

# A Ruthenium Catalyst for Olefin Metathesis Featuring an Anti-Bredt N-Heterocyclic Carbene Ligand

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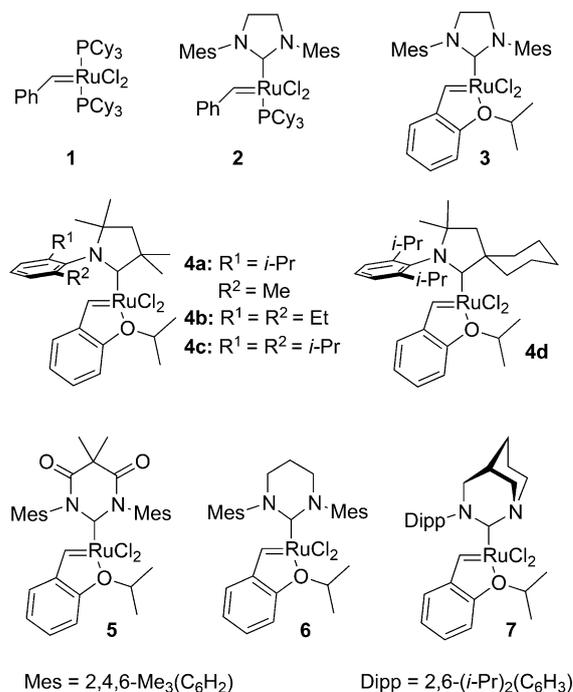
**Abstract:** A ruthenium complex bearing an “anti-Bredt” N-heterocyclic carbene was synthesized, characterized and evaluated as a catalyst for olefin metathesis. Good conversions were observed at room temperature for the formation of di- and tri-substituted olefins by ring-closing metathesis. It also allowed for the ring-opening metathesis polymerization of cyclooctadiene, as well as for the cross-metathesis of *cis*-1,4-diacetoxy-2-butene with allylbenzene, with enhanced *Z/E* kinetic selectivity over classical NHC-based catalysts.

**Keywords:** olefin metathesis; ruthenium; stable carbenes

kyl)(amino)carbenes **4** (CAACs)<sup>[8]</sup> and of di(amido)carbenes **5** (DACs)<sup>[9]</sup> have demonstrated interesting activities and selectivities for several ring-closing metathesis and cross-metathesis reactions.<sup>[10–12]</sup> For instance, DAC-ruthenium complex **5** catalyzes the ring-closing metathesis (RCM) of tetra-substituted olefins, a challenging transformation that is accomplished by only a limited range of metathesis catalysts.<sup>[11,13]</sup> However, note that this was found to be also the case for catalyst **6**, which bears a non-electrophilic NHC with a similar steric environment to **5**. The beneficial effect of  $\pi$ -accepting properties of the ligand is more obvi-

N-Heterocyclic carbene ligands have become key components of the  $[L_2X_2Ru=CHR]$  olefin metathesis catalysts.<sup>[1]</sup> The replacement of one phosphine in catalyst **1** by an imidazolidinylidene (catalyst **2**) results in significant enhancements (Scheme 1), which have been attributed to the superior electronic donation of the carbene ligand and the ensuing increased affinity of the ruthenium center for  $\pi$ -acidic olefins.<sup>[2,3]</sup> Note that an extra gain in stability can be achieved by replacement of the remaining phosphine with a chelating ether (catalyst **3**).<sup>[4]</sup>

For some time, the carbene ligand on ruthenium had been limited to imidazolylidenes, imidazolidinylidenes and closely related cyclic di(amino)carbenes.<sup>[5,6]</sup> These so-called NHCs are poor  $\pi$ -acceptors and cover a narrow range of  $\sigma$ -donation.<sup>[7]</sup> More recently, several examples of  $\pi$ -accepting stable cyclic carbenes have been developed, thus providing new opportunities for tuning the ruthenium center. Complexes of cyclic (al-

