which form a second divalent complex which contains much less hydride (by deuteriolysis) and a smaller percentage of samarium.[26] This latter divalent product can be purified, however, by a subsequent low temperature THF recrystallization to provide purple, crystalline $(C_5Me_5)_2Sm(THF)_2$ (I), identified by analytical,[27] magnetic,[27] infrared,[27] and X-ray diffraction methods. Since this reaction can be conveniently run to provide a recrystallized yield of 0.5 g of I,[28] this metal vapor synthesis provides the first preparative scale route to a soluble divalent organosamarium complex.[29]

I is not only the first soluble divalent organosamarium complex but also the first structurally characterized divalent organosamarium system. Two crystallographically independent molecules are found in the unit cell[30] and do not differ significantly in bonding parameters. Figure 1 presents a view of one of the molecules. Average $Sm-C(\eta^5)$ and $Sm-O$ bond lengths are 2.86 (3) and 2.63 (1) Å, respectively. In comparison, $(C_5Me_5)_2Yb(THF)(C_7H_8)_{0.5}$[10] has $Yb-C(\eta^5)$ and $Yb-O$ distances of 2.66 and 2.41 Å, respectively. The differences in these distances, 0.20 and 0.22 Å, are only slightly larger than the difference in ionic radii of Sm(II) and Yb(II), 0.18^{31}–0.19.[32] The small lengthening can be attributed to the more crowded coordination environment in the disolvated 8-coordinate samarium case.

The ^1H NMR spectrum of I[33] in C_6D_6, the first reported NMR spectrum of a divalent samarium complex, exhibited relatively sharp singlets at δ 2.45 (30 H, $\Delta\nu_{1/2}$ = 8 Hz) and 4.43 (7 H, $\Delta\nu_{1/2}$ = 33 Hz) and a broad absorption at δ 17.99 ($\Delta\nu_{1/2}$ = 92 Hz). Exchange of the solvated THF in I with THF-d_8 gave a complex which displayed only the δ 2.45 absorption. Hence, we assign this absorption to C_5Me_5, the δ 4.32 absorption to the β-CH_2 group most distant from the Sm(II) center, and the broad resonance to the α-CH_2 group. The ^{13}C NMR spectrum of I[34] in C_6D_6 exhibited a pattern of absorptions just the opposite of that found in other pentamethylcyclopentadienyl lanthanide complexes:[35] δ

–73.7 (s, $C_5(CH_3)_5$), 33.4 (t, J = 125 Hz, $\overline{OCH_2CH_2CH_2CH_2}$), 94.62 (q, J = 117 Hz, $C_5(CH_3)_5$), 149.5 ($\overline{OCH_2CH_2CH_2CH_2}$).[36]

Given the large radial size and large reduction potential of Sm(II) compared to the other accessible divalent lanthanides, the

(26) Crystallization from THF at –78 °C gives purple crystals which contain ca. 29% Sm rather than the 35% found in the original THF extract. Deuteriolysis gives HD to D_2 ratios of 1:1 rather than 2:1. If this product is dissolved in THF and subsequently reanalyzed, the % Sm drops to ca. 27 [cf. $(C_5Me_5)_2Sm(THF)_2$, 26.61%] and the HD to D_2 ratio falls to <0.25 (<17% hydride). The red-brown mother liquor remaining after crystallization of I contains divalent samarium hydride complexes based on deuteriolysis, but attempts to isolate crystals from this fraction have not yet been successful.

(27) Recrystallization from THF at –50 °C gives purple crystals which contain 26.1% Sm and have χ_M^{296} = 5490 × 10^{-6}, μ_{eff} = 3.6 μ_B. IR (KBr, cm^{-1}): 3100–2725 s, 2705 w, 1440 s, 1370 w, 1240 m, 1210 w, 1080 s, 1040 s, 950 w, 895 s, 795 m. The charge-transfer absorption in the near-infrared–visible spectrum has no maxima in the visible region.

(28) Vaporization of 3–4 g of Sm into a 0.246 M solution of C_5Me_5H in hexane (3.5–4.5 g in 100–140 mL) provides 0.9–1.2 g of crystalline product after a single crystallization.[26] Yields of a twice crystallized product are ca. 0.5 g.[27]

(29) Solution syntheses of I from halide precursors are conceivable,[9–11,22,23] but given the high reactivity of I, the large size of Sm(II), and the propensity of organolanthanide complexes to form alkali metal halide adducts,[9] it may be difficult to obtain halide free products by solution methods.

