# Cyclopropanation of alkenes mediated by novel chiral Fischer carbene complexes

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**Dedicated to an old friend, Professor Marcial Moreno-Mañas, on the occasion of his 60th birthday**

## Abstract

The cyclopropanation reaction using chiral-at-metal Fischer carbene complexes is examined. Racemic molybdenum and chromium carbene complexes *fac-* and *mer-***1** and *mer-***2**, respectively, undergo cycloaddition to acrylonitrile, methyl acrylate and 1-hexene to give cylopropanes **3** and **4** with *trans/cis* ratio up to 4.7:1. The cyclopropanation of acrylonitrile with the enantiopure carbene complex (+)-*mer-***1** resulted in a modest asymmetric induction of 2:1 for the *trans-*isomer **3a**.

**Keywords:** Cyclopropanation, alkenes, chiral Fischer carbene complexes, group 6, diastereoselective, enantioselective

## Introduction

The asymmetric transfer of carbene moieties onto the prochiral face of an olefin is one of the fundamental reactions in organic chemistry. For example, in 1966 Noyori and Nozaki described the use of a copper complex for asymmetric cyclopropanation that constituted the first asymmetric catalytic reaction in a homogeneous phase.[1] However, the exact nature of the active catalytic species remained undetermined. In 1964, Fischer and Maasböl had already isolated the first transition metal carbene complex of a group 6 element.[2,3] Although at first sight closely related, these two areas of carbene chemistry have encountered a surprisingly different development. While transition metal catalyzed asymmetric cyclopropanations have become a powerful tool for the construction of chiral three-membered ring systems,[4,5] the related process starting from Fischer carbene complexes has met with far more difficulties. It took until 1970

when Fischer and Dötz described a first cyclopropanation process for chromium carbene complexes.[6,7] It has only been recently that in connecting the classical areas of copper-catalyzed cyclopropanation and heteroatom-stabilized Fischer carbene complexes we have been able to show that transmetallation from chromium to copper can be achieved under suitable conditions.[8] Thus, chiral copper carbene complexes of the Fischer type are generated in a straightforward manner.

The reason for the mentioned difficulties in the use of Fischer carbene complexes for direct cyclopropanation[9] can be found in the relatively high stability, due to heteroatom substitution, which results in diminished reactivity under standard reaction conditions. Usually, such cyclopropanations have to be carried out in the presence of an excess of electron-poor olefins and at elevated temperatures.[6,9,10] Donor-substituted olefins are usually prone to undergo metathesis, a reaction path that can only be avoided by working under high CO pressures, and unactivated olefins are usually inert leading only to decomposition of the carbene complex.[11] To circumvent these difficulties, intramolecular versions have been divised.[12] In these reactions, olefinic groups in either the alkoxy or the alkyl groups are readily cyclopropanated.

In the achiral series, the mentioned cyclopropanation of electron-poor olefins yields only moderate diastereoselectivities with normally equimolar *trans/cis* ratios (scheme 1, reaction 1).[13]
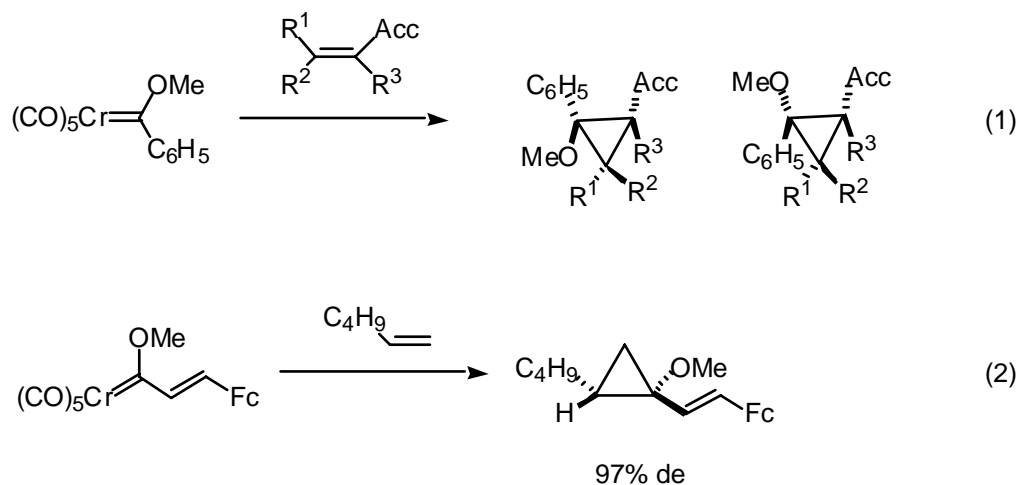


