On the Regioselectivity and Stereoselectivity of the Carbene Transfer from Fischer Carbene Complexes to Trisubstituted Electron-Deficient 1,3-Dienes☆

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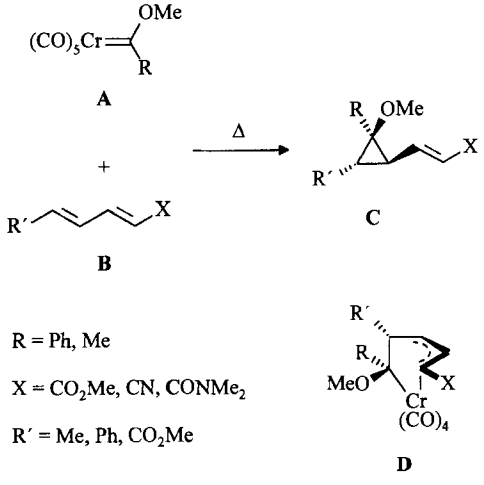
Thermal reactions of Fischer carbene complex **1** with trisubstituted electron-deficient 1,3-dienes **7**, **8**, **23**, **25**, **32**, and **35** provided highly substituted vinylcyclopropanes in good yields. The carbene transfer proceeds highly regioselectively favouring cyclopropanation of the double bond not bearing the ester function. In addition, the diastereoselectivity is generally fairly high in preference of cyclopropanes with the methoxy group *cis*-positioned with respect to the olefin moiety. The reaction of methylcarbene complex **2** with diene ester **8** displays inversed regioselectivity. These observations are discussed together with solvent effects, and a mechanistic rationale is presented.

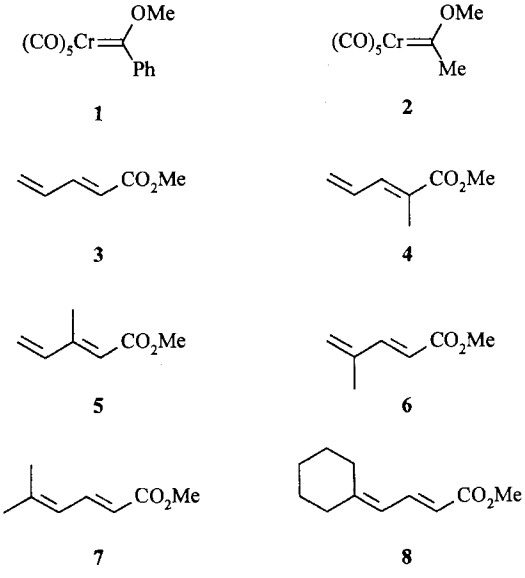
In a preceding report[2] we described thermal reactions of Fischer carbene complexes **A** with 1,4-disubstituted electron-deficient dienes **B** which furnished vinylcyclopropene derivatives **C**. Gratifyingly, these reactions occurred with complete periselectivity, in favour of formal [2 + 1] cycloadditions, and with excellent regioselectivity and good diastereoselectivity producing compounds **C** in high preference. The solvent effects observed are in accordance with a mechanistic proposal which suggests intermediate **D**[2b,3] as crucial for the observed selectivity phenomena.



Since not many studies on the reactivity of Fischer carbene complexes with dienes[4] are known, we further investigated 1,3-dienes with different substitution patterns, in particular trisubstituted electron-deficient compounds, in order to study the dependence of the selectivities with regard to the diene structure.

Results

As Fischer carbene complex we generally employed the phenyl-substituted compound **1**, but in one example we also studied the considerably less reactive methyl-substituted complex **2**. Whereas thermal reactions of **1** with diene esters **3**–**5** provided only polymers or intractable mixtures of many compounds, we could receive clear results when dienes **6**–**8** were used as carbene acceptors.



The slow reaction (90°C, 3 d) of complex **1** with methyl 4-methyl-2,4-pentadienoate (**6**) regioselectively afforded a mixture of the two diastereomers **9a/b** (67:33) in moderate yield. This transformation thus proceeds with the lowest diastereoselectivity observed with diene esters as studied in

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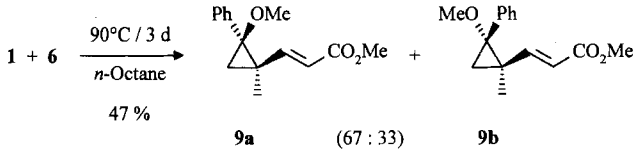
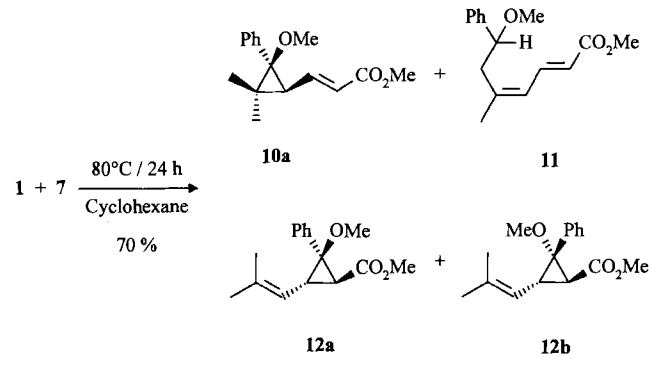
this or the preceding report[2]. In contrast, thermal reaction of **1** with 5,5-disubstituted diene ester **7** gave a good yield of a mixture of regioisomers **10** and **12** and, in addition, of the formal CH insertion product **11**. The "normal" regioisomer was generated as a single diastereomer **10a** while the "wrong" isomer was formed unselectively giving the two isomers **12a/b** in comparable quantities. A mechanism for the formation of **11** will be suggested in the discussion (see below).



9a (67 : 33) **9b**



10a **11**

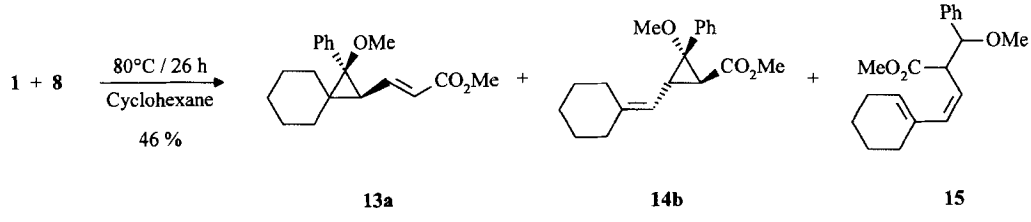
12a **12b**

10a : 11 : 12a : 12b = 60 : 18 : 9 : 13

Diene ester **8**, which is structurally very similar to the acyclic compound **7**, reacted with **1** to produce a mixture of **13a**, **14b**, and a compound to which we attribute structure **15** (see discussion). Again, the major regioisomer **13** was found to be diastereomerically pure (configuration **a**), but astonishingly regioisomer **14** was also formed as a single diastereomer (configuration **b**). Much to our surprise the selectivity of methyl-substituted carbene complex **2** was rather different from that of **1**. The slow reaction with **8** in cyclohexane (80 °C, 87 h) provided a mixture of vinylcyclopropane **16a** with the "wrong" regioisomer **17a** predominating. The small amount (2%) of cyclopentene derivative **18** identified may be caused by thermal rearrangement of **16** or **17** due to the long reaction time[1,5] and not by a direct [4 + 1] cycloaddition. The selectivity of the carbene transfer slightly depends on the solvent. The considerably faster reaction in THF furnished less **17a** and a higher percentage of **16**, now obtained as a mixture of diastereomers.

