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Article

Arene–Ruthenium Complexes of an Acyclic Thiolate–Thioether and Tridentate Thioether Derivatives Resulting from Ring-Closure Reactions

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The reaction of $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = C_6Me_6, 1,4-$MeC_6H_4CHMe_2$) with a large excess of the dianion of bis(2-mercaptoethyl) sulfide, $(HSCH_2CH_2)_2S$, obtained from deprotonation of the dithiol with freshly prepared NaOMe, gives the deep red, monomeric complexes $[(\eta^6\text{-arene})Ru(\eta^3\text{-}C_4H_8S_3)]$ (arene = C_6Me_6 (**5**), 1,4-$MeC_6H_4CHMe_2$ (**6**)) in which the dianion is bound to the metal atom through one thioether and two thiolate sulfur atoms. Complex **5** reacts with $[(\eta^6\text{-}C_6Me_6)RuCl_2]_2$ (**4**) in a 2:1 mole ratio to give a quantitative yield of the chloride salt of a binuclear cation $[\{(\eta^6\text{-}C_6Me_6)Ru\}_2Cl(\mu_2\text{-}\eta^2\text{:}\eta^3\text{-}C_4H_8S_3)]^+$ (**7**) in which the thiolate sulfur atoms of the $[(\eta^6\text{-}C_6Me_6)Ru(\eta^3\text{-}C_4H_8S_3)]$ group bridge to a $(\eta^6\text{-}C_6Me_6)RuCl$ unit. This compound is also obtained directly from the reaction of **4** with the dithiolate, if the Ru dimer is used in large excess. The binuclear complex $[\{(\eta^6\text{-}C_6Me_6)Ru\}_2(MeCN)(\mu_2\text{-}\eta^2\text{:}\eta^3\text{-}C_4H_8S_3)](PF_6)_2\cdot MeCN$, (**9**)$(PF_6)_2\cdot MeCN$, is obtained by treatment of (**7**)Cl with NH_4PF_6 in acetonitrile. Protonation of **5** with HCl gave the mono- and diprotonated derivatives viz. $[(\eta^6\text{-}C_6Me_6)Ru(\eta^3\text{-}C_4H_9S_3)]Cl$, (**8**)Cl, and $[(\eta^6\text{-}C_6Me_6)Ru(\eta^3\text{-}C_4H_{10}S_3)]Cl_2$, (**10**)$Cl_2$, respectively. The reaction of **5** with methyl iodide gives both the mono- and di-S-methylated derivatives. Treatment of **5** with dibromoalkanes, $Br(CH_2)_nBr$ (n = 1–5), effects ring closure to give the $(\eta^6\text{-}C_6Me_6)Ru$ dications containing the trithia mesocyclic zS3 (z = 8–12) ligands, isolated as their PF_6 salts. The X-ray crystal structures of **5**, **6**, the solvates of (**7**)Cl and (**9**)$(PF_6)_2$, and the trithia mesocyclic Ru complexes $(\eta^6\text{-}C_6Me_6)Ru(z$S3$)(PF_6)_2$ (z = 8–11) are reported.

The coordination chemistry of monodentate sulfur donors with arene−ruthenium(II) and arene−osmium(II) complexes is well established. Monodentate thioethers such as dimethyl sulfide and tetrahydrothiophene (R_2S) form unstable complexes $[(\eta^6\text{-arene})RuCl_2(SR_2)]$ and $[(\eta^6\text{-arene})RuCl(SR_2)_2]^+$ (arene = *p*-cymene, 1,3,5-$C_6H_3Me_3$ or C_6Me_6),[1] and confacial bioctahedral tri-μ-thiolato cations $[(\eta^6\text{-arene})_2Ru_2(\mu\text{-}SR)_3]^+$ (R = Et, Ph) are readily obtained from $[(\eta^6\text{-arene})RuCl_2]_2$ and the appropriate thiol.[2−4] Stable, neutral bis(thiolates) $[(\eta^6\text{-}$

p-cymene)Os(SR)_2]$ have been isolated in high yields from the reaction of the monomeric amido complex $[(\eta^6\text{-}p\text{-}$cymene)Os(N-*t*-Bu)]$ or the bis-(*t*-butoxide) complex $[(\eta^6\text{-}p\text{-}cymene)Os(O-\textit{t}\text{-Bu})_2]$ with the thiol; they are monomeric for R = *t*-Bu, 2,6-$Me_2C_6H_3$, and 2,4,6-$Me_3C_6H_2$ and dimeric for R = *p*-MeC_6H_4.[5] The sterically hindered arenethiolates $[2,5\text{-}Me_2C_6H_3S]^-$ and $[2,4,6\text{-i-}Pr_3C_6H_2S]^-$ also give monomeric, 16-electron complexes $[(\eta^6\text{-arene})Ru(SR)_2]$.[6,7] The reaction of $[RuCl_2(PPh_3)_3]$ with 2,6-diphenylthiophenolate anion (DPT) gives a half-sandwich complex $[Ru(DPT)_2$-

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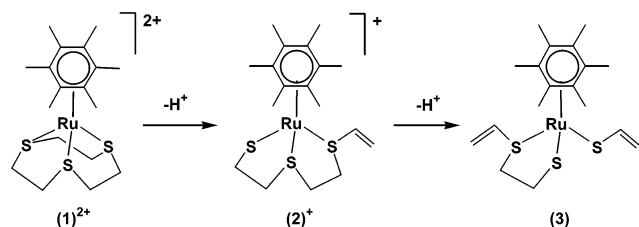(3) Mashima, K.; Mikami, A.; Nakamura, A. *Chem. Lett.* **1992**, 1795.
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Scheme 1

(PPh$_3$)] in which one of the DPT ligands is bound to ruthenium through the aromatic ring as well as through the sulfur atom.[8] However, no arene−ruthenium complexes containing neutral thiols are known that correspond to the extensive series of compounds in the cyclopentadienyl series of general type [(η^5-Cp)Ru(RSH)(L^1)(L^2)]$^+$, where L^1 and L^2 are combinations of CO, t-BuNC, and group 15 donor ligands.[9]

It seemed possible that thiol coordination in the arene−ruthenium series might be stabilized if the thiol were part of a potentially chelating ligand such as a mixed thiolate−thioether. We had already shown that on treatment with KOH, the crown thioether complex [(η^6-C$_6$Me$_6$)Ru{η^3-(9S3)}]$^{2+}$ (**1**) undergoes successive deprotonation at the methylene carbon atoms accompanied by C−S bond cleavage to give the chelate thiolate−thioether complexes **2** and **3** (Scheme 1).[10] We therefore decided to study for comparison the reaction of [(η^6-C$_6$Me$_6$)RuCl$_2$]$_2$ with the anions of bis(2-mercaptoethyl)sulfide (3-thiapentane-1,5-dithiol), (HSCH$_2$CH$_2$)$_2$S. This compound acts as a η^3-tridentate ligand in various early transition metal complexes, such as [NbS-(η^3-SCH$_2$CH$_2$SCH$_2$CH$_2$S)(η^2-SCH$_2$CH$_2$S)]$^{-11}$ and [ReOX(η^3-SCH$_2$CH$_2$SCH$_2$CH$_2$S)] (X = Cl or various SR groups),[12−15] and in the tin(IV) complex [Sn(η^3-SCH$_2$CH$_2$SCH$_2$CH$_2$S)$_2$].[16] It is also possible for one or both thiolate sulfur atoms to form bridges to additional metal atoms, as found in the dinickel(II) complex [Ni$_2$(μ_2-η^1:η^3-SCH$_2$CH$_2$SCH$_2$CH$_2$S)$_2$],[17] the indium(III) dicarbollide complex [(C$_2$B$_9$H$_{11}$)$_2$In$_2$(μ_2-η^1:η^3-SCH$_2$CH$_2$SCH$_2$CH$_2$S)$_2$],[18] and the tripalladium(II) complex [Pd$_3$(μ_2-η^1:η^3-SCH$_2$CH$_2$SCH$_2$CH$_2$S)$_3$],[17] as shown in Figure 1.
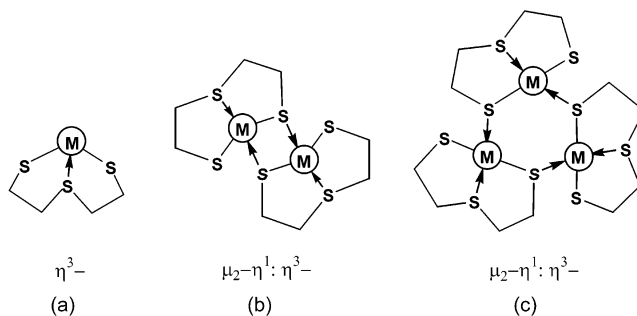
Figure 1. Known bonding modes of S(CH$_2$CH$_2$S$^-$)$_2$.

Scheme 2
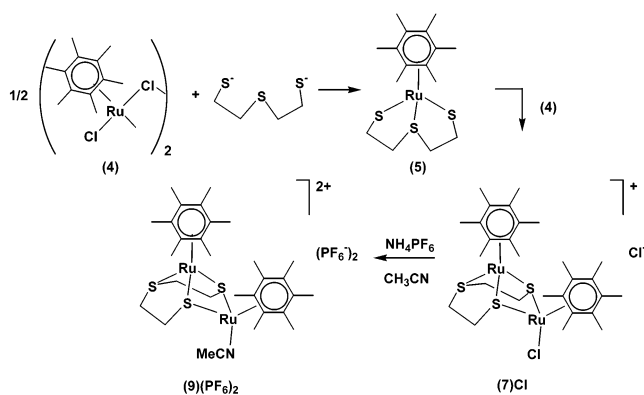
Results and Discussion

Syntheses and Characterization. The reaction of [(η^6-C$_6$Me$_6$)RuCl$_2$]$_2$ (**4**) with 2-mercaptoethyl sulfide can give a complex mixture of products, depending on the extent of deprotonation of the ligand and the molar ratio of the reactants. If the dithiol is completely deprotonated by overnight treatment with an excess of freshly prepared NaOMe and treated with a deficiency of complex **4** (ca. 0.2 mol per mol of dithiol), the only isolated product, in ca. 80% yield based on **4**, is the deep red, crystalline, monomeric complex [(η^6-C$_6$Me$_6$)Ru(η^3-C$_4$H$_8$S$_3$)] (**5**) (Scheme 2), in which 2-mercaptoethyl sulfide adopts its familiar η^3-bonding mode, as confirmed by X-ray crystallography (see in a following section).

