unprecedented among neutral, hexacoordinate 18-electron ruthenium carbene complexes. The fact that hard, neutral O-donor ligands such alcohols or water coordinate to the soft ruthenium center of complex **6** demonstrates a much higher Lewis-acidity of the metal center than for other 16-electron ruthenium carbene complexes. It explains the formation of dimeric complex **5** under non-acidic conditions with the weakly Lewis-basic complex **4**. Under acidic conditions, the catalytic amount HCl obviously converts complex **6** into complex **7** (or alternatively directly into cationic carbyne complex **8a**) instantly after formation which then was demonstrated to undergo dehydrohalogenation with subsequent rearrangement of the C$_3$-spine to complex **3** in thf. As catalytic amounts of acetyl chloride (which should form HCl under reaction conditions), or complex **7** itself, prove sufficient for a complete conversion into the desired product, it is obvious that the first step, the formation of complex **6**, is rate determining for the conversion as there must be sufficient amounts of HCl in the reaction mixture to complete the pathway. The protonation to afford complex **7** (or directly complex **8a**), the *trans*-chloride substitution to form complex **8a** from complex **7**, and the C$_3$-spine rearrangement therefore, have to be significantly faster (Scheme 3).

Nucleophilic bases such as *N,N*-4-dimethylaminopyridine (DMAP) also afforded the loss of one HCl molecule in complex **7** under restoration of the initial allenylidene moiety. A second molecule DMAP coordinated to the metal center in *trans*-position to the carbene moiety to form purplish-blue complex **12** (Scheme 2). The use of <2 equiv. of DMAP will result in a mixture of complexes **6** and **12**. Complex **12** was isolated and the structure was determined via NMR spectroscopy and X-ray diffraction (Fig. 7). The ^{31}P NMR spectrum (CD$_2$Cl$_2$) exhibited one resonance at 23.2 ppm (s). The ^{1}H NMR spectrum

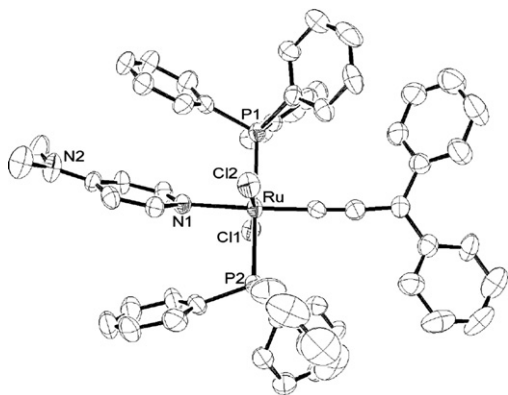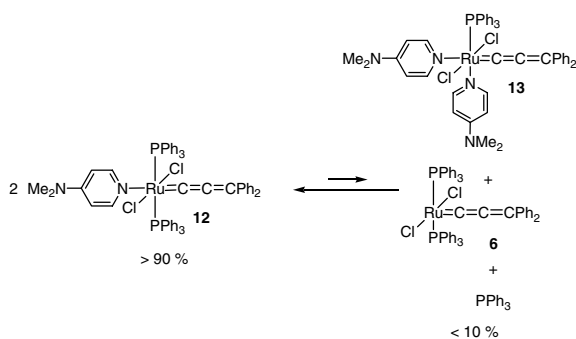Fig. 7. ORTEP diagram of $(DMAP)(PPh_3)_2Cl_2Ru=C=C=CPh_2$ (**12**) (hydrogen atoms omitted for clarity).

displayed only one resonance outside the aromatic area at 2.88 ppm (s, 6H) for the NMe$_2$ protons. Complex **12** is unique as it represents the first hexacoordinate 18-electron Ru carbene complex bearing two phosphine and only one N-donor ligand, in contrast to reports where the reaction of two N-donor ligands replacing one phosphine forming L(N-donor)$_2$Cl$_2$Ru carbene [19,39,40] or L(N-donor)$_3$ClRu$^+$ carbene [38] complexes (L = phosphine or NHC ligand). It should be noted, that dissolution of crystals of complex **12** in CD$_2$Cl$_2$, (and to a lesser degree in d$_6$-benzene) did afford trace amounts of several secondary species which display multiple ^{31}P NMR resonances. Most notably, resonances are observed at 41.4 ppm (s), 31.9 (s) and at −4.7 ppm (s, PPh$_3$) with the same integration values. It appears likely that the signal at 41.4 ppm represents complex $(PPh_3)(DMAP)_2Cl_2Ru=C=C=CPh_2$ (**13**) where one of the PPh$_3$ ligands is replaced by a second DMAP ligand. Thus, a free PPh$_3$ ligand is formed (δ −4.7 ppm) plus a molecule of complex **6** (δ 31.9 ppm). Dissolving pure complex **12** apparently resulted in the formation of an equilibrium with complex **13**, complex **6** and free PPh$_3$ (Scheme 4) which are formed in trace amounts as >90% of the mixture is still present as complex **12**. Upon addition of DMAP to this mixture, the signal intensities of complex **13** (δ 41.4 ppm) and PPh$_3$ (δ −4.7 ppm) slowly increase in a 1:1 ratio, whereas the signal for complex **6** disappears. Addi-

tion of 10 equiv. of DMAP to complex **12** afforded a conversion of approximately 70% after 30 min, however, a strong increase in the formation of secondary products was also observed. It is obvious, that both PPh$_3$ ligands are strongly bonded in complex **12**. Pentacoordinate ruthenium allenylidene complexes are known slow metathesis initiators [14], and this process depends on the rate of phosphine dissociation. In addition, the use of an excess of PPh$_3$ during synthesis and crystallization also may have shifted the equilibrium back to complex **12** that this was the sole isolated product.

