Reactions of Fischer carbene complexes with electron-deficient olefins: scope and limitations of this route to donor-acceptor-substituted cyclopropanes

Anette Wienand, and Hans Ulrich Reissig

Organometallics, **1990**, 9 (12), 3133-3142• DOI: 10.1021/om00162a027 • Publication Date (Web): 01 May 2002

HRMS (*m/e*) calcd for $C_8H_{17}ClSi$ 176.0788, found 176.0814; HRMS (*m/e*) calcd for $C_8H_{17}ClSi$ 177.0822, found 177.0801.

***trans*-1-(Dichloromethylsilyl)-1-hexene (2f)**: ^1H NMR δ 0.80 (s, 3 H), 0.95 (s, 3 H), 1.40 (m, 4 H), 2.20 (dt, J = 7.0, 5.7, Hz, 2 H), 5.75 (d, J = 19.0 Hz, 1 H), 6.51 (d, J = 19.0, 5.7 Hz, 1 H); MS (*m/e*, %) 198 (M^+ + 2, 0.6), 196 (M^+, 1), 183 (1.2), 181 (2.1), 169 (9), 167 (11), 156 (31), 154 (45), 115 (71), 113 (100).

2-(Dichloromethylsilyl)-1-hexene (3f): ^1H NMR δ 0.79 (s, 3 H), 0.94 (t, J = 6.5 Hz, 3 H), 1.40 (m, 4 H), 2.20 (t, J = 7.0 Hz, 2 H), 5.71 (s, 1 H), 5.84 (s, 1 H); MS (*m/e*, %) 198 (M^+ + 2, 2), 196 (M^+, 4), 183 (2.7), 181 (3.9), 169 (9), 167 (12), 156 (10), 154 (15), 115 (71), 113 (100).

***trans*-1-(Trimethoxysilyl)-1-hexene (2g)**: ^1H NMR δ 0.95 (t, J = 6.5 Hz, 3 H), 1.40 (m, 4 H), 2.18 (q, J = 7.0, 6.2 Hz, 2 H), 3.48 (s, 9 H), 5.38 (d, J = 18.9 Hz, 1 H), 6.43 (dt, J = 18.9, 6.2 Hz, 1 H); MS (*m/e*, %) 204 (M^+, 3), 172 (20), 143 (12), 121 (100), 91 (60); HRMS (*m/e*) calcd for $C_9H_{20}O_3Si$ 204.118, found 204.1192 (5).

2-(Trimethoxysilyl)-1-hexene (3g): ^1H NMR δ 0.95 (t, J = 6.5 Hz, 3 H), 1.40 (m, 4 H), 2.20 (t, J = 7.0 Hz, 2 H), 3.48 (s, 9 H), 5.62 (bs, 1 H), 5.75 (bs, 1 H); MS (*m/e*, %), 204 (M^+, 10), 121 (100), 91 (65); HRMS (*m/e*) calcd for $C_9H_{20}O_3Si$ 204.118; found 204.1182 (5).

Acknowledgment. This work was supported by grants from the National Science Foundation, the National Institutes of Health, and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Professor Robert H. Crabtree, Department of Chemistry, Yale University, for sending us a preprint of his related work prior to publication.

Reactions of Fischer Carbene Complexes with Electron-Deficient Olefins: Scope and Limitations of This Route to Donor–Acceptor-Substituted Cyclopropanes[1]

Anette Wienand and Hans-Ulrich Reissig*

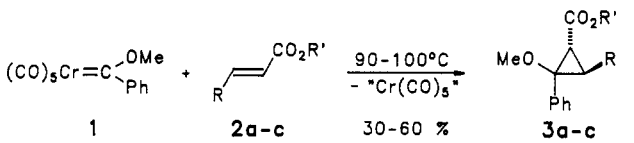
Institut für Organische Chemie der Technischen Hochschule Darmstadt, Petersenstrasse 22, D-6100 Darmstadt, FRG

Received July 10, 1990

The Fischer carbene complex $[(CO)_5Cr{=}C(OMe)Ph]$ (**1**) is able to transfer its carbene ligand to a variety of electron-deficient olefins and provides donor–acceptor-substituted cyclopropanes in good yields. Apt activating groups with respect to the alkene are ester, amide, nitrile, sulfone, and dialkyl phosphonate functions. Methyl vinyl ketone (**19**) affords products in low yield that may arise from an intermediate cyclopropane derivative. Phenyl vinyl sulfoxide (**24**) mainly acts as an oxidizing agent, transforming **1** into methyl benzoate. For olefin **24** and α-(*N*-methylanilino)acrylonitrile we found products that should be formed on an olefin metathesis pathway. The methyl-substituted carbene complex **48** also affords the expected donor–acceptor-substituted cyclopropanes; however, acyclic isomers are formed in higher amounts. The molybdenum and tungsten complexes **55** and **56**, respectively, also furnish cyclopropane derivatives, but the yields are lower than with the chromium compound **1**. Disubstituted olefins and complex **1** still give the cyclopropanes in moderate yields, while all trisubstituted and most of the difunctionalized alkenes do not react with this Fischer carbene complex. The cyclopropanes synthesized can be deprotonated and alkylated or transformed into ring-opened products. These model reactions demonstrate the synthetic potentials of donor–acceptor-substituted cyclopropanes prepared via Fischer carbene complexes.

Introduction

Since the fundamental discovery of carbene complexes by Fischer and co-workers these novel organometallic compounds have found a number of highly interesting applications as building blocks for organic synthesis.[2] Among the very first reactions with the standard chromium carbene complex **1** were the formal [2 + 1] cycloadditions with electron-rich[3] and electron-deficient olefins,[4] which provide difunctional cyclopropanes. Thus, compound **1** and α,β-unsaturated esters **2a–c** furnish the corresponding donor–acceptor-substituted cyclopropanes **3a–c** in reasonable yields (eq 1).



1 **2a–c** 30–60 % **3a–c**

a R, R' = Me **b** R = Ph, R' = Me **c** R = CO_2Et, R' = Et (1)

Donor–acceptor-substituted cyclopropanes—usually prepared by alternative routes—have gained attention because of their high potential to serve as versatile intermediates.[5] They are precursors of a variety of heter-

(1) Wienand, A. Dissertation, Technische Hochschule Darmstadt, 1990.

(2) Reviews: (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, FRG, 1983. (b) Dötz, K. H. *Angew. Chem.* **1984**, *96*, 595; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (c) Aumann, R. *Angew. Chem.* **1988**, *100*, 1512; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1456. (d) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1989; Vol. 1. (e) Hegedus, L. S. In *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989; p 233.

(3) Dötz, K. H.; Fischer, E. O. *Chem. Ber.* **1972**, *105*, 3966. For a review on more recent work in this area see: Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411.

(4) (a) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1970**, *103*, 1273. (b) Dötz, K. H.; Fischer, E. O. *Chem. Ber. 1972*, **105**, 1356. (c) Cooke, M. D.; Fischer, E. O. *J. Organomet. Chem.* **1973**, *56*, 279.

(5) Review: Reissig, H.-U. *Top. Curr. Chem.* **1988**, *144*, 73.

0276-7333/90/2309-3133$02.50/0

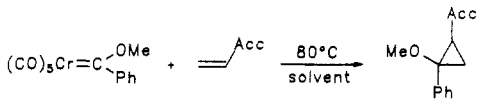
Table I. Reactions of Chromium Carbene Complex 1 with Acceptor-Substituted Olefins

acceptor (Acc)	olefin	solvent	time, h	yield, %	products: cyclopropanes (trans/cis)	products: other	ratio
CO_2Me	4	C_6H_{12}	5.5	75	9	14	39:58:3
$CONMe_2$	5	$(ClCH_2)_2$	3.5	78	10	15, 16	52:45:1:2
CN	6	$(ClCH_2)_2$	5	89	11	17	44:44:12
$PO(OMe)_2$	7	C_6H_{12}	3.5	79	12		50:50
SO_2Ph	8	$(ClCH_2)_2$	2	49	13	18	40:36:24

ocycles or carbocycles, as well as of acyclic 1,4-dicarbonyl compounds and derivatives thereof, including natural products.[6] Interest in this type of cyclopropanes brought us to revisit the Dötz–Fischer reaction of chromium carbene complexes with electron-deficient olefins to explore the scope and limitations of this potentially very valuable route toward functionalized cyclopropanes. Only β-substituted α,β-unsaturated esters had been employed (in large excess) as carbenophiles (eq 1).[4] Also, phenyl-substituted carbene complexes had served as the exclusive carbene source. Here we describe our preparatively relevant results,[7] demonstrating that a rather broad variety of different donor–acceptor-substituted cyclopropanes are accessible by this approach, while a forthcoming paper will deal with the mechanism of the carbene transfer.[8]

Results

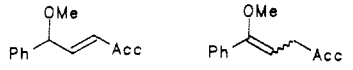
Reactions of Complex 1 with Olefins Bearing Different Electron-Withdrawing Groups. Employing the standard chromium carbene complex **1**, we first screened various olefins with different acceptor groups. As given in eq 2 and Table I *mono*substituted alkenes **4–8** bearing



(2)

1 4 - 8 9 - 13

Acc: CO_2Me, $CONMe_2$, CN, $PO(OMe)_2$, SO_2Ph



14, 15 16 - 18

ester, amide, nitrile, phosphonic ester, and sulfone functions react rather smoothly with **1** to provide the desired cyclopropane derivatives **9–13** in generally good yields.

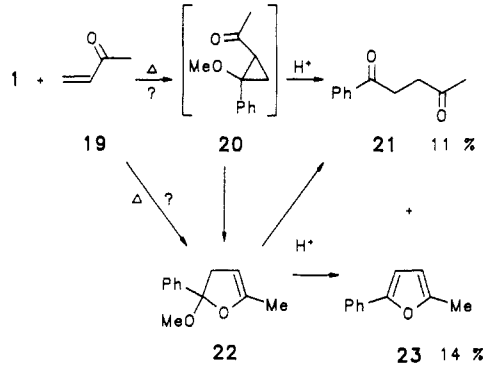
All experiments were performed with *equimolar* amounts of both components at 80 °C. The nature of the solvent used is not very important with respect to yields, as many experiments of **1** with methyl acrylate or acrylonitrile have revealed.[1,8] However, a moderate influence of the solvent polarity on the trans/cis distribution of **9** and **11** was recognized, which is close to 1:1 for the nonpolar solvents such as cyclohexane and 1,2-dichloroethane employed under standard conditions (Table I).

