Trinuclear heterometallic clusters with bridging disulfide and sulfide ligands [(μ_2-S$_2$)(Cp*Ru)$_2$(μ_3-S)(μ_2-S)$_2$MS] derived from diruthenium complex [Cp*RuCl(μ_2-Cl)$_2$RuCp*Cl] and [MS$_4$]$^{2-}$ (M = W, Mo; Cp* = η^5-C$_5$Me$_5$)

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Abstract

Reactions of [Cp*RuCl(μ-Cl)$_2$RuCp*Cl] (2) with excess [MS$_4$]$^{2-}$ (M = W (1a) or Mo (1b)) in tetrahydrofuran at reflux afforded the trinuclear heterometallic clusters with bridging disulfide and sulfide ligands [(μ_2-S$_2$)(Cp*Ru)$_2$(μ_3-S)(μ_2-S)$_2$MS] (M = W (3a) or Mo (3b)). Clusters 3 were also obtained by treatment of an equimolar mixture of 1 and 2 with Li$_2$S$_2$ at room temperature. X-ray analysis was undertaken to clarify the detailed structures of clusters 3. Crystal data for 3a: monoclinic; space group, $P2_1/c$ (No. 14); a = 16.460(2) Å, b = 10.009(3) Å and c = 16.582(2) Å; β = 93.68(1)°; V = 2726(1) Å^3; Z = 4; D_{calc} = 2.07 g cm^{-3}; μ(Mo Kα) = 58.26 cm^{-1}; and $R(R_w)$ = 0.053 (0.065) for 3060 reflections ($|F_o| > 3\sigma(F_o)$). Crystal data for 3b: monoclinic; space group, $P2_1/c$ (No. 14); a = 16.530(6) Å, b = 9.992(3) Å and c = 16.633(6) Å; β = 93.82(3)°, V = 2741(2) Å^3; Z = 4, D_{calc} = 1.84 g cm^{-3}; μ(Mo Kα) = 19.56 cm^{-1}, and $R(R_w)$ = 0.056 (0.064) for 3390 reflections ($|F_o| > 3\sigma(F_o)$). When reacted with excess PEt$_3$, 3a was converted into a trinuclear cluster [Cp*Ru(PEt$_3$)(μ_2-S)$_2$W(μ_2-S)$_2$RuCp*(PEt$_3$)].

Keywords: Ruthenium; Tungsten; Molybdenum; Sulfide cluster; Disulfide; X-ray structure

1. Introduction

The versatile coordination mode of sulfide ligands results in the formation of many molecular transition metal–sulfur clusters with a remarkable structural diversity [1]. These clusters are currently attracting much attention owing to their possible relevance to the active sites of sulfur-containing metalloproteins and metalloenzymes as well as solid metal sulfide catalysts. The electronic and structural flexibility displayed by the synthetic metal–sulfur clusters may lead to the development of their intriguing catalytic activity, although applications of these compounds to the catalytic reactions have still been limited [2]. Metal clusters containing more than two different transition metals are of particular interest [3]. This mainly stems from the expectation that these clusters can exhibit unusually high activity and selectivity in certain chemical transformations ow-

ing to the simultaneous or consecutive activation of substrate molecules on the multinuclear heterometallic centers.

It has already been shown that the tetrathiometallates [MS$_4$]$^{2-}$ (M = W (1a) or Mo (1b)) can serve as good precursors for preparing heterometallic sulfide clusters [4], in which the MS$_4$ moiety is commonly bound to the other metal(s) M' either as a terminal η^2 ligand or a bridging $\eta^2 : \eta^2$ ligand to give multimetallic cores [M'(μ_2-S)$_2$MS$_2$] or [M'(μ_2-S)$_2$M(μ_2-S)$_2$M'] respectively. It is to be noted, however, that the chemistry concerning the organometallic derivatives of tetrathiometallates is still poorly developed [5]. Recent extensive studies on the reactions of the Ru(III) complex [Cp*RuCl(μ_2-Cl)$_2$RuCp*Cl] (2) (Cp* = η^5-C$_5$Me$_5$) as well as the Ru(II) complexes [(Cp*Ru)$_4$(μ_3-Cl)$_4$] and [Cp*Ru(μ_2-OMe)$_2$RuCp*] with various sulfur sources (e.g. RS$^-$, HS$^-$ or S^{2-}) have demonstrated the formation of a series of dinuclear [6], trinuclear [7] and tetranuclear [6h] ruthenium complexes with bridging sulfur ligands. Now we have extended these reac-

