Cyclobutyne Ligands. 3. Synthesis and Characterization of a Disubstituted Cyclobutyne Ligand in the Triosmium Complex Os₃(CO)₉[(μ₃-η²-C₂CH₂C(Me)ᵗBu)](μ₃-S)

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The reaction of 4-*tert*-butyl-4-methyl-1-(phenylthio)cyclobutene with Os₃(CO)₁₀(NCMe)₂ at 25 °C yielded the new complex Os₃(CO)₁₀[μ-PhSC₂CH₂C(Me)ᵗBu](μ-H), **3** (54% yield), by displacement of the MeCN ligands and the addition of the 4-*tert*-butyl-4-methyl-1-(phenylthio)-cyclobutene and the activation of the alkenyl CH bond. Compound **3** was decarbonylated by refluxing in heptane solvent (97 °C) to yield the new compound Os₃(CO)₉[μ₃-SPhC₂CH₂C(Me)ᵗ-Bu](μ-H), **4** (93%), in which the alkenyl double bond of the metalated cyclobutenyl ligand has become coordinated to the cluster. When heated to 125 °C, compound **4** was transformed to the new complex Os₃(CO)₉(μ₃-η²-C₂CH₂C(Me)ᵗBu)(μ₃-S), **5** (60% yield based on **4** consumed). Compound **5** contains a triply bridging 3-methyl-3-*tert*-butylcyclobutyne ligand formed from the metalated cyclobutenyl ligand by cleavage from the sulfur atom in **4**. The phenyl group was also cleaved from the sulfur atom, resulting in the formation of a triply bridging sulfido ligand. The phenyl group and hydride ligand were eliminated, presumably as benzene. The C—C triple bond in **5** is coordinated to three metal atoms in the μ₃-η² mode. The length of the coordinated triple bond in **5** is 1.40(2) Å. All three products were characterized by single crystal X-ray diffraction analysis. Crystal data: (for **3**) space group = *P*2₁/*c*, *a* = 7.764(1) Å, *b* = 17.722-(4) Å, *c* = 21.153(3) Å, *β* = 92.36(1)°, *Z* = 4, 2451 reflections, *R* = 0.023; (for **4**) space group = *P*1̄, *a* = 11.845(2) Å, *b* = 13.196(3) Å, *c* = 9.840(2) Å, *α* = 99.33(2)°, *β* = 113.71(1)°, *γ* = 85.73(1)°, *Z* = 2, 2782 reflections, *R* = 0.024; (for **5**) space group = *P*2₁/*c*, *a* = 9.178(1) Å, *b* = 17.913(4) Å, *c* = 14.329(2) Å, *β* = 93.904(9)°, *Z* = 4, 2157 reflections, *R* = 0.025.

Introduction

We have recently prepared the first example of a metal complex containing the ligand cyclobutyne.[1] Cyclobutyne has not yet been prepared as a free molecule although theoretical calculations show that it could be capable of existence.[2] Metal complexes are well-known to stabilize reactive organic molecules.[3,4] In our original synthesis of the cyclobutyne ligand, a cluster of three metal atoms was used to prepare the ligand on site and provide the stabilization necessary to permit its isolation, Scheme I. This was achieved by the cleavage of a cyclobutenyl group from the molecule phenyl cyclobutenyl thioether by a triosmium cluster complex to yield the complex Os₃(CO)₁₀-(μ-η²-C=CHCH₂CH₂)(μ-SPh), **1**, step A. Subsequent decarbonylation led to activation of the cyclobutenyl CH bond and the transformation of the cyclobutenyl group

Scheme I

into the cyclobutyne ligand and a hydride ligand in the complex Os₃(CO)₉(μ-η²-C₂CH₂CH₂)(μ-SPh)(μ-H), **2**, step B.

The stability of small saturated cyclic hydrocarbons **A** containing the carbon–carbon triple bond has been of interest to chemists for many years.[5] Strain is believed

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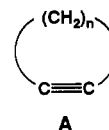
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(3) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.
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to be an important factor in the destabilization of these molecules when the ring contains less than nine carbon atoms.[2,5-8] Accordingly, we have attempted to prepare additional examples of cyclobutyne derived ligands for the purpose of investigating the character of this unusual ligand in greater detail. In this report we describe the synthesis and structural characterization of the methyl tert-butyl derivative of cyclobutyne, 3,3-C̅₂CH₂C̅-(Me)^{t}Bu, as a ligand in a triosmium cluster complex.

Experimental Section

General Procedures. Reactions were performed under a dry nitrogen atmosphere. Reagent grade solvents were stored over molecular sieves and purged with nitrogen prior to use. Os₃-(CO)₁₀(NCMe)₂[9] and 4-tert-butyl-4-methyl-1-(phenylthio)cyclobutene[10] were prepared according to the literature. IR spectra were recorded on a Nicolet 5DXB FT-IR spectrometer. ^{1}H NMR spectra were recorded on Brüker AM-300 and AM-500 FT-NMR spectrometers. Elemental microanalyses were performed by Desert Analytics Organic Microanalysis, Tucson, AZ. TLC separations were performed in air by using silica gel (60 Å, F₂₅₄) on plates (Whatman, 0.25 mm).