The expected cyclopropane derivatives **9–13** were accompanied in varying though reproducible quantities by the acyclic isomers **14–18** (Table I). Control experiments proved that the enol ether derivatives **16–18** were formed by rearrangement from the corresponding cyclopropanes **10**, **11**, and **13**.[1] This cleavage of the strained three-membered ring can be catalyzed either by protons or by organometallic species, as is known for other donor–acceptor-substituted cyclopropanes.[5,9] Larger amounts of these enol ethers were generated in 1,2-dichloroethane as solvent, which is a potential source of traces of HCl. Addition of basic alumina strongly diminished this side reaction. These observations are taken as evidence for proton catalysis.[1]

On the other hand, the acyclic isomers **14** and **15** do not arise from the cyclopropanes **9** and **10** but directly from the olefins and carbene complex **1**. For certain alkenes as precursors,[10] and in particular with acetonitrile as solvent, the amount of these "insertion products" can increase considerably.

It is important to note that approximately 50% of the chromium could be recovered as $Cr(CO)_6$, which precipitates at the sublimation finger introduced (into the reaction flask) during the course of the reaction (see Experimental Section). This setup allows the observation of the reaction progress as well as the recycling of $Cr(CO)_6$ for the preparation of **1**. Our experiments also demonstrate that an excess of olefins is not required to obtain good yields of cyclopropanes. Actually, we had less satisfying results in several cases when 10 equiv of alkenes was used. Possibly the more tedious separation of the desired products from olefin polymers diminished the yield.

The clear results with olefins **4–8** were in contrast with experiments employing other electrophilic alkenes. Starting with methyl vinyl ketone (**19**) and complex **1**, the



expected cyclopropane derivative **20** could not be isolated. Instead, a complex mixture of products was obtained, which was simplified by treatment with 2 N hydrochloric acid to give the 1,4-diketone **21** and furan derivative **23**. After purification both compounds were isolated in low yield.

Formation of these products can be explained either via cyclopropane **20** or via dihydrofuran **22**, which could arise directly by a [4 + 1] cycloaddition[11] of **1** and **19**. Alter-

(6) Zschiesche, R.; Hafner, T.; Reissig, H.-U. *Liebigs Ann. Chem.* **1988**, 1169. Marino, J. P.; Silveira, C.; Comasseto, J.; Petragnani, N. *J. Org. Chem.* **1987**, *52*, 4139.

(7) For a preliminary report see: Wienand, A.; Reissig, H.-U. *Tetrahedron Lett.* **1988**, *29*, 2315. For the use of diene esters see: Buchert, M.; Reissig, H.-U. *Tetrahedron Lett.* **1988**, *29*, 2319. For a short review see: Reissig, H.-U. In *Organometallics in Organic Synthesis 2*; Werner, H., Erker, G., Eds.; Springer-Verlag: Berlin, 1989; p 311.

(8) Wienand, A.; Reissig, H.-U. Manuscript in preparation.

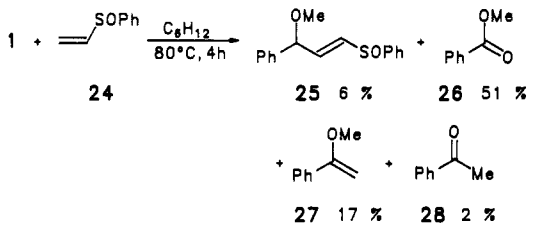
(9) (a) Doyle, M. P.; van Leusen, D. *J. Am. Chem. Soc.* **1981**, *103*, 5917. (b) Reissig, H.-U. *Tetrahedron Lett.* **1985**, *26*, 3943.

(10) Wienand, A.; Reissig, H.-U. *Angew. Chem.* **1990**, *102*, 1156; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1129. Acyclic products of this type had exclusively been obtained from $(CO)_4FeC(OEt)R$ and monosubstituted olefins: Semmelhack, M. F.; Tamura, R. *J. Am. Chem. Soc.* **1983**, *105*, 6750.

natively, the ring enlargement **20** → **22** is possible. ^{1}H NMR analysis of the crude reaction mixture (before acid treatment) suggested the presence of **22** because of a triplet signal appearing at δ 4.85. Diketone **21** is formed by hydrolysis of **22** (or **20**), while **23** is the result of an elimination of methanol from **22**.

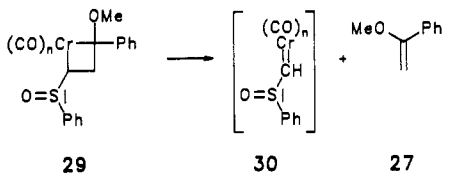
Experiments employing **1** and 2-methyl-1-buten-3-one or 3-penten-2-one as olefins indicate that furan derivatives corresponding to **23** were formed.[1] However, these compounds are only minor components, and they could not be isolated in pure form. Crotonaldehyde and styrene did not provide cyclopropanes or other low-molecular-weight products with **1**. Polymerization of these olefins seems to be the major pathway.

An interesting result was obtained with phenyl vinyl sulfoxide (**24**). Heating this olefin with carbene complex



1 for 4 h afforded a mixture of four compounds, but none of these were the anticipated cyclopropane. The adduct was the insertion product **25**, obtained in 6% yield after purification. The major compound is methyl benzoate (**26**; 51% yield), which was presumably formed from oxidation of **1** by the sulfoxide function of **24**. Similar reactions of Fischer carbene complexes with dimethyl sulfoxide as the oxygen source are known.[12]

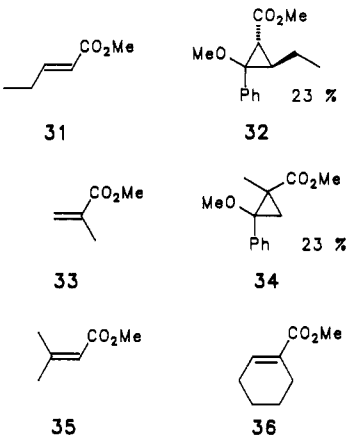
The other two compounds isolated, the enol ether **27** and acetophenone (**28**), must arise by an olefin metathesis process. Hydrolysis of **27** is responsible for the small amount of acetophenone. To our knowledge olefin metathesis has never been observed with Fischer carbene complexes and electron-deficient olefins.[13] Possibly, the intermediate metallacyclobutane **29** is able to split into **27**



and the carbene complex **30** because the sulfoxide moiety might stabilize the carbene center with the sulfur lone pair.[14] Of course, this pathway is speculative, since **30** or products derived thereof could not be detected.

Although 2-nitropropene is an α,α-disubstituted olefin, its reaction with **1** should be mentioned here. Methyl benzoate was the only substance of many products that could be identified. It very likely arises from oxidation of the carbene complex by the nitro function. A control experiment with nitrobenzene and **1** revealed that the nitro group can be an oxygen-transfer reagent, furnishing methyl benzoate **26** rather efficiently.[1] To our knowledge the reaction of Fischer carbene complexes with nitro compounds has so far not been described.[15]

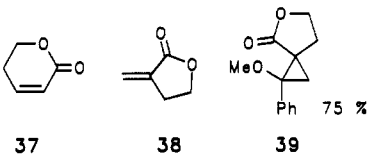
Reactions of Complex 1 with Disubstituted and Trisubstituted Electron-Deficient Alkenes. Fischer and Dötz had already reported on the thermal reactions of carbene complex **1** with an excess of methyl crotonate (**2a**) or methyl cinnamate (**2b**), which provided the corresponding methyl cyclopropanecarboxylates **3a,b** in 60% and 34% yield (eq 1). We obtained similar results employing only equimolar amounts of starting materials. For a further definition of the scope and limitations of this carbene-transfer reaction, we also examined the α,β-unsaturated esters **31**, **33**, **35**, and **36**. While the β-ethyl-



substituted alkene **31** and the α-methyl-bearing olefin **33** provided the expected cyclopropanes **32** and **34** with rather moderate efficiency, the presence of two alkyl groups in compounds such as **35** and **36** apparently prevents the [2 + 1] cycloaddition. No cyclopropanes derived from these trisubstituted alkenes could be detected.

Similarly, when methyl α-phenylacrylate was chosen as the substrate for **1**, no reaction could be observed even after 32 h at 80 °C.[1] Thus, steric hindrance caused by either the number or the size of the substituents seems to be a severe limitation of this route to cyclopropanes.

The two unsaturated lactones **37** and **38** were tested in order to study the influence of a fixed transoid or cisoid conformation of the enoate moiety. Surprisingly, only **38** afforded the expected spirocyclopropanes **39** in good yield, while **37** was completely unreactive.



The failure to transfer the carbene ligand of **1** to **37** must also be compared to the reaction of the carbene complex with methyl isocrotonate (*Z* isomer of compound **2a**), which furnished the corresponding cyclopropanes in moderate yield.[1] Due to the observed lack of stereospecificity, this experiment is of high mechanistic importance and will be described and discussed in a forthcoming paper.[8] In a comparison of **38** and **33**, the higher reactivity of the lactone is remarkable. Possibly, the carbene transfer to the C=C bond requires a cisoid location of the carbonyl

(11) A formal [4 + 1] cycloaddition was reported for complex **48** and an *N*-Acyl imine: Fischer, E. O.; Weiss, K.; Burger, K. *Chem. Ber.* **1973**, *106*, 1581.

(12) (a) Casey, C. P.; Burkhardt, T. J.; Bunell, C. A.; Calabrese, J. *J. Am. Chem. Soc.* **1977**, *99*, 2127. (b) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726.

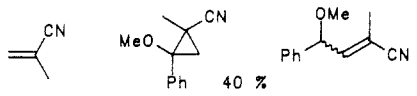
(13) Dötz, K. H.; Pruskil, I. *Chem. Ber.* **1981**, *114*, 1980. Casey, C. P.; Tuinstra, H. E.; Saeman, M. C. *J. Am. Chem. Soc.* **1976**, *98*, 608. See also ref 3.

(14) For the electronic effects of sulfoxide groups see: Shorter, J. In *The Chemistry of Sulphones and Sulfoxides*; Patai, S., Rappoport, Z., Stirling, C., Eds.; Wiley: Chichester, England, 1988; p 483.

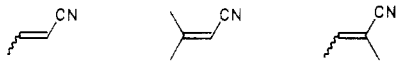
(15) Reactions of complex **1** with nitroso compounds: Herndon, J. W.; McMullen, L. A. *J. Organomet. Chem.* **1989**, *368*, 83. Reactions of complex **56** with nitrosobenzene: Pilato, R. S.; Williams, G. D.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 3665.

moiety. This would also explain the inertness of lactone **37**.

