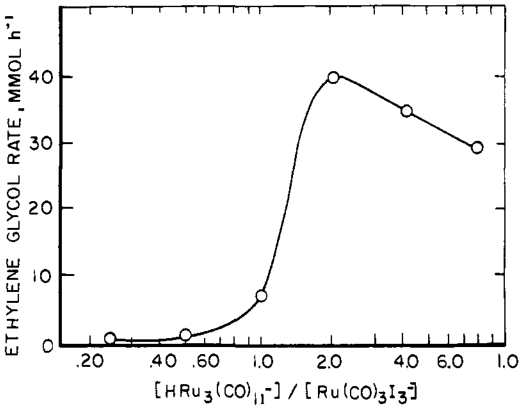

Figure 2. Catalytic activity vs. molar ratio of $HRu_3(CO)_{11}^-$ to $Ru(CO)_3I_3^-$. 75 mL of sulfolane solvent, 0.86 mmol of PPN $[Ru(CO)_3I_3]$, PPN$[HRu_3(CO)_{11}]$ as indicated, 36 mmol of NaI, 850 atm, H_2/CO = 1, 230 °C.

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.

Acknowledgment. I thank Union Carbide Corporation for permission to publish this work and Dr. G. L. O'Connor for his support and encouragement.

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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

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[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.

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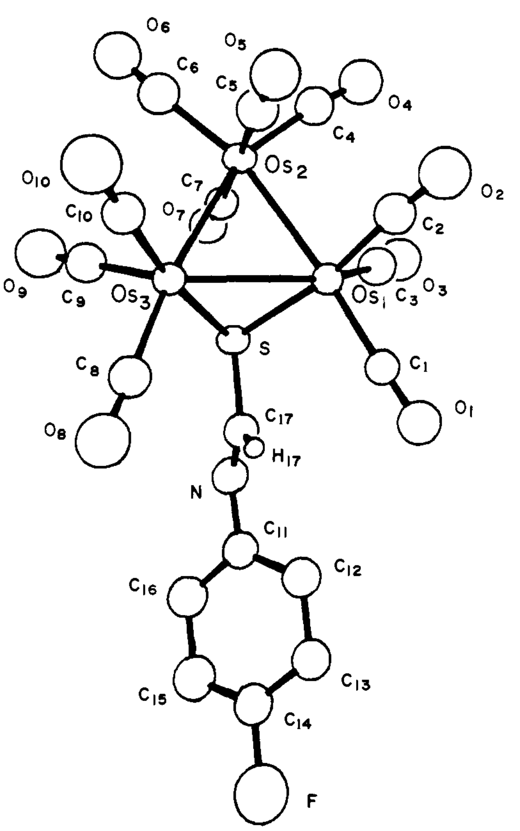

Figure 1. ORTEP drawing of $HOs_3[\mu\text{-}\eta^1\text{-}SC(H)N\text{-}p\text{-}C_6H_4F](CO)_{10}$ showing 50% electron density probability ellipsoids.

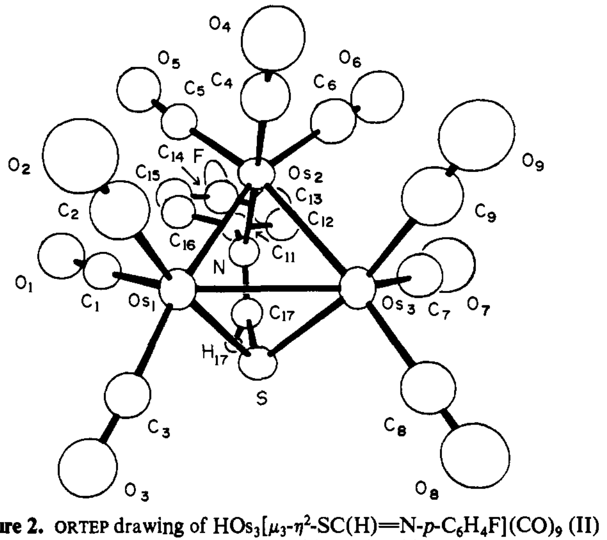

Figure 2. ORTEP drawing of $HOs_3[\mu_3\text{-}\eta^2\text{-}SC(H){=}N\text{-}p\text{-}C_6H_4F](CO)_9$ (II) showing 50% electron density probability ellipsoids.

