Catalytic Cyclopropanation of Fluorine-Containing Alkenes and Dienes with Diazomethane and Methyl Diazoacetate

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The reactivities of various double bonds in fluorine-containing unsaturated compounds toward cyclopropanation with diazomethane and methyl diazoacetate with catalysis by copper, rhodium and palladium compounds were studied. In general, the presence of fluorine atoms attached to the double bond or arranged at neighbouring positions exerted a suppressive effect on the cyclopropanation of this bond. As would be expected, diazomethane in the presence of palladium compounds primarily cyclopropanated less highly substituted double bonds. In the case of 2-fluoro-3-methylbutadiene, the reaction took place at both of the double bonds. When methyl diazoacetate was used, $[Rh_2(OAc)_4]$ was an efficient catalyst, yielding cyclopropanation products on monofluoro-substituted double bonds in alkenes and cycloalkenes. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2004)

Introduction

It is well known that the introduction of fluorine atoms into organic molecules can dramatically affect the chemical properties of compounds and result in valuable products, such as biologically active compounds. In this respect, cyclopropane derivatives with fluorine atoms at different positions in the molecule are of interest. These derivatives can be conveniently synthesized by catalytic cyclopropanation of fluorine-containing unsaturated compounds with diazoalkanes and diazoesters. In particular, compounds from this series have been synthesized in order to obtain precursors of pyrethroid insecticides[1,2] and antibacterial agents.[3,4] Recently[5] we have studied the reactions of diazomethane and methyl diazoacetate with fluorine-containing vinylcyclobutanes and vinylcyclobutene.

The results obtained suggest that the fluorine-containing unsaturated compounds exhibit decreased reactivity in the double bonds (either with or without fluorine atoms at these bonds) in these reactions.[5] Although highly effective catalysts for the cyclopropanation of olefins with diazo compounds have been known for a long time[6−10] there are no systematic study of catalytic reactions of fluorinated olefins with diazoesters and diazoalkanes. In view of the dramatic effects that may be caused by the replacement of particular C−H bonds with C−F bonds, we studied the reactions between fluorinated analogues of unsaturated compounds and aliphatic diazo compounds. The aim of these studies was to examine the effect of the presence of fluorine substituents on the reactivities of various double bonds and to develop methods for the preparation of new fluorine-containing synthons.

For this purpose we synthesized (see Exp.Sect.) the following fluorine-containing alkenes and dienes with fluorine substituents present at different positions in the molecules: 3,3-difluoro-2-methoxy-1-vinyl-1-cyclobutene (**1**), 2-fluoro-3-methyl-1,3-butadiene (**2**), 1-(1-fluorovinyl)-1-methylcyclopropane (**3**), 4-chloro-4,5,5-trifluoro-1-cyclohexene (**4**), 1,2-difluoro-1,4-cyclohexadiene (**5**) and 1-fluoro-2-methyl-1-cyclopentene (**6**). The catalytic cyclopropanation was performed with diazomethane and methyl diazoacetate in the presence of Cu, Rh and Pd compounds.

Results and Discussion

The reaction between 3,3-difluoro-2-methoxy-1-vinyl-1-cyclobutene (**1**) and a twofold to threefold excess of CH_2N_2 in the presence of $[(PhCN)_2PdCl_2]$ occurred with high selectivity of cyclopropanation of the exocyclic double bond to give 3,3-difluoro-2-methoxy-1-cyclopropyl-1-cyclobutene (**7**) in 85−90% yield. The reaction was performed by introduction of gaseous CH_2N_2 in an inert gas flow into a mixture of the olefin and the catalyst at 0−5 °C. The high yield of the resulting cyclopropane **7** is consistent with the fact that palladium catalysts are highly sensitive to steric factors in a substrate, only monosubstituted and strained cyclic double bonds being readily cyclopropanated in the presence of Pd compounds.[8−11] Moreover, in the case of vinylcyclobutene **1**, the activity of the catalyst was high in the course of the overall process. In contrast, the cyclopropanation of related 2,3,3-trifluoro-1-vinyl-1-cyclobutene under analogous conditions gave the corresponding cyclopropylcyclobutene **7** in only approx. 40% yield.[5]

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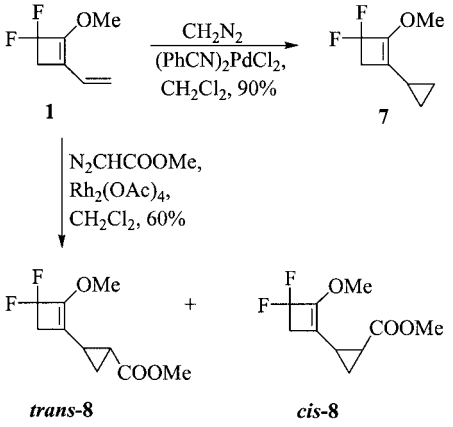
The comparatively low yield of 1-cyclopropyl-2,3,3-trifluoro-1-cyclobutene probably resulted from a parallel reaction in the form of a 1,3-dipolar cycloaddition between diazomethane and 2,3,3-trifluoro-1-vinyl-1-cyclobutene and partial deactivation of the catalyst.[5] The replacement of a fluorine atom by an electron-donor group resulted in methoxyvinylcyclobutene **1** not entering into 1,3-dipolar cycloaddition reactions with either diazomethane or diazoesters.



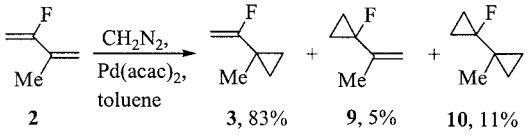
Scheme 1

It should be noted that, in contrast to compounds **1** and **7**, some non-fluorinated cyclobutenes with endocyclic double bonds undergo catalytic cyclopropanation with diazomethane and ethyl diazoacetate.[12−14] The formal cyclopropanation of endocyclic double bonds of fluorinated cyclobutene derivative has occurred in reactions with ethyl diazoacetate and phenyldiazomethane in the absence of catalysts,[15] but this process could be a result of 1,3-dipolar cycloaddition and deazotation reactions.

The catalytic cyclopropanation of the vinylcyclobutene **1** with methyl diazoacetate in the presence of 1 mol% $[Rh_2(OAc)_4]$ in CH_2Cl_2 at an olefin/diazoester molar ratio of 3:1 occurred at the vinyl group to give methyl 2-(3,3-difluoro-2-methoxy-1-cyclobutenyl)cyclopropanecarboxylate (**8**) in 60% total yield as a mixture of *trans* and *cis* isomers in a ratio of 1.2:1. The use of $[Pd(acac)_2]$ at 20 °C or of $[Cu(acac)_2]$ in boiling CH_2Cl_2 was ineffective, with cyclopropanation products **8** being formed in yields of 10% or less. In the former case the reaction occurred very slowly, whereas dimethyl fumarate and maleate were the main products of methyl diazoacetate decomposition. The esters **8** were separated as fractions enriched in *cis* or *trans* isomer (up to 90−93%) by preparative TLC on silica gel. In contrast to those of the cyclopropylcyclobutene **7**, ^1H NMR spectra of isomeric compounds **8** exhibited nonequivalence of methylene protons in a four-membered ring due to the presence of an ester substituent at the cyclopropane unit; this effect was much more pronounced in the *cis* isomer ($\Delta\delta$ = 0.24 ppm) than in the *trans* isomer ($\Delta\delta$ = 0.03 ppm). Analogously, the ^{19}F NMR signals of geminal fluorine atoms in the *cis* isomer exhibited different chemical shifts ($\Delta\delta$ = 2.5 ppm) and split into a doublet with spin−spin coupling constant $^2J_{FF}$ 200 Hz, whereas the signal of the CF_2 group in the *trans* isomer was a weakly broadened singlet.

