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Base-Induced Fragmentation of a Macrocyclic Thioether at an (Arene)ruthenium(II) Center. Generation of $\eta^1(S)$-Ethenethiolate and $\eta^2(C,S)$-Thioacetaldehyde

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Abstract: Treatment of the labile (hexamethylbenzene)ruthenium(II) acetone complex $[(\eta^6\text{-}C_6Me_6)Ru(OCMe_2)_3]^{2+}$ with 1,4,7-trithiacyclononane (9S3) gives the half-sandwich salt $[(\eta^6\text{-}C_6Me_6)Ru(9S3)](PF_6)_2$ (**1**), which undergoes two successive deprotonations at its methylene carbon atoms in the presence of KOH. The products are chelate vinyl thioether complexes, $[(\eta^6\text{-}C_6Me_6)Ru(S(CH{=}CH_2)CH_2CH_2SCH_2CH_2S)]PF_6$ (**2**) (48% isolated yield) and $(\eta^6\text{-}C_6Me_6)Ru(S(CH{=}CH_2)CH_2CH_2S)(SCH{=}CH_2)$ (**3**) (34% isolated yield); the latter also contains the novel $\eta^1(S)$-ethenethiolate ligand. Treatment of **1** or **2** with more than 3 molar equiv of KO-*t*-Bu induces deprotonation of one of the C_6Me_6 methyl groups; addition of the resulting carbanion to the vinyl group of the coordinated thioether of **3** gives $Ru(SCH{=}CH_2)(S(CH_2CH_2CH_2\text{-}\eta^6\text{-}C_6Me_5)CH_2CH_2S)$ (**4**) (50% isolated yield), which contains a tridentate arene−thioether−thiolate ligand in addition to $\eta^1(S)$-ethenethiolate. Complexes **2**−**4** have been characterized by NMR (^1H, ^{13}C) and IR spectroscopy and by single-crystal X-ray structural analysis. Whereas **2** is reconverted into **1** by acid, in the case of **3** and **4** the ethenethiolate groups are protonated to generate cationic complexes containing η^2-thioacetaldehyde, i.e., $[(\eta^6\text{-}C_6Me_6)Ru(S(CH{=}CH_2CH_2CH_2S)(\eta^2\text{-}SCHCH_3)]^+$ (**8**) and $[Ru(\eta^2\text{-}SCHCH_3)(S(CH_2CH_2CH_2\text{-}\eta^6\text{-}C_6Me_5)CH_2CH_2S)]^+$ (**7**), respectively, which exist as diastereomeric mixtures, as shown by ^1H and ^{13}C NMR spectroscopy. Complex **8** undergoes a slower, second protonation of the vinyl thioether to give, after C−S bond formation, $[(\eta^6\text{-}C_6Me_6)Ru(S(\eta^2\text{-}CHCH_3)CH_2CH_2SCH_2CH_2S)]^{2+}$ (**9**).

Introduction

The macrocyclic thioether 1,4,7-trithiacyclononane (abbreviated [9]aneS_3 or, in this paper, 9S3) forms an unusually wide range of transition metal complexes in which it commonly adopts its favored facial endodentate conformation.[2−5] They include a family of homoleptic complexes of the type $[M(9S3)_2]^{n+}$ [2−7] and various mixed complexes in which the 9S3 ligand occupies one face of an octahedron or square pyramid, e.g., $Mo(CO)_3(9S3)$,[8] $ReO_3(9S3)$,[9] $VOCl_2(9S3)$,[10] $[MH(CO)(PPh_3)(9S3)]^+$ (M = Ru, Os),[6] $RuCl_2$ $(PPh_3)(9S3)$,[11] and $[Ni(L\text{-}L)(9S3)]^{2+}$ (L-L = various ditertiary phosphines).[12] There has also been interest in organometallic complexes containing 9S3 as a coligand, e.g., $[M(\eta^4\text{-diene})(9S3)]^+$ (M = Rh, Ir; diene = 1,5-cyclooctadiene or 1,3-butadiene),[13] $[M(C_2H_4)_2(9S3)]^+$ (M = Rh, Ir),[13] $[Os(\eta^6\text{-}4\text{-}MeC_6H_4\text{-}i\text{-}Pr)(9S3)]^{2+}$,[6] $[RuR(CO)(PPh_3)(9S3)]^+$ (R = *p*-MeC_6H_4, CH=CHPh, CPh=CHPh),[14] MRR′(9S3),[15] and $[MR_2R'(9S3)]^+$ (M = Pt, Pd; R,R′ = various alkyl groups, Ph).[15,16] Apart from $Mo(CO)_3(9S3)$,[8] however, there are no examples of 9S3 bound to a zerovalent metal atom.

It has been established that *o*-xylylene or tetramethyl-*o*-xylylene complexes of ruthenium(0) are formed on deprotonation of bis(η^6-1,2-dimethylarene) complexes of ruthenium(II) (eq 1)[17] or of η^6-1,2-dimethylarene complexes of ruthenium(II) containing tertiary phosphines (eqs 2 and 3).[17−19] Depending on the arene and on the auxiliary ligands in the starting material, the *o*-xylylene fragment may be *endo*-coordinated (eq 1 and 2) or *exo*-coordinated (eq 3).

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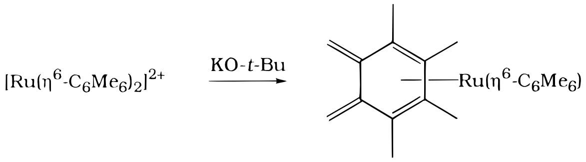

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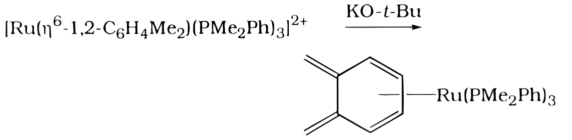

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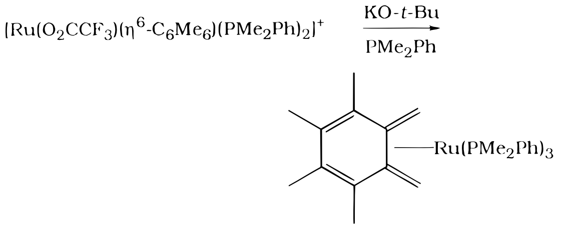

(3)

In attempting to prepare analogous complexes containing 9S3, we found that treatment of $[Ru(\eta^6\text{-}C_6Me_6)(9S3)]^{2+}$ with strong bases causes preferential deprotonation of coordinated 9S3 and C−S bond cleavage, thus fragmenting the macrocycle. This paper expands on our preliminary communication.[20]

Experimental Section

All reactions were carried out under high-purity nitrogen or argon with use of standard Schlenk techniques. Analytical grade acetone was used as supplied. CH_2Cl_2 was distilled from CaH_2 before use. All other solvents were distilled from sodium benzophenone ketyl. Elemental analyses were carried out in-house. NMR spectra were measured on Varian XL200 (^1H at 200.01 MHz; ^{13}C at 50.29 MHz) and Varian Gemini 300 (^1H at 300.10 MHz; ^{13}C at 75.46 MHz) and were referenced to residual $CHDCl_2$ in CD_2Cl_2 or CHD_2CN in CD_3CN. 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.

Commercial potassium *tert*-butoxide was sublimed and stored under nitrogen. The compounds $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$[21] and 9S3[22] were prepared by appropriate literature methods.

Preparations. (a) $[Ru(\eta^6\text{-}C_6Me_6)(9S3)](PF_6)_2$ (1). To a suspension of $[RuCl_2(\eta^6\text{-}C_6Me_6)]_2$ (2.00 g, 3.0 mmol) in acetone (50 mL) at 0 °C was added solid $AgPF_6$ (3.08 g, 12.16 mmol) under nitrogen. An orange solution was formed immediately, and AgCl precipitated. On filtration through a disk of Celite (3 × 3 cm) into a stirred solution of 9S3 (1.08 g, 6.0 mmol) in acetone (50 mL), an initial greenish yellow coloration was observed. After 30 min at ambient temperature, the resultant orange-yellow solution was filtered through a disk of neutral alumina (3 × 4 cm) and concentrated to *ca.* 10 mL in vacuo. Addition of ether (*ca.* 10 mL) and cooling to 0 °C for 3 h gave **1** as a fine, lemon yellow crystalline solid (3.77 g, 5.14 mmol, 86%), which is insoluble in most organic solvents except acetone and acetonitrile. ^1H NMR (CD_3CN): δ 2.25 (s, 18 H, C_6Me_6), 2.78 (m, 12 H, CH_2). ^{13}C NMR (CD_3CN): δ 16.37 ($C_6\mathit{Me}_6$), 36.48 (CH_2), 107.74 (C_6Me_6). FAB-MS: *m/z* 719 (M − CH_2), 607(M − PF_6 − F), 520 (M − $2PF_6$). Anal. Calcd for $C_{18}H_{30}F_{12}P_2RuS_3$: C, 29.47; H, 4.12; F, 31.08; P, 8.44; Ru, 13.63; S, 13.11. Found: C, 29.87; H, 4.27; F, 30.82; P, 8.45; Ru, 13.70; S, 12.98.

