Insertion Reactions of Carbon Dioxide with Triply Bonded Ditungsten Dialkylamido Compounds. Structures and Dynamic Properties of the Resulting Carbamato Complexes

Sir:

Earlier work from our laboratories has shown that there exists an extensive series of compounds containing tungsten-tungsten triple bonds in molecules of the types $W_2(NR_2)_6$, R = CH_3,[1] C_2H_5,[2] and $W_2(NEt_2)_4X_2$, X = Cl,[2] Br,[3] I,[3] CH_3.[4] There is also the compound $W_2(CH_2SiMe_3)_6$ reported first by Wilkinson[5] and recently characterized structurally by us.[6] In addition, it has been shown that CO_2 reacts with mononuclear metal dialkylamido compounds to convert NR_2 ligands to dialkylcarbamato, O_2CNR_2, ligands.[7] In view of these two lines of work it was natural for us to examine the reaction of CO_2 with the dinuclear tungsten dialkylamido compounds.

We find that such reactions proceed readily in the presence of a trace of R_2NH which we believe to function catalytically by reacting with CO_2 to form R_2NCOOH which then attacks a W-NR_2 bond. We find that $W_2(NMe_2)_6$ is converted to $W_2(O_2CNMe_2)_6$, and that the carbon-tungsten bonds in $W_2(NEt_2)_4(CH_3)_2$ remain intact while the W-N bonds are attacked giving $W_2(CH_3)_2(O_2CNEt_2)_4$. Finally, the structures of both products[8] retain their W≡W bonds (W≡W = 2.275 ± 0.004 Å), have two bridging O_2CNR_2 groups and an approximately pentagonal set of bonds to the ligands. Stereoviews of $W_2(CH_3)_2(O_2CNEt_2)_4$ and $W_2(O_2CNMe_2)_6$ are shown in the upper and lower parts, respectively, of Figure 1.

The two structures are closely related. In addition to the essential identity in their W-W bond lengths, the coordination geometry is very similar. Each metal atom is at the apex of a pentagonal pyramid, the basal vertices of which are defined by the two oxygen atoms of a bidentate nonbridging carbamato group (W-O, av, 2.16 Å) one oxygen atom from each of the bridging, bidentate carbamato groups (W-O, av, 2.08 Å) and either a methyl group (W-C, av, 2.20 Å) or the oxygen atom from another carbamato group (W-O, av, 2.07 Å). In each case the molecule has approximate C_{2v} symmetry if the orientations of the ethyl groups are discounted.

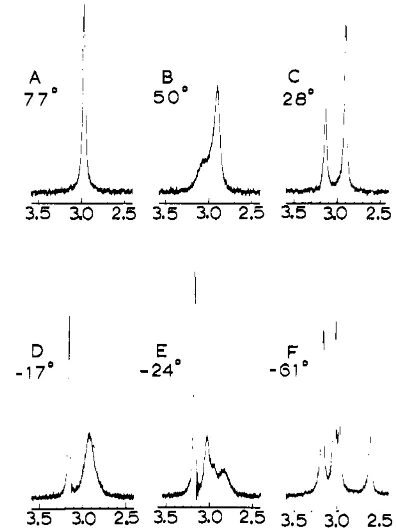

Figure 2. Proton NMR spectra at various temperatures of $W_2(O_2CNMe_2)_6$. Chemical shifts in parts per million are reported relative to hexamethyldisiloxane.

In the case of $W_2(O_2CNMe_2)_6$, the second oxygen atom of the carbamato group that, in effect, replaces the methyl group in $W_2Me_2(O_2CNEt_2)_4$ is also coordinated to the tungsten atom along the extension of the W-W axis (W-O, av, 2.67 Å). We view the bonding as follows: In $W_2(CH_3)_2(O_2CNEt_2)_4$ the tungsten atom uses three orbitals to form the W≡W bond[9a] and five to form the W—O and W—C bonds,[9b] leaving one[9c] empty, while in $W_2(O_2CNMe_2)_6$, the last-mentioned orbital is also used and the tungsten atom attains a radon configuration.