(30) The space group is the triclinic $P\bar{1}$ with a = 15.155 (6) Å, b = 16.141 (6) Å, c = 16.179 (6) Å, α = 55.92 (3)°, β = 65.13 (3)°, γ = 62.18 (3)°, and D_C = 1.33 g cm^{-3} for Z = 4. Least-squares refinement on the basis of 3949 observed reflections led to a final R = $\sum(|F_o| - |F_c|)/\sum|F_o|$ = 0.061. Hydrogen atoms have not been included, and the ring carbon atoms were refined with isotropic temperature factors. The thermal motion of all other atoms was dealt with anisotropically.

(31) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley: New York, 1980; p 1002.

(32) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751–767.

(33) 18.8 mg/mL at 23 °C. The spectrum is temperature and concentration dependent, see ref 10.

(34) 30.3 mg/0.3 mL at 38 °C.[33]

(35) Cf. $(C_5Me_5)_2SmCl_2Li(THF)_2$: ^{13}C NMR (C_6D_6) δ 116.3 (s, C_5Me_5), 68.6 (t, J = 166 Hz, $\overline{OCH_2CH_2CH_2CH_2}$), 25.7 (q, J = 167 Hz, $C_5(CH_3)_5$), 18.2 (t, J = 133 Hz, $\overline{OCH_2CH_2CH_2CH_2}$). Evans, W. J.; Bloom, I., unpublished results.

(36) Signal too weak to observe in undecoupled spectrum.

soluble divalent products of this reaction would be expected to be highly reactive. A preliminary survey of reactivity supports this contention. The crystallized product reacts rapidly with CO, NO, 3-hexyne, HgR_2, and $Co(PR_3)_4$ to form trivalent products. It is also observed to polymerize ethene and functions as a catalyst precursor for catalytic hydrogenation of 3-hexyne to >99% *cis*-3-hexene under mild conditions.[37] These reaction products, as well as the interesting byproducts of this metal vapor reaction, are currently under investigation. On the basis of these results, we anticipate a rich and varied reaction chemistry for divalent organosamarium complexes now that a preparative scale synthesis of a soluble derivative is available.

Supplementary Material Available: Tables of bond distances, bond angles, final fractional coordinates, and thermal parameters and the ORTEP plot of the other crystallographically independent molecule of $(C_5Me_5)_2Sm(THF)_2$ in the unit cell (31 pages). Ordering information is given on any current masthead page.

(37) At 25 °C and 1 atm of H_2, the rate was 0.85 × 10^{-3} turnovers/min based on H_2 uptake.

A Novel Catalytic System for Homogeneous Hydrogenation of Carbon Monoxide: Ruthenium Complexes in the Presence of Iodide Promoters

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Homogeneous catalysts for CO hydrogenation[1–5] and systems modeling their behavior[6,7] have been the subject of much recent research because such catalytic systems offer the potential of selectively converting synthesis gas to chemicals now derived from petroleum. Various metal complexes have been investigated as potential catalysts for synthesis gas conversion in the homogeneous phase. The highest activity has been observed with rhodium catalysts[8] which produce mainly ethylene glycol and methanol, along with smaller amounts of other oxygenates. Cobalt and ruthenium catalysts also produce oxygenates, and complexes of other metals have been found to exhibit only very low or insignificant catalytic activity.[1] Reported here are initial studies of a novel ruthenium-containing catalytic system wich hydrogenates

(1) Fahey, D. R. *J. Am. Chem. Soc.* **1981**, *103*, 136–141 and references therein.

(2) Paxson, T. E.; Reilly, C. A.; Holocek, D. R. *J. Chem. Soc., Chem. Commun.* **1981**, 618–619 and references therein.

(3) Bradley, J. S. *J. Am. Chem. Soc.* **1979**, *101*, 7419–7421.

(4) Dombek, B. D. *J. Am. Chem. Soc.* **1980**, *102*, 6855–6857. See also: Knifton, J. F. *J. Chem. Soc., Chem. Commun.* **1981**, 188–189.

(5) King, R. B.; King, A. D., Jr.; Tanaka, K. *J. Mol. Catal.* **1981**, *10*, 75–83.

(6) (a) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479–490. (b) Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121–127. (c) Headford, C. E. L.; Roper, W. R. *J. Organomet. Chem.* **1980**, *198*, C7–C10.

