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Cyclobutyne Ligands. 4. Ruthenium Carbonyl Clusters Containing Substituted Cyclobutyne Ligands and the First Example of a Quadruply Bridging Cyclobutyne Ligand

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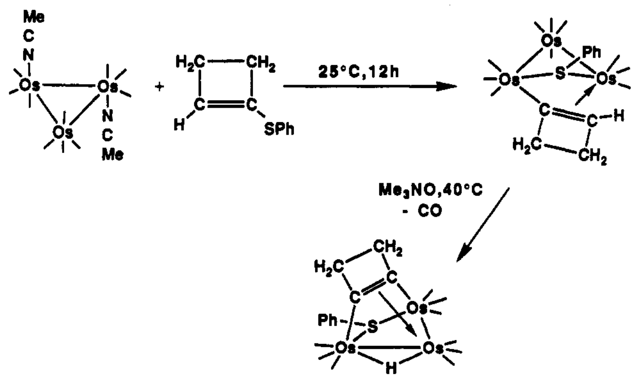
The reaction of 4-*tert*-butyl-4-methyl-1-(phenylthio)cyclobutene with $Ru_3(CO)_{12}$ at 98 °C has yielded four new complexes: $Ru_4(CO)_{12}[\mu_4\text{-}SC_2CH_2C(Me)^tBu]$ (1; 12%), $\{Ru_3(CO)_8[\mu_3\text{-}\eta^2\text{-}C_2CH_2C(Me)^tBu](\mu_4\text{-}S)\}_2$ (2; 1%), $Ru_4(CO)_{11}[\mu_4\text{-}\eta^2\text{-}C_2CH_2C(Me)^tBu](\mu_4\text{-}S)$ (3; 14%), and a trace of $Ru_6(CO)_{16}[\mu_4\text{-}CCHCH{=}C(Me)^tBu](\mu_4\text{-}S)$ (4; 1%). All four products were characterized by single-crystal X-ray diffraction analyses. Compounds 2 and 3 contain new examples of the disubstituted cyclobutyne ligand $C_2CH_2C(Me)^tBu$, formed by the cleavage of the hydrogen atom and the phenylthio group from the cyclobutene ring. Compound 1 contains a quadruply bridging metalated 1-sulfidocyclobutenyl group. It was transformed to compound 3, which contains the first example of a quadruply bridging cyclobutyne ligand. Compound 4 contains six ruthenium atoms arranged in the shape of an edge-bridged square-pyramidal cluster. A sulfido ligand bridges the square base, and a $CH{=}C(Me)^tBu$ substituted-vinylidene ligand bridges one triangle of the square pyramid and the edge-bridging ruthenium atom. Compound 2 is a dimer that can be split by reaction with CO to yield two of the monomeric triruthenium cluster complexes $Ru_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C_2CH_2C(Me)^tBu](\mu_3\text{-}S)$ (5). When heated to 68 °C, compound 5 is decarbonylated and converted back into 2. Compound 5 was also characterized crystallographically. Crystal data for 1: space group $P2_1/c$, $a = 10.014(2)$ Å, $b = 11.662(2)$ Å, $c = 23.642(3)$ Å, $\beta = 92.48(1)°$, $Z = 4$, 2589 reflections, $R = 0.027$. Crystal data for $2{\cdot}C_6H_6$: space group $P2_1/c$, $a = 18.793(3)$ Å, $b = 15.109(3)$ Å, $c = 19.039(4)$ Å, $\beta = 114.89(2)°$, $Z = 4$, 3180 reflections, $R = 0.033$. Crystal data for 3: space group $P\bar{1}$, $a = 10.429(1)$ Å, $b = 11.566(2)$ Å, $c = 10.893(1)$ Å, $\alpha = 89.94(1)°$, $\beta = 98.308(8)°$, $\gamma = 90.36(1)°$, $Z = 2$, 2871 reflections, $R = 0.025$. Crystal data for 4: space group $P2_1/c$, $a = 16.395(2)$ Å, $b = 12.117(3)$ Å, $c = 18.382(3)$ Å, $\beta = 107.01(1)°$, $Z = 4$, 2741 reflections, $R = 0.032$. Crystal data for 5: space group $P2_1/c$, $a = 9.138(2)$ Å, $b = 17.845(3)$ Å, $c = 14.415(2)$ Å, $\beta = 93.29(1)°$, $Z = 4$, 2152 reflections, $R = 0.021$.

Introduction

In our recent studies we have isolated the first examples of the highly strained carbocycle cyclobutyne[1] and the 3,3-^tBu,Me derivative $C_2CH_2C(Me)^tBu$ by complexation to triosmium clusters (e.g. Scheme 1).[2-4] This was achieved by the cleavage of the hydrogen atom and the phenylthio grouping from the corresponding phenyl cyclobutenyl thioethers. The cyclobutyne ligands are stabilized by coordination of the triple bond to the metal atoms. This apparently reduces the strain at the C–C multiple bond sufficiently to permit the existence of the ligand at room temperature. This reduction was indicated by the length of the carbon–carbon bond.

Scheme 1



We have now extended these studies to the cluster chemistry of ruthenium. Since the metal–metal bonds of ruthenium clusters are generally weaker than those of osmium, we have found a tendency of the clusters to fragment and subsequently reassemble into stable clusters with higher metal nuclearity. As a result, we have been able to isolate the first example of a tetranuclear metal cluster containing a quadruply bridging substituted cyclobutyne ligand. 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

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[2] (a) Adams, R. D.; Chen, G.; Qu, X.; Wu, W.; Yamamoto, J. H. *Organometallics* 1993, *12,* 2404. (b) Adams, R. D.; Chen, G.; Qu, X.; Wu, W.; Yamamoto, J. H. *J. Am. Chem. Soc.* 1992, *114,* 10 977.

[3] Adams, R. D.; Chen, G.; Qu, X.; Wu, W.; Yamamoto, J. H. *Organometallics* 1993, *12,* 3426.

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distillation under nitrogen from the appropriate drying agents (sodium/benzophenone for THF, sodium for toluene, and CaH_2 for CH_2Cl_2 and hexane), stored over molecular sieves, and deoxygenated by purging with nitrogen prior to use. $Ru_3(CO)_{12}$ was purchased from Strem Chemicals, Inc. 4-*tert*-Butyl-4-methyl-1-(phenylthio)cyclobutene was prepared according to the literature.[5] IR spectra were recorded on a Nicolet 5DXB FT-IR spectrophotometer. ^1H NMR spectra were recorded on Bruker AM-300 and AM-500 FT-NMR spectrometers. Mass spectra were run on a VG Model 70SQ mass spectrometer using electron impact ionization with 70-eV ionizing voltage and direct-inlet sample additions. Elemental microanalyses were performed by Desert Analytics Organic Microanalysis, Tucson, AZ. TLC separations were performed in air by using silica gel (60 Å, F_{254}) on plates (Analtech, 0.25 mm).

Reactions of $Ru_3(CO)_{12}$ with 4-*tert*-Butyl-4-Methyl-1-(Phenylthio)cyclobutene. A 25.0-mg amount of 4-*tert*-butyl-4-methyl-1-(phenylthio)cyclobutene (0.108 mmol) and a 192.0-mg amount of $Ru_3(CO)_{12}$ (0.300 mmol) were dissolved in 25 mL of heptane. The solution was heated to reflux for 4 h. The solvent was then removed in vacuo, and the residue was first separated by column chromatography using silica gel to remove unreacted $Ru_3(CO)_{12}$ (120 mg), which eluted first. The remaining colored material was collected and subsequently separated by TLC using hexane solvent for elution. This yielded four products in the following order of elution: 11.5 mg of orange $Ru_4(CO)_{12}[\mu_4\text{-}S(C_6H_5)C_2CH_2C(Me)^tBu]$ (1; 12% yield), 1.0 mg of yellow $\{Ru_3(CO)_8[\mu_3\text{-}\eta^2\text{-}C_2CH_2C(Me)^tBu](\mu_4\text{-}S)\}_2$ (2; 1%), 13.5 mg of yellow $Ru_4(CO)_{11}[\mu_4\text{-}\eta^2\text{-}C_2CH_2C(Me)^tBu](\mu_4\text{-}S)$ (3; 14%), and 2.0 mg of black $Ru_6(CO)_{16}[\mu_4\text{-}CCHCH{=}C(Me)^tBu](\mu_4\text{-}S)$ (4; 1%). Longer reaction periods did not give higher yields of the products. Spectroscopic data for the products are given as follows. IR (ν_{CO} in hexane, cm^{-1}) for 1: 2095 (m), 2069 (vs), 2039 (s), 2025 (m), 2016 (w), 2006 (w), 2000 (m), 1945 (w, broad). ^1H NMR (δ in $CDCl_3$) for 1: 3.00 (d, 1H, $^2J_{HH}$ = 13.9 Hz), 2.23 (d, 1H, $^2J_{HH}$ = 13.9 Hz), 1.21 (s, 9H), 1.07 (s, 3H). Anal. Calcd (found) for 1: C, 28.17 (28.30); H, 1.56 (1.43). IR (ν_{co} in hexane, cm^{-1}) for 2: 2084 (s), 2052 (s), 2036 (vs), 2020 (m), 2008 (m), 2004 (m), 1993 (m), 1969 (m). ^1H NMR (δ in $CDCl_3$) for 2: 3.23 (d, 1H, $^2J_{HH}$ = 14.0 Hz), 3.07 (d, 1H, $^2J_{HH}$ = 14.1 Hz), 2.35 (d, 1H, $^2J_{HH}$ = 14.0 Hz), 2.24 (d, 1H, $^2J_{HH}$ = 14.1), 1.23 (s, 3H), 1.05 (s, 3H), 1.02 (s, 9H), 0.96 (s, 9H). The mass spectrum of 2 showed the parent ion *m/e* 1364 and ions corresponding to the loss of each of 2–16 carbonyl ligands. IR (ν_{co} in hexane, cm^{-1}) for 3: 2091 (m), 2067 (s), 2059 (s), 2037 (vs), 2026 (s), 2016 (m), 2003 (m), 1988 (m), 1894 (w), 1856 (m). ^1H NMR (δ in $CDCl_3$) for 3: 2.06 (d, 1H, $^2J_{HH}$ = 14.0 Hz), 1.48 (d, 1H, $^2J_{HH}$ = 14.0 Hz), 0.63 (s, 9H), 0.55 (s, 3H). $^{13}C\{^1H\}$ NMR at 25 °C (δ in CD_2Cl_2): 27.67 (CMe_3) 29.6 (*Me*), 35.86 (CMe_3), 52.74 (CH_2), 60.60 ($C(Me)^tBu$), 182.04 ($\equiv$C), 190.92 ($\equiv$C), 200.33 (11 CO). Anal. Calcd (found) for 3: C, 27.69 (27.78); H, 1.42 (1.62). IR (ν_{co} in hexane, cm^{-1}) for 4: 2095 (w), 2070 (vs), 2048 (vs), 2043 (s), 2032 (m), 2027 (m), 2020 (m), 1999 (w), 1985 (w). ^1H NMR (δ in $CDCl_3$) for 4: 5.76 (d, 1H, $^3J_{HH}$ = 9.3 Hz), 5.53 (dq, 1H, $^3J_{HH}$ = 9.3 Hz, $^4J_{HH}$ = 1.2 Hz), 1.89 (d, 3H, $^4J_{HH}$ = 1.2 Hz), 1.03 (s, 9H). The mass spectrum of 4 showed the parent ion *m/e* 1209 and ions corresponding to the loss of each of the 16 carbonyl ligands.

