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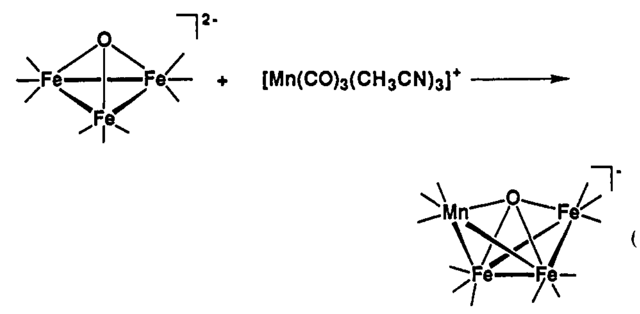
A Butterfly Cluster Containing a Bridging Acetamidato Ligand. Synthesis, Structure, and Bonding for $[MnRu_3(CO)_{12}(\eta^2\text{-}\mu_3\text{-}NC(\mu\text{-}O)CH_3)]^-$

Organometallic clusters containing carbido,[1] nitrido,[2] or sulfido[3] ligands are numerous, but relatively few contain the oxo ligand,[4] and until recently, the highest oxygen connectivity was μ_3.[5] Metal clusters containing the μ_4-oxygen ligand were recently prepared in our laboratory.[6,7] The rarity of μ_4-oxo clusters and the desire to understand the reactivity of the oxo ligand led to the present research. We describe here the formation of $[MnRu_3(CO)_{12}(\eta^2\text{-}\mu_3\text{-}NC(\mu\text{-}O)CH_3)]^-$ (**1**), a butterfly cluster containing a bridging acetamidato ligand, which appears to result from a μ_3-O cluster.

The iron oxo cluster $[PPN]_2[Fe_3(CO)_9(\mu_3\text{-}O)]$ (PPN^+ = bis(triphenylphosphine)nitrogen(1+)) was first synthesized by reaction of $[PPN]_2[Fe_3(CO)_{11}]$ with air,[5a] and it is a useful starting material for the synthesis of higher nuclearity oxo clusters (eq 1).[6,7] In an analogous fashion, $[PPN]_2[Ru_3(CO)_{11}]$[8] in acetone solution was treated with dry air in an attempt to synthesize $[PPN]_2[Ru_3(CO)_9(\mu_3\text{-}O)]$. The infrared spectrum of this solution (ν_{CO} 2015 (m), 1964 (vs), 1922 (s), 1905 (m) cm^{-1}) is similar to that of the iron oxo cluster, but only an orange-brown oil could be isolated, indicating a mixture of products. The FAB-MS of the oil also is consistent with a mixture of products. Various oxygen atom transfer agents,[9] such as nitrous oxide, iodosylbenzene, and oxygen gas, yielded similar results. Since a pure oxo cluster was not isolated, we investigated reactions of the oil, with the thought that an oxo-cluster component might exhibit distinctive reactivity.



(1)

An acetone solution of the above reaction mixture was combined with 1 equiv of $[Mn(CO)_3(CH_3CN)_3]PF_6$,[10] in an attempt to mimic reaction 1. Solvent was removed under vacuum, and the resulting dark brown oil was extracted with diethyl ether to give a product (6.6% yield based on $[PPN]_2[Ru_3(CO)_{11}]$) with an infrared spectrum ($\nu_{CO}(Et_2O)$ 2051 (vw), 2005 (vs), 1989 (s), 1970 (m), 1924 (w), 1863 (vw), 1818 (w) cm^{-1}) similar to those for $[Fe_3Mn(CO)_{12}(\mu_4\text{-}O)]^-$ and $[MnRu_3(CO)_{13}(\mu_4\text{-}C)]^-$.[6,11] EDAX indicates the presence of P, Mn, and Ru. Red-brown X-ray-quality crystals were grown by layering pentane onto a concentrated ether solution of the reaction product.