Reaction of Os₃(CO)₁₀(NCMe)₂ with 4-tert-Butyl-4-methyl-1-(phenylthio)cyclobutene. A 40.0-mg amount of 4-tert-butyl-4-methyl-1-(phenylthio)cyclobutene (0.172 mmol) and a 150.0-mg amount of Os₃(CO)₁₀(NCMe)₂ (0.161 mmol) were dissolved in 50 mL of CH₂Cl₂. The solution was stirred at 25 °C for 30 h. The solution was then concentrated in vacuo and separated by TLC using hexane solvent. This yielded 94.0 mg of yellow Os₃(CO)₁₀[μ-PhSC̅₂CH₂C̅(Me)^{t}Bu](μ-H) (54%), 3. IR (ν_{co} in hexane, cm⁻¹) for 3: 2104 (w), 2063 (vs), 2053 (m), 2023 (s), 2009 (m), 2004 (m), 1995 (m), 1983 (w), 1977 (w). ^{1}H NMR for 3 (δ in CDCl₃): 7.57–7.34 (m, 5H), 2.49 (d, 1H, $^2J_{HH}$ = 13 Hz), 1.81 (d, 1H, $^2J_{HH}$ = 13 Hz), 1.02 (s, 3H), 0.47 (s, 9H), –14.90 (s, 1H). Anal. Calc for 3 (found): C, 27.72 (27.67); H, 1.86 (1.56).

Synthesis of Os₃(CO)₉[μ₃-PhSC̅₂CH₂C̅(Me)^{t}Bu](μ-H), 4. A 50.0-mg amount of 3 (0.0462 mmol) was dissolved in 25 mL of heptane. The solution was heated to reflux for 1 h. After cooling to room temperature, the solvent was then removed in vacuo, and the residue was separated by TLC using hexane solvent. This yielded only one compound: 45.3 mg of yellow Os₃(CO)₉[μ₃-PhSC̅₂CH₂C̅(Me)^{t}Bu](μ-H), 4 (93%). IR for 4 (ν_{co} in hexane, cm⁻¹): 2092 (s), 2065 (vs), 2036 (vs), 2017 (s), 2006 (m), 1996 (m), 1982 (m), 1977 (w), 1966 (w). ^{1}H NMR for 4 (δ in CDCl₃) (The compound exists in solution as a mixture of two isomers in equilibrium in a 2.2/1 ratio at 25 °C): (major isomer) 7.42–7.20 (m), 2.91 (d, 1H, $^2J_{HH}$ = 14 Hz), 2.43 (d, 1H, $^2J_{HH}$ = 14 Hz), 1.40 (s, 3H), 0.99 (s, 9H), –17.20 (s, 1H); (minor isomer) 7.42–7.20 (m), 3.07 (d, 1H, $^2J_{HH}$ = 14 Hz), 2.56 (d, 1H, $^2J_{HH}$ = 14 Hz), 1.35 (s, 3H), 0.82 (s, 9H), –17.30 (s, 1H). Anal. Calc for 4 (found): C, 27.32 (27.51); H, 1.91 (1.68).

Synthesis of Os₃(CO)₉(μ₃-η²-C̅₂CH₂C̅(Me)^{t}Bu)(μ₃-S), 5. A 30-mg amount of 4 (0.0284 mmol) was dissolved in 25 mL of

Table I. Crystal Data for Compounds 3–5

compound	3	4	5
formula	Os₃SO₁₀C₂₅H₂₀	Os₃SO₉C₂₄H₂₀	Os₃SO₉C₁₈H₁₄
fw	1083.09	1055.08	976.96
cryst syst	monoclinic	triclinic	monoclinic
lattice params			
a (Å)	7.764(1)	11.845(2)	9.178(1)
b (Å)	17.722(4)	13.196(3)	17.913(4)
c (Å)	21.153(3)	9.840(2)	14.329(2)
α (deg)	90.0	99.33(2)	90.0
β (deg)	92.36(1)	113.71(1)	93.904(9)
γ (deg)	90.0	85.73(2)	90.0
V (Å³)	2908.2(8)	1389(1)	2350(1)
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)
Z	4	2	4
ρ_{calc} (g/cm³)	2.47	2.52	2.76
μ(Mo Kα) (cm⁻¹)	132.1	138.2	163.2
temp (°C)	20	20	20
$2\theta_{max}$ (deg)	42.0	44.0	43.0
no. of obs refns ($I > 3\sigma$)	2451	2782	2157
goodness of fit	1.19	1.30	1.42
residuals: R; R_w	0.023; 0.024	0.024; 0.025	0.025; 0.027
largest peak in final diff map	0.57	0.57	0.93

octane. The solution was heated to reflux for 1.5 h. After cooling to room temperature, the solvent was removed, and the residue was separated by TLC using hexane solvent. This yielded, in the order of elution, 5.6 mg of yellow compound 5 (60%, based on compound 4 consumed) and 19.9 mg of unreacted 4. Note the yield of 5 is not increased by using longer reaction periods. IR for 5 (ν_{co}, in hexane, cm⁻¹): 2097 (w), 2074 (vs), 2054 (m), 2017 (s), 2004 (m), 1995 (m). ^{1}H NMR for 5 (δ in CDCl₃): 3.61 (d, 1H, $^2J_{HH}$ = 15 Hz), 2.53 (d, 1H, $^2J_{HH}$ = 15 Hz), 1.20 (s, 3H), 1.01 (s, 9H). Anal. Calc for 5 (found): C, 22.13 (22.12); H, 1.44 (1.26).

Crystallographic Analyses. Crystals of 3 suitable for X-ray diffraction analysis were grown from a solvent mixture of dichloromethane and hexane by slow evaporation of the solvent at 10 °C. Crystals of 4 suitable for X-ray diffraction analysis were grown from a solvent mixture of dichloromethane and hexane by slow evaporation of the solvent at 25 °C. Crystals of 5 were grown from solution in a solvent mixture of dichloromethane and methanol by slow evaporation of solvent at –20 °C. All crystals used in intensity measurements were mounted in thinwalled 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 AFC6 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 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.[11a] Anomalous dispersion corrections were applied to all nonhydrogen atoms.[11b] All non-hydrogen atoms were refined with anisotropic thermal parameters. Full matrix least-squares refinements minimized the function: $\sum_{hkl}w(|F_o| - |F_c|)^2$ where w = $1/\sigma(F)^2$, $\sigma(F) = \sigma(F_o^2)/2F_o$, and $\sigma(F_o^2) = [\sigma(I_{raw})^2+(0.02I_{net})^2]^{1/2}/Lp$.