a triangular cluster of three osmium atoms with a triply bridging η^2-thioformamido ligand. The sulfur atom bridges one edge of the cluster while the nitrogen atom is coordinated to the third metal atom. The carbon–sulfur bond retains its single bond character, C(17)–S = 1.774 (15) Å while the carbon–nitrogen bond, C-(17)–N = 1.250 (17) Å, remains double. A single hydride ligand observed in the ^1H NMR spectrum is believed to occupy a bridging position along the Os(1)–Os(3) bond in the large cavity circumscribed by the carbonyl groups C(2)–O(2), C(3)–O(3), C(8)–O-(8), and C(9)–O(9).

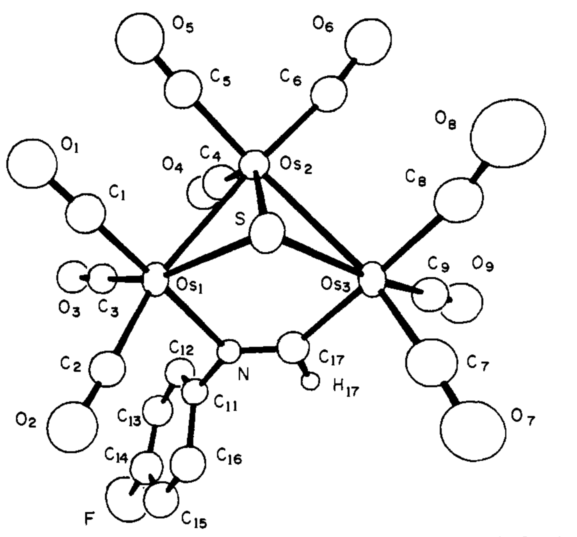

Figure 3. ORTEP drawing of $HOs_3(\mu_3\text{-}S)(\mu\text{-}HC{=}N\text{-}p\text{-}C_6H_4F)(CO)_9$ (III) showing 50% electron density probability ellipsoids.

When refluxed for 15 min, octane solutions of II turn bright yellow, and a new yellow complex (III) is formed in 62% yield. On the basis of IR and ^1H NMR spectroscopies[10] and an X-ray crystallographic analysis we formulate III as $HOs(\mu_3\text{-}S)[\mu\text{-}\eta^2\text{-}HC{=}N\text{-}p\text{-}C_6H_4F](CO)_9$.[3,11] Its molecular structure is shown in Figure 3.[12] The molecule consists of an "open" cluster of three osmium atoms linked by two metal–metal bonds, a triply-bridging inorganic sulfide ligand, and an η^2-formimidoyl ligand which bridges the open edge of the cluster. The C(17)–N internuclear distance at 1.213 (14) Å is indicative of a double bond. The hydrogen atom on C(17) (not observed crystallographically) was identified by its characteristic ^1H NMR shift δ 11.11.[13,14] The Os(2)–Os(3) metal–metal bond at 2.988 (1) Å is significantly longer than the Os(1)–Os(2) bond at 2.836 (1) Å and suggests that the hydride ligand bridges this edge of the cluster.

The formation of III obviously occurs via cleavage of the carbon–sulfur bond in II. Subsequent attack by the sulfide ligand on the third osmium atom should induce cleavage of the metal–metal bond and produce III directly. Two principal effects of the activation and desulfurization of this thioformamido ligand can be attributed to its polynuclear coordination: (1) It contributes to the localization of the π electrons between the carbon and nitrogen atoms and thus causes a lowering of the carbon–sulfur bond order. (2) The coordination of the nitrogen atom brings the ligand into a position where the osmium–carbon bond can be formed either immediately following or perhaps in concert with the cleavage of the carbon–sulfur bond. This example of the activation of a thioformamido ligand about a trinuclear site is a process that can be readily envisaged to occur at a trinuclear site on a metallic surface. In this regard cluster compounds might truly serve as models for surface-related phenomena.[15]

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(9) Selected bond distances (Å) and angles (deg) for II are Os(1)–Os(2) = 2.817 (1), Os(1)–Os(3) = 2.860 (1), Os(2)–Os(3) = 2.824 (1), Os(2)–N = 2.193 (11), Os(1)–S = 2.456 (4), Os(3)–S = 2.449 (4), S–C(17) = 1.774 (15), C(17)–N = 1.250 (17); Os(1)–S–Os(3) = 71.3 (1), Os(1)–S–C(17) = 104.5 (5), Os(3)–S–C(17) = 104.8 (5), S–C(17)–N = 121.9 (11).

