2 were different anomeric mixtures, they were hydrolyzed into their corresponding C_3 monoacetates.[14] Both synthetic and naturally derived substances proved to be the same 3.7:1 anomeric mixture and, finally, exhibited the same properties: $[\alpha]_D$ -9.8° (*c* 1.43, CH_2Cl_2) natural series, $[\alpha]_D$ -9.7° (*c* 0.51, CH_2Cl_2) synthetic series.

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Supplementary Material Available: Experimental procedures including NMR, IR, and mass spectral data (71 pages). Ordering information is given on any current masthead page.

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(15) Both synthetic and naturally derived **2** were crystallized from ethyl acetate/hexane. A mixed melting point of these materials was undepressed.

Synthesis of a New Type of Metal Dithiolene Complex via an Induced Reaction of Acetylenes with a Ruthenium Sulfide

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The reactions of unsaturated organic compounds with naked main-group ligands is an active area of coordination chemistry.[1] The present contribution to this field involves the chemically induced reaction of a soluble ruthenium sulfide with acetylenes. This project has resulted in the characterization of the simplest ruthenium sulfido complex and a unique bonding mode for a 1,2-alkene disulfide (dithiolene) ligand.

Our starting material was $Cp^*_2Ru_2S_4$ (**1**, $Cp^* = \eta^5\text{-}C_5Me_4Et$), a highly soluble, air-stable, intensely blue compound.[2] Compound **1** was prepared in ca. 15% yield from the reaction of 3.02 g of $Cp^*_2Ru_2(CO)_4$[3] and 0.62 g of S_8 in 125 mL of boiling toluene for 18 h. The crude product was flash chromatographed on silica gel (CH_2Cl_2) and crystallized from cold hexane. An X-ray diffraction study showed that **1** is properly formulated as $Cp^*_2Ru_2(\mu,\eta^2\text{-}S_2)(\mu,\eta^1\text{-}S_2)$ comparable to the recently reported iron analogues.[4] Whereas the Ru–S distances are normal for the $\mu,\eta^2\text{-}S_2$, the Ru-S distances for the parallel (μ,η^1) S_2 are quite short at 2.20 Å and indicate multiple bonding[5] between the ruthenium centers and this disulfur ligand.

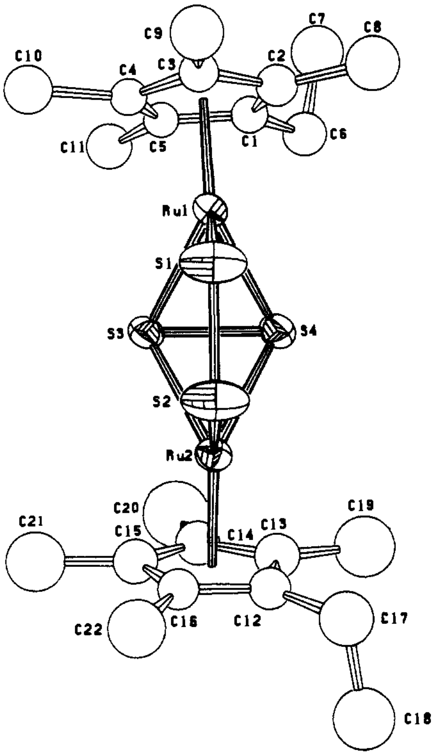

Figure 1. ORTEP of the $(C_5Me_4Et)_2Ru_2S_4$ molecule (**1**). Representative distances (Å) and angles (deg): Ru(1)–S(1), 2.195 (4); Ru(1)–S(3), 2.382 (4); S(1)–S(2), 2.020 (5); S(3)–S(4), 2.050 (4); Ru(1)–S(1)–S(2), 112.9 (2); Ru(1)–S(3)–Ru(2); 104.1 (1); Ru(1)–S(3)–S(4), 64.9 (1). The S···S distances between the two S_2 subunits are 3.39–3.42 Å.

