complex. The optimized structure of triplet adduct **3d** at the unrestricted HF/6-31G* level is shown in Figure 4.[16] It is interesting that the O–O and Si–O bond distances and the Si–O–O angle are almost equal to those in the silanone oxide intermediate in the reaction of silylene with triplet oxygen.[5c] A calculation of vibrational frequencies predicts that the O–O stretching frequency in **3d** is near 1083 cm^{-1} ($\nu_{calcd}/1.126$)[5c,17] and shifts by 57 cm^{-1} to 1026 cm^{-1} upon ^{18}O substitution. These are in good agreement with those observed for **3a**. A peroxonium ion structure (**4**) in the singlet state may be considered as an alternative disilirane–oxygen adduct. We also calculated the vibrational frequencies of peroxonium intermediate **4d** derived from the reaction of **1d** with singlet oxygen at the HF/6-31G* level.[18] The absence of a band in the range 1000–1100 cm^{-1} in the IR spectra of **4d**, which can be assigned to the O–O stretching vibration, may exclude the intermediacy of **4a**. We therefore conclude that the labile intermediate formed in charge-transfer photooxygenation of **1a** can be represented by structure **3a**. A probable pathway to triplet adduct **3a** may be a direct reaction from the excited donor–acceptor complex between **1a** and oxygen (see Scheme I), as in the case of charge-transfer photooxygenation of tetramethylethylene[13] and sulfides[6] in a cryogenic oxygen matrix.

Acknowledgment. This work was supported in part by a grant from the Ministry of Education, Science and Culture in Japan.

Supplementary Material Available: Tables of physical properties of new compounds (**1b**, **1c**, **2b**, and **2c**) and HF/6-31G* vibrational frequencies of **1d**–oxygen adducts **3d** and **4d** and their isotopomers (2 pages). Ordering information is given on any current masthead page.

(16) The addition of **1d** to triplet oxygen to yield **3d** was 12.6 kcal/mol exothermic at the MP2/6-31G*//HF/6-31G* level.

(17) Kudo, T.; Nagase, S. *J. Phys. Chem.* **1984**, *88*, 2833.

(18) Singlet adduct **4d** is 28.9 kcal/mol more stable than triplet adduct **3d** at the MP2/6-31G*//HF/6-31G* level. The collapse of **4d** to product **2d** is 61.4 kcal/mol exothermic at the same level.

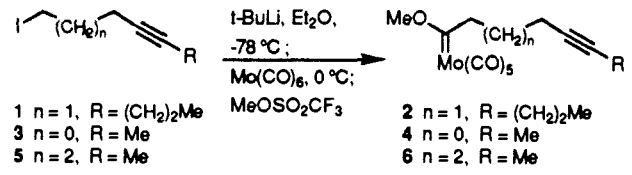
Molybdenum Carbene Complexes: Trapping of in Situ Generated Vinylcarbene Complexes with Electron-Poor Olefins

Daniel F. Harvey* and Matthew F. Brown

Department of Chemistry-0506
University of California, San Diego
La Jolla, California 92093-0506

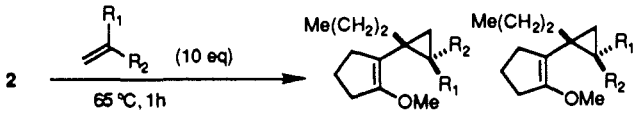
Received May 3, 1990

Fischer carbene complexes of chromium and tungsten have been found to participate in a wide variety of synthetically used transformations.[1] Investigations into the reactivity of Fischer carbene complexes of molybdenum have been reported to a lesser extent.[2] Recently, we reported that molybdenum-based Fischer



1 n = 1, R = $(CH_2)_2Me$ **2** n = 1, R = $(CH_2)_2Me$
3 n = 0, R = Me **4** n = 0, R = Me
5 n = 2, R = Me **6** n = 2, R = Me

