Preparation of hydrosulfido- and hydroselenido-bridged diruthenium complexes with π-arene co-ligands and their conversion into new cubane-type sulfido or selenido clusters

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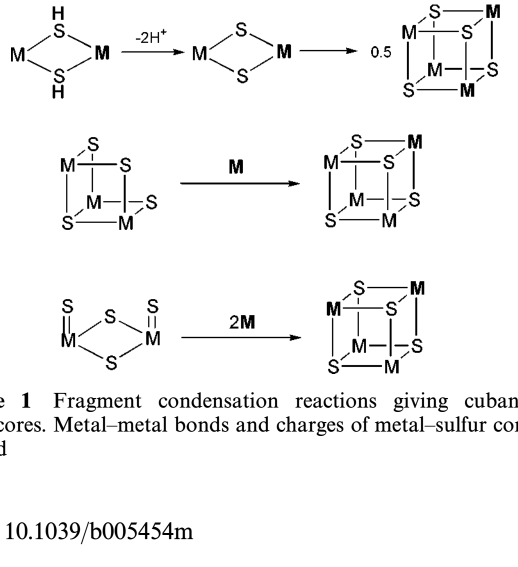
The Ru(II)-arene complex $(CymRuCl)_2(\mu\text{-}Cl)_2$ (Cym = η^6-*p*-$MeC_6H_4Pr^i$) dissolved in CH_2Cl_2 reacted with H_2S gas or *in situ*-generated H_2Se to afford the hydrosulfido- and hydroselenido-bridged diruthenium complexes $(CymRuCl)_2(\mu\text{-}EH)_2$ (E = S **2**, Se **3**). Complexes **2** and **3** were converted further into the cubane-type tetraruthenium sulfido and selenido clusters $(CymRu)_4(\mu_3\text{-}E)_4$ (E = S **4**, Se **5**) by treatment with NEt_3 in benzene. The reactions are presumed to proceed *via* coupling of the diruthenium species $(CymRu)_2(\mu\text{-}E)_2$ initially formed by dehydrochlorination of **2** and **3**. The structures of new compounds **2**, **3**, **4** and **5** have been determined in detail by X-ray crystallography.

Among the numerous transition metal-sulfur clusters hitherto synthesized, those containing the cubane-type M_4S_4 core[1–4] are of particular interest owing principally to their relevance to the active sites of certain biological and industrial catalysts. In this respect, compounds containing Fe_4S_4,[2] $MoFe_3S_4$,[3] and Mo_4S_4[4] cores have been extensively studied in relation to iron–sulfur proteins, nitrogenases, and hydrodesulfurization catalysts, respectively. Our studies on the chemistry of cubane-type clusters have been aimed at syntheses of those consisting of a much wider range of metals and heavier chalcogens in pursuit of more intriguing physical properties and reactivities.

We have recently prepared a series of cubane-type clusters with desired compositions of metals *via* rational synthetic routes, which include, for example, dimerization of the coordinatively unsaturated $M_2(\mu\text{-}S)_2$ fragments generated *in situ* from $M_2(\mu\text{-}SH)_2$ moieties through deprotonation,[5] as well as incorporation of either a metal into the missing vertex of the incomplete cubane-type M_3S_4 core[6,7] or two metals into the $MS(\mu\text{-}S)_2MS$ template[8] (Scheme 1). The first method, starting from dinuclear hydrosulfido complexes, has proved to be remarkably versatile and homo- and heterometallic cluster cores such as Ru_4S_4, Rh_4S_4, Ir_4S_4, $Ti_2Rh_2S_4$, $Ti_2Ir_2S_4$, $Ti_2Ru_2S_4$ and $TiRu_3S_4$ have been afforded *via* this route. More recently it has been demonstrated that the selenido clusters $(Cp^*M)_4(\mu_3\text{-}Se)_4$ (M = Rh, Ir; Cp* = η^5-C_5Me_5) are also accessible by an analogous route.[9]



Scheme 1 Fragment condensation reactions giving cubane-type M_4S_4 cores. Metal–metal bonds and charges of metal–sulfur cores are omitted

