Reactions of Fischer Carbene Complexes with Siloxydienes: Formation of Cycloheptadiene and Cyclopentene Derivatives—Formal [2+1] Cycloaddition Followed by Cope Rearrangement Versus Formal [3+2] Cycloaddition with or without Preceding Carbene-Ligand Metathesis

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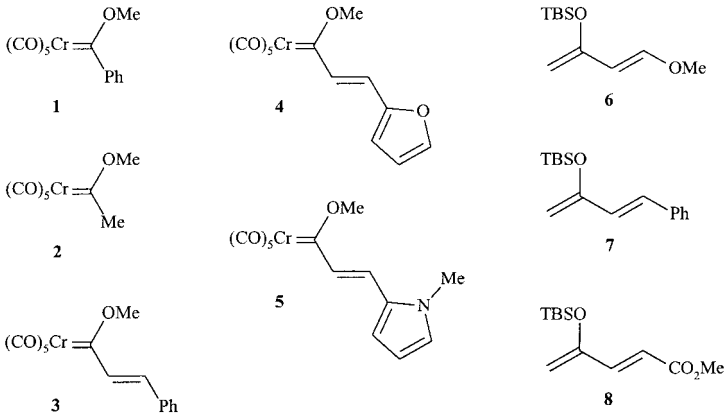
Abstract: Thermal reactions of the α,β-unsaturated Fischer carbene complexes **3**–**5** with the siloxydienes **6** and **7** mainly furnished the expected cyclohepta-1,4-dienes such as **9**, **10**, **12**, **14**, and **15**, whose formation is explained by a formal [2+1] cycloaddition followed by Cope rearrangement. The rather electron-rich carbene complex **5** also afforded the cyclopentene derivatives **11** and **16** as by-products, which are probably formed by two distinct mechanisms. Single diastereomers of the cyclopentene derivatives **17** and **18** were isolated as the exclusive products of the reactions of **3** and **4**, respectively, with the donor/acceptor-substituted 1,3-diene **8**. This process is interpreted as a metalla Diels–Alder reaction to form a chromacyclohexene intermediate **25**, which subsequently undergoes fragmentation to give cyclopentene derivatives with the required constitution. Most surprisingly, the reactions of simple carbene complexes **1** or **2** with the siloxydienes **7** or **8** yielded cyclopentene derivatives **19** and **20** that do not contain the carbene ligand of the precursor complexes. Instead, the constitution of the isolated products can be accounted for by a formal diene dimerization with fragmentation of a methylene unit. Their formation can be interpreted by an unprecedented sequence of carbene-ligand metathesis followed by a metalla Diels–Alder reaction and reductive fragmentation. All these results illustrate the great importance of electronic fine-tuning in the precursors involved in reactions of Fischer carbene complexes with 1,3-dienes.

Keywords: carbene complexes · chromium · cycloadditions · metathesis · rearrangements · silicon

Introduction

In systematic investigations we have explored the ability of Fischer carbene complexes such as **1**–**5** to serve as the carbene source for the preparation of functionalized cyclopropane derivatives.[1] Chromium complexes **1** and **2** underwent the expected formal [2+1] cycloaddition with simple electron-deficient alkenes,[2] and their thermal reactions with electron-poor 1,3-dienes proceeded with surprisingly high regio- and stereoselectivity, which resulted in the formation of some interestingly functionalized vinylcyclopropane derivatives.[3] Reactions of the α,β-unsaturated carbene complexes **3**–**5** were less predictable. A delicate balance was observed between formal [2+1] and [3+2] cycloaddition, which seemed to depend on the carbene-complex substituent, the alkene, and the solvent.[4]



Unfortunately, all our attempts to treat the unsaturated carbene complexes **3**–**5** with electron-deficient 1,3-dienes were not successful. The expected divinylcyclopropane derivatives would have had a particularly interesting substitution pattern, and their Cope rearrangements to functionalized

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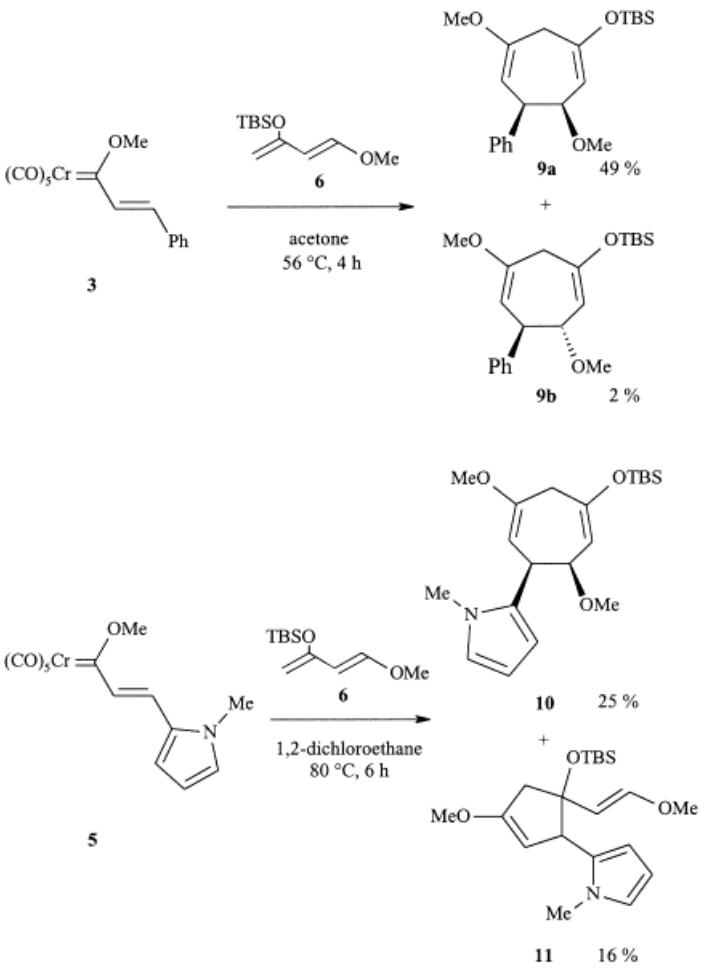
cycloheptadiene derivatives[5] would have opened new synthetic options. However, thermal reactions of these carbene complexes with the siloxy-substituted 1,3-dienes **6**,[6] **7** (electron-rich), or **8** (electronically ambiguous) were performed successfully (TBS = Si*t*BuMe$_2$). They gave expected, but also unprecedented results,[7] which are described herein in detail.

