ORGANOMETALLICS

Cyclobutyne ligands. 1. Synthesis and reactivity of a cyclobutyne ligand in a triosmium complex, including a structural characterization of the first cyclobutyne ligand in the complex [cyclic] Os3(CO)9(.mu.3-.eta.2-C2CH2CH2)(.mu.-SPh)(.mu.-H)

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Organometallics, **1993**, 12 (8), 3029-3035• DOI: 10.1021/om00032a027 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Cyclobutyne Ligands. 1. Synthesis and Reactivity of a Cyclobutyne Ligand in a Triosmium Complex, Including a Structural Characterization of the First Cyclobutyne Ligand in the Complex $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2CH_2CH_2)(\mu\text{-}SPh)(\mu\text{-}H)$

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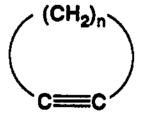
Received April 27, 1993

The reaction of the triosmium complex $Os_3(CO)_{10}(NCMe)_2$ with 1-(phenylthio)cyclobutene, $PhSC{=}CHCH_2CH_2$, at 25 °C resulted in the formation of the two products $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C{=}CHCH_2CH_2)(\mu\text{-}SPh)$ (**1**) and $Os_2(CO)_6(\mu\text{-}\eta^2\text{-}C{=}CHCH_2CH_2)(\mu\text{-}SPh)$ (**2**) by the addition of the 1-(phenylthio)cyclobutene and cleavage of the carbon–sulfur bond to the cyclobutenyl group. The formation of **2** involved in addition a partial degradation of the metal cluster. Both products were characterized by X-ray diffraction analysis, and both complexes were found to contain a $\mu\text{-}\eta^2$-cyclobutenyl ligand bridging two metal atoms. When treated with Me_3NO in a refluxing CH_2Cl_2 solution, compound **1** was converted to **2** (21% yield) and the new complex $Os_3(CO)_9(\mu\text{-}\eta^2\text{-}C_2CH_2CH_2)(\mu\text{-}SPh)(\mu\text{-}H)$, **3** (35% yield). Complex **3** was characterized by X-ray diffraction analysis and was found to contain a triply bridging cyclobutyne ligand formed by the cleavage of the alkenyl C–H bond in the cyclobutenyl ligand and the transfer of the hydrogen atom to the metal atoms. When heated to 125 °C, compound **3** was transformed into two new products: $Os_2(CO)_6(\mu\text{-}C_2CH_2CH_2C_6H_4S)$ (**4**) (36%) and $Os_3(CO)_8[\mu_3\text{-}SC_6H_4CCHC(H)Me](\mu\text{-}H)$ (**5**) (10%). For comparisons, the compound $Os_3(CO)_9(\mu\text{-}\eta^2\text{-}MeC_2Me)(\mu\text{-}SPh)(\mu\text{-}H)$ (**6**) was also synthesized. All six compounds **1**–**6** were structurally characterized by single-crystal X-ray diffraction analysis. The C–C triple bond in **3** is coordinated to three metal atoms in the classical $\mu_3\text{-}\eta^2$ mode. The length of the coordinated triple bond in **3** is 1.37(2) Å. In **6** it is slightly longer at 1.42(2) Å. In compound **4** the cyclobutyne ligand was coupled to the thiolate phenyl group at an ortho position and the cluster was reduced to two metals. Compound **5** contains a metalated methylallyl group that is also coupled to the thiolate phenyl group at an ortho position. The allyl grouping in **5** was apparently formed by a ring-opening transformation of the the cyclobutyne ligand. Crystal data: for **1**, space group = $P2_1$, a = 13.638(2) Å, b = 17.582(4) Å, c = 9.946(2) Å, β = 93.01(2)°, Z = 4, 3264 reflections, R = 0.046; for **2**, space group = $P\bar{1}$, a = 9.565(2) Å, b = 12.388(2) Å, c = 7.951(2) Å, α = 102.74(1)°, β = 98.85(1)°, γ = 85.23(1)°, Z = 2, 1836 reflections, R = 0.034; for **3**, space group = $P2_1/n$, a = 10.954(2) Å, b = 16.540(3) Å, c = 12.495(2) Å, β = 91.98(2)°, Z = 4, 2233 reflections, R = 0.033; for **4**, space group = $P\bar{1}$, a = 14.432(2) Å, b = 16.057(3) Å, c = 7.787(2) Å, α = 90.85(2)°, β = 93.20(1)°, γ = 77.47(1)°, Z = 4, 2678 reflections, R = 0.044; for **5**, space group = $P\bar{1}$, a = 14.109(3) Å, b = 14.542(4) Å, c = 11.509(4) Å, α = 105.98(2)°, β = 106.44(2)°, γ = 92.51(2)°, Z = 4, 2744 reflections, R = 0.045; for **6**, space group = $P2_1/n$, a = 11.008(2) Å, b = 16.759(2) Å, c = 12.560(2) Å, β = 91.45(1)°, Z = 4, 2773 reflections, R = 0.038.

Introduction

Saturated strained ring hydrocarbons containing the carbon–carbon triple bond (**A**) have aroused the curiosity of chemists for many years.[1] Strain is believed to become a major factor in the stability of these molecules when the ring contains less than nine carbon atoms.



A

Cyclooctyne, n = 6, is the smallest pure cycloalkyne that has been isolated,[2] although tetramethylcycloheptyne has also been isolated,[3] and there is spectroscopic evidence for the existence of cyclohexyne at low temperatures.[4] A note in a recent report referred to spectroscopic evidence that was tentatively assigned to the molecule cyclopentyne.[5a] Theoretical calculations have indicated that the molecule, cyclobutyne, $C{\equiv}CCH_2CH_2$, lies on an

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energy minimum, but as yet there is no conclusive experimental evidence for the existence of this molecule in the free state.[5] Calculations have indicated that cyclopropyne does not lie on an energy minimum and probably has the poorest chance for existence of all the cycloalkynes.[6]

The ability of metal atoms to complex and stabilize highly reactive small molecules is well-known.[7,8] Recently, metal complexes of cyclopentyne[9] and a *gem*-dimethylcyclopentyne[10] were isolated. We now wish to 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 preliminary report of this study has been published.[11]

Experimental Section

General Procedures. Reactions were performed under a dry nitrogen atmosphere. Reagent grade solvents were dried over sodium and deoxygenated by purging with nitrogen prior to use. $Os_3(CO)_{10}(NCMe)_2$[12] and 1-(phenylthio)cyclobutene[13] were prepared according to literature. IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer, ^1H NMR spectra were recorded on a Bruker AM-300 FT-NMR spectrometer, and mass spectra were recorded on a VG Model 70SQ mass spectrometer. Elemental microanalyses were performed by Oneida Research Services, Inc., Whitesboro, NY. TLC separations were performed in air by using silica gel (60 Å, F_{254}, 0.25-mm thickness).

