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Synthesis and metathesis reactions of a phosphine-free dihydroimidazole carbene ruthenium complex

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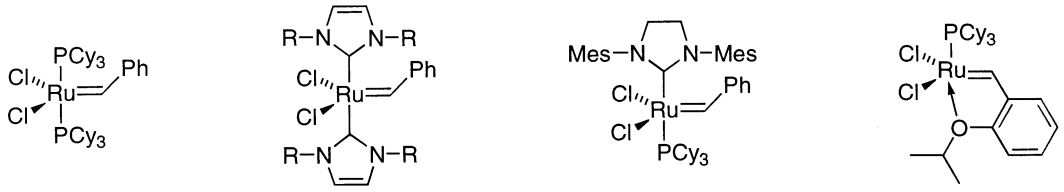
Abstract

Synthesis and activity in ring closure metathesis (RCM) and cross metathesis (CM) of the phosphine-free 1,3-dimesityl-4,5-dihydroimidazole-2-ylidene (IHMes) ruthenium alkoxybenzylidene complex **6** are reported.

Keywords: carbene complex; olefin metathesis; ruthenium; homogenous catalysis.

The introduction of *N*-heterocyclic carbenes as Lewis basic ligands into ruthenium–alkylidene complexes of the Grubbs type **1** has strongly encouraged the development of new highly active metathesis catalysts (Fig. 1).[1] It was shown that complexes **2**, in which both phosphines are replaced by more Lewis basic diaminocarbene ligands, exhibit a higher stability but are less reactive in RCM and CM reactions.[1a,f] Probably, the catalytically active $14e^-$ species is formed more slowly in comparison with the bisphosphine complex due to the stronger carbene metal bond.[1c]



1 **2** **3** **4**

Figure 1. Ruthenium carbene complexes for olefin metathesis (Cy = cyclohexyl, Mes = C_6H_2-2,4,6-Me_3)

This drawback has been overcome by the use of the sterically demanding IMes- and IHMes-ligands because they enable the selective replacement of only one phosphine moiety by

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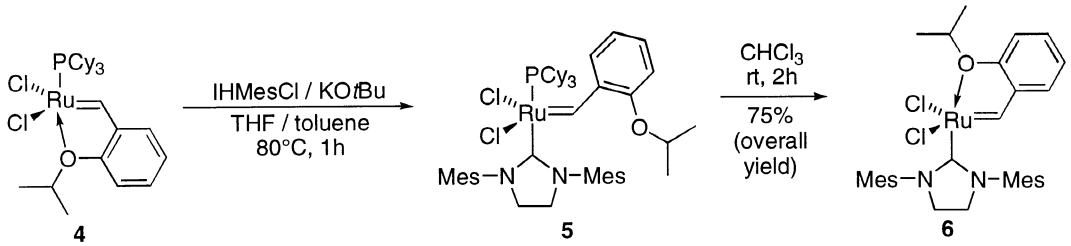
the *N*-heterocyclic carbene. These mixed complexes such as **3** bearing one phosphine as a leaving ligand show increased stability and activity in RCM and CM reactions.[1b,f]

We were interested in IHMes–Ru complexes with a non-phosphine leaving ligand with regard to different selectivities and reactivities. Recently, Hoveyda et al. have shown that *O*-chelating benzylidene moieties can be used for such purposes, providing complexes such as **4** exhibiting extraordinary stability against water and oxygen. Another advantage is the more facile purification by flash chromatography (FC).[2]

Herein, we report the synthesis of IHMes-*o*-isopropoxybenzylidene-ruthenium dichloride **6** and its behaviour in some metathesis reactions.[3]

As shown above, **6** can be obtained in 75% yield in two steps starting from **4**. Treatment of **4** with 1.2 equiv. of IHMesCl and 1.2 equiv. KO*t*Bu in THF/toluene at 80°C leads to the formation of a pink intermediate **5** still bearing the PCy_3 moiety. This suggests that the IHMes ligand replaces the isopropoxy group. Compound **5** can be isolated and was fully characterised. Formation of the desired complex is achieved by stirring of **5** at room temperature in $CHCl_3$ for two hours (Scheme 1). The green crystalline product **6** can be separated from the liberated phosphine by flash chromatography using CH_2Cl_2 as the eluent. The structure of this complex was confirmed by ^1H, ^{13}C NMR, HR-MS and X-ray analysis.[4] Like **4**, complex **6** shows a great stability against water and oxygen and can be stored under ambient atmosphere at room temperature.



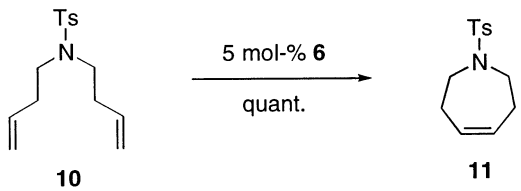
Scheme 1.

Catalyst **6** was tested in several metathesis reactions and compared with **3**.[5] We have found that the exchange of the PCy_3 ligand with the isopropyl ether leads to different reactivities.

In contrast to **3**, which proved to be an excellent catalyst for yne-ene CM,[6] analogous reactions with catalyst **6** yielded only traces of the desired products. Polymerisation of the alkyne component was not observed.

