

Selective C-H Bond Activation of Substituted and Unsubstituted Linear Alkanes by a Rhodium Trispyrazolylborate Complex

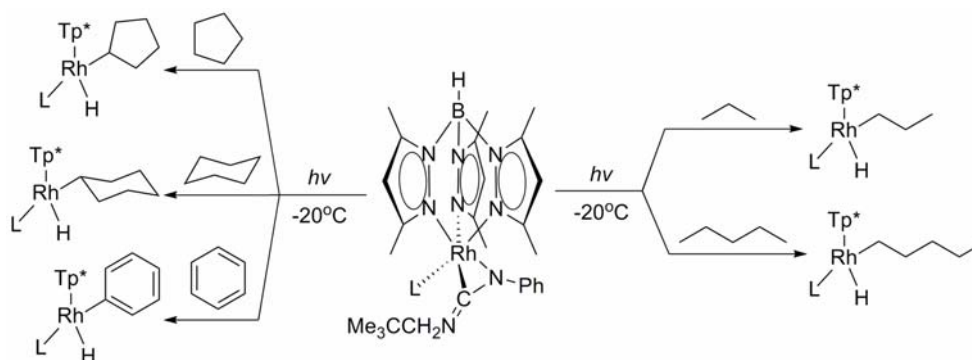
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The need for new energy sources and chemical feed stocks has been a recent driving force behind several areas of chemical research. While both abundant and inexpensive, the relative chemical inertness of alkanes due to strong C-H bonds makes them difficult to use as a carbon source. Even as a fuel source, some small alkanes, such as methane, are both expensive and dangerous to liquefy and transport, and are often burned on-site. Therefore, the ability to selectively activate and functionalize strong C-H bonds, along with an understanding of what influences selective bond activation, is desired¹.

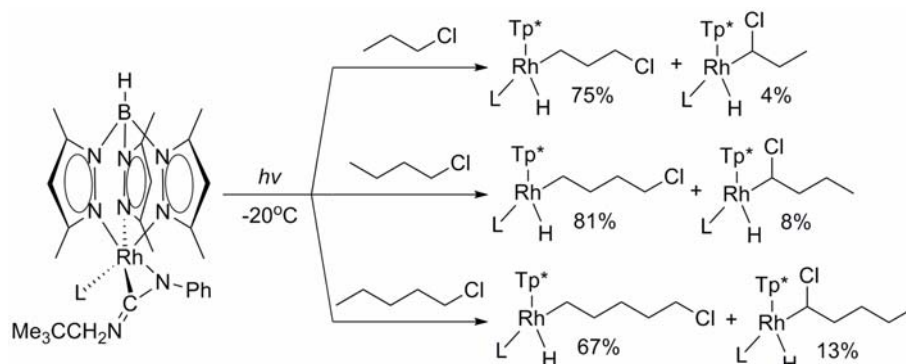
Jones *et al.* reported the activation of both aromatic and aliphatic hydrocarbons complexed to the 16 e⁻ fragment [Tp^{*}RhL] (Tp^{*} = tris(3,5-dimethylpyrazole)borate, L = neopentylisocyanide), generated by the loss of a photolabile carbodiimide ligand (Scheme 1)². The reaction of linear C₁-C₆ alkanes with this fragment resulted in selective cleavage of the stronger primary C-H bonds without evidence for the oxidative addition of the weaker secondary C-H bonds. The [Tp^{*}RhL] fragment was determined to be more selective towards primary C-H bond activation of alkanes than previously reported [Cp^{*}Ir(PMe₃)] and [Cp^{*}Rh(PMe₃)] fragments^{3,4}.



Scheme 1. Activation of benzene and cyclic and linear alkanes by [Tp^{*}RhL].

In order to investigate the observed selectivity of primary over secondary C-H bonds, a series of secondary alkyl hydride complexes (Tp^{*}RhL(H)R R = *i*-propyl, *sec*-butyl) were prepared from the corresponding alkyl chlorides. Once formed, the secondary alkyl hydride complexes slowly isomerized to the corresponding primary alkyl hydride complexes⁵. This isomerization process was determined to occur via an intramolecular mechanism. Competition studies using alkanes of varying length resulted in a preference towards C-H bond activation of the longer chain. From this study, it was calculated that the coordination of secondary C-H bonds to the metal fragment was 1.5 times faster than coordination of primary C-H bonds. Moreover, the rate of oxidative addition of a primary C-H bond to the metal fragment was determined to be 64 times faster than oxidative addition of a secondary C-H bond⁶. From this data, Jones proposed that initial coordination to any C-H bond leads eventual migration to, and oxidative addition of a primary C-H bond.

In order to understand the effects of reactive functional groups present on the alkanes, a series of chloropentanes were reacted with the $[\text{Tp}^*\text{RhL}]$ fragment, resulting in the selective activation of terminal C-H bonds with no activation of the C-Cl bond observed⁷. Selective C-H bond activation was observed upon treatment of the metal fragment with 1-chloroalkanes resulting in terminal C-H activation forming the major, kinetic product⁸. As the length of the 1-chloroalkanes increased, the amount of a minor, thermodynamic product attributed to the C-H bond activation adjacent to the chlorine (α -C-H) increased (Scheme 2). Competition reactions between methylchloride and 1-chloroalkanes showed there was no preference towards activation of the longer 1-chloroalkanes, unlike the trend observed with unsubstituted alkanes. Therefore, the activation of the 1-chloroalkanes must occur by a different mechanism than unsubstituted alkanes. It is likely that the C-H bond activation of 1-chloroalkanes occurs via coordination of the α -C-H bond to the metal fragment followed by migration to the terminal C-H bond and subsequent oxidative addition to give the kinetically favored product.



Scheme 2. Selective C-H activation of 1-chloroalkanes by $[\text{Tp}^*\text{RhL}]$.

A comparison of the reductive elimination of chloroalkyl hydrides and the corresponding parent alkyl hydrides found that the chloroalkyl hydrides eliminate at a slower rate. Furthermore, as the length of the chloroalkyl chain increased, the rate for reductive elimination converged with the rate for the unsubstituted alkyl hydride. This convergence of rate was attributed to the decreased inductive effect from the chlorine in longer carbon chains. A competition reaction between methane and methylchloride determined that the bond strength of the metal-chloromethyl bond was stronger than the metal-methyl bond by at least 2 kcal/mol^{8,9}.

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