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Polymeric Dicarbonyl Ruthenium(I) Acetate - An Efficient Catalyst for Alkene Cyclopropanation with Diazoacetates

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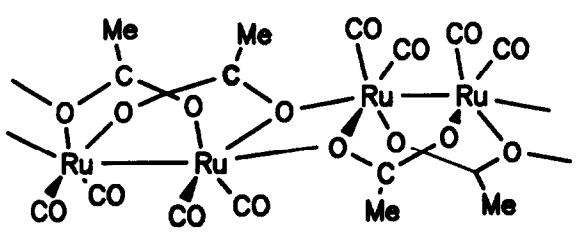
Abstract The polymeric complex $[Ru_2(CO)_4(\mu\text{-}OAc)_2]_n$ is the first Ru(I) catalyst that efficiently catalyzes cyclopropanation of alkenes with diazoacetic esters The related dinuclear catalyst $Ru_2(CO)_4(\mu\text{-}OAc)_2(MeCN)_2$ shows a similar performance only for cyclopropanation of monosubstituted alkenes

For the cyclopropanation of alkenes with diazo compounds, a variety of highly efficient copper-, palladium-, and rhodium-based catalysts are available[1] The catalytic process is believed to involve metal-carbene intermediates that are responsible for the chemo- and stereoselectivity observed in these reactions[2-6] Although the available catalysts, especially the rhodium(II) carboxylates and copper(I) triflate, have proven their value in many instances, the search for alternative catalysts goes on Recently, ruthenium(II) carboxylates[7,8] and ruthenacarboranes[9] have been introduced as efficient cyclopropanation catalysts, both of which are superior to the Ru(II,III) complex $Ru_2(OAc)_4Cl$ investigated earlier[2] $Ru_3(CO)_{12}$ has been reported to catalyze cyclopropanation of an electron-rich alkene (*n*-butyl vinyl ether)[10], but has not been evaluated further for other alkenes

We wish to introduce now the polymeric complex $[Ru_2(CO_4)(\mu\text{-}OAc)_2]_n$ (**1**)[11] and the dinuclear bis(acetonitrile) complex $Ru_2(CO)_4(\mu\text{-}OAc)_2(MeCN)_2$ (**2**)[11] as the first ruthenium(I) complexes that exhibit a remarkable catalytic activity for alkene cyclopropanation with diazoacetates In contrast to **1**, the complex **2** has a good solubility in the alkenes investigated, it also catalyzes efficiently cyclopropanation of monosubstituted alkenes, but less so of more highly alkyl-substituted alkenes.



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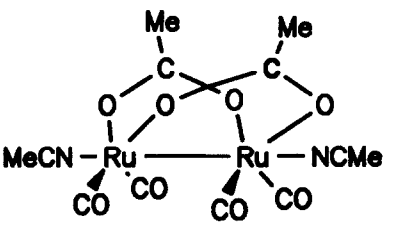

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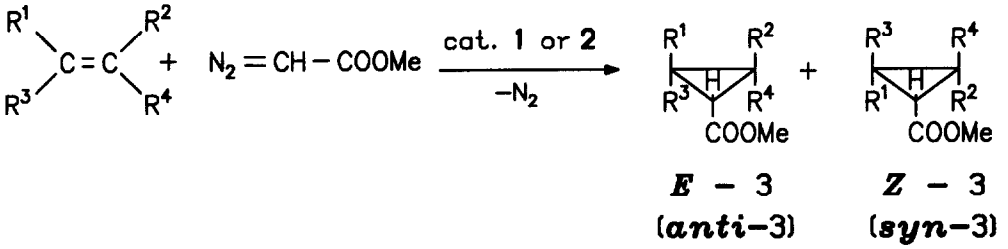
Results and Discussion

Synthesis of cyclopropanes **3** from methyl diazoacetate (MDA) and the appropriate alkene with **1** as catalyst succeeds at room temperature (Table 1) Typically, 1 mol-% of catalyst is applied, but with styrene and MDA, even smaller amounts of **1** were found to be sufficient (0 3 mol-%: overall reaction time 48 h, 87 % yield, 0 5 mol-% 16 h, 95%). The formal carbene dimers, dimethyl maleate and fumarate, constitute by-products in these reactions Their formation can be greatly reduced by keeping the diazoester concentration very low (high dilution and slow addition to the alkene / catalyst mixture)