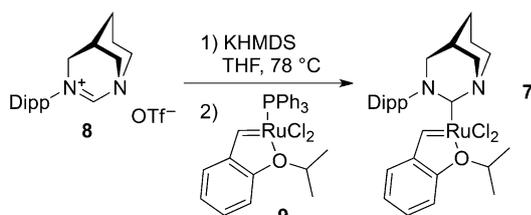
**Scheme 1.**

ous in the CAAC series. Indeed, complex **4a** has the highest reported TON value (340,000) for ethenolysis reactions to date.<sup>[12]</sup> It vastly surpasses the more traditional catalysts **1–3** (TONs of only 2,000–5,000). Note that sterics also play a role, as **4b** is more active than **4c** or **4d** by several orders of magnitude. More generally, both subtle changes in electronic and steric properties of the ligands can account for dramatic changes in activity, stability or selectivity. Therefore there is no single best ruthenium catalyst for all metathesis transformations, and new improvements in the field require a continuous effort to design new catalysts.<sup>[13]</sup>

We recently reported “anti-Bredt” N-heterocyclic carbenes featuring one nitrogen atom in a strained bridgehead position.<sup>[14]</sup> These ligands are significantly more  $\pi$ -accepting than NHCs, while retaining their strong  $\sigma$ -donation. They also feature a unique low steric hindrance on the side of the bridgehead nitrogen. Interestingly, they were found to be superior to CAAC and cyclic di(amino)carbenes as ligands for the gold-catalyzed intermolecular hydroamination of alkynes by hydrazine.<sup>[15]</sup> In addition, they allow for the challenging gold(I)-catalyzed hydroarylation of *N,N*-di(alkyl)anilines.<sup>[16]</sup> Herein we report the synthesis of the “anti-Bredt” NHC ruthenium complex **7** and its evaluation as a catalyst, using a set of standardized olefin metathesis reactions.<sup>[13]</sup>

Complex **7** was synthesized by deprotonation of the anti-Bredt imidazolium salt **8** in THF at  $-78^\circ\text{C}$ , generating the free carbene, followed by the addition *in situ* of ruthenium complex **9** (Scheme 2). The consumption of **9** and the formation of free triphenylphosphine were monitored by  $^{31}\text{P}$  NMR spectroscopy. After completion of the reaction and work-up, complex **7** was isolated as green crystals in 89% yield and fully characterized, including a single crystal X-ray diffraction study.<sup>[17]</sup>

In the solid state, the ruthenium center of **7** has a distorted square-pyramidal environment, the apical position being occupied by the benzylidene ligand (Figure 1). The Ru1–C1 (192.6 pm) and Ru1–O1 (232.4 pm) bond lengths are comparable to those in CAAC-complexes **4**.<sup>[10]</sup> In contrast, the tetrahydropyrimidin-2-ylidene complex **6** features a significantly longer Ru1–C1 bond length (204.8 pm).<sup>[11]</sup> This is consistent with an increased double bond character of the metal-carbene bond of the anti-Bredt NHC complex,



Scheme 2. Synthesis of complex **7**.