**Scheme 1.** "Classical" cyclopropanation and elevated diastereoselective cyclopropanation. Fc = ferrocenyl.

Alternatively, better diastereoselectivities can be obtained from reaction with conjugated systems either in the olefinic partner or in the carbene.[14] Within this approach we have recently described exceptionally high diastereoselectivities from reactions of $\alpha,\beta$-unsaturated chromium carbene complexes with simple olefins (scheme 1, reaction 2).[15]

In 1973, Fischer and Cooke used a chiral phosphine to modify the metal center in such a way that chirality transfer could occur in an enantioselective manner (scheme 2).[16] However, only a

symmetrical substrate was reported and apart from the observation that the product appeared to be optically active, no further studies were undertaken.
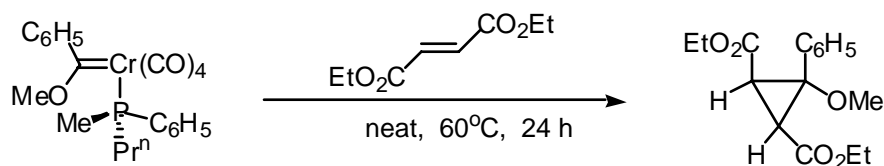


**Scheme 2.** Enantioselective cyclopropanation.

We have recently devised a novel approach for the synthesis of chiral Fischer carbene complexes of group 6 metals (Chart 1).[17,18] This approach consists of a modification of the metal coordination sphere via exchange of two CO ligands for a chiral, CO-emulating bidentate phosphite ligand.[19] Such ligands have been described by Kündig[20] and *trans*-1,2-bis{bis[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]phosphinoxy}cyclopentane proved best for our purposes. Thus, the three different types of complexes (*fac*-**1**, *mer*-**1** of Mo and *mer*-**2** of Cr) were obtained by thermal complexation.[17,19] Since the chiral information is directly placed at the metal fragment, enantioselective compounds of this type should bear an enormous potential for the development of novel asymmetric processes based on Fischer carbene complexes.[21]

Here, we describe the first results on the use of these complexes for the diastereo- and enantioselective cyclopropanation reaction.
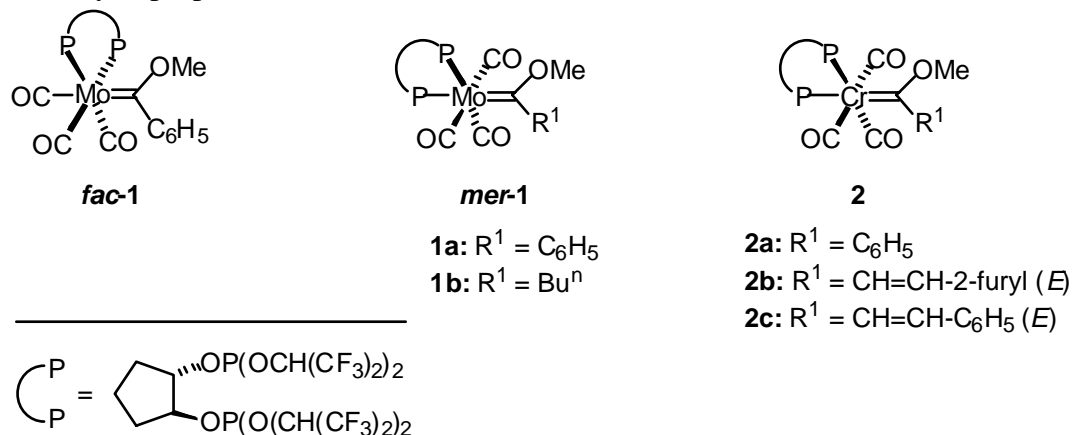