(b) $[(\eta^6\text{-}C_6Me_6)\overline{Ru(S(CH{=}CH_2)CH_2CH_2SCH_2CH_2S})]PF_6$ (2). A slurry of **1** (367 mg, 0.5 mmol) and freshly powdered KOH (91 mg, 1.62 mmol) in THF (25 mL) was stirred under nitrogen at room temperature. The mixture slowly turned orange and finally deep red. After 1.5 h, the product mixture was concentrated to dryness in vacuo, and the residue was extracted with CH_2Cl_2 (4 × 5 mL). The combined extracts were filtered through Celite (1 × 3 cm) to remove KPF_6 and the excess of KOH. The orange-red filtrate and washings were combined and concentrated to 1−2 mL, and ether (*ca.* 0.2 mL) was added. Overnight cooling at 0 °C gave dark red crystals of **2** (0.14 g, 0.24 mmol, 48%). The mother liquor contained a mixture of starting material (**1**) and complexes bearing vinyl protons, of which **3** (described below) was the main component. Orange-red crystals of **2** suitable for study by X-ray diffraction were obtained by allowing hexane to diffuse into a saturated solution in CH_2Cl_2 for 2 days at room temperature. ^1H NMR (CD_2Cl_2): δ 1.99−3.02 (m, CH_2), 2.12 (s, 18H, C_6Me_6), 5.83−5.92 (two overlapping d, 2H, J = 18.7, 9.3, $=C\mathit{H}_2$), 6.49−6.62 (m, 1H, $C\mathit{H}{=}CH_2$). ^{13}C NMR (CD_2Cl_2): δ 15.31(J = 129, $C_6\mathit{Me}_6$), 29.67 (J = 139), 35.01 (J = 143), 37.80 (J = 145), 45.35 (J = 142) (each CH_2), 101.55 (C_6Me_6), 126.46 (J = 163, $=CH_2$), 126.71 (J = 183, =CH). IR (cm^{-1}, KBr): 1599 m [ν(C=C)], 840 vs, br [ν(PF)], 585 s [δ(PF)]. FAB-MS: *m/z* 589 (M), 561 (M − $2CH_2$), 547-(M − $3CH_2$). Anal. Calcd for $C_{18}H_{29}F_6PRuS_3$: C, 36.79; H, 4.97; F, 19.40; P, 5.27; Ru, 17.20; S, 16.37. Found: C, 36.98; H, 4.93; F, 19.68; P, 5.28; Ru, 17.31; S, 16.73.

(c) $(\eta^6\text{-}C_6Me_6)\overline{Ru(S(CH{=}CH_2)CH_2CH_2S})(SCH{=}CH_2)$ (3). An orange solution of **2** (117 mg, 0.2 mmol) in CH_2Cl_2 (8 mL) was stirred with freshly powdered KOH (20 mg, 0.36 mmol) at ambient temperature. As there was no obvious color change, the progress of the reaction was monitored by occasional testing of the toluene-solubility of the solid residue obtained by evaporating small aliquots of the reaction mixture to dryness. After 4 h, the resultant solution was concentrated to dryness and the product was extracted into toluene (4 × 2 mL). The filtered orange extract was concentrated to *ca.* 1 mL, and hexane (*ca.* 1 mL) was added. Cooling at 0 °C for 2 h gave dark red crystals of **3** (30 mg, 0.068 mmol, 34%) and a trace of dark red oil. The residue from the toluene treatment was extracted with CH_2Cl_2 (3 × 2 mL). On workup, this gave unreacted starting material (**2**) (*ca.* 60 mg, 50% recovery), contaminated with some unidentified material that showed a six-line multiplet (centered at δ 7.20) due to vinyl protons and a $C_6\mathit{Me}_6$ singlet at 2.19 in its ^1H NMR spectrum.

X-ray quality crystals of **3** were obtained as orange-red plates from a saturated solution in CH_2Cl_2 layered with hexane after 2 days at 0 °C. ^1H NMR (CD_2Cl_2): δ 1.97 (s, 20 H, C_6Me_6, CH_2S), 2.33 (m, 4 H, CH_2S), 4.74 (dd, 1H, J = 9.5, 2.1, =C*H*H(*cis*)), 5.05 (dd, 1H, J = 16.8, 2.1, =CH*H* (*trans*)), 5.56 (d, 1H, J = 9.1, =C*H*H(*cis*)), 5.66 (d, 1H, J = 16.6, =CH*H*(*trans*)), 6.45−6.57(8 line m, 2H, 2C*H*=). ^{13}C NMR (CD_2Cl_2, −40 °C): δ 14.51 (J = 128, $C_6\mathit{Me}_6$), 27.91 (J = 140), 43.83 (J = 142) (each CH_2), 96.03 (C_6Me_6), 107.73 (J = 157, $=CH_2$), 120.85 (J = 161, $=CH_2$), 129.44 (J = 184, =CH) 145.64 (J = 165, =CH). IR (cm^{-1}, KBr): 1590 (s), 1555 (s) [ν(C=C)]. FAB-MS: *m/z* 442 (M) (plus higher mass fragments), 383, 356, 324, 295, 260. Anal. Calcd for $C_{18}H_{23}RuS_3$: C, 48.95; H, 6.39; S, 21.78. Found: C, 47.53, 49.55; H, 6.78, 5.53; S, 21.19.

(d) $\overline{Ru(SCH{=}CH_2)(S(CH_2CH_2CH_2\text{-}\eta^6\text{-}C_6Me_5)CH_2CH_2S})$ (4). To a stirred suspension of **1** (367 mg, 0.5 mmol) in THF (20 mL) under nitrogen at ambient temperature was added KO-*t*-Bu (227 mg, 2.02 mmol). An orange coloration developed instantaneously, and KPF_6 precipitated. After 15 min, the mixture was concentrated to dryness in vacuo and the residue was extracted with CH_2Cl_2 (5 × 5 mL). The combined extracts were filtered through a disk of Celite (2 × 3 cm) and concentrated to *ca.* 1 mL. Slow addition of ether (2−3 mL) with stirring caused **4** to precipitate as a fine orange solid (116 mg, 0.262 mmol, 53%). The mother liquor contained **3** and other unidentified vinyl thioether complexes. A similar yield of **4** was obtained with the use of 3 molar equiv of KO-*t*-Bu. X-ray quality crystals of **4** were obtained as thick, dark red needles from a saturated solution in CH_2Cl_2/ether after 5 days at −20 °C. ^1H NMR (CD_2Cl_2): δ 1.93, 1.95, 2.01, 2.07, 2.10 (each s, 15 H, C_6Me_5), 1.55−1.70 (m, 1H), 2.10−2.28 (m, 4H), 2.39−2.66 (m, 3H), 3.23 (dt, 1H, sepn = 10.3, 3.9) (CH_2), 4.76 (dd, 1H, J = 9.6, 1.8, =C*H*H(*cis*)), 5.03 (dd, 1H, J = 16.8, 2.0, =CH*H* (*trans*), 6.40 (dd, 1H, J = 16.8, 9.7, =CH). ^{13}C NMR (CD_2Cl_2): δ 14.69, 14.89, 14.94, 15.03, 16.78 (each J = 128, $C_6\mathit{Me}_5$), 24.39

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(*J* = 125), 26.60 (*J* = 130), 26.79 (*J* = 139), 31.10 (*J* = 139), 45.21 (*J* = 141) (each $\mathrm{CH_2}$), 91.27, 91.88, 92.26, 94.32, 98.67, 102.96 ($C_6\mathrm{Me_5}$), 109.01 (*J* = 157, $=\mathrm{CH_2}$), 144.29 (*J* = 163, 2.2, $=$CH). IR (KBr, $\mathrm{cm^{-1}}$): 1556 (s) [ν(C$=$C)]. EI-MS: *m/z* 442 (M), 410 (M − S), 383. Anal. Calcd for $\mathrm{C_{18}H_{23}RuS_3}$: C, 48.95; H, 6.38; Ru, 22.88; S, 21.78. Found: C, 48.94; H, 5.93; Ru, 22.55; S, 21.42.

Treatment of **1** with 1 molar equiv of KO-*t*-Bu in THF and extraction of the solid product with $\mathrm{CH_2Cl_2}$ gave unchanged **1** (*ca.* 50%) and a 1:1 mixture of **2** and **3**, mixed with small amounts of unidentified vinyl thioether complexes, from which **2** was isolated in *ca.* 14% yield. Reaction of **1** with an excess of KO-*t*-Bu in $\mathrm{CD_2Cl_2}$ for 1.5 h gave a 1:1 mixture of **3** and **4** as the main product.

(e) Conversion of 2 into 4. To **2** (*ca.* 10 mg) and an excess of KO-*t*-Bu (*ca.* 10 mg) was added THF (*ca.* 0.5 mL). The mixture was stirred at room temperature for 5 min and evaporated to dryness in vacuo. The ^{1}H NMR spectrum of a $\mathrm{CD_2Cl_2}$ extract showed that **4** was the main product.