Transformation of 1 to 3. A 16.0-mg amount of 1 (0.018 mmol) and a 2.0-mg amount of Me_3NO (0.027 mmol) were dissolved in 10 mL of CH_2Cl_2. The solution was heated to reflux for 2 days. The solvent was then removed in vacuo, and the residue was separated by TLC using hexane solvent. This yielded the major product: 4.0 mg of yellow $Ru_4(CO)_{11}(\mu_4\text{-}S)[\mu_4\text{-}CCCH_2C(Me)^tBu]$ (3; 26%).

Synthesis of $Ru_3(CO)_9[\mu_3\text{-}CCCH_2C(Me)(^tBu)](\mu_3\text{-}S)$ (5). A 13.0-mg amount of 2 (0.010 mmol) was dissolved in 25 mL of CH_2Cl_2. The solution was purged with CO for 5 min, and the reaction flask was closed. The resulting solution was stirred at 25 °C for 12 h. The solvent was then removed in vacuo, and the residue was separated by TLC using hexane as solvent. This yielded the major product: 11.0 mg of yellow $Ru_3(CO)_9(\mu_3\text{-}S)[\mu_3\text{-}CCCH_2C(Me)(^tBu)]$ (5; 81% yield). IR data for 5 (ν_{co}, in hexane, cm^{-1}): 2098 (m), 2077 (vs), 2049 (s), 2030 (s), 2016 (m), 2006 (s), 1669 (w). ^1H NMR data for 5 (δ in $CDCl_3$): 3.38 (d, 1H, $^2J_{HH}$ = 14 Hz), 2.50 (d, 1H, $^2J_{HH}$ = 14 Hz), 1.23 (s, 3H), 1.03 (s, 9H). The mass spectrum of 5 showed the parent ion *m/e* 711 and ions corresponding to the loss of each of the eight carbonyl ligands.

Decarbonylation of 5. An 8.0-mg amount of 5 (0.0113 mmol) was dissolved in 15 mL of hexane and was heated to reflux for 30 min. The solvent was removed in vacuo, and the residue was separated by TLC using hexane as solvent. This yielded 6.1 mg of 2 (80%).

Reaction of 5 with $Ru(CO)_5$. An 8.0-mg amount of 5 (0.0113 mmol) was dissolved in 15 mL of cyclohexane. The solution was heated to reflux under a slow purge of CO, and $Ru(CO)_5$ (~0.083 mmol) dissolved in 20 mL of hexane solution was then added via a dropping funnel over a period of 10 min. The solution was refluxed for an additional 30 min, while the slow CO purge was continued. During this time, the yellow solution turned to orange. The reaction solution was concentrated and some $Ru_3(CO)_{12}$ was separated (yellow first band) by using a silica gel column and eluting with hexane solvent. The yellow second band was largely $Ru_4(CO)_{11}(\mu_4\text{-}S)[\mu_4\text{-}CCCH_2C(Me)^+Bu]$, (3) and was further purified by TLC using hexane elution solvent to give 6.8 mg of 3 (69% yield).

Crystallographic Analyses. Crystals of 1 suitable for X-ray diffraction analysis were grown from a solution of a solvent mixture of dichloromethane and hexane by slow evaporation of the solvent at 25 °C. Crystals of 2 suitable for X-ray diffraction analysis were grown from a solution of a solvent mixture of benzene and methanol by slow evaporation of the solvent at 25 °C. Crystals of 3 were grown from a solution of a solvent mixture of dichloromethane and hexane by slow evaporation of the solvent at 25 °C. Crystals of 4 were grown from a solution of hexane by slow evaporation of the solvent at −15 °C. Crystals of 5 were grown from a solution of a solvent mixture of dichloromethane and hexane by slow evaporation of the solvent at −15 °C. All crystals were mounted in thin-walled glass capillaries. All diffraction measurements were made on a Rigaku AFC6S automatic diffractometer at 20 °C 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 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.[6a] Anomalous dispersion corrections were applied to all non-hydrogen atoms.[6b] 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 $\sigma(F_o^2) = [\sigma(I_{raw})^2 + (0.02I_{net})^2]^{1/2}/Lp$.

Compound 1 crystallized in the monoclinic crystal system. The space group $P2_1/c$ was assumed and confirmed by the successful solution and refinement of the structure. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were located and refined with isotropic thermal parameters.

Compound 2 crystallized in the monoclinic crystal system. The space group $P2_1/c$ was assumed and confirmed by the successful solution and refinement of the structure. All non-

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[6] (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.

Table 1. Crystal Data for Compounds 1–5

formula	$Ru_4SO_{12}C_{21}H_{14}$	$Ru_6S_2O_{16}C_{34}H_{28}{\cdot}C_6H_6$	$Ru_4SO_{11}C_{20}H_{14}$	$Ru_6SO_{16}C_{25}H_{14}$	$Ru_3SO_9C_{18}H_{14}$
fw	894.67	1441.24	866.66	1208.85	709.57
cryst syst	monoclinic	monoclinic	triclinic	monoclinic	monoclinic
lattice params					
a (Å)	10.014(2)	18.793(3)	10.429(1)	16.395(2)	9.138(2)
b (Å)	11.662(2)	15.109(3)	11.566(2)	12.117(3)	17.845(3)
c (Å)	23.642(3)	19.039(4)	10.893(1)	18.382(3)	14.415(2)
α (deg)	90.0	90	89.94(1)	90	90
β (deg)	92.48(1)	114.89(2)	98.308(8)	107.01(1)	93.29(1)
γ (deg)	90.0	90	90.36(1)	90	90
V (Å^3)	2758.4(7)	4904(4)	1300.0(5)	3492(2)	2347(1)
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
Z value	4	4	2	4	4
ρ_{calc} (g/cm^3)	2.15	1.95	2.21	2.30	2.01
μ(Mo Kα) (cm^{-1})	22.37	19.12	23.67	26.06	19.99
$2\theta_{max}$ (deg)	45.0	41.0	45.0	42	42
no. of obs reflns ($I > 3\sigma$)	2589	3180	2871	2741	2152
no. of variables	399	547	370	433	280
goodness of fit	1.30	1.24	1.71	1.59	1.40
residuals: R; R_w	0.027; 0.027	0.033; 0.033	0.025; 0.029	0.032; 0.032	0.021; 0.022
abs cor	empirical	empirical	empirical	none	empirical
largest peak in final diff map	0.51	0.91	0.54	0.58	0.36
transmissn coeff, max/min	1.00/0.92	1.00/0.95	1.00/0.88		1.00/0.75
max shift/error on final cycle	0.00	0.01	0.05	0.03	0.00

hydrogen atoms of the complex were refined with anisotropic thermal parameters. In the final stages of the analysis one molecule of benzene was found in the lattice. This was added, and the carbon atoms were refined with isotropic thermal parameters. All hydrogen atoms were calculated by assuming idealized geometries. The contributions of all of the hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compound **3** 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 cyclobutyne ligand was found to contain a disorder between the *tert*-butyl and methyl groups. This produced two different positions for the saturated carbon atoms C(2) and C(3) in the four-membered carbon ring. A 50/50 disorder model was satisfactorily refined. All of the non-hydrogen atoms were refined with anisotropic thermal parameters. The positions of hydrogen atoms were calculated by assuming idealized geometry. The scattering contributions of all hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compound **4** crystallized in the monoclinic crystal system. The space group $P2_1/c$ was assumed and confirmed by the successful solution and refinement of the structure. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were calculated by assuming idealized geometry. The contributions of all of the hydrogen atoms were added to the structure factor calculations, but their positions were not refined.

