ORGANOMETALLICS

Cyclobutyne ligands. 2. Reactions of cyclobutyne triosmium complex [cyclic] Os3(CO)9(.mu.3-.eta.2-C2CH2CH2)(.mu.-SPh)(.mu.-H) with diphenylacetylene

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Organometallics, **1993**, 12 (9), 3426-3430• DOI: 10.1021/om00033a012 • Publication Date (Web): 01 May 2002

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

Cyclobutyne Ligands. 2. Reactions of the Cyclobutyne Triosmium Complex $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2CH_2CH_2)(\mu\text{-}SPh)(\mu\text{-}H)$ with Diphenylacetylene

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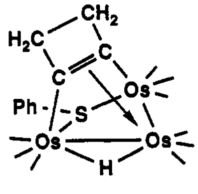
Received March 16, 1993

The reaction of the triosmium complex $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2CH_2CH_2)(\mu\text{-}SPh)(\mu\text{-}H)$ (1) with diphenylacetylene at 97 °C resulted in the formation of three products: the known compound $Os_2(CO)_6(\mu\text{-}\eta^2\text{-}C{=}CHCH_2CH_2)(\mu\text{-}SPh)$ (2) (11% yield) and two new compounds $Os_3(CO)_7[\mu\text{-}C(Ph)(H)C(Ph)][(\mu\text{-}C(Ph)CCH_2CH_2)(\mu_3\text{-}S)$ (3) (28% yield) and $Os_3(CO)_7(\mu\text{-}C(Ph)C(Ph)CCCH_2CH_2)(\mu\text{-}SPh)(\mu\text{-}H)$ (4) (25% yield). Both new compounds were characterized by single-crystal X-ray diffraction analysis. Compound **3** contains a σ-π coordinated phenylcyclobutenyl ligand formed by the transfer of the phenyl group from the thiolate ligand to the cyclobutyne ligand and a σ-π coordinated 1,2-diphenylvinyl ligand formed by the insertion of one molecule of $PhC{\equiv}CPh$ into the metal–hydrogen bonds. Compound 4 contains a metallacycle formed by the coupling of one molecule of $PhC{\equiv}CPh$ to the cyclobutyne ligand. Crystal data: for **3a**, space group = $P2_1/n$, a = 17.401(3) Å, b = 7.981(1) Å, c = 22.304(4) Å, β = 100.26(1)°, Z = 4, 3048 reflections, R = 0.030; for 4, space group = $P\bar{1}$, a = 11.815(2) Å, b = 12.260(2) Å, c = 11.492(3) Å, α = 102.91(2)°, β = 110.86(1)°, γ = 92.44(1)°, Z = 2, 3274 reflections, R = 0.043.

Introduction

Strained-ring hydrocarbons that contain the carbon–carbon triple bond as the only element of unsaturation have been of interest to chemists for many years.[1] Tetramethylcycloheptyne is the smallest cycloalkyne that has been isolated,[2] although there is spectroscopic evidence for cyclohexyne[3] and cyclopentyne.[4a] Although theoretical calculations have indicated that the molecule cyclobutyne, $C{\equiv}CCH_2CH_2$ lies on an energy minimum, there is as yet no conclusive experimental evidence for the existence of this molecule in the free state.[4]

The ability of metal atoms to complex and stabilize highly reactive small molecules is well-known,[5,6] and recently, metal complexes of cyclopentyne[7] and a *gem*-dimethylcyclopentyne[8] were isolated.



1

We recently prepared the first example of a metal complex $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2CH_2CH_2)(\mu\text{-}SPh)(\mu\text{-}H)$ (1) that contains a cyclobutyne ligand.[9] We have now investigated the reaction of 1 with diphenylacetylene. Two new products were formed: one contains a phenylcyclobutenyl ligand formed by a shift of the phenyl ring from the thiolato sulfur atom to the cyclobutyne ligand; the other contains a metallacycle formed by the coupling of the cyclobutyne ligand to 1 equiv of diphenylacetylene. The results of this study are reported here.