(7) Dombek, B. D. *J. Am. Chem. Soc.* **1979**, *101*, 6466–6468.

(8) For example, rates (mmol products per mmol metal per unit time) reported in ref 1 (at 1973 atm, 230 °C) are 1.2 × 10^{-1} s^{-1} for rhodium catalysis and 1.2 × 10^{-2} s^{-1} for cobalt catalysis. Another source[9] includes a rate for rhodium catalysis (to the major products) at 1020 atm, 270 °C, of 1.2 × 10^{-1} s^{-1}. The reported[3] rate for ruthenium catalysis at 1300 atm, 268 °C, is 8.5 × 10^{-3} s^{-1}.

(9) Kaplan, L.; Walker, W. E. German Offen. 2643971 (to Union Carbide Corp.), 1977. U.S. Patent Application 618021, 1975.

Table I. Typical Catalytic Reactions of H_2/CO with $Ru_3(CO)_{12}$ and KI

Ru, mmol	KI, mmol	solvent[a]	P, atm[b]	T, °C	t, h	CH_3OH, g	$(CH_2OH)_2$, g	CH_3CH_2OH, g
6	18	NMP	544	250	0.77	5.44	1.34	1.00
6	120	NMP	1020	240	0.13	9.59	2.34	0.88
3	60	18-C-6	544[c]	250	0.63	8.51	0.48	1.60
15	60	18-C-6	850	200	0.47	6.86	3.76	0.49
30	180	Sulf	408	200	2.00	5.50	2.41	0.80
30	180	Sulf	850	180	1.68	2.76	6.42	0.35

[a] 75 mL of solvent; NMP = 1-methyl-2-pyrrolidinone; 18-C-6 = 18-Crown-6; Sulf = sulfolane. [b] H_2/CO = 1 unless otherwise noted. [c] H_2/CO = 1.5.

Table II. Rates to Products in Reactions with Potassium Salts[a]

salt	CH_3OH, mmol h^{-1}	$(CH_2OH)_2$, mmol h^{-1}
none	13.9	nd[b]
KI	202	43.5
KBr	81.3	17.2
KCl	39.7	6.9
KF	44.7	1
K_3PO_4	60.0	1.9
KO_2CCH_3	55.8	1.5

[a] 75 mL of sulfolane, 6 mmol of Ru, 18 mmol of salt, 850 atm, H_2/CO = 1, 230 °C. [b] Not detected.

CO at rates comparable to those observed for rhodium catalysts[10] and with selectivity characteristics unlike those previously found for ruthenium catalysts.[11]

Ruthenium complexes have been reported to produce only one-carbon products (methanol and methyl formate) from H_2/CO, even under quite high pressures.[3-5,12] It has been shown that two-carbon (glycol ester) products could also be obtained from these reactions by use of a carboxylic acid solvent/promoter.[4] The catalyst is believed to be the same in both reactions; similar overall activity is observed, and $Ru(CO)_5$ is the predominant ruthenium component in both. In the course of our continued studies of synthesis gas conversion by ruthenium complexes, ionic iodide promoters were found to possess a remarkable ability to enhance simultaneously the overall activity of the system and the selectivity to two-carbon products, especially ethylene glycol and ethanol (eq 1).[14] The ethanol is largely a secondary product, on the basis

$$H_2/CO \xrightarrow{Ru_3(CO)_{12}, I^-} CH_3OH + HOCH_2CH_2OH + CH_3CH_2OH \quad (1)$$

of studies of product distribution as a function of reaction time. Other products (which are usually minor fractions) include propanol, methane, glycerine, and glycol acetals of acetaldehyde and glycolaldehyde. The aldehydes are presumed to be precursors of ethanol and glycol, in accord with model studies[7] and a general mechanism[1] previously described. Only small amounts of glycol ethers are normally observed.

Results of some typical experiments are tabulated in Table I. It is evident that the activity and selectivity of the system can be

(10) For comparison with the data of note 8, Table I includes a rate to the major products at 1020 atm, 240 °C, of 1.3 × 10^{-1} s^{-1}.

(11) After submission of this manuscript, a communication appeared which reports studies on a similar ruthenium-catalyzed system in quaternary phosphonium salt melts: Knifton, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 3959–3961. Although the essential chemistry in the melt system appears to be the same as that reported here, substantial differences in behavior are also obvious. Observations in the melt system are apparently complicated by ion pairing and solubility phenomena, secondary reactions, and perhaps also by salt decomposition.