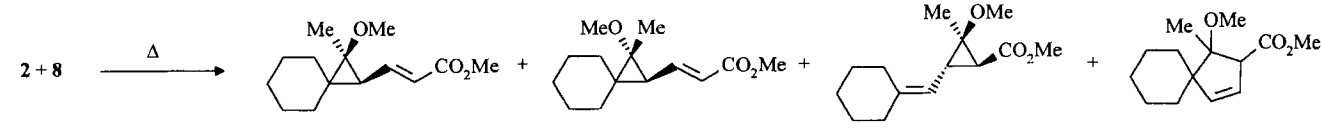
We also wanted to study diene esters in which the terminal double bond is fully incorporated into a carbocycle. For this purpose the (*Z*,*E*) diene esters **24** and **26** and the (*E*,*E*) diene esters **23** and **25**, were synthesized by standard procedures.

Thermal reaction of the cyclopentene derivative **23** with complex **1** proceeded highly selectively and was relatively fast (80 °C, 24 h). The carbene transfer occurred exclusively to the endocyclic trisubstituted π bond, and only one diastereomer of **27** was detected (configuration **a**). The minor product **28a/b** (3:1) probably arises from **27a** by vinylcyclopropane-cyclopentene rearrangement, although the conditions are remarkably mild for this process. It should be noted that **28a/b** differ only in the configuration at the centre bearing the ester function while the other two stereo-



13a **14b** **15**

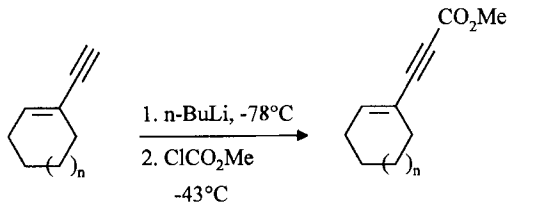
13a : 14b : 15 = 78 : 13 : 9

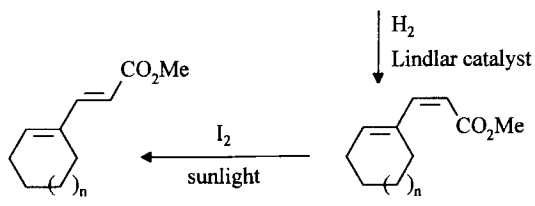


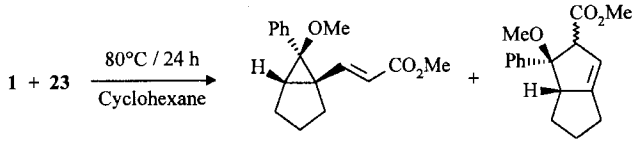
16a **16b** **17a** **18**

	16a	:	16b	:	17a	:	18	Yield
Cyclohexane, 80°C, 87 h	28	:	0	:	70	:	2	60 %
THF, 64°C, 23 h	36	:	7	:	57	:	0	63 %

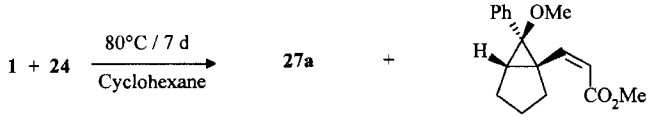
genic carbons have the same relative configuration as in their precursor. A detailed discussion of this and related rearrangements will be presented in a future report[5]. In the reaction of **1** with the corresponding (*Z*,*E*) diene **24** the carbene complex was consumed very slowly, and only a low material balance could be achieved. The expected product **29a** was identified together with isomeric vinylcyclopropane **27a**, both isolated in very low yield. Also, a dimer arising from **24** (or **23**) by Diels-Alder reaction could be detected (13% yield)[1]. It is probable that **27a** is formed via **23** by thermal isomerization of **24**.



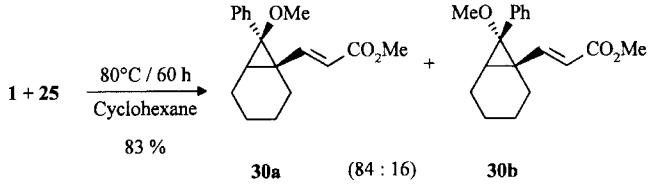


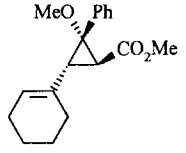


27a : 28a,b = 91 : 9 [28a : 28b = 3 : 1]

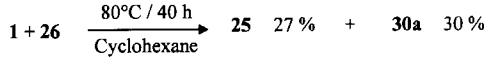


Considering the high selectivity of the combination **1/23** it was rather unexpected that the homologous diene ester **25** enfolded a remarkably lower regio- and stereoselectivity. The carbene transfer from **1** to **25** provided a mixture of three primary products **30a/b** and **31b** (76:14:10). Reaction of **1** with (*Z*,*E*) diene **26** gave **30a** in low yield and (*E*,*E*) diene **25**. Therefore it must be assumed that **26** isomerized to the more stable **25** which than reacts with **1** to furnish **30a** as major component. A control experiment revealed that this isomerization occurs indeed when catalytic amounts of **1** are present, but not without complex catalysis. It should also be realized that the reaction of **1** with **25** is relatively slow (compared with cyclopentene derivative **23**), as demonstrated by the fact that some diene ester could be reisolated.

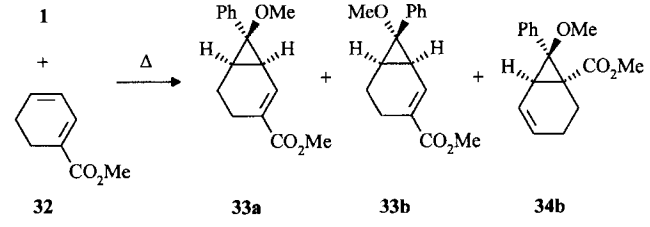




31b **30a : 30b : 31b = 76 : 14 : 10**



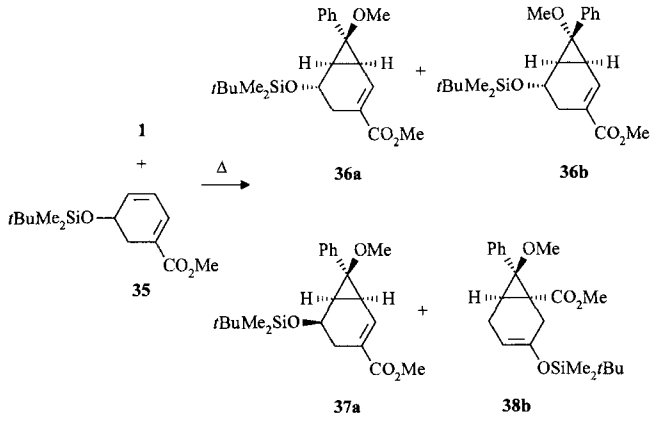
Finally we investigated two dienes where both double bonds were endocyclic. The reaction of cyclohexadiene derivative **32** with carbene source **1** was again highly regioselective and afforded only 2% of the cyclopropane derivative **34b** with the ester function attached to the three-membered ring. The expected major regioisomer was isolated in 48% yield and with very high diastereoselectivity. Consistent with all earlier results this [2 + 1] cycloaddition was accelerated when performed in THF instead of *n*-octane, but the stereo- and regioselectivity dropped considerably.



