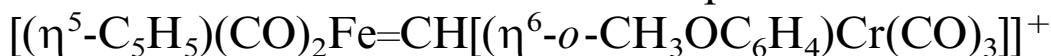


Communication

The origin of diastereoselectivity in cyclopropanation reactions of the iron carbene complex



Qinwei Wang, M. Mahmun Hossain *

Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee WI 53201, USA

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Abstract

The origin of diastereoselectivity in cyclopropanation reactions of the iron carbene complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}=\text{CH}[(\eta^6\text{-}o\text{-CH}_3\text{OC}_6\text{H}_4)\text{Cr}(\text{CO})_3]]^+$ has been investigated. The chromium participation has been proved by the upfield shifts of both ^1H - and ^{13}C -NMR for $\text{C}_\alpha\text{-H}$ and C_α , which stabilized the iron carbene and may result in a late transition-state for the cyclopropanation reaction via tricarbonylchromium-complexed iron carbene. Hence, *trans* selectivity is expected. However, when using aromatic alkenes, a π stacking effect may exist during the transition-state, resulting in the *cis* selectivity for cyclopropanation. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Iron carbene; Cyclopropanation; Transition-state; Diastereoselectivity; π Stacking

Due to continuing interest in asymmetric cyclopropanation reactions via chiral iron carbene complexes, we have employed tricarbonylchromium-complexed iron carbenes *R* and *S* $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}=\text{CH}[(\eta^6\text{-}o\text{-CH}_3\text{OC}_6\text{H}_4)\text{Cr}(\text{CO})_3]]^+$ (**1**) successfully for excellent asymmetric induction, and also expanded the scope of these chiral-at-carbene-ligand iron carbenes by reacting them with a series of styrene derivatives [1]. The carbene **1** reacted with styrene derivatives gave mainly *cis*-cyclopropanes. This was consistent with the dicarbonyl iron carbene complexes $(\text{Cp}(\text{CO})_2\text{Fe}=\text{CHR}^+)$ which are known to exhibit high *cis* selectivity in carbene transfer reactions to alkenes [2]. In contrast, we recently observed that the cyclopropanation reaction of carbene **1** with propene gave predominantly *trans* cyclopropane (*cis:trans*, 1:7), whereas, the uncomplexed iron carbene **2** gave mostly *cis* cyclopropane from propene (*cis:trans*, 5:1). The reaction of propene with dicarbonyl iron carbene complexes is a well-documented reaction and has always provided cyclopropanes with high *cis* selectivity [2], therefore, the observed *trans* selectivity with carbene **1** is unusual.

This result triggered our interest to explore the origin of *cis/trans* selectivity in cyclopropanation of alkenes via carbene **1**. Here, we would like to report our exciting preliminary findings in the origin of the diastereoselectivity in cyclopropanation reactions with tricarbonylchromium-complexed iron carbenes (see Fig. 1).

Cyclopropanes were prepared by the reaction of iron carbene **1** with corresponding alkenes using the procedure described earlier (Scheme 1) [1]. The resulting *cis/trans* ratios for the cyclopropanes **5** are listed in Table 1. With styrene and styrene-derivatives carbene **1** produced, primarily, *cis* cyclopropanes (entry 2–5). With α -methyl styrene carbene **1** also gave high *cis:trans* ratio (entry 1), whereas, with buta-1,3-diene and propene carbene **1** produced mainly *trans* cyclopropanes (entry 6–7).