Now we have found that the chloro-bridged diruthenium(II) complex $(CymRuCl)_2(\mu\text{-}Cl)_2$, **1**, can readily be converted into the hydrosulfido- or hydroselenido-bridged complexes $(CymRuCl)_2(\mu\text{-}EH)_2$ (Cym = η^6-*p*-$MeC_6H_4Pr^i$; E = S **2**, Se **3**), which undergo dehydrochlorination and subsequent dimerization to give new cubane-type tetraruthenium(II) chalcogenido clusters $(CymRu)_4(\mu\text{-}E)_4$ (E = S **4**, Se **5**) having a 72-electron Ru_4 core. From an organometallic perspective, metal clusters with η^6-arene ligands are still rare as are η^6-arene complexes with chalcogenido ligands. In this paper, details of the synthesis and characterization of **2**, **3**, **4** and **5** are described.

Results and discussion

Syntheses and characterization of 2 and 3

The chemistry of $\{(\eta^6\text{-arene})RuCl\}_2(\mu\text{-}Cl)_2$ is known to often resemble that of the isoelectronic $\{(\eta^5\text{-cyclopentadienyl})MCl\}_2(\mu\text{-}Cl)_2$ (M = Rh, Ir),[10] and it is also true for the complexes containing chalcogen ligands. The reactions of $\{(\eta^6\text{-arene})RuCl\}_2(\mu\text{-}Cl)_2$ with $PhSSiMe_3$, PhSH–LiMe, or NaEAr (E = S, Se, Te) have been reported to afford the organochalcogenolato complexes $[\{(\eta^6\text{-arene})Ru\}_2(\mu\text{-}EPh)_3]^+$ (E = S, Se, Te) and $(\eta^6\text{-arene})Ru(EAr)_2$ (EAr = 2,6-$SC_6H_3Me_2$, 2,4,6-$SC_6H_2Pr^i_3$, 2,4,6-$SeC_6H_2Me_3$),[11] while the related Cp*Rh or Cp*Ir complexes such as $[(Cp^*M)_2(\mu\text{-}SR)_3]^+$ (M = Rh, R = Me, C_6F_5, *p*-C_6H_4F; M = Ir, R = *p*-C_6H_4F, CF_3, Et) and $Cp^*Ir(SR)_2$ (R = C_6F_5, *p*-C_6F_4H) are also available by the analogous procedures.[12] As for the chalcogenido clusters, compounds having the $\{(\eta^6\text{-arene})Ru\}_4(\mu_3\text{-}E)_4$ core are unprecedented, although the trinuclear clusters $[(CymRu)_3(\mu_3\text{-}E)_2]^{2+}$ (Cym = η^6-*p*-$MeC_6H_4Pr^i$; E = S, Se) have been known for some time.[13]

When H_2S gas was bubbled through a THF suspension of **1**

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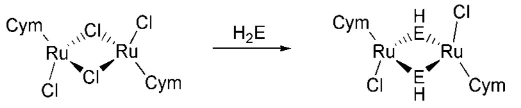
at room temperature, the hydrosulfido-bridged diruthenium complex **2** was obtained in 63% yield. It has also been found that the hydroselenido analog **3** is available in 54% yield from **1** and 2 equiv. of H$_2$Se generated *in situ* from NaSeH-aqueous HCl at 0 °C in CH$_2$Cl$_2$ [eqn. (1)]. Complexes **2** and **3** were characterized by elemental analyses, spectral data, and X-ray diffraction. It is to be noted that hydroselenido complexes fully characterized by X-ray analysis are extremely rare: examples are the Ir and Rh bridging-hydroselenido complexes described in our previous paper[9] (see below) as well as the Al terminal-hydroselenido complexes reported quite recently.[14] Reactions of **1** with NaSH and NaSeH in place of H$_2$S and H$_2$Se, respectively, hardly proceeded and **1** was recovered almost quantitatively, presumably because of the low solubilities of **1** and NaEH in THF. By contrast, it was reported previously that **1** and NaSH dissolved in MeOH did react to give [(CymRu)$_3$(μ_3-S)$_2$]$^{2+}$.[13a]