(f) Protonation of 2. To an orange solution of **2** (30 mg, 0.05 mmol) in $\mathrm{CH_2Cl_2}$ (2 mL) was added dropwise with stirring an ethereal solution (0.5 mL) containing 0.125 mL of 60% $\mathrm{HPF_6}$ (*ca.* 0.05 mmol). The solution immediately turned yellow, and **1** precipitated in the form of a yellow solid (30 mg, 0.041 mmol, 80%). The mother liquor contained some unchanged starting material (**2**) and an unidentified complex that contained no 9S3.

(g) Protonation of 3. An orange-brown solution of **3** was prepared in situ by stirring an orange-red solution of **2** (30 mg, 0.05 mmol) in $\mathrm{CD_2Cl_2}$ (0.6 mL) with powdered KOH (5 mg, 0.09 mmol) for 2 h at ambient temperature (21 °C). It was filtered through a cannula into a 5-mm serum-capped NMR tube and then cooled to −78 °C. Into the cooled solution was injected $\mathrm{CF_3COOH}$ (8 μL, 0.11 mmol). The ^{1}H and ^{13}C NMR spectra were measured at −60 °C. The sample was then allowed to warm up to room temperature, and the ^{1}H NMR spectrum was remeasured. The spectrum was then monitored over 55 h, after which no further change was observed. A proton-coupled ^{13}C spectrum was finally measured. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, −60 °C): δ 1.34 (d, 3H, *J* = 6.7, $\mathrm{CHC}H_3$), 2.05 (s, 18H, $\mathrm{C_6Me_6}$), 2.10−3.30 (m, 4H, $\mathrm{SCH_2CH_2S}$), 5.51 (q, 1H, *J* = 6.7, $\mathrm{C}H\mathrm{CH_3}$), 5.87 (d, 1H, *J* = 8.9, $=\mathrm{C}H\mathrm{H}$(*cis*)), 6.08 (d, 1H, *J* = 16.5, $=\mathrm{CH}H$ (*trans*)), 6.26−6.34 (dd, 1H, $=$CH). ^{13}C NMR ($\mathrm{CD_2Cl_2}$, −60 °C): δ 15.05 (*J* = 129, $\mathrm{C_6}Me_6$), 25.76 (*J* = 129, $\mathrm{CH}C\mathrm{H_3}$), 29.36 (*J* = 144, $\mathrm{CH_2S}$), 35.05 (*J* = 149, $\mathrm{CH_2S}$), 65.98 (*J* = 158, $C\mathrm{HCH_3}$), 99.56 ($C_6\mathrm{Me_6}$), 125.89 (*J* = 185, $=$CH), 127.64 (*J* = 164, $=\mathrm{CH_2}$). Peaks due to $\mathrm{CF_3CO_2^-}$ at δ 114.14 (J_{CF} = 286) and 159.24 (J_{CF} = 41) were also observed. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 21 °C): Peaks as listed above, together with new peaks at δ 1.65 (d, *J* = 6.8, $\mathrm{CHC}H_3$), 2.11 (s, $\mathrm{C_6}Me_6$), 5.09 (q, *J* = 6.7, $\mathrm{C}H\mathrm{CH_3}$), 5.96 (d, *J* = 8.4, $=\mathrm{C}H\mathrm{H}$(*cis*)), 6.16 (d, *J* = 18.0, $=\mathrm{CH}H$(*trans*), 6.57−6.65 (dd, $=$CH); ratio of isomers *ca.* 1:3. After 55 h: ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 21 °C) δ 1.59 (d, *J* = 6.8, $\mathrm{CHC}H_3$), 2.29 (s, $\mathrm{C_6}Me_6$), 2.75−3.5 (m, $\mathrm{CH_2S}$), 4.62 (q, *J* = 7.1, $\mathrm{C}H\mathrm{CH_3}$) and 1.90 (d, *J* =7.6, $\mathrm{CHC}H_3$), 2.33 (s, $\mathrm{C_6Me_6}$), 2.75−3.5 (m, $\mathrm{CH_2S}$), 6.15 (q, *J* = 7.6, $\mathrm{C}H\mathrm{CH_3}$); ratio of isomers *ca.* 1:10. ^{13}C NMR ($\mathrm{CD_2Cl_2}$, 21 °C), minor isomer, δ 15.98 (*J* = 131, $\mathrm{C_6}Me_6$), 22.74 (*J* = 134, $\mathrm{CH}C\mathrm{H_3}$) ($C\mathrm{HCH_3}$ signal not observed); major isomer, δ 16.35 (*J* = 130, $\mathrm{C_6}Me_6$), 36.75 (*J* = 148, $\mathrm{CH}C\mathrm{H_3}$), 38.77 (*J* = 147, $\mathrm{CH_2S}$), 88.25 ($C\mathrm{HCH_3}$, *J* = 162, $C\mathrm{HCH_3}$).

Similar results were obtained with $\mathrm{HPF_6}$ in place of $\mathrm{CF_3CO_2H}$.

(h) Protonation of 4. Into an orange-red solution of **4** (20 mg, 0.045 mmol) in $\mathrm{CD_2Cl_2}$ (0.6 mL) in a 5-mm NMR tube at −50 °C was injected $\mathrm{CF_3COOH}$ (7 μL, 0.09 mmol). The solution immediately became reddish brown. The ^{1}H and ^{13}C NMR spectra were measured with the probe temperature maintained at −40 °C (i) immediately after addition of the acid and (ii) after allowing the solution to warm to ambient temperature. ^{1}H NMR ($\mathrm{CD_2Cl_2}$, −40 °C): δ 1.29 (d, 3H, *J* = 7.0, $\mathrm{CHC}H_3$), 1.96 (s, 3H), 2.00 (s, 3H), 2.07 (s, 3H), 2.33 (s, 6H) ($\mathrm{C_6Me_5}$), 2.09−2.30 (m), 2.50−2.75 (m), 2.90−3.36 (m) ($\mathrm{CH_2S}$), 5.41 (1H, *J* = 7.0, $\mathrm{C}H\mathrm{CH_3}$). ^{13}C NMR ($\mathrm{CD_2Cl_2}$, −40 °C): δ 14.75, 15.54, 16.06, 16.85 ($\mathrm{C_6}Me_5$), 23.74 ($\mathrm{CH}C\mathrm{H_3}$), 25.59, 25.87, 29.10, 31.42, 35.22 ($\mathrm{CH_2S}$), 66.20 ($C\mathrm{HCH_3}$), 95.19, 97.56, 97.92, 100.27, 104.20 ($C_6\mathrm{Me_5}$). ^{1}H NMR ($\mathrm{CD_2Cl_2}$, 21 °C): minor isomer, δ 1.34 (d, *J* = 7.0, $\mathrm{CHC}H_3$), 2.01, 2.05, 2.11, 2.37, 2.38 ($\mathrm{C_6Me_5}$), 5.43 (q, *J* = 7.0, $\mathrm{C}H\mathrm{CH_3}$); major isomer, δ 1.62 (d, *J* = 7.0, $\mathrm{CHC}H_3$), 1.96, 1.97, 2.10, 2.40, 2.44 ($\mathrm{C_6Me_5}$), 4.93 (q, *J* = 7.0, $\mathrm{CHC}H_3$). ^{13}C NMR ($\mathrm{CD_2Cl_2}$, 21 °C): δ 15.44, 15.48, 15.60, 16.33, 17.24 ($\mathrm{C_6}Me_5$), 24.15 ($\mathrm{CHC}H_3$), 70.97 ($C\mathrm{HCH_3}$), 94.70, 96.15, 98.02, 98.60, 100.65, 104.08 ($C_6\mathrm{Me_5}$). Ratio of isomers: *ca.* 1:10.

Attempts to isolate the protonation products obtained as described in paragraphs g and h, either at ambient temperature or at −78 °C, invariably gave a red oil.

Crystal Structure Analyses

Data Collection and Processing. Single crystals of **2** and **4** and an epoxy-resin-coated fragment cleaved from a large plate-like crystal of **3** were each mounted on a Philips PW1100/20 diffractometer, which was equipped with a graphite monochromator and used Cu Kα radiation. Lattice parameters were determined by least-squares analysis of the 2θ angles of 25 reflections 115° $< 2\theta <$ 128° (for **2**), 122° $< 2\theta <$ 128° (for **3**), and 63° $< 2\theta <$ 73° (for **4**). (λ(Cu Kα_1) = 1.540 56 Å used for **2** and **3**; λ(Cu K$\bar{\alpha}$) = 1.5418 Å used for **4**).

Crystallographic data are given in Table 1. Three standard reflections were measured periodically (every 120 min for **2** and **4** and 90 min for **3**) and showed decreases in intensity during data collection of 3, 6 and 7% for **2**, **3**, and **4**, respectively. The data were corrected for these decreases[23] and for absorption.[24]

Methods and techniques used for structure solution are given in Table 1. Data reduction and refinement computations were performed with XTAL3.0;[25] atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from ref 26. In complex **2**, disorder was observed at C(71) and for atoms F(2), F(3), F(5), and F(6), in each case the atom being represented by two sites of reduced occupancy. The hexamethylbenzene hydrogen atoms were not located in a difference map, and their orientation relative to the ring could not be inferred, so these atoms have not been included in the model. The hydrogen atoms of the other ligand were placed at calculated positions ($r_{\mathrm{C-H}}$ = 0.95 Å) for use in structure factor calculations. Hydrogen atom parameters were not refined, but were periodically recalculated. Anisotropic displacement factors were employed for full-occupancy non-hydrogen atoms and isotropic displacement factors for disordered atoms and hydrogen atoms. Refinement was continued until all shift-error ratios were <0.22. Maximum and minimum heights in a final difference map were 1.1 and −0.7 e Å^{-3}, respectively, the major features being within the disordered $\mathrm{PF_6^-}$ group.