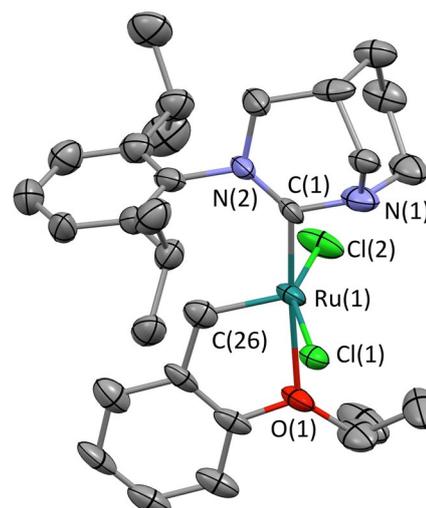


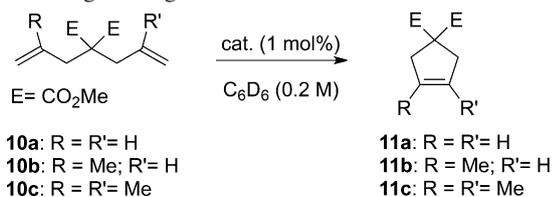
Figure 1. Solid state structure of **7** with ellipsoids drawn at 50% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ): Ru1–C1 1.926(6), Ru1–O1 2.324(4), Ru1–C26 1.813(7), Ru1–Cl1 2.3374(16), Ru1–Cl2 2.3278(17), N1–C1 1.452(8), N2–C1 1.330(8), N1–C1–N2 114.6(5), C1–Ru1–C26 105.4(3), Cl1–Ru1–Cl2 154.27(7).

which is due to the superior  $\pi$ -accepting capabilities of the carbene.

The *N*-aryl substituent of the stable carbene is located above the benzylidene ligand. Interestingly, the same orientation was found in CAAC-complexes **4**. This was interpreted as the result of negative steric interactions, which would prevent the alkyl groups of the quaternary carbon of CAAC to approach the benzylidene proton.<sup>[10]</sup> This explanation is clearly irrelevant in the case of the anti-Bredt NHC ligand, which features a non-bulky distorted amino group in place of the quaternary carbon of CAACs. The preferred conformation of **7** in the solid state could be governed by unfavorable steric interactions between the chlorides and the *N*-2,6-di(isopropyl)phenyl groups. This is suggested by the examination of the hypothetical structure resulting from the simple  $180^\circ$  rotation of the ligand around the C–Ru bond of **7**, which brings the isopropyl groups in very close proximity to the chlorine atoms (see the Supporting Information). The shortest carbon-chloride distance is 278 pm, the Van der Waals radii of these atoms being 170 pm and 175 pm, respectively. However, note that we found no evidence that the solid-state conformation is maintained in solution.

Complex **7** promotes the classical ring-closing metathesis (RCM) of diethyl dialkylmalonate **10a**. After 30 min at room temperature, 90% of the starting material was converted into the corresponding cyclopentene **11a** with 1% catalyst loading. Complete conversion was reached within 2 h (Table 1, entries 1 and 2). In contrast, catalysts bearing bulky CAAC **4c** and **4d**,

**Table 1.** Ring-closing metathesis of malonate derivatives.



Entry	Catalyst	Substrate	Temp.	Time	Conv.
1	<b>7</b>	<b>10a</b>	25 °C	30 min	90%
2	<b>7</b>	<b>10a</b>	25 °C	2 h	99%
3 <sup>[a]</sup>	<b>2</b>	<b>10a</b>	30 °C	30 min	97%
4 <sup>[a]</sup>	<b>3</b>	<b>10a</b>	30 °C	20 min	98%
5 <sup>[a]</sup>	<b>4b</b>	<b>10a</b>	30 °C	15 min	95%
6 <sup>[a]</sup>	<b>4c</b>	<b>10a</b>	60 °C	3 h	97%
7 <sup>[a]</sup>	<b>4d</b>	<b>10a</b>	60 °C	10 h	95%
8 <sup>[b]</sup>	<b>5</b>	<b>10a</b>	60 °C	20 min	85%
9 <sup>[b]</sup>	<b>6</b>	<b>10a</b>	60 °C	30 min	74%
10	<b>7</b>	<b>10b</b>	30 °C	1 h	90%
11	<b>7</b>	<b>10b</b>	30 °C	12 h	90%
12 <sup>[a,c]</sup>	<b>2</b>	<b>10b</b>	30 °C	45 min	95%
13 <sup>[a,c]</sup>	<b>3</b>	<b>10b</b>	30 °C	45 min	95%
14 <sup>[a]</sup>	<b>4b</b>	<b>10b</b>	30 °C	1 h	95%
15	<b>7</b>	<b>10c</b>	60 °C	12 h	0%
16	<b>7</b>	<b>10c</b>	100 °C	12 h	0%
17 <sup>[a,c]</sup>	<b>2</b>	<b>10c</b>	100 °C	1 h	26%
18 <sup>[a,c]</sup>	<b>3</b>	<b>10c</b>	100 °C	1 h	64%
19 <sup>[a]</sup>	<b>4b</b>	<b>10c</b>	60 °C	> 48 h	0%
20 <sup>[b]</sup>	<b>5</b>	<b>10c</b>	100 °C	20 h	29%
21 <sup>[b]</sup>	<b>6</b>	<b>10c</b>	100 °C	24 h	19%