1 E = S (**2**), Se (**3**) (1)

The IR spectra showed the ν(S–H) band at 2511 cm^{-1} for **2** and the ν(Se–H) band at 2253 cm^{-1} for **3**, which are in good agreement with those of the Rh complexes (Cp*RhCl)$_2$(μ-SH)$_2$, **6**, (2511 cm^{-1}) and (Cp*RhCl)$_2$(μ-SeH)$_2$, **7**, (2247 cm^{-1}), respectively. In each of the ^{1}H NMR spectra for **2** and **3** dissolved in C$_6$D$_6$, two sets of signals characteristic of the Cym and EH protons appeared, indicating the presence of *syn* and *anti* isomers with respect to the two μ-EH groups, as observed previously for the isostructural Rh complexes **6** and **7** and their Ir analogs (Cp*IrCl)$_2$(μ-EH)$_2$ (E = S **8**,[5b] Se **9**[9]), as well as the Ru(III) complex (Cp*RuCl)$_2$(μ-SH)$_2$, **10**.[5a] For **2** the SH resonances observed at δ 0.41 and 0.48 due to the *syn* and *anti* isomers, respectively, were integrated to be in a 2 : 1 ratio, while the SeH signals at δ -2.50 and -2.44 for the *syn* and *anti* forms of **3** appeared in a 5 : 3 intensity ratio. Assignment of the SH and SeH resonances to either the *syn* or *anti* isomers is based on the appearance of the corresponding Cym resonances as two sets of signals with the same intensities for the former and as only one set for the latter. These chemical shifts of the SH and SeH protons are comparable to those of the Cp*Rh and Cp*Ir complexes **6**–**9**. It is to be noted that the SH signals in **10** are somehow highly deshielded to be observed at δ 5.11 and 5.13. The signals due to *p*-MeC$_6$H$_4$Pr^i groups are consistent with the structure containing two Cym ligands in mutually *trans* positions for both the *syn* and *anti* isomers.

The X-ray diffraction studies have demonstrated that **2** and **3** are isomorphous, each having a crystallographic inversion center at the midpoint between the two ruthenium atoms (see Fig. 1 for **3**). Their molecular structures are analogous to those of the X-ray analyzed **6**–**8** as well as the spectroscopically characterized **9**, given that the Rh or Ir atoms and the Cp* ligands are replaced by Ru and the Cym ligand, respectively. Important interatomic distances and angles in **2** and **3** are listed in Table 1. The structures of {(η^6-arene)RuCl}$_2$(μ-Cl)$_2$ (arene = hexamethylbenzene, trindane, ethyl benzoate, tetralin) reported previously are also related closely to those of **2** and **3** with comparable Ru–(arene centroid) and Ru–Cl$_{\text{terminal}}$ distances.[15] The hydrogen atoms bound to S or Se were found in the difference-Fourier map, whereby the position of the SeH hydrogen in **3** is unequivocally determined [Se–H, 1.44(6) Å]. However, the SH hydrogen atom in **2** was observed at two disordered positions [S–H, 1.41(5), 1.32(8) Å]. The Ru···Ru distances at 3.6577(4) Å in **2** and 3.8104(6) Å in **3** indicate the absence of any bonding interaction as expected from the 18-electron count for these Ru centers. The Ru–S distances in **2** [2.4040(7) and 2.4049(7) Å] are unexceptional as are those for the Ru–(μ-SR) bonds around the coordinatively saturated Ru(II) atoms.[5c,11a,b,16] These interatomic distances in **2** are longer than those in the Cp*Ru(III)-hydrosulfido complex **10**, which has a Ru–Ru single bond [Ru–S, 2.310(1) and 2.319(2); Ru–Ru, 2.822(1) Å].[5a] Diruthenium arene complexes bridged only by two chalcogenolate ligands are hitherto unknown; a benzenethiolate complex with the analogous composition was shown to have a cationic structure with bridging thiolate and chloro ligands [{(η^6-C$_6$Me$_6$)Ru}$_2$(μ-SPh)$_2$(μ-Cl)]Cl.[11a]

