

activity of $I_2(SO_3F)_6$ in the liquid phase remains essentially constant as dilution causes the higher polymer(s) to dissociate.

$I(SO_3F)_3$ is yellow in both the solid and liquid states. The sample of mole fraction 0.746 was green. Samples of smaller mole fraction appeared in bulk to be black, but thin films showed some green color down to mole fraction 0.53. Below this concentration, thin films were dark brown.

Over much of the range of composition the liquid had little tendency to wet the glass container. A film might flow from the wall completely or it might leave isolated drops of liquid.

Since the reaction of I_2 with $I(SO_3F)_3$ or ISO_3F is slow at room temperature and since many samples were heated to obtain complete reaction, it seems likely that subsequent cooling to obtain melting points carried the materials to temperatures low enough to prevent existence of true equilibrium among molecular species at some of the observed melting points. It is not certain that this was the case, however, and it seems likely that the observed melting points were close to those which would have been obtained at true equilibrium. Nmr spectra taken at 110° contained only one line, thereby indicating a rather rapid exchange among molecular species at this temperature. The line was rather broad.

Materials listed in Table I at mole fractions 0.131, 0.250, 0.499, and 0.753 had compositions close to those of the iodine fluorosulfates listed in Table II. In each case the observed range of melting for these samples was about 1.5° with most of the material melting close to the indicated melting point. Compositions of eutectic mixtures and the corresponding eutectic temperatures given in Table II were taken from the graph of melting point vs. composition (Figure 1). For each of the first three eutectics the onset of melting of mixtures of nearby composition was observed to be close to the temperature given in Table II. The eutectic point listed as -52° really was not observed. From the data of Table I, it appears that the mole fraction of $S_2O_6F_2$ at the eutectic point was 0.999 or more. The eutectic temperature must be only slightly below the melting point of pure $S_2O_6F_2$, which is listed as -52.0° , the value discussed above in the Experimental Section.

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Chemistry of Bis(fluoroformyl) Peroxide. Isomerization and Disproportionation

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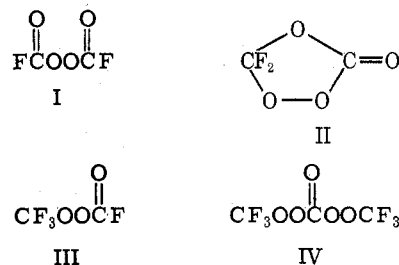
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Bis(fluoroformyl) peroxide was shown to isomerize to the ozonide of the unknown difluoroketene. The isomerization was effected at low temperature with either activated KF or trimethylamine and was shown to be reversible. Strong bases, such as CsF and trimethylamine, also catalyzed the disproportionation of $C_2F_4O_4$ to bis(trifluoromethyl) bis(peroxy)carbonate, $(CF_3OO)_2CO$, and trifluoromethyl fluoroformyl peroxide, CF_3OOCOF . These reactions constitute new syntheses for these compounds. Fragmentation patterns are reported for all peroxides studied in this work as well as infrared data.

Introduction

Much of the chemistry of bis(fluoroformyl) peroxide (I)¹ has been devoted to the elucidation of its reaction chemistry as a radical source.²⁻⁵ One of the more interesting of these reactions was the complex, low-yield reactions of I with difluorodiazene to give fluoroformyl perfluoromethyl peroxide.⁵ As part of a study of acyl fluorides we were interested in both the conversion of the $-C(O)F$ moiety to the CF_3O group and the reactions of I with Lewis bases. Indeed, the action of bases such as alkali fluorides on I have given two distinct sets of products depending on the strength of the base. With a weak base such as KF, I is converted to the ozonide of difluoroketene, 3,3-difluoro-2,4,5-trioxacyclopentanone (II). Strong bases, such as CsF, cause the peroxide (I)

to disproportionate in high yields to peroxide III and to bis(trifluoromethyl) bis(peroxy)carbonate (IV).



Experimental Section

Apparatus and Materials.—Reactions were conducted in stainless steel cylinders and the products were separated and purified using a stainless steel-Teflon FEP vacuum line. Pressures were measured by means of a Heise Bourdon tube pressure gauge. Infrared spectra were taken on Perkin-Elmer Infracords 137 and 337 using 5-cm path length stainless steel or Kel-F cells fitted with AgCl windows. The ^{19}F nmr spectra were obtained using a Varian Associates high-resolution nmr spectrometer

(1) A. J. Arvia, P. J. Aymonino, C. H. Waldow, and H. J. Schumacher, *Angew. Chem.*, **72**, 169 (1960).

