

Appendix B

Miscellaneous C-H-Activated Catalysts

Introduction

This chapter contains several miscellaneous C-H-activated complexes that were partially prepared and characterized. Many of these complexes have not been fully characterized (e.g., ^{13}C NMR spectra and HRMS are lacking), but there is good reason to believe that the target complex was formed based on ^1H NMR spectroscopy and qualitative evidence such as color changes. Selected unsuccessful attempts at other complexes will also be presented. The primary product in these unsuccessful attempts was either an unidentified decomposition product, or a ruthenium hydride species. I will try to briefly discuss the rationale behind the preparation of each complex in a manner that is useful for future researchers.

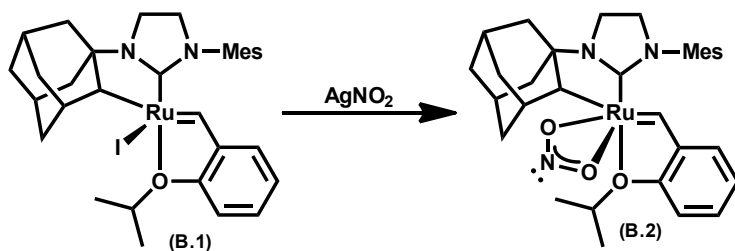


Figure B.1. Preparation of **B.2**

Nitrite Catalyst

Before focusing on the nitrate catalysts presented in Chapter 6, we also prepared a catalyst with a nitrite X-type ligand (Figure B.1). This catalyst was successfully prepared and preliminary results indicate its reactivity is on par with its nitrate-based cousins. Interesting redox chemistry may be possible at the nitrite ligand.

A 20 mL scintillation vial in the glove box was charged with **B.1** (13 mg,

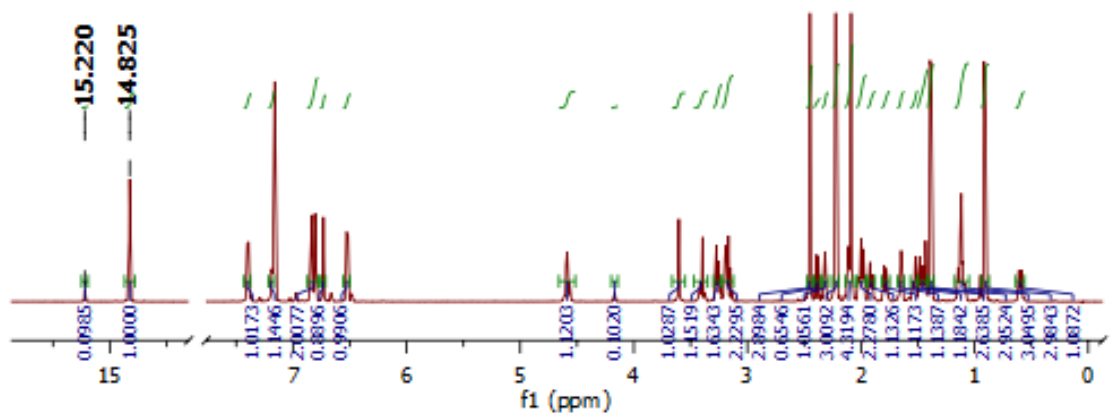


Figure B.2. ^1H NMR (600 MHz, C_6D_6) spectrum of **B.2** at RT. Peak at $\delta = 15.22$ ppm is unknown impurity

0.019 mmol) and AgNO_2 (14 mg, 0.096 mmol) and THF (1 mL) was added. The suspension was stirred vigorously until a color change from brown to red/purple was observed (ca. 3–5 min). The solution was immediately filtered, washing with THF, and concentrated. The resulting residue was triturated with Et_2O to give **B.2** (10 mg, 87%). Note that similar to the formation of the nitrate catalysts in Chapter 6, prolonged exposure of **B.1** (or **B.2**) to AgNO_2 resulted in complete decomposition.