<sup>[a]</sup> Ref.<sup>[10a]</sup>

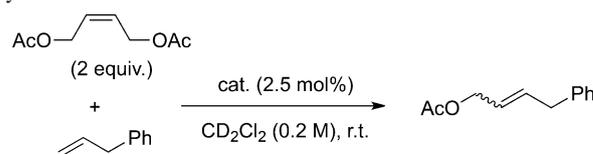
<sup>[b]</sup> Ref.<sup>[11]</sup>

<sup>[c]</sup> Ref.<sup>[13]</sup>

6-membered ring NHC **5**, and DAC **6** require higher temperature to reach decent conversions (entries 6–9). Complex **7** compares well with benchmark catalysts **2** and **3** and CAAC-complex **4b**, which benefits from a smaller N-aryl substituent than in **4c** and **4d** (entries 3–5). This remains the case for the synthesis of the more challenging trisubstituted olefin **11b** (entries 10–14). However, whereas 90% of the starting material **10b** was transformed within 30 min in presence of 1% of **7**, the conversion did not improve after one night, likely due to decomposition of the catalyst.

Complex **7** did not catalyze the formation of the tetra-substituted olefin **11c** from malonate (entries 15 and 16). CAAC ligands (catalysts **4a–c**), which are comparable to anti-Bredt NHCs in terms of electronic properties, suffer from the same limitation, whereas **2** and **3** afford up to 64% conversion (entries 17–19). Robustness of the catalyst is known to play a key role in the very challenging RCM of **10c**, which typically occurs at elevated temperatures.<sup>[13]</sup> This is well illustrated by **5** and **6**, which are moderately active in RCM (entries 8 and 9), but have a good thermal stability and still allow for the formation of **11c** at 100 °C

**Table 2.** Cross-metathesis of *cis*-1,4-diacetoxy-2-butene with allylbenzene.



Entry	Catalyst	Time [h]	Conversion (% <i>E</i> )
1	<b>7</b>	1	52% (70)
2	<b>7</b>	3	98% (70)
3 <sup>[a]</sup>	<b>2</b>	0.5	79% (91)
4 <sup>[a]</sup>	<b>3</b>	0.5	72% (91)
5 <sup>[b]</sup>	<b>4b</b>	1	60% (66)

<sup>[a]</sup> Ref.<sup>[13]</sup>

<sup>[b]</sup> Ref.<sup>[10b]</sup>

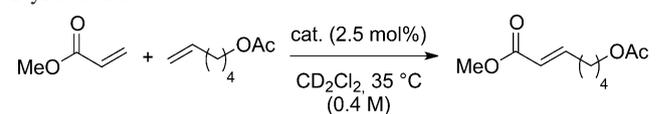
(entries 20 and 21). Note that even after a night at 100 °C complex **7** could still be detected by <sup>1</sup>H NMR. This suggested that the catalyst could survive the experimental conditions and was just inert toward the substrate.

Catalyst **7** was also tested in cross-metathesis reactions. With 2.5% catalyst loading, the reaction between *cis*-1,4-diacetoxy-2-butene and allylbenzene reached 98% conversion in 3 h. Relative to catalysts **2** and **3**, **7** is slightly less active, but exhibits an enhanced *Z/E* ratio at higher conversion (Table 2, entries 1–3). Note that similar kinetic selectivity was reported with CAAC-based catalyst **4b** (entry 4).

