in the crystal are conserved in solution, but the molecules are fluxional. For $W_2(O_2CNMe_2)_6$, the spectra (Figure 2) in CH_2Cl_2 are particularly easy to interpret. At −60 °C there are four signals of relative intensities 4:4:2:2 assignable to methyl groups of bridging O_2CNMe_2, the nonbridging bidentate O_2CNMe_2 that has equivalent methyl groups and the proximal and distal methyl groups of the remaining O_2CNMe_2 ligand. Between −60 and −30 °C interchange of the distal and proximal methyl groups becomes rapid enough to broaden their resonances and between −30 and −17° these and the line due to the other nonbridging O_2CNMe_2 coalesce so that we have a two-line spectrum with relative intensities of 4:8. The more intense signal sharpens between −17 and +28°. At still higher temperatures these two signals also broaden and coalesce, showing that all three ligand types undergo rapid scrambling.

We believe that the ready formation of these compounds and the presence of two bridging O_2CNR_2 groups is of great significance because such compounds may constitute the point of departure for a transformation of triply-bonded W_2 species to quadruply bonded ones. For example, homolytic removal of one univalent group, X, from each metal atom in an $M_2X_2(O_2CNR_2)_4$ molecule, accompanied or followed by movement of the two bidentate nonbridging O_2CNR_2 groups into a bridging posture would produce an $M_2(O_2CNR_2)_4$ species similar to the known xanthato compound,[10] $Mo(S_2COEt)_4$ and the many $M_2(O_2CR)_4$ compounds.[11,12]

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(8) Crystal Data. For $W_2(CH_3)_2(O_2CNEt_2)_4$: space group, $P2_1/c$; $a = 16.014$ (4), $b = 10.433$ (4), $c = 18.983$ (5) Å; $\beta = 107.51$ (2)°; $Z = 4$. Mo radiation. 2671 reflections having $I > 3\sigma(I)$ and $2\theta \leq 45°$. Refined anisotropically to $R_1 = 0.040$, $R_2 = 0.054$. For $W_2(O_2CNMe_2)_6$: space group, $P\bar{1}$; $a = 12.018$ (2), $b = 16.516$ (4), $c = 11.630$ (3) Å; $\alpha = 111.09$ (2)°, $\beta = 107.26$ (2)°, $\gamma = 91.00$ (2)°; $Z = 2$. Mo radiation. 3317 reflections having $I > 3\sigma(I)$ and $2\theta \leq 45$. Refined anisotropically to $R_1 = 0.073$, $R_2 = 0.103$.

(9) (a) A σ orbital (probably p_z or d_{z^2}) and d_{xz}, d_{yz}. (b) A σ orbital (probably s) along with p_x, p_y, d_{xy}, $d_{x^2-y^2}$. (c) A σ orbital, probably p_z or d_{z^2}.

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An Electron Filtering Membrane

Sir:

In our study of the oxidization of water by Mn(IV) porphyrin complex modeling *photosystem II*,[1,2] we found that a very effective electron transport could be achieved by use of an appropriately modified lecithin membrane[3] under conditions where material transport was negligibly small.

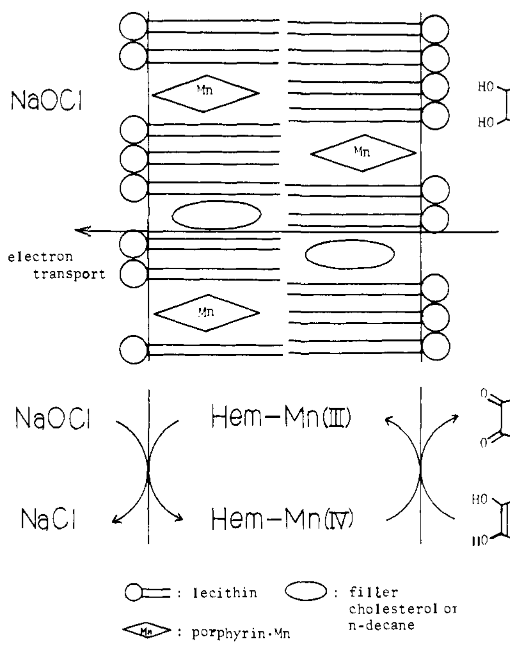


Figure 1.