Catalysts with Chiral Carboxylates

Theoretical calculations have established that the C-H activated catalysts most likely proceed through a side-bound ruthenacycle intermediate.¹ Therefore, the ligands in these catalysts may be better able to influence ruthenacyclobutanes. In order to examine this, we prepared C-H catalysts with chiral carboxylates for enantioselective olefin metathesis (i.e., asymmetric ring-opening cross-metathesis).²

A multitude of commercially available chiral carboxylic acids are available

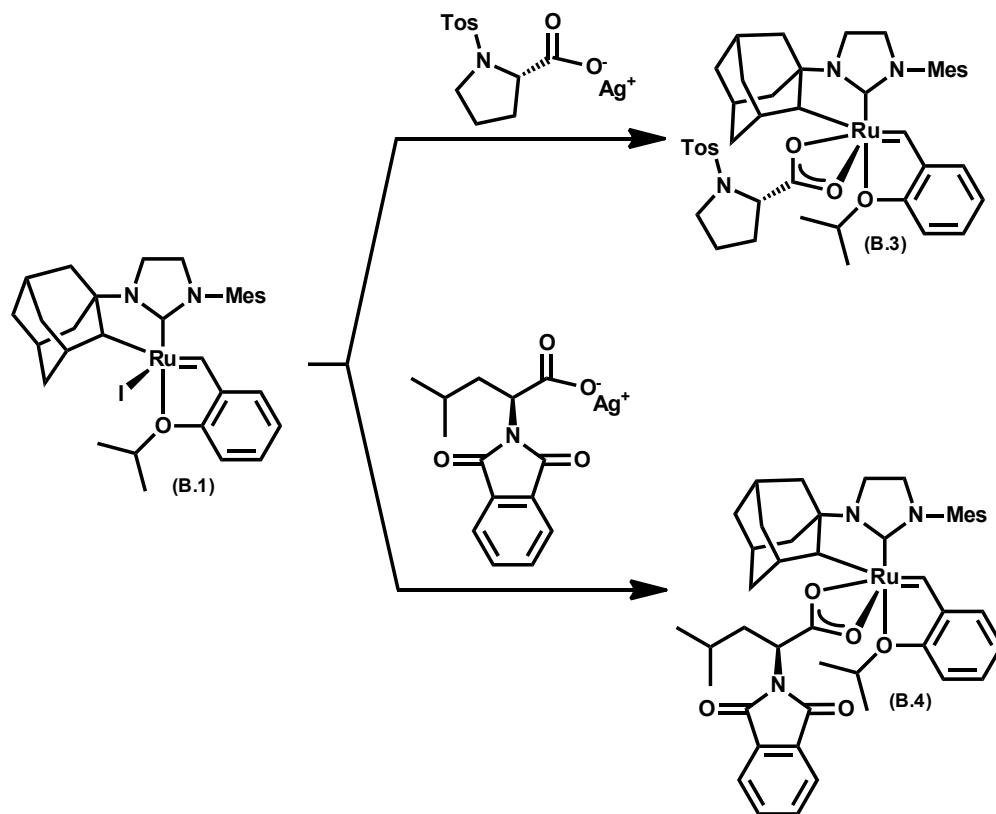


Figure B.3. Preparation of **B.3** and **B.4**

because of their prevalence in enantioselective rhodium-catalyzed cyclopropanation reactions.³ Following the conversion of two selected acids to their corresponding silver salts, transmetalation onto **B.1** was affected using the procedures discussed in Chapter 6 (Figure B.3). The ¹H NMR spectra of both **B.3** and **B.4** contained three resonances each in the benzylidene region (Figure B.4). In the case of **B.3**, these resonances were found to interconvert on the NMR timescale as evidenced by a 2D ROESY spectrum (Figure B.5). In contrast, the benzylidene resonances of **B.4** did not interconvert by ROESY. At this point, it is unclear what structures these benzylidene resonances represent.