Compound **5** crystallized in the monoclinic crystal system. The space group $P2_1/c$ was assumed and confirmed by the successful solution and refinement of the structure. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were calculated by assuming idealized geometry. The 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 $Ru_3(CO)_{12}$ in heptane at reflux yielded four new complexes: $Ru_4(CO)_{12}[\mu_4\text{-}S\overline{C_2CH_2C}(Me)^tBu]$ (**1**; 12%), $\{Ru_3(CO)_8[\mu_3\text{-}\eta^2\text{-}\overline{C_2CH_2C}(Me)^tBu](\mu_4\text{-}S)\}_2$ (**2**; 1%); $Ru_4(CO)_{11}[\mu_4\text{-}\eta^2\text{-}\overline{C_2CH_2C}(Me)^tBu](\mu_4\text{-}S)$ (**3**; 14%), and $Ru_6(CO)_{16}[\mu_4\text{-}CCHCH{=}C(Me)^tBu](\mu_4\text{-}S)$ (**4**; 1%). All four products were characterized by IR, ^1H 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 molecule contains four metal atoms arranged in the form of a butterfly tetrahedron. The dihedral angle between the two triruthenium planes Ru(1), Ru(3), Ru(4) and Ru(2), Ru(3), Ru(4) is 162.93°. There is a 1-sulfido-4-*tert*-butyl-4-methylcyclobutenyl grouping bridging one face of the cluster. The sulfur atom bridges the Ru(2)–Ru(4) edge, and the carbon atom C(4) bridges the opposite edge Ru(1)–Ru(3). The C(1)–C(4) bond in the four-membered ring is short (1.378(9) Å) and indicative of a C–C double bond. Atom C(1) is also weakly bonded to the metal Ru(3) (Ru(3)–C(1) = 2.433(6) Å), and the coordination of the two carbon atoms of the 4-*tert*--butyl-4-methylcyclobutenyl grouping is similar to that of bridging σ,π-alkenyl groups coordinated to triosmium[7] and triruthenium[8] clusters. The metal–metal bonds that are bridged by the sulfur and carbon atom C(4) are the shortest in the cluster (Ru(1)–Ru(3) = 2.7614(9) Å and Ru(2)–Ru(4) = 2.715(1) Å). The diagonal bond Ru(3)–Ru(4) = 2.7614(9) Å is intermediate, and the unbridged bonds Ru(2)–Ru(3) = 2.886(1) Å and Ru(1)–Ru(4) = 2.913(1) Å are the longest. Each metal atom has three carbonyl ligands. All are linear, except C(41)–O(41) and C(33)–O(33), which are weak semibridging ligands. In accord with the solid structure, the two hydrogen atoms on carbon C(3) are spectroscopically inequivalent in the ^1H NMR spectrum in solution: δ 3.00 (d) and 2.23 (d) with the typical *geminal* coupling constant $^2J_{HH}$ = 13.9 Hz.

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. The molecule contains six metal atoms arranged in two groups of three and can be viewed as a dimer of the grouping $Ru_3(CO)_8[\mu_3\text{-}\eta^2\text{-}\overline{C_2CH_2C}(Me)^tBu](\mu_3\text{-}S)$. Each grouping

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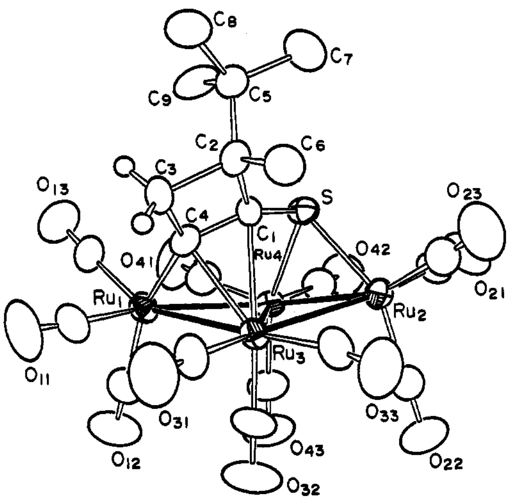

Figure 1. ORTEP diagram or $Ru_4(CO)_{12}[\mu_4\text{-}SC_2CH_2C(Me)\text{-}{}^tBu]$ (1) showing 50% probability thermal ellipsoids.

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

atom	*x*	*y*	*z*	*B*(eq) (Å²)
Ru(1)	0.49308(06)	0.89452(05)	0.85214(03)	2.81(3)
Ru(2)	0.81521(06)	0.62137(05)	0.92843(02)	2.96(3)
Ru(3)	0.72191(06)	0.85499(05)	0.91867(02)	2.50(3)
Ru(4)	0.56048(06)	0.66319(05)	0.89001(02)	2.61(3)
S	0.75068(18)	0.65021(15)	0.83234(07)	2.74(8)
O(11)	0.5148(06)	1.1498(06)	0.8424(03)	6.6(4)
O(12)	0.2587(06)	0.9096(06)	0.9328(03)	6.8(4)
O(13)	0.3430(06)	0.8956(06)	0.7383(03)	6.5(4)
O(21)	0.8337(07)	0.3627(05)	0.9223(03)	7.1(4)
O(22)	0.7672(08)	0.6174(06)	1.0549(03)	7.7(4)
O(23)	1.1180(07)	0.6346(06)	0.9247(03)	7.0(4)
O(31)	0.7710(07)	1.1132(06)	0.9240(03)	7.1(4)
O(32)	0.5651(06)	0.8692(06)	1.0245(03)	6.7(4)
O(33)	0.9829(06)	0.8634(06)	0.9889(03)	6.7(4)
O(41)	0.3273(07)	0.6609(06)	0.8045(03)	7.7(4)
O(42)	0.5186(07)	0.4041(05)	0.8829(03)	6.4(4)
O(43)	0.3926(06)	0.6605(06)	0.9939(03)	6.6(4)
C(1)	0.7775(06)	0.7984(05)	0.8235(03)	2.2(3)
C(2)	0.8814(06)	0.8657(06)	0.7898(03)	2.6(3)
C(3)	0.7750(08)	0.9650(07)	0.7918(04)	3.1(4)
C(4)	0.6837(07)	0.8848(06)	0.8237(03)	2.5(3)
C(5)	0.9010(07)	0.8184(06)	0.7292(03)	3.0(3)
C(6)	1.0131(08)	0.8904(08)	0.8221(04)	3.6(4)
C(7)	0.9986(10)	0.7189(08)	0.7302(05)	4.6(5)
C(8)	0.9586(10)	0.9125(08)	0.6927(04)	4.5(5)
C(9)	0.7703(10)	0.7805(10)	0.7006(04)	5.0(5)
C(11)	0.5061(07)	1.0527(08)	0.8476(03)	3.6(4)
C(12)	0.3414(08)	0.9014(07)	0.9031(04)	4.1(4)
C(13)	0.3945(08)	0.8940(07)	0.7813(04)	4.1(4)
C(21)	0.8236(08)	0.4591(08)	0.9238(03)	4.1(4)
C(22)	0.7853(08)	0.6190(07)	1.0077(04)	4.2(4)
C(23)	1.0065(09)	0.6278(07)	0.9271(03)	4.0(4)
C(31)	0.7500(08)	1.0185(07)	0.9199(03)	4.0(4)
C(32)	0.6234(08)	0.8601(07)	0.9838(04)	4.4(4)
C(33)	0.8889(08)	0.8405(07)	0.9600(03)	4.2(4)
C(41)	0.4166(09)	0.6800(07)	0.8355(04)	4.3(4)
C(42)	0.5398(08)	0.4997(07)	0.8861(03)	3.7(4)
C(43)	0.4561(08)	0.6657(07)	0.9554(03)	4.2(4)

Table 3. Intramolecular Distances for 1[a]

Ru(1)–Ru(3)	2.7614(9)	C(1)–C(2)	1.550(9)
Ru(1)–Ru(4)	2.913(1)	C(1)–C(4)	1.378(9)
Ru(1)–C(4)	2.054(7)	C(2)–C(3)	1.58(1)
Ru(2)–Ru(3)	2.886(1)	C(2)–C(5)	1.56(1)
Ru(2)–Ru(4)	2.715(1)	C(2)–C(6)	1.52(1)
Ru(2)–S	2.359(2)	C(3)–C(4)	1.53(1)
Ru(3)–Ru(4)	2.8250(9)	C(5)–C(7)	1.52(1)
Ru(3)–C(1)	2.433(6)	C(5)–C(8)	1.53(1)
Ru(3)–C(4)	2.288(6)	C(5)–C(9)	1.51(1)
Ru(4)–S	2.395(2)	Ru–C (av)	1.91(1)
S–C(1)	1.763(7)	C–O (av)	1.19(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]

Ru(3)–Ru(1)–Ru(4)	59.65(2)	Ru(4)–S–C(1)	97.7(2)
Ru(3)–Ru(1)–C(4)	54.4(2)	C(2)–C(1)–C(4)	96.0(5)
Ru(3)–Ru(2)–Ru(4)	60.49(2)	C(1)–C(2)–C(3)	83.5(5)
Ru(1)–Ru(3)–Ru(2)	117.45(3)	C(1)–C(2)–C(5)	114.1(5)
Ru(1)–Ru(3)–Ru(4)	62.83(2)	C(1)–C(2)–C(6)	115.1(6)
Ru(2)–Ru(3)–Ru(4)	56.75(2)	C(3)–C(2)–C(5)	113.6(6)
Ru(1)–Ru(4)–Ru(2)	118.11(3)	C(3)–C(2)–C(6)	114.7(7)
Ru(1)–Ru(4)–Ru(3)	57.52(2)	C(5)–C(2)–C(6)	112.8(6)
Ru(2)–Ru(4)–Ru(3)	62.76(2)	C(2)–C(3)–C(4)	89.1(5)
Ru(2)–S–Ru(4)	69.64(5)	C(1)–C(4)–C(3)	91.3(5)
Ru(2)–S–C(1)	102.5(2)	Ru–C–O (av)	176(1)