The influence of additional substituents is very similar with unsaturated nitrile derivatives. However, the situation is complicated due to the higher tendency to give acyclic isomers by the competing insertion reaction of the carbene ligand into the β-CH bond of these olefins. While acrylonitrile (**6**) and **1** provided the expected cyclopropane **11** in good yield (eq 2, Table I), α-methylacrylonitrile (**40**)



40 **41** (~2:1) **42** 40 %

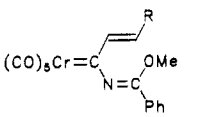


43 **44** **45**

gave a 2:1 mixture of cyclopropane **41** and the insertion product **42** in 40% yield. The (*E*/*Z*)-crotonitriles **43** slowly react with carbene complex **1**, but the result is highly dependent on the solvent employed. In cyclohexane a stereospecific insertion in to the β-CH bond of (*E*/*Z*)-**43** was observed, while in acetonitrile the expected cyclopropyl cyanide predominated.[10] These results will be discussed in the paper dealing with mechanistic details.[8]

Not unexpectedly, the dialkyl-substituted acrylonitrile derivatives **44** and **45** did not afford cyclopropanes. Also, it is interesting to realize that no insertion of the nitrile function of **44** into the chromium–carbene bond of **1** could be observed even under forced conditions. This process is well-known to occur with amino nitriles or similar derivatives,[16] and more recently simple aliphatic and aromatic nitriles have successfully been used to provide new (methyleneamino)carbene complexes.[17] This reaction is known to be reversible. Possibly, the equilibrium of **44** + **1** and the insertion complex is essentially on the side of the starting materials.

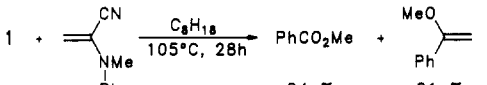
Reactions of Complex 1 with Difunctional Olefins. Whereas the reactions of **1** with dimethyl fumarate and dimethyl maleate are known to be successful in providing the expected cyclopropanes,[4b] this carbene complex and other difunctional olefins such as methyl 4-oxo-2-pentenoate, fumarodinitrile, α-ethoxyacrylonitrile, and α-chloroacrylonitrile did not furnish cyclopropanes or other characterizable organic materials.[1] On the other hand, insertion of β-(dimethylamino)- and β-methoxyacrylonitriles with their nitrile group into the Cr=C bond of **1** afforded the novel alkenyl-substituted complexes **46**.[18]



46a R = NMe_2
46b R = OMe

The corresponding β-dimethylamino acrylic ester did not react at all with **1**, while methyl β-methoxyacrylate gives small amounts of the expected cyclopropane as well as of a second product that remains to be identified with certainty.[19]

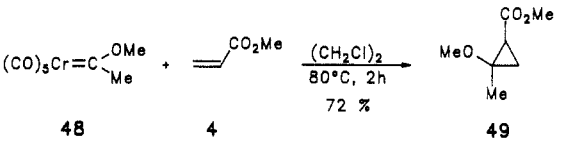
The thermal reaction of **1** with α-(*N*-methylanilino)-acrylonitrile (**47**) is of some interest. The formation of



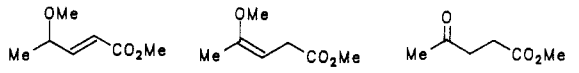
47 **26** 24 % **27** 21 %

enol ether **27** can again be explained by an olefin metathesis pathway involving a chromacyclobutane whose fragmentation to give **27** may be supported by the donor ability of the *N*-methylanilino group. No compounds derived from the second fragmentation product could be identified. However, a relatively large amount of methyl benzoate (**26**) was found. Although we performed all experiments described under dry nitrogen, this oxidation product of **1** was always formed to some degree together with the carbene dimers (*E*)- and (*Z*)-α,α′-dimethoxystilbene[20] when the reaction times were very long (>10 h).

Cyclopropanations with Other Carbene Complexes. The carbene transfer to electron-deficient olefins is not restricted to the standard phenyl-substituted chromium carbene complex **1**. The methoxymethylcarbene complex **48** and methyl acrylate (**4**) furnished a mixture of the



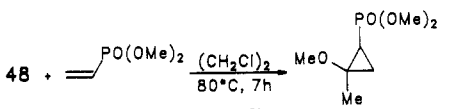
48 **4** 72 % **49**



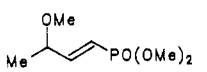
50 **51** **52**

methyl cyclopropanecarboxylates **49** (trans:cis = 66:34), the β-CH insertion product **50**, and methyl levulinate (**52**) (**49**:**50**:**52** = 38:33:29) in 72% yield. Compound **52** should arise from the hydrolysis of enol ether **51**, which was probably formed by acid-catalyzed rearrangement of cyclopropane **49**.

Dimethyl vinylphosphonate **7** and complex **48** gave the cyclopropane **53** together with the acyclic isomer **54** in excellent yield (**53**:**54** = 70:30). In general, the methyl-



7 **53** 91 %



54

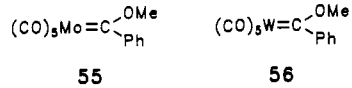
substituted carbene complex **48** exhibits a rather high tendency to undergo the β-CH insertion reaction. It is reasonable to assume that other alkyl-substituted chromium carbene complexes behave similarly to **48**. Recently, Herndon and Tumer reported on the successful reactions of electron-deficient alkenes with (cyclopropylcarbene)-chromium complexes, providing donor–acceptor-substituted cyclopropylcyclopropanes in good yield.[21] Even

(16) Fischer, H.; Schubert, U.; Märkl, R. *Chem. Ber.* **1981**, *114*, 3412. Fischer, H.; Märkl, R. *Chem. Ber.* **1985**, *118*, 3683.
(17) Wulff, W. D.; Dragisich, V.; Huffman, J. C.; Kaesler, R. W.; Yang, D. C. *Organometallics* **1989**, *8*, 2196.
(18) Wienand, A.; Reissig, H.-U.; Fischer, H.; Hofmann, J. *Chem. Ber.* **1989**, *122*, 1589.
(19) Hofmann, B.; Reissig, H.-U. Unpublished results.
(20) Fischer, E. O.; Heckl, B.; Dötz, K. H.; Müller, J.; Werner, H. *J. Organomet. Chem.* **1969**, *16*, 29.
(21) Herndon, J. W.; Tumer, S. U. *Tetrahedron Lett.* **1989**, *30*, 4771. Herndon, J. W.; Tumer, S. U. *J. Org. Chem.*, in press.

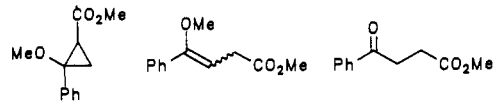
nonactivated dienes could be converted into vinylcyclopropanes. One example for an intramolecular cyclopropanation of an electron-deficient alkene involving an alkyl-substituted chromium carbene complex has also been described.[22]

On the other hand, we used several heteroaryl- or alkenyl-substituted carbene complexes to prepare cyclopropanes bearing heterocyclic substituents or alkenyl groups.[19] Since some of these reactions are complicated by the formation of five-membered ring systems, they will be discussed separately.[23]

Fischer and Dötz had already reported[4] that the molybdenum and tungsten complexes related to **1** are also able to transfer the methoxyphenylcarbene ligand to methyl crotonate (**2a**). The dependence of the cis/trans selectivity on the metal involved was taken as evidence that the cyclopropane **3a** was not formed via a free carbene. In a few orientating experiments we also employed the carbene complexes **55** and **56**. The molybdenum complex



55 **56**



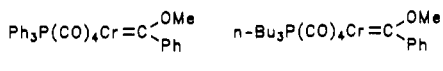
9 **57** **58**

55 and methyl acrylate (**4**) also provided the expected cyclopropane **9**, albeit not very efficiently (49% yield) and without any stereoselectivity. As a minor component the γ-oxo ester **58** was found, which arises from the cyclopropane **9** via the enol ether **57**. Interestingly, no insertion product **14** could be detected.

The major problem with molybdenum compounds such as **55** is that they are considerably less stable than **1**, which makes their synthetic use rather inefficient. However, a recent communication reports that the molybdenum *n*-butylmethoxycarbene complex and electron-poor olefins afford the corresponding cyclopropanes at relatively low temperatures in good yields.[24]

The tungsten complex **56** is remarkably less reactive than **1** or **55**. Thus, it had to be heated with methyl acrylate (**4**) for 6 h at 100 °C to furnish the cyclopropane **9** in 24% yield. Again, no β-CH insertion product **14** was detected. In summary, the chromium complexes seem to provide the best results because of their stability, reactivity, and the yields of cyclopropanes received. Possibly, the in situ use of molybdenum compounds could help to increase their value for cyclopropanation reactions.

We also briefly examined the triphenylphosphine- and tributylphosphine-substituted carbene complexes **59** and **60**. Reactions of **59** with methyl acrylate (**4**) or methyl

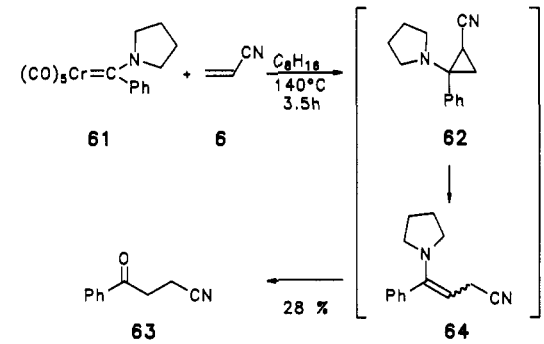


59 **60**

14 **57**

crotonate (**2a**) gave results very similar to those for standard complex **1**.[1] In contrast, the tributylphosphine-substituted complex **60** and methyl acrylate (**4**) provided a rather complex mixture containing only 25% of cyclopropane **9** but approximately 75% of the acyclic isomers **14** and **57**.

Finally, the aminocarbene complex **61** and acrylonitrile **6** were combined. Whereas no reaction occurred at 80 °C,



61 **6** **62** **63** **64**

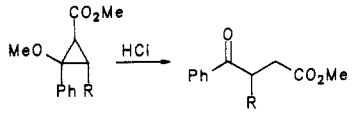
heating to 140 °C in cyclooctane allowed isolation of the γ-keto nitrile **63** in low yield. It arises probably via aminocyclopropane **62** and the enamine **64**. Not surprisingly, the aminocarbene complex **61** is by far less reactive toward electron-deficient olefins than **1**. Similar effects are known for the benzannulation reactions of chromium carbene complexes.[25] On the other hand, aminocyclopropanes such as **62** are more sensitive to thermal ring cleavage.[5] Therefore, chromium aminocarbene complexes will presumably not provide a good route to this type of donor–acceptor-substituted cyclopropanes.

