Highly Functionalized Vinylcyclopropane Derivatives by Regioselective and Stereoselective Reactions of Fischer Carbene Complexes with 1,4-Disubstituted Electron-Deficient 1,3-Dienes☆

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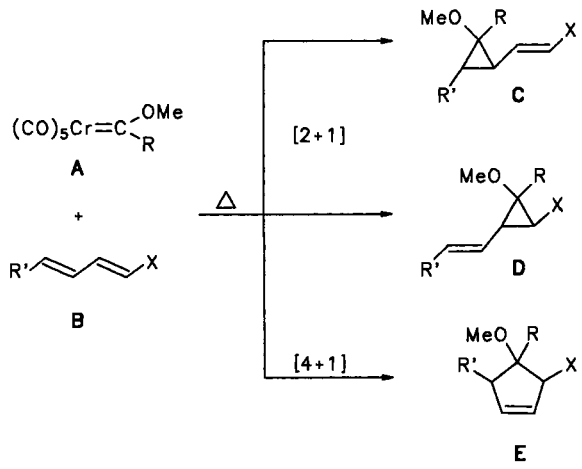
The thermal reaction of Fischer carbene complex **1** with electron-deficient 1,3-dienes such as methyl (*E,E*)-2,4-hexadienoate (**2**) provided functionalized vinylcyclopropanes like **3** in good yields. Similar results were obtained by employing related unsaturated esters **4**, **17**, and **21** or nitrile **6**. The periselectivity as well as regioselectivity of these carbene-transfer reactions are generally very high, and the diastereomer with the methoxy group *cis*-positioned with respect to the olefinic moiety is largely favoured (>85:15). A mechanistic rationale of these observations is given. Double adducts were only formed as minor sideproducts in these reactions, but by employing amide **13** as electron-deficient diene they were very easily formed with **1**. The [2 + 1] cycloaddition could also be extended to methylcarbene complex **24** and diene **2**, but the corresponding vinylcyclopropane **25a** was so far only obtained in low yield.

Fischer carbene complexes have recently found a number of interesting applications in selective organic synthesis[2]. Thus, the formal [2 + 1] cycloadditions with electron-rich[3] and electron-deficient alkenes[4] afford functionalized cyclopropane derivatives. We have studied scope and limitations of reactions of complexes **A** with acceptor olefins and found that many donor-acceptor-substituted cyclopropanes[5] can be synthesized, although the diastereoselectivities are generally modest[6]. In this paper we describe our results by employing electron-deficient 1,3-dienes **B**. When we started this programme no reactions of Fischer carbene complexes **A** with 1,3-dienes were known. Coincidently with our preliminary communication[7] Wulff et al.[8] reported on the reaction of an alkenyl-substituted chromium carbene complex with the electron-rich Danishefsky diene. More recently, the groups of Herndon[9] and Harvey[10] described the [2 + 1] cycloadditions of various Fischer carbene complexes to alkyl- and phenyl-substituted dienes which provide vinylcyclopropane derivatives with good selectivities. The reactions of highly electrophilic benzylidene metal complexes with dienes such as cyclopentadiene were also studied[11]. Photochemically induced [2 + 2] cycloaddition reactions of chromium carbene complexes with olefins – including a few 1,3-dienes – leading to cyclobutanones were reported by Hegedus[12] and Mattay[13].

The reaction of complex **A** with dienes **B** as employed in this project may a priori lead by [2 + 1] cycloadditions to vinylcyclopropanes **C** and **D**, whereas a formal [4 + 1] cycloaddition would provide cyclopentene derivative **E**. In addition, diastereomers can be formed along these routes. Therefore, a first systematic study addresses to the questions of regio-, peri-, and diastereoselectivity. It has also to be investigated which substituents R′ and X (acceptor) are appropriate for this reaction.



We concentrated on electron-deficient 1,4-disubstituted 1,3-dienes, since monosubstituted dienes such as methyl 2,4-pentadienoate were unsuitable substrates – probably due to their high tendency to polymerize[1]. The reactions of carbene complexes with higher substituted 1,3-dienes will be described in due course[14].

Results

The thermal reaction of standard carbene complex **1** with methyl (*E,E*)-2,4-hexadienoate (**2**) in cyclohexane proceeded rather slowly but cleanly afforded vinylcyclopropane derivatives **3a/b** in good yield and with surprisingly high dia-

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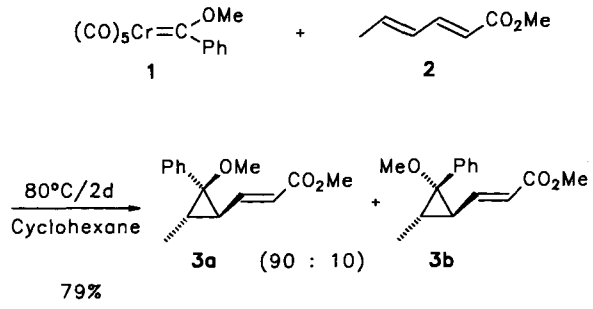
stereoselectivity. Major isomer **3a** was obtained in pure form after one recrystallization from pentane.

