Carbon−Sulfur Bond Formation on the Disulfide Bridging Ligand of a Dinuclear Ruthenium Compound in the Reaction with Acetone

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Received April 21, 1994[⊗]

A novel C−S bond formation has been found in the reaction of $[\{Ru(AN)_3(TMP)_2\}_2(\mu\text{-}S_2)]^{4+}$ with acetone (AN is acetonitrile, and TMP is $P(OMe)_3$). The crystal structure of the resulting compound, $[\{Ru^{III}(AN)_2(TMP)_2\}(\mu\text{-}S_2CH_2COCH_3)\{Ru^{III}(AN)_3(TMP)_2\}](CF_3SO_3)_3\cdot 0.5(CH_3)_2CO$, has been solved by single-crystal X-ray diffraction analysis. The crystal data are as follows: triclinic, space group $P\bar{1}$, $a = 12.238(4)$ Å, $b = 22.248(7)$ Å, $c = 12.344(4)$ Å, $\alpha = 93.29(3)°$, $\beta = 112.69(2)°$, $\gamma = 78.54(3)°$, $V = 3074(2)$ Å^3, and $Z = 2$. The two ruthenium atoms originally bridged by a S_2^{2-} bridging ligand in the starting material are bridged by a $S_2CH_2COCH_3^{3-}$ ligand in the product with the two sulfur-coordinating atoms. In the new bridging ligand, deprotonated acetone, $CH_3COCH_2^-$, is bonded to the S_2^{2-} bridge, forming a C−S bond. The carbonyl oxygen atom of the new bridge coordinates to one of the ruthenium atoms to form a RuOCCS five-membered ring. The S−S distance is 2.067(6) Å, the two Ru−S distances are 2.339(5) and 2.380(5) Å, and the two Ru atoms are attached to the S−S bridging ligand in a trans mode.

Multinuclear transition-metal complexes with sulfur-containing bridging ligands have been investigated to mimic the function of nitrogenase enzymes[1−7] and to study the hydrodesulfurization of thiophene and other organosulfur compounds in the refinement of fossil fuels.[8−15] The latter reactions are usually catalyzed at the surface of transition-metal sulfides. Mechanistic studies of the desulfurization and its reverse reactions in homogeneous solution have been carried out on sulfide- and hydrosulfide-bridged multinuclear transition metal complexes by DuBois[15−19] and Rauchfuss et al.[12−15,20] Sulfide and hydrosulfide ligands exhibit novel C−O cleavage of cyclic ethers, forming a C−S bond;[16] they also undergo addition of alkene, alkyne, and cumulenes.[17,21] Polysulfide coordinated to a transition metal is observed to react with alkyne to form a coordinated dithiolene.[17c]

Table 1. Summary of Crystal Data for **1**

formula	$C_{29.5}F_9H_{59}N_5O_{22.5}P_4Ru_2S_5$	Z	4
fw	1501.1	d_{calcd}, g cm^{-3}	1.62
cryst syst	triclinic	abs coeff (μ), cm^{-1}	8.49
space group	$P\bar{1}$ (No. 2)	radiation (λ, Å)	Mo Kα (0.710 68)
a, Å	12.238(4)	R^a	0.102
b, Å	22.248(7)	$R_w{}^b$	0.111
c, Å	12.344(4)		
V, Å^3	3074(2)	GOF^c	1.33

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ ($w = 1/(\sigma(F)^2 + 0.006566F^2)$). [c] GOF $= [\sum w(|F_o| - |F_c|)^2/\sum(N_{reflecns} - N_{params})]^{1/2}$.

So far the formation of C−S bonds has been observed on only a limited number of transition-metal complexes.[16,17,21] These are mostly alkyne additions to two adjacent S^{2-} ligands and to a S_2^{2-} ligand. By contrast only a few alkene additions are known; these occur on one or two adjacent S^{2-} ligand(s).[17a,21] Cleavage of C−O in tetrahydrofuran leading to C−S bond formation on a S^{2-} bridging ligand[16] is also noteworthy. In the present paper, we report a novel reaction of a disulfide-bridged Ru(III) dimer with acetone: Cleavage of a C−H bond of acetone takes place, and a new C−S bond is formed on the bridging S_2^{2-} in the product, $[\{Ru(AN)_2(TMP)_2\}(\mu\text{-}S_2CH_2COCH_3)\{Ru(AN)_3(TMP)_2\}](CF_3SO_3)_3\cdot 0.5(CH_3)_2CO$ (**1**).

Experimental Section

Preparation of Complex 1. All of the following procedure was carried out under an N_2 atmosphere. To 2 mL of AN (AN is CH_3CN) containing 0.1 g of $[\{RuCl(TMP)_2\}_2(\mu\text{-}Cl)_2(\mu\text{-}S_2)]$ (**2**)[22] was added 0.104 g (4 equiv) of $AgCF_3SO_3$, and the solution was heated at 50 °C for 40 h. After cooling of the solution to room temperature, AgCl was removed by filtration, and the filtrate was dried in vacuo and was

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[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1995.