Complex **5** shows a parent ion in its FAB-mass spectrum together with peaks arising from elimination of methylene and sulfur fragments. The ^{1}H NMR spectrum shows the expected 18 H-singlet at δ 2.05 due to C$_6$Me$_6$ and three multiplets in the same region due to the SCH$_2$ groups. Correspondingly, the ^{13}C{^{1}H} NMR spectrum shows singlets at δ 95.9 and 15.1 arising from the aromatic and methyl carbon atoms, respectively, of coordinated C$_6$Me$_6$, together with a pair of singlets at δ 28.2 and 44.6 due to the inequivalent methylene carbon atoms. The analogous *p*-cymene complex [(η^6-1,4-MeC$_6$H$_4$CHMe$_2$)Ru(η^3-C$_4$H$_8$S$_3$)] (**6**) can be obtained similarly with some difficulty (see Experimental Section) from [(η^6-1,4-MeC$_6$H$_4$CHMe$_2$)RuCl$_2$]$_2$; its structure also has been confirmed by X-ray crystallography (see in a following section). This bis(thiolate)/

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Table 1. NMR Spectral Data

complex	^{1}H[a] arene−CH$_3$	S−CH$_2$	S−H or S−CH$_3$	^{13}C[a] C$_6$Me$_6$	C$_6$Me$_6$	S−CH$_2$	S−CH$_3$
[Ru(C$_6$Me$_6$)(C$_4$H$_8$S$_3$)] **5**	2.05 (s, 18H)	2.09 (m, 2H)		15.1	95.9	28.2	
		2.32 (m, 4H)				44.6	
		2.64 (m, 2H)					
[Ru(MeC$_6$H$_4$CHMe$_2$)(C$_4$H$_8$S$_3$)] **6**	1.21 (d, *J* 5 Hz, 6H, CH*Me$_2$*)	2.10 (m, 2H)		18.2	85.7, 87.2	29.1	
	2.16 (s, 3H, C$_6$H$_4$*Me*)	2.39 (m,[b] 4H)		22.6 (CH)[c]	100.7, 107.2	44.7	
	2.80 (m, 1H, C*H*Me$_2$)	2.64 (m, 2H)		30.5 (CH$_3$)[c]			
	5.26 (dd, ΔH$_A$H$_B$ = 45 Hz, *J* 5 Hz, 4H)						
[{Ru(C$_6$Me$_6$)}$_2$(C$_4$H$_8$S$_3$)Cl]Cl (**7**)Cl	1.95 (s, 18H)	1.52−1.63 (8-line m,[e] 2H)		15.0 (q, *J* 128 Hz)	95.7	34.4 (t, *J* 141 Hz)	
	2.21 (s, 18H)	2.53−2.59 (8-line m,[e] 2H)		16.0	101.1	43.5 (t, *J* 145 Hz)	
		3.13−3.19 (8-line m,[e] 2H)					
		3.87−3.98 (8-line m,[e] 2H)					
[Ru(C$_6$Me$_6$)(C$_4$H$_9$S$_3$)]Cl (**8**)Cl	2.21 (s, 18H)	2.15 (m br,[d] 2H)	2.83 (1H)[f]	15.9	99.3	28.6	
		2.54 and 2.58 (each t br,[d] 2H)				42.8	
		2.75 (t, *J* 4 Hz, 1H)					
		2.78 (t, *J* 4 Hz, 1H)					
[Ru(C$_6$Me$_6$)(C$_4$H$_9$S$_3$)]Cl (**8**)Cl[g]	2.14 (s, 18H)	2.28−2.32 (m br,[d] 4H)	3.55 (1H)[f]				
		2.52−2.61 (7-line m, 2H)					
		2.73 (t *J* 4 Hz, 1H)					
		2.78 (t *J* 4 Hz, 1H)					
[Ru(C$_6$Me$_6$)(C$_4$H$_9$S$_3$)](PF$_6$) (**8**)(PF$_6$)[g]	2.14 (s, 18H)	2.16−2.32 (m,[d] 2H)	2.91 (1H)[f]	15.7	101.5	28.6	
		2.32−2.46 (m,[d] 2H)				41.6	
		2.47−2.54 (6-line m, 2H)					
		2.66−2.74 (6-line m, 2H)					
[Ru(C$_6$Me$_6$)(C$_4$H$_{10}$S$_3$)]Cl$_2$ (**10**)Cl$_2$[g]	2.15 (s, 18H)	2.37 (m br,[d] 4H)	4.39 (2H)[f] ($\nu_{1/2}$ 42 Hz)				
		2.63 (m br,[d] 2H)					
		2.84 (m br,[d] 2H)					
[{Ru(C$_6$Me$_6$)}$_2$(C$_4$H$_8$S$_3$)-(MeCN)](PF$_6$)$_2$ (**9**)(PF$_6$)$_2$[g]	2.07 (s, 18H)	1.71−1.82 (8-line m,[e] 2H)		15.5	100.8	34.8	
	2.21 (s, 18H)	2.58−2.66 (8-line m,[e] 2H)		16.1	103.1	44.4	
		2.81−2.92 (8-line m,[e] 2H)					
		3.38−3.47 (8-line m,[e] 2H)					
[Ru(C$_6$Me$_6$)(C$_4$H$_8$S$_3$Me)](PF$_6$) (**11**)(PF$_6$)[g]	2.11 (s, 18H)	2.20[h] (8-line m, 2H)	2.25 (3H)	15.5	102.1	29.7	18.3
		2.26−2.44 (9-line m,[e] 2H)				35.8	
		2.52−2.61 (8-line m,[e] 1H)				38.4	
		2.78−2.85 (6-line m,[e] 3H)				45.4	
[Ru(C$_6$Me$_6$)(C$_4$H$_8$S$_3$Me$_2$)](PF$_6$)$_2$ (**12**)(PF$_6$)$_2$[g]	2.20 (s, 18H)	2.50 (m,[d] 2H)	2.39 (6H)	16.1	106.9	36.1	21.3
		2.73 (m,[d] 2H)				40.2	
		(3.00, 2.97)[d] (4H)					
[Ru(C$_6$Me$_6$)(8S3)](PF$_6$)$_2$ (**13**)(PF$_6$)$_2$[g]	2.29 (s, 18H)	2.79−3.24 (m, 10H)		16.6	105.7	38.3	
						39.1	
						70.0	
[Ru(C$_6$Me$_6$)(9S3)](PF$_6$)$_2$ (**1**)(PF$_6$)$_2$[g]	2.26 (s, 18H)	2.79 (m, 12H)		16.4	107.7	36.5	
[Ru(C$_6$Me$_6$)(10S3)](PF$_6$)$_2$ (**14**)(PF$_6$)$_2$[i]	2.30 (s, 18H)	1.98−2.10 (m, 1H)		15.9	108.3	23.8	
		2.42−2.58 (m, 1H)				29.9	
		2.81−2.98 (m, 8H)				36.7	
		3.11−3.21 (m, 2H)				38.0	
		3.38−3.44 (m, 2H)					
[Ru(C$_6$Me$_6$)(11S3)](PF$_6$)$_2$ (**15**)(PF$_6$)$_2$[g]	2.17 (s, 18H)	1.47−1.60 (m, 2H)		15.7	107.4	25.4	
		2.24−2.39 (m, 2H)				34.3	
		2.76−2.93 (m, 10H)				35.1	
		3.18−3.25 (m, 2H)				39.0	
[Ru(C$_6$Me$_6$)(12S3)](PF$_6$)$_2$ (**16**)(PF$_6$)$_2$[g]	2.15 (s, 18H)	1.46−1.55 (m, 1H)		15.6	107.2	18.6	
		2.09 (s, 1H)				25.8	
		2.21 (s, 2H)				36.1	
		2.59−2.68 (m, 2H)				36.9	
		2.75−2.88 (m, 5H)				39.4	
		2.91−3.11 (m, 7H)					

[a] In CDCl$_3$ unless otherwise stated. [b] Quartetlike. [c] Belongs to ^{i}Pr side chain. [d] Unresolved. [e] Symmetrical pattern. [f] Observed δ varies from 2.8 ($\nu_{1/2}$ 42 Hz) to 3.7 ($\nu_{1/2}$ 25 Hz). [g] In CD$_3$CN. [h] Center of a multiplet, which is partially obscured by the Me resonance at δ 2.11. [i] In MeOD.

thioether ligand array in complexes **5** and **6** is equivalent to that present in complex **2** (Scheme 1).

If deprotonation of the dithiol is not allowed to proceed to completion, or when **4** is used in excess, for example, ≥0.5 mol per mol of dithiol, the reaction with complex **4** gives **5** in lower yield; a second product, of empirical formula [{(η^6-C$_6$Me$_6$)RuCl}$_2$(C$_4$H$_8$S$_3$)], can be isolated as a dark yellow solid. An independent experiment showed that this product was formed almost quantitatively from the direct

reaction of **5** with **4** (Scheme 2). In its FAB-mass spectrum, the highest mass peaks correspond to the successive loss of two chloride ions from the molecule. The ^{1}H and ^{13}C NMR spectra clearly show the presence of inequivalent C$_6$Me$_6$ groups; there are also four groups of 8-line multiplets due to the four sets of methylene protons in the dithiolate ligand, indicating that the ligand is in a less symmetrical environment than that in **5**. A 10^{-3} M solution of the compound in acetonitrile has a molar conductivity of 150 S cm^2 mol^{-1},

and the slope of the Onsager plot ($\Lambda_0 - \Lambda_M$ vs $c^{1/2}$) is 25.5, typical of 1:1 electrolytes in this solvent[19,20] (Λ_0, Λ_M are the molar conductances at infinite dilution and concentration M, respectively). These data are consistent with a formulation as the chloride salt of a dinuclear cation, $[\{(\eta^6\text{-}C_6Me_6)Ru\}_2\text{-}Cl(\mu_2\text{-}\eta^2{:}\eta^3\text{-}C_4H_8S_3)]^+$, (**7**)Cl, which has been structurally characterized as a solvate containing one molecule of water of crystallization (see in a following section). The dithiol adopts a hitherto unobserved bridging mode, $\mu_2\text{-}\eta^2{:}\eta^3$, in which both thiolate sulfur atoms from one dianion $^-SCH_2CH_2\text{-}SCH_2CH_2S^-$ bridge a pair of metal atoms; in previous examples (see Figure 1b,c), the bridging thiolate groups come from different anions.

