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Communication

The origin of diastereoselectivity in cyclopropanation reactions of the iron carbene complex $[(\eta^5\text{-}C_5H_5)(CO)_2Fe{=}CH[(\eta^6\text{-}o\text{-}CH_3OC_6H_4)Cr(CO)_3]]^+$

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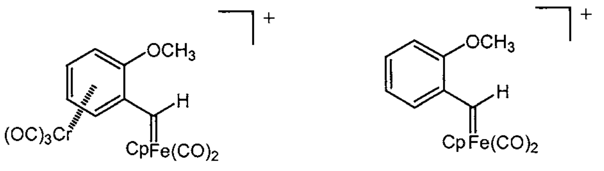
Abstract

The origin of diastereoselectivity in cyclopropanation reactions of the iron carbene complex $[(\eta^5\text{-}C_5H_5)(CO)_2Fe{=}CH[(\eta^6\text{-}o\text{-}CH_3OC_6H_4)Cr(CO)_3]]^+$ has been investigated. The chromium participation has been proved by the upfield shifts of both ^{1}H- and ^{13}C-NMR for C_α–*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* $[(\eta^5\text{-}C_5H_5)(CO)_2Fe{=}CH[(\eta^6\text{-}o\text{-}CH_3OC_6H_4)Cr(CO)_3]]^+$ (**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 ($Cp(CO)_2Fe{=}CHR^+$) 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).



1 **2**

Fig. 1.

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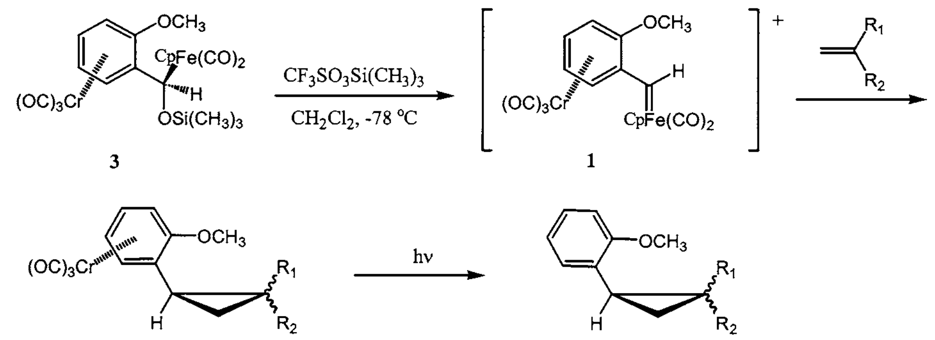


4a, R_1=CH_3, R_2=Ph
4b, R_1=H, R_2=Ph
4c, R_1=H, R_2=*p*-CH_3Ph
4d, R_1=H, R_2=*p*-ClPh
4e, R_1=H, R_2=*p*-CF_3Ph
4f, R_1=H, R_2=-CH=CH_2
4g, R_1=H, R_2=CH_3

5a, R_1=CH_3, R_2=Ph
5b, R_1=H, R_2=Ph
5c, R_1=H, R_2=*p*-CH_3Ph
5d, R_1=H, R_2=*p*-ClPh
5e, R_1=H, R_2=*p*-CF_3Ph
5f, R_1=H, R_2=-CH=CH_2
5g, R_1=H, R_2=CH_3

Scheme 1.

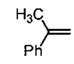
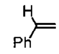
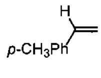
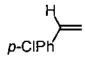
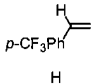
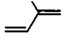
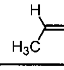
In order to explain the observed *cis*/*trans* selectivity in cyclopropanation reactions involving iron carbenes, a transition-state model was proposed by Brookhart (Fig. 2) [3]. According to this model, for more reactive dicarbonyl systems $Cp(CO)_2Fe{=}CHR^+$, the transition-state is early as shown 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 ^{1}H-NMR for C_α and C_α–*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 ^{1}H-NMR for C_α and C_α–*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**.