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. $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2CH_2CH_2)(\mu\text{-}SPh)(\mu\text{-}H)$ (1) was prepared according to our previous report.[9] IR spectra were recorded on a Nicolet 5DXB FT-IR spectrometer, ^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}) on plates (Whatman, 0.25 mm).

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0276-7333/93/2312-3426$04.00/0

Table I. Crystal Data for Compounds 3 and 4

	3	4
formula	$Os_3SO_7C_{31}H_{20}$	$Os_3SO_7C_{31}H_{20}$
fw	1107.15	1107.15
crystal system	monoclinic	triclinic
lattice params		
a (Å)	17.401(3)	11.815(2)
b (Å)	7.981(1)	12.260(2)
c (Å)	22.304(4)	11.492(3)
α (deg)	90	102.91(2)
β (deg)	100.26(1)	110.86(1)
γ (deg)	90	92.44(1)
V (Å^3)	3048(2)	1503(1)
space group (No.)	$P2_1/n$ (14)	$P\bar{1}$ (2)
Z	4	2
ρ_{calc} (g/cm^3)	2.41	2.45
μ(Mo Kα) (cm^{-1})	126.0	127.8
T (°C)	20	20
$2\theta_{max}$ (deg)	43.0	45.0
no. obs ($I > 3\sigma$)	2894	3274
residuals: R, R_w	0.030, 0.032	0.043, 0.050
goodness-of-fit indicator	1.71	2.75
max shift in final cycle	0.02	0.02
largest peak in final diff map, e/Å^3	1.31	1.71

Reaction of $Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}C_2CH_2CH_2)(\mu\text{-}SPh)(\mu\text{-}H)$ (1) with PhC_2Ph. A solution containing a 13.6-mg (0.014-mmol) amount of 1 and a 4.0-mg (0.022-mmol) amount of PhC≡CPh in 25 mL of heptane was heated to reflux for 30 h. During this time, the color slowly changed from yellow to red. The solvent was removed in vacuo, and the residue was separated by TLC with a hexane/dichloromethane (9/1) solvent mixture. Three major products were obtained. In order of elution these were the previously reported compound $Os_2(CO)_6(\mu\text{-}\eta^2\text{-}C{=}CHCH_2CH_2)(\mu\text{-}SPh)$[9] (2) (1.1 mg, 11%), a new red compound $Os_3(CO)_7[\mu\text{-}C(Ph)(H)C(Ph)][(\mu\text{-}C(Ph)CCH_2CH_2)(\mu_3\text{-}S)$ (3) (4.2 mg, 28% yield), and a new orange compound $Os_3(CO)_7[\mu\text{-}C(Ph)C(Ph)CCCH_2CH_2](\mu\text{-}SPh)(\mu\text{-}H)$ (4) (3.8 mg, 25% yield). Spectroscopic data for 3 are as follows. IR (ν(CO), cm^{-1}, in hexane): 2070 (m), 2043 (m), 2035 (m), 2024 (s), 2020 (vs), 2005 (s), 1978 (m), 1975 (m), 1964 (w), 1955 (w). ^{1}H NMR (δ, in $CDCl_3$): 7.58–6.72 (m, 30H), 5.40 (s, 1H), 5.29 (s, 1H), 3.84–2.90 (m, 8H). The two resonances at δ 5.40 (s, 1H) and 5.29 (s, 1H) have a 4/3 intensity ratio and are assigned to the alkenyl hydrogen atom of the diphenylvinyl ligand. The presence of two resonances indicates that compound 3 exists in solution as a mixture of two isomers. Anal. Calcd for 3: C, 33.60; H, 1.81. Found: C, 34.12; H, 1.61. Spectroscopic data for 4 are as follows. IR (ν(CO), cm^{-1}, in hexane): 2089 (s), 2056 (vs), 2014 (s), 1995 (m), 1983 (w), 1951 (m), 1942 (w). ^{1}H NMR (δ, in $CDCl_3$): 7.36–7.04 (m, 15H), 3.90–3.83 (m, 1H), 3.55–3.47 (m, 1H), 3.40–3.32 (m, 1H), 3.06–2.99 (m, 1H), −14.51 (s, 1H). The mass spectrum of 4 showed the parent ion at m/e = 1108 and ions corresponding to the loss of each of the seven carbonyl ligands.