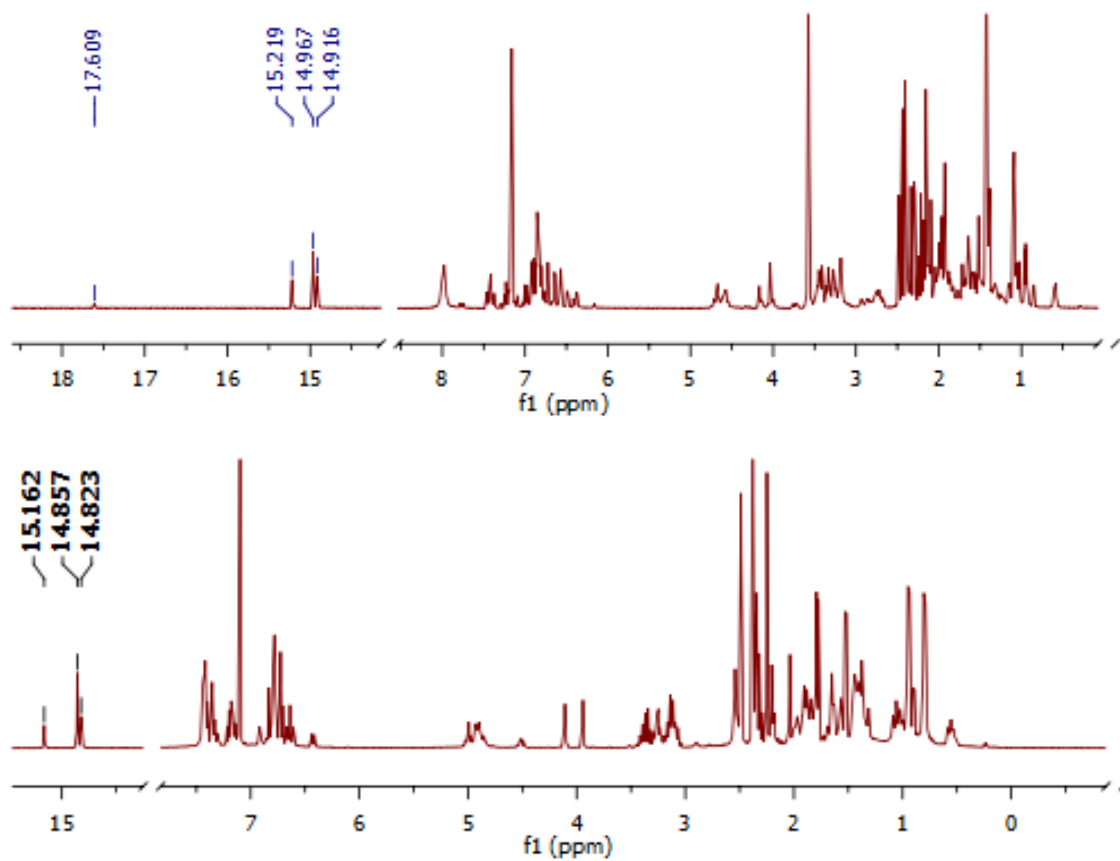


Figure B.4. ¹H NMR (400 MHz, C₆D₆) spectrum of **B.3** (top) and **B.4** (bottom) at RT