(1) Pelikan, P.; Boca, R. *Coord. Chem. Rev.* **1984,** *55,* 55.
(2) Henderson, R. A.; Leigh, G. J.; Pickett, G. J. *Adv. Inorg. Chem. Radiochem.* **1983,** *27,* 198.
(3) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978,** *78,* 589.
(4) Dilworth, J. R.; Richards, R. L. In *Comprehensive Organometallic Chemistry;* Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982; Chapter 60, pp 1073−1106.
(5) Hidai, M. In *Molybdenum Enzymes;* Spiro, T. G., Ed.; J. Wiley: New York, 1985; p 759.
(6) Chatt, J.; Fakley, M. E.; Hitchcock, P. B.; Richards, R. L.; Luong-Thi, N. T. *J. Organomet. Chem.* **1979,** *172,* C55.
(7) Kim, J.; Rees, D. C. *Nature* **1992,** *360,* 553.
(8) Gellman, A. J.; Nieman, D.; Somorjai, G. A. *J. Catal.* **1987,** *92,* 103.
(9) Kwart, H.; Schuit, G. C. A.; Gates, B. C. *J. Catal.* **1980,** *61,* 128.
(10) Massoth, F. *J. Catal.* **1977,** *47,* 300.
(11) Spies, G. H.; Angelici, R. J. *J. Am. Chem. Soc.* **1985,** *107,* 5569.
(12) Bucknor, S. M.; Draganjac, M.; Rauchfuss, T. B.; Ruffing, C. J.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1984,** *106,* 5379.
(13) Luo, S.; Rauchfuss, T. B.; Gan, Z. *J. Am. Chem. Soc.* **1993,** *115,* 4943.
(14) Skaugset, A. E.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1992,** *114,* 8521.
(15) Luo, S.; Skaugset, A. E.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1992,** *114,* 1732.
(16) Godziela, G.; Tonker, T.; DuBois, M. R. *Organometallics* **1989,** *8,* 2220.
(17) (a) Mckenna, M.; Wright, L. L.; Miller, D. J.; Tanner, L.; Haltiwanger, R. C.; DuBois, M. R. *J. Am. Chem. Soc.* **1983,** *105,* 5329. (b) Bolinger, C. M.; Rauchfuss, T. B. *Inorg. Chem.* **1982,** *21,* 3947. (c) Draganjac, M.; Coucouvanis, D. *J. Am. Chem. Soc.* **1983,** *105,* 139.
(18) Bernatis, P.; Laurie, J. C. V.; DuBois, M. R. *Organometallics* **1990,** *9,* 1607.
(19) DuBois, M. R. *Chem. Rev.* **1989,** *89,* 1.
(20) Rauchfuss, T. B.; Rodgers, D. P. S.; Wilson, S. R. *J. Am. Chem. Soc.* **1986,** *108,* 3114.
(21) Birnbaum, J.; Laurie, J. C. V.; DuBois, M. R. *Organometallics* **1990,** *9,* 156.
(22) Matsumoto, T.; Matsumoto, K. *Chem. Lett.* **1992,** 559.

0020-1669/95/1334-0658$09.00/0

Table 2. Positional and Thermal Parameters for $[\{Ru_2(CH_3CN)_5(P(OCH_3)_3)_4\}(\mu\text{-}S_2CH_2COCH_3)](CF_3SO_3)_3{\cdot}0.5(CH_3)_2O$

