Cationic Ruthenium Allenylidene Complexes as Catalysts for Ring Closing Olefin Metathesis

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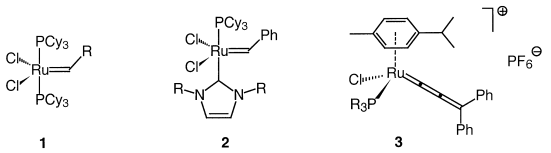
Abstract: A series of well accessible cationic ruthenium allenylidene complexes of the general type $[(\eta^6\text{-arene})(R_3P)RuCl(=C=C=CR'_2)]^+ X^-$ is described which constitute a new class of pre-catalysts for ring closing olefin metathesis reactions (RCM) and provide an unprecedented example for the involvement of metal allenylidenes in catalysis. They effect the cyclization of various functionalized dienes and enynes with good to excellent yields and show a great tolerance towards an array of functional groups. Systematic variations of their basic structural motif have provided insights into the essential parameters responsible for catalytic activity which can be enhanced further by addition of Lewis or Brønsted acids, by irradiation with UV light, or by the adequate choice of the "non-coordinating" counterion X^-. The latter turned out to play a particularly important role in determining the rate and selectivity of the reaction. A similarly pronounced influence is exerted by remote substituents on the allenylidene residue which indicates that this ligand (or a ligand derived thereof) may remain attached to the metal throughout the catalytic process. X-ray crystal structures of the catalytically active allenylidene complexes **3b**·PF_6 and **15**·OTf as well as of the chelate complex **10** required for the preparation of the latter catalyst are reported.

Keywords: alkenes · allenylidenes · catalysts · metathesis · ruthenium

Introduction

The advent of well defined ruthenium-based metathesis pre-catalysts has triggered an explosive growth of interest in this transformation both from the organic and polymer chemists' communities.[1] In particular, the *neutral 16-electron* ruthenium carbene complexes **1** (R = Ph, CH=CPh_2) developed by Grubbs and co-workers turned out to be exceedingly useful tools which set the standards in the field.[2] These reagents combine a high catalytic activity with a good to excellent tolerance towards polar functional groups and have found many applications to the synthesis of complex target molecules and the preparation of speciality polymers.[1, 3] Among the numerous variations on the ligand sphere of **1** carried out in search for an even better application profile,[4] replacement of one phosphine ligand by a N-heterocyclic carbene moiety was recently found to impart a significant increase in activity as well as stability in solution. Therefore it is very likely that complexes of type **2** will gain similar popularity and importance.[5, 6]



Although the rapidly increasing demand has led to the development of improved methods for the preparation of Grubbs carbenes,[7] the recent literature also documents a search for alternative metathesis initiators of comparable performance and improved accessibility.[8] In this context, we have recently introduced the ruthenium allenylidene complex **3**·PF_6 as a versatile pre-catalyst for various ring-closing metathesis (RCM) reactions.[9] This *cationic 18-electron* species not only provides an unprecedented example for the involvement of metal allenylidene complexes in catalytic C–C-bond formation reactions,[10, 11] but is also very easily prepared from commercially available precursors. Moreover, substantial variations of its basic structural motif are possible which hold the promise that the performance and scope of this type of metathesis catalyst can be properly adjusted.

In the following we summarize our investigations in this field. Among the series of allenylidene complexes prepared during the course of this study we were able to identify metathesis pre-catalysts that are significantly more active than compounds **3a**·PF_6 and **3b**·PF_6 originally used. This screen-

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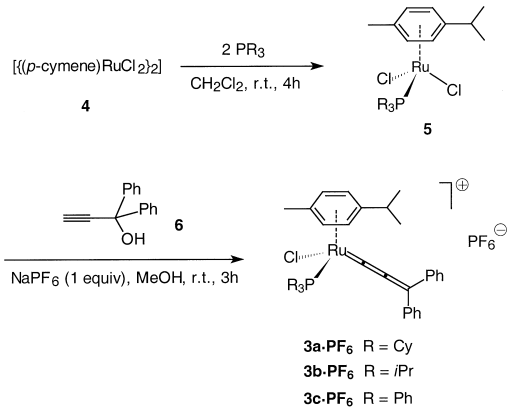
ing has also revealed a subtle, cooperative influence of the individual ligands around the central metal atom and has shown that the seemingly most remote moiety, namely the "non-coordinating" anion, plays a key role in determining the catalytic activity and selectivity of the cationic Ru^{II} template.

Results and Discussion

General synthesis methods: A most attractive feature of cationic complexes such as **3** stems from the ease of formation of the Ru=C bond of their allenylidene entity,[12] which is obtained by reaction of a suitable 16-electron Ru^{II} template formed in situ with a propargyl alcohol in the presence of a non-coordinating anion.

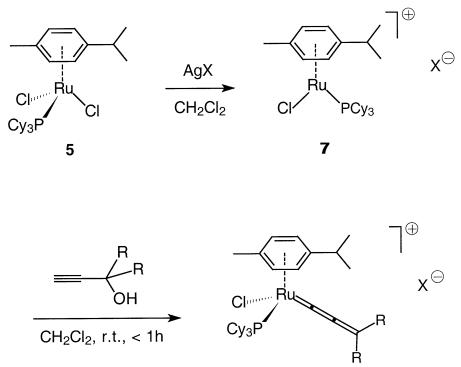
Specifically, treatment of the commercially available, air-stable compound $[\{(p\text{-cymene})RuCl_2\}_2]$ (**4**) with 1 equiv of phosphine leads to the essentially quantitative formation of the corresponding monomeric species $[(p\text{-cymene})(R_3P)RuCl_2]$ (**5**).[13] The latter reacts with propargylic alcohols (e.g. **6**) in the presence of $NaPF_6$ (or $NaBPh_4$ etc.) in MeOH at ambient temperature to form the desired Ru-allenylidene complexes which are obtained as violet to dark-red solids (Method **A**, Scheme 1). As long as the phosphine R_3P is



Scheme 1. Preparation of ruthenium allenylidene complexes under protic conditions (Method **A**).

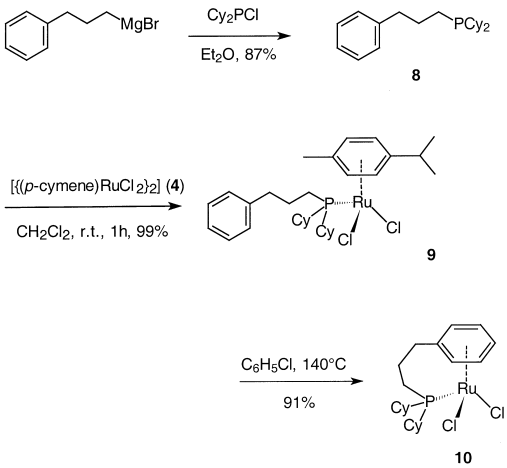
sterically encumbered, subsequent attack of MeOH does not take place on the electrophilic α-C of the resulting allenylidene which would lead to the formation of catalytically inert Fischer-carbene complexes of the type $[(p\text{-cymene})(R_3P)Cl\text{-}Ru{=}CH(OMe){-}CH{=}CPh_2]$.[14]

Replacing the alkali metal salts by AgX ($X = PF_6^-$, OTf^-, BF_4^- etc.) results in an even more practical and flexible method for the preparation of allenylidene complexes under aprotic conditions (Method **B**, Scheme 2).[24] Thus, treatment of compound **5** with AgX in CH_2Cl_2 yields the cationic 16-electron species **7** which can be isolated and stored under argon for several months without noticeable decomposition. Compound **7** reacts rapidly with suitable propargylic alcohol derivatives in CH_2Cl_2 at ambient temperature to afford the corresponding ruthenium allenylidene complexes in excellent yields.



Scheme 2. Preparation of ruthenium allenylidene complexes under aprotic conditions (Method **B**).

As shown in Table 1, these methods give access to a set of structurally diverse ruthenium allenylidene complexes by variation of the phosphine, the allenylidene substituent, and the counterion. Further modifications are possible by replacing the *p*-cymene entity with other arenes as outlined in Scheme 3. Cleavage of the commercial dimer **4** with phos-



Scheme 3. Preparation of the chelate complex **10**.

phine **8** followed by an intramolecular substitution of the cymene ligand in **9** with the tethered phenyl ring at 140 °C in chlorobenzene delivers complex **10**,[15] which is then processed into the allenylidene species **15** as described above according to methods **A** or **B**.