A single-crystal X-ray structure determination reveals that the anionic cluster is not the expected $[MnRu_3(CO)_{12}(\mu_4\text{-}O)]^-$ but instead is $[MnRu_3(CO)_{12}(\eta^2\text{-}\mu_3\text{-}NC(\mu\text{-}O)CH_3)]^-$ (Figure 1).[12]

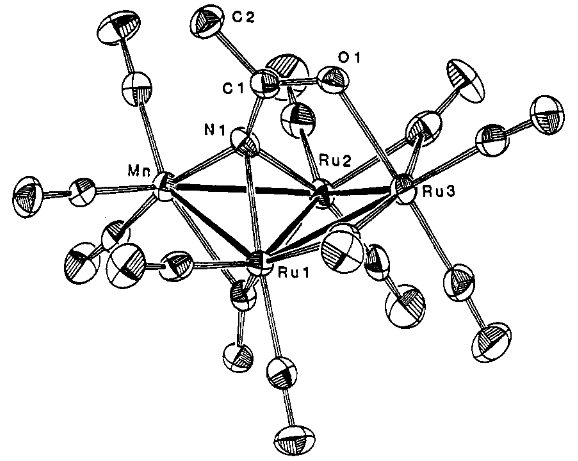


Figure 1. Structure of the anion $[MnRu_3(CO)_{12}(\eta^2\text{-}\mu_3\text{-}NC(\mu\text{-}O)CH_3)]^-$ (**1**) showing 50% probability ellipsoids.

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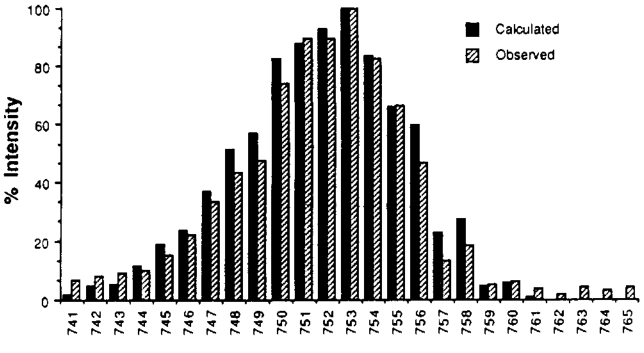


Figure 2. Calculated (black) and observed (dashed) isotopic ion distributions for the $(M)^-$ cluster ion in the negative-ion FAB-MS of $[PPN][MnRu_3(CO)_{12}(\eta^2\text{-}\mu_3\text{-}NC(\mu\text{-}O)CH_3)]$.

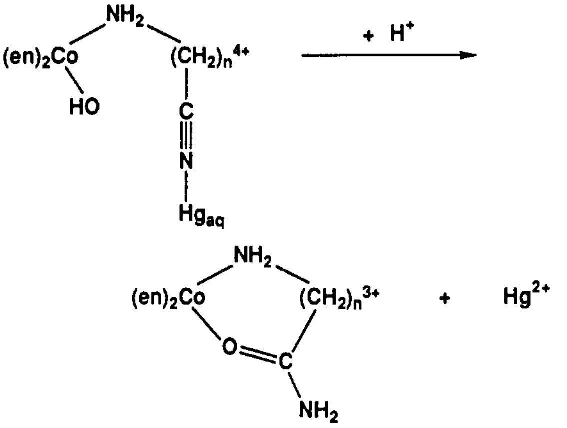
The cluster $[MnRu_3(CO)_{12}(\eta^2\text{-}\mu_3\text{-}NC(\mu\text{-}O)CH_3)]^-$ has a four-metal butterfly geometry with nine terminal carbonyl ligands, three on the manganese and two on each ruthenium. Two carbonyl ligands bridge between the wingtip and hinge Ru atoms, and one μ_3-CO ligand caps the Mn-Ru1-Ru2 face opposite to the acetamidato ligand $(\eta^2\text{-}\mu_3\text{-}NC(\mu\text{-}O)CH_3)$. The acetamidato ligand bridges between the wings of the butterfly and is μ_3-N-bonded to Mn, Ru1, and Ru2 and O-bonded to the wingtip ruthenium atom, Ru3.

