η^6-Mesityl,η^1-Imidazolinylidene – Carbene – Ruthenium(II) Complexes: Catalytic Activity of their Allenylidene Derivatives in Alkene Metathesis and Cycloisomerisation Reactions

Bekir Çetinkaya,*[a] Serpil Demir,[b] Ismail Özdemir,[b] Loïc Toupet,[c] David Sémeril,[d] Christian Bruneau,[d] and Pierre H. Dixneuf*[d]

Abstract: The reaction of electron-rich carbene-precursor olefins containing two imidazolinylidene moieties [(2,4,6-$Me_3C_6H_2CH_2$)$\overline{NCH_2CH_2N(R)C}$=]$_2$ (**2a**: R = CH_2CH_2OMe, **2b** R = CH_2Mes), bearing at least one 2,4,6-trimethylbenzyl (R = CH_2Mes) group on the nitrogen atom, with [$RuCl_2$(arene)]$_2$ (arene = *p*-cymene, hexamethylbenzene) selectively leads to two types of complexes. The cleavage of the chloride bridges occurs first to yield the expected (carbene)(arene)ruthenium(II) complex **3**. Then a further arene displacement reaction takes place to give the chelated η^6-mesityl,η^1-carbene – ruthenium complexes **4** and **5**. An analogous η^6-arene,η^1-carbene complex with a benzimidazole frame **6** was isolated from an in situ reaction between [$RuCl_2$(*p*-cymene)]$_2$, the corresponding benzimidazolium salt and cesium carbonate. On heating, the $RuCl_2$(imidazolinylidene)(*p*-cymene) complex **8**, with *p*-methoxybenzyl pendent groups attached to the N atoms, leads to intramolecular *p*-cymene displacement and to the chelated η^6-arene,η^1-carbene complex **9**. On reaction with AgOTf and the propargylic alcohol HC≡$CCPh_2OH$, compounds **4** – **6** were transformed into the corresponding ruthenium allenylidene intermediates (**4** → **10**, **5** → **11**, **6** → **12**). The in situ generated intermediates **10** – **12** were found to be active and selective catalysts for ring-closing metathesis (RCM) or cycloisomerisation reactions depending on the nature of the 1,6-dienes. Two complexes [$RuCl_2$-{η^1-$\overline{CN(CH_2C_6H_2Me_3\text{-}2,4,6)CH_2CH_2N}$-($CH_2CH_2OMe$)}($C_6Me_6$)] **3** with a monodentate carbene ligand and [$RuCl_2${η^1-$\overline{CN[CH_2(\eta^6\text{-}C_6H_2Me_3\text{-}2,4,6)]CH_2CH_2N}$-($CH_2C_6H_2Me_3$-2,4,6)}] **5** with a chelating carbene – arene ligand were characterised by X-ray crystallography.

Keywords: alkene metathesis · arenes · carbenes · catalysis · cycloisomerisation · ruthenium

[a] Prof. B. Çetinkaya
Ege University, Faculty of Science, Chemistry Department
Bornova 35100 Izmir (Turkey)
Fax: (+90) 232-3888264
E-mail: Çetinkaya@fenfak.ege.edu.tr

[b] S. Demir, Dr. I. Özdemir
Inönü University, Chemistry Department
44069 Malatya (Turkey)
Fax: (+90) 422-3410037
E-mail: iozdemir@inonu.edu.tr

[c] Dr. L. Toupet
Groupe Matière Condensée et Matériaux
UMR 6626 Université de Rennes – CNRS
Université de Rennes l, 35042 Rennes (France)
Fax: (+33) 2-23-23-67-17
E-mail: loic.toupet@univ-rennes1.fr

[d] Prof. P. H. Dixneuf, Dr. D. Sémeril, Dr. C. Bruneau
Institut de Chimie de Rennes
UMR 6509 Organométalliques et Catalyse – CNRS
Université de Rennes 1, 35042 Rennes (France)
Fax: (+33) 2-23-23-69-39
E-mail: pierre.dixneuf@univ-rennes1.fr

Introduction

Nucleophilic carbenes have been shown to behave as phosphine mimics[1] and N-heterocyclic carbenes of the 1,3-imidazolylidene and 1,3-imidazolinylidene type are currently used in transition metal chemistry as ancillary ligands.[2] This is largely due to their recently revealed ability to create specific catalytic activity,[3–5] and attempts are currently being made to modify the coordination sphere of the metal with the hope of finding an even better application profile. For instance, the replacement of one phosphine ligand from the alkene metathesis catalyst precursors $RuCl_2$(=CHPh)(PCy_3)$_2$ and $RuCl_2$[=CHC_6H_4-(*o*-O*i*Pr)](PCy_3) by sterically hindered N-heterocyclic carbene moieties was recently found to impart significant increases in activity as well as stability in solution.[6, 7] Substantial variations of these carbene basic structural motifs promise that the performance and scope of the catalysts can be properly adjusted.

 DOI: 10.1002/chem.200204533

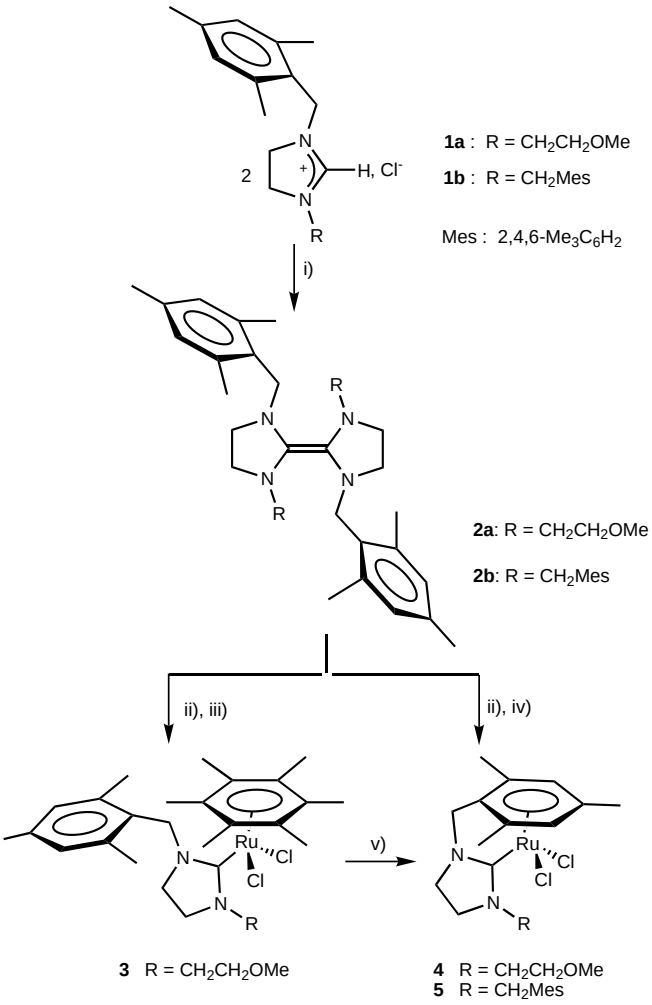
Previous work from our research groups in this area has focussed on the elaboration of olefins as electron-rich heterocyclic carbene precursors to allow the formation of chelating carbenes,[5] and on the rapidly developing chemistry of η^6-arene–ruthenium(II) complexes containing substituted imidazolidin-2-ylidenes.[8] We have now considered the possibility of generating heterocyclic carbenes that have a pendent arene group to evaluate their ability to chelate the ruthenium atom, stabilise the complex or create catalytic activity. We report here the study of the first mixed arene–imidazolidin-2-ylidene metal chelating complexes and their transformation into catalysts, via ruthenium–allenylidene species, for both alkene ring-closing metathesis (RCM) and the cycloisomerisation of dienes. A preliminary account of some of these results has been published.[9]

Results and Discussion

The synthesis of heterocyclic carbene precursors **1** and **2**, bearing at least one 2,4,6-trimethylbenzyl group linked to a nitrogen atom has been attempted, since the methylene group linking the mesityl group to the carbene nitrogen atom was expected to provide enough flexibility for the mesityl group to coordinate a metal site at the same time as the carbene. The 4,5-dihydroimidazolium salts **1a** and **b** were first prepared by a similar procedure to that originally developed by Lappert et al.[10] (Scheme 1). The 4,5-dihydroimidazolium salts **1** were selectively dehydrochlorinated on deprotonation with NaH, and the electron-rich olefins **2a** and **2b** were obtained in good yield (85%). They possess a bisimidazolin-2-ylidene structure with one (**2a**) or two (**2b**) trimethylbenzyl groups linked to a nitrogen atom.

