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# Polyphosphine Anion Radicals

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Electron spin resonance (esr) spectra have been obtained for the anion radicals of 1,2,3,4-tetrakis(trifluoromethyl)-1,2-diphosphacyclobut-3-ene, $(CF_3C)_2(PCF_3)_2$, and 1,2,3,4,5-pentakis(trifluoromethyl)-1,2,3-triphosphacyclopent-4-ene, $(CF_3C)_2(PCF_3)_3$, prepared by electrolytic reduction at low temperature. The observed $^{19}F$ and $^{31}P$ hyperfine coupling constants indicate that the unpaired electron is localized mainly in the carbon-carbon double bond and that little delocalization to the phosphorus atoms occurs. Reduction of the two compounds with alkali metals led to anion radicals of decomposition products of the parent phosphines. Attempts to generate anion radicals from the cyclopolyphosphines, $(CF_3P)_4$ and $(CH_3P)_5$, or 3,4-bis(trifluoromethyl)-1,2-dithietene, $(CF_3C)_2S_2$, were unsuccessful.

## Introduction

Previous work[2] has established that it is possible to generate anion radicals from the cyclopolysilanes $[(CH_3)_2Si]_4$, $[(CH_3)_2Si]_5$, and $[(CH_3)_2Si]_6$ by a low-temperature electrochemical technique. Because the hyperfine coupling is equivalent for all of the methyl protons in each of the $[(CH_3)_2Si]_n\cdot^-$ anion radicals, it was suggested that the unpaired electron in these species occupies a delocalized molecular orbital which may involve the silicon 3d orbitals.[2] Since 3d orbital participation has also been invoked in connection with the bonding in cyclopolyphosphines[3,4] and polyphosphine heterocycles,[5] it seemed appropriate to attempt the generation of anion radicals from these types of compounds. The dithietene, $(CF_3C)_2S_2$, was included because of its obvious similarity to the polyphosphine heterocycle $(CF_3C)_2(PCF_3)_2$.

## Experimental Section

**Materials.** The compounds $(CF_3P)_4$,[3] $(CH_3P)_5$,[6] $(CF_3C)_2(PCF_3)_2$,[5] $(CF_3C)_2(PCF_3)_3$,[5] and $(CF_3C)_2S_2$[7] were made and purified according to literature methods. The solvents dimethyl ether, 1,2-dimethoxyethane (DME), tetrahydrofuran (THF), hexamethylphosphoramide (HMPA), and 2-methyltetrahydrofuran (MeTHF) were dried and distilled prior to use.

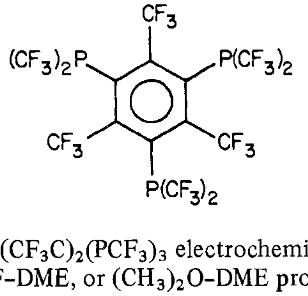
**Electron Spin Resonance Spectra.** First-derivative esr spectra were determined using a Varian V-4502-13 X-band spectrometer equipped with a Varian V-4532 dual cavity. Sample temperature was regulated with a Varian V-4540 variable-temperature controller and insert dewar. Temperatures reported are believed accurate to ±5°. Anion radicals were produced either electrolytically by reduction at low temperatures in the sample cavity in a special electrolytic cell[8] or by alkali metal reduction at −95 or −126°. In the electrolytic experiments tetra(*n*-butyl)ammonium perchlorate was used as a supporting electrolyte. The XY recorder was calibrated with tetracene cation radical, and *g* values were measured by comparison with the *g* value of peroxylaminedisulfonate anion,[9] using the dual cavity.

Simulated esr spectra were calculated by a computer program written in Fortran 63 for the CDC 1604 and 3600 computers at the UWCC.[10] A constant line width of 0.40 G was used.

## Results and Discussion

No radical species were observed when dimethyl ether-DME solutions of $(CF_3P)_4$, $(CH_3P)_5$, or $(CF_3C)_2S_2$ were reduced either chemically (NaK alloy) or electrochemically at −125°. Failure to observe a radical anion for $(CF_3C)_2S_2$ is probably due to rapid cleavage to the stable dithietene dianion. Similar ring opening may also account for the lack of anion radical products from the cyclophosphines.

