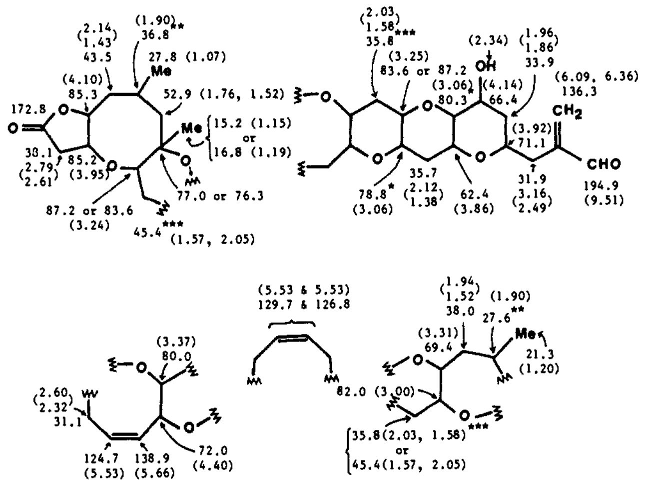

Figure 1. Partial structures of **6** proposed by COSY, heteroCOSY, and decoupling experiments. The attached numbers denote ^{13}C NMR (^{1}H NMR) chemical shifts, ppm in CD_2Cl_2.[11] The signals with asterisks are interchangeable.

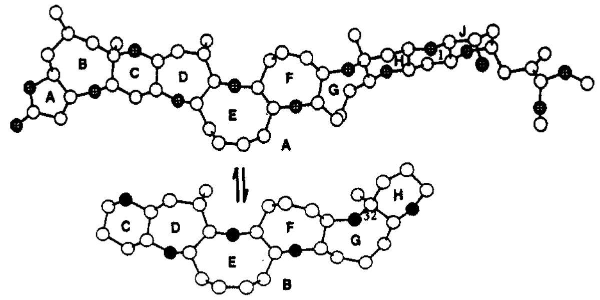

Figure 2. (A) Computer-generated perspective drawing of the final X-ray model of compound **7**. Hydrogens are omitted for clarity, and no absolute configuration is implied. Oxygen atoms are cross-hatched. (**B**) Partial perspective drawing of the molecule with ring G in crown form.

presence of Dowex 50W-X8 (H^+ form) at 45 °C for 1 h. Since **7** yielded **6** quantitatively upon treatment with aqueous acid, there was no structural alteration of the rest of the molecule during the acid treatment. the ^{1}H NMR spectrum of **7** is very similar to that of **6** except for the signals associated with the acetal moiety.

Compound **7** crystallized in the monoclinic space group $C2$ with $a = 27.249$ (5), $b = 10.572$ (2), $c = 21.739$ (4) Å, and $\beta = 128.85$ (2)°. One molecule of composition $C_{51}H_{76}O_{14}$ formed the symmetric unit. All unique diffraction maxima with $2\theta \leq 114°$ were collected on a computer-controlled four-circle diffractometer using graphite monochromated Cu K$\bar{\alpha}$ radiation (1.541 78 Å) and variable speed, 1° ω-scans. Of the 3504 reflections measured in this fashion, 2777 (79%) were judged observed ($|F_0| \geq 3\sigma(F_0)$).[12] The structure solution was difficult, but eventually a phasing model was found. Full-matrix least-squares refinements with anisotropic nonhydrogen atoms and isotropic hydrogens have converged to a standard crystallographic residual of 0.050 for the observed reflections. Additional crystallographic details are available and are described in the supplementary material.