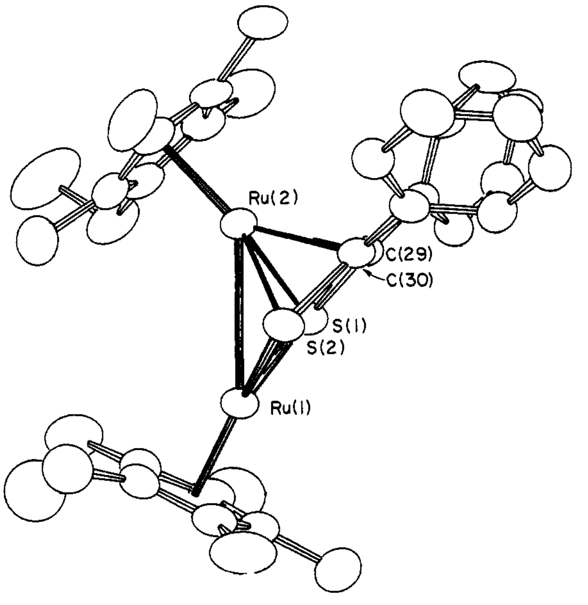

Figure 2. ORTEP of the $(C_5Me_4Et)_2Ru_2S_2C_2Ph_2$ molecule (**3**). Representative distances (Å) and angles (deg): Ru–Ru, 2.980 (1); Ru(1)–S(1), 2.253 (3); Ru(2)–S(1), 2.428 (3); Ru–Si(1)–Ru, 79.00 (8); Ru(1)–S(1)–C(29), 109.5 (3); Ru(2)–S(1)–C(29), 60.7 (3).

A compound tentatively identified as $Cp^*_4Ru_4S_6$ (**2**) was also isolated in ca. 20% yield in the synthesis of **1**.[6] Compound **2** is

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(1) (a) Oxide reactions: Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1986**, *108*, 507. Collman, J. P.; Kodadek, T.; Raybuck, S. A., Brauman, J. T.; Papazian, L. M. *J. Am. Chem. Soc.* **1985**, *108*, 507. Herrmann, W. A.; Serrano, R.; Küsthardt, U.; Ziegler, M. L.; Guggolz, E., Zahn, T. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 515. (b) Sulfide reactions: Adams, R. D.; Wang, S. *Organometallics* **1985**, *4*, 1902. Rajan, O. A.; McKenna, M.; Noordik, J.; Haltiwanger, R. C., Rakowski DuBois, M. *Organometallics* **1984**, *3*, 831. Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *J. Am. Chem. Soc.* **1983**, *103*, 6321. (c) Phosphinidine reactions: Lunnis, J.; MacLaughlin, S. A.; Taylor, N. J.; Carty, A. J.; Sappa, E. *Organometallics* **1985**, *4*, 2066. Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456.

(2) Anal C, H, S. FABMS (m/z, ^{102}Ru) 630 (P^+); ^{1}H NMR (δ in ppm, J in Hz, $CDCl_3$) 2.23 (q, 4 H, 7.3), 1.92 (s, 12 H), 1.87 (s, 12 H), 1.10 (t, 6 H, 7.4). Compound **1** crystallized from hexane in the space group $P\bar{1}$, with cell dimensions a = 18.386 (4) Å, b = 18.868 (4) Å, c = 8.564 (3) Å, α = 98.64 (2)°, β = 91.12 (2)°, γ = 117.48 (2)°, V = 2592 (1) Å^3, Z = 4, ρ_{exp} = 1.60 g cm^{-3}, for $\pm h,\pm k,+l$ in the range $3.0° < 2\theta < 46°$. These data were averaged to (R_{av} = 0.018). The structure 7256 independent reflections was solved by direct methods (SHELX), refined with use of 4377 intensities ($I > 2.58\ \sigma(I)$) to R = 0.053 and R_w = 0.067.

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(5) Millar, M. M.; O'Sullivan, T.; de Vries, N.; Koch, S. A. *J. Am. Chem. Soc.* **1985**, *107*, 3714.