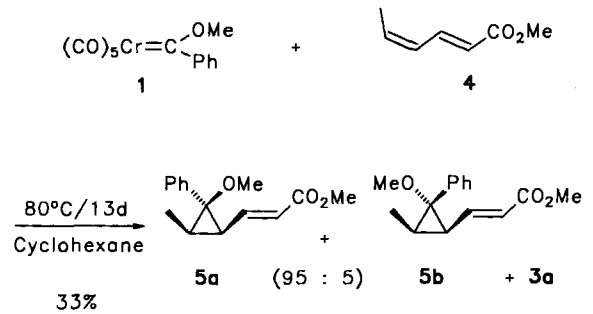


(in MeCN, 80°C, 16h: **3a**:**3b** = 70 : 30, 91% yield)

Regioisomeric cyclopropanes (type **D**), cyclopentene derivatives (**E**), acyclic isomers[6], or double adducts (see below) could not be detected in the crude product. The transformation rate **2** → **3** can be compared with that of the addition of **1** to methyl crotonate which requires similar conditions (80°C, 40 h)[4,15]. These rather slow reactions of chromium carbene complexes were best performed under argon, otherwise the formation of methyl benzoate by oxidation of **1** by traces of oxygen cannot be avoided. We recently found that the reaction of **1** with **2** can be dramatically enhanced when more polar solvents such as acetonitrile, tetrahydrofuran, or acetone are used. The yield was even slightly higher in acetonitrile, but the diastereoselectivity was inferior to that obtained with cyclohexane as solvent[16].

The conversion **2** → **3** is stereospecific with respect to the C–C double bond attacked. It was therefore of interest to combine **1** with the stereoisomeric (*E*,*Z*)-diene **4**. This reaction took considerably longer under standard conditions and furnished a mixture of three isomeric vinylcyclopropanes in low yield.

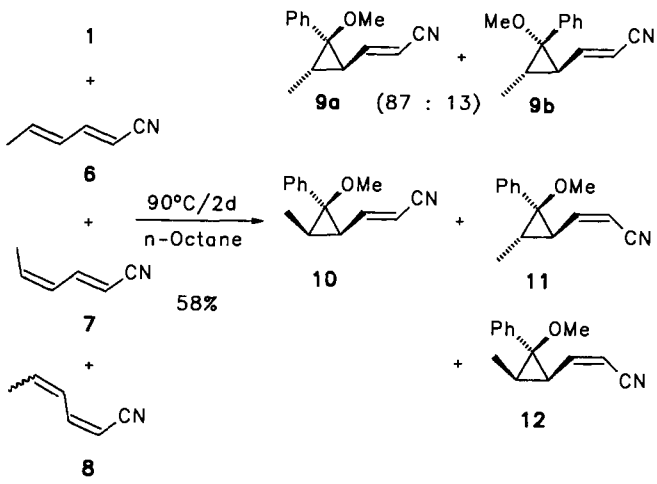
The expected products **5a/b** were the major components, however, diastereomer **3a** was also found with a proportion of 24%, which can be explained by a nonstereospecific [2 + 1] cycloaddition involving an intermediate able to stereoisomerize[16]. However, a further experiment (4 d, 100°C, *n*-octane)[1] with **1** and **4** demonstrated that under the reaction conditions diene **4** isomerizes to the more stable (*E*/*E*)-diene **2** which was isolated together with unconsumed **4** (8% of **2** and 17% of **4** reisolated). Therefore, the "wrong" diastereomer **3a** may stem from the reaction of **1** with **2**,



5a : **5b** : **3a** = 72 : 4 : 24

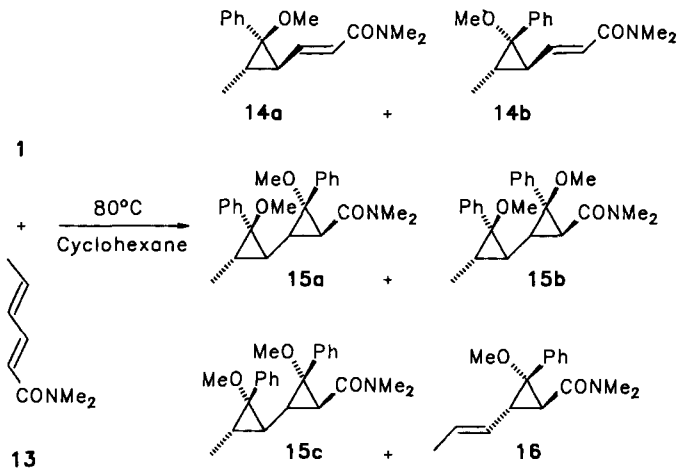
and the [2 + 1] cycloaddition of the complex to **4** may also be stereospecific.