atom	*x/a*	*y/b*	*z/c*	$B_{eq}{}^{a}$ (Å^2)	atom	*x/a*	*y/b*	*z/c*	$B_{eq}{}^{a}$ (Å^2)
Ru1	0.6478(1)	0.1842(1)	0.8360(1)	4.69	C11	0.9618(23)	0.2808(17)	0.9198(24)	13.72
Ru2	0.1749(1)	0.3251(1)	0.6627(1)	4.27	C12	0.6222(35)	0.3360(24)	0.6697(42)	21.86
S1	0.4663(4)	0.2407(2)	0.8339(4)	5.28	C13	0.6939(46)	0.3516(21)	0.9992(41)	23.23
S2	0.3565(4)	0.2651(2)	0.6617(4)	6.02	C21	0.6295(32)	0.2183(18)	1.1967(24)	16.38
P1	0.7389(5)	0.2624(2)	0.8601(5)	6.51	C22	0.9437(42)	0.1480(29)	1.1639(54)	28.04
P2	0.7121(4)	0.1682(3)	1.0296(4)	5.98	C23	0.7054(37)	0.0695(19)	1.1026(54)	21.42
P3	0.0815(4)	0.2466(2)	0.5990(4)	5.67	C31	0.1796(26)	0.1639(10)	0.4811(22)	10.22
P4	0.1396(5)	0.3555(3)	0.4818(5)	6.69	C32	0.0157(40)	0.1653(15)	0.7012(31)	20.31
O1	0.5479(12)	0.1088(6)	0.7976(12)	7.58	C33	−0.1462(27)	0.2825(20)	0.4609(51)	22.31
C1	0.4089(14)	0.1753(8)	0.8586(17)	6.02	C41	0.1630(28)	0.3117(13)	0.2806(20)	12.33
C2	0.4527(17)	0.1167(9)	0.8126(18)	6.84	C42	0.3320(29)	0.4116(16)	0.5185(29)	14.03
C3	0.3870(21)	0.0670(12)	0.7897(24)	10.79	C43	−0.0487(36)	0.4460(20)	0.3744(47)	23.90
N1	0.7925(13)	0.1208(7)	0.8369(15)	6.37	S3	0.5685(6)	0.3985(4)	0.2954(8)	10.00
N2	0.5923(12)	0.1902(7)	0.6476(13)	5.63	F11	0.4576(27)	0.4830(14)	0.3863(21)	22.24
N3	0.0210(12)	0.3773(7)	0.6606(12)	5.98	F12	0.4554(24)	0.5088(11)	0.2260(22)	19.49
N4	0.2096(12)	0.3069(7)	0.8388(13)	5.38	F13	0.3464(17)	0.4401(13)	0.2455(20)	17.82
N5	0.2637(12)	0.3989(7)	0.7443(13)	5.71	C4	0.4465(38)	0.4627(15)	0.2847(48)	14.65
C1n	0.8662(21)	0.0847(11)	0.8300(18)	7.93	O11s	0.5475(32)	0.3888(13)	0.1726(26)	24.10
C2n	0.9607(24)	0.0299(12)	0.8266(27)	13.93	O12s	0.6681(20)	0.4266(18)	0.3674(29)	23.79
C3n	0.5605(24)	0.1961(13)	0.5550(21)	10.16	O13s	0.5387(25)	0.3489(10)	0.3310(23)	17.74
C4n	0.5185(39)	0.2125(19)	0.4401(32)	19.44	S4	0.2817(19)	0.1264(7)	0.0995(13)	18.06
C5n	−0.0605(17)	0.4105(9)	0.6629(14)	5.56	O21s	0.3976(68)	0.1164(35)	0.1306(63)	36.88^{b}
C6n	−0.1770(16)	0.4490(10)	0.6632(21)	8.65	O22s	0.2266(64)	0.1711(33)	0.1391(64)	36.55^{b}
C7n	0.2389(16)	0.3094(9)	0.9378(21)	6.89	O23s	0.2073(59)	0.1116(30)	−0.0096(62)	34.66^{b}
C8n	0.2897(25)	0.3116(12)	1.0702(18)	10.69	C5	0.2246(56)	0.0462(30)	0.1278(60)	23.46^{b}
C9n	0.3037(19)	0.4345(9)	0.8131(20)	7.27	F21	0.3310(64)	0.0341(31)	0.0564(62)	42.38^{b}
C10n	0.3466(26)	0.4821(11)	0.8931(20)	10.99	F22	0.2560(38)	0.0962(20)	0.2584(37)	28.23^{b}
O11	0.8752(12)	0.2442(8)	0.9099(18)	11.99	F23	0.3674(35)	0.0510(17)	0.2389(33)	24.75^{b}
O12	0.7116(24)	0.2996(13)	0.7441(23)	17.84	S5,C6	0.9320(15)	1.0179(10)	0.4717(17)	14.51^{b}
O13	0.7101(27)	0.3151(11)	0.9340(32)	22.84	F31	0.8823(35)	0.9799(18)	0.3766(35)	13.36^{b,c}
O21	0.6328(19)	0.2075(9)	1.0914(15)	13.13	F32	0.9591(53)	1.0676(27)	0.4170(52)	21.02^{b,c}
O22	0.8332(20)	0.1700(20)	1.1002(21)	25.22	F33	0.7090(128)	1.0456(59)	0.4674(114)	41.91^{b,c}
O23	0.7007(35)	0.1091(11)	1.0595(21)	20.36	O31s	1.1666(92)	0.9999(44)	0.4919(79)	25.66^{b,c}
O31a	0.0620(42)	0.2141(21)	0.4814(26)	10.99^{c}	O32s	0.8414(58)	1.0647(29)	0.4748(50)	16.83^{b,c}
O31b	0.1648(27)	0.1814(11)	0.5829(28)	7.70^{c}	S6,C7	0.0217(16)	0.5304(8)	−0.0248(16)	12.60^{c}
O32a	0.1128(35)	0.1962(15)	0.7046(27)	7.70^{c}	F41	0.0995(43)	0.5619(21)	0.0467(40)	13.50^{b,c}
O32b	0.0402(41)	0.2296(15)	0.6932(37)	10.35^{c}	F42	−0.0749(32)	0.5604(16)	−0.1260(30)	10.65^{b,c}
O33a	−0.0681(26)	0.2695(15)	0.5670(33)	8.29^{c}	F43	0.0873(40)	0.4694(22)	−0.0899(40)	15.37^{b,c}
O33b	−0.0327(29)	0.2507(17)	0.4777(37)	9.42^{c}	O41s	−0.0494(53)	0.5740(26)	0.0452(51)	16.44^{b,c}
O41	0.1798(16)	0.3021(8)	0.4098(13)	10.36	O42s	−0.0063(61)	0.5330(30)	−0.1408(58)	17.32^{b,c}
O42	0.1953(17)	0.4106(8)	0.4684(15)	10.87	O43s	0.1391(37)	0.5345(20)	0.0424(35)	9.40^{b,c}
O43	0.0015(16)	0.3801(9)	0.4002(14)	10.37					

[a] $B_{eq} = (8/3\pi)[a^2a^{*2}U_{11} + b^2b^{*2}U_{22} + c^2c^{*2}U_{33} + aba^*b^* (\cos\gamma)U_{12} + aca^*c^* (\cos\beta)U_{13} + bcb^*c^* (\cos\alpha)U_{23}]$. [b] Isotropic thermal parameters. [c] The occupancies are 0.5.

redissolved in 5 mL of acetone. After the solution was left at room temperature for 1 h, the blue color of the solution faded to pale blue. The solution was then filtered, and the filtrate was vacuum-condensed to 3 mL. After 3 days standing with ether vapor diffusion, the solution formed a red-brown oily precipitate, which was filtered off, and the solution was again set for crystallization by ether-vapor diffusion. Blue plate crystals of **1** were obtained with 72% yield. The crystals can be recrystallized either from AN or acetone with ether-vapor diffusion. Anal. Calcd for $C_{29.5}F_9H_{59}N_5O_{22.5}P_4Ru_2S_5$: C, 23.60; H, 3.96; N, 4.67. Found: C, 23.45; H, 4.08; N, 4.50.