***E* − 3** (*anti*−3) ***Z* − 3** (*syn*−3)

Complex **1** is a yellow solid that initially does not dissolve in the reaction mixtures, but disappears partly or completely during the course of the reactions In order to provide entirely homogeneous reaction conditions, we used catalyst **2** which is well soluble in most of the alkenes used Disappointingly, the cyclopropane yields were consistently lower by ca 35% than those obtained with **1** as catalyst under analogous conditions at 20 °C (Table 1, entries 2,6) At elevated temperature, however, monosubstituted alkenes (styrene, ethyl vinyl ether) are again cyclopropanated in high yield, whereas no improvement was observed for cyclopropanation of 2,3-dimethyl-2-butene The low yield in the latter case may be caused by a destruction of the active catalyst Mixing of diazoester, catalyst, and alkene for entry 12 produces a black-colored solution that subsequently turns pale-yellow with concomitant formation of a brown-red precipitate In contrast, the solutions remain yellow and homogeneous throughout the reaction for entries **3** and **7**

Thus, catalyst **2** cannot compete with **1** in terms of general efficiency for alkene cyclopropanation, despite of its good solubility in the liquid alkenes This seems to contradict general experience, but it should be taken into account that neither **1** nor **2** are likely to be the active catalysts since the ruthenium atoms are coordinatively saturated in both cases[12] In order to generate a metal carbene intermediate that is generally assumed to be involved in these carbenoid transformations[1], ligand exchange must take place Introduction of a carbene ligand at ruthenium is likely to break up the polymeric structure of **1** (which would explain why insoluble **1** is gradually consumed during the reactions), whereas it occurs by displacement of a weakly-bound acetonitrile ligand in **2**

The yields of cyclopropanes **3** resulting from monosubstituted or 1,1-disubstituted alkenes and **1** or **2** (at elevated temperature) (Table 1, entries 1,3,4,5,7,10) compare well with those obtained in the reactions catalyzed by $Rh_2(OAc)_4$[2,3,5], but are somewhat lower for the cyclopropanes derived from the 1,2-disubstituted and tetrasubstituted alkenes (entries 8,9,11) The stereoselectivities of carbene transfer to styrene, 1-hexene, and cyclohexene resemble those obtained in the $Rh_2(OAc)_4$-catalyzed reactions In the case of ethyl vinyl ether and 2,3-dihydrofuran, catalysis by **1** remarkably increases the diastereomer excess of the sterically more favored (*E*)-cyclopropane, which may be attributed at least in part to a fast epimerization and ring-opening isomerization of (Z)-**3** (syn-**3**) by the catalyst[13] On the other hand, the *cis*-selectivity observed for cyclopropanation of α-methylstyrene (entry 10) contrasts with *E*/*Z* ratios of 1 5 and 0 98 in the reactions catalyzed by $Cu(acac)_2$[14] and $Rh_2(OAc)_4$ (ethyl diazoacetate instead of MDA)[5], respectively The stereochemical assignments rest upon the interpretation of the ^1H NMR

spectra as given in the literature[14-16]. The assignments are corroborated further by the ^{13}C NMR spectra (Table 2). Most significant is the mutual shielding of the carbon atoms that are attached to the cyclopropane ring and belong to vicinal *cis*-positioned substituents, certainly a consequence of the well-precedented γ-effect. As a consequence of this effect, the carbonyl signal of the major isomer (*E* in 1,2-disubstituted cyclopropanes and *anti* in the bicyclo[n.1 0]alkanes) is consistently found at lower field as compared to the minor isomer

Table 1. Formation of Cyclopropanes **3** from Alkenes and Methyl Diazoacetate (MDA) Catalyzed by **1** or **2**