The interpretation of the reaction of **1** with (*E*,*E*)-2,4-hexadienenitrile (**6**) was complicated by the presence of small amounts of stereoisomers **7** and **8**. This resulted in a mixture of five isomeric vinylcyclopropane derivatives **9**–**12** as illustrated. Again, the diastereoselectivity with respect to the formation of major components **9a/b** is very good.



6 : **7** : **8** = 88 : 6 : 6 **9a** : **9b** : **10** : **11** : **12** = 69 : 10 : 9 : 7 : 5

When (*E*,*E*)-*N*,*N*-dimethylhexadienamide (**13**) is employed the outcome of the reaction with carbene complex **1** is highly dependent on the ratio of starting materials. The use of an excess of diene **13** (10 equiv.) led to the expected vinylcyclopropanes **14a/b** as major products – again formed with good diastereoselectivity –, but even under these conditions we found 10% of double adduct **15a**. In addition, 2% of regioisomeric monoadduct **16** could be identified. When complex **1** was used in excess, the formation of the bicyclopropyl derivatives **15** occurred almost exclusively. A 95:5

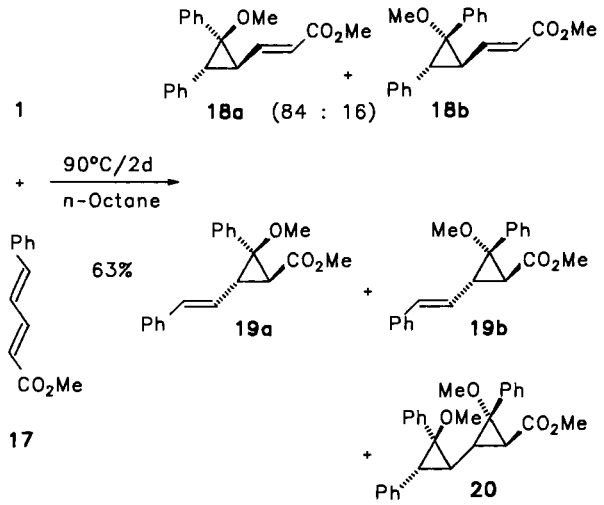


Ratio 1:13	Time	Yield	14a : 14b : 16 : 15a : 15b : 15c
1:10	2h	89%	81 : 7 : 2 : 10 : - : -
2.2:1	19h	78%	- : - : 5 : 71 : 15 : 9
Stereoselectivity			92 : 8 | 83 : 17

mixture of **15**:**16** was obtained by employing 2.2 equiv. of **1**; vinylcyclopropanes **14** were not detected.

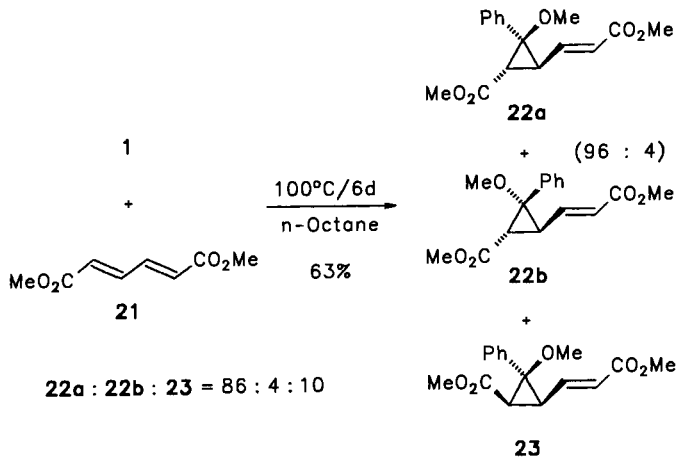
Another striking feature of these reactions is their high rate compared to similarly substituted 1,3-dienes. The product ratios as obtained prove that double-adduct formation is even faster than the generation of the preceding vinylcyclopropanes **14**. The notion that **15** is formed via **14** and probably not via regioisomer **16** can be deduced from the rather constant low proportion of **16**, independent of the starting-material ratio. In addition, the double bond in **16** should not be activated with respect to a carbene complex attack since acceptor or donor substituents are absent. We are not able to present a conclusive explanation for the exceptional behaviour of amide **13**. The related reaction of **1** with acrylic acid dimethylamide proceeds uneventfully[6] and without a perceivably higher rate compared to other simple olefins[15].

The regioselectivity of the [2 + 1] cycloaddition of **1** to methyl (*E,E*)-5-phenyl-2,4-pentadienoate (**17**) is high but not complete. Thus, a mixture of five compounds was obtained containing the expected vinylcyclopropanes **18a/b** as major compounds. Minor products were regioisomers **19a/b** and double adduct **20**. The 5-phenyl group lowers the regioselectivity compared to a methyl substituent in this position (see **2** → **3**).



