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Cyclobutyne Ligands. 5. C–H Bond Cleavage versus Ring Opening of σ,π-Coordinated Cyclobutenyl Ligands

Richard D. Adams,* Linfeng Chen, and Xiaosu Qu

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

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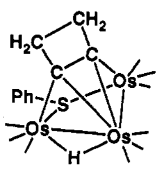
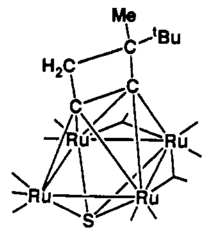
The reaction of 1-bromocyclobutene with $Os_3(CO)_{10}(NCMe)_2$ at 25 °C yielded two new complexes: $Os_3(CO)_{10}(\mu\text{-Br})(\mu\text{-}\overline{CCHCH_2CH_2})$ (**1**; 44%) and $Os_3(CO)_9(\mu\text{-Br})(\mu_3\text{-}CCHCH_2CH_2)$ (**2**; 16%). Compound **1** contains a bridging σ,π-coordinated cyclobutenyl and a bridging bromo ligand across the open edge of a triosmium cluster. Compound **2** contains a metalated σ,π-coordinated bridging alkenyl ligand. Compound **2** was obtained from **1** in good yield both by thermal- and irradiation-induced ring-opening cleavage of a carbon–carbon bond of the cyclobutenyl ligand. Compound **1** was decarbonylated by treatment with Me_3NO at 0 °C and was converted into a mixture of **2** (37%) and the new compound $Os_3(CO)_9(\mu\text{-Br})(\mu_3\text{-}\eta^2\text{-}\overline{C_2CH_2CH_2})(\mu\text{-H})$ (**3**; 8%). Compound **3** contains a new example of a triply bridging cyclobutyne ligand formed by the transfer of the alkenyl hydrogen atom of the cyclobutenyl ligand to the metal atoms. Interestingly, compound **3** could not be transformed to **2** by either thermal or photochemical methods. Crystal data for **1**: space group $P\bar{1}$, $a = 15.577(1)$ Å, $b = 20.220(3)$ Å, $c = 9.555(2)$ Å, $\alpha = 91.39(2)°$, $\beta = 94.30(2)°$, $\gamma = 93.54(1)°$, $Z = 6$, 5295 reflections, $R = 0.027$. Crystal data for **2**: space group $P2_1/n$, $a = 13.348(3)$ Å, $b = 9.588(3)$ Å, $c = 15.036(3)$ Å, $\beta = 108.93(2)°$, $Z = 4$, 1753 reflections, $R = 0.034$. Crystal data for **3**: space group $P\bar{1}$, $a = 9.237(2)$ Å, $b = 13.922(5)$ Å, $c = 7.779(2)$ Å, $\alpha = 92.57(2)°$, $\beta = 111.32(2)°$, $\gamma = 88.31(2)°$, $Z = 2$, 1727 reflections, $R = 0.029$.

Introduction

We have recently prepared and characterized the first examples of the highly strained carbocycle cyclobutyne[1] ($\overline{C_2CH_2CH_2}$) and its 3-^{t}Bu-3-Me derivative $\overline{C_2CH_2C}(Me)^t$Bu through its complexation to triosmium,[2–4] triruthenium,[5] and tetraruthenium[5] cluster complexes (e.g. $Os_3(CO)_9(\mu\text{-SPh})[\mu_4\text{-}\eta^2\text{-}\overline{CCHCH_2CH_2}](\mu\text{-H})$ (**A**) and $Ru_4(CO)_{11}(\mu_4\text{-S})[\mu_4\text{-}\eta^2\text{-}\overline{C_2CH_2C}(Me)^tBu]$ (**B**)). These were made through reactions of suitable cluster precursor complexes with the appropriate phenyl cyclobutenyl thioethers by the cleavage of the hydrogen atom and the phenylthio groupings from the alkene portion of the cyclobutenyl group. The coordination of the triple bond of the cyclobutynes to the metal atoms apparently reduces the strain at the C–C multiple bond sufficiently to permit the ligand to exist at room temperature.



A



B

We have now investigated the reaction of 1-bromocyclobutene with $Os_3(CO)_{10}(NCMe)_2$. We have found that the bromine atom is readily cleaved from the cyclobutenyl group upon reaction with the cluster, and it is also possible to transform this cyclobutenyl ligand into a cyclobutyne ligand, but most interestingly, we have found a new transformation that involves an opening of the cyclobutenyl ring by a cleavage of one of its carbon–carbon bonds. The results of this study are reported here.

Experimental Section

General Procedures. Reactions were performed under a dry nitrogen atmosphere. Reagent grade solvents were purified by distillation under nitrogen from the appropriate drying agents (sodium/benzophenone for THF, sodium for toluene, and CaH_2 for CH_2Cl_2 and hexane) and stored over molecular sieves and deoxygenated by purging with nitrogen prior to use. 1-Bromocyclobutene was prepared according to the published procedures of Abell and Chiao,[6] except that *trans*-1,2-dibromocyclobutane was directly synthesized by bromination of cyclobutene, which was prepared according to the literature.[7] $Os_3(CO)_{10}(NCMe)_2$ was prepared according to the literature procedure.[8] UV–vis irradiations were performed by using an externally positioned 360-W medium-pressure mercury lamp purchased from Gates Inc., Long Island, NY, on solutions in Pyrex glassware. IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AM-300 FT-NMR spectrometer. Elemental microanalyses were performed by Desert Analytics Microanalysis, Tucson, AZ. TLC

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separations were performed in air on silica gel (60 Å, F_{254}) using plates (Analtech, 0.25 mm) or on Al_2O_3 (60 Å, F_{254}) using plates (Merck, 0.25 mm).

