Organometallics 1992, *11*, 607–613

Formation of Thioruthenium Carbonyl Clusters via a Thioallyl Cation Complex

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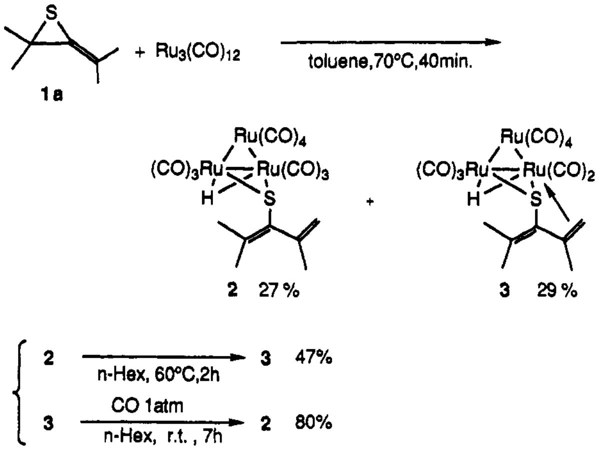
Received June 25, 1991

Tetramethylallene episulfide (**1a**) reacts with $Ru_3(CO)_{12}$ to afford the oxidative addition hydride clusters $Ru_3(CO)_{10}[\mu\text{-}S(C{=}CMe_2)C(Me){=}CH_2](\mu\text{-}H)$ (**2**) and $Ru_3(CO)_9[\mu\text{-}S(C{=}CMe_2)C(Me){=}CH_2](\mu\text{-}H)$ (**3**), respectively. The structure of **2** was characterized crystallographically. The cluster **2** undergoes decarbonylation at 60 °C to form **3** in 47% yield. The cluster **3** can regenerate **2** by bubbling with carbon monoxide under 1 atm of pressure at room temperature, in 80% yield. The chemical correlations leave little doubt about the structure of **3** which has a six-electron donating $(\mu\text{-}S)(\mu\text{-}H)\eta^2$-dimethylpentadiene ligand. The reaction of 1-*tert*-butyl-3,3-diphenylallene 1-episulfide (**1b**) with $Ru_3(CO)_{12}$ resulted in the formation of the cluster $Ru_3(CO)_{10}[2\text{-}(\mu\text{-}S)\text{-}1\text{-}tert\text{-butyl-3-phenylindene}](\mu\text{-}H)$ (**5**). The X-ray structure of **5** shows that intramolecular cyclization has occurred besides C–S bond cleavage. The thioallyl cation complexes **9** and **10** are the intermediates of the formation of clusters **2** and **5**. Upon warming to 80–120 °C, **2** and **5** were finally converted to desulfurized products 2,4-dimethyl-1,3-pentadiene (**6**) (quantitative) and 1-*tert*-butyl-3-phenylindene (**7**) (56%) along with thio cluster $HRu_5(CO)_{15}[2\text{-}(\mu\text{-}S)\text{-}1\text{-}tert\text{-butyl-3-phenylindene}](\mu_4\text{-}S)$ (**8**) (30%).

Introduction

The sulfur ligand has been played central roles in transition-metal chemistry, which exhibits a wide variety of structural geometries and electron-donating capabilities.[1] The cyclic thioethers are also able to serve as a ligand through coordination of sulfur atoms. Recently, studies on the reactions of transition-metal clusters with cyclic thioethers have been widely explored,[2] because of the importance of the hydrodesulfurization (HDS) process.[3] Allene episulfides[4-6] are methylene homologues of thiirane, which easily cleaves the C–S bond to produce β-thioallyl due to a high internal strain. We had already reported formation of (η^4-β-thioallyl)iron tricarbonyl complexes by the reaction of allene episulfides with diiron nonacarbonyl.[7] We report here the formation of thioruthenium carbonyl clusters by the reaction of allene episulfides with triruthenium dodecacarbonyl via thioallyl cation complexes and desulfurization reactions of these thio clusters.

Scheme I



Results and Discussion

Reaction of Tetramethylallene Episulfide (1a) with $Ru_3(CO)_{12}$. The reaction of 1,1,3,3-tetramethylallene episulfide (**1a**) with $Ru_3(CO)_{12}$ has yielded the complexes $Ru_3(CO)_{10}[\mu\text{-}S(C{=}CMe_2)C(Me){=}CH_2](\mu\text{-}H)$ (**2**) and $Ru_3(CO)_9[\mu\text{-}S\text{-}(C{=}CMe_2)C(Me){=}CH_2](\mu\text{-}H)$ (**3**) in yields of 27% and 29%, respectively (Scheme I). The ^1H NMR spectra of **2** and **3** showed the characteristic upfield μ-H resonance at −15.30 and −13.46 ppm in addition to the olefin methylene protons. So the ligands of **2** and **3** are thought to be formed by transfer of a methyl proton of **1a** to the metal–metal bond.[8,9] Although the IR and ^{13}C

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Table I. Crystallographic Data for Diffraction Studies

compd	2	5	8
empirical formula	$Ru_3SO_{10}C_{17}H_{12}$	$Ru_3SO_{10}C_{29}H_{20}$	$Ru_5S_2O_{15}C_{34}H_{20}$
fw	711.55	863.75	1238.01
cryst syst	monoclinic	orthorhombic	monoclinic
lattice params			
a, Å	15.524 (4)	12.795 (2)	24.229 (13)
b, Å	9.901 (1)	14.202 (6)	11.790 (3)
c, Å	30.860 (8)	17.580 (2)	14.830 (8)
α, deg			
β, deg	99.96 (1)		105.33 (2)
γ, deg			
V, $Å^3$	4671.7	3194.6	4085.8
space group	*C*2/*c* (No. 15)	$P2_12_12_1$ (No. 19)	$P2_1/n$ (No. 14)
Z	8	4	4
D_{calc}, g/cm^3	2.02	1.80	2.01
*F*000	2728	1688	2384
μ(Mo Kα), cm^{-1}	20.1	14.9	19.3
temp, °C	23	23	23
$2\theta_{max}$, deg	50	50	50
no. of observns ($I > 3\sigma(I)$)	3389	3002	5496
no. of variables	280	388	508
residuals: *R*; R_w	0.046; 0.057	0.027; 0.041	0.042; 0.048
goodness of fit indicator	3.67	2.86	4.31
max shift in final cycle	0.12	0.59	0.22
largest peak in final diff map, e/$Å^3$	0.39	0.58	1.07

Table II. Intramolecular Distances (Å) for 2

Ru(1)-Ru(2)	2.839 (1)	Ru(3)-S(1)	2.394 (2)
Ru(1)-Ru(3)	2.828 (1)	Ru(3)-C(301)	1.91 (1)
Ru(1)-S(1)	2.397 (3)	Ru(3)-C(302)	1.90 (1)
Ru(1)-C(101)	1.90 (1)	Ru(3)-C(303)	1.91 (1)
Ru(1)-C(102)	1.97 (1)	S(1)-C(11)	1.80 (1)
Ru(1)-C(103)	1.90 (1)	O-C(av)	1.13 (2)
Ru(1)-H(1)	1.57 (2)	C(11)-C(12)	1.36 (2)
Ru(2)-Ru(3)	2.819 (1)	C(11)-C(13)	1.47 (2)
Ru(2)-C(201)	1.92 (1)	C(12)-C(121)	1.51 (2)
Ru(2)-C(202)	1.92 (1)	C(12)-C(122)	1.54 (2)
Ru(2)-C(203)	1.92 (1)	C(13)-C(131)	1.51 (2)
Ru(2)-C(204)	1.95 (1)	C(13)-C(132)	1.37 (1)
Ru(2)-H(1)	1.89 (2)		

