usually two or more metal centers are required to activate the SR ligand in this manner.[19] In the few cases where a single metal center abstracts sulfur from alkane thiols or thioethers, it is in a high oxidation state and therefore an exceedingly electrophilic center.[20] Provided a more general synthetic route to other cationic zirconocene thiolato derivatives may be uncovered, potential exists for a more detailed study of the C–S bond-cleavage step in these systems. We are also exploring the possibility of trapping the presumed intermediate, "$Cp_2Zr{=}S$", which should be highly reactive.[21]

Acknowledgment. Funding from the Natural Sciences and Engineering Research Council of Canada and the University of Guelph is gratefully acknowledged.

Supplementary Material Available: Tables of hydrogen atom parameters, crystallographic details, anisotropic thermal parameters, and complete interatomic distances and angles (7 pages). Ordering information is given on any current masthead page.

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Reaction of $Fe(\eta\text{-}C_5H_4)_2S_3$ with $M_3(CO)_{12}$ (M = Ru, Os). Structure of $Fe(\eta\text{-}C_5H_4S)_2Ru_2(CO)_6$ and $Fe(\eta\text{-}C_5H_4S)_2(\mu_3\text{-}S)Os_4(CO)_{11}$

William R. Cullen,* Ana Talaba, and Steven J. Rettig

Chemistry Department, University of British Columbia, Vancouver, BC, Canada V6T 1Z1

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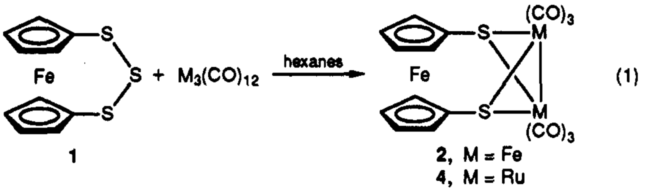
Summary: The thermal reaction of 1,2,3-trithia[3]ferrocenophane (1) with $Ru_3(CO)_{12}$ in refluxing hexanes affords the complex $Fe(\eta\text{-}C_5H_4S)_2Ru_2(CO)_6$ (4) in moderate yield. The reaction of 1 with $Os_3(CO)_{12}$ yields $Fe(\eta\text{-}C_5H_4S)_2(S)Os_2(CO)_6$ (5) in low yield in refluxing cyclohexane and four products in moderate to low yields in refluxing toluene. These compounds were identified as the diosmium species $Fe(\eta\text{-}C_5H_4S)_2Os_2(CO)_6$ (6), the triosmium species $Fe(\eta\text{-}C_5H_4S)_2Os_3(CO)_{10}$ (7), and the tetraosmium species $Fe(\eta\text{-}C_5H_4S)_2(\mu_3\text{-}S)Os_4(CO)_{11}$ (8) and $Fe(\eta\text{-}C_5H_4S)_2(\mu_3\text{-}S)_2Os_4(CO)_{10}$ (9). Only complexes 4 and 8 were characterized by using X-ray crystallography. The common sawhorse geometry is found for 4, with the $Fe(\eta\text{-}C_5H_4S)_2$ group bridging the two $Ru(CO)_3$ moieties. The osmium cluster 8 consists of a μ_3-S ligand bridging a spiked triangle of osmium atoms with the $Fe(\eta\text{-}C_5H_4S)_2$ ligand bridging the spike Os–Os bond. Both structures have eclipsed and nearly parallel cyclopentadienyl rings. Crystals of 4 are monoclinic, with $a = 7.685$ (3) Å, $b = 13.866$ (4) Å, $c = 18.225$ (2) Å, $\beta = 96.43$ (2)°, $Z = 4$, and space group $P2_1/n$, and those of 8 are also monoclinic, with $a = 11.872$ (2) Å, $b = 14.230$ (3) Å, $c = 16.543$ (4) Å, $\beta = 101.20$ (2)°, $Z = 4$, and space group $P2_1/n$. The structures were solved by the Patterson method and were refined by full-matrix least-squares procedures to $R = 0.028$ and 0.033 for 3773 and 4262 reflections with $I \geq 3\sigma(I)$, respectively.

Bishop and Davison[1a] first reported that ferrocene derivatives with donor atoms in the 1,1′-positions, for example $Fe(\eta\text{-}C_5H_4PPh_2)_2$, can coordinate to some transition metals to give chelate complexes such as $(L\text{-}L)Mo(CO)_4$, and a number of workers have since made contributions to this field.[1]

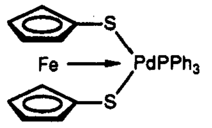
The isolation of 1,2,3-trithia[3]ferrocenophane (1)[2] provided a route to ferrocene-1,1′-dithiol and bidentate dithiolate complexes. A series of 1,3-dithia[3]-ferrocenophanes of main-group elements was prepared from the dithiol and the appropriate halide.[3] The reaction of 1 with $Fe_3(CO)_{12}$ afforded 2[4] (eq 1). 1 was also reacted with low-valent, coordinatively unsaturated transition-metal species such as tetrakis(triphenylphosphine)palladium(0). The product proved to be 3, which contains a Fe→Pd bond, rather than the expected dithiolate derivative.[5,6]



(1)

1

2, M = Fe
4, M = Ru



3

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This note describes the reaction of 1 with the cluster carbonyls $M_3(CO)_{12}$ (M = Ru, Os). Our objective was to investigate the possibility of preparing compounds with Fe→M bonds (M = Os, Ru) analogous to 3 in the knowledge that such compounds are available by reacting ferrocenylphosphines with these carbonyls.[7] There was also the possibility that further examples of ferrocyne and ferrodicyne complexes would be obtained.[8] Unfortunately neither possibility eventuated and the isolated products all contain the ferrocenedithiolato ligand.