Structural Assignments. Comparison with literature NMR data[26,27] allowed a straightforward and unambiguous determination of the configuration of the cyclopropanes obtained. Most significant in the ^{1}H NMR spectra of 2-phenyl-substituted derivatives is that substituents or protons cis to this group are more shielded than those located trans to the aromatic ring. For the acyclic isomers of type **14–18** the olefinic signals in the ^{1}H NMR spectra are most indicative. Thus, **14** and **15** display absorptions typical for (*E*)-acrylate derivatives (δ 6–7), while **16–18** show enol ether signals in the range δ 4.5–5.5. The ^{13}C NMR data, where available, fully support these structural assignments.

Subsequent Reactions of the Donor–Acceptor-Substituted Cyclopropanes Prepared. Donor–acceptor-substituted cyclopropanes such as **3**, **9**, and **10** are precursors of 1,4-dicarbonyl compounds.[5] However, due to the relatively stable 2-alkoxy groups, rather harsh acidic conditions are required to cleave the cyclopropane ring.[28] Attempts to prepare the more useful trimethylsiloxy-substituted cyclopropanes[29] from Fischer carbene complexes were not successful because of the very limited stability of these siloxycarbene complexes.[30]

Nevertheless, we did perform a few model reactions with the cyclopropanes described in this paper, demonstrating their synthetic potential. While **9** could be converted into methyl γ-oxo carboxylate **58** with 2 N hydrochloric acid at room temperature, the methyl-substituted compound **3a** gave the expected ring-cleavage product **65** only after

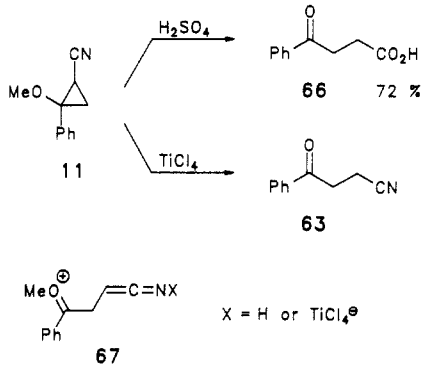
(22) Korkowski, P. F.; Hoye, T. R.; Rydberg, D. B. *J. Am. Chem. Soc.* **1988**, *110*, 2676.
(23) For examples providing vinylcyclopropanes see ref 7.
(24) Harvey, D. F.; Brown, M. F. *Tetrahedron Lett.* **1990**, *31*, 2529.
(25) See ref 2b,d.
(26) Reichelt, I.; Reissig, H.-U. *Chem. Ber.* **1983**, *116*, 3985.
(27) Booth, H. In *Progress in Nuclear Magnetic Resonance Spectroscopy*; Pergamon Press: Oxford, England, 1969; Vol. 5, p 149.
(28) Wenkert, E. *Acc. Chem. Res.* **1980**, *13*, 27.
(29) Kunkel, E.; Reichelt, I.; Reissig, H.-U. *Liebigs Ann. Chem.* **1984**, 512.
(30) Fischer, E. O.; Selmayr, T.; Kreissl, F. R.; Schubert, U. *Chem. Ber.* **1977**, *110*, 2574.



9	R = H	**58**	71 %
3a	R = Me	**65**	73 %

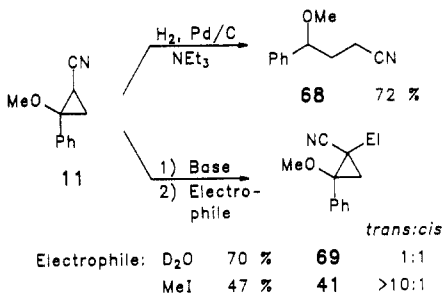
brief heating in concentrated HCl.

A few preliminary experiments were performed with the acrylonitrile-derived cyclopropane **11**. Treatment with concentrated sulfuric acid gave the γ-oxo carboxylic acid **66**, and use of titanium tetrachloride followed by aqueous



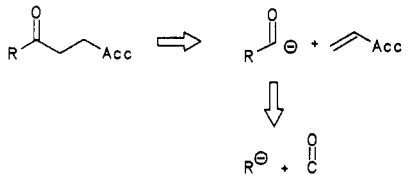
workup brought about the transformation **11** → **63** rather efficiently. Mechanistically these ring-opening reactions are presumed to involve attack of the (Lewis) acid at the acceptor substituent, thereby enhancing the lability of the cyclopropane bond between the donor and acceptor group bearing carbon atoms. Heterolytic cleavage of this bond should provide the oxonium ion **67**,[31] which is trapped by nucleophiles (water), finally leading to the isolated compounds with a γ-keto functionality.

A rather smooth ring opening of nitrile **11** occurred upon hydrogenolysis with a poisoned palladium catalyst. As expected,[32] the cyclopropane bond between the donor and the acceptor substituents was cleaved exclusively to afford the methyl ether **68**. Finally, compound **11** was depro-



tonated with base (*n*-butyllithium or LDA) to generate the corresponding cyclopropyl anion. Treatment with D_2O gave the deuterated material **69** as a mixture of diastereomers. On the other hand, alkylation employing methyl iodide afforded only the trans isomer of **41**. This behavior is typical for cyclopropyl anions bearing a β-alkoxy[26] or a β-trialkylsiloxy group.[33] Other substitution reactions at the cyclopropane ring should be achievable by use of different electrophiles. They should allow the synthesis of cyclopropane derivatives that are not (efficiently) available by the carbene transfer from **1** to the corresponding olefin.

A retrosynthetic analysis of the dicarbonyl products obtained from the cyclopropanes after ring cleavage demonstrates that the carbene complex served as an equivalent to an acyl anion. The carbene complex route described in this paper supplements existing synthetic methods,[34] since other starting materials are involved.



Conclusion

The experiments described in this paper illustrate that the carbene complex route to donor–acceptor-substituted cyclopropanes is a valuable alternative to other known methods.[5] The phenyl-substituted chromium carbene complex **1** gave very satisfactory results for many electron-deficient olefins. Thus, the scope of this formal [2 + 1] cycloaddition is considerably larger than the early findings of Fischer and Dötz indicate. However, the method is limited to mono- and disubstituted olefins; trisubstituted alkenes do not react with **1**. We assume that steric hindrance is responsible for the decreasing reactivity of olefins with increasing numbers of substituents.

The methyl-substituted complex **48** also provided good yields of addition products; however, besides the cyclopropanes, higher amounts of acyclic compounds were found in these reactions. Molybdenum or tungsten carbene complexes do not offer advantages over the chromium compounds. As is to be expected, the aminocarbene complex **61** is rather unreactive toward electron-poor olefins.

Oxidation of the carbene complex **1** occurred with a nitroalkene or a vinyl sulfoxide. Also, an olefin metathesis pathway is involved for certain alkenes. The mechanistic significance of these observations will be discussed together with other experiments in a paper dealing with the mechanism of the carbene transfer to electron-deficient alkenes.[8] The work outlined here is a confirmation of the high utility of Fischer carbene complexes in organic synthesis.

Experimental Section

The complexes **1**,[20] **48**,[35] **55**,[36] **56**,[37] **59**,[38] **60**,[38] and **61**[39] were prepared by literature procedures. α-Methylene-γ-butyrolactone (**38**) was prepared according to ref 40 and dimethyl vinylphosphonate was obtained from BASF AG (Ludwigshafen, FRG); all other olefins employed were commercially available. Solvents were dried by standard methods (CaH_2 or molecular sieve).

IR spectra: Beckman IR 5A. ^1H NMR spectra: Varian EM 360 (60 MHz), Bruker WM 300 (300 MHz, internal reference

(31) Reissig, H.-U.; Böhm, I. *Tetrahedron Lett.* **1983**, *24*, 715.
(32) Brückner, C.; Reissig, H.-U. *Chem. Ber.* **1987**, *120*, 617, 627 and references therein.
(33) Reissig, H.-U.; Böhm, I. *J. Am. Chem. Soc.* **1982**, *104*, 1735. Reichelt, I.; Reissig, H.-U. *Liebigs Ann. Chem.* **1984**, 531. For a more detailed discussion see ref 5.
(34) For related methods see: Hegedus, L. S.; Perry, R. J. *J. Org. Chem.* **1985**, *50*, 4955. Seyferth, D.; Hui, R. C. *J. Am. Chem. Soc.* **1985**, *107*, 4551. Pouilhès, A.; Thomas, S. E. *Tetrahedron Lett.* **1989**, *30*, 2285. Recent review on acyl anions and their equivalents: Ager, D. J. In *Umpoled Synthons*; Hase, T. A.; Ed.; Wiley: Chichester, England, 1987; p 19.
(35) Aumann, R.; Fischer, E. O. *Chem. Ber.* **1968**, *101*, 954.
(36) Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445.
(37) Fischer, E. O.; Schubert, U.; Kleine, W.; Fischer, H. *Inorg. Synth.* **1979**, *19*, 165.
(38) Fischer, E. O.; Fischer, H. *Chem. Ber.* **1974**, *107*, 657. Complex **59** was not reported in this paper but was analogously obtained in analytically pure form according to the procedure given.
(39) Fischer, E. O.; Leupold, M. *Chem. Ber.* **1972**, *105*, 599.
(40) (a) Murray, A. W.; Reid, R. G. *J. Chem. Soc., Chem. Commun.* **1984**, 132. (b) Murray, A. W.; Reid, R. G. *Synthesis* **1985**, 35.

Table II. ^{1}H NMR Data for Cyclopropane Derivatives 9–13 (δ, 300 MHz, $CDCl_3$, Coupling Constants in Hz)

compd	Ph (5 H, m)	OMe (3 H, s)	ABX system of 1-H, 3-H (3 H) 1-H	3-H[a]	3-H[b]	J_{trans}[c]	J_{cis}[c]	J_{gem}	other signals
trans-**9**	7.50–7.26	3.14	2.34	1.81	1.53	6.8	9.4	5.7	3.44 (s, 3 H, CO_2Me)
cis-**9**	7.50–7.26	3.22	2.15	1.98	1.49	7.0	8.8	6.0	3.75 (s, 3 H, CO_2Me)
trans-**10**	7.42–7.22	3.19	2.45	1.99	1.40	6.9	9.7	6.0	3.04, 2.67 (2 s, 3 H each, NMe_2)
cis-**10**	7.42–7.22	3.24	3.04	1.98	1.56	7.3	12.1	9.0	3.01, 3.00 (2 s, 3 H each, NMe_2)
trans-**11**	7.60–7.29	3.14	2.01	1.67	1.66	7.0	10.0	6.0	
cis-**11**	7.60–7.29	3.30	1.79	1.71	1.55	6.5	9.5	6.0	
trans-**12**	7.58–7.52 (2 H) 7.42–7.28 (3 H)	3.12		1.8–1.2[d]					3.45, 3.35 [(2 d, J = 11.1, 10.8, 3 H each, $P(OMe)_2$)]
cis-**12**	7.38 (2 H) 7.35 (3 H)	3.28	1.80 (22.2)[e]	1.65 (12.5)[e]	1.30 (0.8)[e]	5.6	10.4	7.7	3.81, 3.78 [(2 s, J = 11.2, 10.7, 3 H each, $P(OMe)_2$)]
trans-**13**	7.69–7.13	3.32	2.70	2.25	1.87	6.7	9.5	6.6	7.69–7.13 (m, 5 H, SO_2Ph)
cis-**13**	7.69–7.13	3.06	3.09	2.27	1.74	6.6	10.0	6.5	7.69–7.13 (m, 5 H, SO_2Ph)

[a] Trans with respect to 1-H. [b] Cis with respect to 1-H. [c] Coupling 1-H/3-H. [d] m; assignment not possible. [e] Coupling with P in Hz.