The deprotonation reaction of the salt that leads to the formation of the olefin **2** can be monitored by ^{13}C NMR spectroscopy. Thus, the resonance for the N-CH-N carbon in **1** (ca. 160 ppm) vanishes and the relatively high-field-shifted resonance for the olefinic carbon atom appears at about 135 ppm. This observation excludes the existence of the stable corresponding free carbene since their typical values fall in the 210–240 ppm range.[11] Rather, this carbene dimerises into olefin **2** as soon as formed.

Treatment of **2a**, the source of an asymmetrical carbene, with $[RuCl_2(C_6Me_6)]_2$ in boiling toluene for 4 h afforded the expected carbene–ruthenium(C_6Me_6) complex **3** in 78% yield. By contrast, the reaction of the same precursor **2a** with $[RuCl_2(p\text{-cymene})]_2$, under the same conditions led to complex **4** in 84% yield. It contains the chelating mixed arene–carbene ligand, thus showing the facile displacement of the *p*-cymene ligand at 110°C. Treatment of **2b** with both $[RuCl_2(p\text{-cymene})]_2$ and $[RuCl_2(C_6Me_6)]_2$ led to the formation of the same complex **5** with one coordinated and one pendent mesityl group. Thus, depending on the nature of both the arene and olefin used, the derived carbene behaves as a monodentate carbene ligand, bonded to the metal directly through the carbene carbon atom (**3**) or as an 8-electron polydentate ligand, bonded to the metal atom through both the carbene carbon and the mesityl group, acting as a chelating ligand (**4** and **5**). It is noticeable that the *p*-cymene

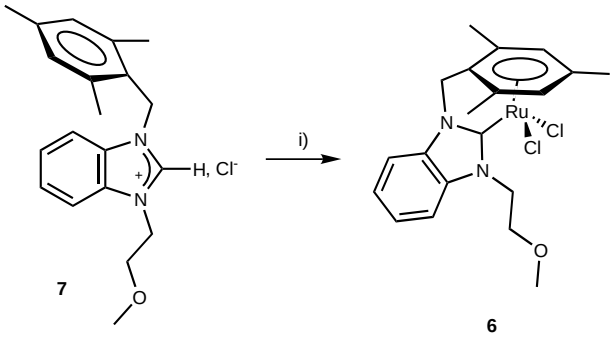


Scheme 1. Synthesis and reactivity of electron-rich olefins: i) NaH, THF; ii) $[RuCl_2(arene)]_2$ (arene = *p*-$MeC_6H_4CHMe_2$, C_6Me_6), 100°C, PhMe; iii) $[RuCl_2(C_6Me_6)]_2$ + **2a**; iv) $[RuCl_2(p\text{-cymene})]_2$ + **2a** or **2b**, or $[RuCl_2(C_6Me_6)]_2$ + **2b**; v) *p*-xylene, 140°C.

is displaced much more readily than the C_6Me_6 ligand. Complex **3**, however, can be converted to the chelated product **4** on reflux in *p*-xylene (140°C); this is consistent with a stronger C_6Me_6–Ru bond than *p*-cymene–Ru bond. These observations indicate that the first reaction step consists of the conversion of the starting dinuclear ruthenium complex to the mononuclear (arene)(carbene)ruthenium complexes, such as **3**, which upon further heating afford the complexes **4** and **5** by substitution of the arene (*p*-cymene or C_6Me_6) by the mesityl group attached to the carbene.

To examine whether this two-step transformation has a more general character, the benzimidazolium salt[10] **7**, which gives a less electron-releasing carbene than the 4,5-dihydroimidazolium salts, was evaluated in the same type of reaction. It is noteworthy that a different, more direct process was attempted this time. It has recently been shown that heating $[RuCl_2(p\text{-cymene})]_2$, 4,5-dihydroimidazolium salt and Cs_2CO_3 in toluene afforded an in situ prepared catalyst for enyne or alkene metathesis that was more active that the isolated complex $RuCl_2$(imidazolinylidene)(*p*-cymene).[12] It was suggested that the catalyst resulted from the coordination of the

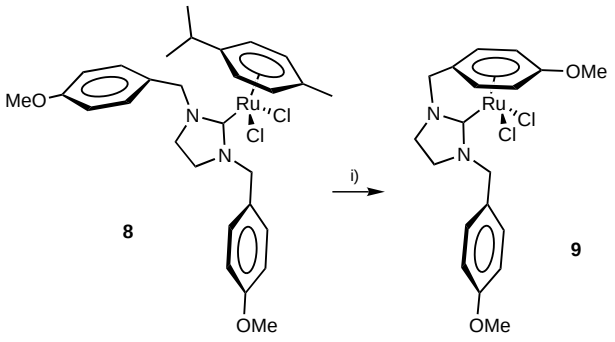
carbene, formed in situ on imidazolium-salt deprotonation with Cs_2CO_3, with concomitant displacement of the (*p*-cymene) ligand. Thus, the benzimidazolium salt **7** was heated with $[RuCl_2(p\text{-cymene})]_2$ in toluene at 110 °C for 7 hours in the presence of an excess of cesium carbonate. Complex **6**, with the mesityl group η^6-coordinated to the ruthenium atom, was obtained in 78% yield (Scheme 2). This result shows for



Scheme 2. i) $[RuCl_2(p\text{-cymene})]_2$, Cs_2CO_2, toluene, 110 °C.

the first time that Cs_2CO_3 is able to generate a ruthenium-coordinated imidazolylidene group from imidazolium salt in refluxing toluene, as was postulated for the in situ generation of carbene – ruthenium(II) catalysts,[12] and that the *p*-cymene ligand can be easily displaced on heating.

Upon comparison with earlier work, a dramatic contrast appears between the 1,3-imidazolin-2-ylidene carbene with $R = CH_2C_6H_5$ and those arising from either **2a**, **2b** or **7** with pendent CH_2Mes groups in terms of their coordinative behaviour towards $[RuCl_2(p\text{-cymene})]_2$. The carbene derived upon coordination to $[RuCl_2(p\text{-cymene})]_2$ of the carbene-precursor olefin with $R = CH_2Ph$ is not able to further react in an intramolecular manner to displace the *p*-cymene ligand.[5] On the other hand, such a process occurs rather rapidly with the carbene derived from **2b** or **7** ($R = CH_2$Mes). Moreover, study of the carbene complex **8**,[13] with only one electron-donating methoxy group on the benzyl substituent, has shown that, on heating, it can be converted to complex **9**, which contains the chelating mixed arene – carbene ligand, thus *p*-cymene displacement occurs (Scheme 3).



Scheme 3. i) 140 °C, *p*-xylene.

These observations show that, on heating, the $RuCl_2$(carbene)(*p*-cymene) complexes loose their arene ligand and that, when a more electron-rich arene ligand is present, this may lead to the preferential coordination of this arene group such as in the transformations to **4**, **5** and **9**.

The above complexes, **4** – **6** and **9**, are the first examples of carbene – ruthenium(II) complexes containing a chelating formal 8-electron arene – carbene ligand. All of the new products **3** – **6** and **9** were obtained as orange-brown crystalline complexes in good yields. They are air stable and soluble in dichloromethane. Their structure was confirmed by NMR and mass spectroscopy, elemental analysis and X-ray diffraction studies for **3** and **5**.

The NMR spectra were particularly diagnostic as to the nature of the bonding in these new complexes, establishing that they have either ruthenium – mesityl or pendent mesityl groups. Thus, the chemical shifts of the metal-bound 2,4,6-trimethylbenzyl protons in complexes **4** – **6** are found at higher fields ($\Delta\delta = 1.4$ ppm) than in the pendent 2,4,6-trimethylbenzyl group. The ^{1}H NMR spectra of **3** and **6** have two resonances for the arene-ring protons, and the ^{13}C NMR spectra have six signals for the corresponding ring carbon atoms. ^{1}H,^{1}H COSY and HETCOR NMR studies were required to assign methylene signals in complexes **3** and **6**. The nonequivalence of each proton in both CH_2 groups indicates the absence of any symmetry element in the complex, in perfect agreement with the solid-state structure. The remarkable high-field ^{13}C NMR resonances of the carbene carbon atoms, in the 200 – 210 ppm range, are similar to those observed for other ruthenium – carbene complexes.[5, 8] The typical (carbene)C=Ru carbon singlet for **3** is at lower field (210.26 ppm) than for the corresponding chelated complex **4** (200.14 ppm). The CH_2Mes substituent on the second N atom of **5** does not show a noticeable effect on the chemical shift (199.95 ppm).