tions to those of 2 with MS_4^{2-}, which have resulted in the isolation of novel trinuclear heterometallic clusters containing two Cp*Ru units connected by both the S_2 ligand and the MS_4 moiety, $[(\mu_2\text{-}S_2)(Cp^*Ru)_2(\mu_3\text{-}S)(\mu_2\text{-}S)_2MS]$ (M = W (**3a**) or Mo (**3b**)). It should be noted that the binding mode of the MS_4 fragment to the two Ru atoms displayed in **3** is quite unique. In this paper, we wish to describe the details of the synthesis and the structures of clusters **3**. Part of this work has appeared previously in a preliminary form [8].
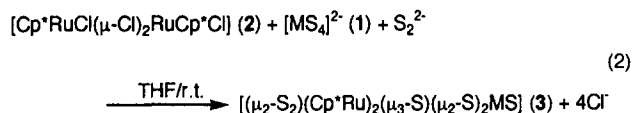
2. Results and discussion

2.1. Preparation of clusters 3

Treatment of **2** with excess $[NH_4]_2 \cdot$ **1a** in tetrahydrofuran (THF) at reflux gave a brown–green suspension. From the filtrate the WRu_2 cluster **3a** was isolated as green crystals with a 13% yield based on **2**. The $MoRu_2$ analogue **3b** was obtained as green crystals similarly but the yield was considerably lower (5%). Clusters **3** are highly soluble into both polar and non-polar organic solvents and their ^1H NMR spectra show a sharp singlet assignable to the Cp* methyl protons at 1.93 and 1.81 ppm for **3a** and **3b** respectively. As demonstrated by X-ray crystallography (vide infra), clusters **3** consist of two Cp*Ru units connected by both the MS_4 and the S_2 bridges. The coordinated S_2 moiety apparently arises from the degradation of **1** and the stoichiometry of these reactions may be represented as Eq. (1) although the presence of 'MS_2' in the reaction mixtures could not be confirmed despite attempts to purify the insoluble solid products. Formation of the S_2 ligand from **1** was also observed in the reactions of $[Cp^*RuCl(\mu\text{-}SPr^i)]_2\text{-}RuCp^*Cl]$ with **1** to give $[Cp^*Ru(\mu\text{-}\eta^1:\eta^1\text{-}S_2)(\mu\text{-}SPr^i)_2RuCp^*]$ [8], details of which will be reported elsewhere.
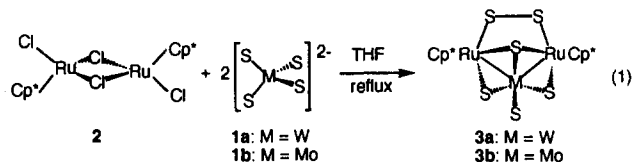
In the present reaction, it is not clear whether the S_2 moiety is formed in the coordination sphere of the Ru or not. One possible mechanism may involve the formation of the intermediate species containing a $Ru(\mu\text{-}MS_4)Ru$ unit and its successive decomposition to a $Ru(\mu_2\text{-}S_2)Ru$ moiety, although such reaction courses towards disulfide ligands have, to our knowledge, not yet been demonstrated. However, the formation of a diselenide ligand was previously reported from the reac-

tion of $[Ni(acac)_2]$ with $[WSe_4]^{2-}$, in which the initial trinuclear product $[Se_2W(\mu\text{-}Se)_2Ni(\mu\text{-}Se)_2WSe_2]^{2-}$ is smoothly converted into $[(\eta^2\text{-}Se_2)Ni(\mu\text{-}Se)_2WSe_2]^{2-}$ when dissolved in dimethylformamide (DMF) [9]. On the contrary, the mechanism involving a free S_2^{2-} ion generated from $[MS_4]^{2-}$ cannot be excluded, since the thermal reaction of **1** in DMF affording $[M_3S_9]^{2-}$ is claimed to proceed with concurrent formation of S_2^{2-} [10]. The latter mechanism has led to the another reaction system to prepare **3**. Thus by treatment of an equimolar mixture of **1** and **2** in THF with Li_2S_2 at room temperature also afforded **3**. However, the yield of **3** was as low as that of the former system; 14% for **3a** and less than 5% for **3b**.