Compound 3 crystallized in the monoclinic crystal system. The space group $P2_1/c$ was established on the basis of the systematic absences observed in the data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. The hydride ligand was located and refined with an anisotropic thermal parameter. All hydrogen atoms on the ligands were calculated by assuming idealized

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(11) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1975; Vol. IV, Table 2.2B, pp 99–101. (b) *Ibid.*, Table 2.3.1, pp 149–150.
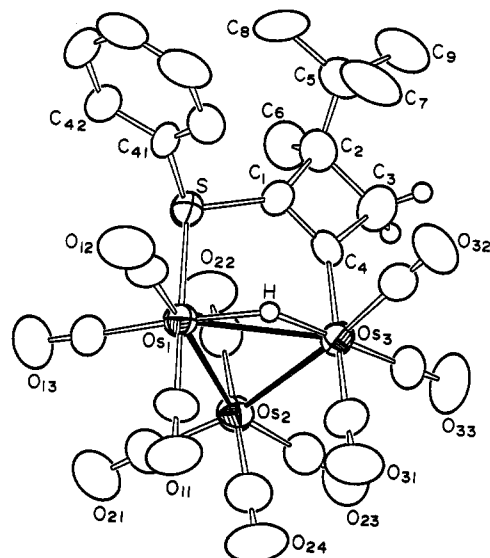
Figure 1. ORTEP diagram of Os₃(CO)₁₀[μ-SPhC₂CH₂C(Me)ᵗ-Bu](μ-H), **3**, showing 50% probability thermal ellipsoids.

geometries. The contributions of all of the hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

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. The position of the hydride ligand was obtained in a chemically reasonable position from a difference Fourier map, but it could not be refined to a convergence. It was thus added as a constant contribution only. All other hydrogen atom positions were calculated by assuming idealized geometries. Their contribution were added to the structure factor calculations, but their positions were not refined.

Compounds **5** crystallized in the monoclinic crystal system. The space group $P2_1/c$ was determined uniquely from the systematic absences observed in the data. The structure was solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. The positions of hydrogen atoms on the ligands were calculated by assuming idealized geometries. The scattering contributions of all hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Results

The reaction of 4-*tert*-butyl-4-methyl-1-(phenylthio)-cyclobutene with Os₃(CO)₁₀(NCMe)₂ yielded the new complex Os₃(CO)₁₀[μ₃-SPhC₂CH₂C(Me)ᵗBu](μ-H), **3**, in 54% yield. Compound **3** was characterized by IR, ¹H NMR, and single crystal X-ray diffraction analyses, and an ORTEP diagram of its molecular structure is shown in Figure 1. Final atomic positional parameters are listed in Table II, and selected interatomic distances and angles are listed in Tables III and IV. The molecule consists of a triangular triosmium cluster of three metal atoms with ten linear terminal carbonyl ligands. The 4-*tert*-butyl-4-methyl-1-(phenylthio)cyclobutene ligand has undergone an activation at the alkenyl CH bond of the cyclobutenyl grouping. This ligand bridges an edge of the cluster with the carbon atom and the thioether sulfur atom occupying axial coordination sites. The Os–C and Os–S distances are not unusual, 2.10(1) and 2.495(3) Å. The C(1)–C(4) distance of 1.34(1) Å is typical of a C–C double bond, as

Table II. Positional Parameters and B(eq) for Os₃(CO)₁₀[μ-SPhC₂CH₂C(Me)ᵗBu](μ-H), 3

atom	x	y	z	B(eq) (Å²)
Os(1)	0.19813(06)	0.06991(02)	0.135339(19)	3.30(2)
Os(2)	0.48018(06)	0.08970(03)	0.22878(02)	3.59(2)
Os(3)	0.18121(06)	0.18686(02)	0.236409(19)	3.32(2)
S	0.2782(03)	0.17103(15)	0.05990(12)	3.5(1)
O(11)	0.0949(12)	−0.0511(05)	0.2267(04)	6.7(5)
O(12)	−0.1285(11)	0.0286(05)	0.0579(04)	6.3(5)
O(13)	0.4344(11)	−0.0360(05)	0.0652(04)	6.5(5)
O(21)	0.7132(12)	−0.0403(05)	0.1919(05)	7.2(6)
O(22)	0.6487(11)	0.1827(05)	0.1266(04)	6.7(5)
O(23)	0.6899(12)	0.1675(05)	0.3356(05)	7.4(6)
O(24)	0.3311(11)	−0.0105(06)	0.3321(04)	7.0(6)
O(31)	0.0195(12)	0.0828(06)	0.3341(04)	7.9(6)
O(32)	−0.1407(10)	0.2864(05)	0.2311(04)	6.2(5)
O(33)	0.3928(11)	0.2822(06)	0.3294(04)	7.1(6)
C(1)	0.2760(14)	0.2561(06)	0.1031(05)	3.8(6)
C(2)	0.3428(18)	0.3375(06)	0.0915(06)	5.6(7)
C(3)	0.3317(17)	0.3424(07)	0.1658(05)	5.9(7)
C(4)	0.2676(12)	0.2597(05)	0.1663(05)	3.0(5)
C(5)	0.2196(19)	0.3922(07)	0.0555(06)	6.1(8)
C(6)	0.5255(16)	0.3430(07)	0.0675(06)	5.5(7)
C(7)	0.0333(17)	0.3833(07)	0.0778(07)	7.2(8)
C(8)	0.221(02)	0.3793(08)	−0.0153(06)	8(1)
C(9)	0.2786(18)	0.4741(07)	0.0695(07)	7.0(8)
C(11)	0.1419(15)	−0.0048(06)	0.1930(06)	4.6(6)
C(12)	−0.0038(16)	0.0476(06)	0.0842(05)	4.3(6)
C(13)	0.3461(15)	0.0027(06)	0.0925(05)	4.1(6)
C(21)	0.6274(15)	0.0084(08)	0.2043(06)	5.3(7)
C(22)	0.5768(14)	0.1513(07)	0.1647(06)	4.7(6)
C(23)	0.6118(16)	0.1385(07)	0.2950(06)	4.9(7)
C(24)	0.3799(14)	0.0271(07)	0.2925(06)	4.8(6)
C(31)	0.0863(15)	0.1208(07)	0.2973(06)	5.0(7)
C(32)	−0.0188(16)	0.2494(06)	0.2324(05)	4.0(6)
C(33)	0.3101(16)	0.2457(07)	0.2954(06)	4.7(6)
C(41)	0.1051(14)	0.1778(06)	0.0014(04)	3.6(5)
C(42)	0.1492(14)	0.1593(06)	−0.0599(05)	3.9(6)
C(43)	0.0212(18)	0.1625(07)	−0.1075(05)	4.9(7)
C(44)	−0.1435(17)	0.1825(07)	−0.0944(07)	5.4(7)
C(45)	−0.1874(14)	0.2004(07)	−0.0328(05)	5.4(7)
C(46)	−0.0581(16)	0.1988(06)	0.0152(05)	4.7(6)
H	0.070(12)	0.132(05)	0.181(04)	6(2)