The proton NMR spectra show that the structures observed

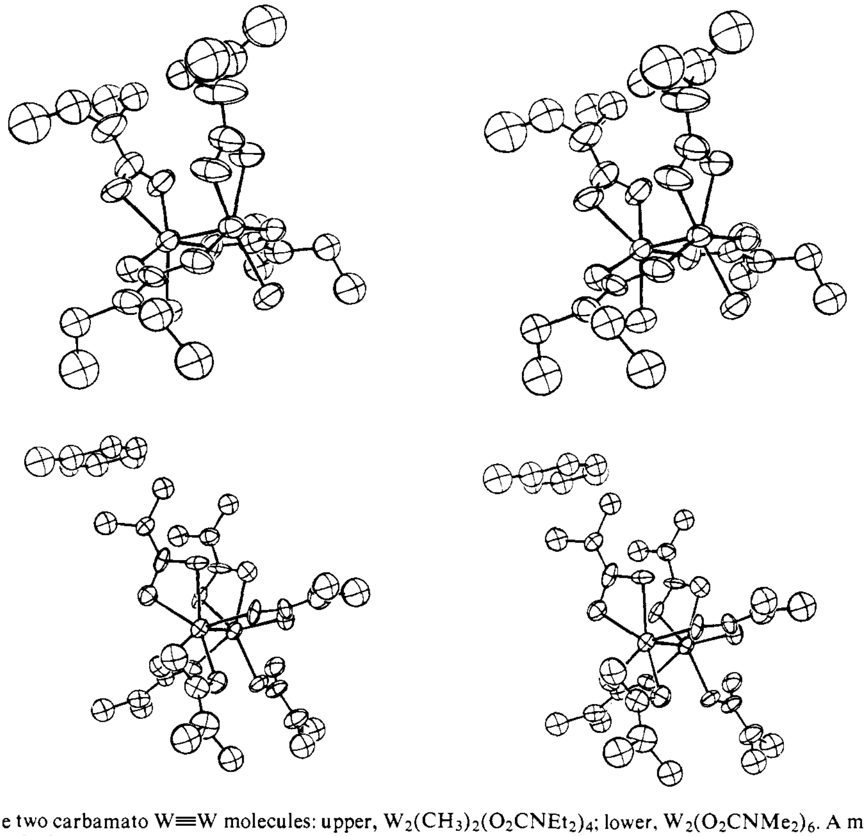

Figure 1. Stereoviews of the two carbamato W≡W molecules: upper, $W_2(CH_3)_2(O_2CNEt_2)_4$; lower, $W_2(O_2CNMe_2)_6$. A molecule of toluene of crystallization is also shown for the latter.

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] $Mo_2(S_2COEt)_4$ and the many $M_2(O_2CR)_4$ compounds.[11,12]

References and Notes

(1) M. H. Chisholm, F. A. Cotton, M. Extine, and B. R. Stults, *J. Am. Chem. Soc.*, **98**, 4477 (1976).
(2) M. H. Chisholm, F. A. Cotton, M. Extine, M. Millar, and B. R. Stults, *J. Am. Chem. Soc.*, **98**, 4486 (1976).
(3) M. H. Chisholm, F. A. Cotton, M. Extine, and B. R. Stults, unpublished studies.
(4) M. H. Chisholm, F. A. Cotton, M. Extine, M. Millar, and B. R. Stults, *Inorg. Chem.*, in press.
(5) W. Mowat, A. J. Shortland, G. Yagupsky, M. Yagupsky, N. J. Hill, and G. Wilkinson, *J. Chem. Soc., Dalton Trans.*, 533 (1972).
(6) M. H. Chisholm, F. A. Cotton, M. Extine, and B. R. Stults, *Inorg. Chem.*, in press.
(7) M. H. Chisholm and M. Extine, *J. Am. Chem. Soc.*, **96**, 6214 (1974).
(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, $P1$; $a = 12.018$ (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}.
(10) L. Ricard, P. Karagiannidis, and R. Weiss, *Inorg. Chem.*, **12**, 2179 (1973).
(11) F. A. Cotton, *Chem. Soc. Rev.*, **4**, 27 (1975).
(12) The work described here has been supported by the National Science Foundation (Grant Nos. GP33142X and MPS 73-05016) and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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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.

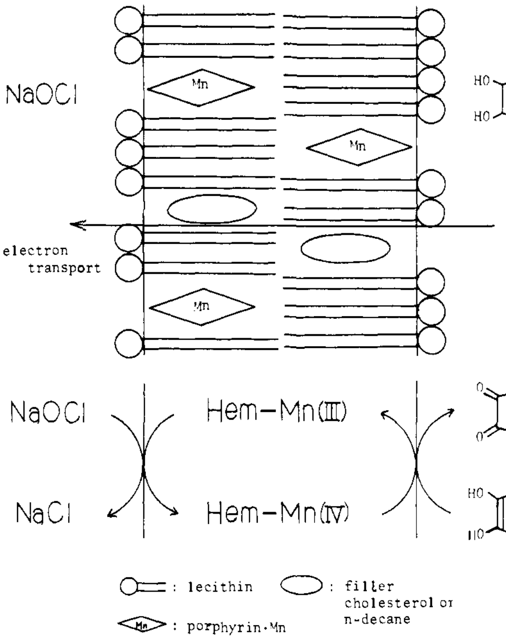


Figure 1.

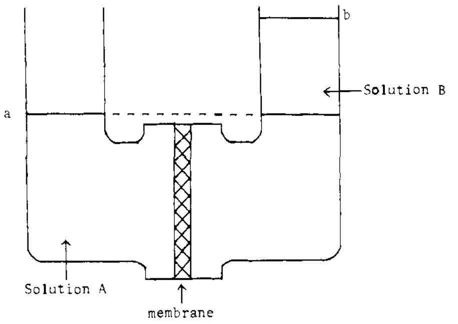
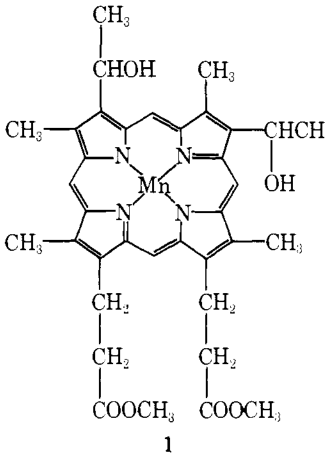


Figure 2. Electron filtering apparatus.

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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