Structure: Crystals suitable for X-ray analysis have been obtained from the allenylidene complexes $[(p\text{-cymene})RuCl(PiPr_3)(=C=C=CPh_2)]PF_6$ (**3b**·PF_6)[16] and $[(\eta^6\text{-}C_6H_5\text{-}(CH_2)_3\text{-}PCy_2)RuCl(=C=C=CPh_2]OTf$ (**15**·OTf)[17] as well as from the chelate complex $[(\eta^6\text{-}C_6H_5\text{-}(CH_2)_3\text{-}PCy_2)RuCl_2]$ (**10**)[18] required for the preparation of the latter catalyst (Figures 1–3, Table 2).

A comparison of these three structures shows significant differences between the neutral complex **10** on one hand and the cationic species **3b**·PF_6 and **15**·OTf on the other hand (see Figure 4). While the arene ring in all three complexes is slightly tilted, leading to a ring slippage of less than 0.1 Å, the neutral species **10** exhibits a significantly shorter Ru-ring

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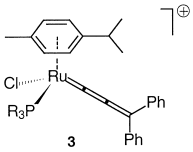
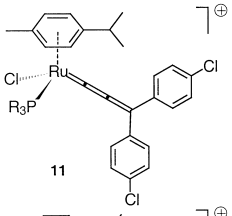
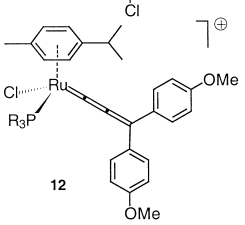
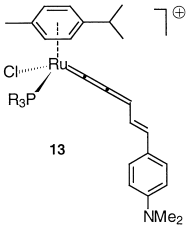
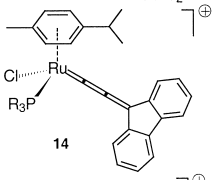
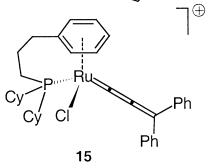
Table 1. Preparation of cationic ruthenium allenylidene complexes.

Allenylidene fragment	R_3P	X^-	Nr	Method	Yield [%]
 3	Ph_3P	PF_6^-	**3c**·PF_6	**A**	93
	$PiPr_3$	PF_6^-	**3b**·PF_6	**A**	95
		OTf^-	**3b**·OTf	**B**	92
	Cy_3P	PF_6^-	**3a**·PF_6	**A**	97
		BPh_4^-	**3a**·BPh_4	**A**	80
		BF_4^-	**3a**·BF_4	**B**	89
		OTf^-	**3a**·OTf	**B**	95
 11	Cy_3P	BF_4^-	**11**·BF_4	**B**	52
		OTf^-	**11**·OTf	**B**	87
 12	Cy_3P	OTf^-	**12**·OTf	**B**	79
 13	Cy_3P	BF_4^-	**13**·BF_4	**B**	80
 14	Cy_3P	BF_4^-	**14**·BF_4	**B**	[a]
 15	–	PF_6^-	**15**·PF_6	**A**	83
		OTf^-	**15**·OTf	**B**	91

[a] Not determined.

centroid distance than its cationic counterparts reflecting the different electronic nature of the Ru^{II} centre. Both allenylidene species show very similar Ru=C bond distances which agree well with that of similar cumulene complexes found in the Cambridge Structural Database [1.88(3) Å for 50 hits]. The C=C double bonds of the allenylidene moiety are of different length, with the one closer to the metal centre being shorter by approximately 0.12(3) Å. The allenylidene moiety is not linear in either complex. This phenomenon is also precedented in the Database and no preference for either angle to deviate more from linearity could be found in the recorded cases.

Furthermore, the trimethylene bridge present in **15**·OTf does not change the geometry around the Ru centre as compared to that of the non-chelated complex **3b**·PF_6. Especially the P-Ru-ring centroid angle lies within the expected value of 131(3)° obtained from 111 observations of ruthenium-(η^6-arene)-phosphine complexes. Similar complexes having only two methylene units in the tether, however, show significant deviations because their P-Ru-ring centroid angles are reduced to 120.65° and 120.73°, respectively.[19]

RCM reactions catalyzed by ruthenium allenylidene complexes: A preliminary assessment of the performance of these complexes in ring-closing metathesis (RCM) using *N*,*N*-diallyltosyl amide (**16**) as the substrate revealed a strong correlation with the nature of the phosphine. In line with previous observations,[2] their catalytic activity decreases in the order $PCy_3 > PiPr_3 \gg PPh_3$ (Table 3). With **3a**·PF_6 (2.5 mol%) as the catalyst, diene **16** is quantitatively cyclized to dihydropyrrole **17** after 4 h reaction time in toluene at 80 °C (entry 5). Dichloromethane can also be used, although the

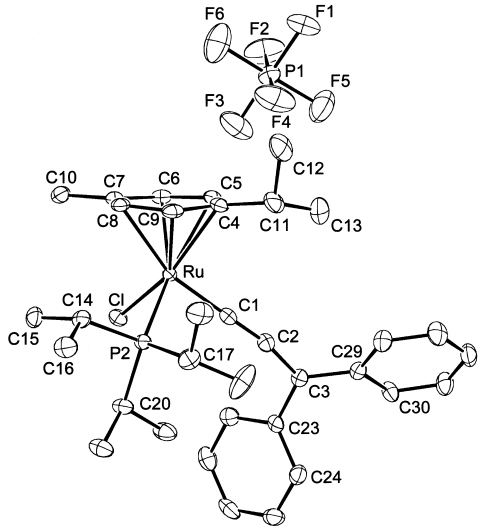


Figure 1. Molecular structure of **3b**·PF_6, anisotropic displacement parameters are drawn at 50% probability, hydrogens atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–C2 1.253(5), C1–Ru 1.894(3), C2–C3 1.361(5), P2–Ru 2.3814(9), Cl–Ru 2.3862(8), C2-C1-Ru 174.6(3), C1-C2-C3 168.8(4), C1-Ru-P2 90.54(10), C1-Ru-Cl 87.07(10), P2-Ru-Cl 88.53(3).

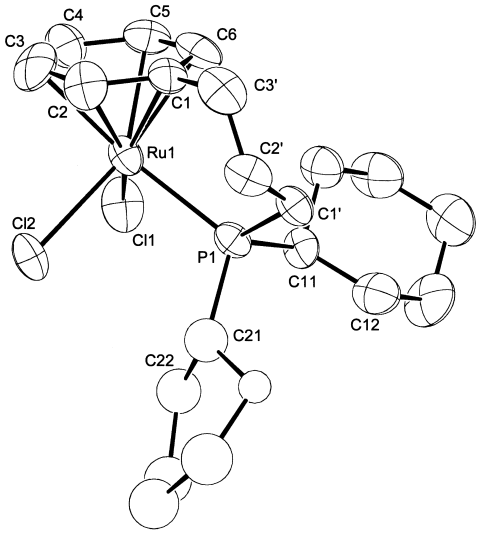


Figure 3. Molecular structure of **10**, anisotropic displacement parameters are drawn at 50% probability, hydrogens atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1–P1 2.347(3), Ru1–Cl1 2.417(3), Ru1-Cl2 2.420(3), P1–C1′ 1.840(12), C1′–C2′ 1.518(16), C2′–C3′ 1.506(18), C3′–C1 1.522(17), P1-Ru1-Cl1 87.13(12), P1-Ru1-Cl2 93.49(11), Cl1-Ru1-Cl2 86.13(12), C1′-P1-Ru1 111.7(4), C2′-C1′-P1 113.5(8), C3′-C2′-C1′ 113.3(10), C2′-C3′-C1 115.1(10), C2-C1-C6 118.9(12), C2-C1-C3′ 121.2(11), C6-C1-C3′ 119.8(11).

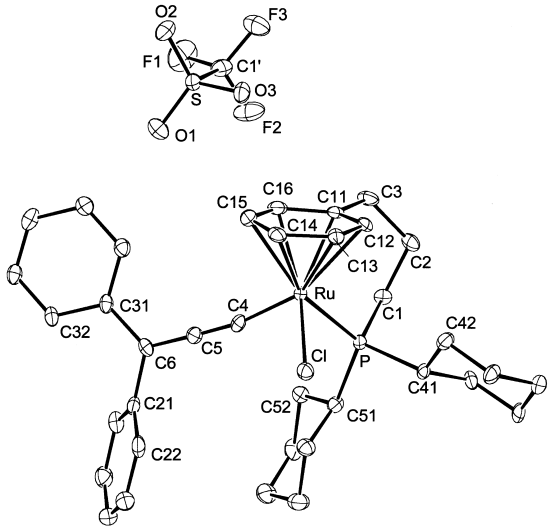


Figure 2. Molecular structure of **15**·OTf, anisotropic displacement parameters are drawn at 50% probability, hydrogens atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru–C4 1.903(4), Ru–P 2.3360(11), Ru–Cl 2.3901(11), P–C1 1.821(4), C1–C2 1.539(5), C2–C3 1.533(6), C3–C11 1.510(6), C4–C5 1.244(5), C5–C6 1.364(5), C4-Ru-P 90.28(12), C4-Ru-Cl 92.41(13), P-Ru-Cl 87.20(4), C1-P-Ru 109.65(14), C2-C1-P 116.5(3), C3-C2-C1 112.2(3), C11-C3-C2 115.2(4), C5-C4-Ru 170.9(4), C4-C5-C6 178.4(5), C16-C11-C12 119.0(4), C16-C11-C3 122.3(4), C12-C11-C3 118.3(4).