(2) R. L. Cauble and G. H. Cady, *J. Amer. Chem. Soc.*, **89**, 5161 (1967).

(3) W. B. Fox and G. Franz, *Inorg. Chem.*, **5**, 946 (1966).

(4) A. J. Arvia, P. J. Aymonino, and H. J. Schumacher, *Z. Phys. Chem. (Frankfurt am Main)*, **28**, 393 (1961).

(5) R. L. Talbott, *J. Org. Chem.*, **33**, 2095 (1968).

operating at 56.4 Mc. Samples were sealed in Pyrex and CFCl_3 was employed as the internal standard. Mass spectral data were obtained with a CEC 21-103C mass spectrometer. The density was determined using a Pyrex pycnometer fitted with a Fischer-Porter Teflon valve and calibrated prior to use with mercury. Cesium and potassium fluorides were fused and then powdered in a drybox prior to use.

Preparation of Bis(fluoroformyl) Peroxide (I).—A modified literature⁶ technique was used in the preparation of peroxide I. A stream of CO (200 cm^3/min) and O_2 (750 cm^3/min) was premixed in a Pyrex bulb as was a stream of F_2 (400–450 cm^3/min) and O_2 (1000 cm^3/min) in a separate Pyrex bulb. The two gas streams were then mixed in a Pyrex manifold and passed through a Pyrex reactor coil (1.5 in. o.d. $\times$ 30 ft, 8 l. volume) heated in a water bath to $+55^\circ$. Following the glass reactor coil were two T-traps cooled at -80° with Dry Ice/Freon 11 slush. Unreacted gas was finally passed through a H_2SO_4 bubbler into the atmosphere. After the desired reaction period (usually 4 hr), the entire system was flushed with oxygen. Using a vacuum system, the product was transferred at ambient temperature into a stainless steel cylinder chilled to -196° . A typical 4 hr experiment produced 97 g of peroxide I representing a 63% yield based on CO used. (Caution! It is extremely important to keep the reactant mixture ratio constant. In preliminary work at our laboratory a number of serious explosions destroyed the glass apparatus when an imbalance in reactants occurred.)

Preparation of Trifluoroformyl Fluoroformyl Peroxide (III) and Bis(trifluoromethyl) Bis(peroxy)carbonate (IV).—A 75-ml prepassivated stainless steel Hoke cylinder was loaded with 5 g of powdered CsF and evacuated and then I (1210 cm^3 , 54.0 mmol) added at -196° . The cylinder was warmed from -196 to -78° over several hours. The cylinder was further warmed from -78 to -40° and maintained at this temperature for the duration of the experiment (27 days). Products of the reaction were separated by fractional condensation at -95 , -112 , -126 , and -196° . Noncondensable product gases were pumped through the -196° trap and vented. The -126° fraction contained (299 cm^3 , 13.3 mmol) peroxide III as identified by its infrared spectrum⁷ and mass spectrum (Table I). This represents a 49%

TABLE I
MASS PATTERNS OF III AND IV

<i>m/e</i>	Ion	—Rel intens—	
		$\text{CF}_3\text{OOC}(=\text{O})\text{F}$	$(\text{CF}_3\text{OO})_2\text{C}=\text{O}$
148	$\text{C}_2\text{F}_4\text{O}_8^+$	1.27	
129	$\text{C}_2\text{F}_3\text{O}_8^+$	1.19	17.53
113	$\text{C}_2\text{F}_3\text{O}_2^+$	0.54	7.33
85	CF_3O^+	1.92	3.27
82	CF_2O_2^+	0.98	
69	CF_3^+	100.00	100.00
66	CF_2O^+	20.38	
63	CFO_2^+	20.00	
50	CF_2^+	2.46	1.27
47	CFO^+	73.85	34.07
44	CO_2^+	31.54	46.53
32	O_2^+	4.23	
31	CF^+	5.19	2.27
28	CO^+	18.46	17.33

