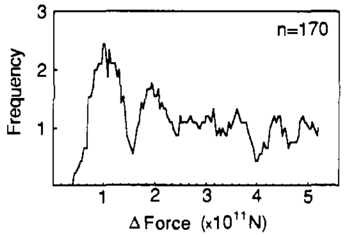


Figure 3. Distribution of differences between 170 pairs of adhesion measurements from one experiment. The measurements were divided into 4×10^{-13} N bins, and data was smoothed by a five-point averaging. There is a well-defined peak at 1.2×10^{-11} N. The next multiple can also be seen, but higher multiples are lost because of peak broadening.

peared to be a CO_2-driven pH decrease. The cantilevers were 120 or 200 μm, V-shaped, with spring constants of roughly 0.2 or 0.04 N/m, respectively.[14,16]

At pH 5 the adhesive force between silicon nitride AFM tips and glass in water is generally 5×10^{-9} to 4×10^{-8} N,[17] while at pH > 9.3 the adhesion is reduced below the limits of detection and the interaction is strongly repulsive (Figure 1). In the high-resolution experiments the adhesion is measured at pH 8.5–9, where the adhesive force is about 0.5×10^{-9} to 1.5×10^{-9} N. As this curve (Figure 1C, but with analog control) was examined closely over time, it became evident that the adhesive interaction fluctuated in discrete steps (Figure 2). A large number of these events ($n > 4000$) were examined, and the difference in adhesive force between pairs of scans was tabulated. The criteria for counting an interaction were that the two measurements were immediately sequential (i.e., within 2 s, to minimize drift), that the path of the trace was identical before and after the jump off, and that the difference between two jumps was less than 1.8 nm. The latter was an arbitrary number selected to limit the size of the data set, while including several multiples of the discrete interaction. The smoothed distribution of all events that satisfied these criteria from one experiment is shown in Figure 3. A similar distribution was seen for several experiments; however, variability prevented pooling of data from separate experiments. The oscilloscope traces and the distribution plot clearly show the discrete nature of the adhesive interaction between silicon nitride and glass of roughly 1×10^{-11} N.

The high density of silanol groups on both surfaces leads us to suggest that these discrete interactions may be due to variations in the number of hydrogen bonds formed between the surfaces at subsequent contacts.[18,19] Indeed the strength of the interaction is of the order of magnitude expected for a single hydrogen bond. Since there is also a repulsive double layer present, the force of adhesion measured from cantilever deflection should be an underestimate of the actual bond force. Another possible explanation of the data stems from the breakdown of the continuum properties of water near surfaces.[20] Israelachvili and Pashley[10] have shown that ordered water layers near a mica surface caused oscillations in the measured force as two surfaces were brought together. It is possible that the quantized adhesion described here results from the tip pulling away from different force minima generated by the ordered water layers. In fact, the depth of the corresponding energy wells may be sufficiently near kT (at jump-off) to allow the tip to jump between the different wells, effectively resulting in a Boltzman sampling. Several other explanations for the data such as digital signal noise, drift, double layer repulsion, and other adhesive forces have been considered, but do not provide adequate explanations for the data.

The observation of a quantized adhesive interaction between silicon nitride and glass presents a potentially important phenomenon. The most likely explanations for the effect are individual hydrogen bonds being resolved or force minima from ordered hydration layers. While the exact mechanism remains to be determined, the results demonstrate that the AFM has the sensitivity for studying subtle details of intermolecular forces.

Acknowledgment. This research was supported by the Office of Naval Research (J.P.C., C.B.P., J.H.H.), the National Science Foundation Solid State Physics Grant DMR89-17164 (P.K.H.), and by fellowship awards from the Colvin and Merck Funds (J.H.H.). Equipment was supplied by Digital Instruments. We thank J. Israelachvili, W. Ducker, and D. Leckband for insightful discussions.

---

(16) Preliminary results from direct measurements suggest that spring constants can vary by a factor of 2 for the same type of cantilever within a wafer (Cleveland *et al.*, unpublished observation). The average value for the V-shaped 200 μm long with 36 μm wide legs cantilever measured to date is 0.04 N/m, though no calibrated cantilevers were available for this study.