$$[Cp^*RuCl(\mu\text{-}Cl)_2RuCp^*Cl]\ (2) + [MS_4]^{2-}\ (1) + S_2^{2-}$$

$$\xrightarrow{\text{THF/r.t.}} [(\mu_2\text{-}S_2)(Cp^*Ru)_2(\mu_3\text{-}S)(\mu_2\text{-}S)_2MS]\ (3) + 4Cl^- \qquad (2)$$

2.2. Description of the structures of 3

The X-ray analysis has been carried out to disclose the detailed structures of **3** by using the single crystals of both **3a** and **3b**. The structures of these two clusters are essentially identical and the ORTEP drawing of **3a** is shown in Fig. 1. Selected bond distances and angles in **3** are listed in Table 1. In **3**, two Cp*Ru units are connected by a $cis\text{-}\eta^1:\eta^1\text{-}S_2$ ligand as well as an MS_4 moiety. The MS_4 fragment is bound to two Ru atoms by three S atoms, one of which bridges the M and two Ru atoms in a μ_3 fashion and the other two are each bound to the M and Ru atoms in a μ_2 manner. The coordination geometry around M with the four S ligands is a slightly distorted tetrahedron with the S–M–S angles varying from 106.6(2) to 112.1(2)° for **3a** and from 106.2(1) to 112.3(2)° for **3b**. Interatomic distances

$$\begin{array}{c}\text{Cl}\diagdown\text{Ru}\diagup\text{Cl}\diagdown\text{Ru}\diagup\text{Cp}^* \\ \text{Cp}^*\diagup\ \ \ \text{Cl}\ \ \ \diagdown\text{Cl} \\ \mathbf{2}\end{array} + 2\begin{bmatrix}\text{S}\diagdown\text{M}\diagup\text{S} \\ \text{S}\diagup\ \diagdown\text{S}\end{bmatrix}^{2-} \xrightarrow[\text{reflux}]{\text{THF}} \text{Cp}^*\text{Ru}\diagdown\diagup\text{RuCp}^* \qquad (1)$$

$$\begin{array}{lll}\mathbf{2} & \mathbf{1a}: \text{M} = \text{W} & \mathbf{3a}: \text{M} = \text{W} \\ & \mathbf{1b}: \text{M} = \text{Mo} & \mathbf{3b}: \text{M} = \text{Mo}\end{array}$$
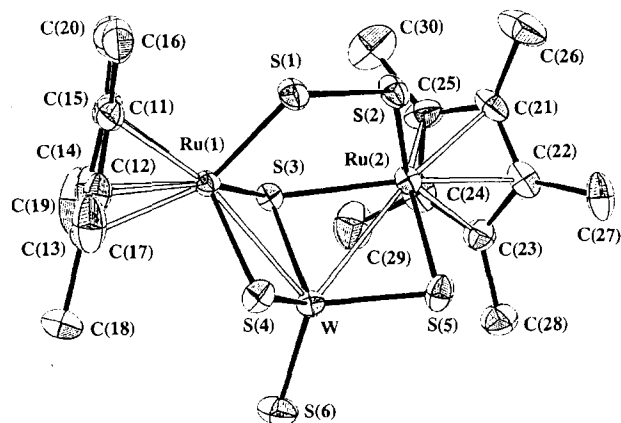
Fig. 1. An ORTEP drawing of **3a** with atom-numbering scheme. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) in **3a** and **3b**