For complex **3**, a difference electron density map suggested that one of the hydrogen atoms of each of five of the methyl groups was antiperiplanar to ruthenium; in contrast, at C(51) one hydrogen atom appeared to be periplanar. Coordinates for the methyl hydrogen atoms were calculated ($r_{\mathrm{C-H}}$ = 0.95 Å) on the basis of these assumptions. Hydrogen atoms were also generated on the other ligands. Hydrogen atom parameters were not refined, but were periodically recalculated. Anisotropic and isotropic displacement factors were employed for non-hydrogen and hydrogen atoms, respectively. Refinement was continued until all shift-error ratios were <0.04. Maximum and minimum heights in a final difference map were 1.9 and −0.8 e Å^{-3}, respectively, all major features being close to the ruthenium atom. Data reduction and refinement computations were performed as for **2**.

Non-hydrogen atoms in **4** were refined with anisotropic displacement factors. Hydrogen atoms were located in difference maps, and coordinates were refined; hydrogen atoms on methyl groups were adjusted to give idealized geometry and refined with Waser-type restraints.[27] In the final cycle the maximum shift-error ratio was 0.14. Maximum and minimum heights in a final difference map were 0.38 and −0.42 e Å^{-3}, respectively, the major features being near the ruthenium atom. Data reduction and refinement computations were

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(23) Churchill, M. R.; Kalra, K. L. *Inorg. Chem.* **1974**, *13*, 1427.

(24) de Meulenaer, J.; Tompa, H. *Acta Crystallogr.* **1965**, *19*, 1014.

(25) *XTAL 3.0 Reference Manual;* Hall, S. R., Stewart, J. M., Eds.; Universities of Western Australia and Maryland: Nedlands, Australia, and College Park, MD, 1990.

(26) *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99−101, 149−150; distributed by Kluwer Academic Publishers, Dordrecht, Holland.

(27) (a) Waser, J. *Acta Crystallogr.* **1963**, *16*, 1091. (b) Olthof-Hazekamp, R. "CRYSLQ" in ref 25.

Table 1. Crystal and Refinement Data for Compounds **2**−**4**

	2	**3**	**4**
(a) Crystal Data			
chemical formula	$C_{18}H_{29}F_6PRuS_3$	$C_{18}H_{28}RuS_3 \cdot 0.5CH_2Cl_2$	$C_{18}H_{28}RuS_3$
fw	587.64	484.14	441.67
cryst syst	orthorhombic	monoclinic	triclinic
space group	*Pbca*	*C2/c*	$P\bar{1}$
a, Å	12.910(1)	15.543(1)	8.017(1)
b, Å	14.611(1)	9.579(1)	9.028(1)
c, Å	25.056(1)	28.555(1)	14.349(1)
α, deg			100.87(1)
β, deg		93.48(1)	91.92(1)
γ, deg			113.62(1)
V, Å^3	4726.3	4243.9	927.6
Z	8	8	2
ρ_{calc}, g cm^{-3}	1.652	1.515	1.581
μ[Cu *K*α], cm^{-1}	90.8	100.1	100.5
T, K	293(1)	293(1)	298(1)
cryst dimens mm	0.30 × 0.12 × 0.18	0.27 × 0.36 × 0.15	0.19 × 0.08 × 0.11
F(000)	2384	1992	456
(b) Data Collection and Processing			
diffractometer	Philips PW1100/20	Philips PW1100/20	Philips PW1100/20
X-radiation	Cu*K*α	Cu*K*α	Cu*K*α
λ, Å	1.5418	1.5418	1.5418
scan mode	$\theta-2\theta$	$\theta-2\theta$	$\theta-2\theta$
ω-scan width	$1.1 + 0.142 \tan \theta$	$1.2 + 0.142 \tan \theta$	$1.2 + 0.142 \tan \theta$
scan rate, deg mm^{-1}	2	6	1.5
background counts (s)	8	3	12
$2\theta_{max}$ (deg)	128	128	128
min, max *h*, *k*, *l*	0, 15	−18,0	−9,0
	0, 17	0, 11	−9,10
	0, 29	−33, 32	−16, 16
no. of unique data	3919	3528	3092
no. of data refined	2975[$I > 3\sigma(I)$]	2997[$I > 3\sigma(I)$]	2898[$I > 3\sigma(I)$]
no. of variables	255	214	284
abs corr	analytical	analytical	analytical
min, max corr	0.227-0.426	0.085-0.352	0.287-0.518
g × 10^{-4} [a]	0.36(5)	0.45(6)	0.26(2)
(c) Structure Analysis and Refinement			
structure soln	direct methods (SHELXS-86) and diff Fourier techniques	direct methods (SHELXS-86) and diff Fourier techniques	Patterson and diff Fourier techniques
refinement	full-matrix least squares minimizing $\sum w(\lvert F_o \rvert - \lvert F_c \rvert)^2$	full-matrix least squares minimizing $\sum w(\lvert F_o \rvert - \lvert F_c \rvert)^2$	full-matrix least squares minimizing $\sum w(\lvert F_o \rvert - \lvert F_c \rvert)^2$
weighting scheme *w*	$[\sigma^2(F) + (0.0004)F^2]^{-1}$	$[\sigma^2(F) + (0.0009)F^2]^{-1}$	$[\sigma^2(F) + (0.0004)F^2]^{-1}$
R[b]	0.051	0.059	0.020
R_w[c]	0.070	0.080	0.033
GOF[d]	2.31	2.09	1.38

[a] g is final value of Zachariasen extinction parameter. [b] $R = \sum \lvert\lvert F_o \rvert - \lvert F_c \rvert\rvert / \sum \lvert F_o \rvert$. [c] $R_w = [\sum w(\lvert F_o \rvert - \lvert F_c \rvert)^2 / \sum (w F_o^2)]^{1/2}$. [d] GOF $= [\sum w(\lvert F_o \rvert - \lvert F_c \rvert)^2/(m - n)]^{1/2}$, where m = number of unique reflections and n = number of variables.

performed as for **2** and **3**. Final parameters for the non-hydrogen atoms in complexes **2**−**4** are available in the supporting information.

Results

Deprotonation of Coordinated 9S3. The precursor [Ru(η^6-C_6Me_6)(9S3)]$^{2+}$ (**1**) was obtained in high yield as its yellow PF_6 salt by displacement of the labile acetone molecules in [Ru(η^6-C_6Me_6)($OCMe_2$)$_3$]$^{2+}$ by 9S3 (eq 4); the tris(acetone) complex was generated in situ by treatment of [$RuCl_2$(η^6-C_6Me_6)]$_2$ with $AgPF_6$ in acetone.[28] The symmetrical half-sandwich structure of **1** is confirmed by the ^{1}H NMR spectrum, which shows a symmetrical multiplet at δ 2.78 due to the methylene protons of 9S3, and by the ^{13}C NMR spectrum, which shows a singlet at δ 36.48 due to equivalent methylene carbon atoms; typical C_6Me_6 resonances are also present in both spectra.

A suspension of **1** and 3 molar equiv of KOH in THF reacted at ambient temperature over a period of 1.5 h to give a deep red solution, from which was isolated the tridentate bis(thioether) thiolate complex [(η^6-C_6Me_6)Ru(S(CH═CH_2)(CH_2)$_2$S(CH_2)$_2$S)]PF_6 (**2**) as air-stable, dark red crystals in 48% yield (Scheme 1); the yield can be improved to 62% by use of 1−1.5 molar equiv of KOH for a longer reaction time (24 h). The mother liquor contained a mixture of the starting material (**1**) and a mixture of species of which the neutral compound (η^6-C_6Me_6)Ru(S(CH═CH_2)(CH_2)$_2$S)(SCH═CH_2) (**3**), containing η^1-ethenethiolate (vinyl mercaptide) and a bidentate thioether−thiolate ligand, was the main component. A longer reaction time (2.5 h) gave **3** as the principal product together with **2** and another unidentified vinyl thioether complex having a C_6Me_6 singlet at δ (CH_3) 2.19 in the ^{1}H NMR spectrum. It was not possible to separate **3** from this latter complex. Pure **3** in solution was best obtained from the reaction of **2** with 2−3 molar equiv of KOH in CH_2Cl_2 for *ca.* 4 h (Scheme 1).