Experimental Section

Reactions were performed under a nitrogen atmosphere by using conventional Schlenk procedures; solvents were freshly purified and distilled. Ruthenium carbonyl $Ru_3(CO)_{12}$ was prepared by carbonylation of methanol solutions of $RuCl_3 \cdot xH_2O$ at 125 °C and 55–60 atm.[9] Commercially available osmium carbonyl $Os_3(CO)_{12}$ was used. Column chromatography was carried out by using silica gel (230–400 mesh). Preparative TLC separations were carried out by using commercial silica gel coated glass plates (0.5-mm thickness). Reagent-grade solvents were used for routine column chromatography. Product mixtures were monitored throughout all experimental procedures by using TLC on aluminum-backed silica gel coated plates (0.2-mm thickness). ^1H NMR spectra were recorded by using Bruker WH200, Varian XL-300, and Bruker WH400 spectrometers. Chemical shifts are reported in ppm and quoted relative to tetramethylsilane (TMS) as an external standard.

Low-resolution mass spectra, electron ionization (EI, probe temperature 120–150 °C) and fast atom bombardment (FAB), were recorded on Kratos MS 50 and AEI MS-9 spectrometers, and infrared spectra were determined by using a Perkin-Elmer 598 instrument.

Elemental analyses were performed by Mr. Peter Borda of this department.

Preparation of 1,2,3-Trithia[3]ferrocenophane (1). The reaction of sulfur with dilithioferrocene in 1,2-dimethoxyethane was carried out as described in the literature.[2] The ether extracts of the resulting reaction mixture were evaporated to afford a dark gum.

Chromatographic examination (TLC) showed two major products and traces of three other compounds. The analytically pure ferrocenophane was isolated by using column chromatography on silica and petroleum ether/dichloromethane (80/20) as eluent. Removal of the solvent afforded 1,2,3-trithia[3]-ferrocenophane (1) as an orange crystalline mass (yield 45%).

The second band to elute was characterized as diferrocenyl sulfide, a yellow crystalline solid (yield ~20%). ^1H NMR ($CDCl_3$): δ 4.30 (s, 8), 4.16 (s, 10). Mass spectrum (EI; selected m/z (relative intensity)): 402 (100, M^+), 370 (4.7), 306 (39.1). This chromatographic workup gives better results than the procedure described in the literature.[2]

Reaction of 1 with $Ru_3(CO)_{12}$. (a) In Hexane. A 100-mL three-necked flask equipped with a magnetic stirbar and a reflux condenser was charged with 0.550 g (1.96 mmol) of $Fe(C_5H_4)_2S_3$, 2.500 g (3.92 mmol) of $Ru_3(CO)_{12}$, and 50 mL of hexane. The resulting suspension was stirred, heated at reflux for 18 h, cooled to room temperature, and filtered. The solid was extracted with dichloromethane (30 mL), and the extract was combined with the brown residue obtained by evaporating the filtrate. Part of the solvent was removed under vacuum, and the remaining solution was transferred onto a silica gel chromatographic column. The reaction product 4 and $Ru_3(CO)_{12}$ (~60% total) coeluted with petroleum ether as eluent. Compound separation was achieved by preparative TLC (petroleum ether or petroleum ether/dichloromethane (80/20) as eluent). Orange-red crystals of 4 were obtained after solvent removal and crystallization from hexane/dichloromethane (25/75) (yield 35%). ^1H NMR ($CDCl_3$): δ 4.34 (pseudo t, 4), 4.03 (pseudo t, 4). IR (CH_2Cl_2; ν_{CO}, cm^{-1}): 2090 (s), 2060 (s), 2040 (w), 2015 (s, br). Mass spectrum (EI; selected m/z (relative intensity)): 620 (100, M^+), 592 (34.3), 564 (23.6), 536 (26.1), 508 (28.3), 480 (48.5), 452 (85.7, M^+ – 6 CO).

(b) In Cyclohexane. The reaction of 1 with $Ru_3(CO)_{12}$ was carried out in cyclohexane by following the same procedure as for the reaction in hexane. Orange-red crystals of 4 were obtained in lower yield (~10%). A brown band which did not elute with a variety of solvents (petroleum ether, petroleum ether/dichloromethane, dichloromethane, ethylacetate, methanol) comprised ~75% of the mixture transferred onto the silica gel column.