Entry	R^1	R^2	R^3	R^4	Catalyst/ Method[a]	Reaction Time [h][b]	Temp. [°C]	Yield of **3** [%][c]	*E*-**3**/*Z*-**3** [d,e]
1	Ph	H	H	H	**1**/A	12/4	20	95	1.6
2					**2**/A	8/12	20	58	2.3
3					**2**/B	5/2	60	94	1.5
4	Bu	H	H	H	**1**/A	12/4	20	67	2.0
5	EtO	H	H	H	**1**/A	12/4	20	89	4.5
6					**2**/A	8/36	20	54	11.9
7					**2**/B	5/2	36	83	5.4
8	$-(CH_2)_4-$		H	H	**1**/A	12/4	20	68	3.7
9	$-(CH_2)_2O-$		H	H	**1**/A	12/4	20	62[f]	>97:<3
10	Ph	H	Me	H	**1**/A	12/4	20	91	0.67
11	Me	Me	Me	Me	**1**/A	12/4	20	47[g]	-
12					**2**/B	5/2	60	12[h]	-

[a] Method A MDA (20 mmol), diluted in alkene and CH_2Cl_2, is added over 8-12 h to a suspension of the catalyst (0 2 mmol) in excess alkene and CH_2Cl_2 - Method B· MDA (20 mmol), diluted in alkene, is added over 5 h to a solution of catalyst (0 2 mmol) in excess alkene kept at the indicated temperature For further details, see Experimental Section

[b] Time of addition / subsequent time for complete decomposition of MDA.

[c] Yield of distilled cyclopropanes **3**. Dimethyl maleate and dimethyl fumarate were observed as by-products

[d] *Anti/syn* for entries 8 and 9

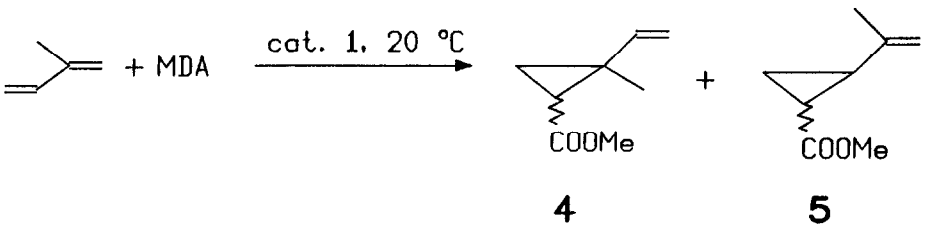
[e] Determined by ^1H NMR (400 MHz)

[f] Mixture of anti-**3** and (2,3-dihydro-4-furyl)acetate, ratio 9 1

[g] Dimethyl maleate and fumarate were isolated in 36 and 15 % yield, resp

[h] Dimethyl maleate and fumarate were isolated in 57 and 30 % yield, resp

Carbene transfer to isoprene with MDA/**1** yields the cyclopropanes **4** (56%, E/Z = 0.92) and **5** (36%, E/Z = 2 5) The preference for the more electron-rich 1,1-disubstituted double bond of the diene has been observed before for rhodium- and copper-catalyzed reactions[17,18] In fact, for the cyclopropanation catalyzed by **1** and by $Rh_2(OAc)_4$, the yields of **4** and **5**, the regioselectivity (**4**/**5**) and the stereoselectivity for **4** (E/Z ratios of 0 97[18] and 1 1[3] have been reported) are nearly identical. Only the ratio *E*-**5**/*Z*-**5** is higher than with any other catalyst used before



4 5

Table 2. ^{13}C NMR Data of Cyclopropanes **3** (solvent $CDCl_3$, δ values in ppm)[a]

R^1	R^2	R^3	R^4	Isomer	*C*HCO	CR^1R^3	CR^2R^4	OMe	CO	Other Signals
Ph	H	H	H	*Z*	25.3	23.7	11.0	51.04	171.0	136.2 (i-Ph)
				E	26.0	21.4	16.7	51.52	173.4	139.7 (i-Ph)
Bu	H	H	H	*Z*[b]	21.7	17.7	13.2	51.06	173.1	13.7 (Me); 22.1, 26.4, 32.5 (CH_2)
				E[b]	22.7	19.7	15.2	51.17	174.6	13.7 (Me); 22.1, 31.1, 31.6 (CH_2)
$-(CH_2)_4-$		H	H	*syn*	21.6	16.2	16.8	50.64	171.9	18.2, 20.9 (CH_2)
				anti	25.2	21.8	21.8	51.04	174.8	20.7, 22.5 (CH_2)
Me	Me	Me	Me		35.4	29.9	29.9	50.6	172.3	16.4, 23.3 (Me)