The reaction of complex **7** with methanol without addition of extra base yielded the Fischer-type vinylmethylidene complex **14** (Scheme 2). Instead of deprotonation of the C$_\beta$ atom, the *trans* chloride was replaced by a methoxide adding to the C$_\alpha$-atom converting the carbyne to a carbene moiety. The product precipitated almost quantitatively from the reaction solution (refluxing methanol plus 2 equiv. PPh$_3$ open to air) as a brown powder. Complex **14** was characterized via NMR spectroscopy and X-ray diffraction (Fig. 8) and represents the α,β-addition product of complex **6** with methanol. The ^{31}P NMR spectrum (CD$_2$Cl$_2$) exhibited one resonance at 29.8 ppm (s), and the ^{1}H NMR spectrum displayed two characteristic resonances outside the aromatic area at 3.15 ppm (s, 3H) for the methoxy group and 5.33 ppm (s, 1H) for the C$_\beta$-hydrogen atom. The nucleophile addition proceeds at the α-carbon atom in contrast to reports of cationic CpRu vinylcarbyne complexes adding soft nucleophiles to the γ-carbon atom of the C$_3$-spine [36]. Addition of alcohols across the C$_\alpha$–C$_\beta$ bond of cationic vinylidene complexes to form Fischer-carbene complexes had been reported before [42]. The mechanism of the addition was not investigated in these reactions. Very likely the nucleophilic attack precedes the proton transfer to the C$_\beta$ atom in these transformations. It is unlikely the reaction proceeds via the dicationic carbyne complex as the cationic vinylidene precursor was obtained by protonation using strong acids
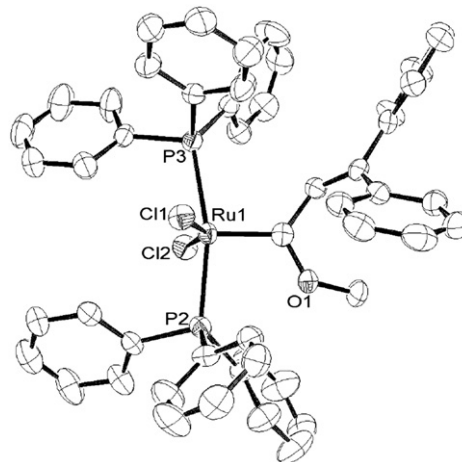

Scheme 4. Equilibrium between mono-DMAP complex **12** and complexes **13**, **6** and PPh$_3$ in CD$_2$Cl$_2$.

Fig. 8. ORTEP diagram of $(PPh_3)_2Cl_2Ru=C(OMe)–CH=CPh_2$ (**14**) (hydrogen atoms omitted for clarity).

and thus, weakly acidic alcohols should not afford a second protonation step at the C_β atom. The formation of complex **14** proceeds in reverse order, first protonation of the C_β atom in complex **6**, then nucleophilic attack with subsequent deprotonation at the C_α atom, as the protonation is already accomplished with the formation of complex **7**. Interestingly, we were not able, even after several hours of reflux in 2-propanol, to obtain the corresponding Fischer-carbene complex bearing an OiPr substituent. As it was demonstrated that 2-propanol is too bulky to coordinate to the ruthenium center of complex **6** upon treatment of complex **7** with base, it suggests that *trans*-chloride substitution versus methanol may be crucial to the substitution reaction. The resulting cationic intermediate carbyne complex **8b** certainly possesses a more electrophilic C_α-atom which could be more readily attacked by the weakly nucleophilic alcohol.

The formation of complex **15** from complex **7** with acetic acid, another weakly basic nucleophile, was accomplished by sonication of the slurry of complex **7** in 2-propanol and a large excess of AcOH for 4 h (Scheme 2). In the same fashion, chloride substitution takes place with the weakly nucleophilic acetate adding to the C_α-atom. To the best of our knowledge, this is the first example of the addition of a carboxylate to a carbyne carbon atom to form a Fischer-carbene complex. Similar to the formation of complex **14**, we propose that the nucleophilic addition is preceded by the chloride substitution in *trans*-position to the allenylidene group to form the cationic complex **8c**. As a result, the ruthenium center became more susceptible towards nucleophilic attack at the C_α atom. The acetate group additionally coordinates back to the metal center to form a chelating vinylmethylidene group under *trans* to *cis* isomerization of the chloride ligand. Complex **15** was characterized via NMR spectroscopy and X-ray diffraction (Fig. 9). The ^{31}P NMR spectrum (CD$_2$Cl$_2$) exhibited one resonance at 18.3 ppm (s), and the ^{1}H NMR
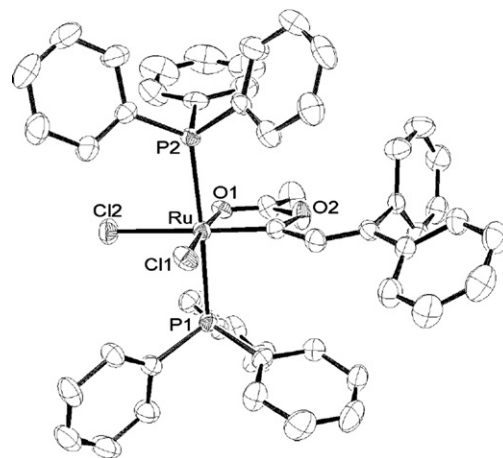

Fig. 9. ORTEP diagram of (PPh$_3$)$_2$Cl$_2$Ru=C(O–COMe)–CH=CPh$_2$ **15** (hydrogen atoms omitted for clarity).

spectrum displayed one characteristic resonance outside the aromatic area at 1.01 ppm (s, 3H) for the acetyl methyl group whereas the signal for the C_β-hydrogen atom is masked by the aromatic proton signals.

2.2. Structural investigations

The structures in solid state of complexes **5**, **7**, **9–12**, **14** and **15** could be determined via X-ray crystallography. Relevant bond distances and angles of the allenylidene complexes **5**, **9–12** are summarized in Table 1 and those of complexes **7**, **14** and **15** in Table 2. All complexes exhibit a distorted octahedral environment at the ruthenium center with exception of pentacoordinated 16-electron complex **14** which is distorted tetragonal pyramidal.

In complex **5**, three bridging μ-Cl ligands face-connect both octahedra. As expected, all (μ-Cl)–Ru–(μ-Cl) (between 78.18(3)° and 82.39(3)°) and Ru–(μ-Cl)–Ru angles (between 83.15(3) and 85.90(3)°) are significantly smaller than 90°.