Reaction of 1 with $Os_3(CO)_{12}$. (a) In Hexane. A mixture of 1 (0.28 g, 0.10 mmol) and $Os_3(CO)_{12}$ (0.100 g, 0.11 mmol) in a three-necked flask was stirred and heated in hexanes (40 mL) at reflux for 18 h. The reaction mixture was monitored by using TLC with petroleum ether/dichloromethane (80/20) as eluent. No reaction was evident after 18 h.

(b) In Cyclohexane. A mixture of 1 (0.28 g, 0.10 mmol) and $Os_3(CO)_{12}$ (0.100 g, 0.11 mmol) was stirred and heated in cyclohexane (40 mL) at reflux for 44 h. A dark brown suspension was produced. Chromatographic examination (TLC) indicated the presence of four main compounds (of which 1 and $Os_3(CO)_{12}$ represented ~60%) and traces of another four. The reaction mixture was filtered, and the isolated solid was extracted with pentane and then with dichloromethane. The extracts were combined with the filtrate, and the solvent was removed under reduced pressure. Preparative TLC (pentane/dichloromethane 50/50) afforded only one product in a reasonable yield (10%). Crystals of this yellow solid, 5, could not be obtained from a range of dichloromethane/hexane and dichloromethane/pentane mixtures, toluene, or dichloromethane/methanol (layer technique). ^1H NMR ($CDCl_3$): δ 4.57 (pseudo t, 4), 4.28 (pseudo t, 4). IR (CH_2Cl_2; ν_{CO}, cm^{-1}): 2095 (s), 2075 (w), 2040 (w), 2005 (s, br). Mass spectrum (EI; selected m/z (relative intensity)): 830 (35.0, M^+), 802 (9.4), 774 (12.1), 746 (10.0), 718 (30.4), 690 (22.0), 662 (43.8, M^+ – 6 CO), 630 (5.1).

(c) In Toluene. The reaction in toluene was carried out by using the same procedure described above. The reaction mixture was stirred and heated at reflux for 18 h. The color changed from yellow-orange to orange and then to red. A red solution with a brown precipitate was finally obtained. The solvent was removed under vacuum to yield a brown-red residue that was almost completely soluble in dichloromethane. Chromatographic examination (TLC) indicated the presence of five main compounds and traces of another four. The brown-red mixture was slurried in dichloromethane with silica gel, and after solvent removal, the gel was applied onto the top of a silica gel column. Elution with petroleum ether/dichloromethane (6/1) gave five bands (yellow, orange, yellow-orange, yellow, and brown), but the last two did not elute from the column. The yellow and orange fractions contained five compounds. Isolation of four of these was achieved by careful repeated chromatography. Slow evaporation of the solvent afforded yellow-orange crystals of compound 6 (yield 10%), orange-yellow crystals (needles) of 7 (yield 10%), dark red crystals of 8 (yield 25%), and orange crystals (stars) of 9 (yield 8%). Compounds 6 and 7 could not be recrystallized from toluene and a range of dichloromethane/pentane and dichloromethane/hexane mixtures. Compound 9 resisted attempts at recrystallization from a range of dichloromethane/pentane mixtures. 6: ^1H NMR ($CDCl_3$) δ 4.31 (pseudo t, 4), 4.04 (pseudo t, 4); IR (CH_2Cl_2; ν_{CO}, cm^{-1}) 2090 (w), 2060 (s), 2040 (w), 1990 (s); mass spectrum (FAB; selected m/z) 854 (M^+), 826, 798, 770, 742, 714, 686, 658, 630 (M^+ – 8 CO), 532, 476. Anal. Calcd for $C_{18}H_8FeO_8Os_2S_2$: C, 25.29; H, 0.94. Found: C, 25.70, H, 1.12. 7: ^1H NMR ($CDCl_3$) δ 4.64 (pseudo t, 4), 4.34 (pseudo t, 4); IR (CH_2Cl_2; ν_{CO}, cm^{-1}) 2075 (w), 2050 (s), 2020 (s, br), 1995 (s, br); mass spectrum (EI; selected m/z (relative intensity)) 1100 (16.4, M^+), 1072 (6.5), 1044 (8.9), 1016 (14.8), 988 (13.5), 960 (8.4), 932 (18.6), 904 (13.8), 876 (12.0), 848 (10.0), 820 (25.4, M^+ – 10 CO), 798 (16.4, $Os_3(CO)_7S^+$), 788 (8.00), 602 (4.9, Os_3S^+). 8: ^1H NMR ($CDCl_3$) δ 4.88 (m, 2), 4.34 (m, 2), 4.23 (m, 2), 407 (m, 2); IR (CH_2Cl_2; ν_{CO}, cm^{-1}) 2100 (s), 2080 (s), 2055 (s), 2010 (w, br), 1720 (s, br); mass spectrum (EI; selected m/z (relative intensity)) 1350 (25.8, M^+), 1322 (16.9), 1238 (9.1), 1210 (26.1), 1182 (17.1), 1154 (14.2), 1126 (11.9), 1098 (13.9),