[a] Data for the remaining cyclopropanes of Table 1 have already been reported[14]
[b] Assignments are based on *J*-modulated spin-echo experiments

We have also checked the ability of **1** to catalyze alkene cyclopropanation with methyl diazo(trimethylsilyl)acetate **6** The diazo carbon atom of **6** is both sterically shielded and rendered less nucleophilic than in MDA by the $SiMe_3$ substituent Thus, diazoester **6** provides a further test for the performance of **1** as a carbene transfer catalyst

Diazoester **6** is only decomposed at elevated temperatures (60-80 °C), as expected, but cyclopropanes **7** are still obtained in good yield (Table 3) Two other catalysts which decompose **6** already at 20 °C, Cu(I) triflate and Rh(II) perfluorobutyrate, also produce cyclopropanes **7** from styrene and 1-hexene, though in somewhat lower yield[19] In contrast to **1**, however, they furnish no cyclopropane with cyclohexene, but only the product of carbene insertion into an allylic C-H bond. This result underlines the excellent cyclopropanation activity of our new ruthenium(I) catalyst **1** The cyclopropanation of 1-hexene was accompanied by a small amount of the metathesis product $BuCH=C(SiMe_3)COOMe$ The low yield and the failure to detect similar olefins in the other cases indicate that **1**, in contrast to $Ru_2(OAc)_4$[7], is not an effective metathesis catalyst under the given reaction conditions

According to the diastereomer ratio for **7a-c**, the sterically favored isomer prevails, i e. the trimethylsilyl group occupies the less substituted side of the cyclopropane ring The stereochemical assignment is based on ^1H and ^{13}C NMR criteria For **7a**, the phenyl ring causes the expected high-field shift of the *cis*-$SiMe_3$ and *cis*-COOMe proton signals as compared to the same groups in *trans* position For **7b** and

7c, the protons of $SiMe_3$ and COOMe are slightly deshielded, when the neighboring alkyl groups are in *cis* position[20] In the ^{13}C NMR spectra, the C=O signal is shifted to higher field when the alkyl and ester groups are *cis* to each other, again, this is in agreement with the *γ-syn*-effect mentioned above.

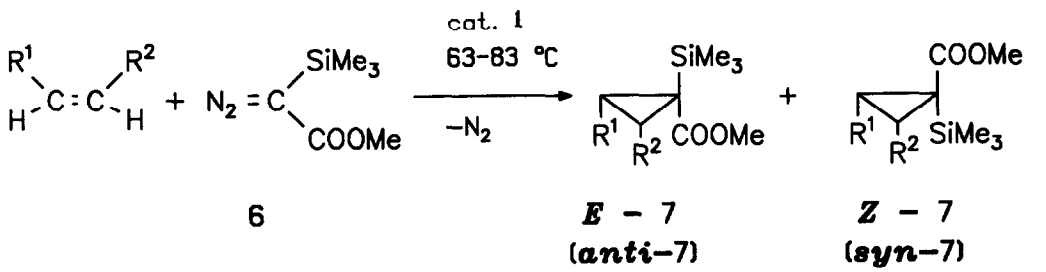
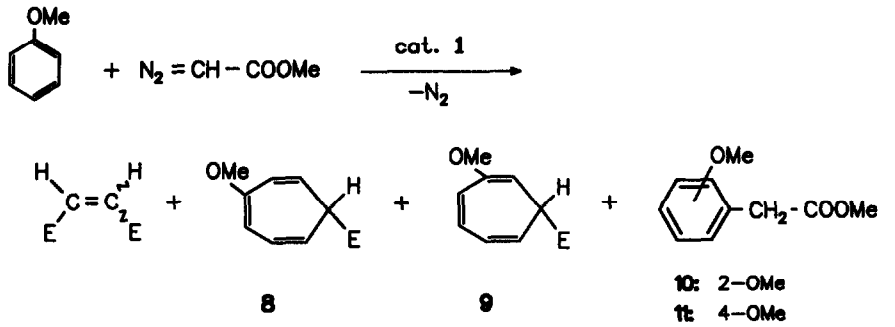