18a : **18b** : (**19a** + **19b**) : **20** ≈ 80 : 15 : 3 : 2

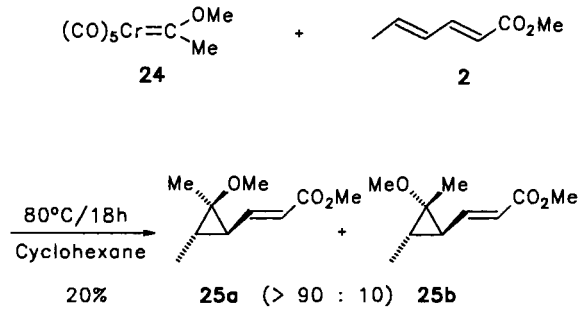
The very slow thermal reaction of dimethyl (*E,E*)-2,4-hexadien-1,6-dioate (**21**) with carbene complex **1** gave the two vinylcyclopropanes **22a/b** with excellent diastereoselectivity. Surprisingly, ca. 10% of the product mixture consisted of stereoisomer **23**. Since starting material **21** was isomerically pure and generation of the corresponding thermodynamically less stable (*Z,E*)-diene under the reaction conditions employed is rather unlikely[17], we have to assume an isomerization **22** → **23**. The reaction conditions make this process rather likely because similar *trans/cis* isomerizations and ring enlargements to give cyclopentene derivatives were found in other examples[1,18].



(in THF, 64°C, 45h: **22a** : **22b** = 80 : 20, 86% yield)

When the reaction of **1** with **21** was executed in tetrahydrofuran as solvent it proceeded dramatically faster and with higher yield, but with lower diastereoselectivity. However, the "wrong" stereoisomer **23** was not formed under these milder reaction conditions.

The cyclopropanations of simple 1,3-dienes with Fischer carbene complexes are not limited to aryl-substituted compounds such as **1**[9,10]. The reaction of methylcarbene complex **24** with electron-deficient diene **2** also furnished a vinylcyclopropane derivative **25a**, but after chromatographic purifications this compound was obtained in only 20% yield.



Stereoisomer **25b** was detected in other chromatography fractions, but it could not be obtained in pure form. Nevertheless, the diastereoselectivity of the [2 + 1] cycloaddition can be estimated to exceed 90:10. The formation of **25** from **24** and **2** is accompanied by the generation of unknown byproducts with considerably higher molecular weight. Further experiments (in polar solvents) are required to improve the mass balance of this reaction and to answer the question of regioselectivity more definitely.

Discussion

The results described here demonstrate that Fischer carbene complexes **A** react with electron-deficient 1,3-dienes **B** with excellent periselectivity and regioselectivity to afford vinylcyclopropanes of type **C**. There is no evidence for the formation of [4 + 1] cycloadducts **E**, and regioisomers **D**

Table 1. Preparation of vinylcyclopropanes from carbene complexes **1** and **24** and 1,3-dienes (according to the general procedure; purification method A: Kugelrohr distillation; B: column chromatography on silica gel)

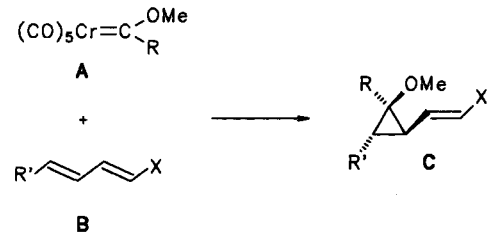
Complex g (mmol)	1,3-Diene g (mmol)	Solvent (ml)	Temp. °C	Time	Product	Purification Method	Yield g
6.25 **1** (20.0)	3.78 **2** (30.0)	Cyclohexane (50)	80	2 d	**3a/3b** (90 : 10)	A[a]	79 % 3.89
0.312 **1** (1.00)	0.189 **2** (1.50)	Acetonitrile (2.5)	80	16 h	**3a/3b** (70 : 30)	A	91 % 0.224
0.850 **1** (2.70)	0.380 **4** (3.00)	Cyclohexane (10)	80	13 d	**5a/5b/3a** (72 : 4: 24)	A[b]	33 % 0.220
2.50 **1** (8.00)	1.12 **6,7,8** (12.0)	n-Octane (20)	90	2 d	**9a/9b/10/11/12** (69 : 10 : 9 : 7 : 5)	B[c]	58 % 0.981
0.620 **1** (2.00)	2.78 **13** (20.0)	Cyclohexane (10)	80	2 h	**14a/14b/16/15a** (81 : 7 : 2 : 10)	B[d]	89 % 0.445
1.02 **1** (3.30)	0.208 **13** (1.50)	Cyclohexane (7)	80	19 h	**16/15a/15b/15c** (5 : 71 : 15 : 9)	B[e]	78 % 0.434
2.81 **1** (9.00)	3.38 **17** (18.0)	n-Octane (15)	90	2 d	**18a/18b/19a/b/20** (80 : 15 : 3 : 2)	B[f]	63 % 1.73
1.25 **1** (4.00)	2.74 **21** (16.0)	n-Octane (20)	100	6 d	**22a/22b/23** (86 : 4 : 10)	B[g]	63 % 0.730
0.312 **1** (1.00)	0.342 **21** (2.00)	Tetrahydrofuran (5)	64	45 h	**22a/22b** (80 : 20)	B[h]	86 % 0.250
1.00 **24** (4.00)	5.05 **2** (40.0)	Cyclohexane (15)	80	18 h	**25a**	A[i]/B[j]	20 % 0.148