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Table I. Crystallographic Data[a]

compd	4	8
formula	$C_{16}H_8FeO_6Ru_2S_2$	$C_{21}H_8FeO_{11}Os_4S_3$
fw	618.34	1349.11
color, habit	orange, plate	green, prism
cryst size, mm	0.05 × 0.35 × 0.40	0.18 × 0.24 × 0.28
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$
a, Å	7.685 (3)	11.872 (2)
b, Å	13.866 (4)	14.230 (3)
c, Å	18.225 (2)	16.543 (4)
β, deg	96.43 (2)	101.20 (2)
V, Å^3	1929.8 (8)	2741.4 (9)
Z	4	4
D_{calc}, g/cm^3	2.128	3.269
$F(000)$	1192	2400
μ(Mo Kα), cm^{-1}	24.96	192.86
transmissn factors	0.51–1.00	0.51–1.00
scan type	ω–2θ	ω–2θ
scan range, deg in ω	1.21 + 0.35 tan θ	0.94 + 0.35 tan θ
scan rate, deg/min	32	32
data collected	$+h,+k,\pm l$	$+h,+k,\pm l$
$2\theta_{max}$, deg	60	60
cryst decay	negligible	negligible
total no. of rflns	6248	8661
no. of unique rflns	5856	8301
R_{merge}	0.039	0.078
no. of rflns with $I \geq 3\sigma(I)$	3773	4262
no. of variables	277	362
R	0.028	0.033
R_w	0.035	0.037
GOF	1.36	1.33
max Δ/σ (final cycle)	0.002	0.03
residual density, e/Å^3	−0.74 to +0.95	−1.44 to +1.75 (near Os)

[a] Conditions and additional details: temperature 294 K, Rigaku AFC6S diffractometer, Mo Kα radiation (λ = 0.71069 Å), graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1, up to 8 rescans), $\sigma^2(F^2) = [S^2(C + 4B) + (0.03F^2)^2]/(L_p)^2$ (S = scan rate, C = scan count, B = normalized background count), function minimized $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and GOF $= [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$. Values given for R, R_w, and GOF are based on those reflections with $I \geq 3\sigma(I)$.

Table II. Final Atomic Coordinates (Fractional) and B_{eq} Values (Å^2) for 4[a]

atom	x	y	z	B_{eq}
Ru(1)	0.65202 (4)	0.50267 (2)	0.21415 (2)	3.51 (1)
Ru(2)	0.42115 (4)	0.37446 (2)	0.15062 (1)	3.19 (1)
Fe(1)	0.40068 (6)	0.36069 (4)	0.38669 (3)	3.17 (2)
S(1)	0.3471 (1)	0.50111 (6)	0.23109 (4)	2.99 (3)
S(2)	0.6541 (1)	0.33404 (7)	0.24470 (5)	3.45 (3)
O(1)	0.8551 (6)	0.5943 (3)	0.3506 (2)	9.2 (2)
O(2)	0.9552 (4)	0.4585 (4)	0.1272 (2)	8.4 (2)
O(3)	0.5528 (5)	0.6794 (3)	0.1204 (2)	8.0 (2)
O(4)	0.1258 (5)	0.2302 (3)	0.1655 (2)	7.7 (2)
O(5)	0.6359 (6)	0.2692 (3)	0.0455 (2)	9.4 (3)
O(6)	0.2480 (5)	0.4918 (3)	0.0222 (2)	7.1 (2)
C(1)	0.2936 (4)	0.4638 (2)	0.3184 (2)	3.1 (1)
C(2)	0.3611 (6)	0.5056 (3)	0.3874 (2)	4.0 (2)
C(3)	0.2728 (6)	0.4612 (3)	0.4430 (2)	4.7 (2)
C(4)	0.1532 (5)	0.3950 (4)	0.4100 (2)	4.8 (2)
C(5)	0.1636 (5)	0.3959 (3)	0.3324 (2)	3.8 (1)
C(6)	0.5886 (4)	0.3042 (2)	0.3319 (2)	3.1 (1)
C(7)	0.6633 (5)	0.3416 (3)	0.4008 (2)	4.0 (2)
C(8)	0.5866 (6)	0.2914 (4)	0.4573 (2)	4.9 (2)
C(9)	0.4687 (7)	0.2250 (3)	0.4239 (2)	5.1 (2)
C(10)	0.4688 (6)	0.2310 (3)	0.3457 (2)	4.0 (2)
C(11)	0.7790 (7)	0.5623 (3)	0.3000 (3)	5.7 (2)
C(12)	0.8459 (6)	0.4767 (4)	0.1610 (3)	5.5 (2)
C(13)	0.5954 (6)	0.6151 (3)	0.1566 (3)	5.2 (2)
(C14)	0.2381 (6)	0.2816 (3)	0.1592 (2)	4.7 (2)
C(15)	0.5523 (7)	0.3058 (4)	0.0845 (2)	5.8 (2)
C(16)	0.3084 (6)	0.4472 (3)	0.0702 (2)	4.4 (2)

[a] $B_{eq} = {}^8/_3\pi^2\sum\sum U_{ij}a_i a_j(\mathbf{a}_i \cdot \mathbf{a}_j)$.