The metal-metal bond distances are typical of those observed in ruthenium butterfly[13] and Ru-Mn clusters[14] (Ru1-Ru2 = 2.7347 (6) Å, Ru1-Ru3 = 2.7670 (7) Å, Ru2-Ru3 = 2.7421 (6) Å, Ru1-Mn = 2.7937 (8) Å, Ru2-Mn = 2.6965 (8) Å). The nitrogen of the acetamidato ligand is bonded to the metal framework, closer to the wingtip manganese atom (Mn-N1 = 1.918 (3) Å) than to the hinge ruthenium atoms (Ru1-N1 = 2.126 (3) Å, Ru2-N1 = 2.116 (3) Å). The N1-C1 distance of 1.326 (5) Å is intermediate between a single and a double nitrogen-carbon bond distance; the C1-O1 distance of 1.264 (5) Å is between a single and a double carbon-oxygen bond distance. On the basis of these bond distances, the bridging acetamidato ligand appears to have allyl-like bonding. The O1-Ru3 distance of 2.182 (3) Å is short enough to be considered a bonding interaction. The C1-C2 distance of 1.483 (6) Å between the carbons in the bridging ligand can be considered a normal single bond.

The observed dihedral angle between the wings of the butterfly clusters range from 90 to 180°. This angle is influenced by the electronic structure, the coordinating properties of the bridging ligand, and the steric interaction between ligands.[13] For $[MnRu_3(CO)_{12}(\eta^2\text{-}\mu_3\text{-}NC(\mu\text{-}O)CH_3)]^-$ (**1**) the dihedral angle between the two deltahedral metal fragments is 145.2°, a much more open configuration compared to other butterfly clusters with a ligand bridging the wingtips. For example, the butterfly $Ru_4(CO)_{12}(\eta^2\text{-}\mu_4\text{-}C_2Ph_2)$ has a hinge angle of 115.5°,[15] and $[Fe_4(CO)_{12}(\mu_4\text{-}CCO_2Me)]^-$ has a 129.9° hinge angle.[16] An example of a very open butterfly is the compound $Ru_4(CO)_8(DAB)_2$ (DAB = 1,4-diazabutadiene), which has a dihedral angle of 142.2°.[17] The large dihedral angle in **1** appears to be a result of the spatial requirements of the acetamidato ligand when it serves as a six-electron donor to yield the expected 62 cluster valence electron count.[18]

A negative-ion fast atom bombardment mass spectrum (FAB-MS) of $[PPN][MnRu_3(CO)_{12}(\eta^2\text{-}\mu_3\text{-}NC(\mu\text{-}O)CH_3)]$ (taken in an *n*-nitrobenzyl alcohol (*n*-NBA) matrix) contained an *m/z* 752.8 ion as the most abundant species. The isotropic distribution of the associated envelope matched the isotopic distribution expected, $[MnRu_3(CO)_{12}(\eta^2\text{-}\mu_3\text{-}NC(\mu\text{-}O)CH_3)]^-$ (Figure 2). The fragmentation pattern indicates loss of six consecutive carbonyl ligands (*m/z* 725, 697, 669, 641, 613, 585) and loss of $C(O)CH_3$ from the bridging acetamidato ligand (*m/z* 725, 697, 669, 641, 613, 585) and loss of $C(O)CH_3$ from the bridging acetamidato ligand (*m/z* 542). Thus, the mass spectral data are consistent with the X-ray structural data on the cluster.

It appears likely that the acetamidato ligand arises from the reaction of $[Ru_3(CO)_9(\mu_3\text{-}O)]^{2-}$ with the nitrile ligand of an incoming $[Mn(CO)_3(CH_3CN)_3]^+$ ion. Both acid and base hydrolyses are known to convert nitriles to amides.[19] In general, the hydrolysis requires forcing conditions such as the use of strong mineral acids[20] or HO_2^-, a strong nucleophile.[21] The facile process in the present reaction may arise from the electron-acceptor character of the $[Mn(CO)_3]^+$ moiety along with the close proximity of the ruthenium-bound oxo ligand and coordinated acetonitrile in the cluster-building reaction. An analogue of this proposed mechanism is the intramolecular nucleophilic attack of a cobalt-bound OH ligand on a mercury-bound nitrile proposed by Buckingham et al., eq 2.[22]



