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Letter

First ruthenium complexes with a chelating arene carbene ligand as catalytic precursors for alkene metathesis and cycloisomerisation†

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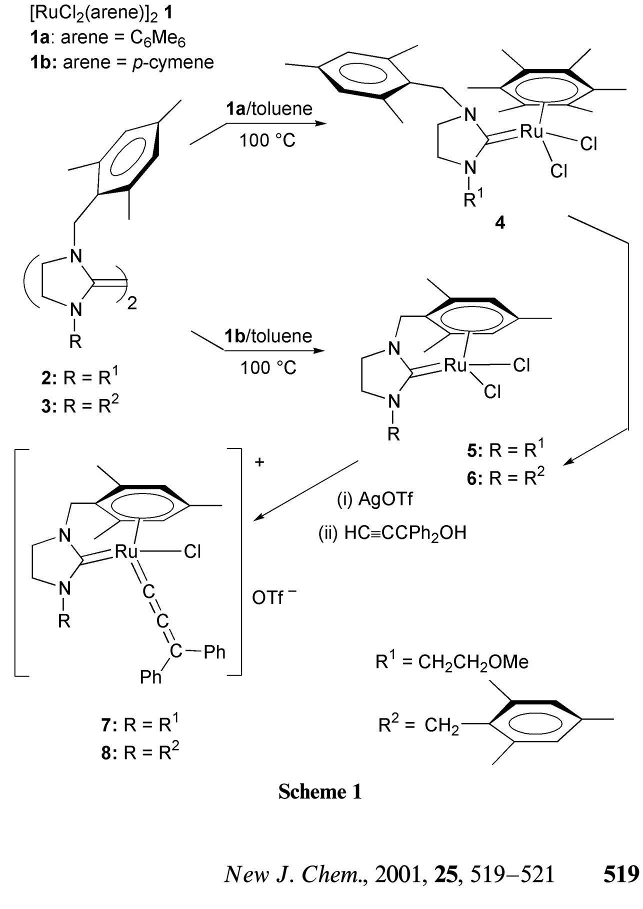
Electron-rich carbene precursors 2 and 3, containing the imidazolidin-2-ylidene moiety with one (2) and two (3) pendent *N*-(2,4,6-trimethylbenzyl) groups, on reaction with $[RuCl_2(arene)]_2$ lead to ruthenium(II) complexes 5 and 6 containing the chelating 8-electron mixed arene–carbene ligand; the X-ray diffraction crystal structure of $RuCl_2\{\eta^1\text{-}CN[CH_2(\eta^6\text{-}2,4,6\text{-}Me_3C_6H_2)]CH_2CH_2N(CH_2CH_2OMe)\}$ 6, was established. These complexes are precursors of the unstable ruthenium-allenylidene intermediates 7 and 8, but are active catalysts either for selective catalytic alkene metathesis or cycloisomerization, depending on the nature of the 1,6-diene.

Heterocyclic carbene ligands, the imidazol-2-ylidene and imidazolidin-2-ylidene carbenes,[1] are giving a new life to metal complexes as catalyst precursors for a variety of reactions, such as Heck and cross-coupling reactions,[2] cyclopropanation[3] or synthesis of furans.[4] Recently, they have also been used as key ligands to promote alkene,[5–7] enyne[8] and ene-yne cross[9] metathesis. The chemistry of electron-rich and bulky imidazolidin-2-ylidene ruthenium complexes is a rapidly developing area in the search for more active alkene metathesis catalysts and the discovery of new catalytic reactions.

It was shown previously that arene-ruthenium-allenylidene complexes associated with an electron-rich, bulky phosphine ligand promote alkene and enyne metathesis catalysis,[10] whereas their association with a bulky imidazol-2-ylidene ligand does not increase their catalytic activity.[11] In our search to improve both the activity and stability of the catalytic species, we have attempted to generate allenylidene-ruthenium(II) intermediates, coordinated to an 8-electron ligand, containing an electron-releasing carbene ligand and a pendent chelating arene group.

We now wish to report (i) the first synthesis of 8-electron, chelating mixed arene imidazolidin-2-ylidene metal complexes, (ii) their transformation into new ruthenium-allenylidene catalyst species, (iii) which selectively lead either to diene cycloisomerisation or ring-closing metathesis (RCM) catalytic reactions, depending on the nature of the 1,6-diene substrate. In order to introduce an imidazolidin-2-ylidene ligand, containing a pendent aryl group, in a metal complex, the new electron-rich alkenes **2** and **3** were first prepared by dehydrochlorination from the corresponding imidazolidinium salts.[12]

