toward the natural product by inhibiting diketopiperazine formation.

The ^1H NMR, ^{13}C NMR, and mass spectra of synthetic westiellamide ($[\alpha]^{21}_D = 130.0°$, $c = 0.1$, MeOH)[26] were identical to those reported for the natural sample. With the exception of the valine β-H, which is shifted upfield, the ^1H NMR data for cyclotetramer **9** are very similar to those for trimer **1** and show that **9** has C_4 symmetry in the NMR time average at 22 °C in $CDCl_3$. The vicinal ^3J (NHCH) of 9.7 Hz in **9** corresponds to a $HN^{\alpha}CH$ dihedral angle of $180° > \theta > 160°$ with the valyl groups axial and the NH directed to the center of the molecule. Contrary to the related cyclooctapeptide ascidiacyclamide, which has two oxazoline and two thiazole subunits and adopts a rectangular form in solution and the solid state,[27] tetramer **9** is likely to adopt a novel square conformation with oxazolines located at each corner of the ring. This conformational preference is especially relevant for the formation of coordination complexes similar to expanded porphyrin[28] systems. The ease of formation of the 24-membered ring under the reaction conditions also suggests the possibility that **9** is a still unidentified product of *Westiellopsis* or *Lissoclinum* species. (See Figure 1.)

We are presently investigating further applications of oxazolines in cyclopeptide chemistry and the conformational and metal-chelating properties of westiellamide and macrocycle **9**, as well as further analog structures.

Acknowledgment. This work was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Central Research Development Fund of the University of Pittsburgh. C.P.M. also acknowledges the DOE for a fellowship award.

Supplementary Material Available: Experimental synthetic procedures and data for **1**, **4**, and **6**–**9** (3 pages). Ordering information is given on any current masthead page.

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[26] Natural westiellamide: $[\alpha]_D = 130°$, $c = 0.1$, MeOH.[4]

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Cyclobutyne: The Ligand. The Synthesis and Molecular Structure of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}\overline{C_2CH_2C}H_2)(\mu\text{-SPh})(\mu\text{-H})$

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Although theoretical calculations have indicated that the molecule cyclobutyne, $\overline{C{\equiv}CCH_2C}H_2$, lies on an energy minimum, there is as yet no conclusive experimental evidence for the existence of this molecule in the free state.[1] The ability of metal atoms to complex and stabilize highly reactive small molecules is well-known, and through complexation numerous species that would otherwise have been inaccessible have now been prepared and studied.[2] We now report that by using the stabilizing influence of three metal atoms we have been able to prepare and isolate the first example of a metal complex containing the ligand "cyclobutyne".

A cyclobutenyl grouping was introduced into a triosmium cluster complex by the reaction of $Os_3(CO)_{10}(NCMe)_2$[3] with 1-(phenylthio)cyclobutene,[4] $PhS\overline{C{=}CHCH_2C}H_2$, at 25 °C. This yielded two products: $Os_2(CO)_6(\mu\text{-}\eta^2\text{-}\overline{C{=}CHCH_2C}H_2)(\mu\text{-SPh})$, **1** (44%), and $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}\overline{C{=}CHCH_2C}H_2)(\mu\text{-SPh})$, **2** (34%), by the addition of the 1-(phenylthio)cyclobutene and cleavage of the carbon–sulfur bond to the cyclobutenyl group.[5] The RS and cyclobutenyl groups are bridging ligands in both complexes. The molecular structures of **1** and **2** were established by single-crystal X-ray diffraction analyses, and an ORTEP drawing of the molecular structure of **2** is shown in Figure 1.[6] The η^2-cyclobutenyl ligand and a benzenethiolato ligand bridge the two metal atoms that are not mutually bonded in an open triosmium cluster. The formation of **1** involved in addition a degradation of the cluster to two metal atoms. Cleavage of RS substituents from unsaturated hydrocarbon groupings by triosmium clusters has been observed previously.[7]

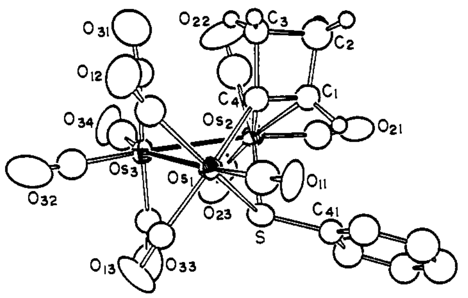

Figure 1. An ORTEP diagram of $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}\overline{C{=}CHCH_2C}H_2)(\mu\text{-SPh})$, **2**. Selected interatomic distances (Å) for two independent molecules are Os(1)–Os(3) = 2.905 (2) [2.900 (2)], Os(2)–Os(3) = 2.938 (2) [2.958 (2)], Os(1)–C(4) = 2.06 (3) [2.16 (2)], Os(2)–C(4) = 2.39 (3) [2.40 (3)], Os(2)–C(1) = 2.53 (3) [2.41 (3)], and C(1)–C(4) = 1.38 (4) [1.29 (4)].