Crystallographic Analyses. Crystals of 3 and 4 suitable for X-ray diffraction analysis were grown from solutions in pentane solvent by slow evaporation of the solvent at 25 °C. All crystals used in diffraction analyses 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 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 based on three azimuthal (ψ) scans were applied to the data in each analysis. Neutral-atom scattering factors were calculated by the standard procedures.[10a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[10b] Full-matrix least-squares refinements minimized the function

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

where

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

and

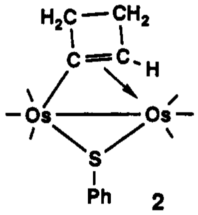
$$\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$$

Compound 3 crystallized in the monoclinic crystal system. The space group $P2_1/n$ was established on the basis of the systematic absences observed during the collection of the intensity data. 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 hydride ligand was located and refined by using an isotropic thermal parameter. The positions of the hydrogen atoms on the ligands were calculated by assuming idealized geometries and C–H distances of 0.95 Å. 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 was $P\bar{1}$ 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. One of the phenyl rings, C(51)–C(56), was found to exhibit a 2-fold rotational disorder. Both orientations were refined with 50% occupancy and isotropic thermal parameters for the atoms. All other non-hydrogen atoms were refined with anisotropic thermal parameters. The hydride ligand was located and refined on its positional parameters only. The positions of all hydrogen atoms on the ligands were calculated by assuming idealized geometries. Their contributions were added to the structure factor calculations, but their positions were not refined.

Results

The reaction of complex 1 with PhC≡CPh in refluxing heptane solvent for 30 h yielded three products: $Os_2(CO)_6(\mu\text{-}\eta^2\text{-}C{=}CHCH_2CH_2)(\mu\text{-}SPh)$ (2) (11% yield), $Os_3(CO)_7[\mu\text{-}C(Ph)(H)C(Ph)][(\mu\text{-}C(Ph)CCH_2CH_2)(\mu_3\text{-}S)$ (3) (28% yield), and $Os_3(CO)_7[\mu\text{-}C(Ph)C(Ph)CCCH_2CH_2](\mu\text{-}SPh)(\mu\text{-}H)$ (4) (25% yield). Compound 2 was obtained previously in our studies of the thermal transformations of the complex $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C{=}CHCH_2CH_2)(\mu\text{-}SPh)$,[9] which is the precursor to 1. It is not a product of the reaction of 1 with PhC≡CPh and will not be discussed further here.



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Compounds 3 and 4 are new, and both compounds were characterized by IR, ^{1}H NMR, and single-crystal X-ray diffraction analyses. An ORTEP diagram of the molecular

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[10] (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.

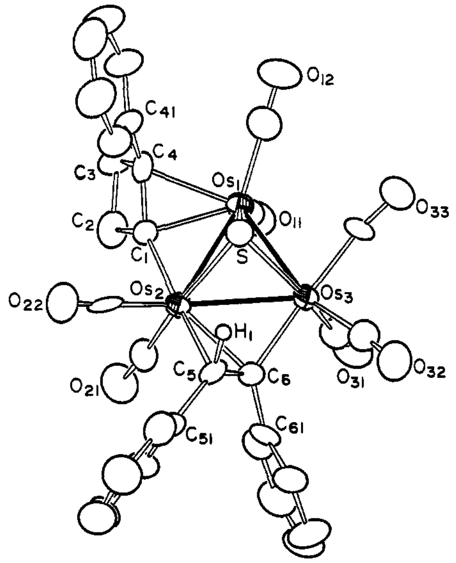

Figure 1. ORTEP diagram of $Os_3(CO)_7[\mu\text{-}C(Ph)(H)C(Ph)][(\mu\text{-}\overline{C(Ph)CCH_2CH_2})(\mu_3\text{-}S)]$ (**3**) showing 50% probability thermal ellipsoids.

