

Introduction

Light olefins obtained by steam cracking of higher paraffins serve as precursors to oxygenated solvents, fuel additives, and organic building blocks. Olefin hydration or hydroalkoxylation reactions of olefins provide the means to forge carbon-oxygen bonds, with strong acids serving as traditional promoters of these transformations. Acid catalysis has been remarkably successful for many substrates including methyl *tert*-butyl ether (MTBE), a fuel additive whose use has been limited by regulatory and environmental concern in recent decades. In contrast, hydroalkoxylation catalysts which proceed via traditional organometallic mechanisms are remarkably limited in terms of activity, scope, and the conditions required to effect C-O bond formation. Our PRF-funded research program has been investigating the role of iridium allyls in the formation and cleavage reactions of tertiary ethers. In addition, we have been exploring the reactivity of cationic bis(phosphine)iridium complexes in reductive ether silylation, a project which grew out of initial observations on the reactivity of cationic iridium allyls.

Iridium allyls in C-O bond formation and cleavage

In our proposal we identified that dehydrogenation of a simple cationic bis(phosphine)iridium dihydride complex in MTBE gave rise to a methallyl complex (**1**) resulting from C-O bond cleavage. We published these findings and a preliminary discussion of the proposed mechanism of this stoichiometric transformation prior to the beginning of the grant period.¹ The catalytic cleavage of MTBE to methanol and isobutene is not thermodynamically favorable at modest reaction temperatures, but in initial studies under catalytic conditions, **1** is found to give > 70 turnovers in 18 hours at 65 °C (Figure 1). To provide driving force we also conducted examined MTBE cleavage under hydrogenolysis conditions. **1** is found to catalyze the hydrogenolysis of MTBE to methanol and isobutane under H₂, with a brief survey of conditions yielding > 200 turnovers in 18 hours at 65 °C. The addition of the organic base 2,6-lutidine reduces the efficiency of MTBE hydrogenolysis to roughly 5 TON in the same time period, but the observation that catalysis still occurs under basic conditions allows us to rule out a simple acid-promoted mechanism. We hypothesize that the reduction in reaction rate in the presence of base likely results from competition for catalyst binding sites. We have also found that **1** is a catalyst for the hydroalkoxylation of isobutene with a variety of aliphatic alcohols, though the reaction rates observed to-date have been modest. The development of improved systems is ongoing.

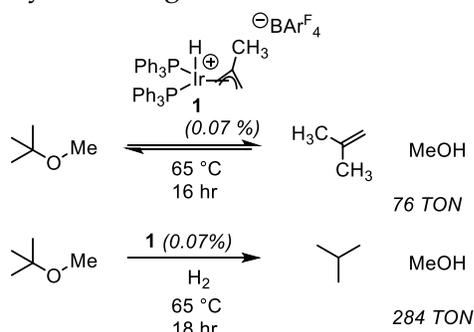


Figure 1. MTBE cleavage and hydrogenolysis by **1**.

Observations on electron-deficient catalyst variants

In an effort to investigate the effect of increasing the electrophilicity of the methallyl ligand we prepared the catalyst variant **3** with less electron-releasing phosphines (Figure 2). This change significantly alters the reactivity of the resulting complex in comparison to **1**. The hydrido allyl **3** can be observed spectroscopically only in 1,2-difluorobenzene, as the metal hydride is capable of serving as a potent Brønsted acid. Indeed **3** is rapidly deprotonated even by simple alkyl ethers.

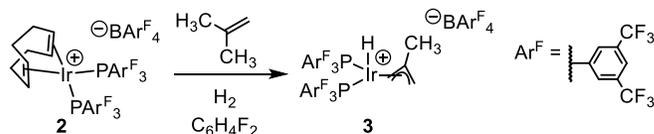


Figure 2. Synthesis of the Brønsted-acidic methallyl monohydride **3**.

