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Note

# A one-pot synthesis of cyclopropanes from aromatic aldehydes and styrene via iron carbene complexes

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**Abstract**

A one-pot preparation of cyclopropanes from aromatic aldehydes and styrene via iron carbene complexes is reported. The preparation consisted of a sequence of reactions, involving initial addition of aldehyde to the Fp anion, followed by chlorotrimethylsilane and finally styrene in the presence of trimethylsilyltriflate.

*Keywords:* Catalysis; Cyclopropanation; Iron complexes; Carbene complexes

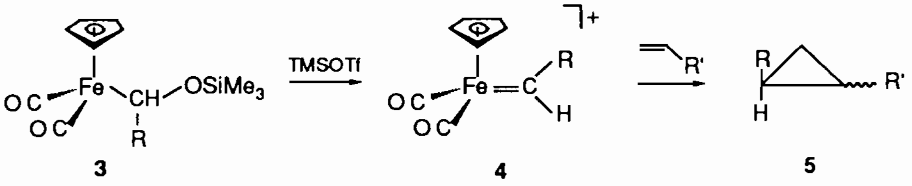
## 1. Introduction

Recently, we developed a new method [1] for the preparation of the α-siloxyalkyliron complexes **3** by treatment of the Fp anion **1** with aldehydes in the presence of chlorotrimethylsilane. The α-siloxyiron complexes **3** were found to be very useful reagents for cyclopropanation reactions. In the presence of trimethylsilyl triflate, **3** were converted to the corresponding iron carbene complexes **4** which efficiently transferred their carbene ligands to alkenes, producing cyclopropanes **5** (Scheme 1). During our study, we observed that handling of the α-siloxyiron complexes **3** was difficult, because they were air and temperature sensitive. Currently, we wish to report our preliminary studies of a one-pot preparation of cyclopropanes from the Fp anion **1**, as well as aldehydes and alkenes in the presence of two electrophilic silanes, without isolation of the carbene precursors, α-siloxyiron complexes **3**.

## 2. Results and discussion

Treatment of the Fp anion **1** with aldehydes **2** in the presence of chlorotrimethylsilane, followed by treatment with triflate and styrene, provided cyclopropanes **5** in moderate yields better or comparable to the multistep procedures reported earlier [2] (Scheme 2). This preparation consisted of a sequence of reactions performed in one simple, side-arm flask.

During this study, we noted that two different types of silicon electrophiles were deemed necessary for these cyclopropanation reactions. Use of 2–2.5 equiv. of trimethylsilyl triflate alone did not produce cyclopropanes. To determine whether there was any formation of carbene precursor, $CpFe(CO)_2[CH(OSiMe_3)C_6H_5]$ (**3a**), the reaction of the Fp anion and benzaldehyde in the



Scheme 1.

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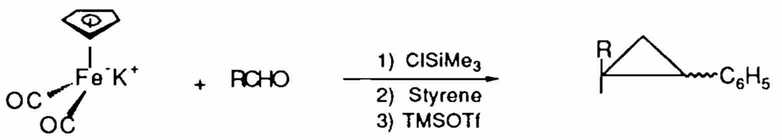

**1** **2a**: R = $C_6H_5$ **5a**: R = $C_6H_5$, 48% (all cis)
**2b**: R = $p$-$CH_3C_6H_4$ **5b**: R = $p$-$CH_3C_6H_4$, 28% (all cis)
**2c**: R = $p$-$OCH_3C_6H_4$ **5c**: R = $p$-$OCH_3C_6H_4$, 27% (cis/trans:1/3)

Scheme 2.

presence of 1 equiv. of trimethylsilyl triflate was conducted. Formation of the carbene precursor **3a** was not observed. Instead, from the reaction a 49% yield of CpFe(CO)$_2$SiMe$_3$ and a 20% yield of iron Lewis acid, [CpFe(CO)$_2$(THF)]$^{+}$ $^{-}$OSO$_2$CF$_3$, were isolated while the remainder was iron dimer.

It is readily apparent, from these unoptimized results, that the one-pot preparation of cyclopropanes, without isolation of $\alpha$-siloxy complexes **3**, is quite promising [2]. Reaction of benzaldehyde with styrene exhibited very high *cis* selectivity, which is consistent with the reaction of carbene precursor **3a** with styrene [1]. Reaction of $p$-methylbenzaldehyde with styrene also gave only *cis* cyclopropane **5b**. Treatment of $p$-methoxybenzaldehyde with styrene showed a different selectivity compared to the multi-step one. It yielded **5c** with the *trans* isomer as the major product (*trans*/*cis*, 3/1) and it is in contrast to the treatment of the precursor, CpFe(CO)$_2$[CH(OSiMe$_3$)C$_6$H$_4$OCH$_3$] (**3c**) with styrene in the presence of triflate in CH$_2$Cl$_2$ (*trans*/*cis*, 1/4) [1].

In conclusion, we report here a one-pot cyclopropanation reaction, via an iron carbene complex. This method eliminates problems associated with the isolation of the unstable carbene precursors, $\alpha$-siloxyalkyliron complexes. Work is underway to expand the scope of this reaction to include a larger variety of aldehydes and alkenes, as well as to optimize yields.

## 3. Experimental

### 3.1. General procedure

A 1.15–1.59 mmol sample of FpK [3] was dissolved in 30 ml of THF, cooled to −78 °C, and 2.39–3.44 mmol of aldehyde added dropwise. After stirring the mixture for 1–3 h at −78 °C, 1.15–1.59 mmol of chlorotrimethylsilane were added. Stirring was continued for 1 h and the temperature was maintained at −78 °C. To this reaction mixture, 2.29–3.18 mmol of styrene were added dropwise, with subsequent treatment of 1.15–1.75 mmol of trimethylsilyl triflate and stirred for 1 h at −78 °C[1]. After this, 60–70 ml of pentane were added to precipitate all of the iron salts. The cold solution was extracted with a saturated sodium bicarbonate solution, separated and passed through a short column of neutral alumina (Brockmann Activity Grade 3). The solvent was removed by distillation under atmospheric pressure. The residue was columned by a silica gel column[2] using 1–5% ethyl acetate–pentane to obtain pure cyclopropanes. The crude reaction mixture was analyzed by $^{1}$H NMR and/or by Hewlett-Packard 5880A GC to determine the *cis*/*trans* ratio.

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[1] With $p$-methoxybenzaldehyde the reaction mixture was warmed to −35 °C and stirred for 30 min. With $p$-methylbenzaldehyde the reaction mixture was warmed up to −50 °C and stirred for 30 min.

[2] Neutral alumina (Brockman Activity Grade 2) was used with the $p$-anisaldehyde reaction.