(12) Ruthenium complexes have previously been reported to produce glycol and glycerine,[13] but the results could not be reproduced; it is believed that these products were formed by rhodium deposited on the reactor walls in previous experiments: Jenner, G.; Kiennemann, A.; Bagherzadah, E.; Deluzarche, A. *React. Kinet. Catal. Lett.* **1980**, *15*, 103–112.

(13) Deluzarche, A.; Fonseca, R.; Jenner, G.; Kiennemann, A. Erdoel Kohle, Erdgas, Petrochem. **1979**, *32*, 313–316.

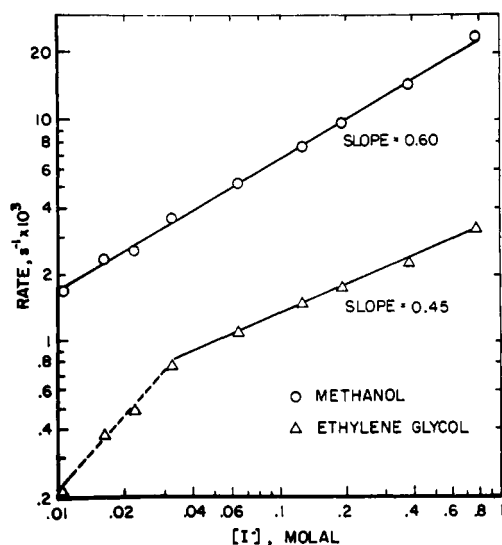(14) Dombek, B. D. European Patent Application 0013008 (to Union Carbide Corp.), 1979.

Figure 1. Log–log plot of reaction rate vs. NaI concentration. Sulfolane solvent, 0.064 m Ru, 850 atm, H_2/CO = 1, 230 °C.

modified very significantly by varying reaction conditions, including temperature, pressure, and catalyst component concentrations. Salts which do not contain iodide are less effective promoters, as shown by Table II. However, many ionic promoters offer an activity advantage over the unpromoted system. The identity of the cation associated with the iodide anion has little effect on activity or selectivity in sulfolane solvent; lithium, sodium, potassium, cesium, and bis(triphenylphosphine) iminium iodides give very similar results.

The effect of promoter concentration on rates has been studied over a broad range; raising the iodide concentration causes a progressive increase in catalyst activity for both methanol and glycol products, as seen in Figure 1. The dependences are nonintegral (suggesting equilibria involving the iodide ion) and are different for the two products; higher iodide concentrations shift the product distribution toward methanol. However, the glycol rate dependence on iodide concentration is significantly higher at I^-/Ru ratios below about 0.5. Other experiments carried out at constant iodide concentration and varying Ru levels exhibit maximum observed rates (to both methanol and glycol) near this same ratio. The possible significance of this unique promoter/metal ratio will be addressed below.

Reaction solutions after catalysis have been found to contain largely the Ru complexes $HRu_3(CO)_{11}^{-}$ [15] and $Ru(CO)_3I_3^{-}$ [16] [no $Ru(CO)_5$ is observed], which are apparently formed by the reaction of eq 2. Indeed, we have found that this reaction occurs

$$^7/_3Ru_3(CO)_{12} + 3I^- + H_2 \rightarrow$$
$$2HRu_3(CO)_{11}^{-} + Ru(CO)_3I_3^{-} + 3 CO \quad (2)$$
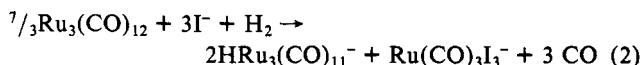
even under very mild conditions (25 °C, 1 atm of H_2). The minimum I^-/Ru ratio required for complete reaction of the $Ru_3(CO)_{12}$ is 0.43; hence catalytic reaction mixtures with less than

(15) Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Suss, G. *J. Chem. Soc., Dalton Trans.* **1979**, 1356–1361.

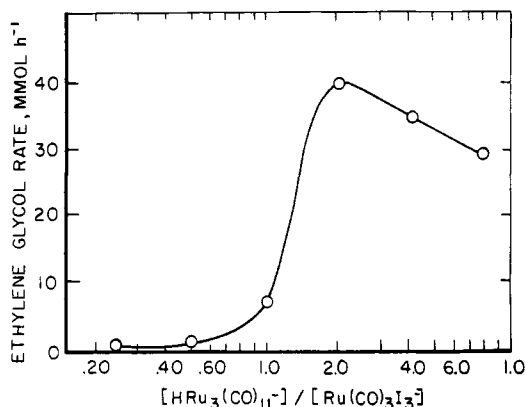(16) Cleare, M. J.; Griffith, W. P. *J. Chem. Soc. A* **1969**, 372–380.

