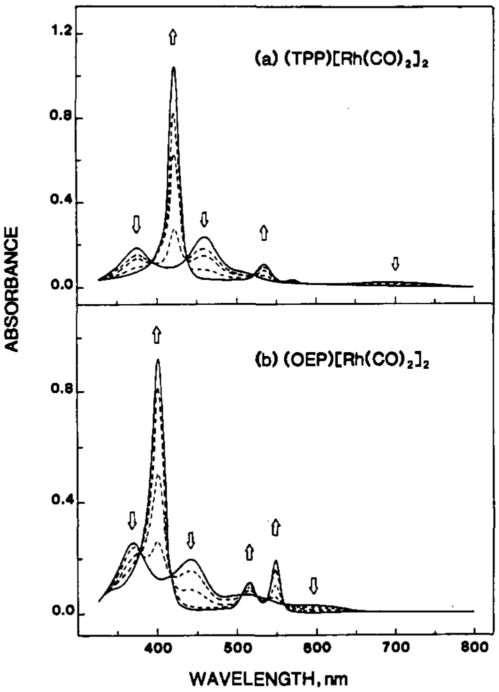

Figure 2. Electronic absorption spectra for the oxidation of (a) 1.2×10^{-5} M $(TPP)[Rh(CO)_2]_2$ at 0.95 V and (b) 1.4×10^{-5} M $(OEP)[Rh(CO)_2]_2$ at 0.90 V in PhCN containing 0.2 M TBAP.

$(CO)_2]_2$ indicates formation of $[(OEP)Rh]^+$ (Figure 2b). These spectral details are summarized in Table I. It should also be noted that negligible photochemical reactivity of $(P)[Rh(CO)_2]_2$ occurred on the spectroelectrochemical time scale (about 2–4 min). This was verified by independent photolysis experiments under the same experimental conditions.

Oxidation of $(P)[Rh(CO)_2]_2$ was monitored in the CO region of the infrared spectrum by spectroelectrochemical techniques. $(OEP)[Rh(CO)_2]_2$ is characterized[1-5] by two M–CO absorption bands at 2053 and 1990 cm^{-1}. Upon oxidation, an intermediate is observed with absorption bands at 2094 and 2035 cm^{-1}. The intensities of the new bands are substantially less than those of the original spectrum and may indicate that a large concentration of the intermediate cannot be generated. The large shift in the CO absorption bands reflects an oxidation of the metal and a decrease in the metal π back-bonding ability. After bulk electrolysis of $(OEP)[Rh(CO)_2]_2$ no absorptions associated with a M–CO band are observed. In addition, frozen solutions of electrooxidized compound do not have an ESR signal, consistent with formation of $[(P)Rh]^+$.

Oxidation of $(TPP)[Rh(CO)_2]_2$ produces similar results. The initial spectrum of $(TPP)[Rh(CO)_2]_2$ has two M–CO bands at 2050 and 1994 cm^{-1}, and the oxidized intermediate has two M–CO absorption bands at 2070 and 2031 cm^{-1}. No M–CO absorption bands are observed in the infrared region after bulk electrolysis of $(TPP)[Rh(CO)_2]_2$.

Reaction Scheme. The overall oxidation/reduction scheme of $(P)[Rh(CO)_2]_2$ is given in Figure 3. The two successive reductions result in formation of a porphyrin π anion radical and dianion. These electron additions are given by reactions 1 and 2.