Treatment of (**7**)Cl with NH_4PF_6 in acetonitrile for 3 days at ambient temperature led to 57% conversion to the salt $[\{(\eta^6\text{-}C_6Me_6)Ru\}_2(\mu_2\text{-}\eta^2{:}\eta^3\text{-}C_4H_8S_3)(MeCN)](PF_6)_2$, (**9**)$(PF_6)_2$, as shown in Scheme 2, while a similar reaction in CH_2Cl_2 only effected metathetical exchange of the anion in (**7**)Cl. The dithiolate in **9** adopts the same $\mu_2\text{-}\eta^2{:}\eta^3$ coordination mode as found in cation **7**.

Protonation Products. Complex **5** in CH_2Cl_2 underwent instantaneous protonation at -78 °C, producing $[(\eta^6\text{-}C_6Me_6)\text{-}Ru(\eta^3\text{-}C_4H_9S_3)]Cl$, (**8**)Cl, in 76% yield and (**8**)PF_6 in 92% yield from the use of 1 mole equivalent of HCl and 2 mole equivalents of HPF_6, respectively. In the NMR spectrum, the thiol proton of these two salts was observed as a broad peak, the chemical shift of which varied from δ 2.8 ($\nu_{1/2}$ 42 Hz) to δ 3.7 ($\nu_{1/2}$ 25 Hz) in different solvents (see Table 1). The IR spectrum of salt (**8**)PF_6 shows a band at 2495 cm^{-1} assigned to S$-$H stretching. It was found that 60 molar equivalents of acid were required to convert **5** completely into its diprotonated derivative, $[(\eta^6\text{-}C_6Me_6)Ru(\eta^3\text{-}C_4H_{10}S_3)]\text{-}Cl_2$, (**10**)$Cl_2$, which was unstable in solution, readily decomposing to **7** and a minor unidentified monoruthenium species possessing a ^1H NMR resonance at δ 2.05. The use of less acid (up to 30 mole equivalents) led to the isolation of mainly the monoprotonated species in admixture with the diprotonated salt and small amounts of diruthenium species. In the proton NMR spectrum, the C_6Me_6 resonance of (**10**)$^{2+}$ is just 0.01 ppm downfield from that of (**8**)$^+$, and the thiol resonance is observed as a broad peak at δ 4.4 ($\nu_{1/2}$ 42 Hz). The interaction of (**8**)Cl with **4** or **5** also led to the formation of (**7**)Cl (Scheme 3).

Methylation. The thiolate sulfur atoms in **5** could be methylated. The reaction in THF with slightly more than 1 mole equivalent of methyl iodide yielded instantaneously an orange precipitate of the monomethylation derivative $[(\eta^6\text{-}C_6Me_6)Ru(\eta^3\text{-}C_4H_8S_3Me)]I$, (**11**)I. The formation of the yellow dimethylated derivative $[(\eta^6\text{-}C_6Me_6)Ru(\eta^3\text{-}C_4H_8S_3\text{-}Me_2)]I_2$, (**12**)$I_2$, required an overnight reaction with 24 mole equivalents of methyl iodide in methanol. In this solvent, the initially formed (**11**)I is soluble and undergoes further methylation (Scheme 4). Both cations have been isolated as their PF_6 salts.

Scheme 3
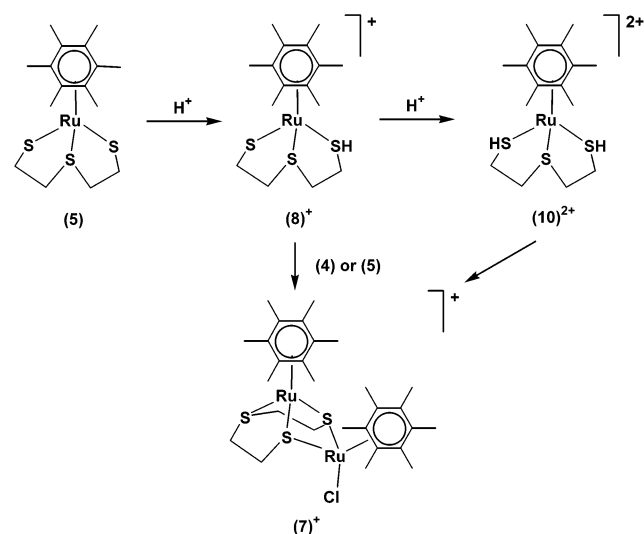
Scheme 4
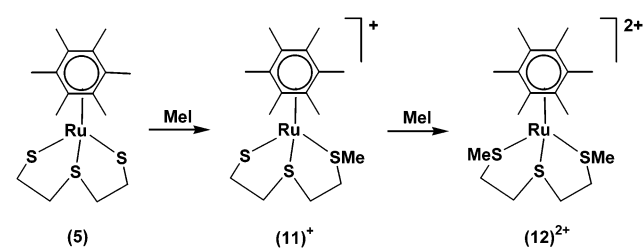
Ring Closure Reactions. Coordinated thiolate is a good nucleophile; for example, the dianion of bis(2-mercapto-ethyl)sulfide in its $Mo(CO)_3$ complex undergoes ring closure on reaction with 1,2-dibromoethane to form $[Mo(CO)_3(9S3)]$,[21,22] and similar reactions have been carried out on benzene-1,2-dithiolate in its ruthenium(II) complex *cis*-[Ru-$(CO)_2(1,2\text{-}C_6H_4S_2)_2]^{2-}$.[23,24] We found that neutral complex **5** also undergoes ring closure when treated with α,ω-dibromoalkanes, $Br(CH_2)_nBr$ ($n = 1-5$), at room temperature to give the macrocyclic thioether complexes $[(\eta^6\text{-}C_6Me_6)\text{-}Ru\{\eta^3\text{-}(zS3)\}]^{2+}$ ($z = 8$, (**13**)$^{2+}$; $z = 9$, (**1**)$^{2+}$; $z = 10$, (**14**)$^{2+}$; $z = 11$, (**15**)$^{2+}$; $z = 12$, (**16**)$^{2+}$; isolated as PF_6 salts, in 41, 92, 77, 72, and 22% yields, respectively (Scheme 5). Such crown trithiaether metal complexes are commonly prepared via ligand substitution by the cyclic ligands, producing homoleptic bis(ligand) coordination compounds from metal salts, or mixed-sandwich organometallic complexes from their respective precursor complexes containing acetone, halo, carbonyl, and/or phosphine ligands.[10,22,25−30]

Spectral Properties. The ^1H NMR spectra of the complexes show a singlet at δ 1.95−2.30 for the methyl protons

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(22) Smith, R. J.; Salek, S. N.; Went, M. J.; Blower, P. J.; Barnard, N. J. *J. Chem. Soc., Dalton Trans.* **1994**, 3165 and references therein.
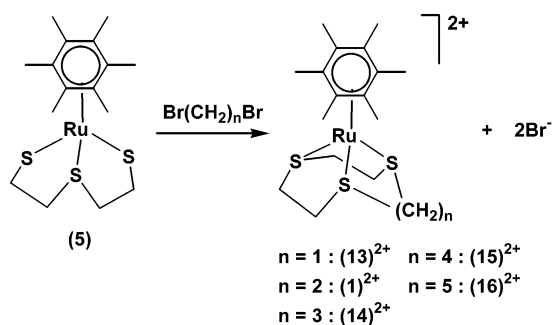(23) Sellmann, D.; Böhlen, E. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37*, 1026.
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(26) Bell, M. N.; Blake, A. J.; Christie, R. M.; Gould, R. O.; Holder, A. J.; Hyde, T. I.; Schröder, M.; Yellowlees, L. J. *J. Chem. Soc., Dalton Trans.* **1992**, 2977.
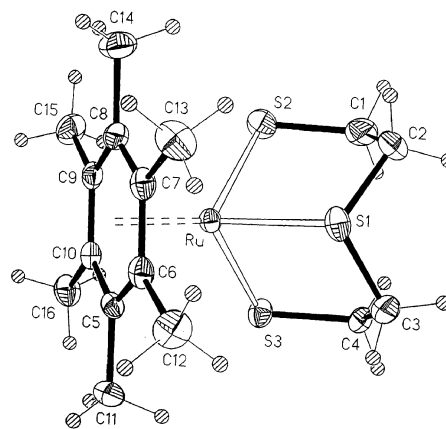
Scheme 5

n = 1 : (13)$^{2+}$ n = 4 : (15)$^{2+}$
n = 2 : (1)$^{2+}$ n = 5 : (16)$^{2+}$
n = 3 : (14)$^{2+}$

Figure 2. Molecular structure of **5**. Thermal ellipsoids are drawn at the 50% probability level.

Figure 3. Molecular structure of **6**. Thermal ellipsoids are drawn at the 50% probability level.

Figure 4. Molecular structure of (**7**)$^+$. Thermal ellipsoids are drawn at the 50% probability level.
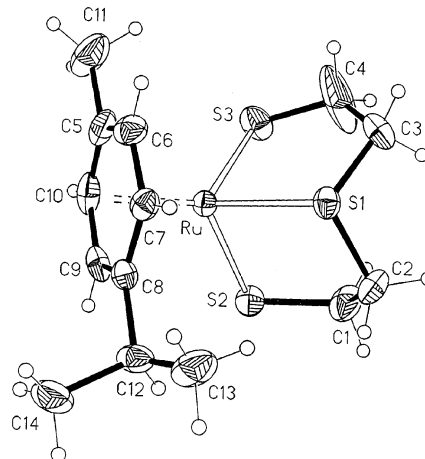
on the C_6Me_6 ring while the SCH_2 protons are usually observed as sets of multiplets at δ 1.46−3.98. In particular, the dinuclear complexes, (**7**)$^{2+}$ and (**9**)$^{2+}$, possess four sets of distinctive 8-line multiplets. In the ^{13}C NMR spectra, the signal for the C_6Me_6 methyl carbons are found between δ 15.0 and 16.6 ppm and the ring carbons at δ 95.7−108.3. The detailed NMR spectral data of all the complexes are given in Table 1, and the IR data are in Supporting Information.