2-Fluoro-3-methyl-1,3-butadiene (**2**) is the simplest conjugated diene containing an alkyl group at a double bond and a fluorine atom at the other double bond in internal positions. This compound was cyclopropanated by a procedure in which diazomethane was generated in situ.[16] A twofold molar amount of *N*-methyl-*N*-nitrosourea was added to a mixture of a 40% KOH solution and diene **2** in toluene in the presence of a catalytic amount of $[Pd(acac)_2]$, which approximately corresponded to a diene/CH_2N_2 molar ratio equal to 1:1.5.

In this case, 1-(1-fluorovinyl)-1-methylcyclopropane (**3**) was isolated as the main product in about 80% yield. The ^1H and ^{19}F NMR spectra of this product contained signals due to the fluorovinyl group, which were analogous to the signals of the starting olefin, with the characteristic spin−spin coupling constants $^3J_{H,F\text{-}trans}$ = 50.1 and $^3J_{H,F\text{-}cis}$ = 16.6 Hz for the $H_2C{=}CF$ fragment.

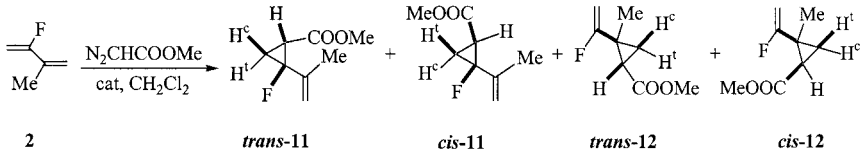


Scheme 2

However, 1-fluoro-1-isopropenylcyclopropane (**9**, approx. 5%) and 1-fluoro-1-(1-methylcyclopropyl)cyclopropane (**10**, 11%) were also detected in the reaction mixture along with compound **3**. The formation of compounds **9** and **10** is indicative of the cyclopropanation of a fluorinated double bond.

Indeed, the repeated cyclopropanation of compound **3** with diazomethane in the presence of $[Pd(acac)_2]$ under the specified conditions at an olefin/*N*-methyl-*N*-nitrosourea molar ratio equal to 1:3 resulted in bicyclopropyl derivative **10** in good yield. This is the first example of the successful cyclopropanation of a fluorine-substituted double bond with diazomethane in the presence of a palladium catalyst. Note that the activity of this double bond is lower than the activity of a methyl-substituted double bond in diene **2** or 2-methyl-1,3-butadiene.[17]

The cyclopropanation of the fluorodiene **2** with methyl diazoacetate in the presence of $[Rh_2(OAc)_4]$, $[Cu(acac)_2]$ or $[(PhCN)_2PdCl_2]$ as catalyst occurred at both of the double bonds and result in the formation of isomeric esters **11** and **12**. In this case, with the use of a threefold excess of diene **2** under the same conditions, the total yield of monoadducts decreased on going from Rh compounds to Cu and Pd compounds (Table 1) with a simultaneous increase in the amount of dimethyl fumarate and maleate. Moreover, the amount of products of the cyclopropanation of a fluorinated double bond was greater (by a factor of 1.2−1.3) with



2 *trans*-11 *cis*-11 *trans*-12 *cis*-12

Scheme 3

Table 1. Composition of cyclopropanation products of fluorinated olefins **2**, **3** and 2-methyl-1,3-butadiene with methyl (ethyl[a]) diazoacetate in the presence of different catalysts

Starting compound	Catalyst	Cyclopropanation of H_2C=CX bond where X = F or H			Cyclopropanation of H_2C=C(Me) bond		
		Products	Yield (%)	*cis/trans* ratio	Products	Yield (%)	*cis/trans* ratio
 **2**	$Rh_2(OAc)_4$	**11**	44	1.1 : 1	**12**	40	1 : 1
	$Cu(acac)_2$		34	1.1 : 1		27	1 : 1
	$(PhCN)_2PdCl_2$		19	1 : 1.9		36	1 : 2
 **3**	$Rh_2(OAc)_4$	**13**	88	1.4 : 1			
	$Cu(acac)_2$		75	1.5 : 1			
	$(PhCN)_2PdCl_2$		18	1 : 1			
	$Rh_2(OAc)_4$	[b]	36	1 : 1.8	[c]	57	1 : 1.1
	$Cu(acac)_2$		18	1 : 3.3		37	1 : 1.3
	$(PhCN)_2PdCl_2$		16	1 : 1		8	1 : 1.1

[a] Ethyl diazoacetate was used for cyclopropanation of 2-methyl-1,3-butadiene (see ref.[9]). [b] Ethyl *cis*- and *trans*-2-isopropenylcyclopropanecarboxylate. [c] Ethyl *cis*- and *trans*-1-methyl-2-vinylcyclopropanecarboxylate.

the use of Rh and Cu compounds as catalysts, whereas cyclopropanation in the presence of Pd compounds primarily occurred at a methylated double bond (ratio **11**:**12** = 1:1.9).

Three fractions enriched in different isomers were separated by column chromatography and unambiguously identified by their ^1H and ^{19}F NMR spectra. As evidenced by the positions of the fluorine signals in the ^{19}F NMR spectra (Table 2), a characteristic difference between the regioisomers involves the presence of a fluorovinyl fragment or a fluorocyclopropane unit in one or the other pair of isomers, respectively. Moreover, in the former case, the ^1H NMR spectra contain signals due to the fluorovinyl group with spin−spin coupling constants $^3J_{H,F\text{-}trans}$ = 50 and $^3J_{H,F\text{-}cis}$ = 16 Hz in the olefin region, whereas signals due to an isopropenyl fragment with low spin−spin coupling constants from methyl protons were observed in the latter case. The *cis* and *trans* forms of the compounds were attri-

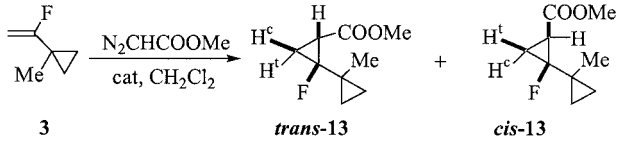
Table 2. ^1H and ^{19}F NMR spectra of cyclopropanecarboxylates **11**−**13** (δ, ppm; *J*, Hz)

Compound	1-H	3-H[c]	3-H[t]	$=CH_2$ or *c*-C_3H_4	CH_3	OCH_3	$^3J_{cis}$	$^3J_{trans}$	^2J	$^3J_{H,F}$ (*cis*)	$^3J_{H,F}$ (*trans*)	^{19}F
cis-**11**	2.02 m	1.44 ddd	2.00 m	5.12 dq, 5.02 m $J_{H,F}$ = 2.7	1.79 dd ^4J = 1.0 and 1.2 Hz	3.76 s	8.7	7.4	6.5	19.7	3.5, 13.0	−188.7, br. dd, $^2J_{H,F}$ = 20.7, $^2J_{H,F}$ = 10.4
trans-**11**	2.34 ddd	1.60 ddd	1.77 ddd	5.17 m	1.87 dd ^4J = 1.1 and 2.5 Hz	3.69 s	10.2	7.6	6.9	18.5, 19.2	13.0	−163.3, br. dd, $^2J_{H,F}$ = 18.5, $^2J_{H,F}$ = 13.0
cis-**12**	1.76 dd	1.10 ddd $J_{H,F}$ = 4.8	1.61 ddd $J_{H,F}$ = 3.0	4.70 dd, 4.48 dd J = 3.2	1.38 s	3.69 s	7.7	5.6	5.3	15.5	48.8	−97.6, br. dd, $^2J_{H,F}$ = 50.0, $^2J_{H,F}$ = 17.8
trans-**12**	2.13 dd	1.43 dd	1.29 ddd $J_{H,F}$ = 1.5	4.64 dd, 4.43 dd J = 3.3	1.38 s	3.72 s	8.5	6.3	4.6	17.6	49.5	−109.3, br. dd, $^2J_{H,F}$ = 48.5, $^2J_{H,F}$ = 15.5
cis-**13**	1.78 m	0.99 ddd	1.75 m	0.33−0.72 m	1.29 s	3.71 s	8.6	7.4	6.3	19.5	3.6, 11.5	−187.2, br. t, $^2J_{H,F}$ = 10.9
trans-**13**	2.26 ddd	1.32 ddd	1.22 ddd	0.33−0.72 m	1.19 s	3.69 s	10.2	7.3	6.9	18.4, 19.0	12.6	−159.6. br. dd, $^2J_{H,F}$ = 30.7, $^2J_{H,F}$ = 15.8

buted from the positions of signals due to cyclopropane protons and spin−spin coupling constant values. In particular, the signal highest upfield, at δ = 1.10 ppm, in the ^{1}H NMR spectra was ascribed to the 3-H^a proton in *cis* isomer **12** as the most shielded proton among the four isomeric structures.