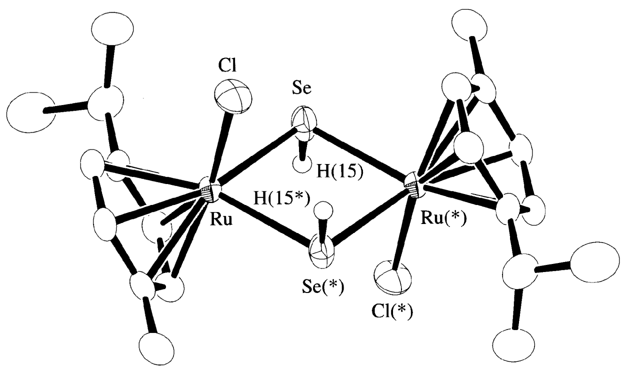
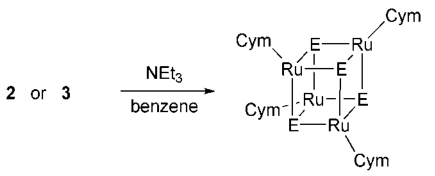


Fig. 1 Molecular structure of **3**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity except for the hydroselenido ligand.

Formation of the cubane-type Ru$_4$E$_4$ clusters

Treatment of **2** and **3** with NEt$_3$ in benzene at room temperature readily produced the cubane-type ruthenium chalcogenido clusters **4** and **5** [eqn. (2)]. It is interesting to note that the reactions of **3** with sulfido compounds such as Na$_2$S and



E = S (**4**), Se (**5**) (2)

Table 1 Selected interatomic distances (Å) and angles (°) in the new compounds **2**–**5**

	2 (E = S)	**3** (E = Se)
Ru···Ru*	3.6577(4)	3.8104(6)
Ru–E	2.4040(7)	2.5105(5)
Ru–E*	2.4049(7)	2.5146(5)
Ru–Cl	2.4091(6)	2.411(1)
Ru–C	2.155(3)–2.223(2)	2.159(4)–2.222(4)
Ru–(centroid or Cym)	1.676(3)	1.683(4)
E–Ru–E*	80.97(2)	81.38(2)
E–Ru–Cl	84.38(3)	83.94(3)
E*–Ru–Cl	86.26(3)	86.46(4)
Ru–E–Ru*	99.03(2)	98.62(2)
Ru–Se–H		101(2)
Ru–Se*–H*		95(2)
	4 (E = S)	**5** (E = Se)
Ru···Ru	3.6108(4)–3.6500(6)	3.7819(9)–3.829(1)
Ru–E	2.380(1)–2.412(2)	2.497(1)–2.529(1)
Ru–C	2.196(5)–2.268(6)	2.17(1)–2.26(1)
Ru–(centroid of Cym)	1.702(6)–1.721(8)	1.70(2)–1.71(1)
E–Ru–E	80.35(5)–80.94(5)	80.48(4)–81.38(4)
Ru–E–Ru	97.73(5)–99.51(4)	97.44(4)–99.32(4)

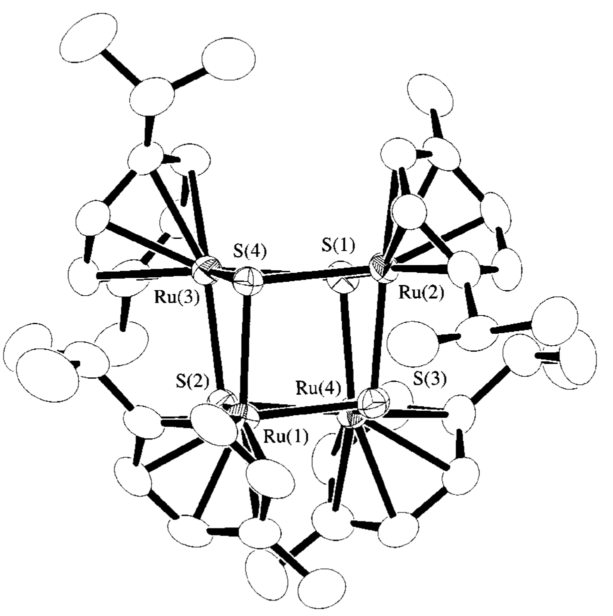


Fig. 2 Molecular structure of **4**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

$S(SiMe_3)_2$ do not afford **4** but $[(CymRu)_3(\mu_3\text{-}S)_2]^{2+}$.[13a] As demonstrated for the syntheses of several homo- and heterometallic cubanes (*vide supra*), it is presumed that **4** and **5** also result from the coupling of two $(CymRu)_2(\mu\text{-}E)_2$ (E = S, Se) species generated *in situ* by the dehydrochlorination of **2** and **3**, although no intermedate species were able to be isolated or detected.