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

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.19403(03)	0.04747(06)	0.08094(02)	3.14(2)
Os(2)	0.30231(02)	0.08808(06)	0.00531(02)	2.90(2)
Os(3)	0.15174(03)	0.26182(06)	–0.01378(02)	3.14(2)
S	0.26672(16)	0.3010(04)	0.07223(14)	3.2(1)
O(11)	0.0887(05)	–0.2469(13)	0.0429(04)	5.7(5)
O(12)	0.1318(06)	0.0697(14)	0.1993(05)	6.4(6)
O(21)	0.3121(06)	–0.2124(13)	–0.0758(05)	6.6(6)
O(22)	0.4797(05)	0.1191(13)	0.0438(05)	6.3(5)
O(31)	0.0374(05)	0.0518(15)	–0.0942(05)	7.0(6)
O(32)	0.1322(06)	0.6045(14)	–0.0765(05)	6.8(6)
O(33)	0.0400(05)	0.3361(15)	0.0662(05)	6.3(5)
C(1)	0.2987(06)	–0.0845(14)	0.0733(05)	2.8(5)
C(2)	0.2940(07)	–0.2771(14)	0.0727(07)	4.4(6)
C(3)	0.2828(08)	–0.2732(17)	0.1401(06)	5.0(7)
C(4)	0.2981(06)	–0.0820(15)	0.1379(06)	3.5(6)
C(5)	0.3206(06)	0.3206(15)	–0.0534(05)	3.4(6)
C(6)	0.2462(06)	0.2535(15)	–0.0721(05)	3.2(5)
C(11)	0.1294(06)	–0.1339(19)	0.0586(06)	4.0(6)
C(12)	0.1548(08)	0.0601(17)	0.1546(07)	4.4(7)
C(21)	0.3074(07)	–0.0923(17)	–0.0469(06)	4.2(7)
C(22)	0.4119(08)	0.1005(16)	0.0275(05)	4.0(6)
C(31)	0.0860(07)	0.1370(19)	–0.0674(06)	4.6(7)
C(32)	0.1402(07)	0.4790(19)	–0.0525(07)	4.6(7)
C(33)	0.0869(07)	0.2922(18)	0.0391(06)	4.1(6)
C(41)	0.3409(07)	0.0094(16)	0.1914(06)	3.8(6)
C(42)	0.3954(07)	0.1328(19)	0.1861(06)	4.8(7)
C(43)	0.4386(09)	0.201(02)	0.2380(09)	7(1)
C(44)	0.4291(11)	0.149(03)	0.2938(09)	8(1)
C(45)	0.3760(12)	0.026(03)	0.2997(08)	8(1)
C(46)	0.3315(09)	–0.0365(20)	0.2482(07)	6.0(8)

structure of **3** 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 cluster of three metal atoms with a triply bridging sulfido ligand. The metal–metal and metal–sulfur distances are similar to those found in the complex $Os_3(CO)_9(\mu_3\text{-}CO)(\mu_3\text{-}S)$.[11] There is also a phenylcyclobutenyl ligand bridging one edge of the cluster, Os(1)–Os(2) = 2.7628(8) Å, and a 1,2-diphenylvinyl ligand bridging one of the other edges, Os(2)–Os(3) = 2.7777(7) Å. Both of these ligands exhibit the classic η^2-σ-π coordination and serve as three-electron donors.[12] Thus,

Table III. Intramolecular Distances for 3[a]

Os(1)–Os(2)	2.7628(8)	Os(3)–C(6)	2.13(1)
Os(1)–Os(3)	2.6986(8)	C(1)–C(2)	1.54(2)
Os(1)–S	2.413(3)	C(1)–C(4)	1.44(2)
Os(1)–C(1)	2.14(1)	C(2)–C(3)	1.55(2)
Os(1)–C(4)	2.27(1)	C(3)–C(4)	1.55(2)
Os(2)–Os(3)	2.7777(7)	C(4)–C(41)	1.48(2)
Os(2)–S	2.415(3)	C(5)–C(6)	1.40(1)
Os(2)–C(1)	2.06(1)	C(5)–C(51)	1.53(2)
Os(2)–C(5)	2.33(1)	C(6)–C(61)	1.52(2)
Os(2)–C(6)	2.25(1)	Os–C(av)	1.89(2)
Os(3)–S	2.422(3)	O–C(av)	1.15(2)

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

Table IV. Intramolecular Bond Angles for 3[a]