Results

Reactions of Danishefsky's diene 6: Transfer of the carbene ligand of complex **3** to the 1,3-diene **6** occurred smoothly over 4 h under reflux in acetone to provide two stereoisomeric cyclohepta-1,4-diene derivatives **9a** and **9b** (96:4) in 51% yield. The reaction in 1,2-dichloroethane at 80 °C gave a similar result (Scheme 1). We assume that the unexpected, minor isomer **9b** is formed from **9a** during chromatography.[8] The *cis* configuration of the major component **9a** is indicated by the coupling constant of 2.9 Hz for 6-H and 7-H (cf. 8.2 Hz for **9b**) and is supported further by mechanistic considerations (see Discussion).

Combination of the pyrrolyl-substituted carbene complex **5** with Danishefsky's diene **6** also produced a cycloheptadiene derivative **10** as a major component (25% yield); however, a second isomer was also isolated, which we assign as structure **11**. Although its configuration could not be determined, the constitution proposed is very likely because its ^{1}H NMR spectrum is very similar to those for the related cyclopentene derivatives obtained from **5**,[4] but significantly different from regioisomeric systems such as **17**, **19**, or **20**. Again, complex **5** tends to undergo formal [3+2] cycloadditions.[4]

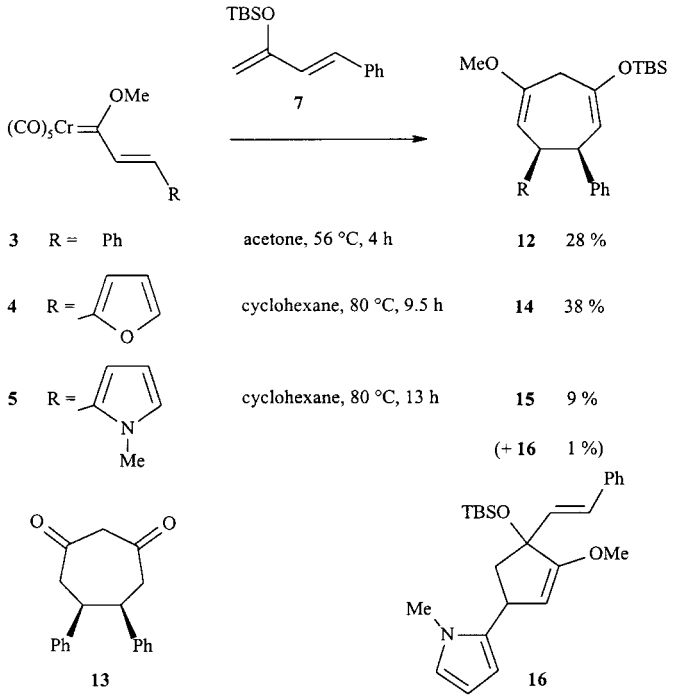


Scheme 1. Reactions of complexes **3** and **5** with Danishefsky's diene **6**.

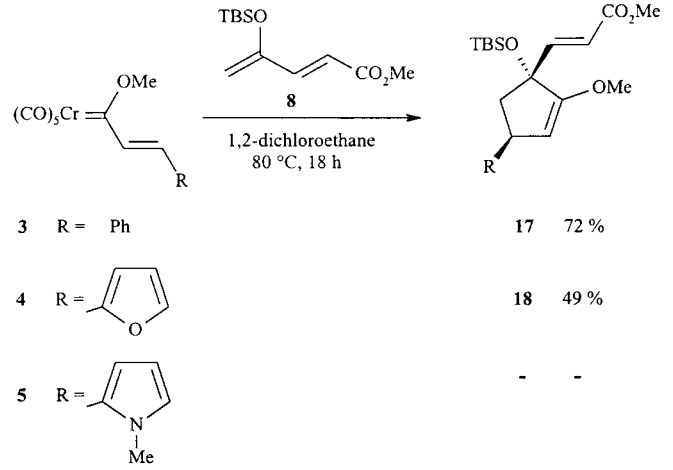
Abstract in German: *Beim Erwärmen der α,β-ungesättigten Fischer-Carbenkomplexe **3**–**5** mit den Siloxydienen **6** und **7** entstanden hauptsächlich die erwarteten 1,4-Cycloheptadiene **9**, **10**, **12**, **14** und **15**, deren Bildung durch formale [2+1]-Cycloaddition und anschließende Cope-Umlagerung erklärt werden kann. Der relativ elektronenreiche Carbenkomplex **5** lieferte zusätzlich die Cyclopentenderivate **11** und **16** als Nebenprodukte, die wahrscheinlich mit zwei unterschiedlichen Mechanismen gebildet werden. Nach der Umsetzung von **3** oder **4** mit dem donor-acceptor-substituierten 1,3-Dien **8** wurden ausschließlich die Cyclopentene **17** und **18** in diastereomerenreiner Form isoliert. Diese Reaktion wird als Metalla-Diels–Alder-Reaktion mit dem Chromacyclohexen **25** als Zwischenstufe gedeutet, das zu den Cyclopentenderivaten mit der geforderten Konstitution fragmentiert. Überraschenderweise wurden nach der Umsetzung der einfachen Carbenkomplexe **1** oder **2** mit den Siloxydienen **7** oder **8** die Produkte **19** und **20** isoliert, denen der Carbenligand fehlt. Stattdessen fand eine formale Diendimerisierung unter Abspaltung einer Methyleneinheit statt. Dieses Ergebnis kann als bisher unbekannte Folge von Carbenligandmetathese, Metalla-Diels–Alder-Reaktion und reduktiver Fragmentierung interpretiert werden. Alle Ergebnisse demonstrieren die große Bedeutung der elektronischen Feinabstimmung in den Ausgangskomponenten für die Reaktionen von Fischer-Carbenkomplexen mit 1,3-Dienen.*

Reactions of the phenyl-substituted siloxydiene 7: As in the reactions of Danishefsky's diene **6**, the siloxydiene **7** furnished mainly cycloheptadiene derivatives in moderate to low yields. Only compounds **12** and **14** could be isolated from the reaction with the carbene complexes **3** and **4**, whereas the pyrrolyl-substituted complex **5** afforded a 9:1 mixture of the expected **15** and the cyclopentene derivative **16** in low yield (Scheme 2). The NMR spectra of **16** are quite different from those of **11**, but are related to those of the cyclopentene derivatives **17**–**20**. Therefore, we propose structure **16** for this minor product. The structure and configuration of cycloheptadiene **12** were confirmed by hydrolysis with 2 N HCl to give the C_S-symmetric cyclohepta-1,3-dione **13**; a similar experiment with **14** resulted in its complete decomposition.[9]

Reactions of the methoxycarbonyl-substituted siloxydiene 8: In contrast to the electron-rich siloxydienes **6** and **7**, reactions of the electronically ambiguous methoxycarbonyl-substituted siloxydiene **8** with carbene complexes **3** and **4** afforded only cyclopentene derivatives. Compounds **17** and **18** were formed with high diastereoselectivity, but **17** was accompanied by a small quantity (ca. 3%) of an isomeric cyclopentene whose structure could not be determined unequivocally because of its low concentration (Scheme 3). The connectivity