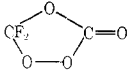
yield based on 1 mol of peroxide III from 2 mol of peroxide I. The following vapor pressure-temperature data were observed ($^\circ\text{C}$, mm): -78.9 , 12; -63.5 , 42; -57.0 , 64.5; -45.9 , 144; -31.5 , 325; -24.5 , 482. The vapor pressure-temperature relationship⁸ is described by the equation, $\log P_{\text{mm}} = 8.4092 - 1423.8/T^\circ\text{K}$. The normal boiling point calculated from the equation is -15.7° . The melting point was observed at -128 to -129° . The derived ΔH_{vap} is 6.54 kcal/mol and the Trouton constant is 25.4. The following temperature-density data were obtained ($^\circ\text{C}$, cm^3): -50.5 , 1.654; -46.3 , 1.638; -44.4 , 1.637; -42.2 , 1.621; -39.8 , 1.626; -37.0 , 1.616; -34.3 , 1.606; -31.7 , 1.598; -30.0 , 1.596; -28.8 , 1.584; -28.0 ,

1.588; -26.0 , 1.575; -22.9 , 1.563; -22.6 , 1.561; -17.5 , 1.543; -17.4 , 1.547; -13.1 , 1.529; -9.4 , 1.515; -8.8 , 1.511; -7.6 , 1.504; and $+23.3$, 1.368. The temperature-density relation is described by the equation $d(\text{cm}^3) = 1.4750 - 4.311 \times 10^{-5}t_c - 1.539 \times 10^{-7}t_c^2$. The observed molecular weight (by gas density) was 149, calculated 148.

The -95° fraction contained approximately 1.5 ml of a clear liquid at ambient temperature which was identified as bis(trifluoromethyl) bis(peroxy)carbonate by infrared⁹ and mass spectra (Table I). This fraction was further purified by fractionation through a -80° trap. The physical properties⁹ were obtained on a slightly contaminated sample. The molecular weight (by gas density) was 222 (calculated 230), vapor pressure at 27.0° was 170 mm with an estimated boiling point of 55° , and density at 23° was 1.64 cm^3 . The ^{19}F nmr shows a single peak at $\phi + 69.56$. The small amount of impurity is yet to be identified. The 1.5 ml of product (2.5 g) represents an approximately 48% yield based on 1 mol of carbonate from 3 mol of peroxide I.

Isomerization of Bis(fluoroformyl) Peroxide. Preparation of 3,3-Difluoro-2,4,5-trioxacyclopentanone (II) (Difluoroketene Oxonide). A. Using Potassium Fluoride.—A 30-ml prepassivated stainless steel Hoke cylinder was loaded with 2 g of powdered KF and evacuated, and then I (258 cm^3 , 11.5 mmol) added at -196° . The cylinder was warmed from -196 to -80° and kept at this temperature for 36 days. Products of the reaction were separated by fractional condensation at -95 , -112 , and -196° . The -95° fraction contained unreacted I (213 cm^3 , 9.5 mmol) as identified by its infrared spectrum. The -112° fraction contained II (10.4 cm^3 , 0.46 mmol) which was identified by its mass spectrum (Table II), ^{19}F nmr and infrared spectrum

TABLE II
MASS PATTERNS OF $\text{C}_2\text{F}_2\text{O}_4$ ISOMERS

<i>m/e</i>	Ion	—Rel intens—	
			
82	CF_2O_2^+	100.00	
66	CF_2O^+	39.46	3.62
63	CFO_2^+	11.21	2.13
60	CO_2^+	1.43	
50	CF_2^+	22.42	
47	CFO^+	56.95	31.49
44	CO_2^+	80.72	100.00
32	O_2^+	47.98	8.09
31	CF^+	6.28	1.11
28	CO^+	30.40	15.97
19	F^+	1.79	0.49
17	O^+	17.94	13.85
12	C^+	13.39	11.92

(Figure 1). The observed molecular weight (by gas density) was 124.1, calculated 126.