Reaction of $Os_3(CO)_{10}(NCMe)_2$ with 1-Bromocyclobutene. A 50.0-mg amount of $Os_3(CO)_{10}(NCMe)_2$ (0.054 mmol) and a 22.0-mg amount of 1-bromocyclobutene (0.165 mmol) were dissolved in 25 mL of CH_2Cl_2. The solution was stirred at room temperature for 24 h. The solvent was then removed in vacuo, and the residue was first separated on silica gel to yield 35.0 mg of an orange band. This orange band was crystallized from a solution of diethyl ether and pentane at −15 °C to yield 23.0 mg of orange flaky crystals of $Os_3(CO)_{10}(\mu\text{-Br})(\mu\text{-CCHCH}_2\text{CH}_2)$ (1; 44%) and 8.0 mg of a pale yellow residue of $Os_3(CO)_9(\mu\text{-Br})(\mu_3\text{-CCHCH}_2\text{CH}_2)$ (2; 16%). Spectroscopic data are as follows. IR (ν_{CO} in hexane, cm^{-1}) for 1: 2106 (w), 2067 (s), 2056 (m), 2021 (vs), 2014 (m), 2001 (m), 1992 (w), 1979 (w). ^{1}H NMR (δ in $CDCl_3$) for 1: 6.07 (s, 1H), 3.40–3.37 (m, 2H), 3.25–3.22 (m, 2H). Anal. Calcd (found) for 1: C, 17.08 (17.06); H, 0.51 (0.33). IR (ν_{CO} in hexane, cm^{-1}) for 2: 2101 (w), 2081 (vs), 2055 (vs), 2027 (m), 2019 (s), 2008 (s), 1999 (w), 1984 (w), 1975 (w). ^{1}H NMR (δ in $CDCl_3$) for 2: 5.07 (dddd, 1H, $^2J_{HH}$ = 16.0 Hz, $^3J_{HH}$ = 9.4 Hz, $^3J_{HH}$ = 5.8 Hz, $^3J_{HH}$ = 4.0 Hz), 4.89 (dddd, 1H, $^2J_{HH}$ = 16.0 Hz, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 5.4 Hz, $^3J_{HH}$ = 1.0 Hz), 4.26 (d, 1H, $^3J_{HH}$ = 4.0 Hz), 3.30 (ddd, 1H, $^2J_{HH}$ = 12.4 Hz, $^3J_{HH}$ = 9.4 Hz, $^3J_{HH}$ = 5.4 Hz), 2.62 (ddd, 1H, $^2J_{HH}$ = 12.4 Hz, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 5.8 Hz). Anal. Calcd (found) for 2: C, 16.32 (16.25); H, 0.52 (0.44).

Pyrolysis of $Os_3(CO)_{10}(\mu\text{-Br})(\mu\text{-CCHCH}_2\text{CH}_2)$ (1). A 20.0-mg amount of 1 (0.020 mmol) was dissolved in 15 mL of hexane. The solution was heated to reflux for 30 min. The solvent was then removed in vacuo, and the residue was separated by TLC using hexane solvent. This yielded the only product: 13.8 mg of yellow $Os_3(CO)_9(\mu\text{-Br})(\mu_3\text{-CCHCH}_2\text{CH}_2)$ (2; 71%).

Photolysis of 1. A 20.0-mg amount of 1 (0.020 mmol) was dissolved in 15 mL of hexane. The solution was irradiated with a medium-pressure mercury arc lamp for 30 min. The solvent was then removed in vacuo, and the residue was separated by TLC using hexane solvent. This yielded the only product: 14.0 mg of yellow $Os_3(CO)_9(\mu\text{-Br})(\mu_3\text{-CCHCH}_2\text{CH}_2)$ (2; 72%).

Reaction of 1 with Me_3NO. A 25.0-mg amount of $Os_3(CO)_{10}(\mu\text{-Br})(\mu\text{-CCHCH}_2\text{CH}_2)$ (0.025 mmol; 1) and a 2.0-mg amount of Me_3NO (0.026 mmol) were dissolved in 25 mL of CH_2Cl_2. The solution was stirred at 0 °C for 2 days. The solvent was then removed in vacuo, and the residue was separated by TLC on Al_2O_3 to yield, in order of elution: 2.0 mg of pale yellow $Os_3(CO)_9(\mu\text{-Br})(\mu_3\text{-C}_2\text{CH}_2\text{CH}_2)(\mu\text{-H})$ (3; 8%), 9.0 mg of pale yellow $Os_3(CO)_9(\mu\text{-Br})(\mu_3\text{-CCHCH}_2\text{CH}_2)$ (2; 37%). Spectroscopic data for compound 3 are as follows. IR (ν_{CO} in hexane, cm^{-1}) for 3: 2110 (w), 2083 (s), 2065 (vs), 2040 (s), 2020 (s), 2015 (s), 1998 (m), 1991 (w), 1980 (w). ^{1}H NMR (δ in $CDCl_3$) for 3: 4.22 (d, 2H, $^2J_{HH}$ = 10.5 Hz), 3.54 (d, 2H, $^2J_{HH}$ = 10.5 Hz), −16.65 (s, 1H). Anal. Calcd (found) for 3: C, 16.32 (16.38); H, 0.52 (0.53).

Attempted Pyrolysis of $Os_3(CO)_9(\mu\text{-Br})(\mu_3\text{-CCCH}_2\text{CH}_2)(\mu\text{-H})$ (3). A 4.0-mg amount of 3 was dissolved in 10 mL of octane. The solution was heated to reflux for 1 h. The IR spectrum of the reaction solution showed only 3, which was recovered essentially quantitatively after TLC. The TLC showed no evidence for the formation of any compound 2.

Photolysis of 3. A 4.0-mg amount of 3 was dissolved in 10 mL of hexane. The solution was irradiated (UV–vis) for 1 h. The solvent was then removed in vacuo. The residue was separated by TLC using hexane solvent to yield a small amount of unreacted 3, and a dark base line band was observed which could not be removed from the silica gel. There was no evidence for the formation of any compound 2.

Crystallographic Analyses. Crystals of 1 suitable for X-ray diffraction analysis were grown from a solution in a solvent mixture of diethyl ether and pentane by slow evaporation of the solvent at −14 °C. Crystals of 2 suitable for X-ray diffraction analysis were grown from a solution in a solvent mixture of dichloromethane and hexane by slow evaporation of the solvent at 5 °C. Crystals of 3 were grown from a solution in a solvent mixture of diethyl ether and pentane by slow evaporation of the solvent at 5 °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. 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 1. 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) corrections were applied to the data in each analysis. Neutral atom scattering factors were calculated by the standard procedures.[9a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[9b] All structures were solved by a combination of direct methods (MITHRIL) and difference Fourier syntheses. 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 $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$. For all three structures the positions of all hydrogen atoms were calculated by assuming idealized geometries. The contributions of the hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Table 1. Crystal Data for Compounds 1–3

	1	2	3
formula	$Os_9Br_3O_{30}C_{42}H_{15}$	$Os_3BrO_9C_{13}H_5$	$Os_3BrO_9C_{13}H_5$
fw	983.69	955.68	955.68
cryst syst	triclinic	monoclinic	triclinic
lattice params			
a (Å)	15.577(1)	13.348(3)	9.237(2)
b (Å)	20.220(3)	9.588(3)	13.922(5)
c (Å)	9.555(2)	15.036(3)	7.779(2)
α (deg)	91.39(2)	90	92.57(2)
β (deg)	94.30(2)	108.93(2)	111.32(2)
γ (deg)	93.54(1)	90	88.31(2)
V (Å^3)	2994(2)	1820.1(8)	930.9(4)
space group	$P\bar{1}$ (No. 2)	$P2_1/_n$ (No. 14)	$P\bar{1}$ (No. 2)
Z	6	4	2
ρ_{calc} (g/cm^3)	3.27	3.49	3.41
μ(Mo Kα) (cm^{-1})	211.01	231.32	226.14
temp (°C)	20	20	20
$2\theta_{max}$ (deg)	43.0	45.0	43.0
no. of obs reflns ($I > 3\sigma$)	5295	1753	1727
goodness of fit	1.42	1.63	1.86
residuals: R; R_w	0.027; 0.026	0.034; 0.034	0.029; 0.031
abs cor	empirical	empirical	analytical
largest peak in final diff map (e/Å^2)	1.42	1.00	1.88