Table III. Intramolecular Distances for 3ᵃ

Os(1)–Os(2)	2.9100(7)	Os(3)–C(33)	1.88(1)
Os(1)–Os(3)	2.9844(7)	Os(3)–H	1.7(1)
Os(1)–S	2.495(3)	S–C(1)	1.76(1)
Os(1)–C(11)	1.86(1)	S–C(41)	1.79(1)
Os(1)–C(12)	1.91(1)	O–C(av)	1.15(1)
Os(1)–C(13)	1.91(1)	C(1)–C(2)	1.55(1)
Os(1)–H	1.79(9)	C(1)–C(4)	1.34(1)
Os(2)–Os(3)	2.9001(7)	C(2)–C(3)	1.58(2)
Os(2)–C(21)	1.92(1)	C(2)–C(5)	1.54(2)
Os(2)–C(22)	1.91(1)	C(2)–C(6)	1.53(2)
Os(2)–C(23)	1.91(1)	C(3)–C(4)	1.55(1)
Os(2)–C(24)	1.93(1)	C(5)–C(7)	1.55(2)
Os(3)–C(4)	2.10(1)	C(5)–C(8)	1.51(2)
Os(3)–C(31)	1.91(1)	C(5)–C(9)	1.55(2)
Os(3)–C(32)	1.91(1)		

ᵃ Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

expected. The other C–C distances in the four membered ring are single, C(1)–C(2) = 1.55(1) Å, C(2)–C(3) = 1.58(2) Å, and C(3)–C(4) = 1.55(1) Å. The C–S distance to the metalated cyclobutenyl grouping is also normal, 1.76(1) Å. The bulky *tert*-butyl grouping is oriented exo to the cluster, presumably to minimize the steric interactions with the axial carbonyl ligand C(22)–O(22). The hydride ligand bridges the Os(1)–Os(3) bond, which is lengthened slightly to 2.9844(7) Å, as expected for bridging hydride ligands.[12] It exhibits the usual highly shielded resonance shift in the ¹H NMR spectrum, δ = −14.90 ppm.

Table IV. Intramolecular Bond Angles for 3[a]

Os(2)–Os(1)–Os(3)	58.93(2)	S–C(1)–C(2)	134.5(8)
Os(2)–Os(1)–S	98.49(6)	S–C(1)–C(4)	123.9(8)
Os(3)–Os(1)–S	88.79(6)	C(2)–C(1)–C(4)	98.3(9)
Os(1)–Os(2)–Os(3)	61.82(2)	C(1)–C(2)–C(3)	82.1(8)
Os(1)–Os(3)–Os(2)	59.26(2)	C(2)–C(3)–C(4)	89.2(8)
Os(1)–Os(3)–C(4)	84.0(3)	Os(3)–C(4)–C(1)	134.9(8)
Os(2)–Os(3)–C(4)	92.6(2)	Os(3)–C(4)–C(3)	134.4(7)
Os(1)–S–C(1)	106.0(3)	C(1)–C(4)–C(3)	90.5(9)
Os(1)–S–C(41)	106.9(4)	Os–C(av)–O	176(1)
C(1)–S–C(41)	106.1(5)		

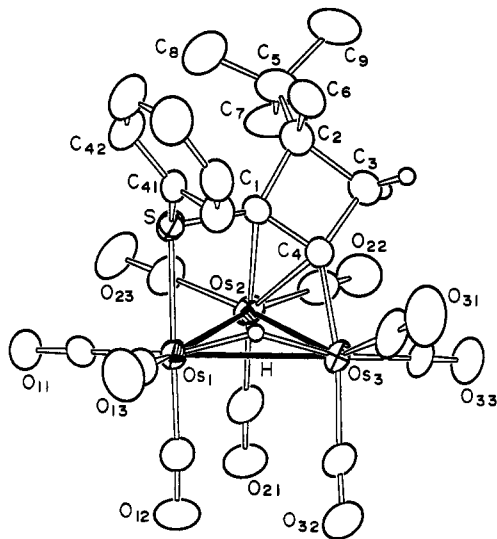[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Figure 2. ORTEP diagram of $Os_3(CO)_9[\mu_3\text{-}SPhC_2CH_2C(Me)^t\text{-}Bu](\mu\text{-}H)$, 4, showing 50% probability thermal ellipsoids.