Reaction of $Os_3(CO)_{10}(NCMe)_2$ with 1-(Phenylthio)cyclobutene. A 40-mg amount of 1-(phenylthio)cyclobutene (0.247 mmol) and a 150-mg amount of $Os_3(CO)_{10}(NCMe)_2$ (0.161 mmol) were dissolved in 50 mL of CH_2Cl_2. The solution was stirred at room temperature for 12 h. The solvent was removed, and the residue was separated by TLC using hexane solvent. This yielded, in the order of elution, 49.9 mg of yellow $Os_2(CO)_6(\mu$-η^2-$C{=}CHCH_2CH_2)(\mu$-SPh) (**2**) (44%) and 54.5 mg of yellow $Os_3(CO)_{10}(\mu$-η^2-$C{=}CHCH_2CH_2)(\mu$-SPh) (**1**) (34%). IR (ν(CO), in hexane) for **1**: 2102 (m), 2061 (vs), 2051 (m), 2018 (vs), 2013 (m), 2003 (w), 1994 (w), 1985 (w), 1975 cm^{-1} (w). ^1H NMR for **1** (δ, in $CDCl_3$): 7.187–7.358 (m, 5H), 5.409 (s, 1H), 3.098–3.125 (m, 2H), 3.004–3.030 (m, 2H). IR (ν(CO), in hexane) for **2**: 2085 (m), 2056 (vs), 2009 (s), 1998 (s), 1982 cm^{-1} (m). ^1H NMR (δ, in $CDCl_3$): 2.29–2.36 (m, 0.5H), 2.49–2.56 (m, 0.5H), 2.96–3.06 (m, 1H), 3.23–3.35 (m, 0.5H), 3.36–3.45 (m, 1H), 3.55–3.62 (m, 1H), 4.60–4.61 (m, 0.5H), 7.07–7.25 (m, 5H, Ph). The presence of multiplets with approximately half-integral intensities indicates that **2** exists in solution as a mixture of two isomers in approximately equal amounts. Anal. Calc (found) for **1**: C, 23.71 (23.82); H, 0.995 (0.78). Calc (found) for **2**: C, 27.01 (27.08); H, 1.41 (1.23%).

Reaction of 1 with Me_3NO. A 62.0-mg amount of **1** (0.0612 mmol) and a 4.5-mg amount of Me_3NO (0.0612 mmol) were dissolved in 40 mL of CH_2Cl_2, and the solution was heated to reflux for 30 h. The solvent was removed, and the residue was separated by TLC using hexane solvent. This yielded, in the order of elution, 9.8 mg of yellow **2** (21%) and 23 mg of yellow $Os_3(CO)_9(\mu$-η^2-$C_2CH_2CH_2)(\mu$-SPh)(μ-H), (**3**) (35%). IR (ν(CO) in hexane) for **3**: 2103 (w), 2079 (vs), 2053 (s), 2031 (m), 2018 (m), 2013 (s), 1994 (w), 1979 cm^{-1} (w). ^1H NMR at 27 °C (δ, in $CDCl_3$) for **3**: −17.48 (s, 1H), 4.34 (d, 2H, $^2J_{H-H}$ = 10.5 Hz), 3.67 (d, 2H, $^2J_{H-H}$ = 10.5 Hz), 7.35 (s, 1H, Ph), 7.25–7.13 (m, 4H, Ph). ^1H NMR at −73 °C (δ, in CD_2Cl_2) for **3**: −17.60 (s, 1H), 3.50 (m, 1H), 3.67 (m, 1H), 4.20 (m, 1H), 4.36 (m, 1H), 7.12 (m, 2H), 7.20 (m, 2H), 7.33 (s, 1H). $^{13}C\{^1H\}$ NMR at −68 °C (δ, in CD_2Cl_2) for **3**: 50.5, 51.0 (CH_2); 128.5, 128.9, 132.1, 140.0 (Ph); 168.5, 169.8, 171.8, 172.2, 175.5, 176.0, 177.7, 178.9, 181.6 (CO); 156.9 ($\equiv$*C*CH_2), 193.9 ($\equiv$$CCH_2$). $^{13}C\{^1H\}$ NMR at 25 °C (δ, in $CDCl_3$) for **3**: 142.0, 131.9, 128.9, 128.5 (Ph); 50.6 (CH_2). Anal. Calc (found) for **3**: C, 23.17 (22.97); H, 1.02 (0.99).

Pyrolysis of $Os_3(CO)_9(\mu$-η^2-$C_2CH_2CH_2)(\mu$-SPh)(μ-H) (3). A solution of compound **3** (20 mg, 0.020 mmol) in 25 mL of octane was heated to reflux for 20 h. After cooling, the solvent was removed in vacuo. The residue was dissolved in a minimal amount of dichloromethane and was separated by TLC on silica gel. Elution with hexane solvent yielded two products: 5.1 mg of $Os_2(CO)_6(\mu$-$C_2CH_2CH_2C_6H_4S)$ (**4**) (36%) as a pale yellow band and 1.9 mg of $Os_3(CO)_8[\mu_3$-$SC_6H_4CCHC(H)Me](\mu$-H) (**5**) (10%) as a yellow band. Trace amounts of other products were obtained, but these could not be characterized due to their very low yields. IR for **4** (ν(CO), in hexane) 2086 (m), 2059 (vs), 2014 (s), 2002 (vs), 1987 cm^{-1} (m). ^1H NMR (δ, in $CDCl_3$) for **4**: 7.18–7.08 (m, 3H), 6.88 (dt, 1H, J_{H-H} = 7.4, 1.7 Hz), 3.95–3.80 (s, br, 1H), 3.64–3.36 (s, br, 1H), 3.20–3.05 (s, br, 1H), 2.80–2.65 (s, br, 1H). The mass spectrum of **4** showed the parent ion at *m/e* = 710 and ions corresponding to the loss of each of the six carbonyl ligands. IR data (ν(CO), in hexane) for **5**: 2093 (s), 2062 (vs), 2023 (vs), 2018 (vs), 2004 (m), 1989 (w), 1955 cm^{-1} (m). ^1H NMR data (δ, in CD_2Cl_2) for **5**: 7.79–7.63 (m, 2H), 7.18–7.11 (m, 2H), 7.16 (dd, 1H, $^3J_{H-H}$ = 7.2 Hz, $^4J_{H-H}$ = 1.7 Hz), 2.33 (d, 3H, $^3J_{H-H}$ = 5.9 Hz), 2.04 (dqd, 1H, $^3J_{H-H}$ = 7.2 Hz, $^3J_{H-H}$ = 5.9 Hz, $^4J_{H-H}$ = 1.3 Hz), −13.00 (d, 1H, $^4J_{H-H}$ = 1.3 Hz). Coupling constants were established by a series of single-frequency ^1H decoupling experiments. The mass spectrum of **5** showed the parent ion at *m/e* = 958 and ions corresponding to the loss of each of the eight carbonyl ligands.