The catalyst was significantly less active in cross-metathesis of hex-5-en-1-yl acetate with methyl acrylate, a very challenging electron-poor olefin. Indeed only 23% conversion was obtained after 20 h under standard conditions, whereas the reaction reaches completion within 2–8 h with catalysts **2** and **3** (Table 3).

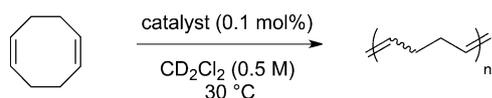
Finally, we confirmed that **7** could promote ring-opening metathesis polymerization (ROMP).<sup>[1g,18]</sup> For this reaction the stability of the catalyst has usually a marginal role, the catalytic activity having the major contribution to the overall catalytic performance.<sup>[13]</sup> According to NMR monitoring, the polymerization of

**Table 3.** Cross-metathesis of methyl acrylate with hex-5-en-1-yl acetate.



Entry	Catalyst	Time [h]	Conversion
1	<b>7</b>	20	23%
2 <sup>[a]</sup>	<b>2</b>	2	98%
3 <sup>[a]</sup>	<b>3</b>	8	96%

<sup>[a]</sup> Ref.<sup>[13]</sup>

**Table 4.** Ring-opening metathesis polymerization of cycloocta-1,5-diene.

Entry	Catalyst	Time [min]	Conversion
1	<b>7</b>	60	98%
2 <sup>[a]</sup>	<b>1</b>	60	32%
3 <sup>[a]</sup>	<b>2</b>	6	99%
4 <sup>[a]</sup>	<b>3</b>	6	99%

<sup>[a]</sup> Ref.<sup>[13]</sup>

cyclooctadiene occurred in 1 hour in the presence of 0.1% of **7**. This is in line with the results obtained in the previous test reactions. Indeed this fair activity is moderate when compared to benchmark catalysts **2** and **3**, which afford 99% polymerization within 6 min under similar conditions (Table 4).

In conclusion, the anti-Bredt NHC ruthenium complex **7** was synthesized, characterized and evaluated as a catalyst for olefin metathesis reactions. It was found to be highly active in RCM, with good and fast conversions being observed at room temperature for the formation of di- and tri-substituted olefins. However, it was inactive for the formation of tetra-substituted olefins. It allowed for ROMP, as well as for the cross-metathesis of *cis*-1,4-diacetoxy-2-butene with allylbenzene with a 70% *E* selectivity at 98% conversion. It is a poor catalyst for the more challenging cross-metathesis of hex-5-en-1-yl acetate with methyl acrylate.

The fact that these results are reminiscent of the activity of catalyst **4b** is in line with the similarity of anti-Bredt NHCs and CAACs in terms of electronic properties. Previous screening of CAAC-based catalysts demonstrated the importance of tuning the steric environment of the ruthenium center, especially by varying the N-substituent of the carbene ligand. However, in the case of anti-Bredt NHCs, only the free carbene bearing a 2,3-di(isopropyl)phenyl amino group is available. To date, all attempts to deprotonate precursors of these carbenes featuring smaller N-substituents have led to side-reactions under kinetic control, such as the formation of azomethine ylides. Therefore, the synthetic challenge of increasing the structural diversity of anti-Bredt NHC ruthenium complexes remains to be addressed.