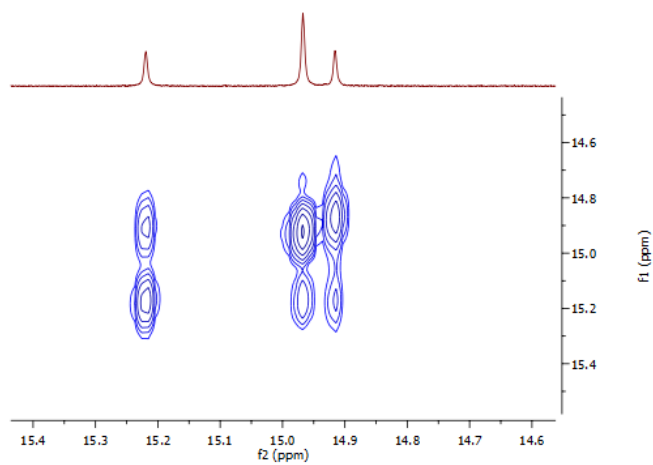


Figure B.5. 2D ROESY of **B.3** showing chemical exchange

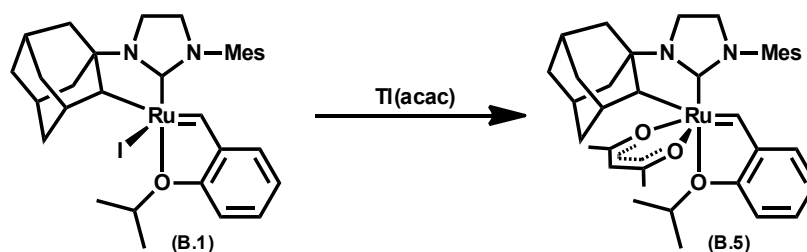


Figure B.6. Preparation of **B.5**

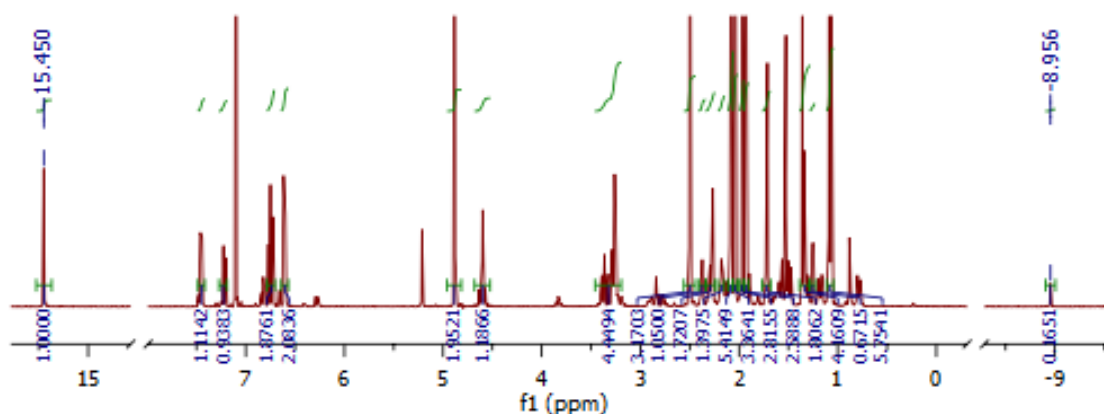


Figure B.7. ^1H NMR (400 MHz, C_6D_6) spectrum of **B.5**

Acetylacetonate (acac) Complexes

In addition to carboxylates, the iodide ligand in **B.1** can also be replaced with acac ligands (Figure B.6). When **6.1** was exposed to Ti(acac) according to the general procedure in Chapter 6, complex **6.5** and an unidentified Ru-H complex were recovered (Figure B.6 and B.7). Complex **6.5** was found to be inactive under standard homodimerization conditions. It's possible that this inactivity may be rem