Collection and Reduction of X-ray Data. A crystal of **1** (0.4 × 0.25 × 0.15 mm^3) was subjected to single-crystal X-ray diffraction analysis. Since the crystal is very unstable in air at room temperature, X-ray measurement was made on a epoxide-resin coated crystal at −30 °C. Unit cell parameters were obtained from a least-squares fit of 24 reflections in the range $21° < 2\theta < 25°$ measured on a Rigaku AFC-5R four-circle diffractometer using graphite-monochromated Mo Kα radiation (0.710 68 Å). Taking the above measures ensured no serious deterioration of the crystal was observed during the measurement; therefore no decay correction was applied. Azimuthal scans of several reflections indicated no need for an absorption correction. The crystal data are given in Table 1, and the details of the data collection are in supplementary Table S1. The Lorentz-polarization correction was made to the collected data, but no absorption correction was applied since the absorption coefficient is small.

Solution and Refinement of the Structure. The structure of **1** was solved by direct methods and subsequent Fourier techniques. All the non-hydrogen atoms in the complex cation were located and were refined anisotropically by a full-matrix least-squares method, by using the program Shelxs76/86. One of the counteranions was found to be distributed in two orientations on a crystallographic center of symmetry and was refined isotropically. One of the remaining two counteranions was refined anisotropically, whereas the other was refined isotropically, since the thermal motion was very large. Although elemental analysis and the ^{1}H NMR spectrum indicate that 0.5 molecule of acetone is contained per molecule, the acetone molecule could not be located unequivocally by X-ray analysis and, therefore, was not included in the calculation.

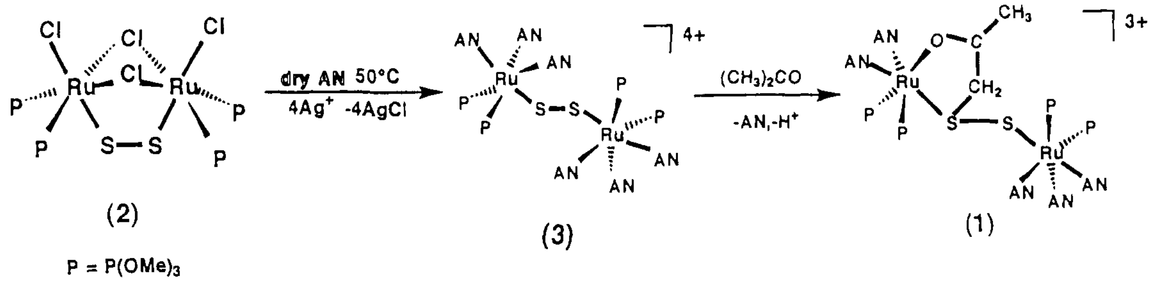
The final atomic positional and thermal parameters for **1** are listed in Table 2. The anisotropic thermal parameters are deposited in Table S2.

Physical Measurements. ^{1}H and ^{31}P{^{1}H} NMR spectra were recorded on a JEOL JNM-EX270WB and GE Omega500. Since **1** is unstable and highly reactive, no internal standard was added to the sample solution. The ^{1}H chemical shifts are expressed relative to the small amount of CD_2HCN in the solvent CD_3CN, whose signal was set at 1.96 ppm. ^{31}P chemical shifts are referenced to an external standard of free TMP in CD_3CN at 140 ppm.

Results and Discussion

Preparation and Properties of the Complex. The synthesis of **1** is illustrated in Scheme 1. Complex **1** is very unstable in

Scheme 1



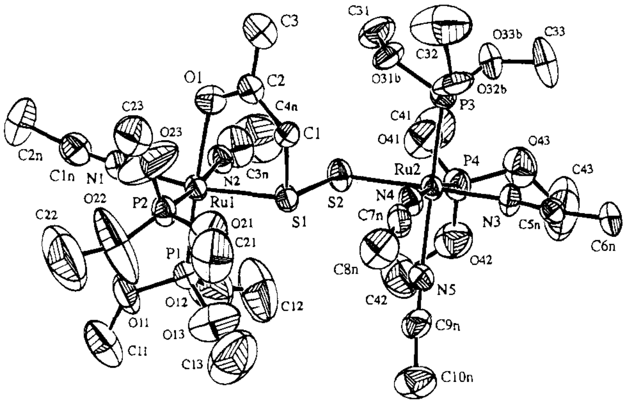


Figure 1. Molecular structure of **1**.

air, especially toward humidity, and must be kept under dry N_2, preferably at 5 °C or lower.

The first step of the synthesis of **1** includes in situ preparation of $[\{Ru(AN)_3(TMP)_2\}_2(\mu\text{-}S_2)]^{4+}$ (**3**) by reacting 4 equiv of $AgCF_3SO_3$ with **2** at 50 °C for 40 h. The isolation and the crystal structure of **3** will be reported elsewhere.[23] Compound **3** thus prepared reacts with acetone to give **1**. The destination of the proton removed from the acetone was not determined. Compound **1** does not have any proton on either the bridging S_2^{2-} or the counteranions, which was confirmed by ^1H NMR spectroscopy. Therefore, the proton must remain in the solution.

