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Professor James P. Stambuli, The Ohio State University; AFOSR Final Report

Contract/Grant Title: Site-selective alkane dehydrogenation of fatty acids

Contract/Grant#: FA9550-10-1-0532

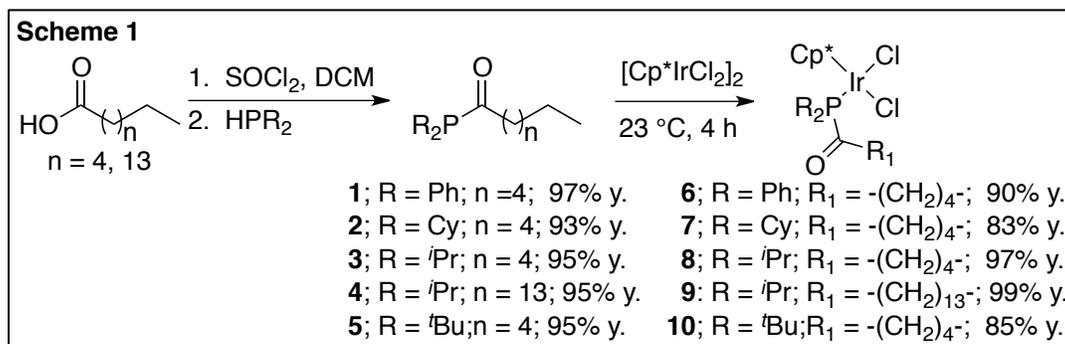
Final Reporting Period: 15 September 2011 to 14 September 2011

Professor James P. Stambuli
The Ohio State University

Final Report

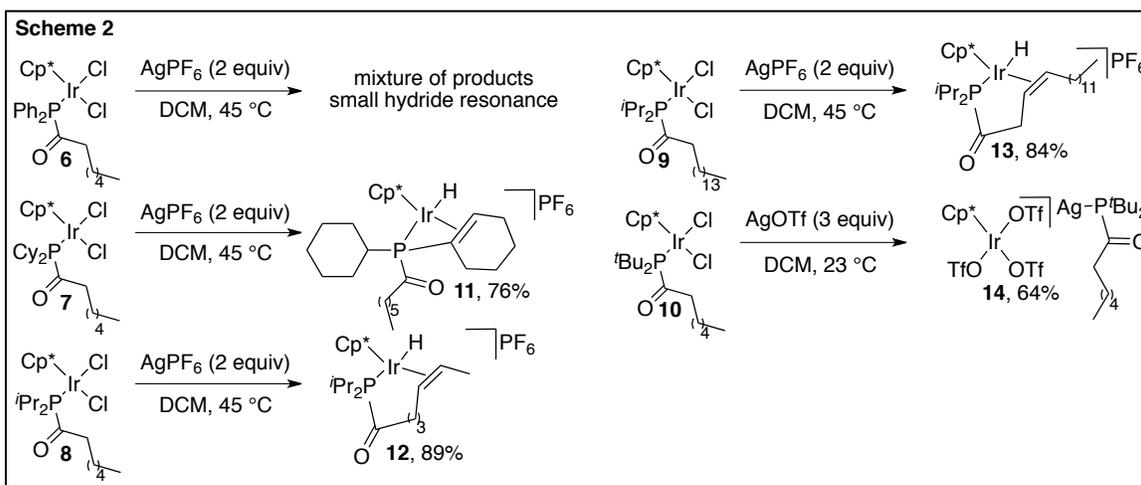
The proposed research examines the site-selective dehydrogenation of alkanes. The alkanes employed were fatty acids and related derivatives prepared from this renewable resource material. The design and development of a system that demonstrates, for the first time, the site-selective dehydrogenation of an acyclic alkane is described in the report below.

Rather than employ highly basic trialkyl phosphine ligands in our initial reactions, the lesser-known acyl phosphine class of ligands were employed. The initial thoughts were to use less basic ligands so that the coordinate ligand and olefin would be easier to be replaced by an additional ligand, and hence allow the possibility for the catalyst to turn over. We were intrigued by the limited employment of these types of ligands in transition metal catalysis, as well as the ability to directly incorporate fatty acids into the ligand. The preparation of the acyl phosphines (**1-5**) was easily accomplished starting from the corresponding saturated carboxylic (Scheme 1). Because of the lack of basicity in the phosphine, electron-rich 1,2,3,4,5-pentamethylcyclopentadiene (Cp*) ligand was chosen to increase the electron density to the complex. Reaction of the corresponding acyl phosphines with $[\text{Cp}^*\text{IrCl}_2]_2$ provided the desired complexes (**6-10**) in excellent yields.