Table 1
Selected bond distances (pm) and bond angles (°) for allenylidene complexes **5**, **9**, **10**, **11** and **12**

	5[c]	**9**	**10**	**11**	**12**
Ru–C_α	186.0(4)	183.6(4)	183.3(6)	184.8(9)	190.2(4)
C_α–C_β	124.6(5)	125.0(4)	123.6(7)	124.4(11)	119.0(5)
C_β–C_γ	135.7(5)	135.4(5)	138.4(8)	134.5(11)	139.7(5)
Ru–P	233.52(10)	242.09(9)	238.55(16)	238.5(2)	239.80(11)
	238.79(11)	248.37(9)	239.02(16)	239.2(2)	243.93(10)
Ru–Cl	243.52(9)	237.38(9)	237.22(16)	237.7(2)	239.13 (11)
	246.24(10)	235.85(9)	236.54(17)	237.1(2)	239.32(11)
Ru–L[a,b]	248.37(9) (Cl)	229.8(2) (O)	225.5(4) (O)	225.7(5) (O)	225.0(3) (N)
Ru–C_α–C_β	171.6(3)	177.8(3)	177.1(5)	179.1(8)	179.3(4)
C_α–C_β–C_γ	170.1(4)	176.5(4)	178.9(6)	177.8(9)	175.3(4)
P–Ru–P	101.85(4)	172.41(3)	179.01(6)	179.41(9)	178.89(4)
Cl–Ru–Cl	79.29 (3)	159.24(3)	162.20(6)	163.89(8)	172.86(3)
	82.39(3)				
	78.33(3)				

[a] Distance to binding atom of the ligand *trans* to the allenylidene moiety.
[b] Binding atom given in brackets following value.
[c] Distances and angles given for ruthenium center bearing the allenylidene moiety.

Table 2
Selected bond distances (pm) and bond angles (°) for carbyne complex **7** and vinylmethylidene complexes **14** and **15**

	7	14	15
Ru–C$_\alpha$	172.5(7)	185.5(5)	186.2(5)
C$_\alpha$–C$_\beta$	137.9(9)	146.3(7)	143.4(7)
C$_\beta$–C$_\gamma$	137.6(9)	134.9(8)	134.7(7)
Ru–P	244.27(15)	236.91(17)	240.96(12)
	245.79(15)	241.80(18)	241.97(12)
Ru–Cl	235.90(15)	233.93(17)	239.63(12)
	240.93(15)	235.70(17)	250.39(13)[a]
	249.66(17)[a]		
Ru–C$_\alpha$–C$_\beta$	167.1(5)	124.0(4)	134.1(3)
C$_\alpha$–C$_\beta$–C$_\gamma$	127.7(7)	120.1(5)	130.3(5)
P–Ru–P	176.33(6)	166.53(5)	177.06(4)
Cl–Ru–Cl	175.01(6)	150.06(6)	98.03(5)

[a] Distance to Cl *trans* to the carbyne or carbene moiety.

All other *cis*-angles at the Ru centers between the terminal ligands vary between 86.40(4)° and 102.03(4)° with the P–Ru–P angles widened to 101.85(4)° and 99.36(4)°, respectively. The angles along the C$_3$-spine also are deviating somewhat from linearity (Ru–C$_\alpha$–C$_\beta$: 171.6(3)°, C$_\alpha$–C$_\beta$–C$_\gamma$: 170.1(4)°) which could be a consequence of C–H π-interactions to spatially close ligand hydrogen atoms. This was been observed for other allenylidene complexes [14,43]. The Ru-(μ-Cl) distances vary between 242.16(8) pm and 253.10(10) pm which makes them slightly longer than the Ru–Cl$_{terminal}$ distance (239.96(9) pm). The Ru–P distances are longer at the metal bearing the allenylidene group (233.52(10) pm and 238.79(11) pm) than for the terminal chloride substituted (227.00(11) pm and 229.80(11) pm). The Ru–C$_\alpha$ distance (186.0(4) pm) is relatively short for 18-electron Ru–allenylidene complexes (typical range 187–192 pm) [40,44] but significantly longer than the carbene distances (179 pm) observed for the only two reported 16-electron Ru–allenylidene complexes [14]. The C–C distances in the C$_3$-spine, C$_\alpha$–C$_\beta$: 124.6(5) pm (typical range 125–127 pm) and C$_\beta$–C$_\gamma$: 135.7(5) (typical range 132–135 pm), are in the common range for allenylidene complexes [14,43,44].

In complex **7**, all *cis*-angles at the metal vary between 84.34(6)° and 96.60(2)° and the *trans*-angles between 175.01(6)° and 178.90(2)°, respectively. As expected, the C$_3$-spine has lost the linearity at the C$_\beta$ atom (Ru–C$_\alpha$–C$_\beta$: 167.1(5)°, C$_\alpha$–C$_\beta$–C$_\gamma$: 127.7(7)°). However, the angle at the C$_\alpha$ atom also is somewhat significantly bent and smaller than any other such angle observed with ruthenium carbyne complexes (168.8(4)–179.9(7)°) [36,45]. This may come as a result of steric interference with the terminal phenyl groups. The closest non-bonding contacts of the C$_\alpha$ and the C$_\beta$ atoms are to the *ortho*-C*H* of one of the spine-phenyl groups (272.4 pm and 286.9 pm). The Ru–Cl distances *cis* to the carbyne moiety are 235.90(15) pm and 240.93(15) pm whereas the *trans*-Cl bond is elongated to 249.66 (17) pm. The Ru–C$_\alpha$ distance (172.5(7) pm) is in the range of previously reported ruthenium carbyne complexes

(170.3(9)–176.6(3) pm) [36,45]. The C–C distances in the C$_3$-spine (C$_\alpha$–C$_\beta$: 137.9(9) pm and C$_\beta$–C$_\gamma$: 137.6(9) pm) are almost identical and in similar range as the literature complex. Interestingly, such similar bond distances, despite different bonding orders in the C$_3$-spine, was also observed for ruthenium vinylmethylidene complexes [17c].

