

Conformers of the axially most-electronegative type (Ia) and in which the stannole ring spans one axial and one equatorial position (Ib)²¹ can interconvert by a pseudorotation mechanism which may go through a tetragonal pyramidal (Id) as shown.²²⁻²⁴ Ic, combining both the axial-bromine and stannole ring spanning axial and equatorial positions, or the tetragonal pyramidal Id could give rise to the observed cyclopentadienyl group nonequivalence through a stannole ring nonplanarity. Such magnetic nonequivalence arising from a preferred dissymmetric diene conformation is proposed for the related (4-bromo-1,2,3,4-tetraphenyl-*cis,cis*-1,3-butadienyl)dimethyltin bromide,¹⁶⁻¹⁸ but is less likely for I. Formulation of a lithium ion association with the stannole ring in dicyclopentadienylstannole with a bromide counterion which would rationalize the temperature-dependent spectra in terms of a dissociation of the complex is ruled out by the lack of chemical shift dependence on temperature, and by the presence of a tin-bromide shift in the infrared. Chemical shifts are sensitive to the metal ion, Li⁺ or Tl⁺, however, and the lack of appreciable conductivity in nitrobenzene suggests significant ion pairing.

The synthesis of I can proceed through either 1-bromo-1-cyclopentadienylstannole followed by adduct formation with C₅H₅⁻ anion or dicyclopentadienylstannole with subsequent bromide ion uptake. The appearance of both cyclopentadienyltin resonances from the onset of reaction argues against the former.

Tetraorganotin compounds show no Lewis acidity, yet the as yet unisolated 1,1-dicyclopentadienyl-2,3,4,5-tetraphenylstannole apparently takes up bromide ion during its formation from lithium or thallium cyclopentadiene in THF-hexane to give the [R₄SnBr]⁻ anion rather than precipitating the metal bromide.²⁵

Acidity studies on other cyclopentadienyltin derivatives are proceeding.

Acknowledgments. Our work is supported by the National Science Foundation through Grant 16,544. We thank Drs. E. A. Williams and J. D. Cargioli of the General Electric Research and Development Center for the carbon-13 spectra, Mr. D. L. Tomaja for the tin-119m Mössbauer spectra, the M&T Chemical Co. for the generous gift of organotin starting materials, and Professors J. A. Zubieta and R. J. Zwarich for helpful discussions.

References and Notes

- (1) Mp 167.5–168.0°; MS P⁺ (a dibromo-monetin polyisotopic ion) at *m/e* 638 (mol wt = 638 (calcd)); tin-119m Mössbauer spectrum *IS* = 1.51 ± 0.06, *QS* = 2.51 ± 0.12 mm/sec.
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- (21) Based on these structures and hybridization arguments, the downfield resonance in the carbon-13 spectrum which has the smaller $J^{117,119\text{Sn}-13\text{C}}$ value can be assigned to the axial-cyclopentadiene group. The tin coupling in the proton spectrum is smaller for the downfield resonance only at lower temperatures.
- (22) Pseudorotation about either of the tin attachments to the stannole ring as a pivot would place the ring in a diequatorial position with a stannole angle C–Sn–C = 120°. Such an expansion of the ring angle at tin would be accompanied by considerable strain.
- (23) Square pyramidal intermediates have been proposed to rationalize the temperature-dependent proton NMR of 2-biphenylbis(4,4'-bitolyl)antimony whose singlet methyl resonance collapses to a quartet at –60° (ΔE^\ddagger = 11.6 kcal/mol) (D. Hellwinkel and M. Bach, *Naturwissenschaften*, **56**, 214 (1969); *J. Organomet. Chem.*, **17**, 389 (1969)).
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Received September, 16, 1974

Protonated Chloromethyl Alcohol and Chloromethyl Ethers. Proof for the Intermediacy of the Elusive Chloromethyl Alcohol¹

Sir:

Chloromethyl alcohol, although suggested to be an intermediate in chloromethylation with formaldehyde and hydrogen chloride,² was not directly observed or substantiated by any evidence.

Encouraged by our previous preparation and study of protonated fluoromethyl alcohol,³ we have extended our investigations and report now our success in directly observing (by low temperature NMR spectroscopy) protonated chloromethyl alcohol and a series of related protonated chloromethyl ethers.