If small differences due to the use of methyl diazoacetate or ethyl diazoacetate are ignored, the fluorine-substituted double bond in fluorodiene **2** is more active than the unsubstituted double bond in 2-methyl-1,3-butadiene if Rh or Cu compounds are used as catalysts (Table 1). Because the above catalysts generate electrophilic carbenoid species, and as cyclopropanation occurs, as a rule, at electronically enriched double bonds,[8,18] it is believed that electron density in fluorodiene **2** is noticeably displaced from the methyl-substituted double bond to the fluorovinyl unit.

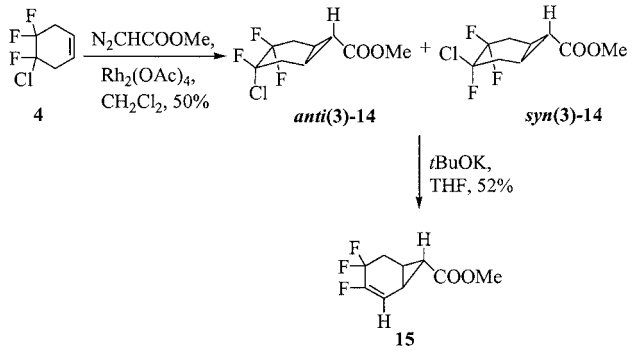
The catalytic cyclopropanation of the fluorine-substituted double bond in vinyl fluoride **3** with methyl diazoacetate in the presence of [$Rh_2(OAc)_4$], [$Cu(acac)_2$] or [$Pd(acac)_2$] resulted in isomeric esters **13**, the compositions of which changed only slightly depending on the nature of a catalyst. However, the total yields of these bicyclopropanes dramatically decreased on going from Rh and Cu compounds to [$Pd(acac)_2$] (Table 1).



Scheme 4

The fluorocyclopropane ring protons of both isomers of **13** and the corresponding protons in isomeric fluorocyclopropanes **11** exhibited analogous ^{1}H NMR signals (Table 2). Previously,[3] in the case of catalytic cyclopropanation of α-fluorovinylbenzene with ethyl diazoacetate, it had been found that, among catalysts based on Cu, Rh, and Pd compounds, copper compounds such as [$Cu(acac)_2$] were most effective. However, our results obtained in the cyclopropanation of fluorodiene **2** and vinyl fluoride **3** suggest that rhodium compounds, in particular, [$Rh_2(OAc)_4$], are more preferable.

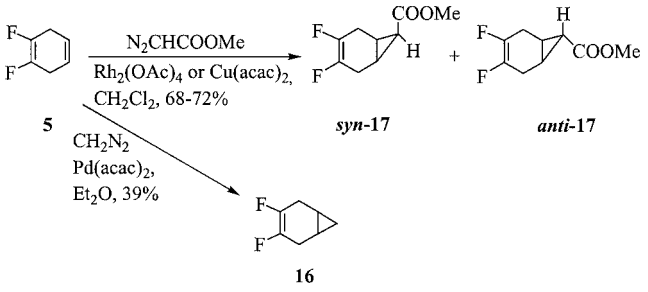
We also studied the catalytic cyclopropanation of fluorine-containing cycloalkenes with or without fluorine atoms at double bonds. We found that the double bond in 4-chloro-4,5,5-trifluoro-1-cyclohexene (**4**) was scarcely cyclopropanated with diazomethane in the presence of [$Cu(acac)_2$], [$(PhCN)_2PdCl_2$] or [$Pd(acac)_2$]. Interaction between cycloalkene **4** and methyl diazoacetate in the presence of [$Rh_2(OAc)_4$] occurred successfully, however, to result in the methyl esters of 3-chloro-3,4,4-trifluoro[4.1.0]bicycloheptane-7-carboxylic acid **14** in a total yield of about 50%. According to GLC data, these esters were formed as a difficult to separate mixture of two isomers in an approximately equal ratio. These isomers are very similar in properties, and the OCH_3 group protons manifest themselves as a singlet in the ^{1}H NMR spectra ($CDCl_3$). This suggests that the isomerism of esters **14** is due to different positions of F and Cl atoms at C-3 and a more stable *anti* arrangement of the ester group, which is at a distant position with respect to substituents at C-3, in both of the isomers.



Scheme 5

Note that the signal of the CF_2 group of one of the isomers appeared in the ^{19}F NMR spectrum as a broadened singlet, whereas the corresponding signal of the other isomer appeared as two broadened doublets with the geminal spin−spin coupling constant J_{FF} = 257 Hz. The dehydrochlorination of compound **14** in the presence of *t*BuOK in THF resulted in the formation of an isomer of methyl 3,4,4-trifluorobicyclo[4.1.0]hept-2-ene-7-carboxylate (**15**). The *trans* configuration of the cyclopropane unit in compound **15** was attributed from ^{1}H NMR spectral data. Indeed, the upfield signals at δ = 1.6−2.0 ppm due to the cyclopropane protons were multiplets with maximum spin−spin coupling constant J_{trans} = 5 Hz. This fact confirms our suggestion about the *anti* arrangement of the ester group in esters **14**.

Unlike the cyclohexene **4**, 1,2-difluorocyclohexa-1,4-diene (**5**) underwent cyclopropanation with diazomethane in the presence of [$Pd(acac)_2$], but the reaction occurred only in low yield. Thus, with the use of a sevenfold to tenfold excess of CH_2N_2 and with the addition of the catalyst to a mixture of the reactants, only approx. 40% conversion of the starting diene **5** was reached. In this case, a cyclopropanation product, which was identified by its ^{1}H and ^{19}F NMR spectra as 3,4-difluorobicyclo[4.1.0]hept-3-ene (**16**), was formed. The use of CuCl as a catalyst also resulted in adduct formation at the non-fluorinated double bond, but the compound was obtained in a very low yield (3−5%).

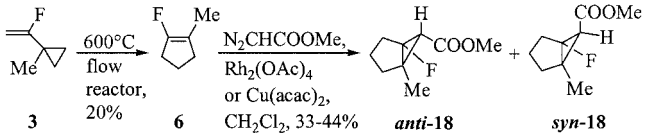


Scheme 6

The cyclopropanation of diene **5** with methyl diazoacetate in the presence of $[Rh_2(OAc)_4]$ or $[Cu(acac)_2]$ occurred with the same regioselectivity and resulted in the methyl 3,4-difluorobicyclo[4.1.0]hept-3-ene-7-carboxylate (**17**) in total yields of 72 or 67%, respectively. The esters **17** were formed as a mixture of *anti* and *syn* isomers in a ratio of (2−2.1):1 and were separated as fractions enriched in *anti* or *syn* isomer (up to 90−93%) by preparative TLC on silica gel. The *trans* configuration of the cyclopropane unit in the major isomer **17** was attributed because the upfield signals due to the cyclopropane protons in the ^1H NMR spectra at $\delta = 1.6-1.8$ ppm were multiplets with maximum spin−spin coupling constant $J_{trans} = 3$ Hz.