Figure 2 is a computer-generated perspective drawing of the final X-ray model.[13] This structure is in excellent agreement with the structural information obtained from NMR analysis. A remarkable feature of the structure is the unprecedented presence of all ring systems from five- to nine-membered in a single molecule. Another conspicuous structural feature is that in the crystal form, the molecule has a 90° twist at ring G. The molecule is essentially composed of two perpendicularly linked polycyclic sheets, rings A–F and rings H–J. In the solid state, ring G has the boat-chair (BC) form instead of the crown form. In brevetoxin B and its derivatives, the molecules are essentially planar. It is speculated that **6** undergoes a rather slow conformational change between the BC and crown form in solution.[14] This would explain the unusual peak broadening or disappearance of certain signals, particularly those of the protons and carbons around ring G, experienced in the NMR studies. In retrospect, this is the major cause of our failure to assign the structure for the central portion of the molecule in spite of extensive use of modern NMR techniques. Molecular mechanics calculations[15] indicate that the BC form is more stable than the crown form by a modest 2.9 kcal/mol. Most of the energy difference is associated with angle strain at the G-ring oxygen and C-32.

The structure elucidation of **6** also establishes another natural toxin GB-7 (**8**)[10] mp 295 °C dec, since **8** was determined to be the alcohol derivative of brevetoxin A on the basis of ^{1}H and ^{13}C NMR spectra. The spectra were superimposable except that the signals belonging the α-methylene aldehyde are replaced by those of α-methylene carbinol [δ (CD_2Cl_2) 4.05 (CH_2OH), 4.93 and 5.08 (terminal methylene)].

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Supplementary Material Available: Tables of ^{13}C and ^{1}H NMR signal assignment for **6** and fractional coordinates, thermal parameters, interatomic distances, interatomic angles, and torsional angles for **7** (10 pages). Ordering information is given on any current masthead page.

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[12] The crystallographic programs employed are described in: Roll, D. M.; Chang, C. W. J.; Scheuer, P. J.; Gray, G. A.; Shoolery, J. N.; Matsumoto, G. K.; Van Duyne, G. D.; Clardy, J. *J. Am. Chem. Soc.* **1985**, *107*, 2916–2920.

[13] The X-ray analysis did not afford the absolute configuration, which is currently under investigation.

[14] Hendrickson, J. B. *J. Am. Chem. Soc.* **1964**, *86*, 4854–4866.

[15] Allinger, N. L. *Adv. Phys. Org. Chem.* **1976**, *13*, 1 and references therein.

Pentacyclo[12.2.2.2^{2,5}.2^{6,9}.2^{10,13}]-1,5,9,13-tetracosatetraene and Its Reaction with AgOTf. Synthesis of a Square-Planar d^{10} Organometallic Complex

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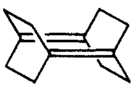
We reported recently on the synthesis of tetracyclo[8.2.2.2^{2,5}.2^{6,9}]-1,5,9-octadecatriene (**2**) and remarked that this substance might be considered as a member of a class of compounds made of n six-membered rings joined by double bonds at their C1 and C4 positions to form a large overall ring.[1] The smallest member of the class, diene **1**, has also been reported recently.[2] We felt that the third member of the class, tetraene



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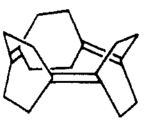

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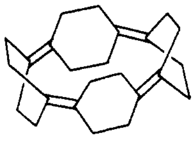

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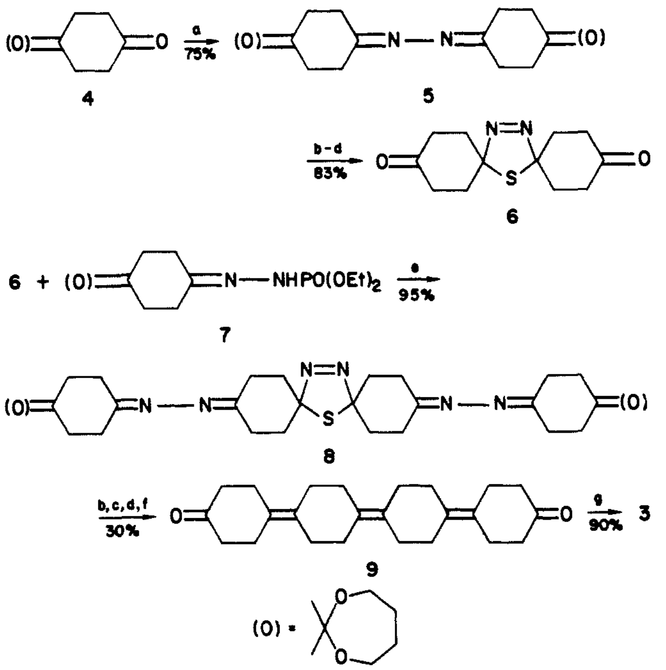
[1] McMurry, J. E.; Haley, G. J.; Matz, J. R.; Clardy, J. C.; Van Duyne, G.; Gleiter, R.; Schafer, W.; White, D. H. *J. Am. Chem. Soc.* **1984**, *106*, 5018.