(17) Most low-resolution measurements were made with 120-μm V-shaped cantilevers with spring constants of 0.2 N/m. Since the total adhesive force is load dependent, these values are lower for the 200-μm cantilevers.

(18) The density of silanol groups on silicon nitride and typical glass surfaces is about 5 hydroxyl groups per nm^2. Iler, R. K. *The Chemistry of Silica*; Wiley and Sons: New York, 1979. Bousse, L.; Mostarshed, S. *J. Electroanal. Chem.* **1991**, *302*, 269–274. Amino groups on the surface of silicon nitride are only about 1% as frequent as hydroxyl groups, and their contribution is here considered negligible. Bousse, L.; Mostarshed, S. *J. Electroanal. Chem.* **1991**, *302*, 269–274.

(19) The pK_a of surface silanol groups is usually 6–7; however, as these two surfaces are brought into contact, the pK_a will shift up substantially (often 1–3 units in other systems). The silanols will therefore be partially protonated, though the exact protonation state is not known.

(20) Granick, S. *Science* **1991**, *253*, 1374–1379.

A New Type of Bridging Carbonyl Ligand: μ_3-η^2, and not One but Two

Richard D. Adams,* Zhaoyang Li, Jau-Ching Lii, and Wengan Wu

Department of Chemistry and Biochemistry
University of South Carolina
Columbia, South Carolina 29208

Received March 13, 1992

Bridging coordination is a principal mode for the activation of CO by metal cluster complexes.[1] It is believed to play a key role in the transformations of CO on metal surfaces.[2] A variety of bridging coordination modes for CO have been characterized. These range from the simple two-center carbon bridge A to the complex μ_4-η^2 B.[1] Triply bridging carbonyl ligands that have been characterized include μ_3-η^1 C and μ_3-η^2 D.[3] There are also a number of variations of these forms in which Lewis acid centers are strongly associated to the oxygen atom.[1a] We now wish to report what appears to be a new triple bridge, E, in which the carbon atom bridges two of the metals of an *open* triangle and the oxygen atom alone is coordinated to the third one.

The compound $Ru_8Pt_2(CO)_{23}(\mu_3\text{-}H)_2$[4] (**1**) was isolated in 22% yield from the reaction of $Ru_4Pt_2(CO)_{18}$[5] with $Ru_4(CO)_{13}(\mu\text{-}H)_2$

---

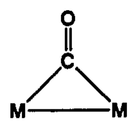
(1) (a) Horwitz, C. P.; Shriver, D. F. *Adv. Organomet. Chem.* **1984**, *23*, 219. (b) Shriver, D. F.; Sailor, M. J. *Acc. Chem. Res.* **1988**, *21*, 374. (c) Chisholm, M. H.; Folting, K.; Hampden-Smith, M. J.; Hammond, C. E. *J. Am. Chem. Soc.* **1989**, *111*, 7283. (d) Chisholm, M. H.; Hammond, C. E.; Huffman, J. C.; Johnston, V. J. *J. Organomet. Chem.* **1990**, *394*, C16. (e) Chisholm, M. H.; Folting, K.; Johnston, V. J.; Hammond, C. E. *J. Organomet. Chem.* **1990**, *394*, 265. (f) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Organometallics* **1985**, *4*, 986. (g) Brun, P.; Dawkins, G. M.; Green, M.; Miles, A. D.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, *92*, 6.

(2) (a) Blyholder, G.; Lawless, M. *J. Chem. Soc., Chem. Commun.* **1990**, 632. (b) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479.

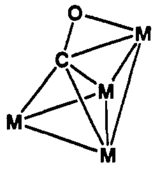
(3) Herrmann, W. A.; Biersack, H.; Ziegler, M. L.; Weidenhammer, K.; Siegel, R.; Rehder, D. *J. Am. Chem. Soc.* **1981**, *103*, 1692.

