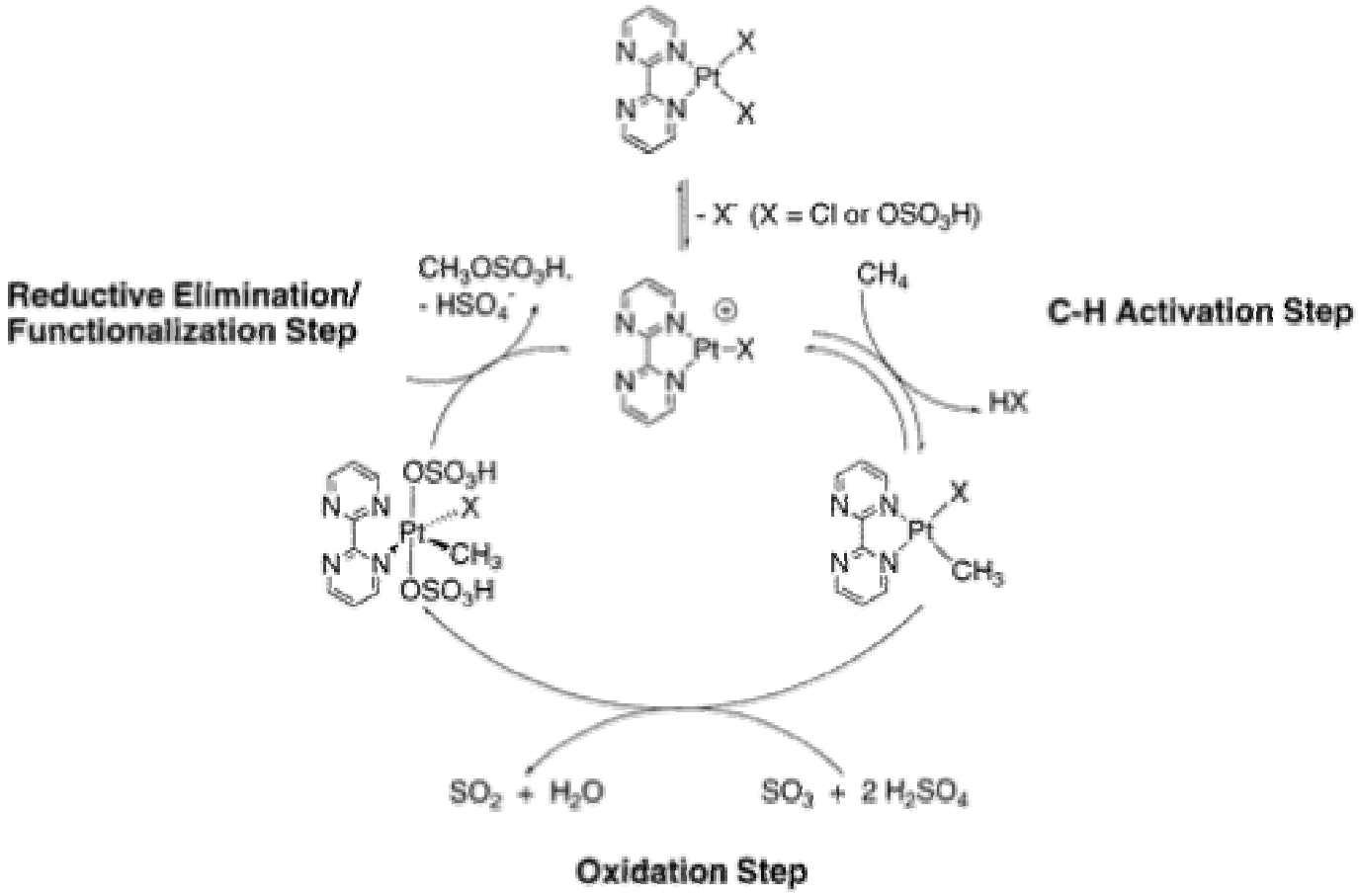
Catalytica Process/Shilov Chemistry

Methane is the major constituent of natural gas, which is an abundant and inexpensive natural resource. Currently its high transportation cost and low reactivity prevent it from being used fully as a major feedstock for the chemical industry.

It has been known since the early 1970s based on Shilov's C-H activation reactions ($[PtCl_4]^{2-}$/$[PtCl_6]^{2-}$ in aqueous acetic acid) that Pt(II) can activate C-H bonds in methane. Further, Pt(IV) can be used to oxidize methane to methanol. Methanol is very stable compare to methane in oxidation. Therefore, Catalytica process was proposed base on Shilov's reaction to convert methane to methyl bisulfate in good yield at relatively low temperature in fuming sulfuric acid with (bipyrimidine)$PtCl_2$ as a catalyst. The process can be divided into three steps.

(1) formation of a 14-electron cationic platinum(II) complex, which reacts with methane to form a platinum(II) methyl compound
(2) oxidation of this material to a platinum(IV) methyl sulfonate compound
(3) reductive elimination of methyl bisulfate and loss of a bisulfate ligand to regenerate the catalyst.

Figure#1



It has been proven difficult to derivatize methane cleanly, specifically, and in high yield. Recent work has focused on sulfonating methane with fuming sulfuric acid. This is motivated by the facts that, one, the presence of the highly oxidized sulfonate group lessens the chance of further oxidation at carbon, two, the ready hydrolysis of the sulfonate group provides the commodity chemical methanol, and three, the SO_2 byproduct readily oxidizes to SO_3, providing the plausible catalytic cycle.

The recent report from Dr. Periana and co-workers from University of Southern California provides great promise. They found that methane reacts with fuming sulfuric acid solvent at modest temperatures (ca. 200 °C) in the presence of (bipyrimidine)$PtCl_2$ to give only methyl bisulfate, with minimal production of byproducts. Yields of >70% of methanol, from hydrolysis of methyl bisulfate, were obtained.

Figure#2