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Lewis Acid-Promoted Addition of Allyl(cyclopentadienyl)iron(II) Dicarbonyl To Aldehydes: A New Aldehyde Allylation Method

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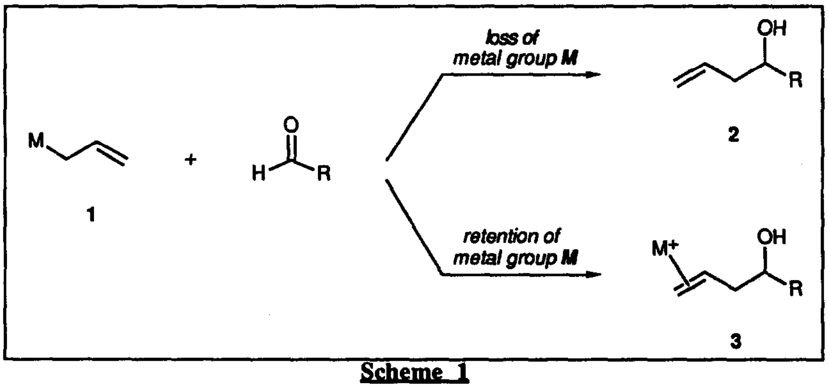
Key Words: Lewis acid-promoted addition; allyl(cyclopentadienyl)iron(II) dicarbonyl; aldehyde allylation; homoallylic alcohols, cationic iron-olefin complexes

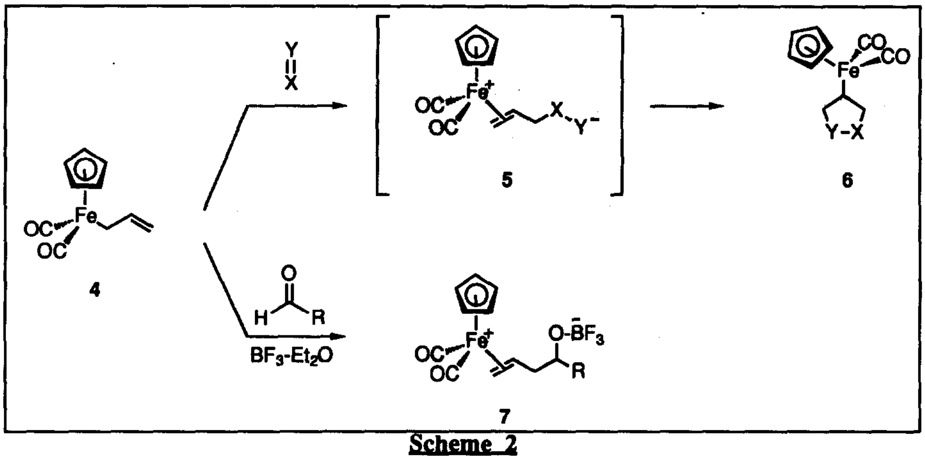
Abstract: *The Lewis acid-promoted addition of allyliron(II) reagent 4 to aldehydes provides zwitterionic iron-olefin complexes 7 as isolable yellow salts. Treatment of the iron complexes with NaI in wet acetone affords homoallylic alcohols 8.*

The addition reactions of allylmetallic reagents to carbonyl compounds are among the most reliable and well-studied carbon-carbon bond forming processes developed to date.[1] A wide variety of allylmetallic reagents 1, including those in which M= Li, Mg, B, Al, Zn, Zr, Ti, Mo, Cr, Si, and Sn, react with aldehydes to provide homoallylic alcohols 2 (top, **Scheme 1**). It should be pointed out that in each of these systems, the metal group M is consumed during the course of the reaction or upon hydrolytic workup. *In this communication, we report a new aldehyde allylation procedure in which the metal group M is preserved within the product in the form of a stable metal-olefin complex 3* (bottom, **Scheme 1**). As a consequence of the electrophilic nature of the metal complex[2,3], we envision that additional functionality may be introduced directly onto the double bond.