Table 3 Cyclopropanation of Alkenes with Methyl Diazo(trimethylsilyl)acetate (**6**) Catalyzed by **1**

Cyclo-propane	R^1	R^2	Reaction temp. [°C]	Yield of 7 [%][a]	*E/Z*[b] (*anti/syn*)
7a	Ph	H	70	70	1.8
7b	Bu	H	63	89[c]	3.4
7c	$-(CH_2)_4-$		83	54	7.0

[a] Yield of isolated products
[b] Determined by ^1H NMR spectroscopy (200 MHz).
[c] The cyclopropane was accompanied by a small amount of $BuCH=C(SiMe_3)COOMe$ (5% yield, 2 isomers, ratio 3 2.1).

The electrophilic nature of the metal-carbene intermediate derived from **1** and MDA becomes obvious from experiments to cyclopropanate benzene and anisole. Decomposition of MDA in an excess of benzene catalyzed by **1** (1 mol-%) furnished only the formal carbene dimers, dimethyl fumarate and maleate, whereas carbene transfer to the more electron-rich anisole [slow addition of MDA to an excess of anisole containing **1** (1 mol-%), 20 °C] was more successful Besides the carbene dimers (62%), two of the three regioisomeric methoxycycloheptatriene-7-carboxylates, **8** and **9** (total yield 24%, **8**/**9** = 12.5), as well as (2-methoxyphenyl)- and (4-methoxyphenyl)acetates **10** (3%) and **11** (3%) were obtained after column chromatography A comparison with Rh(II) carboxylate catalysts[1,21] is instructive. $Rh_2(OAc)_4$ is quite inefficient in promoting alkoxycarbonylcarbene transfer to benzene, whereas the more electrophilic $Rh_2(O_2CCF_3)_4$ is the catalyst of choice for acylcarbene transfer to aromatic molecules This comparison shows again the similarity between catalyst **1** and $Rh_2(OAc)_4$ The regioselectivity observed in the anisole reaction catalyzed by **1**, on the other hand, is strongly different from that reported for $Rh_2(O_2CCF_3)_4$ as catalyst, where the 3-, 1-, and 2-methoxy derivatives of methyl 1,3,5-cycloheptatriene-7-carboxylate have been obtained in yields of 56, 29, and 8 % , respectively[21]



8 **9**

In summary, we have described the first efficient Ru(I) catalyst for alkene cyclopropanation with diazoesters The catalyst **1** is easily accessible[11,22] and easy-to-handle. Cyclopropanation succeeds not only with methyl diazoacetate, but also with sterically shielded disubstituted methyl diazo(trimethylsilyl)-acetate In terms of electrophilicity, efficiency, regio- and (partly) stereoselectivity, **1** compares remarkably well with $Rh_2(OAc)_4$ A comparison of current prizes of ruthenium and rhodium derivatives also recommends **1** as a distinctly less costly alternative

Experimental

General information NMR spectra Bruker WP 200 (^{1}H. 200 MHz, ^{13}C 50 3 MHz) and Bruker AM 400 (^{1}H 400 MHz; ^{13}C 100 6 MHz). All spectra were recorded in $CDCl_3$ with TMS as internal standard IR spectra Perkin-Elmer IR 397, wavenumbers [cm^{-1}] are given. Elemental analyses Perkin-Elmer EA 2400 $[Ru_2(CO)_4(\mu\text{-}OAc)_2]_n$ (**1**) and $Ru_2(CO)_4(\mu\text{-}OAc)_2(MeCN)_2$ (**2**) were prepared by literature methods[11] All cyclopropanation reactions were carried out under an argon atmosphere.