Allenylidene complexes **9–11** display the same coordination sphere around the ruthenium center as expected. Methanol and water complexes **10** and **11** exhibit very similar bond distances and angles around the metal center. Ethanol complex **9** exhibits a slightly longer Ru–O distance to the ligand (229.8(2) pm) in comparison to complexes **10** (225.5(4) pm) and **11** (225.7(5) pm) presumably due to increased steric crowding at the metal center. Due to the same effect, the Ru–P distances are also elongated in complex **9** (242.09(9) pm and particularly 248.37(9) pm) whereas these distances all lie in between 238.5(2) pm and 239.2(2) pm for complexes **10** and **11**. This steric effect is also visible in the bond angles around the metal center. The *trans*-phosphine angles for complex **9** (P–Ru–P: 172.41(3)°) is smaller by more than 6° than in complexes **10** and **11**, and the *trans*-chlorine angle (Cl–Ru–Cl: 159.24(3)°) by approx. 3°. Additionally, the *cis* O–Ru–P angles are also significantly widened in complex **9** (93.77(3)° and 93.91(6)°) by an average of approx. 3° in comparison to complexes **10** and **11**. The angles along the C$_3$-spine are close to linearity in all complexes (smallest Ru–C$_\alpha$–C$_\beta$ (**10**): 177.1(5)°, smallest C$_\alpha$–C$_\beta$–C$_\gamma$ (**9**): 176.5(4) °). The Ru–Cl distances for all three complexes are in a narrow range between 235.85(11) pm (**9**) and 237.7(2) pm (**11**). The Ru–C$_\alpha$ distances are similarly close between 183.3(6) pm (**10**) and 184.8(9) pm (**11**) and like complex **5** (*vide supra*) at the short end to other 18-electron Ru–allenylidene complexes (typical range 187–192 pm) [41]. The bond distances along the C$_3$-spine (**9**: C$_\alpha$–C$_\beta$: 125.0(4) pm and C$_\beta$–C$_\gamma$: 135.4(5) pm; **10**: C$_\alpha$–C$_\beta$: 123.6(7) pm and C$_\beta$–C$_\gamma$: 138.4(8) pm; **11**: C$_\alpha$–C$_\beta$: 124.4(11) pm and C$_\beta$–C$_\gamma$: 134.5(11) pm) are similar to complex **5** and other ruthenium allenylidene complexes [14,43,44]. The angles along the C$_3$-spine do not deviate more than 3.5° from linearity which should exclude significant C–H π-interactions to spatially close ligand hydrogen atoms.

In complex **12**, all *cis*-angles vary between 84.87(4)° and 94.45(4)° (both Cl–Ru–P) and the three *trans*-angles (C–Ru–N: 177.67(15)°, P–Ru–P: 178.89(4)°, Cl–Ru–Cl: 172.86(3)°) are close to linearity, much more so than in isoelectronic complexes **9–11**. The angles along the C$_3$-spine also are close to linearity (Ru–C$_\alpha$–C$_\beta$: 179.3(4)°, C$_\alpha$–C$_\beta$–C$_\gamma$: 175.3(4)°). The Ru–N distance (225.0(3) pm) is much shorter than other reported Ru–N distances for pyridines coordinated *trans* to the carbene moiety [19c], and also shorter than the Ru–O distances in complexes **9–11**. This indicates a very strong interaction between metal and N-donor ligand. The Ru–C$_\alpha$ distance (190.2(4) pm) is in the general range (187–192 pm) for 18-electron Ru–allenylidene complexes [41] and somewhat longer than in complexes **5** and **9–11**. The C–C distances in the C$_3$-spine, C$_\alpha$–C$_\beta$:

119.0(5) pm (typical range 125–127 pm) and C_β–C_γ: 139.7(5) (typical range 132–135 pm), exhibit noticeable shortening of the internal bond and extension of the terminal bond which indicates an increased level of conjugation in the allenylidene system.

Complex **14** possesses the only pentacoordinate ruthenium center in the series of investigated complexes. The structure is somewhat distorted tetragonal pyramidal. All P–Ru–Cl *cis* angles are smaller than 90° in the range between 87.14(6)° and 89.46(6)° whereas the C_α–Ru–P(Cl) *cis* angles are all larger than 90° in a range between 93.07(18)° and 106.89(16)°. This indicates a strong steric interference of the vinylmethylidene group with the other metal ligands pushing them out of co-planarity with the metal center. This effect can also be seen with the *trans*-angles, P–Ru–P: 166.53(5)° and particularly Cl–Ru–Cl: 150.06(6)°, which are significantly smaller than 180°. The angles in the C_3-spine now are very close to the expected 120° with Ru–C_α–C_β: 124.0(4)° and C_α–C_β–C_γ: 120.1(5)°. In comparison to the previously published pentacoordinate 16-electron ruthenium vinylmethylidene complex (Ru–C_α: 176 pm) [17c,46], the Ru–C_α distance (185.5(5) pm) is somewhat elongated which may be a result of the steric interference with the other metal ligands and/or a result of lower conjugation. The C–C distances in the C_3-spine, C_α–C_β: 146.3(7) pm and C_β–C_γ: 134.9(8), are elongated for the internal and shortened for the terminal bond in comparison the literature complex (C_α–C_β: 138.0 pm and C_β–C_γ: 136.2) [17c] indicating a lower degree of conjugation along the C_3-spine. Such may be a result of the heteroatom substitution at C_α which has become part of the conjugated system.

Due to the chelating acetate ligand, vinylmethylidene complex **15** is distorted octahedral. All *cis*-angles vary in a broad range between 80.11(17)° (the chelate O–Ru–C) and 98.03(5)° (Cl–Ru–Cl) and the three *trans*-angles (C_α–Ru–Cl: 167.14(15)°, P–Ru–P: 177.06(4)°, O–Ru–Cl: 174.69(10)°) are deviating more or less strongly from linearity. The angles along the C_3-spine are larger than 120° (Ru–C_α–C_β: 134.1(3)°, C_α–C_β–C_γ: 130.3(5)°). The Ru–O distance (210.9(3) pm) is much shorter than the Ru–O distances in complexes **9-11**. The Ru–C_α distance (186.2(5) pm) is similar to complex **14**. The C–C distances in the C_3-spine, C_α–C_β: 143.4(7) pm and C_β–C_γ: 134.7(7), are similarly elongated for the internal and shortened for the terminal bond as in complex **14** in comparison the literature vinylmethylidene complex (C_α–C_β: 138.0 pm and C_β–C_γ: 136.2) [17c] as a result of lower conjugation in the C_3-spine.