[2] (a) Wiberg, K. B.; Matturro, M.; Adams, R. *J. Am. Chem. Soc.* **1981**, *103*, 1600. (b) Wiberg, K. B.; Matturro, M. G.; Okarma, P. J.; Jason, M. E. *J. Am. Chem. Soc.* **1984**, *106*, 2194.

Scheme I.[a] Synthesis of Pentacyclo[$12.2.2.2^{2,5}.2^{6,9}.2^{10,13}$]-1,5,9,13-tetracosatetraene



[a](a) N_2H_4; EtOH; (b) H_2S, CH_3CN; (c) $Pb(OAc)_4$, CH_2Cl_2; (d) HCl, H_2O, CH_2Cl_2; (e) NaH, THF; (f) toluene, Δ; then $P(OEt)_3$, Δ; (g) $TiCl_3/Zn/Cu$, dimethoxyethane, 48 h addition, Δ.

3, might be particularly interesting because it might be capable of complexing metal ions in its cavity.

Tetraene 3 was prepared as shown in Scheme I. Reaction of hydrazine with the tetramethylene monoacetal of 1,4-cyclohexanedione[3] (4) gave the symmetrical azine 5, which was converted into diketothiadiazoline 6 on treatment with H_2S in acetonitrile followed by oxidation with lead tetraacetate and hydrolysis with aqueous acid. Coupling[4] of 6 with phosphonohydrazide 7 and then gave 8. Addition of H_2S to 8, oxidation with lead tetraacetate, deprotection by treatment with aqueous acid, and heating, first in toluene to effect a 3-fold extrusion of nitrogen and then in triethyl phosphite to remove sulfur, gave diketone 9.[5] Slow addition of diketone 9 over a 48-h period to a refluxing slurry of $TiCl_3/Zn/Cu$ in dimethoxyethane according to our previously published general procedure[6] provided tetraene 3 in 90% yield.[7] Single-crystal X-ray analysis confirmed the structure and indicated a distance of 5.11 Å between double bonds across the ring.

If tetraene 3 is to act as an eight-electron, square-planar ligand for complexation with d^8 or d^{10} metals, stringent criteria must be met. First, the symmetries and energy levels of ligand and metal orbitals must be compatible (this may be a source of difficulty with d^{10} metals, which do not adopt square-planar geometry); second, the size of the ligand's cavity (5.11-Å diameter) requires a metal-to-carbon bond distance of approximately 2.5 Å; third, the metal atom or ion must be stripped of all other ligands, including solvent, before it will be able sterically to enter the cavity.

Of the transition metals that might meet these criteria, Ag(I) was chosen because it is known[8] to form silver–olefin complexes with bond lengths of 2.4–2.6 Å and because its weakly ligated trifluoromethanesulfonate (triflate) salt is readily available. When powdered tetraene 3 was added to a stirred solution of silver triflate in tetrahydrofuran (THF) at room temperature, the normally insoluble olefin dissolved within minutes to form a homogeneous solution from which a new white powder slowly precipitated. Recrystallization of the powder from THF yielded a crystalline silver–olefin complex (66%) that was shown by ^1H and ^{13}C NMR spectra to have a highly symmetrical structure.[9] In addition, the ^{13}C NMR spectrum showed carbon–silver coupling indicative of a static, stable complex. Single-crystal X-ray analysis[10] confirmed the structure of the complex as 10 (Figure 1). Compound 10 proved stable to air, heat, light, and hydroxylic solvents under conditions that instantly destroy normal silver–olefin π complexes. To our knowledge, this is the first example, both of a static silver–olefin complex and of a square-planar d^{10} organometallic complex. We are continuing our work in hope of generating complexes of 3 with other metals.