Compounds 1 and 3 both crystallized in the triclinic crystal system. The space group $P\bar{1}$ was assumed and confirmed by the successful solution and refinement of each structure. For compound 1 all non-hydrogen atoms were refined with anisotropic thermal parameters. For compound 3 all non-hydrogen atoms, except carbon C(1) of the cyclobutyne ligand, were refined with anisotropic thermal parameters. Attempts to refine C(1) with an anisotropic thermal parameter yielded a highly distorted ellipse, and an isotropic thermal parameter was thus used in the final refinement. The positions of all hydrogen atoms were calculated by assuming idealized geometries. The position of the hydride ligand was calculated using the program HYDEX.[10]

Compound 2 crystallized in the monoclinic crystal system. The space group $P2_1/n$ was identified on the basis of the patterns of systematic absences observed in the data. All non-hydrogen atoms were refined with anisotropic thermal parameters.

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(10) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

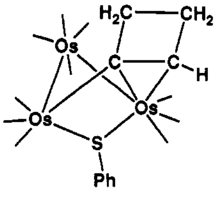
Table 2. Positional Parameters and B(eq) Values for 1

atom	x	x	z	B(eq) (Å^2)	atom	x	y	z	B(eq) (Å^2)
Os(1A)	0.29727(03)	–0.00038(02)	0.45457(06)	3.18(3)	C(1A)	0.1738(08)	0.0593(06)	0.3904(18)	3.8(7)
Os(1B)	0.55695(03)	0.26977(02)	0.40655(06)	2.95(2)	C(1B)	0.5349(08)	0.3845(06)	0.3856(15)	3.2(6)
Os(1C)	–0.04022(03)	0.36818(02)	0.68847(06)	3.01(2)	C(1C)	0.0446(08)	0.3782(06)	0.9052(14)	3.3(6)
Os(2A)	0.21856(04)	0.09255(02)	0.20073(07)	3.74(3)	C(2A)	0.0908(10)	0.0285(08)	0.442(02)	7(1)
Os(2B)	0.49171(03)	0.37454(02)	0.16790(06)	2.86(2)	C(2B)	0.5938(09)	0.4311(06)	0.4831(17)	4.6(8)
Os(2C)	0.16226(03)	0.39859(02)	0.81079(06)	3.07(2)	C(2C)	0.0143(10)	0.3316(07)	1.0200(16)	5.0(8)
Os(3A)	0.25593(04)	–0.04476(03)	0.16004(07)	3.88(3)	C(3A)	0.1238(12)	0.0521(08)	0.594(02)	6(1)
Os(3B)	0.64292(03)	0.29980(02)	0.14806(06)	3.05(2)	C(3B)	0.5470(10)	0.4058(07)	0.6051(16)	4.8(8)
Os(3C)	0.10404(04)	0.28684(03)	0.62810(07)	3.67(3)	C(3C)	–0.0636(09)	0.3763(07)	1.0326(16)	4.8(8)
Br(A)	0.36527(09)	0.10745(06)	0.35750(17)	4.30(7)	C(4A)	0.2034(09)	0.0783(07)	0.5277(19)	4.7(8)
Br(B)	0.41231(08)	0.26612(06)	0.25031(16)	3.72(6)	C(4B)	0.4906(09)	0.3625(06)	0.4992(18)	4.3(7)
Br(C)	0.06381(08)	0.47083(06)	0.64866(16)	3.58(6)	C(4C)	–0.0261(08)	0.4162(06)	0.9173(14)	3.4(6)
O(11A)	0.1975(07)	–0.1265(05)	0.5275(13)	7.2(7)	C(11A)	0.2331(09)	–0.0788(07)	0.5015(18)	4.9(8)
O(11B)	0.7342(07)	0.2973(05)	0.5550(13)	6.1(6)	C(11B)	0.6674(10)	0.2855(06)	0.4969(16)	4.0(7)
O(11C)	–0.1331(07)	0.2426(05)	0.7761(14)	6.9(7)	C(11C)	–0.0978(08)	0.2891(07)	0.7425(17)	4.4(8)
O(12A)	0.3715(08)	0.0286(06)	0.7557(13)	6.9(7)	C(12A)	0.3420(10)	0.0220(07)	0.6453(18)	4.4(8)
O(12B)	0.4801(07)	0.2146(05)	0.6680(12)	5.8(6)	C(12B)	0.5057(09)	0.2361(07)	0.5687(18)	4.2(7)
O(12C)	–0.1980(07)	0.4497(05)	0.6769(12)	5.9(6)	C(12C)	–0.1382(10)	0.4200(07)	0.6885(16)	4.1(7)
O(13A)	0.4550(07)	–0.0751(05)	0.3997(13)	6.0(6)	C(13A)	0.3938(10)	–0.0478(07)	0.4141(16)	4.1(7)
O(13B)	0.6025(07)	0.1332(05)	0.3054(12)	5.2(6)	C(13B)	0.5868(08)	0.1854(07)	0.3402(15)	3.5(7)
O(13C)	–0.0816(07)	0.3321(05)	0.3782(13)	5.8(6)	C(13C)	–0.0639(09)	0.3448(07)	0.4953(19)	4.2(8)
O(21A)	0.1738(08)	0.2345(05)	0.2645(13)	6.8(7)	C(21A)	0.1931(10)	0.1812(07)	0.2421(18)	4.9(8)
O(21B)	0.3352(08)	0.4503(06)	0.2254(14)	7.0(7)	C(21B)	0.3936(10)	0.4216(07)	0.2030(17)	4.3(7)
O(21C)	0.2083(07)	0.5178(05)	1.0103(13)	5.7(6)	C(21C)	0.1914(08)	0.4737(07)	0.9359(18)	3.9(7)
O(22A)	0.2975(10)	0.1336(07)	–0.0761(16)	10(1)	C(22A)	0.2691(12)	0.1193(07)	0.031(02)	6(1)
O(22B)	0.4350(07)	0.3398(05)	–0.1432(13)	5.8(6)	C(22B)	0.4574(09)	0.3524(06)	–0.0284(18)	3.9(7)
O(22C)	0.3156(07)	0.4221(05)	0.6252(13)	6.2(6)	C(22C)	0.2592(09)	0.4149(06)	0.6951(18)	4.1(7)
O(23A)	0.0418(10)	0.0610(06)	0.0513(19)	11(1)	C(23A)	0.1102(13)	0.0727(07)	0.109(02)	6(1)
O(23B)	0.5986(06)	0.4961(05)	0.0973(12)	5.7(6)	C(23B)	0.5588(09)	0.4496(07)	0.1206(16)	4.3(7)
O(23C)	0.2548(07)	0.3041(05)	1.0002(12)	6.1(6)	C(23C)	0.2195(09)	0.3394(07)	0.9245(17)	4.0(7)
O(31A)	0.4342(08)	0.0157(06)	0.0933(15)	7.9(8)	C(31A)	0.3682(13)	–0.0065(08)	0.1196(18)	6(1)
O(31B)	0.7526(06)	0.4166(05)	0.2969(12)	5.2(5)	C(31B)	0.7110(09)	0.3731(06)	0.2442(16)	3.7(7)
O(31C)	0.1366(07)	0.3789(05)	0.3825(13)	6.3(6)	C(31C)	0.1239(09)	0.3450(06)	0.4738(17)	3.9(7)
O(32A)	0.3195(07)	–0.1845(05)	0.1981(14)	7.0(7)	C(32A)	0.2944(10)	–0.1311(07)	0.1877(17)	4.9(8)
O(32B)	0.7940(08)	0.2096(06)	0.1829(15)	7.9(8)	C(32B)	0.7355(10)	0.2413(07)	0.1755(16)	4.5(8)
O(32C)	0.0030(08)	0.1813(05)	0.4371(17)	8.1(8)	C(32C)	0.0359(10)	0.2216(07)	0.5103(18)	4.8(8)
O(33A)	0.0704(07)	–0.0928(05)	0.2215(14)	6.8(7)	C(33A)	0.1389(12)	–0.0724(07)	0.2030(17)	5.1(8)
O(33B)	0.5195(07)	0.1905(05)	–0.0040(13)	6.3(6)	C(33B)	0.5631(10)	0.2313(07)	0.0545(17)	4.4(8)
O(33C)	0.0826(07)	0.2012(05)	0.8827(14)	6.9(7)	C(33C)	0.0865(08)	0.2369(06)	0.7938(19)	4.4(8)
O(34A)	0.1977(10)	–0.0521(06)	–0.1522(15)	9.1(9)	C(34A)	0.2172(12)	–0.0480(08)	–0.035(02)	6(1)
O(34B)	0.6894(07)	0.3510(06)	–0.1351(12)	6.4(6)	C(34B)	0.6704(09)	0.3333(07)	–0.0287(20)	4.6(8)
O(34C)	0.1738(08)	0.0593(06)	0.3904(18)	3.8(7)	C(34C)	0.2194(11)	0.2597(07)	0.6214(19)	5.1(9)