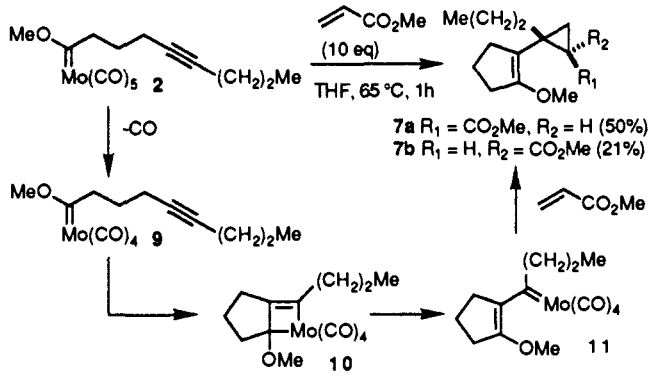
Figure 1.



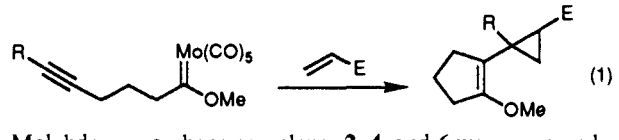
(in THF) R_1 = CN, R_2 = H **12a** 40% **12b** 26%
(in toluene) R_1 = H, R_2 = $PO(OMe)_2$ **13a** 47% **13b** 32%
(in THF) R_1 = Me, R_2 = CO_2Me **14a** 23% **14b** 11%

Figure 2.

Scheme I



carbene complexes would readily cyclopropanate electron-poor olefins in good yield.[3] This cyclopropanation process was found to occur under milder conditions and at a faster rate than the analogous process with chromium- and tungsten-derived complexes.[4] Reported herein is the extension of this cyclopropanation process to the trapping of in situ generated molybdenum vinylcarbene complexes (see eq 1).[5] We believe this to be the first example of the intermolecular trapping of an in situ generated vinylcarbene complex by an alkene.



Molybdenum carbene complexes **2**, **4**, and **6** were prepared as shown in Figure 1.[6] Methylation of the intermediate lithium alkoxide has been found to proceed smoothly with $MeOSO_2CF_3$ or $MeOSO_2F$.[7] This procedure proceeds in higher yield and with better reproducibility than the more commonly employed Me_3OBF_4 procedure.[8] Earlier reports have suggested that mo-

(1) For recent reviews, see: (a) Casey, C. P. *React. Intermed. (Wiley)* **1985**, *3*, 109. (b) Dötz, K. H. *Transition Met. Carbene Complexes* **1983**, 191. (c) Wulff, W. D.; Tang, P. C.; Chan, K. S.; McCallum, J. S.; Yang, D. C.; Gilbertson, S. R. *Tetrahedron* **1985**, *41*, 5813.

(2) (a) Fischer, E. O.; Maasböl, A. *Chem. Ber.* **1967**, *100*, 2445. (b) Dötz, K. H.; Fischer, E. O. *Chem. Ber.* **1972**, *105*, 1356. (c) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1972**, *105*, 3966. (d) Hegedus, L. S.; Schultze, L. M.; Toro, J.; Yijun, C. *Tetrahedron* **1985**, *41*, 5833. (e) Juneau, K. J.; Hegedus, L. S.; Roepke, F. W. *J. Am. Chem. Soc.* **1989**, *111*, 4762. (f) Doyle, M. P.; Davidson, J. G. *J. Org. Chem.* **1980**, *45*, 1538. (g) Wulff, W. D.; Kaesler, R. W.; Peterson, G. A.; Tang, P. C. *J. Am. Chem. Soc.* **1985**, *107*, 1060. (h) Wulff, W. D.; Yang, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 6726. (i) Aumann, R.; Uphoff, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 357. (j) Aumann, R.; Heinen, H. *Chem. Ber.* **1988**, *121*, 1739. (k) Aumann, R.; Heinen, H. *Chem. Ber.* **1986**, *119*, 2289. (l) Aumann, R.; Heinen, H. *Chem. Ber.* **1985**, *118*, 4186. (m) Aumann, R.; Kuckert, E.; Heinen, H. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 978. (n) Lam, C. T.; Senoff, C. V. *J. Organomet. Chem.* **1974**, *70*, 273. (o) Brandvold, T. A.; Wulff, W. D. *J. Am. Chem. Soc.* **1990**, *112*, 1645. (p) Hegedus, L. S.; Schultze, L. M.; Montgomery, J. *Organometallics* **1989**, *8*, 2189. (q) Aumann, R.; Hinterding, P. *Chem. Ber.* **1989**, *122*, 365. (r) Fischer, H.; Markl, R. *Chem. Ber.* **1985**, *118*, 3683.

