ABSTRACT

THESIS: Anodic Oxidation Induced [2+2] Carbon-Carbon Coupling Reactions of Terminal Alkenes using Organo-Re(II) Electron Transfer Mediator

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The radical cation, $[ReCp(CO)_3]^+$ (**1**$^+$, Cp = η^5-C_5H_5) has been utilized to initiate radical-based intermolecular carbon-carbon coupling reactions of unsubstituted terminal alkenes. Characterization of the **1**/**1**$^+$ couple was recently made possible by the application of the weakly coordinating anion $[B(C_6F_5)_4^-]$ of the supporting electrolyte. The very nature of the **1**/**1**$^+$ couple ($E_{1/2}$ = 1.16 V vs. $Fc^{0/+}$) makes **1**$^+$ a powerful one-electron oxidizing agent. The *in situ* anodic generation of **1**$^+$ by electrolysis at 1.3 V initiates coupling reactions between excessively added linear alkenes with individual $E_{1/2}$ values exceeding 1.8 V. The exceptional catalytic oxidation process between **1**$^+$ and each terminal alkene is theorized to occur by means of an electron-transfer mechanism. Carbon-carbon coupling reactions for 1-octene, 1,7-octadiene, and 1-hexene have been conducted, as well as focused experiments with increased concentrations of 1-octene to a 1:50 (**1**:1-octene) mole ratio was employed. Primary products of these reactions were unique to each alkene and 1-octene produced cyclobutyl-derivative major products. Catalytic bulk oxidation of **1** in each case was exhausted in < 25 min., following the passage of 0.01 - 0.3 F/mol of alkenes. Products from these coupling reactions were obtained in **60-73%** yields and identified by GC-MS, ^{1}H-NMR, ^{13}C-NMR, DEPT, and HMQC NMR spectroscopic data analyses. The mechanisms of these reactions will be discussed. Presented is an efficient synthetic tool of [2+2] carbon-carbon coupling reactions under mild conditions and the pertinent ramifications therein.