Concentration of solutions of **3** in dichloromethane, toluene, or ether tends to precipitate a film on the vessel walls and finally an oil, insoluble in ether or toluene. The dark red crystals of **3** obtained in low yield from the addition of hexane to the

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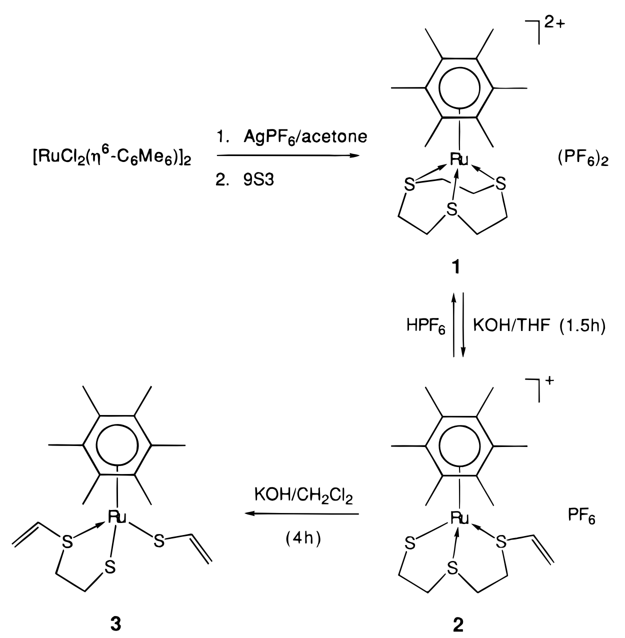
[28] Bennett, M. A.; Matheson, T. W.; Robertson, G. B.; Steffen, W. L.; Turney, T. W. *J. Chem. Soc., Chem. Commun.* **1979**, 32.

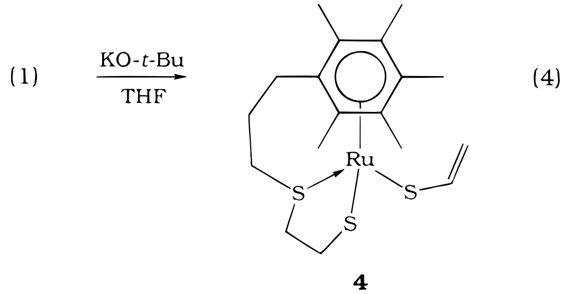
Scheme 1



concentrated solution were always contaminated by this oil, which may be a polymeric decomposition product.

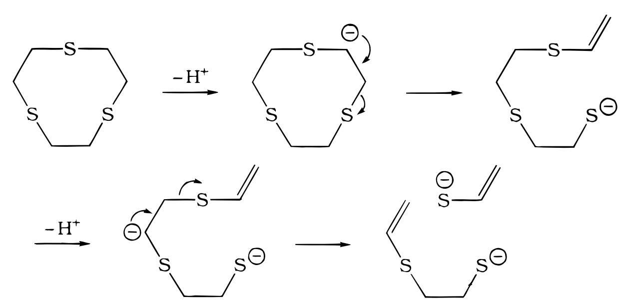
The structures of **2** and **3** have been established by X-ray crystallography (see below), although spectroscopic data already provided a preliminary indication. Both complexes contain parent ion peaks in their FAB mass spectra. The presence of a vinyl group in **2** is evident from a pair of proton multiplets in a 1:2 ratio at δ 6.56 and δ 5.93−5.84 due to the α- and β-protons, respectively, and a pair of resonances in the ^{13}C NMR spectrum at δ 126.7 (d, $J = 183$ Hz) and δ 126.5 (t, $J = 163$ Hz) due to the α- and β-vinyl carbon atoms. The ^{13}C NMR spectrum of **3** contains two pairs of vinyl resonances, at δ 129.4 (d, $J = 184$ Hz, C_α) and δ 120.8 (t, $J = 161$ Hz, C_β), and δ 145.6 (d, $J = 165$ Hz, C_α) and δ 107.7 (t, $J = 157$ Hz, C_β). The resemblance of the chemical shifts and coupling constants of the first pair to the corresponding parameters in **2** suggests that these resonances belong to the vinyl thioether group; hence the second pair is assigned to ethenethiolate. Correspondingly, there are two sets of AMX vinyl resonances in the ^{1}H NMR spectrum of **3**. The IR spectrum of **2** exhibits a band of medium intensity at 1599 cm^{-1} assignable to ν(C=C) of the vinyl thioether, whereas the spectrum of **3** contains two strong bands, at 1590 and 1555 cm^{-1}, assigned to the vinyl thioether and to ethenethiolate, respectively, *cf.* 1580 cm^{-1} in free ethenethiol.[29]

Deprotonation of **1** with 3−4 molar equiv of KO-*t*-Bu in THF at room temperature immediately gave an orange solution, from which the complex $Ru(SCH{=}CH_2)(S(CH_2CH_2CH_2\text{-}(\eta^6\text{-}C_6Me_5)\text{-}CH_2CH_2S)$ (**4**) was isolated in *ca.* 50% yield as dark red, air-stable crystals that are sparingly soluble in toluene and ether, but readily soluble in THF and CH_2Cl_2. **4** contains an unusual η^6-arene−thioether−thiolate strapping ligand derived by addition of monodeprotonated C_6Me_6 to the vinyl thioether group of **3**. It is the main product of reaction of **2** with an excess of KO-*t*-Bu in THF; small amounts of byproducts having $C_6\mathit{Me}_6$ resonances at δ 1.82, 1.91, and 2.20 are also present. A similar reaction in CD_2Cl_2 gave **3** after 20 min and a 1:1 mixture of **3** and **4** after 1.5 h, as shown by ^{1}H NMR spectroscopy. **4** is not formed if **1** is treated with less than 2 equiv of KO-*t*-Bu; use of 1 equiv of KO-*t*-Bu gave a 50% conversion into a 1:1 mixture of **2** and **3**, together with other unidentified materials, and treatment with 2.5 equiv of KO-*t*-Bu gave an inseparable mixture of complexes. **4** is unaffected by a large excess of KO-*t*-Bu.



4

Scheme 2[a]



[a] Run(η^6-C$_6$Me$_6$) omitted for clarity.

The X-ray structure of **4** has been described in our preliminary communication.[20] Consistent with the structure, the ^{1}H NMR spectrum shows five singlets between δ 1.93 and 2.10 due to the inequivalent methyl groups of the η^6-arene ring, an AMX pattern between δ 4.5 and 6.5 arising from the vinyl protons of the ethenethiolate group, and a series of multiplets between δ 1.55 and 3.23 due to the methylene groups. Corresponding resonances are observed in the ^{13}C NMR spectrum; the chemical shifts and coupling constants of the vinyl carbon atoms [δ 109.0, $J_{CH} = 157$ Hz, C_α and δ 144.4, $J_{CH} = 163$ Hz, Cβ] are similar to those assigned to the ethenethiolate group in **3**. There is a strong band at 1556 cm^{-1} in the IR spectrum of **4** due to ν(C=C) of the ethenethiolate group.

Complexes **2** and **3** are probably formed by successive C−S bond cleavages resulting from base-induced deprotonations of the acidic C−H bonds adjacent to the coordinated thioether group (Scheme 2). The cleavages may occur in undetected intermediates containing Ru−C σ-bonds or Ru−(η^2-CH=S) bonds; *cf.* the formation of a Co−C σ-bonded complex by deprotonation of $[Co(NH_2CH_2CH_2CH_2SCH_2CH_2NH_2)_2]Cl$[30] and the formation of the cyclometalated complex $[(\eta^6\text{-}C_6H_6)Ru(o\text{-}C_6H_4CH{=}SCH_2\text{-}o\text{-}C_6H_4CH_2SCH_2)]BF_4$ from 2,11-dithia[3.3]-orthocyclophane.[31] The first deprotonation/cleavage sequence opens the 9S3 ring, generating the 3,6-dithia-1-octenethiolate ligand in **2**, and the second breaks this into the ethenethiolate and 3-thia-1-pentenethiolate in **3**. The first sequence is analogous to the deprotonation of $[M(9S3)_2]^{3+}$ (M = Co, Rh, Ir), which is induced by weak bases such as Et_3N or water at pH > 4 and is reversed by acid (eq 5).[32] A similar process occurs on

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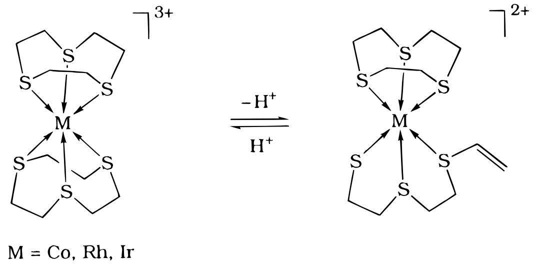
(29) Strausz, O. P.; Hikida, T.; Gunning, H. E. *Can. J. Chem.* **1965**, *43*, 717.

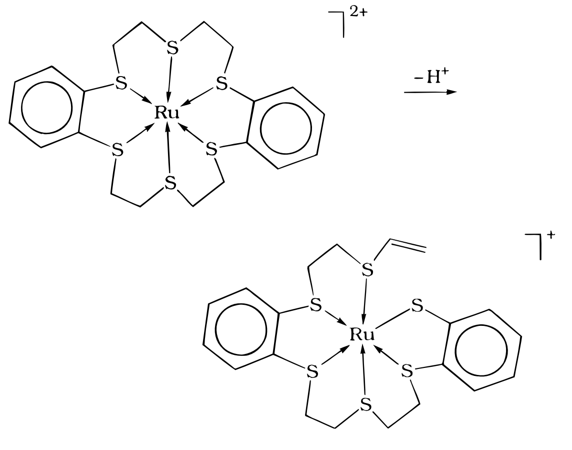
(30) Bjerrum, M. J.; Gajhede, M.; Larsen, E.; Springborg, J. *Inorg. Chem.* **1988**, *27*, 3960.