Pyrolysis of 1. A 25-mg amount of **1** (0.025 mmol) was dissolved in 25 mL of heptane. The solution was heated to reflux for 1 h. The solvent was removed. The residue was separated by TLC in hexane to yield, in the order of elution, 8.0 mg of yellow compound **2** (25%), 7.2 mg of yellow compound **3** (30%), and 1.1 mg of yellow compound **5** (5%).

Synthesis of $Os_3(CO)_9(\mu$-SPh)(μ_3-$MeC_2Me)(\mu$-H) (6). (1) For the synthesis of $Os_3(CO)_9(\mu$-$MeC_2Me)(\mu$-CO), an excess of MeC$\equiv$CMe was added via a syringe to a solution containing 50 mg of $Os_3(CO)_{10}(NCMe)_2$ in 30 mL of CH_2Cl_2. The color of the solution changed immediately from yellow to red. After 1 h of stirring at 25 °C, the solvent was removed and the residue was separated by TLC using hexane solvent to yield 33.6 mg of $Os_3(CO)_9(\mu$-$MeC_2Me)(\mu$-CO) (69% yield). This material is spectroscopically identical to the compound with the same formula that was prepared by a different method.[14]

(2) A 10.0-μL amount of PhSH was added to a solution of $Os_3(CO)_9(\mu$-CO)(μ_3-MeC_2Me)[14] (25 mg, 0.028 mmol) in 25 mL of heptane, and the reaction mixture was heated to reflux for 30 min. After cooling, the solvent was removed in vacuo, and the residue was separated by TLC on silical gel using hexane as eluent to yield 16.2 mg of $Os_3(CO)_9(\mu$-SPh)(μ_3-$MeC_2Me)(\mu$-H) (**6**) (59%) as a yellow solid. IR (ν(CO), in hexane) for **6**: 2101 (m), 2076 (vs), 2049 (vs), 2013 (s), 2008 (s), 1991 (m), 1984 (w), 1974 cm^{-1} (m). ^1H NMR (δ, in $CDCl_3$) for **6**: 7.24–7.11 (m, 5H), 3.42 (s, 6H), −16.16 (s, 1H). $^{13}C\{^1H\}$ NMR at −68 °C (δ, in CD_2Cl_2) for **6**: 38.1, 39.2 (Me); 128.6, 129.1, 132.2, 141.6 (d, J_{C-H} = 2.5 Hz) (Ph); 170.1 (J_{C-H} = 10.2 Hz), 170.8 (d, J_{C-H} = 2.9 Hz), 171.8 (d, J_{C-H} = 2.9 Hz), 173.3 (d, J_{C-H} = 10.2 Hz), 175.5 (s), 176.9 (d, J_{C-H} = 0.3 Hz), 177.0 (s), 177.4 (s), 179.8 (d, J_{C-H} = 4.5 Hz) (CO); 140.0 (d, J_{C-H} = 4.0 Hz) ($\equiv$*C*Me), 182.6 (s) ($\equiv$*C*Me). The small couplings that

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Table I. Crystal Data for Compounds 1–5

	1	2	3	4	5	6
formula	$Os_3SO_{10}C_{20}H_{10}$	$Os_2SO_6C_{16}H_{10}$	$Os_3SO_9C_{19}H_{10}$	$Os_2SO_6C_{16}H_8$	$Os_3SO_8C_{18}H_{10}$	$Os_3SO_9C_{19}H_{12}$
fw	1012.95.	710.71	979.90	708.70	956.93	986.96
crystal system	monoclinic	triclinic	monoclinic	triclinic	triclinic	monoclinic
lattice params						
a (Å)	13.638(2)	9.565(2)	10.954(2)	14.432(2)	14.109(3)	11.008(2)
b (Å)	17.582(4)	12.388(2)	16.540(3)	16.057(3)	14.542(4)	16.759(2)
c (Å)	9.946(2)	7.951(2)	12.495(2)	7.787(2)	11.509(4)	12.560(2)
α (deg)	90.0	102.74(1)	90.0	90.85(2)	105.98(2)	90.00
β (deg)	93.01(2)	98.85(1)	91.98(2)	93.20(1)	106.44(2)	91.45(1)
γ (deg)	90.0	85.23(1)	90.0	77.47(1)	92.51(2)	90.00
V (Å^3)	2382(1)	906.8(3)	2262(1)	1758.8(5)	2158(3)	2316(1)
space group (No.)	$P2_1$ (4)	$P\bar{1}$ (2)	$P2_1/n$ (14)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$P2_1/n$ (14)
Z	4	2	4	4	4	4
ρ_{calc} (g/cm^3)	2.82	2.60	2.88	2.68	2.94	2.83
μ(Mo Kα) (cm^{-1})	161.2	141.5	169.6	145.9	177.7	165.7
T, (°C)	23	23	23	20	20	20
$2\theta_{max}$ (deg)	46.0	43.1	44.0	42.0	40.0	46.0
No. obs ($I > 3\sigma$)	3264	1836	2233	2678	2744	2773
residuals: R, R_w	0.046, 0.055	0.034, 0.039	0.033, 0.037	0.044, 0.053	0.045, 0.044	0.038, 0.044
goodness-of-fit	2.03	2.52	1.79	2.13	1.81	2.47
largest peak in final E map (e/Å^3)	2.45	2.80	1.64	2.04	1.83	2.15

were observed in this spectrum are due to coupling to the hydride that was not effectively decoupled. Anal. Calcd (found) for **6**: C, 23.10 (23.19); H, 1.22 (1.11).