Table III. Intramolecular Bond Angles (deg) for 2

Ru(2)-Ru(1)-Ru(3)	59.68 (3)	Ru(1)-S(1)-Ru(3)	72.34 (7)
Ru(2)-Ru(1)-S(1)	81.02 (6)	Ru(1)-S(1)-C(11)	118.2 (3)
Ru(2)-Ru(1)-H(1)	39 (2)	Ru(3)-S(1)-C(11)	110.7 (3)
Ru(3)-Ru(1)-S(1)	53.78 (6)	S(1)-C(11)-C(12)	118.1 (8)
S(1)-Ru(1)-C(101)	91.2 (4)	S(1)-C(11)-C(13)	118.6 (8)
S(1)-Ru(1)-C(102)	102.7 (4)	C(12)-C(11)-C(13)	123 (1)
S(1)-Ru(1)-C(103)	165.6 (4)	C(11)-C(12)-C(121)	123 (1)
Ru(1)-Ru(2)-Ru(3)	59.98 (3)	C(11)-C(12)-C(122)	122 (1)
Ru(1)-Ru(2)-H(1)	31 (7)	C(121)-C(12)-C(122)	115 (1)
Ru(1)-Ru(3)-Ru(2)	60.34 (3)	C(11)-C(13)-C(131)	116.0 (9)
Ru(1)-Ru(3)-S(1)	53.88 (6)	C(11)-C(13)-C(132)	121 (1)
Ru(2)-Ru(3)-S(1)	81.47 (6)	C(131)-C(13)-C(132)	123 (1)
S(1)-Ru(3)-C(301)	94.2 (3)	Ru(1)-H(1)-Ru(2)	109 (2)
S(1)-Ru(3)-C(302)	94.2 (3)	Ru-C-O(av)	176 (0)
S(1)-Ru(3)-C(303)	169.5 (4)		

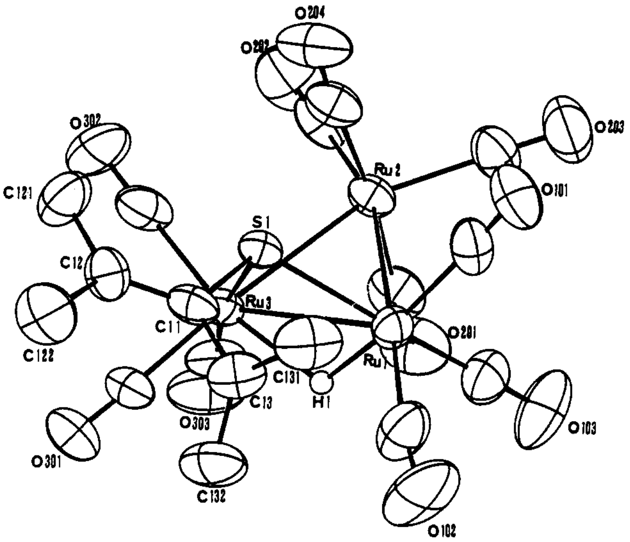

Figure 1. ORTEP drawing of $Ru_3(CO)_{10}[\mu\text{-}S(C{=}CMe_2)C(Me){=}CH_2](\mu\text{-}H)$ (2).

absorptions of 2 and 3 suggested the carbonyl stoichiometry, the spectroscopic data were not sufficient to confirm the ligand structure of 2 and 3. X-ray diffraction analyses of 2 was undertaken and an ORTEP drawing of the molecular structure of 2 is shown in Figure 1. Selected interatomic distances and angles are listed in Tables II and III. The molecule contains a closed triangular cluster of three metal atoms with a $S(C{=}CMe_2)C(Me){=}CH_2$ ligand bridging the edge of the cluster. Three metal–metal bonds including the unbridged and bridged Ru–Ru bonds, 2.839 (1), 2.819 (1), and 2.828 (1) Å, are very similar to the Ru–Ru distances found in $Ru_3(CO)_{12}$, 2.854 (4) Å.[10] The metal–sulfur distances, 2.394–2.397 Å, are similar to the metal–sulfur distances found for bridging thiolato ligands in triruthenium cluster complexes, which usually lies in the range 2.38–2.40 Å.[11] The C–S distance 1.80 Å is a typical of a C–S single bond. Thus the X-ray structure of 2 reveals that the thiolato and hydride ligand bridge the same metal–metal bond. The olefin methylene proton resonances of 3 at 3.20 and 3.52 ppm are further upfield than those of 2 (4.55 and 4.88 ppm). Similarly, the olefin carbon resonances of 3 appear at 62.2 (t) and 96.8 (s) ppm, indicating the presence of metal coordination of one olefin unit. These values are appreciably upfield of the corresponding resonances of 2 (119.9 (t) and 128.1 (s) ppm).

When heated at 60 °C for 2 h, 2 converted to 3 in 47% yield. 3 was allowed to react with carbon monoxide at room temperature for 7 h to afford 2 in 80% yield. This chemical correlation as well as the nice agreement with the expected isotope pattern in the mass spectra of 3 established the carbonyl stoichiometry of 3 as $Ru_3(CO)_9$. Consequently, in the structure of 3, one of the terminal CO

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Scheme II

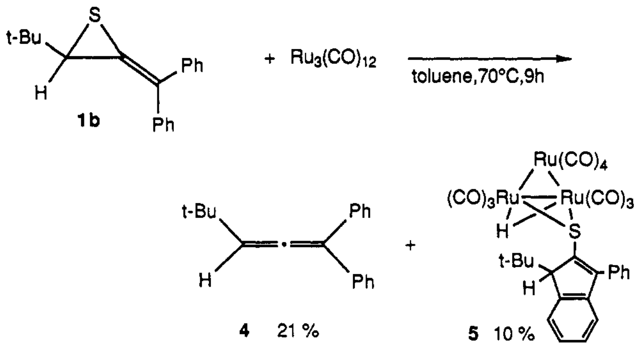

Table IV. Intramolecular Distances (Å) for 5

Ru(1)-Ru(2)	2.833 (1)	C(2)-C(211)	1.48 (1)
Ru(1)-Ru(3)	2.821 (1)	C(2)-C(221)	1.51 (1)
Ru(1)-S	2.414 (2)	C(3)-C(31)	1.60 (1)
Ru(1)-C(101)	1.95 (1)	C(3)-C(216)	1.53 (1)
Ru(1)-C(102)	1.94 (1)	C(31)-C(32)	1.54 (2)
Ru(1)-C(103)	1.92 (1)	C(31)-C(33)	1.54 (2)
Ru(1)-H(1)	2.06 (0)	C(31)-C(34)	1.54 (2)
Ru(2)-Ru(3)	2.834 (1)	C(211)-C(212)	1.40 (1)
Ru(2)-S	2.414 (3)	C(211)-C(216)	1.40 (1)
Ru(2)-C(201)	1.93 (1)	C(212)-C(213)	1.38 (2)
Ru(2)-C(202)	1.91 (1)	C(213)-C(214)	1.41 (2)
Ru(2)-C(203)	1.91 (1)	C(214)-C(215)	1.43 (2)
Ru(2)-H(1)	1.76 (3)	C(215)-C(216)	1.40 (1)
Ru(3)-C(301)	1.95 (1)	C(221)-C(222)	1.38 (1)
Ru(3)-C(302)	1.97 (1)	C(221)-C(226)	1.42 (1)
Ru(3)-C(303)	1.95 (1)	C(222)-C(223)	1.43 (2)
Ru(3)-C(304)	2.03 (1)	C(223)-C(224)	1.43 (2)
S-C(1)	1.777 (9)	C(224)-C(225)	1.34 (2)
C(1)-C(2)	1.35 (1)	C(225)-C(226)	1.42 (2)
C(1)-C(3)	1.55 (1)	O-C(av)	1.11 (7)

ligands of **2** is replaced by the olefin unit of the thiolato ligand, while the S atom and hydride are μ-bonded to the two rutheniums, as shown in Scheme I.

