

## Transition Metal Activation of Carbon-Hydrogen Bonds

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The cleavage of carbon-hydrogen (C-H) bonds is a crucial step in the functionalization of saturated hydrocarbons [1]. Such functionalization processes are employed in the conversion of crude oil and coal into more readily utilized fuels. Heterogeneous catalysts currently used to catalyze C-H bond scission reactions require high temperatures and are often not sufficiently selective [2]. Due to the increased product selectivity observed with homogeneous transition metal catalysts [3], their potential use in C-H bond activation has received increased interest in recent years.

### Intramolecular Activation

The first example of homogeneously promoted activation was reported by Kleinman in 1963 [1b]. In this case the mechanism of the C-H bond scission is assisted by bringing the bond into close contact with a metal center. This occurs if the hydrocarbon group is part of a ligand which is pre-coordinated to the metal [4]. These reactions are termed "cyclometallations" or "orthometallations".

### Intermolecular Activation

Intermolecular C-H bond activation is less common than intramolecular activation. In the presence of  $\text{PtCl}_4^{2-}$  salts, simple alkanes catalytically undergo deuterium exchange in  $\text{D}_2\text{O}/\text{CH}_3\text{CO}_2\text{D}/\text{DCl}$  at  $100^\circ\text{C}$  [5]. Though this example dates to 1969, further progress in this area has been made only recently. This progress was prompted by the realization that an unsaturated metal center facilitates reaction with the alkane [3].  $\text{IrH}_2(\text{Me}_2\text{CO})_2(\text{PPh}_3)_2^+$  [6] and  $\text{L}_2\text{ReH}_7$  ( $\text{L} = (\text{p-F-C}_6\text{H}_4)_3\text{P}$ ,  $\text{PPh}_3$ ,  $(\text{p-MeC}_6\text{H}_4)_3\text{P}$ ,  $\text{PEt}_2\text{Ph}$ ) [7] can dehydrogenate cyclic alkanes with the aid of 3,3-dimethyl-1-butene as a hydrogen acceptor. Similarly  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{PMe}_3)\text{H}_2$  [8] and  $(\eta^5\text{-C}_5\text{Me}_5)\text{Ir}(\text{CO})_2$  [9] add free alkanes. In the latter two cases [8,9], the intermediate hydridoalkyl metal species has been isolated. These systems [6-9] are stoichiometric, not catalytic.

### Clean Metal Surface Studies

Since metal surfaces display enhanced C-H bond activation, it is believed that homogeneous systems which mimic active surface sites are more likely to lead to useful homogeneous catalysts [6b]. For example, "steps" and "kinks" on surfaces have been shown to be more active than "terrace" sites [10,11]. These sites differ from the bulk metal in that they are less coordinatively saturated and possess asymmetric orbital arrays [11].

C-H bond cleavage on a metal surface may occur via a 3-center-2-electron bond [10]. Models for such systems exist in transition metal chemistry [12]. Perhaps a deeper understanding of heterogeneous catalysts can be obtained through such modelling of metal surfaces.

## References

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