(10) IR: ν(CO) (hexane) 2108 m, 2079 vs, 2048 vs, 2027 w, 2017 m, 2008 s, 1988 m, 1983 m, 1973 m. ^1H NMR ($CDCl_3$): at 25 °C δ 11.11 (s, 1 H), 7.04 (m, 2 H), 6.75 (m, 2 H), −16.28 (s, 1 H); at −60 °C, isomer A, δ 11.60 (s, 1 H), 7.04 (m, 2 H), 6.74 (m, 2 H), −15.46 (s, 1 H); isomer **B**, 10.78 (s, 1 H), 7.04 (m, 2 H), 6.74 (m, 2 H), −16.93 (s, 1 H). Ratio A/**B** = 1:2.

(11) Space group $P2_1/n$; at 25 °C, $a = 11.562$ (2) Å, $b = 16.879$ (3) Å, $c = 11.952$ (4) Å, $\beta = 111.66$ (3)°, $Z = 4$, $\rho_{\text{calcd}} = 3.00$ g/cc. The structure was solved by the heavy atom method. Least-squares refinement on 2314 reflections produced the final residuals $R_1 = 0.063$ and $R_2 = 0.067$.

(12) Selected bond distances (Å) and angles (deg) for III are Os(1)–Os(2) = 2.836 (1), Os(2)–Os(3) = 2.988 (1), Os(1)···Os(3) = 3.779 (1), Os(1)–S = 2.422 (3), Os(2)–S = 2.386 (4), Os(3)–S = 2.464 (4), Os(1)–N = 2.205 (11), Os(3)–C(17) = 2.051 (13), C(17)–N = 1.213 (14); Os(1)–Os(2)–Os(3) = 80.88 (2), Os(1)–S–Os(2) = 72.28 (10), Os(2)–S–Os(3) = 76.04 (11), Os(1)–S–Os(3) = 101.32 (13), Os(1)–N–C(17) = 118.5 (10), Os(3)–C-(17)–N = 136.1 (12).

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Interestingly, it was recently reported that $Co_2(CO)_8$ cleaves sulfur from thioamides to give the cluster compounds $(\mu_3\text{-S})(\mu\text{-R}^1C{=}NR^2)Co_3(CO)_7$, R^1 = Me, Ph; $R^2 = C_6H_{11}$, but since no intermediates were observed, the state of aggregation of the cluster that existed when the desulfurization occurred is not known.[16]

The desulfurization of organic molecules is a reaction of interest regarding the purification of fossil fuels.[17] Recently, organometallic complexes have attracted attention as desulfurization agents.[18]

Acknowledgment. This research was supported by the Division of Basic Energy Sciences of the U.S. Department of Energy under Contract DE-AC02-78ER04900 and the Alfred P. Sloan Foundation through a fellowship to R.D.A. We wish to thank Engelhard Industries for a loan of osmium tetroxide and Dr. B. F. G. Johnson of the University Chemical Laboratories, Cambridge, for converting it into $Os_3(CO)_{12}$ for us. NMR studies were supported by Grant CHE-7916210 from the National Science Foundation.

Supplementary Material Available: Complete tables of fractional atomic coordinates, bond distances and angles are available for all three structures (12 pages). Ordering information is given on any current masthead page.

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Fully Functionalized Thiol Vesicles: Structure and Esterolytic Properties

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Exceptional attention has focused on synthetic surfactant vesicles because of their ability to model biological membranes and their potential use as "chemical machines"; i.e., highly organized reagent assemblies designed to perform specific chemical tasks.[2,3] Electron microscopy has been an essential tool in the structural characterization of vesicles but is limited to the examination of "fixed" specimens. Accordingly, spectroscopic[4] or chemically reactive[5] reporter molecules have been designed to probe vesicular microenvironments. Several probes have detected substantial molecular ordering in vesicles, particularly in multilamellar types.