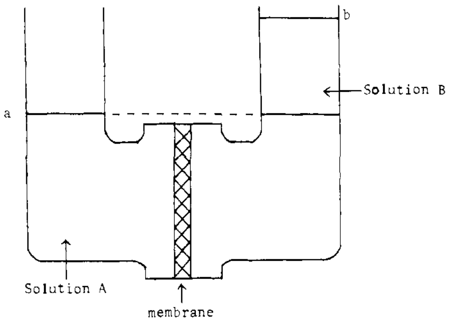
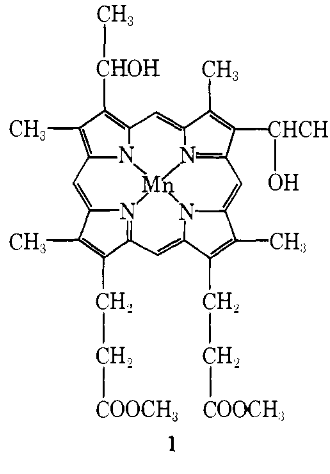


Figure 2. Electron filtering apparatus.

Now we wish to report that the hematoporphyrin Mn(III) complex **1** (hereafter, abbreviated as Hm·Mn(III)) intercalated in a lecithin membrane translocates electrons in the direction of the arrow in Figure 1. The membranes, prepared from lecithin, an appropriate filler (*n*-decane[4] or cholesterol[5]), and Hm·Mn(III), were supported on a millipore filter (2000 Å; Japan Millipore Ltd.). The membranes, supported by filters, were placed into the apparatus shown in Figure 2. With properly constructed membranes, no appreciable change in the levels of solution A (level a) or solution B (level b) was observed during a period of 48 h.

After being placed in position, Hm·Mn(III) membrane was treated with an aqueous solution of NaOCl[6] (ca. 3%



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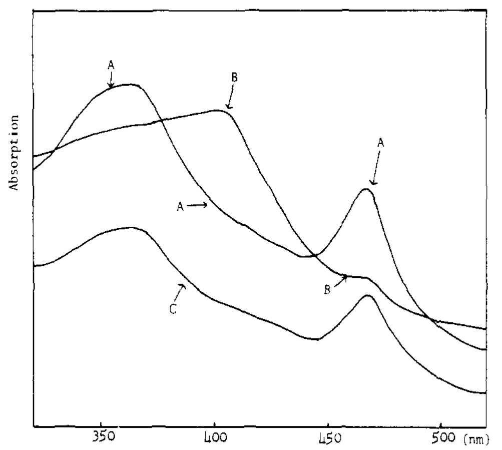

Figure 3. Electronic spectrum of a lecithin membrane: A, Hm·Mn(III) membrane; B, treatment of A with NaOCl for 1 min; C, treatment of B with aqueous ascorbic acid for 1 min.

concentration) containing KCl(1.0 M) to adjust its ionic strength. After 1 min, most of the Mn(III) in the membrane was effectively converted into Mn(IV) (more than 80%) as ascertained by electronic spectral changes as shown in Figure 3. Spectra were obtained after washing the membranes rapidly three times with aqueous alkaline solution (pH 12) to remove traces of NaOCl absorbed on the surface.

The Hm·Mn(IV) in the membrane was stable enough for spectroscopic measurements. The Mn(IV) membranes were then treated with aqueous ascorbic acid (0.01 M), containing KCl (1.0 M), for 1 min. After rapid washing with the aqueous solution of pH 12, Hm·Mn(IV) was estimated by electronic spectral changes, which showed that most of the Hm·Mn(IV) was converted to Hm·Mn(III) (70–80%) (Figure 3).