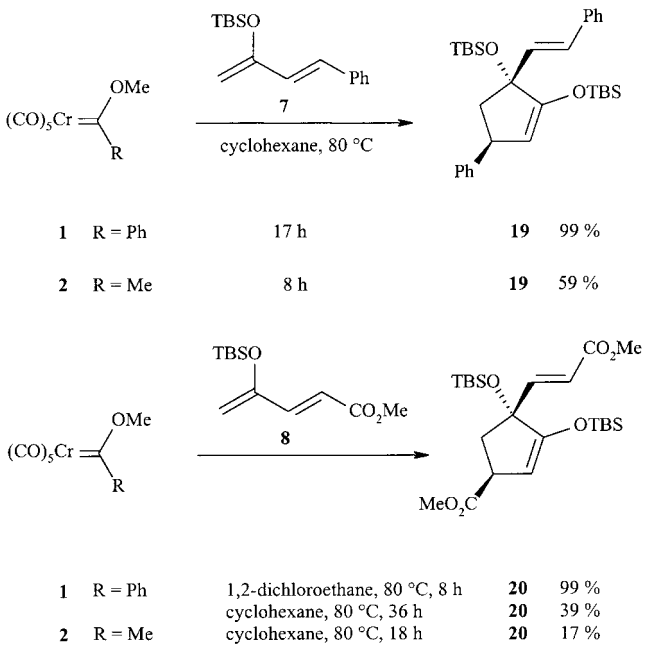
Scheme 2. Reactions of complexes **3**–**5** with siloxydiene **7**.



Scheme 3. Reactions of complexes **3**–**5** with the substituted siloxydiene **8**.

of the atoms in the structure **18** was confirmed by ^{13}C 2D-INADEQUATE spectroscopy, while the configurations of **17** and **18** (as depicted) were ascertained from ^{1}H NOESY spectra. Reaction of **8** with complex **5** gave a very complicated mixture of products which could not be distinguished. No experiments have been performed with carbene complexes where R = alkyl, but they ought to behave in a similar manner to complex **3**.

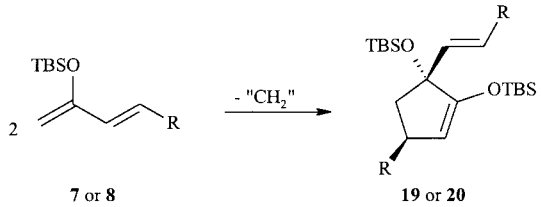
Reactions of carbene complexes 1 and 2 with siloxydienes: Although our reactions of **1** or **2** with the Danishefsky's diene **6** did not give any clear results, the outcome of their reactions with the less electron-rich dienes **7** and **8** was very surprising, as the carbene ligands of **1** and **2** were not incorporated into the products **19** or **20** (isolable in excellent yields) (Scheme 4). The constitution and relative configuration of **19** and **20** were



Scheme 4. Reactions of complexes **1** and **2** with siloxydienes **7** and **8**.

determined from their 1D- and 2D-INADEQUATE NMR spectra (used to establish the connectivity), and also from their by 2D-NOESY NMR spectra.

These cyclopentene derivatives are formally generated by a previously unknown diene dimerization with fragmentation of a methylene unit (Scheme 5).



Scheme 5. Diene dimerization with fragmentation of a methylene unit.

Discussion

Formation of cycloheptadienes: Formation of cycloheptadiene derivatives such as **9**, **10**, **12**, **14**, and **15** is easily explained and has been reported frequently in the literature.[6] The most plausible mechanism involves a regio- and stereoselective carbene transfer from complexes **3**, **4**, or **5** to the dienes **6** or **7**, which yields a *cis*-divinylcyclopropane derivative such as **22**. This then undergoes a Cope-type [3,3] sigmatropic rearrangement to afford **23** (Scheme 6). Although this sequence looks straightforward and has been proposed several times,[6] there is no obvious explanation for the stereoselectivity of the formal [2+1] cycloaddition of the carbene ligand to the participating dienes. Similar [2+1] cycloadditions with Fischer carbene complexes and other alkenes often proceed with low diastereoselectivity.[2–4] It may be that generation of the metallacyclobutane, which should precede cyclopropane formation, is reversible. Therefore, only diastereomer **21** produces **22**, because reductive elimination of the $(CO)_4Cr$

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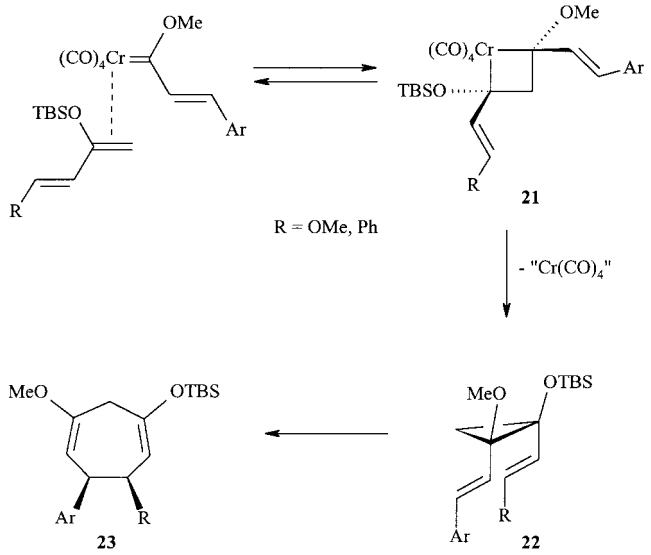
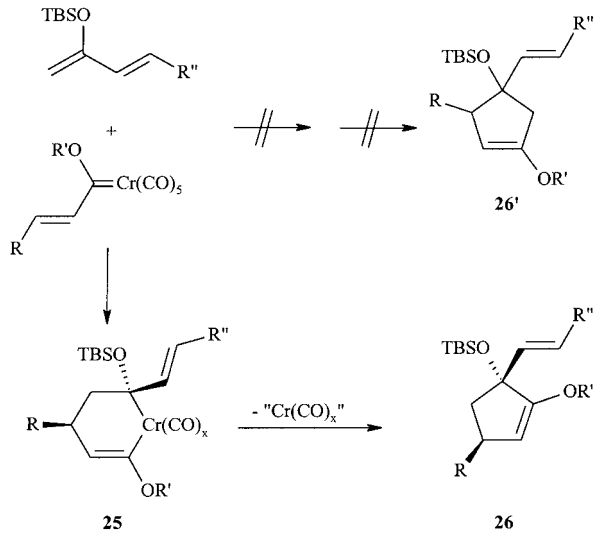


Scheme 6. Formation of cycloheptadiene derivative **23** via **21** and **22**.

fragment is strongly assisted by two *cis* oxygen functionalities.[10] However, we are not able to exclude the formation of *trans*-divinylcyclopropanes, which could then rearrange to *cis*-**22** under the reaction conditions.[11] An intermediate diradical would be reasonably stabilized by the substituents. In addition, a *trans*–*cis* isomerization catalyzed by the chromium complex is conceivable.