	33a	:	33b	:	34b	Yield
n-Octane, 90°C, 2 d	90	:	6	:	4	50 %
THF, 64°C, 15 h	81	:	11	:	8	83 %

Siloxy-substituted cyclohexadiene derivative **35** is easily available from the furan methyl acrylate Diels-Alder adduct[6]. With this chiral (racemic) compound the diastereofacial selectivity of the carbene transfer could be studied. Its reaction with **1** gave a mixture of four isomers **36a/b**, **37a**, and **38b**. In THF the "wrong" regioisomer **38b** was formed in 30% while in cyclohexane its percentage in the product mixture was somewhat lower. Compound **38b** is not the primary product of the addition to the cyclohexa-

diene 1,2-double bond, but a (metal catalyzed) π-bond isomerization[7] must be assumed bringing the remaining double bond into conjugation with the siloxy function. The major regioisomers **36**, **37** show that the carbene transfer proceeded with diastereoselectivity with respect to the carbene substituents favouring formation of isomers **a**, and that the diastereofacial selectivity was moderate (ca. 5:1) in favour of the isomers **36** with the cyclopropane ring in *trans* position with respect to the siloxy group. The solvent effect on the stereoselectivity was low.



(all compounds are racemic)

	36a	36b	37a	38b	Yield
Cyclohexane, 80°C, 86 h	46	13	15	26	54 %
THF, 64°C, 43 h	52	8	10	30	100 % (crude)

When we compare the reactions of **1** with **32** and the similar diene **35** it is remarkable that the regioselectivity of **35** is much lower. One may speculate whether the influence of the additional siloxy group in **35** is only of sterical nature or whether its electronic effects are also decisive.

Structural Assignments

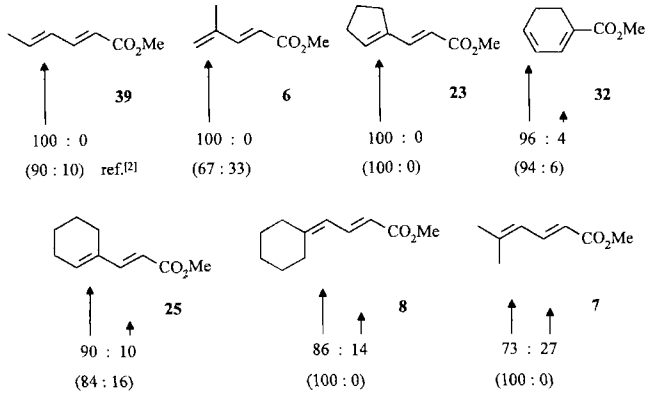
The constitution and configuration of all vinylcyclopropanes were determined by ^{1}H- and ^{13}C-NMR spectroscopy as described in a preceding paper[2] and in ref.[1]. A few stereochemical assignments had to be supported by NOE experiments. Thus, irradiation of the signal of the methyl group of **17a** (in hexadeuterioacetone) caused an enhancement of the olefinic signal at δ = 4.67, whereas irradiation to the methoxy group induced an enhancement of the cyclopropane 3-H. For regioisomer **16a** a strong NOE was observed between the methoxy signal and the olefinic 3-H signal. These observations heavily support the configurations for **17a** and **16a** as depicted above. Also, irradiation of the phenyl signal of **33a** (in hexadeuteriobenzene) caused a strong enhancement of the signals of the two bridgehead protons thus proving the assignment for this compound.

Discussion

Periselectivity: As earlier found for reactions of Fischer carbene complexes **1** or **2** with disubstituted dienes to type **B**[2], the carbene transfer proceeds again with excellent periselectivity in favour of [2 + 1] cycloadducts when trisubstituted electron-deficient dienes were employed. Although small quantities of cyclopentene derivatives could be identified in a few cases these were very likely not to be formed by direct [4 + 1] cycloaddition but by a thermal vinylcyclopropane/cyclopentene rearrangement[5]. Even for cisoid-fixed 1,3-dienes such as **32** and **35** the [4 + 1] cycloaddition is disfavoured.

Regioselectivity: The regioselectivities of the carbene transfer from complex **1** to the different diene esters are summarized in Scheme 1.

Scheme 1. Regioselectivity of the carbene transfer from **1** to diene esters in hydrocarbon solvents (values in parenthesis: diastereoselectivity)



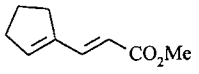
This collection demonstrates that the addition to the remote double bond, not bearing the methoxycarbonyl function, is intrinsically highly favoured. If there is one additional alkyl group at C-5 or C-4 as for diene esters **39** and **6** the regioselectivity is very high (100:0), whereas two substituents at C-5 and C-2 (as for **32**) or at C-5 and C-4 (as for **25**) moderately diminish the regioselectivity. The higher selectivity of diene **23** compared with the homologue **25** may be connected with the strain of the cyclopentene double bond favouring the reaction at this site. Even stronger erosion of the regioselectivity was observed for dienes such as **8** and **7** with two alkyl groups at C-5. Thus, the intrinsic preference for the remote double bond is apparently moderated when steric hindrance by substituents is operating. Interestingly, methylcarbene complex **2** is more sensitive to these effects. Whereas the reaction of **2** with methyl 2,4-hexadienoate (**39**) showed complete carbene transfer to the remote double bond[2], the diene ester **8** accepts the carbene at the less substituted double bond with moderate preference. In no case double adducts were observed which could form by addition of two carbene ligands to the dienes.

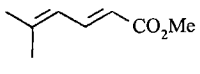
Stereoselectivity: The diastereofacial selectivity of the carbene transfer was marginally investigated employing chiral diene ester **35**, and it turned out to be only moderate. However, as already observed for disubstituted dienes[2], the noninduced diastereoselectivity is usually good to excellent favouring formation of isomer **a** (see Scheme 2). No correlation of the diastereoselectivity with the regioselectivity, and thus with the substitution pattern, could be recognized.

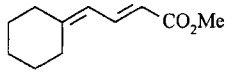
But further inspection of our results revealed some relation between the reactivity of the diene esters and the stereoselectivity of the carbene transfer. The reaction times as indicated in the individual experiments can be taken as crude criteria for the reactivity of the corresponding diene, since the consumption of carbene complex **1** could be visually followed by the colour change of the reaction mixture[8].

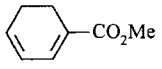
as ligand to provide an 18-e configuration at the metal centre. This chelate effect can plausibly explain the favoured formation of stereoisomers **a** by metal elimination from **G**. When formation of **G** is the rate determining step the correlation between reactivity and diastereoselectivity is reasonable. It is unclear why higher substitution degree enhances the reactivity; possibly, the ring closure **F** → **G** is facilitated by electron-donating alkyl substituents. A π complex **E** may

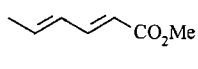
Scheme 2. Reactivity and diastereoselectivity of reactions of diene esters with complex **1**



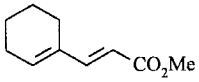


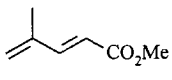


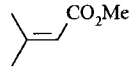


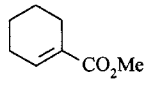


	23	**7**	**8**	**32**	**39**
reaction time (ca. 80°C)	24 h	24 h	26 h	48 h	48 h
diastereoselectivity (**a** : **b**)	100 : 0	100 : 0	100 : 0	94 : 6	90 : 10