Results

Two products, $Os_3(CO)_{10}(\mu\text{-Br})(\mu\text{-}\overline{\text{CCHCH}_2\text{C}}\text{H}_2)$ (1; 44% yield) and $Os_3(CO)_9(\mu\text{-Br})(\mu_3\text{-CCHCH}_2\text{CH}_2)$ (2; 16% yield), were obtained from the reaction of 1-bromocyclobutene with $Os_3(CO)_{10}(NCMe)_2$ at 25 °C over 24 h. Both products were characterized by IR, ^{1}H NMR, and single-crystal X-ray diffraction analyses.

An ORTEP diagram of the molecular structure of compound 1 is shown in Figure 1. Final atomic positional parameters are listed in Table 2, and selected interatomic distances and angles are listed in Tables 3 and 4. The crystal contains three independent molecules in the asymmetric unit. All three molecules are structurally similar, and each consists of an open triangular cluster of three osmium atoms. There is a σ,π-coordinated cyclobutenyl ligand bridging the open edge of the cluster on one side of the triosmium plane and a bridging bromo ligand across the open edge on the other side of the triosmium plane. The molecule is very similar to the complex $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}\overline{\text{CCHCH}_2\text{C}}\text{H}_2)(\mu\text{-SPh})$ (4) obtained from the reaction of 1-(phenylthio)cyclobutene with $Os_3(CO)_{10}(NCMe)_2$, except that 4 contains a bridging benzenethiolato ligand at the location of the bridging bromo ligand in 1.[2] The nonbonding Os(1)···Os(2) = 3.313(1) Å [3.298(1), 3.296(1) Å] is not significantly different from that in 4 (Os···Os = 3.305(2) Å [3.310(2) Å]). The values in brackets correspond to other independent molecules in the crystal lattice. The C–C distances around the four-membered ring are not unusual, and as expected, the coordinated double bond (C(1)–C(4) = 1.39(2) Å [1.40(2), 1.39(2) Å]) is slightly shorter than the C–C single bonds (C(1)–C(2) = 1.52(2) Å [1.52(2), 1.54(2) Å], C(2)–C(3) = 1.56(3) Å [1.50(3), 1.57(2) Å], C(3)–C(4) = 1.51(2) Å [1.51(2), 1.51(2) Å]). The Os(1)–Os(3) bond distance is significantly longer than the Os(1)–Os(2) distance in each of the three molecules. This may be due simply to steric effects, since the number of atoms coordinated to Os(1) is 1 larger than the number of atoms coordinated to Os(2). A similar effect was observed in 4. The other dimensions of 1 are similar to those found in related triosmium cluster complexes.[11] The alkenyl hydrogen atom on carbon C(4) exhibits a characteristically deshielded shift (δ 6.07 ppm) in the ^{1}H NMR spectrum.



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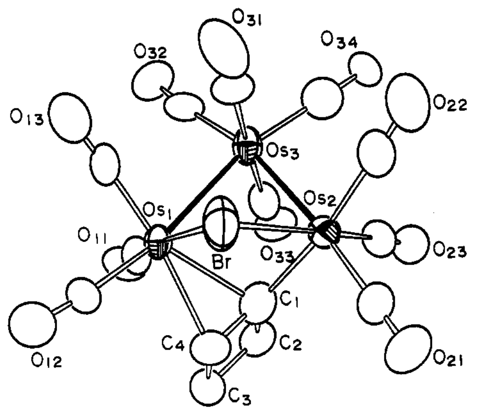


Figure 1. ORTEP diagram of $Os_3(CO)_{10}(\mu\text{-}Br)(\mu\text{-}\overline{CCHCH_2CH_2})$ (1) showing 50% probability thermal ellipsoids. The hydrogen atoms are not shown.