Crystallographic Analyses. Crystals of **1** suitable for X-ray diffraction analysis were grown from solution in benzene solvent by slow evaporation of the solvent at 25 °C. Crystals of **2** were grown from a solution in a solvent mixture of dichloromethane and hexane by slow evaporation of the solvent at 25 °C. Crystals of **3** were grown from solution in a solvent mixture of benzene and heptane by slow evaporation of solvent at 25 °C. Crystals of **4**–**6** were grown from solution in a solvent mixture of dichloromethane and hexane by slow evaporation of solvent at 25 °C. All crystals used in data collection were mounted in thin-walled glass capillaries. Diffraction measurements were made on a Rigaku AFC6S automatic diffractometer by using graphite-monochromated Mo Kα radiation. The unit cells were determined from 15 randomly selected reflections obtained by using the diffractometer automatic search, center, index, and least-squares routines. Crystal data, data collection parameters, and results of the analyses are listed in Table I. All data processing was performed on a Digital Equipment Corp. VAXstation 3520 computer by using the TEXSAN structure-solving program library obtained from the Molecular Structure Corp., The Woodlands, TX. Lorentz–polarization (Lp) and empirical absorption corrections were applied to the data in each analysis. Neutral-atom scattering factors were calculated by the standard procedures.[15a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[15b] Unless described otherwise below, the positions of all hydrogen atoms on the ligands were calculated by assuming idealized geometries with C–H = 0.95 Å. Their contributions of the calculated hydrogen atoms were added to the structure factor calculations, but their positions were not refined. Full-matrix least-squares refinements minimized the function

$$\Sigma_{hkl} w(|F_o| - |F_c|)^2$$

where

$$w = 1/\sigma(F)^2, \quad \sigma(F) = \sigma(F_o^2)/2F_o$$

and

$$\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$$

Compound **1** crystallized in the monoclinic crystal system. The space group $P2_1$ was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. The crystal contains two symmetry-independent molecules in the asymmetric unit, but both molecules are structurally similar. All metal and oxygen atoms were refined with anisotropic thermal parameters. The carbon atoms were refined with isotropic thermal parameters. A test of the enantiomorph was made by inverting the coordinates of all atoms and refining again; however, this did not produce an improvement in the R factors, and the original configuration was thus retained.

Compound **2** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of the hydrogen atoms on the cyclobutenyl ligand were located and refined on their positional parameters.

Compounds **3** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was determined uniquely from the systematic absences observed during the collection of data. The structures were solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All metal and oxygen atoms were refined with anisotropic thermal parameters. The carbon atoms were refined with isotropic thermal parameters. The hydride ligand was located in difference Fourier syntheses but could not be adequately refined. It was included as a fixed contribution only.

Compound **4** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All metal and oxygen atoms were refined with anisotropic thermal parameters. The carbon atoms were refined with isotropic thermal parameters.

Compound **5** crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of the structure. There are two independent molecules in the asymmetric crystal unit. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All metal and oxygen atoms were refined with anisotropic thermal parameters. The carbon atoms were refined with isotropic thermal parameters. The position of the hydride ligand was obtained by calculation using the energy minimization program HYDEX.[16]

Compound **6** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was assumed and confirmed by the successful solution and refinement of the structure. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. All non-hydrogen atoms were

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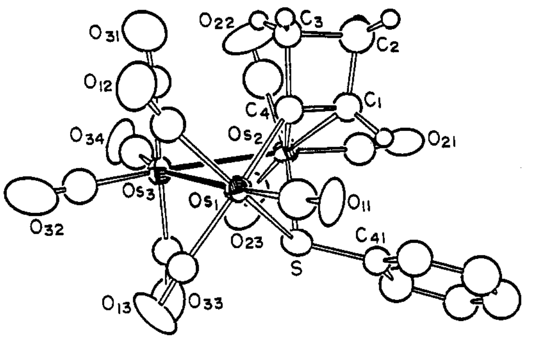

Figure 1. ORTEP diagram of $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}\overline{C{=}CH\text{-}CH_2CH_2})(\mu\text{-SPh})$ (1) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) for two independent molecules: Os(1)–Os(3) = 2.905(2) [2.900(2)], Os(2)–Os(3) = 2.938(2) [2.958(2)], Os(1)···Os(2) = 3.305(2) [3.310(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) = 2.35(3) [2.41(3)], C(1)–C(4) = 1.38(4) [1.29(4)], C(1)–C(2) = 1.54(5) [1.47(4)], C(2)–C(3) = 1.56(5) [1.50(4)], C(3)–C(4) = 1.59(4) [1.54(3)].

refined with anisotropic thermal parameters. The hydride ligand was located in a difference Fourier map and refined on its positional parameters.

Results

The reaction of $Os_3(CO)_{10}(NCMe)_2$ with 1-(phenylthio)-cyclobutene, $PhS\overline{C{=}CHCH_2CH_2}$, at 25 °C has yielded two products: $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}\overline{C{=}CHCH_2CH_2})(\mu\text{-SPh})$ (1) (34%) and $Os_2(CO)_6(\mu\text{-}\eta^2\text{-}\overline{C{=}CHCH_2CH_2})(\mu\text{-SPh})$ (2) (44%). Both products were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. In the crystal of 1 there are two independent molecules in the asymmetric unit. Both molecules are structurally similar, and an ORTEP diagram of the molecular structure of one of these molecules is shown in Figure 1. The molecule consists of an open triosmium cluster containing an η^2-σ-π coordinated cyclobutenyl ligand bridging the open edge of the cluster, Os(1)···Os(2) = 3.305(2) Å [3.310(2) Å]. The value in brackets corresponds to the second molecule in the crystal. A benzenethiolato ligand bridges the same edge of the cluster through its sulfur atom. The C–C distances around the four-membered ring are not exceptional, and as expected, the coordinated double bond, C(1)–C(4) = 1.38(4) Å [1.29(4) Å], is slightly shorter than the C–C single bonds, C(1)–C(2) = 1.54(5) Å [1.47(4) Å], C(2)–C(3) = 1.56(5) Å [1.50(4) Å], and C(3)–C(4) = 1.59(4) Å [1.54(3) Å], although the standard deviations are large in all cases. The other dimensions of 1 are similar to those of various related triosmium cluster complexes.[17]

An ORTEP diagram of the molecular structure of compound 2 is shown in Figure 2. This molecule also contains an η^2-σ-π bridging cyclobutenyl ligand and a bridging benzenethiolato ligand, but in this case the molecule has only two metal atoms and they are mutually bonded, Os(1)–Os(2) = 2.7620(9) Å. The six carbonyl ligands are arranged in the classic "sawhorse" fashion.

When compound 1 was treated with Me_3NO in a refluxing solution of CH_2Cl_2, it was decarbonylated and transformed into compound 2 in 21% yield and the new compound $Os_3(CO)_9(\mu\text{-}\eta^2\text{-}\overline{C_2CH_2CH_2})(\mu\text{-SPh})(\mu\text{-H})$ (3) in 35% yield. Compound 3 was characterized by IR, ^1H and ^{13}C NMR, and single-crystal X-ray diffraction analyses.