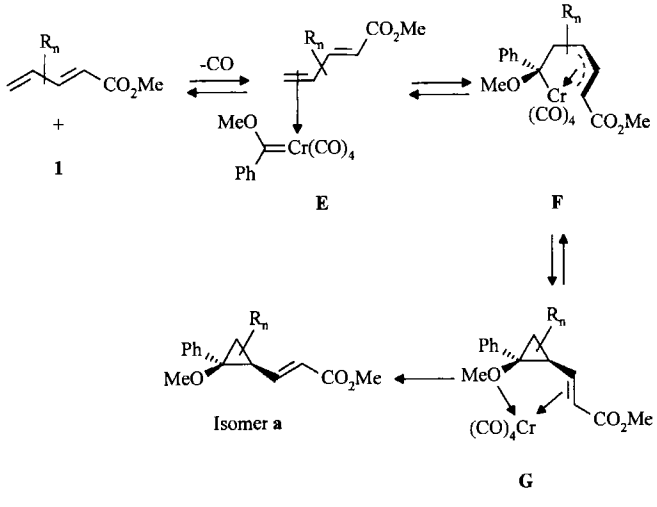


	25	**6**	**40**	**41**
	60 h	> 72 h (3d, 90°C)		
	84 : 16	67 : 33		

Although the sequence given in Scheme 2 must only be a rough qualitative estimate, the good correlation between rate and diastereoselectivity is puzzeling. Reactive diene esters accept the carbene highly selective, whereas less reactive dienes such as **6** display only very moderate diastereoselectivity. We cannot rigorously exclude equilibration (by ring opening/ring closure) for systems requiring long reaction times (**25** and **6**), however, the temperatures employed and, in particular, the absence of cyclopentene derivatives[5] make thermodynamic control rather unlikely. With respect to reactivity, Scheme 2 clearly demonstrates that diene esters bearing two additional alkyl substituents are considerably more reactive than monoalkyl-substituted compounds – the position of the alkyl groups being of minor importance. The relatively low reactivity of diene **25** is not clear. The particularly fast consumption of **23** may be an effect of the cyclopentene ring strain which often accelerates cycloadditions. It should also be emphasized at this point of discussion that several diene esters are considerably more reactive than the related α,β-unsaturated ester. Thus, no reaction of **1** with olefins **40** and **41**, respectively, could be achieved[8b]. This observation must be compared with smooth transformations of dienes **7**, **8**, **23**, and **25**.

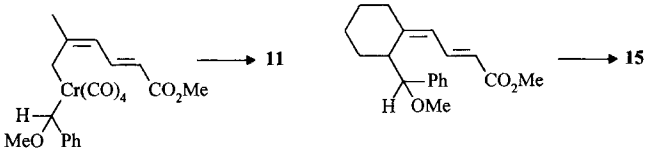
Although we are far from full understanding of all reactivity and selectivity effects, our results are in accord with the earlier suggestion[2b,3] that a crucial intermediate in the carbene transfer should be the reversibly generated η^1-alkyl-η^3-allyl complex **F** which precedes vinylcyclopropane complex **G**. Here the alkene unit and the alkoxy group serve

also be produced in the sequence of steps, and precede generation of complex **F**. Its formation could also be faster when the diene bears two alkyl groups.



The solvent effects observed in several cases also support these mechanistic suggestions. The donor solvent THF increases the rate and decreases diastereoselectivity and regioselectivity. Intermediate **G** must now compete with an alternative 18-e complex where the alkoxy group is replaced by a solvent molecule as ligand. Thus the chelate effect as operating in **G** is not necessary and higher percentages of isomers **b** are formed.

Side products: Two side products not derived from vinylcyclopropane derivatives were detected in small amounts. Compound **11** could be the result of an insertion of **1** into one of the six allylic C–H bonds of diene ester **7**. Formation of intermediate **H** seems plausible and should give **11** by reductive elimination of $Cr(CO)_4$ which is possibly stabilized by the diene moiety[9].



H **42**

The structure of side product **15** formed in the reaction of **1** with **8** could not unambiguously be established, the spectroscopic data together with mechanistic considerations, however, make suggestion **15** likely. Again an insertion into an allylic C–H bond to afford an intermediate similar to **H** is reasonable, but product **42** apparently undergoes a 1,5-sigmatropic rearrangement to compound **15**.

The results presented in this study demonstrate that the carbene transfer from Fischer carbene complexes to dienes is a rather general process occurring with considerably regio- and stereoselectivity. The related reactions with other functionalized dienes will be reported in a subsequent paper.

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Experimental

For general information see refs.[8b,8c]. The 1,3-dienes and carbene complexes were prepared according to literature procedures: **1**[10], **2**[11], **6**[12], **7**[13], **8**[14], **32**[15], **35**[6]. Solvents were dried by standard methods (CaH_2 or molecular sieves).

General Procedure for the Reactions of Carbene Complexes with 1,3-Dienes: The reactions were performed in a flask equipped with a stirring bar and sublimation finger as described in refs.[8b,8c]. The carbene complex and the diene were dissolved in the corresponding solvent under dry Ar, and the solution was heated at reflux temp. for the time indicated in the individual experiments. The reaction mixture was filtered through a short pad of Celite (ca. 4 cm, elution with pentane/ether, 4:1), the solvents were evaporated in vacuo, and the product was purified by removal of $Cr(CO)_6$ and excess diene by kugelrohr distillation. The residue was further purified as described in the individual experiments. Chromatography means column chromatography with silica gel 60 (Merck, 0.063–0.200 mm, eluation with mixtures of *n*-hexane = h and ethyl acetate = ea). For spectroscopic and analytical data of vinylcyclopropanes see Tables 1–5.

Methyl (E)-3-(2-Methoxy-1-methyl-2-phenylcyclopropyl)-2-propenoate (**9a, b**): According to the general procedure, a solution of 1.86 g (6.00 mmol) of **1** and 0.960 g (7.50 mmol) of **6** in 10 ml of *n*-octane was heated for 3 d at 90°C. The crude product was distilled in a kugelrohr oven (170°C/0.02 Torr) providing 0.971 g (66%) of **9a/9b** (67:33, purity ca. 85%). Chromatography (h/ea, 6:1) afforded 0.621 g (43%) of pure **9a/9b** (60:40) and 0.127 g (9%) of a mixture containing **9a/9b** and the corresponding cyclopentene derivative[5] (4:39:36:21). For data see Tables 1–3.

Methyl (E)-3-(2-Methoxy-3,3-dimethyl-2-phenylcyclopropyl)-2-propenoate (**10a**): According to the general procedure, a solution of 0.240 g (0.77 mmol) of **1** and 0.420 g (3.00 mmol) of **7** in 3 ml of cyclohexane was heated for 24 h at 80°C. Kugelrohr distillation (100°C/0.05 Torr) gave a mixture of **10a**, **11**, **12a**, and **12b** (0.140 g, 70%, 60:18:9:13) as analyzed by GC. By preparative HPLC (elution with h/ea, 98:2) pure samples of **10a**, **12a**, **12b**, and **11** were obtained in low quantity. Data of **10a** Tables 1–3, **12a**, **12b** Tables 4 and 5, and **11**: ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.42 (dd, *J* = 12.0, 15.0 Hz, 1H, 3-H), 7.34 (m_c, 5H, Ph), 6.02 (dd, *J* = 0.5, 12.0 Hz, 1H, 4-H), 5.71 (d, *J* = 15.0 Hz, 1H, 2-H), 4.25 (dd, *J* = 6.0, 8.0 Hz, 1H, 7-H), 3.73, 3.20 (2 s, 3H each, OMe), 2.84 (dd, *J* = 8.0, 13.5 Hz, 1H, 6-H), 2.54 (dd, *J* = 6.0, 13.5 Hz, 1H, 6-H), 1.83 (s, 3H, Me). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 167.9, 56.7 (s, q, CO_2Me), 146.2, 141.2 (2 s, Ph, C-5), 140.6 (d, C-3), 128.4, 127.8, 126.6, 125.9, 118.8 (5 d, Ph, C-2,4), 82.8 (d, C-7), 51.4 (q, OMe), 41.6 (t, C-6), 25.3 (q, Me).