Figure 2. Catalytic activity vs. molar ratio of $HRu_3(CO)_{11}^-$ to $Ru(CO)_3I_3^-$. 75 mL of sulfolane solvent, 0.86 mmol of PPN [$Ru(CO)_3I_3$], PPN[$HRu_3(CO)_{11}$] as indicated, 36 mmol of NaI, 850 atm, H_2/CO = 1, 230 °C.

this amount of iodide might be expected to exhibit anomalous behavior (as seen in Figure 1) if equilibria forming the products of eq 2 are favorable under catalytic conditions. Thus, the correspondence in the unusual I^-/Ru stoichiometry at ambient and catalytic conditions is at least consistent with these complexes being the stable form of the catalyst during reaction.

The ruthenium complexes formed by eq 2 have been prepared as their bis(triphenylphosphine)iminium (PPN) salts and examined *individually* for catalytic activity in CO hydrogenation reactions. Neither PPN[$HRu_3(CO)_{11}$] or PPN [$Ru(CO)_3I_3$] exhibit more than relatively low activity, either in the presence or in the absence of added iodide promoters, and they can be observed unchanged (by infrared spectroscopy) after the reactions. However, synthetic mixtures of the two complexes do possess catalytic activity, as illustrated in Figure 2. Optimum activity is obtained at a 2:1 molar ratio of $HRu_3(CO)_{11}^-$ to $Ru(CO)_3I_3^-$, which is also the proportion in which they are formed from $Ru_3(CO)_{12}$ by eq 2. In view of these results, it is interesting to note that the hydridic character of the hydrogen atom in $HRu_3(CO)_{11}^-$ has recently been demonstrated[17] and that reactions of hydride reagents with electrophilic metal carbonyl complexes have been shown to lead to stoichiometric reduction of CO.[18] Possible reaction pathways based on these observations are under investigation.

Ionic iodide promoters (and to a lesser extent, other promoters) have been shown here to cause a major change in the behavior of ruthenium complexes in catalytic synthesis gas conversion. This is evident both in the identity of the products and in the activity of the system, as compared with those of the unpromoted system. Our earlier studies of ruthenium catalysis in a carboxylic acid solvent/promoter suggested that a glycol product was obtained in that system because a catalytic intermediate normally formed in the unpromoted system was trapped by the reactive solvent and converted to a product not otherwise obtained.[4] The function of the iodide promoter appears to be somewhat different, since it leads to catalytic precursors (and presumably intermediates) not available in the unpromoted system. It seems very plausible that solvent/promoter combinations can be found which will greatly increase the activity of metal complexes found to have little activity for CO hydrogenation in simple screening studies. Finally, it may be significant that the two most active systems for homogeneous synthesis gas conversion (the Rh[19] and Ru/I$^-$ systems) appear to contain anionic metal cluster hydrides. The possible involvement of these species in CO hydrogenation is a subject of current study.

(17) Shore, S. G., personal communication.
(18) (a) Casey, C. P.; Neumann, S. M. *J. Am. Chem. Soc.* **1978**, *100*, 2544–2545. (b) Gladysz, J. A.; Tam, W. *Ibid.* **1978**, *100*, 2545–2547.
(19) Vidal, J. L.; Walker, W. E. *Inorg. Chem.* **1980**, *19*, 896–903.

The Importance of Trinuclear Coordination in the Activation and Desulfurization of a Thioformamido Ligand by a Triosmium Cluster

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It has been proposed that polynuclear coordination of organic molecules to transition-metal cluster compounds can lead to a greater degree of ligand activation than can mononuclear coordination.[1] We have now discovered that triosmium clusters can readily desulfurize thioformamido ligands and that polynuclear coordination does play a key role in the activation of the ligand.