Our attempts to perform the cyclopropanation of the resulting compounds **16** and **17** at a fluorinated double bond with a diazoester or diazomethane and with Cu, Rh and Pd compounds as catalysts were unsuccessful; nor were products of C−H insertion formed in detectable amounts. In this context it is interesting to note that reactions between diene **5** and dichloro- or chlorofluorocarbene generated from $CHCl_2X$ (X = Cl, F) and NaOH in the presence of phase-transfer catalyst occurred with inverted regioselectivity and were accompanied by the predominant formation of a cyclopropane adduct at a difluorinated double bond (ratio of 6.5:1).[19]

Because a difluoro-substituted double bond in cyclohexene was inert in catalytic cyclopropanation with diazo compounds, we studied the reactivity of a cycloalkene that simultaneously possessed a fluorine atom and a methyl group at the double bond. For this purpose we used 1-fluoro-2-methyl-1-cyclopentene (**6**), which was prepared in about 20% yield under severe conditions by the vinylcyclopropane−cyclopentene isomerization[20−22] of the vinylcyclopropane **3** in a flow reactor at 600 °C.



Scheme 7

We found that the fluorocyclopentene **6** entered into a catalytic cyclopropanation reaction with methyl diazoacetate in the presence of rhodium and copper catalysts to form mixtures of isomeric methyl 1-fluoro-5-methylbicyclo[3.1.0]-hexane-6-carboxylates (**18**) in total yields of about 30 and 43%, respectively, with a 1:1.1 ratio between *anti* and *syn* isomers.

Fluorine-containing by-products were formed in both cases, particularly with the use of $[Rh_2(OAc)_4]$ as a catalyst. The products of :CHCOOMe insertion into the allyl C−H bonds of fluorocyclopentene **6** might be among these products. Indeed, insertion reactions into cycloalkene C−H bonds are most typical of the use of Rh compounds.[8,23]

The target cyclopropanes *anti*- and *syn*-**18** were separated by preparative TLC and characterized by ^1H and ^{19}F NMR spectroscopy. The spectra of *syn*-**18** exhibited the appearance of a spin−spin coupling constant $J_{H,F} = 19$ Hz, which is characteristic of *cis*-arranged H and F atoms in a cyclopropane ring; in *anti*-**18**, this spin−spin coupling constant was as low as 4 Hz.

Conclusion

Generally, the study of [1+2] cycloadditions between aliphatic diazo compounds and fluorinated unsaturated compounds has exhibited an inhibitory effect of fluorine atoms at a double bond on the catalytic reaction with a carbenoid, particularly, in the case of tetrasubstituted double bonds containing two vicinal fluorine atoms. In the great majority of cases $[Rh_2(OAc)_4]$ was the most effective catalyst for cyclopropanation of double bonds of fluorine-containing alkenes with diazoesters. Copper compounds are the catalysts of choice in cases of [1+2] cycloadditions between diazoacetates and monofluorinated sterically hindered double bonds, while palladium complexes are the effective catalysts for the cyclopropanation of fluorinated olefins with diazomethane. The successful cyclopropanation of a fluorine-substituted double bond with diazomethane in the presence of a palladium catalyst has been carried out for the first time.

Experimental Section

General Remarks: The ^1H and ^{13}C spectra, ^{13}C COSY/proton and NOESY decoupled experiments were recorded with Bruker AM 300 (^1H, 300.13 and ^{13}C, 75.5 MHz) and Bruker DRX 500 (^1H, 500.13 and ^{13}C, 125.8 MHz) instruments with solutions in $CDCl_3$ containing 0.05% Me_4Si as the internal standard. The ^{19}F NMR spectra were measured with a Bruker AC 200 machine (188.3 MHz); the chemical shifts are given relative to CCl_3F. Mass spectra were obtained on a Finnigan MAT INCOS-50 instrument or a MS-30 "Kratos" machine (EI, 70 eV, a 30 m RSL-200 or SE-54 capillary column or a direct inlet system). Elemental analyses were performed with a Perkin−Elmer (Series II) C,H,N-analyzer 2400. The preparative TLC was carried out on 20 × 20 cm plate with a nonfixed layer of neutral Al_2O_3 or silica gel (Merck kieselgel 60) plates (0.25 mm). Reactions were monitored by TLC on Merck kieselgel 60 F_{254} (0.25 mm) plates, which were viewed by UV inspection. The starting compound 2-chloro-1,1,2-trifluoro-3-vinylcyclobutane[24] was prepared by the described methods. The catalysts $[Cu(acac)_2]$, $[Pd(acac)_2]$, $[(PhCN)_2PdCl_2]$ and $[Rh_2(OAc)_4]$ were purchased from Merck.

3,3-Difluoro-2-methoxy-1-vinyl-1-cyclobutene (1): A solution of MeONa (6.49 g, 0.12 mol) in methanol (20 mL) was added over 10 min to 2-chloro-2,3,3-trifluoro-1-vinylcyclobutane (6.83 g, 0.04 mol), and the reaction mixture was heated at reflux for 5 h. The mixture was cooled, and the precipitate was filtered off. Diethyl ether (100 mL) was added to the filtrate, and the mixture was washed initially with aqueous HCl (3%, 100 mL) and then with a saturated NaCl solution (4 × 100 mL). After drying with anhydrous Na_2SO_4 and vacuum distillation, 4.39 g (75%) of 3,3-difluoro-2-methoxy-1-vinylcyclobutene (**1a**) was obtained, b.p. 48−49 °C (42 Torr). ^1H NMR (200 MHz, $CDCl_3$, 25 °C): $\delta = 2.66$ (t, $J =$

4 Hz, 2 H, H-4), 3.86 (s, 3 H, OMe), 5.19 (d, J_{trans} = 18.0 Hz, 1 H, =CH_2), 5.25 (d, J_{cis} = 10.0 Hz, 1 H, =CH_2), 6.62 (dd, J_{trans} = 18.0, J_{cis} = 10.0 Hz, 1 H, =CH), ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 37.2 (t, $J_{C,F} \approx$ 22.0 Hz, C-4), 57.7 (s, OMe), 117.4 (t, $^3J_{C,F}$ = 18.0 Hz, C-1), 118.1 (s, =CH), 118.5 (t, $^1J_{C,F}$ = 274.0 Hz, CF_2), 126.6 (s, =CH_2), 141.49 (t, $^2J_{C,F}$ = 23.0 Hz, C-2) ppm. ^{19}F NMR (188.3 MHz, $CDCl_3$, CCl_3F, 25 °C): δ = −107.7 (br. s, CF_2) ppm. EIMS (probe, 70 eV): *m*/*z* (%) = 146 (87) $[M]^+$, 131 (5) $[M - Me]^+$, 127 (10) $[M - F]^+$, 115 (40), 103 (50), 97 (20), 91 (5), 83 (58), 77 (38), 67 (45), 53 (77), 44 (25), 39 (100). $C_7H_8F_2O$ (146.1): calcd. C 57.53, H 5.52; found C 57.40, H 5.39.

2-Fluoro-3-methyl-1,3-butadiene (2): Precondensed isobutylene (60 mL, 35 g, 0.625 mol) and dichlorofluoromethane (70 mL) were added in sequence to a solution of benzyltriethylammonium chloride (1.5 g) in CH_2Cl_2 (100 mL), cooled to −40 °C. After addition of the reactants, the temperature of the mixture was increased to −10 °C, and a 50% KOH solution was added with intense stirring. The rate of addition (over 1.5−2 h) was controlled so that the reaction mixture was not heated above −6 °C and the condensation of evaporated reactants in the reflux condenser was not very intense. The reaction mixture was then additionally stirred for 30−50 min at −6 °C and gradually heated to 20 °C. The mixture was diluted with water, the organic layer was washed with water, and the aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL). The organic extracts were dried with anhydrous $CaCl_2$, and, after distillation, 1-chloro-1-fluoro-2,2-dimethylcyclopropane (63 g, b.p. 73−75 °C) was obtained. A 50% solution of the resulting compound in heptane with an inert carrier gas flow was then passed through a pyrolyzer at 450−455 °C for 7−8 h. The pyrolyzer was washed with 8 g of heptane; the resulting pyrolysis products were neutralized with a 5% NaOH solution, dried with $CaCl_2$ and distilled at atmospheric pressure, and 2-fluoro-3-methyl-1,3-butadiene (**2**, 41 g, 76%) with b.p. 46.5−46.8 °C was obtained. The spectroscopic characteristics of this product were consistent with published data.[25]