(31) Hanton, L. R.; Kemmitt, T. *J. Chem. Soc., Chem. Commun.* **1991**, 700.

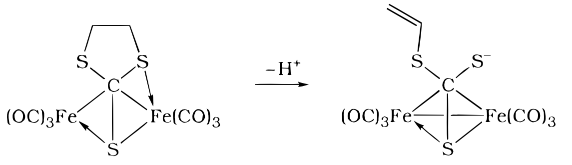
treatment of the six-coordinate ruthenium(II) dication of dibenzo-18S6 (eq 6) with NaOMe, although this process is irreversible.[33] Also, coordinated ethylenetrithiocarbonate in (μ-η^2-SCS(CH$_2$)$_2$S)-Fe$_2$(CO)$_6$ is deprotonated by LiN-*i*-Pr$_2$ to generate a *S*-vinyl group at the trithiocarbonate carbon atom (eq 7).[34]



(5)



(6)



(7)

We assume that KO-*t*-Bu causes deprotonation of one of the methyl protons of coordinated C$_6$Me$_6$ forming the carbanion **5** (Scheme 3), a process which is known to occur readily for cationic methyl-substituted arene complexes of iron,[35] ruthenium,[17−19] and manganese.[36] The exocyclic methylene groups so formed are powerful nucleophiles, and carbanion **5** is well placed to undergo an intramolecular Michael addition to the thioether vinyl group of coordinated CH$_2$=CHSCH$_2$CH$_2$S$^-$. This process generates carbanion **6**, which acquires a proton on workup to give the observed product **4**. The use of an excess of KO-*t*-Bu thus allows all the steps of Schemes 2 and 3 to proceed in one pot without isolation of the intermediates.

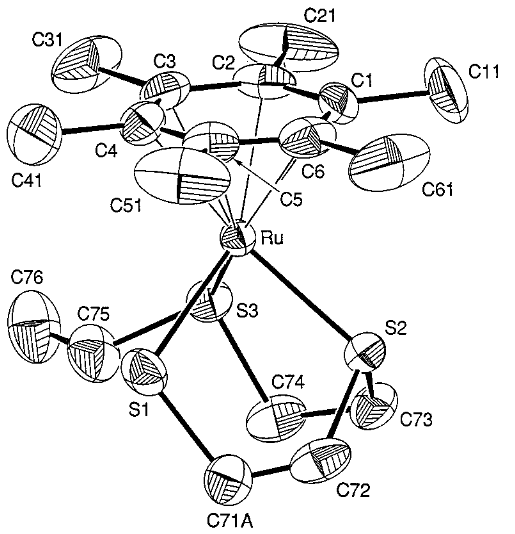
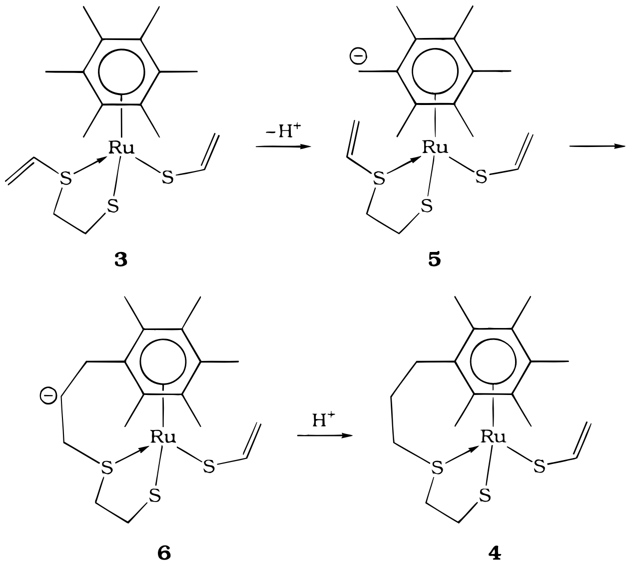


Figure 1. Thermal ellipsoid diagram of [(η^6-C$_6$Me$_6$)Ru(S(CH=CH$_2$)CH$_2$CH$_2$SCH$_2$CH$_2$S)]$^+$ (**2**) with atom labeling. Only one location is shown for disordered C(71). Ellipsoids show 30% probability levels; hydrogen atoms are omitted for clarity.

Scheme 3



Crystal Structures of 2−4. The molecular structures are shown in Figures 1−3, and important bond lengths and angles are listed in Tables 2−4, respectively. All three complexes possess the half-sandwich arrangement typical of (arene)-ruthenium(II) complexes. In **2** and **3**, the C$_6$Me$_6$ rings are essentially planar, whereas in **4** carbon atom C(6) is displaced *ca.* 3° out of the plane formed by the remaining arene carbon atoms toward ruthenium, presumably as a consequence of the presence of the trimethylene chain linking the arene ring and one sulfur atom. The coordinated vinyl thioether groups in **2** and **3** are characterized by C=C distances of 1.25(1) Å (**2**) and 1.23(1) Å (**3**) and C−S distances of 1.77(1) Å (**2**) and 1.789(9) Å (**3**); *cf.* the C=C bond length of 1.289(21) Å in [Rh-(S(CH=CH$_2$)CH$_2$CH$_2$SCH$_2$CH$_2$S)(9S3)](PF$_6$)$_2$ (eq 5).[32] In the ethenethiolate ligand, the C=C distances [1.32(1) Å (**3**), 1.298-(7) Å (**4**)] are significantly longer, and the C−S distances [1.737(8) Å (**3**), 1.745(5) Å (**4**)] are significantly shorter, than the corresponding separations in the vinyl thioether groups, consistent with delocalization of negative charge from sulfur to the C=C bond in ethenethiolate. The Ru−S (aliphatic thioether) distances [2.320(2) Å (**2**), 2.3549(6) Å (**4**)] are close to the range 2.33−2.35 Å found in the bis(macrocyclic thioether) complexes of ruthenium(II) [Ru(9S3)$_2$]Y$_2$ (Y = BPh$_4$,[37] OTf[38])

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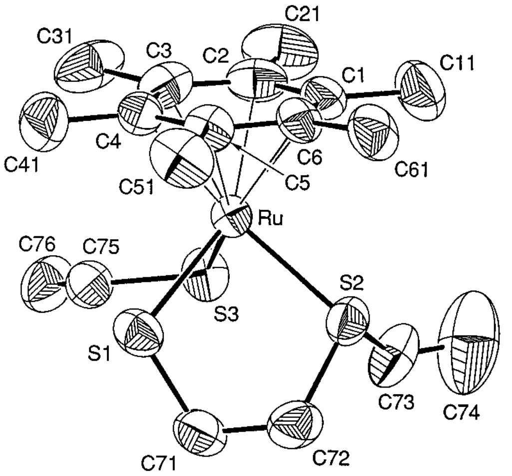

Figure 2. Thermal ellipsoid diagram of (η^6-C_6Me_6)Ru(S(CH=CH_2-CH_2CH_2S)(SCH=CH_2) (**3**) with atom labeling. Ellipsoids show 50% probability levels; hydrogen atoms are omitted for clarity.

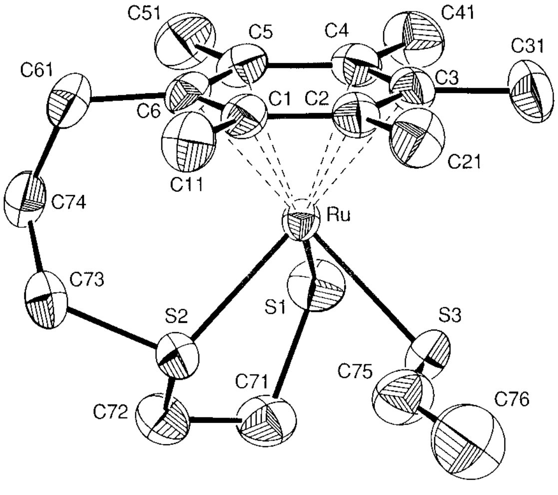

Figure 3. Thermal ellipsoid diagram of Ru(SCH=CH_2)(S(CH_2CH_2-CH_2-η^6-C_6Me_5)CH_2CH_2S) (**4**) showing labeling of selected atoms. Ellipsoids show 50% probability levels; hydrogen atoms are omitted for clarity.

and [Ru(dibenzo-18S6)]$(PF_6)_2$[39] and also agree well with the Ru−S (thioether) separation of 2.331(2) Å observed in [(η^6-C_6H_6)Ru(*o*-C_6H_4CH=SCH$_2$-*o*-$C_6H_4CH_2SCH_2$)]BF_4.[31]

