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Increased Ring Closing Metathesis Activity of Ruthenium-Based Olefin Metathesis Catalysts Coordinated with Imidazolin-2-ylidene Ligands

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Abstract: The novel air and water tolerant, imidazolinylidene-substituted ruthenium-based complex **3**, has been prepared starting from $RuCl_2(=CHPh)(PCy_3)_2$ **2** and shown to exhibit increased ring-closing metathesis activity at elevated temperature compared to that of the parent complex **2**. Di-, tri-, and even tetra-substituted cycloolefins were successfully prepared from corresponding diene precursors using catalytic amounts of **3** in moderate to excellent yields.

With the advent of efficient catalysts, the olefin metathesis reaction has emerged as a powerful tool for the formation of C-C bonds.[1] Widely used well-defined alkylidene-metal complexes for this transformation include the alkoxy imido molybdenum complex **1**[2] and the benzylidene ruthenium complex **2**.[3] The molybdenum complex **1** exhibits the higher reactivity of the two towards a broad range of substrates with many steric or electronic variations;[4] however, it also suffers from high sensitivity to air and moisture and decomposition upon storage. To increase the utility of the ruthenium family of complexes by increasing the activity and/or selectivity, a number of derivatives of **2** have been prepared. These derivatives of **2** include bidentate salicylaldimine ruthenium complexes[5] and binuclear ruthenium complexes.[6] The recent reports from the Herrmann group on the derivatization of **2** with imidazolinylidene ligands[7] prompted us to explore this family of complexes for use in organic applications. Herein, we report a ruthenium-based imidazolinylidene complex **3**, showing a ring closing metathesis activity comparable to that of the molybdenum complex **1**, yet exhibiting a remarkable air and water stability similar to that of the parent benzylidene ruthenium complex **2**.

Herrmann et al. prepared a novel class of ruthenium complexes **4** by substituting both of the phosphine with imidazolinylidene ligands.[7] Although these complexes showed little if any improvements in applications to ROMP and RCM, their potential activity expected from the ligand's basicity and steric bulk[8] led us to explore some of the other members of the Arduengo imidazolinylidene ligand family.[9] Of the number of 1,3-diaryl-imidazolin-2-ylidene ligands that were tried, only the 2,6-disubstituted aryl systems including the 1,3-

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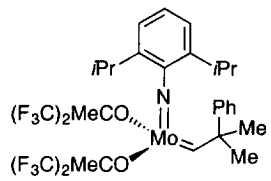
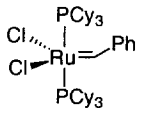
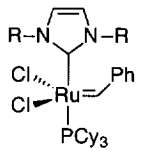
dimesityl-imidazolin-2-ylidene ligand gave clean substitution products. In contrast to the Herrmann systems, this ligand displaced only one of the two phosphines to produce **3**.[10] This new derivative of **2** allows many of the desirable RCM reactions to be carried out with ruthenium complexes.



1

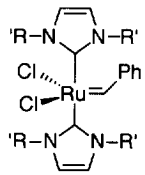


2



R = C_6H_2-2,4,6-$(CH_3)_3$

3

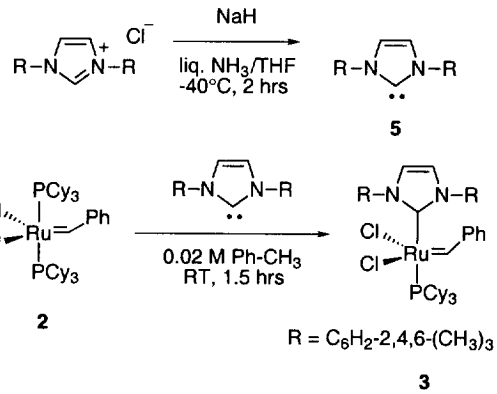


R' = C_6H_{11}, C_3H_7

4

The monosubstituted imidazolinylidene complexes can be prepared using Herrmann's procedure,[7] provided that the substituents on the imidazole ring are sufficiently bulky to prevent disubstitution (Scheme 1). The imidazolinylidene ligand **5**[9] is conveniently synthesized from the corresponding salt with sodium hydride in liquid ammonia/THF[11] and can be isolated or used without purification in the subsequent step. The ligand exchange reaction in toluene[12] is rapid at room temperature and the product **3**[13] is isolated as a pinkish-brown microcrystalline solid that can be purified by recrystallization from pentane at –78°C.