Os(2)–Os(1)–Os(3)	61.13(2)	C(2)–C(3)–C(4)	86(1)
Os(2)–Os(1)–S	55.12(8)	Os(1)–C(4)–C(1)	66.0(6)
Os(3)–Os(1)–S	56.23(7)	Os(1)–C(4)–C(3)	109.9(8)
Os(1)–Os(2)–Os(3)	58.30(2)	Os(1)–C(4)–C(41)	117.6(8)
Os(1)–Os(2)–S	55.05(7)	C(1)–C(4)–C(3)	93(1)
Os(3)–Os(2)–S	55.07(7)	C(1)–C(4)–C(41)	136(1)
Os(1)–Os(3)–Os(2)	60.58(2)	C(3)–C(4)–C(41)	122(1)
Os(1)–Os(3)–S	55.90(8)	C(6)–C(5)–C(51)	125(1)
Os(2)–Os(3)–S	54.82(7)	C(5)–C(6)–C(61)	121(1)
C(2)–C(1)–C(4)	91(1)	Os(3)–C(33)–O(33)	169(1)
C(1)–C(2)–C(3)	89(1)	Os–C(av)–O	176(2)

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

with three metal–metal single bonds, each of the metal atoms achieves the 18-electron configuration. The C–C distances around the four-membered ring are normal, and as expected, the coordinated double bond, C(1)–C(4) = 1.44(2) Å, is slightly shorter than the C–C single bonds, C(1)–C(2) = 1.54(2) Å, C(2)–C(3) = 1.55(2) Å, and C(3)–C(4) = 1.55(2) Å, and are very similar to the values found for the unsubstituted σ-π cyclobutenyl ligands found in the complexes **2** and $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}\overline{C{=}CHCH_2CH_2})(\mu\text{-}SPh)$ that we reported previously.[9] In solution, compound **3** exists as a mixture of two isomers, as evidenced by the presence of two resonances at 5.40 (s) and 5.29 (s) ppm in a 4/3 ratio that were assigned to the alkenyl hydrogen atom on the σ-π diphenylvinyl ligand. Isomers of **3** could be formed by the coordination of the different faces of the two σ-π alkenyl ligands.[12,13]

An ORTEP diagram of the molecular structure of **4** 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. The molecule consists of a triangular cluster of three metal atoms with a benzenethiolato ligand bridging the Os(2)–Os(3) edge of the cluster. The most interesting ligand contains the four coordinated carbon atoms, C(1), C(2), C(5), and C(6). The group is π-bonded to Os(2) and forms a metallacycle through σ-bonding of C(1) and C(6) to Os(1). The ligand was clearly formed through the coupling of the cyclobutyne ligand to one molecule of PhC_2Ph through the formation of the carbon–carbon bond C(2)–C(5). Dimetalated dienyl ligands such as this are commonly formed by the coupling of two alkynes in polynuclear metal complexes.[14] The ligand serves as a six-electron donor. There is one bridging

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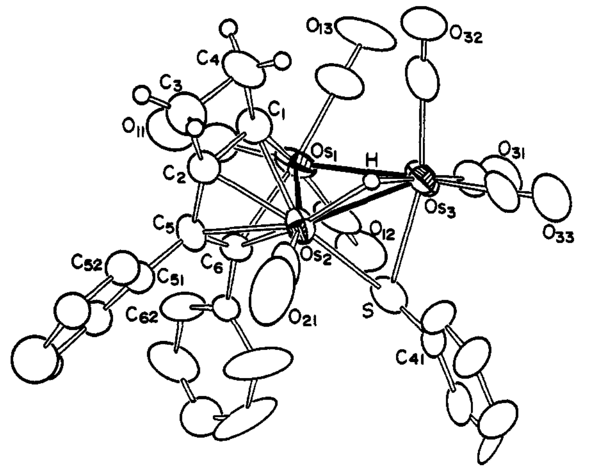


Figure 2. ORTEP diagram of $Os_3(CO)_7(\mu\text{-}C(Ph)C(Ph)CCH_2CH_2)(\mu\text{-}SPh)(\mu\text{-}H)$ (4) showing 50% probability thermal ellipsoids.