4-Chloro-4,5,5-trifluoro-1-cyclohexene (4): A mixture of chlorotrifluoroethylene (152 g, 1.3 mol) and 1,3-butadiene (71 g, 1.3 mol) was passed through a quartz tube (20 mm inner diameter; 60 cm long) at a temperature of 505 °C and at an average rate of 0.4 mol/h. The products at the reactor outlet were condensed in a water-cooled vessel, and low-boiling components were collected in a trap cooled to −78 °C. After the fractional distillation of liquid pyrolysis products, 4-chloro-4,5,5-trifluoro-1-cyclohexene[26] (**4**, 125.2 g, 56%) was obtained (b.p. 82−84 °C at 120 Torr). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 2.89 (m, 4 H, 3-H, 6-H), 5.65 (m, 2 H, 1-H, 2-H) ppm. ^{19}F NMR (188.3 MHz, $CDCl_3$, CCl_3F, 25 °C): δ = −122.2 (br. s, 1 F, CFCl), −111.2 and −113.0 (both br. d, 1 + 1 F, $^1J_{FF}$ = 245 Hz, CF_2) ppm. EIMS (probe, 70 eV): *m*/*z* (%) = 172 (5) and 170 (19) $[M]^+$, 151 (2), 149 (7), 134 (30), 113 (53), 106 (24), 95 (30), 90 (19), 84 (85), 77 (19), 69 (21), 64 (10), 59 (49), 49 (100).

1,2-Difluoro-1,4-cyclohexadiene (5): A mixture of zinc powder (35 g, 0.538 mol), dry DMF (150 mL), and concentrated hydrochloric acid (2 mL) was stirred for 10 min, and 4-chloro-4,5,5-trifluoro-1-cyclohexene (**4**, 30 g, 0.176 mol) was added. The mixture was heated at 95−100 °C for 10 h with stirring, after which it was cooled to 20 °C and filtered. The filtrate was diluted with water (500 mL) and extracted with diethyl ether (3 × 60 mL). The extract was washed with water (2 × 50 mL) and dried with $CaCl_2$. Fraction distillation afforded the product **5** (16.5 g, 81%) with b.p. 113−116 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 3.02 (m, 4 H, 3-H and 6-H), 5.09 (m, 2 H, 4-H and 5-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 27.60 (m, C-3 and C-6), 122.37 (m, C-4 and C-5), 249.89 (dd, $^1J_{C,F}$ = 249.9, $^2J_{C,F}$ = 10.52 Hz, C-1 and C-2) ppm. ^{19}F NMR (188.3 MHz, $CDCl_3$, CCl_3F, 25 °C): δ = −142.4 (br. s) ppm. EIMS (probe, 70 eV): *m*/*z* (%) = 116 (100) $[M]^+$, 97 (21) $[M - F]^+$, 39 (16). $C_6H_6F_2$ (116.1): calcd. C 62.07, H 5.21; found C 61.84, H 5.03.

1-Fluoro-2-methyl-1-cyclopentene (6): 1-(1-Fluorovinyl)-1-methylcyclopropane (**3**, 3.8 g, 0.038 mol) was passed through a quartz tube (0.6 cm inner diameter; 18 cm long) filled with quartz beads by 2:3 and flushed with an argon flow at 600 °C for 80 min. The reaction products were collected in a trap cooled to −60 °C. The pyrolysis products collected were condensed in vacuo and were then distilled at atmospheric pressure. 1-Fluoro-2-methyl-1-cyclopentene (**6**, 750 mg, 20%) was obtained as a colourless liquid, b.p. 72−74 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.59 (m, 3 H, Me), 1.85 (m, 2 H, 4-H); 2.20 (m, 2 H, 3-H), 2.4 (m, 2 H, 5-H) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 10.6 (s, Me), 18.7 (d, $^3J_{C,F}$ = 9.3 Hz, C-4), 29.2 (d, $^2J_{C,F}$ = 21.7 Hz, C-5), 32.1 (d, $^3J_{C,F}$ = 8.1 Hz, C-3), 128.7 (d, $^2J_{C,F}$ = 40.7 Hz, C-2), 155.3 (d, $^1J_{C,F}$ = 269.5 Hz, C-1) ppm. ^{19}F NMR (188.3 MHz, $CDCl_3$, CCl_3F): δ = −131.38 (br. s) ppm. EIMS (probe, 70 eV): *m*/*z* (%) = 99 (38) $[M - H]^+$, 84 (48) $[M - H - Me]^+$, 67 (20), 55 (32), 43 (100). C_6H_9F (100.1): calcd. C 71.97; H 9.06; found C 71.80, H 9.00.

1-Cyclopropyl-3,3-difluoro-2-methoxy-1-cyclobutene (7): A twofold to threefold excess of diazomethane was passed at 0−5 °C over 2 h through a solution of vinylcyclobutene **1a** (2.05 g, 0.014 mol) and $[(PhCN)_2PdCl_2]$ (0.053 g, 0.14 mmol) in CH_2Cl_2 (3 mL). Diazomethane was generated in a special reactor by the decomposition of *N*-methyl-*N*-nitrosourea (5.8 g, 0.057 mol) and purged with argon. After completion of the reaction, the mixture was filtered through a layer of Al_2O_3 (approx. 1 cm) and fractionated at atmospheric pressure in the presence of hydroquinone. 1-Cyclopropyl-3,3-difluoro-2-methoxycyclobutene (**7a**, 2.02 g, 90%) was obtained as a colourless liquid, b.p. 146−148 °C. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.60 and 0.75 ppm (both m, 2 H, 2′-H and 3′-H), 1.76 (m, 1 H, 1′-H), 2.32 (t, *J* = 2.6 Hz, 2 H, 4-H), 3.82 (s, 3 H, Me) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 4.6 (c, C-2′, C-3′), 7.7 (t, $J_{C,F}$ = 4.6 Hz, C-1′), 36.9 (t, $J_{C,F}$ = 22.0 Hz, C-4), 57.1 (s, Me), 118.4 (t, $^1J_{C,F}$ = 142.0 Hz, CF_2), 122.4 (t, $^3J_{C,F}$ = 18.0 Hz, C-1), 141.0 (t, $^2J_{C,F}$ = 22.0 Hz, C-2) ppm. ^{19}F NMR (188.3 MHz, $CDCl_3$, CCl_3F): δ = −107.6 (br. s, CF_2) ppm. EIMS (probe, 70 eV): *m*/*z* (%) = 160 (50) $[M]^+$, 145 (52) $[M - Me]^+$, 129 (30) $[M - OMe]^+$, 109 (27), 102 (15), 97 (63), 84 (100). $C_8H_{10}F_2O$ (160.2): calcd. C 59.99, H 6.29; found C 60.17, H 6.14.

Cyclopropanation of 2-Fluoro-3-methyl-1,3-butadiene (2) with Diazomethane: *N*-Methyl-*N*-nitrosourea (0.5 g) and $[Pd(acac)_2]$ (0.018 g, 0.059 mmol) were added with intense stirring to a cooled (−5 °C) mixture of the olefin **2** (2.5 g, 0.029 mol) in toluene (10 mL) and aqueous KOH (45%, 10 mL). Additional *N*-methyl-*N*-nitrosourea (5.4 g) was then added in portions over 15 min (the total amount was 0.058 mol). Upon completion of gas release, the organic layer was separated and analysed by GLC and ^{19}F NMR spectroscopy. Along with a small amount of the starting fluoroisoprene **2**, the reaction mixture contained 83% 1-(1-fluorovinyl)-1-methylcyclopropane (**3**), 5% 1-fluoro-1-isopropenylcyclopropane (**9**), and 11% 1-fluoro-1-(1-methylcyclopropyl)cyclopropane (**10**). The mixture was fractionated at atmospheric pressure. The following compounds were obtained: 1.45 g of fluorovinylcyclopropane **3** (b.p. 66.7−67.9 °C) and 0.85 g of fluorovinylcyclopropane **3** containing fluorocyclopropane **9** as an impurity (the total yield of fluorovinylcyclopropane **3** was 78%); 0.3 g of a mixture of **3**, **9**, and **10** in a ratio of 1.2:1: 1 (b.p. 68−105°C); and 0.1 g of the pure fluorobicyclopropane **10** (b.p. 105−106 °C).