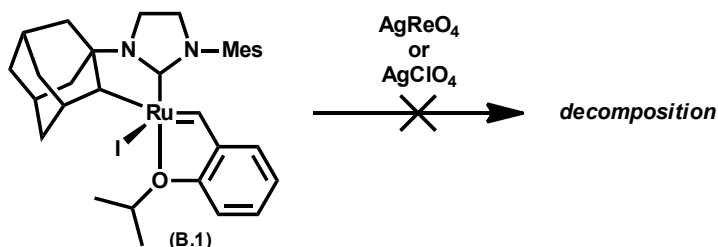


Figure B.7. Attempted preparation of ReO_4^- and ClO_4^- complexes

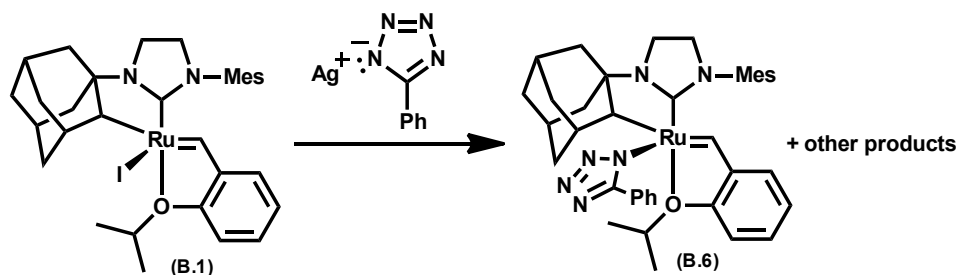


Figure B.8. Tetrazolate complex **B.6**

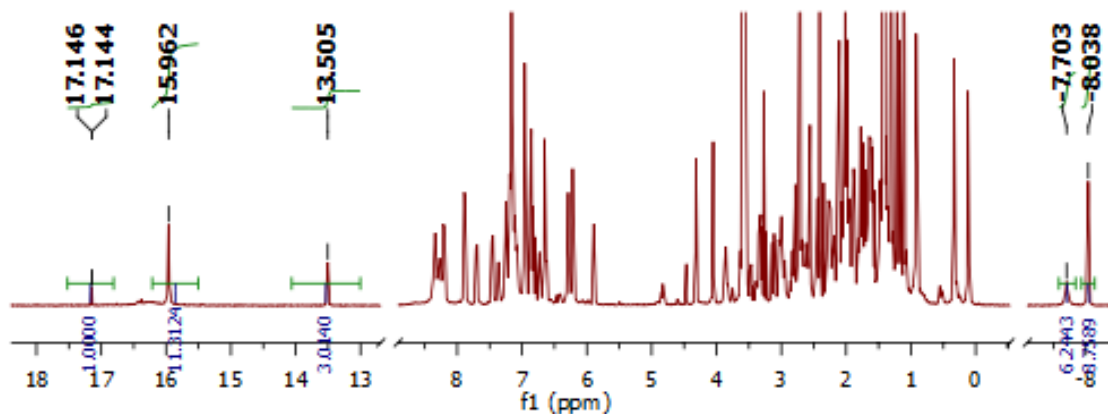


Figure B.9. ^1H NMR (400 MHz, C_6D_6) spectrum of crude reaction mixture from Figure B.8

edied through the addition of exogenous acid (see Chapter 2).

Perchlorate and Perrhenate Ligands

In the hopes finding similar ligands to nitrate, we also attempted to replace the iodide ligand in **B.1** with the heavily oxygenated ligands perchlorate (ClO_4^-) and perrhenate (ReO_4^-), but these reactions resulted in complete decomposition. Extreme care should be taken when handling these heavily oxygenated compounds as they are explosive.

Tetrazolate Complexes

Tetrazolate-type ligands, as close analogues of carboxylates, were also briefly examined (Figure B.8). When **B.1** was exposed to silver (I) phenyl tetrazolate, a mixture of products, starting material, and hydrides was observed (Figure B.9). This may indicate that C-H-activated species with tetrazolate ligands are thermally unstable and decompose under the reaction conditions. However, no attempts were made to isolate or purify the complex mixture.

Sulfonate Complexes

Sulfonate ligands have previously been used in olefin metathesis catalysts, and displayed improved selectivity for Z-olefins compared to halide-ligated catalysts.⁴ Therefore we attempted to prepare C-H-activated catalysts containing sulfonate ligands. Exposure of **B.1** to silver (I) tosylate resulted in the formation of the desired sulfonate complex, but this product quickly decomposed in solution at RT into a mixture of unidentified hydride species. Despite this result, different substituted sulfonates may yield more stable complexes.

References

- (1) Liu, P.; Xu, X.; Dong, X.; Keitz, B. K.; Herbert, M. B.; Grubbs, R. H.; Houk, K. N. *J. Am. Chem. Soc.* **2012**, *134*, 1464.
- (2) (a) La, D. S.; Sattely, E. S.; Ford, J. G.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2001**, *123*, 7767. (b) (1) Berlin, J. M.; Goldberg, S.; Grubbs, R. H. *Angew. Chem. Int. Ed.* **2006**, *45*, 7591.

(3) Trindade, A. F.; Coelho, J. A. S.; Afonso, C. A. M.; Veiros, L. F.; Gois, P. M. P.

ACS Catalysis **2012**, 2, 370.

(4) Teo, P.; Grubbs, R. H. *Organometallics* **2010**, 29, 6045.