[a] Two distillations; partially crystalline product; recrystallization from pentane afforded pure **3a** (2.49 g, 51 %). - [b] Further purification by radial chromatography (chromatotron, silica gel plate, pentane/ether, 15 : 1). - [c] (Hexane/EtOAc, 15 : 1), three fractions obtained. - [d] (Hexane/EtOAc, 1 : 15), four fractions obtained, 71 % of pure **14a**. - [e] (Hexane/EtOAc, 1 : 5), five fractions obtained. - [f] (Hexane/EtOAc, 6 : 1), three fractions obtained; recrystallization from hexane afforded pure **18a**. - [g] (Hexane/EtOAc, 4 : 1), two fractions obtained, 55 % of pure **22a**. - [h] (Hexane/EtOAc, 4 : 1), three fractions obtained, 67 % of pure **22a**. - [i] 30°C/0.05 Torr. - [j] (Hexane/EtOAc, 10 : 1), three fractions obtained, 20 % of pure **25a**; **25b** was detected in the other fractions.

Table 2. IR data and melting points (boiling points) of vinylcyclopropanes **3a/b**, **5a**, **9**, **14a**, **15a**, **18a**, **22a**, and **25a**.

Compound	Solvent	IR (ν, cm^{-1}) CH	CO	C=C	other	m.p. (b.p.)
3a/3b	$CHCl_3$	3100-3000, 2960, 2840	1705	1640	-	43.5 - 44.5°C (**3a**, from pentane) (b.p. 140°C/0.02 Torr)
5a	film	3100-3000, 2950, 2850	1715	1635	-	(b.p. 120°C/0.1 Torr)
9	film	3060-3020, 2960-2940, 2830	-	1640	2220 (C≡N)	-
14a	film	3080-3000, 2990-2860, 2820	1650	1610	-	91 - 92°C (from hexane)
15a	film	3080-3010, 3000-2940, 2830	1650	-	-	121 - 123°C (from hexane)
18a	$CHCl_3$	3100-3000, 2960, 2840	1705	1640	-	98 - 99 °C (from hexane)
22a	$CHCl_3$	3100-3000, 2960, 2840	1725	1650	-	62 - 63°C (from hexane)
25a	$CHCl_3$	3100-3000, 2960, 2840	1710	1635	-	-

are detected in only less than 5% in one case. Double adducts are found as sideproducts only; however, for unknown reasons the formation of these compounds occurs with particular ease by starting with the unsaturated amide **13**.

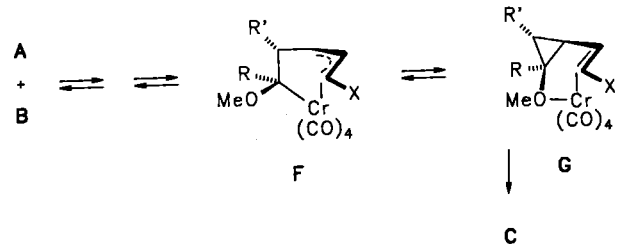


The diastereoselectivity of the [2 + 1] cycloaddition of **1** to electron-deficient 1,3-dienes is rather high in favour of the diastereomer of **C** as illustrated above (at least 84:16). This preference may be explained by a mechanism proposed by Harvey and Lund[10] for the reactions of simple 1,3-dienes. Crucial intermediates are the reversibly generated η^3-allyl complex **F** and vinylcyclopropane complex **G** where the olefinic unit and the alkoxy substituent coordinate to the metal. Thus, by contraction to the three-membered ring (**F** → **G**) the 18-e configuration at the metal atom is maintained. In contrast, formation of the **b** isomer would involve a 16-e intermediate since the *trans*-alkoxy group is not available for coordination to the metal atom.

Table 3. ^{1}H-NMR data of vinylcyclopropanes **3a**, **3b**, **5a**, **5b**, **9a**, **9b**, **10**, **11**, **12**, **14a**, **14b**, **18a**, **18b**, **22a**, **22b**, **23**, **25a**, and **25b** (300 MHz, $CDCl_3$, δ values, coupling constants in Hz as given in parentheses).