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

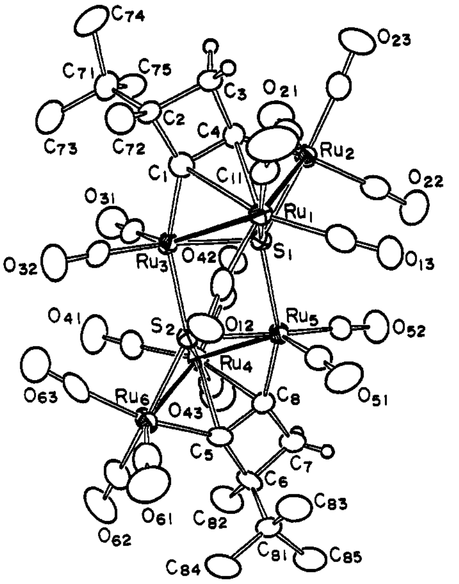

Figure 2. ORTEP diagram of $\{Ru_3(CO)_8[\mu_3\text{-}\eta^2\text{-}C_2CH_2C(Me)^tBu](\mu_4\text{-}S)\}_2$ (2) showing 45% probability thermal ellipsoids.

contains one triply bridging $C_2CH_2C(Me)^tBu$ cyclobutyne ligand. The two groups are joined by coordinate bonds between the sulfur atom of one group and a ruthenium atom of the second group. This results in the formation of a Ru–S–Ru–S four-membered ring. Similar dimers were obtained by the decarbonylation of the related phenylacetylene complexes $Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{-}PhC_2H)(\mu_3\text{-}S)$ and $Ru_3(CO)_8(PMe_2Ph)(\mu_3\text{-}\eta^2\text{-}PhC_2H)(\mu_3\text{-}S)$.[9] The metal–metal and metal–sulfur bond distances in both 2 and the acyclic alkyne dimers are similar. Notably, the donor–acceptor bonds Ru(3)–S(2) and Ru(5)–S(1) (2.507(3) and 2.506(3) Å) are significantly longer than those within the cluster units (2.409(3), 2.377(3), 2.376(3), 2.422(3), 2.370(3), and 2.369(3) Å). The carbon–carbon distances are not significantly different from those found in the triosmium cluster complex $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C_2CH_2C(Me)^tBu](\mu_3\text{-}S)$ (6), which also contains the $C_2CH_2C(Me)^tBu$ cyclobutyne ligand.[4] The C–C distances for the multiple bonds in the two cyclobutyne ligands in 2 are 1.42(1) and 1.43(1) Å. The corresponding distance for the cyclobutyne ligand in 6 is 1.40(2) Å. The C–C multiple-bond distance for the cyclobutyne ligand $C_2CH_2CH_2$ in $Os_3(CO)_9[\mu_3\text{-}\eta^2\text{-}C_2CH_2CH_2](\mu\text{-}SPh)$ (7) is 1.37(2) Å.[2] These distances also compare favorably with the value found for $Ru_3(CO)_9[\mu_3\text{-}$

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

atom	*x*	*y*	*z*	*B*(eq) (Å^2)
Ru(1)	0.33215(05)	0.42687(06)	0.58526(05)	2.85(4)
Ru(2)	0.20390(05)	0.31749(06)	0.55558(05)	3.03(4)
Ru(3)	0.27990(05)	0.46879(06)	0.42724(05)	2.76(4)
Ru(4)	0.09415(05)	0.66219(06)	0.33446(05)	3.22(4)
Ru(5)	0.15163(05)	0.61196(06)	0.49060(05)	2.70(4)
Ru(6)	0.22634(06)	0.76333(07)	0.36228(06)	3.68(5)
S(1)	0.19894(16)	0.45614(19)	0.49469(16)	2.8(1)
S(2)	0.22820(16)	0.62326(18)	0.41891(16)	2.8(1)
O(11)	0.4861(06)	0.3472(06)	0.7027(05)	7.6(5)
O(12)	0.4105(05)	0.6020(06)	0.5768(05)	5.4(5)
O(13)	0.2973(05)	0.4823(06)	0.7208(05)	5.5(5)
O(21)	0.0725(06)	0.2250(06)	0.4258(06)	7.0(5)
O(22)	0.1092(06)	0.3935(07)	0.6418(06)	7.1(6)
O(23)	0.2591(06)	0.1500(06)	0.6523(05)	6.4(5)
O(31)	0.1742(05)	0.4245(06)	0.2630(05)	6.4(5)
O(32)	0.4170(05)	0.5093(06)	0.3881(05)	6.0(5)
O(41)	0.1051(06)	0.6255(08)	0.1831(05)	7.9(6)
O(42)	0.0257(05)	0.4801(07)	0.3339(05)	5.9(5)
O(43)	−0.0693(06)	0.7373(07)	0.2478(06)	8.5(6)
O(51)	0.2622(06)	0.6744(06)	0.6482(05)	6.5(5)
O(52)	0.0208(05)	0.5967(06)	0.5427(05)	6.4(5)
O(61)	0.3730(06)	0.8428(07)	0.4825(07)	8.3(6)
O(62)	0.1723(07)	0.9219(07)	0.2556(07)	9.6(7)
O(63)	0.3085(06)	0.6731(07)	0.2704(06)	7.5(6)
C(1)	0.3166(06)	0.3467(07)	0.4712(06)	3.0(5)
C(2)	0.3747(06)	0.2738(07)	0.4716(06)	2.8(5)
C(3)	0.3496(06)	0.2222(07)	0.5296(06)	3.1(5)
C(4)	0.2899(06)	0.2974(07)	0.5191(06)	2.7(5)
C(5)	0.1494(06)	0.7924(07)	0.4101(06)	3.3(5)
C(6)	0.1036(06)	0.8713(07)	0.4219(07)	3.6(5)
C(7)	0.0626(06)	0.8045(07)	0.4550(07)	3.8(5)
C(8)	0.1175(06)	0.7332(07)	0.4483(06)	3.0(5)
C(11)	0.4298(08)	0.3762(08)	0.6560(07)	3.7(6)
C(12)	0.3805(07)	0.5365(09)	0.5740(06)	3.7(6)
C(13)	0.3107(07)	0.4623(08)	0.6705(08)	4.2(6)
C(21)	0.1206(07)	0.2605(08)	0.4758(08)	4.5(7)
C(22)	0.1421(07)	0.3631(08)	0.6092(08)	4.3(6)
C(23)	0.2386(07)	0.2139(09)	0.6180(07)	3.9(6)
C(31)	0.2139(07)	0.4431(08)	0.3248(08)	3.9(6)
C(32)	0.3652(07)	0.4918(08)	0.4019(07)	3.9(6)
C(41)	0.1036(07)	0.6421(09)	0.2409(08)	4.9(7)
C(42)	0.0521(07)	0.5499(09)	0.3419(06)	3.9(6)
C(43)	−0.0069(08)	0.7123(09)	0.2814(07)	5.1(7)
C(51)	0.2202(07)	0.6471(08)	0.5891(07)	3.8(6)
C(52)	0.0709(07)	0.6003(08)	0.5235(07)	3.9(6)
C(61)	0.3168(08)	0.8134(10)	0.4354(09)	5.6(8)
C(62)	0.1940(08)	0.8630(09)	0.2967(09)	6.1(8)
C(63)	0.2794(08)	0.7100(09)	0.3046(08)	5.5(8)
C(71)	0.3488(07)	0.2240(08)	0.3936(06)	3.8(6)
C(72)	0.4606(06)	0.3003(08)	0.5045(06)	4.1(6)
C(73)	0.3696(08)	0.2753(09)	0.3352(08)	6.2(7)
C(74)	0.3917(08)	0.1337(09)	0.4065(08)	6.0(7)
C(75)	0.2610(08)	0.2050(08)	0.3552(07)	4.9(6)
C(81)	0.1549(07)	0.9386(07)	0.4856(07)	3.9(6)
C(82)	0.0470(08)	0.9194(08)	0.3494(08)	6.1(7)
C(83)	0.2148(07)	0.8912(08)	0.5587(08)	5.5(7)
C(84)	0.2018(08)	0.9994(08)	0.4561(09)	6.3(7)
C(85)	0.1035(08)	0.9976(08)	0.5097(08)	6.1(7)
C(101)	0.5724(09)	−0.0171(11)	0.3290(10)	8.1(4)
C(102)	0.5391(10)	−0.0803(11)	0.2717(09)	7.9(4)
C(103)	0.4812(10)	−0.1311(11)	0.2672(09)	8.0(4)
C(104)	0.4514(09)	−0.1241(10)	0.3213(09)	7.4(4)
C(105)	0.4823(09)	−0.0625(11)	0.3773(09)	7.3(4)
C(106)	0.5396(09)	−0.0109(10)	0.3820(09)	7.5(4)

η^2-$\overline{\mathrm{C_2CH_2C}}$(Me)^{t}Bu]($\mu_3$-S) (**5**), the ruthenium homologue of **6** (see below).