3. Conclusions

The primary goal of the presented research was to investigate the formation of ruthenium 3-phenylindenylidene complex **3**, precursor to a powerful class of olefin metathesis catalysts, from its precursor **4**. The originally described, synthetic procedure from complex **4** and 1,1-diphenyl-2-propyn-1-ol in thf under reflux lacked reliability

and we have demonstrated that adding catalytic amounts of acetyl chloride under otherwise similar reaction conditions results in complete and reliable formation of this compound. We have identified dinuclear allenylidene complex **5** as a low-reactive intermediate which is formed under non-acidic conditions. Complex **5** can be converted into complex **3** under acidic conditions with 1,1-diphenyl-2-propyn-1-ol in thf, but the conversion is only moderately successful, as long reaction times cause partial formation of degradation products leaving some unreacted complex **5** in the reaction mixture. We conclude that complex **5** may be an intermediate of a lesser reaction pathway to the formation of complex **3**. The reaction of complex **4** and 1,1-diphenyl-2-propyn-1-ol in CH_2Cl_2 under reflux in the presence of excess amounts of conc. HCl afforded the new carbyne complex **7**, an HCl addition product of allenylidene complex **6**. Complex **7** can be completely converted into complex **3** in thf under reflux and thus, complex **7** very likely represents an intermediate of the major pathway to the formation of complex **3**. Complex **7** is a versatile complex and can be converted to different types of carbene complexes. A molecule HCl can be abstracted from complex **7** with triethylamine, a non-coordinating base, to form the new 16-electron allenylidene complex **6** which can be crystallized as 18-electron complexes adding small alcohols (MeOH, EtOH) or water to the vacant coordination site *trans* to the allenylidene group to give complexes **9–11**. The addition of 2-PrOH does not afford stable coordination. Stronger N-donor ligand DMAP (2 equiv.) reacts with complex **7** to give unique diphosphine-mono-N-donor ruthenium allenylidene complex **12** which is formed in contrast to previously reported monophosphine-di-N-donor ruthenium carbene complexes upon addition of N-donor ligands. The formation of complexes **9–12** is unique in comparison to other ruthenium carbene complexes, which proves the relatively strong Lewis acidity of the allenylidene complex **6**. This acidity makes the reaction conditions for the formation of complex **3** plausible. The acid will be needed to form intermediate **7**, preventing the formation of slow-reacting side product **5** with nucleophilic complex **4**. The solvent thf is needed to replace the *trans*-chloride ligand of complex **7** during the reaction to form the cationic intermediate species **8a**. The α-carbon atom of intermediate **8a** has an elevated electrophilicity and thus enables the rearrangement of the allenylidene into the 3-phenylindenylidene group. For the first time, evidence has been produced to formulate a mechanism for the formation of complex **3**. The electrophilicity of the α-carbon atom of complex **7** is also observed in reaction of weakly basic nucleophiles such as methanol and acetic acid which also affords HCl abstraction, however with the nucleophile attacking the α-carbon atom of the carbyne ligand instead of the metal center. The formed vinylmethylidene Fischer-carbene complexes **14** and **15** are produced in high yields. Due to the fact that 2-propanol is not affording this transformation, it is likely that the reactive species are cationic intermediates **8b** and **8c** bearing a methanol or acetic acid

molecule *trans* to the carbyne moiety. A similar intermediate cannot be formed with 2-propanol due to steric constraints as shown in reaction with complex **6**. To the best of our knowledge, complex **15** is the first example of the addition of a carboxylic acid to the α-carbon atom of an allenylidene complex.

4. Experimental

4.1. General procedures

All experiments with organometallic compounds (unless stated otherwise) were performed under dry nitrogen atmosphere using standard Schlenck techniques or in an MBraun drybox ($O_2 < 2$ ppm). NMR spectra were recorded at a Varian Inova Instrument (300.1 MHz for ^{1}H, and 121.4 MHz for ^{31}P). ^{1}H NMR spectra were referenced to the residual solvent (d_6-benzene δ 7.15 ppm, CD_2Cl_2 δ 5.32 ppm), ^{31}P NMR spectra were referenced using H_3PO_4 (δ 0 ppm) as external standard. IR spectra were recorded with a Nicolet Nexus 470 FT-IR instrument. For sonication, a Fischer Scientific Ultrasonic Cleaner FS 30 was used. The bath temperature was set to 30 °C. Crystal data was obtained for complex **14** on a Bruker AXS Smart system, and for complexes **5**, **7**, **9–12** and **15** on an Oxford Diffraction Gemini S system.

4.2. Materials and methods

Diethyl ether and thf were dried by passage through solvent purification (MBraun-Auto-SPS) and CH_2Cl_2, d_6-benzene and CD_2Cl_2 were degassed prior to use. No purification was performed with other solvents. Reagents were purchased from commercial sources and used without further purification. $(PPh_3)_{3-4}RuCl_2$ [26] **4** was prepared according to the literature.

4.3. (PPh$_3$)$_2$Cl$_2$Ru(3-phenylindenylidene) (3) [22]

Method A: Acetyl chloride (0.10 mL, mg, mmol) was added to a solution of $(PPh_3)_{3-4}RuCl_2$ (**4**) (2.032 g, M™ 1000 g/mol, 2 mmol) and 1,1-diphenyl-2-propyn-1-ol (434 mg, 2.09 mmol) in thf (70 mL) and stirred under reflux for 90 min. The purple solution was cooled to room temperature and the solvent was removed under reduced pressure. 2-propanol (50 mL) was added and the residue was dispersed in the solvent under sonication at 30 °C for 30 min. The slurry was filtered in air and washed with 3×20 mL 2-propanol. The residue was dried in a vacuum oven for 3 h at 60 °C to yield pure complex **3** (1.532 g, 1.72 mmol, approx. 86%) as purple powder. *Method B:* Complex **7** (233 mg, 0.252 mmol) was heated in a solution of PPh$_3$ (103 mg, 0.39 mmol) in thf (15 mL) under reflux for 90 min. The work-up procedure was identical with Method A, using 20 mL and 3×10 mL 2-propanol. Yield (186 mg, 0.209 mmol, 83%). *Method C:* Complex **7** (67 mg, 0.073 mmol) was added to a solution of (PPh$_3$)$_{3-4}$ RuCl$_2$ (**4**) (690 mg, approx. 0.690 mmol) and 1,1-diphenyl-2-propyn-1-ol (178 mg, 0.86 mmol) in thf (40 mL) and stirred under reflux for 2 h. The work-up procedure was identical with Method A, using 30 mL and 3×10 mL 2-propanol. Yield (608 mg, 0.684 mmol, approx. 90%).