Complex **1** is diamagnetic as judged from the normal ^1H and ^{31}P NMR spectra with sharp peak profiles (see later section); in spite of this the complex is a Ru(III) dinuclear compound. Several previously reported Ru(III) dimer complexes with a S_2^{2-} bridging ligand, $[\{RuCl(TMP)_2\}_2(\mu\text{-}Cl)_2(\mu\text{-}S_2)]$,[22] $[\{Ru(Cp)(PMe_3)_2\}_2(\mu\text{-}S_2)](SbF_6)_2$[24] (Cp is cyclopentadienide), $[\{Ru(NH_3)_5\}_2(\mu\text{-}S_2)]Cl_4{\cdot}2H_2O$,[25] $[\{Ru(PPh_3)\text{'}S_4\text{'}\}_2(\mu\text{-}S_2)]$[26] ('$S_4$' is 1,2-bis[(2-mercaptophenyl)thio]ethane(2−)), and $[\{(\eta^5\text{-}C_5Me_5)Ru\}_2(\mu\text{-}SPr^i)_2(\mu\text{-}S_2)]$[27] ($C_5Me_5$ is pentamethylcyclopentadienide), are also diamagnetic, and this is caused by a distinct electronic structure of the *trans*-RuSSRu chromophore. A qualitative MO description of the RuSSRu core[25b,26] revealed a distinct π-MO that accommodates the two unpaired electrons of the two Ru(III) atoms as an electron pair.

Complex **1** fairly easily decomposes in AN at room temperature to become dark blue. The dark blue color means the RuSSRu core or its derivatives are retained (the bridging S_2^{2-} might be modified); however, the decomposition product has not yet been identified.

Structure of 1. The molecular structure of **1** is shown in Figure 1. Compound **1** is a 34 electron dimer lacking a direct metal−metal bond. The two ruthenium atoms are bridged by a disulfide ligand, to which deprotonated acetone $CH_3COCH_2^-$ is attached through a C−S bond. The carbonyl oxygen of the $CH_3COCH_2^-$ is coordinated to one of the Ru atoms. The H_α abstraction is apparently facilitated by coordination of the acetone oxygen atom to the Ru atom. Although several dinuclear transition-metal complexes with a disulfide bridging ligand are known,[24,25,28,29] any reaction on a bridging disulfide ligand was not known previously. Only one reaction is however known, in which a terminal chelating disulfide reacts with an acetylene derivative.[30] The present reaction revealed an unexpectedly high reactivity of a disulfide bridging ligand. The reaction should be compared to those of the bridging sulfide ligand S^{2-} in dinuclear molybdenum complexes;[16−19,21] the sulfide bridging ligands are known to undergo protonation, and various alkylations take place by insertion of alkenes in the S−H bond. These facts reveal that the sulfide ligands in the dimolybdenum complexes receive nucleophilic attack. We have carefully searched for the possible existence of a proton on the disulfide ligand or on the triflate by ^1H NMR in the range −20 to 10 ppm; however, no such proton was detected.

The two Ru atoms are trans to the disulfide. The literature values of S−S distances in disulfide complexes are mostly in the range 2.01−2.05 Å.[20,24−27,29,31] The S−S distance of 2.067(6) Å in **1** is slightly longer; however, this is reasonable, considering that the ligand is not a simple disulfide S_2^{2-} but is $S_2CH_2COCH_3^{3-}$. The major bond distances and bond angles are listed in Tables 3 and 4, respectively. All bond distances and angles are deposited in Tables S3 and S4. Both Ru atoms are Ru(III), as judged from the Ru−P(phosphite) distances: Ru(II)−P distances are usually in the range 2.32−2.35 Å,[32−34] whereas Ru(III)−P distances are in the range 2.24−2.30 Å.[22,24,28] These data includes both PR_3 and $P(OR)_3$, and no appreciable difference is observed between the two types of ligands. The Ru−S and S−S distances of **1** are compared with those of other diruthenium complexes in Table 5. The Ru−S(disulfide) distances are known to be shorter than the Ru−S(dialkyl sulfides, alkyane thiolates, and thiophenes) distances, which is due to the strong π-donation from the disulfide to the ruthenium

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(23) Matsumoto, K.; Matsumoto, T.; Kawano, M.; Ohnuki, H.; Shichi, Y.; Nishide, T. Manuscript in preparation.

(24) Amarasekera, J.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1987**, *26*, 3328.

(25) (a) Elder, R. C.; Trkula, M. *Inorg. Chem.* **1977**, *16*, 1048. (b) Kim, S.; Otterbein, E. S.; Rava, R. P.; Isied, S. S.; Filippo, J. S., Jr.; Waszcyak, J. V. *J. Am. Chem. Soc.* **1983**, *105*, 336.

(26) Sellmann, D.; Lechner, P.; Knoch, F.; Moll, M. *J. Am. Chem. Soc.* **1992**, *114*, 922.

(27) Mizobe, Y.; Hosomizu, M.; Kawabata, J.; Hidai, M. *J. Chem. Soc., Chem. Commun.* **1991**, 1226.

(28) Amarasekera, J.; Rauchfuss, T. B.; Rheingold, A. L. *Inorg. Chem.* **1987**, *26*, 2017.

(29) Müller, A.; Jagermann, W.; Enemark, J. H. *Coord. Chem. Rev.* **1882**, *46*, 245.

