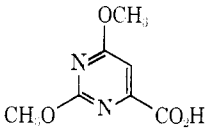
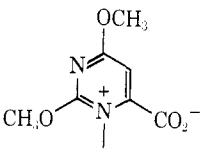
has precedent.[8] In path B under neutral conditions **3** is considered to be in equilibrium with the zwitterion **7**[9] which is the active species giving the ylide **8** in this route to **4**. Decarboxylations by such a route have considerable analogy for other heteroaromatic acids, and **6** and **8** have been suggested earlier as possible intermediates.[10]

Comparison of the rates of decarboxylation of **9** and **10**[11] provides a semiquantitative estimate of a zwitterionic pathway. In contrast to the smooth decarboxylation of the carboxylate anion of **3** in isoquinoline at 206°, the carboxylate anion of **9**, which cannot give a dipole-stabilized carbanion, does not decarboxylate under those conditions. Accordingly, the neutral carboxylic acid in the form of **9** is also considered to be unreactive[9a] and the facile decarboxylation of this acid with a first-order rate constant of 1.3×10^{-2} sec^{-1} in the neutral solvent sulfolane at 206° is attributed solely to a zwitterionic pathway involving **11**. If the



9



10, R = CH_3
11, R = H

rate constant for the decarboxylation of **11** is estimated to be 5×10^4 sec^{-1} by extrapolation from the reaction of **10** at lower temperatures, the equilibrium constant for zwitterion formation required by the observed rate of decarboxylation of **9** is 2.6×10^{-7}.

The above study of **9** may be used in an assessment of the decarboxylation of **3** *via* **7** by the kinetic model method which was successfully used earlier to distinguish neutral and zwitterionic processes in hydrogen–deuterium exchange of pyrimidones.[10] The value of K_z for **3** may be estimated by attenuating the equilibrium constant for **9** by the ratio of base ionization constants of *N*-methyl-2-pyridone to 2-methoxypyridine.[12] Not unexpectedly this approximation yields a value of K_z for **3** (3×10^{-10}) about three orders of magnitude smaller than that for **9**. As before, using k_z estimated at 5×10^4 sec^{-1} gives $K_z k_z$, the calculated rate constant for path B, equal to 0.2×10^{-4} sec^{-1}, which is in reasonable agreement with the experimentally observed rate constant 7.6×10^{-4} sec^{-1}. Accordingly, pathway B *via* the zwitterion is the preferred mechanism for the decarboxylation of formally neutral 1,3-dimethylorotic acid.

To the extent that **3** is a valid model for the enzymatic decarboxylation of **1**, an obvious role, which could account for several powers of ten of the effectiveness of the enzyme, for orotate decarboxylase is to increase the effective zwitterion concentration by reaction of one of the carbonyl oxygens in the pyrimidone with a proton or other suitable electron-deficient center either prior to or in the transition state for decarboxylation. Further studies are in progress.

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(10) P. Beak and R. Watson, *Tetrahedron*, **27**, 953 (1971), and references cited therein. An alternative to **7** and **8** which has the proton on O-4 is clearly possible.

(11) The zwitterion **10** is prepared in mixture with a neutral ester by hydrolysis of the corresponding pyrimidinium ester. The zwitterion has been characterized by nmr spectroscopy and hydrolysis to 1-methylorotic acid.

(12) E. J. Cohn and J. T. Edsall, Ed., "Proteins, Amino Acids, and Peptides As Ions and Dipolar Ions," Hafner Publishing Co., New York, N. Y., 1943; A. R. Katritzky, Ed., "Physical Methods in Heterocyclic Chemistry," Vol. I, Academic Press, New York, N. Y., 1963; E. Arnett and C. Douty, *J. Amer. Chem. Soc.*, **86**, 409 (1964).