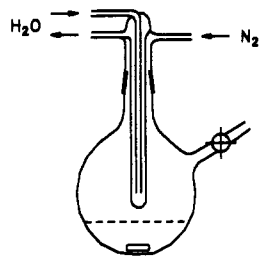


Figure 1. Reaction flask for the cyclopropanations according to the general procedure.

TMS). ^{13}C NMR spectra: Bruker WM 300 (75.5 MHz, internal reference $CDCl_3$). Mass spectra: Varian Model MAT 311A. Boiling points of compounds obtained refer to the temperature in a Büchi Kugelrohr oven. Melting points: SMP-20 apparatus (Büchi), uncorrected values. Radial chromatography: Chromatotron (Harrison Research, Model 7924), silica gel plates.

General Procedure for the Reactions of Carbene Complexes with Olefins. The reactions were performed in a flask equiped with a stirring bar and sublimation finger (Figure 1), which served as a condenser for the boiling solvent or olefin and also trapped the $Cr(CO)_6$ liberated during the reaction. The carbene complex was dissolved in the corresponding solvent under an atmosphere of dry N_2 and treated with the olefin at the temperature indicated in the individual experiments. After disappearance of the color of the carbene complex (most often a color change from red to green could be observed) the mixture was worked up according to one of the procedures A–C: (A) filtration through a short pad of Celite, evaporation of the solvent, removal of $Cr(CO)_6$ at 50 °C/0.5 Torr, and Kugelrohr distillation of the residue; (B) evaporation, addition of diethyl ether, filtration through a short pad of Celite, the remainder of the procedure then analogous to A; (C) dissolution in CH_2Cl_2/Et_2O (4:1), filtration through a short pad of Celite, evaporation, dissolution in CH_2Cl_2/Et_2O (4:1), the remainder of the procedure then analogous to A.

Reaction of Complex 1 with Methyl Acrylate (4). According to the general procedure, 1 (1.56 g, 5.00 mmol) and methyl acrylate (0.433 g, 5.00 mmol) in 10 mL of cyclohexane were heated to 80 °C for 5.5 h. Filtration through a short pad of Al_2O_3 and then workup analogous to A and distillation (120 °C/0.02 Torr) provided 0.773 g (75%) of methyl 2-methoxy-2-phenylcyclopropanecarboxylate (**9**)[41] and methyl 4-methoxy-4-phenyl-2-butenoate (**14**; *trans*-**9**:*cis*-**9**:**14** = 39:58:3). IR (film): 3070, 3040, 3000, 2950 (CH), 2830 (OMe), 1735 (C=O), 1610, 1590, 1510 (C=C) cm^{-1}. ^{13}C NMR ($CDCl_3$) for **14**: δ 147.6 (d, C-3), 132.4, 130.1–125.9 (s, 3 d, Ph), 120.5 (d, C-2), 82.5 (d, C-4), 56.7 (q, OMe); due to the low concentration of **14** the signals of the CO_2Me group could not be identified.

Reaction of Complex 1 with Acrylic Acid Dimethylamide (5). According to the general procedure, 1 (0.626 g, 2.00 mmol) and **5** (0.198 g, 2.00 mmol) in 10 mL of 1,2-dichloroethane were heated to 80 °C for 3.5 h. Workup (A) and distillation (110 °C/0.02 Torr) provided 0.343 g (78%) of 2-methoxy-2-phenylcyclopropanecarboxylic acid dimethylamide (**10**) and traces of acyclic isomers **15** and **16** (*trans*-**10**:*cis*-**10**:**15**:**16** = 52:45:1:2). IR (film): 3060, 3040, 3020, 2940 (CH), 2840 (OMe), 1625 (C=O), 1600, 1580, 1500 (C=C) cm^{-1}. Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81; N, 6.39. Found: C, 70.87; H, 7.89; N, 5.98. ^{13}C NMR ($CDCl_3$) for (*E*)-**16**: δ 129.6, 128.7–125.2 (s, 3 d, Ph), 106.8 (d, C-3), 58.4 (q, OMe), 31.1 (t, C-2); other signals not unambiguously determinable.

Reaction of Complex 1 with Acrylonitrile (6). According to the general procedure, 1 (0.672 g, 2.15 mmol) and acrylonitrile (**6**; 0.114 g, 2.15 mmol) in 10 mL of 1,2-dichloroethane were heated to 80 °C for 5 h. Workup (A) and distillation (110 °C/0.02 Torr) provided 0.332 g (89%) of 2-methoxy-2-phenylcyclopropyl cyanide (**11**)[42] and 4-methoxy-4-phenyl-3-butenenitrile (**17**; *trans*-**11**:*cis*-**11**:(*E*)-**17**:(*Z*)-**17** = 44:44:9:3). IR (film): 3060, 3020, 2950 (CH), 2840 (OMe), 2245 (CN), 1610, 1590, 1500 (C=C) cm^{-1}. Anal. Calcd for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.05. Found: C, 76.57; H, 6.62; N, 7.61.

Reaction of Complex 1 with Dimethyl Vinylphosphonate (7). According to the general procedure, 1 (0.626 g, 2.00 mmol) and **7** (0.274 g, 2.00 mmol) in 10 mL of cyclohexane were heated to 80 °C for 3.5 h. Workup (A) and distillation (150 °C/0.02 Torr) provided 0.406 g (79%) of dimethyl (2-methoxy-2-phenylcyclopropyl)phosphonate (**12**; *trans*-**12**:*cis*-**12** = 50:50). IR (film): 3090, 3060, 3000, 2960 (CH), 2860, 2840 (OMe), 1600, 1580, 1495 (C=C), 1255 (P=O) cm^{-1}. Anal. Calcd for $C_{12}H_{17}O_4P$: C, 56.25; H, 6.69. Found: C, 55.85; H, 6.49.

Reaction of Complex 1 with Phenyl Vinyl Sulfone (8). According to the general procedure, 1 (0.626 g, 2.00 mmol) and **8** (0.336 g, 2.00 mmol) in 10 mL of 1,2-dichloroethane were heated to 80 °C for 2 h. Workup (A) and radial chromatography (pentane:ethyl acetate = 4:1) provided 0.280 g (49%) of 2-methoxy-2-phenylcyclopropyl phenyl sulfone (**13**) and 3-methoxy-3-phenyl-2-propenyl phenyl sulfone (**18**; *trans*-**13**:*cis*-**13**:(*E*)-**18**:(*Z*)-**18** = 40:36:12:12). IR (film): 3080, 3040, 3020, 2950 (CH), 2840 (OMe), 1690 (C=O), 1600, 1585, 1500 (C=C), 1350, 1150 (SO_2) cm^{-1}. Anal. Calcd for $C_{16}H_{16}O_3S$: C, 66.64; H, 5.59. Found: C, 66.55; H, 5.36.

Reaction of Complex 1 with Methyl Vinyl Ketone (19). According to the general procedure, 1 (3.13 g, 10.0 mmol) and **19** (0.705 g, 10.0 mmol) were heated without solvent to 80–90 °C for 4.5 h. The reaction mixture was dissolved in CH_2Cl_2/Et_2O (4:1) and the solution filtered through a short pad of Al_2O_3. Evaporation gave the crude product, which was dissolved in 7 mL of THF, and the solution was stirred with 4 mL of 2 N HCl for 26 h at room temperature. Extraction with diethyl ether provided 1.31 g of a brownish liquid, which was purified by distillation (80–120 °C/0.02 Torr) and radial chromatography (pentane:ethyl acetate = 4:1) to give 0.187 g (11%) of 1-phenylpenta-1,4-dione (**21**)[43] and

(41) Sanders, V.; Weyerstahl, P. *Chem. Ber.* **1978**, *111*, 3879.

(42) Doyle, M. P.; van Leusen, D. *J. Org. Chem.* **1982**, *47*, 5326.

(43) Stetter, H.; Schmitz, P. H.; Schreckenberg, M. *Chem. Ber.* **1977**, *110*, 1971.

Table III. ^{13}C NMR Data for Cyclopropane Derivatives 9–13 (δ, 75.5 MHz, $CDCl_3$)

compd	Ph (s, 3 d)	C-2 (s)	OMe (q)	C-1 (d)	C-3 (t)	other signals
trans-**9**	139.0, 130.0–126.4	70.5	54.5	29.2	17.9	170.5, 51.8 (s, q, CO_2Me)
cis-**9**	134.6, 130.0–126.4	70.0	55.6	29.8	19.2	169.8, 51.8 (s, q, CO_2Me)
trans-**10**	140.1, 128.7–127.1	68.8	54.6	31.9	15.5	167.8 (s, C=O), 37.2, 35.2 (2 q, NMe_2)
cis-**10**	135.4, 128.7–127.1	66.8	55.8	31.9	15.9	171.6 (s, C=O), 35.6, 34.2 (2 q, NMe_2)
trans-**11**	135.7, 128.8–126.8	68.0	54.4	18.9	12.6	118.4 (s, CN)
cis-**11**	133.3, 128.8–126.8	66.9	55.1	20.5	11.9	118.4 (s, CN)
trans-**12**	135.0, 129.7, 128.6, 128.0	67.2[a]	54.5	20.8 (193.4)[b]	15.7 (5.1)[b]	52.3, 52.1 [2 dq, $P(OMe)_2$][a]
cis-**12**	138.8, 128.4, 127.9, 126.7	66.8 (5)[b]	55.5	22.8 (189.0)[b]	17.2 (5.3)[b]	52.7, 52.6 [2 dq, J = 25.9, 24.5,[b] $P(OMe)_2$]
trans-**13**	137.4, 129.8–126.7	68.1	55.8	47.7	17.0	141.5, 129.8–126.7 (s, 3 d, SO_2Ph)
cis-**13**	131.8, 129.8–126.7	69.1	54.4	46.4	16.7	140.4, 129.8–126.7 (s, 3 d, SO_2Ph)

[a] Coupling to P not determinable. [b] Coupling with P in Hz.