Methyl (E)-3-(2-Methoxy-2-phenylspiro[2.5]oct-1-yl)-2-propenoate (**13a**): According to the general procedure, a solution of 1.25 g (4.00 mmol) of **1** and 1.44 g (8.00 mmol) of **8** in 10 ml of cyclohexane was heated for 26 h at 80°C. The crude product was purified by chromatography (h/ea, 15:1): fraction 1, 0.095 g (8%) of **13a**, **14b**, **15** (18:74:8); fraction 2, 0.456 g (38%) of **13a**, **15** (90:10). Data of **13a** (Tables 1–3), **14b** (Tables 4 and 5), and **15**: ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.26 (m_c, 5H, Ph), 6.45 (dd, *J* = 10.0, 11.5 Hz, 1H, 3-H), 5.83 (d, *J* = 11.5 Hz, 1H, 4-H), 5.41 (m_c, 1H, 1′-H), 4.31–4.20 (m, 2H, 2-H, =CH), 3.63 (s, 3H, CO_2Me), 3.18 (s, 3H, OMe), 2.12–1.33 (m, 8H, CH_2). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 166.6 (s, CO), 150.2 (d, C-4), 140.4, 137.0 (2 s, =C, Ph), 129.3, 128.4, 127.5 (3 d, Ph), 124.9, 119.4 (2 d, C-3, =CH), 87.9 (d, C-1′), 56.9 (q, OMe), 52.1, 50.9 (q, d, OMe, C-2), 29.7, 27.5, 23.0, 22.2 (4 t, CH_2).

Methyl (E)-3-(2-Methoxy-2-methylspiro[2.5]oct-1-yl)-2-propenoate (**16a, b**): According to the general procedure, a solution of 0.750 g (3.00 mmol) of **2** and 1.62 g (9.00 mmol) of **8** in 10 ml of cyclohexane was heated for 87 h at 80°C. The crude product was purified by chromatography (h/ea, 10:1): fraction 1, 16 mg of **18** (impure); fraction 2, 0.105 g (15%) of **16a**, **16b** (96:4); fraction 3, 0.036 g (5%) of **16a**, **17a** (33:67); fraction 4, 0.276 g (39%) of **17a**. Data of **16a, b** (Tables 1–3), **17a** (Tables 4 and 5), and **18**: ^1H NMR ($CDCl_3$, 300 MHz): δ = 6.18, 5.62 (2 dd, *J* = 2.5, 6.5 and 2.0, 6.5 Hz, 1H each, HC=CH), 3.71, 3.35 (2 s, 3H each, OMe), other signals are hidden by signals of impurities. – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 173.9 (s, CO), 139.1, 125.3 (2 d, HC=CH), 89.1 (s, *C*–OMe), 58.5 (d, *C*–CO), 54.6 (s, spiro C), 51.7, 51.5 (2 q, OMe), 33.0, 31.6, 26.3, 23.7, 23.5 (5 t, CH_2), 15.0 (q, Me). – An experiment was analogous performed with **2** (0.500 g, 2.00 mmol) and **8** (1.08 g, 6.00 mmol) in THF (8 ml). After heating to 64°C for 23 h it provided a crude product, which was purified by chromatography as above: fraction 1, 0.138 g (29%) of **16a**, **16b**, **17a** (78:15:7), fraction 2, 0.162 g (34%) of **17a**.

Methyl 3-(1-Cyclopenten-1-yl)-2-propynoate (**20**): According to a procedure of Brandsma et al.[16], 26.7 g (0.290 mol) of 1-ethynylcyclopentene (**19**)[17], 124 ml (2.97 mmol) of *n*-butyllithium in THF (150 ml), and 45 ml (0.580 mol) of methyl chloroformate gave after aqueous workup and kugelrohr distillation (100°C/1 Torr) 35.9 g (82%) of pure **20**. – ^1H NMR ($CDCl_3$, 300 MHz): δ = 6.43 (broad s, 1H, =CH), 3.79 (s, 3H, OMe), 2.51 (m_c, 4H, CH_2), 1.95 (quint., *J* = 7.5 Hz, 2H, CH_2). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ =

154.3, 52.4 (s, q, CO_2Me), 145.5, 122.8 (d, s, HC=C), 84.1, 81.4 (2 s, C≡C), 35.4, 33.6, 23.0 (3 t, CH_2). – IR (film): $\tilde{\nu}$ = 3050, 2950, 2850 cm^{-1} (CH), 2210 (C≡C), 1710 (CO), 1600 (C=C). – $C_9H_{10}O_2$ (150.2): calcd. C 71.98, H 6.71; found C 71.61, H 6.85.

Methyl 3-(1-Cyclohexen-1-yl)-2-propynoate (**22**): According to a procedure of Brandsma et al.[16], 31.2 g (0.290 mol) of 1-ethinylcyclohexene (**21**)[17], 140 ml (0.320 mol) of *n*-butyllithium in THF (200 ml), and 45.4 ml (0.585 mol) of methyl chloroformate afforded after aqueous workup and kugelrohr distillation (56 °C/0.1 Torr) 31.8 g (66%) of crude **22** which was further purified by chromatography (h/ea, 10:1). Product **22** was obtained as colourless liquid (24.3 g, 51%). – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.46 (m_c, 1 H, =CH), 3.78 (s, 3 H, CO_2Me), 2.15, 1.63 (2 m_c, 4 H each, CH_2). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 154.7, 52.6 (s, q, CO_2Me), 142.4, 118.4 (d, s, HC=C), 88.8, 78.3 (2 s, C=C), 28.1, 26.0, 21.9, 21.1 (4 t, CH_2). – IR (film): $\tilde{\nu}$ = 3025, 2930, 2860 cm^{-1} (CH), 2200 (C≡C), 1705 (CO), 1640 (C=C). – $C_{10}H_{12}O_2$ (164.2): calcd. C 73.15, H 7.36; found C 72.87, H 7.64.

Methyl (Z)-3-(1-Cyclopenten-1-yl)-2-propenoate (**24**): Analogously to a reported procedure[18], 2.00 g (13.3 mmol) of **20** was hydrogenated in the presence of Lindlar catalyst (0.280 g of Pd/$CaCO_3$ treated with 0.15 ml of quinoline) in 100 ml of hexane/ethyl acetate (1:1). After consumption of 0.75 equiv. of hydrogen the catalyst was filtered off, the solvents were evaporated, and the residue was purified by chromatography (h/ea, 15:1) providing 0.915 g (46%) of pure **24**. – ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.58, 5.64 (2 d, *J* = 12.5 Hz, 1 H each, HC=CH), 6.16 (broad s, 1 H, =CH), 3.71 (s, 3 H, CO_2Me), 2.61, 2.40, 1.93 (2 m_c, quint., *J* = 7.5 Hz, 2 H each, CH_2). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 166.9, 51.1 (s, q, CO_2Me), 141.3, 138.1, 116.4 (3 d, =CH), 33.2, 32.5, 24.3 (3 t, CH_2), quaternary C not detected.