Molecular Structures. The molecular geometries of the monomeric, neutral complexes, [(η^6-arene)Ru(η^3-$C_4H_8S_3$)] (arene = C_6Me_6 (**5**), 1,4-MeC$_6$H$_4$CHMe$_2$ (**6**)), and of the binuclear salts, [{(η^6-C_6Me_6)Ru}$_2$Cl(μ_2-η^2:η^3-$C_4H_8S_3$)]Cl·H$_2$O, (**7**)Cl·H$_2$O, and [{(η^6-C_6Me_6)Ru}$_2$(MeCN)(μ_2-η^2:η^3-$C_4H_8S_3$)](PF$_6$)$_2$·MeCN, (**9**)(PF$_6$)$_2$·MeCN, are shown in Figures 2−5, respectively. Selected bond distances and angles for complexes **5** and **6** are listed in Table 2; those for (**7**)-Cl·H$_2$O and (**9**)(PF$_6$)$_2$·MeCN are collected in Table 3. A comparison of selected angles and nonbonded distances of these complexes and those described in following paragraphs is given in Table 4.
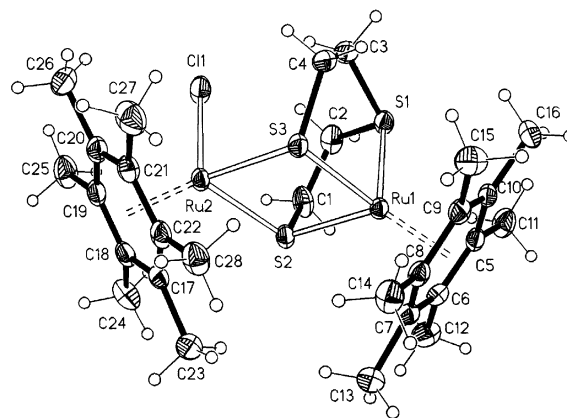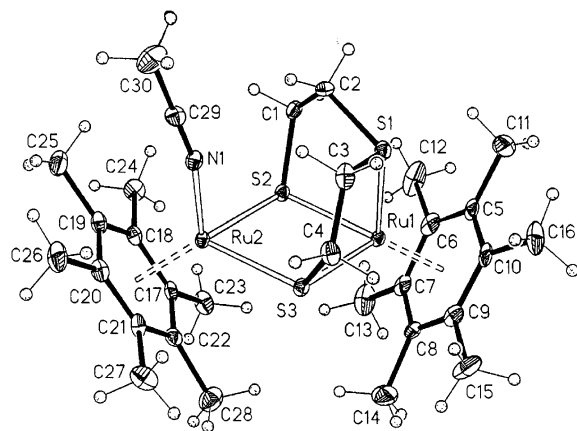
In these four complexes, the ruthenium atoms are surrounded in the usual piano-stool arrangement by the planar η^6-arene ring together with two thiolate sulfur atoms and one thioether sulfur atom of the $C_4H_8S_3$ dianion. The structures of **5** and **6** differ only in a slight twist of the aromatic ring relative to the sulfur atoms. The Ru−S(thioether) bond lengths in **5** and **6** [2.3396(10) and 2.3428-(12) Å, respectively] are shorter than the Ru−S(thiolate) separations [2.3763(13)−2.3858(13) Å], lying in the range 2.25−2.35 Å found in the bis(mesocyclic thioether) complexes of ruthenium(II), [Ru(9S3)$_2$]Y$_2$ (Y = BPh$_4$,[31] OTf [32]), [Ru(dibenzo-(18S6))](PF$_6$)$_2$,[33] and [CpRu(9S3)](PF$_6$)$_2$;[25] a similar trend was found in the thiolate−thioether complexes **2** and **3**[10b] and the Cp* analogue of **5**.[34] The Ru−S(thioether)

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distances in the cationic binuclear complexes (**7**)Cl·H$_2$O and (**9**)(PF$_6$)$_2$·MeCN (2.30 Å) appear to be significantly shorter than those in the neutral complexes **5** and **6**. The thiolate bridges in the binuclear complexes are not symmetrical, the Ru−S distances to the ruthenium atom to which the thioether sulfur atom is bound being consistently ca. 0.06 Å less than those to the ruthenium atom bearing Cl$^-$ or MeCN. The bite angle of the tridentate ligand in the binuclear complexes [56.4(1)°] is smaller than in the mononuclear complexes

Figure 5. Molecular structure of (**9**)$^{2+}$. Thermal ellipsoids are drawn at the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) of Monoruthenium Complexes

	5	6
Ru−C(5)	2.258(3)	2.252(5)
Ru−C(6)	2.245(3)	2.246(5)
Ru−C(7)	2.235(3)	2.201(4)
Ru−C(8)	2.248(4)	2.252(4)
Ru−C(9)	2.219(4)	2.184(4)
Ru−C(10)	2.226(3)	2.187(5)
Ru−S(1)	2.3396(10)	2.3428(12)
Ru−S(2)	2.3851(10)	2.3763(13)
Ru−S(3)	2.3807(10)	2.3858(13)
S(1)−Ru−S(2)	85.18(4)	85.69(5)
S(1)−Ru−S(3)	85.41(4)	85.18(5)
S(2)−Ru−S(3)		89.54(5)
S(3)−Ru−S(2)	92.18(4)	

Table 3. Selected Bond Lengths (Å) and Angles (deg) of Diruthenium Cationic Complexes

	(**7**)Cl·H$_2$O	(**9**)(PF$_6$)$_2$·MeCN
Ru(1)−C(5)	2.228(7)	2.235(10)
Ru(1)−C(6)	2.239(7)	2.225(10)
Ru(1)−C(7)	2.265(7)	2.293(10)
Ru(1)−C(8)	2.265(7)	2.249(10)
Ru(1)−C(9)	2.250(7)	2.219(10)
Ru(1)−C(10)	2.232(7)	2.245(10)
Ru(1)−S(1)	2.3032(19)	2.297(2)
Ru(1)−S(2)	2.3653(19)	2.360(2)
Ru(1)−S(3)	2.3672(19)	2.367(2)
Ru(2)−N(1)		2.046(8)
Ru(2)−C(17)	2.205(7)	2.211(10)
Ru(2)−C(18)	2.232(8)	2.209(9)
Ru(2)−C(19)	2.242(8)	2.239(10)
Ru(2)−C(20)	2.229(8)	2.262(10)
Ru(2)−C(21)	2.235(8)	2.223(11)
Ru(2)−C(22)	2.209(7)	2.236(10)
Ru(2)−S(2)	2.414(2)	2.391(2)
Ru(2)−S(3)	2.415(2)	2.410(2)
Ru(2)−Cl(1)	2.416(2)	
S(1)−Ru(1)−S(2)	86.16(7)	86.24(9)
S(1)−Ru(1)−S(3)	86.17(7)	86.54(9)
S(2)−Ru(1)−S(3)	79.09(7)	79.29(8)
S(2)−Ru(2)−S(3)	77.22(7)	77.82(8)
S(2)−Ru(2)−Cl(1)	96.29(8)	
S(3)−Ru(2)−Cl(1)	96.21(8)	
N(1)−Ru(2)−S(2)		95.6(2)
N(1)−Ru(2)−S(3)		97.5(2)
Ru(1)−S(2)−Ru(2)	101.84(8)	101.83(9)
Ru(1)−S(3)−Ru(2)	101.74(8)	101.05(9)

[64.9(1)° **5**; 63.1(1)° **6**]. Consequently, the S···S nonbonded distance [S(2)−S(3)] is shorter in the former than in the latter [3.01(1) Å vs 3.39(1) Å (av)]. The molecular structures of

(**1**)$^{2+}$ and of (**13**)$^{2+}$−(**15**)$^{2+}$ each contain a (η^6-arene)Ru moiety coordinated to a cyclic trithia ligand in a three-legged piano-stool arrangement. The complex cation (**1**)$^{2+}$, which we had previously synthesized directly from 9S3,[10] contains the ligand in its normal favored facial endodentate conformation.[29,30,35,36] The ORTEP plots of (**13**)$^{2+}$−(**15**)$^{2+}$ are illustrated in Figure 6a−c. The 8S3 complex cation (**13**)$^{2+}$ is the first of its kind; the 2-substituted derivatives of the cyclic eight-membered compound, 1,3,6-trithiacyclooctane, were synthesized a few years ago,[37] but there have been no reports of its ligation properties.

There are now numerous examples of the ligation of the cyclic thiaether 10S3 to metal centers from the work of Grant and co-workers.[25,38,39] In the (**14**)$^{2+}$ complex, the (10S3) ligand is facially coordinated in tridentate syn endodentate mode, with a plane of symmetry through the Ru atom and S(1) which bisects the six-membered chelate and arene rings. The trithia ligand adopts the [2323]A (see Figure 7) boat−chair−boat conformation in which the six-membered chelate ring possesses a chair conformation, in contrast to the [1324] boat conformation it adopts in Grant's Cp analogue, though [CpFe(10S3)]$^+$ also possesses a chair conformation of the sulfur ligand.[25,40]

It had been observed that the chair conformation is normally adopted by this ligand in its coordination to first row transition metals, but it appears that, in addition to the size of the central metal atom,[25] the ancillary ligands bear much influence on the conformation mode of the coordination, because the trisulfur ligand adopts a chair conformation in [Ru(10S3)$_2$]$^{2+}$ [39] and a boat form in [CpRu(10S3)]$^+$ and [Mo(10S3)(CO)$_3$].[41] The cation (**15**)$^{2+}$ containing an (11S3-147) ligand is the first such complex to be structurally characterized, though complexes of this ligand and its isomer (11S3−148) have recently been synthesized for trivalent Co and divalent Fe, Ru, Co, Ni, Pd, and Hg.[42] The ligand assumes the [12323]A conformation (see Figure 7) but with the sulfur atoms all syn endodentate; in the chairlike conformation, the C(5)C(6)C(7) portion of the seven-membered chelate ring points toward the arene ring. The PF$_6^-$ salt of the (**16**)$^{2+}$ cation, isolated in low yield, contains a (12S3-147) cyclic ligand, which only bears an analogy in ring size, but not in structure, to the known symmetrical (12S3-159) ligand.[27,43] The bond parameters of the PF$_6^-$ salts of (**1**)$^{2+}$ and of (**13**)$^{2+}$−(**15**)$^{2+}$ are given in Table 5, which

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(40) For the notation used for different conformation modes, see: (a) Setzer, W. N.; Cacioppo, E. L.; Guo, Q.; Grant, G. J.; Kim, D. D.; Hubbard, J. L.; VanDerveer, D. G. *Inorg. Chem.* **1990**, *29*, 2672. (b) Setzer, W. N.; Guo, Q.; Meehan E. J., Jr.; Grant, G. J. *Heteroat. Chem.* **1990**, *1*, 425. (c) Dale, J. *Acta Chem. Scand.* **1973**, *27*, 1115, 1130.
(41) Grant, G. J.; Carpenter, J. P.; Setzer, W. N.; VanDerveer, D. G. *Inorg. Chem.* **1989**, *28*, 4128.
(42) Grant, G. J.; Shoup, S. S.; Baucom, C. L.; Setzer, W. N. *Inorg. Chim. Acta* **2001**, *317*, 91