B. Using Trimethylamine.—A sample of I (719 cm^3 , 33.5 mmol) was condensed into a 30-ml Hoke cylinder containing a catalytic amount of $(\text{CH}_3)_3\text{N}$ (2.8 cm^3 , 0.13 mmol). The cylinder was maintained at -80° for 5 days after which it was fractionated in the vacuum line through traps cooled at -95 , -112 , and -196° . The -95° fraction consisted of I (48.0 cm^3 , 2.15 mmol) contaminated with a small amount of $(\text{CF}_3\text{OO})_2\text{C}=\text{O}$. The -112° fraction contained II (12.0 cm^3 , 0.54 mmol) and the -196° fraction contained III (15.8 cm^3 , 0.70 mmol) with 76.2 cm^3 of COF_2 and CO_2 .

Isomerization of the Oxonide (II).—The oxonide II (17.9 cm^3 , 0.80 mmol) was condensed into a 30-ml stainless steel Hoke cylinder containing activated KF. The reactor was thermostatted at -80° for 5 days after which the volatile contents were fractionated through traps maintained at -95 , -126 , and -196° . The -95° fraction contained bis(fluoroformyl) peroxide I (6.5 cm^3 , 0.74 mmol), the -126° trap contents were the oxonide II (6.1 cm^3 , 0.27 mmol), and the -196° fraction was essentially carbonyl fluoride (17.7 cm^3 , 0.79 mmol) contaminated with CO_2 .

(6) A. J. Arvia, P. J. Aymonino, and H. J. Schumacher, *Z. Anorg. Allg. Chem.*, **316**, 327 (1962).

(7) R. L. Cauble and G. H. Cady, *J. Org. Chem.*, **35**, 2094 (1968).

(8) The vapor pressure-temperature relationship was recently reported by D. DesMarteau, *Inorg. Chem.*, **9**, 2179 (1970). Our data differ very slightly with a lower boiling point (-15.7° vs. -14.2°) and give a greater ΔH_{vap} .

(9) Data on pure IV have been reported by P. A. Bernstein, F. A. Hohorst, and D. D. DesMarteau, *J. Amer. Chem. Soc.*, **93**, 3882 (1971).

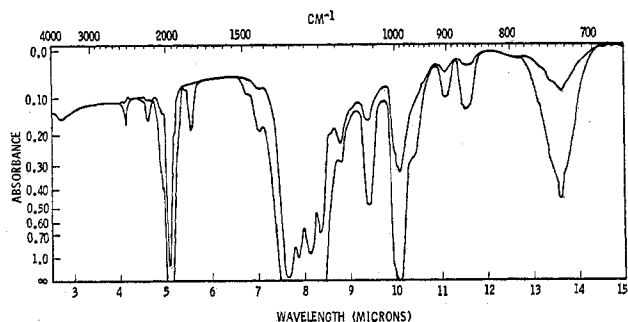
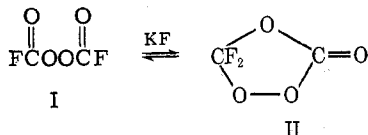


Figure 1.—Infrared spectrum of 3,3-difluoro-2,4,5-trioxacyclopentanone.

Results

The peroxide I was found to react with alkali fluorides at temperatures below ambient. With KF, a reversible reaction led to the formation of the new compound II

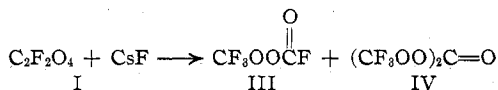


The new compound is colorless in all phases. It is of marginal stability and this, coupled with the small quantities obtained, precluded the determination of its physical properties. The purification procedure did show that it is more volatile than its isomer I. The ozonide II is unusual in that it represents an ozonized derivative of the unknown unsaturated difluoroketene without using ozone.

The identification of II was unambiguous through the ^{19}F nmr and its mass cracking pattern. The ^{19}F nmr spectrum was observed in CFCl_3 solution. The single resonance expected for this molecule was observed at $\delta +60.8$. Further, the relative intensity compared to the solvent was in good agreement with the ratio of ^{19}F components in the prepared solution. The latter measurement supports the assignment as a species containing two equivalent fluorines as in II. The chemical shift is in reasonable agreement with other fluorinated peroxides⁵ although shifted downfield by several ppm. No additional ^{19}F resonances were noted.

Mass patterns for both I and II are shown in Table II for a convenient comparison. As would be predicted, the fragmentation patterns are quite dissimilar inasmuch as the base peak for II is m/e 82 (CF_2O_2^+) while the same peak is nonexistent from the fragmentation of I. The small peak from I at mass number 66 (CF_2O^+) is most certainly due to a rearrangement upon impact. If it were due to isomerization of I to II in the mass spectrometer inlet system (or sample bulb), the companion peak at m/e 50 (CF_2^+) should be present at about half the intensity of the 66 peak. The absence of this peak then confirms a rearrangement in the mass spectrometer upon electron impact.