**Chart 1.** Chirally modified Fischer carbene complexes **1-2** with a chiral bisphosphite ligand P^P.

## Results and Discussion

### Cyclopropanation reaction with racemic complexes 1,2

Given the generally good reactivity of Fischer carbene complexes towards electron-acceptor substituted carbon-carbon double bonds we turned our attention on cyclopropanation with this

class of olefins. First, complex *fac*-**1** was chosen for optimization of reaction conditions. In the presence of 14 equivalents of acrylonitrile, carbene transfer from complex **1** was found to occur smoothly at a temperature between 40 and 60°C (Table 1). When acetonitrile was chosen as solvent, high conversion could be achieved and the product mixture contained the two isomeric cyclopropanes **3a** and **4a** in a *trans:cis* ratio ranging from 3.5:1 (at 60°C) to 4.0:1 (at 40°C). This is a rather high value for molybdenum carbene complexes since due to thermolability these compounds normally tend to give no diastereoselectivities at all. Carrying out the reaction in other polar solvents such as methanol or DMF required longer reaction times and resulted in lower yields and diastereoselectivities. The reaction did not proceed in THF and in the non-polar solvent hexane. A strong solvent dependence must thus be concluded that has no precedence for this type of reaction. Apparently, only the aprotic, highly polar solvent acetonitrile ensures sufficiently high reactivity in this case.
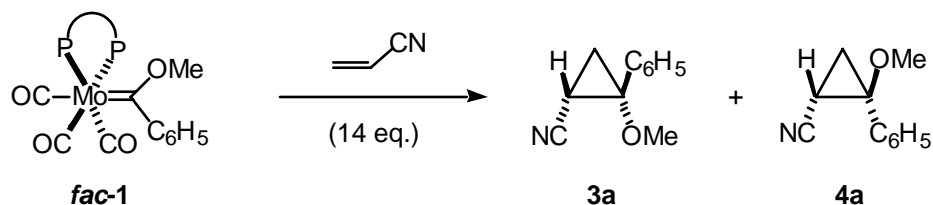


**Table 1.** Cyclopropanation of acrylonitrile with complex *fac*-**1**

| Entry | Solvent | Temp.(°C) | Time (h) | Yield[a] (%) | *trans:cis*[b] (**3a:4a**) |
|-------|---------|-----------|----------|--------------|----------------------------|
| 1 | CH$_3$CN | 60 | 5 | 81 | 3.5:1 |
| 2 | CH$_3$CN | 40 | 12 | 77 | 4.0:1 |
| 3 | CH$_3$OH | 60 | 40 | 14 | 3.0:1 |
| 4 | DMF | 50 | 26 | 23 | 2.0:1 |
| 5 | THF | 50 | 17 | - | - |
| 6 | *n*-C$_6$H$_{14}$ | 60 | 40 | - | - |

[a] Yields for isolated cyclopropane mixtures.
[b] Ratio as determined from integration of the respective methoxy signals of **3a** and **4a**.

Since acetonitrile had turned out to be the solvent of choice it was maintained throughout the following reactions investigating scope and limitation regarding the olefinic component. The results for general cyclopropanation reactions of molybdenum complex *mer*-**1** with electron-poor olefins are given in Table 2.
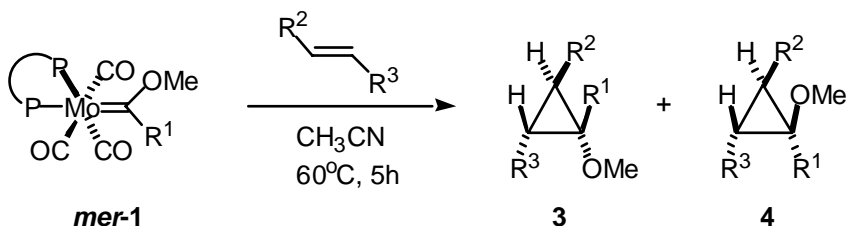
**Table 2.** Diastereoselective cyclopropanation with complex *mer*-**1**

| Entry | $R^1$ | $R^2$ | $R^3$ | Products | Yield[a] (%) | *trans*:*cis*[b] (**3**:**4**) |
|-------|-------|-------|-------|----------|--------------|-------------------------|
| 1 | $C_6H_5$ | H | CN | **3a** + **4a** | 84 | 4.7:1 |
| 2 | *n*Bu | H | CN | **3b** + **4b** | 89 | 2.0:1 |
| 3 | $C_6H_5$ | H | $CO_2Me$ | **3c** + **4c** | 88 | 2.0:1 |
| 4 | $C_6H_5$ | Me | CN | - | - | - |
| 5 | $C_6H_5$ | H | CH=N-Bu$^t$ | - | - | - |
| 6 | $C_6H_5$ | H | CO-Me | - | - | - |

[a] Yields for isolated cyclopropane mixtures.