Reaction of *tert*-Butyldiphenylallene Episulfide (1b) with $Ru_3(CO)_{12}$. The reaction of 1-*tert*-butyl-3,3-diphenylallene 1-episulfide (**1b**) with $Ru_3(CO)_{12}$ has yielded the corresponding allene **4** and $Ru_3(CO)_{10}[2\text{-}(\mu\text{-}S)\text{-}1\text{-}$*tert*-butyl-3-phenylindene$](\mu\text{-}H)$ (**5**) in yields of 21% and 10%, respectively (Scheme II). The formation of allene is assumed to be the preferred reaction pathway like the reactions of metal carbonyl cluster complexes with thiiranes.[2] The μ-hydride resonance (−15.32 ppm) and ten carbonyl resonances of **5** demand that **5** have the same $Ru_3(CO)_{10}(\mu\text{-}SR)$ skeleton as **2**, and the ligand structure finally was assigned by X-ray analyses. An ORTEP drawing of the molecular structure of **5** is shown in Figure 2. Selected interatomic distances and angles are listed in Tables IV and V. Compound **5** consists of a closed triangular cluster of three ruthenium atoms with ten linear terminal carbonyl ligands distributed about the cluster, as shown in Figure 2. Compound **5** also contain a 1-*tert*-butyl-3-phenylindene-2-thiolato ligand and the hydride ligand, both of which bridge the same Ru–Ru bond. The Ru–Ru, Ru–S, and C–S bond lengths are comparable with the corresponding values observed in **2**. The X-ray structure of **5** demonstrates the existence of a facile intramolecular cyclization process that leads to the indenyl framework of the thiolato ligand.

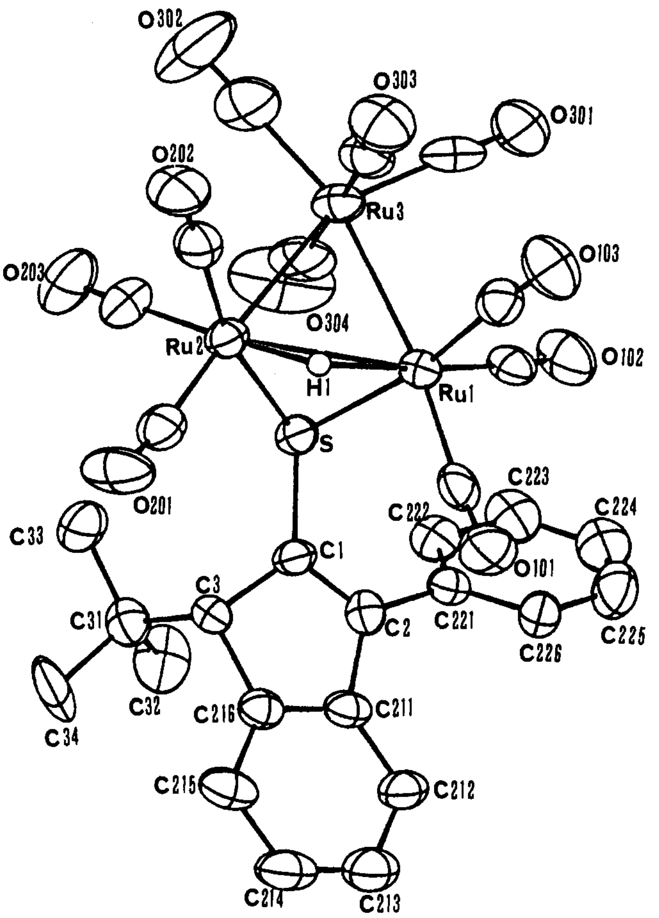

Figure 2. ORTEP drawing of $Ru_3(CO)_{10}[2\text{-}(\mu\text{-}S)\text{-}1\text{-}$*tert*-butyl-3-phenylindene$](\mu\text{-}H)$ (**5**).

Table V. Intramolecular Bond Angles (deg) for 5

Ru(2)-Ru(1)-Ru(3)	60.15 (3)	C(1)-C(2)-C(211)	108.8 (8)
Ru(2)-Ru(1)-S	54.09 (6)	C(1)-C(2)-C(221)	127.7 (9)
Ru(2)-Ru(1)-H(1)	38 (3)	C(211)-C(2)-C(221)	123.5 (8)
Ru(3)-Ru(1)-S	81.74 (6)	C(1)-C(3)-C(31)	112.0 (8)
S-Ru(1)-C(101)	95.2 (3)	C(1)-C(3)-C(216)	99.1 (7)
S-Ru(1)-C(102)	96.6 (3)	C(31)-C(3)-C(216)	110.6 (8)
S-Ru(1)-C(103)	169.4 (3)	C(3)-C(31)-C(32)	111.6 (8)
Ru(1)-Ru(2)-Ru(3)	59.73 (3)	C(3)-C(31)-C(33)	109.4 (9)
Ru(1)-Ru(2)-S	54.07 (6)	C(3)-C(31)-C(34)	108.0 (9)
Ru(1)-Ru(2)-H(1)	46 (4)	C(32)-C(31)-C(33)	110 (1)
Ru(3)-Ru(2)-S	81.47 (7)	C(32)-C(31)-C(34)	110 (1)
S-Ru(2)-C(201)	102.5 (4)	C(33)-C(31)-C(34)	107.3 (8)
S-Ru(2)-C(202)	166.3 (3)	C(2)-C(211)-C(212)	130.2 (9)
S-Ru(2)-C(203)	93.0 (4)	C(2)-C(211)-C(216)	107.5 (8)
Ru(1)-Ru(3)-Ru(2)	60.12 (3)	C(3)-C(216)-C(211)	111.1 (9)
Ru(1)-S-Ru(2)	71.85 (8)	C(3)-C(216)-C(215)	128.0 (8)
Ru(1)-S-C(1)	109.8 (3)	C(2)-C(221)-C(222)	118.9 (8)
Ru(2)-S-C(1)	118.7 (4)	C(2)-C(221)-C(226)	119.7 (9)
S-C(1)-C(2)	122.2 (7)	Ru-C-O(av)	176 (1)
S-C(1)-C(3)	126.0 (6)	Ru(1)-H(1)-Ru(2)	95 (3)
C(2)-C(1)-C(3)	111.7 (8)		

Mechanisms for the Reaction of Allene Episulfides 1a or 1b with $Ru_3(CO)_{12}$. The initial step of the reaction of allene episulfides **1a** or **1b** with $Ru_3(CO)_{12}$ is the coordination of thiirane by $Ru_3(CO)_{10}$, as shown in Scheme III. The coordination of sulfur to two metal atoms has been observed previously in the reaction of the triosmium carbonyl cluster with thietanes,[3d] which is necessary to activate the coordinated thietane ring. The C–S bond cleavage of the thiirane ring produces an allyl cation and a negative charge on the thiolato sulfur, i.e. the thioallyl cation type intermediates **9** and **10**. The negative charge delocalizes into the metal atoms of the cluster shown in Scheme III. The subsequent proton transfer from the ligand to the metal–metal bond affords **2** and **5**. We disfavor an alternative mechanism that involves direct γ or δ C–H activation since the transformation of **1b** to **5** obviously undergoes intramolecular cationic cyclization. Therefore the ruthenium cluster behaves like a Lewis acid in these reactions, similar to the protic acid catalyzed rearrangement of allene episulfide via the thioallyl cation.[12]