Table 3. Intramolecular Distances for 1[a]

Os(1A)–Os(3A)	2.945(1)	Os(2C)–Br(C)	2.630(1)
Os(1A)–Br(A)	2.588(1)	Os(2C)–C(1C)	2.13(1)
Os(1A)–C(1A)	2.38(1)	C(1A)–C(2A)	1.52(2)
Os(1A)–C(4A)	2.35(1)	C(1A)–C(4A)	1.39(2)
Os(1B)–Os(3B)	2.955(1)	C(1B)–C(2B)	1.52(2)
Os(1B)–Br(B)	2.604(1)	C(1B)–C(4B)	1.40(2)
Os(1B)–C(1B)	2.38(1)	C(1C)–C(2C)	1.54(2)
Os(1B)–C(4B)	2.38(1)	C(1C)–C(4C)	1.39(2)
Os(1C)–Os(3C)	2.9482(9)	C(2A)–C(3A)	1.56(3)
Os(1C)–Br(C)	2.607(1)	C(2B)–C(3B)	1.50(2)
Os(1C)–C(1C)	2.37(1)	C(2C)–C(3C)	1.57(2)
Os(1C)–C(4C)	2.36(1)	C(3A)–C(4A)	1.51(2)
Os(2A)–Os(3A)	2.8947(9)	C(3B)–C(4B)	1.51(2)
Os(2A)–Br(A)	2.634(2)	C(3C)–C(4C)	1.51(2)
Os(2A)–C(1A)	2.10(1)	Os–C (av)	1.91(2)
Os(2B)–Os(3B)	2.8913(8)	C–O (av)	1.14 (2)
Os(2B)–Br(B)	2.617(1)	Os(1A)···Os(2A)	3.313(1)
Os(2B)–C(1B)	2.14(1)	Os(1B)···Os(2B)	3.298(1)
Os(1C)···Os(2C)	3.296(1)		

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

Table 4. Intramolecular Bond Angles for 1[a]

Os(1A)–Os(3A)–Os(2A)	69.12(2)	C(2C)–C(1C)–C(4C)	91(1)
Os(1B)–Os(3B)–Os(2B)	68.66(2)	C(1A)–C(2A)–C(3A)	89(1)
Os(1C)–Os(3C)–Os(2C)	68.87(2)	C(1B)–C(2B)–C(3B)	89(1)
Os(1A)–Br(A)–Os(2A)	78.76(4)	C(1C)–C(2C)–C(3C)	87(1)
Os(1B)–Br(B)–Os(2B)	78.33(4)	C(2A)–C(3A)–C(4A)	85(1)
Os(1C)–Br(C)–Os(2C)	78.03(4)	C(2B)–C(3B)–C(4B)	87(1)
Os(1A)–C(1A)–Os(2A)	95.1(5)	C(2C)–C(3C)–C(4C)	86(1)
C(2A)–C(1A)–C(4A)	90(1)	C(1A)–C(4A)–C(3A)	96(1)
Os(1B)–C(1B)–Os(2B)	93.7(5)	C(1B)–C(4B)–C(3B)	94(1)
C(2B)–C(1B)–C(4B)	90(1)	C(1C)–C(4C)–C(3C)	96(1)
Os(1C)–C(1C)–Os(2C)	94.2(5)	Os–C–O (av)	177(2)

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

An ORTEP diagram of the molecular structure of compound 2 is shown in Figure 2. Final atomic positional parameters are listed in Table 5, and selected interatomic distances and angles are listed in Tables 6 and 7. This molecule also consists of an open cluster of three osmium atoms. As in 1, the metal–metal bonds are different in length (Os(1)–Os(3) = 2.932(1) Å and Os(2)–Os(3) = 2.845(1) Å). This molecule contains an $OsCCHCH_2CH_2$ metallacyclic ring formed by the insertion of one of the osmium atoms into the C–CH_2 carbon–carbon bond of the cyclobutenyl ring. The C–C bond was completely cleaved, and the C(1)–C(2) distance increased from 1.52(2) Å in 1 to 2.67(2) Å in 2. The carbon C(1) is bonded to all three metal atoms, but the distance Os(3)–C(1) in the metallacyclic ring is by far the shortest (Os(1)–C(1) = 2.19(2) Å, Os(2)–C(1) = 2.27(2) Å, Os(3)–C(1) = 1.93(1) Å). Carbon C(4) is still bonded to Os(2) (Os(2)–C(4) = 2.30(2) Å), and the C(1)–C(4) bond still has some multiple-bond character (1.40(2) Å). The C(1)–C(4) grouping could be viewed as an alkenylidene grouping. C(2) and C(3) are methylene groups, and C(2) is bonded directly to atom Os(1) (Os(1)–C(2) = 2.20(2) Å). Since the molecule is chiral, all of the hydrogen atoms are inequivalent. Accordingly, the ^1H NMR spectrum shows resonances for five separate hydrogen atoms: δ = 5.07 (dddd, 1H, $^2J_{HH}$ = 16.0 Hz, $^3J_{HH}$ = 9.4 Hz, $^3J_{HH}$ = 5.8 Hz, $^3J_{HH}$ = 4.0 Hz), 4.89 (dddd, 1H,

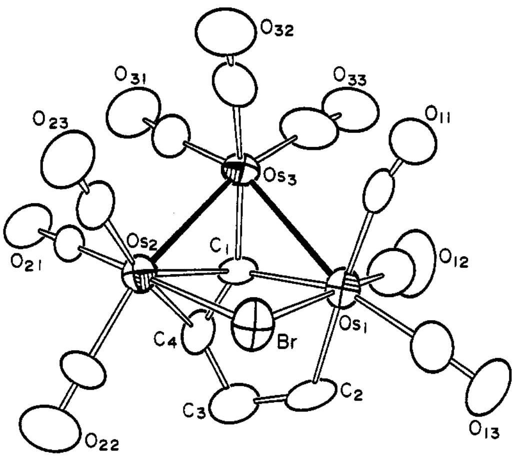


Figure 2. ORTEP diagram of $Os_3(CO)_9(\mu\text{-}Br)(\mu_3\text{-}CCHCH_2CH_2)$ (2) showing 50% probability thermal ellipsoids. The hydrogen atoms are not shown.