[b] Ratio as determined from integration of the respective methoxy signals of **3** and **4**.

Three observations from Tables 1,2 are noteworthy. First, the two isomeric molybdenum carbene complexes *fac*- and *mer*-**1** yield different diastereoselectivities towards acrylonitrile. While *fac*-**1** gives a ratio of up to 4:1 (MeCN, 40°C) in favor of the *trans*-isomer, this ratio is increased to 4.7:1 (MeCN, 60°C) when *mer*-**1** is used. These results are in relation with a thermal isomerization[17,18] from the *fac*-configured complex to the more stable *mer*-complex occurring in the same temperature range (around 60°C) as applied to the cyclopropanation. Apparently, this isomerization has also a significant influence on the diastereoselectivity. Consequently, cyclopropanations with *fac*-**1** should either be carried out at temperatures that are low enough to avoid isomerization or, alternatively, complex *mer*-**1** should be used directly.

Secondly, only mono-substituted olefins were found to show reactivity. Any attempt to employ olefins with a different substitution pattern (entry 4) was unsuccessful. However, this observation is not too surprising since it is known that steric hindrance on the alkene, either caused from the number of substituents or from their bulkiness, limits the reactivity of Fischer carbene complexes in [2+1]-cycloadditions.[22] Enaldimines and enones do also not react (entries 5,6), most probably due to electronic reasons.

Finally, the diastereoselectivities are in all cases significantly higher than those reported from the respective series with pentacarbonyl complexes.[23] As the present cyclopropanation relies on the use of chiral ligand-modified Fischer carbene complexes the beneficial influence of the chiral ligand on the stereochemical course of the [2+1]-cycloaddition is obvious. Furthermore, unlike the case of [2+1]-cycloadditions with pentacarbonyl carbene complexes no products derived from formal $C_\beta$-H insertion reactions[24] were ever detected.

Next, attention was turned to the related chromium complexes *mer*-**2** (Table 3). Again, only the monosubstituted olefins acrylonitrile and methyl acrylate showed reactivity towards phenyl-substituted carbene complex *mer*-**2a**, indicating that the observed limitation is not metal specific (see entries 1-3). We were delighted to find that the cyclopropanation reaction could be successfully extended not only to α,β-unsaturated chromium carbene complexes *mer*-**2b,c** (entries 4,5) but also to unactivated olefins (entry 6).

The influence on the reaction course as exercised by the chiral ligand can be observed from the increase in diastereoselectivity in these reactions. In this context, no diastereoselectivity was reported for the cyclopropanation reaction of acrylonitrile with the corresponding pentacarbonyl[(methoxy)(phenyl)methylene]chromium(0) complex.[23] The diastereomeric ratio for reaction with methyl acrylate was reported to be 19% in favor of the *cis*-isomer.[22] The 50% *de* reached from the reaction of **mer**-**2** with acrylic nitrile thus represent a considerable improvement in diastereoselectivity while in the case of methyl acrylate an inversion in diastereoselectivity occurred.
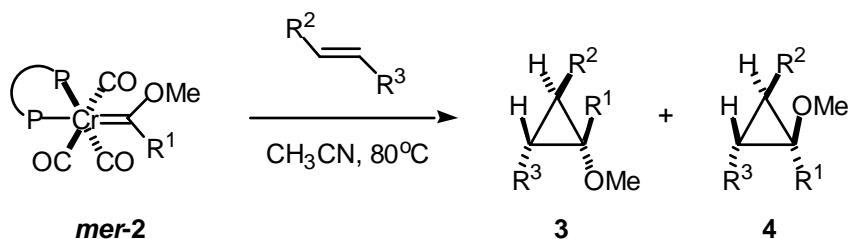