A clean solution of protonated chloromethyl alcohol **1** was obtained when anhydrous HCl was introduced into a

Table I. ¹H NMR Data of Protonated Chloromethyl Alcohol and Chloromethyl Alkyl Ethers^a

	H ₁	H ₂	H ₃	H ₄	H ₅	H ₆	Coupling constants, Hz
$\text{ClCH}_2\overset{\oplus}{\text{O}}\text{H}_2$	11.67 (t)	6.40 (t)					$J_{12} = 4.8$
$\text{ClCH}_2\overset{\oplus}{\text{O}}\text{CH}_3$	11.40 (m)	6.38 (d)				4.82 (d)	$J_{12} = 4.8$ $J_{16} = 3.3$
$\text{ClCH}_2\overset{\oplus}{\text{O}}\text{CH}_2\text{CH}_3$	11.00 (p)	6.40 (d)	5.37 (d,q)			1.90 (t)	$J_{12} = 5.0$ $J_{13} = 3.4$ $J_{36} = 7.4$
$\text{ClCH}_2\overset{\oplus}{\text{O}}\text{CH}_2\text{CH}_2\text{Cl}$	11.70 (p)	6.37 (d)	5.27 (d,t)	4.16 (t)			$J_{12} = 4.2$ $J_{34} = 4.2$
$\text{ClCH}_2\overset{\oplus}{\text{O}}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	11.17 (m)	6.37 (d)	5.27 (m)	3.90 (t)	2.26 (m)		$J_{12} = 4.5$ $J_{45} = 5.3$
$\text{ClCH}_2\overset{\oplus}{\text{O}}\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\overset{\oplus}{\text{O}}\text{CH}_2\text{Cl}$	11.83 (m)	6.43 (br s)	5.28 (m)			2.50 (m)	

^a Spectra were obtained from a Varian A56/60A spectrometer at -80° in SO_2 . Chemical shifts in δ (ppm) refer to a capillary TMS and the multiplicities are given in parentheses: s, singlet; d, doublet; t, triplet; q, quartet; p, quintet; m, multiplet; br, broad.

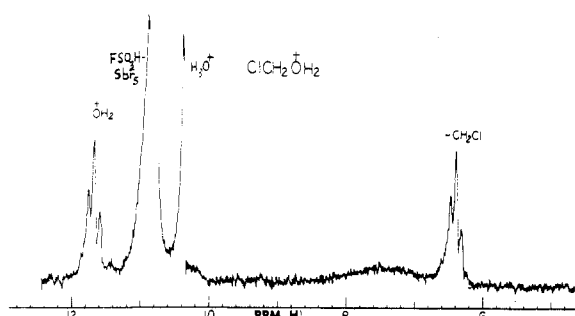
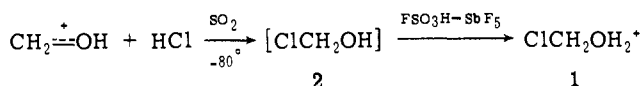
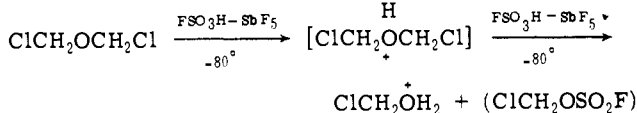
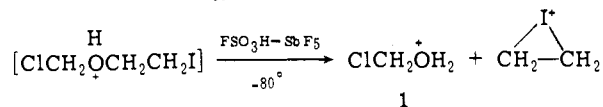
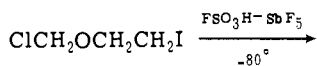


Figure 1. ¹H NMR spectrum of protonated chloromethyl alcohol in $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2$ solution at -80° .

solution of protonated formaldehyde in $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2$ at -80° . The direct observation of **1** proves the intermediacy in the reaction



of chloromethyl alcohol **2**.

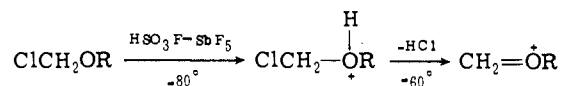


The ¹H NMR spectrum of **1** (Figure 1) shows the $-\overset{\oplus}{\text{O}}\text{H}_2$ triplet at δ 11.67 ($J_{\text{H-H}} = 4.8$ Hz) and the methylene triplet at δ 6.40. There is no evidence of exchange, including chlorine-fluorine exchange (which would show characteristic H-F coupling as found in $\text{FCH}_2\text{OH}_2^+$).