(2)

The bridging acetamidato ligand is rare, but it has been observed in the butterfly cluster $[HOs_4(CO)_{12}(\mu_3\text{-}N(CO)CH_3)MPPh_3]$ (M = Au, Cu)[23] and in the tetrabridged dirhodium compounds $[Rh_2(CH_3CONH)_4(MPh_3)_2]$ (M = P, As, Sb)[24] and $[Rh_2(CH_3CO_2)_n(CH_3CONH)_{4-n}]$ (n = 0–3).[25] A bridging acetamidato ligand was also proposed for the triangular cluster $[Os_3(CO)_{10}(\mu\text{-}H)(NHCOR)]$ (R = H, Me, Ph, Et, Pr).[26] Complex **1** provides the only known example of an N- and O-bonded acetamidato ligand bridging four metals.

Acknowledgment. We are grateful for support of this work by Department of Energy Grant No. DE-FG02-86-ER13640.

Supplementary Material Available: Tables of crystal structure data, positional parameters, anisotropic thermal parameters, and bond distances and angles, a figure showing the atom-numbering scheme for

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(12) $[PPN][MnRu_3(CO)_{12}(\eta^2\text{-}\mu_3\text{-}NC(\mu\text{-}O)CH_3)]$: M_r = 1289.91; triclinic space group $P\bar{1}$ (No. 2); a = 11.494 (2) Å, b = 13.546 (2) Å, c = 16.619 (3) Å, α = 94.81 (1)°, β = 106.14 (1)°, γ = 94.04 (1)°, V = 2464 (1) Å^3; Z = 2; d_{calcd} = 1.74 g cm^{-3}; μ(Mo Kα) = 12.5 cm^{-1}. The structure was solved by direct methods (SHELXS 86) and refined by using TEXSAN 4.0. Full-matrix least-squares refinement yielded $R(F)$ = 0.029 and $R_w(F)$ = 0.043 for 5841 reflections with $I > 3\sigma(I)$ measured on a CAD4 diffractometer up to 2θ = 46° at −120 °C (Mo Kα radiation, λ = 0.71069 Å).

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[PPN][MnRu$_3$(CO)$_{12}$(η^2-μ_3-NC(μ-O)CH$_3$)], and an ORTEP diagram of the anion (11 pages); a listing of structure factors (40 pages). Ordering information is given on any current masthead page.

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New Synthetic Route to the Hydridospherosiloxanes O_h-$H_8Si_8O_{12}$ and D_{5h}-$H_{10}Si_{10}O_{15}$

Oligomeric silsesquioxanes are compounds of general formula $(XSiO_{1.5})_n$ where n is an even number ($n \geq 4$) and X is either H, Cl, or any of a large number of organic groups.[2-5] The name "spherosiloxanes" is sometimes used to describe these compounds,[6,7] since they have polyhedral structures that are topologically equivalent to a sphere.

The first hydridospherosiloxane was synthesized serendipitously in 1959 by Müller, Köhne, and Sliwinski[8] (<1% yield from $HSiCl_3$) and shown to be O_h-$H_8Si_8O_{12}$. Subsequently, in 1970 an improved synthesis of this compound was reported by Frye and Collins[3] (ca. 13% yield from $HSi(OCH_3)_3$). They also reported an unusual preparative procedure that yielded a mixture of hydridospherosiloxanes in highly variable yields (15–35% from $HSiCl_3$). Agaskar, Day, and Klemperer reported in 1987[9] that a modification of this procedure gave more reproducible yields (>30%) and also described a purification protocol that yielded gram quantities of four pure hydridospherosiloxanes. The structures of these compounds O_h-$H_8Si_8O_{12}$, D_{5h}-$H_{10}Si_{10}O_{15}$, D_{2d}-$H_{12}Si_{12}O_{18}$, and D_{3h}-$H_{14}Si_{14}O_{21}$, which were obtained in ca. 0.5, 3.5, 3.5, and 0.5% yields, respectively, are shown in Figure 1.