Electrochemical reduction of $(CF_3C)_2(PCF_3)_2$ in THF or $(CH_3)_2O$-DME produced an anion radical (I) attributable to the parent molecule, over the temperature range −100 to −60°. The esr spectrum of I and a computer simulation are shown in Figure 1. Reduction of $(CF_3C)_2(PCF_3)_2$ with NaK or Li-HMPA in THF, $(CH_3)_2O$-DME or THF-DME produced an anion radical of a decomposition product III. The radical III must be at least a dimer and more probably a trimer of $(CF_3)_2C_2(PCF_3)_2$, because over 400 lines appear in the esr spectrum (Figure 2). The spectrum contains ten main groups of lines with a splitting between the groups of ~20 G. This suggests hyperfine coupling with three equivalent $-CF_3$ groups; a possible structure for the radical is



Reduction of $(CF_3C)_2(PCF_3)_3$ electrochemically at −130° in THF, MeTHF-DME, or $(CH_3)_2O$-DME produces the anion radical II attributable to the parent molecular structure initially. The esr spectrum and a computer simulation are shown in Figure 3. However, II is unstable and even at −130° slowly transforms to the anion radical of hexakis(trifluoromethyl)benzene. Reduction of $(CF_3C)_2(PCF_3)_3$ with sodium-potassium alloy in a variety of solvents from −140 to −60° always produced the hexakis(trifluoromethyl)benzene anion radical IV. The $^{19}F$ hyperfine splitting constant and *g* value (Table I) found for radical IV are in good agreement with published data.[11,12] The decomposition of this phosphine to form a cyclic trimer is somewhat analogous to the cyclization of 1,1-bis(trimethylsilyl)ethylene found by Gerson and coworkers.[13]

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(1) (a) Department of Chemistry, University of Wisconsin. (b) Department of Chemistry, University of Texas at Austin.

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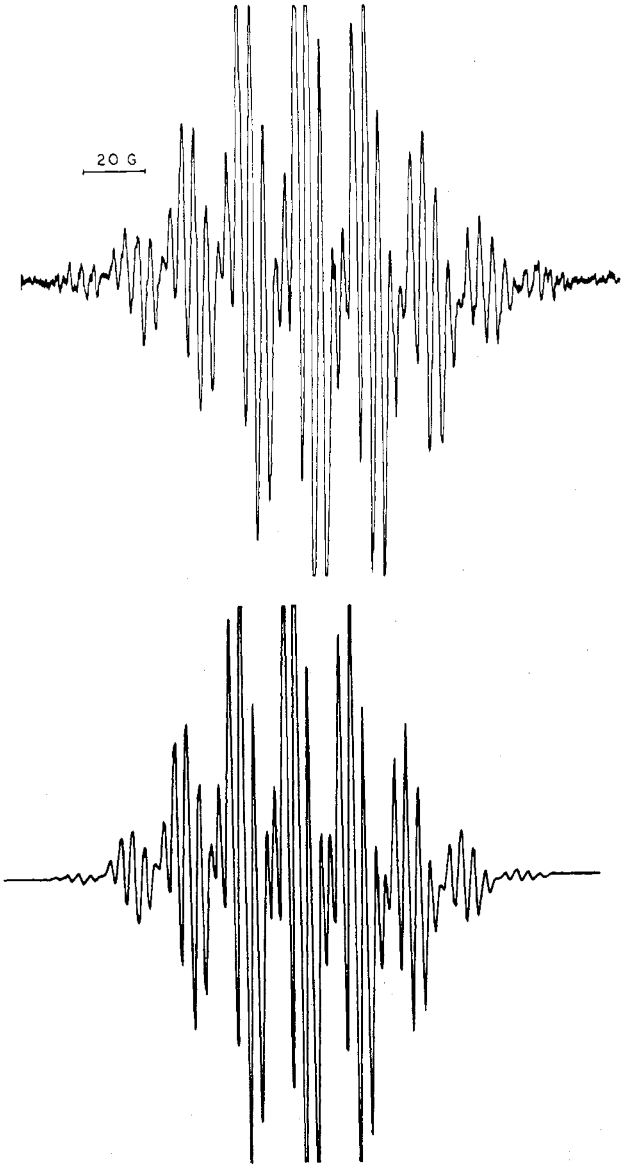

**Figure 1.** Above, esr spectrum of $(CF_3C)_2(PCF_3)_2\cdot^-$ (I) in THF at −80°; below, computer simulation using splitting constants in Table I.