The first oxidation of $(P)[Rh(CO)_2]_2$ is a one-electron process (reaction 3) and ultimately results in formation of a Rh(III) species. This may occur via an intramolecular electron-transfer reaction, i.e., a reaction between Rh(I) and Rh(II) in the same porphyrin molecule. After formation of Rh(III), this metal ion is inserted into the porphyrin plane with loss of Rh^0, which is observed as an insoluble black precipitate after bulk oxidation of the complexes. An intermolecular electron-transfer reaction may also occur with the generation of $[(P)Rh]^+$ and Rh^0. In both schemes, $[(P)Rh]^+$ is generated as the only porphyrin species in solution. The second and third oxidation waves observed in the cyclic voltammograms in PhCN (reactions 4 and 5) correspond to reactions of this species. The oxidation properties of $[(TPP)Rh]^+$ have been previously discussed.[16]

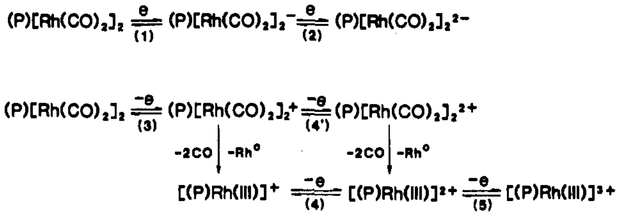

Figure 3. Reaction scheme of $(P)[Rh(CO)_2]_2$ for reduction and oxidation.

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Registry No. $(TPP)[Rh(CO)_2]_2$, 88083-36-7; $(TPP)[Rh(CO)_2]_2^-$, 109152-56-9; $(TPP)[Rh(CO)_2]_2^{2-}$, 109152-57-0; $(TPP)[Rh(CO)_2]_2^+$, 109152-59-2; $(TPP)[Rh(CO)_2]_2^{2+}$, 109152-60-5; $(OEP)[Rh(CO)_2]_2$, 51320-70-8; $(OEP)[Rh(CO)_2]_2^-$, 109182-00-5; $(OEP)[Rh(CO)_2]_2^{2-}$, 109152-58-1; $(OEP)[Rh(CO)_2]_2^+$, 109182-01-6; $(OEP)[Rh(CO)_2]_2^{2+}$, 109152-61-6; $[(TPP)Rh]^+$, 98756-66-2; $[(TPP)Rh]^{3+}$, 109152-62-7; $[(OEP)Rh]^+$, 99327-15-8; $[(OEP)Rh]^{3+}$, 109152-63-8; Rh, 7440-16-6.

Contribution from the Department of Chemistry,
University of Georgia, Athens, Georgia 30602

(Dialkylamido)selenium Derivatives

R. B. King* and S. A. Sangokoya

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The extensive applications of SeO_2 as an oxidant in organic chemistry[1] suggests that (dialkylamido)selenium(IV) derivatives might be useful in organic synthesis as sources of dialkylamino groups under potentially oxidizing conditions. However, relatively little is known about the preparation and properties of (dialkylamido)selenium derivatives. Furthermore, such derivatives have received essentially no attention since the report by Paetzold and Rönsch in 1965[2] on the preparation and properties of $(Me_2N)_2SeO$. Since that time selenium-77 NMR spectroscopy (^{77}Se: $I = {}^1/_2$, natural abundance 7.6%, receptivity 5.26×10^{-4} that of the proton) has been shown to be a useful method for the characterization of organoselenium compounds.[3-6] Accordingly, we have reinvestigated and extended these original results by Paetzold and Rönsch[2] using selenium-77 NMR as a method for the analysis of reaction mixtures and products isolated therefrom. This paper summarizes our results in this area.

Experimental Section

Selenium-77 NMR spectra were taken on a multinuclear JEOL FX-90Q spectrometer operating at a nominal frequency of 17.04 MHz in the pulsed Fourier-transform mode. For chemical shift determinations the spectrum was calibrated against an external sample of dimethyl selenide