Cyclopropanation of alkenes with methyl diazoacetate catalyzed by **1** *or* **2**; *general procedure* Alkenes were generally purified by distillation prior to use A solution of methyl diazoacetate (20 mmol) in alkene (20 mmol) and dichloromethane (50 ml) is added at 20 °C during 8-12 h via an automatic pump to a stirred mixture of alkene (180 mmol) and dichloromethane (20 ml) containing the catalyst [**1** (0 086 g, 0 2 mmol) or **2** (0 103 g, 0.2 mmol)] Stirring is continued until the evolution of N_2 has ceased (4-36 h, see Table 1), and the solvent and excess alkene are removed by distillation at ambient pressure (except for styrene and α-methylstyrene which were removed by column chromatography on silica gel, eluant low-boiling petroleum ether) Cyclopropanes **3** are isolated by column chromatography [80 g of silica gel, eluant pentane/ether, 5 1] as the first fraction (followed by dimethyl fumarate and dimethyl maleate) and purified further by distillation Diastereomeric mixtures could not be separated in this manner For yields and diastereomer ratios, see Table 1

All cyclopropanes **3** so obtained were characterized by ^{1}H and ^{13}C NMR spectra as well as by elemental analysis ^{1}H NMR data have been reported before in the literature[14-16], ^{13}C NMR data are given in Table 2

Cyclopropanation of isoprene A mixture of *methyl (E)-* and *(Z)-2-methyl-2-vinylcyclopropane-1-carboxylate* (**4**) and *methyl (E)-* and *(Z)-2-(1-methylvinyl)-cyclopropane-1-carboxylate* (**5**) was obtained Assignment of the individual regioisomers and diastereomers was possible by the close similarity of the ^{1}H NMR data with those reported for the corresponding ethyl esters[2,3] Isomer ratios were determined by integration of the ^{1}H NMR spectrum (400 MHz) of the mixture

Cyclopropanation of alkenes with methyl diazo(trimethylsilyl)acetate (6) catalyzed by **1**; *general procedure* A solution of **6**[23] 0.42 g, 2.4 mmol) in the alkene (10 ml) is added over 1.5-2 h at a controlled rate to a stirred suspension of **1** (35 mg, 0.081 mmol, 3.4 mol-%) in the alkene (10 ml) kept at the temperature that is given in Table 2. Stirring is continued until evolution of N_2 has ceased (6-8 h). The mixture is filtered over neutral alumina (ca. 10 g) to remove the catalyst, excess alkene is distilled off at ambient pressure, and the cyclopropane is isolated by vacuum distillation or column chromatography [Merck Lobar columns, LiChroprep Si-60, 40-63 μm, eluant petroleum ether / ether (9:1)].

*Methyl (E)-and (Z)-2-phenyl-1-trimethylsilyl-1-cyclopropanecarboxylate (***7a***)* Chromatographic separation of the reaction mixture yields first oligomers of styrene, then cyclopropane **7a** as a mixture of diastereomers (70%, *E*/*Z* ratio 1.8). - ^{1}H NMR (200 MHz): *Z*-**7a**: δ = -0.18 (s, $SiMe_3$), 1.42 (dd, *J* = 6.8, 4.0 Hz, 1 H), 1.72 (dd, *J* = 8.8, 4.0 Hz, 1 H), 2.84 (dd, *J* = 8.8, 6.8 Hz, 1 H), 3.75 (OMe), 7.28 (m, Ph). *E*-**7a**: δ = 0.12 ($SiMe_3$), 1.25 (dd, *J* = 8.1, 4.9 Hz, 1 H), 1.96 (dd, *J* = 6.5, 4.9 Hz, 1 H), 2.40 (dd, *J* = 8.1, 6.5 Hz, 1 H), 3.35 (OMe), 7.28 (m, Ph). - ^{13}C NMR *Z*-**7a**: δ = -1.2 ($SiMe_3$), 15.8 (C-3), 20.1 (C-1), 32.1 (C-2), 51.7 (OMe), 137.8 (ipso-Ph), 176.7 (C=O). - *E*-**7a**: δ = -2.6 ($SiMe_3$), 14.2 (C-3), 23.5 (C-1), 28.2 (C-2), 51.2 (OMe), 137.4 (ipso-Ph), 172.7 (C=O). -IR (neat): 1710 (C=O). - Anal. Calcd for $C_{14}H_{20}O_2Si$ (248.4): C, 67.69; H, 8.11. Found: C, 67.6; H, 7.9.