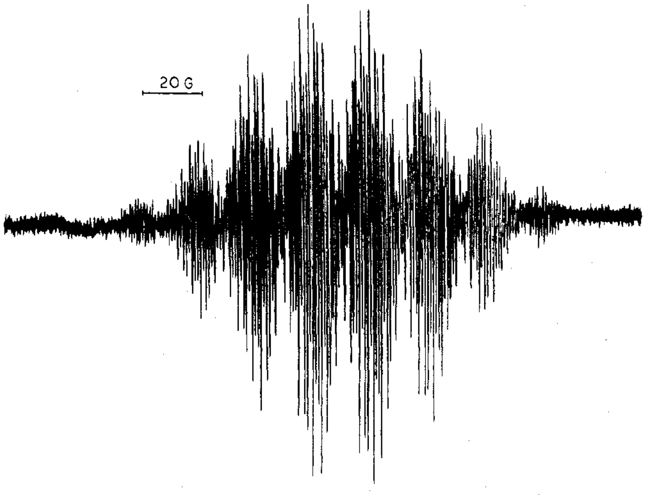

**Figure 2.** Esr spectrum of radical III in THF-DME at −20°.

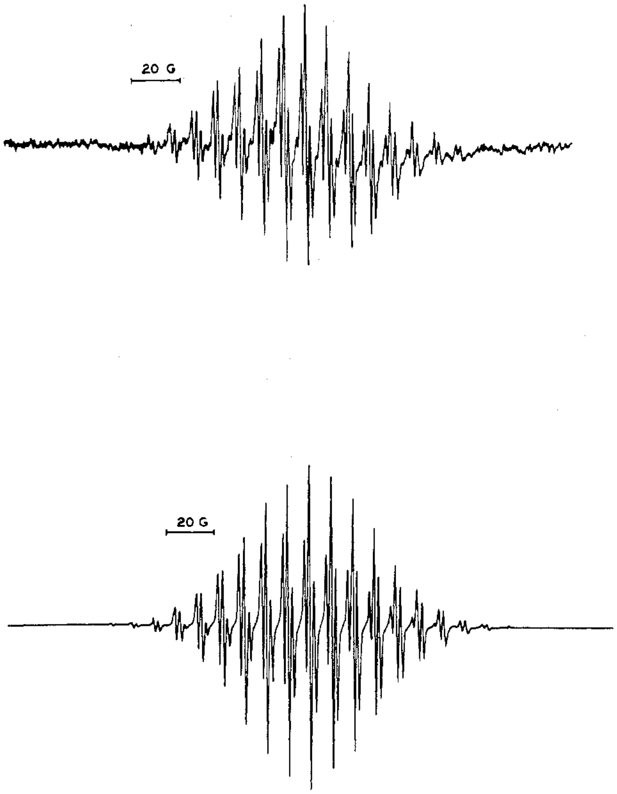

**Figure 3.** Above, esr spectrum of $(CF_3C)_2(PCF_3)_3\cdot^-$ (II) in THF at −100°; below, computer-simulated spectrum of II assuming splitting constants listed in Table I.

Hyperfine splitting constants and *g* values for I-III are given in Table I. In both I and II there are two sets of six equivalent fluorines, so an ambiguity arises concerning the assignment of the fluorine coupling constants. Assignment of the larger couplings (*ca.* 18 G) to the fluorines of the trifluoromethyl groups attached to the ethylenic carbon atoms in I and II, respectively, is preferred because, as indicated by the small coupling to the remote P-$CF_3$ fluorines in II (0.15 G), the coupling constants diminish with increasing number of bonds from the ethylenic linkage (see Figure 4 for the structures of I and II).