1-(1-Fluorovinyl)-1-methylcyclopropane (3): ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.53 (ddd, *J* = 6.0, *J* = 3.5, *J* = 1.3 Hz, 2 H, 2-H^a and 3-H^a), 0.98 (dd, *J* = 6.0, *J* = 3.5 Hz, 2 H, 2-H^b and 3-H^b), 1.23 (s, 3 H, Me), 4.28 (dd, *J* = 50.1, *J* = 2.9 Hz, 1 H, =CH_2), 4.50 (dd, *J* = 16.6, *J* = 2.9 Hz, 1 H, =CH_2) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 12.9 (d, $^3J_{C,F}$ = 2.8 Hz, C-2 and C-3), 16.6 (d, $^2J_{C,F}$ = 27.6 Hz, C-1), 21.2 (d, $^3J_{C,F}$ = 4.13, Me), 87.0 (d, $^2J_{C,F}$ = 23.3 Hz, =CH_2), 169.4 (d, $^1J_{C,F}$ = 253 Hz, =CH) ppm. ^{19}F NMR (188.3 MHz, $CDCl_3$, CCl_3F, 25 °C): δ = −106.1 (br. dd, $J_{H,F}$ = 50.1, $J_{H,F}$ = 16.6 Hz) ppm. EIMS (probe, 70 eV): *m*/*z* (%) = 100 (23) $[M]^+$, 85 (53) $[M - Me]^+$, 77 (19), 72 (15), 67 (12), 65 (35), 59 (42), 57 (17), 53 (27), 51 (35), 44 (33), 39 (100).

1-Fluoro-1-isopropenylcyclopropane (9): ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.50 (m, 2 H, 2-H^a and 3-H^a), 1.12 and 1.22 (both m, 1 + 1 H, 2-H^b and 3-H^b), 1.72 (s, 3 H, Me), 4.95 (m, 1 H, =CH_2), 5.05 (m, 1 H, =CH_2) ppm. ^{19}F NMR (188.3 MHz, $CDCl_3$, CCl_3F, 25 °C): δ = −179.5 (br. s) ppm. EIMS (probe, 70 eV): *m*/*z* (%) = 100 (15) $[M]^+$, 85 (100), 65 (33), 39 (79). C_6H_9F (for mixture of isomers) (100.1): calcd. C 71.97, H 9.06; found C 71.81, H 8.95.

1-Fluoro-1-(1-methylcyclopropyl)cyclopropane (10): The cyclopropanation of vinylcyclopropane **3** (0.5 g, 0.005 mol) was carried out in the same way as used in the treatment of 2-fluoro-3-methyl-1,3-butadiene (**2**) with diazomethane, but with the use of a mixture of pentane and dichloromethane as solvent instead of toluene. The organic layer was separated and solvents were removed. Along with a small amount of the starting vinylcyclopropane **3**, the reaction mixture contained about 97% of compound **10** (by GLC). ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.52, 0.84 and 0.94 (all m, 6 + 1 + 1 H, H of cyclopropane rings), 1.23 (s, 3 H, Me) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 9.51 (d, $^2J_{C,F}$ = 13.5 Hz, C-2 and C-3), 11.66 (d, $^3J_{C,F}$ = 4.7 Hz, Me), 17.75 (d, $^2J_{C,F}$ = 27.3 Hz, C-1′), 20.89 (s, C-2′ and C-3′), 84.21 (d, $^1J_{C,F}$ = 212.0 Hz, C-1) ppm. ^{19}F NMR (188.3 MHz, $CDCl_3$, CCl_3F, 25 °C): δ = −178.5 (br. s) ppm. EIMS (probe, 70 eV): *m*/*z* (%) = 114 (7) $[M]^+$, 99 (82) $[M - Me]^+$, 86 (100), 67 (42), 39 (97). $C_7H_{11}F$ (114.1): calcd. C 73.65, H 9.71; found C 73.52, H 9.56.

3,4-Difluorobicyclo[4.1.0]hept-3-ene (16): $[Pd(acac)_2]$ (0.068 g, 0.22 mol) was added at 0°C with intense stirring to a solution of 1,2-difluorocyclohexa-1,4-diene (**5**, 2.94 g, 0.025 mol) and CH_2N_2 (approx. 0.25 mol) in diethyl ether. Upon completion of gas release, the mixture was condensed with care in vacuo and fractionated at atmospheric pressure. 3,4-Difluorobicyclo[4.1.0]hept-3-ene (**16**, 1.27 g) was obtained as a colourless liquid (b.p. 129−130°C), yield 39%. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 0.29 (dd, *J* = 11.0, *J* = 5.0 Hz, 1 H, 7-H$_a$), 0.69 (dt, *J* = 8.5, *J* = 5.0 Hz, 1 H, 7-H$_b$), 1.08 (m, 2 H, 4-H and 5-H), 2.55 (m, 2 H, 3-H$_b$ and 6-H$_b$), 2.70 (m, 1 H, 6-H$_a$), 2.78 (m, 1 H, 3-H$_a$) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 7.34 (s, C-5), 9.40 (m, C-3 and C-7), 24.75 (m, C-4 and C-6), 139.5 (dd, $^1J_{C,F}$ = 247.9, $^2J_{C,F}$ = 11.1 Hz, C-3 and C-4) ppm. ^{19}F NMR (188.3 MHz, $CDCl_3$, CCl_3F): δ = −141.9 (br. s) ppm. EIMS (probe, 70 eV): *m*/*z* (%) = 130 (83) $[M]^+$, 115 (100), 109 (63), 79 (12), 63 (10), 39 (33). $C_7H_8F_2$ (130.1): calcd. C 64.61, H 6.20; found C 64.51, H 6.06.

Cyclopropanation of 2-Fluoro-3-methyl-1,3-butadiene (2) with Methyl Diazoacetate (General Procedure): A solution of methyl diazoacetate (1.0 g, 0.01 mol) in CH_2Cl_2 (5 mL) was added at 20 °C over 5 h to a stirring mixture of diene **2** (2.6 g, 0.03 mol) and 0.1 mmol of a catalyst {$[Rh_2(OAc)_4$, $[Cu(acac)_2]$, or $[(PhCN)_2PdCl_2]$} in CH_2Cl_2 (8 mL). When the reaction was complete, the solvent and an excess of the starting olefin **2** were removed in vacuo, and the residue was dissolved in diethyl ether. The resulting solution was passed through a silica gel layer (1 cm). The solvent was then evaporated, and the reaction mixture was analysed by ^{1}H and ^{19}F NMR spectroscopy (Table 1). The reaction mixture obtained with the use of $[Rh_2(OAc)_4]$ as a catalyst was separated by column chromatography on silica gel (column, 3.5 × 18 cm; eluent: ethanol/hexane; gradient of ethanol concentration, from 0 to 5%; total eluent volume, 0.6 L). Three fractions enriched in isomers *cis*-**12** and *trans*-**12**, *trans*-**12** and *trans*-**11**, and *trans*-**11** and *cis*-**11** were obtained (oily colourless liquid); the total yield of cyclopropanes **11** and **12** was 1.33 g (84%) (Table 2). $C_8H_{11}FO_2$ (158.2): calcd. C 60.75, H 7.01; found C 60.61, H 6.87.

Isomer *cis*-12: EIMS (probe, 70 eV): *m*/*z* (%) = 158 (5) $[M]^+$, 143 (18) $[M - Me]^+$, 127 (20) $[M - OMe]^+$, 103 (100), 99 (90), 83 (10), 79 (65), 69 (15), 59 (90), 53 (36), 47 (13), 39 (57).

Isomer *trans*-12: EIMS (probe, 70 eV): *m*/*z* (%) = 158 (5) $[M]^+$, 143 (13) $[M - Me]^+$, 127 (27) $[M - OMe]^+$, 116 (15), 103 (27), 98 (90), 83 (10), 79 (60), 71 (10), 63 (06), 59 (100).