Table III. Final Atomic Coordinates (Fractional) and B_{eq} Values (Å^2) for 8[a]

atom	x	y	z	B_{eq}
Os(1)	0.40998 (3)	0.55015 (3)	0.20184 (2)	1.99 (1)
Os(2)	0.62405 (3)	0.45283 (4)	0.24281 (3)	2.40 (2)
Os(3)	0.62438 (4)	0.64387 (3)	0.25486 (3)	2.39 (2)
Os(4)	0.17890 (3)	0.55246 (4)	0.14614 (3)	2.26 (2)
Fe(1)	0.2339 (1)	0.5428 (1)	0.4106 (1)	2.86 (6)
S(1)	0.5357 (2)	0.5405 (2)	0.3328 (2)	2.3 (1)
S(2)	0.2781 (2)	0.4327 (2)	0.2356 (2)	2.3 (1)
S(3)	0.2808 (2)	0.6652 (2)	0.2423 (2)	2.5 (1)
O(1)	0.4327 (8)	0.7012 (7)	0.0773 (6)	4.9 (5)
O(2)	0.4274 (8)	0.4118 (7)	0.0655 (6)	4.9 (5)
O(3)	0.8573 (7)	0.4279 (8)	0.3517 (6)	5.2 (5)
O(4)	0.5400 (9)	0.2599 (8)	0.2869 (7)	5.6 (5)
O(5)	0.7145 (9)	0.4226 (9)	0.0850 (7)	6.5 (6)
O(6)	0.7216 (9)	0.6871 (8)	0.1007 (6)	5.9 (6)
O(7)	0.540 (1)	0.8334 (7)	0.3067 (7)	5.6 (5)
O(8)	0.8567 (8)	0.6670 (9)	0.3657 (6)	5.5 (5)
O(9)	−0.0622 (7)	0.5497 (7)	0.1836 (6)	4.1 (4)
O(10)	0.128 (1)	0.7072 (7)	0.0156 (6)	5.7 (5)
O(11)	0.1260 (8)	0.4009 (8)	0.0125 (6)	5.3 (5)
C(1)	0.2475 (8)	0.4347 (7)	0.3354 (7)	2.3 (4)
C(2)	0.137 (1)	0.4337 (9)	0.3548 (7)	3.1 (5)
C(3)	0.148 (1)	0.427 (1)	0.4398 (8)	3.9 (6)
C(4)	0.268 (1)	0.419 (1)	0.4749 (8)	4.1 (6)
C(5)	0.330 (1)	0.4239 (9)	0.4124 (7)	3.0 (5)
C(6)	0.2557 (9)	0.6569 (9)	0.3433 (7)	2.7 (4)
C(7)	0.147 (1)	0.659 (1)	0.3670 (7)	3.6 (5)
C(8)	0.165 (1)	0.660 (1)	0.4540 (8)	4.3 (6)
C(9)	0.283 (1)	0.658 (1)	0.4837 (8)	4.2 (6)
C(10)	0.340 (1)	0.656 (1)	0.4178 (8)	3.4 (5)
C(11)	0.435 (1)	0.646 (1)	0.1267 (7)	3.3 (5)
C(12)	0.432 (1)	0.4602 (9)	0.1206 (8)	3.1 (5)
C(13)	0.769 (1)	0.436 (1)	0.3086 (7)	3.5 (5)
C(14)	0.569 (1)	0.332 (1)	0.2647 (9)	4.0 (6)
C(15)	0.680 (1)	0.432 (1)	0.1435 (8)	3.6 (6)
C(16)	0.683 (1)	0.672 (1)	0.1595 (8)	3.6 (6)
C(17)	0.570 (1)	0.763 (1)	0.2832 (8)	3.5 (5)
C(18)	0.769 (1)	0.659 (1)	0.3227 (7)	3.6 (5)
C(19)	0.028 (1)	0.551 (1)	0.1700 (7)	3.2 (5)
C(20)	0.147 (1)	0.649 (1)	0.0673 (8)	3.6 (5)
C(21)	0.148 (1)	0.457 (1)	0.0643 (7)	3.6 (5)

[a] $B_{eq} = {}^8/_3\pi^2\sum\sum U_{ij}a_i a_j(\mathbf{a}_i \cdot \mathbf{a}_j)$.

1070 (14.5), 1042 (36.6, M$^+$ − 11 CO), 1010 (6.4), 798 (7.7, $Os_3(CO)_7S^+$). Anal. Calcd for $C_{22}H_8FeO_{11}Os_4S_3$: C, 18.66; H, 0.59. Found: C, 19.00; H, 0.80. **9**: ^{1}H NMR ($CDCl_3$) δ 5.09 (m, 2), 4.68 (m, 2), 4.35 (m, 2), 4.28 (m, 2); IR (CH_2Cl_2; ν_{CO}, cm^{-1}) 2110 (w), 2085 (s), 2060 (w), 2030 (s, br), 2100 (w); mass spectrum (EI; selected m/z (relative intensity)) 1354 (8.7, M$^+$), 1242 (5.4), 1186 (5.7), 1074 (8.2, M$^+$ − 10 CO), 1070 (7.1).