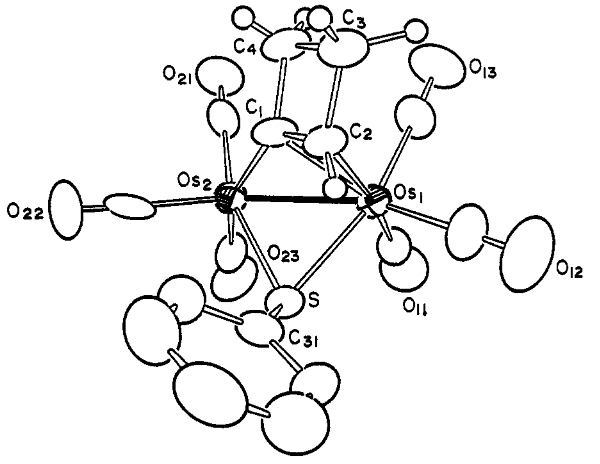

Figure 2. ORTEP diagram of $Os_2(CO)_6(\mu\text{-}\eta^2\text{-}\overline{C{=}CH\text{-}CH_2CH_2})(\mu\text{-SPh})$ (2) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å): Os(1)–Os(2) = 2.7620(9), Os(1)–C(1) = 2.28(1), Os(2)–C(1) = 2.07(1), Os(1)–C(2) = 2.29(1), C(1)–C(2) = 1.40(2), C(1)–C(4) = 1.53(2), C(2)–C(3) = 1.52(2), C(3)–C(4) = 1.53(2).

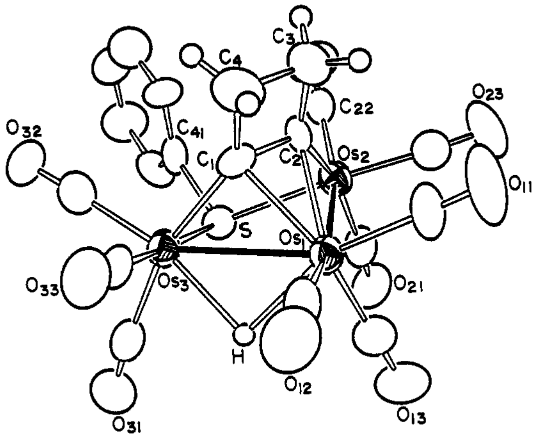

Figure 3. ORTEP diagram of $Os_3(CO)_9(\mu\text{-}\eta^2\text{-}\overline{C_2CH_2CH_2})(\mu\text{-SPh})(\mu\text{-H})$ (3) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å): Os(1)–Os(2) = 2.830(1), Os(1)–Os(3) = 2.940(1), Os(2)–S = 2.458(4), Os(3)–S = 2.447(4), Os(1)–C(1) = 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), C(3)–C(4) = 1.52(2).

An ORTEP diagram of the molecular structure of 3 is shown in Figure 3. Like 1, this molecule also consists of an open triosmium cluster with a benzenethiolato ligand bridging the open edge of the cluster through its sulfur atom, Os(2)···Os(3) = 3.859(1) Å. The cyclobutenyl ligand was transformed into a "cyclobutyne" ligand, $\overline{C_2CH_2CH_2}$, via a C–H bond activation step that shifted the alkenyl hydrogen atom to the cluster. The cyclobutyne ligand bridges all three metal atoms in the classical μ_3-η^2 mode observed for coordinated alkynes.[18] The hydrogen atom was shifted to the cluster to become a hydride ligand that bridges the Os(1)–Os(3) bond, $\delta = -17.48$ ppm. The metal–carbon bond distances are not unusual: Os(1)–C(1) = 2.22(1) Å, Os(3)–C(1) = 2.12(2) Å, Os(1)–C(2) = 2.26(2) Å, and Os(2)–C(2) = 2.06(2) Å. The carbon–carbon bond distances in the ring are normal although the coordinated triple bond, C(1)–C(2) = 1.37(2) Å, is significantly shorter

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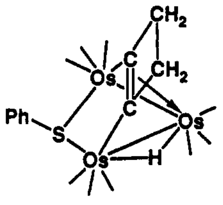
[17] Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1.

[18] (a) Raithby, P. R.; Rosales, M. J. *Adv. Inorg. Chem. Radiochem.* **1985**, *29*, 169. (b) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203.

than the carbon–carbon single bonds, C(1)–C(4) = 1.54(2) Å, C(2)–C(3) = 1.51(2) Å, and C(3)–C(4) = 1.52(2) Å. 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.[19] In the limit, a resonance structure **B** can be drawn in which



B

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. Thus, the C(1)–C(2) distance is significantly longer than that of an uncoordinated C–C triple bond. It is believed that it is the stabilization provided by such coordination that has made the isolation of complex **3** possible. The C_4 ring is completely planar and is inclined 73.7° from the Os_3 plane. The cyclobutyne ligand serves as a four-electron donor, and all three metal atoms achieve 18-electron configurations.

For the purpose of structural spectroscopic comparisons, we have prepared and characterized the related alkyne complex $Os_3(CO)_9(\mu\text{-}\eta^2\text{-}MeC_2Me)(\mu\text{-}SPh)(\mu\text{-}H)$ (**6**), which contains the unstrained alkyne MeC≡CMe as a ligand. This complex will be described below.

The methylene protons of the cyclobutyne ligand appear as two doublets at δ 4.34 (2H, $^2J_{H-H}$ = 10.5 Hz) and 3.67 (2H, $^2J_{H-H}$ = 10.5 Hz) in the ^1H NMR spectrum due to an averaging of the CH_2 groups by a rapid exchange of the hydride ligand between the two metal–metal bonds, ΔG^*_{273} = 13.2 kcal/mol,[18] but this process does not average the two hydrogen atoms in a given methylene group. At low temperatures (e.g. −73 °C) the hydride exchange is slow on the NMR time scale and four complex multiplets are observed at 3.50, 3.67, 4.20 and 4.36 ppm. A similar hydride exchange was observed in compound **6**; *vide infra*. Due to its dynamical activity, the methylene resonances of the cyclobutyne ligand were observed as a singlet, 50.6 ppm, in the ^{13}C NMR spectrum of **3** at room temperature and the resonances of the alkyne and CO ligands were not observed; however, the complete spectrum was observed at −68 °C: CH_2, 50.5, 51.0; CO, 168.5, 169.8, 171.8, 172.2, 175.5, 176.0, 177.7, 178.9, 181.6; CCH_2, 156.9, 193.9 ppm. The alkyne chemical shifts are not anomalous[20] and are only slightly less shielded than the alkyne carbon resonances observed for **6**. Compound **3** was also obtained in a 30% yield simply by heating a solution in heptane solvent to reflux for 1 h. However, significant amounts of **2**, 25% yield, and a small amount of a new compound $Os_3(CO)_8[\mu_3\text{-}SC_6H_4CCHC(H)Me](\mu\text{-}H)$ (**5**), 5% yield, were also obtained under these conditions. Compound **5** appears to have been derived from **3** by a thermal transformation and will be described below.