	3a (M = W)	**3b** (M = Mo)
Bond distances (Å)		
M–Ru(1)	2.864(2)	2.860(2)
M–Ru(2)	2.880(2)	2.874(2)
Ru(1) Ru(2)	3.977(2)	3.975(2)
S(1)–S(2)	1.991(7)	1.991(5)
M–S(3)	2.257(4)	2.266(3)
M–S(4)	2.210(5)	2.223(4)
M–S(5)	2.214(5)	2.224(4)
M–S(6)	2.147(6)	2.127(5)
Ru(1)–S(1)	2.224(5)	2.229(4)
Ru(1)–S(3)	2.366(5)	2.370(3)
Ru(1)–S(4)	2.357(5)	2.348(4)
Ru(2)–S(2)	2.216(5)	2.220(4)
Ru(2)–S(3)	2.373(5)	2.360(3)
Ru(2)–S(5)	2.359(6)	2.355(4)
Ru(1)–C	2.18(2)–2.29(2)	2.17(2)–2.27(2)
Ru(2)–C	2.21(2)–2.29(2)	2.21(2)–2.30(1)
Bond angles (°)		
S(3)–M–S(4)	106.9(2)	106.8(1)
S(3)–M–S(5)	106.6(2)	106.2(1)
S(3)–M–S(6)	110.8(2)	111.5(2)
S(4)–M–S(5)	108.5(2)	108.0(2)
S(4)–M–S(6)	111.6(2)	111.7(2)
S(5)–M–S(6)	112.1(2)	112.3(2)
S(1)–Ru(1)–S(3)	90.7(2)	90.1(1)
S(1)–Ru(1)–S(4)	100.0(2)	99.7(2)
S(3)–Ru(1)–S(4)	98.9(2)	99.6(1)
S(2)–Ru(2)–S(3)	90.2(2)	90.3(1)
S(2)–Ru(2)–S(5)	100.7(2)	100.4(2)
S(3)–Ru(2)–S(5)	98.5(2)	99.2(1)
Ru(1)–S(1)–S(2)	116.3(3)	116.6(2)
Ru(2)–S(2)–S(1)	116.8(3)	116.3(2)
M–S(3)–Ru(1)	76.5(1)	76.1(1)
M–S(3)–Ru(2)	76.9(1)	76.8(1)
Ru(1)–S(3)–Ru(2)	114.1(2)	114.3(1)
M–S(4)–Ru(1)	77.6(2)	77.4(1)
M–S(5)–Ru(2)	78.0(2)	77.7(1)

between two Ru atoms at 3.977(2) Å for **3a** and 3.975(2) Å for **3b** suggest the absence of any bonding interaction, while the W–Ru distances at 2.864(2) and 2.880(2) Å as well as the Mo–Ru distances at 2.860(2) and 2.874(2) Å imply the presence of the M–Ru bonds.

The S_2 ligand in **3** coordinates to two Ru atoms in a cis-η^1 : η^1 manner and the two Ru and two S atoms are coplanar. The Ru–S distances of 2.224(5) and 2.216(5) Å in **3a** and 2.229(4) and 2.220(4) Å in **3b** are substantially shorter than the common Ru–S single bond, which generally exceeds 2.3 Å. The S–S bond lengths at 1.991(7) Å for **3a** and 1.991(5) Å for **3b** are also shorter than that in H_2S_2 (2.055 Å) and Me_2S_2 (2.038 Å) [11]. These features together with the Ru–S–S angles observed in the range 116–117° may be interpreted in terms of the presence of the $d\pi$–$p\pi$ interaction between the Ru and S atoms and concurrent delocalization of these π electrons over the S–S bond, as previously

proposed for the diiron complex $[CpFe(\mu_2\text{-}S_2)(\mu_2\text{-}SEt)_2FeCp]^{n+}$ ($Cp = \eta^5\text{-}C_5H_5$; $n = 0[12]$, 1 [12a]). The diamagnetic nature of **3** in spite of the presence of two Ru(III) centers without any direct bonding interactions may presumably be explained by the spin coupling through the S_2 ligand as proposed previously for $[CpFe(\mu_2\text{-}S_2)(\mu_2\text{-}SR)_2FeCp]$ [12] and its Cp^*Ru analogue [8].