X-ray Crystallographic Analyses. Crystallographic data for $Fe(\eta\text{-}C_5H_4S)_2Ru_2(CO)_6$ (**4**) and $Fe(\eta\text{-}C_5H_4S)_2(\mu_3\text{-}S)Os_4(CO)_{11}$ (**8**) appear in Table I. The final unit-cell parameters were obtained by least squares on the setting angles for 25 reflections with 2θ = 42.7–49.1° for **4** and 42.3–48.7° for **8**. The intensities of three standard reflections, measured every 200 reflections throughout the data collection, remained constant for both compounds. The data were processed[10] and corrected for Lorentz and polarization effects and absorption (empirical, based on azimuthal scans for four reflections).

Both structures were solved by heavy-atom methods, the coordinates of the metal atoms being determined from the Patterson functions and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. All non-hydrogen atoms of both complexes were refined with anisotropic thermal parameters. Hydrogen atoms were refined with isotropic thermal parameters for **4** and were fixed in idealized positions (C–H = 0.98 Å, $B_H = 1.2B_{\text{bonded atom}}$ for **8**. Corrections for secondary extinction were applied for both structures, the final values of the extinction coefficient being 3.32×10^{-7} for **4** and 1.28×10^{-7} for **8**. Neutral atom scattering factors for all atoms and anomalous dispersion

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(10) TEXSAN/TEXRAY structure analysis package, which includes versions of the following: DIRDIF, direct methods for difference structures, by P. T. Beurskens; ORFLS, full-matrix least squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; ORTEP II, illustrations, by C. K. Johnson.

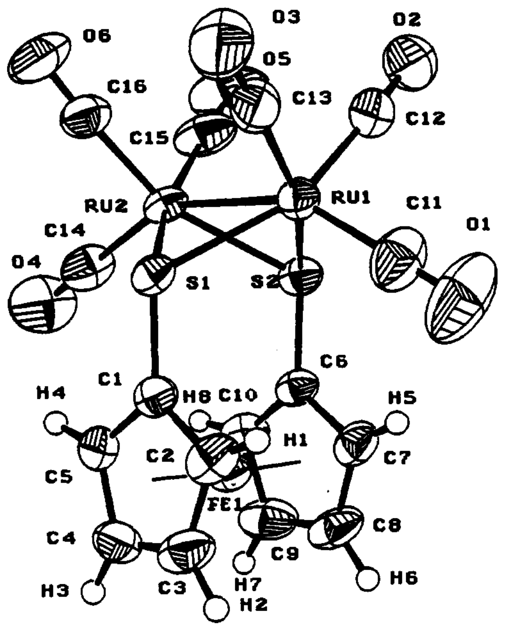

Figure 1. Perspective view of 4 (50% probability thermal ellipsoids are shown for the non-hydrogen atoms). Selected bond lengths (Å) and angles (deg): Ru(1)-Ru(2) = 2.6812 (7), Ru(1)-S(1) = 2.398 (1), Ru(2)-S(1) = 2.397 (1), S(1)-C(1) = 1.765 (3); Ru(2)-Ru(1)-S(1) = 55.99 (3), Ru(1)-Ru(2)-S(1) = 56.01 (3), Ru(2)-Ru(1)-C(11) = 151.9 (1), S(1)-Ru(1)-S(2) = 86.70 (3), Ru(1)-S(2)-Ru(2) = 67.83 (2).

corrections for the non-hydrogen atoms were taken from ref 11. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Tables II and III. Tables of complete bond lengths and angles, hydrogen atom parameters, anisotropic thermal parameters, and complete planes are included as supplementary material.

Results and Discussion

The thermal reaction of 1 with $Ru_3(CO)_{12}$ in refluxing hexane affords complex 4, an orange-red air-stable solid that is soluble in common solvents (eq 1). The formulation of 4 as an electron-precise dinuclear complex is supported by the spectroscopic data and a solid-state single-crystal X-ray analysis (Figure 1).

The ^1H NMR spectrum consists of two pseudotriplets at δ 4.03 and 4.34 corresponding to the α and β protons of the C_5H_4S rings. The chemical shift difference of 0.31 ppm between these multiplets is comparable with that found for the presumably isostructural derivative 2.[4] The solid-state structure of 2 was not determined.

The structure of 4 shows that the dithiolate symmetrically bridges the two $Ru(CO)_3$ moieties. The Ru-Ru separation of 2.6812 (7) Å is similar to that found in other ruthenium dimers (average 2.70 Å),[12] and the overall sawhorse arrangement is as commonly found.[13] Each sulfur atom is symmetrically bound to the two ruthenium atoms.