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Table I. Products from Selenium Dioxide and Secondary Amines

product	mp, °C	anal				NMR spectra, δ			
			% C	% H	% N	^{77}Se	N–H	other proton	^{13}C
$[Me_2NH_2]_2[Se_2O_5]$	oil					1375	9.6	2.6 s	34.5
$[Et_2NH_2]_2[Se_2O_5]$	dec. 62	calcd	24.9	6.2	7.3	1368	9.78	3.02 q, 1.36 t	40.9, 11.1
		found	25.3	6.7	7.2				
$[n\text{-}Pr_2NH_2]_2[Se_2O_5]$	dec. 104	calcd	32.6	7.2	6.3	1371	9.42	2.68 m, 1.63 m, 0.80 t	48.2, 19.2, 11.2
		found	33.7	7.6	6.4				
$[i\text{-}Pr_2NH_2]_2[Se_2O_5]$	dec. 144	calcd	32.6	7.2	6.3	1364	9.30	3.31 m, 1.40 d	46.6, 19.6
		found	31.4	7.5	6.0				

in a sealed NMR tube. Tetramethylsilane was used as an internal standard so that proton and carbon-13 NMR spectra could be obtained on the same samples and the same spectrometer. Chemical shifts (δ) are reported in parts per million *down*field from internal tetramethylsilane (for proton and carbon-13) and external pure dimethyl selenide (for selenium-77). All reported NMR chemical shifts were obtained in $CDCl_3$ solution.

All reactions were carried out in an efficient hood with solid sodium hydroxide traps used to decompose noxious acidic materials in the effluent vapors before they were passed into the hood exhaust. A dry nitrogen atmosphere was always provided for the following three operations: (a) carrying out reactions; (b) handling (dialkylamido)selenium compounds that are sensitive to oxygen and/or moisture; (c) filling evacuated vessels containing potentially air-sensitive materials. When necessary Schlenkware[7] or a polyethylene glovebag was used to provide the dry nitrogen atmosphere. Before use all solvents were distilled under nitrogen over appropriate drying agents (Na/benzophenone or metal hydrides, except for chlorinated solvents). The −72 °C reaction temperature used for several of the reactions was obtained from an acetone/dry ice bath.

Melting and decomposition points were taken in capillaries and are uncorrected. Microanalyses (C,H,N) were performed by Atlantic Microanalytical Laboratory, Atlanta, GA, and were difficult because of the extreme hygroscopicity of many of the (dialkylamido)selenium derivatives. In addition, reliable chlorine analyses could not be obtained from this source because of selenium interference.

The organosilicon reagents were purchased from Petrarch Systems, Inc., Bristol, PA, or were synthesized from trimethylchlorosilane and the secondary amine in pentane, hexane, or diethyl ether according to a published procedure.[8] All other starting materials including $SeCl_4$ were purchased from standard commercial suppliers, mainly Alfa Products of Morton Thiokol, Inc., Danvers, MA, or Aldrich Chemical Company, Milwaukee, WI.

Preparation of $SeOCl_2$. The following method for the preparation of $SeOCl_2$ from SeO_2 and Me_3SiCl is considerably simpler than the reported[9] method from SeO_2 and HCl followed by dehydration with H_2SO_4.

A mixture of 134 g (1235 mmol) of Me_3SiCl and 54.8 g (494 mmol) of SeO_2 was stirred at room temperature. Within an hour almost all of the solid SeO_2 dissolved, and an oily layer began to separate. After being stirred overnight at room temperature, the system was heated for 6 h at 80 °C (oil bath temperature). Excess Me_3SiCl was removed in a water-pump vacuum (~25 mmHg) and the $(Me_3Si)_2O$ byproduct by atmospheric pressure distillation (bp 97 °C). Vacuum distillation of the residue gave 69.2 g (84% yield) of orange liquid $SeOCl_2$: bp 45 °C (0.6 mmHg); infrared ν(Se=O) 915 cm^{-1}; Selenium-77 NMR in $CDCl_3$ δ 1497.

A similar reaction of Me_3SiCl with SeO_2 in an 8:1 mole ratio gave only $SeOCl_2$ with no evidence for further substitution of oxygen with chlorine, in contrast to the reported[10] reaction of SeO_2 with excess $SOCl_2$, which gives $SeCl_4$.