(4) $Ru_4Pt_2(CO)_{18}$[5] (30.0 mg, 0.0231 mmol) and 18.0 mg (0.0233 mmol) of $Ru_4(CO)_{13}(\mu\text{-}H)_2$ were dissolved in 30 mL of heptane and heated to reflux for 45 min. The products were separated by TLC on silica gel with a hexane/CH_2Cl_2 (2/1) solvent mixture. This yielded the following, in order: 2.1 mg of a mixture of $Ru_4(CO)_{12}(\mu\text{-}H)_4$ and $Ru_3(CO)_{12}$, 12.0 mg of unreacted $Ru_4(CO)_{13}(\mu\text{-}H)_2$, 2.1 mg of unreacted $Ru_4Pt_2(CO)_{18}$, and 8.9 mg of dark green $Ru_8Pt_2(CO)_{23}(\mu_3\text{-}H)_2$ (**1**) (22%). For **1**: IR (ν_{CO} in CH_2Cl_2) 2074 (vs), 2046 (w), 2033 (w); ^{1}H NMR (δ in CD_2Cl_2) −15.79 (2 H, J_{Pt-H} = 22.2 Hz). Satisfactory elemental analyses have been obtained.

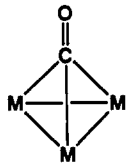
0002-7863/92/1514-4918$03.00/0



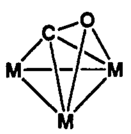
A



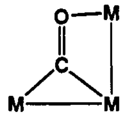
B



C



D



E

in refluxing heptane solvent. Compound **1** was characterized by single-crystal X-ray diffraction analyses,[6,7] and an ORTEP drawing of its molecular structure is shown in Figure 1. The molecule consists of an edge-shared bioctahedral cluster of eight ruthenium and two platinum atoms and 23 carbonyl ligands. The platinum atoms occupy the edge-sharing sites, and there are two triply bridging hydride ligands (located and refined crystallographically, δ −15.79 ppm, $^2J_{\text{Pt-H}}$ = 22.2 Hz) on triruthenium faces on opposite sides of the cluster. The ruthenium apices of the octahedra are also joined by metal–metal bonds, and one of these is unusually short: Ru(5)–Ru(6) = 2.580 (2) Å vs Ru(7)–Ru(8) = 2.738 (2) Å. The shortness may reflect unsaturation in the cluster. Compound **1** is also electron deficient by the amount of two electrons according to the usual electron counting procedures.[8] Anticipating high reactivity, we investigated its reaction with 1,2-bis(diphenylphosphino)ethane, dppe.

When compound **1** was allowed to react with dppe at 0 °C for 2 h, the adduct Ru$_8$Pt$_2$(CO)$_{23}$(dppe)(μ-H)$_2$ (**2**) was formed.[9] Compound **2** was characterized by single-crystal X-ray diffraction analyses,[7,10] and an ORTEP drawing of its molecular structure is shown in Figure 2. This compound consists of a face-shared bioctahedral cluster of nine metal atoms with a ruthenium "spike", Ru(8), extending from one of the outer Ru$_3$ triangles. The bridging hydride ligands were located crystallographically (^{1}H NMR δ −7.71 (1 H, dd, $J_{\text{P-H(cis)}}$ = 10 Hz, $J_{\text{P-H(trans)}}$ = 29 Hz), −18.09 (1 H, s)). There are four bridging carbonyl ligands of the type A, but most interestingly there are *two* μ_3-η^2 carbonyl ligands of the type E, C(53)–O(53) and C(63)–O(63), that bridge adjacent Ru–Ru bonds through their carbon atoms on the outer Ru$_3$ triangle and are coordinated to the spike through their oxygen atoms: Ru(8)–O(53) = 2.24 (1) Å, Ru(8)–O(63) = 2.16 (1) Å. The CO distances, C(53)–O(53) = 1.21 (2) and C(63)–O(63) = 1.23 (2) Å, of these ligands are significantly longer than those of the other carbonyl ligands, which could reflect a significant reduction in the CO bond order. This was also indicated by their low-frequency absorption in the infrared spectrum at 1612 cm^{-1}.[11] The long distances, Ru(8)···C(53) = 2.75 (1) and Ru(8)···C(63) = 2.74 (1) Å, indicate that there is no significant bonding between