When heated to reflux in heptane solvent (97 °C), compound **3** was decarbonylated and transformed into the new compound $Os_3(CO)_9[\mu_3\text{-}SPhC_2CH_2C(Me)^t Bu](\mu\text{-}H)$, **4**, in 93% yield. Compound **4** was characterized by IR, ^1H NMR, and single crystal X-ray diffraction analyses, and an ORTEP diagram of its molecular structure is shown in Figure 2. Final atomic positional parameters are listed in Table V, and selected interatomic distances and angles are listed in Tables VI and VII. This compound also consists of a triangular triosmium cluster of three metal atoms but has only nine carbonyl ligands, three on each metal atom. The metalated phenyl cyclobutenyl thioether ligand has been transformed into a triply bridging ligand through coordination of the cyclobutenyl C–C double bond. This C–C group bridges the Os(2)–Os(3) bond in the usual $\mu\text{-}\eta^2$, σ + π coordination mode. As a result of its coordination, the C(1)–C(4) double bond has lengthened to 1.40(1) Å. The S–C(1) bond is also slightly longer than that in **3**, 1.80(1) Å. Interestingly, the *tert*-butyl group in **4** is also oriented exo to the cluster. However, a simple coordination of the C–C double bond of the cyclobutenyl group in **3** should lead to the isomer **A** having an endo *tert*-butyl group; see Scheme II. The observed structure of **4** could then be obtained by a σ–π flip. Flipping transformations of σ–π coordinated alkenyl groups are a well established low energy process.[13] Nonbonded steric

Table V. Positional Parameters and B(eq) for
$Os_3(CO)_9[\mu_3\text{-}SPhC_2CH_2C(Me)^t Bu](\mu\text{-}H)$, 4

atom	x	y	z	B(eq) (Å²)
Os(1)	0.87154(04)	0.27484(03)	0.48175(05)	3.29(2)
Os(2)	0.88756(04)	0.34558(03)	0.77553(05)	3.29(2)
Os(3)	0.92970(04)	0.13601(03)	0.71902(04)	3.27(2)
S	0.6643(02)	0.30375(19)	0.4663(03)	3.5(1)
O(11)	0.8575(08)	0.4879(06)	0.3976(10)	6.8(4)
O(12)	1.1457(07)	0.2729(06)	0.5535(10)	6.3(4)
O(13)	0.8077(09)	0.1501(08)	0.1702(10)	7.6(5)
O(21)	1.1604(07)	0.3790(06)	0.8766(09)	5.8(4)
O(22)	0.9241(08)	0.3722(07)	1.1032(10)	6.7(4)
O(23)	0.8000(08)	0.5640(06)	0.7165(11)	7.7(4)
O(31)	0.8204(10)	−0.0777(07)	0.6143(11)	8.6(5)
O(32)	1.1858(08)	−0.0820(07)	0.7180(10)	7.0(4)
O(33)	1.0268(08)	0.1186(06)	1.0493(09)	6.5(4)
C(1)	0.6865(08)	0.2737(07)	0.6474(11)	3.3(4)
C(2)	0.5874(10)	0.2627(09)	0.7109(13)	5.1(5)
C(3)	0.6946(10)	0.2007(09)	0.8229(13)	5.2(5)
C(4)	0.7724(08)	0.2050(07)	0.7306(11)	3.4(4)
C(5)	0.5258(13)	0.3528(11)	0.7706(17)	7.1(7)
C(6)	0.4890(10)	0.1802(10)	0.5981(13)	6.0(6)
C(7)	0.6186(12)	0.4265(11)	0.8921(19)	8.7(8)
C(8)	0.4406(16)	0.4048(14)	0.640(02)	11(1)
C(9)	0.4462(14)	0.3099(14)	0.8401(19)	9(1)
C(11)	0.8624(09)	0.4084(09)	0.4288(13)	4.5(5)
C(12)	1.0439(11)	0.2730(08)	0.5305(12)	4.4(5)
C(13)	0.8312(10)	0.1988(09)	0.2860(14)	4.9(5)
C(21)	1.0570(11)	0.3666(08)	0.8348(12)	4.7(5)
C(22)	0.9084(10)	0.3613(09)	0.9794(15)	5.1(5)
C(23)	0.8315(11)	0.4815(09)	0.7381(14)	5.5(6)
C(31)	0.8641(12)	0.0008(09)	0.6510(12)	5.3(5)
C(32)	1.0911(11)	0.1034(09)	0.7162(12)	4.8(5)
C(33)	0.9892(10)	0.1226(08)	0.9249(13)	4.6(5)
C(41)	0.5571(09)	0.2135(08)	0.3245(11)	3.7(4)
C(42)	0.4451(10)	0.2535(09)	0.2358(13)	5.6(5)
C(43)	0.3600(12)	0.1873(12)	0.1279(16)	7.3(7)
C(44)	0.3838(13)	0.0851(12)	0.1026(14)	7.0(7)
C(45)	0.4991(12)	0.0470(09)	0.1888(14)	5.7(6)
C(46)	0.5842(10)	0.1107(09)	0.2983(12)	4.6(5)
H	0.8426	0.1665	0.5323	4.0

Table VI. Intramolecular Distances for 4[a]