Reaction of $SeOCl_2$ with Dimethylamine. The following reaction is patterned after the reaction reported by Paetzold and Rönsch[2] except for the use of selenium-77 NMR to follow the course of the reaction.

Excess dimethylamine is condensed at −40 °C into a solution of 48.4 g (290 mmol) of $SeOCl_2$ in 200 mL of hexane. The reaction mixture was allowed to warm slowly to 0 °C. The reaction mixture was filtered from the considerable amount of precipitated dimethylammonium chloride. Concentration of the filtrate at 25 mmHg and cooling in a −10 °C freezer gave pale yellow solid $(Me_2N)_2SeO$ (82% yield (lit.[2] 73%)): mp 42 °C (lit.[2] 42–43 °C); selenium-77 NMR δ 1215; proton NMR δ 2.73; carbon-13 NMR δ 35.4.

A solution of this $(Me_2N)_2SeO$ in dichloromethane was kept at room temperature for 5 days. The selenium-77 NMR spectrum of this solution after that time showed disappearance of the δ 1215 resonance from $(Me_2N)_2SeO$ but the appearance of a major peak at δ 974 as well as minor peaks at δ 1362, 1188, 600, and 340. Dichloromethane was removed at 25 mmHg, and the residue was extracted with hexane. Decanting the hexane extract followed by evaporation of the hexane at ~25 mmHg and vacuum distillation gave $(Me_2N)_2Se$: bp 32 °C (0.7 mmHg); selenium-77 NMR δ 978; yields up to 30%.

Attempts to improve the yield of $(Me_2N)_2Se$ by deoxygenation of $(Me_2N)_2SeO$ by adding Ph_3P, n-Bu_3P, or $(Me_2N)_3P$ resulted in complete decomposition with formation of the corresponding phosphine selenide, as indicated by phosphorus-31 and selenium-77 NMR spectra of the reaction mixtures.

Preparation of i-$Pr_2NSe(O)Cl$. (a) From $SeOCl_2$ and i-Pr_2NH. A solution of 12.1 g (73 mmol) of $SeOCl_2$ in 300 mL of pentane was treated at −78 °C with 14.7 g (145 mmol) of diisopropylamine. The reaction mixture was allowed to warm slowly to room temperature and then stirred at room temperature for 2 h. The reaction mixture was filtered from the precipitated diisopropylammonium chloride. Concentration of the filtrate and cooling in a −10 °C freezer precipitated white i-$Pr_2NSe(O)Cl$: 65% yield; dec pt 66 °C; selenium-77 NMR δ 1441 (broad); proton NMR δ 4.3 (septet) and 1.34 (doublet); carbon-13 NMR δ 48.7 and δ 22.6. Anal. Calcd for $C_6H_{14}ClNOSe$: C, 31.3; H, 6.1; N, 6.1. Found: C, 31.6; H, 6.6; N, 6.1.

(b) From $SeOCl_2$ and i-Pr_2NSiMe_3. A solution of 5.1 g (29 mmol) of i-Pr_2NSiMe_3 in 30 mL of tetrahydrofuran and 30 mL of hexane was treated at −78 °C with 2.42 g (14.6 mmol) of $SeOCl_2$. The reaction mixture was allowed to warm to −5 °C. Concentration of the mixture at ~25 mmHg precipitated white solid i-$Pr_2NSe(O)Cl$: 68% yield; dec pt 62 °C; identified by elemental analyses (C, H, N) and NMR spectra (^{77}Se, ^{1}H, and ^{13}C).

Isolation of $[i\text{-}Pr_2NSe(O)]_2O$. A solution of 29.5 g (292 mmol) of diisopropylamine in 300 mL of pentane was treated with 12.1 g (73 mol) of $SeOCl_2$ at −72 °C. The reaction mixture was then allowed to warm slowly to 0 °C. The reaction mixture was filtered from the precipitated diisopropylammonium chloride. Concentration of the filtrate and cooling in a −10 °C freezer precipitated white $[i\text{-}Pr_2NSe(O)]_2O$: 66% yield, mp 79 °C dec; selenium-77 NMR δ 1310 and 1299; proton NMR δ 4.23 (septet), 3.83 (multiplet), and 1.29 (overlapping doublets); carbon-13 NMR δ 44.9, 24.3, and 23.9. Anal. Calcd for $C_{12}H_{28}N_2O_3Se_2$: C, 35.5; H, 6.9; N, 6.9. Found: C, 35.0; H, 7.1; N, 6.8.

