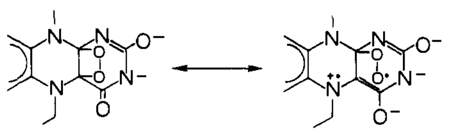
intermediate followed by coupling of substrate and 10a-dihydroflavin peroxide radicals (eq 24) is the covalent counterpart of the superoxide mechanism of eq 22 or the reaction of substrate with a complex composed of FlEt· and $O_2^{-}\cdot$. We know of no precedent in the literature for 1e⁻ reduction of a dioxetane accompanied by C–O bond scission. However, as in the nucleophilic addition mechanism, the C(4) carboxyl group may serve as an electron sink and the dioxetane itself may possess a radical character (eq 25).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Acknowledgment. This work was supported by grants from the National Institutes of Health and National Science Foundation. T.C.B. gratefully acknowledges support as a Guggenheim Fellow.

Communications to the Editor

Synthesis and X-ray Structural Characterization of the $[Rh_{22}(\mu_3\text{-}CO)_7(\mu\text{-}CO)_{18}(CO)_{12}]^{4-}$ Anion Containing a Large Close-Packed Cluster with an ABAC Sequence of Compact Layers

Sir:

During our studies on the rhodium carbonyl cluster compounds of high nuclearity containing fragments of metal lattices, we have isolated and structurally characterized the anions $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$ ($n = 2, 3$),[1,2] $[Rh_{14}(CO)_{25}]^{4-}$,[3] $[Rh_{14}H(CO)_{25}]^{3-}$,[4] and $[Rh_{15}(CO)_{27}]^{3-}$.[3] We now wish to report the synthesis and X-ray characterization of the new $[Rh_{22}(CO)_{37}]^{4-}$ anion.

This anion was first observed as a minor byproduct in the synthesis of $[Rh_{15}(CO)_{27}]^{3-}$,[3] where it was sometimes present in the sodium fraction of the alkali metals salts. It has now been synthesized by refluxing for 4–6 h under nitrogen mixtures of $Rh_4(CO)_{12}$ and NaOH in 2-propanol in the ratio of one OH^- for every 5–5.5 Rh atoms. A mixture of brown products is formed from which the $[Rh_{22}(CO)_{37}]^{4-}$ anion can be separated, after filtration, evaporation to dryness in vacuo, and dissolution in water, by fractional precipitation of the sodium salts. After separation of an eventual first fraction at 2.5% NaCl concentration (which contains another new species, namely, the $[Rh_{14}(CO)_{26}]^{2-}$ anion[5]), addition of NaCl up to 9% causes the separation of $Na_4[Rh_{22}(CO)_{37}]$ in tiny brown crystals with a metallic appearance.[6] The yields are rather low, 1–10% depending on experimental conditions. The corresponding bulky cation salts can be obtained by metathesis in alcohols.

The characteristic IR spectrum of the sodium salt in THF (Figure 1) shows bands at 2020 (vs), 2010 (sh m), 1990 (vw), 1940 (w), 1880–1860 (m br), 1815 (sh m), 1803 (ms), and 1765 (w) cm⁻¹, which are possibly in accord with the X-ray structure. However, the spectrum in other solvents such as MeCN changes markedly in the bridging CO stretching region, showing bands at 2015 (vs), 1925 (w br), 1860 (sh), 1850 (ms br), 1835 (m sh), and 1805 (m br) cm⁻¹, suggesting that the anion in solution can adopt carbonyl stereochemistries different from that of the solid state depending on the solvent. This hypothesis seems to be confirmed by preliminary results from ^{13}C NMR spectroscopy.[7]

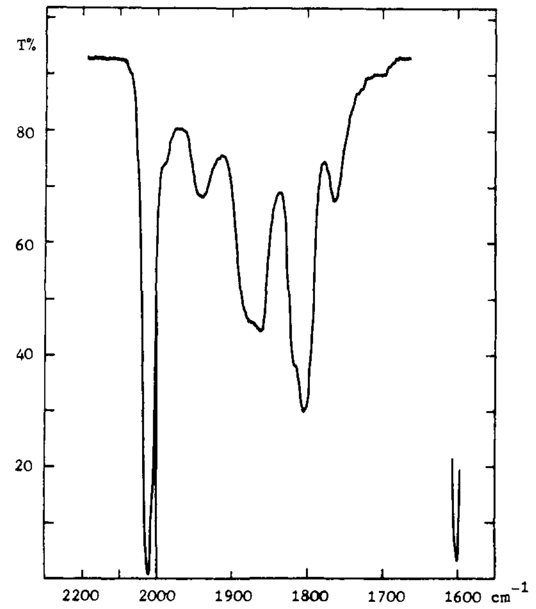
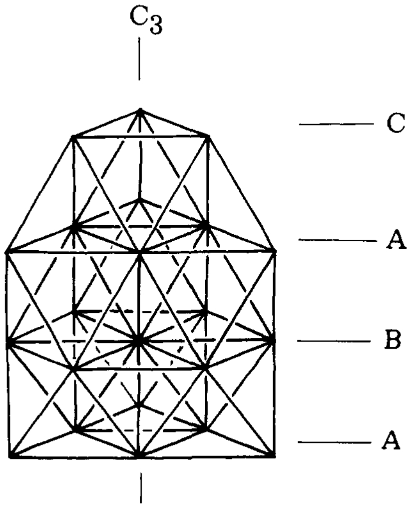


Figure 1. IR spectrum of $Na_4[Rh_{22}(CO)_{37}]$ in THF solution.