A number of well-defined S_2 complexes have appeared to date, in which the S_2 ligand displays diversified coordination modes to one or more metal centers [13]. However, complexes containing the cis-μ_2-η^1 : η^1-S_2 ligand coordinated to two metals are relatively limited. These complexes can further be classified into two types, i.e. complexes containing an essentially planar M–S–S–M moiety and those having a non-planar M–S–S–M unit less commonly observed, which are summarized in Table 2.

In **3**, there exist three types of sulfide ligand, i.e. one μ_3-S ligand, two μ_2-S ligands and one terminal S ligand. For the μ_3-S ligand, the Ru–S–Ru angles (**3a**; 114.1(2)°, **3b**; 114.3(1)°) are much wider than the Ru–S–M angles (76–77°), whereas the M–S bonds (**3a**, 2.257(4) Å; **3b**, 2.266(3) Å) are significantly shorter than the Ru–S bonds (**3a**, 2.366(5) and 2.373(5) Å; **3b**, 2.360(3) and 2.370(3) Å). The latter feature is also observed for the μ_2-S ligands. Thus the M–S distances at 2.210(5) and 2.214(5) Å in **3a** and 2.223(4) and 2.224(4) Å in **3b** are shorter than the Ru–S distances at 2.357(5) and 2.359(6) Å in **3a** and 2.348(4) and 2.355(4) Å in **3b**. Analogously, longer Ru–S bonds at 2.377(6) and 2.394(6) Å than the W–S bonds both at 2.212(6) Å have been reported for $[CpRu(MeNC)(\mu_2\text{-}S)_2W(\mu_2\text{-}S)_2RuCp(MeNC)]$ [5e]. It is also to be noted that the M–S distances in **3** increase in the order M–S(terminal) < M–S(μ_2) < M–S(μ_3).

2.3. Reactions of 3a with PEt_3

Treatment of **3a** with excess PEt_3 in THF at room temperature resulted in the loss of the S_2 ligand in **3a** and a trinuclear cluster $[Cp^*Ru(PEt_3)(\mu_2\text{-}S)_2W(\mu_2\text{-}S)_2RuCp^*(PEt_3)]$ (**4**) was isolated with a 15% yield as red crystals:

+ 2Et_3PS
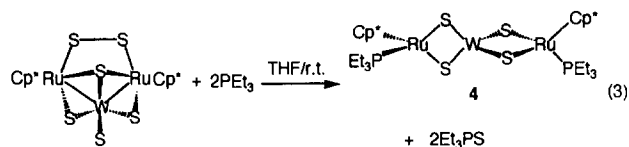
The ^1H NMR spectrum of **4** exhibits only one doublet, one doublet of quartets, and one doublet of triplets assignable to the Cp^*, methylene and methyl protons