Isomer *trans*-11: EIMS (probe, 70 eV): *m*/*z* (%) = 158 (3) $[M]^+$, 143 (15) $[M - Me]^+$, 138 (2) $[M - HF]^+$, 127 (27) $[M - OMe]^+$, 116 (17), 103 (28), 98 (92), 83 (11), 79 (60), 67 (10), 59 (100).

Isomer *cis*-11: EIMS (probe, 70 eV): *m*/*z* (%) = 158 (3) $[M]^+$, 143 (18) $[M - Me]^+$, 127 (26) $[M - OMe]^+$, 103 (100), 99 (90), 83 (10), 79 (62), 69 (17), 59 (92).

Cyclopropanation of 1-(1-Fluorovinyl)-1-methylcyclopropane (3) with Methyl Diazoacetate: The cyclopropanation of 1-(1-fluorovinyl)-1-methylcyclopropane (**3**) was carried out by the same way as used for the treatment of 2-fluoro-3-methyl-1,3-butadiene (**2**) with methyl diazoacetate. The reaction mixtures were analysed by ^{1}H and ^{19}F NMR spectroscopy (Table 1). In the case in which $[Rh_2(OAc)_4]$ was used as catalyst the isomers were separated by TLC on silica gel (eluent: hexane/diethyl ether, 5:1; R_f = 0.6 for *trans* isomer **13** and R_f = 0.5 for *cis* **13** and characterized by ^{1}H and ^{19}F NMR spectra (Table 2) as enriched fractions up to 90−93% (oily colourless liquid).

Isomer *cis*-13: EIMS (probe, 70 eV): *m*/*z* (%) = 171 (1) $[M - H]^+$, 152 (6) $[M - HF]^+$, 124 (10), 117 (33), 93 (50), 85 (70), 77 (44), 73 (22), 65 (21), 59 (21), 55 (100).

Isomer *trans*-13: EIMS (probe; 70 eV): *m*/*z* (%) = 171 (1) $[M - H]^+$, 152 (4) $[M - HF]^+$, 117 (32), 97 (49), 93 (45), 85 (71), 81 (13), 77 (40), 73 (23), 65 (24), 59 (62), 55 (100). $C_9H_{13}FO_2$ (for mixture of isomers) (172.2): calcd. C 62.78, H 7.61; found C 62.59, H 7.48.

Methyl 2-(3,3-Difluoro-2-methoxy-1-cyclobutenyl)cyclopropanecarboxylate (8): The cyclopropanation of vinylcyclobutene **1a** was carried out by the same way as used for the treatment of 2-fluoro-3-methyl-1,3-butadiene (**2**) with methyl diazoacetate. The reaction in the presence of $[Rh_2(OAc)_4]$ produced methyl 2-(3,3-difluoro-2-methoxy-1-cyclobutenyl)cyclopropanecarboxylate (**8**) in a total yield of about 60%, as a mixture of *trans* and *cis* isomers in a ratio of 1.2:1. The mixture was distilled in vacuo (bath temperature of 100 °C, 0.5 Torr). The isomers were separated by TLC on silica gel (eluent: hexane/diethyl ether, 5:1; R_f = 0.4 and 0.3 for *trans*-**8** and *cis*-**8**, respectively) and characterized as enriched fractions up to 90−93% (oily colourless liquid). The interaction between alkene **1a** and methyl diazoacetate in the presence of $[Cu(acac)_2]$ or $[(PhCN)_2PdCl_2]$ occurred only in low yields.

Isomer *trans*-8: ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.15 (ddd, J_{gem} = 4.4, J_{trans} = 6.1, J_{cis} = 8.3 Hz, 1 H, 3-H$_a$), 1.45 (dt, J_{trans} =

5.4, J_{cis} = 8.3 Hz, 1 H, 1-H), 1.87 (ddd, J_{cis} = 8.3, J_{trans} = 5.4, J_{gem} = 4.4 Hz, 1 H, 3-H_b), 2.21 (m, 1 H, 2-H), 2.4 (m, 2 H, 4′-H), 3.71 (s, 3 H, COOMe), 3.84 (s, 3 H, OMe) ppm. ^{19}F NMR (188.3 MHz, $CDCl_3$, CCl_3F): δ = −108.7 (br. s, CF_2) ppm.

Isomer *cis*-8: ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.25 (dt, J_{cis} = 8.2, J_{gem} = 4.9 Hz, 1 H, 3-H_a), 1.40 (dt, J_{cis} = 8.3, J_{trans} = 6.4 Hz, 1 H, 1-H), 1.45 (dt, J_{trans} = 6.4, J_{gem} = 4.9 Hz, 1 H, 3-H_b), 1.96 (m, 1 H, 2-H), 2.26 (br. dt, J_{gem} = 10, J = 3 Hz, 1 H, 4′-H_a), 2.5 (ddd, J_{gem} = 10, J = 4.0, J = 2.0 Hz, 1 H, 4′-H_b), 3.62 (s, 3 H, COOMe), 3.68 (s, 3 H, OMe) ppm. ^{19}F NMR (188.3 MHz, $CDCl_3$, CCl_3F, 25 °C): δ = −107.8 and −110.4 (both br. d, $^2J_{FF} \approx$ 200 Hz, CF_2) ppm.

Mixture of Isomers: EIMS (probe, 70 eV): *m*/*z* (%): 218 (60) $[M]^+$, 203 (10) $[M - Me]^+$, 183 (30) $[M - Me - HF]^+$, 171 (20), 159 (100), 139 (30), 127 (50), 115 (35), 109 (40), 97 (30), 81 (40), 59 (40), 52 (40), 45 (30), 39 (60). $C_{10}H_{12}F_2O_3$ (218.2): calcd. C 55.05, H 5.54; found C 55.18, H 5.67.

Methyl 3-Chloro-3,4,4-trifluorobicyclo[4.1.0]heptane-7-carboxylate (14): The cyclopropanation of 4-chloro-4,5,5-trifluoro-1-cyclohexene (**4**) was carried out in the same way as used for treatment of 2-fluoro-3-methyl-1,3-butadiene (**2**) with methyl diazoacetate. In the presence of $[Rh_2(OAc)_4]$ as the catalyst, methyl 3-chloro-3,4,4-trifluorobicyclo[4.1.0]heptane-7-carboxylate (**14**) was obtained in 50% total yield as a difficult to separate mixture of two diastereomers in an approximately equal ratio (colourless oily liquid, b.p. 89−90 °C, 1 Torr). The olefin **4** was hardly cyclopropanated with methyl diazoacetate in the presence of $[Cu(acac)_2]$ or $[(PhCN)_2PdCl_2]$.

Mixture of Isomers (14): ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.77 (m, 3 H, 1-H, 6-H, 7-H), 2.32−3.08 (m, 4 H, 2-H, 5-H), 3.69 (s, 3 H, OMe) ppm. EIMS (probe; 70 eV): *m*/*z* (%) = 244 (2) and 242 (6) $[M]^+$, 207 (22) $[M - Cl]^+$, 175 (4), 127 (20), 111 (15), 84 (100). $C_9H_{10}ClF_3O_2$ (242.6): calcd. C 44.55, H 4.15; found C 44.42, H 4.26.

Isomer 14a: ^{19}F NMR (188.3 MHz, $CDCl_3$, CCl_3F): δ = −111.1 (br. s, CF_2), −120.9 (br. s, CFCl) ppm.

Isomer 14b: ^{19}F NMR (188.3 MHz, $CDCl_3$, CCl_3F, 25 °C): δ = −104.6 and −109.3 (both br. d, $^2J_{FF}$ = 255 Hz, CF_2), −122.31 (br. s, CFCl) ppm.