The carbene precursors **2** and **3** were reacted with the ruthenium complex sources $[RuCl_2(arene)]_2$, **1a** (arene = C_6Me_6) and **1b** (arene = *p*-cymene), in toluene at 100 °C for 4 h (Scheme 1). From **1a** and the alkene **2**, the carbene complex **4** was isolated in 78% yield. No corresponding complex was formed under similar conditions with the bulky precursor **3** and **1a**. By contrast, from **1b** the chelating complexes **5** and **6** were obtained in 84 and 91% yield, respectively. They result from the expected cleavage of the chloro bridges, but also from the ready displacement of the *p*-cymene ligand and coordination of the 8-electron mixed arene-carbene ligand. No intermediate still containing the *p*-cymene ligand, analogous to **4**, could be observed during the reaction, and this is consistent with the rather weak *p*-cymene–ruthenium bonding. Heating complex **4**, in xylenes at 140 °C for 3 h, led to intramolecular arene displacement and complete conversion into complex **5**, which was isolated in 82% yield. ^1H NMR appeared to be a



Scheme 1

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† Electronic supplementary information (ESI) available: synthetic procedures and selected spectroscopic data for **4–8**. See http://www.rsc.org/suppdata/nj/b1/b100264n/

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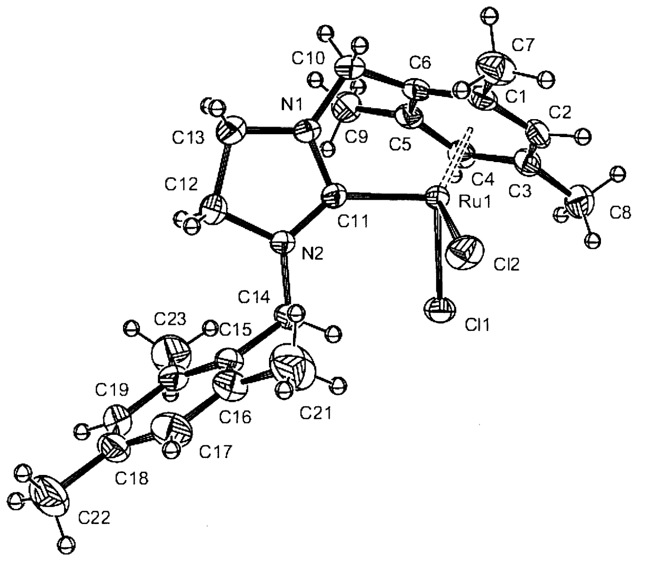


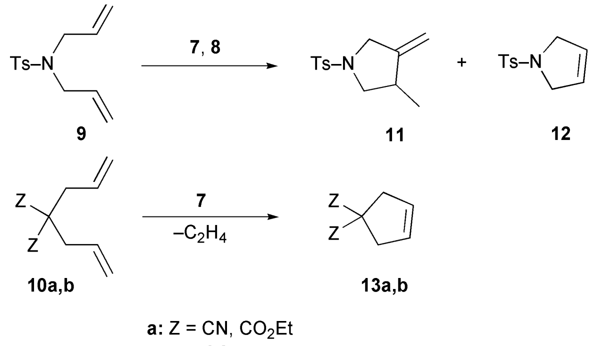
Fig. 1 ORTEP drawing illustrating the structure of complex **6**.

powerful diagnostic tool for establishing the coordination of the mesityl group in complexes **5** and **6**, as the aryl protons are shifted upfield by *ca.* 0.4 ppm, as shown in the ^{1}H NMR spectra of **4**, **5** and **6**.†

The X-ray study of complex **6** (Fig. 1, Table 1)[13] shows both coordinated and non-coordinated mesityl groups, with a cyclic carbene plane almost orthogonal to the coordinated mesityl group plane. It is noteworthy that in the η^1-carbene complex **4**, the cyclic carbene plane makes an angle of 87.0° with the ruthenium–arene axis,[14] whereas in complex **6** the corresponding angle is only 23.7°, illustrating the strong distorsion of the carbene ligand due to the coordination of one N-substituent.

Table 1 Selected bond lengths (Å) and angles (°) for **6**

Ru(1)–C(11)	2.040(3)	Ru(1)–C(4)	2.191(3)
N(1)–C(11)	1.347(3)	Ru(1)–C(5)	2.194(2)
N(2)–C(11)	1.328(3)	Ru(1)–C(2)	2.280(2)
N(1)–C(10)	1.460(3)	Ru(1)–C(3)	2.318(3)
Ru(1)–C(6)	2.111(2)	C(10)–C(6)	1.503(4)
Ru(1)–C(1)	2.161(2)	C(1)–C(6)–C(10)	121.9(3)
		C(5)–C(6)–C(10)	117.1(2)



a: $Z = CN, CO_2Et$
b: $Z = CO_2Et$

Scheme 2

Complexes **4**, **5** and **6** were used as precursors for the catalytic alkene metathesis of diallyltosylamide at 80 °C and show no activity for RCM reactions. Complexes **5** and **6** were thus transformed into the corresponding allenylidene complexes on reaction at room temperature with 1 equiv. of silver triflate in dichloromethane and then with 1.1 equiv. of propargyl alcohol, $HC\equiv CCPh_2OH$, for 15 min according to the procedure described for $[Ru=C=C=CPh_2(Cl)(PR_3)(arene)]^+X^-$ catalyst precursors.[10a,b] Complexes **7** and **8** were quantitatively formed and were isolated as violet solids for ^{1}H NMR and catalytic studies. They were not stable enough for analysis and ^{13}C NMR, likely due to the distortion of the carbene ligand. However, they showed a characteristic (C=C=C) IR absorption band at 1965 cm^{-1}, the ^{1}H NMR spectra revealed the presence of a coordinated mesityl moiety linked to a NCH_2-mesityl group with very different diastereotopic protons as well as the CPh_2 group.†