Table 2
Complexes containing the cis-μ_2-η^1 : η^1-S$_2$ ligand

Complex	S–S distance (Å)	M–S–S–M torsion angle (°)	Reference
Planar M–S–S–M			
[(μ_2-S$_2$)(Cp*Ru)$_2$(μ_3-S)(μ_2-S)$_2$WS]	1.991(7)		This work
[(μ_2-S$_2$)(Cp*Ru)$_2$(μ_3-S)(μ_2-S)$_2$MoS]	1.991(5)		This work
[(Cp*Ru)$_2$(μ_2-S$_2$)(μ_2-S^{i}Pr)$_2$]	2.008(6)		[8]
[(η^5-C$_5$Me$_4$Et)Ru)$_2$(μ_2-η^1 : η^1-S$_2$)(μ_2-η^2 : η^2-S$_2$)]	2.020(5) [a]		[14]
[{RuCl(TMP)$_2$}$_2$(μ_2-S$_2$)(μ_2-Cl)$_2$] [b]	1.971(4)		[15]
[(CpFe)$_2$(μ_2-S$_2$)(μ_2-SEt)$_2$]	2.023(3)		[12b]
[(CpFe)$_2$(μ_2-S$_2$)(μ_2-SEt)$_2$]$^+$	1.987(1)		[12a]
[(CpFe)$_2$(μ_2-η^1 : η^1-S$_2$)(μ_2-η^2 : η^2-S$_2$)]	1.999(8) [a]		[16]
[(Cp*Fe)$_2$(μ_2-η^1 : η^1-S$_2$)(μ_2-η^2 : η^2-S$_2$)]	2.021(2) [a]		[17]
[{(η^5-C$_5$H$_4$Me)V}$_2$(μ_2-η^1 : η^1-S$_2$)(μ_2-η^2 : η^2-S$_2$)(μ_2-S)]	2.023(2) [a]		[18]
[{(η^5-C$_5$H$_4$Pr^i)V}$_2$(μ_2-S$_2$)(μ_2-S)$_2$]	2.027(3)		[19]
Non-planar M–S–S–M			
[(Ru(MeCN)(TMP)$_2$}$_2$(μ_2-S$_2$)(μ_2-N$_2$H$_4$)$_2$]$^{3+}$	2.009(5)	31.9(3)	[20]
[{RuCl(TMP)$_2$}$_2$(μ_2-S$_2$)(μ_2-N$_2$H$_4$)(μ_2-Cl)]	2.002(3)	16.1(2)	[15b]
[{Mo(NO)}$_4$(μ_2-η^1 : η^1-S$_2$)$_2$(μ_2-η^2 : η^2-S$_2$)$_4$(μ_4-O)]	2.079(5) [a]	ND [c]	[21]
[{Cp*Mo(η^2-S$_2$)}$_2$(μ_2-S$_2$)]	2.040(5)	59.7	[22]

[a] Value for μ_2-η^1 : η^1-S$_2$ ligand.
[b] TMP = trimethylphosphite.
[c] ND, not described.

respectively, indicating that the structure of **4** has a twofold symmetry. This feature is comparable with that observed previously in the Cp and η^5-C$_5$H$_4$Me analogues of **4** with PPh$_3$ or PMe$_3$ ligands, which were derived from the reactions, e.g. between [CpRu(PPh$_3$)$_2$Cl] and [PPh$_4$]$_2$ · **1a** [5e].

3. Experimental section

3.1. General comments

All manipulations were carried out under a nitrogen atmosphere. Solvents were dried and distilled under nitrogen before use. Compounds [NH$_4$]$_2$ · **1** [23], **2** [24], and Li$_2$S$_2$ [25] were prepared according to the literature methods, while PEt$_3$ was commercially obtained and used without further purification. Elemental analyses were done at the Elemental Analysis Laboratory, Department of Chemistry, Faculty of Science, The University of Tokyo. Electron probe microanalysis (EPMA) was carried out using a Kevex μX 7000 energy dispersive-type X-ray analyzer. NMR spectra were recorded on a JEOL GX-400 spectrometer.

3.2. Preparation of 3a

(1) A mixture containing [NH$_4$]$_2$ · **1a** (393 mg, 1.13 mmol) and **2** (174 mg, 0.283 mmol) in THF (8 cm^3) was refluxed for 6 h with stirring. The resulting mixture was filtered and the filtrate was dried in vacuo. The residue was extracted with benzene, and ether was

added to the concentrated extract. The dark-green crystals deposited were filtered off and dried in vacuo (32.1 mg, (13%)) Anal. Found: C, 28.53; H, 3.48. C$_{20}$H$_{30}$Ru$_2$S$_6$W Calc.: C, 28.30; H, 3.57%. ^{1}H NMR (CDCl$_3$): δ 1.93 (s, Cp*) ppm.

(2) A mixture of [NH$_4$]$_2$ · **1a** (87.9 mg, 0.25 mmol), **2** (150 mg, 0.243 mmol) and Li$_2$S$_2$ (23.1 mg, 0.296 mmol) in THF (10 cm^3) was stirred for 16 h at room temperature. From the resultant mixture was isolated **3a** by the same work-up as described above (29.4 mg (14%)).