An ORTEP diagram of the molecular structure of compound **3** is shown in Figure 3. Final atomic positional parameters are listed in Table 8, and selected interatomic distances and angles are listed in Table 9 and 10. The molecule was disordered in the crystal such that the Me and ^{t}Bu groups were interchanged. This resulted in two closely spaced positions for both of the uncoordinated ring carbons. This disorder model was refined very well. The molecules consists of a rhomboidal cluster of four metal

Table 6. Intramolecular Distances for 2[a]

Ru(1)–Ru(2)	2.777(1)	Ru(5)–S(1)	2.506(3)
Ru(1)–Ru(3)	2.816(1)	Ru(5)–S(2)	2.370(3)
Ru(1)–S(1)	2.409(3)	Ru(5)–C(8)	2.00(1)
Ru(1)–C(1)	2.39(1)	Ru(6)–S(2)	2.369(3)
Ru(1)–C(4)	2.28(1)	Ru(6)–C(5)	2.05(1)
Ru(2)–S(1)	2.377(3)	C(1)–C(2)	1.55(1)
Ru(2)–C(4)	2.03(1)	C(1)–C(4)	1.42(1)
Ru(3)–S(1)	2.376(3)	C(2)–C(3)	1.58(1)
Ru(3)–S(2)	2.507(3)	C(3)–C(4)	1.55(1)
Ru(3)–C(1)	2.02(1)	C(5)–C(6)	1.54(1)
Ru(4)–Ru(5)	2.807(2)	C(5)–C(8)	1.43(1)
Ru(4)–Ru(6)	2.771(1)	C(6)–C(7)	1.55(1)
Ru(4)–S(2)	2.422(3)	C(7)–C(8)	1.53(1)
Ru(4)–C(5)	2.40(1)	Ru–C (av)	1.90(1)
Ru(4)–C(8)	2.29(1)	O–C (av)	1.14(1)

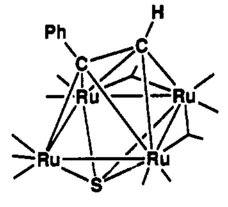
[a] Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses.

Table 7. Intramolecular Bond Angles for 2[a]

Ru(2)–Ru(1)–Ru(3)	91.95(4)	C(1)–C(4)–C(3)	92.0(8)
S(1)–Ru(3)–S(2)	77.9(1)	C(6)–C(5)–C(8)	91.6(8)
Ru(5)–Ru(4)–Ru(6)	91.85(4)	C(5)–C(6)–C(7)	87.7(8)
S(1)–Ru(5)–S(2)	78.0(1)	C(6)–C(7)–C(8)	87.6(8)
C(2)–C(1)–C(4)	93.6(9)	C(5)–C(8)–C(7)	92.5(9)
C(1)–C(2)–C(3)	86.4(7)	Ru–C–O (av)	176(1)
C(2)–C(3)–C(4)	87.8(7)		

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

atoms. On one side of the cluster there is a quadruply bridging sulfido ligand, while on the other side there is the quadruply bridging substituted cyclobutyne ligand $\overline{\mathrm{C_2CH_2C}}$(Me)^{t}Bu. The unsaturated C(1)–C(4) distance 1.416(7) Å in the cyclobutyne ligand is not significantly different from those found in compounds **2**, **5**, and **6**. Thus, it can be concluded that the μ_4 coordination probably produces a stabilization of the cyclobutyne that is very similar to that of the μ_3 coordination. This C–C distance is also very similar to the alkyne C–C distances of 1.395(6) and 1.411(6) Å reported for the compounds Ru$_4$(CO)$_{11}$(μ_4-η^2-HC$_2$Ph)(μ_4-S) (**8**)[10] and Ru$_5$(CO)$_{13}$(μ_4-η^2-HC$_2$Ph)(μ_4-S)(**9**),[10] respectively, which contain unstrained HC$_2$Ph ligands, and 1.402(6) Å reported for the PhC$_2$Ph ligand in the phosphinidene complex Ru$_4$(CO)$_{11}$(μ_4-η^2-PhC$_2$Ph)(μ_4-PPh).[11] The metal–sulfur distances are similar to those found for **8** and **9** and other ruthenium cluster complexes that contain quadruply bridging sulfido ligands.[12] The molecule contains 11 carbonyl ligands. Nine are linear terminal ligands, and two are bridges spanning the Ru-



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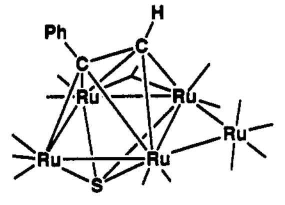

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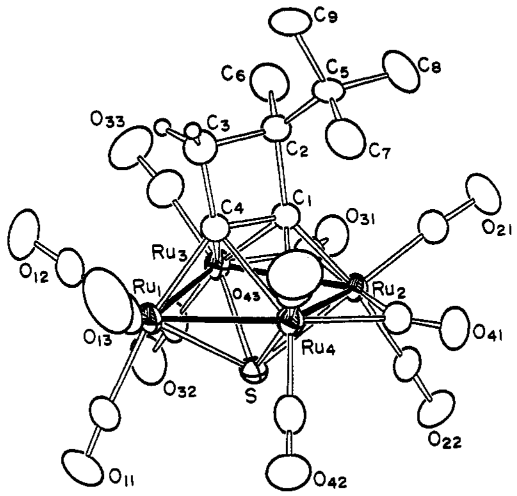


Figure 3. ORTEP diagram of $Ru_4(CO)_{11}[\mu_4\text{-}\eta^2\text{-}\overline{C_2CH_2C}(Me)^tBu](\mu_4\text{-}S)$ (3) showing 50% probability thermal ellipsoids.

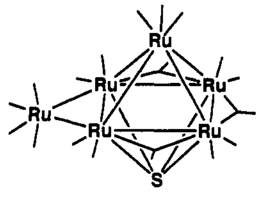
Table 8. Positional Parameters and *B*(eq) Values for 3

atom	*x*	*y*	*z*	*B*(eq) (Å^2)
Ru(1)	0.17351(04)	0.25112(04)	0.92830(04)	4.16(2)
Ru(2)	0.15762(04)	0.25100(04)	0.54748(04)	3.47(2)
Ru(3)	0.18637(04)	0.41164(04)	0.73733(04)	3.92(2)
Ru(4)	0.18606(04)	0.09076(04)	0.73766(04)	3.91(2)
S	0.03836(12)	0.25066(13)	0.72669(12)	3.80(6)
O(11)	−0.0855(05)	0.2497(06)	1.0324(05)	9.3(3)
O(12)	0.3006(07)	0.4411(07)	1.0899(05)	12.4(5)
O(13)	0.3016(07)	0.0632(07)	1.0916(05)	12.6(5)
O(21)	0.2896(05)	0.2533(06)	0.3192(04)	9.7(3)
O(22)	−0.1041(04)	0.2490(04)	0.3771(04)	6.0(2)
O(31)	0.1566(04)	0.5143(04)	0.4782(04)	5.9(2)
O(32)	−0.0347(05)	0.5602(05)	0.7882(05)	8.5(3)
O(33)	0.3587(06)	0.6152(05)	0.8256(06)	9.4(3)
O(41)	0.1562(04)	−0.0133(04)	0.4789(04)	5.9(2)
O(42)	−0.0357(05)	−0.0610(05)	0.7884(05)	8.4(3)
O(43)	0.3566(06)	−0.1111(05)	0.8286(06)	9.6(3)
C(1)	0.3196(05)	0.2519(05)	0.6885(04)	3.8(2)
C(2A)	0.4747(17)	0.2914(13)	0.7009(16)	3.9(7)
C(2B)	0.4717(15)	0.2210(16)	0.7011(15)	4.3(7)
C(3A)	0.468(03)	0.2850(18)	0.843(03)	5(1)
C(3B)	0.471(03)	0.2271(19)	0.848(03)	5(1)
C(4)	0.3225(05)	0.2517(05)	0.8188(05)	4.4(3)
C(5A)	0.5653(11)	0.1992(13)	0.6506(11)	4.0(6)
C(5B)	0.5659(12)	0.2964(16)	0.6493(12)	5.2(8)
C(6)	0.5141(07)	0.4161(06)	0.6634(07)	6.6(4)
C(7)	0.5142(07)	0.0840(06)	0.6647(07)	6.8(4)
C(8A)	0.569(03)	0.2171(19)	0.510(03)	7(1)
C(8B)	0.568(03)	0.282(02)	0.512(03)	7(1)
C(9A)	0.702(03)	0.2164(20)	0.725(03)	7(1)
C(9B)	0.704(03)	0.2764(20)	0.711(03)	7(1)
C(11)	0.0096(07)	0.2503(07)	0.9985(05)	6.0(4)
C(12)	0.2501(08)	0.3710(08)	1.0305(06)	7.5(4)
C(13)	0.2468(08)	0.1326(08)	1.0299(06)	7.8(5)
C(21)	0.2449(06)	0.2529(06)	0.4090(05)	5.5(3)
C(22)	−0.0072(06)	0.2497(05)	0.4387(05)	4.3(3)
C(31)	0.1642(05)	0.4417(06)	0.5524(05)	4.7(3)
C(32)	0.0518(07)	0.5057(06)	0.7692(05)	5.6(3)
C(33)	0.2983(07)	0.5379(07)	0.7898(06)	6.2(4)
C(41)	0.1649(05)	0.0609(06)	0.5528(05)	4.6(3)
C(42)	0.0494(07)	−0.0052(06)	0.7689(05)	5.5(3)
C(43)	0.2965(07)	−0.0335(06)	0.7916(06)	6.0(4)

(2)–Ru(3) and Ru(2)–Ru(4) bonds. This arrangement is similar to that found in 8. The ^{13}C NMR spectrum of 3 at 25 °C exhibits an intense singlet at 200.33 ppm that is attributed to an average signal of the 11 carbonyl ligands. Evidently, the molecule is dynamically active and all of the CO ligands are averaged on the NMR time scale at 25 °C. Attempts to obtain spectra at lower temperatures were unsuccessful due to the low solubility of the complex. Two small resonances were observed at 182.04 and 190.92 ppm. These are attributed to the coordinated alkyne carbon atoms. The alkyne resonances for the cyclobutyne ligand in 7 were observed at 156.9 and 193.9 ppm.[2] If the cyclobutyne and sulfido ligands serve as four-electron donors, the complex contains a total of 62 valence electrons, which is two less than that required by the 18-electron rule, but if the cluster is viewed as a pentagonal-bipyramidal core consisting of the atoms Ru_4SC_2, its total polyhedral electron count is 70, which is in agreement with the polyhedral skeletal electron pair theory.[13]