Stronger bases than KF were found to give irreversible reaction of I. With CsF, I was converted to tri-fluoromethyl fluoroformyl peroxide (III) and bis(tri-



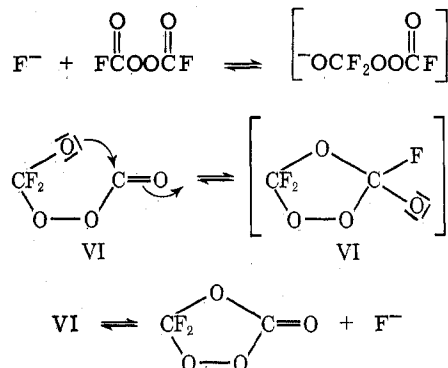
fluoromethyl) bis(peroxy)carbonate (IV). The reaction is essentially quantitative with roughly equivalent amounts of III and IV formed.

Stable mass patterns were obtained for both III and IV and are shown in Table I. These augment the data reported earlier⁵ with only one notable exception. For IV we find no m/e at 66 (CF_2O^+) while the cited work offered this as a prominent peak. An infrared trace for II is given in Figure 1.

Discussion

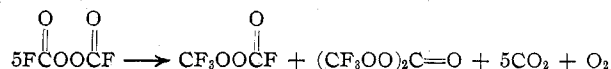
The action of certain Lewis bases on bis(fluoroformyl) peroxide gives two sets of products, depending on the basicity of the fluoride used. With KF, isomerization occurs with an equilibrium being established. While not precisely measured it appeared that equilibrium is established at -80° after several days with II being present as high as 18 mol %. Some decomposition to COF_2 was generally encountered and further complicated precise equilibrium measurements. The reverse reaction may be slower in attaining an equilibrium mixture inasmuch as pure II gave only a 50-50 mixture of I and II after a 5 day period over KF.

The action of KF on either component I or II appears to be rather straightforward and undoubtedly involves an addition of F^- to a carbonyl group carbon



Cyclization probably occurs as suggested for the synthesis of perfluoro- β -oxa- δ -valerolactone.¹⁰ Further, the good material balances obtained in analyzing the volatile products precluded the existence of complexes (bracketed structures above) remaining in the solid phase at ambient temperature.

A considerably stronger base, CsF, upon reaction with I gives no isomeric product at the temperatures tested. Instead, the formation of III and IV takes place exclusively. Further, these peroxides are formed in essentially equimolar amounts. Although not precisely substantiated, the stoichiometry for the formation of these materials is approximately

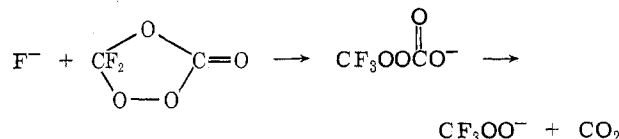


It is significant that CsF and I effect no formation of the ozonide II. This may be interpreted by (i) examining the potential sites of nucleophilic attack on II and (ii) relating these to the nucleophilicity of the attacking base. Two sites for attack are possible and are, of course, the two carbons. An attack at the carbonyl carbon apparently only effects the isomerization reaction which has been shown to be reversible.

(10) J. R. Throckmorton, *J. Org. Chem.*, **34**, 3438 (1969).

Because of the probable pronounced polarization of the C=O bond, the carbon is electron deficient to the extent that the weaker bases, such as KF, can effectively react. Thus, the isomerization reaction is effected by all bases capable of adding to C=O bonds.

The other potential acid site in II, the CF₂ group, must be susceptible to F⁻ attack only in the case where the cation is large as in CsF. This postulate is consistent with the ring opening reactions of perfluoroalkylene oxides where it was shown that only strong F⁻ bases such as CsF could cause ring opening.¹¹ The attacking CsF then leads to an irreversible reaction with the elimination of CO₂. The postulated peroxide



(11) J. A. Young, *Fluorine Chem. Rev.*, **1**, 370 (1967).

salt, CsOOCF₃, likely accounts for both III and IV.¹²

It is noteworthy that only isomerization of I or II occurs with KF and disproportionation occurs exclusively with CsF. When a catalytic amount of trimethylamine is used with I, both the isomerization reaction and disproportionation reaction occur suggesting that a transitory quaternary fluoride is of base strength between KF and CsF. This suggestion was not tested directly through the use of a fluoride such as R₄NF.