Table IV. ^1H NMR Data for the Acyclic Isomers 14–18 (300 MHz, $CDCl_3$)

compd	Ph (5 H, m)	OMe (3 H, s)	2-H (1-H for 18)	3-H, (2-H for 18)	4-H	signals of the Acc groups
(*E*)-**14**	7.60–7.17	3.30	6.05 (dd, J = 16.0, 2.0 Hz, 1 H)	6.95 (dd, J = 16.0, 5.0 Hz, 1 H)	4.73 (dd, J = 5.0, 2.0 Hz, 1 H)	3.68 (s, 3 H, CO_2Me)
(*E*)-**15**	7.42–7.22	*a*	5.01 (1 H)[b]	*a*	4.12 (1 H)[b]	$CONMe_2$[a]
(*E*)-**16**	7.49–7.20	3.53	1.24 (d, J = 8.0 Hz, 2 H)	5.48 (t, J = 8.0 Hz, 1 H)		3.07, 2.99 (2 s, 3 H each, NMe_2)
(*E*)-**17**[c]	7.50–7.22	3.64	2.86 (d, J = 8.0 Hz, 2 H)	4.62 (t, J = 8.0 Hz, 1 H)		
(*Z*)-**17**[c]	7.50–7.22	3.49	3.11 (d, J = 6.0 Hz, 2 H)	5.03 (t, J = 6.0 Hz, 2 H)		
(*E*)-**18**	7.69–7.13	3.69	3.81 (d, J = 8.0 Hz, 2 H)	4.79 (t, J = 8.0 Hz, 1 H)		7.69–7.13 (m, 5 H, SO_2Ph)
(*Z*)-**18**	7.69–7.13	3.11	4.09 (d, J = 7.0 Hz, 2 H)	5.11 (t, J = 7.0 Hz, 1 H)		7.69–7.13 (m, 5 H, SO_2Ph)

[a] Signals hidden. [b] Coupling constants not determinable. [c] Compare ref 42.

0.216 g (14%) of 4-methyl-1-phenylfuran (**23**).[44] ^1H NMR ($CDCl_3$) of **21**: δ 8.10–7.86, 7.60–7.22 (2 m, 2 H, 3 H, Ph), 3.37–3.12 (m, 2 H, 3-H), 2.97–2.70 (m, 2 H, 2-H), 2.23 (s, 3 H, Me). Data for **23**: ^1H NMR (300 MHz, $CDCl_3$) δ 7.64–7.57, 7.38–7.30, 7.22–7.16 (3 m, 2 H, 2 H, 1 H, Ph), 6.53 (d, J = 3.2 Hz, 1 H, 3-H), 6.04 (m, allylic coupling to Me, 1 H, 4-H), 2.35 (broad s, 3 H, Me); ^{13}C NMR ($CDCl_3$) δ 152.3, 151.9 (2 s, C-2, C-5), 131.2, 128.7, 126.7, 123.3 (s, 3 d, Ph), 107.7, 105.8 (2 d, C-3, C-4), 13.7 (q, Me); IR (film) 3080, 3060, 3000 (=CH), 2960, 2920 (CH), 2860 (OMe), 1590 (C=C) cm^{-1}; MS (EI) *m/e* (%) 158 (100, M^+), 157 (40), 129 (14), 115 (40), 105 (12), 77 (18), 50 (16), 41 (40).

Reaction of Complex 1 with Phenyl Vinyl Sulfoxide (24). According to the general procedure, 1 (0.626 g, 2.00 mmol) and **24** (0.304 g, 2.00 mmol) were heated in 10 mL of cyclohexane to 80 °C for 4 h. Workup (A) and distillation provided 0.211 g (76%) of a mixture containing methyl benzoate (**26**), α-methoxystyrene (**27**), 3-methoxy-3-phenyl-1-propenyl phenyl sulfoxide (**25**), and acetophenone (**28**; **26**:**27**:**25**:**28** = 62:21:15:2). ^1H NMR (300 MHz, $CDCl_3$): **26**, δ 8.12–7.88, 7.68–7.07 (2 m, 2 H, 3 H, Ph), 3.90 (s, 3 H, CO_2Me); **27**, δ 7.68–7.08 (m, 5 H, Ph), 4.61, 4.17 (2 d, J = 3 Hz, 1 H each, $=CH_2$); **25**, δ 7.68–7.07 (m, 10 H, 2 Ph), 6.49 (dd, J = 16, 9 Hz, 1 H, 2-H), 5.27 (d, J = 9 Hz, 1 H, 3-H), 5.26 (d, J = 16 Hz, 1 H, 1-H), 3.70 (s, 3 H, OMe); **28**, δ 7.68–7.07 (m, 5 H, Ph), 1.63 (s, 3 H, Me).

Reaction of Complex 1 with Methyl 2-Pentenoate (31). According to the general procedure, 1 (0.626 g, 2.00 mmol) and **31** (0.228 g, 2.00 mmol) in 10 mL of cyclohexane were heated to 80 °C for 76 h. Workup (A) and distillation provided a red liquid, which was dissolved in diethyl ether. Addition of Al_2O_3 and oxidation by atmospheric oxygen removed unconsumed complex 1. Filtration and distillation (100 °C/0.02 Torr) afforded 0.140 g of a mixture of methyl 3-ethyl-2-methoxy-2-phenylcyclopropanecarboxylate (**32**, 23%; *trans*-**32**:*cis*-**32** = 20:80), (*Z*)-α,α′-dimethoxystilbene[20] (3%), and methyl benzoate (**26**, 8%). ^1H NMR (300 MHz, $CDCl_3$): *trans*-**32**, δ 7.48–7.27 (m, 5 H, Ph), 3.77 (s, 3 H, CO_2Me), 3.01 (s, 3 H, OMe), 2.20 (q, J = 7.0 Hz, 1 H, 3-H), 2.07 (d, J = 7.0 Hz, 1 H, 1-H), 0.87 (t, J = 7.0 Hz, 3 H, Me), signal of CH_2 hidden; *cis*-**32**, δ 7.48–7.27 (m, 5 H, Ph), 3.47 (s, 3 H, CO_2Me), 3.15 (s, 3 H, OMe), 2.03 (dt, J = 6.8, 7.0 Hz, 1 H, 3-H), 1.90 (d, J = 6.8 Hz, 1 H, 1-H), 1.68 (dq, J = 7.0, 7.4 Hz, 2 H, CH_2), 1.15 (t, J = 7.4 Hz, 3 H, Me); (*Z*)-α,α′-dimethoxystilbene, δ 7.17 (s, 10 H, 2 Ph), 3.60 (s, 6 H, OMe). ^{13}C NMR ($CDCl_3$): *trans*-**32**, δ 129.9–127.9 (3 d, Ph), 54.8 (q, OMe), 51.9 (q, CO_2Me), 35.1 (d, C-1), 29.8 (d, C-3), 21.6 (t, CH_2), 12.8 (q, Me); *cis*-**32**, δ 135.6, 129.8, 128.2, 128.1 (s, 3 d, Ph), 74.3 (s, C-2), 54.9 (q, OMe), 51.5 (q, CO_2Me), 33.6, 33.5 (2 d, C-1, C-3), 19.5 (t, CH_2), 13.9 (q, Me).

Reaction of Complex 1 with Methyl Methacrylate (33). According to the general procedure, 1 (0.626 g, 2.00 mmol) and **33** (0.201 g, 2.00 mmol) were heated without solvent to 90–100 °C for 15 h. Workup (C) and distillation (70 °C/0.02 Torr) provided 0.103 g (23%) of methyl 2-methoxy-1-methyl-2-phenylcyclopropanecarboxylate (**34**; *trans*-**34**:*cis*-**34** = 55:45). ^1H NMR (300 MHz, $CDCl_3$): *trans*-**34**, δ 7.50–7.26 (m, 5 H, Ph), 3.26 (s, 3 H, CO_2Me), 3.15 (s, 3 H, OMe), 2.03, 1.50 (2 d, J = 5.8 Hz, 1 H each, 3-H), 1.58 (s, 3 H, 1-Me); *cis*-**34**, δ 7.50–7.26 (m, 5 H, Ph), 3.76 (s, 3 H, CO_2Me), 3.11 (s, 3 H, OMe), 1.92, 1.19 (2 d, J = 6.1 Hz, 1 H each, 3-H), 0.95 (s, 3 H, 1-Me). ^{13}C NMR ($CDCl_3$): *trans*-**34**, δ 172.6, 51.5 (s, q, CO_2Me), 132.9, 129.5, 128.7, 128.1 (s, 3 d, Ph), 71.7 (s, C-2), 54.8 (q, OMe), 33.2 (s, C-1), 22.2 (t, C-3), 14.8 (q, 1-Me); *cis*-**34**, δ 172.3, 52.1 (s, q, CO_2Me), 135.8, 129.2, 128.2, 127.9 (s, 3 d, Ph), 71.6 (s, C-2), 54.9 (q, OMe), 33.2 (s, C-1), 20.0 (t, C-3), 17.5 (q, 1-Me). IR (film): 3100–3030 (=CH), 3000–2800 (CH), 1720 (C=O), 1600, 1575, 1490 (C=C) cm^{-1}. Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 71.55; H, 7.45.

Reaction of Complex 1 with α-Methylene-γ-butyrolactone (38). According to the general procedure, 1 (0.626 g, 2.00 mmol) and **38** (0.396 g, 4.00 mmol) in 10 mL of 1,2-dichloroethane were heated to 80 °C for 3 h. Workup (A) and distillation (150 °C/0.02 Torr) provided 0.328 g (75%) of 1-methoxy-1-phenyl-5-oxaspiro[2.4]heptan-4-one (**39**; *trans*-**39**:*cis*-**39** = 55:45). Fractional crystallization allowed separation of a small portion of *cis*-**39**, thus allowing assignment of the NMR signals to the individual isomers. ^1H NMR (300 MHz, $CDCl_3$): *trans*-**39**, δ 7.36–7.27 (m, 5 H, Ph), ABXY system (δ_A 4.45, δ_B 4.35, δ_X 2.75, δ_Y 2.46, J_{AB} = 9.0, J_{AX} = 2.7, J_{AY} = 9.2, J_{BX} = 7.4, J_{BY} = 9.7, J_{XY} = 13.2 Hz, 1 H each, 6-H, 7-H), 3.18 (s, 3 H, OMe), 2.02, 1.36 (2 d, J = 6.0 Hz, 1 H each, 2-H); *cis*-**39**, δ 7.46–7.32 (m, 5 H, Ph), ABXY system (δ_A 4.30, δ_B 4.10, δ_X 2.17, δ_Y 1.58, J_{AB} = 9.0, J_{AX} = 9.0, J_{AY} = 2.1, J_{BX} = 10.5, J_{BY} = 7.0, J_{XY} = 13.0 Hz, 1 H each, 6-H, 7-H), 3.24 (s, 3 H, OMe), 2.02, 1.78 (2 d, J = 6.4 Hz, 1 H each, 2-H). ^{13}C NMR ($CDCl_3$): *trans*-**39**, δ 175.4 (s, C=O), 134.1, 129.1, 128.4, 128.2 (s, 3 d, Ph), 71.4 (s, C-1), 66.1 (t, C-6), 55.0 (q, OMe), 33.5 (s, C-3), 25.9 (t, C-2), 20.9 (t, C-7); *cis*-**39**, δ 174.7 (s, C=O), 135.6, 129.3, 128.9, 128.4 (s, 3 d, Ph), 72.8 (s, C-1), 65.4 (t, C-6), 55.9 (q, OMe), 34.0 (s, C-3), 28.4 (t, C-2), 20.3 (t, C-7). IR (film): 3100–3000 (=CH), 3000–2800

(44) Nishio, T.; Omote, Y. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1703.