X-ray structures: To gauge the steric factors at play with the dangling and coordinated CH_2Mes system, structural studies were carried out on complexes **3**[14] and **5**.[15] ORTEP diagrams of **3** and **5** with selected data are presented in Figures 1 and 2, respectively. In both compounds, the ruthenium atoms have pseudooctahedral geometry with the arene occupying three adjacent sites of the octahedron. The most striking feature of **5** is that the carbene ring is almost orthogonal to the coordinated 2,4,6-trimethylbenzyl ring; the dihedral angle C_t-Ru-C11-N1 is 23.7° whereas the corresponding angle in **3** is 87.0°. This can be attributed to the strong distortion of the carbene ligand due to the coordination of one N substituent. The Ru=C separation in **3** (2.086 Å) is significantly longer than that in **5** (2.040 Å).

Electrochemical studies of complexes 3 – 6: The complexes **3** – **6**, which contain pendent or η^6-coordinated 2,4,6-trimethylbenzyl-substituted carbene ligands have been studied by cyclic voltammetry in order to evaluate the electron richness of the complexes. The measurements were performed in dichloromethane containing 40 mmol of complex and nBu$_4$NPF$_6$ (0.026 or 0.05 M) as supporting electrolyte. The corresponding data are compiled in Table 1. It shows that each carbene complex gives a reversible oxidation process at 100 or 200 mV s^{-1}. The nature of the substituent on the second

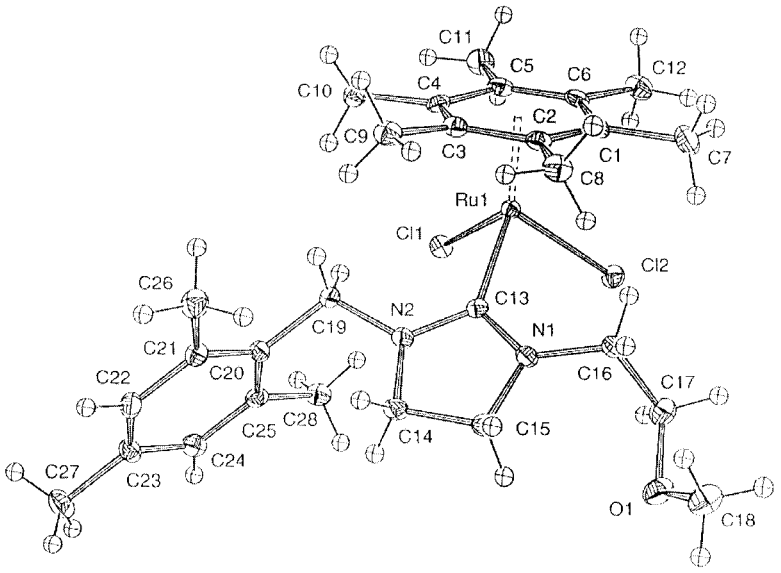


Figure 1. Molecular structure of **3**, hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1−C13 2.086(3), Ru1−C1 2.206(4), Ru1−C2 2.2114, Ru1−C3 2.220(4), Ru1−C4 2.192(3), Ru1−C5 2.271(4), Ru1−C6 2.260(4), Ru1−Cl1 2.4218(9), Ru1−Cl2 2.4281(9), C13-Ru1-C4 118.90(14), C13-Ru1-C1 119.56(14), C4-Ru1-C1 80.68(14), C13-Ru1-C2 93.48(13), C4-Ru1-C2 68.45(14), C13-Ru1-Cl1 90.99(10), C13-Ru1-Cl2 89.79(10).

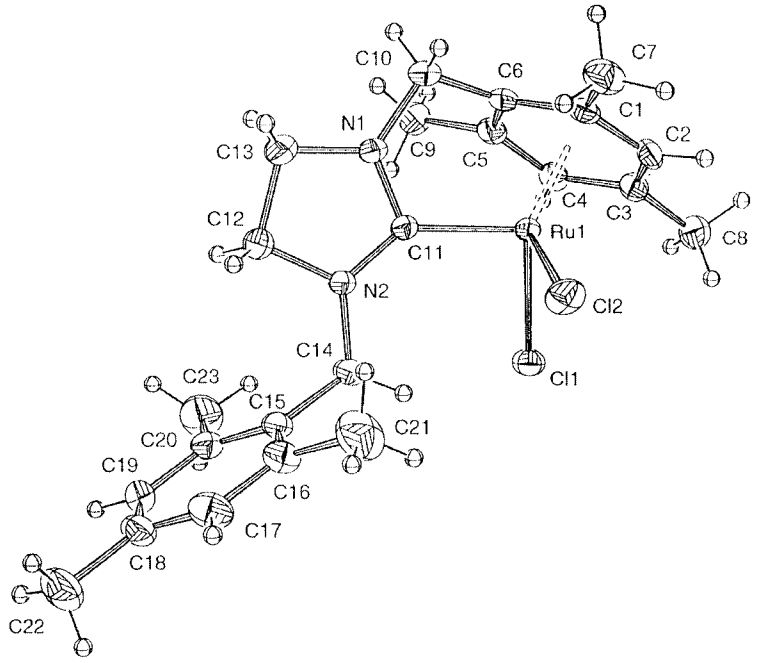


Figure 2. Molecular structure of **5**, hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru1−C11 2.040(3), N1−C11 1.347(3), N2−C11 1.328(3), N1−C10 1.460(3), Ru1−C2 2.280(2), Ru1−C3 2.318(3), Ru1−C4 2.191(3), Ru1−C5 2.194(2), Ru1−C6 2.111(2), C10−C6 1.503(4), C1-C6-C10 121.9(3), C5-C6-C10 117.1(2).

nitrogen atom of the carbene ligand, chelated or not, does not significantly modify the oxidation potentials. These data show that the electron richness of the complexes arises more from the nature of the coordinated arene ($C_6Me_6 > CH_2C_6H_2Me_3 >$ *p*-cymene) than from the type of carbene ligand.

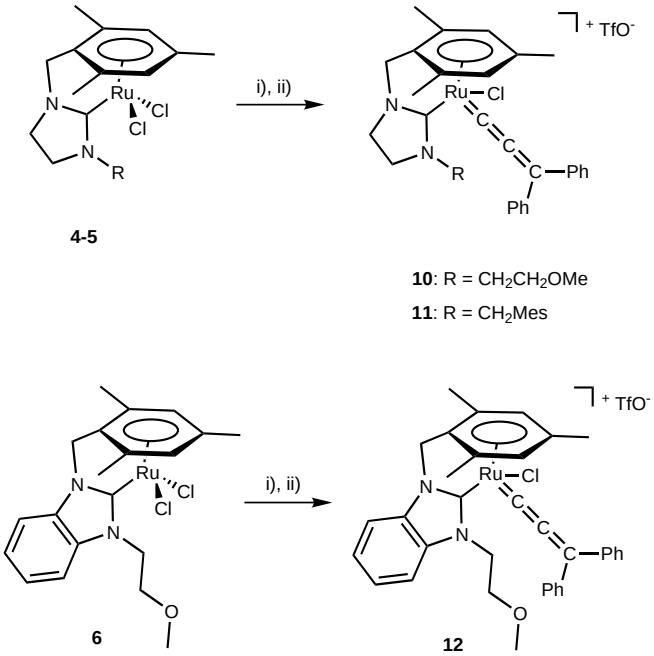
Ring-closing metathesis and cycloisomerisation reactions catalysed by ruthenium – allenylidene – carbene complexes: In addition to Grubbs' catalyst, the ruthenium(II) – allenylidene complexes of the type $[RuCl(=C=C=CPh_2)(PCy_3)(p\text{-cymene})]^+X^-$ have been shown to be active in ring-closing metathesis reactions (RCM) of dienes.[22] The high stability of complexes **4** – **6**, owing to the chelate effect, in addition to the tuneable nature of the R group on nitrogen provides a new perspective on the potential of such complexes as catalyst precursors. They have been tested as catalysts in the RCM reaction of diallyltosylamide at 80 °C, with 2.5 mol % of complex, but showed no activity for the RCM reaction, as expected from the absence of an active carbene moiety (e.g.=CHR). To activate the neutral complexes **4** – **6**, it was necessary to remove the strongly bound chloride ligand and introduce an allenylidene ligand. This was done by treatment of complexes **4** – **6** with 1.2 equivalents of 1,1-diphenylprop-2-yn-1-ol and 1 equivalent of silver triflate at room temperature in CH_2Cl_2[23] (Scheme 4). The ruthenium – allenylidene complexes **10** – **12** were quantitatively obtained as dark violet, air-sensitive solids, but they decomposed quite rapidly in solution and were not stable enough for analysis and ^{13}C NMR spectroscopy. Their structure is based on previously known preparations of ruthenium – allenylidene complexes from analogous precursors[22, 23] and on their ^1H NMR and IR spectra. Because of their instability, the ruthenium – allenylidene complexes were in situ generated just before the addition of the diene and the catalytic reaction.