Scheme III

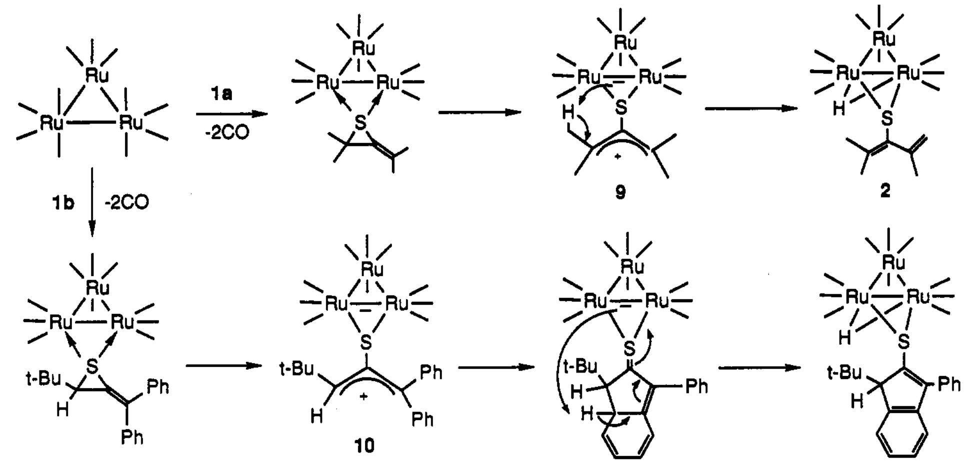

Table VI. Intramolecular Distances (Å) for 8

Ru(1)–Ru(2)	2.766 (1)	Ru(4)–C(43)	1.922 (8)
Ru(1)–Ru(3)	3.19 (0)	Ru(5)–S(2)	2.321 (2)
Ru(1)–Ru(4)	4.50 (3)	Ru(5)–C(51)	1.93 (1)
Ru(1)–Ru(5)	2.784 (1)	Ru(5)–C(52)	1.88 (1)
Ru(1)–S(2)	2.414 (2)	Ru(5)–C(53)	1.90 (1)
Ru(1)–C(11)	1.92 (1)	S(1)–C(1)	1.768 (7)
Ru(1)–C(12)	1.837 (9)	O–C(av)	1.13 (3)
Ru(1)–C(13)	1.93 (1)	C(1)–C(2)	1.36 (1)
Ru(1)–H(1)	2.09 (8)	C(1)–C(5)	1.52 (1)
Ru(2)–Ru(3)	4.52 (7)	C(2)–C(3)	1.50 (1)
Ru(2)–Ru(4)	4.25 (3)	C(2)–C(201)	1.47 (1)
Ru(2)–Ru(5)	2.889 (1)	C(3)–C(4)	1.39 (1)
Ru(2)–S(2)	2.332 (2)	C(3)–C(6)	1.39 (1)
Ru(2)–C(21)	1.895 (9)	C(4)–C(5)	1.52 (1)
Ru(2)–C(22)	1.93 (1)	C(4)–C(9)	1.37 (1)
Ru(2)–C(23)	1.90 (1)	C(5)–C(501)	1.62 (1)
Ru(3)–Ru(4)	2.699 (1)	C(6)–C(7)	1.41 (1)
Ru(3)–Ru(5)	4.50 (9)	C(7)–C(8)	1.42 (1)
Ru(3)–S(1)	2.417 (2)	C(8)–C(9)	1.39 (2)
Ru(3)–S(2)	2.672 (2)	C(201)–C(202)	1.39 (1)
Ru(3)–C(31)	1.869 (8)	C(201)–C(206)	1.41 (1)
Ru(3)–C(32)	1.95 (1)	C(202)–C(203)	1.41 (1)
Ru(3)–C(33)	1.92 (1)	C(203)–C(204)	1.39 (2)
Ru(3)–H(1)	1.33 (9)	C(204)–C(205)	1.38 (2)
Ru(4)–Ru(5)	4.34 (2)	C(205)–C(206)	1.42 (2)
Ru(4)–S(1)	2.443 (2)	C(501)–C(202)	1.51 (1)
Ru(4)–S(2)	2.351 (2)	C(501)–C(203)	1.53 (2)
Ru(4)–C(41)	1.95 (1)	C(501)–C(204)	1.51 (2)
Ru(4)–C(42)	1.89 (1)		