Methyl 3,4,4-Trifluorobicyclo[4.1.0]hept-2-ene-7-carboxylate (15): Potassium *tert*-butoxide (0.93 g, 0.0083 mol) was added under argon at −20°C to a solution of methyl 3-chloro-3,4,4-trifluorobicyclo[4.1.0]heptane-7-carboxylate (**14**, 0.67 g, 0.0028 mol) in THF (15 mL). The mixture was stirred under argon at this temperature for 8 h, and was then neutralized with a solution of HCl in THF. The suspension obtained was passed through a silica gel layer (1 cm) and distilled in vacuo (b.p. 85−86° °C, 1 Torr). Methyl 3,4,4-trifluorobicyclo[4.1.0]hept-2-ene-7-carboxylate (**15**) was obtained as a colourless, oily liquid; yield 300 mg, 52%. ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.65 (ddd, J_{trans} = 5.0, 3.5, 2.0 Hz, 1 H, 7-H), 2.00 (m, 1 H, 6-H), 2.08 (m, 1 H, 1-H), 2.52 (dddd, J = 26.5, J = 15.5, J = 12.8, J = 5.0 Hz, 1 H, 5-H_b), 2.78 (m, 1 H, 5-H_a), 6.0 (dddd, J = 12.5, J = 5.5, J = 3.5, J = 0.8 Hz, 1 H, 2-H), ppm. ^{19}F NMR (188.3 MHz, $CDCl_3$, CCl_3F): δ = −136.4 (m, CF), −104.05 (br. t, $^1J_{FF}$ 274, J_{FH} = 12.8 Hz, CF_2), −83.10 (br. dd, $^1J_{FF}$ 274, $^2J_{FF}$ = 47.0, J_{FH} = 22.0 Hz, CF_2,), ppm. EIMS (probe, 70 eV): *m*/*z* (%) = 206 (5) $[M]^+$, 186 (3) $[M - HF]^+$, 175 (22), 172 (18), 163 (50), 154 (11), 153 (31), 148 (30), 145 (15), 142 (13), 128 (20), 127 (100). $C_9H_9F_3O_2$ (206.2): calcd. C 52.43, H 4.40; found C 52.59, H 4.49.

Methyl 3,4-Difluorobicyclo[4.1.0]hept-3-ene-7-carboxylate (17): The cyclopropanation of 1,2-difluoro-1,3-cyclohexadiene (**5**) was carried out by the same way as used for treatment of 2-fluoro-3-methyl-1,3-butadiene (**2**) with methyl diazoacetate. In the presence of $[Rh_2(OAc)_4]$ methyl 3,4-difluorobicyclo[4.1.0]hept-3-ene-7-carboxylate (**17**) was obtained in 72% total yield as a mixture of *anti* and *syn* isomers in a ratio of approx. 2:1. In the presence of Cu catalyst the compound **17** was obtained in 68% total yield (ratio of *anti* and *syn* 2.1:1). The isomers obtained were separated by TLC on silica gel (eluent: hexane/diethyl ether, 3:1; R_f = 0.5 and 0.4 for *anti*-**17** and *syn*-**17**, respectively) and characterized as enriched fractions up to 90−93% (colourless oily liquid, b.p. 75−76 °C, 1 Torr). The interaction between the alkene **5** and methyl diazoacetate in the presence of $[(PhCN)_2PdCl_2]$ occurred only in very low yield (< 5%).

Isomer *anti*-17: ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.67 (br. t, J_{trans} = 3.0 Hz, 1 H, 7-H), 1.75 (m, 2 H, 1-H, 6-H), 2.58−2.78 (m, 4 H, 2-H, 5-H), 3.70 (s, 3 H, Me) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 20.9 (m, C-1 and C-6), 23.0 (br. s, C-7), 24.5 (m, C-2 and C-5), 52.0 (s, Me), 139.2 (dd, $^1J_{C,F}$ = 249, $^2J_{C,F}$ = 11.5 Hz, C-3 and C-4), 173.94 (s, CO) ppm. ^{19}F NMR (188.3 MHz, $CDCl_3$, CCl_3F, 25 °C): δ = −141.2 (br. s, =CF) ppm. EIMS (probe, 70 eV): *m*/*z* (%) = 188 (11) $[M]^+$, 168 (22) $[M - HF]^+$, 157 (13), 127 (32), 109 (38), 98 (100), 83 (30), 77 (18), 59 (29), 51 (20), 43 (11), 39 (27).

Isomer *syn*-17: ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.55 (m, 2 H 1-H, 6-H), 1.75 (m, 1 H, 7-H), 2.58−2.78 (m, 4 H, 2-H, 5-H), 3.68 (s, 3 H, Me) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$, 25 °C): δ = 14.9 (m, C-1 and C-6), 22.0 (br. s, C-7), 23.0 (m, C-2 and C-5), 51.6 (s, Me), 140.1 (dd, $^1J_{C,F}$ = 247, $^2J_{C,F}$ = 11.8 Hz, C-3 and C-4), 169.9 (s, CO) ppm. ^{19}F NMR (188.3 MHz, $CDCl_3$, CCl_3F): δ = −141.3 (br. s, =CF) ppm. EIMS (probe, 70 eV): *m*/*z* (%) = 188 (10) $[M]^+$, 168 (21) $[M - HF]^+$, 157 (21), 136 (23), 127 (83), 114 (16), 109 (100), 97 (20), 77 (31), 63 (13), 59 (40), 51 (38), 43 (17), 39 (45). $C_9H_{10}F_2O_2$ (for mixture of isomers) (188.2): calcd. C 57.45, H 5.36; found C 57.31, H 5.18.

Methyl 1-Fluoro-5-methylbicyclo[3.1.0]hexane-6-carboxylate (18): The cyclopropanation of 1-fluoro-2-methyl-1-cyclopentene (**6**) was carried out by the same way as used for treatment of 2-fluoro-3-methyl-1,3-butadiene (**2**) with methyl diazoacetate. In the presence of $[Rh_2(OAc)_4]$ or $[Cu(acac)_2]$, methyl 1-fluoro-5-methylbicyclo-[3.1.0]hexane-6-carboxylate (**18**) was obtained in 33 or 44% total yields as mixtures of two isomers (ratio of *anti* and *syn* 1.4 : 1 and 2.1 : 1). The isomers obtained were separated by TLC on silica gel (eluent: heptane/diethyl ether, 3:1; R_f = 0.64 and 0.53 for *anti*-**18** and *syn*-**18**, respectively) and characterized as enriched fractions up to 92−95% (colourless oily liquid, b.p. 95−100 °C, 45 Torr). The interaction of the alkene **6** with methyl diazoacetate in the presence of $[(PhCN)_2PdCl_2]$ occurred with a very low yield (< 5%).

Isomer *anti*-18: ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.12 (br. d, $J_{H,F}$ = 18.7 Hz, 1 H, H-6), 1.43 (s, 3 H, Me), 1.73 (m, 4 H, 3-H and 4-H), 2.22 (m, 2 H, 2-H), 3.70 (s, 3 H, OMe) ppm. ^{19}F NMR (188.3 MHz, $CDCl_3$, CCl_3F, 25 °C): δ = −188.29 (br. t, $J_{H,F}$ = 14.7 Hz) ppm. EIMS (probe, 70 eV): *m*/*z* (%) = 173 (75) $[M + H]^+$, 141 (25) $[M - OMe]^+$, 113 (100), 93 (43), 77 (20), 40 (30).

Isomer *syn*-18: ^{1}H NMR (200 MHz, $CDCl_3$, 25 °C): δ = 1.23 (d, $J_{H,F}$ = 4.0 Hz, 1 H, 6-H), 1.31 (s, 3 H, Me), 1.80 (m, 4 H, 3-H and 4-H), 2.32 (m, 2 H, 2-H), 3.69 (s, 3 H, OMe) ppm. ^{19}F NMR (188.3 MHz, $CDCl_3$, CCl_3F): δ = −206.2 (br. s) ppm. EIMS (probe, 70 eV): *m*/*z* (%) = 173 (25) $[M + H]^+$, 141 (22) [M −

OMe]$^+$, 113 (100), 93 (70), 59 (22), 40 (28). $C_9H_{13}FO_2$ (for mixture of isomers) (172.2): calcd. C 62.78, H 7.61; found C 62.91, H 7.64.

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