It was found that compound 1 can be decarbonylated and transformed into 3 in 26% yield by treatment with Me_3NO in refluxing methylene chloride solvent. Similar transformations involving acyclic alkynes linked to phosphorus and sulfur have been reported previously.[11,14]

A minor product having the formula $Ru_6(CO)_{16}[\mu_4\text{-}CCHCH{=}C(Me)^tBu](\mu_4\text{-}S)$ (4; 1%) was also isolated. An ORTEP diagram of the molecular structure of compound 4 is shown in Figure 4. Final atomic positional parameters are listed in Table 11, and selected interatomic distances and angles are listed in Tables 12 and 13. The molecule contains six metal atoms arranged in the form of an edge-shared square pyramid. There is a quadruply bridging sulfido ligand across the square base. This portion of the molecule is very similar to that of the compounds $Ru_6(CO)_{18}(\mu_4\text{-}S)$ (10)[12b] and $Ru_6(CO)_{17}(\mu\text{-}H)_2(\mu_4\text{-}S)$ (11).[15] In addition, compound 4 also contains a quadruply bridging $CH{=}C(Me)^tBu$ substituted-vinylidene ligand. The carbon C(1) is bonded to four metal atoms, three in the square pyramid and also the edge-bridging ruthenium Ru(6). The carbon C(2) is bonded only to Ru(6). The C(1)–C(2) distance is short (1.43(1) Å) and indicative of some multiple-bond character, and there is a full double bond between the carbons C(3) and C(4) (1.33(1) Å). The hydrogen atom H(1) resonates at 5.76 ppm and is coupled ($^3J_{HH}$ = 9.3 Hz) to H(2) at 5.53 ppm. The latter is weakly coupled ($^4J_{HH}$ = 1.2 Hz) to the hydrogen atoms on the methyl group C(6). Similarly coordinated μ_4-vinylidene ligands have been reported previously.[16] Unlike 9 and 10, 4 has no bridging carbonyl ligands, although one (C(43)–O(43)) is semibridging (Ru(4)–C(43)–O(43) = 161(1)°).



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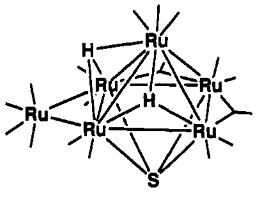

11

It was found that the dimer 2 could be split easily by treatment with CO at 25 °C for 12 h to yield two of the triruthenium complexes $Ru_3(CO)_9[\mu_3\text{-}\overline{C_2CH_2C}(Me)^tBu](\mu_3\text{-}S)$ (5) in 81% yield. For comparison of its metrical parameters with related cyclobutyne containing molecules, compound 5 was also subjected to a careful X-ray structural analysis. An ORTEP diagram of the molecular structure of compound 5 is shown in Figure 5. Final atomic positional parameters are listed in Table 14, and selected

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[15] Adams, R. D.; Babin, J. E.; Tasi, M. A.; Wolfe, T. A. *New J. Chem.* **1988**, *12*, 481.

[16] (a) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197. (b) Bruce, M. I.; Swincer, A. G. *Adv. Organomet. Chem.* **1983**, *22*, 59.

Table 9. Intramolecular Distances for 3[a]

Ru(1)–Ru(3)	2.8058(7)	C(1)–C(2B)	1.61(2)
Ru(1)–Ru(4)	2.8015(7)	C(1)–C(4)	1.416(7)
Ru(1)–S	2.432(1)	C(2A)–C(3A)	1.56(4)
Ru(1)–C(4)	2.091(5)	C(2A)–C(5A)	1.57(2)
Ru(2)–Ru(3)	2.7640(6)	C(2A)–C(6)	1.57(2)
Ru(2)–Ru(4)	2.7635(6)	C(2B)–C(3B)	1.60(3)
Ru(2)–S	2.462(1)	C(2B)–C(5B)	1.48(2)
Ru(2)–C(1)	2.113(5)	C(2B)–C(7)	1.71(2)
Ru(2)–C(31)	2.207(7)	C(3A)–C(4)	1.55(3)
Ru(2)–C(41)	2.201(7)	C(3B)–C(4)	1.56(3)
Ru(3)–S	2.411(2)	C(5A)–C(7)	1.45(2)
Ru(3)–C(1)	2.417(5)	C(5A)–C(8A)	1.55(3)
Ru(3)–C(4)	2.421(6)	C(5A)–C(9A)	1.55(3)
Ru(3)–C(31)	2.024(6)	C(5B)–C(6)	1.50(2)
Ru(4)–S	2.399(2)	C(5B)–C(8B)	1.51(4)
Ru(4)–C(1)	2.432(5)	C(5B)–C(9B)	1.51(3)
Ru(4)–C(4)	2.430(6)	Ru–C (av)	1.89(1)
Ru(4)–C(41)	2.024(6)	O–C (av)	1.14(1)
C(1)–C(2A)	1.67(2)		

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

Table 10. Intramolecular Bond Angles for 3[a]

Ru(3)–Ru(1)–Ru(4)	82.89(2)	C(3A)–C(2A)–C(5A)	115(1)
Ru(3)–Ru(2)–Ru(4)	84.36(2)	C(1)–C(2B)–C(3B)	86(1)
Ru(1)–Ru(3)–Ru(2)	95.64(2)	C(1)–C(2B)–C(5B)	122(1)
Ru(1)–Ru(4)–Ru(2)	95.75(2)	C(3B)–C(2B)–C(5B)	117(2)
Ru(1)–S–Ru(2)	115.01(5)	C(2A)–C(3A)–C(4)	92(2)
Ru(1)–S–Ru(3)	70.81(4)	C(2B–C(3B)–C(4)	87(1)
Ru(1)–S–Ru(4)	70.89(4)	C(1)–C(4)–C(3A)	93(1)
Ru(2)–S–Ru(3)	69.12(4)	C(1)–C(4)–C(3B)	95(1)
Ru(2)–S–Ru(4)	69.29(4)	Ru(2)–C(31)–O(31)	135.0(5)
Ru(3)–S–Ru(4)	101.01(5)	Ru(3)–C(31)–O(31)	143.5(5)
C(2A)–C(1)–C(4)	92.2(7)	Ru(2)–C(41)–O(41)	135.7(5)
C(2B)–C(1)–C(4)	92.1(7)	Ru(4)–C(41)–O(41)	142.7(5)
C(1)–C(2A)–C(3A)	83(2)	Ru–C–O (av)	176(1)
C(1)–C(2A)–C(5A)	114(1)		

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

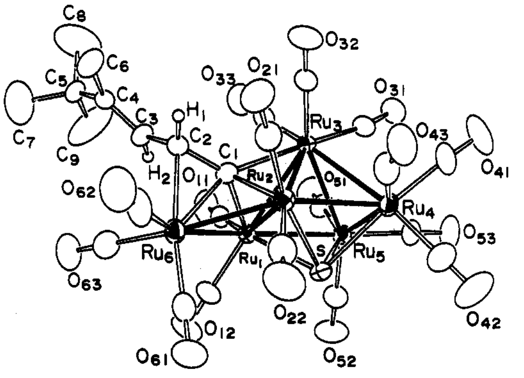

Figure 4. ORTEP diagram of $Ru_6(CO)_{16}[\mu_4\text{-}CCHCH{=}C(Me)^tBu](\mu_4\text{-}S)$ (4) showing 35% probability thermal ellipsoids.

Table 11. Positional Parameters and *B*(eq) Values for 4

atom	*x*	*y*	*z*	*B*(eq) (Å^2)
Ru(1)	0.32152(05)	0.19970(07)	0.19299(04)	2.96(4)
Ru(2)	0.15057(05)	0.17953(07)	0.18566(05)	3.38(4)
Ru(3)	0.19461(05)	0.28495(07)	0.06715(04)	3.12(4)
Ru(4)	0.13353(05)	0.40883(08)	0.17365(05)	3.83(4)
Ru(5)	0.30657(05)	0.42568(07)	0.17720(05)	3.33(4)
Ru(6)	0.25648(06)	–0.00248(08)	0.22469(05)	3.82(4)
S	0.25156(17)	0.3148(02)	0.26131(14)	3.6(1)
O(11)	0.4556(06)	0.1882(07)	0.1105(05)	7.0(5)
O(12)	0.4632(06)	0.1180(08)	0.3270(05)	8.2(5)
O(21)	0.0020(05)	0.0477(08)	0.0878(05)	6.9(5)
O(22)	0.0958(06)	0.1165(09)	0.3245(06)	8.4(6)
O(31)	0.1717(05)	0.5059(07)	–0.0142(05)	6.0(4)
O(32)	0.0319(06)	0.1955(08)	–0.0435(06)	9.1(5)
O(33)	0.2923(07)	0.2059(09)	–0.0397(05)	9.2(6)
O(41)	0.0426(07)	0.5885(09)	0.0648(06)	10.2(7)
O(42)	0.1045(07)	0.5432(11)	0.3016(07)	11.3(8)
O(43)	–0.0401(06)	0.3074(08)	0.1439(07)	8.7(6)
O(51)	0.4121(06)	0.4424(07)	0.0670(05)	6.7(5)
O(52)	0.4625(06)	0.4780(09)	0.3094(05)	8.1(5)
O(53)	0.2525(06)	0.6656(08)	0.1644(06)	8.2(6)
O(61)	0.3013(07)	0.0317(09)	0.3972(05)	8.7(6)
O(62)	0.1232(06)	–0.1784(08)	0.2156(06)	8.3(6)
O(63)	0.4011(06)	–0.1670(08)	0.2376(06)	7.7(5)
C(1)	0.2273(06)	0.1087(08)	0.1273(06)	3.4(5)
C(2)	0.2217(06)	0.0003(09)	0.0956(05)	3.4(5)
C(3)	0.2860(06)	–0.0445(09)	0.0616(06)	3.8(5)
C(4)	0.2751(06)	–0.1296(09)	0.0139(06)	3.2(5)
C(5)	0.3424(07)	–0.1674(09)	–0.0216(07)	4.4(6)
C(6)	0.1942(08)	–0.1925(10)	–0.0086(08)	6.6(7)
C(7)	0.3689(12)	–0.2830(15)	0.0053(12)	12(1)
C(8)	0.3141(12)	–0.170(02)	–0.1040(09)	14(1)
C(9)	0.4222(11)	–0.1021(17)	0.0027(12)	14(1)
C(11)	0.4038(07)	0.1910(09)	0.1429(06)	4.3(5)
C(12)	0.4068(08)	0.1446(10)	0.2774(07)	5.3(6)
C(21)	0.0561(07)	0.0971(10)	0.1245(07)	4.7(6)
C(22)	0.1198(07)	0.1386(10)	0.2727(08)	5.2(6)
C(31)	0.1821(08)	0.4287(10)	0.0211(07)	4.9(6)
C(32)	0.0919(08)	0.2282(09)	0.0004(06)	5.0(6)
C(33)	0.2570(08)	0.2343(10)	0.0037(07)	5.1(6)
C(41)	0.0767(08)	0.5215(11)	0.1023(08)	6.2(7)
C(42)	0.1147(08)	0.4924(12)	0.2535(08)	6.2(7)
C(43)	0.0306(09)	0.3273(11)	0.1557(08)	6.1(7)
C(51)	0.3702(08)	0.4357(10)	0.1074(07)	5.0(6)
C(52)	0.4044(08)	0.4593(10)	0.2607(07)	4.8(6)
C(53)	0.2673(07)	0.5748(11)	0.1689(07)	5.1(6)
C(61)	0.2850(08)	0.0193(10)	0.3325(08)	5.3(6)
C(62)	0.1746(09)	–0.1145(11)	0.2206(08)	6.1(7)
C(63)	0.3478(08)	–0.1072(11)	0.2331(07)	5.1(7)