4.4. (PPh$_3$)$_2$ClRu(μ-Cl)$_3$(PPh$_3$)$_2$Ru=C=C=CPh$_2$ (5)

Method A: A solution of $(PPh_3)_{3-4}RuCl_2$ (**4**) (1.782 g, approx. 1.78 mmol) and 1,1-diphenyl-2-propyn-1-ol (385 mg, 1.85 mmol) in 40 mL thf was heated and stirred under reflux for 45 min. The purple solution was cooled to room temperature and the solvent was removed under reduced pressure. Diethyl ether (50 mL) was added and the residue was dispersed in the solvent under sonication at 30 °C for 30 min. The slurry was filtered in air and washed with 3×20 mL diethyl ether. The residue was dried in a vacuum oven for 60 min at 60 °C to yield pure complex **5** (1.218 g, 0.769 mmol, approx. 86%) as reddish-purple powder. X-ray quality crystals of complex **5** were obtained from a concentrated solution in CH_2Cl_2 containing approx. 4 equiv. of PPh$_3$ by vapor diffusion of diethyl ether in a closed vessel at −20 °C. *Method B:* A solution of $(PPh_3)_{3-4}RuCl_2$ (**4**) (278 mg, approx. 0.278 mmol) and 1,1-diphenyl-2-propyn-1-ol (61 mg, 0.293 mmol) in 15 mL CH_2Cl_2 was heated and stirred under reflux for 2 h. The purple solution was cooled to room temperature and the solvent was removed under reduced pressure. Analogous to Method A, diethyl ether (20 mL) was added and the residue was dispersed in the solvent under sonication at 30 °C for 30 min. The slurry was filtered in air and washed with 3×10 mL diethyl ether. The residue was dried in a vacuum oven for 60 min at 60 °C to yield pure complex **5** (176 mg, 0.110 mmol, approx. 79%) as reddish-purple powder. ^{1}H NMR (CD_2Cl_2, 20 °C, 300.1 MHz) $\delta = 7.66$ (d, $^3J(^1H^1H) = 7.5$ Hz, 4H), 7.62 (m, 4H), 6.90 (t, $^3J(^1H^1H) = 7.5$ Hz, 4H, =C(C$_6$H$_5$)$_2$), 7.28–7.52 (m, 12H), 7.06–7.28 (m, 24H), 6.92–7.06 (m, 18H) 6.76 (m, 6H, P(C$_6$H$_5$)$_3$); ^{31}P NMR (CD_2Cl_2, 20 °C, 121.4 MHz) $\delta = 48.3$ (s, 2P), 39.8 (d, $^2J(^{31}P^{31}P) = 27.8$ Hz, 1P), 38.6 (d, $^2J(^{31}P^{31}P) = 27.8$ Hz, 1P); ^{31}P NMR (CD_2Cl_2, 20 °C, 121.4 MHz) $\delta = 51.4$ (d, $^2J(^{31}P^{31}P) = 37.8$ Hz), 48.9 (d, $^2J(^{31}P^{31}P) = 37.8$ Hz), 40.8 (d, $^2J(^{31}P^{31}P) = 26.6$ Hz), 37.0 (d, $^2J(^{31}P^{31}P) = 26.6$ Hz); IR (20 °C, solid) v (cm^{-1}) 1930 (s, C=C=C).

4.5. (PPh$_3$)$_2$Cl$_3$Ru C–CH=CPh$_2$ (7)

Aqueous HCl$_{conc.}$ (0.3 mL, approx. 3 mmol) was added to a solution of $(PPh_3)_{3-4}RuCl_2$ (**4**) (1.678 g, approx. 1.68 mmol) and 1,1-diphenyl-2-propyn-1-ol (376 mg, 1.81 mmol) in 100 mL CH_2Cl_2 and stirred under reflux for 90 min. The yellow–brown solution was cooled to room temperature and transferred in air into 2-propanol (100 mL). During the transfer, a yellow precipitate was formed. The resulting slurry was reduced to 80 mL under reduced pressure and sonicated at 30 °C for 2 min. The

slurry was filtered in air and washed with 2×20 mL 2-propanol and once with 20 mL of diethyl ether. The residue was dried in a vacuum oven for 2 h at 60 °C to yield pure complex **7** (1.306 g, 1.41 mmol, approx. 84%) as yellow powder. X-ray quality crystals of complex **7** were obtained from a concentrated solution in CH_2Cl_2 containing approx. 4 equiv. of PPh$_3$ by layer-diffusion of an approx. 10-fold volume of 2-propanol in a closed test tube at room temperature. ^{1}H NMR (CD$_2$Cl$_2$, 20 °C, 300.1 MHz) $\delta = 5.67$ (t, $^4J(^{31}P^1H) = 2.4$ Hz, 1H, C$_\beta H$), 7.21 (m, 2H), 7.66–7.78 (m, 6H), 7.44 (d, $^3J(^1H^1H) = 7.5$ Hz, 2H, =C(C$_6H_5$)$_2$), 8.56–8.68 (m, 12H), 7.61–7.68 (m, 18H), 6.92–7.06 (m, 18H, P(C$_6H_5$)$_3$); ^{31}P NMR (CD$_2$Cl$_2$, 20 °C, 121.4 MHz) $\delta = 13.6$.

4.6. $(PPh_3)_2Cl_2Ru{=}C{=}C{=}CPh_2$ (**6**)

Triethylamine (1.0 mL, 0.7 g, 7 mmol) was added to a slurry of complex **7** (289 mg, 0.313 mmol) and PPh$_3$ (125 mg, 0.48 mmol) in methanol (25 mL) under non-inert conditions. After the addition, the vessel was immediately closed with a septum and sonicated for 15 min at 30 °C. During that time, the yellow slurry turned deep red. The slurry was filtered in air and washed with 3×10 mL methanol. The residue was dried in a vacuum oven for 3 h at 60 °C to yield pure complex **6** (198 mg, 0.223 mmol, 71%) as bright red powder. ^{1}H NMR (d_6-benzene, 20 °C, 300.1 MHz) $\delta = 7.40$ (d, $^3J(^1H^1H) = 7.5$ Hz, 4H), 7.08 (m, $^3J(^1H^1H) = 7.5$ Hz, 2H), 6.70 (m, 4H, =C(C$_6H_5$)$_2$), 7.96 (m, 12H), 6.86–7.02 (m, 18H, P(C$_6H_5$)$_3$); ^{31}P NMR (d_6-benzene, 20 °C, 121.4 MHz) $\delta = 30.9$. IR (20 °C, solid) v (cm^{-1}) 1906 (s, C=C=C).