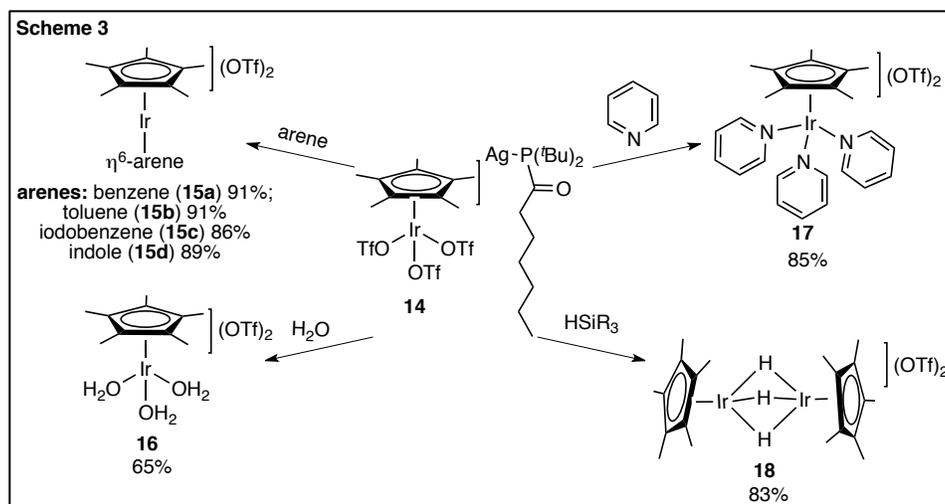


The above complexes were reacted in the presence of silver salts at mild temperatures to provide an unsaturated metal center that would be more reactive toward C-H activation of the alkane (Scheme 2). The diphenylphosphine complex **6** was shown to react with silver trifluoromethanesulfonate (AgOTf) at ambient temperature to yield

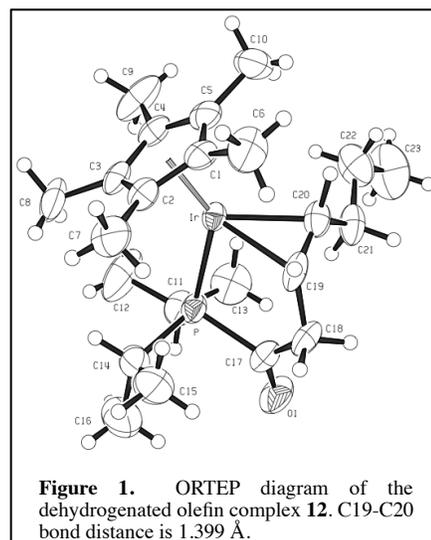
the bis triflate complex. Upon warming this complex to 45 °C in dichloromethane various hydridic signals were observed in the ^1H NMR spectrum, indicating a C-H bond activation event had occurred. However, no products were isolated from the complex reaction mixture. Interestingly, the dicyclohexylphosphine complex **7** underwent dehydrogenation of one of the cyclohexyl groups on the phosphine. Diisopropyl phosphine Complex **8** reacted with AgOTf at room temperature to give a mixture of M-H species along with the bis triflate complex. However, when silver hexafluorophosphate (AgPF_6) was employed instead of AgOTf, and the solution was warmed to 45 °C in CH_2Cl_2 , a single complex containing a metal hydride signal in the ^1H NMR spectrum was observed. Due to coordination of the olefin, it was difficult to determine if dehydrogenation had occurred by simple ^1H NMR spectroscopic analysis as no peak appeared above 3.5 ppm). Complex **9**, which contains a derivative of palmitic acid, also was site-selectively dehydrogenated at the β,γ positions of the alkane.



When *tert*-butyl was the alkyl group on the acylphosphine and reacted with AgOTf, the anionic complex **14** was formed. The reactivity of this complex was probed and the results have been published earlier this year (Scheme 3). The complex readily underwent reaction with arenes to product η^6 iridium arene complexes (**15a-15d**). In the presence of water or pyridine, the triflate ligands were easily displaced to produce the corresponding aqua or pyridyl complexes (**16-17**). Finally, the addition of trialkylsilanes produced the bridged hydride dimer **18** in 83% yield.



An X-ray quality crystal of **12**, was grown by carefully layering a saturated CH_2Cl_2 solution of the product with Et_2O . An ORTEP diagram of the unsaturated ligand complex **12** is shown in Figure 1. The C19-C20 bond distance was found to be 1.399 Å, which is indicative of a C=C double bond. The hydride ligand was not located in the X-ray diffractometer; however, a signal in the hydride region of the ^1H NMR spectrum displays a doublet at -17.2 ppm. This resonance becomes a singlet upon ^{31}P decoupling of the ^1H NMR spectrum. Moreover, the sum of the bond angles around the iridium center (352°) indicates a distorted tetrahedral coordination, as opposed to trigonal planar, and thus provides more evidence for the presence of a hydride.



The site-selective dehydrogenation of a single C-C bond on an alkyl chain is described. During the discovery of this catalyst, a novel anionic iridium complex was also discovered and its reactivity was investigated and described in a recent publication. In addition to this being the first report of a site-selective alkane dehydrogenation, only mild temperatures (45°C) needed to promote this reaction. Future work will investigate the development of a catalytic variant of this reaction.