Protonation Studies. Only the first deprotonation of coordinated 9S3 (Schemes 1 and 2) is reversible; treatment of **2** with HPF_6 regenerates **1**. Treatment of complex **4** in CD_2Cl_2 with CF_3CO_2H or HPF_6 at −40 °C causes the vinyl resonances in the ^1H and ^{13}C NMR spectra to disappear. They are replaced by a 3H doublet at δ 1.29 and a 1H quartet at δ 5.41 (J = 7 Hz) characteristic of a CH_3CH group; the corresponding resonances in the ^{13}C NMR spectrum appear at δ 23.74 and 66.20, respectively. The other features of the NMR spectrum of **4** show only small changes of chemical shift. When the solution is allowed to warm to 21 °C, a second CH_3CH resonance pattern appears at δ 1.62 (d, 3H) and 4.93 (q, 1H, J = 7 Hz) in the ^1H NMR spectrum and at δ 24.15 and 70.97 in the ^{13}C NMR spectrum. At equilibrium, the final ratio of the two species is 1:4; this does not change when the solution is cooled again to −40 °C. Treatment of the solution with KO-

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for Non-Hydrogen Atoms in [(η^6-C_6Me_6)Ru(S(CH=$CH_2CH_2CH_2SCH_2CH_2$S)]PF_6 (**2**)[a]

Ru−S(1)	2.374(2)	Ru−S(2)	2.320(2)
Ru−S(3)	2.346(2)	Ru−C(1)	2.246(9)
Ru−C(2)	2.231(8)	Ru−C(3)	2.228(9)
Ru−C(4)	2.215(8)	Ru−C(5)	2.232(10)
Ru−C(6)	2.216(9)	S(1)−C(71A)	1.86(2)
S(1)−C(71B)	1.75(2)	S(2)−C(72)	1.83(1)
S(2)−C(73)	1.789(9)	S(3)−C(74)	1.82(1)
S(3)−C(75)	1.77(1)	C(1)−C(2)	1.41(2)
C(1)−C(6)	1.47(1)	C(1)−C(11)	1.50(2)
C(2)−C(3)	1.45(1)	C(2)−C(21)	1.55(2)
C(3)−C(4)	1.38(1)	C(3)−C(31)	1.56(1)
C(4)−C(5)	1.37(1)	C(4)−C(41)	1.55(2)
C(5)−C(6)	1.37(2)	C(5)−C(51)	1.53(2)
C(6)−C(61)	1.54(1)	C(71A)−C(72)	1.30(2)
C(71B)−C(72)	1.50(2)	C(73)−C(74)	1.49(1)
C(75)−C(76)	1.25(1)	Ru−cen	1.727
S(1)−Ru−S(2)	85.17(7)	S(1)−Ru−S(3)	90.04(7)
S(2)−Ru−S(3)	85.93(7)	S(1)−Ru−cen	125.6
S(2)−Ru−cen	128.1	S(3)−Ru−cen	128.2
Ru−S(1)−C(71A)	103.2(6)	Ru−S(1)−C(71B)	103.2(6)
Ru−S(2)−C(72)	106.1(3)	Ru−S(2)−C(73)	106.0(3)
C(72)−S(2)−C(73)	102.6(4)	Ru−S(3)−C(74)	104.3(3)
Ru−S(3)−C(75)	112.3(4)	C(74)−S(3)−C(75)	98.0(5)
S(1)−C(71A)−C(72)	119(1)	S(1)−C(71B)−C(72)	114(1)
S(2)−C(72)−C(71A)	115(1)	S(2)−C(72)−C(71B)	115.1(9)
S(2)−C(73)−C(74)	113.0(6)	S(3)−C(74)−C(73)	110.8(7)
S(3)−C(75)−C(76)	124(1)		

[a] Cen is the centroid of C(1)−C(6): (0.2760, 0.6399, 0.6186).

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for Non-Hydrogen Atoms in [(η^6-C_6Me_6)Ru(S(CH=$CH_2CH_2CH_2$S)(SCH=CH_2)·0.5CH_2Cl_2 (**3**)[a]

Ru−S(1)	2.380(2)	Ru−S(2)	2.367(2)
Ru−S(3)	2.401(2)	Ru−C(1)	2.233(8)
Ru−C(2)	2.230(8)	Ru−C(3)	2.240(9)
Ru−C(4)	2.204(7)	Ru−C(5)	2.241(7)
Ru−C(6)	2.259(7)	S(1)−C(71)	1.820(9)
S(2)−C(72)	1.817(9)	S(2)−C(73)	1.777(9)
S(3)−C(75)	1.737(8)	C(1)−C(2)	1.41(1)
C(1)−C(6)	1.43(1)	C(1)−C(11)	1.54(1)
C(2)−C(3)	1.41(1)	C(2)−C(21)	1.50(1)
C(3)−C(4)	1.43(1)	C(3)−C(31)	1.52(1)
C(4)−C(5)	1.43(1)	C(4)−C(41)	1.51(1)
C(5)−C(6)	1.40(1)	C(5)−C(51)	1.54(1)
C(6)−C(61)	1.52(1)	C(71)−C(72)	1.50(1)
C(73)−C(74)	1.23(2)	C(75)−C(76)	1.32(1)
C(8)−Cl	1.71(1)	Ru−cen	1.727
S(1)−Ru−S(2)	84.21(7)	S(1)−Ru−S(3)	88.67(7)
S(1)−Ru−cen	127.5	S(2)−Ru−S(3)	89.46(6)
S(2)−Ru−cen	127.1	S(3)−Ru−cen	126.5
Ru−S(1)−C(71)	101.8(3)	Ru−S(2)−C(72)	106.0(3)
Ru−S(2)−C(73)	112.3(4)	C(72)−S(2)−C(73)	101.0(5)
Ru−S(3)−C(75)	107.4(3)	C(2)−C(1)−C(6)	119.9(7)
C(2)−C(1)−C(11)	120.5(7)	C(6)−C(1)−C(11)	119.6(7)
C(1)−C(2)−C(3)	120.1(7)	C(1)−C(2)−C(21)	121.2(8)
C(3)−C(2)−C(21)	118.6(8)	C(2)−C(3)−C(4)	120.0(7)
C(2)−C(3)−C(31)	122.6(8)	C(4)−C(3)−C(31)	117.4(8)
C(3)−C(4)−C(5)	119.6(7)	C(3)−C(4)−C(41)	122.4(7)
C(5)−C(4)−C(41)	117.9(8)	C(4)−C(5)−C(6)	119.8(7)
C(4)−C(5)−C(51)	119.4(7)	C(6)−C(5)−C(51)	120.7(7)
C(1)−C(6)−C(5)	120.5(7)	C(1)−C(6)−C(61)	117.4(7)
C(5)−C(6)−C(61)	122.2(7)	S(1)−C(71)−C(72)	109.0(6)
S(2)−C(72)−C(71)	112.7(6)	S(2)−C(73)−C(74)	127(1)
S(3)−C(75)−C(76)	125.1(7)		

[a] Cen is the centroid of C(1)−C(6): (0.2914, 0.6921, 0.5697).

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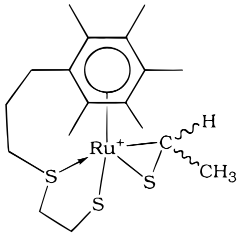
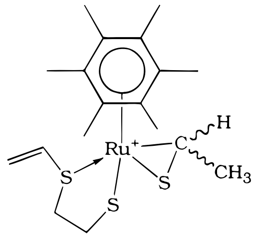
t-Bu regenerates **4**, together with unidentified byproducts. These observations are consistent with protonation of the ethenethiolate group in **4** to form the cationic complex **7** containing η^2-thioacetaldehyde. Such a compound can clearly exist as a pair of diastereomers.



7



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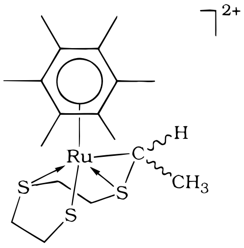

9

One of the vinyl groups of **3** is also protonated immediately by CF3CO$_2$H at −78 °C. The presence of an isopropyl group and of the remaining vinyl group is evident from the ^{1}H and ^{13}C NMR spectra (see Experimental Section), and the IR spectrum shows a ν(C=C) band at 1605 cm^{-1}, which is close to the value of 1599 cm^{-1} found for complex **2**. These observations indicate that protonation occurs at the ethenethiolate group of **3** to give a cationic thioacetaldehyde complex **8**, in which the vinyl thioether group remains intact. As in the case of **7**, this can exist as a pair of diastereomers. The second isomer is formed when the solution is brought to room temperature and predominates at equilibrium (1:3 ratio). As expected, the second species also shows characteristic CH$_3$CH and vinyl group resonances in its ^{1}H NMR spectrum. Unfortunately, all attempts to isolate **7** and **8** in solid form with noncoordinating anions gave red, oily intractable materials.

When the solution of **8** in CF$_3$CO$_2$H is allowed to stand, a second, much slower reaction takes place to give an approximately 1:10 ratio of isomers, each containing a single isopropyl group. The complete absence of vinyl resonances suggests that the vinyl thioether group of **8** has been protonated and that the resulting electrophile, SCH$_2$C$^+$H$_2$, attacks the nucleophilic sulfur atom of coordinated ethenethiolate to give the dicationic complex **9**. This process is analogous to the reformation of **1** from **2** in the presence of HPF$_6$.