Formation of cyclopentene derivatives: The formation of the cyclopentene derivative **11** follows a previously described pathway.[4] The particularly electron-rich nature of the carbene ligand in **5** apparently favors rearrangement of a metallacyclobutane intermediate **21** to an η^3-complex **24**, which then undergoes reductive elimination to give by-product **11** (Scheme 7). The reactions of **5** with highly electron-deficient olefins provided exclusively the cyclopentene derivatives,[4] when noncoordinating solvents such as cyclohexane or 1,2-dichloroethane were employed. However, the reaction of **5** with Danishefsky's diene **6** slightly favors reductive fragmentation of **21** to yield a 60:40 distribution between the cycloheptadiene and cyclopentene.

The cyclopentene derivatives **16**, **17**, and **18** have a different substitution pattern to **11**, which suggests that an alternative mechanism is operative. We propose a [4+2] cycloaddition of the electron-poor chromadiene system as 4_π component to the terminal double bond of the siloxydienes **7** or **8** as 2_π contributor. The chromacyclohexene intermediate **25** formed with regio- and *endo*-selectivity then undergoes reductive elimination of the metal fragment with retention of configuration to furnish the cyclopentene derivative **26** (Scheme 8).



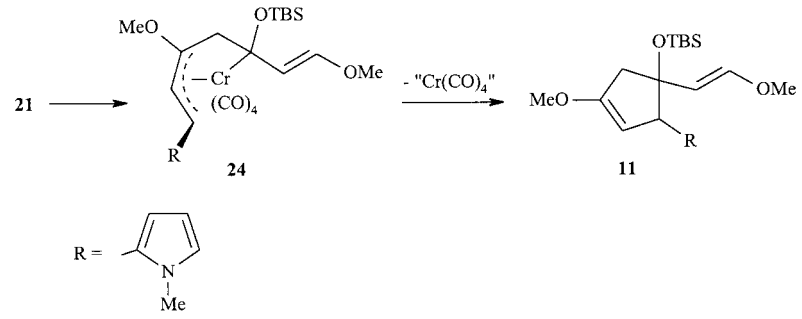
Scheme 8. Formation of **26** by the proposed [4+2] cycloaddition.

The more usual [3+2] pathway via an intermediate analogous to **24** would have afforded regioisomer **26′**.

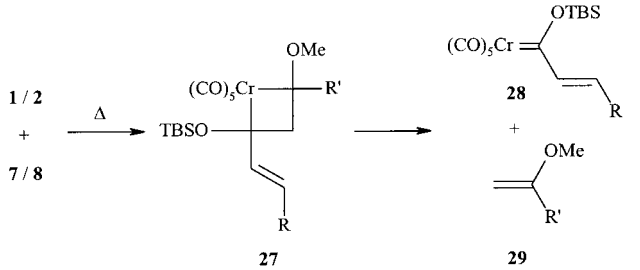
Examples of metalladiene Diels–Alder reactions are rare but have been noted before.[12] As for all [4+2] cycloadditions of two diene systems, an exchange of the diene and dienophile role in our examples would also lead to identical products when the cycloaddition is followed by a [3,3] sigmatropic rearrangement. This sequence could also deliver the chromacyclohexene **25**, but there is no evidence to support this more complicated mechanism in our examples.[13]

Reactions without incorporation of the carbene ligands: A more sophisticated interpretation is needed for the unexpected formation of cyclopentene derivatives **19** and **20** (by reaction of **1** or **2** with siloxydienes **7** or **8**), since the carbene ligand from the precursors **1** or **2** was not incorporated into the products. The results can be explained plausibly by the generation of new α,β-unsaturated carbene complexes **28** by initial carbene-ligand metathesis.[14] Formation of **28** should proceed via the chromacyclobutane intermediates **27** to afford the enol ethers **29** as by-products (Scheme 9). In fact, after reaction of **1** with **8**, 1-methoxy-1-phenylethene (**29**; $R' = C_6H_5$) was identified unambiguously in the crude product by ^{1}H NMR spectroscopy.

The new unsaturated carbene complexes **28** are probably highly reactive, as the siloxy group should be a considerably weaker donor substituent. The donor/acceptor-substituted car-



Scheme 7. Generation of the η^3-complex **24** with subsequent reductive elimination of $Cr(CO)_4$ to yield compound **11**.



Scheme 9. Formation of **28** and **29** via the chromacyclobutane intermediate **27**.

bene complex **28** ($R = CO_2CH_3$) should be particularly reactive. Subsequent reaction of **28** to give **19** or **20** may occur by the metalla Diels–Alder pathway as proposed above. The carbene-ligand metathesis/cycloaddition sequence explains why **1** and **2** gave identical products.

Conclusion

Although we do not understand entirely the effects of substituents in the reactions of unsaturated carbene complexes with 1,3-dienes, certain tendencies can be recognized. Electron-rich dienes such as Danishefsky's diene **6** and compound **7** produce mainly *cis*-divinylcyclopropanes, and subsequently cycloheptadiene derivatives. The very electron-rich unsaturated carbene complex **5** is exceptional in giving cyclopentenes as minor components by either the usual [3+2] cycloaddition pathway (with **6**) or the metalla Diels–Alder mechanism (with **7**). This latter route is generally preferred when the donor/acceptor-substituted diene **8** is used. Surprisingly, the carbene-ligand metathesis is faster than the cycloaddition pathways when simple carbene complexes such as **1** or **2** are treated with the siloxydienes **7** and **8**. The highly reactive carbene complexes **28** are generated in situ and favor the metalla Diels–Alder pathway to provide cyclopentene derivatives. This sequence of reactions of carbene complexes results in a previously unknown diene dimerization with fragmentation of a methylene unit. Electron-deficient 1,3-dienes behave normally in reactions with carbene complexes **1** and **2** and yield vinylcyclopropane derivatives.[3] With the unsaturated complexes **3**–**5** however, no clear results were obtained. The generation of cyclopentene and cycloheptadiene derivatives as described in this report is also of synthetic interest, as both types of carbocycles are highly functionalized and are therefore suitable for further synthetic investigations. Our results highlight new facets of the chemistry of Fischer carbene complexes and emphasize their versatility in organic synthesis.[15]

Experimental Section

All reactions were performed under argon in flame-dried reaction flasks.[2d] For further general information see ref. [3]. Starting materials were prepared by known procedures: **1**,[16] **2**,[17] **3**,[18] **4**,[18] **5**,[18] **6**,[19] **7**,[20] **8**.[21]

General procedure for the reactions of carbene complexes with siloxydienes: The carbene complex and the siloxydiene were dissolved in the appropriate solvent and then refluxed for the time indicated in the individual experiments. The reaction mixture was filtered through a short pad of Celite (ca. 4 cm, elution with Et_2O), the solvents were evaporated in vacuo, and $Cr(CO)_6$ was removed by rotary evaporation (0.02 mbar, 25 °C). Further methods of purification are described in the individual experiments.