Preparation of $(i\text{-}Pr_2N)_2Se$. A solution of 29.5 g (292 mmol) of diisopropylamine in 300 mL of diethyl ether was treated at −78 °C with 12.1 g (73 mmol) of $SeOCl_2$. After the reaction mixture was warmed to 0 °C, the precipitated diisopropylammonium chloride was removed by filtration. Concentration of the filtrate at 25 mmHg followed by cooling in a −10 °C freezer precipitated 12.5 g (61% yield) of white $(i\text{-}Pr_2N)_2Se$: mp 39 °C; selenium-77 NMR δ 1167; proton NMR δ 3.55 (septet) and 1.35 (triplet); carbon-13 NMR δ 44.8, 24.1, and 23.7. Anal. Calcd for $C_6H_{14}N_2Se$: C, 51.6; H, 10.1; N, 10.0. Found: C, 51.3; H, 10.0; N, 9.9.

Preparation of $(OC_4H_8N)_2Se$. A solution of 9.3 g (58 mmol) of morpholinotrimethylsilane in 30 mL of tetrahydrofuran and 30 mL of hexane was treated dropwise with stirring at −72 °C with 4.8 g (29 mmol) of $SeOCl_2$. The reaction mixture was allowed to warm slowly to room temperature over a period of 5 h. Concentration and cooling the reaction mixture to 0 °C gave a white precipitate, which was filtered and washed with three 30-mL portions of hexane to give 6.2 g (86% yield) of $(OC_4H_8N)_2Se$: dec pt 151 °C; selenium-77 NMR δ 1082; carbon-13 NMR δ 67.4 and 49.3. Anal. Calcd for $C_8H_{16}N_2O_3Se$: C, 38.2; H, 6.4; N, 11.2. Found: C, 36.9; H, 6.9; N, 10.7. Attempts to purify this compound by recrystallization resulted in gradual decomposition to give red selenium.

Reactions of $SeCl_4$ with Me_2NSiMe_3. (a) Isolation of $(Me_2N)_3SeCl$. A solution of 2.4 g (11 mmol) of $SeCl_4$ in 20 mL of tetrahydrofuran was treated at −72 °C with 7.0 g (60 mmol) of (dimethylamino)trimethylsilane. Volatile materials were removed in vacuum while the mixture was warmed to room temperature. The residue was washed with three 20-mL

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portions of tetrahydrofuran and dried in vacuum to give 1.9 g (70% yield) of white $(Me_2N)_3SeCl$: dec pt 84 °C; selenium-77 NMR δ 1122; proton NMR δ 2.85; carbon-13 NMR δ 40.2. Anal. Calcd for $C_6H_{18}ClN_3Se$: C, 29.2; H, 7.4; N, 17.0. Found: C, 29.1; H, 7.4; N, 17.0.

(b) Isolation of $(Me_2N)_2SeCl_2$. A solution of 3.5 g (16 mmol) of $SeCl_4$ in 30 mL of tetrahydrofuran was treated at −72 °C with a solution of 3.72 g (32 mmol) of (dimethylamino)trimethylsilane in 20 mL of pentane. The reaction mixture first became deep red-orange and then gradually became yellow upon further stirring. After one hour at the low temperature, the reaction mixture was stirred for 3 h at room temperature. Solvent was removed in vacuum from the resulting yellow-orange slurry. The residue was treated with a mixture of 20 mL of tetrahydrofuran and 30 mL of pentane. The bright yellow precipitate was filtered and dried in vacuum to give 2.5 g (55 % yield) of $(Me_2N)_2SeCl_2$: dec pt 77 °C; selenium-77 NMR δ 1316; proton NMR δ 3.1; carbon-13 NMR δ 40.9. Anal. Calcd for $C_4H_{12}Cl_2N_2Se$: C, 20.2; H, 5.1; N, 11.8; Cl, 29.8. Found C, 20.1; H, 5.2; N, 11.7; Cl8 29.6.