Discussion

Removal of one proton from a coordinated chelating thioether and subsequent C−S bond cleavage is well established[30−33] and may be favored in the case of 9S3 and other cyclic thioethers by relief of ring strain. The successive ocurrence of two such processes in 9S3 coordinated to [Ru(η^6-C$_6$Me$_6$)]$^{2+}$ is remarkable in view of the electron-donating ability of the arene ligand and presumably is a reflection of the affinity of the ruthenium(II) center for thiolate ligands. Clearly, the C−S bond cleavages reported here differ mechanistically from those observed in early transition metal thiolate complexes. For example, the conversion of the ethane-1,2-dithiolato complex [Nb(SCH$_2$CH$_2$S)$_3$]$^-$ into [NbS(SCH$_2$CH$_2$S)(SCH$_2$CH$_2$SCH$_2$CH$_2$S)]$^-$ is believed to proceed by initial attack of H$^+$ or ROH on a dithiolate sulfur atom,[40] and a molybdenum arenethiolate bond can be cleaved by an adjacent Mo−H bond.[41]

Table 4. Selected Interatomic Distances (Å) and Angles (deg) for Non-Hydrogen Atoms in $\overline{\text{Ru(SCH=CH}_2\text{(S(CH}_2\text{CH}_2\text{CH}_2\text{-(}\eta^6\text{-C}_6\text{Me}_5\text{)CH}_2\text{CH}_2\text{S}}$) (**4**)[a]

Ru−S(1)	2.3664(10)	Ru−S(2)	2.3549(6)
Ru−S(3)	2.4155(8)	Ru−C(1)	2.242(3)
Ru−C(2)	2.234(3)	Ru−C(3)	2.224(2)
Ru−C(4)	2.214(3)	Ru−C(5)	2.224(3)
Ru−C(6)	2.204(3)	S(1)−C(71)	1.821(3)
S(2)−C(72)	1.832(4)	S(2)−C(73)	1.828(3)
S(3)−C(75)	1.745(5)	C(1)−C(2)	1.423(4)
C(1)−C(6)	1.449(4)	C(1)−C(11)	1.506(5)
C(2)−C(3)	1.441(5)	C(2)−C(21)	1.509(4)
C(3)−C(4)	1.408(4)	C(3)−C(31)	1.509(4)
C(4)−C(5)	1.453(4)	C(4)−C(41)	1.518(6)
C(5)−C(6)	1.410(5)	C(5)−C(51)	1.518(5)
C(6)−C(61)	1.523(4)	C(61)−C(74)	1.526(4)
C(71)−C(72)	1.502(6)	C(73)−C(74)	1.514(5)
C(75)−C(76)	1.298(7)	Ru−cen	1.702
S(1)−Ru−S(2)	85.54(3)	S(1)−Ru−S(3)	84.87(3)
S(1)−Ru−cen	126.1	S(2)−Ru−S(3)	84.04(3)
S(2)−Ru−cen	131.5	S(3)−Ru−cen	128.9
Ru−S(1)−C(71)	102.6(1)	Ru−S(2)−C(72)	105.3(1)
Ru−S(2)−C(73)	110.3(1)	C(72)−S(2)−C(73)	99.3(2)
Ru−S(3)−C(75)	107.9(2)	Ru−C(1)−C(2)	71.2(2)
Ru−C(1)−C(6)	69.6(2)	Ru−C(1)−C(11)	131.3(2)
C(2)−C(1)−C(6)	119.1(3)	C(2)−C(1)−C(11)	118.8(3)
C(6)−C(1)−C(11)	122.1(2)	Ru−C(2)−C(1)	71.8(2)
Ru−C(2)−C(3)	70.7(2)	Ru−C(2)−C(21)	131.5(2)
C(1)−C(2)−C(3)	120.5(2)	C(1)−C(2)−C(21)	120.3(3)
C(3)−C(2)−C(21)	119.2(3)	Ru−C(3)−C(2)	71.5(1)
Ru−C(3)−C(4)	71.1(1)	Ru−C(3)−C(31)	128.9(2)
C(2)−C(3)−C(4)	119.9(3)	C(2)−C(3)−C(31)	119.2(3)
C(4)−C(3)−C(31)	120.9(3)	Ru−C(4)−C(3)	71.9(1)
Ru−C(4)−C(5)	71.3(1)	Ru−C(4)−C(41)	128.7(2)
C(3)−C(4)−C(5)	120.3(3)	C(3)−C(4)−C(41)	120.7(3)
C(5)−C(4)−C(41)	119.0(3)	Ru−C(5)−C(4)	70.5(2)
Ru−C(5)−C(6)	70.7(2)	Ru−C(5)−C(51)	128.5(2)
C(4)−C(5)−C(6)	119.5(3)	C(4)−C(5)−C(51)	118.6(3)
C(6)−C(5)−C(51)	121.7(3)	Ru−C(6)−C(1)	72.4(2)
Ru−C(6)−C(5)	72.2(2)	Ru−C(6)−C(61)	127.4(2)
C(1)−C(6)−C(5)	120.6(2)	C(1)−C(6)−C(61)	120.1(3)
C(5)−C(6)−C(61)	119.3(3)	C(6)−C(61)−C(74)	115.1(3)
S(1)−C(71)−C(72)	109.8(3)	S(2)−C(72)−C(71)	110.2(2)
S(2)−C(73)−C(74)	116.2(3)	C(61)−C(74)−C(73)	114.5(3)
S(3)−C(75)−C(76)	127.7(5)		

[a] Cen is the centroid of C(1)−C(6): (0.5657, 0.1288, 0.6380).

The base-induced fragmentation of [Ru(η^6-C$_6$Me$_6$)(9S3)]$^{2+}$ forms coordinated ethenethiolate (vinyl mercaptide), a hitherto missing member of the family of alkane- and arenethiolate ligands,[42] and represents a kind of reversal of the construction of coordinated 9S3, in the form of Mo(CO)$_3$(9S3), from the thioether dithiolate anion [Mo(CO)$_3$(SCH$_2$CH$_2$SCH$_2$CH$_2$S)]$^{2-}$ and 1,2-dibromoethane.[43]

Protonation of η^1-ethenethiolate generates η^2-thioacetaldehyde, a ligand that is unstable in the free state.[44] Thioaldehydes can be stabilized by coordination to a transition metal center; in most cases, e.g., W(CO)(η^2-S$_2$CNEt$_2$)(η^2-SCNEt$_2$)(η^2-SCHR)

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(R = Ph, Me),[45] Rh(η^5-C_5H_5) (η^2-CHSMe)(P-*i*-Pr_3),[46] Zr(η^5-C_5H_5)$_2$(η^2-SCHR) (R = Me, various aryl groups),[47] and [Re(η^5-C_5H_5)(NO)(PPh_3)(η^2-SCHR)]$^+$ (R = H, Me, various aryl groups),[48,49] the ligand is *dihapto*. However, in the aromatic thioaldehyde complexes $W(CO)_5$(SCHAr)[50] and [Ru(η^5-C_5H_5)-L_2(SCHAr)]$^+$ [51] (L_2 = various monodentate and bidentate P donors), the ligand is predominantly S-bound, although there is spectroscopic evidence for a dynamic equilibrium between η^1-S and η^2-C,S forms for Ar = Ph, *p*-$C_6H_4CF_3$, and *p*-C_6H_4-Me in the $W(CO)_5$ series and for L_2 = 2PMe_3, $Me_2PCH_2CH_2$-PMe_2 and Ar = Ph, *p*-C_6H_4Cl in the [Ru(η^5-C_5H_5)L_2]$^+$ series. The S-bonded form shows a characteristically deshielded C*H*S resonance in the region δ 8.5−12, whereas in the η^2-C,S complexes this resonance occurs in the range δ 3−5. This evidence supports our *dihapto* formulation for **7** and **8**. The slow conversion of **8** into **9** in CF_3CO_2H indicates that the sulfur atom of η^2-$SCCHCH_3$ can still behave as a nucleophile; precedent for this type of reaction is provided by the methyl triflate induced methylation at sulfur in the η^2-thioformaldehyde complexes Os(η^2-CH_2S)$(CO)_2(PPh_3)_2$[52] and Rh(η^5-C_5H_5)(η^2-CH_2S)(PMe_3)[46] to give cationic complexes containing η^2-CH_2-SMe.

Conclusions

(1) In the presence of base, 1,4,7-trithiacyclononane (9S3) coordinated to the electrophilic fragment [Ru(η^6-C_6Me_6)]$^{2+}$ undergoes stepwise fragmentation as a result of C−S bond cleavage, leading to species containing coordinated vinyl thioethers and η^1(*S*)-ethenethiolate. The likelihood of fragmentation of coordinated crown thioethers under basic conditions should be kept in mind in view of the widespread use of these ligands in coordination chemistry.

(2) The vinyl thioether ligand undergoes an intramolecular Michael addition with the carbanion $C_6Me_5CH_2^-$ derived from coordinated C_6Me_6, and η^1(*S*)-ethenethiolate is protonated to form η^2-thioacetaldehyde. These properties indicate that vinylsulfur ligands could prove to be versatile building blocks in coordination chemistry.

Supporting Information Available: Coordinates for non-hydrogen and hydrogen atoms, isotropic displacement factors, displacement factors for non-hydrogen atoms, complete listing of bond distances, bond angles, and torsion angles, and selected least-squares planes for **2**−**4** (40 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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