**Phosphorus Spin Densities in I and II.** Estimation of the phosphorus spin densities in I and II requires a knowledge of the carbon spin densities. In turn the latter are estimated from the fluorine coupling constants. Unfortunately very few data are available for $CF_3$-substituted free radicals.[11,12,14] However, it is evident from fluorine contact shift measurements[15] on nickel chelates and from a single-crystal esr study of the perfluorosuccinic acid radical[16] that direct transfer of spin to β-fluorine atoms occurs. This means that a two-term empirical relationship of the type

$$a^{F}_{CF_3} = Q^{F}_{C-CF_3}\rho_C + Q^{F}_{FC}\rho_F \qquad (1)$$

should be employed when relating fluorine coupling constants, $a^{F}_{CF_3}$, to carbon spin densities, $\rho_C$. The second term of eq 1 accounts for fluorine splitting from spin density in a 1s or 2s fluorine orbital due to coupling with spin density in a 2p fluorine orbital. However, there are insufficient data to permit independent evaluation of $Q^{F}_{C-CF_3}$ and $Q^{F}_{FC}$ so we

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**Table I.** Coupling Constants and *g* Values for Polyphosphine Anion Radicals

| Anion radical | No. lines in set | Coupling constant, G | Assignment | Temp, °C | *g* (±0.0001) | Temp, °C |
|---|---|---|---|---|---|---|
| | | 18.00 ± 0.10[a] | *P* | −110 | 2.00255[b] | −110 |
| I | 9 | 18.60 | C–C*F*$_3$ | | | |
| | 7 | 3.93 | P–C*F*$_3$ | | | |
| II | 3 | 10.90 ± 0.10 | C–*P* | −100 | 2.0028 | −80 |
| | 7 | 18.05 | C–C*F*$_3$ | | | |
| | 7 | 8.85 | C–P–C*F*$_3$ | | | |
| | 2 | 0.5[c] | P–*P*–P | | | |
| | 4 | 0.15[c] | P–PC*F*$_3$–P | | | |
| III | 10[d] | 20 | 3CF$_3$? | | 2.0021 | −35 |
| IV | 19 | 7.59 | CF$_3$ | −60 | 2.0031 | −80 |

[a] Accidental near-degeneracy giving nine lines rather than 3 × 7 = 21. [b] ±0.00005. [c] Estimated coupling, observed only as a contribution to line width. [d] ~400 lines over 200 G; not assigned.

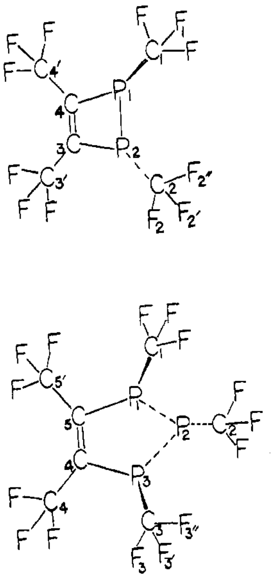

**Figure 4.** Proposed structures for $(CF_3C)_2(PCF_3)_2\cdot^-$ (I) and $(CF_3C)_2(PCF_3)_3\cdot^-$ (II).

are obliged to use the simplified relationship

$$a^F{}_{CF_3} = Q^F{}_{C-CF_3}\rho^\pi{}_C \qquad (2)$$

Studies with the hexakis(trifluoromethyl)benzene[11,12] and para CF$_3$-substituted nitrobenzene[14d] anion radicals suggest that 47 G is a reasonable value for $Q^F{}_{C-CF_3}$. This leads to the following estimates for the carbon spin densities in I and II: $\rho_{C_3} = \rho_{C_4} = 0.39$ for I and $\rho_{C_4} = \rho_{C_5} = 0.39$ for II; in both I and II about 80% of the total spin density appears to be on the ethylenic carbon atoms. (See Figure 4 for the numbering system.)