2-*tert*-Butyldimethylsiloxy-4,7-dimethoxy-6-phenylcyclohepta-1,4-diene (**9**): According to the general procedure, a solution of **3** (237 mg, 0.70 mmol) and **6** (214 mg, 1.00 mmol) in acetone (5 mL) was heated for 4 h at 56 °C. The crude product (249 mg) was purified by chromatography (silica gel, hexane/ethyl acetate, 10:1) to give pure **9a** (72 mg) and a mixture of **9a** and **9b** (87:13, 56 mg) as colorless liquids (yield = 51 %).

9a: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.25-7.04$ (m, 5H; Ph), 4.78, 4.74 (d, dd, $J = 5.5$ Hz, $J = 5.9$, 1.0 Hz, 1H each; 1-H, 5-H), 4.14, 3.85 (2ddd, $J = 5.5$, 2.9, 1.0 Hz, $J = 5.9$, 2.9, 1.0 Hz, 1H each; 6-H, 7-H), 3.51, 3.34 (2s, 3H each; 4-OMe, 7-OMe), 3.32 (br. d, $J = 18.6$ Hz, 1H; 3-H), 2.79 (d, $J = 18.6$ Hz, 1H; 3-H), 0.94, 0.15 (2s, 9H, 6H; $OSiMe_2tBu$); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 153.3$, 129.5, 127.7, 126.3 (s, 3d, Ph), 149.8, 142.5 (2s, C-2, C-4), 107.6, 98.3 (2d, C-1, C-5), 79.4 (d, C-7), 56.7, 54.3 (2q, 4-OMe, 7-OMe), 46.0 (d, C-6), 39.0 (t, C-3), 25.6, 17.9, −4.6, −4.7 (q, s, 2q, $OSiMe_2tBu$).

9b: ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.25-7.04$ (m, 5H; Ph), 4.91, 4.68 (dd, d, $J = 4.8$, 1.0 Hz, $J = 5.3$ Hz, 1H each; 1-H, 5-H), 4.02, 3.81–3.69 (ddd, m, $J = 8.2$, 4.8, 1.0 Hz, 1H each; 6-H, 7-H), 3.48, 3.19 (2s, 3H each; 4-OMe, 7-OMe), 2.83 (d, $J = 18.4$ Hz, 1H; 3-H), 0.95, 0.17 (2s, 9H, 6H; $OSiMe_2tBu$); signal of the second 3-H is hidden by other signals; ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 154.5$, 128.5, 128.1, 127.1 (s, 3d, Ph), 151.5, 143.7 (2s, C-2, C-4), 107.2, 98.0 (2d, C-1, C-5), 79.7 (d, C-7), 56.6, 54.3 (2q, 4-OMe, 7-OMe), 47.4 (d, C-6), 38.7 (t, C-3), 25.5, 17.9, −4.4, −4.5 (q, s, 2q, $OSiMe_2tBu$).

9a, **9b**: IR (film): $\tilde{\nu} = 3060$, 3035, 2990, 2955, 2930 (CH), 2850 (OMe), 1635, 1615, 1490, 1460, 1450 cm^{-1} (C=C); $C_{21}H_{32}O_3Si$ (360.6): calcd C 69.95, H 8.95; found C 69.60, H 8.60.

***cis*-2-*tert*-Butyldimethylsiloxy-4,7-dimethoxy-6-(*N*-methyl-2-pyrrolyl)cyclohepta-1,4-diene** (**10**) and **4-*tert*-butyldimethylsiloxy-1-methoxy-4-(2-methoxyethenyl)-3-(2-*N*-methylpyrrolyl)cyclopent-1-ene** (**11**): According to the general procedure, a solution of **5** (512 mg, 1.50 mmol) and **6** (322 mg, 1.50 mmol) in 1,2-dichloroethane (5 mL) was heated for 6 h at 80 °C. The crude product (385 mg) was purified by chromatography (silica gel, hexane/ethyl acetate, 10:1) to give **11** (85 mg, 16 %) and **10** (140 mg, 25 %) as slightly yellow liquids.

10: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.55$ (t, $J = 2.2$ Hz, 1H; pyrrole-H), 6.09 (m_c, 2H; pyrrole-H), 4.96 (dd, $J = 5.6$, 1.2 Hz, 1H; 1-H), 4.66 (d, $J = 5.8$ Hz, 1H; 5-H), 4.13 (ddd, $J = 5.6$, 2.5, 1.3 Hz, 1H; 7-H), 3.88–3.84 (m, 1H; 6-H), 3.46 (d,* $J = 18.6$ Hz, 1H; 3-H), 3.62, 3.50, 3.35 (3s, 3H each; 4-OMe, 7-OMe, NMe), 2.75 (d, $J = 18.6$ Hz, 1H; 3-H), 0.96, 0.20, 0.19 (3s, 9H, 3H, 3H; $OSiMe_2tBu$); *further long-range couplings could not be determined; ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 153.4$, 150.3 (2s, C-2, C-4), 133.9, 121.3,** 106.3 (s, 2d, pyrrole-C), 107.6, 97.8 (2d, C-1, C-5), 78.9 (d, C-7), 56.6, 54.4 (2q, 4-OMe, 7-OMe), 38.8 (t, C-3), 38.2 (d, C-6), 34.1 (q, NMe), 25.7, 17.9, −4.6, −4.7 (q, s, 2q, $OSiMe_2tBu$); **signal of increased intensity; $C_{20}H_{33}NO_3Si$ (363.6): calcd C 66.07, H 9.15, N 3.85; found C 66.24, H 9.47, N 3.68.

11: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.54$ (t, $J = 2.2$ Hz, 1H; pyrrole-H), 6.49, 4.19 (2d, $J = 12.7$ Hz, 1H each; HC=CH), 6.02 (t, $J = 3.1$ Hz, 1H; pyrrole-H), 5.82 (dd, $J = 3.1$, 2.2 Hz, 1H; pyrrole-H), 4.48 (m_c, 1H; 2-H), 3.94 (m_c, 1H; 3-H), 3.69, 3.57, 3.24 (3s, 3H each; OMe, OMe, NMe), 2.72 (dt, $J = 16.3$, 1.3 Hz, 1H; 5-H), 2.46 (br. d, $J = 16.3$ Hz, 1H; 5-H), 0.85, 0.12, 0.09 (3s, 9H, 3H, 3H; $OSiMe_2tBu$); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta =$ 158.2 (s, C-1), 146.2 (d, HC=*C*HOMe), 133.5, 121.9, 108.1 (s, 2d, pyrrole-C), 106.5 (d, pyrrole-C, H*C*=CHOMe), 95.3 (d, C-2), 83.5 (s, C-4), 56.5, 55.5 (2q, 2OMe), 54.4 (d, C-3), 46.0 (t, C-5), 34.3 (q, NMe), 25.9, 19.1, −2.5, −2.8 (q, s, 2q, $OSiMe_2tBu$). The amount of **11** obtained was not sufficient for a correct elemental analysis.