(3) Harvey, D. F.; Brown, M. F. *Tetrahedron Lett.* **1990**, *31*, 2529.

(4) For a recent review of cyclopropane formation via Fischer carbene complexes, see: Brookhart, M.; Studabaker, W. B. *Chem. Rev.* **1987**, *87*, 411.

(5) For related examples of the intramolecular trapping of in situ generated vinylcarbene complexes with olefins, see: (a) Korkowski, P. F.; Hoye, T. R.; Rydberg, D. R. *J. Am. Chem. Soc.* **1988**, *110*, 2676. (b) Hoye, T. R.; Rehberg, G. M. *Organometallics* **1989**, *8*, 2070. (c) Parlier, A.; Rudler, H.; Platzer, N.; Fontanille, M.; Soum, A. *J. Organomet. Chem.* **1985**, *287*, C8. (d) Parlier, A.; Rudler, H.; Platzer, N.; Fontanille, M.; Soum, A. *J. Chem. Soc., Dalton Trans.* **1987**, 1041. (e) Alvarez, C.; Parlier, A.; Rudler, H.; Yefsah, R.; Daran, J. C.; Knobler, C. *Organometallics* **1989**, *8*, 2253.

(6) Iodide **1** was prepared from the commercially available 1-chloro-4-octyne (NaI, acetone, reflux; 97% yield). Iodide **3** was prepared from the commercially available 3-pentyn-1-ol [(a) MsCl, Et_3N, CH_2Cl_2; (b) NaI, acetone, reflux, 77% yield]. Iodide **5** was prepared from commercially available 5-hexyn-1-ol [(a) TMSCl, Et_3N, CH_2Cl_2, 78% yield; (b) *n*-BuLi, THF, MeI, 91% yield; (c) TBAF, THF, 91% yield; (d) MsCl, Et_3N, CH_2Cl_2; (e) NaI, acetone, reflux, 90% yield].

(7) Casey, C. P.; Cyr, C. R.; Boggs, R. A. *Synth. Inorg. Met.-Org. Chem.* **1973**, *3*, 249.

(8) Aumann, R.; Fischer, E. O. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 879.

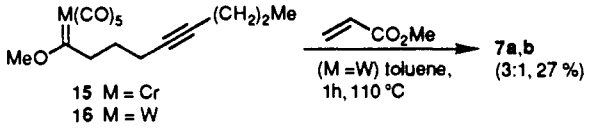
0002-7863/90/1512-7806$02.50/0 © 1990 American Chemical Society

lybdenum carbene complexes are unstable and difficult to handle.[2a,d] We have found that molybdenum carbene complexes **2**, **4**, and **6** are relatively stable. No significant decomposition of these complexes was observed after storage at −10 °C for 1 week.

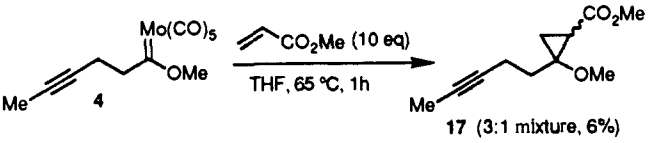
Mild thermolysis (65 °C, THF, 1 h) of complex **2** in the presence of methyl acrylate (10 equiv) led directly to a mixture of vinylcyclopropanes **7a** and **7b** in 71% yield. The presumed pathway for this transformation is outlined in Scheme I. Initial dissociation of CO leads to coordinatively unsaturated complex **9**. Intramolecular cyclization of **9** to **10** and subsequent ring opening generates vinylcarbene complex **11**.[9] Cyclopropanation of methyl acrylate by complex **11** gives vinylcyclopropanes **7a** and **7b**. The stereoselectivity observed in this process is similar to that observed in previous cyclopropanation studies.[10]