(30) Halbert, T. R.; Pan, W.-H.; Stiefel, E. I. *J. Am. Chem. Soc.* **1983**, *105*, 5476.

(31) Kawano, M.; Hoshino, C.; Matsumoto, K. *Inorg. Chem.* **1992**, *31*, 5158.

(32) Kawano, M.; Watanabe, T.; Matsumoto, K. *Chem. Lett.* **1992**, 2389.

(33) Uemura, H.; Kawano, M.; Watanabe, H.; Matsumoto, T.; Matsumoto, K. *Inorg. Chem.* **1992**, 5137.

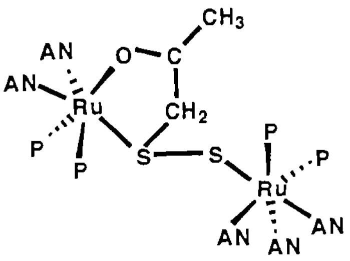
(34) Kato, T.; Kawano, M.; Taniguchi, H.; Funaki, M.; Moriyama, H.; Sato, T.; Matsumoto, K. *Inorg. Chem.* **1992**, 26.

Table 3. Bond Distances (Å) of [{$Ru_2(CH_3CN)_5(P(OCH_3)_3)_4$}-($\mu$-$S_2CH_2COCH_3$)]$(CF_3SO_3)_3$·$0.5(CH_3)_2O$

Ru1−S1	2.339(5)	Ru2−S2	2.380(5)
Ru1−P1	2.204(6)	Ru2−P3	2.224(6)
Ru1−P2	2.233(5)	Ru2−P4	2.223(6)
Ru1−O1	2.202(15)	Ru2−N3	2.016(15)
Ru1−N1	2.045(16)	Ru2−N4	2.095(16)
Ru1−N2	2.160(16)	Ru2−N5	2.143(16)
S1−S2	2.067(6)	N1−C1n	1.12(3)
S1−C1	1.83(2)	N2−C3n	1.06(3)
O1−C2	1.24(3)	N3−C5n	1.14(2)
C1−C2	1.48(3)	N4−C7n	1.13(3)
C2−C3	1.45(4)	N5−C9n	1.16(3)
P1−O11	1.53(1)	C1n−C2n	1.53(4)
P1−O12	1.58(3)	C3n−C4n	1.35(5)
P1−O13	1.52(3)	C5n−C6n	1.53(3)
P2−O21	1.57(2)	C7n−C8n	1.51(3)
P2−O22	1.42(2)	C9n−C10n	1.44(3)
P2−O23	1.43(3)	C41−O41	1.55(3)
P3−O31a	1.54(4)	C42−O42	1.57(4)
P3−O31b	1.66(3)	C43−O43	1.48(5)
P3−O32a	1.65(4)	C11−O11	1.44(4)
P3−O32b	1.53(6)	C12−O12	1.29(5)
P3−O33a	1.71(3)	C13−O13	1.15(6)
P3−O33b	1.61(3)	C21−O21	1.32(4)
P4−O41	1.56(2)	C22−O22	1.30(5)
P4−O42	1.57(2)	C23−O23	1.04(6)
P4−O43	1.61(2)	C31−O31a	1.65(5)
		C31−O31b	1.36(5)
		C32−O32a	1.49(7)
		C32−O32b	1.54(6)
		C33−O33a	1.30(6)
		C33−O33b	1.39(5)

Table 4. Bond Angles (deg) of [{$Ru_2(CH_3CN)_5(P(OCH_3)_3)_4$}-($\mu$-$S_2CH_2COCH_3$)]$(CF_3SO_3)_3$·$0.5(CH_3)_2O$

P1−Ru1−S1	96.7(2)	P3−Ru2−S2	91.3(2)
P2−Ru1−S1	90.4(2)	P4−Ru2−S2	86.5(2)
P2−Ru1−P1	92.1(2)	P4−Ru2−P3	92.8(2)
O1−Ru1−S1	81.8(4)	N3−Ru2−S2	178.6(5)
O1−Ru1−P1	175.4(4)	N3−Ru2−P3	89.4(5)
O1−Ru1−P2	92.3(4)	N3−Ru2−P4	92.3(5)
N1−Ru1−S1	169.3(5)	N4−Ru2−S2	96.1(4)
N1−Ru1−P1	93.9(5)	N4−Ru2−P3	93.1(5)
N1−Ru1−P2	88.2(5)	N4−Ru2−P4	173.4(5)
N1−Ru1−O1	87.6(6)	N4−Ru2−N3	85.1(6)
N2−Ru1−S1	93.6(4)	N5−Ru2−S2	90.9(4)
N2−Ru1−P1	91.4(5)	N5−Ru2−P3	173.0(5)
N2−Ru1−P2	174.4(4)	N5−Ru2−P4	93.9(5)
N2−Ru1−O1	84.3(6)	N5−Ru2−N3	88.6(6)
N2−Ru1−N1	87.2(6)	N5−Ru2−N4	80.0(6)
S2−S1−Ru1	108.2(3)	C2−O1−Ru1	119.0(13)
C1−S1−Ru1	96.2(6)	C2−C1−S1	114.6(17)
C1−S1−S2	101.7(6)	C1−C2−O1	120.3(19)
S1−S2−Ru2	107.5(3)	C3−C2−O1	119.6(20)
		C3−C2−C1	120.1(22)