	CO_2Me s, 3 H	2′-OMe s, 3 H	2-H d, 1 H	3-H dd, 1 H	1′-H dd, 1 H	3′-H 1 H	3′-R	2′-Ph m_c, 5 H
3a	3.75	3.04	6.07 (15.5)	6.96 (10.5, 15.5)	1.92 (6.0, 10.5)	1.75, dq (6.0, 6.5)	0.83, d (6.5) 3H	7.36
3b	3.61	3.13	5.84 (15.5)	a)	a)	a)	1.41, d (6.5) 3 H	7.36
5a	3.74	3.20	6.04 (15.5)	7.04 (10.5, 15.5)	2.09, t (10.5)	1.71, dq (6.5, 10.5)	1.37, d (6.5) 3 H	7.34
5b	a)	a)	6.06 (15.5)	a)	a)	a)	1.02, d (6.5) 3 H	7.34
9a	-	3.02	5.52 (16.0)	6.66 (10.0, 16.0)	1.92 (6.0, 10.0)	1.78, quint (≈ 6.0)	0.84, d (6.5) 3 H	7.36
9b	-	3.20	5.27 (16.0)	5.75 (10.0, 16.0)	1.8 - 1.75, m 2 H		1.41, d (6.0) 3 H	7.34
10	-	3.17	5.48 (16.0)	6.74 (10.5, 16.0)	a)	a)	1.35, d (6.5) 3 H	7.36
11	-	3.01	5.36 (10.5)	6.43, t (10.5)	a)	a)	0.86, d (6.5) 3 H	7.33
12	-	a)	5.08 (11.0)	6.57, t (11.0)	a)	a)	1.46, d (6.0) 3 H	7.33
14a	3.13, 3.05, 3.03 b)		6.52 (15.0)	6.92 (10.0, 15.0)	1.94 (6.5, 10.0)	1.72, quint (6.5)	0.81, d (6.5) 3 H	7.36
14b	3.14, 2.96, 2.91 b)		6.21 (15.0)	6.06 (10.0, 15.0)	1.81 (6.0, 10.0)	1.69, quint (6.0)	1.41, d (6.0) 3 H	7.36
18a	3.76	3.15	6.20 (15.5)	7.11 (10.0, 15.5)	2.66 (6.5, 10.0)	2.93, d (6.5)	7.22, 7.05, 6.75-6.60 s, m_c, m, 5 H, 3 H, 2 H	
18b	3.62	2.82	5.95 (15.5)	6.23 (10.0, 15.5)	2.68 (6.5, 10.0)	a)	7.50-7.05 m, 10 H	
22a	3.76	3.10	6.19 (15.5)	6.92 (10.0, 15.5)	2.91 (6.0, 10.0)	2.55, d (6.0)	3.49, s 3 H	7.36
22b	3.64	3.07	6.10 - 5.95 m, 2 H		3.01 (6.5, 9.0)	2.53, d (6.5)	3.81, s 3 H	7.36
23	3.77	3.19	6.07 (16.0)	7.64 (10.0, 16.0)	2.42, t (10.0)	2.55, d (10.0)	3.76, s 3 H	7.40
25a	3.71	3.25	5.87 (15.5)	6.78 (10.5, 15.5)	1.22 - 1.06, m 2 H		1.11, d (6.5)	1.38, s 3 H c)
25b	3.70	3.30	5.88 (15.5)	6.56 (10.5, 15.5)	1.39 (6.0, 10.5)	1.08, quint (6.0)	1.20, d (6.0)	1.40, s 3 H c)

a) Signal hidden by other signals, no unambiguous assignment possible. - b) 3 s, 3 H each, NMe_2 and OMe. - c) 2′-Me.



The observation of considerably lower diastereoselectivity in solvents of higher donor quality, in particular in acetonitrile or acetone, supports this interpretation. Now an external ligand takes over the part of the alkoxy group in **G** and therefore makes the formation of the **b** diastereomer less unfavourable. These mechanistic speculations may oversimplify, but plausibly explain our experiments. A more detailed discussion will also deal with the possiblity of primary π-complex formation and involvement of metallacyclobutanes which may precede the generation of intermediates **F** and **G**[16]. From a synthetic point of view, the regioselective [2 + 1] cycloadditions described here make vinylcyclopropanes such as **3** easily available which can serve as starting materials for further transformations.

Structural Assignments

The constitution and configuration of all vinylcyclopropanes could be determined on the basis of ^{1}H-NMR and ^{13}C-NMR data (see Tables 3 and 4). As an example spectroscopic data of **3a/b** are briefly discussed[19]. The *trans*-propenoate moiety in both diastereomers is deduced from the coupling constant of 15.5 Hz; a coupling of the olefinic proton (3-H) with the vicinal cyclopropane proton in the range of 10.5 Hz is taken as evidence for the bisected conformation of the vinylcyclopropane unit. The coupling constants for the cyclopropane protons are 6.0 Hz which is typical of the *trans* arrangement. Most important for the configurational assignments are the strongly differing chemical shifts of the methyl group. In diastereomer **3a** the signal appears at high field (δ = 0.83) due to the *cis*-positioned phenyl group, while isomer **3b** shows this signal at low field (δ = 1.41) caused by the *cis*-methoxy group. Similar arguments[1] were used for all other vinylcyclopropanes and the double adducts described in this paper.