***cis*-2-*tert*-Butyldimethylsiloxy-4-methoxy-6,7-diphenylcyclohepta-1,4-diene** (**12**): According to the general procedure, a solution of **3** (677 mg, 2.00 mmol) and **7** (651 mg, 2.50 mmol) in acetone (5 mL) was heated for 4 h at 56 °C. After a second filtration through a short pad of Celite (elution with hexane), the crude product (894 mg) was purified by chromatography (alumina, hexane) to yield siloxydiene **7** (110 mg) and **12** (230 mg, 28 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.14-7.04$ (m, 6H; Ph), 6.81–6.70 (m, 4H; Ph), 4.96, 4.57 (dd, d, $J = 6.1$, 2.2 Hz, $J = 6.5$ Hz, 1H each; 1-H, 5-H), 4.08–3.97, 3.75–3.65 (2m, 1H each; 6-H, 7-H), 3.82 (br. d, $J = 18.4$ Hz, 1H; 3-H),

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3.44 (s, 3H; OMe), 2.62 (d, $J = 18.4$ Hz, 1H; 3-H), 0.90, 0.14, 0.11 (3s, 9H, 3H, 3H; $OSiMe_2tBu$); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 154.8$, 148.5 (2s, C-2, C-4), 143.0, 141.2, 130.2, 129.3, 127.7, 127.2, 126.4 (2s, 5d, Ph), 111.3, 98.4 (2d, C-1, C-5), 54.7 (q, OMe), 50.0, 47.2 (2d, C-6, C-7), 38.5 (t, C-3), 25.8, 18.1, −4.2, −4.3 (q, s, 2q, $OSiMe_2tBu$); $C_{21}H_{32}O_3Si$ (360.6): calcd C 69.95, H 8.95; found C 68.91, H 8.91.

***cis*-3,4-Diphenylcycloheptan-1,6-dione** (**13**): A solution of **12** (104 mg, 0.28 mmol) in THF (4 mL) was stirred with 2N HCl (2 mL) for 1 h at 20 °C. The mixture was diluted with water (5 mL), extracted with dichloromethane (3 × 10 mL), and the combined organic layers were then dried over Na_2SO_4. After evaporation of solvent, **13** (49 mg, 71%) was obtained as colorless liquid, which crystallized in the refrigerator (m.p. 107–109 °C). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.15$–7.07 (m, 6H; Ph), 6.74–6.70 (m, 4H; Ph), AB-system ($\delta_A = 3.94$, $\delta_B = 3.56$, $J_{AB} = 17.3$ Hz, 1H each; 7-H), 3.74–3.66 (m, 2H; 3-H, 4-H), 3.21 (dd, $J = 15.3$, 11.4 Hz, 2H; 2-H, 5-H), 2.78 (dd, $J = 15.3$, 5.2 Hz, 2H; 2-H, 5-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 204.7$ (s, C-1, C-6), 139.6, 128.5, 128.4, 127.3 (s, 3d, Ph), 58.5 (t, C-7), 46.4 (d, C-3, C-4), 46.1 (t, C-2, C-5); IR (film): $\tilde{\nu} = 3050$, 3030, 2940, 2900, 2850 (CH), 1720, 1700 cm^{-1} (C=O); $C_{19}H_{18}O_2$ (278.4): calcd C 81.99, H 6.52; found C 80.97, H 6.61.

***cis*-2-*tert*-Butyldimethylsiloxy-6-(2-furyl)-4-methoxy-7-phenylcyclohepta-1,4-diene** (**14**): According to the general procedure, a solution of **4** (656 mg, 2.00 mmol) and **7** (521 mg, 2.00 mmol) in cyclohexane (5 mL) was heated for 9.5 h at 80 °C. After a second filtration through a pad of Celite, the crude product (674 mg) was purified by chromatography (silica gel, hexane/ethyl acetate, 9:1) to give **14** (298 mg, 38%). ^1H NMR (300 MHz, $CDCl_3$): $\delta =$ 7.15 (m_c, 3H; Ph), 6.86–6.83 (m, 2H; Ph), 6.27 (m_c, 2H; furyl-H), 5.82 (d, $J = 3.2$ Hz, 1H; furyl-H), 5.06, 4.39 (dd, br. d, $J = 6.0$, 2.4 Hz, $J = 6.9$ Hz, 1H each; 1-H, 5-H), 4.28, 4.01 (dd, dt, $J = 6.9$, 2.7 Hz, $J = 6.0$, 3.2 Hz, 1H each; 6-H, 7-H), 3.81, 2.66 (d, br. d, $J = 18.5$ Hz, 1H each; 3-H), 3.49 (s, 3H; OMe), 0.96, 0.20, 0.18 (3s, 9H, 3H, 3H; $OSiMe_2tBu$); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 155.9$, 140.7, 111.4, 105.9 (s, 3d, furyl-C), 147.8, 140.6 (2s, C-2, C-4), 140.8, 129.5, 127.0, 126.2 (s, 3d, Ph), 110.1, 94.6 (2d, C-1, C-5), 54.7 (q, OMe), 47.5, 39.7 (2d, C-6, C-7), 38.4 (t, C-3), 25.7, 17.9, −4.4, −4.5 (q, s, 2q, $OSiMe_2tBu$). The high sensitivity of **14** towards oxygen precluded any correct elemental analysis.

***cis*-2-*tert*-Butyldimethylsiloxy-4-methoxy-6-(2-*N*-methylpyrrolyl)-7-phenylcyclohepta-1,4-diene** (**15**) and **5-*tert*-butyldimethylsiloxy-1-methoxy-3-(2-*N*-methylpyrrolyl)-5-(2-phenylethenyl)cyclopent-1-ene** (**16**): According to the general procedure, a solution of **5** (680 mg, 2.00 mmol) and **7** (650 mg, 2.50 mmol) in cyclohexane (5 mL) was heated for 13 h at 80 °C. The crude product (800 mg, yellow oil) was purified by chromatography first on silica gel (hexane/ethyl acetate, 20:1) and then on alumina (hexane/ethyl acetate, 50:1). Thus, **7** (236 mg) was recovered and **15**/**16** were obtained as a 90:10 mixture (71 mg, 10% yield).