Scheme I



Studies on the $^{13}C\{^{103}Rh\}$ INDOR and ^{103}Rh NMR spectra are in progress. No hydride signal can be detected in the ^1H NMR spectrum from τ −50 to +58 either at room temperature or at −90 °C.

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(1) Albano, V. G.; Ceriotti, A.; Chini, P.; Ciani, G.; Martinengo, S.; Anker, W. M. *J. Chem. Soc., Chem. Commun.* **1975**, 860.

(2) Albano, V. G.; Ciani, G.; Martinengo, S.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1979**, 978.

(3) Martinengo, S.; Ciani, G.; Sironi, A.; Chini, P. *J. Am. Chem. Soc.* **1978**, *100*, 7096.

(4) Ciani, G.; Sironi, A.; Martinengo, S. *J. Organomet. Chem.* **1980**, *192*, C-42.

(5) Martinengo, S.; Ciani, G.; Sironi, A., to be published.

(6) In the fractional crystallization of the sodium salts, the required NaCl concentration is reached by dropping in, while stirring, the proper amount of a concentrated NaCl solution. The solution is then left to crystallize 3–4 h or more before filtration of every fraction. If the relative band intensities in the bridging COs region of the IR spectrum are not as in Figure 1, the product should be redissolved and the fractional precipitation repeated.

(7) Martinengo, S.; Heaton, B. T., unpublished results.

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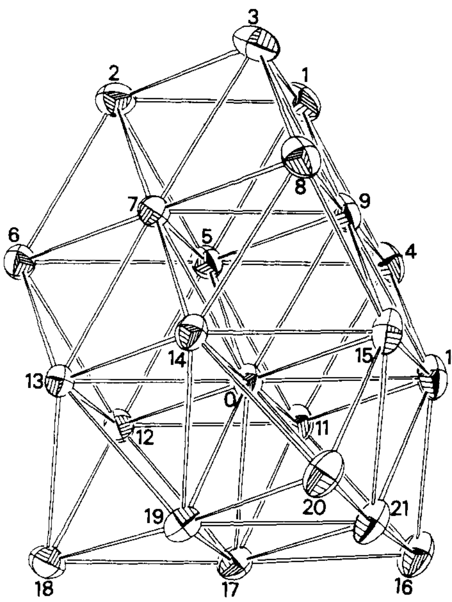

Figure 2. View of the metal atom cluster with the atomic numbering.

Crystals of the triethyl-*n*-propylammonium salt suitable for the X-ray analysis[8] were obtained by slow diffusion of a solution of $[NEt_3Pr]Br$ in 2-propanol into a solution of the sodium salt in methanol.

The $[Rh_{22}(CO)_{37}]^{4-}$ anion contains a compact close-packed metal atom cluster formed by superimposition of four pieces of compact layers (6/7/6/3) with an idealized C_{3v} symmetry. The sequence of layers is of the type ABAC, resulting in a mixed hcp/ccp arrangement as shown in Scheme I. The ccp moiety, formed by the three upper layers, is a 7/6/3 array of T_d symmetry (*i.e.*, a truncated supertetrahedron with four seven-atom faces). The hcp moiety, consisting of the three lower layers, is a 6/7/6 array of D_{3h} symmetry, which can be described as a centered "twinned-cuboctahedron" (like that present in the $[Rh_{13}H_{5-n}(CO)_{24}]^{n-}$ anions[1,2]) capped on the six square faces.

A view of the bare cluster is shown in Figure 2. The metallic polyhedron, containing one interstitial atom, exhibits two types of large faces: a basal six-metal triangle (normal to the threefold axis) and three lateral seven-metal centered hexagons. In the hcp moiety there are three surface butterflylike cavities. The 22 metal atoms occupy 7 different kinds of sites, with metal-metal connectivities ranging from 12 to 4. The array contains 11 tetrahedral and 7 octahedral holes. The 72 Rh-Rh bond lengths show only small variations, ranging from 2.729 (2) to 2.883 (2) Å, with an overall mean value of 2.798 Å.