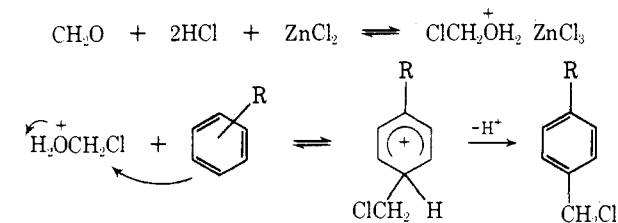
Protonated chloromethyl alcohol is less stable than protonated fluoromethyl alcohol³ and decomposes at temperatures above -65° . As a matter of fact its observation was unexpected and considered remarkable, because fluorine is so unique in stabilizing one carbon atom species (such as CF_3O^+ , etc.) that in no way could any analogy be expected. Attempts to prepare higher homologous protonated α -chloro-

alkyl alcohols failed. Protonated acetaldehyde^{3b} was unaffected by adding HCl.

A series of chloromethyl alkyl ethers was also protonated in $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2\text{ClF}$ solution at -70° , giving the corresponding chloromethyl alkyloxonium ions. ¹H NMR data are summarized in Table I. Protonated chloromethyl alkyl ethers are less stable than the parent, unsubstituted aliphatic ethers⁵ and slowly eliminate hydrogen chloride at -60° to form alkoxy-carbenium ions.⁶ No cleavage giving protonated chloromethyl alcohol could be observed.



The exact nature of the reactive chloromethylating agent in electrophilic aromatic chloromethylations was never established. $\text{CH}_2\text{O}^+\text{H}$ and $^+\text{CH}_2\text{Cl}$ are the species frequently suggested.⁷ It is highly improbable that the chloromethyl cation exists in any chloromethylation systems. The demonstration in the present work, that the hydroxycarbenium ion with HCl gives chloromethyl alcohol, which in acidic media is observed in its relatively stable protonated form, i.e., the chloromethyloxonium ion, allows one to suggest that the latter can be a reactive intermediate in chloromethylation with formaldehyde-HCl systems



This suggestion is in accord with kinetic data of chloromethylations⁷ (showing first-order dependence in aromatics and formaldehyde) and would eliminate the need to suggest either the chlorocarbenium ion ($^+\text{CH}_2\text{Cl}$) or the hydroxycarbenium ion to be directly involved. In the same manner protonated (or Lewis acid complexed) chloromethyl alkyl ethers are the probable alkylating agents in chloromethylations with these ethers.

We feel that our present findings shed new light on the mechanistic aspects of chloromethylation and may also contribute to understanding the nature of the reactive alkylating species involved in the *in vitro* carcinogenic activity of chloromethyl ethers and related formaldehyde systems.⁸

Acknowledgement. Support of our work by the National Science Foundation and the National Institutes of Health is gratefully acknowledged.

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Received January 4, 1975

Linear Trinuclear Copper(II) Complex with a Spin-Doublet Ground State

Sir:

There have been several reports¹⁻⁶ of oxygen-bridged trinuclear copper(II) complexes that exhibit varying degrees of antiferromagnetic behavior. The molecular structures⁷⁻⁹ for a representative number of these complexes have revealed only two kinds of trinuclear copper clusters. Both consist of triangular arrays (I and II) of copper ions but differ in the kind of bridging oxygen atoms (μ_2 or μ_3), the