Table 1. ^{1}H-NMR data of cyclopropane derivatives **9a**, **b**, **10a**, **13a**, **16a**, **b**, **27a**, **29a**, **30a**, **b**, **33a**, **b**, **36a**, **b**, and **37a** ($CDCl_3$, 300 MHz, δ values, coupling constants in Hz given in parentheses)

Compound	Ph	HC=CH-CO_2Me			OMe	Cyclopropane-H	Other Signals
	m_c, 5 H	dd, 1 H	d, 1 H	s, 3 H	s, 3 H		
9a	7.34	-[a]	5.90 (16.0)	3.74	3.14	1.43 (s) (2 H)	0.88 (s, 3 H, Me)
9b	7.32	6.20 (d) (15.5)	5.77	3.60	3.14	1.25, 1.21 (5.5)[b]	1.51 (s, 3 H, Me)
10a	7.36	7.00 (10.5, 15.5)	6.09 (15.5)	3.75	3.04	1.95 (d) (10.5)	1.39, 0.81 (2 s, 3 H each, Me)
13a	7.34	7.05 (11.0, 15.5)	6.13 (15.5)	3.74	3.02	1.97 (d) (11.0)	1.90, 1.52-1.30, 1.26, 1.11, 0.92-0.80 (3 m_c, 2 m, 10 H, CH_2)
16a	-	6.91 (11.0, 15.5)	5.92 (15.5)	3.71	3.28	1.76-1.25 (m)	1.76-1.25 (m, 10 H, CH_2), 1.42 (s, 3 H, Me)
16b	-	6.63 (11.0, 15.5)	5.96 (15.5)	-[c]	-[c]	-[c]	-[c]
27a	7.36	7.43 (d) (16.0)	6.00	3.76	3.06	2.18-2.02, 1.97-1.72, 1.42-1.22, 0.26-0.14 (4 m, 2 H, 3 H, 1 H, 1 H, CH, CH_2)	
29a	7.51-7.26 (m)	6.59 (d) (12.0)	5.96	3.76	3.08	2.17-2.03, 1.91-1.69, 1.40-1.26, 0.27-0.13 (4 m, 2 H, 3 H, 1 H, 1 H, CH, CH_2)	
30a	7.35	7.23 (d) (16.0)	5.98	3.75	3.04	1.79 (dd) (4.0, 8.5)	2.10-1.92, 1.75-1.07, 0.98-0.78 (3 m, 2 H each, CH_2), 1.66, 1.49 (2 ddd, 5.0, 8.5, 14.0 and 4.5, 9.0, 14.0, 1 H each, CH_2)
30b	7.30	6.19 (d) (16.0)	5.72	3.58	3.13	1.74 (dd) (3.0, 8.0)	2.08-1.94, 1.93-1.81, 1.65-1.25 (3 m, 2 H, 2 H, 4 H, CH_2)
33a[d]	7.13	7.43 (2.5, 6.5)	-	3.50	2.88	1.82 (dd) (6.5, 8.5) 1.35 (dd) (4.5, 8.5)	2.74, 2.10, 2.58-2.43, 1.60-1.43 (2 broad dd, 7.5, 17.0 and 8.0, 15.0, 2 m, 1 H, 1 H, 1 H, 1 H, CH_2)
33b	7.32	7.10 (3.5, 5.5)	-	3.80	3.01	-[c]	2.50-2.30, 1.78-1.55 (2 m, 3 H, 3 H, CH, CH_2)
36a[e]	7.21	7.48 (2.5, 6.0)	-	3.51	2.83	2.10 (dd) (6.0, 9.0) 1.77 (ddd) (2.0, 5.0, 9.0)	4.63 (dt, 2.5, 5.0, 1 H, CH), 3.08, 2.90-2.80 (dt, 2.5, 17, m, 1 H each, CH_2), 0.95, 0.09, 0.05 (3 s, 9 H, 3 H, 3 H, OSi*t*BuMe_2)
36b[e]	7.19	7.43 (1.5, 8.5)	-	3.47	2.90	-[c]	0.71, 0.09, -0.18 (3 s, 9 H, 3 H, 3 H, OSi*t*BuMe_2)[c]
37a[e]	7.15	7.32 (1.5, 8.5)	-	3.52	3.08	2.21 (dd) (6.0, 8.5)[c]	4.31 (ddd, 4.5, 8.0, 9.0, 1 H, CH), 3.20 (broad dd, 8.0, 17.0, 1 H, CH), 1.02, 0.10, 0.09 (3 s, 9 H, 3 H, 3 H, OSi*t*BuMe_2)[c]

[a] Signal hidden by the Ph signal. – [b] AB system. – [c] Signals hidden by those of the major isomer. – [d] In C_6D_6. – [e] In C_6D_6/CH_2Cl_2.

Table 2. ^{13}C-NMR data of cyclopropane derivatives **9a**, **b**, **10a**, **13a**, **16a**, **b**, **27a**, **29a**, **30a**, **b**, **33a**, **b**, **36a**, **b**, and **37a** [$CDCl_3$, 75.5 MHz, Ph signals for all compounds except for **16a**, **b**: s (δ = 141–133), 3 d (δ = 130–126)]

Compound	HC=CH d	HC=CH d	CO_2Me s	CO_2Me q	OMe q	Cyclopropane-C s	Cyclopropane-C d	Cyclopropane-C d	Other Signals
9a	153.1	118.0	167.2	51.3	54.7	74.6	30.7 (s)	25.3 (t)	17.9 (q, Me)
9b	153.8	117.3	167.0	51.2	54.7	73.8	31.1 (s)	25.6 (t)	15.2 (q, Me)
10a	147.3	120.6	166.9	51.4	55.4	76.6	34.7	32.8 (s)	24.8, 15.6 (2 q, Me)
13a	147.4	120.2	166.9	51.2	55.1	77.2	34.1	39.7 (s)	34.5, 26.2, 26.1, 25.3, 24.5 (5 t, CH_2)
16a	148.2	119.5	166.9	51.1	54.5	71.2	37.8	39.4 (s)	34.1, 26.3, 26.2, 25.3, 25.2 (5 t, CH_2) 15.8 (q, Me)
16b	147.5	120.6	-[a]	-[a]	53.8	72.1	36.8	39.8 (s)	31.8, 28.4, 25.5 (3 t, CH_2), 12.5 (q, Me)
27a	152.0	117.6	167.5	51.4	54.1	75.7	43.0 (s)	41.4	28.3, 26.6, 22.7 (3 t, CH_2)
29a	149.8	120.8	166.8	51.1	53.9	73.6	41.1 (s)	40.5	31.7, 27.0, 23.6 (3 t, CH_2)
30a	154.9	116.9	167.7	51.3	54.1	75.9	31.5 (s)	32.9	23.4, 20.3, 20.1, 19.9 (4 t, CH_2)
30b	155.2	115.7	166.8	51.6	54.9	74.0	30.1 (s)	27.7	20.9, 20.6, 20.0, 18.1 (4 t, CH_2)
33a	134.3	128.7 (s)	167.7	51.5	56.6	76.5	29.5	24.0	22.1, 16.6 (2 t, CH_2)
33b	139.0	125.7 (s)	168.0	51.8	55.6	73.4	26.7	20.4	24.0, 15.0 (2 t, CH_2)
36a[b]	134.1	-[a]	167.2	51.2	56.9	74.5	37.7	24.1	62.5 (d, CH), 33.2 (t, CH_2), 25.9, 18.2, -0.5 (q, s, q, Si*t*BuMe$_2$)
36b[b]	138.6	-[a]	-[a]	51.2	55.1	78.3	-[a]	-[a]	61.9 (d, CH), 25.4, 17.6 (q,s, Si*t*BuMe$_2$), 16.4 (t, CH_2)
37a[b]	133.7	-[a]	-[a]	-[a]	56.0	76.6	33.7	28.1	66.5 (d, CH), 22.6 (t, CH_2), 25.5 (q, Si*t*BuMe$_2$)[a]

[a] Signal hidden by other signals. – [b] In C_6D_6/CH_2Cl_2.