(6) Anal. C, H, S. FDMS (m/z, ^{102}Ru) 1196 (P^+), 1164 (P^+ - S), 1132 (P^+ - 2S), 1047 (P^+ - Cp^*); ^{1}H NMR (see ref 2, C_6D_6) 2.45 (q, 2 H, 7.5), 2.31 (q, 4 H, 7.7), 2.11 (m, 8 H), 2.05 (s, 6 H), 1.78 (s, 6 H), 1.77 (s, 6 H), 1.69 (s, 6 H), 1.64 (s, 6 H), 1.63 (s, 6 H), 1.60 (s, 6 H), 1.24 (t, 3 H, 7.60), 0.98 (t, 6 H, 7.4), 0.89 (t, 3 H, 7.6).

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formed in similar yield when toluene solutions of **1** are treated with 1 equiv of tri-*n*-butylphosphine (PBu_3) at 70 °C for 2 h followed by evaporation and trituration with aqueous methanol. This unusual species can be easily crystallized from cold hexane. The ^1H NMR spectrum of **2** shows three nonequivalent Cp* ligands (1:1:2) and its structure is suggested to resemble that for $Cp_4Fe_4S_2(S_2)_2$.[7] The conversion of **1** into a larger cluster is reminiscent of our previous observation that $(MeCp)_2V_2S_4$ reacts with PBu_3 to give $(MeCp)_4V_4S_4$.[8]

When toluene solutions of **1** are treated with PBu_3 (2 equiv) *in the presence* of diphenylacetylene (1 equiv, 70 °C, 2 h) one obtains, after solvent evaporation and trituration with methanol, $Cp^*{}_2Ru_2S_2C_2Ph_2$ (**3**) as red brown crystals from pentane in ca. 70% yield (eq 1).[9] It is important to note that compound **1** does

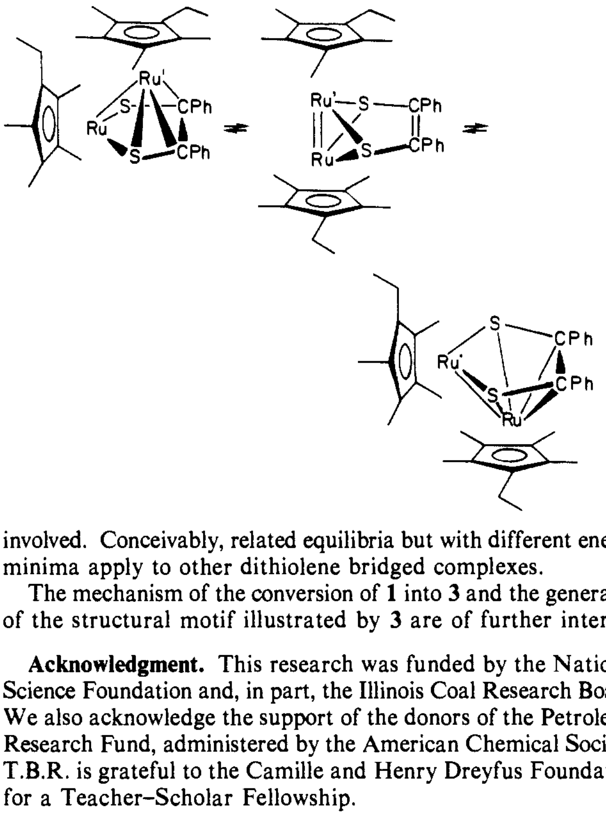
$$Cp^*{}_2Ru_2S_4 + R_2C_2 + 2PBu_3 \rightarrow Cp^*{}_2Ru_2S_2C_2R_2 + 2SPBu_3 \quad (1)$$

$$R_2 = Ph_2\ (\mathbf{3}),\ PhH,\ H_2$$

not react with Ph_2C_2 (2 equiv, 70 °C, 2 weeks). Furthermore compound **2** is not an intermediate in the dithiolene synthesis since it can be recovered in good yield after attempted reaction with Ph_2C_2 (2 equiv), alone or in the presence of PBu_3 (2 equiv). The dithiolene synthesis also works well for acetylene and phenylacetylene.[10] The reaction of **1**, PBu_3 (*1 equiv*), and C_2H_2 (2 atm) gave ~25% yield of $Cp^*{}_2Ru_2S_2C_2H_2$;[10] chromatographic workup of the products returned ~35% yield of **1**.