Table V. Positional Parameters and *B*(eq) for 4

atom	*x*	*y*	*z*	*B*(eq), Å^2
Os(1)	0.92948(06)	0.17050(05)	0.12314(06)	4.71(3)
Os(2)	0.82556(06)	0.33250(05)	0.23942(05)	3.82(2)
Os(3)	0.89227(06)	0.17087(06)	0.36970(07)	5.83(3)
S	0.6858(04)	0.1931(04)	0.2471(04)	6.1(2)
O(11)	1.0002(12)	0.1850(11)	−0.0984(13)	7.1(6)
O(12)	0.7496(12)	−0.0503(10)	−0.0037(13)	7.9(6)
O(13)	1.1520(12)	0.0565(11)	0.2462(14)	8.9(6)
O(21)	0.7255(17)	0.5414(11)	0.3361(14)	9.3(8)
O(31)	0.8724(13)	−0.0858(12)	0.2990(16)	8.9(7)
O(32)	1.1711(12)	0.2076(14)	0.5072(13)	8.6(7)
O(33)	0.8500(15)	0.1731(17)	0.6168(17)	10.7(9)
C(1)	1.0075(13)	0.3398(11)	0.2191(13)	3.9(5)
C(2)	0.9419(13)	0.4226(11)	0.1679(13)	3.7(5)
C(3)	1.0432(16)	0.5197(13)	0.2563(16)	5.8(7)
C(4)	1.1122(16)	0.4263(15)	0.3134(17)	6.7(7)
C(5)	0.8222(13)	0.3899(11)	0.0664(12)	3.6(5)
C(6)	0.7848(12)	0.2721(11)	0.0391(11)	3.1(5)
C(11)	0.9723(16)	0.1772(16)	−0.0163(16)	5.4(7)
C(12)	0.8174(16)	0.0297(15)	0.0420(18)	6.2(7)
C(13)	1.0692(16)	0.0990(15)	0.2005(18)	6.4(7)
C(21)	0.7616(17)	0.4601(13)	0.3013(14)	5.1(7)
C(31)	0.8796(16)	0.0097(18)	0.326(02)	7.0(9)
C(32)	1.072(02)	0.1931(17)	0.4549(18)	7.0(9)
C(33)	0.8644(19)	0.1755(18)	0.525(02)	8(1)

Table VI. Intramolecular Distances for 4[a]

Os(1)–Os(2)	2.725(1)	Os(3)–S	2.406(4)
Os(1)–Os(3)	3.017(1)	Os(3)–H	1.9(1)
Os(1)–C(1)	2.11(1)	S–C(41)	1.81(2)
Os(1)–C(6)	2.23(1)	C(1)–C(2)	1.41(2)
Os(2)–Os(3)	2.722(1)	C(1)–C(4)	1.50(2)
Os(2)–S	2.364(4)	C(2)–C(3)	1.53(2)
Os(2)–C(1)	2.24(2)	C(2)–C(5)	1.44(2)
Os(2)–C(2)	2.21(1)	C(3)–C(4)	1.56(2)
Os(2)–C(5)	2.24(1)	C(5)–C(6)	1.42(2)
Os(2)–C(6)	2.12(1)	OS–C(av)	1.91(3)
Os(2)–H	1.9(1)	O–C(av)	1.13(2)

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

Table VII. Intramolecular Bond Angles for 4[a]

Os(2)–Os(1)–Os(3)	56.31(3)	C(1)–C(2)–C(5)	120(1)
C(1)–Os(1)–C(6)	75.5(5)	C(3)–C(2)–C(5)	147(1)
Os(1)–Os(2)–Os(3)	67.27(3)	C(2)–C(3)–C(4)	85(1)
Os(1)–Os(2)–S	90.9(1)	C(1)–C(4)–C(3)	89(1)
Os(3)–Os(2)–S	55.9(1)	C(2)–C(5)–C(6)	111(1)
Os(1)–Os(3)–Os(2)	56.42(3)	C(2)–C(5)–C(51)	122(1)
Os(1)–Os(3)–S	83.3(1)	C(5)–C(6)–C(61)	121(1)
Os(2)–Os(3)–S	54.5(1)	C(6)–C(5)–C(51)	128(1)
C(2)–C(1)–C(4)	92(1)	Os–C(av)–O	178(2)
C(1)–C(2)–C(3)	93(1)		