## Experimental Section

### General Considerations

Experiments were performed under an inert atmosphere of dry argon, using standard Schlenk and dry-box techniques,

dry and oxygen-free solvents. Toluene, THF and pentane were distilled over sodium under argon atmosphere prior use. Dichloromethane was dried *via* elution through a solvent column drying system. CD<sub>2</sub>Cl<sub>2</sub> and C<sub>6</sub>D<sub>6</sub> were distilled from CaH<sub>2</sub>. Allylbenzene, tridecane, and *cis*-1,4-diacetoxy-2-butene were distilled from anhydrous potassium carbonate prior to use. KHMDS, ethyl acrylate, hex-5-en-1-yl acetate, and anthracene were purchased from Aldrich, stored under Ar, and otherwise used as received. 1,5-Cyclooctadiene was distilled under Ar immediately prior to the polymerization reaction. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker Avance 300 spectrometer. Chemical shifts are given relative to SiMe<sub>4</sub> and referenced to the residual solvent signal. Melting points were measured with an Electrothermal MEL-TEMP apparatus. All metathesis reactions were conducted according to the protocol described in ref.<sup>[13]</sup>

### {3-(2,6-Diisopropylphenyl)-1,3-diaza[3.3.1]non-2-ylidene[dichloro(2-isopropoxyphenylmethylene)-ruthenium (7)}

Under an argon atmosphere, amidinium triflate **8**<sup>[14]</sup> (140 mg, 0.32 mmol) was dissolved in THF (6 mL) and slowly added to a stirred solution of KHMDS (70 mg, 0.35 mmol) in THF (3 mL) at -78 °C. After 5 min, Cl<sub>2</sub>Ru[=CHC<sub>6</sub>H<sub>4</sub>-*o*-(*i*-Pr)]PPh<sub>3</sub> **9** (158 mg, 0.27 mmol)<sup>[19]</sup> in THF (10 mL) was added. The resulting mixture was warmed up to room temperature and stirred overnight. The volatiles were removed under vacuum. The residues were washed two times with pentane and the product was extracted three times with toluene. The combined toluene fractions were concentrated under vacuum and pentane was slowly layered, affording compound **7** as green crystals; yield: 145 mg (89%); mp 130–133 °C. MS: *m/z* = 605.1638 [M+H]<sup>+</sup>, calculated for C<sub>29</sub>H<sub>41</sub>N<sub>2</sub>ORuCl<sub>2</sub>: 605.1636; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ = 16.2 (s, 1H), 7.6–7.2 (m, 4H), 6.9–6.8 (m, 3H), 5.30 (m, 1H), 5.09 (pseudo sept, *J* = 6 Hz, 1H), 3.8–3.6 (m, 3H), 3.51 (d, *J* = 12 Hz, 1H), 3.36 (d, *J* = 12 Hz, 1H), 3.18 (sept, *J* = 6 Hz, 2H), 2.62 (m, 1H), 2.2–1.5 (m, 4H), 1.79 (d, *J* = 6 Hz, 3H), 1.77 (d, *J* = 6 Hz, 3H), 1.30 (d, *J* = 6 Hz, 3H), 1.24 (d, *J* = 6 Hz, 3H), 0.94 (d, *J* = 6 Hz, 3H), 0.88 (d, *J* = 6 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz): δ = 295.8 (Ru=CH), 253.3 (RuCN<sub>2</sub>), 152.5 (C<sub>aro</sub>), 146.7 (C<sub>aro</sub>), 146.5 (C<sub>aro</sub>), 144.1 (C<sub>aro</sub>), 142.0 (C<sub>aro</sub>), 130.2 (CH<sub>aro</sub>), 129.6 (CH<sub>aro</sub>), 125.5 (CH<sub>aro</sub>), 125.3 (CH<sub>aro</sub>), 123.1 (CH<sub>aro</sub>), 121.9 (CH<sub>aro</sub>), 113.0 (CH<sub>aro</sub>), 74.6 (OCH), 62.2 (CH<sub>2</sub>), 52.3 (CH<sub>2</sub>), 50.5 (CH<sub>2</sub>), 30.9 (CH), 29.7 (CH<sub>2</sub>), 29.2 (CH<sub>2</sub>), 28.2 (CH<sub>3</sub>), 27.7 (CH<sub>3</sub>), 25.9 (CH<sub>3</sub>), 25.7 (CH<sub>3</sub>), 24.1 (CH<sub>3</sub>), 23.9 (CH), 22.2 (CH<sub>3</sub>).

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