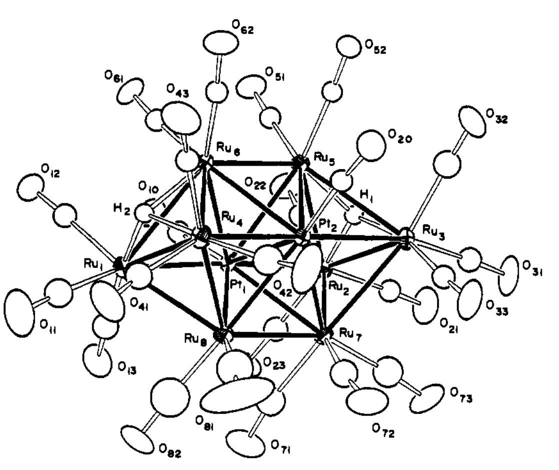


Figure 1. ORTEP diagram of Ru$_8$Pt$_2$(CO)$_{23}$(μ_3-H)$_2$ (**1**). Selected interatomic distances (Å) are as follows: Pt(1)–Pt(2) = 2.754 (1), Ru(1)–Ru(4) = 3.031 (2), Ru(1)–Ru(6) = 2.922 (2), Ru(4)–Ru(6) = 2.922 (2), Ru(2)–Ru(3) = 2.985 (2), Ru(2)–Ru(5) = 2.956 (2), Ru(3)–Ru(5) = 2.915 (2), Ru(5)–Ru(6) = 2.580 (2), Ru(7)–Ru(8) = 2.738 (2), Ru(1)–H(2) = 1.6 (1), Ru(4)–H(2) = 2.0 (1), Ru(6)–H(2) = 2.0 (2), Ru(2)–H(1) = 1.7 (1), Ru(3)–H(1) = 1.8 (1), Ru(5)–H(1) = 1.8 (2).

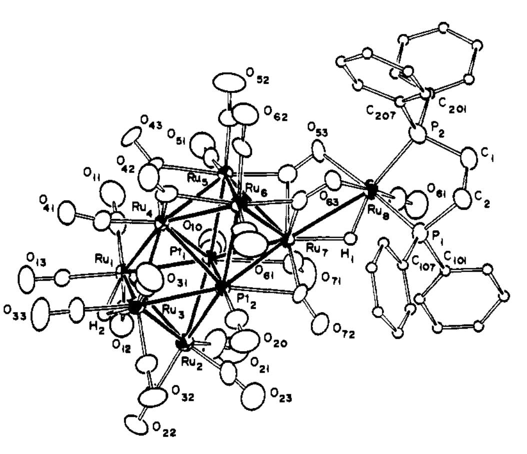


Figure 2. ORTEP diagram of Ru$_8$Pt$_2$(CO)$_{23}$(dppe)(μ-H)$_2$ (**2**). Selected interatomic distances (Å) are as follows: Pt(1)–Pt(2) = 2.5914 (9), Ru(1)–Ru(3) = 3.007 (2), Ru(7)–Ru(8) = 3.002 (2), Ru(1)–H(2) = 1.9 (1), Ru(3)–H(2) = 1.9 (1), Ru(7)–H(1) = 1.9 (1), Ru(8)–H(1) = 1.6 (1), Ru(8)–O(53) = 2.24 (1), Ru(8)–O(63) = 2.16 (1), C(53)–O(53) = 1.21 (2), C(63)–O(63) = 1.23 (2), Ru(8)···C(53) = 2.75 (1), Ru(8)···C(63) = 2.74 (1).

---

(5) Adams, R. D.; Chen, G.; Wang, J. G.; Wu, W. *Organometallics* **1990**, *9*, 1339.

(6) Crystals of **1** were obtained by crystallization from solutions in dichloromethane/hexane (4/1) at 25 °C. Crystal data: space group = $P2_1/n$, a = 20.454 (3) Å, b = 17.676 (4) Å, c = 10.219 (2) Å, β = 90.42 (1)°, Z = 4, 2584 reflections, R = 0.031.

