Electrochemically-Controlled, Ruthenium-Catalyzed Olefin Metathesis

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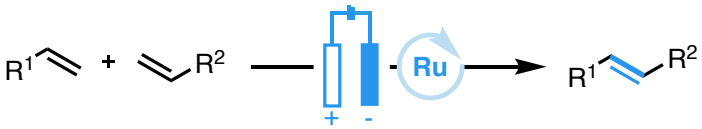

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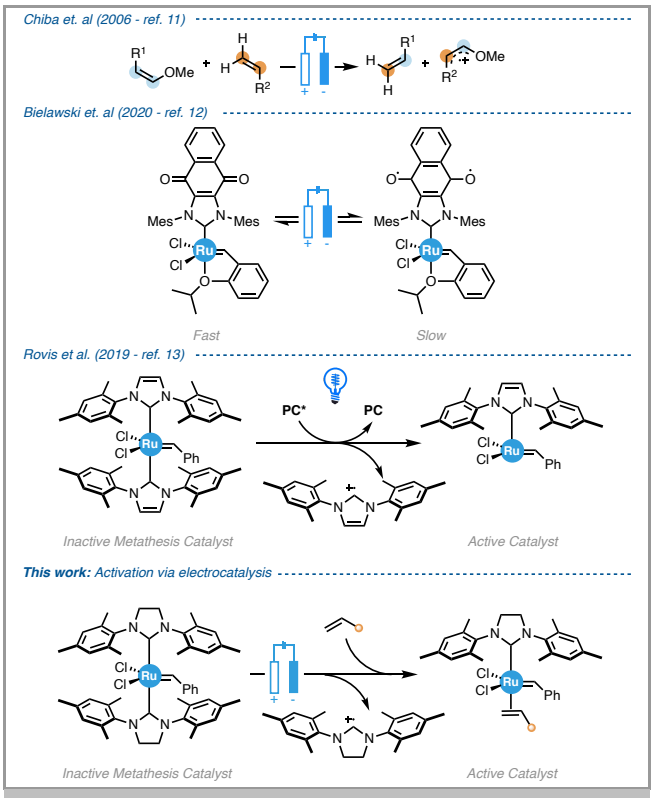
Abstract We report the development of a system to electrochemically-control Ruthenium-catalyzed olefin metathesis. Catalyzed by a commercially-available bis-NHC Ru complex, this system displays a broad substrate scope with very short reaction times, as well as excellent levels of temporal control over metathesis with only electricity as a stimulus.

Key words electrochemistry, electrocatalysis, olefin metathesis, Ruthenium catalysis

Olefin metathesis is one of the most valuable reactions in organic chemistry for the formation of C=C bonds, as reflected by its widespread application in synthetic chemistry,[1] materials science,[2] and polymer science.[3] In recent years, there has been a push to develop methods of controlling metathesis, or more specifically, activate latent metathesis catalysts on demand via external stimuli.[4] Harnessing control over metathesis is important for the efficient production of more complex materials.[5,6] Several reports have achieved such control over metathesis using stimuli, including acid,[7] sonication,[8] light,[9] and electricity.

Electrochemistry, in particular, has gained recent attraction as an external stimulus for chemical reactions—the applied current or voltage can be easily and precisely manipulated throughout the reaction.[10] This unique advantage has inspired significant efforts to enable olefin metathesis electrochemically. For example, Chiba described a metal-free method of triggering cross-metathesis (CM) between enol ethers and alkenes upon the application of an oxidizing potential.[11] More recently, Bielawski extended this approach to ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP) reactions, reporting a redox-switchable Ru catalyst of which the catalytic activity could be toggled between fast and slow states depending on the polarity of the applied potential.[12] While the electrochemical activation of metathesis is well-demonstrated, existing methods to harness temporal control over the reaction remain limited.



Scheme 1 Previous work on controlled olefin metathesis.

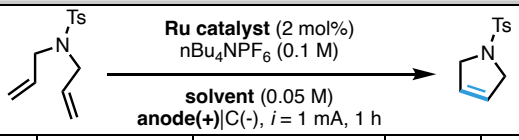
Previously, we disclosed a method of controlling olefin metathesis using visible light photoredox catalysis.[13] Through the combination of a latent bis-NHC, $(IMes)_2RuCl_2(CHPh)$, catalyst and triphenylpyrilium tetrafluoroborate as the photocatalyst, high levels of spatiotemporal control over metathesis were accomplished. As an orthogonal strategy, we envisioned that the reactivity of the metathesis catalyst could be controlled with electricity as the stimulus instead of light. In the photoredox system, activation of the metathesis catalyst involves oxidation by the excited photocatalyst, and its deactivation relies on reduction by the reduced photocatalyst.

