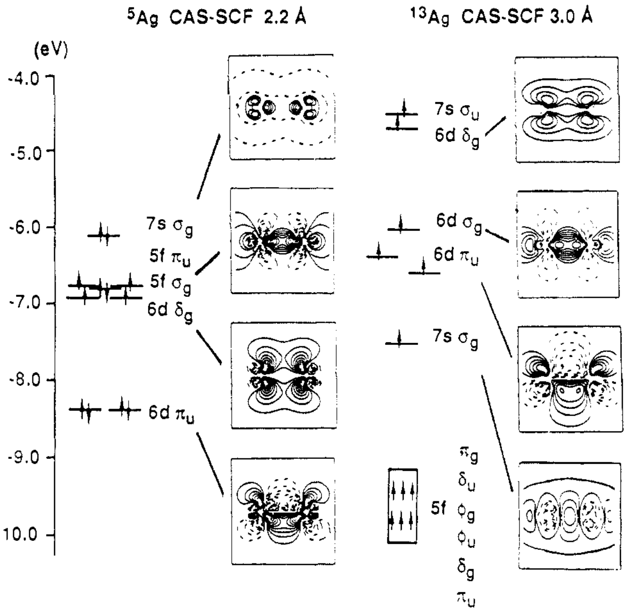

Figure 1. CAS-SCF occupied orbital energy diagrams and contour plots for ^{5}Ag and ^{13}Ag states of U_2. MOs are plotted on a 12 au × 12 au grid, with contour lines at levels of −0.34 to 0.34 au in steps of 0.02 au.

The lowest energy SBL state for U_2 is ^5A_g ($^5\Sigma_g^+$), corresponding to the $7s\sigma_g^2 d\pi_u^4 f\sigma_g^2 d\delta_g^2(t) f\pi_u^2(t)$ configuration. CAS-SCF orbital energies for this state are shown in Figure 1. The MO contour diagrams reveal significant overlaps for $7s\sigma_g$, $f\sigma_g$, and $d\pi_u$, giving an approximate quadruple bond. The energy minimum for these states is at 2.2 Å, 0.6 Å shorter than in the bulk metal.[9] However, this state is not bound with respect to the separated atoms. SCF calculations place the ^5A_g state 740 kJ/mol above the separated atoms; at the SRCI level it is still unbound by 340 kJ/mol.

In contrast to the apparently unbound SBL states, a set of 22 high-spin states with shallow potential minima at 3.0–3.8 Å and approximate harmonic frequencies of 85–105 cm^{-1} were found to lie below the separated atoms in energy. Surprisingly, the lowest energy configuration, $^{13}A_g$ ($^{13}\Delta_g$), has 12 unpaired electrons: $(5f)^6 7s\sigma_g^1 7s\sigma_u^{*1} d\sigma_g^1 d\pi_u^2 d\delta_g^1$. The orbital energies for this state, which has a minimum energy at 3.0 Å, are given in Figure 1. The MO contours for the $7s\sigma_g$, $d\sigma_g$, $d\pi_u$, and $d\delta_g$ MOs show strong overlaps, yielding an approximate double bond. At the SCF level, this state lies 400 kJ/mol below the separated atoms. With SRCI the difference is reduced to 160 kJ/mol.

The improved correlation treatment from SCF to CAS-SCF to SRCI calculations leads to a decrease in the ^5A_g (SBL) energy relative to those of the $^{13}A_g$ (LBL) and atomic states. Although additional correlation effects should lower the ^5A_g energy further, the state may remain unbound even at the highest level of theory. On the other hand, the LBL states may become approximately isoenergetic with the separated atoms when additional correlation effects are considered.

The picture emerging for U_2 is not unlike the complex and controversial one for its analogous 12-valence-electron transition-metal dimers, Cr_2 and Mo_2.[8,10] The simple f-orbital overlap model[4] is an inadequate description of the bonding in U_2: the relatively poor overlap of the U 5f orbitals does not foster U-U bond formation, especially at the sacrifice of electron exchange. Nevertheless, the SBL states show steep potential curves and may indicate the existence of bound metastable species. The LBL states exhibit flat potential curves. Although it is possible that these bound states are artifacts of an incomplete correlation treatment, the diffuse 6d and 7s orbitals of the uranium atom should have optimal overlap at long bond lengths, and these states may remain bound at even higher computational accuracy. Calculations with improved correlation treatment and spin-orbit CI are in progress.

Acknowledgment. We acknowledge the support of the U.S. Department of Energy and the Ohio Supercomputer Center. We thank Professor R. M. Pitzer for helpful discussions and for the uranium basis set.