Reactions of SeO_2 with Secondary Amines (Table I). The dialkylammonium selenite salts listed in Table I were obtained by treatment of SeO_2 with excess secondary amine either in the absence of a solvent or in the presence of an inert solvent such as tetrahydrofuran. Before use in these experiments commercial SeO_2 was stirred for 24 h at room temperature with excess tetrahydrofuran in order to remove unidentified slightly red impurities. The purified SeO_2 was then filtered and dried in vacuum for about 48 h. In a typical experiment 3.4 g (31 mmol) of purified SeO_2 was stirred overnight at room temperature in 50 mL of diisopropylamine. The highly deliquescent white precipitate was filtered and purified by dissolving in chloroform or dichloromethane and reprecipitating by concentration in vacuum after addition of hexane. Elemental analyses in Table I are based on the $[R_2NH_2]_2[Se_2O_5]$ formulation, but these salts appear to have a strong tendency to pick up water to form the corresponding $[R_2NH_2][HSeO_3]$ salt in accord with the known[11] tendency for the $Se_2O_5^{2-}$ ion to undergo facile hydrolysis to give $HSeO_3^-$.

Results and Discussion

A. $SeOCl_2$ Reactions. Analogy with other acid chlorides suggests the facile reaction of $SeOCl_2$ with secondary amines to give the corresponding dialkylamides, $(R_2N)_2SeO$, according to

$$SeOCl_2 + 4R_2NH \rightarrow (R_2N)_2SeO + 2[R_2NH_2]Cl \qquad (1)$$

In 1965 Paetzold and Rönsch[2] investigated this type of reaction with both dimethylamine and diethylamine but were able to isolate the corresponding dialkylamide, namely $(Me_2N)_2SeO$, only in the case of dimethylamine. We investigated reactions of this type with a greater variety of secondary amines including not only dimethylamine and diethylamine but also di-*n*-propylamine, diisopropylamine, morpholine, and 2,6-dimethylpiperidine, using selenium-77 NMR to follow the course of such reactions. However, the only $(R_2N)_2SeO$ derivative that we were able to characterize definitively was the $(Me_2N)_2SeO$ previously reported.[2] Difficulties in isolating other $(R_2N)_2SeO$ derivatives include their very high hydrolytic sensitivity giving ultimately $[R_2NH_2]_2[Se_2O_5]$ and $[R_2NH_2][HSeO_3]$, their facile reduction to selenium(II) derivatives of the type $(R_2N)_2Se$, and difficulty in separating sensitive products from the dialkylammonium chloride byproduct in eq 1. Paetzold and Rönsch[2] report $(Me_2N)_2SeO$ not only to be extremely sensitive toward hydrolysis but also to explode upon attempted distillation.

An interesting reaction of $(Me_2N)_2SeO$ reported by Paetzold and Rönsch[2] is its deoxygenation upon standing at room temperature to give $(Me_2N)_2Se$. The selenium-77 NMR spectrum of this reaction mixture exhibited not only a major resonance at δ 974 shown to be $(Me_2N)_2Se$ and a minor resonance at δ 1362 from the $[Me_2NH_2]_2[Se_2O_5]$ hydrolysis product but also minor resonances at δ 1188, 600, and 340 that have not yet been identified. Attempts to improve the low yield of $(Me_2N)_2Se$ from the deoxygenation of $(Me_2N)_2SeO$ by addition of a trivalent phosphours derivative (Ph_3P, n-Bu_3P, or $(Me_2N)_3P$) resulted in complete destruction of the selenium compound to give the corresponding phosphine selenide.