Scheme 1

Our studies have focused on the use of allyl(cyclopentadienyl)iron(II) dicarbonyl complex (4), which is easily prepared by metallation of allyl chloride with sodium [(cyclopentadienyl)iron(II) dicarbonyl] (NaFp) according to the method of Green (**Scheme 2**).[4] The nucleophilic nature of allyliron reagent 4 has been examined extensively by Rosenblum[5], as well as by Wojcicki[6], Baker[7], and Green[4], in reactions with highly-activated organic and inorganic electrophiles. For allyliron additions to multiple bonds X=Y (i.e. electron-deficient olefins)



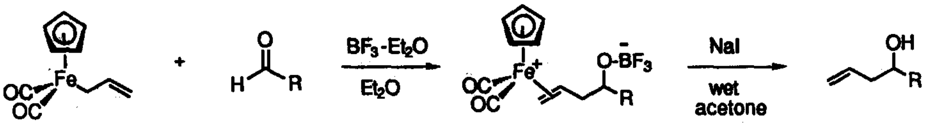
Scheme 2

formal [3+2]-cycloadducts **6** are typically isolated as a result of facile ring closure of an initial zwitterionic organoiron complex **5**.[8] Surprisingly, the reaction of allyliron reagent **4** with *aldehydes* has yet to be reported. In our laboratory we have found that with the use of a Lewis acid[9] to enhance the electrophilicity of the carbonyl center and to stabilize the resulting alkoxide, allyliron reagent **4** adds to aliphatic and aromatic aldehydes to produce zwitterionic iron-olefin complexes **7**. These complexes, which are formed as bright yellow salts, can be isolated by filtration and stored under an inert atmosphere.[10] The complexes show characteristic infrared CO stretching bands at 2075 cm^{-1} and 2035 cm^{-1}, respectively, and a sharp Cp-$\underline{H}$ resonance at 5.1 ppm (CD_2Cl_2) in the proton NMR spectrum. For further characterization, the iron complexes were treated with NaI[5] in wet acetone to give homoallylic alcohols **8** (see **Table**).[11]

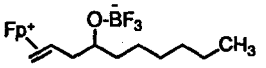
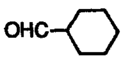
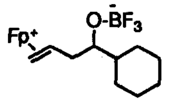
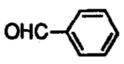
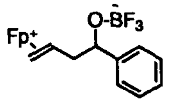
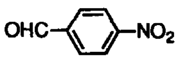
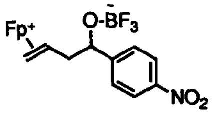
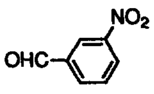
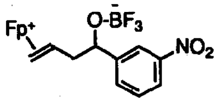
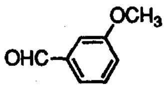
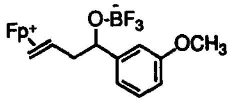
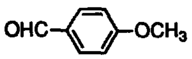
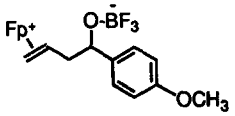
Of the Lewis acids examined (BF_3-Et_2O, $TiCl_4$, $SnCl_4$, $AlBr_3$, TMS triflate), BF_3-etherate is the most effective. *The allylation reactions do not occur in the absence of Lewis acid.* Although an excess amount of *Lewis acid* (3 equivalents) does not dramatically affect the reaction, the use of a two-fold excess of the *allyliron reagent* leads to significantly lower yields of homoallylic alcohols **8**. Diethyl ether is the preferred solvent for the addition reactions in that the iron-olefin complexes **7** are completely insoluble in this solvent, and can be easily filtered from the reaction mixture. Methylene chloride and THF are also effective solvents, although the increased solubility of the olefin complexes in these solvents make the isolation of the complexes more difficult. Reactions do not proceed to any appreciable extent when carried out in hexane. Thus, optimal yields of homoallylic alcohols **8** are obtained when the allylation reactions are conducted in diethyl ether at 0°C using 1.2 equivalents of allyliron reagent **4** and 1.5 equivalents of Lewis acid.[12]