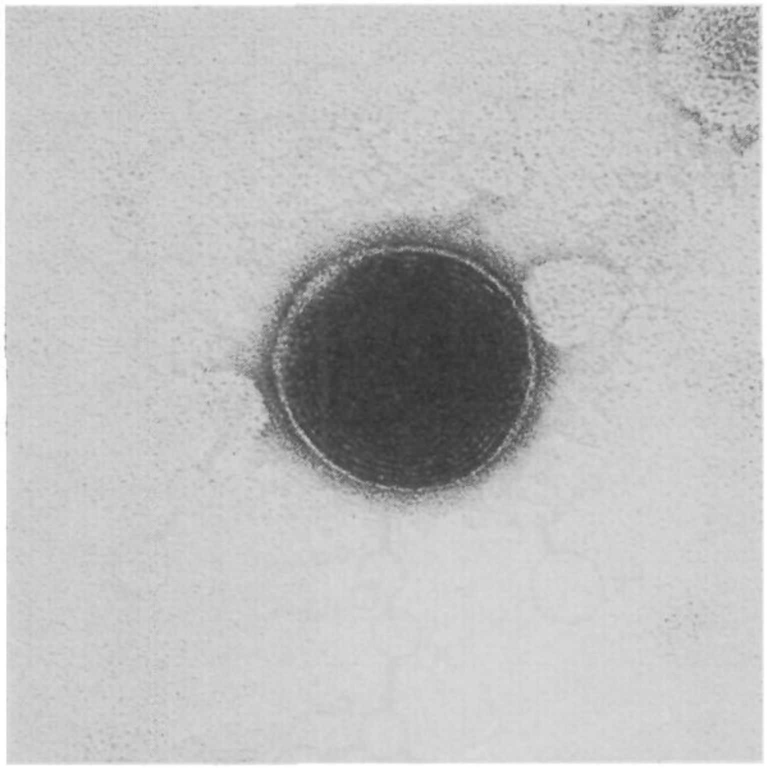

Figure 1. Electron micrograph of vesicular **1** on a Formvar carbon-coated copper grid; magnification, ×230000.

The existence of ordered, stable, membrane-enclosed vesicles, offering unique microenvironments, invites vigorous exploitation; for example, the extension of micellar chemistry[6] to vesicles: the bimolecular cleavage of active esters in alkylammonium ion vesicles,[7] unimolecular decarboxylation,[8] and various photochemical reactions.[9] Of special interest is the formation of vesicles from amino acid derivatives, where the incorporated chirality and functionality permit innate and induced circular dichroism[10] and chiral chemical discrimination.[11]

Our concern centers on *functionalized* vesicles as organic reagents and bioorganic models.[2a,12] Very little has been done in this area. The cleavage of *p*-nitrophenyl esters is catalyzed by hydrophobic imidazole[7] or thiol[13] reagents when both substrate and reagent are noncovalently bound to $R_2N^+Me_2$ vesicles, but the vesicles themselves are not functionalized. Perhaps the sole chemical utilization of synthetic functional vesicles is the enantioselective cleavage of activated phenylalanine esters by vesicles constructed from a histidine-derived surfactant.[11b]

We now report (a) the synthesis of *N*,*N*-dihexadecyl-*N*-(β-mercaptoethyl)-*N*-methylammonium chloride (**1**), (b) the subsequent preparation and characterization of *fully functionalized* thiol vesicles of **1**, and (c) some chemical properties of these vesicles, including distinguishable "inner" and "outer" reactions. The esterolytic reactivity of vesicular **1** is also compared to that of *micellar* **2**[14] and vesicle-bound heptanethiol.[13]

$$(n\text{-}C_{16}H_{33})_2N^+(CH_3)CH_2CH_2SH,Cl^-$$

1

$$n\text{-}C_{16}H_{33}N^+(CH_3)_2CH_2CH_2SH,Cl^-$$

2

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(1) Special Graduate School Fellow, Rutgers University.

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