Table 4. Selected Nonbonded Distances (Å) and Angles (deg)

	5	6	(7)Cl·H$_2$O	(9)(PF$_6$)$_2$·MeCN	(13)(PF$_6$)$_2$	(1)(PF$_6$)$_2$	(14)(PF$_6$)$_2$	(15)(PF$_6$)$_2$
S1···S2	3.198(2)	3.209(2)	3.189(3)	3.184(3)	3.207(3)	3.204(3)	3.1601(13)	3.1971(18)
S1···S3	3.202(2)	3.200(2)	3.191(3)	3.197(3)	3.246(3)	3.201(3)	3.1601(13)	3.1591(18)
S2···S3	3.434(2)	3.354(2)	3.013(3)	3.015(3)	2.728(3)	3.195(3)	3.384(13)	3.5409(18)
X−Ru^a	1.73	1.72	1.74	1.74	1.74(1)	1.75(1)	1.75(1)	1.75(1)
			1.71	1.72				
Ru···Ru			3.71	3.69				
S1−Ru−S2	85.18(4)	85.69(5)	86.16(7)	86.24(9)	88.39(7)	87.28(9)	85.61(3)	86.89(5)
S1−Ru−S3	85.41(4)	85.18(5)	86.17(7)	86.54(9)	86.34(9)	87.05(9)	85.61(3)	85.45(5)
S2−Ru−S3	92.18(4)	89.54(6)	79.09(7)	79.29(8)	70.32(7)	86.75(9)	93.72(5)	98.47(5)
S2···S1···S3	64.9	63.1	56.4	56.4	50.0(1)	60.0(1)	64.7(1)	67.7(1)
X−Ru−S1	129.5	129.6	123.9	124.8	128.2(1)	127.4(1)	127.3(1)	125.0(1)
X−Ru−S2	126.1	125.1	132.4	131.6	133.8(1)	128.3(1)	125.9(1)	125.3(1)
			127.1	125.8				
X−Ru−S3	125.3	127.9	132.4	131.9	130.0(1)	126.3(1)	125.9(1)	124.3(1)
			127.1	127.1				
X−Ru−Y			121.5	121.7				

^{a} X is the centroid of the arene rings. Y is coordinated Cl$^-$ or MeCN on Ru2.
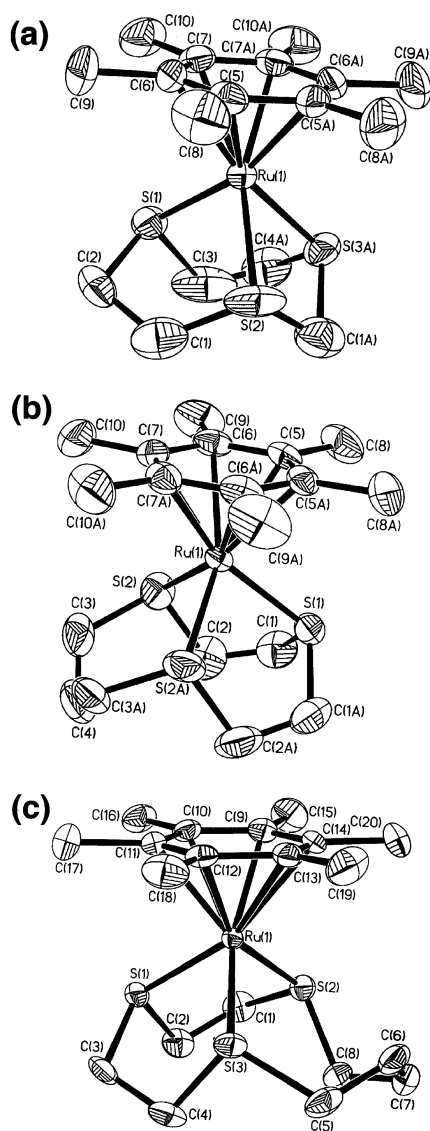
Figure 6. Molecular structures of (a) (13)$^{2+}$, (b) (14)$^{2+}$, (c) (15)$^{2+}$. Thermal ellipsoids are drawn at the 50% probability level.

also shows a comparison with bond parameters of similar trithia complexes of Ru(II).

The deviation between the six Ru(1)−C(arene) bonds is greatest for the 11S3 complex (15)$^{2+}$, in which the longest bond Ru(1)−C(13) is on the same side as the seven-membered chelate ring. The S2−Ru1−S3 bite angle increases with the length of the −S(CH$_2$)$_n$S− chelate, ranging from 70.31° for $n = 1$ to 98.47° for $n = 4$. Bite angles of the other four-membered chelates in all the complexes in the table fall within the range from 82.97° for [CpRu(10S3)]$^+$ to 89.18° for [CpRu(9S3)]$^+$, and the narrow range 85.45−88.39° for the four C$_6$Me$_6$ complexes (1)$^{2+}$ and (13)$^{2+}$−(15)$^{2+}$, there being a narrow deviation between the two angles in each of the complexes. Selected angles and nonbonded distances are presented in Table 4. It is noted that the variation of the S2···S1···S3 angle correlates well with the length of methylene chain linking S2 and S3.

Conclusion

We have shown that bis(2-mercaptoethyl)sulfide forms a variety of arene−ruthenium(II) complexes containing coordinated anionic thiolate, neutral thiol, and neutral thioether groups in various combinations and have established that the dianion S(CH$_2$CH$_2$S$^-$)$_2$ can bridge two ruthenium atoms in a hitherto unobserved μ_2-η^2:η^3 bonding mode. Ring closure reactions based on nucleophilic additions of dibromoalkanes to the thiolate sulfur atoms of [(η^6-arene)Ru(η^3-C$_4$H$_8$S$_3$)] (5) have provided dicationic (η^6-C$_6$Me$_6$)Ru complexes containing trithia mesocyclic zS3 ligands ($z = 8−12$).

Experimental Section

All reactions were carried out under high-purity nitrogen or argon with use of standard Schlenk techniques. CH$_2$Cl$_2$ and CH$_3$CN were distilled from CaH$_2$, (CH$_3$)$_2$CO from molecular sieves and CH$_3$OH from magnesium methoxide before use. All other solvents were distilled from sodium benzophenone ketyl. Elemental analyses were carried out in the Microanalytical Laboratory of the Research School of Chemistry, Australian National University, or of the Department

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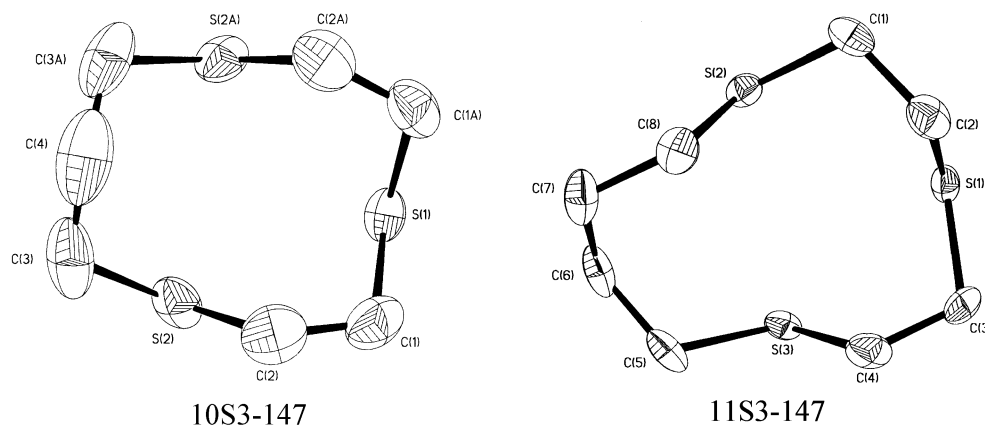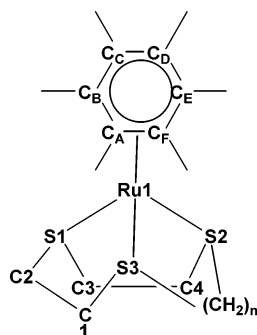
10S3-147   11S3-147

Figure 7. ORTEP diagrams of (10S3) and (11S3) ligands in (**14**)$^{2+}$ and (**15**)$^{2+}$, respectively.

Table 5. Comparison of Selected Bond Lengths (Å) and Bond Angles (deg) of Related Complexes

	[(C$_6$Me$_6$)Ru-(8S3)]$^{2+}$ ^{a}	[(C$_6$Me$_6$)Ru-(9S3)]$^{2+}$ ^{a}	[Ru(9S3)$_2$]$^{2+}$ ^{30}	[(Cp)Ru-(9S3)$_2$]$^+$ ^{23}	[(C$_6$Me$_6$)Ru-(10S3)]$^{2+}$ ^{a}	[Ru(10S3)$_2$]$^{2+}$ ^{37}	[(Cp)Ru-(10S3)$_2$]$^+$ ^{23}	[(C$_6$Me$_6$)-Ru(11S3)]$^{2+}$ ^{a}
n	1	2	2	2	3	3	3	4
Ru1−C$_A$	2.247(4)	2.248(9)			2.252(3)			2.242(5)
Ru1−C$_B$	2.247(4)	2.248(9)			2.252(3)			2.249(5)
Ru1−C$_C$	2.249(4)	2.249(9)			2.261(3)			2.252(5)
Ru1−C$_D$	2.249(4)	2.252(9)			2.261(3)			2.260(5)
Ru1−C$_E$	2.260(4)	2.256(9)			2.263(3)			2.266(5)
Ru1−C$_F$	2.260(4)	2.260(9)			2.263(3)			2.284(5)
Ru1−S1	2.302(2)	2.320(2)	2.3436(5)	2.256(2)	2.3319(12)	2.339(1)	2.302(2)	2.3151(13)
Ru1−S2	2.384(2)	2.323(2)	2.3437(6)	2.323(2)	2.3186(8)	2.347(1)	2.346(2)	2.3341(13)
Ru1−S3	2.3536(16)	2.329(2)	2.3385(6)	2.288(2)	2.3186(8)	2.339(1)	2.346(2	2.3410(13)
S1−Ru1−S2	86.34(9)	87.28(9)	87.72(2)	88.39(8)	85.61(3)	87.3(1)	82.97(7)	86.89(5)
S1−Ru1−S3	88.39(7)	87.05(9)	87.67(2)	88.18(8)	85.61(3)	87.8(1)	82.97(7)	85.45(5)
S2−Ru1−S3	70.32(7)	86.75(9)	87.65(2)	86.73(10)	93.72(5)	93.3(1)	104.10(12)	98.47(5)