Designed Syntheses of the $Mo_2Cl_9^{3-}$ Anion and the New $Mo_2Cl_9^{2-}$ Anion

Sir:

Although the structures,[1] chemistry,[2] and properties[3] of the bioctahedral anions, $M_2Cl_9^{3-}$ (M = Mo or W), have received considerable attention, the synthetic methods used in the formation of these anions from mononuclear reactants remain rather haphazard and are not entirely rational by any means. The basic difficulty in any rational approach starting with mononuclear reactants is the stereospecific formation of the face-shared polyhedron having three chlorine bridges. Our current strategy for the solution of this problem employs the notion that MCl_6^{n-} (n = 0, 1, and 2) can serve as an easily reduced tridentate ligand which can displace CO ligands on a trigonal face of a metal carbonyl halide, such as $M(CO)_5Cl^-$ or $M(CO)_4Cl_3^-$. The displacement of CO, which accompanies bridge formation, should be facilitated by concomitant electron transfer. Any additional CO ligands which remain after bridge formation should be readily lost because of the rather high formal oxidation state of the metal to which they are attached. Thus, the scheme which we envision is an oxidation–reduction reaction which proceeds by an inner sphere or bridging mechanism. If $M(CO)_4Cl_3^-$ is used as a reducing agent, the scheme is

$$MCl_6^{n-} + M(CO)_4Cl_3^- \xrightarrow[-3CO]{} Cl_3MCl_3M(CO)Cl_3^{(n+1)-} \xrightarrow[-CO]{} Cl_3MCl_3MCl_3^{(n+1)-}$$

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(3) (a) R. Saillant and R. A. D. Wentworth, *Inorg. Chem.*, 7, 1606 (1968); (b) R. Saillant and R. A. D. Wentworth, *ibid.*, **8**, 1226 (1969); (c) J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc. A*, 57 (1969); (d) I. E. Grey and P. W. Smith, *Aust. J. Chem.*, **22**, 121 (1969); (e) P. D. W. Boyd, P. W. Smith, and A. G. Wedd, *ibid.*, **22**, 653 (1969); (f) I. E. Grey and P. W. Smith, *ibid.*, **22**, 1627 (1969).

Since the average oxidation state of the product is dependent solely upon the oxidation state of the metal in MCl_6^{n-}, this scheme indicates that it should be possible to prepare not only $Mo_2Cl_9^{3-}$ from MCl_6^{2-} but also $Mo_2Cl_9^{2-}$ from MCl_6^{-}. (The $W_2Cl_9^{2-}$ anion was previously obtained from the oxidation of $W_2Cl_9^{3-}$ with molecular halogens.[2c]) Indeed, we are now able to report the successful syntheses of $Mo_2Cl_9^{3-}$ and the new anion, $Mo_2Cl_9^{2-}$, according to this strategy and the following reactions

$$MoCl_6^{2-} + Mo(CO)_4Cl_3^{-} \longrightarrow Mo_2Cl_9^{3-} + 4CO \quad (1)$$

$$\left.\begin{aligned} MoCl_5 + Cl^- &\longrightarrow MoCl_6^- \\ MoCl_6^- + Mo(CO)_4Cl_3^- &\longrightarrow Mo_2Cl_9^{2-} + 4CO \end{aligned}\right\} \quad (2)$$

Both reactions were conducted at the millimolar level in CH_2Cl_2 contained in glass vessels connected to a vacuum line. Procedures have been previously described.[4] Reaction 1 proceeded with the liberation of 87% of the available CO after 30 hr and the formation of orange $[(n\text{-}C_3H_7)_4N]_3Mo_2Cl_9$ (50% yield) in addition to some $Mo(CO)_6$ and an unknown carbonyl species. Complete evolution of CO occurred in reaction 2 after 24 hr and the yield of dark greenish brown $[(n\text{-}C_4H_9)_4N]_2Mo_2Cl_9$ was virtually quantitative. Satisfactory elemental analyses were obtained in both cases. The two compounds are also easily distinguished by their electronic absorption spectra and their magnetic properties (Table I). The temperature dependence

Table I. The Electronic Spectra and Magnetic Properties of the $Mo_2Cl_9^{3-}$ and $Mo_2Cl_9^{2-}$ Anions

Compound	ν,[a] cm^{-1}	μ_{eff},[b] BM
$[(n\text{-}C_3H_7)_4N]_3Mo_2Cl_9$	~13,200 (23)[c]	1.29 (302°)
	14,920 (33)	0.84 (204°)
	18,950 (638)	Diamagnetic (86°)
	23,300 (608)	
$[(n\text{-}C_4H_9)_4N]_2Mo_2Cl_9$	10,250 (163)	2.06 (300°)
	12,800 (171)	1.87 (236°)
	15,280 (265)	1.65 (140°)
		1.61 (95°)