Thus, the ruthenium – allenylidenes **10** – **12** were in situ generated in toluene or chlorobenzene, then dienes **13** were added, and the solution mixture was heated to 80 °C. Depending on the nature of the 1,6-diene (**13a** – **d**) and the solvent, it is possible to selectively obtain either a metathesis (**14**), a cycloisomerisation (**15**) or an isomerisation product (**16**) (Scheme 5).

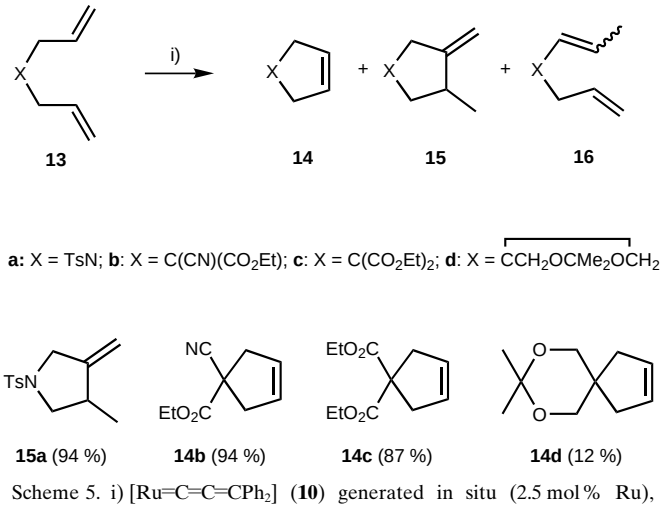
Table 1. Cyclic voltammetry data for carbene – ruthenium complexes.[a]

Compound	$E_{1/2}$ (Ru^{III}/Ru^{II}) [V versus SCE]	ΔE_p [mV]
3	0.969	63
4	0.965	75
5	0.979	74
6	0.959	66
$[RuCl_2\{\eta^1\text{-}CN(CH_2CH_2OMe)CH_2CH_2N(Me)\}(p\text{-}MeC_6H_4CHMe_2)]$[8a]	1.122[b]	111
$[RuCl_2\{\eta^1\text{-}CN(CH_2CH_2OMe)CH_2CH_2N(Me)\}(C_6Me_6)]$[8a]	0.958[b]	122
$[RuCl_2\{\eta^1\text{-}CN(CH_2Ph)CH_2CH_2N(CH_2Ph)\}(p\text{-}MeC_6H_4CHMe_2)]$[5a]	1.270	125

[a] *E* vs. SCE; Pt working electrode: 200 mV s^{-1}; recorded in CH_2Cl_2 with nBu_4NPF_6 (0.026 M) as supporting electrolyte. [b] *E* vs. SCE; Pt working electrode: 100 mV s^{-1}; recorded in CH_2Cl_2 with nBu_4NPF_6 (0.05 M) as supporting electrolyte.



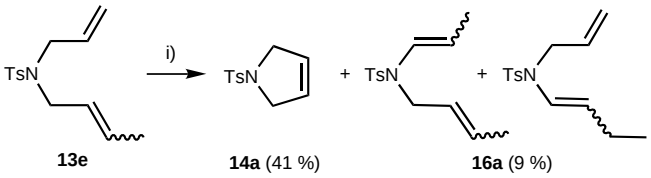
Scheme 4. i) AgOTf; ii) CH≡CC(OH)Ph_2, CH_2Cl_2, RT.



Scheme 5. i) [Ru=C=C=CPh_2] (**10**) generated in situ (2.5 mol% Ru), 80 °C.

With diallyltosylamide **13a** the ruthenium – allenylidene complex **10** gave a full conversion after 4 hours at 80 °C in chlorobenzene, and the cycloisomerisation product **15a** was obtained in 94% yield together with the metathesis product **14a** in 6% yield (Scheme 5). When the reaction was carried out in toluene, the activity decreased. After 4 hours only 25% conversion was observed, and products **14a** and **15a** were obtained in 4 and 21% yield, respectively.

To force complex **10** to produce the metathesis product **14a**, the introduction of a methyl substituent at the double bond (**13e**) was necessary (Scheme 6). In this case, after 10 hours in chlorobenzene at 80 °C, compound **14a** was obtained in 41% with 9% of different allylic isomerisation products **16a**.



Scheme 6. i) [Ru=C=C=CPh_2] (**10**) generated in situ (2.5 mol% Ru), 80 °C.

With 1,6-carbodienes **13b – d** instead of bisallylamides, only metathesis products **14b – d** were obtained (Scheme 5). However, the reactivity of the complex **10** depends dramatically on the nature of the solvent. For example, with the diene **13c** bearing two ester substituents, the best conversion was observed in chlorobenzene contrary to diene **13b** and **13d**, which were more easily transformed in toluene (Table 2).

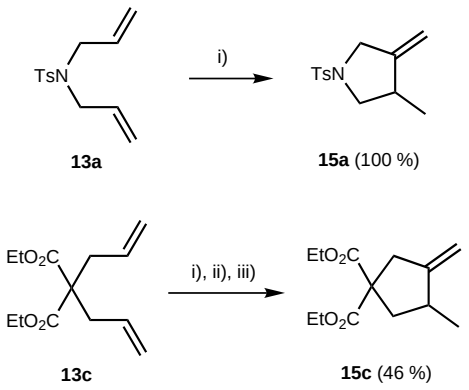
Table 2. Metathesis reaction catalysed by the in situ generated complex **10**.

diene	Conditions[a] Solvent	*t* [h]	Product	Yield (%)[b]
13b	chlorobenzene	5	**14b**	(67)
13b	toluene	6	**14b**	(94)
13c	chlorobenzene	5	**14c**	(87)
13c	toluene	5	**14c**	(8)
13d	chlorobenzene	5	–	
13d	toluene	5	**14d**	(12)

[a] Solvent (2.5 mL), diene **13** (0.5 mmol), **4** (2.5 mol%), AgOTf (2.5 mol%), HC≡$CCPh_2OH$ (3 mol%), 80 °C. [b] Determined by gas chromatography.

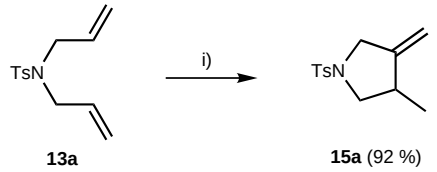
With the 1,6-dienes **13a** and **13c**, the ruthenium precursor **11** selectively gave the cycloisomerisation products **15a** and **15c** (Scheme 7). Like catalyst **10**, catalyst **11** was very sensitive to the nature of the solvent and catalysis conditions. For example with the diene **13a**, full conversion was observed after 4 hours at 80 °C in toluene compared with 84% conversion in chlorobenzene. Product **15c** was obtained preferentially in chlorobenzene and after UV activation of the ruthenium precursor before heating.

The benzimidazolinylidene – ruthenium – allenylidene **12** was less reactive than the catalyst precursors **10** and **11**, possibly because of its aromatic carbene nature and thus its weaker electron-releasing character. However, it gave 92% of



Scheme 7. i) [Ru=C=C=CPh$_2$] (**11**) generated in situ (2.5 mol% Ru), 80 °C; ii) UV, 30 min; iii) 80 °C, chlorobenzene.

cycloisomerisation product **15a** from diene **13a** after 10 hours at 80 °C in toluene (Scheme 8).



Scheme 8. i) [Ru=C=C=CPh$_2$] (**12**) generated in situ (2.5 mol% Ru), 80 °C, toluene, 10 h.

The above results show the most striking evidence that *the nature of the diene and that of the solvent dramatically influence the nature of the diene's transformation by a given catalyst*. Indeed with the same precursor **10**, diene **13a** leads to 94% of **15a**, whereas carbodienes **13b** and **13c** lead to **14b** (67%) and **14c** (87%), respectively, under similar conditions.