The phosphorus spin densities on I and α-phosphorus spin densities on II have been estimated by the method of Hunter and Symons[17] which is based on the approximation

$$100\frac{a^x}{A^x} = \rho_x U_x + \Sigma\rho_y U^x{}_{yz} \qquad (3)$$

In eq 3 $a^x$ is the observed isotropic nuclear hyperfine coupling constant for atom x, $A^x$ is the isotropic nuclear hyperfine coupling constant for one unpaired electron in the valence shell s orbital of x, $\rho_x$ and $\rho_y$ are the spin densities in a valence p orbital on atom x and on adjacent atom y, respectively, and $U_x$ and $U^x{}_{yx}$ are empirically evaluated proportionality constants. As applied to the present problem we have

$$\frac{100(\pm a^P)}{3640} = \rho_P(2.2) + \rho_C(-0.9) \qquad (4)$$

For both I and II we shall employ the value $\rho_C = 0.39$ (*vide supra*). The solutions to eq 4 depend on the sign of $a^P$. If the positive values $a^P = +18.0$ and $+10.90$ G are employed, the phosphorus spin densities are calculated to be +0.39 and +0.29 on I and the α-phosphorus atoms of II, respectively. For $a^P = -18.0$ and $-10.90$ G the corresponding $\rho_P$ values are −0.07 and +0.03. The first solution is rejected because the spin densities are too large; *e.g.*, for I spin densities of $\rho_C = 0.39$ and $\rho_P = 0.39$ would give a total density of 1.56 in the $C_2P_2$ ring. The negative value of the phosphorus spin density in I would imply a spin-polarization mechanism for transferring spin from carbon to phosphorus. However, the Hunter and Symons treatment[17] neglects any effect of spin density in the phosphorus 3d orbitals. Previous studies[18] indicate that this might be an important consideration. Obviously, too much emphasis should not be placed on the above values for the phosphorus spin densities because of the necessarily crude theoretical treatment. However, we believe that the $\rho_C$ and $\rho_P$ values can be taken to indicate that most of the spin density is located on the ethylenic carbons of both I and II. A similar conclusion has been drawn in the case of the positive radical ions $H_2\dot{C}-\overset{+}{P}Ph_3$[19] and $Ph_2\dot{C}-\overset{+}{P}Ph_3$.[20]

The electron distributions in I and II may differ markedly from those in the neutral molecules $(CF_3C)_2(PCF_3)_2$ and $(CF_3C)_2(PCF_3)_3$,[5] whose electronic spectra were interpreted on the basis of pπ–dπ overlap between the olefinic bond and the phosphorus 3d orbitals. Possibly, the large uv shift is due to the inclusion of a small amount of 3d character into the π orbitals, as proposed for thiophene.[21,22]

**P–CF$_3$ Fluorine Coupling Constants.** The fluorine coupling constants for P–CF$_3$ groups are quite large in view of the small estimated spin densities on the α-phosphorus atoms of I and II. This raises the question of a direct (through-space) interaction between the p orbitals on these fluorine atoms and the olefinic double bond. This type of interaction has been invoked by Sheppard[23] to interpret, *e.g.*, $^{19}F$ nmr chemical shifts and by Sheidler and Bolton[14c] in their study of the $(CF_3)_2NO\cdot$ free radical. A through-space mechanism may also explain why the P–CF$_3$ fluorine coupling con-

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stant is larger in II than in I (8.85 *vs.* 3.93 G). Assuming a ring-puckering coordinate of the type described for 2,5-dihydrofuran[24] (*i.e.*, the five-membered ring of II bends about the $P_1$-$P_3$ diagonal, and no stretching of the P–C, C=C, and P–P bonds and no deformations of the P–P–P or C=C–P angles occur), two conformations of II can be described (Figure 4), one with the 2-trifluoromethyl group inclined toward the C=C bond and the other with the 2-trifluoromethyl group inclined away from the olefinic bond. In the former conformation the 1 and 3 trifluoromethyl groups are very close to the $\pi$ electrons of the C=C bond. A time-averaged ring-puckering vibration in II may thus lead to a smaller distance between the C-P-$CF_3$ fluorine atoms and the olefinic bond than in I. In the latter the $C_4$-$P_1$-$P_2$ and $C_3$-$P_2$-$P_1$ bond angles are necessarily ~80-85°; hence the $C_4$-$P_1$-$C_1$ and $C_3$-$P_2$-$C_2$ bond angles are ~115°, thus increasing the distance between the fluorine atoms and the double bond.[25]