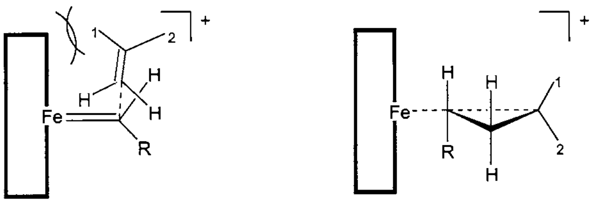
Based on the proposed model, for the less reactive iron carbene **1** the transition state will be late and *trans* selectivity is expected (Fig. 4). Indeed, the reaction of carbene **1** with propene gave a 1:7 *cis*:*trans* ratio, suggesting a late transition-state. While with the more reactive uncomplexed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



6

(early transition state)

7

(late transition state)

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

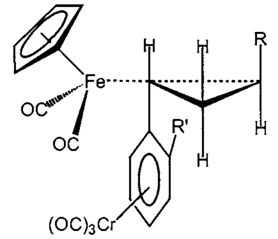


Fig. 4.

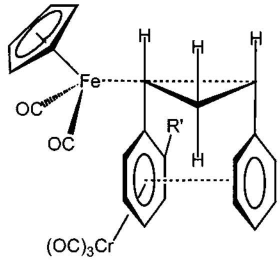


Fig. 5.

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.

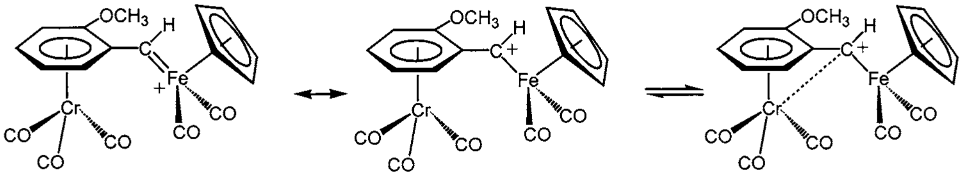


Fig. 3.

Acknowledgements

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References

[1] (a) Q. Wang, M.F. Mayer, C. Brennan, F. Yang, M.M. Hossain, D.S. Grubisha, D. Bennett, Tetrahedron 56 (2000) 4881. (b) Q. Wang, F. Yang, H. Du, M.M. Hossain, D. Bennett, D.S. Grubisha, Tetrahedron Asymmetry 9 (1998) 3971. (c) R.D. Theys, M.M. Hossain, Tetrahedron Lett. 36 (1995) 5113.

[2] (a) M. Brookhart, W.B. Studabaker, Chem. Rev. 87 (1987) 411. (b) R.D. Theys, R.M. Vargas, Q. Wang, M.M. Hossain, Organometallics 17 (1998) 1333.

[3] M. Brookhart, Y. Liu, E.W. Goldman, D.A. Timmers, G.D. Williams, J. Am. Chem. Soc. 113 (1991) 927.

[4] (a) S.G. Davies, T.D. McCarthy, in: F.G. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 12, Pergamon, New York, 1995, p. 1039. (b) M. Acampora, A. Ceccon, M.D. Farra, G. Giacometti, G. Rigatti, J. Chem. Soc. Perkin Trans. 2 (1977) 483. (c) P.A. Downton, B.G. Sayer, M. McGlinchey, J. Organometallics 11 (1992) 3281.

[5] G.A. Olah, S.H. Yu, J. Org. Chem. 41 (1976) 1694.

[6] For carbene **1**: ^{1}H-NMR δ: 13.7/13.3 (Fe=CH), ^{13}C-NMR δ: 275.8/258.8 (Fe = CH); For uncomplexed carbene **2**: ^{1}H-NMR δ: 16.3 (Fe=CH), ^{13}C-NMR δ: 320.1 (Fe=CH).

[7] S. Top, G. Jaouen, J. Org. Chem. 46 (1981) 78.

[8] (a) R.H. Mitchell, T.K. Vinod, G.W. Bushnell, J. Am. Chem. Soc. 112 (1990) 3487. (b) G.B. Jones, B.J. Chapman, J.E. Mathews, J. Org. Chem. 63 (1998) 2928.

[9] (a) D. Bourissou, O. Guerret, F.P. Gabbaï, G. Bertrand, Chem. Rev. 100 (2000) 39. (b) S. Goumri-Magnet, T. Kato, H. Gornitzka, A. Baceiredo, G. Bertrand, J. Am. Chem. Soc. 122 (2000) 4464.