(7) Diffraction measurements at 20 °C were made on a Rigaku AFC6S four-circle diffractometer using Mo Kα radiation. The structure solution and refinement were made by using the TEXSAN structure solving program library (v. 5.0) of the Molecular Structure Corp., The Woodlands, TX. An absorption correction was applied to the data.

(8) Mingos, D. M. P.; May, A. S. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH: New York, 1990.

(9) **1** (20.0 mg, 0.0108 mmol) and 4.3 mg (0.0108 mmol) of (PPh$_2$)$_2$C$_2$H$_4$ were allowed to react in 80 mL of CH$_2$Cl$_2$ at 0 °C for 2 h. A total of 2.6 mg of the blue-green product Ru$_8$Pt$_2$(CO)$_{23}$(dppe)(μ-H)$_2$ (**2**) (10% yield) was isolated by TLC on silica gel with a CH$_2$Cl$_2$/hexane (5/3) solvent mixture. For **2**: IR (ν_{CO} in CH$_2$Cl$_2$) 2084 (w), 2051 (m, sh), 2039 (m, sh), 2029 (vs), 1612 (m); ^{1}H NMR (δ in CD$_2$Cl$_2$, −57 °C) −7.71 (dd, $J_{\text{P-H(cis)}}$ = 10 Hz, $J_{\text{P-H(trans)}}$ = 29 Hz), −18.09 (s, 1 H).

(10) Crystals of **2** were obtained by crystallization from solutions in a mixture of dichloromethane/hexane (2/1) at 5 °C. Crystal data: space group = $P2_1/c$, a = 10.503 (2) Å, b = 20.659 (4) Å, c = 28.379 (5) Å, β = 94.36 (1)°, Z = 4, 4553 reflections, R = 0.032. Nonintegral quantities of CH$_2$Cl$_2$ are cocrystallized in the lattice at two different sites.

(11) Ru$_3$(CO)$_{12}$ was enriched with ^{13}CO at 125 °C by using 99% ^{13}CO in a Parr high-pressure reactor in ethanol solvent. This was subsequently converted to Ru(CO)$_5$[12a] and Ru$_4$(CO)$_{13}$(μ-H)$_2$[12b] using ^{13}CO. The Ru(CO)$_5$ was converted to Pt$_2$Ru$_4$(CO)$_{18}$[5] and then allowed to react with the enriched Ru$_4$(CO)$_{13}$(μ-H)$_2$ to yield **1**, which was subsequently converted to **2** containing greater than 50% ^{13}CO by reaction with dppe. The IR spectrum of this sample shows a new absorption at 1568 cm^{-1}, which is the expected location of the mass-reduced absorption observed at 1612 cm^{-1} in the unenriched sample and confirms this absorption to be related to the CO ligands. Two weak absorptions observed at 1575 and 1437 cm^{-1} in the unenriched sample of **2** appear unshifted in the enriched sample, indicating that they are unrelated to the CO ligands. It is somewhat unexpected that the two bridging CO ligands produce only one absorption.[13] Evidently, their coupling is so weak that one unresolved absorption is observed.

(12) (a) Huq, R.; Poë, A. J.; Charola, S. *Inorg. Chim. Acta* **1980**, *38*, 121. (b) Cauty, A. J.; Johnson, B. F. G.; Lewis, J. *J. Organomet. Chem.* **1972**, *43*, C35.

(13) Adams, R. D.; Babin, J. E.; Tasi, M. *Inorg. Chem.* **1988**, *27*, 2618.

these atoms, in contrast to other examples of η^2-bridging CO ligands.[1,3,14] Each ligand serves as a four-electron donor. Two electrons are donated by the carbon atom to the pair of metal atoms that it bridges, and two electrons from the oxygen are donated to the metal Ru(8). Since the oxygen atoms of both bridging carbonyl ligands are bonded to the same metal atom, the carbon atoms are brought into an unusually close nonbonding contact: C(53)···C(63) = 2.46 (2) Å. Similar close contacts have been shown to facilitate the formation of carbon–carbon bonds between CO ligands under reducing conditions.[15] Efforts to achieve this are in progress.

Acknowledgment. This research was supported by the National Science Foundation Grant No. CHE-8919786.

Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters (27 pages); tables of observed and calculated structure factors (49 pages). Ordering information is given on any current masthead page.

---

(14) Colton, R.; Commons, C. J.; Hoskins, B. F. *J. Chem. Soc., Chem. Commun.* **1975**, 363.

(15) (a) Bianconi, P. A.; Williams, I. D.; Engeler, M. P.; Lippard, S. J. *J. Am. Chem. Soc.* **1986**, *108*, 311. (b) Hoffmann, R.; Wilker, C. N.; Lippard, S. J.; Templeton, J. L.; Brower, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 146.

Synthesis and Structure of a Tetrasilacyclohexyne[1]

Yi Pang, Alan Schneider, and Thomas J. Barton*

Ames Laboratory (U.S. Department of Energy) and
Department of Chemistry
Iowa State University, Ames, Iowa 50011

Mark S. Gordon and Marshall T. Carroll

Department of Chemistry
North Dakota State University
Fargo, North Dakota 58105

Received November 4, 1991
Revised Manuscript Received April 20, 1992

Although strained cycloalkynes have received considerable experimental[2] and theoretical[3] attention for many years, the smallest isolable rings are seven-membered.[4] We report here the synthesis, chemical and structural characterization, and ab initio calculations of the first isolable[5] six-membered ring containing a carbon–carbon triple bond.

In a continuation of our program of synthesis and study of silylene–acetylene polymers[6] we were surprised to find that pentasilacycloheptyne (**2**)[7] could be directly synthesized in 80% yield simply by the condensation of dilithioacetylene[6] and 1,5-dichlorodecamethylpentasilane (**1**). Considerably more surprising was the discovery that the analogous coupling of LiC≡CLi and 1,4-dichlorooctamethyltetrasilane (**3**) afforded octamethyltetrasilacyclohexyne (**4**) in 65% yield as a colorless liquid, easily purified by chromatography on silica gel.[8]

Table I. NMR Comparison of Cycloalkynes **2**, **4**, and **5**

cycloalkyne	^{13}C NMR [C≡C/SiCH$_3$] (δ)	^{29}Si NMR (δ)
$Me_3SiC{\equiv}CSiMe_3$	113.02/0.10	
c-$(Me_2Si)_6C{\equiv}C$, **5**	117.77/−3.10, −5.14, −6.24	−35.4, −38.9, −39.9
2	123.22/−3.16, −5.91, −6.04	−33.3, −34.7, −38.7
4	135.66/−3.02, −6.51	−17.8, −30.6

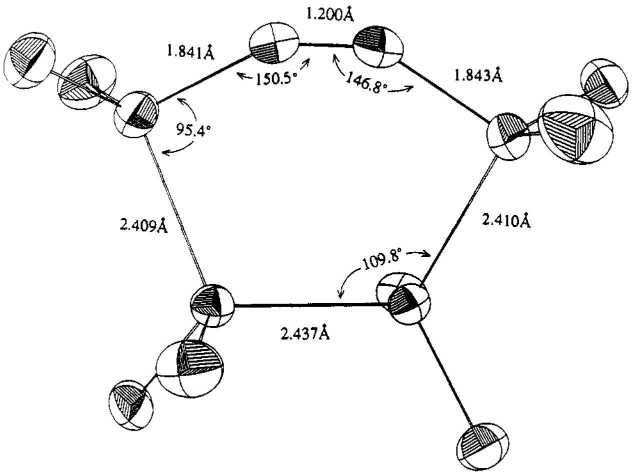
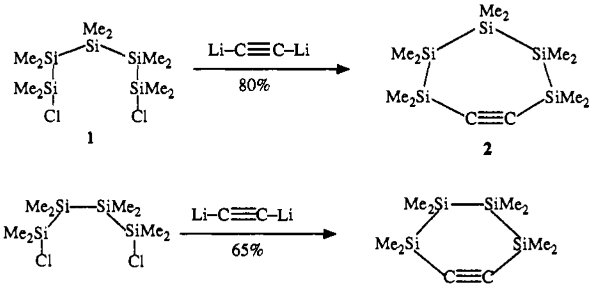


Figure 1. ORTEP diagram of octaisopropyltetrasilacyclohexyne (**8**). The methyl groups have been omitted for clarity.