## Conclusion

This study indicates that the unpaired electron of the anion radicals of $(CF_3C)_2(PCF_3)_2$ and $(CF_3C)_2(PCF_3)_3$ occupies a molecular orbital primarily localized on the two ethylenic carbon atoms and that the spin density on the ethylenic carbon atoms is essentially the same in the two anion radicals. If 3d orbitals of phosphorus were important in the molecular orbital occupied by the unpaired electron, one would expect a larger delocalization of unpaired spin density to the phosphorus atoms. The fact that $(PCH_3)_5$, $(PCF_3)_4$, and $(CF_3C)_2S_2$ cannot be reduced to anion radicals suggests also that d orbitals must not greatly stabilize the lowest antibonding MO for these molecules. The relatively easy reduction to anion radicals of the permethylcyclopolysilanes[2] thus appears exceptional among compounds of second-row elements.

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**Registry No.** I, 42423-23-4; II, 42423-24-5; III, 42561-79-5.

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[25] The following bond distances in angstrons were assumed in constructing models I and II: P–P, 2.22; C–P, 1.88; C–F, 1.33; C=C, 1.34; C–C, 1.50.

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# Chalcogen Chemistry. IX.[1] Synthesis of Alkylammonium Dihalocyanoselenate(II) and Trihaloselenate(II) Salts

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Alkylammonium selenocyanates react with sulfuryl chloride or bromine to yield respectively dichloro- and dibromocyanoselenate(II) salts, $R_4NSeX_2CN$ ($R = n\text{-}C_3H_7$, X = Cl, Br; $R = CH_3$, X = Cl). Conductivity and molecular weight data demonstrate the presence of discrete $SeX_2CN$ anions in solution. Solid-state and solution infrared and Raman spectra indicate the $SeX_2CN$ anions are T shaped with halogens occupying the trans positions in the T. Tetraethylammonium trichloro- and tribromoselenate(II) were prepared *via* the reaction of tetraethylammonium selenocyanate with 2 mol of $SO_2Cl_2$ and $Br_2$, respectively. Far-infrared and Raman spectroscopic data are consistent with the presence of planar $[Se_2X_6]^{2-}$ anions of $D_{2h}$ symmetry in the solid state ($I_2Cl_6$ structure). However, conductivity studies indicate the trihaloselenate(II) salts behave as 1:1 electrolytes in nitromethane. Raman spectra strongly support the presence of discrete T-shaped $[SeX_3]^-$ in solution.

There exists a growing awareness of the biological importance of selenium as a trace element and as a cancer inhibitor.[3,4] In general it appears that it is the chemistry of the lower valences of selenium which is involved in its useful biological function.[4] In continuing our investigation of this area we report herein the preparation of some new selenium species derived from selenocyanate.

## Experimental Section

The compounds containing selenium-bromine bonds are fairly stable to the atmosphere, whereas those containing selenium-chlorine bonds are rapidly hydrolyzed. As a precautionary measure and due to the toxicity of most selenium compounds, all preparations and handling operations were carried out in polyethylene glove bags filled with dry dinitrogen. Infrared, Raman, and proton nuclear magnetic resonance spectra and molecular weight and conductivity data were obtained as previously reported.[1,5]

**Chemicals.** Solvents were purified as previously noted.[5] Potassium selenocyanate was prepared by the literature method,[6] except that the melt was slowly poured directly into acetone from which it crystallized. Tetraalkylammonium halides were obtained from Eastman; *n*-propylammonium and *n*-butylammonium salts were used exclusively so that the "*n*" designation is not used further below.

**Tetraalkylammonium Selenocyanates.** Tetramethylammonium selenocyanate was prepared by stirring tetramethylammonium bromide (4.66 g, 30.2 mmol) and potassium selenocyanate (4.36 g, 30.2 mmol) in 50 ml of acetonitrile for 1 hr. Filtration followed by reduction of volume to 20 ml gave a 69% yield of tetramethylammonium selenocyanate. Recrystallization was done in $CH_3CN$-$CCl_4$; dec pt 266-268°, lit.[7] 267-268°. *Anal.* Calcd for $C_5H_{12}N_2Se$: C, 33.53; H, 6.75; N, 15.64. Found: C, 33.48; H, 6.70; N, 15.65.

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