15: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.17$–7.12 (m, 3H; Ph), 6.78–6.75 (m, 2H; Ph), 6.49 (t, $J = 2.1$ Hz, 1H; pyrrole-H), 5.98 (t, $J = 3.1$ Hz, 1H; pyrrole-H), 5.57 (br. s, 1H; pyrrole-H), 5.04, 4.47 (dd, br. d, $J = 6.0$, 2.2 Hz, $J = 6.5$ Hz, 1H each; 1-H, 5-H), 4.09–4.03, 3.71–3.66 (2m, 1H each; 6-H, 7-H), 3.82 (br. d, $J = 18.6$ Hz, 1H; 3-H), 3.45 (s, 3H; OMe), 3.30 (br. s, 3H; NMe), 2.65 (d, $J = 18.6$ Hz, 1H; 3-H), 0.95, 0.20, 0.16 (3s, 9H, 3H, 3H; $OSiMe_2tBu$); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 154.4$, 149.1 (2s, C-2, C-4), 141.5, 130.0, 127.4, 126.5 (s, 3d, Ph), 133.9, 121.4, 108.2, 106.6 (s, 3d, pyrrole-C), 111.3, 98.8 (2d, C-1, C-5) 54.8 (q, OMe), 48.2, 38.6 (2d, C-6, C-7), 38.6 (t, C-3), 33.6 (q, NMe), 26.2, 18.2, −4.1, −4.2 (q, s, 2q, $OSiMe_2tBu$).

16: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.35$–7.10 (m, 5H; Ph), 6.61, 6.27 (2d, $J = 15.9$ Hz, 1H each; HC=CH), 6.54 (t, $J = 2.2$ Hz, 1H; pyrrole-H), 6.04 (t, $J = 3.1$ Hz, 1H; pyrrole-H), 5.90 (dd, $J = 3.1$, 2.2 Hz, 1H; pyrrole-H), 4.77 (d, $J = 2.1$ Hz, 1H; 2-H), 4.02 (ddd, $J = 7.0$, 6.0, 2.1 Hz, 1H; 3-H), 3.66, 3.58 (2s, 3H each; OMe, NMe), 2.50 (dd, $J = 13.0$, 7.0 Hz, 1H; 4-H), 1.88 (dd, $J = 13.0$, 6.0 Hz, 1H; 4-H), 0.12, 0.10 (2s, 3H each; $OSiMe_2$); signal of the *tert*-butyl group is identical to that of **15**; ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta =$ 128.7, 128.2, 126.8 (3d, Ph), 121.9, 106.8, 104.7 (3d, pyrrole-C), 100.0 (d, C-2), 84.3 (s, C-5), 57.1 (q, OMe), 47.6 (t, C-4), 26.2, −2.9, −3.1 (3q, $OSiMe_2tBu$); other signals could not be identified. The small amount and the high sensitivity of **15**/**16** towards oxidation precluded any correct elemental analysis.

Methyl *E*-3-(1-*tert*-butyldimethylsiloxy-2-methoxy-4-phenylcyclopent-2-en-1-yl)propenoate (**17**): According to the general procedure, a solution of **3** (680 mg, 2.00 mmol) and **8** (730 mg, 3.00 mmol) in 1,2-dichloroethane (10 mL) was heated for 18 h at 80 °C. The crude product (905 mg) was purified by chromatography (silica gel, hexane/ethyl acetate, 10:1) to give a mixture of **17** with siloxydiene **8** (547 mg), and a 86:14 mixture of **17** with an isomer (182 mg, 23%). From the fraction which contained the starting material **8,** compound **17** was readily removed by rotary evaporation (0.02 mbar, 50 °C). The resulting colorless residue was pure **17** (407 mg, 52%), which crystallized in the refrigerator (m.p. 60–63 °C). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.26$–7.08 (m, 5H; Ph), 6.90, 6.02 (2d, $J = 15.4$ Hz, 1H each; HC=CH), 4.69 (d, $J = 1.9$ Hz, 1H; 3′-H), 3.96 (ddd, $J = 7.8$, 6.2, 1.9 Hz, 1H; 4′-H), 3.65, 3.59 (2s, 3H each; CO_2Me, OMe), 2.43 (dd, $J =$ 14.2, 7.8 Hz, 1H; 5′-H), 1.95 (dd, $J = 14.2$, 6.2 Hz, 1H; 5′-H), 0.87, 0.05, 0.04 (3s, 9H, 3H, 3H; $OSiMe_2tBu$); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 167.2$ (s, CO_2Me), 160.8 (s, C-2′), 152.3 (d, C-3), 145.7, 128.5, 126.9, 126.4 (s, 3d, Ph), 119.0 (d, C-2), 102.8 (d, C-3′), 83.8 (s, C-1′), 56.9, 51.4 (2q, CO_2Me, OMe), 49.1 (t, C-5′), 44.2 (d, C-4′), 25.8, 18.4, −3.0, −3.1 (q, s, 2q, $OSiMe_2tBu$); IR (film): $\tilde{\nu} = 3070$, 3030, 3020, 2960, 2940, 2900 (CH), 1720 (C=O), 1660, 1640, 1600 cm^{-1} (C=C); $C_{22}H_{32}O_4Si$ (388.6): calcd C 68.00, H 8.30; found C 67.86, H 8.37.

The following signals are assigned to an unknown isomer of **17**: ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.73$, 6.33 (2d, $J = 16.0$ Hz, 1H each; HC=CH), 3.68 (s, 3H; OMe); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 175.0$ (s, CO_2Me), 156.9 (s), 152.0, 117.9 (2d), 103.8 (d), 52.1, 51.8 (2q, CO_2Me, OMe), 43.5 (d), 40.3 (t), 25.7, 18.2, −3.1, −3.4 (q, s, 2q, $OSiMe_2tBu$).