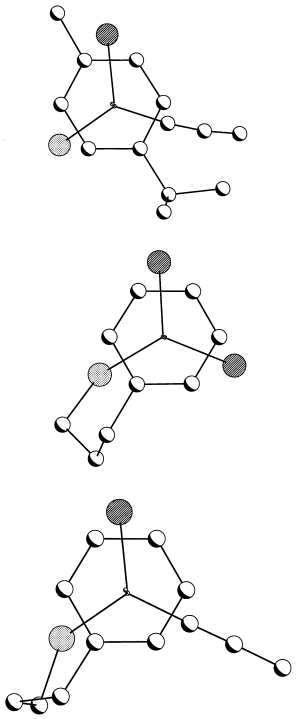


Figure 4. Top view of the η^6-arene moiety and first Ru-ligand sphere in **3b**·PF_6, **10**, and **15**·OTf (top to bottom). Ring centroids and central metal atom are drawn with very small radii to visualize the ring slippage. For all three structures the "matching enantiomers" have been selected with regard to ligand sequence coordinated to the metal atom (chlorine: hatched-, phosphorus: dotted pattern).

turnover frequency of **3b**·PF_6 is lower in this particular reaction medium (entry 3).

Having established the optimum reaction conditions, we applied catalyst **3a**·PF_6 as a "first-generation" allenylidene catalyst for RCM to a set of representative diene substrates. As can be seen from Table 4, it applies to the formation of essentially all ring sizes ≥ 5 and provides good to excellent yields in most of the cases. The results are comparable to those obtained in reactions catalyzed by the ruthenium carbene **1**. Only for the 10-membered ring of jasmine ketolactone **33** (entry 9),[20] and to a minor extent for the bicyclic derivative **31** (entry 8),[21] the allenylidene complex **3a**·PF_6 turned out to be somewhat less efficient. This is tentatively ascribed to its limited stability in toluene solution at 80 °C; the formation of

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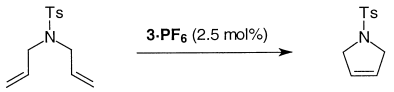
Table 2. Relevant structural data of complexes **3b**·PF_6, **15**·OTf and **10**.

Structural element	**3b**·PF_6	**10**	**15**·OTf
Ru–ring centroid [Å]	1.816	1.701	1.812
P-Ru-ring centroid [°]	128.5	127.3	127.3
Ru–P [Å]	2.3814(9)	2.348(3)	2.337(1)
Ru–Cl [Å]	2.3862(8)	2.417(3)/2.420(3)	2.391(1)
Ru=**C**=C=CPh_2 [Å]	1.894(3)	–	1.903(4)
Ru=**C**=**C**=CPh_2 [Å]	1.253(5)	–	1.245(6)
Ru=C=**C**=**C**Ph_2 [Å]	1.361(5)	–	1.365(5)
Ru=**C**=**C**=CPh_2 [°]	174.6(3)	–	170.9(4)
Ru=**C**=**C**=**C**Ph_2 [°]	168.8(4)	–	178.4(5)

Table 3. Screening of the catalytic activity of the allenylidene complexes **3**·PF_6.



16 17

Entry	Catalyst	Solvent	Additive	T [°C]	t [h]	Yield (%)[a]
1	**3c**·PF_6	toluene	–	80	3	2
2	**3b**·PF_6	toluene	–	80	3	66
3	**3b**·PF_6	CH_2Cl_2	–	40	26	95 (76)
4	**3a**·PF_6	toluene	–	80	3	79
5	**3a**·PF_6	toluene	–	80	4	100 (83)
6	**3a**·PF_6	toluene	cymene (50%)	80	3	47
7	**3a**·PF_6	toluene	PCy_3 (5%)	80	3	31

[a] GC yield (isolated yield).

the medium-sized rings requires particularly long reaction times (up to 100 h) and high dilution conditions, and decomposition of the active species seems to occur with a rate similar to that of productive RCM. Gratifyingly, however, complex **3a**·PF_6 performs well in the macrocyclic series: smooth cyclizations of the conformationally flexible dienes **36** and **38** to the 16- and 18-membered cycloalkenes **37** (entry 11) and **39** (entry 12), have been achieved. As previously described,[22a,b] hydrogenation of compound **37** under standard conditions leads to the macrocyclic musk Exaltolide®, which is used as a valuable perfume ingredient. Furthermore, compound **35** (entry 10) was obtained in good yield which upon deprotection affords the azamacrolide epilachnene, a potent insect repellant alkaloid isolated from the pupae of the Mexican beetle *Epilachnar varivestis*.[22b] Finally, disaccharide **41** obtained by cyclization of the polyfunctional diene **40** (entry 13) constitutes an advanced intermediate en route to tricolorin A, a carcinostatic resin glycoside isolated from *Ipomoea tricolor*.[23]

The examples displayed in Table 4 illustrate the excellent compatibility of the allenylidene catalyst **3a**·PF_6 with various functional groups including ethers, esters, amides, sulfonamides, ketones, acetals, glycosides, carbamates, silyl ethers, aryl halides and even unprotected secondary hydroxyl groups.

Effect of the escorting counterion: In an attempt to identify an even better "second-generation" analogue of **3a**·PF_6, a series of cationic complexes differing in the nature of the counterion has been studied. As can be concluded from Table 5, the counterion exerts a remarkable effect on the reactivity as well as selectivity of ruthenium allenylidene

Table 4. RCM reactions catalyzed by the cationic ruthenium allenylidene complex **3a**·PF_6 (2.5–5 mol%) in toluene at 80 °C.

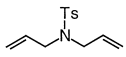
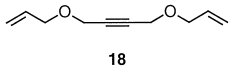
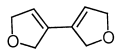
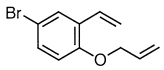
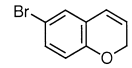
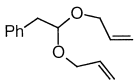
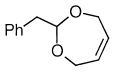
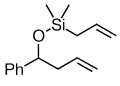
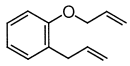
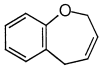
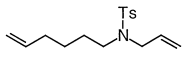
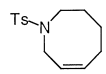
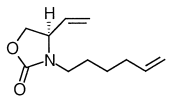
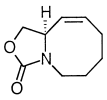
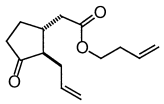
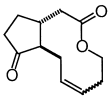
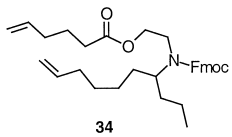
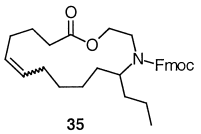
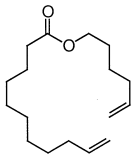
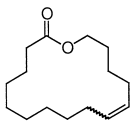
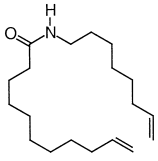
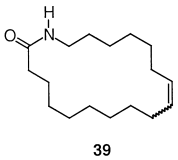
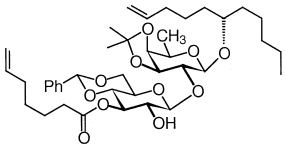
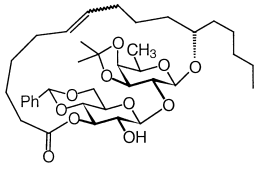
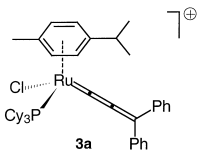
Entry	Substrate	Product	Yield (%)
1	 **16**	 **17**	83
2	 **18**	 **19**	86
3	 **20**	 **21**	93
4	 **22**	 **23**	88
5	 **24**	 **25**	77
6	 **26**	 **27**	86
7	 **28**	 **29**	75
8	 **30**	 **31**	66
9	 **32**	 **33**	40
10	 **34**	 **35**	79
11	 **36**	 **37**	90
12	 **38**	 **39**	73
13	 **40**	 **41**	85