When heated to 125 °C for 20 h, compound **3** was transformed into two new compounds: $Os_2(CO)_6(\mu\text{-}\overline{C_2CH_2C}H_2C_6H_4S)$ (**4**) (36% yield) and $Os_3(CO)_8[\mu_3\text{-}SC_6H_4CCHC(H)Me](\mu\text{-}H)$ (**5**) (10% yield). Both products were characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses. The crystal of **4** contains two independent molecules in the asymmetric unit. Both molecules are structurally similar, and an ORTEP diagram of the molecular structure of one of these molecules is shown in Figure 4. The molecule contains only two metal atoms. The cyclobutyne ligand was transformed into an aryl-substituted cyclobutenyl group through the coupling of one of the alkyne carbon atoms to the phenyl group of the thiolate ligand at an ortho position. The cyclobutenyl ligand bridges the metal atoms in an η^2-σ-π fashion analogous to that found in **2**. The sulfur atom bridges the two metal atoms symmetrically, and the six carbon ligands are arranged in the sawhorse geometry as observed in **2**. The C–C distances in the cyclobutenyl ring are similar to those in **2** (Å): C(1)–C(4) = 1.45(3) [1.40(3)], C(1)–C(2) = 1.50(3) [1.51(3)], C(2)–C(3) = 1.56(4) [1.54(4)], C(3)–C(4) = 1.49(3) [1.54(3)]. The values in brackets correspond to the second molecule in the crystal.

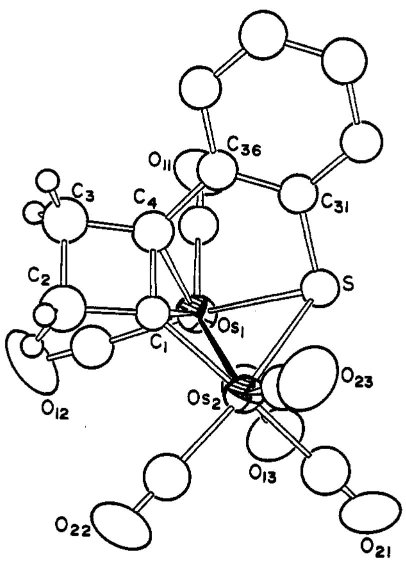


Figure 4. ORTEP diagram of $Os_2(CO)_6(\mu\text{-}\overline{C_2CH_2C}H_2C_6H_4S)$ (**4**) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) for two independent molecules: Os(1)–Os(2) = 2.774(1) [2.777(2)], Os(1)–C(1) = 2.29(2) [2.25(2)], Os(2)–C(1) = 2.02(2) [2.08(2)], Os(1)–C(4) = 2.27(2) [2.32(2)], C(1)–C(4) = 1.45(3) [1.40(3)], C(1)–C(2) = 1.50(3) [1.51(3)], C(2)–C(3) = 1.56(4) [1.54(4)], C(3)–C(4) = 1.49(3) [1.54(3)], C(4)–C(36) = 1.50(3) [1.47(3)].

The crystal of compound **5** also contains two independent molecules in the asymmetric unit. Both molecules are structurally similar, and an ORTEP diagram of the molecular structure of one of the molecules is shown in Figure 5. The complex contains three metal atoms in the form of a closed triangular cluster. As in **4**, the aryl ring of the thiolato ligand in **5** contains a substituent at the ortho position, but in this case it is a 3-methylallyl grouping that is metalated by the osmium atom Os(2) at the α-carbon atom C(4). The allyl grouping is also π-bonded to the neighboring metal atom Os(3). The metal–carbon and carbon–carbon distances associated with the allyl grouping are normal (Å): Os(2)–C(4) = 2.16(3) [2.18(3)], Os(3)–C(4) = 2.24(3) [2.25(3)], Os(3)–C(2) = 2.23(3) [2.18(3)], Os(3)–C(3) = 2.21(3) [2.18(2)]. The allyl grouping in **5** was apparently formed by a ring-opening transformation of the four-carbon ring system. The hydride ligand was not located in the structural analysis. Its position was

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[19] Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456.

[20] (a) Aime, S.; Gobetto, R.; Milone, L.; Osella, D.; Violano, L.; Arce, A. J.; De Sanctis, Y. *Organometallics* **1991**, *10*, 2854. (b) Farrugia, L. J.; Howard, J. A. K.; Mitrprachachon, F. G. A.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1981**, 162. (c) Evan, J.; McNulty, G. S. *J. Chem. Soc., Dalton Trans.* **1984**, 79.

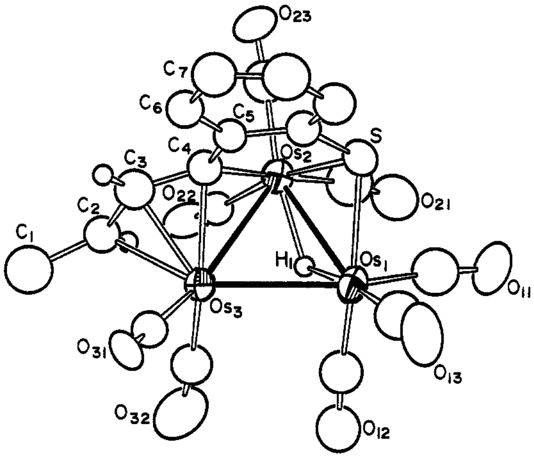

Figure 5. ORTEP diagram of $Os_3(CO)_8[\mu_3\text{-}SC_6H_4CCHC(H)Me](\mu\text{-}H)$ (**5**) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å) for two independent molecules: Os(1)–Os(2) = 2.896(2) [2.892(2)], Os(1)–Os(3) = 2.879(2) [2.879(2)], Os(2)–Os(3) = 2.889(2) [2.896(2)], Os(1)–S = 2.434(9) [2.400(9)], Os(2)–S = 2.397(8) [2.43(1)], Os(2)–C(4) = 2.16(3) [2.18(3)], Os(3)–C(4) = 2.24(3) [2.25(3)], Os(3)–C(2) = 2.23(3) [2.18(3)], Os(3)–C(3) = 2.21(3) [2.18(2)], C(2)–C(3) = 1.49(4) [1.41(4)], C(3)–C(4) = 1.40(4) [1.32(4)], C(4)–C(5) = 1.42(4) [1.47(4)].