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(10) See, for example: (a) Morse, M. D. *Chem. Rev.* **1986**, *86*, 1049. (b) Bursten, B. E.; Schneider, W. F. In *Metal-Metal Bonds and Clusters in Chemistry and Catalysis*; Fackler, J. P., Ed.; Plenum Press: New York, in press.

Spectroscopic Studies on Charge-Transfer Photooxygenation of Disiliranes

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Much attention has been drawn to the reaction of organosilicon compounds with molecular oxygen in recent years. It is well-known that strained silicon–silicon σ-bonds are oxidized exothermically with molecular oxygen to afford disiloxanes as monooxygenated products.[1,2] In spite of the significance of aerobic oxygenation of organosilicon compounds, few mechanistic investigations were carried out.[1,2] Recently we have reported the results on singlet oxygenation of disilirane[3] and oxadisilirane[4] to give 1,2,3,5-dioxadisilolane and 1,2,4,3,5-trioxadisilolane, demonstrating that the silicon–silicon σ-bond is a good electron donor toward singlet oxygen.[3] Our interest in photochemical oxygenation[5] has led us to investigate the direct charge-transfer (CT) photochemical reaction of a silicon–silicon σ-bond with molecular oxygen.[6] We report here the charge-transfer photooxygenation of disilirane and oxadisilirane on the basis of the IR spectroscopic observation of a disilirane–oxygen adduct in a cryogenic oxygen matrix together with ab initio calculations.

The UV absorption spectrum of 1,1,2,2-tetramesityl-1,2-disilirane (**1a**)[3,7] in an oxygen-saturated solvent such as methylene chloride or acetonitrile reveals a weak broad contact CT band with a maximum at 300 nm. The main continuum is seen up to ca.

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† University of Tsukuba.
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(1) (a) Carberry, E.; West, R. *J. Organomet. Chem.* **1966**, *6*, 582. (b) Ishikawa, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1970**, 612. (c) Tamao, K.; Kumada, M.; Ishikawa, M. *J. Organomet. Chem.* **1971**, *31*, 17. (d) Atwell, W. H.; Uhlmann, J. G. *Ibid.* **1973**, *52*, C21. (e) Sakurai, H.; Kobayashi, T.; Nakadaira, Y. *Ibid.* **1978**, *162*, C43. (f) Seyferth, D.; Vick, S. C. *Ibid.* **1977**, *125*, C11. (g) Masamune, S.; Tobita, H.; Murakami, S. *J. Am. Chem. Soc.* **1983**, *105*, 6524. (h) Masamune, S.; Kabe, Y.; Collins, S.; Williams, D. J.; Jones, R. *Ibid.* **1985**, *107*, 5552. (i) Davidson, I. M. T.; Ostah, N. A.; Seyferth, D.; Duncan, D. P. *J. Organomet. Chem.* **1980**, *187*, 297. (j) Weidenbruch, M.; Schafer, A. *Ibid.* **1984**, *269*, 231.

(2) Yokelson, H. B.; Millevolte, A. J.; Gillette, G. R.; West, R. *J. Am. Chem. Soc.* **1987**, *109*, 6865.

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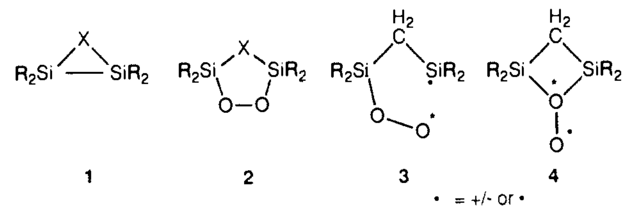
(4) Ando, W.; Kako, M.; Akasaka, T.; Kabe, Y. *Tetrahedron Lett.* **1990**, *31*, 4177.

(5) (a) Akasaka, T.; Ando, W. *J. Am. Chem. Soc.* **1987**, *109*, 1260. (b) Akasaka, T.; Kako, M.; Sonobe, H.; Ando, W. *Ibid.* **1988**, *110*, 494. (c) Akasaka, T.; Nagase, S.; Yabe, A.; Ando, W. *Ibid.* **1988**, *110*, 6270.

(6) Akasaka, T.; Yabe, A.; Ando, W. *J. Am. Chem. Soc.* **1987**, *109*, 8085.