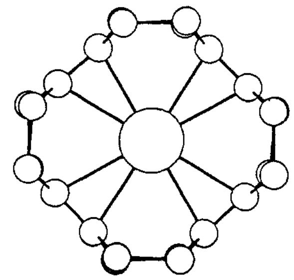


Figure 1. Computer-generated X-ray crystal structure of silver–olefin complex **10**.

Acknowledgment. This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and by the National Science Foundation (Grant CHE-8207890).

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(3) Hyatt, J. A. *J. Org. Chem.* **1983**, *48*, 129.

(4) Baldwin, J. E.; Bottaro, J. C. *J. Chem. Soc., Chem. Commun.* **1982**, 624.

(5) Barton, D. H. R.; Willis, B. J. *J. Chem. Soc., Perkin Trans. 1* **1972**, 305.

(6) (a) McMurry, J. E.; Kees, K. L. *J. Org. Chem.* **1977**, *42*, 2655. (b) McMurry, J. E. *Acc. Chem. Res.* **1983**, *16*, 405.

(7) Data for triene 3: mp >300 °C; ^1H NMR ($CDCl_3$) AA'BB' δ 1.9–2.2 (m, 16 H), 2.2–2.5 (m, 16 H); ^{13}C NMR ($CDCl_3$) δ 129.56, 27.90.

(8) (a) Allen, F. H.; Rogers, D. *Chem. Commun.* **1967**, 588. (b) Streib, W. E.; Jackson, R. B.; *J. Am. Chem. Soc.* **1967**, *89*, 2539. (c) Kang, H. C.; Hanson, A. W.; Eaton, B.; Boekelheide, V. *J. Am. Chem. Soc.* **1985**, *107*, 1979.

(9) Data for complex 10: mp 145 °C dec; ^1H NMR ($CDCl_3$) AA'BB' δ 2.11 (m, 16 H), 2.87 (m, 16 H); ^{13}C NMR ($CDCl_3$) δ 135.15, 135.12, 28.76, 28.74.

(10) Crystals of 10 formed in the monoclinic space group $P2_1/c$ with a = 16.189 (2) Å, b = 9.814 (1) Å, c = 16704 (2) Å, and β = 60.92 (2)°. Block-diagonal least-squares refinements with anisotropic nonhydrogen atoms and isotropic hydrogens converged to a residual of 0.060 for the 2319 observed reflections. Complete structural details will be given in a subsequent publication.

First Insertion of NO into a Transition-Metal Cluster–Carbon Bond: Regioselective Formation, Structure, and Reactions of the First Alkanenitrile Oxide Complexes

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The chemistry of NO in the presence of transition metals is receiving considerable current attention because of its role in air pollution,[1] its potential in organic synthesis by carbon–nitrogen bond formation,[1,2] and an increasing interest in its basic features.[3]

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(1) Panday, K. K. *Coord. Chem. Rev.* **1983**, *51*, 69.

(2) (a) Seidler, M. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 6110. (b) Becker, P. N.; Bergman, R. G. *Organometallics* **1983**, *2*, 787; *J. Am. Chem. Soc.* **1983**, *105*, 2985. (c) Middleton, A. R.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1980**, 1880, 1898. (d) Schoonover, M. W.; Baker, E. C.; Eisenberg, R. *J. Am. Chem. Soc.* **1979**, *101*, 1880. (e) Clement, R. A.; Klabunde, U.; Parshall, G. W. *J. Mol. Catal.* **1978**, *4*, 87.