The two cyclopentadienyl rings are nearly parallel, the dihedral angle between the rings being only 5.38°. This small tilt is close to that observed in $(Fe(\eta\text{-}C_5H_4SR)_2)MX_2$ (R = *i*-Bu, M = Pd, Pt, X = Cl) (1.90°)[1c] and is significantly smaller than that found in some 2-metalla[3]ferrocenophanes such as (1,1′-ferrocenedithiolato-*S*,*S*′,*Fe*)(triphenylphosphine)platinum(II) (21.0°), the platinum analogue of 3.[6a] The rings exhibit an eclipsed conformation and are virtually planar; the largest deviation of any carbon from the mean plane is 0.055 Å. In 1 the sulfur atoms in the 1- and 3-positions are coplanar with the eclipsed cyclopentadienyl rings;[14] however, in 4 the two sulfur atoms are displaced outward from these planes (mean 0.147 Å).

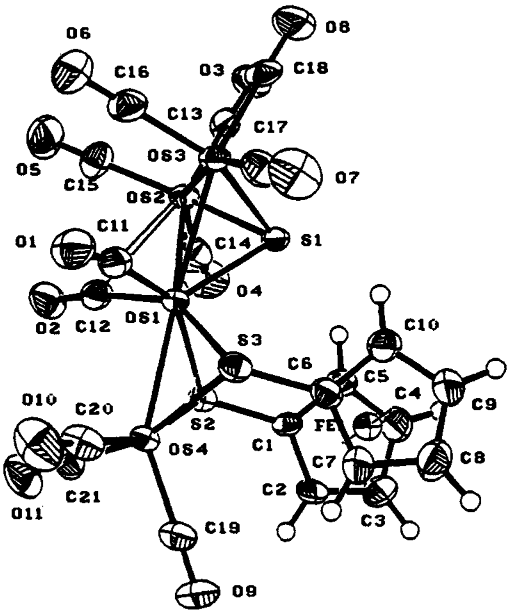

Figure 2. Perspective view of 8 (50% probability thermal ellipsoids are shown for the non-hydrogen atoms). Selected bond lengths (Å) and angles (deg): Os(1)-Os(2) = 2.8576 (7), Os(1)-Os(3) = 2.8563 (7), Os(1)-Os(4) = 2.7192 (7), Os(2)-Os(3) = 2.7257 (9), Os(1)-S(1) = 2.385 (3), Os(1)-S(2) = 2.428 (3), Os(2)-S(1) = 2.341 (3), Os(4)-S(2) = 2.410 (3); Os(2)-Os(1)-Os(3) = 56.98 (2), Os(2)-Os(1)-Os(4) = 151.45 (3), Os(1)-S(1)-Os(3) = 74.42 (8), Os(1)-S(2)-Os(4) = 68.40 (7), Os(1)-C(11)-Os(3) = 72.5 (4).

Not unexpectedly, the thermal reaction of 1 with $Os_3(CO)_{12}$ requires a higher temperature to initiate than the reaction with $Ru_3(CO)_{12}$. There is no reaction in refluxing hexanes, but a low yield of a molecule of formula $Fe(\eta\text{-}C_5H_4S)_2(S)Os_2(CO)_6$ (5) is obtained in refluxing cyclohexane. Reaction in refluxing toluene affords one diosmium complex, $Fe(\eta\text{-}C_5H_4S)_2Os_2(CO)_8$ (6), and one triosmium complex, $Fe(\eta\text{-}C_5H_4S)_2Os_3(CO)_{10}$ (7), both in low yield, and two tetraosmium complexes, $Fe(\eta\text{-}C_5H_4S)_2(\mu_3\text{-}S)Os_4(CO)_{11}$ (8) and $Fe(\eta\text{-}C_5H_4S)_2(\mu_3\text{-}S)_2Os_4(CO)_{10}$ (9), in moderate and low yield, respectively.

Complex 8 was characterized by X-ray analysis (Figure 2). The structure reveals a spiked triangular configuration of osmium atoms. A sulfido ligand triply bridges the osmium triangle, while each S atom of the ferrocenedithiolate ligand bridges the two osmium atoms, Os(1) and Os(4), that form the spike bond. The bridges are again essentially symmetrical with equal S-Os distances. There are two weak semibridging interactions in the molecule that involve the two carbonyls attached to Os(1). The triply bridging sulfide and the semibridging carbonyls shorten the Os-Os bonds of the Os_3 triangle (average 2.8132 Å) relative to the value found in the parent carbonyl $Os_3(CO)_{12}$ (average 2.877 Å).[15] The spike Os-Os bond (Os(1)-Os(4) = 2.7192 (7) Å) is shorter than any of the Os-Os bonds of the tri-

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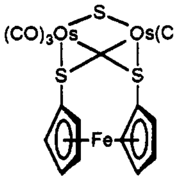

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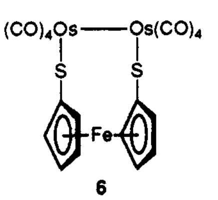

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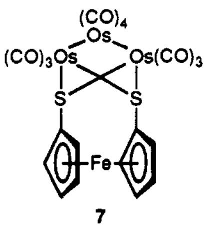