Os(1)–Os(2)	2.8238(9)	Os(3)–C(31)	1.91(1)
Os(1)–Os(3)	3.0309(9)	Os(3)–C(32)	1.94(1)
Os(1)–S	2.403(3)	Os(3)–C(33)	1.89(1)
Os(1)–C(11)	1.90(1)	Os(3)–H	1.80
Os(1)–C(12)	1.90(1)	S–C(1)	1.80(1)
Os(1)–C(13)	1.91(1)	S–C(41)	1.80(1)
Os(1)–H	1.69	C(1)–C(2)	1.56(1)
Os(2)–Os(3)	2.7796(8)	C(1)–C(4)	1.40(1)
Os(2)–C(1)	2.39(1)	C(2)–C(3)	1.58(1)
Os(2)–C(4)	2.26(1)	C(2)–C(5)	1.51(2)
Os(2)–C(21)	1.88(1)	C(2)–C(6)	1.59(2)
Os(2)–C(22)	1.90(1)	C(3)–C(4)	1.54(1)
Os(2)–C(23)	1.91(1)	O–C(av)	1.14(1)
Os(3)–C(4)	2.05(1)		

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

repulsions between the ^{t}Bu group and the phenyl ring in **A** may be the source of its destabilization relative to **4**. The hydride ligand was located in the structural analysis as a bridge across the long Os(1)–Os(3) bond, 3.0309(9) Å, but it could not be refined. In solution **4** exists as a mixture of two isomers, as indicated by a doubling of all of the expected proton resonances (e.g. δ = −17.20 and −17.30 ppm for the hydride ligands). The interconversion of these isomers is still slow on the ^1H NMR time scale even at 100 °C. Isomers could be formed simply by repositioning the hydride ligand as a bridge on one of the other metal-

(12) (a) Teller, R. G.; Bau, R. *Struct. Bonding* **1981**, *44*, 1. (b) Churchill, M. R. In *Transition Metal Hydrides*; Bau, R., Ed.; Advances in Chemistry Series No. 167; American Chemical Society: Washington, DC 1978.

(13) (a) Farrugia, L. J.; Chi, Y.; Tu, W.-C. *Organometallics* **1993**, *12*, 1616 and references therein. (b) Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1.

Table VII. Intramolecular Bond Angles for 4[a]

Os(2)–Os(1)–Os(3)	56.56(2)	S–C(1)–C(4)	127.6(7)
Os(2)–Os(1)–S	72.90(7)	C(2)–C(1)–C(4)	96.3(7)
Os(3)–Os(1)–S	91.83(6)	C(1)–C(2)–C(3)	82.7(7)
Os(1)–Os(2)–Os(3)	65.48(2)	C(2)–C(3)–C(4)	89.9(7)
Os(1)–Os(3)–Os(2)	57.96(2)	Os(2)–C(4)–C(1)	77.3(7)
Os(1)–S–C(1)	98.9(3)	Os(2)–C(4)–C(3)	119.1(7)
Os(2)–C(1)–S	95.5(4)	Os(3)–C(4)–C(1)	133.4(7)
Os(2)–C(1)–C(2)	128.6(7)	Os(3)–C(4)–C(3)	136.9(7)
Os(2)–C(1)–C(4)	67.8(5)	C(1)–C(4)–C(3)	89.7(7)
S–C(1)–C(2)	128.6(7)	Os–C(av)–O	177(1)

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Scheme II

3   A   4
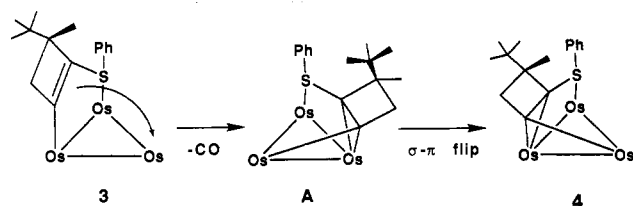
metal bonds, but two isomers could also be formed by changing the σ + π coordination of the cyclobutenyl grouping (see Scheme II) or by changing the chirality of the sulfur atom through an inversion of configuration. One cannot distinguish among these possibilities with the available data.

When heated to 125 °C, compound **4** was transformed to the cyclobutyne complex Os₃(CO)₉(μ_3-η^2-C₂CH₂C(Me)^t-Bu)(μ_3-S), **5**, in 60% yield based on the amount of compound **4** consumed. Compound **5** was characterized by IR, ¹H NMR, and single crystal X-ray diffraction analyses, and an ORTEP diagram of its molecular structure is shown in Figure 3. Final atomic positional parameters are listed in Table VIII, and selected interatomic distances and angles are listed in Tables IX and X. This compound consists of an open triangular cluster of three metal atoms with three linear terminal carbonyl ligands on each metal atom. There is a triply bridging sulfido ligand on one side of the cluster and a triply bridging methyl-*tert*-butylcyclobutyne ligand on the other side. The metal–metal and metal–sulfur distances, Os(1)–Os(2) = 2.8069(9) Å, Os(2)–Os(3) = 2.8282(7) Å, Os(1)–S = 2.393(3) Å, Os(2)–S = 2.432(3) Å, Os(3)–S = 2.388(3) Å, are very similar to those found in the molecule Os₃(CO)₉(μ_3-S)₂, Os–Os = 2.814(1) and 2.812(1) Å and Os–S = 2.392(2), 2.415(1), 2.454(2), 2.434(2), 2.390(2), and 2.402(2) Å, respectively.[14] The acetylene C–C bond in the cyclobutyne ligand, C(1)–C(4) = 1.40(2) Å, is typical of the C–C bond found for triply bridging alkynes[15] and slightly but not significantly longer than that found for the cyclobutyne ligand in 2, 1.37(2) Å.[1] The other C–C distances in the four membered ring are typical of C–C single bonds: C(1)–C(2) = 1.57(1) Å, C(2)–C(3) = 1.56(2) Å, and C(3)–C(4) = 1.54(1) Å. The four carbon ring is nearly planar. No atom deviates by more than 0.04 Å from the least-squares plane. The plane of the cyclobutyne ligand is inclined 79.8° from the plane of the three metal atoms. The coordination of alkynes to trimetallic centers can be viewed as a combination of the σ-donation and π-acceptance that leads to a reduction of

(14) Adams, R. D.; Horváth, I. T.; Segmüller, B. E.; Yang, L.-W. *Organometallics* **1983**, *2*, 144.