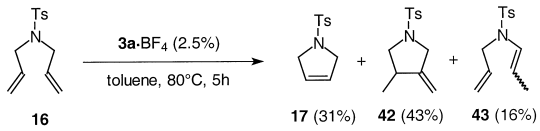
Table 5. Effect of the counterion on the efficiency of cyclization of diene **16** to product **17**.[a]

Allenylidene fragment	Counterion	T [°C]	GC Yield [%]
	PF_6^-	80	95
	BPh_4^-	80	91
	OTf^-	80	99
		20[b]	90
	$B(C_6F_5)_4^-$	80	23
3a	BF_4^-	80	31[c]

[a] The reactions were carried out with 2.5 mol % of the catalyst in toluene for 5 h unless stated otherwise. [b] After 19 h reaction time. [c] Together with the cycloisomerization product **42** (43 %) and isomerized starting material **42** (16 %), see text.

complexes of this type.[24] Whereas cation **3** escorted either by PF_6^-, BPh_4^- or OTf^- leads to excellent results when applied at 80 °C in toluene solution, the particular combination **3**·OTf was found to be effective even at ambient temperature. This improvement is tentatively ascribed to the weakly coordinating character of the triflate group which may assist in the decomplexation of the *p*-cymene ligand from the 18-electron allenylidene pre-catalyst and may also potentially stabilize the resulting 14-electron Ru^{II} species in solution.[25]

In strong contrast, however, the same allenylidene entity **3** having either a $B(C_6F_5)_4^-$ or a BF_4^- counterion behaves poorly and gives rise to significant side reactions. In the latter case, a cycloisomerization of diene **16** to the methylenecyclopentane derivative **42** as well as simple isomerization of the substrate to diene **43** seriously compete with RCM (Scheme 4).[26]



Scheme 4. Effect of the escorting anion: reactivity pattern of complex **3a**·BF_4.

In order to see if this deviation from the regular path is due to the well-known equilibrium between BF_4^- and BF_3+F^- in solution or to the in situ formation of ruthenium hydride species,[26, 27] a series of control experiments has been carried out (Table 6). Surprisingly enough, the addition of nBu$_4$NF results in a dramatic decrease of catalytic activity (entry 2), whereas administering catalytic amounts of $BF_3 \cdot Et_2O$ restores the RCM activity of complex **3**·BF_4 and suppresses cycloisomerization almost completely (entry 3). This result is reminiscent of previous reports that the addition of DCl[28] or certain Lewis acids (CuCl,[29] Ti(OiPr)$_4$[30]) leads to superior results in reactions employing the standard Grubbs catalyst **1**, most likely by removing one of its basic phosphine ligands.

Having excluded that F^- or BF_3 account for the formation of product **42**, we speculated if incidental hydrolysis of **3**·BF_4 liberates traces of HBF_4 which may protonate the Ru^{II} centre and thereby lead to the in situ formation of ruthenium hydride species. In order to investigate this possibility, experiments using complex **3a**·PF_6 were carried out in order to study the response of the system to the addition of excess HBF_4 (20 equiv relative to Ru). Once again, a significantly enhanced catalytic activity for RCM was noticed although at the expense of a much shorter lifetime of the catalyst in solution (Table 6, entry 4). Under these conditions it was possible to cyclize substrate **16** to cycloalkene **17** in excellent yield even at ambient temperature (entry 5). The use of triflic acid instead of HBF_4 is similarly effective (entry 6). In line with the results summarized above, decoordination of the phosphine ligand seems to be responsible for the enhanced activity because the NMR spectrum shows the instantaneous formation of Cy_3PH^+ BF_4^- [^{31}P NMR: $\delta = 32.6$ (d, $J = 467$ Hz); ^{1}H NMR: $\delta = 5.6$ (d m, $J = 467$ Hz)]. Since no cycloisomerization of **16** to product **42** was observed, however, one can exclude that HBF_4 formed in situ upon incidental hydrolysis of **3**·BF_4 plays no role in determining the reaction pathway; the observed product distribution depicted in Scheme 4 therefore reflects the intrinsic reactivity of this particular allenylidene complex.

Effect of the allenylidene residue: Methods **A** and **B** described above allow to prepare a variety of cationic ruthenium complexes differing in the nature of their allenylidene substituents simply by changing the propargylic alcohol reagent.

The allenylidene ligand was found to exert a pronounced influence on the course and selectivity of the catalytic reaction. Thus, it is possible to switch from RCM to predominant cycloisomerization simply by varying the distal *para*-substituents on the phenyl rings of the allenylidene units (Table 7). Note, however, that the trend is different in the OTf^- and in the BF_4^- series (cf. entries 1/5 and 2/6). Although it is too early to rationalize this subtle behaviour, these experiments seem to indicate that the allenylidene moiety (or a ligand derived thereof) serves as a residual ligand to the Ru-template throughout the entire catalytic reaction. This notion

Table 6. Effect of additives on the reactivity and selectivity of cationic allenylidene complexes (2.5 mol %) in reaction with diene **16** in toluene solution.

Entry	Complex	Additive [mol %]	T [°C]	t [h]	Product distribution **17** (%)	**42** (%)
1	**3a**·BF_4	–	80	5	31	43
2		nBu$_4$NF (5 %)	80	4	7.5	
3		$BF_3 \cdot Et_2O$ (10 %)	80	4	97.5	2.5
4	**3a**·PF_6	$HBF_4 \cdot Et_2O$ (50 %)	80	0.5	98	
5		$HBF_4 \cdot Et_2O$ (50 %)	20	1	79	
6		F_3CSO_3H (50 %)	20	1	75	

Table 7. Effect of the allenylidene substituent on the product distribution in reactions of diene **16**.[a]

Entry	Catalyst	Conversion (%)	Product distribution (GC) **17** (%)	**42** (%)	**43** (%)
1	**3a**·BF_4	90	31	43	16
2	**11**·BF_4	97	90	7	–
3	**13**·BF_4	96	60	36	traces
4	**14**·BF_4	85	56	29	traces
5	**3a**·OTf	99	99	–	–
6	**11**·OTf	91	46	45	traces
7	**12**·OTf	99	85	14	–

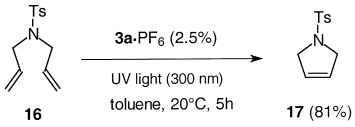
[a] All reactions have been carried out in toluene at 80 °C using 2.5 mol % of the catalyst.

0947-6539/00/0610-1852 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 10

is supported by the fact that the cationic complex **7** lacking the allenylidene unit constitutes a rather poor catalyst for RCM. These results suggest, however, that the allenylidene catalysts described herein differ fundamentally from the Grubbs carbenes **1**, in which the electronic properties of the Ru=CHR fragment of the catalyst precursor intervene only in the initiation phase when this group is cleaved off by reaction with the olefinic substrate and gets replaced by the $Ru=CH_2$ unit of the propagating species.[31] This intriguing aspect is subject of further study in our laboratories.

Photochemical activation: Recently it has been demonstrated that [(*p*-cymene)$RuCl_2(Cy_3P)$] (**5**) converts into an efficient metathesis catalyst upon photochemical irradiation.[8c,d] Although the precise nature of the active species in solution is still unknown, a light-induced decomplexation of the *p*-cymene ligand liberating a reactive 14-electron Ru^{II} entity is believed to trigger the catalytic process. Since a similar dissociation of the arene may occur during the initiation of the allenylidene complexes,[25] experiments have been carried out to see if their reactivity can also be enhanced by photochemical treatment.

Complex **3a**·PF_6 shows absorption maxima at $\lambda_{max} = 516$ nm ($\varepsilon = 5900\,l\,mol^{-1}\,cm^{-1}$) caused by the allenylidene ligand and at $\lambda_{max} = 294$ nm ($\varepsilon = 7800\,l\,mol^{-1}\,cm^{-1}$) attributed to the coordinated arene. In line with our expectations, constant irradiation with UV light (300 nm) near the latter maximum fosters the metathesis activity to such an extent that RCM of diene **16** proceeds at ambient temperature rather than at 80 °C (Scheme 5). Similarly, irradiation of a solution of



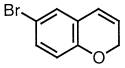
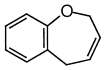
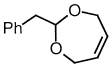
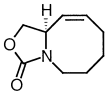
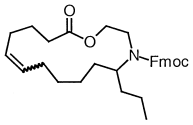
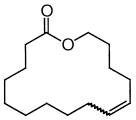
Scheme 5. Photochemical activation of RCM catalyzed by ruthenium allenylidene complexes.

catalyst and substrate for 30 min followed by heating of the mixture to 50 °C in the dark also results in significantly increased reaction rates. This photochemical activation protocol turned out to be particularly convenient in preparative terms and has been successfully applied to a set of enyne substrates which convert into substituted 3-vinyl-2,5-dihydrofuran derivatives under these conditions.[9b]

Catalytic activity of allenylidene chelate complexes: Although the *reactivity* of the "first-generation" ruthenium allenylidene complex **3a**·PF_6 is slightly lower than that of the standard Grubbs carbene **1**, the results summarized above have shown different ways to adjust this parameter either i) by changing the "non-coordinated" anion from PF_6^- to OTf^-, ii) by adding Brønsted or Lewis acids to the reaction mixture, and/or iii) by photochemical means. What remains to be solved, however, is the issue of *stability* which was found to be the limiting factor in applications to the synthesis of medium-sized rings (vide supra). With the idea in mind that chelation may potentially stabilize the propagating species in its "resting" state in solution, we have prepared complexes **15**·PF_6 and **15**·OTf (vide supra) and have checked their particular application profiles (Table 8).