Acknowledgment.—We are indebted to Dr. J. Muirhead for the ¹⁹F nmr data and Mr. S. Cohz for the mass cracking patterns. We also wish to thank Dr. K. O. Christe for many helpful discussions. This work was supported in part under Contract F04711-C-67-0007 through the Air Force Rocket Propulsion Laboratory, Air Force System Command, Edwards, California.

(12) The salts of CF₃OOH were shown to be intermediates in the synthesis of III and IV in ref 9.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, MARYGROVE COLLEGE, DETROIT, MICHIGAN 48221, AND THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN 48104

The Synthesis of a Cyclic Fluorodialkylaminophosphine and Its Coordination with Boron Acids. The Formation of a Unique Dialkylaminophosphine Cation

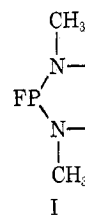
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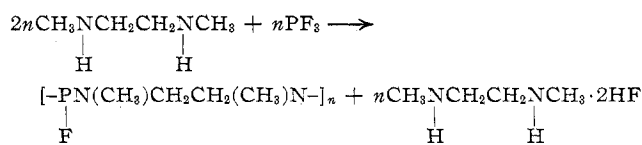
The synthesis of a new cyclic fluorodialkylaminophosphine ligand is reported. It is 2-fluoro-1,3-dimethyl-1,3,2-diazaphospholidine (I). Nuclear magnetic resonance and infrared techniques have been used to demonstrate that in the borane adduct bonding occurs *via* the phosphorus atom. Trifluoroborane, on the other hand, combines with a nitrogen atom of the base in a 1:1 mole ratio to give the first reported adduct of this type which is stable to fluorine shift and phosphorus–nitrogen bond cleavage. Reaction of I with an excess of trifluoroborane is shown conclusively by nmr techniques to result in the reversible formation of the unique cation–anion system, [CH₃NCH₂CH₂(CH₃)NP]⁺[B₂F₇]⁻. The cation has also been isolated as the stable [CH₃NCH₂CH₂(CH₃)NP]⁺[PF₆]⁻ species by the reaction between I and PF₅.

Introduction

Compounds of the type F₂PNR₂ and FP[NR₂]₂ have been described^{2–5} and it has been shown conclusively by X-ray and/or nmr studies that bonding takes place *via* the phosphorus atom when these ligands react with boron hydrides.^{2b,5} On the other hand, though all available evidence indicates boron–nitrogen bonding in trifluoroborane adducts of these ligands, their instability to halogen shift and P–N bond cleavage have prohibited the structural studies needed to make an unequivocal decision.^{2b,5} In the present paper we report the synthesis of the cyclic fluorodialkylaminophosphine 2-fluoro-1,3-dimethyl-1,3,2-diazaphospholidine, I, and its reactions with B₂H₆, BF₃, and PF₅.



1. Synthesis of CH₃NCH₂CH₂(CH₃)NPF (I).—The reaction of PF₃ with an excess of (CH₃)₂NH yields FP[N(CH₃)₂]₂.^{2b,5} By analogy, it was thought that the reaction of PF₃ with an excess of *N,N'*-dimethylethylenediamine should result in formation of either a polymeric species



or a cyclic fluorodialkylaminophosphine, as follows.

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(1) American Chemical Society Petroleum Research Fund Scholars.

(2) (a) H. Noth and H. J. Vetter, *Chem. Ber.*, **96**, 1298 (1963); (b) S. Fleming, Ph.D. Dissertation, University of Michigan, 1963.

(3) R. G. Cavell, *J. Chem. Soc.*, 1992 (1964).

(4) R. Schmutzler, *Inorg. Chem.*, **3**, 415 (1964).

(5) S. Fleming and R. W. Parry, *ibid.*, **11**, 1 (1972).

(6) M. D. LaPrade and C. E. Nordman, *ibid.*, **8**, 1669 (1969).