The molecular structures of **4** and **5** have been unequivocally determined by X-ray crystallography. An ORTEP drawing of **4** is shown in Fig. 2, while pertinent interatomic distances and angles in **4** and **5** are summarized in Table 1. Clusters **4** and **5** have an essentially identical structure except for the larger core volume of **5** than that of **4**, mainly because of the difference in the atomic radius between S and Se. There exist no crystallographically imposed symmetries within both molecules, although the Ru_4E_4 core displays a pseudo T_d symmetry. No bonding interactions were observed between the Ru atoms, which is consistent with the 72-electron count for the Ru_4 cores in these clusters. The Ru_4S_4 cubanes are slightly distorted with acute E–Ru–E (80–82°) and obtuse Ru–E–Ru (97–100°) angles. M–E–M bond angles wider than 90° are commonly observed for those associated with the two metal atoms without a direct M—M bond in M_4E_4 cubane cores.

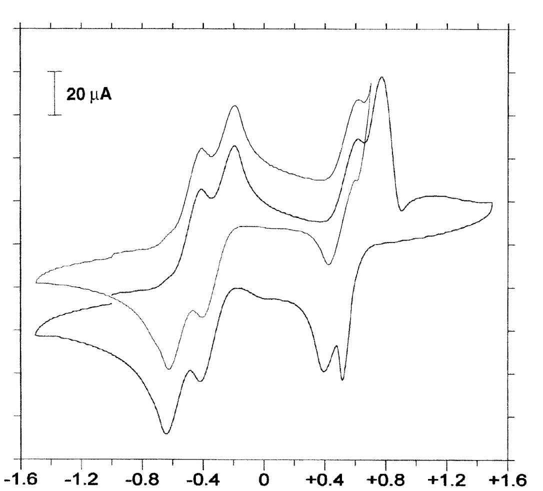


Fig. 3 Cyclic voltammogram of **4** dissolved in CH_2Cl_2–0.1 M $[Bu^n_4N][BF_4]$ with a Pt working electrode *vs.* SCE. Scan rate: 200 mV s^{-1}.

A series of cubane-type Ru_4E_4 (E = S, Se, Te) clusters with η^5-cyclopentadienyl ligands have already been reported. However, these include either the 66-electron clusters $[Cp'_4Ru_4(\mu_3\text{-}E)_4]^{2+}$ [$Cp'_4 = Cp^*_4$, E = S; $Cp'_4 = (C_5H_4Me)_4$, E = S, Se, Te; $Cp'_4 = (C_5H_4SiMe_3)_4$, E = S; $Cp'_4 = Cp^*_2Cp_2$, E = S] or the 68-electron clusters $Cp'_4Ru_4(\mu_3\text{-}E)_4$ [$Cp'_4 = Cp^*_4$, E = S, Se, Te; $Cp'_4 = (C_5H_4Me)_4$, E = S, Se, Te; $Cp'_4 = (C_5H_4SiMe_3)_4$, E = S; $Cp'_4 = Cp^*_2Cp_2$, E = S], whose cores consist formally of three or two Ru–Ru single bonds, respectively.[5a,c,17,18] Although $Fe_4(\mu_3\text{-}E)_4(CO)_{12}$ (E = S, Se)[19] and $Os_4(\mu_3\text{-}O)_4(CO)_{12}$[20] have long been known, 72-electron Ru_4E_4 clusters are still quite rare. To our knowledge, the only structurally determined example of this type is $Ru_4(\mu_3\text{-}Se)_4(CO)_{10}(\mu\text{-}Ph_2PCH_2PPh_2)$,[21] whereas the relevant hydroxide-bridged clusters $[\{(\eta^6\text{-}C_6H_6)Ru\}_4(\mu_3\text{-}OH)_4][SO_4]_2$[22] and $[(Cp'Ru)_4(\mu_3\text{-}OH)_4]$ (Cp′ = Cp*, C_5Me_4Et)[23] are known for some time. The Ru–Se distances in **5** [2.497(1)–2.529(1) Å] are slightly longer than those in $(Cp^*Ru)_4(\mu_3\text{-}Se)_4$ (2.43–2.49 Å)[18d] but shorter than those in $Ru_4(\mu_3\text{-}Se)_4(CO)_{10}(\mu\text{-}Ph_2PCH_2PPh_2)$ [2.549(1)–2.577(1) Å].[21]