Methyl (Z)-3-(1-Cyclohexen-1-yl)-2-propenoate (**26**): Analogously to the procedure above, 3.60 g (21.9 mmol) of **22** provided after chromatography (h/ea, 20:1) 0.840 g (23%) of pure **26**. – ^1H NMR ($CDCl_3$, 300 MHz): δ = 6.33, 5.58 (dd, d, *J* = 1.0, 12.5 and 12.5 Hz, 1H each, HC=CH), 6.02 (m_c, 1H, =CH), 3.71 (s, 3H, CO_2Me), 2.20, 1.62 (2 m_c, 4H each, CH_2). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 167.4, 51.4 (s, q, CO_2Me), 144.8, 136.0, 115.4 (3 d, =CH), 135.3 (s, =C), 26.9, 26.3, 22.6, 21.8 (4 t, CH_2). – IR (film): $\tilde{\nu}$ = 3025, 2940, 2860 cm^{-1} (CH), 1720 (CO), 1620 (C=C). – $C_{10}H_{14}O_2$ (166.2): calcd. C 72.26, H 8.49; found C 72.08, H 8.58.

Table 3. IR data [film except **27a** (KBr), all compounds except **13a** 3100–3000 cm^{-1} (CH)] and elemental analyses obtained for compounds **9a/b**, **10a**, **13a**, **16a**, **17a**, **27a**, **29a**, **30a**, **33a**, and **36a**

Compound	IR (ν, cm^{-1}) CH	CO	C=C			C	H
9a/9b	2960, 2830	1720	1640	$C_{15}H_{18}O_3$ (246.3)	Calcd.	73.15	7.36
					Found	73.09	7.52
10a	2960, 2830	1750	1635	$C_{16}H_{20}O_3$ (260.3)	Calcd.	73.82	7.64
					Found	73.62	7.69
13a	3050, 3015 2920, 2840	1715	1630	$C_{19}H_{24}O_3$ (300.4)	Calcd.	75.97	8.05
					Found	75.50	8.05
16a[a]	2930, 2850	1715	1625	$C_{14}H_{22}O_3$ (238.3)	Calcd.	70.56	9.30
					Found	70.09	9.15
17a	2930, 2850	1730	-	-[b]	-		
27a	2950, 2820	1710	1625	$C_{17}H_{20}O_3$ (272.3)	Calcd.	74.97	7.40
					Found	75.07	7.55
29a	2950, 2830	1720	1625	-[b]	-		
30a	2940, 2860	1715	1625	$C_{18}H_{22}O_3$ (286.4)	Calcd.	75.50	7.74
					Found	75.36	7.78
33a	3000-2900 2830	1705	1640	$C_{16}H_{18}O_3$ (258.3)	Calcd.	74.40	7.02
					Found	73.86	7.13
36a[c]	2950, 2925 2855	1710	1635	$C_{22}H_{32}O_4Si$ (388.6)	Calcd.	67.95	8.30
					Found	67.75	8.30

[a] Obtained from a mixture of **16a**, **b**, **17a**. – [b] Lack of material did not allow elemental analysis. – [c] Obtained from a mixture of **36a**, **b**, **37a**.

Methyl (E)-3-(1-Cyclopenten-1-yl)-2-propenoate (**23**): Analogously to a procedure of Elvidge et al.[19], a solution of 0.915 g (6.02 mmol) of **24** in ethyl acetate (50 ml) was treated with an iodine crystal and exposed to daylight for 7 d. Kugelrohr distillation (80°C/0.1 Torr) furnished 0.486 g (53%) of pure **23**. – ^1H NMR ($CDCl_3$, 60 MHz): δ = 7.60, 5.75 (2 d, *J* = 16.0 Hz, 1H each, HC=CH), 6.20 (broad s, 1H, =CH), 3.75 (s, 3H, CO_2Me), 2.50, 2.20–1.40 (m_c, m, 4H, 2H, CH_2).

Methyl (E)-3-(1-Cyclohexen-1-yl)-2-propenoate (**25**): Analogously to the procedures above, a solution of 3.60 g (21.9 mmol) of **22** in hexane (50 ml) was hydrogenated (0.75 g of $Pd/CaCO_3$, 0.18 ml of quinoline). After consumption of 0.75 equiv. of hydrogen the crude mixture was treated with an iodine crystal and exposed to daylight for 1 d (sunny day). Chromatography (h/ea, 30:1) afforded 1.24 g (34%) of pure **25** as colourless liquid. – ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.29, 5.76 (2 d, *J* = 16.0 Hz, 1H each, HC=CH), 6.17 (m_c, 1H, =CH), 3.74 (s, 3H, CO_2Me), 2.21–2.12, 1.73–1.60 (2 m, 4H each, CH_2). – ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 168.0, 51.2 (s, q, CO_2Me), 148.2, 138.7, 114.0 (3 d, =CH), 134.8 (s, =C), 26.3, 24.0, 21.9* (3 t, CH_2), * signal of double intensity.

Methyl (E)-3-(6-Methoxy-6-phenylbicyclo[3.1.0]hexan-1-yl)-2-propenoate (**27a**): According to the general procedure, a solution of 0.468 g (1.50 mmol) of **1** and 0.708 g (4.72 mmol) of **23** in 5 ml

of cyclohexane was heated for 24 h at 80°C. The crude product was purified by chromatography (h/ea, 10:1): fraction 1, 0.030 g (7%) of **28a**, **28b** (25:75); fraction 2, 0.274 g (67%) of **27a** as colourless crystals (m.p. 90–92°C). Data of **27a** see Tables 1–3, data of **28a/28b** will be reported in a subsequent publication[5].

Methyl (Z)-3-(6-Methoxy-6-phenylbicyclo[3.1.0]hexan-1-yl)-2-propenoate (**29a**): According to the general procedure, a solution of 0.620 g (1.99 mmol) of **1** and 0.380 g (2.50 mmol) of **24** in 5 ml cyclohexane was heated for 7 d at 80°C. The crude product was purified by chromatography (h/ea, 7:1): fraction 1, 0.038 g (7%) of **29a**; fraction 2, 0.050 g (13%) of a **24** dimer; fraction 3, 0.030 g (6%) of **27a**. Data of **29a** see Tables 1–3, data of **24** dimer see ref.[1].

