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Allylation and [3+2]-Cycloaddition Reactions of Imines With Allyl(cyclopentadienyl)iron(II) Dicarbonyl Complexes

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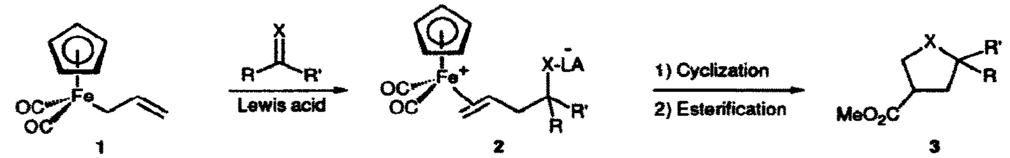
Key Words: Lewis acid-promoted addition; allyl(cyclopentadienyl)iron(II) dicarbonyl complexes; imine allylation; pyrrolidines, iron-olefin π-complexes

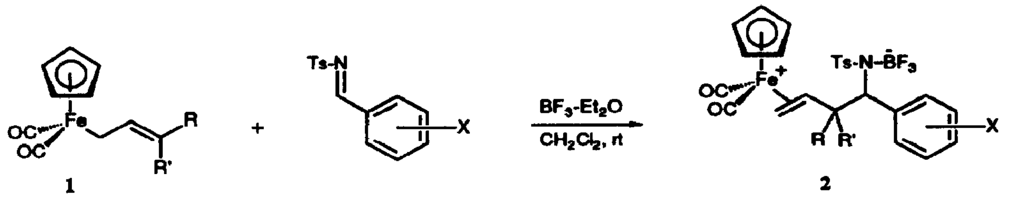
Abstract: *Allyl(cyclopentadienyl)iron(II) dicarbonyl (1) reacts with N-tosylimines to give either iron-olefin complexes 2 or pyrrolidines 3, depending on the quantity and nature of the Lewis acid and the work-up procedure.*

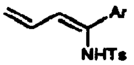
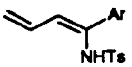
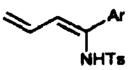
The reaction of allylic metal reagents with carbonyl compounds[1] and, to a lesser extent, imines[2] is a well-known procedure for the preparation of homoallylic alcohols or homoallylic amines, respectively. Recently, we described an extension of this methodology using the transition metal complex, allyl(cyclopentadienyl)iron(II) dicarbonyl[3] (**1**), which leads to the formation of zwitterionic iron-olefin π-complexes **2** where X=O.[4,5] We have shown that, under appropriate conditions, π-adducts **2** can be converted to tetrahydrofuran esters **3** (X=O) by heterocyclization of the alkoxide onto the electrophilic iron-olefin complex, and subsequent esterification of the resulting iron furan.[6] In this paper we report that this allylation procedure can also be applied to N-tosylimines for the synthesis of acyclic π-complexes **2** (X=NTs) or pyrrolidine esters **3** (X=NTs).[7,8]



To begin our studies, we first examined the reaction of allyliron complexes with aromatic tosylimines using BF_3-etherate as the promoter (**Table 1**). The reactions were conducted by adding freshly prepared allyliron reagent[3] (3 mmol) to a stirred solution of the imine (1mmol) and BF_3-etherate (3 mmol) in CH_2Cl_2 at rt. After stirring for 12 h, the reaction mixture can be diluted with Et_2O to precipitate the zwitterionic π-adduct (which can be isolated by filtration through a fine-pore glass frit), or treated directly with NaI in moist acetone to afford the homoallylic amine.[9] It appears that these additions require a strong electron-withdrawing group on the imine nitrogen, since reaction of the parent allyliron complex (R=R'=H) with the N-*phenyl*imine of benzaldehyde gives a much lower yield of the π-complex (23%), while the corresponding N-*benzyl*imine or N-*butyl*imine fail to react with the allyliron complex.[10] When 3-methoxyallyliron complex **1b** is used, the 1,2-syn homoallylic amine is obtained as a *single* diastereomer (after demetalation with NaI) along with a considerable amount of a 1-amino-1,3-diene.[11,12] Formation of the diene can be avoided altogether using 3-benzyloxyallyliron complex **1c**, which reacts with imines to give a mixture of the syn and anti allylation products after demetalation.

Table 1. BF$_3$-Promoted Additions of Allyliron Complexes to N-Tosylimines



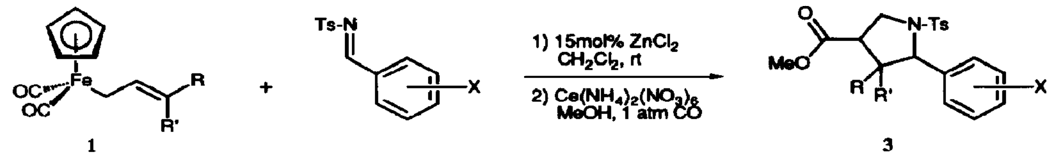
Allyliron complex	Imine	Isolated yield of homoallylic amine[a]
1a R = R' = H	X = H	70%
	X = 3-OMe	50%
	X = 3-NO$_2$	88%
	X = 4-NO$_2$	20%
1b R = H; R' = OMe	X = H	47% (syn isomer) +  (23%)
	X = 3-OMe	43% (syn isomer) +  (20%)
	X = 3-NO$_2$	39% (syn isomer) +  (22%)
1c R = H; R' = OCH$_2$Ph	X = H	84% (2.5:1 syn:anti)[b]
	X = 3-OMe	84% (2.5:1 syn:anti)[b]
	X = 3-NO$_2$	72% (2.5:1 syn:anti)[b]

[a] Yields are based on the isolated amount of demetalated homoallylic amine after flash chromatography.