4.7. Crystallization and NMR experiments with complex **6** affording complexes **9**–**11**

Complex **6** (20 mg) and approx. 4 equiv. of PPh$_3$ were dissolved in CH_2Cl_2 (**9**), or a 90:10 v/v mixture of CH_2Cl_2 methanol (**10**), or in a 90:5:5 v/v mixture of CH_2Cl_2, water and 2-propanol (2 mL each) in a scintillation vial and placed in a closed vessel containing diethyl ether (15 mL). The vessel was stored at −20 °C to afford crystals of complexes **9**–**11** suitable for X-ray diffraction after 3–6 days. ^{31}P NMR (d_6-benzene, 20 °C, 121.4 MHz) were obtained adding 2.0 μL of O-donor via microliter syringe to a solution of 2 mg of complex **6** in d_6-benzene (0.6 mL) which was placed in an NMR tube sealed with a rubber septum. **9** (EtOH): $\delta = 27.0$, **10** (MeOH): $\delta = 27.6$, **11** (H$_2$O): $\delta = 27.5$.

4.8. $(PPh_3)_2(C_7H_{10}N_2)Cl_2Ru{=}C{=}C{=}CPh_2$ (**12**)

4-N,N-dimethylaminopyridine (39 mg, 0.32 mmol) was added to a slurry of complex **7** (146 mg, 0.158 mmol) and PPh$_3$ (87 mg) in 2-propanol (15 mL) under non-inert conditions. After the addition, the vessel was immediately closed with a septum and sonicated for 90 min at 30 °C. During that time, the yellow slurry turned deep blue. The slurry

was filtered in air and washed with 3×10 mL methanol. The residue was dried in a vacuum oven for 3 h at 60 °C to yield pure complex **12** (91 mg, 0.090 mmol, 57%) as purplish-blue powder. X-ray quality crystals of complex **12** were obtained from a concentrated solution in CH_2Cl_2 containing approx. 4 equiv. of PPh$_3$ by vapor diffusion of diethyl ether in a closed vessel at −20 °C. ^{1}H NMR (CD$_2$Cl$_2$, 20 °C, 300.1 MHz) $\delta = 8.16$ (d, $^3J(^1H^1H) = 7.5$ Hz, 2H), 5.74 (d, $^3J(^1H^1H) = 7.5$ Hz, 2H), 2.88 (s, 6H, DMAP-H), 6.85-7.73 (m, 40H, =C(C$_6H_5$)$_2$ and P(C$_6H_5$)$_3$); ^{31}P NMR (CD$_2$Cl$_2$, 20 °C, 121.4 MHz) $\delta = 23.2$; IR (20 °C, solid) v (cm^{-1}) 1886 (s, C=C=C).

4.9. $(PPh_3)_2Cl_2Ru{=}C(OCH_3){-}CH{=}CPh_2$ (**14**)

Complex **7** (245 mg, 0.265 mmol) was dispersed in a solution of PPh$_3$ (104 mg, 0.40 mmol) in methanol (15 mL) and heated under reflux open to the air for 15 minutes. In that time, the initially yellow solution turned almost clear and a brown precipitate formed. The precipitate was filtered and washed with 3×10 mL methanol. The residue was dried in a vacuum oven for 3 h at 60 °C to yield pure complex **14** (239 mg, 0.260 mmol, 98%) as yellowish-brown powder. X-ray quality crystals of complex **14** were obtained from a concentrated solution in CH_2Cl_2 containing approx. 4 equiv. of PPh$_3$ by vapor diffusion of diethyl ether in a closed vessel at −20 °C. ^{1}H NMR (CD$_2$Cl$_2$, 20 °C, 300.1 MHz) $\delta = 5.33$ (s, 1H, C$_\beta H$), 3.15 (s, 3H, OCH_3), 6.88–7.66 (m, 40H, =C(C$_6H_5$)$_2$ and P(C$_6H_5$)$_3$); ^{31}P NMR (CD$_2$Cl$_2$, 20 °C, 121.4 MHz) $\delta = 29.7$.

4.10. $(PPh_3)_2Cl_2Ru = C(OAc){-}CH{=}CPh_2$ (**15**)

Complex **7** (178 mg, 0.193 mmol) was dispersed in a solution of PPh$_3$ (132 mg, 0.50 mmol), acetic acid (2.0 mL, 2.1 g, 35 mmol) in 2-propanol (15 mL) in a closed vessel under non-inert conditions and sonicated for 4 h at 30 °C. During that time, the initially yellowish orange slurry turned yellowish-green. The precipitate was filtered and washed with 3×10 mL methanol. The residue was dried in a vacuum oven for 3 h at 60 °C to yield pure complex **15** (117 mg, 0.123 mmol, 64%) as yellowish-green powder. X-ray quality crystals of complex **15** were obtained from a concentrated solution in CH_2Cl_2 containing approx. 4 equiv. of PPh$_3$ by vapor diffusion of diethyl ether in a closed vessel at −20 °C. ^{1}H NMR (CD$_2$Cl$_2$, 20 °C, 300.1 MHz) $\delta = 1.01$ (s, 3H, C(O)–CH_3), 7.47 (m, 2H), 7.03 (d, $^3J(^1H^1H) = 8.1$ Hz, 2H), 6.44 (d, $^3J(^1H^1H) = 8.7$ Hz, 2H), 7.64–7.74 (m, 14H), 7.16–7.37 (m, 21H, =C(C$_6H_5$)$_2$, P(C$_6H_5$)$_3$ and C$_\beta H$); ^{31}P NMR (CD$_2$Cl$_2$, 20 °C, 121.4 MHz) $\delta = 18.3$.