Methyl (E)-3-(7-Methoxy-7-phenylbicyclo[4.1.0]heptan-1-yl)-2-propenoate (**30a, b**): According to the general procedure, a solution of 1.25 g (4.00 mmol) of **1** and 0.870 g (5.24 mmol) of **25** in 10 ml of cyclohexane was heated for 60 h at 80°C. The crude product was purified by chromatography (h/ea, 20:1): fraction 1, 0.086 g (8%) of **31b**; fraction 2, 0.140 g (12%) of **30b**; fraction 3, 0.719 g (63%) of **30a**. Data of **30a, b** (Tables 1–3), data of **31b** (Tables 4 and 5). – In an analogous experiment a solution of 0.470 g (1.51 mmol) of **1** and 0.300 g (1.80 mmol) of **26** was heated for 40 h to 80°C. From the crude product mixture 0.080 g (27%) of **25** was removed by kugelrohr distillation (50°C/0.05 Torr). The residue was purified by radial chromatography (petroleum ether/ea, 7:1) which provided 0.130 g (30%) of spectroscopically pure **30a**.

Whereas diene **26** did not isomerize under purely thermal conditions (cyclohexane, 2 d, 80°C), an analogous experiment in the presence of 0.1 equiv. of **1** resulted in mixture containing **26** (ca. 12%), **25** (ca. 6%), and a **25** dimer[1].

Methyl 7-Methoxy-7-phenylbicyclo[4.1.0]-2-heptene-3-carboxylate (**33a, b**): According to the general procedure, a solution of 1.86 g (6.00 mmol) of **1** and 1.65 g (12.0 mmol) of **32** in 10 ml of *n*-octane was heated for 2 d at 90°C. The crude product was purified by chromatography (h/ea, 15:1): fraction 1, 0.075 g (5%) of **34b**, **33b**, and unknown components (40:20:40); fraction 2, 0.062 g (4%) of **33a**, **33b** (50:50); fraction 3, 0.665 g (43%) of pure **33a**. Data of **33a, b** see Tables 1–3, data of **34b** Tables 4 and 5. – In

Table 4. ^{1}H-NMR data of cyclopropane derivatives **12a, b, 14b, 17a, 31b, 34b**, and **38a** ($CDCl_3$, 300 MHz, δ values, coupling constants in Hz given in parentheses)

Compound	Ph m_c, 5 H	HC=CH d, 1 H	HC=CH d, 1 H	CO_2Me s, 3 H	OMe s, 3 H	Cyclopropane-H d, 1 H	Cyclopropane-H 1 H	Other Signals
12a	7.39	-	4.25 (1.0, 9.0)[a]	3.79	3.06	2.21 (6.5)	2.98 (dd) (6.5, 9.0)	1.77, 1.55 (2 d, 1.0, 6 H, Me)
12b	7.36	-	5.17 (9.0)[b]	3.47	3.11	2.19 (6.5)	2.84 (dd) (6.5, 9.0)	1.85, 1.80 (2 broad d, 1.0, 6 H, Me)
14b	7.35	-	5.10 (9.0)	3.47	3.12	2.20 (6.5)	2.89 (dd) (6.5, 9.0)	2.37, 2.17, 1.59 (3 m_c, 2 H, 2 H, 6 H, CH_2)
17a	-	-	4.67 (7.5)[b]	3.70	3.26	-[c]	2.61 (t) (7.5)	2.27-2.25, 2.07, 1.53 (m, 2 m_c, 3 H, 2 H, 6 H, CH, CH_2), 1.39 (s, 3 H, Me)
31b	7.43-7.26 (m)	5.69 (m_c)	-	3.47	3.07	2.63 (7.5)	2.48 (d) (7.5)	2.25-2.14, 2.13-2.06, 1.75-1.56 (3 m, 2 H, 2 H, 4 H, CH_2)
34b	7.31	5.90-5.84[d]	6.45 (10.0)[b]	3.34	3.10	2.60, 2.31-1.64 (2 m, 1 H, 4 H, CH, CH_2)		
38a	7.35	5.59 (s)[b]	-	3.40	3.16	2.47-2.06 (m, 5 H, CH, CH_2), 1.00, 0.25, 0.24 (3 s, 9 H, 6 H, OSi*t*BuMe$_2$)		

[a] Septet. – [b] Broad signal. – [c] See other signals. – [d] m.

Table 5. ^{13}C-NMR data of cyclopropane derivatives **12a, b, 14b, 17a, 31b, 34b**, and **38b** [$CDCl_3$, 75.5 MHz, Ph signals for all compounds except **17a**: s (δ = 141–123), 3 d (δ = 139–126)]

Compound	CO_2Me s	CO_2Me q	C=CH s	C=CH d	OMe q	Cyclopropane-C s	Cyclopropane-C d	Cyclopropane-C d	Other Signals
12a	169.9	51.7	135.3	119.9	54.5	74.3	32.4	32.3	25.1, 18.3 (2 q, Me)
12b	170.5	51.6	135.3	119.3	54.7	73.8	35.9	30.5	25.8, 18.7 (2 q, Me)
14b	170.4	51.5	143.3	115.9	54.6	73.8	36.0	29.6	37.0, 29.6, 28.4, 27.6, 26.6 (5 t, CH_2)
17a	170.1	51.4	144.4	116.0	54.1	68.7	35.2	30.5	36.5, 29.5, 28.2, 27.3, 26.3 (5 t, CH_2), 16.4 (q, Me)
31b	170.1	51.1	123.9	129.9	54.3	73.4	36.8	31.0	28.9, 24.9, 22.6, 21.9 (4 t, CH_2)
34b	171.5	51.6 (d)	129.4	119.6	55.5	79.7	34.7 (s)	28.5	22.3, 15.4 (2 t, CH_2)
38b	171.8	51.6	-	-	55.4	78.4	26.7	-[a]	152.2, 97.2 (s, d, OC=CH), 27.4, 17.5 (2 t, CH_2), 25.8, 18.1, -4.2 (q, s, q, OSi*t*BuMe$_2$)

[a] Signal hidden by other signals.

an analogous experiment a solution of 0.624 g (2.00 mmol) of **1** and 0.412 g (3.00 mmol) of **32** in 5 ml of THF was heated for 15 h to 64°C. The crude product was purified by chromatography (h/ea, 15:1): fraction 1, 0.012 g (2%) of **34b**; fraction 2, 0.053 g (10%) of **34b**, **33b** (50:50); fraction 3, 0.037 g (7%) of **33a**, **33b**, **34b** (50:40:10); fraction 4, 0.331 g (64%) of pure **33a**.

Methyl 5-(tert-Butyldimethylsiloxy)-7-methoxy-7-phenylbicyclo[4.1.0]-2-heptene-3-carboxylate (**36a**, **36b**, **37a**): According to the general procedure, a solution of 0.468 g (1.50 mmol) of **1** and 0.670 g (2.50 mmol) of **35** in 5 ml of cyclohexane was heated for 86 h at 80°C. The crude product was purified by chromatography (h/ea, 20:1): fraction 1, 0.155 g (27%) of **38b** and unknown components (ca. 50:50); fraction 2, 0.232 g (40%) of **36a**, **36b**, **37a** (62:18:20). By HPLC further enrichment of these components was possible thus allowing assignment of the NMR signals to the isomers. – In an analogous experiment a solution of 0.626 g (2.00 mmol) of **1** and 0.805 g (3.00 mmol) of **35** in 7 ml of THF was heated for 43 h at 64°C. The pale yellow crude product (0.778 g, 100%) was pure according to NMR spectroscopy: **36a**:**36b**:**37a**:**38b** = 52:8:10:30 (Tables 1–5).

☆ Dedicated to Professor *Rolf Huisgen* on the occasion of his 75th birthday.

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