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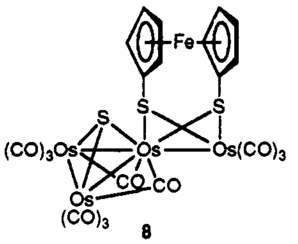

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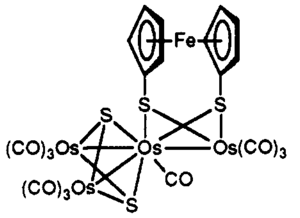

9

angle. The Os–S distances (average 2.354 Å) are similar to the average values of 2.405 and 2.390 Å found respectively in the open cluster compound $Os(\mu_3\text{-}S)_2(CO)_9$[16] and the closed cluster compound $Os_3(\mu\text{-}S)(\mu\text{-}H)_2(CO)_9$.[17] The Os–S–Os angles are faily acute; however, they lie in the range 65–75° reported for M–S–M angles in cluster compounds.[18]

The two cyclopentadienyl rings are eclipsed and nearly parallel, the dihedral angle between the two rings being only 5.91°. This small tilt is close to that observed in the ruthenium complex 4 (5.38°). The rings are virtually planar, while the two sulfur atoms (S(2) and S(3)) are displaced outward from the Cp ring planes (average 0.150 Å) again as in 4.

The semibridging carbonyls of 8 may well become more symmetrical in solution, because a strong absorption is seen in the bridging carbonyl region of the infrared spectrum of this compound.

Compound 9 proved to be very difficult to purify, and good microanalytical data were not obtained. The structure shown is based on strong spectroscopic evidence. First, the ^1H NMR spectrum is very similar to that of 8, showing four equal-intensity multiplets. Second, the mass spectrum indicates that 9 has one less CO group and one more sulfur atom than 8. The mass spectra of 8 and 9 show $Os_4(S)Fe(C_5H_4S)_2^+$ and $Os_4(S)_2Fe(C_5H_4S)_2^+$ ions after the loss of 11 and 10 carbonyls, respectively, and the ion $Os_4(CO)_8^+$ is present in the spectra of both 8 and 9. These data indicate that 8 and 9 are related as indicated.

Similar problems with purity were encountered with 5 and 7. The structures suggested for these two molecules seem reasonable on the basis of the spectroscopic data, particularly the mass spectrum and the ^1H NMR spectra, which indicate a symmetrical structure. The mass spectrum of 5 shows stepwise loss of six CO groups and one sulfur atom. The resulting ion $Fe(C_5H_4S)_2Os_2^+$ is also seen in the mass spectrum of 6, where the parent ion corresponds to the formulation $Fe(C_5H_4S)_2Os_2(CO)_8$. Microanalytical data for 6 support this, and a possible structure is as indicated.

The reaction of 1 with $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ under mild conditions affords intractable solids. Similar results were obtained when ((dimethylamino)methyl)-1,2,3-trithia[3]ferrocenophane was reacted with a variety of transition-metal complexes such as $Ru_3(CO)_{12}$ and Pd(COD)-Cl_2.[19]

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and NATO for financial support.

Supplementary Material Available: Tables of bond lengths and angles, hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least-squares planes for 4 and 8 (29 pages). Ordering information is given on any current masthead page.

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Additions and Corrections

Frank Bottomley* and Selami Karslioglu: Organometallic Oxides: Preparation and Properties of the Diamagnetic Trinuclear Cluster $\{[(\eta\text{-}C_5Me_5)Nb(\mu\text{-}Cl)(\mu\text{-}O)]_3\}^+$ and Related Chloride–Oxides of Niobium. **1992**, *11*, 326.

The crystal structure of $\{2^+\}_2\{Zn_6Cl_{14}^{2-}\}$ can be described in the monoclinic space group $C2/m$, with cell dimensions a = 23.592 (4) Å, b = 17.806 (2) Å, c = 11.117 (2) Å, and β = 105.97 (1)°. The cell is related to the triclinic $P\bar{1}$ used in the refinement by the transformation matrix −1,1,1, 0,−1,1, 100. The structure has been rerefined in $C2/m$ using new data (by Dr. Paul D. Boyle). The disorder in the $Zn_6Cl_{14}^{2-}$ anions and η-C_5Me_5 rings which was reported using $P\bar{1}$ remains in $C2/m$. The distances and angles in the $[Nb(\mu\text{-}Cl)(\mu\text{-}O)]_3$ core are identical within experimental error to those reported using $P\bar{1}$. Therefore, there is no change in the discussion or conclusions of the paper. Complete details of the $C2/m$ refinement are available as supplementary material.

Supplementary Material Available: Tables of crystal and refinement data, positional and thermal parameters, and bond distances and angles for the refinement in space group $C2/m$ and a table comparing dimensions of $\{2^+\}_2\{Zn_6Cl_{14}^{2-}\}$ in $P\bar{1}$ and $C2/m$ (7 pages). Ordering information is given on any current masthead page.