We hypothesized that an electrochemical-based system would allow these same redox events to proceed under milder and greener conditions; the electrodes—typically constructed from inexpensive and harmless materials—would serve as the electron transfer agents.[14] Thus, along with its intrinsic precision over reaction control, electrochemistry offers an enhanced, cost-effective, and sustainable strategy for initiating and controlling metathesis. Herein, an electrochemically-enabled olefin metathesis system with excellent temporal control is described.

To test the viability of this electrochemical method, we investigated the RCM of *N,N*-diallyl-tosylamide using the mixed bis-NHC complex **Ru$_1$,** which we recently showed may be activated by Deep Red light photoredox catalysis,[15] in the presence of different anode materials and solvents (Table 1, Entries 1-4). Anode screening showed that copper is the optimal anode material with acetone as the solvent (12%). However, extending the reaction time did not result in an appreciable increase in yield, and a considerable amount of the starting material was observed to decompose. Considering the narrow potential window of acetone,[16] we hypothesized that the solvent was being reduced electrochemically and the resulting product was inhibiting the Ru catalyst. To minimize solvent reactivity, dichloromethane (DCM) was added as a co-solvent. Gratifyingly, there was no decomposition, with 3:1 DCM:acetone providing the highest yield (70%, Table 1, Entries 5 and 6). Interestingly, the reaction still proceeds when acetone is eliminated, furnishing a slightly diminished yield (63%, Table 1, Entry 7).

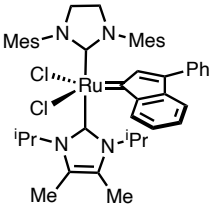
We then turned our attention to screening alternative ruthenium complexes because extending the reaction time, unfortunately, did not lead to an improvement in yield, which was likely due to eventual catalyst death. To our delight, switching to the commercially-available bis-SIMes complex **Ru$_2$**, previously reported by Grubbs,[17] afforded 97% yield of diallyltosylamide in one hour using a constant current system set to 1 mA (Table 1, Entry 8). With such an extremely privileged substrate for RCM, we lowered the reaction time to 5 minutes and obtained 92% yield (Table 1, Entry 9). Control experiments demonstrate that an applied current is necessary. No conversion was observed in the absence of current and electrodes (Table 1, Entry 10), and only a trace amount of product is obtained when the electrodes are in solution without an applied current (<5%, Table 1, Entry 11). The background reactivity observed when the electrodes are immersed in solution could be explained by a residual current flowing between the two electrodes,[18] potentially activating the Ru complex.

Table 1 RCM Optimization



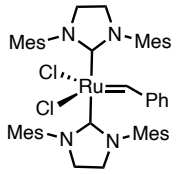
Entry	Ru catalyst	Solvent	Anode	Yield[b]
1	Ru_1	Acetone	C	0
2	Ru_1	Acetone	Pt	0
3	Ru_1	Acetone	Cu	12
4	Ru_1	Acetone	Zn	0
5	Ru_1	1:1 DCM:Acetone	Cu	46
6	Ru_1	3:1 DCM:Acetone	Cu	70
7	Ru_1	DCM	Cu	63
8	Ru_2	3:1 DCM:Acetone	Cu	97
9[c]	Ru_2	3:1 DCM:Acetone	Cu	92
10[d]	Ru_2	3:1 DCM:Acetone	Cu	0
11[e]	Ru_2	3:1 DCM:Acetone	Cu	trace

Ru Catalysts



$RuCl_2(SIMes)(I^iPrMe)(Ind)$

(Ru_1)



$RuCl_2(CHPh)(SIMes)_2$

(Ru_2)

[a]All optimization reactions were conducted on a 0.1 mmol scale. [b]Yield by ^{1}H NMR using mesitylene as internal standard. [c]Reaction time 5 minutes. [d]Reaction conducted without an applied current and without electrodes in solution. [e]Reaction conducted without an applied current.

With optimized conditions in hand, we explored the scope with respect to other metathesis reactions (Figure 1). For RCM, higher yields are achieved for diallyl esters and diallyl tosylamides of various ring sizes compared to our visible light system[13] (88-98%). Despite being somewhat susceptible to oxidation, good yields are obtained for ethers (63-69%). More substituted alkenes proved to be challenging substrates because of their steric bulk, giving low yields. Cross-metathesis (CM) with Type I and Type II olefins[19] also works with this system (17-54%), as well as ring-opening cross-metathesis (ROCM) (25-31%), and ring-opening metathesis polymerization (ROMP) (52-59% conversion). Interestingly, during the ROMP scope, it was observed that the polymer developed on the surface of the anode, supporting our initial hypothesis that catalyst activation proceeds through an oxidative pathway (Figure S2).