^{a} This work.

of Chemistry, National University of Singapore. NMR spectra were measured on Varian Gemini 300 (^{1}H at 300.10 MHz; ^{13}C at 75.46 MHz) or Bruker 300 MHz FT NMR spectrometers and were referenced to residual CHCl$_3$ in CDCl$_3$, CHD$_2$CN in CD$_3$CN or CHD$_2$OD in CD$_3$OD. Coupling constants (*J*) are in hertz. Mass spectra were measured on a VG Micromass 7070F instrument, and IR spectra on a Perkin-Elmer 683 spectrometer. Conductivity measurements were carried out at 298 K on 2 × 10^{-5} to 5 × 10^{-3} M solutions in acetonitrile, using a WTW LFD 550 instrument. 2-Mercaptoethyl sulfide was obtained from Aldrich and used as supplied. The compounds [(η^6-arene)RuCl$_2$]$_2$ (arene = C$_6$Me$_6$ (**4**); 1,4-MeC$_6$H$_4$CHMe$_2$) were prepared as reported in the literature.[44]

Reactions of [(η^6-C$_6$Me$_6$)RuCl$_2$]$_2$ (4) with 2-Mercaptoethyl Sulfide, S(CH$_2$CH$_2$SH)$_2$. (a) To a suspension of sodium methoxide (freshly generated from sodium (85 mg, 3.70 mmol) and evacuated to dryness) in THF (15 mL) was injected 2-mercaptoethyl sulfide

(0.23 mL, 1.76 mmol), and the mixture was stirred overnight. To the gel-like suspension was added solid **4** (253 mg, 0.38 mmol) and the mixture stirred at ambient temperature. A deep red coloration developed instantaneously. After 3.5 h, the mixture was evacuated to dryness and extracted with toluene−acetonitrile (4:1, 15 mL), followed by toluene (5 mL). The extracts were filtered through Celite and concentrated to ca. 5 mL, and ether (2 mL) was added. Cooling at −30 °C for 30 min gave [(η^6-C$_6$Me$_6$)Ru(η^3-C$_4$H$_8$S$_3$)] (**5**) as a fine, deep red, crystalline solid (250 mg, 0.60 mmol, 79% yield). A second crop was obtained from the supernatant (yield 13 mg, 0.031 mmol, 4%). FAB$^+$-MS: *m/z* 416 [M]$^+$, 356 [M − S(CH$_2$)$_2$]$^+$, 328 [M − S(CH$_2$)$_4$]$^+$, 296 [M − S$_2$(CH$_2$)$_4$]$^+$, and unidentified lower molecular weight fragments. Anal. Calcd for C$_{16}$H$_{26}$RuS$_3$: C, 46.2; H, 6.3; S, 23.1. Found: C, 46.3; H, 6.3; S, 23.4.

(b) To a suspension of sodium methoxide (freshly generated from sodium (23 mg, 1 mmol)) in THF (10 mL) was injected 2-mercaptoethyl sulfide (0.065 mL, 0.5 mmol), and the mixture was

(44) Bennett, M. A.; Huang, T.-N.; Matheson, T. W.; Smith, A. K. *Inorg. Synth.* **1982**, *21*, 74.

stirred for 1.5 h. To the suspension was added solid **4** (0.167 g, 0.25 mmol), and the mixture was stirred at ambient temperature for 1.75 h. The reddish orange suspension was evaporated to dryness, giving a brick-red residue, which was extracted with 1:1 toluene−acetonitrile (30 mL). The extract was filtered through Celite, concentrated to 5 mL, and cooled at −78 °C for 2 h. Complex **5** was obtained as a deep red crystalline solid, which was collected by filtration (120 mg, 0.29 mmol, 58% yield). Addition of ether (5 mL) to the mother liquor, followed by cooling at 0 °C, gave [{(η^6-C$_6$Me$_6$)Ru}$_2$Cl(μ_2-η^2:η^3-C$_4$H$_8$S$_3$)]Cl, (**7**)Cl, (30 mg, 0.040 mmol, 16% yield). FAB$^+$-MS: m/z 715 [M − Cl]$^+$, 679 [M − 2Cl]$^+$, and lower molecular fragments at 651, 621, 591, 554, 524, 497, 461, 423, 389, 356, 328, 296, and 257. Anal. Calcd for C$_{28}$H$_{44}$-Cl$_2$Ru$_2$S$_3$: C, 44.9; H, 5.9; Cl, 9.5; S, 12.8. Found: C, 45.0; H, 6.1; Cl, 10.2; S, 11.7. Conductivity in acetonitrile at 295 K, Λ_M (1 × 10^{-3} M) = 150 S cm^2 mol^{-1}, and the slope of the Onsager plot of (Λ_0 − Λ_M) versus $c^{1/2}$ = 25.5, where Λ_M and Λ_0 represent molar conductance at concentration M and infinite dilution, respectively.[12]

Monoprotonation of 5. (a) With HCl. Into a vigorously stirred solution of **5** (143 mg, 0.34 mmol) in CH$_2$Cl$_2$ (10 mL), cooled to −78 °C, was injected 1 molar equivalent of HCl (270 μL, 1.24 M prepared by diluting the concentrated acid in MeOH). An immediate color change from reddish orange to yellowish orange was observed. The solution was stirred for an additional 15 min and then concentrated to half of its volume. Ether was added dropwise to the stirred solution, causing the monoprotonated salt (**8**)Cl to precipitate as an orange solid. This was filtered, washed with ether (3 × 5 mL), and dried (116 mg, 0.26 mmol, 76% yield). FAB$^+$-MS: m/z 416 [M − Cl − H]$^+$, 356 [M − Cl − S(CH$_2$)$_2$]$^+$, 328 [M − Cl − S(CH$_2$)$_4$]$^+$, 296 [M − Cl − S$_2$(CH$_2$)$_4$]$^+$. The product was converted into its PF$_6$ salt by reaction with NH$_4$PF$_6$ in acetonitrile. Subsequent recrystallization in acetonitrile−ether at −31 °C gave red orthorhombic-shaped crystals of (**8**)PF$_6$. Anal. Calcd for C$_{16}$H$_{27}$F$_6$PRuS$_3$: C, 34.2; H, 4.9; F, 20.3; P, 5.5; S, 17.1. Found: C, 34.1; H, 4.8; F, 20.1; P, 6.1; S, 16.8. A similar reaction using 2 molar equivalents of HCl followed by a similar metathesis with NH$_4$PF$_6$ in acetonitrile gave a 3:1 molar mixture of microcrystalline orange crystals of (**8**)PF$_6$ and well-formed polyhedral yellow crystals of (**9**)(PF$_6$)$_2$·MeCN.

(b) With HPF$_6$. Into a vigorously stirred solution of **5** (100 mg, 0.24 mmol) in CH$_2$Cl$_2$ (10 mL), cooled to −78 °C, was injected 2 molar equivalents of dilute HPF$_6$ (0.7 mL, 0.68 M prepared by diluting 60% HPF$_6$ in MeOH). An immediate color change from reddish orange to yellowish orange was observed. The solution was stirred for a further 15 min and then concentrated to half of its volume. Hexane was added dropwise to the stirred solution to precipitate out orange solids of (**8**)PF$_6$, which were then filtered, washed with hexane (3 × 5 mL), and dried (125 mg, 0.22 mmol, 92% yield).

Diprotonation of 5. To a vigorously stirred solution of **5** (50 mg, 0.12 mmol) in MeOH (10 mL) at −78 °C was added dropwise 2.9 mL of approximately 1.2 M HCl in MeOH (i.e., 29 molar equivalents of acid to **5**). A color change from reddish orange to orange-yellow was observed. After stirring for 30 min, the solution was concentrated to half of its volume, and ether solvent was added via a syringe giving a dark red oil, which, after trituration with ether and evacuation to dryness, gave a proton NMR spectrum almost identical to that of (**8**)Cl. A similar workup of the mother liquor gave again an orange oil which after repeated trituration with a trace of MeOH and ether at −78 °C yielded an orange solid (ca. 5 mg). Anal. Calcd for C$_{16}$H$_{28}$Cl$_2$RuS$_3$: C, 39.3; H, 5.8. Found: C, 39.5; H, 6.0, formulated as [(η^6-C$_6$Me$_6$)Ru(η^3-C$_4$H$_8$S$_3$H$_2$)]Cl$_2$, (**10**)Cl$_2$, which was also supported by the proton NMR spectrum.

The compound was found to be unstable in the CD$_3$CN solution, with 80% conversion within 5 h at room temperature into the dinuclear species **7** and a minor amount of a monoruthenium compound possessing an arene ^{1}H NMR Me resonance at δ 2.05. Dissolving the precipitated oily product in THF and stirring for ca. 15 min yielded orange solids of the dinuclear complex (**7**)Cl.

An NMR experiment showed that the treatment of 10 mg of **5** with 60 molar equivalents of HCl resulted in total conversion to the diprotonated species (**10**)Cl$_2$.

Monomethylation. Into a vigorously stirred solution of **5** (153 mg, 0.37 mmol) in THF (35 mL), was injected methyl iodide (25 μL, 0.40 mmol). An orange solid started to form immediately. The suspension was stirred for an additional 15 min. The solids were filtered, washed with THF (10 mL), followed by ether (2 × 10 mL), and then dried under vacuum. The dried solids were then dissolved in MeOH (5 mL). NH$_4$PF$_6$ (100 mg, ca. 0.6 mmol) was added to the stirred solution, whereupon orange solids immediately precipitated. After stirring a further 30 min, the mixture was concentrated to half of its volume and then filtered. The solids were washed with ether and then extracted with acetonitrile (5 mL). Filtration removed the white ammonium salts. The filtrate was layered with ether (2 mL); after a day at −31 °C, red crystals of the monomethylated derivative [(η^6-C$_6$Me$_6$)Ru(η^3-C$_4$H$_8$S$_3$Me)]PF$_6$, (**11**)PF$_6$, were collected (112 mg, 0.20 mmol, 54% yield). FAB$^+$-MS: m/z 431 [M − PF$_6$]$^+$, 371 [M − PF$_6$ − S(CH$_2$)$_2$]$^+$, 356 [M − PF$_6$ − S(CH$_2$)$_2$ − Me]$^+$, 328 [M − PF$_6$ − S(CH$_2$)$_4$ − Me]$^+$, 296 [M − PF$_6$ − S$_2$(CH$_2$)$_4$ − Me]$^+$, 282 [M − PF$_6$ − S$_2$(CH$_2$)$_6$- Me]$^+$. FAB$^-$ -MS: m/z 145 (PF$_6^-$). Anal. Calcd for C$_{17}$H$_{29}$F$_6$PRuS$_3$: C, 35.5; H, 5.1; F, 19.8; P, 5.4; S, 16.7. Found: C, 35.5; H, 5.2; F, 19.5; P, 5.7; S, 16.5.