[b] Diastereomeric ratios refer to the 1,2-syn/anti mixture of the demetalated homoallylic amines and were determined by integration of non-overlapping signals in the 400 MHz ^{1}H NMR spectrum. We have not yet been able to assign the facial orientation of the metal moiety in the iron-olefin π-complex.

We next investigated the reactions of allyliron complexes with tosylimines under catalytic Lewis acid conditions. The experimental procedure for these cycloadditions is the same as that described above, except that 15 mol% ZnCl$_2$ is utilized in place of BF$_3$-etherate. After stirring for 24 h at rt, the reaction mixture is then cooled to -78°C and treated with a methanolic solution of ceric ammonium nitrate (3 molar equiv) under an atmosphere of CO. Evaporation and flash chromatography of the crude product affords the pyrrolidine methyl esters as a mixture of diastereomers (**Table 2**).[9] Reactions at rt in CH$_2$Cl$_2$ give better results than those at lower temperature (-20°C) or in Et$_2$O, and if TiCl$_4$ or BF$_3$-Et$_2$O is used as catalyst, none of the expected [3+2]-adduct is obtained. We also observe that the cycloaddition involving crotyliron complex **1d** gives only two diastereomeric cycloadducts.[13]

Table 2. $ZnCl_2$-Catalyzed [3+2]-Cycloadditions of Allyliron Complexes to N-Tosylimines

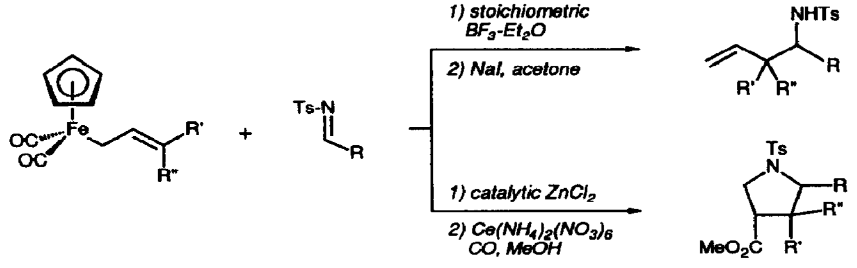


Allyliron complex	Imine	Isolated yield, diastereomeric ratio[a]
1a R = R' = H	X = H	55% (2.5:1)
	X = 3-NO_2	42% (2.5:1)
1d R = Me; R' = H	X = H	28% (2 isomers, 2.5:1)[b]

[a] Diastereomeric ratios were determined by integration of non-overlapping signals in the 400 MHz ^1H NMR spectrum of the mixture.

[b] The relative stereochemistry of these adducts has not yet been firmly established.

To summarize, we have shown that allyl(cyclopentadienyl)iron dicarbonyl complexes react with N-tosylimines under Lewis acid conditions to provide either homoallylic amines or pyrrolidines, depending on the amount and type of Lewis acid and the workup procedure. Current efforts are focussed on the application of this methodology to the preparation of selected naturally-occurring pyrrolidines and related ring systems.



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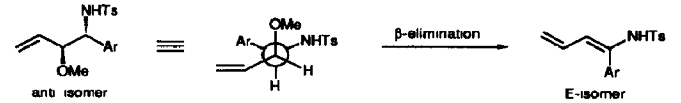
8. Pyrrolidines have also been prepared by BF_3-etherate catalyzed addition of allyltrimethylsilane to α-amino aldehyde derivatives. Kiyooka, S.-i.; Shiomi, Y.; Kira, H.; Kaneko, Y.; Tanimori, S. *J. Org. Chem.* **1994**, *59*, 1958.
9. The homoallylic amines and pyrrolidine esters were purified by flash chromatography and gave acceptable ^1H NMR, infrared, MS, and HRMS spectral data.
10. In contrast to related work cited in reference 7a, our attempts to add the allyliron complexes to *in situ*-generated N-tosylimines of aryl or aliphatic aldehydes failed to produce the desired allylation adduct.
11. Although both syn- and anti-addition products are most likely formed in the allylation reaction, apparently only the anti-isomer eliminates methanol to give the diene. We have tentatively assigned the E-geometry to the diene on the assumption that β-elimination from the anti-isomer of the homoallylic amine occurs via an anti-orientation of the proton and methoxy group (see below). The 1,2-syn homoallylic amine is less prone to elimination, and can be recovered after prolonged exposure to the work-up and purification conditions.



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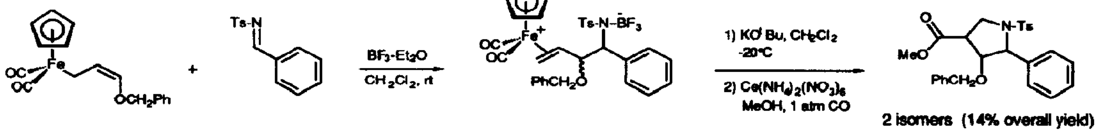
13. Although the initial allylation step most likely gives a mixture of diastereomeric π-adducts, two of these complexes may not cyclize due to unfavorable interactions between the methyl substituent and the iron moiety. A similar outcome was observed for the cyclization of π-adducts prepared from the 3-benzyloxyallyliron complex (below). Thus, treatment of the diastereomeric mixture of π-complexes with potassium t-butoxide in CH_2Cl_2, followed by esterification with methanolic ceric ammonium nitrate, gave only two cycloadducts.



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