Both of them give satisfactory results with a representative set of substrates although the reaction rates are lower than those of their non-chelated analogues **3a**·PF_6 and **3a**·OTf, respectively. The yield for the rather difficult formation of the [6.3.0]-bicyclic skeleton depicted in entry 5, however, remains rather poor. Therefore we conclude that the lifetime of the actual catalyst in solution has not been increased by introducing the chelating ligand and that the presently available ruthenium allenylidene complexes are outperformed by the more stable carbene catalysts **1** and **2** in applications requiring long reaction times.

Table 8. RCM catalyzed by allenylidene chelate complexes **15**·PF_6 and **15**·OTf.[a]

Entry	Product	**15**·PF_6		**15**·OTf	
		t [h]	Yield [%]	*t* [h]	Yield [%]
1		2	89	1	92
2		16	93		
3		2	86	3	88
4		5.5	88		
5		72	30[b]	150	47[b]
6		41	79		
7				12	83

[a] All reactions were carried out in toluene at 80 °C using 5 mol % of the catalyst unless stated otherwise. [b] With 10 mol % of the catalyst.

Conclusion

A series of well accessible cationic ruthenium allenylidene complexes of the general type [η^6-arene)$(R_3P)RuCl(=C=C=CR'_2)]^+ X^-$ is described which constitute a new class of pre-catalysts for ring closing olefin metathesis reactions (RCM) and provide an unprecedented example for the involvement of metal allenylidene complexes in catalysis. Systematic variations of their basic structural motif have provided insight into the essential parameters responsible for catalytic activity which can be enhanced by using (Lewis) acidic additives, by irradiation with UV light, or by the proper choice of the "non-coordinating" counterion X^-. From the

mechanistic point of view, however, these activation methods seem to intervene at different levels: whereas the most effective counterion OTf^- as well as the photochemical procedure are likely to facilitate the decoordination of the arene ligand and thereby create an electronically unsaturated Ru^{II} template responsible for catalysis in solution, the prime site of interactions of additives such as BF_3 or HBF_4 seems to be the basic phosphine. Furthermore, a pronounced influence of substituents on the allenylidene residue was noticed on the course and selectivity of the reaction which indicates that this ligand (or a ligand derived thereof) may remain attached to the metal throughout the catalytic process. This surprising notion is supported by the fact that we were unable to identify any by-product formed by reaction of the allenylidene unit with the olefinic substrate. Therefore the role of the allenylidene seems to be distinctly different from that of the carbene entity of the classical Grubbs-type catalysts **1** which is cleaved off during the initial activation phase. Together with the lack of direct spectroscopic evidence for the propagating species in solution, these data suggest that the mode of action of cationic ruthenium allenylidene pre-catalysts is rather complex and requires further in-depth physico-chemical studies before a conclusive mechanistic picture can be drawn.

Experimental Section

General: All reactions were carried out under Ar in pre-dried glassware using Schlenk techniques. The solvents were dried by distillation over the following drying agents and were transferred under Ar: toluene (Na/K alloy), CH_2Cl_2 (CaH_2), Et_2O (Mg/anthracene), MeOH (MeONa). Flash chromatography: Merck silica gel 60 (230–400 mesh). NMR: Spectra were recorded on a Bruker AC200 or DMX300 spectrometer in $CDCl_3$ or CD_2Cl_2 as the solvents; chemical shifts (δ) are given in ppm relative to TMS. IR: Nicolet FT-7199. MS (EI): Finnigan MAT 8200 (70 eV). Elemental analyses: Dornis&Kolbe, Mülheim, Germany. All commercially available substrates were used as received.

[(*p*-Cymene)RuCl$_2$(PCy$_3$)] (5): PCy_3 (0.566 g, 2.018 mmol) and [(*p*-cymene)$RuCl_2]_2$ (**4**; 0.618 g, 1.09 mmol) were dissolved in CH_2Cl_2 (40 mL) and the mixture was stirred for 16 h at ambient temperature. The solvent was evaporated, the residue was washed with Et_2O (2 × 25 mL) and dried in vacuo. This afforded the title compound as a red-brown powder (1.06 g, 90 %). ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 26.0$. The other analytical data were in accordance with those reported in the literature.[13]

Preparation of cationic ruthenium allenylidene complexes

Method A: **[(*p*-cymene)RuCl(PCy$_3$)(=C=C=CPh$_2$)]$^+$ [PF$_6$]$^-$ (3a·PF$_6$)**: A solution of $NaPF_6$ (99 mg, 0.589 mmol), [(*p*-cymene)$RuCl_2$(PCy$_3$)] (**5**; 344 mg, 0.586 mmol) and 1,1-diphenylpropynol (**6**; 243 mg, 1.168 mmol) in MeOH (30 mL) was stirred for 3 h at ambient temperature. The solvent was evaporated and the residue was washed with Et_2O (2 × 20 mL) in order to extract the excess of the propargylic alcohol. The crude **3a**·PF_6 was dissolved in CH_2Cl_2 (2 × 10 mL) and the remaining NaCl was filtered off. Evaporation of the solvent, washing of the residue with Et_2O (20 mL) and drying of the product in vacuo afforded complex **3a**·PF_6 as a violet powder (504 mg, 97 %). ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 58.8$ (PCy_3), −140.8 (PF_6^-); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.87$ (d m, 4H, $J = 7.2$ Hz), 7.75 (m, 2H), 7.48 (m, 4H), 6.63 (d m, 1H, $J = 6.6$ Hz), 6.47 (d m, 1H, $J = 6.5$ Hz), 6.11 (d m, 1H, $J = 6.7$ Hz), 6.02 (d m, 1H, $J = 6$ Hz), 2.72 (hept, 1H), 2.20 (br m, 3H), 2.20 (s, 3H), 2.10–0.90 (m, 30H), 1.29 (m, 6H); ^{13}C NMR (75 MHz, CD_2Cl_2, 193 K): $\delta = 282$ (C_α), 187.6 (C_β), 166.2 (C_γ), 144.6, 141.8, 133.5, 132.4, 128.9, 127.8, 127.2, 124.8, 30.8, 26.8, 25.5, 24.3, 23.0, 19.5, 17.8; IR: 3057, 3026, 2932, 2854, 1959, 1594, 1490, 1448, 840, 557 cm^{-1}; anal. calcd for $C_{43}H_{57}ClF_6P_2Ru$: C 58.26, H 6.48; found C 58.39, H 6.44.

[(*p*-Cymene)RuCl(P*i*Pr$_3$)(=C=C=CPh$_2$)]$^+$ [PF$_6$]$^-$ (3b·PF$_6$): A solution of $NaPF_6$ (64 mg, 0.384 mmol), [(*p*-cymene)$RuCl_2$(P*i*Pr$_3$)] (117 mg, 0.251 mmol) and 1,1-diphenylpropynol (**6**; 63 mg, 0.302 mmol) in MeOH (15 mL) was stirred for 4 h at ambient temperature. The solvent was evaporated and the residue was washed with Et_2O (3 × 20 mL). The NaCl formed during the reaction was removed by dissolving the crude **3b**·PF_6 in CH_2Cl_2 (2 × 10 mL). Evaporation of the solvent, washing of the residue with Et_2O (20 mL) and drying of the product in vacuo afforded complex **3b**·PF_6 as a violet powder (182 mg, 95 %). ^{31}P NMR (81 MHz, $CDCl_3$): $\delta =$ 68.14 (P*i*Pr$_3$), −143.69 (PF_6^-); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.86$ (d, 4H, $J = 7.1$ Hz), 7.75 (t, 2H, $J = 7.1$ Hz), 7.48 (t, 4H, $J = 7.1$ Hz), 6.62 (br d, 1H, $J = 6.9$ Hz), 6.54 (br d, 1H, $J = 6.9$ Hz), 6.09 (m, 2H), 3.05–2.50 (m, 4H), 2.33 (s, 3H), 1.51 (d, 3H, $J = 7.2$ Hz), 1.42 (d, 3H, $J = 7.2$ Hz), 1.35–1.10 (m, 18H); IR: 3058, 2932, 2876, 1945, 1587, 1487, 839, 557 cm^{-1}; anal. calcd for $C_{34}H_{45}ClF_6P_2Ru$: C 53.30, H 5.92, P 8.09; found C 53.19, H 5.73, P 8.05.