Table 5. Positional Parameters and *B*(eq) Values for 2

atom	*x*	*y*	*z*	*B*(eq) (Å^2)
Os(1)	0.24443(06)	0.16026(07)	0.96887(05)	3.33(3)
Os(2)	0.26254(06)	–0.14002(08)	1.11399(05)	3.21(3)
Os(3)	0.26154(06)	–0.13479(08)	0.92452(05)	3.26(3)
Br	0.14347(15)	0.08202(19)	1.08116(13)	4.02(8)
O(11)	0.1634(12)	0.4609(14)	0.9637(10)	5.8(8)
O(12)	0.3871(15)	0.2398(19)	0.8593(13)	9(1)
O(13)	0.0443(15)	0.0946(14)	0.7991(11)	7.9(9)
O(21)	0.4003(12)	–0.3965(14)	1.1537(11)	6.3(7)
O(22)	0.3105(14)	–0.0806(17)	1.3215(11)	7.2(9)
O(23)	0.0619(12)	–0.3127(15)	1.0689(10)	6.0(8)
O(31)	0.3766(13)	–0.4048(17)	0.9375(12)	7.2(9)
O(32)	0.0400(11)	–0.2701(16)	0.8358(10)	5.9(8)
O(33)	0.3093(13)	–0.0612(19)	0.7454(10)	7.4(9)
C(1)	0.3447(12)	–0.0200(16)	1.0277(11)	2.6(7)
C(2)	0.3688(18)	0.241(02)	1.0936(15)	6(1)
C(3)	0.4191(17)	0.137(02)	1.1646(15)	6(1)
C(4)	0.4076(14)	–0.0058(17)	1.1219(13)	3.7(9)
C(11)	0.1885(16)	0.346(02)	0.9642(13)	5(1)
C(12)	0.3309(18)	0.215(02)	0.8986(16)	6(1)
C(13)	0.1188(19)	0.1015(17)	0.8607(14)	4(1)
C(21)	0.3517(15)	–0.2987(18)	1.1384(12)	3.7(8)
C(22)	0.2879(16)	–0.1034(20)	1.2450(13)	4(1)
C(23)	0.1366(17)	–0.2491(19)	1.0871(13)	4(1)
C(31)	0.3339(16)	–0.301(02)	0.9368(14)	5(1)
C(32)	0.1195(19)	–0.218(02)	0.8645(13)	5(1)
C(33)	0.2917(19)	–0.096(03)	0.8110(17)	7(1)

Table 6. Intramolecular Distances for 2[a]

Os(1)–Os(3)	2.932(1)	Os(3)–C(1)	1.93(1)
Os(1)–Br	2.590(2)	C(1)–C(4)	1.40(2)
Os(1)–C(1)	2.19(2)	C(2)–C(3)	1.45(3)
Os(1)–C(2)	2.20(2)	C(3)–C(4)	1.50(2)
Os(2)–Os(3)	2.845(1)	Os–C (av)	1.92(2)
Os(2)–Br	2.606(2)	C–O (av)	1.13(2)
Os(2)–C(1)	2.27(2)	C(1)···C(2)	2.67(2)
Os(2)–C(4)	2.30(2)		

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

Table 7. Intramolecular Bond Angles for 2[a]

Os(3)–Os(1)–Br	87.95(5)	Os(2)–C(1)–Os(3)	84.9(5)
C(1)–Os(1)–C(2)	74.9(7)	Os(2)–C(1)–C(4)	73(1)
Os(3)–Os(2)–Br	89.51(5)	Os(3)–C(1)–C(4)	150(1)
C(1)–Os(2)–C(4)	35.7(6)	Os(1)–C(2)–C(3)	115(1)
Os(1)–Os(3)–Os(2)	76.39(3)	C(2)–C(3)–C(4)	111(2)
Os(1)–Br–Os(2)	86.89(6)	C(1)–C(4)–C(3)	118(1)
Os(1)–C(1)–C(4)	115(1)	Os–C–O (av)	175(2)

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

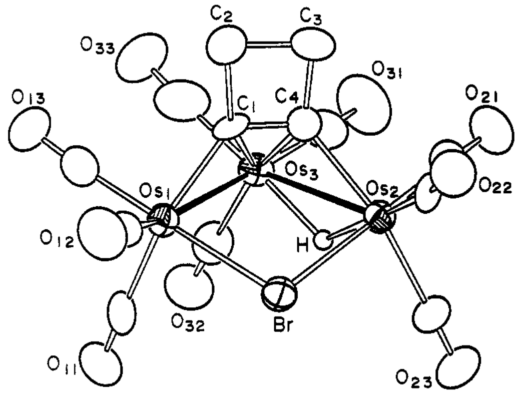


Figure 3. ORTEP diagram of $Os_3(CO)_9(\mu\text{-}Br)(\mu_3\text{-}\eta^2\text{-}C_2CH_2CH_2)(\mu\text{-}H)$ (**3**) showing 50% probability thermal ellipsoids. The hydrogen atoms are not shown.

$^2J_{HH}$ = 16.0 Hz, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 5.4 Hz, $^3J_{HH}$ = 1.0 Hz), 4.26 (d, 1H, $^3J_{HH}$ = 4.0 Hz), 3.30 (ddd, 1H, $^2J_{HH}$ = 12.4 Hz, $^3J_{HH}$ = 9.4 Hz, $^3J_{HH}$ = 5.4 Hz), 2.62 (ddd, 1H, $^2J_{HH}$ = 12.4 Hz, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 5.8 Hz). These are complicated by numerous couplings. The hydrogen atoms of the methylene groups are uniquely identified by their characteristically large *geminal* couplings ($^2J_{HH}$ = 16.0 Hz and $^2J_{HH}$ = 12.4 Hz).

Table 8. Positional Parameters and *B*(eq) Values for 3

atom	*x*	*y*	*z*	*B*(eq) (Å²)
Os(1)	0.44269(07)	0.29349(05)	0.89984(08)	3.07(3)
Os(2)	–0.00564(07)	0.32216(04)	0.76226(08)	2.94(3)
Os(3)	0.19411(08)	0.20078(05)	0.61601(08)	3.19(3)
Br	0.23909(18)	0.42339(11)	0.9143(02)	3.50(7)
O(11)	0.5584(14)	0.4290(10)	0.6744(17)	5.6(6)
O(12)	0.6353(16)	0.3628(10)	1.2891(17)	6.3(7)
O(13)	0.6831(16)	0.1389(10)	0.9185(19)	6.2(7)
O(21)	–0.2879(16)	0.2014(10)	0.5650(18)	5.9(7)
O(22)	–0.0876(14)	0.3429(09)	1.1061(17)	5.3(6)
O(23)	–0.1576(14)	0.5093(10)	0.5718(18)	6.0(6)
O(31)	–0.0895(19)	0.0942(12)	0.347(02)	8.3(9)
O(32)	0.3029(15)	0.2928(09)	0.3382(17)	5.9(7)
O(33)	0.3908(19)	0.0193(11)	0.622(02)	7.8(8)
C(1)	0.2928(19)	0.1914(11)	0.929(02)	3.9(7)
C(2)	0.298(02)	0.0971(14)	1.020(03)	4.5(9)
C(3)	0.118(02)	0.1078(14)	0.959(03)	5(1)
C(4)	0.1378(18)	0.1964(11)	0.869(02)	3.4(3)
C(11)	0.5208(18)	0.3818(13)	0.762(02)	3.8(8)
C(12)	0.5644(19)	0.3374(12)	1.143(03)	4.0(8)
C(13)	0.592(02)	0.1997(14)	0.904(02)	4.2(8)
C(21)	–0.180(02)	0.2450(14)	0.638(02)	4.2(9)
C(22)	–0.0629(17)	0.3386(11)	0.971(02)	3.2(7)
C(23)	–0.1054(19)	0.4437(13)	0.640(02)	4.1(8)
C(31)	0.014(03)	0.1354(13)	0.448(03)	5(1)
C(32)	0.264(02)	0.2579(13)	0.441(02)	4.3(8)
C(33)	0.321(03)	0.0875(16)	0.617(02)	6(1)