3.3. Preparation of 3b

A suspension containing [NH$_4$]$_2$ · **1b** (6.765 g, 26.0 mmol) and **2** (3.185 g, 5.18 mmol) in THF (65 cm^3) was stirred for 15 h at reflux. The resulting mixture was filtered and the filtrate was dried in vacuo. The residue was crystallized from benzene–ether, yielding **3b** as dark-green crystals (183 mg (5%)). Anal. Found: C, 30.29; H, 4.10. C$_{20}$H$_{30}$MoRu$_2$S$_6$ Calc.: C, 31.57; H, 3.97%. ^{1}H NMR (CDCl$_3$): δ 1.81 (s, Cp*) ppm.

3.4. X-ray crystallography for 3

Single crystals sealed in glass capillaries were mounted on a diffractometer and data collection was performed at room temperature by the use of graphite-monochromated Mo Kα radiation. Lattice parameters were obtained from a least-squares analysis of 20 reflections with $20° < 2\theta < 30°$. Three standard reflections

monitored every 100 reflections showed no significant decay. Intensity data were corrected for Lorentz and polarization effects, and for absorption. Detailed crystallographic data are shown in Table 3.

Both structures of **3a** and **3c** were solved by using the UNIX-III program package [26] at the computer center of The University of Tokyo. Heavy atom positions were determined by the direct-method program SHELXS86 [27]. Subsequent block-diagonal least-squares refinement and difference Fourier maps revealed all non-hydrogen atoms, which were refined anisotropically. Hydrogen atoms were placed at the calculated positions for both **3a** and **3b** and included in the final stage of the refinement with fixed parameters for **3a**, while those in **3b** were refined isotropically. Final atomic coordinates of non-hydrogen atoms are summarized in Table 4.

3.5. Reaction of 3a with PEt₃ to give 4

To a stirred solution of **3a** (90.0 mg, 0.106 mmol) in THF (9 cm³) was added PEt₃ (0.080 cm³, 0.542 mmol). An almost spontaneous color change from green to red was observed. After stirring overnight, the resultant solution was dried and the residue was subjected to silica gel column chromatography. A red band eluted with hexane was collected, concentrated in vacuo and then kept in the refrigerator. The red crystals precipitated were filtered off and dried (16 mg (15%)). EPMA data have suggested the presence of the W, Ru, S and P atoms in the ratio of $1:2:4:2$ in the product. ^{1}H NMR (CDCl$_3$): δ 1.85 (d, $^4J_{P-H} = 1.2$ Hz, 30H, Cp*), 1.41 (dq, $^2J_{J-H} = 3.8$ Hz, $^3J_{H-H} = 7.5$ Hz, 12H, PCH_2), 0.91 (dt, $^3J_{P-H} = 13.9$ Hz, $^3J_{H-H} = 7.5$ Hz, 18H, PCH$_2$CH_3) ppm.

Table 3
X-ray crystallographic data for **3**

	3a	3b
Crystal data		
Formula	$C_{20}H_{30}Ru_2S_6W$	$C_{20}H_{30}MoRu_2S_6$
Formula weight	848.8	760.9
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (Å)	16.460(2)	16.530(6)
b (Å)	10.009(3)	9.992(3)
c (Å)	16.582(2)	16.633(6)
β (°)	93.68(1)	93.82(3)
V (Å³)	2726(1)	2741(2)
Z	4	4
D_{calc} (g cm^{-3})	2.07	1.84
μ (cm^{-1})	58.26	19.56
$F(000)$ (electrons)	1632	1504
Crystal dimensions (mm)	0.40 × 0.28 × 0.05	0.42 × 0.40 × 0.20
Crystal color	Dark green	Dark green
Data collection		
Diffractomer	Rigaku AFC5R	MAC MXC18
Monochromator	Graphite	
Radiation (λ (Å))	Mo Kα (0.7107)	
Temperature	Room temperature	
Maximum 2θ, °	45	50
Scan method	ω–2θ	ω
Scan speed (° min^{-1})	16	16
Reflections measured	$\pm h, +k, +l$	$+h, +k, \pm l$
Absorption correction	ψ method	Gaussian integration method
Transmission factor	1.001–1.851	0.485–0.684
Structure solution and refinements		
Number of parameters refined	263	383
Number of data used ($|F_o| > 3\sigma(F_o)$)	3060	3390
R [a]	0.053	0.056
R_w [b]	0.065	0.064
Maximum residuals (electrons Å^{-3})	2.8 (around W)	0.8 (around Mo)

[a] $R = \Sigma(|F_o| - |F_c|)/\Sigma |F_o|$.
[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w |F_o|^2]^{1/2}$, where $w = 1$.