**Table 3.** Diastereoselective [2+1]-cycloaddition with complexes **mer**-**2**

| Entry | $R^1$ | $R^2$ | $R^3$ | Products | Yield[a] (%) | *trans*:*cis*[b] (**3:4**) |
|-------|-------|-------|-------|----------|--------------|----------------------------|
| 1 | $C_6H_5$ | H | CN | **3a** + **4a** | 74 | 3.0:1 |
| 2 | $C_6H_5$ | H | $CO_2Me$ | **3c** + **4c** | 80 | 1.5:1 |
| 3 | $C_6H_5$ | Me | CN | - | - | - |
| 4 | (*E*)-CH=CH-2-furyl | H | CN | **3d** + **4d** | 75 | 1.7:1[c] |
| 5 | (*E*)-CH=CH-$C_6H_5$ | H | CN | **3e** + **4e** | 70 | 2.5:1[d] |
| 6 | (*E*)-CH=CH-2-furyl | H | *n*Bu | **3f** + **4f** | 78 | 2.0:1[e] |

[a] Yields for isolated cyclopropane mixtures.

[b] Ratio as determined from integration of the respective methoxy signals.

[c] Solvent: DMF.

[d] Solvent: acetonitrile or cyclohexane.

[e] Solvent: THF.

**Enantioselective cyclopropanation reaction**

Given the already rather problematic performance of complexes **1,2** regarding diastereoselectivity, we only briefly addressed the issue of enantioselectivity.

Thus, enantiopure molybdenum complex (+)-**mer**-**1**, derived from (+)-(1*S*,2*S*)-*trans*-1,2-bis{bis[2,2,2-trifluoro-1-(trifluoromethyl)ethoxy]phosphinoxy}cyclopentane, was submitted to cyclopropanation with acrylonitrile at 50°C in acetonitrile. Removal of the volatiles and kügelrohr distillation furnished a 5:1 mixture of *trans*- and *cis*-cyclopropanes in 89% yield. Careful purification (SiO$_2$; hexane/EtOAc 5:1 v/v) allowed for isolation of the major *trans*-diastereoisomer **3a** which was analyzed by chiral HPLC analysis (Chiracel OD-H column), from which an enantiomeric ratio of 2:1 was determined. To the best of our knowledge this represents

the first example of a diastereomerically and enantiomerically enriched [2+1]-cycloaddition between an enantiopure Fischer carbene complex of group 6 and a non-symmetrical olefin.

To summarize, we have shown that novel Fischer carbene complexes of molybdenum **1** and of chromium **2** are able to cyclopropanate electron-poor and unactivated alkenes with high diastereoselectivity. The first asymmetric attempts reveals a rather modest face selectivity. Therefore, optimization of the ligand structure for improvement of the enantiomeric ratio, as well as investigation of complexes **1,2** in other asymmetric reactions is currently under investigation.


## Experimental Section


**General Procedures.** THF, diethylether, *n*-hexane and toluene were distilled from sodium/benzophenone ketyl radical under argon. Dichloromethane was distilled from $CaH_2$ under argon. All other solvents were reagent grade and used as received.

All syntheses of cyclopropanes were repeated at least twice in order to ensure reproducibility. The yields which are reported are average values.

All cyclopropane adducts were identified by comparison of their ^{1}H NMR with those already reported in the literature.[22,23,25]


**General procedure for the cyclopropanation of acrylonitrile, methyl acrylate and 1-hexene in the presence of modified carbene complexes 1-2**

The carbene complex (0.8 mmol) is placed in a well-dried Schlenk flask under an inert atmosphere of nitrogen and dissolved in 30 mL freshly distilled solvent. The olefin (11 mmol, 14 equiv.) is added via syringe and the Schlenk flask is sealed with a glass stopper. The reaction mixture is warmed at 40-80°C for 5-12 hours and then cooled to room temperature. The solvent is removed under reduced pressure and the crude product is submitted for analysis by ^{1}H NMR. Purification of the crude product was carried out by Kügelrohr distillation at a low pressure vacuum pump yielding a yellowish oil that consists of an undetermined mixture of metal-ligand complex and cyclopropanes. Final purification by column chromatography (silica gel, *n*-hexane/ethyl acetate, 5:1, v/v) yields both diastereomeric cyclopropanes which, if desired, can be separated by further column chromatography (silica gel, *n*-hexane/ethyl acetate, 60:1 v/v).

The diastereomeric ratios of the cyclopropane products were determined from the crude ^{1}H NMR spectra by comparison of the methoxy group signals (Tables 1-3).

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