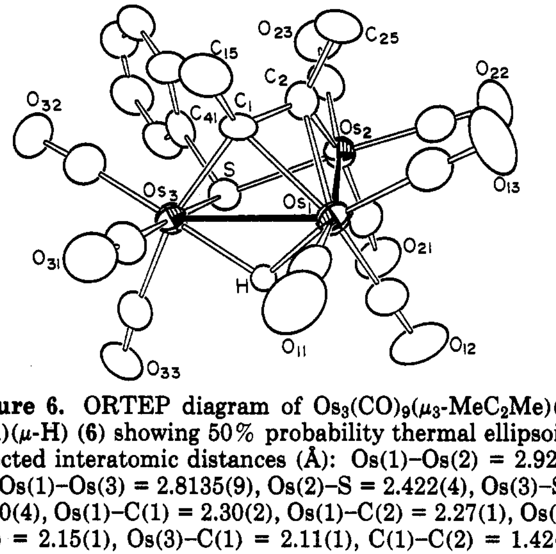

Figure 6. ORTEP diagram of $Os_3(CO)_9(\mu_3\text{-}MeC_2Me)(\mu_3\text{-}SPh)(\mu\text{-}H)$ (**6**) showing 50% probability thermal ellipsoids. Selected interatomic distances (Å): Os(1)–Os(2) = 2.9285(8), Os(1)–Os(3) = 2.8135(9), Os(2)–S = 2.422(4), Os(3)–S = 2.430(4), Os(1)–C(1) = 2.30(2), Os(1)–C(2) = 2.27(1), Os(2)–C(2) = 2.15(1), Os(3)–C(1) = 2.11(1), C(1)–C(2) = 1.42(2), C(1)–C(15) = 1.50(2), C(2)–C(25) = 1.52(2).

determined by an energy minimization calculation using the program HYDEX. The existence of the ligand was confirmed by ^{1}H NMR, $\delta = -13.00$ ppm. It is weakly coupled ($^4J_{H\text{-}H} = 1.3$ Hz) to the hydrogen atom located on atom C(2), which was observed as a multiplet at 2.04 ppm ($^3J_{H\text{-}H} = 7.2$ Hz, $^3J_{H\text{-}H} = 5.9$ Hz, $^4J_{H\text{-}H} = 1.3$ Hz). The hydrogen atom on C(3) exhibits a very deshielded shift, 7.16 ppm ($^3J_{H\text{-}H} = 7.2$ Hz, $^4J_{H\text{-}H} = 1.7$ Hz), where it is overlapped by the multiplets of the aryl ring hydrogen resonances. It is also weakly coupled (1.7 Hz) to one of the aryl hydrogen atoms.

For the purpose of comparison, we have also prepared and characterized the complex $Os_3(CO)_9(\mu\text{-}\eta^2\text{-}MeC_2Me)(\mu\text{-}SPh)(\mu\text{-}H)$ (**6**). Compound **6** was obtained in 59% yield from the reaction of $Os_3(CO)_9(\mu\text{-}CO)(\mu_3\text{-}MeC_2Me)$[14] with PhSH at 98 °C. Details of the structure of **6** were also established by an X-ray crystallographic analysis, and an ORTEP diagram of the molecular structure of **6** is shown in Figure 6. Like **3**, this molecule also consists of an open triosmium cluster with a triply bridging 2-butyne ligand and a benzenethiolato ligand bridging the open edge of the cluster through its sulfur atom. There is one hydride ligand that bridges the Os(1)–Os(3) bond, $\delta = -16.16$ ppm. The metal–carbon bond distances to the alkyne ligand are not significantly different from those found in **3** (Å): Os(1)–C(1) = 2.30(2), Os(1)–C(2) = 2.27(1), Os(2)–C(2) = 2.15(1), Os(3)–C(1) = 2.11(1). The carbon–carbon distance of the coordinated triple bond, 1.42(2) Å, appears to be slightly longer than that observed in **3**, but this is just barely at the significance level (3σ). Like **3**, compound **6** is also dynamical, and only a single methyl resonance was observed, 3.42 ppm, in the ^{1}H NMR spectrum at 27 °C. At −68 °C the two alkyne carbon resonances were observed at 140.0 and 182.6 ppm in the ^{13}C NMR spectrum. These shifts are 12–17 ppm more shielded than those observed for **3**. In a similar way, the ^{13}C resonances of the alkene carbon atoms in *cis*-2-butene (124.6 ppm) are 12.6 ppm more shielded than those in cyclobutene (137.2 ppm).[21]

Discussion

A summary of the results of this study are shown in Scheme I. The reaction of the 1-(phenylthio)cyclobutene with $Os_3(CO)_{10}(NCMe)_2$ leads to addition to the cluster by displacement of the two labile NCMe ligands. The addition is accompanied by a cleavage of the carbon–sulfur bond to the cyclobutenyl group, and the PhS and cyclobutenyl groups become bridging ligands in complexes **1** and **2**. It has been shown previously that the reactions of thioethers with triosmium clusters will lead to the cleavage of one of the carbon–sulfur bonds.[22] The formation of **2** involved addition and degradation of the cluster to two metal atoms. Compound **2** was not investigated further.

When decarbonylated by thermal means or by using Me_3NO, the cyclobutenyl ligand in compound **1** undergoes a C–H activation at the alkenyl carbon atom and is transformed into the cyclobutyne ligand. The hydrogen atom is shifted to the metal atoms to become a hydride ligand. The transformation of hydrogen-substituted μ_3-η^2 alkenyl ligands to alkyne ligands is a well established process.[17] The novel cyclobutyne ligand should contain considerable ring strain, but within the accuracy of our measurements there is no evidence for unusual ring strain in either structural or spectroscopic analyses. Structurally, the cyclobutyne ligand bridges the three metal atoms in a manner analogous to that of other alkynes. For a direct comparison, compound **6** was prepared; see Scheme II. The μ_3-η^2-MeC≡CMe ligand in **6** is coordinated in a manner very similar to that of the cyclobutyne ligand in **3**. The Os–C and alkyne C–C bond distances are not significantly different in the two complexes. Spectroscopically, the ^{13}C resonances of the alkyne carbons in **3** are deshielded relative to those in **6**, but the shift is not significantly larger than that observed in going from *cis*-2-butene to cyclobutene. Therefore, the strain in the cyclobutyne ligand in **3** might be no more than that in cyclobutene and the representation of the cyclobutyne ligand in **3** as a dimetalated cyclobutene **B** might be very accurate. However, when heated, **3** does undergo some very interesting transformations.