Several other electron-poor olefins have been found to readily participate in this transformation. Thermolysis of complex **2** with acrylonitrile, dimethyl vinylphosphonate, and methyl methacrylate led to **12**, **13**, and **14** as mixtures of diastereomers (Figure 2). The major diastereomer in each of these transformations is that in which the cyclopentene ring is anti to the electron-withdrawing group.[10] Cyclization with methyl methacrylate led to the desired cyclopropanes **14a** and **14b** in low isolated yield. Vinylcyclopropanes **14a** and **14b** appear to be less stable than the other vinylcyclopropanes described herein because of the presence of two quaternary centers on the cyclopropane ring.

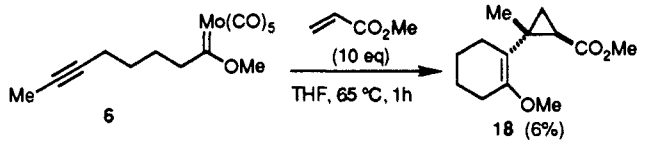
The reactivity of molybdenum carbene complex **2** was compared to that of the analogous chromium- and tungsten-based systems. Carbenes **15** and **16** were prepared by pathways analogous to those presented in Figure 1.[11] Thermolysis of chromium carbene complex **15** in the presence of methyl acrylate (65 °C, 1 h, benzene) led to a complex mixture of products, none of which corresponded to the desired vinylcyclopropane system.[12] Thermolytic chemistry of chromium alkynylcarbene complexes related to **15** has been described.[13] The dominant pathway with these systems appears to be intramolecular cyclization of the carbene complex with the alkyne accompanied by incorporation of carbon monoxide to give a vinylketene complex. In most cases the vinylketene complex undergoes subsequent transformations. In the cyclization of molybdenum carbene complexes **2**, **4**, and **6**, no products resulting from carbon monoxide incorporation were detected. Thermolysis of the more stable tungsten carbene complex **16** in the presence of methyl acrylate (110 °C, 1 h, toluene) led to the desired vinylcyclopropanes **7a** and **7b**. However, the isolated yields of **7a** and **7b** were considerably lower than in the reactions with the analogous molybdenum system.



Cyclization reactions with complexes **4** and **6** were investigated in order to explore the scope of this process. Thermolysis of molybdenum carbene complex **4**, which has a shorter, two-methylene tether between the carbene and the alkyne, did not lead to the desired 2-(1-methyl-2-carbomethoxycyclopropyl)-1-methoxycyclobutene or any identifiable products derived therefrom. Alkynylcyclopropane **17**, resulting from direct cyclopropanation of the carbene complex without initial addition to the alkyne, was the only identifiable product, in 6% isolated yield.



Complex **6**, with the longer, four-methylene tether, when treated with methyl acrylate in THF at 65 °C for 1 h, led to the desired cyclohexenylcyclopropane **18** in 6% yield. This was the only identifiable product that could be isolated from this reaction. Cyclopropanation to give 1-methoxy-1-(5-heptynyl)-2-carbomethoxycyclopropane was not observed. From these studies it appears that the success of the intramolecular cyclization to form the vinylcarbene complex is very dependent on the length of the tether.



In conclusion, we have demonstrated that in situ generated vinylcarbene complexes of molybdenum will react with electron-poor olefins to give vinylcyclopropanes in good yield. Further studies in this area are currently in progress.

Acknowledgment. Support from the Cancer Research Coordinating Committee of the University of California, the donors of the Petroleum Research Fund administered by the American Chemical Society, the American Cancer Society (Junior Faculty Research Award to D.F.H.), and the National Institutes of Health (GM41984-01) is gratefully acknowledged.