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Experimental

For general information see ref.[6]. The 1,3-dienes and carbene complexes were prepared according to literature procedures: **2**[20], **4**[21], **6**–**8**[22], **13**[22], **17**[23], **21**[24], **1**[25], **24**[26]. Solvents were dried by standard methods (CaH_2 or molecular sieves).

General Procedure for the Reactions of Carbene Complex **1** *with 1,3-Dienes:* The reactions were performed in a flask equipped with a stirring bar and sublimation finger as described in ref.[6]. Complex **1** and the diene were dissolved in the corresponding solvent under dry argon and heated to reflux temperature for the time indicated in the individual experiments. The crude product was filtered through a short pad of Celite [ca. 4 cm, eluation with pentane/ether (4:1)], the solvents were evaporated in vacuo, and the product was purified as described in the individual experiments (see Table 1). For spectroscopic and analytical data of vinylcyclopropanes see Tables 2–5.

Spectroscopic Data of Regioisomeric Vinylcyclopropanes **16**, **19a/b**, *and of Double Adducts* **15a/b/c**, **20**

16: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.25 (m, 5H, Ph), 5.87 (qd, *J* = 6.5, 15.0 Hz, 1H, 2′-H), 5.46 (qdd, *J* = 1.5, 9.0, 15.0 Hz, 1H, 1′-H), 3.15, 3.10, 2.71 (3 s, 3H each, OMe, NMe_2), 2.95 (dd, *J* = 6.5, 9.0 Hz, 1H, 3-H), 2.34 (d, *J* = 6.5 Hz, 1H, 1-H), 1.75 (dd, *J* = 1.5, 6.5 Hz, 3H, 2′-Me). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 167.4, 37.1, 36.8 (s, 2 q, $CONMe_2$); 135.3, 128.8, 128.0, 127.9, 127.4, 126.4 (s, 5 d, Ph, C-1′, C-2′); 72.3 (s, C-2); 55.2 (q, OMe); 35.2, 30.9 (2 d, C-1, C-3); 18.1 (q, 2′-Me).

15a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.25 (m, 10H, Ph); 3.29, 3.26, 3.12, 2.66 (4 s, 3H each, NMe_2, OMe); 2.44 (dd, *J* = 7.0,

Table 4. ^{13}C-NMR data of vinylcyclopropanes **3a/b**, **5a**, **9a/b**, **14a**, **18a/b**, **22a/b**, **23**, and **25a**. [75.5 MHz, $CDCl_3$, δ values, Ph signals for all compounds except **25a**: s (δ = 140-134), 3 d (δ = 130-127)]

	C-1 (s)	C-2 (d)	C-3 (d)	C-2′ (s)	C-1′/C-3′ (2d)	3′-Me (q)	2′-OMe (q)	1-OMe (q)
3a	167.0	119.3	149.0	75.1	33.0/30.6	14.2	55.0	51.3
3b	166.7	119.1	149.3	74.1	36.1/27.8	11.8	54.8	51.1
5a	166.8	121.4	145.9	71.5	31.4/28.6	7.9	55.7	51.4
9a	118.2	98.5	154.8	75.4	33.7/30.9	14.1	54.9	-
9b	117.8	96.9	155.3	74.3	36.9/28.1	11.7	54.9	-
14a	166.6	118.6	145.5	74.5	33.0/30.0	14.1	55.0	a)
18a	166.9	120.5	147.5	75.6	40.7/33.8	b)	55.1	51.5
18b	166.5	120.4	147.7	75.1	37.5/36.3	b)	54.5	51.3
22a	166.5	122.5	144.3	74.7	37.0/33.0	c)	55.1	51.5
22b	166.1	122.1	144.5	74.9	34.9/33.6	d)	54.7	51.3
23	166.2	122.5	142.4	72.1	33.9/33.2	e)	55.5	51.2
25a	167.0	118.4	149.8	68.7	36.5/29.7	15.1f)	54.2	51.1

a) 37.2, 35.6 (2q, NMe_2). - b) Additional signals in the phenyl range. - c) 169.0, 52.0 (s, q, 3′-CO_2Me). - d) 168.9, 52.2 (s, q, 3′-CO_2Me). - e) 167.6, 51.8 (s, q, 3′-CO_2Me). - f) 13.4 (q, 2′-Me).

Table 5. Elemental analyses obtained for new compounds **3a**, **5a**, **9**, **14a**, **15a**, **18a**, **22a**, and **25a**.