(7) Masamune, S.; Murakami, S.; Tobita, H. *J. Am. Chem. Soc.* **1983**, *105*, 7776.



a; R=mesityl, X=CH_2 b; R=2,6-diisopropylphenyl, X=O

c; R=2,6-diethylphenyl, X=O d; R=H, X=CH_2

400 nm. Oxygen was bubbled through an acetonitrile solution of **1a** (3×10^{-3} M) that was irradiated at 15 °C with a high-pressure mercury arc lamp through a sharp-cut optical filter (Toshiba L-37 filter; cutoff 360 nm). 1,1,2,2-Tetramesityl-1,2,3,5-dioxadisilolane (**2a**)[3] was obtained by flash column chromatography on silica gel in 36% yield (6% conversion). Very similar results were obtained with 2,2,3,3-tetrakis(2,6-diisopropylphenyl)oxadisilirane (**1b**)[8] and 2,2,3,3-tetrakis(2,6-diethylphenyl)oxadisilirane (**1c**)[8] affording the corresponding 1,2,4,3,5-trioxadisilolanes (**2b** and **2c**) as the major products under the same conditions. If the photolysis of **1a** was carried out under nitrogen, **1a** was recovered quantitatively even after a prolonged irradiation.[7] Addition of 1,4-diazabicyclo[2.2.2]octane as a singlet oxygen quencher[9] or 2,4,6-tri-*tert*-butylphenol as a free-radical scavenger did not affect the oxidation. These control experiments confirm that neither singlet oxygenation[3] nor free-radical oxidation is responsible for the production of **2a** under the reaction conditions.

The UV absorption spectrum of **1a** in solid oxygen matrices[10] reveals the same broad contact CT band with a maximum at 300 nm as seen in the liquid phase (Figure 1). No product was obtained by the photolysis (350–400 nm)[11] of **1a** in an argon matrix at 16 K.[12] The photolysis of **1a** in an oxygen matrix at 16 K, however, caused a smooth photochemical oxygenation, as shown in Figure 2. The reaction intermediates resulting from similar UV irradiation (350–400 nm) of the contact CT band were studied by FT–IR spectroscopy.[6] Irradiation of **1a** isolated in an oxygen matrix at 16 K gave a new species with an intense IR band at 1078 cm^{-1} (Figure 3).[12,13] The species behaves as a single chemical entity (i.e., the IR bands appear and disappear simultaneously at the initial stage of irradiation). Isotopic labeling experiments show that the IR band shifts by 39 cm^{-1} to a lower wave number with $^{18}O_2$ (40% doubly labeled). Upon subsequent annealing of the matrix at temperatures higher than 50 K, the intense band at 1078 cm^{-1} disappeared and the oxygen matrix became cloudy.[14] Product analysis at room temperature showed the formation of **2a** (75%) and 1,2,4-oxadisiletane (25%) by means of spectral analysis.[3] The intense band at 1078 cm^{-1} is ascribable to the characteristic O–O stretching mode in the disilirane–oxygen adduct (**3a**) in the triplet state, as described below. It is noteworthy that the O–O stretching frequency and its isotopic shift in **3a** are close to those (1084 and 40 cm^{-1}) in the silylene–triplet oxygen adduct having a silanone oxide ($R_2Si–O–O$) structure.[5c]

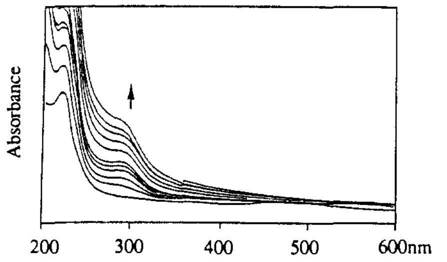


Figure 1. UV spectra of disilirane **1a** matrix-isolated in solid oxygen at 16 K.

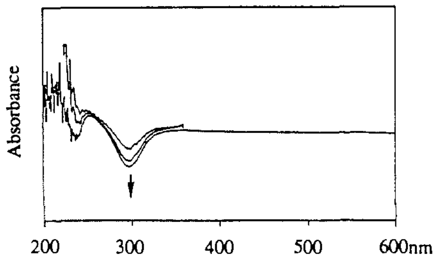


Figure 2. Difference UV spectra obtained upon photolysis of disilirane **1a** matrix-isolated in solid oxygen at 16 K.

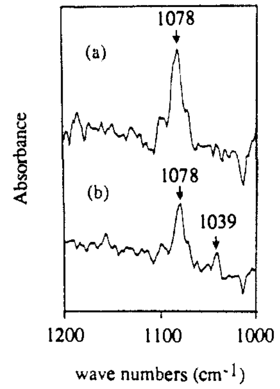


Figure 3. Difference IR spectra obtained upon photolysis of disilirane **1a** matrix-isolated in solid oxygen at 16 K.