Spontaneous transport of ascorbic acid through the lecithin-Hm·Mn(III)-*n*-decane membrane from B (0.01 M ascorbic acid and 1.0 M KCl) to A (1.0 M KCl) was measured by the spectroscopic determination of ascorbic acid (265 nm) in A. It was $(3.8 \pm 0.3) \times 10^{-12}$ mol min^{-1}, ca. 3000 times slower than the reduction of the Mn(IV) membrane by ascorbic acid. The continuous electron transfer through the lecithin-Hm·Mn membrane from the ascorbic acid solution (5.0×10^{-5} M) to the sodium hypochlorite solution (1.3×10^{-1} M) was also studied by use of a salt bridge. The amount of the ascorbic acid oxidized was 7.4×10^{-10} mol min^{-1} (ca. 2.3 turnover per Mn in 25 min), 195 times faster than the rate of spontaneous transport. This strongly indicates that the oxidation-reduction did not result from material transport but from one-way electron transport as shown in Figure 1. Treatment of Mn(IV) membranes with an aqueous solution of pH 4 containing 1.0 M KCl instead of aqueous ascorbic acid again reduced Mn(IV) to Mn(III) as in the homogeneous system,[1] but the rate was considerably slower than that of the ascorbic acid reduction.

These electron translocating membranes are versatile, allowing the preparation of one-way oxidation-reduction electron transport systems or the effective separation of electrons from positive holes.

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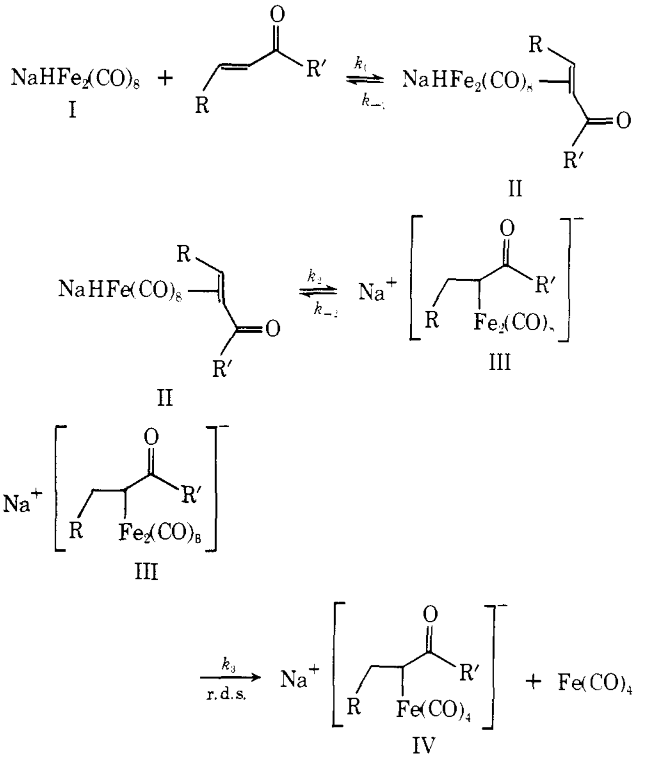
Binuclear Clusters in Organic Synthesis. Synthetic and Mechanistic Studies of the Reduction of α,β-Unsaturated Carbonyl Compounds by $NaHFe_2(CO)_8$

Sir:

Transition metal clusters offer the possibility of reaction paths involving adjacent metal centers acting on a common substrate. Although many studies exist probing the structure,[1] bonding,[1] and fluxional[2] behavior of carbonyl cluster compounds and their hydrides,[3] little is known about their chemical reactivity[4] and correspondingly even less about their detailed reaction mechanisms.[5,6] Only one cluster has been shown to be a useful synthetic reagent.[7]

Scheme I. Proposed Mechanism for the Reduction of α,β-Unsaturated Carbonyl Compounds by $NaHFe_2(CO)_8$



Reactions Occurring after the Rate-Determining Step