Electrochemistry of 4 and 5

Under voltammetric conditions at a glassy carbon electrode, the electrochemical properties of **4** and **5** were investigated. As depicted in Fig. 3, the cyclic voltammogram shows that **4** undergoes four consecutive oxidations, among which initial three steps are obviously reversible. Although the first and second processes as well as the third and fourth processes are not separated clearly, the potentials $E_{1/2}$ for these four waves may be calculated to be about −0.53, −0.31, +0.51 and +0.65 V *vs.* SCE, which are presumably assignable to the series of redox processes $[Ru(II)_4] \rightleftharpoons [Ru(II)_3Ru(III)] \rightleftharpoons [Ru(II)_2Ru(III)_2] \rightleftharpoons [Ru(II)Ru(III)_3] \rightleftharpoons [Ru(III)_4]$. Under identical conditions, **5** exhibited an analogous cyclic voltammogram, whose $E_{1/2}$ values corresponding to these processes are −0.52, −0.32, +0.45 and +0.53 V, respectively, which indicate that the oxidation potentials are affected only slightly upon changing S to Se. Overlapping of the first and second oxidation waves might imply that these processes occur at the two almost equivalent Ru(II) centers without any direct bonding interaction. The large separation of these waves from the mutually overlapping third and fourth waves is presumably owing to the rapid formation of the stable diamagnetic species with one Ru(III)–Ru(III) bond. Cyclic voltammograms for the Ru(III) clusters $\{(MeC_5H_4)Ru\}_4(\mu_3\text{-}E)_4$(E = S, Se, Te) were reported previously by Rauchfuss and his coworkers,[18c] which revealed two consecutive, reversible oxidation waves for E = S. However, these two waves almost overlapped for E = Se, while only one wave attributable to a two-electron process was observed for E = Te. Thus, it was concluded that although the separation of the two potentials changed significantly from 121 mV for E = S to *ca.* 80 mV for E = Se and *ca.* 0 mV for E = Te, the chalcogen exerts only a slight effect on the average of the two potentials $E_{1/2}$ (−0.12, −0.13 and −0.17 V *vs.* Ag/AgCl reference electrode for E = S, Se and Te, respectively) as observed in the present work.

Because of the higher lability of the η^6-arene ligand compared to the η^5-cyclopentadienyl group, **4** and **5** will possibly serve as better precursors to cubane-type clusters of the general formula $Ru_4(\mu_3\text{-}E)_4L_{12}$, where the arene ligand is replaced by L. Further study is in progress to clarify the reactivities of **4** and **5** in this context.

Experimental

Syntheses

All manipulations were performed under nitrogen atmosphere using standard Schlenk techniques. Solvents were dried by common procedures and distilled under nitrogen just before use. Compounds **1**[24] and NaSeH[17,25] were prepared according to the literature methods. Other reagents were commercially obtained and used as received.

^{1}H (400 MHz) NMR spectra were recorded on a JEOL alpha-400 spectrometer in C_6D_6, whereby the chemical shifts were referenced to the signal of C_6D_5H at δ 7.15. IR spectra were recorded on a JASCO FT/IR-420 spectrometer. Elemental analyses were done with Perkin–Elmer 2400 series II CHN analyzer. Electrochemical measurements were made with a BAS CV-50W electrochemical analyzer using a glassy carbon working electrode. Potentials were measured in CH_2Cl_2–0.1 M $[\mathrm{Bu}^n_4\mathrm{N}][\mathrm{BF}_4]$ with SCE as reference.

