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Iron Complexes as Catalysts in Aldol Additions

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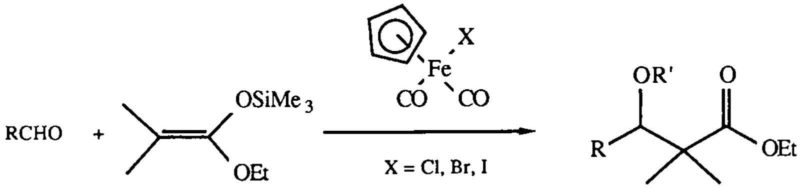
Abstract. *(Dicarbonyl)(η^5-cyclopentadienyl) iron halides function as catalysts for the aldol addition of enolsilanes to aldehydes.*

The use of chiral Lewis acids as catalysts for the asymmetric induction of C-C bond forming reactions has been extensively investigated expecially in the enantioselective variant of the Diels Alder reaction[1]. Less progress has been made in achieving good levels of asymmetric induction in Lewis acid catalyzed aldol reactions (Mukaiyama reaction)[2]. To the best of our knowledge there are two examples of enantioselective addition of enolsilanes to aldehydes which make use of chiral catalysts and only one of them is a truly catalytic process[3].

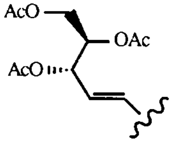
We now report that (dicarbonyl)(η^5-cyclopentadienyl) iron halides (FpX) are effective catalysts in the addition of the silyl ketene acetal **2** to aldehydes **1** (Table).They exhibit turnover and the utility of such material as catalysts in Mukaiyama reactions is further corroborated by the following properties: 1) easy preparation from inexpensive chemicals[4]; 2) stability to air and moisture, in order to avoid strictly anhydrous reaction conditions; 3) susceptibility to chiral modifications by simple exchange of a ligand.



1 **2** **3** R' = H
4 R' = OSiMe$_3$

The reaction works equally well with Fp iodide, bromide and chloride (Table, entries 1-3). Aromatic, aliphatic and α,β-unsaturated aldehydes react to give a mixture of β-siloxy **4** and β-hydroxy esters **3** in a *ca.* 8-10:1 ratio in good to excellent yields. Reaction conditions are extremely mild and no great differences in yields were observed for reactions carried out under nitrogen or in a simply stopped vial. The best yields were obtained by addition of 0.3 equivalents of the iron complex in three portions over 48 hours.

Table. FpX catalyzed aldol addition at r.t..

Entry	R	Solvent	catalyst	reaction time (h)	isolated yield (%)
1	Ph	CH_2Cl_2	FpCl	48	88
2	Ph	CH_2Cl_2	FpBr	48	86
3	Ph	CH_2Cl_2	FpI	48	72
4	Ph	THF	FpCl	48	84
5	$(CH_3)_2CH\text{-}CH_2\text{-}$	CH_2Cl_2	FpCl	48	62
6		CH_2Cl_2	FpCl	48	95

The Fp halide complexes are 18 electron compounds and have no Lewis acid character as such[5]. A mechanism involving the dissociation of the halide ion yielding a coordinatevely unsaturated species which in turn may activate the carbonyl function seems to be unlikely since the reaction proceeds even in a strongly coordinating solvent such as tetrahydrofuran (Table, entry 4). Alternatively, intermediate iron enolates may be formed which are the active nucleophiles in the addition to the aldehyde[6].

Work is in progress to gain further insights on the mechanism of the above reactions and particularly to test diastereselectivity with prochiral silanes as well as asymmetric induction with chiral variants of the catalyst.

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References and Notes

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