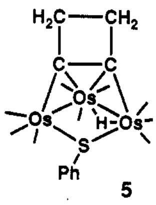
Table 9. Intramolecular Distances for 3[a]

Os(1)–Os(3)	2.837(1)	Os(3)–C(4)	2.22(1)
Os(1)–Br	2.599(2)	C(1)–C(2)	1.51(2)
Os(1)–C(1)	2.09(2)	C(1)–C(4)	1.34(2)
Os(2)–Os(3)	2.954(1)	C(2)–C(3)	1.56(3)
Os(2)–Br	2.567(2)	C(3)–C(4)	1.49(2)
Os(2)–C(4)	2.17(2)	Os–O (av)	1.92(2)
Os(3)–C(1)	2.28(2)	C–O (av)	1.13(2)

Table 10. Intramolecular Bond Angles for 3[a]

Os(3)–Os(1)–Br	86.46(5)	C(1)–C(2)–C(3)	87(1)
Os(3)–Os(2)–Br	84.61(5)	C(2)–C(3)–C(4)	85(1)
Os(1)–Os(3)–Os(2)	84.53(3)	C(1)–C(4)–C(3)	96(1)
Os(1)–Br–Os(2)	97.88(6)	Os–C–O (av)	177(2)
C(2)–C(1)–C(4)	92(1)		

Compound 2 was also formed in 37% yield when compound 1 was treated with Me_3NO at 0 °C for 2 days, but in addition the new compound $Os_3(CO)_9(\mu\text{-}Br)(\mu_3\text{-}C_2CH_2CH_2)(\mu\text{-}H)$ (**3**) was obtained in 8% yield. Compound 3 was also characterized by a single-crystal X-ray diffraction analysis, and an ORTEP diagram of its molecular structure is shown in Figure 3. Final atomic positional parameters are listed in Table 8, and selected interatomic distances and angles are listed in Tables 9 and 10. This molecule also consists of an open cluster of three osmium atoms. Most interestingly, it contains a triply bridging cyclobutyne ligand formed by the decarbonylation of 1 and the cleavage of the alkenyl C–H bond of the cyclobutenyl ligand and transfer of the hydrogen atom to the metal atoms to become a bridging hydride ligand. As expected, the hydride-bridged metal–metal bond Os(2)–Os(3) is significantly longer (2.954(1) Å) than the non-hydride-bridged bond Os(1)–Os(3) (2.837(1) Å). The position of the hydride ligand was not observed crystallographically, but its resonance was clearly visible in the ^1H NMR spectrum (δ –16.65 (s, 1H)). A similar elongation of the hydride-bridged osmium–osmium bond was observed in the cyclobutyne complex $Os_3(CO)_9(\mu\text{-}\eta^2\text{-}CCH_2CH_2)(\mu\text{-}SPh)(\mu\text{-}H)$ (**5**) which was obtained by the decarbonylation of 4.[2] The unsaturated C–C bond of the cyclobutyne ligand (C(1)–C(4)) is slightly shorter than that found in 5 (1.34(2) vs 1.37(2) Å), but this is not significant by the 3σ criterion. It is, however, significantly shorter than the C–C distances found for the substituted cyclobutyne ligands in the complexes $M_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C_2CH_2C(Me)^tBu](\mu_4\text{-}S)$ (**6a**, M = Os, 1.40(2) Å;[4] **6b**, M = Ru, 1.424(7) Å) and the decarbonylated dimer of **6b**, $\{Ru_3(CO)_8[\mu_3\text{-}\eta^2\text{-}C_2CH_2C(Me)^tBu](\mu_4\text{-}S)\}_2$ (7; 1.42(1) and 1.43(1) Å).[5] Calculations have indicated values of 1.258–1.294 Å for the C≡C distance for the free molecule cyclobutyne.[1a] It is well established that the C≡C distance of unstrained alkynes is increased upon coordination to one or more metal atoms.[12] The C≡C distance of the unstrained MeC≡CMe ligand in the complex $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}MeC_2Me](\mu\text{-}SPh)(\mu\text{-}H)$ is 1.42(2) Å.[2a] The C—C bond distances



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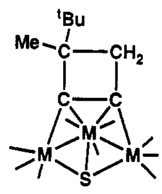

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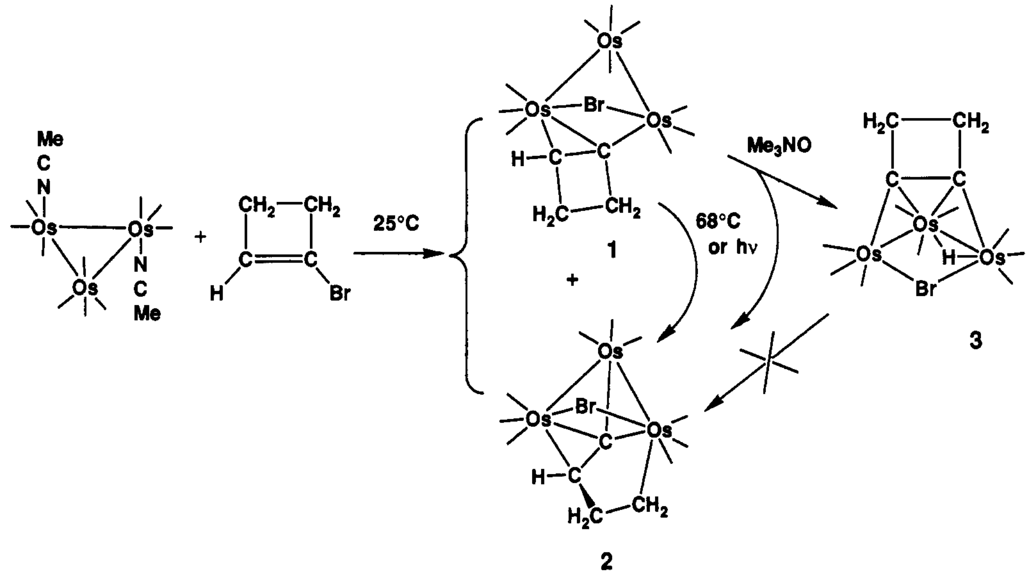
Scheme 1