Compound			Calcd.			Found		
			C	H	N	C	H	N
3a	$C_{15}H_{18}O_3$	(246.3)	73.15	7.36	-	73.07	7.46	-
5a	$C_{15}H_{18}O_3$	(246.3)	73.15	7.36	-	72.88	7.40	-
9	$C_{14}H_{15}NO$	(213.3)	78.83	7.09	6.57	78.49	6.81	6.32
14a	$C_{16}H_{21}NO_2$	(259.2)	74.11	8.16	5.40	74.48	8.26	5.50
15a	$C_{24}H_{29}NO_3$	(379.5)	75.96	7.70	3.69	75.99	7.72	3.80
18a	$C_{20}H_{20}O_3$	(308.4)	77.90	6.54	-	78.07	6.61	-
22a	$C_{16}H_{18}O_5$	(290.3)	66.20	6.25	-	66.74	6.36	-
25a	$C_{10}H_{16}O_3$	(184.2)	65.19	8.47	-	65.43	8.74	-

9.5 Hz, 1H, 1-H); 2.36 (d, J = 7.0 Hz, 1H, 2-H); 1.43 (quint, J = 6.5 Hz, 1H, 3′-H); 1.20 (dd, J = 6.5, 9.5 Hz, 1H, 1′-H); 0.79 (d, J = 6.5 Hz, 3H, 3′-Me). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 167.3, 37.3, 35.1 (s, 2 q, $CONMe_2$); 137.3, 135.5, 129.5, 128.1, 128.0, 127.8 (2 s, 4 d, Ph); 72.2, 71.0 (2 s, C-3, C-2′); 55.6, 55.5 (2 q, OMe); 37.2, 27.2, 26.5, 26.4 (4 d, C-2, C-1, C-1′, C-3′); 14.3 (q, 3′-Me).

15b: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.20 (m, 10H, Ph); 3.36, 3.22, 3.15, 3.06 (4 s, 3H each, NMe_2, OMe); 2.51 (dd, J = 6.5, 9.0 Hz, 1H, 1-H); 2.42 (d, J = 6.5 Hz, 1H, 2-H); 1.27 (quint, J = 6.5 Hz, 1H, 3′-H); 0.40 (d, J = 6.5 Hz, 3H, 3′-Me); 0.23 (dd, J = 6.5, 9.0 Hz, 1H, 1′-H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 167.5, 37.5, 35.6 (s, 2 q, $CONMe_2$); 137.0, 136.7, 129.6, 128.4, 128.1, 128.0, 127.7 (2 s, 5 d, Ph); 72.7, 71.2 (2 s, C-2′, C-3); 55.1, 54.7 (2 q, OMe); 32.8, 29.7, 29.4, 25.8 (4 d, C-1, C-2, C-1′, C-3′); 13.6 (q, 3′-Me).

15c (only a few signals can be assigned): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.34, 3.25, 3.11, 2.70 (4 s, 3H each, NMe_2, OMe); 1.41 (d, J = 7.0 Hz, 3H, 3′-Me). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 167.8, 37.4, 35.3 (s, 2 q, $CONMe_2$); 71.9, 71.0 (2 s, C-3, C-2′); 55.5, 55.4 (2 q, OMe).

19a: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55–6.77 (m, 10H, Ph), 6.57 (d, J = 16.0 Hz, 1H, 2′-H), 5.30 (dd, J = 9.5, 16.0 Hz, 1H, 1′-H), 3.80 (s, 3H, CO_2Me), 3.10 (s, 3H, OMe), 2.30–1.40 (m, 2H, 1-H, 3-H).

19b: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55–6.77 (m, 10H, Ph), 6.41 (d, J = 16.0 Hz, 1H, 2′-H), 5.50 (dd, J = 9.5, 16.0 Hz, 1H, 1′-H), 3.45 (s, 3H, CO_2Me), 3.05 (s, 3H, OMe), 2.47–2.39 (m, 2H, 1-H, 3-H).

20: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.55–6.77 (m, 15H, Ph); 3.46 (s, 3H, CO_2Me); 3.22, 3.06 (2 s, 3H, each, OMe); 2.30–1.40 (m, 4H, 1-H, 2-H, 1′-H, 3′-H). – ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 170.2, 51.6 (s, q, CO_2Me); 137.3–125.7 (Ph); 73.8, 73.2 (2 s, C-3, C-2′); 55.5, 55.3 (2 q, OMe); 37.8, 35.3, 29.8, 27.2 (4 d, C-2, C-3′, C-1, C-1′).

☆ Dedicated to Professor *Klaus Hafner* on the occasion of his 65th birthday.

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[16] A detailed mechanistic interpretation of these results will be presented in a future paper.

[17] If formed, this (*Z*,*E*)-diene should react considerably slower at the (*Z*)-substituted double bond (compare **4**→**5**).

[18] Reasonably stabilized 1,3-zwitterions should be the intermediates involved. The rearrangements of donor-acceptor-substituted vinylcyclopropanes will be reported in a subsequent publication; M. Buchert, H.-U. Reißig, unpublished results.

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