(CH), 1585, 1500, 1480 (C=C) cm^{-1}. Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.05; H, 6.09.

Reaction of Complex 1 with α-Methylacrylonitrile (40). According to the general procedure, **1** (0.775 g, 2.48 mmol) and **40** (0.167 g, 2.48 mmol) in 2 mL of cyclohexane were heated to 80 °C for 8.5 h. Workup (A) and distillation (80 °C/0.02 Torr) provided 0.186 g (40%) of a mixture of 2-methoxy-1-methyl-2-phenylcyclopropyl cyanide (**41**) and 4-methoxy-2-methyl-4-phenyl-2-butenenitrile (**42**; *trans*-**41**:*cis*-**41**:**42** = 32:32:36). Radial chromatography (pentane:ethyl acetate = 4:1) afforded small amounts of pure **42** and a fraction enriched in **41**. ^1H NMR (300 MHz, $CDCl_3$): *trans*-**41**, δ 7.47–7.32 (m, 5 H, Ph), 3.16 (s, 3 H, OMe), 1.84, 1.20 (2 d, J = 6.3 Hz, 1 H each, 3-H), 1.61 (s, 3 H, Me); *cis*-**41**, δ 7.47–7.32 (m, 5 H, Ph), 3.23 (s, 3 H, OMe), 1.70, 1.36 (2 d, J = 6 Hz, 1 H each, 3-H), 1.05 (s, 3 H, Me). IR ($CHCl_3$): 3020, 2940, 2840 (CH), 2240 (CN) cm^{-1}. Anal. Calcd for $C_{12}H_{13}NO$: C, 76.97; H, 7.00; N, 7.48. Found: C, 76.90; H, 7.01; N, 7.27. ^1H NMR ($CDCl_3$): **42**, δ 7.50–7.11 (m, 5 H, Ph), 6.13 (dq, J = 9, 1 Hz, 1 H, 3-H), 5.02 (d, J = 9 Hz, 1 H, 4-H), 3.30 (s, 3 H, OMe), 1.91 (d, J = 1 Hz, 3 H, 2-Me).

Reaction of Complex 1 with 2-(*N*-Methylanilino)acrylonitrile (47). According to the general procedure, **1** (1.25 g, 4.00 mmol) and **47** (0.633 g, 2.00 mmol) in 10 mL of *n*-octane were heated to 105 °C for 28 h. Workup (A) and distillation (50–100 °C/0.02 Torr) provided 0.201 g of a mixture containing **47**, **26**, and **27** (**47**:**26**:**27** = 32:28:40). Calculated yields: 24% for **26** and 21% for **27**.

Reaction of Complex 48 with Methyl Acrylate (4). According to the general procedure, **48** (0.640 g, 2.50 mmol) and methyl acrylate (**4**; 0.215 g, 2.50 mmol) in 10 mL of 1,2-dichloroethane were heated to 80 °C for 2 h. Workup (B) and distillation (50 °C/0.02 Torr) provided 0.260 g (72%) of a mixture of methyl 2-methoxy-2-methylcyclopropanecarboxylate (**49**), methyl (*E*)-4-methoxy-2-pentenoate (**50**), and methyl levulinate (**52**; *trans*-**49**:*cis*-**49**:**50**:**52** = 25:13:33:29). ^1H NMR (300 MHz, $CDCl_3$): **50**, δ 6.84 (dd, J = 15.7, 6.1 Hz, 1 H, 3-H), 5.97 (d, J = 15.7 Hz, 1 H, 2-H), 3.88 (dq, J = 6.1, 6.6 Hz, 1 H, 4-H), 3.68 (s, 3 H, CO_2Me), 3.32 (s, 3 H, OMe), 1.28 (d, J = 6.6 Hz, 3 H, Me). ^{13}C NMR ($CDCl_3$): **50**, δ 166.6, 51.6 (s, q, CO_2Me), 149.4 (d, C-3), 120.9 (d, C-2), 76.2 (d, C-4), 56.6 (q, OMe), 18.4 (q, C-5). The NMR data of **49** and **52** agree with those given in refs 26 and 45.

Reaction of Complex 48 with Dimethyl Vinylphosphonate (7). According to the general procedure, **48** (0.640 g, 2.50 mmol) and **7** (0.341 g, 2.50 mmol) in 10 mL of 1,2-dichloroethane were heated to 80 °C for 7 h. Workup (B) and distillation provided 0.444 g (91%) of a mixture containing dimethyl (2-methoxy-2-methylcyclopropyl)phosphonate (**53**) and dimethyl (*E*)-3-methoxy-1-butenyl-1-phosphonate (**54**; *trans*-**53**:*cis*-**53**:**54** = 42:28:30). ^1H NMR (300 MHz, $CDCl_3$): *trans*-**53**, δ 3.76, 3.75 [2 d, J = 10.8 Hz, 3 H each, $P(OMe)_2$], 3.30 (s, 3 H, OMe), 1.61 (s, 3 H, Me), 1.55–0.83 (m, 3 H, 1-H, 3-H); *cis*-**53**, δ 3.76, 3.74 [2 d, J = 11.2 Hz, 3 H each, $P(OMe)_2$], 3.36 (s, 3 H, OMe), 1.45 (d, J = 2.4 Hz, 3 H, Me), 1.55–0.83 (m, 3 H, 1-H, 3-H); **54**, δ 6.71 (ddd, J = 5.1, 17.3 Hz, J_P = 22.4 Hz, 1 H, 2-H), 5.85 (ddd, J = 1.3, 17.3 Hz, J_P = 20.8 Hz, 1 H, 1-H), 3.95–3.85 (m, 1 H, 3-H), 3.74, 3.73 [2 d, J = 11.5, 11.1 Hz, 3 H each, $P(OMe)_2$], 3.33 (s, 3 H, OMe), 1.28 (d, J = 6.4 Hz, 3 H, 4-H). ^{13}C NMR ($CDCl_3$): *trans*-**53**, δ 61.9 (s, C-2), 54.2 (q, OMe), 52.4 [q, $P(OMe)_2$], 19.2 (dd, J_P = 151 Hz, C-1), 19.1 (t, C-3), 15.9 (q, Me); *cis*-**53**, δ 62.0 (s, C-2), 54.7 (q, OMe), 52.4 [q, $P(OMe)_2$], 19.4 (dd, J_P = 160 Hz, C-1), 19.2 (t, C-3), 15.4 (q, Me); **54**, δ 154.5 (d, C-2), 116.4 (d, C-1), 77.8 (d, C-3), 56.7 (q, OMe), 52.4 [q, $P(OMe)_2$], 18.1 (q, C-4). IR (film): 3000–2800 (CH), 1660, 1630 (C=C), 1250 (P=O) cm^{-1}. Anal. Calcd for $C_7H_{15}O_4P$: C, 43.30; H, 7.79. Found: C, 42.95; H, 7.84.

Reaction of Complex 55 with Methyl Acrylate (4). According to the general procedure, **55** (0.534 g, 1.50 mmol) and **4** (0.129 g, 1.50 mmol) in 10 mL of cyclohexane were heated to 80 °C for 7 h. Workup (A) and distillation (100 °C/0.02 Torr) provided 0.153 g (49%) of a mixture containing cyclopropanes **9** and methyl 4-oxo-4-phenylbutanoate (**58**; *trans*-**9**:*cis*-**9**:**58** = 47:47:6). ^1H NMR ($CDCl_3$): **58**, δ 8.1–7.7, 7.6–7.2 (2 m, 2 H, 3 H, Ph), 3.70 (s, 3 H, CO_2Me), 3.31, 2.75 (2 m, 2 H, 2 H, 3-H, 2-H).[46]

Reaction of Complex 56 with Methyl Acrylate (4). According to the general procedure, **56** (1.11 g, 2.50 mmol) and **4** (0.216 g, 2.50 mmol) were heated without solvent to 100 °C for 6 h. Workup (C), a second filtration through a short pad of Al_2O_3 (elution with 4:1 CH_2Cl_2/Et_2O), and distillation (110 °C/0.02 Torr) provided 0.123 g (24%) of cyclopropanes **9** (*trans*-**9**:*cis*-**9** = 52:48).

Reaction of Complex 60 with Methyl Acrylate (4). According to the general procedure, **60** (0.630 g, 1.30 mmol) and **4** (0.344 g, 4.00 mmol) in 8 mL of tetrahydrofuran were heated to 70 °C for 4 h. Workup (A) and repeated distillation (80–100 °C/0.02 Torr) to separate tributylphosphine provided 0.234 g of a product mixture containing cyclopropanes **9**, acyclic isomers **14** and **57**, methyl benzoate (**26**), and Bu_3P (*trans*-**9**:*cis*-**9**:**14**:(*E*)-**57**:(*Z*)-**57**:**26** = 11:11:34:24:9:11). ^1H NMR (300 MHz, $CDCl_3$): (*E*)-**57**, δ 7.5–7.25 (m, 5 H, Ph), 4.81 (t, J = 7.5 Hz, 1 H, 3-H), 3.71, 3.68 (2 s, 3 H each, CO_2Me, OMe), 3.09 (d, J = 7.5 Hz, 2 H, 2-H); (*Z*)-**57**, δ 7.5–7.25 (m, 5 H, Ph), 5.41 (t, J = 7.1 Hz, 1 H, 3-H), 3.70, 3.52 (2 s, 3 H each, CO_2Me, OMe), 3.33 (d, J = 7.1 Hz, 2 H, 2-H).