Table 4
Atomic coordinates of non-hydrogen atoms in **3**

Atom	x ($\times 10^{-4}$)	y ($\times 10^{-4}$)	z ($\times 10^{-4}$)
3a			
W	2610(1)	262(1)	7760(1)
Ru(1)	3069(1)	−716(1)	6230(1)
Ru(2)	1296(1)	1664(1)	6896(1)
S(1)	1838(3)	−1061(5)	5633(3)
S(2)	959(3)	161(5)	5952(3)
S(3)	2687(3)	1461(4)	6614(3)
S(4)	2922(3)	−1823(5)	7467(3)
S(5)	1321(3)	323(5)	8067(3)
S(6)	3416(4)	1055(7)	8710(3)
C(11)	3647(11)	−1695(24)	5226(12)
C(12)	4046(12)	−2142(19)	5944(13)
C(13)	4446(11)	−1039(23)	6349(11)
C(14)	4286(11)	63(20)	5891(13)
C(15)	3766(12)	−262(23)	5189(11)
C(16)	3235(14)	−2445(36)	4565(17)
C(17)	4126(16)	−3586(27)	6192(21)
C(18)	4959(15)	−1142(37)	7118(14)
C(19)	4598(17)	1472(25)	6070(22)
C(20)	3510(16)	659(35)	4526(17)
C(21)	279(11)	2969(20)	6464(12)
C(22)	241(11)	2802(16)	7294(12)
C(23)	948(11)	3383(21)	7702(11)
C(24)	1418(12)	3916(17)	7106(13)
C(25)	1045(14)	3669(22)	6340(12)
C(26)	−356(17)	2648(27)	5817(17)
C(27)	−468(13)	2185(21)	7694(16)
C(28)	1094(14)	3542(25)	8583(13)
C(29)	2241(16)	4574(29)	7241(17)
C(30)	1313(20)	4082(21)	5541(16)
3b			
Ru(1)	3070(1)	−726(1)	6227(1)
Ru(2)	1302(1)	1643(1)	6892(1)
Mo	2621(1)	264(1)	7748(1)
S(1)	1838(2)	−1085(4)	5638(2)
S(2)	958(2)	125(4)	5957(2)
S(3)	2674(2)	1458(3)	6594(2)
S(4)	2933(3)	−1835(4)	7454(2)
S(5)	1333(3)	306(4)	8060(2)
S(6)	3420(3)	1057(5)	8684(3)
C(11)	3769(9)	−264(18)	5202(9)
C(12)	3682(8)	−1699(18)	5228(9)
C(13)	4048(9)	−2143(16)	5947(9)
C(14)	4431(8)	−1032(17)	6342(8)
C(15)	4278(9)	111(16)	5885(10)
C(16)	3470(14)	578(31)	4481(14)
C(17)	3239(13)	−2544(29)	4590(13)
C(18)	4155(15)	−3601(20)	6201(17)
C(19)	4973(12)	−1103(28)	7129(11)
C(20)	4561(12)	1485(21)	6057(17)
C(21)	1027(11)	3607(15)	6332(10)
C(22)	291(10)	2960(16)	6458(9)
C(23)	243(8)	2786(13)	6287(9)
C(24)	948(9)	3397(13)	7689(8)
C(25)	1440(9)	3889(14)	7097(9)
C(26)	1321(16)	4083(21)	5538(12)
C(27)	−354(12)	2628(23)	5802(12)
C(28)	−454(8)	2169(17)	7705(12)
C(29)	1110(11)	3506(18)	8601(9)
C(30)	2233(11)	4620(17)	7260(13)

4. Supplementary material available

Tables of anisotropic temperature factors of non-hydrogen atoms, atomic coordinates of hydrogen atoms, and extensive bond lengths and angles (9 pages) as well as a listing of observed and calculated structure factors (19 pages) for **3a** and **3b** are available from the author (M.H.) upon request.

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