Scheme IV

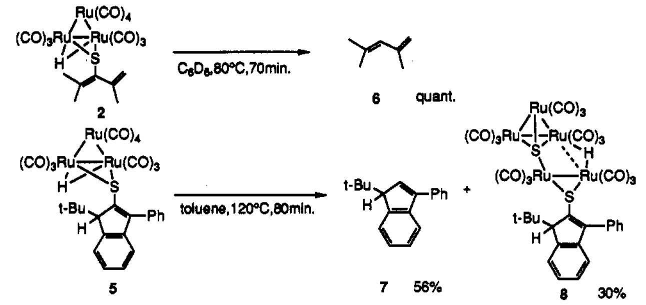

Table VII. Intramolecular Bond Angles (deg) for 8

Ru(2)–Ru(1)–Ru(3)	98 (7)	Ru(2)–S(2)–Ru(4)	130.5 (1)
Ru(2)–Ru(1)–Ru(5)	62.73 (3)	Ru(2)–S(2)–Ru(5)	76.76 (6)
Ru(2)–Ru(1)–S(2)	52.97 (5)	Ru(3)–S(2)–Ru(4)	64.63 (5)
Ru(2)–Ru(1)–H(1)	100 (0)	Ru(3)–S(2)–Ru(5)	129.00 (9)
Ru(3)–Ru(1)–Ru(5)	97 (8)	Ru(4)–S(2)–Ru(5)	136.7 (1)
Ru(3)–Ru(1)–S(2)	54 (9)	S(1)–C(1)–C(2)	122.4 (6)
Ru(5)–Ru(1)–S(2)	52.46 (5)	S(1)–C(1)–C(5)	125.3 (6)
Ru(5)–Ru(1)–H(1)	83 (4)	C(2)–C(1)–C(5)	112.3 (6)
S(2)–Ru(1)–H(1)	49 (1)	C(1)–C(2)–C(3)	107.2 (8)
C(11)–Ru(1)–H(1)	76 (9)	C(1)–C(2)–C(201)	128.5 (7)
C(12)–Ru(1)–H(1)	162 (6)	C(3)–C(2)–C(201)	124.3 (7)
C(13)–Ru(1)–H(1)	102 (7)	C(2)–C(3)–C(4)	108.6 (7)
Ru(1)–Ru(2)–Ru(5)	58.94 (8)	C(2)–C(3)–C(6)	128.1 (9)
Ru(1)–Ru(2)–S(2)	55.74 (6)	C(4)–C(3)–C(6)	123.3 (8)
Ru(5)–Ru(2)–S(2)	51.46 (5)	C(3)–C(4)–C(5)	109.6 (7)
Ru(1)–Ru(3)–Ru(4)	99 (4)	C(3)–C(4)–C(9)	120.0 (8)
Ru(1)–Ru(3)–S(1)	93 (3)	C(5)–C(4)–C(9)	130.3 (9)
Ru(4)–Ru(3)–S(1)	56.73 (6)	C(1)–C(5)–C(4)	100.8 (7)
Ru(4)–Ru(3)–S(2)	51.91 (5)	C(1)–C(5)–C(501)	112.1 (7)
Ru(4)–Ru(3)–H(1)	89 (5)	C(4)–C(5)–C(501)	111.5 (7)
S(1)–Ru(3)–S(2)	71.10 (6)	C(3)–C(6)–C(7)	116 (1)
S(1)–Ru(3)–H(1)	108 (5)	C(6)–C(7)–C(8)	121 (1)
S(2)–Ru(3)–H(1)	42 (5)	C(7)–C(8)–C(9)	120 (1)
C(31)–Ru(3)–H(1)	154 (5)	C(4)–C(9)–C(8)	120 (1)
C(32)–Ru(3)–H(1)	94 (5)	Ru–C–O(av)	175 (7)
C(33)–Ru(3)–H(1)	65 (5)	C(2)–C(201)–C(202)	118.6 (8)
Ru(3)–Ru(4)–S(1)	55.81 (6)	C(2)–C(201)–C(206)	121.2 (8)
Ru(3)–Ru(4)–S(2)	63.46 (6)	C(202)–C(201)–C(206)	120.2 (9)
S(1)–Ru(4)–S(2)	76.42 (7)	C(201)–C(202)–C(203)	120 (1)
Ru(1)–Ru(5)–Ru(2)	58.33 (3)	C(202)–C(203)–C(204)	121 (1)
Ru(1)–Ru(5)–S(2)	55.54 (6)	C(203)–C(204)–C(205)	119 (1)
Ru(2)–Ru(5)–S(2)	51.78 (6)	C(204)–C(205)–C(206)	121 (1)
Ru(3)–S(1)–Ru(4)	67.46 (6)	C(201)–C(206)–C(205)	119 (1)
Ru(3)–S(1)–C(1)	116.0 (3)	C(5)–C(501)–C(502)	109.9 (8)
Ru(4)–S(1)–C(2)	114.4 (3)	C(5)–C(501)–C(503)	108.8 (8)
Ru(1)–S(2)–Ru(2)	71.28 (6)	C(5)–C(501)–C(504)	110.3 (9)
Ru(1)–S(2)–Ru(3)	77.50 (6)	C(502)–C(501)–C(503)	107 (1)
Ru(1)–S(2)–Ru(4)	141.85 (9)	C(502)–C(501)–C(504)	110.5 (9)
Ru(1)–S(2)–Ru(5)	71.99 (5)	C(503)–C(501)–C(504)	109.9 (9)
Ru(2)–S(2)–Ru(3)	129.48 (9)	Ru(1)–H(1)–Ru(3)	135 (8)

Thermolysis of 2 and 5. In the connection with the desulfurization mechanism,[3] the thiolato clusters of 2 and 5 were subjected to thermolysis. 2 was desulfurized at 80 °C to yield 2,4-dimethyl-1,3-pentadiene (6) quantitatively. Heating cluster 5 in toluene at 120 °C gave a desulfurization product 7, 1-*tert*-butyl-3-phenylindene, and a thiopentaruthenium carbonyl cluster 8 in 56% and 30% yield, respectively (Scheme IV). Desulfurization products 6 and 7 were characterized by ^{1}H NMR, ^{13}C NMR, and mass spectra. Formally, the formation of 6 or 7 is the result of migration of μ-H to the C–S bond.[13] Compound 8 was characterized ^{1}H NMR, ^{13}C NMR, IR, and elemental analyses and single-crystal X-ray diffraction analyses. An ORTEP drawing of the molecular structure of 8 is shown in Figure 3. Selected interatomic distances and angles are listed in Tables VI and VII. The molecule consists of triruthenium and diruthenium clusters linked by a quadruply bridging thio ligand. The Ru(1)–Ru(2)–Ru(5)–S(2) grouping is arranged in a closed tetrahedron cluster. The Ru(3)–Ru(4)–S(1) grouping is arranged in the shape of a

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(12) (a) Ando, W.; Hanyu, Y.; Furuhata, T.; Takata, T. *J. Am. Chem. Soc.* **1983**, *105*, 6151. (b) Ando, W.; Itami, A.; Furuhata, T.; Tokitoh, N. *Tetrahedron Lett.* **1987**, *28*, 1787.

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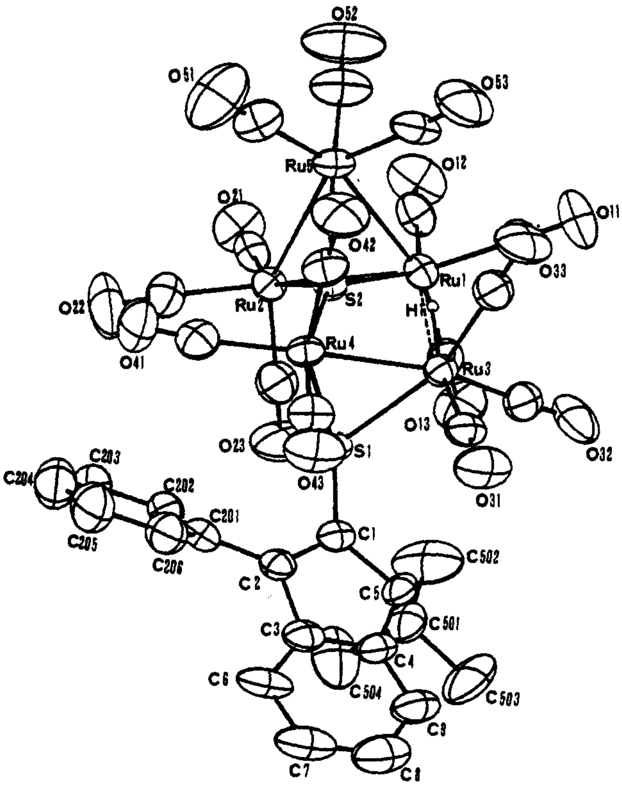


Figure 3. ORTEP drawing of $HRu_5(CO)_{15}[2\text{-}(\mu\text{-}S)\text{-}1\text{-}tert\text{-}butyl\text{-}3\text{-}phenylindene](\mu_4\text{-}S)$ (8).

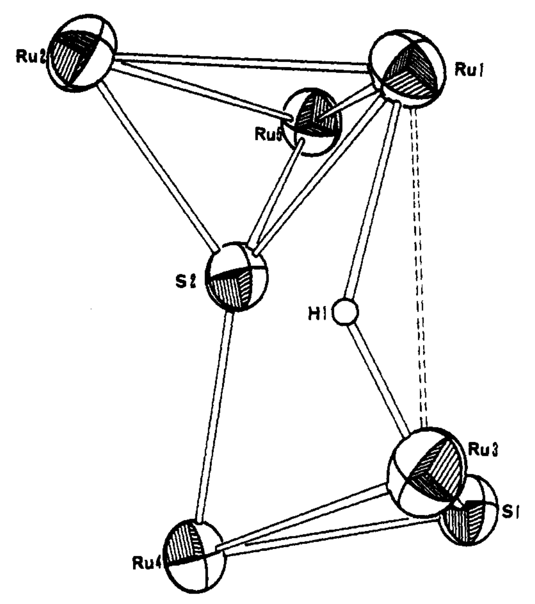
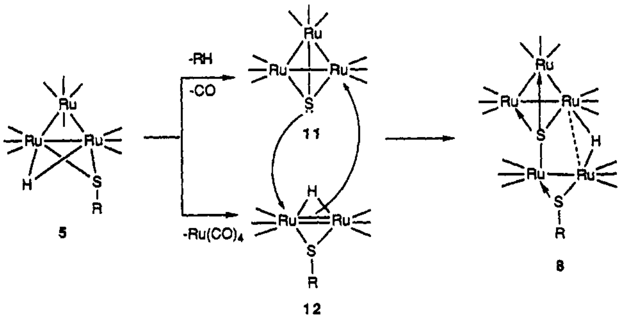


Figure 4. ORTEP drawing of the $HRu_5[\mu_4\text{-}S][\mu\text{-}S]$ core of compound 8.