Reaction of Complex 61 with Acrylonitrile (6). According to the general procedure, **61** (0.703 g, 2.00 mmol) and **6** (0.106 g, 2.00 mmol) in 10 mL of cyclooctane were heated to 140 °C for 3.5 h. Workup (A) and distillation (150 °C/0.02 Torr) provided 90 mg (28%) of impure 4-oxo-4-phenylbutanenitrile (**63**). ^1H NMR ($CDCl_3$): δ 8.0–7.75, 7.6–7.1 (2 m, 2 H, 3 H, Ph), 3.34, 2.70 (2 m_c, 2 H, 2 H, 3-H, 2-H).[47]

Ring Cleavage of Cyclopropane 9 with Acid. Cyclopropane **9** (0.374 g, 1.81 mmol) was dissolved in 5 mL of tetrahydrofuran and the solution stirred with 2 mL of 2 N HCl (39 h, room temperature). Extractive workup provided 0.246 g (71%) of ester **58**.

Ring Cleavage of Cyclopropane 3a with Acid. Cyclopropane **3a**[4b] (0.309 g, 1.32 mmol) was dissolved in 5 mL of methanol and treated with 2 mL of concentrated HCl (2 h, 70 °C). Extractive workup and distillation (100 °C/0.02 Torr) gave 0.224 g (73%) of methyl 3-methyl-4-oxo-4-phenylbutanoate (**65**) as a colorless oil.[46]

Ring Cleavage of Cyclopropane 11 with Acid. Cyclopropane **11** (0.348 g, 2.00 mmol) was heated with 2 mL of aqueous sulfuric acid (50%) to reflux. After the mixture was cooled to room temperature and diluted with 2 mL of water, a pale brown solid precipitated, which was gathered by filtration and dried in vacuo. Thereby 4-oxo-4-phenylbutyric acid (**66**; 0.256 g, 72%) was obtained (colorless crystals, mp 105–110 °C; recrystallization from pentane/ethyl acetate, mp 115–116 °C).[48]

Ring Cleavage of Cyclopropane 11 with $TiCl_4$. A solution of cyclopropane **11** (0.175 g, 1.00 mmol) in 5 mL of dry dichloromethane was stirred with 5 drops of $TiCl_4$ for 3 h at room temperature. Extractive workup provided 0.188 g of an oil containing **63** and impurities (major impurity CH_2Cl_2).

Hydrogenolysis of Cyclopropane 11. A suspension of Pd/C (10%, 0.301 g, 0.287 mmol) in 20 mL of tetrahydrofuran was saturated with hydrogen. Then, triethylamine (47 mg, 0.464 mmol) and cyclopropane **11** (0.500 g, 2.87 mmol) were added and the mixture was treated with hydrogen at atmospheric pressure. After vigorous stirring for 20 h, 50 mL of H_2 was consumed and the mixture was filtered through a pad of Al_2O_3. Evaporation and distillation (130 °C/0.03 Torr) provided 0.303 g (60%) of 4-methoxy-4-phenylbutanenitrile (**68**) as a colorless liquid. ^1H NMR (300 MHz, $CDCl_3$): δ 7.42–7.24 (m, 5 H, Ph), 4.25 (dd, J = 4.8, 8.5 Hz, 1 H, 4-H), 3.23 (s, 3 H, OMe), 2.58–2.47 (m, 1 H, 2-H), 2.36 (ddd, J = 5.8, 7.2, 16.8 Hz, 1 H, 2-H), 2.12–1.90 (m, 2 H, 3-H). ^{13}C NMR ($CDCl_3$): δ 140.4, 128.2, 127.3, 126.5 (s, 3 d, Ph), 119.5 (s, CN), 81.5 (d, C-4), 56.8 (q, OMe), 33.6 (t, C-3), 13.8 (t, C-2). IR (film): 3070, 3040, 2940 (CH), 2840 (OMe), 2250 (CN) cm^{-1}. Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.93; H, 7.21; N, 8.03.

Deuteration of Cyclopropane 11. Under an atmosphere of dry nitrogen cyclopropane **11** (0.348 g, 2.00 mmol) was dissolved in 6 mL of dry tetrahydrofuran and treated at −78 °C with *n*-BuLi (3.00 mmol in hexane) for 2 h. Addition of 2 mL of D_2O, warming to room temperature, extractive workup, and distillation (90

(45) Cerfontain, H.; van Noort, R. C. M. *Synthesis* **1980**, 490.
(46) Kunkel, E.; Reichelt, I.; Reissig, H.-U. *Liebigs Ann. Chem.* **1984**, 802.
(47) Knott, E. B. *J. Chem. Soc.* **1947**, 1190.
(48) Papa, D.; Schwenk, E.; Hankin, H. *J. Am. Chem. Soc.* **1947**, *69*, 3018.

°C/0.02 Torr) provided cyclopropane **69** (0.243 g, 70%) as a 1:1 mixture of cis/trans isomers (degree of deuteration according to ^{1}H NMR >90%).

Methylation of Cyclopropane 11. Cyclopropane **11** (0.348 g, 2.00 mmol, trans:cis = 1:1) was added at −78 °C to a solution of LDA (3.00 mmol) in 6 mL of tetrahydrofuran. After 2 h methyl iodide (0.31 mL, 5.00 mmol) was added and the mixture was warmed to room temperature within 16 h. Extractive workup and distillation (100–130 °C/0.02 Torr) provided 0.176 g (47%) of *trans*-2-methoxy-1-methyl-2-phenylcyclopropyl cyanide (**41**; according to ^{1}H NMR trans:cis > 95:5). ^{13}C NMR ($CDCl_3$): *trans*-**41**, δ 135.0, 128.6, 127.1, 127.0 (s, 3 d, Ph), 121.6 (s, CN), 70.0 (s, C-2), 55.3 (q, OMe), 23.8 (t, C-3), 19.2 (s, C-1), 15.9 (q, Me). For further analytical data see experiment **1** + **40**.

Acknowledgment. We are most grateful for generous support of this work by the Stiftung Volkswagenwerk, the Fonds der Chemischen Industrie, and the Vereinigung von Freunden der Technischen Hochschule zu Darmstadt. We thank BASF AG (Ludwigshafen, FRG) for the donation of chemicals.

Thermal Reactions of Acyloxy and Alkoxy Carbene Complexes with Imines: Metathesis, Acetate Rearrangements, and a New Route to Imino Carbene Complexes via Peterson Type Eliminations

Christopher K. Murray, Benjamin P. Warner, Vera Dragisich, and William D. Wulff*

Searle Chemistry Laboratory, Department of Chemistry, University of Chicago, Chicago, Illinois 60637

Robin D. Rogers

Department of Chemistry, Northern Illinois University, DeKalb, Illinois 60115

Received July 27, 1990

The first examples of the reactions of imines ($R^3N{=}CHR^2$; $R^3 = CH_3$, R^2 = Ph, *p*-MePh) with acetoxy Fischer carbene complexes ($(CO)_5M{=}C(OAc)R^1$; M = Cr, W, R^1 = Ph) are described. The reaction of the chromium complex gives exclusively the *O*-acyl imidate **14** (MeN=C(OAc)Ph), which is the first example of a metathesis of an imine and a carbene complex. The tungsten complex gives a product that results from an unprecedented insertion of the imine into the carbene carbon–heteroatom bond along with the *O*-acyl imidate **14** as a minor product. This new insertion product was characterized by spectroscopic methods and by X-ray diffraction and determined to be the animal carbene complex **13b**. Crystal data for **13b**: space group $P\bar{1}$, $Z = 2$, $a = 8.269$ (3) Å, $b = 10.766$ (5) Å, $c = 13.851$ (7) Å, $\alpha = 68.83$ (5)°, $\beta = 75.97$ (6)°, $\gamma = 81.39$ (4)°, $R = 0.046$, and $R_w = 0.050$ for the 2267 reflections with $F_o \geq 5\sigma(F_o)$. It was determined that this insertion product is the result of an acetate transfer rather than a hydride transfer and that a likely intermediate in the mechanism is the zwitterion that results from initial addition of the imine nitrogen to the carbene carbon. The reaction of the acetoxy carbene complexes $(CO)_5M{=}C(OAc)R^1$ (M = Cr, W, R^1 = Ph, Me, tBu) with *N*-trimethylsilyl imines $Me_3SiN{=}CHR^2$ provides a new method for the synthesis of imino carbene complexes $(CO)_5M{=}C(R^1)N{=}CHR^2$ in a process that involves a Peterson type elimination. In a related reaction, it was found that imino complexes could also be accessed from the reaction of alkoxy carbene complexes $(CO)_5M{=}C(OMe)R^1$ (M = Cr, W, R^1 = Ph, Me, tBu) with *N*-trimethylsilyl imines.

The reaction of Fischer carbene complexes[1] with alkenes to produce cyclopropanes[2,3] has been of longstanding mechanistic interest and more recently of interest in applications to organic synthesis.[4] The corresponding thermal reaction of Fischer carbene complexes with imines to produce aziridines of the type **4** is unknown. The thermal reactions that have been reported led to aminolyses,[5] condensations,[6] or formal [2 + 2] cycloadditions.[7] For example, the reaction of the methyl complex **5** with the *N*-methyl imine of benzaldehyde gives the α,β-unsaturated carbene complex **7**, which is the result of a base-induced condensation and elimination between the relatively acidic complex **5** and the imine.[6] The reaction of **5** with imines less basic than **6** leads only to extensive decomposition of the carbene complex. The photoinduced reaction of Fischer carbene complexes with imines pro-

(1) For recent reviews on the chemistry of Fischer carbene complexes, see: (a) Brown, E. J. *Prog. Inorg. Chem.* **1980**, *27*, 1. (b) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissel, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Deerfield Beach, FL, 1984. (c) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587. (d) Casey, C. P. *React. Intermed.* **1985**, *3*. (e) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081. (f) Wulff, W. D. In *Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI Press: Greenwich, CT, 1989; Vol. 1. (g) Wulff, W. D. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, England, 1990; Vol. 5.

(2) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1972**, *105*, 3966.

(3) For reviews, see: (a) Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411. (b) Doyle, M. P. *Chem. Rev.* **1986**, *86*, 919.

(4) For a listing of recent citations, see footnote 4 in: Murray, C. K.; Yang, D. C.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 5660.

(5) (a) Knauss, L.; Fischer, E. O. *J. Organomet. Chem.* **1971**, *31*, C68. (b) Knauss, L.; Fischer, E. O. *Chem. Ber.* **1970**, *103*, 3744.

(6) Hegedus, L. S.; McGuire, M. A.; Schultze, L. M.; Yijun, C.; Anderson, O. P. *J. Am. Chem. Soc.* **1984**, *106*, 2680.

(7) (a) Barrett, A. G. M.; Brock, C. P.; Sturgess, M. A. *Organometallics* **1985**, *4*, 1903. (b) Barrett, A. G. M.; Mortier, J.; Sabat, M.; Sturgess, M. A. *Organometallics* **1988**, *7*, 2553.

0276-7333/90/2309-3142$02.50/0