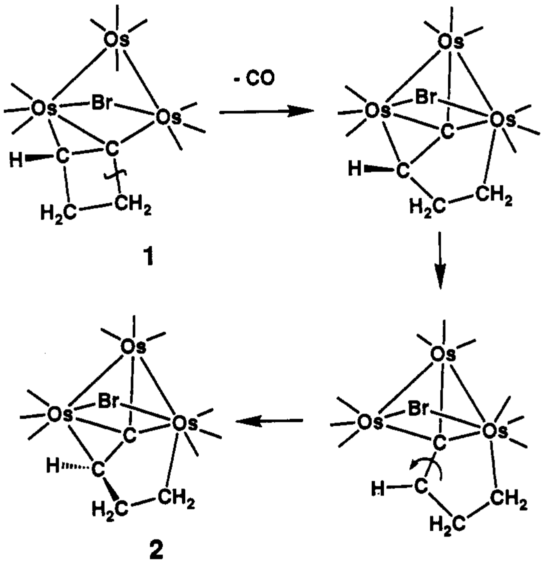
from the alkyne carbons to the methylene groups (C(1)–C(2) = 1.51(2) Å, C(3)–C(4) = 1.49(1) Å) are slightly shorter than the bond between the methylene groups (C(2)–C(3) = 1.56(3) Å), but the difference is of marginal significance. The corresponding distances in **5** are essentially equivalent. The resonances of the methylene hydrogen atoms appear as two doublets at 25 °C: δ 4.22 (2H, $^2J_{HH}$ = 10.5 Hz), 3.54 ppm (2H, $^2J_{HH}$ = 10.5 Hz) in the ^{1}H NMR spectrum. This can be explained by a dynamical process in which the hydride ligand moves rapidly back and forth between the two metal–metal bonds Os(1)–Os(3) and Os(2)–Os(3) and averages the protons in pairs, but those on a given carbon atom remain inequivalent. A similar averaging process was observed in **5**.

To determine the potential of compound **3** to be transformed into **2**, it was treated in two different ways: (1) by heating to reflux for 1 h in a solution in octane solvent (125 °C) and (2) by irradiating (UV–vis) for 1 h in hexane solvent. There was no evidence for the formation of any of compound **2** by either treatment, although the irradiation treatment produced decomposition of a considerable amount of the complex.

Discussion

A summary of the results of this study is shown in Scheme 1. The reaction of $Os_3(CO)_{10}(NCMe)_2$ with 1-bromocyclobutene proceeds by the displacement of the two NCMe ligands and a cluster-opening oxidative addition of the 1-bromocyclobutene in which the bromine atom is cleaved from the cyclobutenyl group. Both the bromine atom and the cyclobutenyl group have adopted bridging coordinations across the open edge of the cluster. This reaction is very similar to the reaction of $Os_3(CO)_{10}(NCMe)_2$ with 1-(phenylthio)cyclobutene.[2] However, unlike the reaction with 1-(phenylthio)cyclobutene, this reaction yielded the second product **2**, formed by a ring opening of the cyclobutenyl ligand. This product was also obtained in good yields by both thermal (68 °C) and photolytic decarbonylation of **1**. This indicates that **1** is a precursor to **2**. Since we had shown previously that the decarbonylation of **4** proceeds with a cleavage of the alkenyl C–H bond to yield the cyclobutyne complex **5**, it occurred to us that the transformation of **1** to **2** might occur via an intermediate similar to **5** containing the cyclobutyne ligand. To demonstrate that this was not the case, we prepared the compound **3**, the cyclobutyne homologue of **5** (albeit in a low yield), by a decarbonylation of **1** with Me_3NO at 0 °C. Efforts to transform **3** to **2** were completely unsuccessful, indicating that it is not an intermediate en route to **2**. Accordingly, we believe that the transformation of **1** to **2** occurs without a cleavage of the alkenyl C–H bond. The first step is probably the loss of the CO ligand. This would produce a vacant site and precipitate the attack of the cluster upon the cyclobutenyl ligand. The ring-opening transformation may be as simple as the insertion of the metal atom Os(2) into the C–CH_2 bond (atoms C(1) and C(2) in Figure 1) of the cyclobutenyl ligand (Scheme 2). This transformation could also be viewed as an oxidative addition of the carbon–carbon bond to the metal atom. The cleavage of carbon–carbon bonds by the oxidative addition of cyclopropanes to platinum atoms has been well studied.[13] We have recently observed examples of the insertion of one metal atom into the

Scheme 2



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[13] (a) Puddephatt, R. J. *Coord. Chem. Rev.* **1980**, *33*, 149. (b) Al-Essa, R. J.; Puddephatt, R. J.; Tipper, C. F. H.; Thompson, P. J. *J. Am. Chem. Soc.* **1980**, *102*, 7546.

carbon–sulfur bond of certain thietanes by metal cluster complexes,[14] but we are unaware of any previous examples of the insertion of metal atoms into the C–C bond of a cyclobutenyl ligand. The expected product would be an isomer of **2** with the orientation of the hydrogen atom being *syn* to the bromo ligand. In **2** the hydrogen atom on C(4) is oriented *anti* to the bromo ligand. The *syn–anti* transformation could be accomplished as easily as a cleavage of the Os(2)–C(4) bond, a rotation about the C(1)–C(4) bond, and a reestablishment of the Os(2)–C(4) bond (see Scheme 2).

The cyclobutyne complex **3** is only the second example of a metal complex containing an unsubstituted cyclobutyne ligand. It was formed by a cleavage of the alkenyl C–H bond induced by the decarbonylation of the cluster by Me_3NO. The formation of the first cyclobutyne complex **5** was obtained by a similar transformation from a precursor containing a σ,π-coordinated cyclobutenyl ligand.[2] Our preliminary studies show that the cyclobutyne ligand is fairly robust.[2] Further studies of its chemistry are in progress.

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Supplementary Material Available: Tables of hydrogen atom positional parameters and anisotropic thermal parameters for all three structural analyses (13 pages). Ordering information is given on any current masthead page.

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[14] (a) Adams, R. D.; Pompeo, M. P. *Organometallics* **1992,** *11,* 103. (b) Adams, R. D.; Belinski, J. A.; Schierlmann, J. A. *J. Am. Chem. Soc.* **1991,** *113,* 9004. (c) Adams, R. D.; Pompeo, M. P. *Organometallics* **1992,** *11,* 2281.