We wish to report here that we have now developed a new synthetic procedure that is extremely easy to implement and that gives a mixture of O_h-$H_8Si_8O_{12}$ and D_{5h}-$H_{10}Si_{10}O_{15}$ (ca. 3.5:1) in ca. 27.2% yield. Pure O_h-$H_8Si_8O_{12}$ can be isolated from the mixture of crystals in ca. 17.5% yield as described below, while pure D_{5h}-$H_{10}Si_{10}O_{15}$ can be isolated from the remainder by following procedures published earlier.[10]

The fundamental feature of this procedure is the use of a partially hydrated metal salt solution to create "scarce-water" hydrolysis conditions similar to those involved in the preparation that uses sulfuric acid.[3,9]

The hydridospherosiloxanes are potentially a very useful class of compounds[11-14] whose chemistry has remained underdeveloped because of the lack of a facile method of making them in synthetically useful quantities. The experimental procedure that is described below should make at least two of these widely accessible, while modifications of this procedure could lead to efficient and convenient synthesis of other compounds of this type.

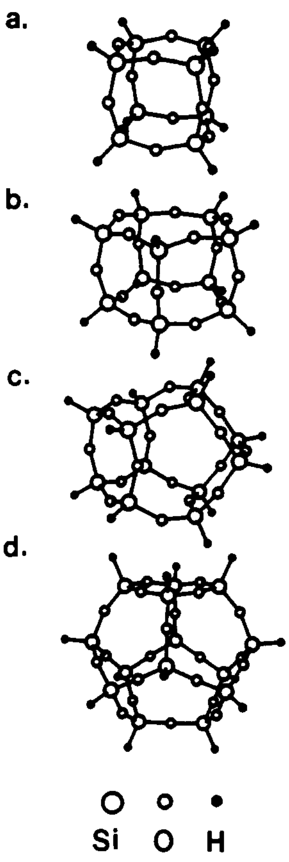

Figure 1. Structures of the four pure hydridospherosiloxanes that have been prepared in gram quantities: (a) O_h-$H_8Si_8O_{12}$; (b) D_{5h}-$H_{10}Si_{10}O_{15}$; (c) D_{2d}-$H_{12}Si_{12}O_{18}$; (d) D_{3h}-$H_{14}Si_{14}O_{21}$.

Experimental Procedure. $FeCl_3$ (anhydrous, 50 g) was taken in a round-bottomed flask, and concentrated HCl (20 mL) was added followed by CH_3OH (40 mL). C_6H_{14} (mixture of isomers, 350 mL) and C_7H_8 (50 mL) were then added, and the biphasic mixture was stirred by a heavy magnetic stirrer. A solution of $HSiCl_3$ (20 mL, ~0.2 mol) in C_6H_{14} (150 mL) was added dropwise by using a pressure-equalizing dropping funnel over a period of 9 h. After an additional 30 min of stirring, the upper hexane layer was transferred to another round-bottomed flask along with some suspended yellow solid (the $FeCl_3$-containing layer can be reused after addition of concentrated HCl).[15] K_2CO_3 (14 g) and $CaCl_2$ (10 g) were added to the flask and the contents stirred overnight. The mixture was filtered, and the filtrate volume was reduced by evaporation until it was ca. 20 mL. The crystals that were deposited weighed 1.86 g after they were separated from the mother liquor and washed with some hexane. The washings were combined with the mother liquor, and the volume was reduced further by evaporation until it was <10 mL. A second crop of crystals was collected (1.02 g) and washed with hexane. The total yield of white crystals was 2.88 g. The mother liquor contained 4.9 g of a soluble product.

^{1}H NMR spectroscopy (C_6D_6, 270 MHz) showed that these crystals were a mixture (ca. 3.5:1) of O_h-$H_8Si_8O_{12}$ (δ = 4.203 ppm)[9] and D_{5h}-$H_{10}Si_{10}O_{15}$ (δ = 4.244 ppm).[9] The total yield based on $HSiCl_3$ was 27.2%.

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(15) The procedure was repeated by using this recycled $FeCl_3$ layer and a drop-in time of only 4.5 h to give O_h-$H_8Si_8O_{12}$ in 16.8% yield based on $HSiCl_3$.