An X-ray diffraction study shows that compound **3** is a square-pyramidal, nido cluster (Figure 2).[11] The most distinctive structural feature of **3** is the bridging dithiolene ligand which is folded over so as to bind to one metal in an η^4 manner. The dithiolene and the Cp* ring carbon atoms are nearly equidistant (±0.02 Å) from Ru(2). Bridging 1,2-dithiolene ligands are common[12] but the present μ-η^2,η^4 form is unique.[13] Structurally, **3** is related to certain diazabutadiene complexes, e.g., $Mn(_2(\mu\text{-}\eta^2,\eta^4\text{-}CH_3NCHCHNCH_3)(CO)_6$,[14] and to the binuclear ferroles $Fe_2(C_4R_4)(CO)_6$.[15] If the μ-η^2,η^4-$R_2C_2S_2$ ligand is viewed as a neutral 8e$^-$ donor, **3** is seen to be an electron-precise 34e$^-$ species. The Ru-Ru distance in **3** is 2.980 (1) Å whereas the Ru-Ru distance in **1** is nonbonding at 3.749 (1) Å.

The ^1H NMR spectrum of **3** consists of four methyl singlets and two methyl triplets showing that the C_5Me_4Et ligands are nonequivalent but suggesting that both lie on a plane of symmetry. At 150 °C in $C_6D_5NO_2$ solution, the separation of the closer pair of methyl singlets in its ^1H NMR spectrum ($\Delta\delta$ = 5.5 Hz at 40 °C) narrows to 1.5 Hz. Therefore ΔG^* for the equivalencing of the two Ru centers is somewhat greater than 95 kJ/mol. We propose that a dynamic equilibrium of the type shown in eq 2 is



(2)

involved. Conceivably, related equilibria but with different energy minima apply to other dithiolene bridged complexes.

The mechanism of the conversion of **1** into **3** and the generality of the structural motif illustrated by **3** are of further interest.

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Supplementary Material Available: Tables of bond distances, bond angles, thermal parameters, fractional coordinates, and structure factor tables for $Cp^*{}_2Ru_2S_2C_2Ph_2$ and $Cp^*{}_2Ru_2S_4$ (43 pages). Ordering information is given on any current masthead page.

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[9] Anal C, H, S. FABMS (*m/z*) 744 (P^+), 566 ($P^+ - Ph_2C_2$); ^1H NMR (C_6D_6) 7.33 and 6.96 (m, 10 H, C_6H_5), 2.50 (q, 2 H, 7.5), 2.20 (q, 2 H, 7.7), 2.04 (s, 6 H), 2.01 (s, 6 H), 1.71 (s, 6 H), 1.66 (s, 6 H), 1.07 (t, 3 H, 7.5); 0.85 (t, 3 H, 7.5).

[10] Characterized by ^1H NMR and FAB mass spectrometry.

[11] Compound **3** crystallized from pentane in the space group $P2_1/n$, with cell dimensions a = 13.222 (3) Å, b = 16.312 (4) Å, c = 15.797 (2) Å, V = 3299 (2) Å^3, β = 104.48 (2)°, Z = 4, ρ_{exp} = 1.47 g cm^{-3}. for $\pm h,-k,+l$ in the range 2.0° < 2θ < 46.0°. These were averaged to (R_{av} = 0.017). The structure, 4576 independent reflections, was solved by direct methods (SHELX), refined with use of 3489 intensities ($I > 2.58\sigma(I)$) to R = 0.033 and R_w = 0.046.

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Selective Deoxygenation of Secondary Alcohols by Photosensitized Electron-Transfer Reaction. A General Procedure for Deoxygenation of Ribonucleosides[1]

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While photosensitized electron-transfer reactions are currently attracting considerable mechanistic interest in organic photochemistry,[2] synthetic methodology based on these reactions has been rather limited.[3] We report a general and practically useful

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