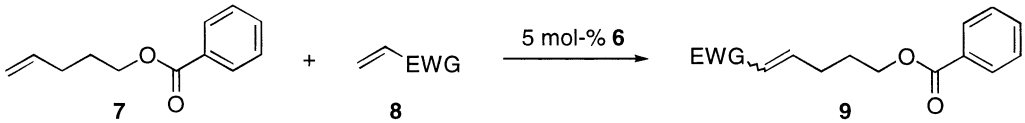
In CM reactions both **3** and **6** show similar behaviour. CM between olefin **7** and electron-deficient olefins is easily accomplished using **6** within 2 h (Table 1).[7]

Ring closure of dienes such as **10** is complete in less than 15 min at room temperature using **6**, whereas **3** requires higher temperatures.



Substantial differences were found in RCM reactions with dienes of types **12** accessible via the Baylis–Hillman reaction.[8,9] These substrates contain a sterically hindered electron deficient and a monosubstituted double bond (Table 2).

Table 1
CM between **7** and various electron-deficient olefins[a]



7 **8** **9**

EWG =	CO_2CH_3	$COCH_3$	CHO	$CON(CH_3)_2$
Yield of **9** (*E*/*Z*)	87% (>20:1)	85% (>20:1)	93% (1:1)	>98%[b] (>20:1)

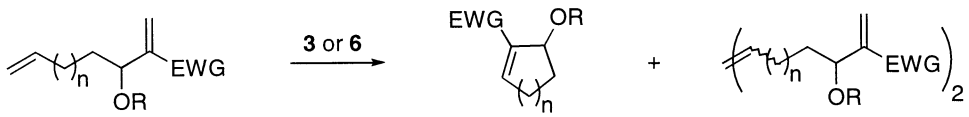
[a] Conditions: CH_2Cl_2, 40°C, [**7**] = 0.05 M, 2 equiv. of **8**.
[b] Yield determined by NMR.

Using **6** dimerisation via the monosubstituted double bond is much more favoured than cyclisation when compared to **3**. However, the dimerisation is reversible. Thus, longer reaction times lead to higher amounts of products of type **13**. For example, in the case of **12a** the ratio of the products switches from 1:5 to 2:1 when the reaction mixture is stirred for 48 h instead of 2 h with no significant change in yield.

Strikingly, catalyst **3** shows a much lower reactivity towards acrylates **12e** and **12f** with unprotected hydroxyl groups than **6**. Diene **12e** is not converted at all and with **12f** a longer reaction time (48 versus 12 h) is required, whereas in the other cases, reaction times with both catalysts are similar.

Another difference in reactivity was found in the reaction of diene **15**.

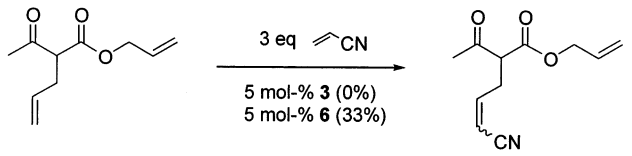
Table 2
RCM reactions[a]



12 **13** **14**

EWG = CO_2CH_3 (entries **a**–**d**) EWG = CN (entries **e**–**h**)	5 mol% **3** ratio **13**:**14** (yield)	5 mol% **6** ratio **13**:**14** (yield)
(**a**) $n=0$, R = H	2:1 (60%)	1:5 (50%)
(**b**) $n=1$, R = H	3:2 (42%)	1:2 (47%)
(**c**) $n=0$, R = TBS	>20:1 (87%)	3:1 (86%)
(**d**) $n=1$, R = TBS	>20:1 (89%)	1:2 (90%)
(**e**) $n=0$, R = H	No reaction	1:5 (40%)
(**f**) $n=1$, R = H	>20:1 (46%)	1:1 (42%)
(**g**) $n=0$, R = TBS	6:1 (90%)	2:1 (92%)
(**h**) $n=1$, R = TBS	>20:1 (86%)	10:1 (90%)

[a] Product ratio determined by NMR spectroscopy after complete conversion of the substrate. Conditions: CH_2Cl_2, 40°C, [**12**] = 0.05 M.



15 16

Both **3** and **6** efficiently catalyse the RCM of **15**. In the presence of acrylonitrile, the use of **6** results in the chemoselective formation of cross metathesis product **16** only. On the other hand, neither RCM nor CM was observed using **3** under identical conditions.

Our results indicate that complex **6** is different from **3** in its catalytic properties with regard to both selectivity and reactivity. As a first conclusion, **6** seems to be a promising catalyst, especially for CM.

Further studies, particularly in the field of cross metathesis, are in progress in our laboratories.

Acknowledgements

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4. Selected analytical data for complexes **5** and **6**:
   Complex **5**: **^{31}P NMR** (80 MHz, $CDCl_3$), $\delta = 29.36$; **^{1}H NMR** (200 MHz, $CDCl_3$), $\delta = 19.88$ (1H, br), 7.41–6.00 (8H), 4.41 (1H, sept), 4.18–3.48 (4H, m), 2.76, 2.59, 2.47, 2.35, 2.13, 1.89 (18H, s), 1.27 (6H, d), 1.83–0.84 (33H); **HR-MS** (FAB): calcd: 906.372, found: 906.374.
   Complex **6**: **^{13}C NMR** (125 MHz, $CDCl_3$), $\delta = 296.5$ (br), 211.1, 152.2, 145.3, 139.1 (br), 138.8, 129.5, 129.3, 122.7, 122.2, 112.9, 74.9, 51.5, 21.0, 19.4 (br); **^{1}H NMR** (500 MHz, $CDCl_3$), $\delta = 16.56$ (1H, s), 7.52–6.77 (8H), 4.90 (1H, sept), 4.18 (4H, s), 2.48 (12H, s), 2.40 (6H, s), 1.27 (6H, d); **HR-MS** (FAB): calcd: 626.140, found: 626.139.
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