The following experimental procedure is representative: To a solution of the aldehyde (1 mmol) and BF_3-etherate (1.5 mmol) in Et_2O (20 mL) at 0°C under an argon atmosphere is added dropwise allyliron reagent **4** (1.2 mmol) in Et_2O (5 mL). During the addition, a bright yellow precipitate forms and stirring is continued for an additional hour. Filtration of the reaction mixture under argon through a Buchner funnel provides adduct **7** as a powdery yellow solid. Addition of NaI (5 mmol) in wet acetone (20 mL) to the yellow solid rapidly produces a black solution indicating the formation of FpI. Evaporation of the reaction mixture and flash chromatography affords homoallylic alcohol **8** as a colorless-to-pale yellow oil.[13]

Table. Lewis-Acid Promoted Aldehyde Additions



4 7 8

Entry	Aldehyde	Iron-olefin complex 7[a]	Yield of alcohol 8 (%)[b]
1			50
2			55
3			76
4			67
5			84
6			74
7			56

[a] Fp$^+$=(cyclopentadienyl)iron(II) dicarbonyl cation

[b] Isolated yields after two successive flash chromatography columns, first with CH_2Cl_2 then with 20% EtOAc in hexane.

Current efforts in our laboratory are aimed at extending this methodology to other types of carbon electrophiles, including ketones and acetals, and examining the diastereoselectivity[14] of the addition process. We are particularly interested in adopting iron-olefin complexes for use as synthetic intermediates. Details of this work will be reported in due course.[15]

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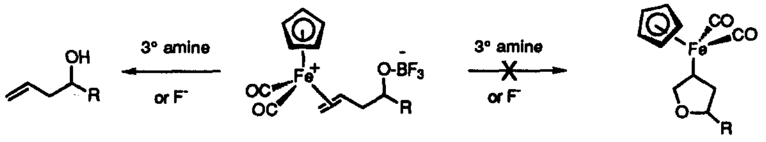
9. Rosenblum has demonstrated that Lewis acids can promote the addition of allyliron reagent **5** to otherwise unreactive pi-systems. See Bucheister, A.; Klemarczyk, P.; Rosenblum, M. *Organometallics* **1**, 1679 (1982). See also Wright, M.E.; Hoover, J.F.; Nelson, G.O.; Glass, R.S. *J. Org. Chem.* **49**, 3059 (1984).
10. Upon exposure to the atmosphere, the yellow solid quickly darkens and eventually becomes a brown oil. The proton NMR spectrum of the brown oil matches that of the original yellow solid, suggesting that the O-BF$_3$ bond of complex **7** undergoes facile hydrolysis. The presence of small amounts of an impurity, identified as an allyliron-BF$_3$ adduct, has thusfar thwarted our efforts to obtain complexes **7** in analytically-pure form.
11. Inspection of the crude reaction mixture by NMR has failed to show any iron-substituted [3+2]-cycloadducts **9** which might be expected to arise from zwitterionic iron-olefin complexes **7**. Furthermore, all attempts to convert zwitterionic complexes **7** to tetrahydrofurans **9** by treatment with tertiary amines (eg. pyridine, diazabicycloundecene) or fluoride ion (eg. Bu$_4$N$^+$F$^-$) have led only to demetallated products **8**.



8 **7** **9**

12. The yields of alcohols **8** can be improved slightly by conducting the addition reactions at -78°C rather than at 0°C. Not surprisingly, electron-rich aromatic systems have lower reactivity towards the mildly nucleophilic allyliron reagent. Indeed, 4-dimethylaminobenzaldehyde is recovered quantitatively from the reaction after stirring with reagent **4** (2 eq) and BF$_3$ (3 eq) at 0°C for 12 hours.
13. Alcohols **8** have been characterized on the basis of IR and proton NMR measurements and by comparison to compounds prepared according to the method of Sakurai (see reference 1).
14. Although the proton NMR spectra (300 MHz) for complexes **7** show only one set of signals in a variety of deuterated solvent systems, we have not conclusively determined whether only one diastereomeric form of the complex is present in solution.
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