Related derivatives are found to promote the oligomerization of isobutene, presumably via an acid-catalyzed path. The remarkable acidity of these complexes does not temper their reactivity as hydrogenation catalysts, therefore we have been able to conduct isobutene dimerization and hydrogenation in tandem with a single catalyst to produce the valuable fuel hydrocarbon isooctane as well as small quantities of the higher oligomers (Figure 3). Under these conditions we suspect that the cationic diene precatalyst **2** is converted to **3** or a related acidic intermediate which acts as a source of Brønsted-acid. The resulting neutral complex is presumably active for olefin hydrogenation. This work is being conducted by senior graduate student Scott Chapp and is ongoing in our laboratory.

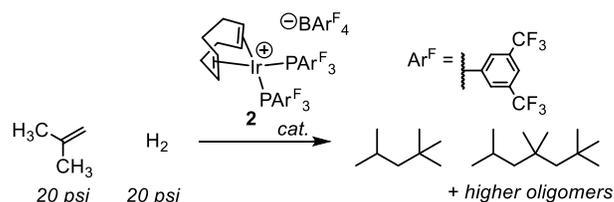


Figure 3. Tandem isobutene oligomerization-hydrogenation to high-octane alkane products.

Ether cleavage via iridium-catalyzed silylation

During the course of our studies on cationic bis(phosphine)iridium complexes we found that **1** is a catalyst for the reductive silylation of ethers to give alkane and silyl ether products. The iridium-catalyzed variant of this transformation was first developed by Brookhart using a cationic bis(phosphine)pincer iridium complex, but no other iridium complexes had been demonstrated to be catalysts since the initial report in 2008.² Although silane reductants are undesirable for the production of low-value products via ether cleavage, the potential for the development of a selective system for the reduction of complex polyether-containing molecules like carbohydrate derivatives has inspired us to explore this transformation in more detail.

We have found that simple cationic bis(phosphine)iridium complexes like **4** serve as catalysts for reductive ether cleavage via silylation. In a recent report we showed that benzylic ethers can be cleaved rapidly in the presence of less-reactive ethers as well as functional groups which are labile under traditional benzyl ether hydrogenolysis conditions.³ Over-reduction is not observed, and the use of simple monodentate phosphines has enabled us to explore a wide variety of catalyst derivatives. Our preliminary experiments on this system grew directly from PRF-funded research efforts, and became part of an NSF-CAREER award which was funded during this grant period. Thus PRF funding of this research program has directly translated to a new NSF-funded research project in our laboratory.

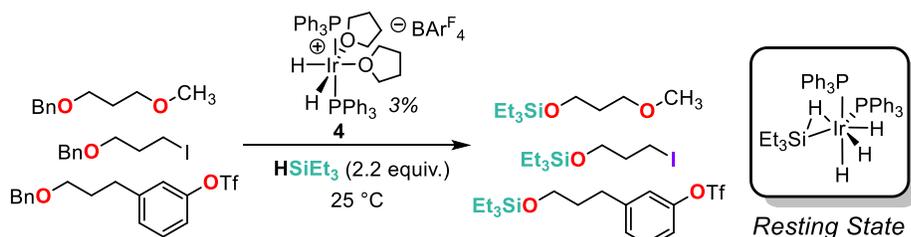


Figure 4. Reductive silylation of benzylic ethers catalyzed by cationic bis(phosphine) complexes.

References

- (1) Chapp, S. M.; Schley, N. D., "Evidence for Reversible Cyclometalation in Alkane Dehydrogenation and C–O Bond Cleavage at Iridium Bis(phosphine) Complexes." *Organometallics* **2017**, *36* (22), 4355-4358.
- (2) Yang, J.; White, P. S.; Brookhart, M., "Scope and Mechanism of the Iridium-Catalyzed Cleavage of Alkyl Ethers with Triethylsilane." *J. Am. Chem. Soc.* **2008**, *130* (51), 17509-17518.
- (3) Jones, C. A. H.; Schley, N. D., "Selective alkyl ether cleavage by cationic bis(phosphine)iridium complexes." *Organic & Biomolecular Chemistry* **2019**, *17* (7), 1744-1748.