Dimethylation. To a deep red solution of **5** (50 mg, 0.12 mmol) in MeOH (5 mL) was added MeI (180 μL, 2.9 mmol). The mixture was stirred overnight, whereupon a yellow solution resulted. This was allowed to react with NH$_4$PF$_6$ (190 mg, 1.16 mmol) with stirring for 1 h, although yellow solids were observed to form almost immediately. The solution was then concentrated to half of its volume, and the yellow solids were filtered, washed with ether (3 × 10 mL), and dried under vacuum. The product was then extracted with CH$_3$CN (5 mL) and the extract filtered through a disk of Celite (1.5 cm thick) to remove the NH$_4^+$ salts. Layering with ether and cooling at −31 °C gave fine yellow needles of [(η^6-C$_6$Me$_6$)Ru(η^3-C$_4$H$_8$S$_3$(Me)$_2$)](PF$_6$)$_2$ (**12**)(PF$_6$)$_2$ (67 mg, 0.091 mmol, 76% yield). FAB$^+$-MS: m/z 591 [M − PF$_6$]$^+$, 465 [fragment not assignable], 445 [M − 2PF$_6$ + H]$^+$, 431 [M − 2PF$_6$ − Me]$^+$, 371 [M$^+$ − 2PF$_6$ − Me − S(CH$_2$)$_2$]$^+$, 356 [M − 2PF$_6$ − 2Me − S(CH$_2$)$_2$]$^+$, 328 [M − 2PF$_6$ − 2Me − S(CH$_2$)$_4$]$^+$, 296 [M − 2PF$_6$ − 2Me − S$_2$(CH$_2$)$_4$]$^+$, 282 [M − 2PF$_6$ − 2Me − S$_2$(CH$_2$)$_6$]$^+$. FAB$^-$ -MS: m/z 145 (PF$_6^-$). Anal. Calcd for C$_{18}$H$_{32}$F$_{12}$P$_2$RuS$_3$: C, 29.4; H, 4.4; F, 31.0; P, 8.4; S, 13.1. Found: C, 29.1; H, 4.1; F, 30.9; P, 8.7; S, 12.9.

Reaction of [(η^6-C$_6$Me$_6$)RuCl$_2$]$_2$ (4) with 5. A suspension of **4** (134 mg, 0.20 mmol) and **5** (160 mg, 0.38 mmol) in THF (20 mL) was stirred at ambient temperature. The color changed gradually from orange-red to yellowish orange with precipitation of some yellow solids. The proton NMR spectrum of an aliquot after 4 h showed that reaction was complete. Filtration followed by washing with THF and ether gave (**7**)(Cl) as a fine light orange solid (280 mg, 0.37 mmol, 97% yield). To a stirred solution of 33 mg (0.044 mmol) of the solid in MeCN (5 mL) was added NH$_4$PF$_6$ (ca. 400 mg, 0.24 mmol); a white precipitate of NH$_4$Cl was formed instantaneously. The suspension was stirred for 3 days at ambient temperature. Subsequent removal of the precipitate, followed by concentration of the filtrate and addition of ether, yielded a light orange solid (27 mg, 0.025 mmol, 57% yield), the proton NMR of

which agrees with the presence of the diruthenium species (**9**)-(PF$_6$)$_2$ with δ(Me) 2.15 and 2.01, in admixture with an equal molar amount of complexes possessing arene methyls at δ 2.18 and 1.96, but apparently no thia ligand. The mother liquor with additional ether gave, after standing for two weeks at −30 °C, more of (**9**)-(PF$_6$)$_2$ as light yellow needle-shaped crystals (4 mg, 0.004 mmol, 9% yield). FAB$^+$-MS: significant fragments at *m/z* 720 [M − 2PF$_6$ − H]$^+$, 679 [M − 2PF$_6$ − MeCN]$^+$, and 340 (^{1}/$_2$[M − 2PF$_6$ − MeCN]$^+$). From a similar reaction with NH$_4$PF$_6$ in CH$_2$Cl$_2$, (**7**)-(PF$_6$) was obtained as the main product (^{1}H and ^{13}C NMR and FAB$^+$-MS spectral data identical with those of (**7**)Cl. FAB$^-$-MS: *m/z* 145 (PF$_6^-$), together with trace amounts of an arene-containing compound(s) possessing δ(Me) 2.06 and 2.00.

Reaction of [(Ru(η^6-C$_6$Me$_6$)(η^3-C$_4$H$_8$S$_3$)] (5) with Dibromoalkanes, Br(CH$_2$)$_n$Br. A typical reaction is described for the case of *n* = 2, as follows: 1,2-Dibromoethane (80 μL, 1.06 mmol) was injected into a reddish orange solution of **5** (100 mg, 0.24 mmol) in MeCN (40 mL) and the mixture stirred at ambient temperature. The color slowly turned to lemon yellow after 1.5 h. To the resultant solution was added solid NH$_4$PF$_6$ (160 mg, 0.98 mmol) with stirring, causing NH$_4$Br to precipitate as a fine white solid. Filtration through a disk (1.5 cm thick) of alumina, followed by concentration of the yellow filtrate to ca. 3 mL, and addition of ether (ca. 1 mL) gave yellow crystals of [(η^6-C$_6$Me$_6$)Ru(η^3-C$_6$H$_{12}$S$_3$)](PF$_6$)$_2$, (**1**)(PF$_6$)$_2$ (160 mg, 0.22 mmol, 91% yield). Spectral data were identical with those previously reported.[10]

For the cases of *n* = 1, 3−5, the reaction was carried out in MeOH in which the product was soluble, so that metathesis of the bromide anion could be effected by direct addition of NH$_4$PF$_6$ to the reaction mixture. A typical procedure is described for *n* = 3 as follows: Into a stirred solution of **5** (40 mg, 0.096 mmol) in MeOH (10 mL) was injected 1,3 dibromopropane (0.30 mL, 2.96 mmol). After 5 h at room temperature, solid NH$_4$PF$_6$ (160 mg, 0.99 mmol) was added and the solution stirred for an additional hour. Concentration to half of its volume gave yellow solids, which were filtered, washed with ether (3 × 10 mL), and dried under vacuo. The product was then extracted with CH$_3$CN (2 × 3 mL), and the extracts were filtered through a disk of Celite (1.5 cm thick) and concentrated to ca. 3 mL and excess ether added to precipitate out yellow solids of [(η^6-C$_6$Me$_6$)Ru(η^3-C$_7$H$_{14}$S$_3$)](PF$_6$)$_2$, (**14**)(PF$_6$)$_2$ (55 mg, 0.074 mmol, 77% yield). FAB$^+$-MS: *m/z* 603 [M − PF$_6$]$^+$, 465, 457 [M − 2PF$_6$ − H]$^+$, 431 [M − 2PF$_6$ − 2CH$_2$ + H]$^+$, 370 [M − 2PF$_6$ − 2CH$_2$ − S(CH$_2$)$_2$]$^+$, 356 [M − 2PF$_6$ − 3CH$_2$ − S(CH$_2$)$_2$]$^+$, 328 [M − 2PF$_6$ − 3CH$_2$ − S(CH$_2$)$_4$]$^+$, 296 [M − 2PF$_6$ − 3CH$_2$ − S$_2$(CH$_2$)$_4$]$^+$, 282 [M − 2PF$_6$ − 3CH$_2$ − S$_2$(CH$_2$)$_6$]$^+$. FAB$^-$-MS: *m/z* 145 (PF$_6^-$). Anal. Calcd for C$_{19}$H$_{32}$F$_{12}$P$_2$RuS$_3$·CH$_3$CN: C, 32.0; H, 4.5; P, 7.9; S, 12.2; N, 1.8. Found: C, 32.0; H, 4.4; P, 7.9; S, 12.0; N, 1.6.

A similar reaction of **5** (0.084 g, 0.20 mmol) with dibromomethane (0.06 mL, 0.86 mmol) for 3 h, followed by a similar workup gave [(η^6-C$_6$Me$_6$)Ru(η^3-C$_5$H$_{10}$S$_3$)](PF$_6$)$_2$, (**13**)(PF$_6$)$_2$ (59 mg, 0.082 mmol, 41% yield). FAB$^+$-MS: *m/z* 575 [M − PF$_6$]$^+$, 431 [M − 2PF$_6$ + H]$^+$, 371 [M − 2PF$_6$ + H − S(CH$_2$)$_2$]$^+$, 355 [M − 2PF$_6$ − CH$_3$ − S(CH$_2$)$_2$]$^+$, 296 [M − 2PF$_6$ − CH$_2$ − S$_2$(CH$_2$)$_4$]$^+$. FAB$^-$-MS: *m/z* 145 (PF$_6^-$). Anal. Calcd for C$_{17}$H$_{28}$F$_{12}$P$_2$RuS$_3$·CH$_3$CN: C, 30.0; H, 4.1; P, 8.1; S, 12.7; N, 1.8. Found: C, 29.5; H, 3.9; P, 8.1; S, 13.0; N, 1.3.

Complex [(η^6-C$_6$Me$_6$)Ru(η^3-C$_8$H$_{16}$S$_3$)](PF$_6$)$_2$, (**15**)(PF$_6$)$_2$, was similarly obtained, from **5** (52 mg, 0.13 mmol) as yellow crystalline plates (69 mg, 0.091 mmol, 72% yield). FAB$^+$-MS: *m/z* 617 [M − PF$_6$]$^+$, 471 [M − 2PF$_6$ − H]$^+$, 444 [M − 2PF$_6$ − 2CH$_2$]$^+$, 413 [M − 2PF$_6$ − S(CH$_2$)$_2$ + H]$^+$, 356 [M − 2PF$_6$ − 4CH$_2$ − S(CH$_2$)$_2$]$^+$, 296 [M − 2PF$_6$ − 4CH$_2$ − S$_2$(CH$_2$)$_4$]$^+$, 282 [M − 2PF$_6$

− 4CH$_2$ − S$_2$(CH$_2$)$_6$]$^+$. FAB$^-$-MS: *m/z* 145 (PF$_6^-$). Anal. Calcd for C$_{20}$H$_{34}$F$_{12}$P$_2$RuS$_3$: C, 31.5; H, 4.5; P, 8.1; S, 12.6. Found: C, 31.6; H, 4.5; P, 7.5; S, 12.1.