The reaction of $H_2Os_3(CO)_{10}$ with p-FC_6H_4NCS at 25 °C yields a yellow product (86% yield) which has been characterized as $HOs_3[\mu$-η^1-$SC(H)N$-p-$C_6H_4F](CO)_{10}$ (I) on the basis of IR and ^1H NMR spectroscopies[2] and an X-ray crystallographic analysis.[3,4] The molecular structure of I is shown in Figure 1.[5] Unlike the related molecules $HOs_3[\mu$-η^2-$OC(H)NAr](CO)_{10}$ which contain η^2-formamido ligands that bridge an edge of the triosmium cluster,[6] I contains a η^1-thioformamido ligand which bridges an edge of the triangular cluster of metal atoms via the sulfur atom only. This ligand was evidently formed by incorporation of one isothiocyanate molecule into the coordination sphere of the cluster and the transfer of one hydride ligand to the carbon atom. The carbon–sulfur distance, $C(17)$-S, at 1.782 (12) Å is long and approaches closely the length of a carbon–sulfur single bond while the carbon–nitrogen distance, $C(17)$-N, at 1.279 (13) Å is typical of a carbon–nitrogen double bond. Apparently, π-electron density, which would normally be delocalized across the entire three-atom S–C–N unit in a ligand of the type has now been localized in the two-atom C–N unit. We feel that this is due in part to the dinuclear coordination of the sulfur atom to the cluster which causes it to assume a trivalent character. A single hydride ligand observed spectroscopically is believed to bridge the $Os(1)$-$Os(3)$ bond on the side of the cluster opposite the thioformamido ligand.

Compound I slowly loses 1 mol of CO when hexane solutions are allowed to stand at room temperature and forms the new red compound $HOs_3[\mu_3$-η^2-$SC(H)N$-p-$C_6H_4F](CO)_9$, II (45% yield in 5 days). Compound II has also been characterized by IR and ^1H NMR spectroscopies[7] and an X-ray crystallographic analysis,[3,8] and its molecular structure is shown in Figure 2.[9] II contains

(1) (a) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1976**, *85*, 451. (b) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479.

(2) IR: ν(CO) (hexane solvent) 2110 w, 2071 vs, 2062 s, 2036 sh, 2027 vs, 2019 s, 2006 m, 1992 w, 1988 w. ^1H NMR (in CDCl$_3$): δ 7.79 (s, 1 H), 7.05 (m, 4 H), −17.42 (s, 1 H).

(3) Diffraction data were collected on an Enraf–Nonius CAD-4 automatic diffractometer. All structure solution and refinement calculations were done on a Digital PDP 11/45 computer by using the Enraf–Nonius SDP program library.

(4) Space group $P2_1/n$; at 27 °C, a = 13.068 (4) Å, b = 12.230 (3) Å, c = 14.517 (4) Å, β = 100.67 (2)°, Z = 4, ρ_{calcd} = 2.93 g/cc. The structure was solved by the heavy atom method. Least-squares refinement on 2698 reflections produced the final residuals R_1 = 0.042 and R_2 = 0.046.

(5) Selected bond distances (Å) and angles (deg) for I are $Os(1)$-$Os(2)$ = 2.861 (1), $Os(1)$-$Os(3)$ = 2.870 (1), $Os(2)$-$Os(3)$ = 2.868 (1), $Os(1)$-S = 2.424 (3), $Os(3)$-S = 2.431 (3), S-$C(17)$ = 1.782 (12), $C(17)$-N = 1.279 (13); $Os(1)$-S-$Os(3)$ = 72.46 (8), $Os(1)$-S-$C(17)$ = 102.6 (4), $Os(3)$-S-$C(17)$ = 103.3 (4), S-$C(17)$-N = 119.7 (8).

(6) Adams, R. D.; Golembeski, N. M.; Selegue, J. P. *Inorg. Chem.* **1981**, *20*, 1242.

(7) IR: ν(CO) (hexane) 2089 m, 2058 s, 2035 vs, 2006 s, 1992 s, 1971 w, 1960 w. ^1H NMR (CDCl$_3$): δ 10.24 (s, 1 H), 7.13 (m, 2 H), 6.89 (m, 2 H), −13.66 (s, 1 H).

(8) Space group $P2_1/c$; at 25 °C, a = 12.545 (4) Å, b = 10.345 (2) Å, c = 17.906 (6) Å, β = 110.21 (3)°, Z = 4, ρ_{calcd} = 2.97 g/cc. The structure was solved by a combination of direct methods (MULTAN) and difference-Fourier techniques. Least-squares refinement on 2252 reflections produced the final residuals R_1 = 0.051 and R_2 = 0.056.