The whole anion is illustrated in Figure 3. The 37 carbonyl groups exhibit a variety of geometries, from terminal to symmetric triple bridging, which are appropriate to reach charge equalization on the various surface metals. Their disposition reduces the idealized symmetry from C_{3v} for the cluster to C_3 for the overall anion.

In order to classify the different types of CO groups, we have assumed a maximum value of ~2.40 Å for a bonding, though weak, Rh-C interaction. On this basis, there are 12 terminal, 18 double-bridging, and 7 triple-bridging carbonyl groups. The 12 terminal ligands are bound 3 to the atoms of the small triangle Rh(1,2,3), 6 to the "corner" atoms of the two large 6-metal triangular layers, and 3 to alternate atoms of the central 7-metal hexagonal layer. Nine of the surface atoms do not bear terminal groups. The mean terminal Rh–C and C–O bond lengths are 1.84 and 1.17 Å, respectively.

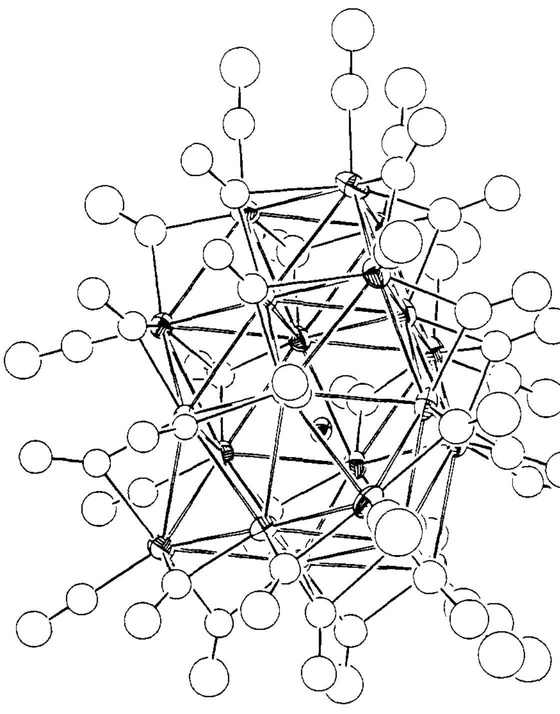

Figure 3. View of the $[Rh_{22}(CO)_{37}]^{4-}$ anion. The metallic cluster is oriented as in Figure 2. For the sake of clarity, the Rh-Rh bonds involving the interstitial metal have been omitted.

Of the 18 double-bridging groups, 15 are symmetric (mean Rh-C and C-O are 2.01 and 1.18 Å) and 3 (bridging the edges Rh(11)-Rh(16), Rh(13)-Rh(18), and Rh(15)-Rh(20)) are asymmetric (mean Rh-C short, Rh-C long, and C-O are 1.94, 2.19, and 1.18 Å, respectively). The 7 triple-bridging CO groups show rather scattered values for the Rh-C bond lengths and 3 are markedly asymmetric (on faces Rh(5,6,12), Rh(7,8,14), and Rh(4,9,10), each with 2 short and 1 long interaction of mean values 2.03 and 2.41 Å).

The anion possesses 276 valence electrons corresponding to 138 cluster valence MOs. An extended Hückel MO calculation on the bare metallic cluster, like those recently performed by Lauher,[9,10] has given 140 cluster valence MOs (280 electrons). This should require the presence of four hydridic atoms, probably interstitial, in accord with the suggestion[10] that such atoms stabilize the internal metal atom. However, as mentioned before, no evidence for hydridic atoms has yet been observed.

This Rh_{22} species is a further and convincing example supporting the view that cluster compounds of high nuclearity are good models of small metallic crystallites covered (or saturated) by ligands. Further work is in progress.

Acknowledgment. This work is dedicated to the memory of the late Professor P. Chini for his continuous encouragement. We thank Dr. A. Magni for preparative assistance and C.N.R. (Italy) for financial support.

Supplementary Material Available: Thermal and positional parameters and Rh-Rh bond distances (4 pages). Ordering information is given on any current masthead page.

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[8] Crystal data for $[Rh_{22}(CO)_{37}][NEt_3(n\text{-}Pr)]_4$: $M = 3877.5$; triclinic; space group $P\bar{1}$ (No. 2) with $a = 23.090$ (7), $b = 14.833$ (5), $c = 15.023$ (6) Å; $\alpha = 107.06$ (4)°, $\beta = 85.53$ (4)°, $\gamma = 91.69$ (4)°; $U = 4903.8$ Å^3; $D_m = 2.61$ (2), $D_c = 2.63$ g cm^{-3} for $Z = 2$. The structure was solved by Patterson and Fourier methods and refined by block-matrix least-squares on the basis of 9093 independent reflections with $\sigma(I)/I \leq 0.40$. The metal atoms were refined anisotropically and all the other atoms isotropically. The current conventional R value is 6.9%.

[9] Lauher, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 5305.
[10] Lauher, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 2604.

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Received May 8, 1980