[(η^6-C$_6$H$_5$-(CH$_2$)$_3$-PCy$_2$)RuCl(=C=C=CPh$_2$)]$^+$ [PF$_6$]$^-$ (15·PF$_6$): The title complex was prepared according to **Method A** from substrate **10** (227 mg, 0.465 mmol), $NaPF_6$ (80 mg, 0.476 mmol) and 1,1-diphenylpropynol (**6**; 193 mg, 0.927 mmol) in MeOH (15 mL). Dark-red powder (301 mg, 81 %). ^{1}H NMR (200 MHz, CD_2Cl_2): $\delta = 7.99$ (m, 2H), 7.81 (m, 4H), 7.58 (m, 4H), 6.61 (m, 1H), 6.46 (m, 2H), 6.34 (m, 1H), 5.50 (m, 1H), 2.63 (m, 3H), 1.95–1.23 (m, 25H); ^{31}P NMR (121.5 MHz, CD_2Cl_2): $\delta = 49.6$, 140.7; IR: 3058, 3025, 2926, 2850, 1966, 1583, 1490, 1445, 840, 747, 698, 557 cm^{-1}; anal. calcd for $C_{36}H_{43}ClF_6P_2Ru$: C 54.88, H 5.50; found C 54.56, H 5.59.

Method B: **Preparation of [(*p*-cymene)RuCl(PCy$_3$)]$^+$ [OTf]$^-$ (7·OTf)**: A solution of [(*p*-cymene)$RuCl_2$(PCy$_3$)] (**5**; 533 mg, 0.91 mmol) in CH_2Cl_2 (45 mL) was added to silver triflate (234 mg, 0.91 mmol). The mixture was stirred for 1 h at room temperature. The solution was filtered and the solvent was evaporated to dryness. Product **7**·OTf (605 mg, 95 %) was obtained as a microcrystalline red powder. ^{31}P NMR (81 MHz, CD_2Cl_2): $\delta = 28.5$ (PCy_3) ^{1}H NMR (200 MHz, $CDCl_3$): 5.8–5.4 (m,4H), 2.77 (hept, 1H, $J = 6$ Hz), 2.37 (m, 3H), 2.11 (s, 3H), 1.95–1.05 (m, 30H), 1.27 (d, 6H, $J = 6$ Hz); anal. calcd for $C_{29}H_{47}ClF_3PSO_3Ru$: C 49.74, H 6.76; found C 49.65, H 6.98.

[*p*-(Cymene)RuCl(PCy$_3$)(=C=C=CPh$_2$)]$^+$ [OTf]$^-$ (3a·OTf): The cationic complex **7** (128 mg, 0.183 mmol) and 1,1-diphenylpropynol (**6**; 60 mg, 0.288 mmol) were dissolved in CH_2Cl_2 (15 mL) and the mixture was stirred for 1 h at room temperature. After filtration and evaporation of the solvent, the residue was washed with diethyl ether (2 × 30 mL) and the product was dried in vacuo. This afforded complex **3**·OTf as a violet powder (155 mg, 95 %). ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 59.21$ (PCy_3); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.87$ (d, 4H, $J = 7$ Hz), 7.74 (t, 2H, $J = 7$ Hz), 7.47 (t, 4H, $J =$ 7 Hz), 6.69 (d, 1H, $J = 6$ Hz), 6.52 (d, 1H, $J = 6$ Hz), 6.29 (d, 1H, $J = 6$ Hz), 6.1 (d, 1H, $J = 6$ Hz), 2.71 (hept, 1H, $J = 7$ Hz), 2.25 (m, 3H), 2.20 (s, 3H), 1.90–1.10 (m, 30H), 1.3 (d, 6H, $J = 7$ Hz); IR: 1957 cm^{-1}; anal. calcd for $C_{44}H_{57}ClF_3PSO_3Ru$: C 59.31, H 6.45; found C 59.26, H 6.55.

[*p*-(Cymene)RuCl(PCy$_3$)(=C=C=CPh$_2$)]$^+$ [BF$_4$]$^-$ (3a·BF$_4$): A solution of $AgBF_4$ (70 mg, 0.359 mmol), [(*p*-cymene)$RuCl_2$(PCy$_3$)] (**5**; 210 mg, 0.359 mmol) and 1,1-diphenylpropynol (**6**; 77 mg, 0.37 mmol) in CH_2Cl_2 (20 mL) was stirred for 1 h at room temperature. The solution was decanted, filtered and the solvent was evaporated. The residue was washed with Et_2O (2 × 30 mL) and dried, thus affording complex **3a**·BF_4 as a violet powder (249 mg, 84 %). ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 59.1$ (PCy_3); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.87$ (d, 4H, $J = 7$ Hz), 7.74 (t, 2H, $J = 7$ Hz), 7.47 (t, 4H, $J = 7$ Hz), 6.69 (d, 1H, $J = 6$ Hz), 6.51 (d, 1H, $J = 6$ Hz), 6.24 (d, 1H, $J = 6$ Hz), 6.06 (d, 1H, $J = 6$ Hz), 2.71 (hept, 1H, $J = 7$ Hz), 2.19 (m, 3H), 2.20 (s, 3H), 1.95–1.05 (m, 30H), 1.29 (d, 6H, $J = 7$ Hz); IR: 1958 cm^{-1}; anal. calcd for $C_{43}H_{57}BClF_4PRu$: C 62.36, H 6.94; found C 62.48, H 7.04.

[*p*-(Cymene)RuCl(PCy$_3$)(=C=C=C(Ph-*p*-Cl)$_2$)]$^+$ [BF$_4$]$^-$ (11·BF$_4$): Complex **11**·BF_4 (295 mg, 52 %) was obtained as a violet powder according to the same procedure from $AgBF_4$ (118 mg, 0.61 mmol), [(*p*-cymene)-$RuCl_2$(PCy$_3$)] (**5**; 359 mg, 0.61 mmol) and 1,1-di(*p*-chlorophenyl) propynol (180 mg, 0.65 mmol) in CH_2Cl_2 (30 mL). ^{31}P NMR (81 MHz, $CDCl_3$): $\delta =$ 60.47 (s, PCy_3); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.00–2.10$ (m, 30H), 1.30 (d, 3H, $J = 7$ Hz), 1.32 (d, 3H, $J = 7$ Hz), 2.21 (s, 3H), 2.32 (m, 3H), 2.70 (hept, 1H, $J = 7$ Hz), 6.17 (d, 1H, $J = 6.5$ Hz), 6.31 (d, 1H, $J = 6.5$ Hz), 6.55 (d, 1H, $J = 6.5$ Hz), 6.72 (d, 1H, $J = 6.5$ Hz), 7.45 (m, 4H), 7.79 (m, 4H); IR: 1956 cm^{-1}; anal. calcd for $C_{43}H_{55}BCl_3F_4PRu$: C 57.57, H 6.18; found C 57.60, H 6.30.

[*p*-(Cymene)RuCl(PCy$_3$)(=C=C=C(Ph-*p*-OMe)$_2$)]$^+$ [OTf]$^-$ (12·OTf): The cationic complex **7** (140 mg, 0.2 mmol) and 1,1-di(*p*-methoxyphenyl)

0947-6539/00/0610-1854 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 10

propynol (**6**; 108 mg, 0.4 mmol) were dissolved in CH_2Cl_2 (15 mL) and the mixture was stirred for 1 h at room temperature. After filtration and evaporation of the solvent, the residue was washed with diethyl ether (2×30 mL) and the resulting product was dried in vacuo, thus affording complex **12**·OTf as a violet powder (151 mg, 79%). ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 53.70$ (PCy_3); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.96 - 6.92$ (m, 8H), 6.60 (d, 1H, $J = 6$ Hz), 6.42 (d, 1H, $J = 6$ Hz), 6.11 (d, 1H, $J = 6$ Hz), 5.85 (d, 1H, $J = 6$ Hz), 3.85 (s, 6H), 2.74 (hept, 1H, $J = 7$ Hz), 2.19 (s, 3H), 2.35–2.19 (m, 3H), 2.02–1.03 (m, 30H), 1.27 (d, 6H, $J = 7$ Hz); IR: 1973 cm^{-1}; anal. calcd for $C_{46}H_{61}ClF_3PSO_5Ru$: C 58.13, H 6.47; found C 58.12, H 6.51.