The transformation of the cyclobutenyl ligand into the cyclobutyne ligand was accomplished by treatment of compound **2** with Me_3NO in 25 mL of CH_2Cl_2 and heating to reflux for 30 h. Two products, **1** and the new complex $Os_3(CO)_9(\mu\text{-SPh})$-

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[5] 1-(Phenylthio)cyclobutene (40 mg, 0.247 mmol) and 150 mg of $Os_3(CO)_{10}(NCMe)_2$ (0.161 mmol) were allowed to react in 25 mL of CH_2Cl_2 at 25 °C for 12 h. The products were separated by TLC using hexane solvent to yield 49.9 mg of yellow $Os_2(CO)_6(\mu\text{-}\eta^2\text{-}\overline{C{=}CHCH_2C}H_2)(\mu\text{-SPh})$, **1** (46%), and 54.5 mg of yellow $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}\overline{C{=}CHCH_2C}H_2(\mu\text{-SPh})$, **2** (34%). IR ($\nu_{CO}$ in hexane) for **1**: 2085 (m), 2056 (vs), 2009 (s), 1998 (s), 1982 (m). For **2**: 2102 (m), 2061 (vs), 2051 (m), 2018 (vs), 2013 (m), 2003 (w), 1994 (w), 1985 (w), 1975 (w). ^1H NMR for **2** (δ in $CDCl_3$): 7.187–7.358 (m, 5 H), 5.409 (s, 1 H), 3.098–3.125 (m, 2 H), 3.004–3.030 (m, 2 H).

[6] For details on the structure of **1**, see the supplementary material. For **2**: space group = $P2_1$, $a = 13.638$ (2) Å, $b = 17.582$ (4) Å, $c = 9.946$ (2) Å, $\beta = 93.01$ (2)°, $Z = 4$, 3264 reflections, $R = 0.046$. The crystal of **2** contains two symmetry independent molecules in the asymmetric crystal unit, but both molecules are structurally similar.

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[8] **2** (62 mg, 0.0612 mmol) and 4.5 mg of Me_3NO (0.0612 mmol) in 25 mL of CH_2Cl_2 were heated to reflux for 30 h. The products were separated by TLC in hexane to yield 9.8 mg of yellow **1** (21%) and 23 mg of greenish yellow $Os_3(CO)_9(\mu\text{-SPh})(\mu_3\text{-}\eta^2\text{-}\overline{C{=}CCH_2C}H_2)(\mu\text{-H})$, **3** (35%). IR ($\nu_{CO}$ in hexane) for **3**: 2103 (w), 2079 (vs), 2053 (s), 2031 (m), 2018 (m), 2013 (s), 1994 (w), 1979 (w). Anal. Calcd for **3** (found): C, 23.17 (22.97); H, 1.02 (0.99). ^1H NMR at 27 °C (in $CDCl_3$): −17.41 (1 H, s), 4.34 (2 H, d, ^2J = 10 Hz), 3.66 (2 H, d, ^2J = 10.5 Hz), 7.35 (1 H, Ph, s), 7.25–7.13 (4 H, Ph, m). At −73 °C (in CD_2Cl_2): −17.60 (1 H, s), 3.50 (1 H, m), 3.67 (1 H, m), 4.20 (1 H, m), 4.36 (1 H, m), 7.12 (2 H, m), 7.20 (2 H, m), 7.33 (1 H, s). $^{13}C\{^1H\}$ NMR at −68 °C (in CD_2Cl_2): CH_2, 50.5, 51.0; Ph, 128.5, 128.9, 132.1, 140.0; CO, 168.5, 169.8, 171.8, 172.2, 175.5, 176.0, 177.7, 178.9, 181.6; $\equiv C$, 156.9, $\equiv C$, 193.9 ppm. $^{13}C\{^1H\}$ NMR at 25 °C (in $CDCl_3$): Ph, 142.0, 131.9, 128.9, 128.5; CH_2, 50.6 ppm.

[9] Crystal data for **3**: space group = $P2_1/n$, $a = 10.954$ (2) Å, $b = 16.540$ (3) Å, $c = 12.495$ (2) Å, $\beta = 91.98$ (2)°, $Z = 4$, 2233 reflections, $R = 0.033$.