Scheme V



closed triangle. S(2) is a quadruply bridging atom that is bonded to Ru(1), 2.414 (2) Å, Ru(2), 2.332 (2) Å, Ru(4), 2.351 (2) Å, and Ru(5), 2.321 (2) Å. As expected,[3c,14] the ruthenium–sulfur distances, 2.321–2.414 Å, are similar to triply bridging thio ligands, 2.35–2.40 Å,[15] and quadruply bridging thio ligands, 2.35–2.43 Å.[16] Diruthenium cluster 8 contains a 1-*tert*-butyl-3-phenylindene-2-thiolato ligand and the hydride ligand. The thiolato sulfur atom S(1) bridges the Ru(3)–Ru(4) bond, 2.699 (1) Å. This metal–metal bond is relatively shorter than those of the triruthenium cluster, as shown in 2 and 5 (2.784, 2.766, and 2.889 Å). This is peculiar in comparison with the sulfur atom bridging Ru–Ru single bonds, 2.828 (1) and 2.833 (1) Å, in 2 and 5, respectively. The Ru–S bond lengths to the thiolato sulfur atom, S(1), 2.443 (2) and 2.417 (2) Å, lie in the expected range for thiolato ligands coordinated to ruthenium and are similar to the Ru–S distances observed in 2 and 5. With close inspection of the cluster framework of 8 (see Figure 4), the Ru(1)–Ru(3) distance is considerably short enough (3.190 Å) to imply anomalous metal–metal bonding,[11] while the other metal–metal distances are completely nonbonding: Ru(1)–Ru(4), 4.503 Å; Ru(2)–Ru(3), 4.527 Å; Ru(2)–Ru(4), 4.253 Å; Ru(3)–Ru(5), 4.509 Å; Ru(4)–Ru(5), 4.342 Å. The hydride ligand was also located between Ru(1) and Ru(3) and ^1H NMR resonance at upfield shift (−18.60 ppm) also suggests the presence of μ-bonded hydride.[9,17] If the electron counting includes the Ru(1) and Ru(2) bond, the molecule is electron precise and metal atoms achieve an 18-electron configuration. One of the electron distribution schemes of 8 is shown in Scheme V. In the mechanistic point of view, two unsaturated intermediates $Ru_3(CO)_9(\mu_3\text{-}S)$ (11) and $HRu_2(CO)_6(\mu\text{-}SR)$ (12) could be formed by the elimination of indene and $Ru(CO)_4$ units from 5, as shown in Scheme V. However, the lack of direct Ru(1)–Ru(2) bond formation could not be neglected. In such a case, the molecule is electron deficient and the Ru(1)–H(1)–Ru(2) group is best considered to be bound by an open three-center two-electron bond. It is proposed that the analogous thioosmium cluster intermediate $Os_3(CO)_9(\mu_3\text{-}S)$ has an important role in the pyrolysis of the osmium thiolato cluster $HOs_3(CO)_{10}(\mu\text{-}SR)$, giving a variety of thioosmium clusters.[18] So it is believed that the thioruthenium intermediate 11 would be very reactive and couple with 12 to lead to the formation of 8.

Experimental Section

General Data. Reagent-grade solvents were distilled from sodium benzophenone ketyl prior to use. Dichloromethane was dried over calcium chloride and then distilled. Tetramethylallene episulfide (**1a**)[4a] was prepared by the published procedures. All reactions were performed under an argon atmosphere unless specified otherwise. Column chromatography was performed by use of Wakogel C-300 (silica gel, 200–300 mesh). Infrared spectra were recorded on a Hitachi 260-50 infrared spectrometer. NMR spectra were run on either a Bruker AM500 or a JEOL EX-90 spectrometer operating at 500 or 90 MHz, respectively. Elemental analyses were carried out by the Chemical Analytical Center of

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[16] (a) Adams, R. D.; Männing, D.; Segmüller, B. E. *Organometallics* **1983**, *2*, 149. (b) μ_4-S four-electron donor: Ru–S 2.44–2.58 Å; ref 2b.

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the University of Tsukuba. Mass spectra and high-resolution mass spectra were obtained on a JEOL JMS SX102A mass spectrometer. All melting points were uncorrected.

(1) Synthesis of 1-*tert*-Butyl-3,3-diphenylallene 1-Episulfide (1b) and 2-Episulfide (1c). **1b** was prepared by thermal decomposition of 2-(2,2-dimethylpropylidene)-5,5-diphenyl-1,3,4-thiadiazoline (**13**). A solution of **13** (87 mg, 0.28 mmol) in 10 mL of benzene was gently refluxed for 40 min. No **13** was detected by TLC. Benzene was evaporated under reduced pressure without heating, and ^{1}H NMR spectral analysis of the residue suggested the products are 1-*tert*-butyl-3,3-diphenylallene 1-episulfide (**1b**) and 1-*tert*-butyl-3,3-diphenylallene 2-episulfide (**1c**) in 65% and 26% yields, respectively (71 mg, 91%). The mixture was purified by silica gel column chromatography to give only **1b** (71 mg, 91%) since **1c** was easily isomerized to **1b** on silica gel, **1b**: white crystals; mp 62.0–65.0 °C; ^{1}H NMR (CCl_4) δ 0.77 (9 H, s), 3.40 (1 H, s), 6.68–7.67 (10 H, m); ^{13}C NMR ($CDCl_3$) δ 27.1 (q), 33.5 (s), 47.3 (d), 125.9 (s), 127.0 (d), 127.3 (d), 127.9 (d), 128.1 (d), 128.2 (d), 128.9 (s), 129.2 (d), 139.6 (s), 140.9 (s). Anal. Calcd for $C_{19}H_{20}S$: C, 81.37; H, 7.18. Found: C, 81.22; H, 7.27. **1c**: ^{1}H NMR (CCl_4) δ 1.23 (9 H, s), 6.13 (1 H, s), 7.00–7.50 (10 H, m).

(2) Preparation of 2-(2,2-Dimethylpropylidene)-5,5-diphenyl-1,3,4-thiadiazoline (13). To *tert*-butylthioketene[19] (ca. 1.32 mmol) in dichloromethane formed by thermal decomposition of 4-(dimethylethyl)-1,2,3-thiadiazole[20] (1.25 g, 8.8 mmol) was added a small excess of diphenyldiazomethane[21] (307 mg, 1.58 mmol) in 1.5 mL of dichloromethane at −30 °C. The mixture was stirred for 2 h at −30 °C. Dichloromethane was evaporated under reduced pressure without heating, and the residue was purified by silica gel column chromatography (eluant, hexane:ether = 10:1).