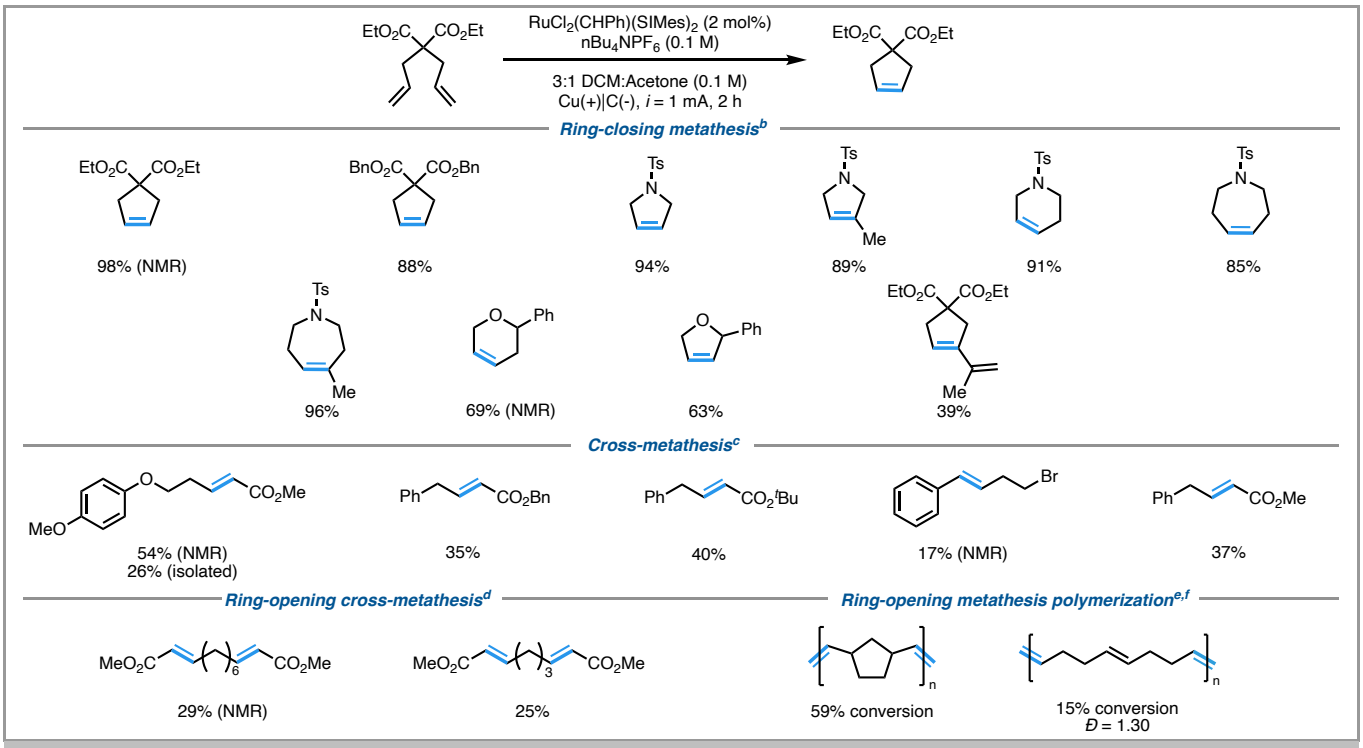


Figure 1 Scope of Metathesis Reactions. [a]All yields isolated unless otherwise noted. NMR yields determined by ^{1}H NMR spectroscopy using mesitylene as internal standard. [b]Conducted on a 0.2 mmol scale. [c]Conditions: left substrate (0.2 mmol), right substrate (0.4 mmol). [d]Conditions: left substrate (0.2 mmol), right substrate (0.6 mmol). [e]Conditions: monomer (0.2 mmol), Ru catalyst (0.02 mol%), 30 min. [f]Percent monomer conversion determined by ^{1}H NMR spectroscopy using mesitylene as internal standard. Polydispersity index determined by GPC

Next, we sought to demonstrate the degree of temporal control we could achieve over metathesis for potential applications in materials science. To this end, on/off experiments for the RCM of *N,N*-diallyl-tosylamide were conducted by subjecting the reaction mixture to alternating periods of applied current and no current, turning the reaction on and off with a simple flip of a switch. Due to the speed at which this reaction occurs, the experiment was conducted at 0 °C, demonstrating good temporal control. Only minimal increases in yield are observed during the off periods (1 to 2%), demonstrating that metathesis can be controlled on demand electrochemically using this Ru catalyst, a promising candidate for applications in materials science.