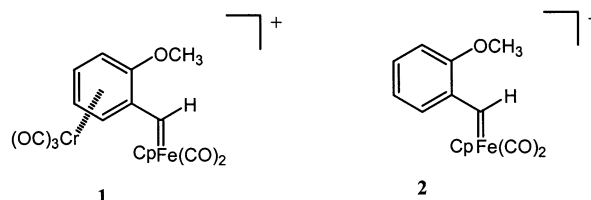
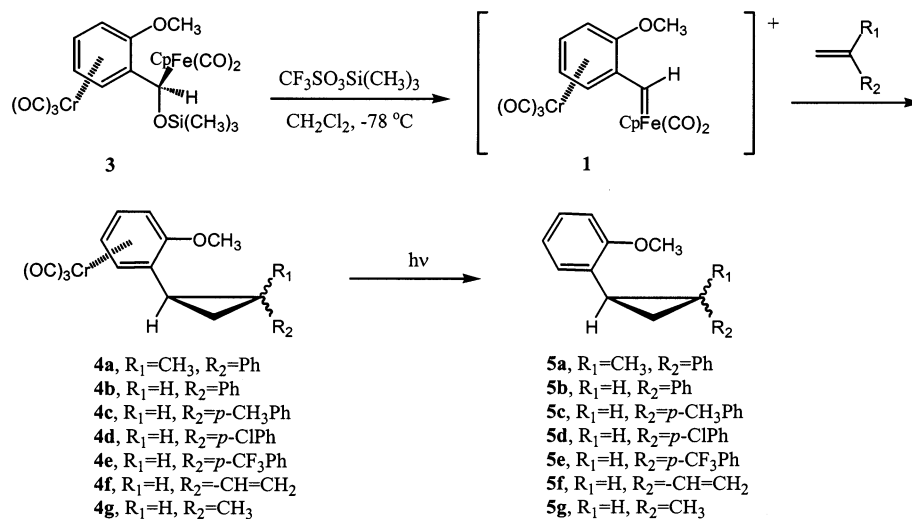


Fig. 1.

* Corresponding author.



Scheme 1.

In order to explain the observed *cis/trans* selectivity in cyclopropanation reactions involving iron carbenes, a transition-state model was proposed by Brookhart (Fig. 2) [3]. According to this model, for more reactive dicarbonyl systems $\text{Cp}(\text{CO})_2\text{Fe}=\text{CHR}^+$, the transition-state is early as shown in **6**. Site 2 would be sterically less crowded than site 1 for substituents, resulting in *cis* selectivity for monosubstituted alkenes [3]. In the late transition-state model **7**, (with less reactive carbene) substituents will prefer site 1 to site 2, and *trans* selectivity will be exhibited in cyclopropanation reactions.

In order to comprehend the origin of diastereoselectivity in the cyclopropanation of the carbene **1** employing the proposed transition-state model, we need to determine whether the transition-state of carbene transfer is 'early' or 'late'. It has been reported that in the chromium-complexed benzylic carbocation the chromium does participate with the positive charge at C_α carbon [4] and this was confirmed by the spectroscopic evidence by Olah [5]. Substantial upfield shifts in ^{13}C - and ^1H -NMR for C_α and $\text{C}_\alpha\text{-H}$ of chromium-complexed benzylic carbocation relative to uncomplexed benzylic carbocation were attributed to the strong participation of chromium [5]. Similar upfield shifts of ^{13}C - and ^1H -NMR for C_α and $\text{C}_\alpha\text{-H}$ of carbene **1** relative to **2** clearly demonstrate a strong participation of chromium with the positive charge of carbene carbon (structure **1'**, Fig. 3) [6]. It is also reported that the chromium participation stabilizes the benzylic carbocation and makes chromium-bound carbocations less reactive, and, in some cases, completely inhibits their reactivities [7]. Similarly, chromium complexation could also make the carbene **1** more stable and less reactive. Experimentally, it was observed that the characteristic purple color of the reaction mixture, assumed to be carbene **1**, persisted for a longer time than that of the corresponding uncomplexed carbene **2**.

Based on the proposed model, for the less reactive iron carbene **1** the transition state will be late and *trans* selectivity is expected (Fig. 4). Indeed, the reaction of carbene **1** with propene gave a 1:7 *cis:trans* ratio, suggesting a late transition-state. While with the more reactive uncomplexed carbene **2**, the transfer to propene gave a 5:1 *cis:trans* ratio via an early transition state.

If the 'late' transition state assumption for carbene transfer reaction with **1** is true, it is surprising to notice that the carbene transfers to styrene and its derivatives

Table 1
Ratio of cyclopropanes **5** from the reaction of carbene **1** with alkenes

Entry	Alkenes	Cyclopropanes	<i>cis</i> : <i>trans</i>
1		5a	30 : 1
2		5b	10 : 1 ^a
3		5c	7 : 1 ^a
4		5d	6 : 1 ^a
5		5e	3 : 1 ^a
6		4f^b	1 : 3
7		5g	1 : 7

^a The result is from ref 1. ^b Unable to obtain cyclopropane **5f** due to its decomposition during photolysis.