$[(\mathrm{CymRuCl})_2(\mu\text{-SH})_2]$ 2. H_2S gas was bubbled through a suspension of **1** (124 mg, 0.203 mmol) in THF (10 mL) for 5 min. The resultant orange-red solution was evaporated to dryness *in vacuo* and the residual solid was crystallized from CH_2Cl_2–hexane. Red crystals of **2** (78 mg, 63% yield) were separated manually from a small amount of dark green oil. ^{1}H NMR (C_6D_6): *syn* isomer: δ 0.41 (s, 2H, SH), 1.68 and 1.88 (s, 3H each, Me), 2.56 and 2.73 (sep, $J = 7.0$ Hz, 1H each, C*H*Me$_2$), 4.39, 4.61, 4.94 and 5.04 (d, $J = 5.9$ Hz, 2H each, C_6H_4); *anti* isomer: δ 0.48 (s, 2H, SH), 1.83 (s, 6H, Me), 2.67 (sep, $J = 7.0$ Hz, 2H, C*H*Me$_2$), 4.56 and 4.86 (d, $J = 6.1$ Hz, 2H each, C_6H_4), 4.65–4.80 (m, 4H, C_6H_4); *syn* : *anti* = 2 : 1; the signals ascribable to Pr^i methyl protons of the *syn* and *anti* isomers in the region δ 1.0–1.15 are overlapped. IR (KBr): ν(SH) 2511 cm^{-1}. Anal. calcd for $C_{20}H_{30}S_2Cl_2Ru_2$: C, 39.53; H, 4.98. Found: C, 39.54; H, 4.99%.

$[(\mathrm{CymRuCl})_2(\mu\text{-SeH})_2]$ 3. To a suspension of **1** (196 mg, 0.321 mmol) and NaSeH (69 mg, 0.67 mmol) in CH_2Cl_2 (7 mL) was added concentrated hydrochloric acid (86 mg, 0.82 mmol) at 0 °C. The mixture was stirred at this temperature for 1 h and then dried over $MgSO_4$. The resultant solution was filtered and hexane was added to the filtrate at −20 °C. Red-brown crystals of **3** precipitated, which were separated manually (121 mg, 54% yield) from a small amount of oily by-product. Single crystals suitable for X-ray analysis were grown by slow diffusion of hexane into a 1,2-dichloroethane solution of **3** at 20 °C over 10 days, although decomposition occurred during this period (24% recovery). ^{1}H NMR (C_6D_6): *syn* isomer: δ −2.50 (s with ^{77}Se satellites, $J_{\mathrm{HSe}} = 43$ Hz, 2H, SeH), 1.75 and 1.95 (s, 3H each, Me), 2.58 and 2.74 (sep, $J = 6.9$ Hz, 1H each, C*H*Me$_2$), 4.42, 4.62, 4.87 and 4.97 (d, $J = 6.0$ Hz, 2H each, C_6H_4); *anti* isomer: δ −2.44 (s with ^{77}Se satellites, $J_{\mathrm{HSe}} = 37$ Hz, 2H, SeH), 1.87 (s, 6H, Me), 2.67 (sep, $J = 6.9$ Hz, 2H), 4.58, 4.70, 4.74 and 4.82 (dd, $J = 5.9$ and 1.3 Hz, 2H each, C_6H_4); *syn* : *anti* = 5 : 3; the signals for Pr^i methyl protons of *syn* and *anti* isomers in the region δ 1.0–1.05 are overlapped. IR (KBr): ν(SeH), 2253 cm^{-1}. Anal. calcd for $C_{20}H_{30}Se_2Cl_2Ru_2$: C, 34.25; H, 4.31. Found: C, 34.25; H, 4.26%.

$[(\mathrm{CymRu})_4(\mu_3\text{-S})_4]$ 4. To a suspension of **2** (61 mg, 0.10 mmol) in benzene (5 mL) was added NEt_3 (42 μL, 0.30 mmol). After stirring of the mixture for 14 h at room temperature, volatile materials were removed under reduced pressure. The residue was extracted with hexane, the extract being concentrated to 4 mL and stored at −78 °C to give **4** as red crystals (46 mg, 86%). Single crystals suitable for X-ray analysis were obtained by cooling a toluene solution of **4** to −78 °C. ^{1}H NMR (C_6D_6): δ 1.30 (d, $J = 6.9$ Hz, 24H, CH*Me*$_2$), 2.09 (s, 12H, Me), 2.92 (sep, $J = 6.9$ Hz, 4H, C*H*Me$_2$), 4.55 and 4.79 (d, $J = 5.6$ Hz, 8H each, C_6H_4). Anal. calcd for $C_{40}H_{56}S_4Ru_4$: C, 44.92; H, 5.28. Found: C, 44.86; H, 5.26%.