Supplementary Material Available: Experimental procedures and spectral data for **2**, **4**, **6**, **7ab**, **12ab**, **13ab**, **14ab**, **15**, **16**, **17ab**, and **18** (9 pages). Ordering information is given on any current masthead page.

(9) The intermediacy of metallocyclobutenes in the reaction of Fischer carbene complexes with alkynes has recently been discussed. See: Hofmann, P.; Hammerle, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 908.

(10) Stereochemistry was assigned on the basis of analysis of ^{1}H NMR spectra and comparison to previous studies. For further discussion, please see the supplementary material. See ref 2b and the following: (a) Wienard, A.; Reissig, H. U. *Tetrahedron Lett.* **1988**, *29*, 2315. (b) Fischer, E. O.; Dötz, K. H. *Chem. Ber.* **1970**, *103*, 1273.

(11) For other methods of preparation of alkyne–carbene complexes of chromium, see: (a) Xu, Y. C.; Wulff, W. D. *J. Org. Chem.* **1987**, *52*, 3263. (b) Wulff, W. D.; Anderson, B. A.; Isaacs, L. D. *Tetrahedron Lett.* **1989**, *30*, 4061.

(12) Several products have been isolated from this reaction and partially characterized. They all appear to result from insertion of carbon monoxide. Details of these studies will be presented in a full account of this work.

(13) (a) Xu, Y. C.; Challener, C. A.; Dragisich, V.; Brandvold, T. A.; Peterson, G. A.; Wulff, W. D.; Williard, P. G. *J. Am. Chem. Soc.* **1989**, *111*, 7269. (b) Wulff, W. D.; Xu, Y. C. *Tetrahedron Lett.* **1988**, *29*, 415. (c) Peterson, G. A.; Kunng, F. A.; McCallum, J. S.; Wulff, W. D. *Tetrahedron Lett.* **1987**, *28*, 1381. (d) Audouin, M.; Blandinieres, S.; Parlier, A.; Rudler, H. *J. Chem. Soc., Chem. Commun.* **1990**, 23.

Protein Microencapsulation of Nonaqueous Liquids

Kenneth S. Suslick* and Mark W. Grinstaff

School of Chemical Sciences
University of Illinois at Urbana-Champaign
505 South Mathews Avenue, Urbana, Illinois 61801

Received June 25, 1990

Vesicles have found diverse and important applications, ranging from microencapsulation of dyes, flavors, and fragrances[1] to drug delivery systems,[2] to the study of membrane structure, function, and reactivity.[3] Many such vesicles are made at least in part from proteins,[4,5] but there has been little understanding of the mech-

(1) (a) Risch, S. J.; Reineceius, G. A. *Flavor Encapsulation*; American Chemical Society: Washington, 1988. (b) Gutcho M. *Capsule Technology and Microencapsulation*; Noyes Group Data: New Jersey, 1972.

(2) (a) Lee, T. K.; Sokoloski, T. D.; Royer, G. P. *Science* **1981**, *213*, 333. (b) Heller, J.; Bake, R. W. *Controlled Release of Biomaterials*; Academic Press: New York, 1980. (c) Burgess, D. J.; Davis, S. S.; Tomlinson, E. *Int. J. Pharm.* **1987**, *39*, 129. (d) Morimoto, Y.; Sugibayashi, K.; Kato, Y. *Chem. Pharm. Bull.* **1981**, *29*, 1433. (e) Jalsenjak, V.; Stolink, S.; Jalsenjak, I. *Acta Pharm. Jugosl.* **1988**, *38*, 297.

(3) (a) Kaler, E. W., et al. *Science* **1989**, *245*, 1371. (b) Fender, J. H. *Acc. Chem. Res.* **1980**, *13*, 7. (c) Gliozzi, A.; Robello, M. *Colloids Surf.* **1989**, *35*, 135. (d) Mcknight, C. A., et al. *J. Bioact. Compat. Polym.* **1988**, *3*, 334.

0002-7863/90/1512-7807$02.50/0 © 1990 American Chemical Society