[(*p*-Cymene)RuCl(PCy$_3$)(=C=C=CH–CH=CH(Ph-*p*-NMe$_2$)]$^+$ [BF$_4$]$^-$ (13·BF$_4$): The title complex (558 mg, 80%) was obtained as a violet powder according to the same procedure from $AgBF_4$ (166 mg, 0.85 mmol), [(*p*-cymene)$RuCl_2(PCy_3)$] (**5**; 498 mg, 0.85 mmol) and 1-(*p*-dimethylaminostyryl)propynol (175 mg, 0.87 mmol) in CH_2Cl_2 (35 mL). ^{31}P NMR (81 MHz, $CDCl_3$): $\delta = 39.98$ (s, PCy_3); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta =$ 8.86 (s, 1H), 7.37 (d, 2H, $J = 8.2$ Hz), 6.91 (d, 2H, $J = 8.2$ Hz), 6.37 (d, 1H, $J = 5.4$ Hz), 5.87 (d, 1H, $J = 6.4$ Hz), 5.64 (s, 2H), 5.46 (d, 1H, $J = 5.4$ Hz), 5.31 (d, 1H, $J = 6.4$ Hz), 3.20–2.60 (br, 7H), 2.30 (br, 3H), 2.05 (s, 3H), 1.27 (d, 6H, $J = 6.9$ Hz), 1.95–1.00 (m, 30H); IR: 1949, 1610 cm^{-1}.

Dicyclohexyl-(3-phenylpropyl)phosphine (8): A solution of 1-bromo-3-phenylpropane (2.389 g, 12 mmol) in Et_2O (25 mL) was added to a stirred suspension of Mg turnings (583 mg, 24 mmol) in Et_2O (10 mL) at such a rate as to maintain gentle reflux. Stirring was continued for 1 h before unreacted Mg was filtered off. A solution of Cy_2PCl (2.528 g, 10.8 mmol) in Et_2O (20 mL) was slowly added to the filtrate at 0 °C and the mixture was kept at that temperature for another 40 min. For work-up, the reaction was quenched with carefully degassed aq. sat. NH_4Cl (50 mL), the aqueous phase was extracted with Et_2O (2×100 mL), the combined organic layers were dried over Na_2SO_4 and the solvent was removed in vacuo. Compound **8** precipitated from the crude product upon standing at room temperature as colourless crystals (2.987 g, 87%). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta =$ 7.31–7.14 (m, 5H), 2.69 (t, $J = 7.7$ Hz, 2H),1.83–1.70 (m, 12H), 1.60–1.36 (m, 4H), 1.24–1.14 (m, 10H); ^{13}C NMR (75.5 MHz): $\delta = 142.6$ (s), 128.5 (s), 128.3 (s), 125.7 (s), 37.7 (d, $J = 12.4$ Hz), 33.5 (d, $J = 13.4$ Hz), 30.6 (s), 30.4 (d, $J = 8.4$ Hz), 29.2 (d, $J = 8.6$ Hz), 27.6–27.4 (m, 4C), 26.7 (s), 21.1 (d, $J = 17.2$ Hz); ^{31}P NMR (121.5 MHz): $\delta = -4.65$; IR: 3026, 2924, 2850, 1604, 1496, 1447, 744, 698 cm^{-1}; MS (EI): *m*/*z* (rel. intensity): 316 (44), 251 (9), 234 (28), 225(41), 212 (23), 192 (17), 151 (29), 130 (100), 117 (18), 91 (20), 83 (41), 55 (74), 41 (47); anal. calcd for $C_{21}H_{33}P$: C 79.70, H 10.51; found C 79.62, H 10.43.

[(*p*-Cymene)$RuCl_2${P(CH$_2$CH$_2$CH$_2$Ph)Cy$_2$}] (9): A solution of [{(*p*-cymene)$RuCl_2$}$_2$] (**4**; 484 mg, 0.789 mmol) and phosphine **8** (500 mg, 1.579 mmol) in CH_2Cl_2 (10 mL) was stirred for 1 h at ambient temperature, the solvent was removed in vacuo, and the residue was recrystallized from THF providing the title complex as a brick-red crystalline solid (785 mg, 79%). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 7.29 - 7.10$ (m, 5H), 5.53–5.49 (m, 4H), 2.77 (q, $J = 6.9$ Hz, 1H), 2.58 (t, $J = 7.6$ Hz, 2H), 2.26–2.21 (m, 2H), 2.18–2.05 (m, 4H), 2.05 (s, 3H), 1.89–1.72 (m, 12H), 1.48–1.42 (m, 2H), 1.38–1.20 (m, 6H), 1.26 (d, $J = 7.0$ Hz, 6H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta =$ 142.2, 128.6, 128.3, 125.9, 107.7, 94.5, 88.5, 88.4, 83.5, 83.4, 30.8, 22.2, 17.9, 37.6–19.2 (19C); ^{31}P NMR (121.5 MHz, CD_2Cl_2): $\delta = 24.69$; IR: 3058, 3024, 2921, 2848, 1602, 1583, 1539, 1495, 1445, 1385, 1270, 747, 699 cm^{-1}; anal. calcd for $C_{31}H_{47}Cl_2PRu$: C 59.80, H 7.61; found: C 59.88, H 7.54.

[(η^6-C$_6$H$_5$-(CH$_2$)$_3$-PCy$_2$)$RuCl_2$] (10):[18] A solution of complex **9** (259 mg, 0.415 mmol) in chlorobenzene (20 mL) was heated to 140 °C for 18 h. After the mixture had been allowed to cool to ambient temperature, the solvent was removed in vacuo, the residue was dissolved in chlorobenzene (1 mL) and the product was precipitated upon slow addition of EtOH. The solids were filtered off and dried in vacuo affording complex **10** as orange crystals (186 mg, 91%). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 6.21$ (t, $J = 5.9$ Hz, 1H), 5.61 (t, $J = 5.8$ Hz, 2H), 5.08 (d, $J = 5.2$ Hz, 2H), 2.49–2.34 (m, 4H), 2.03–1.65 (m, 14H), 1.38–1.19 (m, 10H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta =$ 97.2, 97.1, 96.3, 93.3, 93.2, 80.3, 33.3 (d, $J = 23.7$ Hz), 29.9 (s), 29.0 (d, $J = 1.8$ Hz), 27.7 (s), 27.6 (d, $J = 8.5$ Hz), 27.0 (d, $J = 10.3$ Hz), 26.2 (d, $J = 1.6$ Hz), 25.1 (d, $J = 2.8$ Hz), 15.5 (d, $J = 24.4$ Hz). ^{31}P NMR (121.5 MHz, CD_2Cl_2): $\delta =$ 29.3; IR: 3053, 2928, 2915, 2850, 1504, 1445, 1263, 1115, 806 cm^{-1}; MS (EI): *m*/*z* (rel. intensity): 488 (18), 453 (32), 415 (100), 368 (24), 287 (7), 249 (51), 211 (11), 146 (7), 115 (3), 91 (17), 41 (46) cm^{-1}; anal. calcd for $C_{21}H_{33}Cl_2PRu$: C 51.64, H 6.80; found: C 51.42, H 6.74.

[(η^6-C$_6$H$_5$-(CH$_2$)$_3$-PCy$_2$)RuCl(=C=C=CPh$_2$)]$^+$ OTf$^-$ (15·OTf): AgOTf (103 mg, 0.401 mmol) was added to a solution of complex **10** (197 mg, 0.403 mmol) in CH_2Cl_2 (10 mL). The reaction mixture was stirred for 1 h at ambient temperature, the precipitated silver salts were filtered off and the filtrate was evaporated to dryness affording [{η^6-C$_6$H$_5$-(CH$_2$)$_3$-PCy$_2$}RuCl]$^+$ OTf$^-$ as an orange red powder (214 mg, 88%). A solution of this cationic complex (136 mg, 0.226 mmol) and 1,1-diphenylpropynol (**6**; 47 mg, 0.226 mmol) in CH_2Cl_2 (2 mL) was stirred for 1 h at ambient temperature. Filtration of insoluble residues, evaporation of the solvent, tituration of the crude product with diethyl ether (2×20 mL), followed by drying of the remaining solid in vacuo afforded the title complex as a violet powder (164 mg, 91%). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 8.00 - 7.97$ (m, 4H), 7.84–7.79 (m, 2H), 7.59–7.54 (m, 4H), 6.66 (d, $J = 6.3$ Hz, 1H), 6.49–6.44 (m, 1H), 6.35–6.33 (m, 1H), 5.67–5.65 (m, 1H), 2.64 (m, 3H), 1.89–1.72 (m, 12H), 1.48–1.12 (m, 10H), 0.88–0.86 (m, 2H), 0.63–0.59 (m, 1H); ^{13}C NMR (75 MHz, CD_2Cl_2, 193 K): $\delta = 281.6$ (d, $J = 20.5$ Hz), 181.6, 169.0, 141.3, 134.0, 132.9, 128.8, 109.1, 105.3, 100.1, 87.0, 36.8 (d, $J = 28.6$ Hz), 30.9 (d, $J = 25.2$ Hz), 29.3, 28.0, 26.5 (d, $J = 13.3$ Hz), 25.9 (d, $J = 18.6$ Hz), 25.2 (d, $J = 15.7$ Hz), 23.9, 14.6; ^{31}P NMR (121.5 MHz, CD_2Cl_2): $\delta = 49.9$; IR: 3058, 2921, 2849, 1965, 1585, 1443, 1260, 1149, 1029, 695 cm^{-1}; MS (ESI pos): *m*/*z*: 643 $[M]^+$; anal. calcd for $C_{37}H_{43}ClF_3O_3PRuS$: C 56.09, H 5.47; found C 55.82, H 5.34.