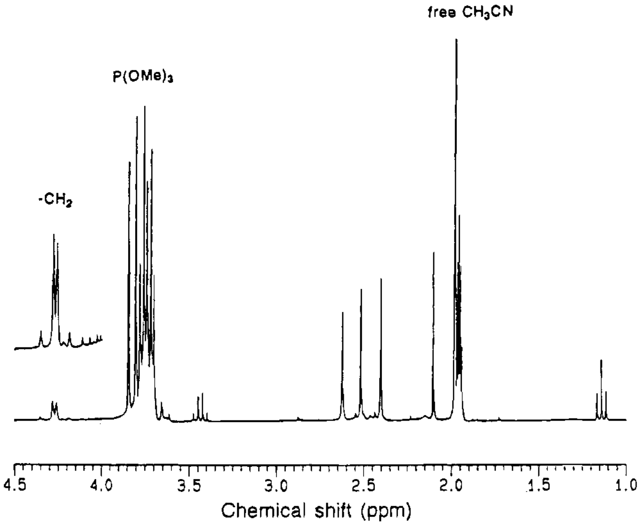


Figure 2. ^1H NMR spectrum of **1** in CD_3CN.

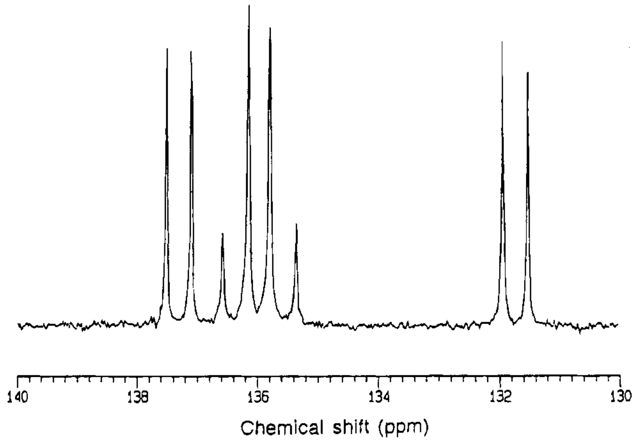


Figure 3. ^{31}P NMR spectrum of **1** in CD_3CN.

atoms.[24,31] The coordination distances around the Ru atoms are normal, and the bond angles around C2 are close to a tetrahedral one. The Ru−N distances trans to the TMP are longer than those trans to the disulfide ligand, indicating that TMP exerts a stronger trans influence than disulfide. A similar tendency was observed previously in [{$Ru^{II,III}(AN)_3(TMP)_2$}$_2$(μ-S_2)]$(PF_6)_3$.[35] A strong structural trans influence of S_2^{2-} is reported for $[(NH_3)_5RuS_2Ru(NH_3)_5]^{4+}$,[25] and the present study shows that the trans influence of TMP might be even stronger. However, other factors such as crystal packing force might also be operating to cause the long bond distances. The Ru−S−S−Ru dihedral angle in **1** is 1.8(2)°, which is almost comparable to that of [{$Ru^{II,III}(AN)_3(TMP)_2$}$_2$(μ-S_2)]$(PF_6)_3$, 0°.[35] The Ru1−O1 distance (2.202(15) Å) in **1** is slightly longer than other Ru(III)−O distances: Ru(III)−$O(OH_2)$ (2.127(8) Å) and Ru(III)−O(carboxylate) (2.050(11)−2.072(13) Å).[36] The S1−C1 distance (1.83(2) Å) is significantly longer than usual single C−S bonds (1.79−1.80 Å) in usual organic sulfur compounds[37] but is comparable to several other C−S bonds coordinated to transition metals with the sulfide sulfur atoms (1.80−1.83 Å).[36]

NMR Studies. The ^1H NMR spectrum of **1** in CD_3CN is shown in Figure 2. The large peak observed around 2 ppm is free AN, which is released from **1** by exchange with CD_3CN. The coordinated AN molecules are observed at 2.41 and 2.52 ppm, each peak intensity corresponding to one AN molecule, and therefore, two AN molecules out of five in the complex are not easily exchanged with the solvent. The peaks around 3.8 ppm are TMP. The singlet at 2.63 ppm is the CH_3 of the coordinated acetonate. The second-order quartet pattern at 4.27 ppm is due to the methylene group of the coordinated acetonate.

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(35) Matsumoto, T.; Matsumoto, K. *Chem. Lett.* **1992**, 1539.

(36) Laurie, J. C. V.; Duncan, L.; Haltiwanger, R. C.; Weberg, R. T.; DuBois, M. R. *J. Am. Chem. Soc.* **1986**, *108*, 6234.

(37) Gzella, A.; Wrzeciono, U. *Acta Crystallogr.* **1991**, *C47*, 980.