Conclusion

The present work describes the synthesis and properties of new chelated, 8-electron arene–carbene–ruthenium complexes. Compounds **4**–**6** and **9** are the first examples of carbene complexes with tethered arene functionality. Sterically demanding CH_2Mes substituent(s) at a N atom of the imidazolidine ring facilitate the displacement of the arene ligand to yield chelated complexes, a process that was not observed with an equivalent CH_2Ph substituent. Although the chelated complexes are inactive, their in situ formed allenylidene derivatives are efficient catalysts for the RCM or cycloisomerisation reactions of 1,6-dienes. Catalytic reactions proceed with very good efficiency and selectivity under relatively mild conditions. However, the chemoselectivity of the reaction dramatically depends on both the diene and solvent nature.

Experimental Section

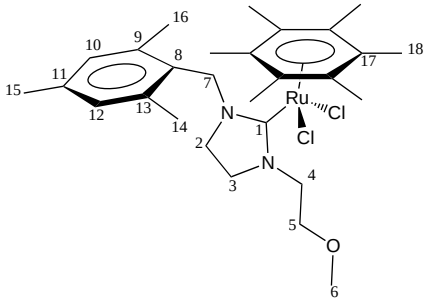
All reactions were performed under an inert atmosphere of N_2 or Ar in predried glassware by using Schlenk techniques. The solvents were dried by distillation over the following drying agents and were transferred under N_2 or Ar: toluene (Na), CH_2Cl_2 (P_2O_5), *n*-hexane (Na), chlorobenzene (P_2O_5), THF (Na/benzophenone). NMR spectra were recorded on a Bruker DPX 200 or RC 300 MHz spectrometer in $CDCl_3$ or CD_2Cl_2; chemical shifts (δ) are given in ppm relative to TMS. The IR spectra were recorded in KBr on a Bruker IFS28 spectrometer.

1-methoxyethyl-3-(2,4,6-trimethylbenzyl)-4,5-dihydroimidazolium chloride (1a): 2,4,6-trimethylbenzyl chloride (1.681 g, 10.1 mmol) was added slowly to a solution of 1-methoxyethyl-4,5-dihydroimidazole (1.273 g, 10 mmol) in DMF (10 mL) at 25 °C, and the resulting mixture was stirred at RT for 6 h. Diethyl ether (15 mL) was added to obtain a white crystalline solid, which was filtered off. The solid was washed with diethyl ether (3 × 15 mL), dried under vacuum and gave 2.64 g (89%) of **1a**. M.p. = 74–75 °C; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 2.15, 2.22 (s, 9H; 3CH_3 Mes), 3.20 (s, 3H; OCH_3), 3.43, 3.57 (t, ^3J(H,H) = 5 Hz, 4H; NCH_2CH_2N), 3.68 (t, ^3J(H,H) = 3.3 Hz, 2H; CH_2CH_2O), 3.82 (t, ^3J(H,H) = 3.3 Hz, 2H; CH_2O), 4.61 (s, 2H; $MesCH_2$), 6.84 (s, 2H; 2CH Mes), 8.72 (s, 1H; NCHN); ^{13}C NMR (50.33 MHz, $CDCl_3$): δ = 19.86, 21.05 (6CH_3 Mes), 45.64 (CH_2CH_2O), 47.20 (CH_2O), 48.16, 48.63 (NCH_2CH_2N), 58.46 (OCH_3), 68.12 (CH_2Mes), 126.87, 129.74, 138.33 (6C arom Mes), 158.07 (NCHN); IR(KBr): $\tilde{\nu}$ = 1651 cm^{-1} (C-N); elemental analysis calcd (%) for $C_{16}H_{25}N_2OCl$ (282.1): C 64.76, H 8.43, N 9.44; found: C 64.44, H 8.47, N, 9.34.

1,3-bis(2,4,6-trimethylbenzyl)-4,5-dihydroimidazolium chloride (1b): Compound **1b** was prepared in the same way as **1a** from 1-(2,4,6-trimethylbenzyl)-4,5-dihydroimidazole (2.021 g, 10 mmol) and 2,4,6-trimethylbenzyl chloride (1.681 g, 10.1 mmol) to give white crystals of **1b**. Yield 3.56 g (96%); m.p. 295–296 °C; ^{1}H NMR (200.13 MHz, $CDCl_3$): δ = 2.30, 2.21 (s, 18H; 6CH_3 Mes), 3.68 (s, 4H; NCH_2CH_2N), 4.86 (s, 4H; CH_2Mes), 6.82 (s, 4H; CH arom Mes), 9.87 (s, 1H; NCHN); ^{13}C NMR (50.33 MHz, $CDCl_3$): δ = 20.38, 21.25 (6CH_3 Mes), 46.64 (2CH_2 NCH_2CH_2N), 47.83 (CH_2Mes), 125.84, 130.14, 138.16, 139.31 (6C arom Mes), 158.46 (NCHN); IR(KBr): $\tilde{\nu}$ = 1660 cm^{-1} (C-N); elemental analysis calcd (%) for $C_{23}H_{31}N_2Cl$ (321.2): C 74.49, H 8.37, N 7.56; found: C 73.97, H 8.59, N 7.49.

1,3,1′,3′tetrakis-(2,4,6-trimethylbenzyl)-[2,2′]bis(1,3-imidazolidinylidene) (2b): The preparation of **2b** was done according to Lappert's procedure.[10] ^{1}H NMR (300.13 MHz, C_6D_6): δ = 2.26 (s, 6H; 2CH_3 Mes), 2.56 (s, 12H; 4CH_3 Mes), 2.75 (s, 4H; NCH_2CH_2N), 4.62 (s, 4H; CH_2Mes), 6.90 (s, 4H; 4CH Mes); ^{13}C NMR (75.47 MHz, C_6D_6): δ = 21.15 (2CH_3 Mes), 21.39 (4CH_3 Mes), 48.03 (NCH_2CH_2N), 51.82 (CH_2Mes), 129.67, 133.40, 136.36, 138.29 (C arom Mes), 132.18 (NCN).

RuCl$_2${η^1-CN(CH$_2$C$_6$H$_2$Me$_3$-2,4,6)CH$_2$CH$_2$N(CH$_2$CH$_2$OMe)}(C$_6$Me$_6$) (3): A solution of the electron-rich olefin **2a** (286 mg, 0.55 mmol) and the ruthenium complex [$RuCl_2(C_6Me_6)]_2$ (334 mg, 0.5 mmol) in degassed toluene (15 mL) was heated in a water bath (95–100 °C) for 4 hours. After the mixture had been cooled to 25 °C, *n*-hexane (15 mL) was added, and the solution was cooled to −15 °C. The precipitated brown solid was filtered and recrystallised from dichloromethane/hexane (10:20 mL). Compound **3** was isolated in 78% yield (463 mg).



^{1}H NMR (300.13 MHz, CD_2Cl_2): δ = 1.99 (s, 18H; H-18), 2.20, 2.25 (s, 6H; H-14 and H-16), 2.34 (s, 3H; H-15), 3.06 (dt, ^2J(H,H) = 11.2 Hz, ^3J(H,H) = 7.2 Hz, 1H; H-3), 3.15–3.24 (m, 2H; H-3 and H-4), 3.24 (s, 3H; H-6), 3.44 (dt, ^2J(H,H) = 11.2 Hz, ^3J(H,H) = 7.2 Hz, 1H; H-2), 3.51–3.57 (m, 2H; H-5), 3.73 (dt, ^2J(H,H) = 11.0 Hz, ^3J(H,H) = 10.8 Hz, 1H; H-2), 4.23 (d, ^2J(H,H) = 13.8 Hz, 1H; H-7), 4.35 (dt, ^2J(H,H) = 9.9 Hz, ^3J(H,H) = 4.1 Hz, 1H; H-4), 6.10 (d, ^3J(H,H) = 13.8 Hz, 1H; H-7), 6.79, 6.81 (s, 2H; H-10 and H-12); ^{13}C NMR (50.33 MHz, CD_2Cl_2): δ = 15.93 (6C; C18), 20.88, 21.02

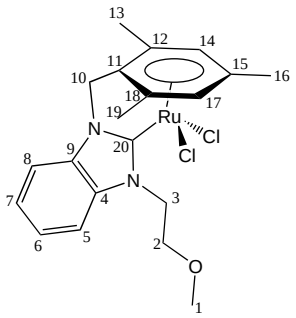
(C14 and C16), 21.54 (C15), 47.76 (C7), 49.73 (C3), 50.06 (C2), 52.03 (C4), 58.83 (C6), 74.73 (C5), 94.39 (6 C17), 129.13, 129.89 (C10 and C12), 130.55 (C8), 137.30, 137.58 (C9 and C13), 140.34 (C11), 210.26 (C1); elemental analysis calcd (%) for $C_{28}H_{42}N_2OCl_2Ru$ (594.2): C 56.56, H 7.07, N 4.71; found: C 56.29, H 6.93, N 4.49.