Representative procedures for RCM

***N*-Tosyl-2,5-dihydropyrrole (17)**: A solution of *N*,*N*-diallyltosylamide (**16**) (259 mg, 1.03 mmol) and the allenylidene complex **3a**·PF_6 (22 mg, 0.0248 mmol, 2.4 mol%) in toluene (5 mL) was stirred for 4 h at 80 °C. The solvent was evaporated and the crude product purified by flash chromatography using diethyl ether/pentane (1:4) as the eluent. This afforded the title compound as a colourless solid (191 mg, 83%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 2.40$ (s, 3H), 4.10 (s, 4H), 5.63 (s, 2H), 7.30 (dm, 1H, $J = 8.6$, 0.7 Hz), 7.70 (dm, 1H, $J = 8.3$, 1.9 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 21.1$, 54.5, 125.1, 129.3, 129.4, 139.2, 143.1; IR (KBr): 3093, 3047, 2951, 2909, 2854, 1928, 1817, 1595, 1540 cm^{-1}; MS: *m*/*z* (rel. intensity): 223 (28) $[M]^+$, 155 (28), 91 (72), 68 (100), 41 (19); $C_{11}H_{13}NO_2S$ (223.3): anal. calcd C 59.17, H 5.83, N 6.27, S 14.36; found C 59.26, H 5.91, N 6.22, S 14.36.

Compounds **19**,[32] **21**,[33] **23**,[34] **25**[35] and **27**[36] were prepared analogously. Their spectral and analytical data are in full agreement with those reported in the literature.

Pentadec-10-enolide (37): **Method A**: Solutions of diene **36** (134 mg, 0.503 mmol) and the ruthenium allenylidene complex **3a**·PF_6 (22 mg, 0.0248 mmol, 4.9 mol%) in toluene (50 mL each) were added over a period of 24 h through two dropping funnels to toluene (25 mL) at 80 °C. Stirring was continued for another 16 h at that temperature prior to evaporation of the solvent and purification of the residue by flash chromatography using diethyl ether/pentane (1:30) as the eluent. This afforded macrocycle **37** as a colourless syrup (108 mg, 90%, *E*/*Z*-mixture).

Method B: A solution of diene **36** (27.9 mg, 0.104 mmol) and of the ruthenium allenylidene complex **15**·OTf (5.3 mg, 0.006 mmol, 6 mol%) in toluene (100 mL) was stirred for 12 h at 80 °C. The solvent was evaporated and the crude product was purified by flash chromatography using diethyl ether/pentane (1:30) as the eluent. This afforded macrocycle **37** as a colourless syrup (20 mg, 0.086 mmol, 83%, *E*/*Z*-mixture). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 5.45 - 5.28$ (m, 2H), 4.18–4.07 (m, 2H), 2.37–2.29 (m, 2H), 2.10–2.00 (m, 4H), 1.72–1.54 (m, 4H), 1.49–1.30 (m, 10H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta =$ 173.9, 131.7, 130.4, 130.1, 129.6, 64.1, 64.0, 34.7, 33.9, 32.0, 29.1, 28.4, 28.4, 28.3, 28.2, 28.1, 28.0, 27.9, 27.6, 27.2, 27.1, 26.6, 26.5, 25.4, 25.2; IR (KBr): 3000, 2928, 2856, 1736, 1461, 1385, 1346, 1252, 1234, 1168, 1152, 1113, 1085, 1024, 969, 719 cm^{-1}; MS: *m*/*z* (rel. intensity): 238 (20) $[M]^+$, 210 (18), 109 (17), 96 (49), 82 (100), 67 (64), 55 (64); $C_{15}H_{26}O_2$ (228.37): calcd C 75.58, H 10.99; found C 75.65, H 11.08.

Compounds **29**,[37] **31**,[21] **33**,[20] **35**,[22b] **39**[22b] and **41**[23] were prepared analogously. Their spectral and analytical data are in full agreement with those reported in the literature.

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[16] Crystal data for compound **3b**·PF_6: $C_{34}H_{45}F_6P_2ClRu$, $M = 766.16\ g\,mol^{-1}$, dark-green crystal with dimensions $0.32 \times 0.32 \times 0.11$ mm, monoclinic *C*2/c (no. 15), at 100 K: $a = 24.2158(10)$, $b = 9.0214(10)$, $c = 30.7593(10)$ Å, $\beta = 93.460(10)^\circ$, $V = 6707.4(8)$ Å^3, $Z = 8$, $\varrho = 1.517\ Mg\,m^{-3}$, $\mu = 0.700\ mm^{-1}$, $\lambda = 0.71069$ Å. X-ray diffraction data for this structure and **15**·OTf were collected using a Siemens SMART-CCD area detector diffractometer employing ω-scans to cover reciprocal space up to $\theta = 27.00^\circ$ with 98.2% completeness, integration of raw data yielded a total of 28486 reflections, merged into 7212 unique reflections with *R*int = 0.0332 after applying Lorentz, polarisation and absorption corrections. All structures were solved by direct methods using SHELXS-97,[38] and atomic positions and displacement parameters were refined using full matrix least-squares based on F^2 using SHELXL-97.[39] Refinement of 473 parameters using all reflections converged at $R = 0.0423$, $wR = 0.1099$, highest residual electron density peak $1.450\ e\,Å^{-3}$. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-132986. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[17] Crystal data for **15**·OTf: $C_{37}H_{43}O_3F_3PSClRu$, $M = 792.26\ g\,mol^{-1}$, dark-red crystals with dimensions $0.18 \times 0.14 \times 0.08$ mm, triclinic $P\bar{1}$ (no. 2), at 100 K: $a = 9.5300(6)$, $b = 10.7797(7)$, $c = 18.8926(12)$ Å, $\alpha = 99.572(2)$, $\beta = 99.855(2)$, $\gamma = 111.010(2)^\circ$, $V = 1729.53(19)$ Å^3, $Z = 2$, $\varrho = 1.521\ Mg\,m^{-3}$, $\mu = 0.690\ mm^{-1}$, $\lambda = 0.71073$ Å. X-ray diffraction data using ω scans up to $\theta = 33.72^\circ$ with 71.1% completenes, yielded a total of 15062 reflections, 9813 unique with *R*int = 0.0558. Refinement of 424 parameters using all reflections converged at $R = 0.0602$, $wR = 0.1238$, highest residual electron density peak $1.025\ e\,Å^{-3}$. CCDC-132988.

[18] Crystal data for compound **10**: $C_{21}H_{33}PCl_2Ru$, $M = 488.41\ g\,mol^{-1}$, orangebrown crystals with dimensions $0.18 \times 0.06 \times 0.02$ mm, monoclinic $P2_1/c$ (no. 14), at 293 K: $a = 16.879(3)$, $b = 8.8795(18)$, $c = 14.917(3)$ Å, $\beta = 106.03(3)^\circ$, $V = 2148.9(8)$ Å^3, $Z = 4$, $\varrho = 1.510\ Mg\,m^{-3}$, $\mu = 1.055\ mm^{-1}$, $\lambda = 0.71073$ Å. X-ray diffraction data were collected using an Enraf-Nonius Kappa area detector diffractometer using ω scans up to $\theta = 25.00^\circ$ with 92.6% completeness, yielding a total of 9042 reflections, 3760 unique with *R*int = 0.0838. Refinement of 208 parameters using all reflections converged at $R = 0.0828$, $wR = 0.2646$, highest residual electron density peak $1.850\ e\,Å^{-3}$. CCDC-132987.

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