Reaction of Tetramethylallene Episulfide (1a, TMAE) with $Ru_3(CO)_{12}$. TMAE (198 mg, 1.54 mmol) (**1a**) was allowed to react with $Ru_3(CO)_{12}$ (210 mg, 0.328 mmol) in 5 mL of benzene at 70 °C for 40 min. After evaporation of the solvent under vacuum, the dark orange residue was chromatographed on a silica gel column (o.d. 3 cm × 15 cm) with hexane as the eluant. After vacuum evaporation of the solvents from the three eluants, the residue was rcrystallized from hexane or hexane:CH_2Cl_2 mixture at room temperature. From the first fraction, 62 mg (27% based on $Ru_3(CO)_{12}$) of **2** as orange crystals was obtained. The second fraction gave $Ru_3(CO)_{12}$ (17 mg). The solvent of the third fraction was removed, and the residue was an orange oil of **3** (64 mg, 29% based on $Ru_3(CO)_{12}$). **2**: mp 105–107 °C dec; ^{1}H NMR (500 MHz, C_6D_6) δ −15.30 (1 H, s), 1.53 (3 H, s), 1.55 (3 H, s), 1.91 (3 H, s), 4.55 (1 H, d), 4.88 (1 H, d); ^{13}C NMR (125 MHz, C_6D_6) δ 22.9 (q), 23.5 (q), 24.3 (q), 119.9 (t), 128.1 (s), 134.26 (s), 142.68 (s), 186.9 (br s), 192.3 (s), 194.1 (s), 198.9 (s), 203.3 (s), 204.6 (s); IR (hexane) ν 2100 (m), 2070 (m), 2055 (s), 2025 (m, sh), 2000 (s), 1990 (s), 1970 (w) cm^{-1}. Anal. Calcd for $Ru_3SO_{10}C_{17}H_{12}$: C, 28.68; H, 1.68. Found: C, 28.69; H, 1.58. **3**: ^{1}H NMR (500 MHz, C_6D_6) δ −13.46 (1 H, s), 1.02 (3 H, s), 1.45 (3 H, s), 1.69 (3 H, s), 3.20 (1 H, s), 3.52 (1 H, s); ^{13}C NMR (125 MHz, C_6D_6) δ 18.4 (q), 20.5 (q), 29.9 (q), 62.2 (t), 96.8 (s), 133.4 (s), 141.4 (s), 188.1 (s), 190.6 (s), 191.3 (s), 199.0 (s), 199.5 (s), 204.7 (s), 206.5 (s), 207.2 (s); IR (hexane) ν 2100 (s), 2060 (s), 2010 (s), 2000 (s), 1980 (m, sh), 1975 (s) cm^{-1}; MS, *m*/*e* 685 (M^+).

Reaction of *tert*-Butyldiphenylallene Episulfide (1b, BDPAE) with $Ru_3(CO)_{12}$. BDPAE (**1b**) (130 mg, 0.46 mmol) was allowed to react with $Ru_3(CO)_{12}$ (97.5 mg, 0.15 mmol) in 2 mL of benzene at 70 °C for 9 h. The following compounds were separated by TLC using hexane as eluant: white crystals of **4** (24 mg, 21%) and orange crystals of **5** (40 mg, 10%). **4**: colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.15 (9 H, s), 5.66 (1 H, s), 7.13–7.46 (10 H, m); ^{13}C NMR ($CDCl_3$) δ 30.3 (q), 33.3 (s), 106.1 (d), 111.0 (s), 126.7 (d), 128.2 (d), 128.3 (d), 137.4 (s), 202.6 (s); IR (CCl_4) ν 1950 cm^{-1}. Exact mass calcd for $C_{19}H_{20}$: *m*/*z* 248.1564. Found: *m*/*z* 248.1553. **5**: mp 136–137 °C dec; ^{1}H NMR (500 MHz, C_6D_6) δ −15.32 (1 H, s), 1.11 (9 H, s), 3.70 (1 H, s), 6.9–7.7 (9 H, m); ^{13}C NMR (125 MHz, C_6D_6) δ 29.7 (q), 37.3 (s), 62.6 (d), 119.6 (d), 124.4 (d), 125.1 (d), 127.1 (d), 128.3 (d), 129.2 (d), 129.4 (d), 130.6 (d), 135.2 (s), 144.6 (s), 145.5 (s), 147.6 (s), 153.5 (s), 185.4 (s), 188.7 (s), 190.9 (s), 191.8 (s), 192.4 (s), 194.4 (s), 198.3 (s), 199.0 (s), 203.0 (s), 204.3 (s); IR (hexane) ν 2100 (s), 2095 (s), 2070 (s, sh), 2065 (s), 2050 (s), 2025 (s, sh), 2010 (s), 2000 (s), 1990 (s), 1975 (m) cm^{-1}. Anal. Calcd for $Ru_3SO_{10}C_{29}H_{20}$: C, 40.31; H, 2.31. Found: C, 40.44; H, 2.22.

Decarbonylation of 2. A solution of **2** (20 mg, 0.0281 mol) in 15 mL of hexane was heated to 60 °C for 2 h. After the solvent was removed in vacuo, the residue was chromatographed by TLC. Elution with hexane separated 1 mg of unreacted **2** from orange **3** (9 mg, 49% based on the amount of **2** consumed).

Carbonylation of 3. A solution of **3** (31 mg, 0.045 mmol) in 20 mL of hexane was bubbled with carbon monoxide at room temperature for 7 h. After removal of the solvent in vacuo, the dark orange residue was chromatographed on silica gel. Elution with hexane yielded **2** (25.8 mg, 80%) as the only isolable product.

Thermolysis of 2. A solution of **2** (20 mg, 0.028 mmol) in 300 μL of benzene-d_6 was heated at 80 °C in a NMR sealed tube. The reaction was monitored by ^{1}H NMR spectroscopy. After 70 min, **2** was completely consumed and converted to 2,4-dimethyl-1,3-pentadiene (**6**)[22] quantitatively. **6**: ^{1}H NMR (500 MHz, C_6D_6) δ 1.64 (3 H, s), 1.71 (3 H, s), 1.77 (3 H, s), 4.87 (1 H, s), 4.99 (1 H, s), 5.70 (1 H, s); ^{13}C NMR (125 MHz, C_6D_6) δ 19.4 (q), 23.8 (q), 26.8 (q), 114.0 (t), 127.8 (d), 133.7 (s), 142.4 (s). Exact mass calcd for C_7H_{12}: *m*/*z* 96.0939. Found: *m*/*z* 96.0935.

Thermolysis of 5. A solution of **5** (18 mg, 0.02 mmol) in 300 μL of toluene was heated to 120 °C in a NMR sealed tube. The reaction was monitored by ^{1}H NMR spectroscopy. After 70 min, **4** was completely consumed. After removal of the solvent in vacuo, the dark orange residue was chromatographed by TLC. Elution with hexane yielded white crystals of **7**[23] (3 mg, 56% based on **5**) and orange crystals of **8** (7.7 mg, 30% based on **5**). **7**: white crystals; ^{1}H NMR (90 MHz, C_6D_6) δ 0.97 (9 H, s), 3.20 (1 H, d, J = 2.0 Hz), 6.46 (1 H, d, J = 2.0 Hz), 7.1–7.6 (9 H, m). Exact mass calcd for $C_{19}H_{20}$: *m*/*z* 248.1564. Found: *m*/*z* 248.1601. **8**: mp 161–162 °C; ^{1}H NMR (500 MHz, C_6D_6) δ −18.60 (1 H, s), 1.07 (9 H, s), 3.43 (1 H, s), 6.9–7.4 (9 H, m); ^{13}C NMR (125 MHz, C_6D_6) δ 29.2 (q), 37.3 (s), 68.5 (s), 119.8 (d), 125.0 (d), 125.4 (d), 127.6 (d), 129.5 (s), 129.9 (d), 134.5 (s), 141.6 (s), 143.8 (s), 145.3 (s), 147.7 (s), 187.0 (s), 195.2 (s), 196.1 (s); IR (hexane) ν 2260 (vw), 2180 (vw), 2125 (vw), 2100 (w), 2070 (s, sh), 2060 (s), 2025 (m), 2010 (m), 1985 (w, sh), 1975 (w) cm^{-1}. Anal. Calcd for $Ru_5S_2O_{15}C_{34}H_{20}$: C, 32.97; H, 1.67. Found: C, 32.88; H, 1.66.