$RuCl_2[\eta^1$-CN{CH$_2$(η^6-C$_6$H$_2$Me$_3$-2,4,6)}CH$_2$CH$_2$N(CH$_2$CH$_2$OMe)] (4): A solution of the electron-rich olefin **2a** (286 mg, 0.55 mmol) and the ruthenium complex $[RuCl_2(p\text{-cymene})]_2$ (306 mg, 0.5 mmol) in degassed toluene (15 mL) was heated in a water bath (95 – 100 °C) for 4 h to give **4** in 84% yield (363 mg) after extraction and crystallisation as for complex **3**. ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta = 2.05$ (s, 6H; 2 CH_3 Mes), 2.19 (s, 3H; CH_3 Mes), 3.18 (s, 3H; OCH_3), 3.42 (d, $^3J(H,H) = 4.2$ Hz, 2H; NCH_2CH$_2$N), 3.70 (d, $^3J(H,H) = 4.2$ Hz, 2H; NCH$_2$CH_2N), 3.64 – 3.97 (m, 4H; NCH$_2$CH$_2$O), 4.05 (s, 2H; NCH$_2$Mes), 5.34 (s, 2H; CH Mes); ^{13}C NMR (50.33 MHz, $CDCl_3$): $\delta = 16.82$ (2 CH_3 Mes), 17.36 (CH_3 Mes), 47.05 (NCH$_2$CH$_2$NC), 48.23 (NCH$_2$Mes), 49.23 (CH_2NCH$_2$CH$_2$), 51.98 (CH_2CH$_2$O), 58.57 (OCH_3), 74.67 (CH$_2$O), 88.47 (2 *ortho*-C Mes), 93.89 (*para* C Mes), 98.89 (2 CH Mes), 100.37 (*ipso*-C Mes), 200.14 (Ru=C); FAB *m/z*: 432.03 $[\mathbf{4}]^+$; elemental analysis calcd (%) for $C_{16}H_{24}N_2OCl_2Ru$ (432.0): C 44.44, H 5.55, N 6.48; found: C 44.23, H 5.49, N 6.22.

Transformation 3 → 4: Complex **3** (594 mg, 1 mmol) in xylene (15 mL) was heated at 140 °C for 3 h to give **4** in 90% yield (389 mg) after extraction and crystallisation as above.

$RuCl_2[\eta^1$-CN{CH$_2$(η^6-C$_6$H$_2$Me$_3$-2,4,6)}CH$_2$CH$_2$N(CH$_2$C$_6$H$_2$Me$_3$-2,4,6)] (5): A solution of the electron-rich olefin **2b** (360 mg, 0.55 mmol) and the ruthenium complex $[RuCl_2(p\text{-cymene})]_2$ (306 mg, 0.5 mmol) in degassed toluene (15 mL) was heated in a water bath (95 – 100 °C) for 4 h to give **5** in 91% yield (460 mg) after extraction and crystallisation as above. ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta = 2.11$ (s, 6H; 2 coord. CH_3 Mes), 2.16 (s, 3H; free CH_3 Mes), 2.19 (s, 9H; 1 coord. CH_3 Mes and 2 free CH_3 Mes), 3.28 (d, $^2J(H,H) = 9.9$ Hz, 2H; NCH_2), 3.64 (d, $^2J(H,H) = 9.0$ Hz, 2H; NCH_2), 4.05 (s, 2H; coord. NCH$_2$Mes), 5.03 (s, 2H; free NCH$_2$Mes), 5.34 (s, 2H; coord. CH Mes), 6.71 (s, 2H; free CH Mes); ^{13}C NMR (50.33 MHz, $CDCl_3$): $\delta =$ 16.94 (2 coord. CH_3 Mes), 17.47 (coord. CH_3 Mes), 20.43 (2 free CH_3 Mes), 20.90 (free CH_3 Mes), 46.88 (CH_2NCH$_2$ coord. Mes), 47.08 (NCH$_2$ coord. Mes), 47.66 (NCH$_2$ free Mes), 48.97 (CH_2NCH$_2$ free Mes), 89.96 (2 *ortho*-C coord. Mes), 92.41 (*para*-C coord. Mes), 97.45 (2 CH coord. Mes), 103.03 (*ipso*-C coord. Mes), 129.18 (2 CH free Mes), 129.33 (*ipso*-C free Mes), 136.99 (*para*-C free Mes), 138.26 (2 *ortho*-C free Mes), 199.95 (Ru=C); FAB *m/z*: 506.08 $[\mathbf{5}]^+$; elemental analysis calcd (%) for $C_{23}H_{30}N_2Cl_2Ru$ (506.1): C 54.54, H 5.93, N 4.71; found: C 54.32, H 5.83, N 5.30.

$RuCl_2[\eta^1$-CN{CH$_2$(η^6-C$_6$H$_2$Me$_3$-2,4,6)}C$_6$H$_4$N(CH$_2$CH$_2$OMe)] (6): A suspension of 1-(methoxyethyl)-3-(2,4,6-trimethylbenzyl)benzimidazolium chloride **7** (0.72 g, 2.10 mmol), Cs_2CO_3 (0.70 g, 2.14 mmol) and $[RuCl_2(p\text{-cymene})]_2$ (0.50 g, 0.82 mmol) was heated under reflux in degassed toluene (20 mL) for 7 h. The reaction mixture was then filtered while hot, and the volume was reduced to about 10 mL before addition of *n*-hexane (15 mL). The precipitate formed was crystallised from CH_2Cl_2/hexane (5:15 mL) to give 0.50 g (78%) of brown crystals.



^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 1.62$ (s, 3H; H-16), 2.05, 2.16 (s, 6H; H-13 and H-19), 3.69 (dd, $^3J(H,H) = 9.5$ Hz, $^3J(H,H) = 10.0$ Hz, 1H; H-2), 4.03 (s, 3H; H-1), 4.31 – 4.44 (m, 2H; H-2 and H-3), 4.93 (d, $^2J(H,H) =$ 15.2 Hz, 1H; H-10), 5.82 (d, $^2J(H,H) = 15.2$ Hz, 1H; H-10), 6.18 – 6.26 (m, 1H; H-3), 6.33, 7.18 (d, $^3J(H,H) = 7.7$ Hz, 2H; H_5 and H_8), 6.53, 6.73 (s, 2H; H_{14} and H_{17}), 6.75, 7.02 (d, $^3J(H,H) = 7.7$ Hz, 2H; H-6 and H-7); ^{13}C NMR (50.33 MHz, $CDCl_3$): $\delta = 19.8$ (C16), 21.1, 21.5 (C13 and C19), 46.2 (C3), 48.0 (C10), 63.6 (C1), 75.3 (C2), 106.7, 109.3 (C5 and C8), 120.8, 121.0 (C6 and C7), 129.2, 129.3 (C14 and C17), 130.8 (C15), 136.0 (C12 and C18), 136.7, 136.9 (C4 and C9), 139.2 (C11), 208.7 (C20).