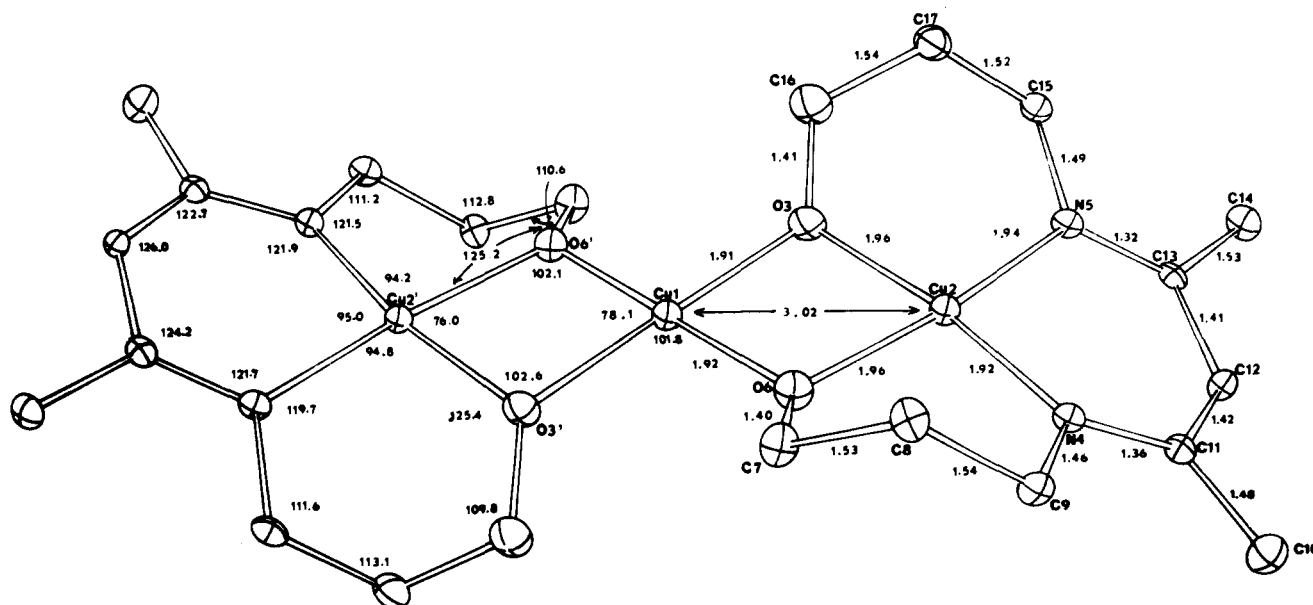
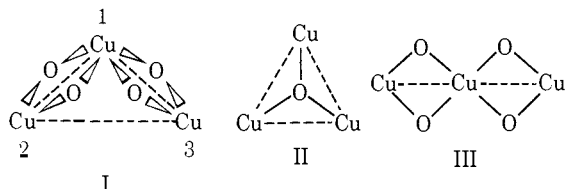


Figure 1. Molecular structure of the trinuclear complex $\text{Cu}_3(\text{C}_{11}\text{H}_{19}\text{N}_2\text{O}_2)_2$, showing all non-hydrogen atoms. Bond distances and bond angles have deviations in the range 0.01-0.02 Å and 0.2-0.6°, respectively.

shape of the triangle (isosceles I or equilateral II), and the degree of exchange coupling between copper ions.

Complexes of type I exhibit subnormal room temperature magnetic moments greater than ~ 1 BM per copper ion; that is, there is still some population of the spin $\frac{3}{2}$ state by the three electrons of the Cu_3 core at room temperature. The magnetic behavior of type I complexes with a few exceptions has been characterized^{5,7,10} by assuming a model based upon three interacting spin $\frac{1}{2}$ species with exchange coupling between the central copper ion and its neighbors (1-2) and (1-3) but no interactions (2-3) between extreme copper ions of the triad.

Complexes of type II, however, exhibit complete spin pairing, so that only the spin-doublet state ($S = \frac{1}{2}$) is populated at room temperature. All type II complexes examined to date by X-ray diffraction have shown the copper ions to be positioned at the corners of an equilateral triangle. We wish to report the first example of a trinuclear copper complex having a spin-doublet ground state in which the copper ions are arranged in a strict linear fashion and joined by μ_2 -bridging oxygen atoms, III.

The compound is the neutral copper(II) complex of the trianion of the tetradentate ligand, IV, formed by the condensation of 2,4-pentanedione and 3-amino-1-propanol. The compound was prepared by the reaction of copper(II) acetylacetonate with potassium hydroxide in neat 3-amino-1-propanol at 100° over a 3-hr period. Although the initial product is contaminated with the red dimeric complex, $[\text{Cu}(\text{PIA})_2]^{11}$ (where PIA is the dianion of ligand V), separation was accomplished by extensive washings in hot absolute alcohol. Crystallization from a mixture of xylenes gave green needle crystals of empirical formula $\text{Cu}_3\text{C}_{22}\text{H}_{38}\text{N}_4\text{O}_4$. Precession photographs (Zr-filtered Mo $K\alpha$ ra-