Scheme 1



5

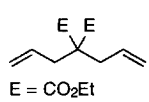
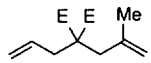
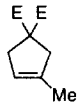
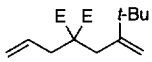
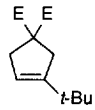
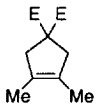
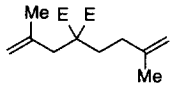
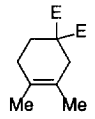
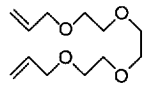
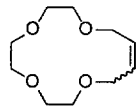
2

R = C_6H_2-2,4,6-$(CH_3)_3$

3

The activity of the complex **3** has been briefly explored as shown in Table 1. Although the new species is less reactive than the parent **2** at room temperature for ring closing metathesis reactions, the reactivity increases dramatically at slightly higher temperatures. For instance, although the ring closure of diethyl diallylmalonate ester (Entry 1) takes hours at room temperature with complex **3**, the reaction is completed within 30 minutes at 40°C with the same carbene catalyst.

Table 1. Results of the RCM with 5 mol% **2** or **3** in 0.05M CD_2Cl_2 at reflux

Entry	Substrate	Product	Time (min)	Yield with **2** (%)[a]	Yield with **3** (%)[a]
1	 E = CO_2Et		30	100	100
2			30	82	100
3			60	N.R.	100
4			90	N.R.	40
5			90	N.R.	95
6			60	39[b]	55 (45)[c]

[a] Yields represent the conversion to product as determined by ^1H NMR. [b] E:Z = ~1.6:1
[c] Isolated yield in parentesis; E:Z~2:1.

In addition, the complex **3** exhibits increased ring closing activity towards sterically demanding olefins. For example, 2-*t*-butyl diethyl diallyl malonate ester (Entry 3) can be cyclized with 5 mol% of **3** in 1 hr, while the corresponding reaction with 5 mol% of **2** does not yield any significant amount of cyclized product.[4] Similarly, tetra-substituted olefins (Entries 4 and 5) can be prepared in moderate to excellent yields using the complex **3**.

Ring closing metathesis of macrocyclic ethers with complex **3** is comparable to that with complex **2**. For instance, triethylene glycol diallyl ether (Entry 6) is cyclized at 40°C to a 45% isolated yield with complex **3** and to a 39% yield with complex **2**.[14] The stereoselectivities of both complexes are similar and the product is obtained as a ~2:1 and a ~1.6:1 mixtures of trans:cis isomers, respectively.

In conclusion, this complex exhibits high olefin metathesis activity in RCM reactions and extends the potential of the ruthenium family of complexes. Di-, tri-, and tetra-substituted olefins can be prepared in moderate to excellent yields. Further detailed studies regarding the

mechanistic description, the scope and limitations, and the steric/electronic tuning of on the complex are under investigation.

Acknowledgements.

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13. Representative procedure for the preparation of **3**: To a solution of imidazolin-2-ylidene ligand **5** (304 mg, 1.0 mmol) in toluene (40 mL) was added a solution of Ru complex **2** (823 mg, 1.0 mmol) in toluene (10 mL) under N_2 atmosphere. The reaction mixture immediately turned from purple to dark red and it was allowed to stir at RT for 1.5 hrs. The reaction mixture was filtered, toluene was evaporated in vacuo and the remaining solid residue was recrystallized from pentane at -78°C thrice to give the desired complex **3** (700 mg, 85%) as a pinkish-brown microcrystalline solid: ^{1}H NMR (C_6D_6, 400 MHz) δ 19.93 (s, 1H), 7.15 (m, 5H), 7.03-6.93 (m, 2H), 6.91(s, 2H), 6.20-6.17 (m, 2H), 2.78-2.45, 2.40-2.00, 1.84, 1.80-1.48, 1.36-0.98 (all m, 51H); ^{31}P NMR (C_6D_6, 161.9 MHz) δ 32.43; HRMS (FAB) $C_{46}H_{63}Cl_2N_2PRu$ [M$^+$] 846.3143, found 846.3116.
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