$RuCl_2[\eta^1$-CN{CH$_2$(η^6-C$_6$H$_4$-*p*-OMe)}CH$_2$CH$_2$N(CH$_2$C$_6$H$_4$-*p*-OMe)] (9): A suspension of complex **8**[13] (0.24 g, 0.5 mmol) in degassed *p*-xylene (15 mL) was heated at 140 °C for 4 h, after the mixture had been cooled at 25 °C, *n*-hexane (15 mL) was added, and then the formed orange solid was filtered and recrystallised from dichloromethane/hexane (10:25 mL) to give **9** as orange crystals. Yield 0.26 g (86%); m.p. = 252 – 252.5 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$): $\delta = 2.83$ (s, 3H; coord. OCH_3), 3.07 (s, 3H; free OCH_3), 3.36 (d, $^3J(H,H) = 8.3$ Hz, 2H; NCH$_2$CH$_2$N), 3.49 (d, $^3J(H,H) =$ 8.3 Hz, 1H; NCH$_2$CH$_2$N), 3.77 (s, 2H; coord. NCH$_2$Ar), 4.74 (s, 2H; free NCH$_2$Ar), 5.22 (d, $^3J(H,H) = 6.63$ Hz, 2H; coord. CH Ar), 6.26 (d, $^3J(H,H) = 6.63$ Hz, 2H; coord. CH Ar), 6.56 (d, $^3J(H,H) = 8.71$ Hz, 2H; free CH Ar), 7.19 (d, $^3J(H,H) = 8.71$ Hz, 2H; free CH Ar); ^{13}C NMR (75.47 MHz, $CDCl_3$): $\delta = 40.33$ (coord. OCH_3), 40.67 (free OCH_3), 47.87, 51.62 (NCH$_2$CH$_2$N), 49.01 (coord. NCH$_2$Ar), 52.86 (free NCH$_2$Ar), 75.46 (2 *ortho*-CH coord. Ar), 76.64 (*ipso*-C coord. Ar), 82.35 (2 *meta*-CH coord. Ar), 87.36 (*para*-C coord. Ar), 112.47 (2 *ortho*-CH free Ar), 124.19 (*ipso*-C free Ar), 130.39 (*meta*-CH free Ar), 150.07 (*para*-C free Ar), 201.19 (Ru=C); elemental analysis calcd (%) for $C_{19}H_{22}N_2O_2Cl_2Ru$ (482.0): C 47.30, H 4.56, N 5.81; found: C 47.16, H 4.35, N 5.69.

[RuCl{η^1-CN[CH$_2$(η^6-C$_6$H$_2$Me$_3$-2,4,6)]CH$_2$CH$_2$N(CH$_2$CH$_2$O-=C=C=CPh$_2$)][TfO] (10): Complex **4** (95 mg, 0.22 mmol) and silver triflate (57 mg, 0.22 mmol) in degassed CH_2Cl_2 (5 mL) were stirred for 15 minutes at room temperature. Then, HC≡CCPh$_2$OH (48 mg, 0.23 mmol) was added, and the reaction mixture was stirred at room temperature for additional 15 min. The purple solution was filtrated with a cannula paper filter, and CH_2Cl_2 was evaporated off under vacuum. Complete conversion into complex **10** was observed by ^{1}H NMR spectroscopy based on the coordinated mesityl protons chemical shifts. ^{1}H NMR (200.13 MHz, CD_2Cl_2): $\delta = 2.09$ (s, 6H; 2 CH_3 Mes), 2.24 (s, 3H; CH_3 Mes), 3.28 – 4.10 (m, 8H; NCH$_2$CH$_2$N and NCH$_2$CH$_2$O), 4.20 – 4.35 (m, 2H; NCH$_2$Mes), 6.27 (s, 1H; CH Mes), 6.32 (s, 1H; CH Mes), 7.50 (t, $^3J(H,H) = 7.5$ Hz, 4H; Ph), 7.77 (t, $^3J(H,H) = 7.5$ Hz, 2H; Ph), 7.91 (t, $^3J(H,H) = 7.5$ Hz, 4H; Ph); IR (KBr): $\tilde{\nu} = 1965$ cm^{-1} (Ru=C=C=C).

[RuCl{η^1-CN[CH$_2$(η^6-C$_6$H$_2$Me$_3$-2,4,6)]CH$_2$CH$_2$N(CH$_2$C$_6$H$_2$Me$_3$-2,4,6)}-(=C=C=CPh$_2$)][TfO] (11): Complex **5** (111 mg, 0.22 mmol) and silver triflate (57 mg, 0.22 mmol) in degassed CH_2Cl_2 (5 mL) were stirred for 15 minutes at room temperature. Then HC≡CCPh$_2$OH (48 mg, 0.23 mmol) was added, and the reaction mixture was stirred at room temperature for additional 15 min. The purple solution was filtrated with a cannula paper filter, and CH_2Cl_2 was evaporated off under vacuum. Complete conversion into complex **11** was observed by ^{1}H NMR spectroscopy based on the coordinated mesityl protons chemical shifts. ^{1}H NMR (200.13 MHz, CD_2Cl_2): $\delta = 2.09$ (s, 6H; 2 CH_3 Mes), 2.17 (s, 3H; CH_3 Mes), 2.19 (s, 9H; 3 CH_3 Mes), 3.21 (d, $^3J(H,H) = 10.2$ Hz, 2H; NCH_2), 3.74 (d, $^3J(H,H) =$ 9.7 Hz, 2H; NCH_2), 4.24 (d, $^2J(H,H) = 18.2$ Hz; 2H, coord. NCH$_2$Mes), 5.80 (d, $^2J(H,H) = 14.0$ Hz, 1H; free NCH$_2$Mes), 5.88 (d, $^2J(H,H) =$ 14.0 Hz, 1H; free NCH$_2$Mes), 6.26 (s, 1H; coord. CH Mes), 6.34 (s, 1H; coord. CH Mes), 6.72 (s, 2H; free CH Mes), 7.47 (t, $^3J(H,H) = 7.5$ Hz, 4H; Ph), 7.74 (t, $^3J(H,H) = 7.5$ Hz, 2H; Ph), 7.95 (t, $^3J(H,H) = 7.5$ Hz, 4H; Ph); IR (KBr): $\tilde{\nu} = 1969$ cm^{-1} (Ru=C=C=C).

Representative procedure for catalysis by using an in situ prepared ruthenium – allenylidene precursor 10 – 12: Ruthenium precursor **4 – 6** (1.25×10^{-2} mmol, 2.5 mol%) and silver triflate (3.2 mg, 1.25×10^{-2} mmol, 2.5 mol%) were introduced into a Schlenk tube under argon. The Schlenk tube was then purged three times, and degassed solvent (toluene or chlorobenzene, 2.5 mL) was added. The reaction mixture was then stirred at room temperature for 15 minutes before the addition of propargylic alcohol HC≡CCPh$_2$OH (2.7 mg, 1.3×10^{-2} mmol, 2.6 mol%). The reaction was stirred at room temperature for an additional 15 minutes. Diene (0.5 mmol) was then added to the purple solution. The reaction mixture was heated at 80 °C. After the mixture had been cooled to room temperature, the solvent was reduced under vacuum. The conversion was determined directly on the crude product by ^{1}H NMR spectroscopy.

Representative procedure for catalysis by using an in situ prepared ruthenium – allenylidene precursor and UV activation: Ruthenium precursor **5** (6.3 mg, 1.25×10^{-2} mmol, 2.5 mol%) and silver triflate (3.2 mg, 1.25×10^{-2} mmol, 2.5 mol%) were introduced into a Schlenk tube under

argon. The Schlenk tube was then purged three times, and degassed chlorobenzene (2.5 mL) was added. The reaction mixture was then stirred at room temperature for 15 minutes before the addition of propargylic alcohol HC≡CCPh$_2$OH (2.7 mg, 1.3×10^{-2} mmol, 2.6 mol%). The reaction mixture was stirred at room temperature for an additional 15 minutes and irradiated with UV for 30 minutes. Then diene **13c** (0.5 mmol) was added to the solution, and the reaction mixture was heated at 80 °C for 5 h. After the mixture had been cooled to room temperature, the solvent was reduced under vacuum, and the conversion was calculated directly on the crude product by ^{1}H NMR spectroscopy.

Acknowledgement

The authors are grateful to the CNRS and Tübitak and to the European Union COST program Action D17 (003) for support.

[1] a) B. Çetinkaya, P. H. Dixneuf, M. F. Lappert, *J. Chem. Soc. Dalton Trans.* **1974**, 1827 – 1833; b) M. F. Lappert, *J. Organomet. Chem*. **1988**, *358*, 185 – 213.

[2] D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39 – 92.

[3] a) W. A. Herrmann, C. Köcher, *Angew. Chem.* **1997**, *109*, 2256 – 2282; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162 – 2187; b) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342 – 1363; *Angew. Chem. Int. Ed.* **2002**, *41*, 1291 – 1309.

[4] a) W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. J. Artus, *Angew. Chem.* **1995**, *107*, 2602 – 2605; *Angew. Chem. Int. Ed. Engl*. **1995**, *34*, 2371 – 2374; b) T. Weskamp, V. P. W. Böhm, W. A. Herrmann, *J. Organomet. Chem*. **1999**, *585*, 348 – 352; c) D. S. McGuinness, K. J. Cavell, *Organometallics* **2000**, *19*, 741 – 748; d) D. S. McGuinness, N. Saendig, B. F. Yates, K. J. Cavell, *J. Am. Chem. Soc.* **2001**, *123*, 4029 – 4040; e) D. S. McGuinness, K. J. Cavell, B. F. Yates, B. W. Skelton, A. H. White, *J. Am. Chem. Soc.* **2001**, *123*, 8317 – 8328.