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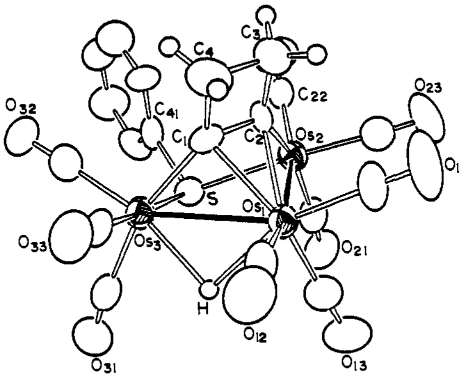
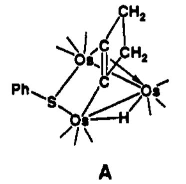


Figure 2. An ORTEP diagram of $Os_3(CO)_9(\mu\text{-}\eta^2\text{-}\overline{C_2CH_2CH_2})(\mu\text{-}SPh)(\mu\text{-}H)$, **3**. Selected interatomic distances (Å) are Os(1)–Os(2) = 2.830 (1), Os(1)–Os(3) = 2.940 (1), Os(1)–C(1) = 2.22 (1), Os(3)–C(1) = 2.12 (2), Os(1)–C(2) = 2.26 (2), Os(2)–C(2) = 2.06 (2), C(1)–C(2) = 1.37 (2), C(1)–C(4) = 1.54 (2), C(2)–C(3) = 1.51 (2), and C(3)–C(4) = 1.52 (2).

$(\mu_3\text{-}\eta^2\text{-}\overline{C_2CH_2}CH_2)(\mu\text{-}H)$, **3**, were formed in the yields 21% and 35%, respectively.[8] Compound **3** was characterized crystallographically, and an ORTEP diagram of its molecular structure is shown in Figure 2.[9] This complex also consists of an open triosmium cluster with a benzenthiolato ligand bridging the open edge as in **2**, but it also has a "cyclobutyne" ligand that serves as a four-electron donor coordinated to all three metal atoms. The transformation of hydrogen-substituted μ_3-η^2-alkenyl ligands to alkyne ligands is a well-established process.[10] The C_4 ring is completely planar and is inclined 73.7° from the Os_3 plane. The ligand has adopted a μ_3-$\|$ coordination mode that is characteristic of alkynes bonded to trimetallic centers.[11] The length of the unsaturated C–C bond, C(1)–C(2), is 1.37 (2) Å and is also typical of alkynes coordinated to trimetallic sites.[11] The other C–C bonds in the ligand are equal in length within experimental error, 1.51 (2)–1.54 (2) Å, and are typical of C–C single bonds. The hydrogen atom that was shifted to the metal atoms bridges the elongated Os(1)–Os(3) bond, $\delta = -17.41$ ppm. It is rapidly exchanging between the two metal–metal bonds on the NMR time scale at 27 °C, $\Delta G^{*}{}_{273} = 13.2$ kcal/mol; thus the methylene groups are equivalent although the protons on each group are inequivalent, $\delta = 4.34$ (2 H, d, $^2J = 10$ Hz), 3.66 (2 H, d, $^2J = 10$ Hz). Due to the dynamics the resonances of the alkyne carbons are not observed at 27 °C; however, they are clearly displayed at 156.9 and 193.9 ppm at −68 °C. These values are also typical of alkynes coordinated to clusters of three metal atoms.[12]

The bonding of alkynes to trimetallic centers can be viewed as a combination of the σ-donation and π-acceptance that leads to a substantial reduction of the C≡C bond order.[13] In the limit, a resonance structure A can be drawn in which the cyclobutyne ligand in **3** is represented as a dimetalated cyclobutene with the C–C π-bond acting as a donor to the third metal atom. It is believed that it is the stabilization provided by such coordination that has made the isolation of complex **3** possible. It is expected that studies of the complexed form of cyclobutyne will reveal some of its reactivity properties and might help to explain its curious absence in the free state.



A

Acknowledgment. This research was supported by the Office of Basic Energy Science of the U.S. Department of Energy.

Supplementary Material Available: An ORTEP diagram of **1** and tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters for **1–3** (30 pages); tables of observed and calculated structure factors for **1–3** (52 pages). Ordering information is given on any current masthead page.

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Solvent-Free Cyclization of Linear Dienes Using Olefin Metathesis and the Thorpe–Ingold Effect

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Received January 27, 1992

The olefin metathesis reaction is of great synthetic utility in polymer chemistry.[1] The recent development of ring-opening (ROMP)[2] and acyclic diene (ADMET)[3] metathesis polymerization reactions has opened new avenues for the synthesis of novel polymeric materials. Recently we used ADMET to synthesize several photochemically active poly(keto olefins)[4] using the catalyst $Mo(CHCMe_2Ph)(NAr)(OCMe(CF_3)_2)_2$ (Ar = 2,6-diisopropylphenyl) (**1**) developed by Schrock and co-workers in 1990.[2g–i] In the course of that work, we discovered that neat samples of highly substituted dienes will cyclize quantitatively via metathesis to give difunctional five- and seven-membered rings instead of the expected linear polymer. Examples of substituted diene cyclizations by metathesis even in the presence of a solvent are rare. Their systematic exploitation in organic synthesis has therefore been limited to two recent studies by Fu and Grubbs, who cyclized

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