*Methyl (E)- and (Z)-2-butyl-1-trimethylsilyl-1-cyclopropanecarboxylate (***7b***)* Chromatographic separation of the reaction mixture yields first oligomers of hexene, then cyclopropane **7b** as a mixture of diastereomers (89%, *E*/*Z* ratio 3.4). - ^{1}H-NMR (400 MHz): δ = -0.02 (s, $SiMe_3$, *E*-isomer), 0.07 (s, $SiMe_3$, *Z*-isomer), 0.6-1.5 (m, all CH, CH_2, and CH_3), 3.58 (s, OMe, *Z*-isomer), 3.60 (s, OMe, *E*-isomer). - ^{13}C NMR *Z*-**7b**: δ = -0.1 ($SiMe_3$), 17.7, 29.6, 30.1, 32.0, 176.8 (C=O), the remaining signals coincide with signals of the major isomer. *E*-**7b**: δ = -2.1 ($SiMe_3$), 14.0 (Me), 16.0 (C-3), 18.2 (C-1), 22.4 (CH_2), 24.7 (C-2), 28.4 (CH_2), 31.6 (CH_2), 51.4 (OMe), 174.6 (C=O). - IR (neat): 1725 (C=O). - Anal. Calcd for $C_{12}H_{24}O_2Si$ (228.4): C, 63.1, H, 10.59. Found: C, 62.9, H, 10.6.
The cyclopropane is contaminated with a trace of *methyl 2-trimethylsilyl-2-heptenoate* (yield: ca. 5%; two isomers, ratio 3:2:1), as evidenced by ^{1}H-NMR and analytical GC-MS. - ^{1}H-NMR (400 MHz), values for the major isomer are given first: δ = 0.08/0.10 ($SiMe_3$), 2.32/? (pseudo-q, CH_2-CH=), 3.67/3.70 (OMe), 6.12/? (t, HC=). - Mass spectrum of major isomer (70 eV): *m/z* = 213 (14%) [M^+], 197 (6), 185 (5), 169 (10), 143 (18), 89 (100).

*Methyl 7-anti- and syn-trimethylsilyl-bicyclo[4.1.0]heptane-7-carboxylate (***7c***)*: After removal of excess cyclohexene, **7c** is isolated by Kugelrohr distillation at 60 °C /0.04 Torr as a mixture of diastereomers (54% yield, *anti*/*syn* = 7:0). - ^{1}H NMR (200 MHz): δ = -0.13 (s, anti-$SiMe_3$), 0.09 (s, syn-$SiMe_3$), 0.7-1.9 (m, all CH, CH_2), 3.46 (s, syn-OMe), 3.52 (s, anti-OMe). - ^{13}C NMR. *anti*-**7c**: δ = -3.3 ($SiMe_3$), 17.2 (C-1,6), 20.4 and 21.0 (C-2,3,4,5), 22.7 (C-7), 50.7 (OMe), 172.8 (C=O). *syn*-**7c**: δ = 1.3 ($SiMe_3$), 20.1 and 20.5 (C-2,3,4,5), 23.5 (C-1,6) C-7 not located, 51.2 (OMe), 177.0 (C=O). - Anal. Calcd for $C_{12}H_{22}O_2Si$ (226.4): C, 63.66, H, 9.80. Found: C, 63.7, H, 9.9.

Reaction of anisole with methyl diazoacetate catalyzed by **1**: A solution of methyl diazoacetate (2.00 g, 20 mmol) in anisole (3 ml) is added over 20 h to a stirred suspension of **1** (0.086 g, 0.2 mmol) in anisole (12 ml). The reaction mixture is then fractionated by column chromatography on silica gel (80 g). Excess anisole is eluated first with low-boiling petroleum ether. Further eluation with ether / petroleum ether (1:9) yields the following fractions: a) A mixture of methyl 3-methoxy- and 2-methoxy-1,3,5-cycloheptatriene-7-carboxylate (**8** and **9**, 0.85 g, 24% yield, **8**/**9** = 12.5), identified by comparison of the ^{1}H NMR spectral data with published[21] values, b) dimethyl fumarate (0.33 g, 23%), c) a mixture of methyl (2-methoxyphenyl)acetate and (4-methoxyphenyl)acetate (**10** and **11**, 0.21 g, 6% yield, **10**/**11** =

1 1), identified by their ^{1}H and ^{13}C NMR[24] spectra Further elution with ether / petroleum ether (3.7) furnished dimethyl maleate (0 56 g, 39%).

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