Methyl *E*-3-[1-*tert*-butyldimethylsiloxy-2-methoxy-4-(2-furyl)cyclopent-2-en-1-yl]propenoate (**18**): According to the general procedure, a solution of **4** (810 mg, 2.47 mmol) and **8** (727 mg, 3.00 mmol) in 1,2-dichloroethane (10 mL) was heated for 18 h at 80 °C. After a second filtration through a pad of Celite (elution with pentane), the brownish crude product (922 mg) was purified by column chromatography (silica gel, hexane/ethyl acetate, 20:1) to yield **18** (457 mg, 49%) as colorless crystals (m.p. 59–64 °C). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.31$ (dd, $J = 1.9$, 0.6 Hz, 1H; furyl-H), 6.94, 6.07 (2d, $J = 15.4$ Hz, 1H each; HC=CH), 6.27 (dd, $J = 3.0$, 1.9 Hz, 1H; furyl-H), 6.00 (dd, $J = 3.0$, 0.6 Hz, 1H; furyl-H), 4.70 (d, $J = 2.1$ Hz, 1H; 3′-H), 4.05 (ddd, $J = 7.9$, 5.4, 2.1 Hz, 1H; 4′-H), 3.72, 3.62 (2s, 3H each; OMe, CO_2Me), 2.43 (dd, $J = 14.0$, 7.9 Hz, 1H; 5′-H), 2.23 (dd, $J = 14.0$, 5.4 Hz, 1H; 5′-H), 0.91, 0.07 (2s, 9H, 6H; $OSiMe_2tBu$); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 167.0$ (s, CO_2Me), 160.7 (s, C-2′), 157.9, 141.2, 110.0, 104.0 (s, 3d, furyl-C), 152.0, 118.9 (2d, C-3, C-2), 99.6 (d, C-3′), 83.2 (s, C-1′), 56.7, 51.3 (2q, OMe, CO_2Me), 44.8 (t, C-5′), 37.3 (d, C-4′), 25.7, 18.2, −3.6, −3.7 (q, s, 2q, $OSiMe_2tBu$); IR (film): $\tilde{\nu} = 3150$, 3125, 3075, 3010, 2960, 2930, 2900 (CH), 2850 (OMe), 1720 (C=O), 1650 cm^{-1} (C=C); $C_{20}H_{30}O_5Si$ (378.6): calcd C 63.46, H 7.99; found C 63.42, H 8.26.

2,3-Bis(*tert*-butyldimethylsiloxy)-5-phenyl-3-(2-phenylethenyl)cyclopent-1-ene (**19**):

From compound **1**: According to the general procedure, a solution of **1** (312 mg, 1.00 mmol) and **7** (781 mg, 3.00 mmol) in cyclohexane (5 mL) was heated for 17 h at 80 °C. The crude product was filtered through a pad of alumina (elution with hexane). After evaporation of solvent, the resulting mixture (702 mg, yellow oil) consisted of **7** and product **19**. Siloxydiene **7** was removed by rotary evaporation (70–90 °C, 0.02 mbar). The residue was pure **19** (502 mg, 99%), as confirmed by NMR spectroscopy.

From compound **2**: According to the general procedure, a solution of **2** (423 mg, 1.69 mmol) and **7** (881 mg, 3.38 mmol) in cyclohexane (5 mL) was heated for 8 h at 80 °C. The crude product was purified by chromatography (silica gel, hexane/ethyl acetate, 10:1) to give a mixture of **19** and **7** (approximately 80:20). Most of the siloxydiene **7** could be removed by rotary evaporation (50 °C, 0.02 mbar) to give a residue (509 mg, 59%), which consisted mainly of **19** (**19**:**7** = 96:4). ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.40$–7.22 (m, 10H; Ph), 6.64, 6.34 (2d, $J = 16.0$ Hz, 1H each; HC=CH), 4.91 (d, $J = 2.0$ Hz, 1H; 1-H), 4.05 (ddd, $J = 8.0$, 6.0, 2.0 Hz, 1H; 5-H), 2.61, 2.11 (2 dd, $J = 14.0$, 8.0 Hz, $J = 14.0$, 6.0 Hz, 1H each; 4-H), 1.01, 1.00 (2s, 9H each; *t*Bu), 0.28, 0.26, 0.20, 0.19 (4s, 3H each; Me); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 157.3$ (s, C-2), 146.3, 137.2 (2s, *ipso*-C-Ph), 134.0, 128.8 (2d, HC=CH), 128.7, 127.2, 126.7 (3d, Ph), 108.3 (d, C-1), 84.7 (s, C-3), 48.5 (t, C-4), 44.0 (d, C-5), 25.9, 25.6 (2q, *t*Bu), 18.4, 18.1 (2s, *t*Bu), −3.0, −4.3, −4.6 (3q, Me); The assignments are proved by the GRAD-INV-CH technique; IR (film): $\tilde{\nu} = 3100$–3000 (CH), 2950–2880 (CH), 1640 cm^{-1} (C=C); $C_{31}H_{46}Si_2O_2$ (506.9): calcd C 73.46, H 9.15; found C 73.45, H 9.11.

Methyl *E*-3-[1,2-bis(*tert*-butyldimethylsiloxy)-4-methoxycarbonylcyclopent-2-en-1-yl]-propenoate (**20**):

From compound **1**: According to the general procedure, a solution of **1** (312 mg, 1.00 mmol) and **8** (727 mg, 3.00 mmol) in 1,2-dichloroethane (5 mL) was heated for 8 h at 80 °C. The crude product was purified by chromatography (silica gel, hexane/ethyl acetate, 15:1) to yield pure **20** (468 mg, 99 %).

An experiment in solution in cyclohexane (36 h, 80 °C) provided a similar result (39 % of **20**). In the crude reaction mixture we also identified 1-methoxy-1-phenylethene (**29**) ($R' = C_6H_5$) by its NMR signals (^{1}H NMR : $\delta = 4.71$, 4.27 (2 d, $J = 2.8$ Hz; CH_2), 3.96 (s, OCH_3); ^{13}C NMR : $\delta = 81.7$ (t, C-2), 160.8 (s, C-1); further signals could not be assigned because of the presence of several other components including **20**).[22]

From compound **2**: According to the general procedure, a solution of **2** (500 mg, 2.00 mmol) and **8** (2.42 g, 10.0 mmol) in cyclohexane (5 mL) was heated for 18 h at 80 °C. The crude product (2.86 g) was purified by chromatography (silica gel, hexane/ethyl acetate, 15:1) to give **20** (158 mg, 17 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.89$, 6.07 (2 d, $J = 15.6$ Hz, 1 H each; HC=CH), 4.79 (d, $J = 2.4$ Hz, 1 H; 2′-H), 3.72, 3.69 (2 s, 3 H each; CO_2Me), 3.57 (ddd, $J = 8.2$, 5.0, 2.4 Hz, 1 H; 3′-H), 2.41 (dd, $J = 14.3$, 5.0 Hz, 1 H; 5′-H), 2.22 (dd, $J = 14.3$, 8.2 Hz, 1 H; 5′-H), 0.88, 0.16, 0.13 (3 s, 9 H, 3 H, 3 H; $OSiMe_2tBu$); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 174.9$, 167.1 (2 s, C-1, *C*O_2Me), 156.8 (s, C-2′), 151.8, 119.6 (2 d, C-2, C-3), 103.6 (d, C-3′), 83.8 (s, C-1′), 52.0, 51.4 (2 q, CO_2Me), 43.4 (d, C-4′), 40.2 (t, C-5′), 25.8, 18.3, −3.8 (q, s, q, $OSiMe_2tBu$); $C_{23}H_{42}Si_2O_6$ (470.8): calcd C 58.68, H 8.99; found C 58.24, H 8.94.

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