[5] H. Kücükbay, B. Çetinkaya, S. Guesmi, P. H. Dixneuf, *Organometallics* **1996**, *15*, 2434 – 2439.

[6] a) C. W. Bielawski, R. H. Grubbs, *Angew. Chem.* **2000**, *112*, 3025 – 3028; *Angew. Chem. Int. Ed.* **2000**, *39*, 2903 – 2906; b) A. K. Chatterjee, J. P. Morgan, M. Scholl, R. H. Grubbs, *J. Am. Chem. Soc.* **2000**, *122*, 3783 – 3784; c) S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, *J. Am. Chem. Soc*. **2000**, *122*, 8168 – 8179; d) T. Weskamp, W. C. Schattenmann, M. Spiegler, W. A. Herrmann, *Angew. Chem.* **1998**, *110*, 2631 – 2633; *Angew. Chem. Int. Ed.* **1998**, *37*, 2490 – 2493; e) A. Fürstner, H. Krause, L. Ackermann, C. W. Lehmann, *Chem. Commun.* **2001**, 2240 – 2241; f) A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, C. W. Lehmann, R. Mynott, F. Stelzer, O. R. Thiel, *Chem. Eur. J.* **2001**, *7*, 3236 – 3253.

[7] a) S. Randl, S. Gessler, H. Wakamatsu, S. Blechert, *Synlett* **2001**, 430 – 432; b) S. Gessler, R. Randl, S. Blechert, *Tetrahedron Lett*. **2000**, *41*, 9973 – 9976; c) H. Wakamatsu, S. Blechert, *Angew. Chem*. **2002**, *114*, 2509 – 2511; *Angew. Chem. Int. Ed.* **2002**, *41*, 2403 – 2405; d) J. S. Kingsbury, J. P. A. Harrity, P. J. Bonitatebus, Jr., A. H. Hoveyda, *J. Am. Chem. Soc.* **1999**, *121*, 791 – 799; e) S. J. Connon, A. M. Dunne, S. Blechert, *Angew. Chem.* **2002**, *114*, 3989 – 3993; *Angew. Chem. Int. Ed.* **2002**, *41*, 3835 – 3838.

[8] a) B. Çetinkaya, I. Özdemir, P. H. Dixneuf, *J. Organomet. Chem*. **1997**, *534*, 153 – 158; b) B. Çetinkaya, I. Özdemir, C. Bruneau, P. H. Dixneuf, *J. Mol. Catal. A* **1997**, *118*, L1-L4; c) B. Çetinkaya, B. Alici, I. Özdemir, C. Bruneau, P. H. Dixneuf, *J. Organomet. Chem.* **1999**, *575*, 187 – 192; d) B. Çetinkaya, I. Özdemir, C. Bruneau, P. H. Dixneuf, *Eur. J. Inorg. Chem.* **2000**, 29 – 32.

[9] B. Çetinkaya, S. Demir, I. Özdemir, L. Toupet, D. Sémeril, C. Bruneau, P. H. Dixneuf, *New J. Chem.* **2001**, *25*, 519 – 521.

[10] E. Çetinkaya, P. H. Hitchcock, H. A. Jasim, M. F. Lappert, K. Spyropoulos, *J. Chem. Soc. Perkin Trans. 1* **1992**, 561 – 567.

[11] a) J. C. C. Chen, I. J. B. Lin, *Organometallics* **2000**, *19*, 5113 – 5121; b) D. S. McGuinness, K. J. Cavell, *Organometallics* **2000**, *19*, 741 – 748; c) E. Peris, J. A. Loch, J. Mata, R. H. Crabtree, *Chem. Commun*. **2001**, 201 – 202.

[12] D. Sémeril, C. Bruneau, P. H. Dixneuf, *Adv. Synth. Catal*. **2002**, *344*, 585 – 595.

[13] I. Özdemir, B. Yigit, B. Çetinkaya, D. Ülkü, M. N. Tahir, C. Arici, *J. Organomet. Chem.* **2001**, *633*, 27 – 32.

[14] Crystal data for compound **3**: $C_{28}H_{42}N_2ORuCl_2$, CH_2Cl_2, $M = 679.53\ g\,mol^{-1}$, orange-brown crystal with dimensions $0.32 \times 0.30 \times 0.15$ mm, monoclinic $P2_1/c$, at 95 K: $a = 9.5630(1)$, $b = 13.1030(1)$, $c = 24.2780(3)$ Å, $\beta = 90.945(4)^\circ$, $V = 3041.72(5)$ Å^3, $Z = 4$, $\rho = 1.484\ Mg\,m^{-3}$, $\mu = 8.92\ cm^{-1}$, $\lambda = 0.71073$ Å. X-ray diffraction data for this structure and **5** were collected by using a NONIUS Kappa CCD with graphite monochromatised $Mo_{K\alpha}$ radiation. The cell parameters were obtained with Denzo and ScaIepack[16] with 10 frames (psi rotation: 1° per frame). The data collection[17] ($2\theta_{max} = 54.0^\circ$) gave 43909 integrated reflections. The data reduction with Denzo and ScaIepack[16] lead to 6932 independent reflections (6352 with $I > 2\sigma(I)$). The structure was solved with SIR-97[18], which reveals all the non-hydrogen atoms of the compound and a dichloromethane molecule. After anisotropic refinement, many hydrogen atoms were found with a Fourier difference. The whole structure was refined with SHELXL-97[19] by the full-matrix least-squares techniques (335 variables and 6352 observations with $I > 2\sigma(I)$, $R = 0.049$, $wR = 0.122$ and residual $\Delta\rho < 1.05\ e\text{Å}^{-3}$). Atomic scattering factors came from the International Tables for X-ray Crysta1lography.[20] Ortep views were realised with PLATON98.[21] See also: CCDC-195933.

[15] Crystal data for compound **5**: $C_{23}H_{30}N_2RuCI_2$, $M = 506.46\ g\,mol^{-1}$, orange-brown crystal with dimensions $0.28 \times 0.22 \times 0.14$ mm, monoclinic, $P2_1/c$, at 293 K, $a = 8.0230(1)$, $b = 8.2340(1)$, $c = 33.3210(5)$ Å, $\beta = 90.401(5)^\circ$, $V = 2201.18(5)$ Å^3, $Z = 4$, $\rho = 1.580\ Mg\,m^{-3}$, $\mu = 9.66\ cm^{-1}$, $\lambda = 0.71073$ Å. X-ray diffraction ($2\theta_{max} = 54.0^\circ$) gives 14669 integrated reflections, the data reduction leads to 4783 independent reflections (4238 with $I > 2\sigma(I)$). Refinement 254 variables and 4783 observations with $I > 2\sigma(I)$ gives $R = 0.038$, $wR = 0.095$ and residual $\Delta\rho < 0.48\ e\text{Å}^{-3}$. See also: CCDC-159033.

[16] Z. Otwinowski, W. Minor in *Methods in Enzymology*, *Macromolecular Crystallography, Part A, Vol. 276* (Eds.: C. W. Carter, R. M. Sweet) Academic Press, London, **1997**, pp. 307 – 326.

[17] Nonius, *KappaCCD Software*, Nonius HV, Delft, The Netherlands, **1999**.

[18] A. Altomare, M. C. Hurla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Molitemi, G. Polidori, R. Spagna, *J. Appl. Cryst*. **1999**, *32*, 115 – 119.

[19] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, **1997**.

[20] A. J. C. Kluwer, *International Tables for X-ray Crystallography*, *Vol. C*, Academic Publishers, Dordrecht, **1992**.

[21] A. L. Spek, PLATON, *A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, **1998**.

[22] a) A. Fürstner, M. Picquet, C. Bruneau, P. H. Dixneuf, *Chem. Commun*. **1998**, 1315 – 1316; b) A. Fürstner, M. Liebl, C. W. Lehmann, M. Picquet, R. Kunz, C. Bruneau, D. Touchard, P. H. Dixneuf, *Chem. Eur. J*, **2000**, *6*, 1487 – 1857.

[23] M. Picquet, D. Touchard, C. Bruneau, P. H. Dixneuf, *New J. Chem*. **1999**, 141 – 143.

Received: October 28, 2002 [F4533]