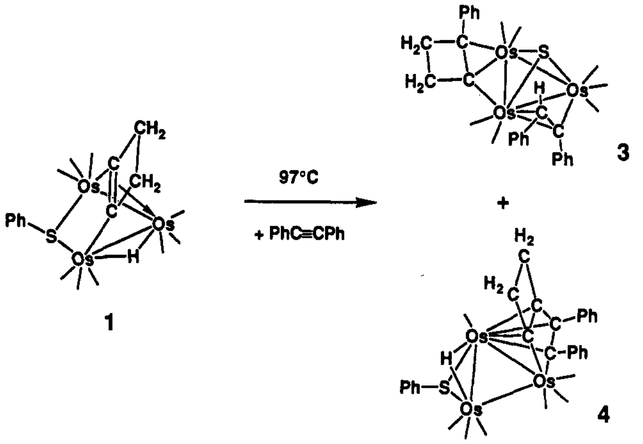
[a] Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

hydride ligand, located and refined crystallographically, that bridges the Os(2)–Os(3) bond, $\delta = -14.51$ ppm. It is well-known that hydride ligands prefer bridging sites proximate to anionic bridging ligands and the usual elongation of the metal–metal bond does not occur in these cases.[15] The cluster in 4 has a total of 48 valence electrons and is electron precise.

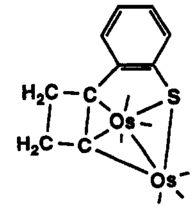
Discussion

A summary of the results of this study are shown in the Scheme I. Two products, 3 and 4, were formed by the combination of compound 1 with PhC≡CPh in refluxing in heptane solvent. On the basis of their structures, it is fairly clear that they must have been formed in competing reactions. A third product, 2, was also formed, but this product was not the result of a PhC≡CPh addition. Compound 2 was obtained previously in our studies of the transformations of the complex $Os_3(CO)_{10}(\mu\text{-}\eta^2\text{-}C{=}CHCH_2CH_2)(\mu\text{-}SPh)$, which is the precursor to 1.

Scheme I



Compound 3 was formed by the loss of one CO ligand and by the transfer of the phenyl group from the thiolato ligand to one of the alkyne carbon atoms of the cyclobutyne ligand. We have observed the thermally induced transfer of a phenyl group from the sulfur atom of a benzenethiolate ligand to other ligands in other triosmium cluster complexes.[16] We have also observed that when compound 1 was heated to 125 °C in the absence of PhC≡CPh, the diosmium compound $Os_2(CO)_6(\mu\text{-}C_2CH_2CH_2C_6H_4S)$ (5)



5

was formed, in which the phenyl ring of the thiolato ligand became coupled to one of the alkyne carbon atoms of the

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cyclobutyne ligand at an ortho position.[9b] However, since **5** contains only two metal atoms, it seems most unlikely that it could be a precursor to **3**. Instead, it seems more likely that **3** and **5** were formed from a common intermediate that has not yet been observed. One molecule of PhC≡CPh was also added to **1** in the formation of **3**. It was inserted into the metal–hydride bond to form the σ-π coordinated diphenylvinyl ligand. The insertion of alkynes into metal–hydride bonds in osmium cluster complexes to form σ-π alkenyl ligands is a very common type of reaction.[12]

The formation of compound **4** is a little more straightforward. It involves a simple decarbonylation of **1** and the addition and coupling of one molecule of PhC≡CPh to the cyclobutyne ligand to yield the metallacyclopentadiene grouping. This is also a common reaction of alkynes in triosmium cluster complexes.[12,17] To date, all of our studies indicate that the chemistry of the cyclobutyne ligand in triosmium cluster complexes is very similar to that of an unstrained alkyne.

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

Supplementary Material Available: Tables of positional parameters for the phenyl rings and hydrogen atoms and anisotropic thermal parameters for both structural analyses (12 pages). Ordering information is given on any current masthead page.

OM930161U

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