Pure, neat **4** slowly decomposes or polymerizes at room temperature but is completely stable when stored as a 20% solution in hexane at 0 °C. The structure of cyclohexyne **4** was initially deduced from its mass (calcd for $C_{10}H_{24}Si_4$ *m/z* 256.09522, found *m/z* 256.09561), ^{1}H NMR (two singlets; δ 0.224, 0.175), ^{13}C NMR, and ^{29}Si NMR spectra. The ^{13}C NMR and ^{29}Si NMR spectral data for permethylhexasilacyclooctyne (**5**),[7] **2**, and **4** are tabulated for comparison in Table I. As anticipated, the most dramatic effect is observed in ^{13}C NMR absorption of the acetylenic carbons, which steadily shifts downfield to the remarkable value of δ 135.7 for **4**. This corresponds to a downfield shift of ca. 23 ppm from the acetylenic resonance of $Me_3SiC{\equiv}SiMe_3$.

Repeated attempts to obtain crystalline **4** were unsuccessful even at low temperatures. Thus, to obtain X-ray structural data

---

(1) Presented in part by Pang, Y., Schneider, A., Ijadi-Maghsoodi, S., and Barton, T. J., at the 24th Organosilicon Symposium, University of Texas, El Paso, TX, April 12, 1991.

(2) (a) Nakagawa, M. *The Chemistry of the Carbon–Carbon Triple Bonds*; Wiley: Chichester, England, 1978; Chapter 15. (b) Krebs, A.; Wilke, J. *Top. Curr. Chem.* **1983**, *109*, 189.

(3) (a) Saxe, P.; Schaefer, H. F. *J. Am. Chem. Soc.* **1980**, *102*, 3239. (b) Fitzgerald, G.; Saxe, P.; Schaefer, H. F. *J. Am. Chem. Soc.* **1983**, *105*, 690. (c) Olivella, S.; Pericas, M. A.; Riera, A.; Sole, A. *J. Am. Chem. Soc.* **1986**, *108*, 6884. (d) Olivella, S.; Pericàs, M. A.; Riera, A.; Solè A. *J. Org. Chem.* **1987**, *52*, 4160. (e) Tseng, J.; Mckee, M. L.; Schevlin, P. B. *J. Am. Chem. Soc.* **1987**, *109*, 5474.

(4) Haase, J.; Krebs, A. *Z. Naturforsch.* **1972**, *27a*, 624.

(5) The half-life of cyclohexyne in dilute CH_2Cl_2 solution at −110 °C is only a few seconds: Wittig, G.; Meske-Schüller, I. *Justus Liebigs Ann. Chem.* **1968**, *65*, 711.

(6) Dilithioacetylene is conveniently prepared by reaction of *n*-butyllithium and trichloroethylene: Ijadi-Maghsoodi, S.; Pang, Y.; Barton, T. J. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 955.

(7) Ando, W.; Nakayama, N.; Kabe, Y.; Shimizu, T. *Tetrahedron Lett.* **1990**, *31*(25), 3597.

(8) Both we and Professor W. Ando reported at the 9th International Symposium on Organosilicon Chemistry, Edinburgh, Scotland, July 1990, GCMS evidence for the synthesis but not isolation of **4**. After this communication was submitted, we learned that the isolation of **4** had been reported the previous month by Professor Ando.[9] Very recently a paper has appeared describing in detail Professor Ando's work in this area, which includes photochemical generation of **4** from **2**.[10]

(9) Hojo, F.; Shimizu, T.; Ando, W. Presented at the 38th Symposium on Organometallic Chemistry, Kyoto, Japan, Oct 1991; Abstract PA203. Ando, W.; Shimizu, K.; Hojo, F.; Sekigawa, S.; Shimizu, T. Presented at the 4th Kyushu International Symposium on Physical Organic Chemistry, Kyushu, Japan, Oct 3, 1991; p 60.

(10) Ando, W.; Hojo, F.; Sekigawa, S.; Nakayama, N.; Shimizu, T. *Organometallics* **1992**, *11*, 1009.