(15) (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.
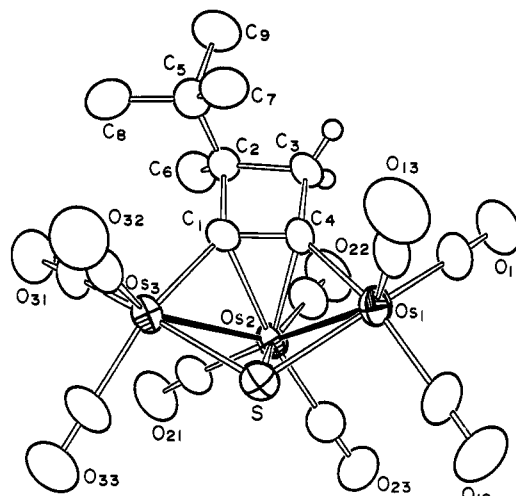

Figure 3. ORTEP diagram of Os₃(CO)₉(μ_3-η^2-C₂CH₂C-(Me)^{t}Bu)(μ_3-S), **5**, showing 50% probability thermal ellipsoids.

Table VIII. Positional Parameters and B(eq) for Os₃(CO)₉(μ_3-η^2-C₂CH₂C(Me)^{t}Bu)(μ_3-S), 5

atom	x	y	z	B(eq) (Å²)
Os(1)	1.03134(05)	0.25048(03)	0.79006(03)	3.02(2)
Os(2)	1.02067(05)	0.09600(03)	0.82167(03)	2.77(2)
Os(3)	0.71739(05)	0.10366(03)	0.84458(03)	3.09(2)
S	0.8946(03)	0.19158(18)	0.90591(20)	3.2(1)
O(11)	1.2444(11)	0.2796(06)	0.6409(07)	6.6(6)
O(12)	1.2289(13)	0.3239(07)	0.9459(08)	7.6(7)
O(13)	0.8350(13)	0.3800(06)	0.7368(08)	6.9(7)
O(21)	0.9518(11)	-0.0561(06)	0.9042(07)	5.6(5)
O(22)	1.2097(12)	0.0310(06)	0.6756(07)	6.8(6)
O(23)	1.2829(10)	0.1184(06)	0.9593(07)	5.6(5)
O(31)	0.5657(13)	-0.0386(07)	0.7737(08)	7.5(7)
O(32)	0.4560(12)	0.2040(07)	0.8193(08)	7.4(7)
O(33)	0.6605(11)	0.0606(07)	1.0488(07)	6.9(6)
C(1)	0.8087(12)	0.1255(07)	0.7196(07)	3.0(6)
C(2)	0.7897(13)	0.1024(07)	0.6134(07)	3.2(6)
C(3)	0.9270(12)	0.1519(07)	0.6010(07)	2.9(6)
C(4)	0.9231(12)	0.1747(06)	0.7047(07)	2.7(5)
C(5)	0.6482(14)	0.1342(08)	0.5641(08)	3.8(6)
C(6)	0.8170(17)	0.0185(08)	0.5954(09)	5.4(8)
C(7)	0.6271(15)	0.2164(09)	0.5847(09)	4.9(7)
C(8)	0.5143(15)	0.0923(09)	0.5882(09)	5.5(8)
C(9)	0.6632(17)	0.1283(10)	0.4570(09)	6.1(9)
C(11)	1.1664(14)	0.2689(08)	0.6973(10)	4.2(7)
C(12)	1.1559(16)	0.2980(08)	0.8892(11)	4.9(8)
C(13)	0.9150(15)	0.3330(08)	0.7589(09)	4.2(7)
C(21)	0.9680(14)	0.0005(08)	0.8730(09)	3.9(7)
C(22)	1.1395(14)	0.0545(08)	0.7298(10)	4.3(7)
C(23)	1.1848(16)	0.1096(08)	0.9091(09)	4.3(7)
C(31)	0.6202(16)	0.0150(09)	0.7989(10)	5.1(8)
C(32)	0.5526(15)	0.1646(09)	0.8310(09)	4.4(7)
C(33)	0.6804(15)	0.0773(08)	0.9734(09)	5.0(8)

the C≡C bond order,[16] and in the limit a resonance structure **B** can be drawn in which the cyclobutyne ligand

B
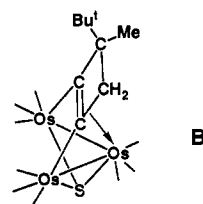
is represented as a dimetalated cyclobutene. Accordingly, the C(1)–C(2) distance is significantly longer than that of

(16) Schilling, B. E. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3456.