Into a stirred solution of **5** (58 mg, 0.14 mmol) in MeOH (12 mL) was injected 1,5-dibromopentane (0.40 mL, 2.94 mmol). After 24 h, there was still no apparent color change from the original red solution. NH$_4$PF$_6$ (211 mg, 1.29 mmol) was added and the mixture allowed to react for 24 h. The solution was then concentrated to dryness giving orange-red solids, which underwent a color change to yellow after 1 week at room temperature. Extraction of the solids with CH$_3$CN (2 × 3 mL) and filtration through a disk of Celite (1.5 cm thick) gave a yellowish brown solution from which was obtained a dark yellow oil upon concentration and addition of ether. Repeated trituration of the oil with a trace of tetrahydrofuran and acetone gave [(η^3-C$_6$Me$_6$)Ru(η^3-C$_9$H$_{18}$S$_3$)](PF$_6$)$_2$, (**16**)(PF$_6$)$_2$, as yellow solid (24 mg, 0.031 mmol, 22% yield). FAB$^+$-MS: *m/z* 631 [M − PF$_6$]$^+$, 485 [M − 2PF$_6$ − H]$^+$, 459 [M − 2PF$_6$ − H − 2CH$_2$]$^+$, 427 [M − 2PF$_6$ − H − S(CH$_2$)$_2$]$^+$, 356 [M − 2PF$_6$ − S(CH$_2$)$_2$ − 5CH$_2$]$^+$, 296 [M − 2PF$_6$ − S$_2$(CH$_2$)$_4$ − 5CH$_2$]$^+$, 282 [M − 2PF$_6$ − S$_2$(CH$_2$)$_6$ − 5CH$_2$]$^+$. FAB$^-$-MS: *m/z* 145 (PF$_6^-$). Anal. Calcd for C$_{21}$H$_{36}$F$_{12}$P$_2$RuS$_3$: C, 32.5; H, 4.7; P, 8.0; S, 12.4. Found: C, 33.1; H, 4.5; P, 8.5; S, 11.2.

Reaction of [(η^6-1,4-MeC$_6$H$_4$CHMe$_2$)RuCl$_2$]$_2$ with 2-Mercaptoethyl Sulfide. To a suspension of sodium methoxide (freshly generated from sodium (23 mg, 1 mmol)) in THF (10 mL) was injected 2-mercaptoethyl sulfide (0.065 mL, 0.5 mmol) and the mixture stirred for 1.5 h. [(η^6-1,4-MeC$_6$H$_4$CHMe$_2$)RuCl$_2$]$_2$ (153 mg, 0.25 mmol) was then added as a solid. A deep red coloration developed instantaneously. After 15 min, the product mixture was evacuated to dryness and extracted with 1:1 toluene−acetonitrile (3 × 7 mL), and the extracts were filtered through Celite. Concentration of the filtrate to ca. 5 mL and addition of *n*-hexane (2 mL), followed by cooling at 0 °C for 30 min, gave [(η^6-1,4-MeC$_6$H$_4$CHMe$_2$)Ru(η^3-C$_4$H$_8$S$_3$)] (**6**) as a fine deep red solid (120 mg, 0.31 mmol, 62% yield), and subsequently a second crop (60 mg, 0.15 mmol, 31% yield) after a day at −78 °C. Attempts at recrystallization resulted in partial degradation. Strangely, these fine solids underwent an unusual solid-state "transformation" over 4 days in a small capped vial at room temperature into crystalline thick plates and large chunky polyhedra, suitable for its complete characterization, including an X-ray diffraction analysis. (FAB$^+$-MS): *m/z* 388 [M]$^+$, 329 [M − S(CH$_2$)(CH$_3$)]$^+$, and lower molecular weight fragments. Anal. Calcd for C$_{14}$H$_{22}$RuS$_3$: C, 43.4; H, 5.7; S, 24.8. Found: C, 43.7; H, 6.3; S, 25.5.

Crystal Structure Determinations. Diffraction-quality crystals were obtained as follows: **5** as reddish-brown prisms from toluene−ether after several days at 0 °C; (**9**)(PF$_6$)$_2$ as orange prisms from acetonitrile−ether after 4 days at 0 °C; (**7**)Cl·H$_2$O as orange polyhedra from acetonitrile−ether after several days at 0 °C; and **6**, as described previously; (**1**)(PF$_6$)$_2$ as yellow cubes, (**13**)(PF$_6$)$_2$ and (**14**)(PF$_6$)$_2$ as yellow orthorhombic crystals, from diffusion of ether into acetonitrile solutions after 4, 5, and 10 days, respectively, at −30 °C; (**15**)(PF$_6$)$_2$ as cubic crystals, from diffusion of ether into a nitromethane solution after 14 days at −30 °C.

Details of crystal parameters, data collection, and structure refinement are summarized in Table 6. Data for compounds **5**, **6**, and (**9**)(PF$_6$)$_2$·MeCN, were collected on a Rigaku AFC6R diffractometer at 296 K while that of compound (**7**)Cl·H$_2$O was collected on a MSC/Rigaku RAXIS-IIC imaging plate at 294 K. Both machines were equipped with graphite monochromated Cu (for compound (**9**)(PF$_6$)$_2$·MeCN) or Mo radiations (for the other three compounds) and a rotating anode generator. Data for compounds

Table 6. Crystal and Refinement Data

	5	**6**	**(7)Cl·H₂O**	**(9)(PF₆)₂·MeCN**	**(13)(PF₆)₂**	**(1)(PF₆)₂**	**(14)(PF₆)₂**	**(15)(PF₆)₂**
formula	$C_{16}H_{26}RuS_3$	$C_{14}H_{22}RuS_3$	$C_{28}H_{46}Cl_2$-ORu_2S_3	$C_{32}H_{50}F_{12}N_2$-$P_2Ru_2S_3$	$C_{32}H_{50}F_{12}N_2$-$P_2Ru_2S_3$	$C_{22}H_{40}F_{12}N_2$-$O_4P_2RuS_3$	$C_{21}H_{35}F_{12}NP_2$-RuS_3	$C_{20}H_{33}F_{12}N$-P_2RuS_3
fw	415.62	387.57	767.87	1051.00	760.64	883.75	788.69	774.66
cryst syst	monoclinic	orthorhombic	monoclinic	hexagonal	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$Pbca$	$P2_1/c$	$P6_5$	$Pnma$	$P2_1/c$	$Pnma$	$P2_1/c$
a, Å	10.678(2)	10.703(4)	9.3192(3)	11.995(4)	9.29190(10)	10.6608(4)	9.7217(4)	8.8575(10)
b, Å	10.247(2)	14.115(3)	17.9876(6)	11.995(4)	9.12350(10)	31.0220(13)	9.0816(4)	32.819(4)
c, Å	15.5890(10)	20.807(4)	21.2085(5)	48.844(8)	33.6347(3)	10.5648(4)	34.0881(13)	10.0280(12)
α, deg	90	90	90	90	90	90	90	90
β, deg	94.98(1)	90	90.00(2)	90	90	107.4450(10)	90	91.992(3)
γ, deg	90	90	90	120	90	90	90	90
V, Å³	1699.3(5)	3143.4(15)	3555.18(18)	6086(3)	2851.37(5)	3333.3(2)	3009.6(2)	2913.3(6)
Z	4	8	4	6	4	4	4	4
μ, mm⁻¹	1.28	1.377	1.194	8.961	0.972	0.855	0.925	0.953
$F(000)$	856	1584	1568	3180	1528	1792	1592	1560
no. indep reflns	3019	2787	7173	3067	3879	8987	5019	4127
no. obsd reflns $[I > 2\sigma(I)]$	2335	1957	6852	2812	18682	34159	26544	19436
no. params refined	187	165	337	491	237	411	221	318
GOF	1.038	1.014	1.191	1.040	1.143	1.157	1.033	1.068
R_F	0.0264	0.0292	0.0753	0.0356	0.051	0.0745	0.0483	0.0784
R_w	0.074	0.0803	0.2362	0.0951	0.1172	0.1562	0.1339	0.2176
$\rho_{max/min}$ (e/Å³)	0.392/−0.418	0.670/−0.386	1.654/−0.902	0.840/−0.370	0.682/−0.631	1.273/−0.968	1.046/−0.742	2.517/−0.976

(**1**)(PF₆)₂ and (**13**)(PF₆)₂−(**15**)(PF₆)₂ were collected on a Bruker APEX AXS diffractometer, equipped with a CCD detector, using Mo Kα radiation. The data were corrected for Lorentz and polarization effects with the SMART suite of programs,[45] and for absorption effects with SADABS.[46] The final unit cell parameters were obtained by least squares on a number of strong reflections. Structural solution and refinement were carried out with the SHELXTL suite of programs.[47] The structure was solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. Organic hydrogens were placed in calculated positions and refined with a riding model. All non-hydrogen atoms were given anisotropic displacement parameters in the final refinement. Refinements were on $\sum[w(F_o^2 - F_c^2)^2]$.

The three compounds, (**13**)(PF₆)₂−(**15**)(PF₆)₂, show disorder of the PF₆ anions; these were modeled with two alternative sites, with appropriate restraints placed. The compound (**13**)(PF₆)₂ also exhibited disorder of the 8S3 ligand; this was modeled with one C and one S atom each occupying two different, alternative sites of equal occupancies. The disordered PF₆ anions in (**9**)(PF₆)₂·MeCN were refined by restraining the P−F and F···F distances to vary within 0.01 and 0.02 Å, respectively.

Supporting Information Available: Tables giving infrared spectral data, additional bond lengths of **5**, and a comparison of selected bond lengths and bond angles of related complexes. CIF data for all the structures, giving atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, and complete listing of interatomic distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(45) *SMART* version 4.05; Siemens Energy & Automation Inc.: Madison, WI.

(46) Sheldrick, G. M. *SADABS*, Software for Empirical Absorption Correction, University of Göttingen, Germany, 1996.

(47) *SHELXTL* version 5.03; Siemens Energy & Automation Inc.: Madison, WI.