The *in situ*-generated intermediates **7** and **8** have been evaluated for the catalytic ring-closing metathesis transformation of the dienes **9** and **10** in chlorobenzene or toluene at 80 °C (Scheme 2). It was found that both catalyst precursors (2.5 mol%) were active. The nitrogen-containing diene **9** with both **7** and **8** selectively afforded the cycloisomerisation product **11** with only traces of the metathesis product **12** (Scheme 2, Table 2). By contrast, the 1,6-dienes **10a,b** were transformed by the same catalyst **7** with very good selectivity into the carbocycles **13a,b** arising from alkene metathesis.

These results show the dramatic influence of the solvent, but especially are a unique example of the influence of the nature of the diene on the resulting selective catalytic transformation: *metathesis* or *cycloisomerisation.* Currently, studies are underway to develop this type of catalyst and understand the duality in catalytic selectivities.

Experimental

A typical procedure for the preparation of the complexes 4, 5 and 6

A solution of alkene **2** or **3** (1.1 mmol) and ruthenium dimer **1a** or **1b** (1.0 mmol) in toluene (15 ml) was heated in a water bath (95–100 °C) for 4 h; after cooling to 25 °C, hexane (15 ml) was added and the solution cooled to −15 °C. The precipitated brown solid was filtered off and recrystallised from dichloromethane–hexane (10 : 20 ml). **4**, **5** and **6** were isolated in 78, 84 and 91% yields, respectively. Characterisation of all products is given in the ESI.†

Table 2 Catalytic metathesis *vs.* cycloisomerisation of dienes **9** and **10**

1,6-Diene	Catalyst[a]	Solvent	Time/h	Conv. (%)[b]	**11** (%)[b]	**12** (%)[b]	**13** (%)[b]
9	**7**	C_6H_5Cl	4	100	94	6	—
9	**7**	Toluene	4	25	21	4	—
9	**8**	C_6H_5Cl	4	84	84	—	—
9	**8**	Toluene	4	100	100	—	—
10a	**7**	C_6H_5Cl	5	67	—	—	67
10a	**7**	Toluene	6	94	—	—	94
10b	**7**	C_6H_5Cl	5	87	—	—	87

[a] The catalyst was prepared *in situ* from **5** or **6** (2.5 mol%), in 2.5 mL of solvent (chlorobenzene or toluene), AgOTf (2.5 mol%), $HC\equiv CCPh_2OH$ (2.6 mol%), 15 min stirring to give **7** or **8**, respectively. The substrate was then added and the solution heated at 80 °C for 4–6 h. [b] Determined by ^{1}H NMR.

Preparation of the ruthenium-allenylidene intermediates 7 and 8

[RuCl$_2${[*N*-(2,4,6-trimethylbenzyl)-*N*-(2-methoxyethyl)]-imidazolidin-2-ylidene}], **5** or [RuCl$_2${1,3-bis[*N*-(2,4,6-trimethylbenzyl)]imidazolidin-2-ylidene}], **6** (100 mg, 0.22 mmol), and 57 mg (0.22 mmol) of silver triflate in 5 ml of degassed CH_2Cl_2 were stirred for 15 min at room temperature. Then, 48 mg (0.23 mmol) of $HC{\equiv}CCPh_2OH$ was added and the solution was stirred again for 15 min at room temperature. After filtration with a canula paper filter, CH_2Cl_2 was evaporated under vacuum. Complete conversion was observed by ^1H NMR based on the coordinated mesityl proton chemical shifts. Characterisation is given in the ESI.†

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13 Crystal data for complex **6**: $C_{23}H_{30}N_2RuCl_2$: $M = 506.46$, monoclinic, space group $P2_1/c$, $a = 8.0230(1)$, $b = 8.2340(1)$, $c = 33.3210(5)$ Å, $\beta = 90.401(5)°$; $U = 2201.18(5)$ Å^{-3}, $T = 293$ K, $Z = 4$, μ(Mo-Kα) = 9.66 cm^{-1}, 14669 integrated measured reflections, $R = 0.038$, $R_w = 0.095$. Data were collected on a NONIUS Kappa CCD with graphite monochromated Mo-Kα radiation. The entire structure was refined with the SHELX97 program by full-matrix least-square techniques. CCDC reference number 159033. See http://www.rsc.org/suppdata/nj/b1/b100264n/ for crystallographic files in CIF or other electronic format.

14 L. Toupet, unpublished results.