Two products **4** and **5** were isolated when **3** was heated to 125 °C. In compound **4** the phenyl ring has become joined to one of the alkyne carbon atoms of the cyclobutyne

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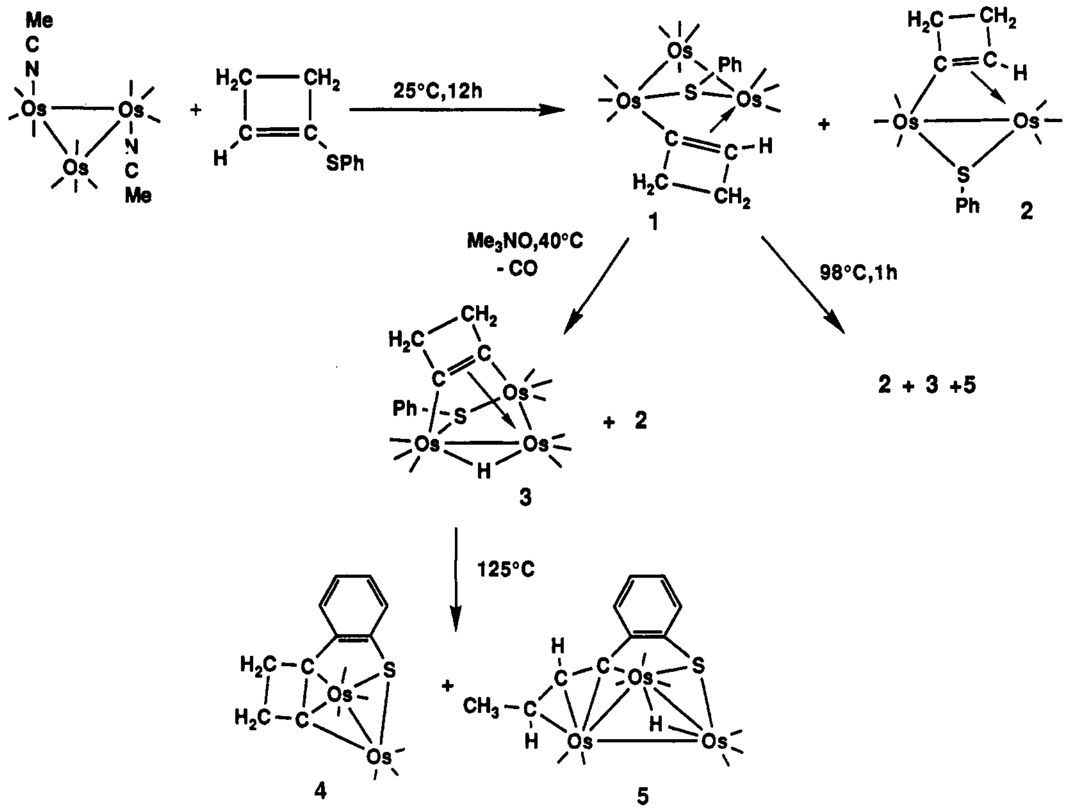
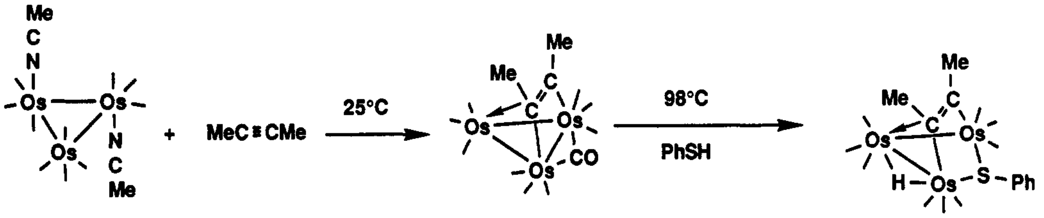
[21] Silverstein, R. M.; Bassler, G. C.; Morril, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley & Sons: New York, 1981; p 263.

[22] (a) Adams, R. D.; Katahira, D. A.; Yang, L.-W. *Organometallics* **1982**, *1*, 235. (b) Boyar, E.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1986**, 1431.

Scheme I



Scheme II



ligand at an ortho position. Ortho C–H activations are well-known in organometallic chemistry,[23] and such a transformation almost certainly preceded the coupling of the two groups. A metal grouping was expelled from the complex in the course of the transformation. This was not recovered, and in the absence of additional evidence, it seems inappropriate to try to speculate upon the nature of the additional transformations that led to the formation of **4**.

Compound **5** is more interesting because the cluster was not fragmented and the cyclobutyne ring was opened. Clearly, a number of transformations occurred in the formation of **5**, one of which includes the coupling of the C_4 chain to an ortho position of the phenyl ring. We have chosen to describe the C_4 grouping as a metalated methylallyl with the Os(2)–C(4) bond as the metalation site. It is not possible to predict at what stage of the transformation to **5** that the ring-opening C–C bond rupture occurred. It is probable that the methyl group in **5** was one of the CH_2 groups in **3** since it seems unlikely that the transformation to **5** involved the addition of three hydrogen atoms to one of the alkyne carbon atoms. Also, in view of the structure of **4**, where the alkyne carbon atom is coupled to an ortho position of the phenyl ring, it seems likely that carbon C(4) in **5** was originally one of the alkyne carbon atoms in **3**. If these assumptions are true, then the site of the C–C bond rupture must have been between one of the alkyne carbon atoms of the C_4 ring and one of the methylene groups. Unfortunately, the low yield of **5** makes the study of this transformation by a selective ^{13}C labeling impractical.

Conclusions

The first example of the cyclobutyne molecule has been prepared and isolated through stabilization by complexation to a metal cluster. The cyclobutyne ligand exhibited no anomalous structural or spectroscopic properties. Interestingly, the C_4 ring was opened when the complex was heated to 125 °C. Further studies of the structure and reactivity of this unusual ligand are in progress.

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

Supplementary Material Available: Tables of positional parameters, bond distances and angles, and anisotropic thermal parameters for the structural analyses of compounds **4–6** (53 pages). Ordering information is given on any current masthead page. Structure factor tables for compounds **1–3** were published previously.[11]

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[23] (a) Parshall, G. W. *Acc. Chem. Res.* **1970**, *3*, 139. (b) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73. (b) Constable, E. C. *Polyhedron* **1984**, *3*, 1037.