Crystallographic Analysis. Orange crystals of dimensions 0.2 × 0.2 × 0.1 mm for **2**, 0.2 × 0.2 × 0.2 mm for **5**, and 0.2 × 0.2 × 0.3 mm for **8**, obtained from slow evaporation of a hexane solution at 25 °C, were used for X-ray analyses. Diffraction measurements were made on an Enraf-Nonius CAD4 computer controlled Kappa axis diffractometer by using graphite-monochromatized Mo Kα radiation. The unit cell was determined and refined from 25 randomly selected reflections obtained by using the CAD4 automatic search, center, index, and least-squares routines. Crystal data and data collection parameters and results of the analyses are listed in Table I. All data processing was performed on a Micro VAX 3100 computer by using the SDP structure solving program obtained from Enraf-Nonius Corp., Delft, Netherlands. The ω–2θ scan technique was adopted varying the ω scan width as a function of θ (ω scan width = $(0.7 + 0.350 \tan\theta)^\circ$). All intensities were corrected for Lorentz and polarization corrections as well as decay correction (−0.1% for **2**, −0.6% for **5**, and −0.5% for **8**). An empirical absorption correction based on a series of ψ scans was also applied to the data. Neutral-atom scattering factors were calculated by the standard procedures.[24a] Anomalous dispersion correction was applied to all non-hydrogen atoms.[24b] Full-matrix least-squares refinements minimized the function $\sum w(|F_o| - |F_c|)^2$, $w = 1$.

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Compound **2** crystallized in the monoclinic crystal system. The systematic absences observed during the collection of data (hkl, $h + k = 2n + 1$; $0kl$, $k = 2n + 1$; $h0l$, $h = 2n + 1$; $hk0$, $h + k = 2n + 1$; $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$) are consistent with either the centrosymmetric space group $C2/c$ or the noncentrosymmetric space group Cc. The successful solution and refinement of the structure confirmed the crystal belonged to the centrosymmetric space group $C2/c$. The coordination of metal atoms was obtained by direct methods (MULTAN), and remaining non-hydrogen atoms were subsequently obtained from difference electron density syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. In the final stage, the μ-hydride atom was located and refined with a fixed isotropic thermal parameter (4 Å^2).

Compound **5** crystallized in the orthorhombic crystal system. The space group $P2_12_12_1$ was identified uniquely on the basis of the systematic absences observed during the collection of data ($h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$). The structure was solved by a combination of direct methods (MULTAN) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. In the final stage, the μ-hydride atom was located and refined with a fixed isotropic thermal parameter (4 Å^2).

Compound **8** crystallized in the monoclinic crystal system. The space group $P2_1/n$ was identified uniquely on the basis of the systematic absences observed during the collection of data ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$). The structure was solved by a combination of direct methods (MULTAN) and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. In the final stage, the μ-hydride atom was located and refined with a fixed isotropic thermal parameter (4 Å^2). The molecular structures with atomic labeling schemes, the bond lengths and angles are given in Figure 1 and Tables II and III for **2**, Figure 2 and Tables IV and V for **5**, and Figure 3, and Tables VI and VII for **8**.

Acknowledgment. This work was supported in part by a Grant-in-Aid for Scientific Research on Priority Areas from the Ministry of Education, Science, and Culture, Japan.

Registry No. **1a**, 61097-65-2; **1b**, 111278-37-6; **2**, 138061-90-2; **3**, 138061-91-3; **4**, 81740-70-7; **5**, 138061-92-4; **6**, 1000-86-8; **7**, 32338-54-8; **8**, 138061-93-5; **13**, 138061-89-9; Ru, 7440-18-8; *tert*-butylthioketene, 54191-76-3.

Supplementary Material Available: For **2**, **5**, and **8**, a textual presentation of experimental procedures and tables of experimental details, positional and thermal parameters, temperature factor expressions, root-mean-square amplitudes, and bond distances and angles (45 pages); listings of intensity data (31 pages). Ordering information is given on any current masthead page.

Thiolato Ligands Derived from Chiral Ferrocenylphosphines: Synthesis and Structure of the Trimeric Copper(I) Complex $[\{(R)\text{-}(S)\text{-CpFe}(\eta^5\text{-C}_5\text{H}_3(1\text{-PPh}_2)(2\text{-CH}(\text{CH}_3)\text{S}))\}\text{Cu}]_3$[†]

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Received August 28, 1991

The reaction of (*R*)-1-[(*S*)-(diphenylphosphino)ferrocenyl]ethyl acetate (**1a**) with KSAc in acetic acid leads to the corresponding thioacetate **4a** in 60% yield. This $\text{S}_\text{N}1$-type transformation occurs cleanly with retention of configuration. The use of other polar solvents was found to give (*R*)-1-[(*S*)-(diphenylthiophosphinyl)ferrocenyl]ethyl acetate (**6**) and only traces of the substitution product. The novel chelating, optically active ligand (*R*)-1-[(*S*)-(diphenylphosphino)ferrocenyl]ethyl mercaptan (**5a**) is obtained by treating **4a** with LiAlH_4 in Et_2O. The reaction of **5a** with $[\text{CuOBu}^t]_4$ (**10**) give the metathesis product $[\{(R)\text{-}(S)\text{-CpFe}(\eta^5\text{-C}_5\text{H}_3(1\text{-PPh}_2)(2\text{-CH}(\text{CH}_3)\text{S}))\}\text{Cu}]$ (**11**) in high yield. **11** was found to be very stable and rather unreactive. It is *trimeric* both in solution and in the solid state. Yellow-orange crystals of **11** are monoclinic, space group $P2_1$, with two molecules in a unit cell of dimensions $a = 13.206$ (1) Å, $b = 18.221$ (2) Å, $c = 16.028$ (1) Å, and $\beta = 113.13$ (1)°. The core of the trimeric complex is constituted by a Cu_3S_3 ring, which adopts a chairlike conformation. The substituents attached to this ring are pseudoequatorially arranged.

Introduction

Chiral ferrocenylphosphines of type **2** bearing a heteroatom-functionalized side chain have been shown, mainly by Hayashi, Kumada, and Ito, to be very effective ligands in numerous asymmetric homogeneous catalytic reactions.[1] The nature of the heteroatom substituent has been so far restricted to dialkylamino groups, mainly because of their ease of introduction starting from the acetate derivatives **1**.[2] The reaction of **1** with an excess of a secondary amine occurs via an $\text{S}_\text{N}1$ mechanism, but with complete retention of configuration at the α-carbon atom of the side chain, due to the involvement of the configurationally stable

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[†] Dedicated to Professor Luigi M. Venanzi on the occasion of his 65th birthday.

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