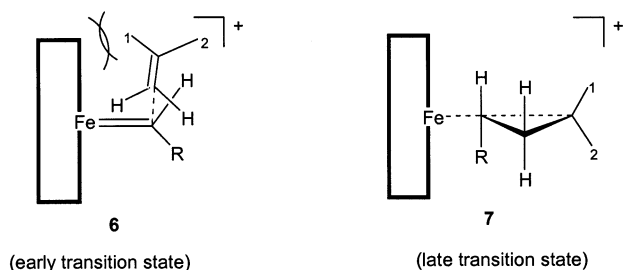


Fig. 2.

all gave mostly *cis* cyclopropanes. This raises the question, what factor is contributing to the *cis* selectivity in cyclopropanation of less reactive chromium-complexed iron carbene **1**? The answer may be the π – π interaction of two phenyl groups during the transition-state, which could keep them *cis* to each other. It is known that the tricarbonylchromium-complexed arene exhibits π – π interaction with another π system referred as the ‘ π stacking’ effect [8]. Such π – π interaction between the two arene groups is possible during the cyclopropanation reaction involving carbene **1** and aromatic alkenes. This interaction could stabilize the transition-state, resulting in *cis* selectivity in cyclopropanation (Fig. 5). If our assumption is true, then the reduction of the π stacking effect by an electron-withdrawing group on styrene could also reduce the *cis* selectivity. Indeed, the *cis:trans* ratio goes down from 10:1 (styrene) to 6:1 (*p*-chlorostyrene), to 3:1 (*p*-trifluoromethylstyrene). The *cis:trans* ratios of cyclopropanes made from *p*-methylstyrene (7:1) and from *p*-trifluoromethylstyrene (3:1) clearly indicate that the selectivity depends mainly on the electronic rather than the steric factor. Recently, the electronic factor was also found to be responsible for the *syn* selectivity in the cyclopropanation reactions of (phosphanyl)(silyl)carbene with styrene and styrene derivatives [9].

In order to further verify the existence of π stacking in the transition-state, we have tested the two other alkenes, α -methyl styrene (entry 1) and buta-1,3-diene (entry 6). In the reaction of carbene **1** with α -methyl styrene, it is predictable that the tricarbonyl chromium arene would obviously select Ph over a CH_3 group as

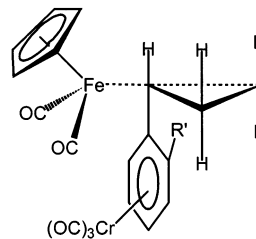


Fig. 4.

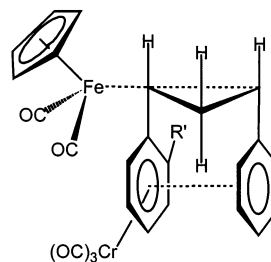


Fig. 5.

its *cis* partner due to the π stacking effect. The resulting very high *cis:trans* ratio (30:1) is consistent with this prediction. When carbene **1** was reacted with buta-1,3-diene, a lower *cis/trans* selectivity was observed (1:3) than for styrene and its derivatives (entries 1–5). This may be because the π stacking effect in this case (only one C=C double bond available) is much weaker than that of arenes. Furthermore, when no π stacking is possible as in the case of propene, the *trans*-selectivity was observed as expected by the late transition-state model.

In summary, the origin of the diastereoselectivity in the reaction of carbene **1** with various alkenes has been investigated. Due to the participation of chromium, the carbene **1** is quite stable and less reactive, resulting in a late transition-state in the carbene transfer reaction. Hence, according to the transition-state-model *trans* selectivity with monosubstituted non-aromatic alkenes is expected. However, with aromatic alkenes a strong π -stacking effect may exist during the transition-state, which results in the *cis* selectivity. Further kinetic and spectroscopic studies are underway and will be published in the near future.

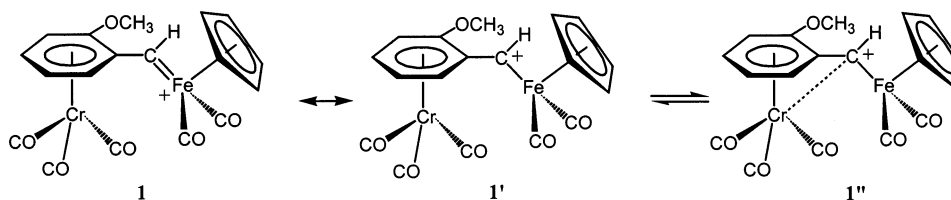


Fig. 3.

Acknowledgements

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