Table 12. Intramolecular Distances for 4[a]

Ru(1)–Ru(2)	2.777(1)	Ru(4)–S	2.411(3)
Ru(1)–Ru(3)	2.816(1)	Ru(5)–S	2.413(3)
Ru(1)–Ru(5)	2.757(1)	Ru(6)–C(1)	2.18(1)
Ru(1)–Ru(6)	2.800(1)	Ru(6)–C(2)	2.27(1)
Ru(1)–S	2.384(3)	C(1)–C(2)	1.43(1)
Ru(1)–C(1)	1.99(1)	C(2)–C(3)	1.48(1)
Ru(2)–Ru(3)	2.796(1)	C(3)–C(4)	1.33(1)
Ru(2)–Ru(4)	2.795(1)	C(4)–C(5)	1.51(1)
Ru(2)–Ru(6)	2.769(1)	C(4)–C(6)	1.48(1)
Ru(2)–S	2.453(3)	C(5)–C(7)	1.51(2)
Ru(2)–C(1)	2.06(1)	C(5)–C(8)	1.45(2)
Ru(3)–Ru(4)	2.870(1)	C(5)–C(9)	1.48(2)
Ru(3)–Ru(5)	2.863(1)	Ru–C (av)	1.90(1)
Ru(3)–C(1)	2.39(1)	O–C (av)	1.14(1)
Ru(4)–Ru(5)	2.826(1)		

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

interatomic distances and angles are listed in Tables 15 and 16. The molecule is structurally analogous to its osmium homologue **6**. It contains one triply bridging substituted cyclobutyne ligand, $\overline{C_2CH_2C}(Me)^tBu$, and one triply bridging sulfido ligand and has only two metal–metal bonds. The metal–metal and metal–sulfur bond distances are very similar to those in **2** and the related molecule $Ru_3(CO)_9[\mu_3\text{-}HCCPh](\mu_3\text{-}S)$ (**12**), which contains the unstrained alkyne ligand HC_2Ph.[10] The Ru–S distances to the outer metal atoms Ru(1) and Ru(3) (2.379(1) and 2.372(2) Å) are significantly longer than the corresponding distances in the two independent molecules found in the crystal of **12** (2.348(4), 2.332(4), 2.345(4), and 2.331(3) Å), although the difference is not large. The Ru-S distance to the central metal atom Ru(2) (2.406(1) Å) is not significantly different from those in **12** (2.410(4) and 2.415(4) Å). The carbon–carbon distances in the ring are not significantly different from those found in **2** or **6**.[4] In particular, the C–C distance for the alkyne carbon–carbon bond C(1)–C(4) (1.424(7) Å) is essentially the same as those found in **2** (1.42(1) and 1.43(1) Å) and **6** (1.40(2) Å) and is also not significantly different from the values 1.42(2) and 1.43(2) Å found for the coordinated alkyne carbon

Table 13. Intramolecular Bond Angles for 4[a]

Ru(2)–Ru(1)–Ru(5)	91.43(4)	Ru(1)–C(1)–Ru(3)	79.4(3)
Ru(2)–Ru(1)–Ru(6)	59.52(3)	Ru(1)–C(1)–Ru(6)	84.2(4)
Ru(3)–Ru(1)–Ru(5)	61.81(3)	Ru(2)–C(1)–Ru(3)	77.4(3)
Ru(5)–Ru(1)–Ru(6)	149.69(4)	Ru(2)–C(1)–Ru(6)	81.4(4)
Ru(1)–Ru(2)–Ru(4)	89.57(4)	Ru(3)–C(1)–Ru(6)	153.8(5)
Ru(1)–Ru(2)–Ru(6)	60.66(3)	C(1)–C(2)–C(3)	123(1)
Ru(4)–Ru(2)–Ru(6)	148.54(4)	C(2)–C(3)–C(4)	126(1)
Ru(2)–Ru(4)–Ru(5)	89.63(4)	C(3)–C(4)–C(5)	123(1)
Ru(1)–Ru(5)–Ru(4)	89.33(4)	C(3)–C(4)–C(6)	121(1)
Ru(1)–Ru(6)–Ru(2)	59.82(3)	C(5)–C(4)–C(6)	116(1)
Ru(1)–C(1)–Ru(2)	86.4(4)	Ru–C–O (av)	176(1)

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

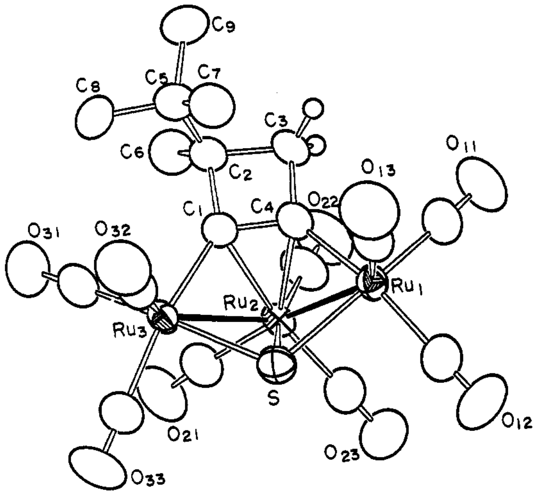

Figure 5. ORTEP diagram of Ru$_3$(CO)$_9$[μ_3-η^2-$\overline{C_2CH_2C}$(Me)-^{t}Bu](μ_3-S) (5) showing 50% probability thermal ellipsoids.

Table 14. Positional Parameters and *B*(eq) Values for 5

atom	*x*	*y*	*z*	*B*(eq) (Å^2)
Ru(1)	1.03056(04)	0.24892(02)	0.78699(03)	3.06(2)
Ru(2)	1.01768(04)	0.09522(02)	0.81718(03)	2.88(2)
Ru(3)	0.71682(04)	0.10357(02)	0.84257(03)	3.11(2)
S	0.89538(15)	0.18990(08)	0.90283(09)	3.93(7)
O(11)	1.2434(05)	0.2767(03)	0.6363(03)	8.0(3)
O(12)	1.2253(06)	0.3274(03)	0.9403(04)	8.7(3)
O(13)	0.8268(06)	0.3754(03)	0.7302(04)	7.8(3)
O(21)	0.9453(05)	–0.0547(02)	0.9042(03)	7.2(3)
O(22)	1.2060(05)	0.0258(03)	0.6731(03)	7.9(3)
O(23)	1.2837(05)	0.1186(03)	0.9513(03)	7.4(3)
O(31)	0.5556(06)	–0.0373(03)	0.7719(03)	9.2(3)
O(32)	0.4650(05)	0.2109(03)	0.8170(03)	7.6(3)
O(33)	0.6519(06)	0.0623(03)	1.0465(03)	8.1(3)
C(1)	0.8060(05)	0.1248(03)	0.7184(03)	3.4(2)
C(2)	0.7860(06)	0.1029(03)	0.6137(03)	4.0(3)
C(3)	0.9255(06)	0.1517(03)	0.5988(03)	4.0(3)
C(4)	0.9249(05)	0.1737(03)	0.7019(03)	3.5(2)
C(5)	0.6455(06)	0.1360(03)	0.5629(04)	4.6(3)
C(6)	0.8065(07)	0.0185(03)	0.5944(04)	5.6(3)
C(7)	0.6252(07)	0.2197(03)	0.5849(04)	5.4(3)
C(8)	0.5070(07)	0.0950(04)	0.5917(04)	6.0(3)
C(9)	0.6586(07)	0.1293(04)	0.4562(04)	6.4(4)
C(11)	1.1648(06)	0.2671(03)	0.6935(04)	5.1(3)
C(12)	1.1532(07)	0.2992(04)	0.8846(05)	5.4(3)
C(13)	0.9082(07)	0.3291(03)	0.7533(04)	4.8(3)
C(21)	0.9606(07)	0.0031(04)	0.8713(04)	5.1(3)
C(22)	1.1325(07)	0.0498(03)	0.7273(04)	5.2(3)
C(23)	1.1839(07)	0.1106(03)	0.9000(05)	5.2(3)
C(31)	0.6156(08)	0.0156(04)	0.7965(04)	5.9(4)
C(32)	0.5591(07)	0.1685(04)	0.8275(04)	5.2(3)
C(33)	0.6766(06)	0.0772(03)	0.9723(04)	5.2(3)