$[(\mathrm{CymRu})_4(\mu_3\text{-Se})_4]$ 5. This complex was obtained as red crystals containing a solvating hexane molecule, $\mathbf{5}\cdot C_6H_{14}$, in 70% yield from **3** by a similar method to that for preparing **4**. Single crystals suitable for X-ray analysis were obtained by cooling a toluene solution to −40 °C. ^{1}H NMR (C_6D_6): δ 1.28 (d, $J = 6.8$ Hz, 24H, CH*Me*$_2$), 2.14 (s, 12H, Me), 2.95 (sep, $J = 6.8$ Hz, 4H, C*H*Me$_2$), 4.60 and 4.78 (d, $J = 5.4$ Hz, 8H each, C_6H_4). Anal. calcd for $C_{46}H_{70}Se_4Ru_4$: C, 41.13; H, 5.25. Found: C, 41.08; H, 5.05%.

X-Ray crystallography

Single crystals of **2**, **3**, $\mathbf{4}\cdot C_7H_8$ and $\mathbf{5}\cdot C_7H_8$ were sealed in glass capillaries under argon and mounted on a Rigaku AFC7R diffractometer equipped with a graphite-monochromated Mo-Kα source. All diffraction studies were done at room temperature. Orientation matrixes and unit cell parameters were derived from the least-squares fit of 25 machine-centered reflections. The intensities of three check reflections were monitored every 150 reflections during data collection, which revealed no significant decay except for $\mathbf{5}\cdot C_7H_8$. Details of the X-ray diffraction study are listed in Table 2.

Structure solution and refinements were carried out by using the teXsan program package.[26] The positions of the non-hydrogen atoms were determined by Patterson methods (PATTY)[27] and subsequent Fourier synthesis (DIRDIF 94).[28] These were refined with anisotropic thermal parameters by full-matrix least-squares techniques except for the disordered

Table 2 Crystallographic data for **2**, **3**, $\mathbf{4}\cdot C_7H_8$ and $\mathbf{5}\cdot C_7H_8$

	2	**3**	$\mathbf{4}\cdot C_7H_8$	$\mathbf{5}\cdot C_7H_8$
Formula	$C_{20}H_{30}S_2Cl_2Ru_2$	$C_{20}H_{30}Cl_2Se_2Ru_2$	$C_{47}H_{64}S_4Ru_4$	$C_{47}H_{64}Se_4Ru_4$
Formula weight	607.62	701.42	1161.54	1349.14
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)	$P2_1/a$ (No. 14)	$P2_1/a$ (No. 14)
a/Å	9.791(1)	9.9109(7)	18.022(1)	18.001(3)
b/Å	11.806(1)	11.9264(8)	16.351(1)	16.653(3)
c/Å	10.532(1)	10.5135(5)	18.111(2)	18.315(3)
β/deg	112.779(7)	112.183(4)	118.101(5)	118.661(10)
U/Å^3	1122.4(2)	1150.7(1)	4708.0(7)	4817(1)
Z	2	2	4	4
ρ_{calc} g cm^{-3}	1.798	2.024	1.639	1.860
μ_{calc}/cm^{-1}	17.73	47.12	14.68	42.84
Crystal size/mm^3	0.8 × 0.4 × 0.3	0.6 × 0.3 × 0.2	0.6 × 0.5 × 0.4	0.4 × 0.2 × 0.2
No. reflections measured	2724	2785	11 172	11 398
No. unique reflections	2580	2639	10 827	11 045
No. reflections observed	2293	2219	7284	5214
R^a	0.021	0.036	0.035	0.040
$R_w{}^b$	0.036	0.046	0.047	0.044

^{a} $R = \Sigma\,\|F_o| - |F_c\|/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o{}^2]^{1/2}$ $\{w = [\{\sigma(F_o)\}^2 + (p^2/4)F_o{}^2]^{-1}\}$.

toluene molecules in $\mathbf{4}\cdot C_7H_8$ and $\mathbf{5}\cdot C_7H_8$, which were treated as the rigid groups. The hydrogen atoms in **2** and **3** were found from the Fourier maps, which were refined isotropically. Other hydrogens were placed at the calculated positions and included in the final stages of the refinements with fixed parameters.

CCDC reference number 440/209. See http://www.rsc.org/suppdata/nj/b0/b005454m/ for crystallographic files in .cif format.

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