To elucidate the mechanism, we investigated the redox behavior of the Ru complex (Figure 3). In accord with our visible light system which employs a similar bis-NHC complex, the cyclic voltammogram of this complex features two distinct peaks at 0.363 and 2.059 V, with the former likely corresponding to the pseudo-reversible Ru(II)/Ru(III) redox couple. The latter is attributed to the oxidation of SIMes, which is proposed to be responsible for the ligand's dissociation from the Ru center and generation of the active metathesis catalyst. This oxidation event appears to be irreversible, which could explain the small amount of product formation during the off periods in the temporal control study.

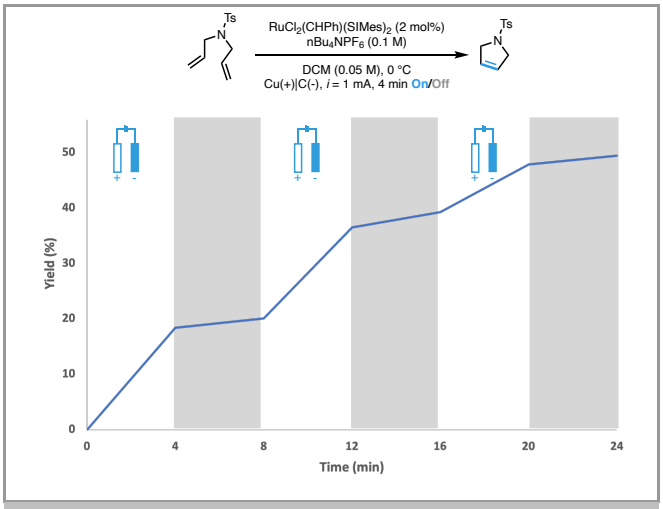


Figure 2 Temporal control over the RCM of *N,N*-diallyl tosylamide.

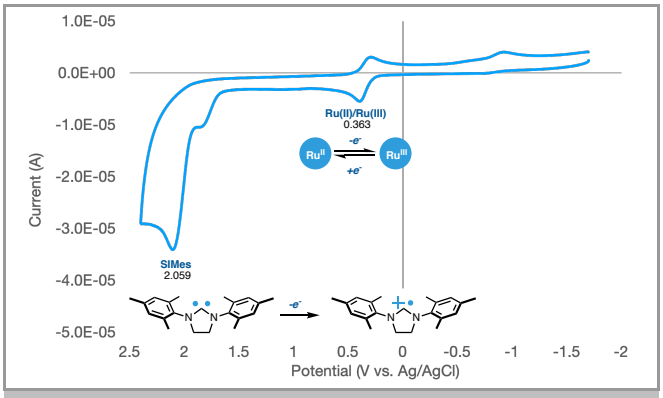


Figure 3 Cyclic voltammogram of $RuCl_2(CHPh)(SIMes)_2$ was measured in a solution of 0.1 M nBu_4NPF_6 in DCM, with a glassy carbon working electrode, Pt wire counter electrode, and Ag/AgCl reference electrode.

We therefore propose the following mechanism for the reaction (Figure 4). First, anodic oxidation of the inactive bis-SIMes Ru complex **I** induces ligand dissociation, generating the active metathesis catalyst **II** and the SIMes radical cation **V**. Reduction of **V** at the cathode produces the free SIMes ligand, which can coordinate to **IV** following metathesis and return the inactive species **I**.

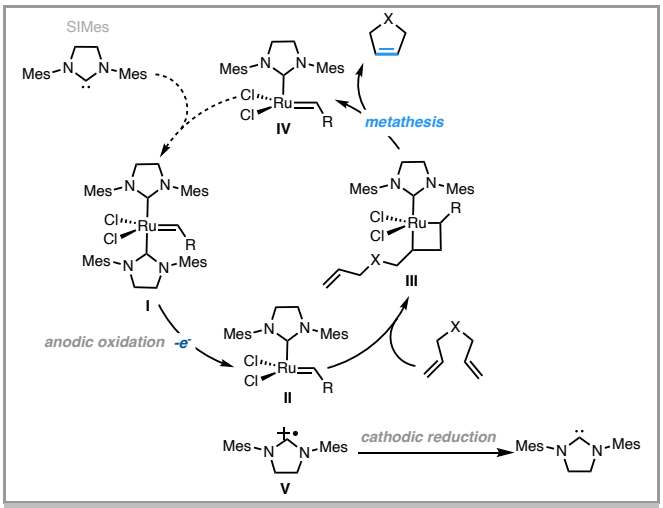


Figure 4 Proposed mechanism.

In summary, we have developed an efficient and facile method to electrochemically-control olefin metathesis. By subjecting a bis(NHC)-ruthenium complex to an electric current, on-demand control over metathesis is achieved with excellent levels of temporal control. We anticipate that this electrochemical strategy will find itself in various applications in materials and polymer science.

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Supporting Information

Supporting Information contains experimental procedures, and compound characterization.

Primary Data

NO.

Conflict of Interest

The authors declare no conflict of interest.

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