Table 15. Intramolecular Distances for 5[a]

Ru(1)–Ru(2)	2.7806(7)	C(1)–C(4)	1.424(7)
Ru(1)–S	2.379(1)	C(2)–C(3)	1.569(7)
Ru(1)–C(4)	2.026(5)	C(2)–C(5)	1.557(8)
Ru(2)–Ru(3)	2.7983(8)	C(2)–C(6)	1.546(7)
Ru(2)–S	2.406(1)	C(3)–C(4)	1.538(7)
Ru(2)–C(1)	2.394(5)	C(5)–C(7)	1.542(8)
Ru(2)–C(4)	2.297(5)	C(5)–C(8)	1.539(8)
Ru(3)–S	2.372(2)	C(5)–C(9)	1.554(8)
Ru(3)–C(1)	2.045(5)	Ru–C (av)	1.910(7)
C(1)–C(2)	1.560(7)	C–O (av)	1.142(7)

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

Table 16. Intramolecular Bond Angles for 5[a]

Ru(2)–Ru(1)–S	54.91(3)	Ru(2)–S–Ru(3)	71.70(4)
Ru(1)–Ru(2)–Ru(3)	91.07(2)	C(2)–C(1)–C(4)	92.3(4)
Ru(1)–Ru(2)–S	54.03(3)	C(1)–C(2)–C(3)	86.7(4)
Ru(3)–Ru(2)–S	53.60(4)	C(2)–C(3)–C(4)	87.8(3)
Ru(2)–Ru(3)–S	54.70(3)	C(1)–C(4)–C(3)	92.9(4)
Ru(1)–S–Ru(2)	71.06(4)	Ru–C–O (av)	177.0(6)
Ru(1)–S–Ru(3)	113.85(6)		

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

atoms in the two independent molecules of **12**.[11] However, it should not be inferred on this basis that the cyclobutyne rings in **2**, **3**, and **5** are strain-free. The C–C–C angles involving the alkyne and the attached phenyl carbon in the two molecules of **12** are 116(1) and 114(1)°. In **5** these angles are approximately 22° smaller at 92.3(4) and 92.9(4)°.

We have also found that compound **5** can be converted to **3** in 69% yield by reaction with Ru(CO)$_5$ in refluxing cyclohexane solvent. Similarly, it was reported that compound **12** will react with Ru(CO)$_5$ to yield the tetraruthenium complex **8**.[10]

Discussion

A summary of the results obtained from our investigation of the reaction of Ru$_3$(CO)$_{12}$ with 4-*tert*-butyl-4-methyl-1-(phenylthio)cyclobutene is shown in Scheme 2. Of the four products that were isolated, only compound **2** is based on triruthenium groupings. Compounds **1** and **3** have a metal nuclearity of 4, and compound **4** has a metal nuclearity of 6. This result is in contrast with the reaction of Os$_3$(CO)$_{10}$(NCMe)$_2$ with 4-*tert*-butyl-4-methyl-1-(phenylthio)cyclobutene, where only trinuclear clusters were formed, even though higher temperatures were required to complete the formation of the cyclobutyne ligand.[4] The changes in metal nuclearity can be attributed to the weaker metal–metal bonds in Ru$_3$(CO)$_{12}$ compared to Os$_3$(CO)$_{10}$(NCMe)$_2$. This allows fragmentation and subsequent reaggregation of the metals into larger and more stable cluster complexes. The tendency of Ru$_3$(CO)$_{12}$ to form higher nuclearity clusters in reactions involving thioethers has been observed previously.[17] In all of the products the phenyl group was cleaved from the sulfur atom and one of the hydrogen atoms was cleaved from the substituted cyclobutenyl group. The fate of these groups was not established in this study, but we have previously observed the formation of benzene in the reactions of benzene thiols with osmium carbonyl clusters,[18] and we suspect that benzene was also formed in the reactions reported here. In compounds **2**–**4** the substituted cyclobutenyl ligand was also cleaved from the sulfur atom. In compounds **2** and **3** this resulted in the formation of substituted cyclobutyne ligands. In compound **4** the four-membered ring was opened to produce an alkenyl-substituted vinylidene ligand. It is possible to convert compound **1** to **3**, which

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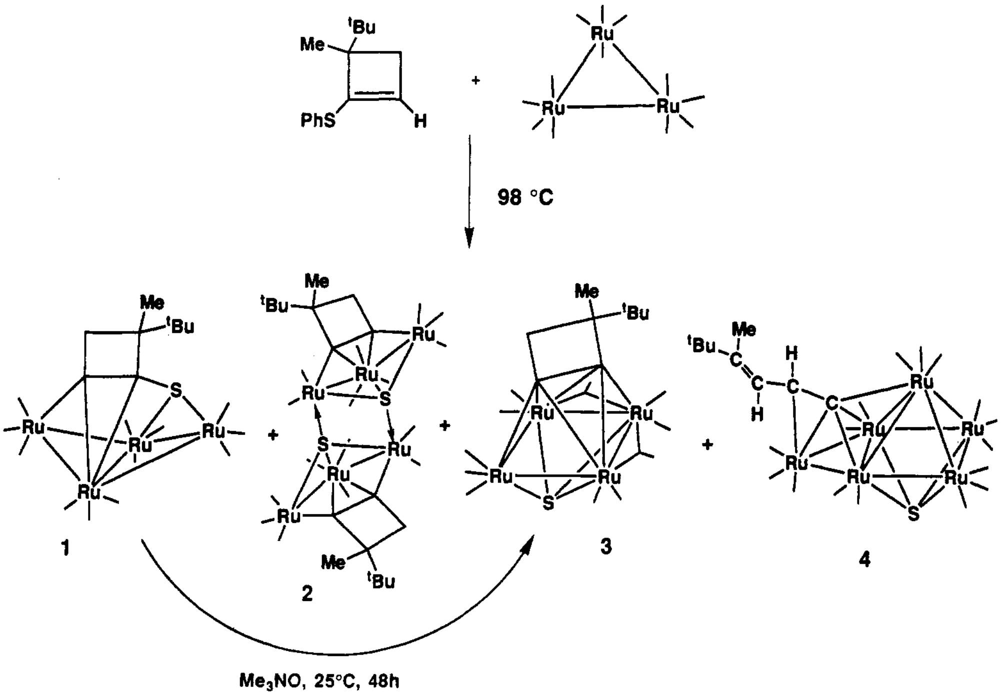
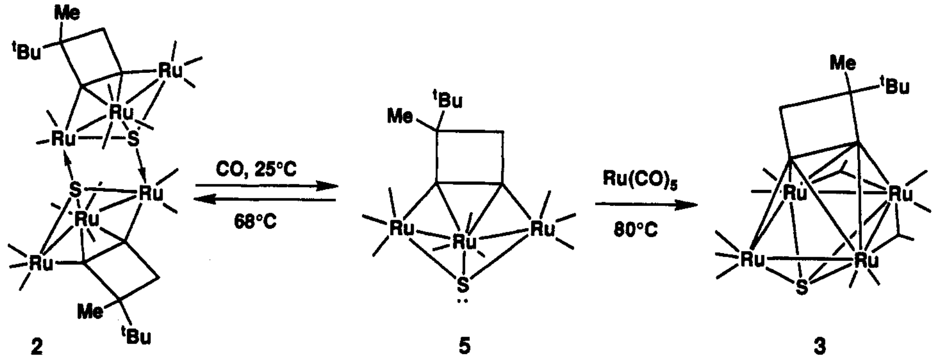
(17) Adams, R. D.; Belinski, J. A. *J. Cluster Sci.* **1990**, *1*, 319.
(18) Adams, R. D.; Yang, L.-W. *J. Am. Chem. Soc.* **1982**, *104*, 4115.

Scheme 2



Scheme 3



suggests that it is probably an intermediate in the formation of 3. Compound 4 was obtained only in very small amounts, and at present we have no information as to how it was formed.

When treated with CO at 1 atm, the dimer 2 was split to yield two of the triruthenium complexes 5 that contain a substituted cyclobutyne ligand (Scheme 3). This reaction is readily reversed by heating to 68 °C. When heated to 80 °C in the presence of $Ru(CO)_5$, compound 5 was enlarged by the addition of a mononuclear ruthenium carbonyl fragment to yield 3. The facile addition of such mononuclear ruthenium fragments to sulfidotriruthenium species could explain why only very small amounts of complex 2 were formed in the original reaction.

We feel that these new results greatly expand our knowledge of the preparation and coordination properties of cyclobutyne ligands. We have now prepared the first example of a quadruply bridging cyclobutyne ligand. It is structurally and spectroscopically similar to the triply bridging cyclobutyne ligands that we have reported in this and previous papers. Our studies show that once it is coordinated to three or more metal atoms, the cyclobutyne ligand is remarkably stable. We are attempting to produce efficient and controlled opening of the cyclobutyne rings in these complexes to see if we can identify the factors that have so far prevented the isolation of this molecule in the free state.

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Supplementary Material Available: Tables of hydrogen atom positional parameters and anisotropic thermal parameters for 1–5 (22 pages). Ordering information is given on any current masthead page.

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