Table 5. Comparison of Selected Distances

complex	Ru−S (Å)	S−S (Å)	−S−S−type	ref
$[\{\mathrm{Ru^{III}(AN)_2(TMP)_2}\}(\mu\text{-}\mathrm{S_2CH_3COCH_3})\{\mathrm{Ru(AN)_3(TMP)_2}\}]\text{-}(\mathrm{CF_3SO_3})_3\cdot 0.5(\mathrm{CH_3})_2\mathrm{CO}$ (**1**)	2.360 (av)	2.067	trans	this work
$[\{\mathrm{Ru^{III}Cl(TMP)_2}\}_2(\mu\text{-}\mathrm{Cl})_2(\mu\text{-}\mathrm{S_2})]$ (**2**)	2.202 (av)	1.971	cis	22
$[\{\mathrm{Ru^{II,III}(AN)_3(TMP)_2}\}_2(\mu\text{-}\mathrm{S_2})](\mathrm{PF_6})_3$	2.322	1.995	trans	28
$[\{\mathrm{Ru^{III}(Cp)(PMe_3)_2}\}_2(\mu\text{-}\mathrm{S_2})](\mathrm{SbF_6})_2$	2.208	1.962	trans	23
$[\{\mathrm{Ru^{III}(NH_3)_5}\}_2(\mu\text{-}\mathrm{S_2})]\mathrm{Cl_4}\cdot 2\mathrm{H_2O}$	2.193 (av)	2.014	trans	24
$[\{\mathrm{Ru^{III}(PPh_3)}\text{‘}\mathrm{S_4}\text{’}\}_2(\mu\text{-}\mathrm{S_2})]$[a]	2.243 (av)	1.991	trans	25
1,4-$[\{\mathrm{MeCp)Ru^{II}(PPh_3)}\}2(\mu\text{-}\mathrm{S_2})_2]$	2.295 (av)	2.046	trans	27
$[\{(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Ru^{III}}\}_2(\mu\text{-}\mathrm{SPr^I})_2(\mu\text{-}\mathrm{S_2})]$	2.212 (av)	2.008	cis	26
$[(\mu_2\text{-}\mathrm{S_2})\{(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{Ru^{III}}\}_2(\mu_3\text{-}\mathrm{S})(\mu_2\text{-}\mathrm{S})_2\mathrm{WS}]$	2.220 (av)	1.991	cis	26
$[\{\eta^5\text{-}\mathrm{C_5Me_4Et)Ru^{III}}\}_2(\mu,\eta^2\text{-}\mathrm{S_2})(\mu,\eta^1\text{-}\mathrm{S_2})]$	2.195	2.020	cis	20
$[\{\mathrm{Ru^{II,III}Cl(TMP)_2}\}_2(\mu\text{-}\mathrm{Cl})(\mu\text{-}\mathrm{N_2H_4})(\mu\text{-}\mathrm{S_2})]$	2.281 (av)	2.002	cis	30

[a] ‘$\mathrm{S_4}$’ is 1,2-bis[(2-mercaptophenyl)thio]ethane(2−).

The singlet at 2.11 ppm is free acetone contained as a solvate molecule in the crystal. These assignments were made by comparing the spectra of **1** with its $(\mathrm{CD_3})_2\mathrm{CO}$- and $\mathrm{CD_3CN}$-substituted compounds, both prepared in the same way as **1** by using the corresponding isotopes. The comparison of the NMR charts for deuterium-substituted and nonsubstituted compounds is deposited as Figure S1. The amount of the solvate acetone was determined as 0.5 per molecule, based on the integrated ^{1}H NMR signal. There was no other ^{1}H signal observed; therefore, the proton released from the acetone is not attached to the sulfur bridge. The observed ^{1}H chemical shifts are as follows: the $-\mathrm{CH_2S}-$ of the acetonate, 4.28 and 4.26 ppm; TMP, 3.84, 3.80, 3.78, 3.76, 3.74, 3.72, and 3.79 ppm; the coordinated acetonate $-\mathrm{CH_3}$, 2.63 ppm; coordinated $\mathrm{CH_3CN}$, 2.52 and 2.41 ppm; free acetone 2.11 ppm; free AN 1.98 ppm. A very weak broad peak was sometimes observed around 6 ppm, which is not, however, a S−H proton, the fact being confirmed by the deuterium-substituted NMR spectra. Compound **1** is not stable at room temperature; **1** in dry AN sealed in an NMR tube is still unstable; it turned from bluish green to dark blue after several days standing at room temperature. The broad ^{1}H NMR signal seems to be due to a small paramagnetic impurity, and we cannot specify the cause and the nature of the impurity; it may be produced by the unavoidable degradation of **1**, or it may be caused by the unavoidable presence of a very trace amount of $\mathrm{H_2O}$ in the solvent. Figure 3 shows the ^{31}P NMR spectrum of **1** measured on a 500 MHz instrument. Totally 8 lines are observed, which correspond to the four TMP molecules, each being split into a doublet. The assignment in Figure 3 was made as follows: since the ligands trans to P3 and P4 are both AN, and these ^{31}P atoms are expected to show similar chemical shifts, the quasi-quartet peaks at 132.80−134.03 ppm were assigned to P3 and P4. Among the remaining P atoms, P1 was assigned to the doublet at 128.95 and 129.37 ppm, since only P1 has an acetonate oxygen atom trans to it, whereas all the other three P atoms have trans AN nitrogen atoms. The Ru−P1 distance is also significantly shorter, compared to the other three Ru−P distances (Table 5). These facts support the assignment of P1 to the doublet that has only one distinct chemical shift among others. The ^{31}P chemical shifts are 134.96, 134.55, 134.03, 133.59, 133.23, 132.80, 129.37, and 128.95 ppm.

Acknowledgment. The present study is financially supported by a Grant-in-Aid for Scientific Research on Priority Area of “Activation of Small Molecules” (04241225) from the Ministry of Education, Science, and Culture of Japan.

Supplementary Material Available: Tables of crystal data, data collection, and refinement details, anisotropic thermal parameters, bond distances, and bond angles and a figure showing ^{1}H NMR spectra for **1** (8 pages). Ordering information is given on any current masthead page.

IC940424S