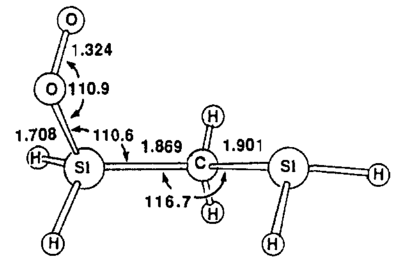
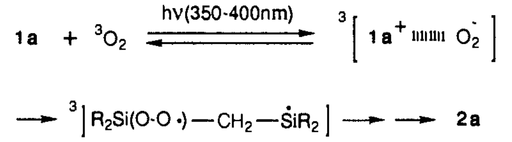


Figure 4. The optimized geometry of **3d** in angstroms and degrees at the unrestricted HF/6-31G* level.

Scheme I



Parallel theoretical studies on the products in the reaction of **1d** with oxygen offer a basis for the possible structure of the adduct **3d**.[15] The silicon–silicon bond with a relatively low ionization energy (IP = 8.9 eV at the HF/6-31G* level) in **1d** compared with IP = 11.4 eV in oxirane can be expected to easily donate the σ-electrons to an oxygen molecule forming a charge-transfer

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(8) **1b** and **1c** were prepared by oxidation of the corresponding disilenes with *m*-chloroperbenzoic acid and dinitrogen oxide,[2] respectively.

(9) Foote, C. S.; Peterson, E. R.; Lee, K.-W. *J. Am. Chem. Soc.* **1972**, *94*, 1032.

(10) The cryogenic apparatus has been described previously.[6]

(11) UV irradiation was carried out by means of a 500-W high-pressure mercury arc lamp (USHIO). A water cell (20 cm) with quartz windows and two sharp-cut optical filters (Toshiba UV-D35 and UV-35 filters) were used at all times to remove the infrared radiation and to select exciting wavelengths (350–400 nm).

(12) Other characteristic absorption bands appeared at 696, 728, 754, 792, 980, 991, 1420, 1480, and 1611 cm^{-1}.

(13) No absorption band assigned to ozone was observed at 1034 cm^{-1}: Hashimoto, S.; Akimoto, H. *J. Phys. Chem.* **1986**, *90*, 529.

(14) The annealing temperature, melting point, and boiling point of oxygen are 26, 54, and 90 K, respectively: Moskovits, M.; Ozin, G. A. In *Cryochemistry*; Moskovits, M., Ozin, G. A., Ed.; Wiley: New York, 1976; p 24.

(15) The program used is GAUSSIAN 88: Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; DeFrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R.; Kahn, L. R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A., Release C: Gaussian Inc., Pittsburgh, PA. Geometries were optimized at the HF/6-31G* level: Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654. Electron correlation was calculated with the MP2 method: Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem.* **1976**, *10*, 1.

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} (ν_{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.

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[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

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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 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.

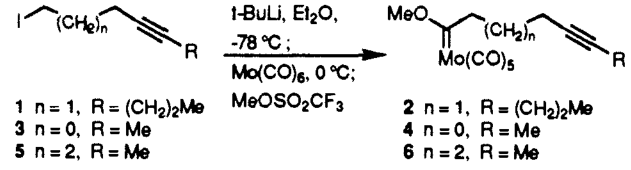


Figure 1.

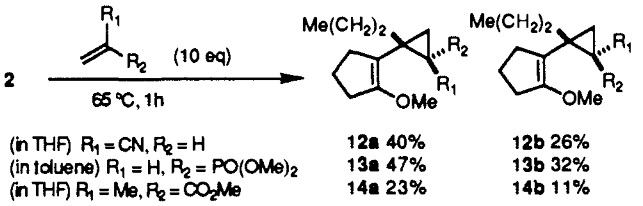
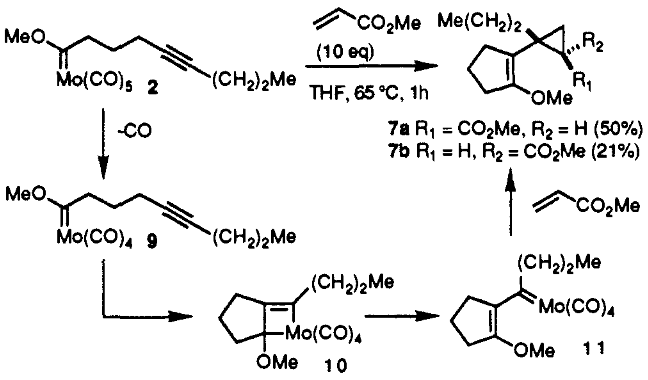
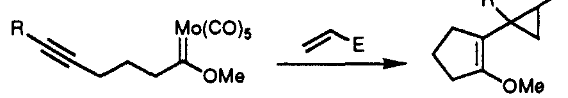


Figure 2.

Scheme I



 (1)

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-

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[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.