[a] Molar extinction coefficients appear in parentheses. [b] Absolute temperatures appear in parentheses. [c] Some fine structure was noted.

of the magnetic moment of $Mo_2Cl_9^{3-}$ is in general accord with a thermal equilibrium between the manifold of antiferromagnetic spin states, $S = 3, 2, 1$, and 0, with $S = 1$ and 0 having only appreciable populations at room temperature. The magnetic moment at that temperature is considerably larger than the value of 0.6 BM found[3b] for $Cs_3Mo_2Cl_9$, but a dependence on the nature of the cation has been previously noted.[3d] The magnetic moment of $Mo_2Cl_9^{2-}$ is constant at about 1.6 BM at temperatures below 100°K, indicating a ground state having one unpaired electron with $g < 2$. As the temperature is increased, the increased magnetic moment is attributed to the thermal population of a manifold of the antiferromagnetic spin states, $S = {}^5/_2, {}^3/_2$, and ${}^1/_2$, with only the last two having appreciable populations at room temperature. The infrared spectrum of $Mo_2Cl_9^{2-}$ between 200 and 400 cm^{-1} resembles that of $W_2Cl_9^{2-}$. Both of these spectra resemble those of the reduced anions, $Mo_2Cl_9^{3-}$ and $W_2Cl_9^{3-}$, and we assume that the oxidized anions retain the bioctahedral structure. A complete description of the magnetic and spectroscopic properties is planned for a subsequent publication.

The $Mo_2Cl_9^{2-}$ anion seems to react with most donor solvents, precluding conductivity measurements. As an example, the anion is instantly reduced by CH_3CN to $Mo_2Cl_9^{3-}$. Rapid, quantitative reduction to $Mo_2Cl_9^{3-}$ also occurs with tin metal and excess alkylammonium halide in CH_2Cl_2.

We believe that this work represents the only synthesis of polynuclear halometalates which purports to have a rational basis. However, the success of the method does not prove the proposed mechanism although it would seem to be the simplest explanation of the results. Moreover, we do not claim that the reaction scheme is universally useful at present since a similar (but not identical) reaction which was designed to yield $W_2Cl_9^{3-}$, *viz.*, $WCl_6 + W(CO)_5Cl^- + 2Cl^- \rightarrow W_2Cl_9^{3-}$, gave instead WCl_6^{2-} and $W(CO)_4Cl_2$ and/or $W(CO)_4Cl_3^-$.[4] It would appear that these products resulted either from an outer sphere mechanism or an inner sphere mechanism followed by decomposition of a bridged intermediate.

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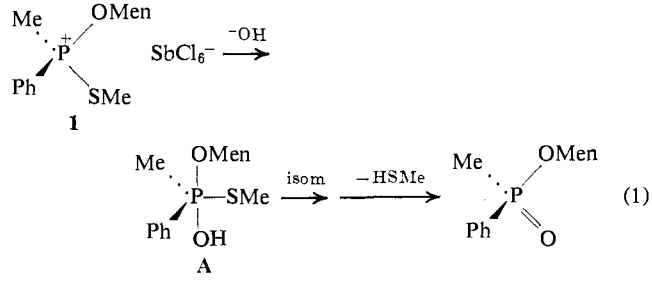
Preferential Mode for Nucleophilic Attack by Methoxide Ion on *O,S*-Dimethyl Phenylphosphonothiolate. A Contrasting Behavior to Reactions on Analogous Phosphonium Salts

Sir:

Recently, the mode for nucleophilic attack by hydroxide ion on menthoxy(methylthio)methylphenylphosphonium hexachloroantimonate (**1**) has been shown[1,2] to be exclusively axial on phosphorus in the face opposite the alkoxy ligand to form intermediate A (eq 1). Eventual loss of the methylthio group only



(1)

after an isomerization results in formation of the product with retention of configuration at phosphorus. In apparent contrast, the neutral ester analog of **1**, *O*-menthyl *S*-methyl phenylphosphonothiolate (**2**), suf-

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