

ZWITTERIONIC HALIDO CYCLOPENTADIENONE IRON COMPLEXES AND THEIR CATALYTIC PERFORMANCE IN HYDROGENATION REACTIONS

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During studies aiming to elucidate the reaction mechanism of hydrogenation reactions using charge-tagged cyclopentadienone iron complexes [1] by mass spectrometry [2], we came across the zwitterionic compound $\text{FeI}(\text{CO})_2\text{-NMe}_3$. This crystalline and air and moisture stable compound constitutes a close analogue to compounds that have been described by Knölker *et al.* [3] in their seminal paper on cyclopentadienone iron complexes. The catalytic activity has however not been described. In this work, we describe the synthesis and full characterization of the halido complexes $\text{FeX}(\text{CO})_2\text{-NMe}_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) by NMR, MS, XRD, IR and elemental analysis. The catalytic performance in hydrogenation and transfer hydrogenation reactions was assessed, establishing the relative reactivity order to be $\text{Cl} < \text{Br} < \text{I}$. All complexes showed activity in the hydrogenation of acetophenone in aqueous solution under hydrogen pressure with up to 93 % conversion (2.5 mol% catalyst loading, 7.5 bar H_2 , 120 °C, $\text{X} = \text{I}$), indicating that the halido ligands can dissociate to form a catalytically active species. The compounds were not active in transfer hydrogenation reactions in boiling isopropanol. With the complex $\text{FeI}(\text{CO})_2\text{-NMe}_3$, experiments involving the addition of iodide and weakly coordinating anions showed the presence of the common ion [4,5] and special ion [6] effects respectively, indicative of the ion pair being involved in the catalytic cycle. (*Manuscript submitted for publication*)

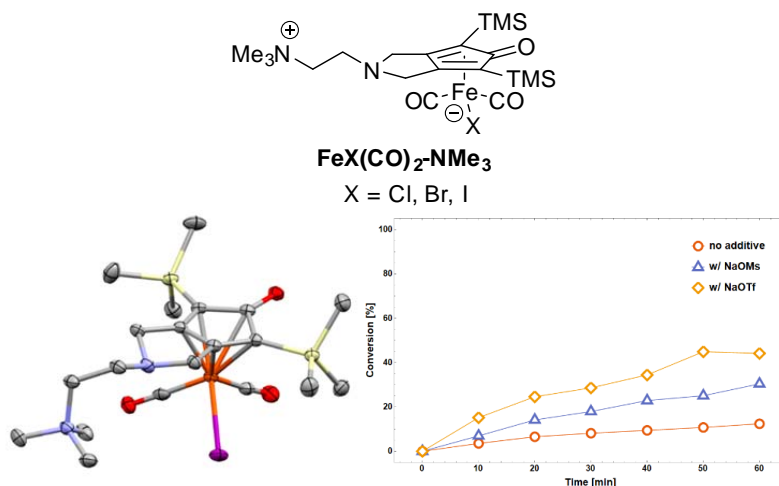


Figure 1. Left: Crystal Structure of $\text{FeI}(\text{CO})_2\text{-NMe}_3$. Right: Kinetic profiles obtained in the hydrogenation of acetophenone in water under hydrogen pressure using $\text{FeI}(\text{CO})_2\text{-NMe}_3$ as the catalyst. The rate enhancement upon addition of NaOMs and NaOTf is attributed to the special salt effect.

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