Table IX. Intramolecular Distances for 5[a]

|			
Os(1)–Os(2)	2.8069(9)	Os(3)–S	2.388(3)
Os(1)–S	2.393(3)	Os(3)–C(1)	2.07(1)
Os(1)–C(4)	2.04(1)	Os(3)–C(31)	1.92(2)
Os(1)–C(11)	1.91(1)	Os(3)–C(32)	1.86(2)
Os(1)–C(12)	1.96(1)	Os(3)–C(33)	1.96(1)
Os(1)–C(13)	1.86(2)	O–C(av)	1.13(1)
Os(2)–Os(3)	2.8282(7)	C(1)–C(2)	1.57(1)
Os(2)–S	2.432(3)	C(1)–C(4)	1.40(2)
Os(2)–C(1)	2.41(1)	C(2)–C(3)	1.56(2)
Os(2)–C(4)	2.32(1)	C(2)–C(5)	1.54(2)
Os(2)–C(21)	1.94(1)	C(2)–C(6)	1.55(2)
Os(2)–C(22)	1.92(1)	C(3)–C(4)	1.54(1)
Os(2)–C(23)	1.91(1)	Os(1)⋯Os(3)	4.017(1)

[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table X. Intramolecular Bond Angles for 5[a]

Os(2)–Os(1)–S	55.09(8)	Os(2)–S–Os(3)	71.84(9)
Os(1)–Os(2)–Os(3)	90.93(2)	C(2)–C(1)–C(4)	93.1(8)
Os(1)–Os(2)–S	53.78(8)	C(1)–C(2)–C(3)	85.6(8)
Os(3)–Os(2)–S	53.36(7)	C(2)–C(3)–C(4)	88.2(8)
Os(2)–Os(3)–S	54.81(7)	C(1)–C(4)–C(3)	92.7(9)
Os(1)–S–Os(2)	71.13(8)	Os–C(av)–O	177(1)
Os(1)–S–Os(3)	114.3(1)		

[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Scheme III
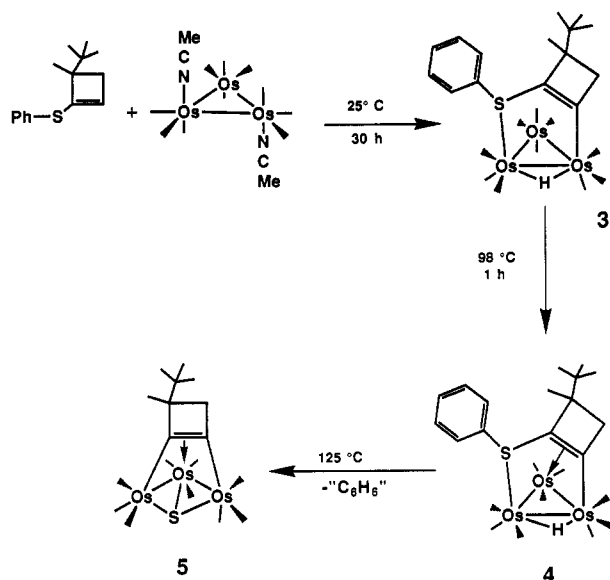
an uncoordinated C–C triple bond. It is believed that it is the stabilization provided by reduction of the C–C bond order that has permitted the isolation of complex 5. The cyclobutyne ligand serves as a four-electron donor, and all three metal atoms achieve 18-electron configurations.

Discussion

In this study we have prepared the second example of a cyclobutyne molecule in a stabilized form through complexation to a metal cluster. A summary of these results is shown in Scheme III. The reaction of 4-*tert*-butyl-4-methyl-1-(phenylthio)cyclobutene with Os₃(CO)₁₀-

(NCMe)₂ led to displacement of the labile NCMe ligands and the addition of 1 equiv of the 4-*tert*-4-methyl-1-(phenylthio)cyclobutene to the cluster. The sulfur atom became coordinated to one of the metal atoms and the cyclobutenyl grouping was metalated at the neighboring metal atom by activation of the CH bond to yield compound **3**. This reaction proceeded quite differently from the reaction of phenyl cyclobutenyl thioether with Os₃(CO)₁₀(NCMe)₂ where the carbon–sulfur bond to the cyclobutenyl group was cleaved initially, Scheme I. One can only speculate why the C–S bond cleavage step in the reaction of the unsubstituted (phenylthio)cyclobutene with Os₃(CO)₁₀(NCMe)₂[1] occurs more readily than the reaction of the 4-*tert*-butyl-4-methyl-1-(phenylthio)cyclobutene, but one obvious difference is the steric bulk at the alkyl-substituted carbon atom. This steric crowding may block the approach of the C–S bond to the metal atoms sufficiently to prevent cleavage by the mechanism that operates in the reaction of the unsubstituted (phenylthio)-cyclobutene.

When compound **3** was heated, the third metal atom was decarbonylated and the carbon–carbon double bond of the cyclobutenyl group became coordinated where the CO group was lost and compound **4** was formed. Finally, when compound **4** was heated to 125 °C, the carbon–sulfur bond was cleaved and the cyclobutyne ligand was formed. At the same time the phenyl group was cleaved from the sulfur atom and both the phenyl group and the hydride ligand were eliminated from the complex. The fate of these two ligands was not determined in this study, but in a related study we have shown that the elimination of a phenyl group and a hydride ligand from the complex Os₃(CO)₁₀(μ-SPh)(μ-H) at 125 °C yields benzene.[17]

This study also provides yet another example of the power of a group of metal atoms to produce novel rearrangement of small organic molecules.[18] In particular, the formation of **3** is almost certainly a two-site two-step process: coordination of the sulfur atom to one metal atom followed by the CH activation at one of the adjacent metal atoms. The decarbonylation of **3** led to involvement of the third metal atom by coordination of the olefin function to form **4**. It is only at this point that the three metal atoms have activated the ligand sufficiently that the carbon–sulfur bond could be cleaved to yield **5**.

(17) Adams, R. D.; Yang, L.-W. *J. Am. Chem. Soc.* **1982**, *104*, 4115.
(18) (a) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1976**, *85*, 451. (b) Adams, R. D.; Horvath, I. T. *Prog. Inorg. Chem.* **1985**, *33*, 127. (c) Adams, R. D. In *Metal–Metal Bonds and Clusters in Chemistry and Catalysis*; Fackler, J. P., Jr., Ed.; Plenum: New York 1990; pp 75–89. (d) Chisholm, M. H. *Ibid.*, pp 55–74.