4.11. Crystal structure determinations of complexes **5, 7, 9–12, 15**

Crystals of **5**, C$_{87}$H$_{70}$Cl$_4$P$_4$Ru$_2$, FW = 1583.37, 291(2) K, Mo Kα radiation, triclinic, space group $P\bar{1}$ (#2),

$a = 14.2366(8)$ Å, $b = 15.310(3)$ Å, $c = 18.9961(16)$ Å, $\alpha = 96.095(11)°$, $\beta = 107.802(6)$, $\gamma = 96.796(9)$; $V = 3869.9(9)$ Å^3, $Z = 2$, $d_{calc} = 1.359$ Mg/m^3, 18772 reflections, 874 parameters, $S = 0.895$, R $[I > 2\sigma(I)] = 0.049$, $wR_2 = 0.096$. Crystals of **7**, a tris-dichloromethane solvate (one disordered), $C_{51}H_{39}Cl_3P_2Ru \cdot 3CH_2Cl_2$, FW = 1178.06, 293(2) K, Mo Kα radiation, monoclinic, $P2_1/n$ (#14), $a = 12.1954(3)$ Å, $b = 24.6253(7)$ Å, $c = 18.5432(5)$ Å, $\beta = 102.650(3)°$, $V = 5433.6(3)$ Å^3, $Z = 4$, $d_{calc} = 1.440$ Mg/m^3, 15711 reflections, 602 parameters, $S = 1.136$, R $[I > 2\sigma(I)] = 0.104$, $wR_2 = 0.194$. Crystals of **9**, $C_{53}H_{46}Cl_2OP_2Ru$, FW = 932.81, 293(2) K, MoKα radiation, monoclinic, $P2_1/c$ (#14), $a = 13.6293(4)$ Å, $b = 18.2506(5)$ Å, $c = 18.4184(5)$ Å, $\beta = 99.784(3)°$, $V = 4514.8(2)$ Å^3, $Z = 4$, $d_{calc} = 1.372$ Mg/m^3, 10462 reflections, 539 parameters, $S = 0.917$, R $[I > 2\sigma(I)] = 0.044$, $wR_2 = 0.065$. Crystals of **10**, $C_{52}H_{44}Cl_2OP_2Ru$, FW = 918.78, 296(2) K, Mo Kα radiation, monoclinic, $C2/c$ (#15), $a = 19.0142(10)$ Å, $b = 23.5771(11)$ Å, $c = 19.5359(6)$ Å, $\beta = 91.000(4)°$, $V = 8756.6(7)$ Å^3, $Z = 8$, $d_{calc} = 1.394$ Mg/m^3, 7800 reflections, 523 parameters, $S = 0.730$, R $[I > 2\sigma(I)] = 0.048$, $wR_2 = 0.063$. Crystals of **11**, $C_{51}H_{42}Cl_2OP_2Ru$, FW = 904.76, 293(2) K, Mo Kα radiation, monoclinic, $C2/c$ (#15), $a = 18.907(4)$ Å, $b = 23.587(2)$ Å, $c = 19.5230(18)$ Å, $\beta = 91.249(17)°$, $V = 8704(2)$ Å^3, $Z = 8$, $d_{calc} = 1.381$ Mg/m^3, 9981 reflections, 520 parameters, $S = 0.892$, R $[I > 2\sigma(I)] = 0.066$, $wR_2 = 0.108$. Crystals of **12**, $C_{58}H_{50}Cl_2N_2P_2Ru$, FW = 1008.98, 293(2) K, Mo Kα radiation, monoclinic, Cc (#9), $a = 10.2434(2)$ Å, $b = 20.4633(5)$ Å, $c = 22.7544(6)$ Å, $\beta = 91.500(2)°$, $V = 4768.0(2)$ Å^3, $Z = 4$, $d_{calc} = 1.406$ Mg/m^3, 12506 reflections, 586 parameters, $S = 0.911$, R $[I > 2\sigma(I)] = 0.045$, $wR_2 = 0.069$. Crystals of **15**, an ethoxyethane solvate (ordered), $C_{53}H_{44}Cl_2O_2P_2Ru$. $C_4H_{10}O$, FW = 1020.98, 293(2) K, Mo Kα radiation, monoclinic, $P2_1/n$ (#14), $a = 13.0221(3)$ Å, $b = 16.6652(4)$ Å, $c = 23.0069(5)$ Å, $\beta = 93.545(2)°$, $V = 4983.3(2)$ Å^3, $Z = 4$, $d_{calc} = 1.361$ Mg/m^3, 14699 reflections, 586 parameters, $S = 1.106$, R $[I > 2\sigma(I)] = 0.086$, $wR_2 = 0.175$. Structures were solved with SHELXS-86 [47]; non-H atoms were modeled with anisotropic vibrational parameters, H-atoms were located in difference electron density maps but placed in idealized positions with isotropic vibrational parameters. Structures were corrected for absorption, and refined by full-matrix least-squares using SHELXL-97 [48], and refined to convergence.

4.12. Crystal structure determination of complex 14

Crystals of **14**, an ethoxyethane solvate (ordered), $C_{48}H_{44}Cl_2OP_2Ru$. $C_4H_{10}O$, FW = 992.90, 218(2) K, Mo Kα radiation, monoclinic, $P2_1/c$ (#14), $a = 10.308(5)$ Å, $b = 23.384(12)$ Å, $c = 20.360(10)$ Å, $\beta = 99.042(11)°$, $V = 4846(4)$ Å^3, $Z = 4$, $d_{calc} = 1.361$ Mg/m^3, 8528 reflections, 543 parameters, $S = 1.025$, R $[I > 2\sigma(I)] = 0.050$, $wR_2 = 0.119$. A single crystal of **14** was placed in inert oil, mounted on a glass pin, and transferred to the cold gas stream of the diffractometer. Data were collected using graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. The structure of complex **14** was solved by direct methods using SHELXS-97 and refined using SHELXL-97 [48]. Non-hydrogen atoms were found by successive full-matrix least-squares refinement on F^2 and refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions and refined using a riding model. A disordered diethyl ether solvent molecule was refined isotropically.

Appendix A. Supplementary material

CCDC 651174, 651173, 651172, 651171, 651170, 651169, 652073 and 651168 contain the supplementary crystallographic data for **5**, **7**, **9**, **10**, **11**, **12**, **14** and **15**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.08.005.

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