In our previously reported studies on (dialkylamido)phosphorus derivatives the bulky diisopropylamido group was used to stabilize compound types such as $(i\text{-}Pr_2N)_2PH$,[12] i-Pr_2NPH_2,[13] and $(i\text{-}Pr_2N)_4P_4$[14] not found for the smaller dimethylamido group. In an attempt to use an analogous idea to obtain more stable (dialkylamido)selenium derivatives, the reactions of $SeOCl_2$ with diisopropylamine were investigated under various conditions. Under mild conditions in a nonpolar solvent (pentane) the reaction of $SeOCl_2$ with diisopropylamine could easily be stopped to give the monosubstituted product i-$Pr_2NSe(O)Cl$ as a white solid. This product appeared to be significantly more stable than the not very stable $Me_2NSe(O)Cl$ obtained by Paetzold and Rönsch[2] from $(Me_2N)_2SeO$ and $SeOCl_2$ in equimolar quantities. Attempts to introduce a second diisopropylamido group by reaction of $SeOCl_2$ with diisopropylamine in pentane solution in a 1:4 mole ratio resulted instead in partial hydrolysis of the initially formed i-$Pr_2NSe(O)Cl$ to $[i\text{-}Pr_2NSe(O)]_2O$, still containing only one diisopropylamido group per selenium. The course of the hydrolysis of i-$Pr_2NSe(O)Cl$ to $[i\text{-}Pr_2NSe(O)]_2O$ was also followed by selenium-77 NMR by adding drops of water to a $CDCl_3$ solution of i-$Pr_2NSe(O)Cl$ in an NMR tube. The binuclear formulation of $[i\text{-}Pr_2NSe(O)]_2O$ is supported by the presence of two singlets in its selenium-77 NMR spectrum at δ 1310 and 1299 indicative of *meso* and *dl* diastereomers arising from the presence of two asymmetric selenium atoms in the molecule analogous to the asymmetric carbon atoms in tartaric acid. If the reaction of $SeOCl_2$ with excess diisopropylamine is conducted in a coordinating solvent (diethyl ether), rapid reduction of selenium(IV) to selenium(II) occurs with concurrent introduction of two diisopropylamido groups to give $(i\text{-}Pr_2N)_2Se$ as a white solid melting slightly above room temperature. This product appears to be the most readily accessible $(R_2N)_2Se$ derivative. The carbon-13 NMR spectrum of $(i\text{-}Pr_2N)_2Se$ exhibits two closely spaced methyl resonances of equal intensity at δ 24.1 and 23.7, indicating two different types of methyl groups possibly arising from steric hindrance of free rotation of the bulky diisopropylamido groups. These studies on the reaction of $SeOCl_2$ with diisopropylamine suggests that the use of a weakly coordinating solvent such as diethyl ether facilities the reduction of selenium(IV) to selenium(II) in this type of system. The oxidation product from these reactions has not been identified.

A possible way to circumvent the need to separate very sensitive (dialkylamido)selenium derivatives from dialkylammonium chloride byproducts from their preparation is to use the trimethylsilyl derivative of the secondary amine rather than the free secondary amine as the source of dialkylamido groups in the reaction with $SeOCl_2$ according to the following sequence of reactions:

$$SeOCl_2 + R_2NSiMe_3 \rightarrow R_2NSe(O)Cl + Me_3SiCl \qquad (2a)$$

$$R_2NSe(O)Cl + R_2NSiMe_3 \rightarrow (R_2N)_2SeO + Me_3SiCl \qquad (2b)$$

The Me_3SiCl byproduct is volatile (bp 57 °C) and thus can be removed in vacuum along with the solvent. However, Me_3SiCl is quite reactive and appeared to destroy a number of the expected (dialkylamido)selenium products so that the scope of this preparative method was somewhat limited. Nevertheless, the reaction of i-Pr_2NSiMe_3 with $SeOCl_2$, even in a 2:1 rather than 1:1 mole ratio, provided an alternative synthesis of i-$Pr_2NSe(O)Cl$. In addition, reaction of the morpholino derivative $OC_4H_8NSiMe_3$ with $SeOCl_2$ gave a white solid formulated as the selenium(II) derivative $(OC_4H_8N)_2Se$ on the basis of its relatively high field selenium-77 resonance at δ 1082. For comparison, the bis(dimethylamido)selenium(IV) derivative $(Me_2N)_2SeO$, and the bis(dimethylamido)selenium(II) derivative $(Me_2N)_2Se$ exhibit selenium-77 resonances at δ 1215 and 978, respectively.

The $SeOCl_2$ used for this research was prepared mostly by a new method, namely the reaction of SeO_2 with trimethylchlorosilane:

$$SeO_2 + 2Me_3SiCl \rightarrow SeOCl_2 + (Me_3Si)_2O \qquad (3)$$

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This method has the advantages of relatively simple manipulations and no apparent risk of overreaction to form $SeCl_4$ in contrast to the reported[10] reaction of SeO_2 with $SOCl_2$.

B. $SeCl_4$ Reactions. Reactions of $SeCl_4$ with secondary amines are complicated by difficulties in separating the selenium products from the dialkylammonium chloride byproducts. Accordingly, the substitution of chlorine atoms in $SeCl_4$ with dimethylamido groups was investigated by using Me_2NSiMe_3. Thus reaction of $SeCl_4$ with excess Me_2NSiMe_3 was found to give a white solid, which is sparingly soluble in tetrahydrofuran, is much more resistant toward hydrolysis than the other (dialkylamido)selenium derivatives and analyses for $(Me_2N)_3SeCl$. This product is formulated as the tris(dimethylamido)selenonium salt $[(Me_2N)_3Se]^+Cl^-$ containing a cation analogous to that in $[(Me_2N)_3S]^+[BF_4]^-$ obtained from the reaction of SF_4 with $(Me_2N)_3B$.[15] Reaction of $SeCl_4$ with a smaller amount of Me_2NSiMe_3 gave a more soluble and much more hydrolysis-sensitive yellow solid analyzing for $(Me_2N)_2SeCl_2$, which could either be a tetracoordinate nonionic selenium(IV) derivative or an ionic selenonium salt $[(Me_2N)_2SeCl]^+Cl^-$. Unfortunately, neither of these (dimethylamido)selenium(IV) chlorides formed crystals that were suitable for resolving these structural uncertainties by X-ray crystallography. Furthermore, these compounds were insufficiently soluble in nonreactive ionizing solvents for meaningful conductivity measurements.

C. SeO_2 Reactions. The ultimate hydrolysis products of (dialkylamido)selenium(IV) derivatives are the dialkylammonium salts $[R_2NH_2]_2[Se_2O_5]$. A number of authentic samples of such salts (Table I) were prepared by reactions of SeO_2 with excess secondary amine in order to provide information on their NMR spectra and other properties for comparison with hydrolysis products. The products, although ionic, did not exhibit high conductivities in nitromethane since they are salts of the weakly basic dialkylamines with the weakly acidic H_2SeO_3 ($K_1 \sim 3.5 \times 10^{-3}$)[16] and thus in solution dissociate into the un-ionized free amine and free selenious acid. Ionic formulations are supported by the Nujol mull infrared spectrum of the diisopropylammonium derivative, which exhibited relatively strong bands at 865, 808, and 620 cm^{-1} close to bands found[17] in authentic $HSeO_3^-$ salts (e.g., strong bands at 875, 845, 825, 790, 615, and 605 cm^{-1} in solid $NaHSeO_3$). The selenium-77 NMR spectra of the products listed in Table I all exhibit a single resonance at δ 1369 ± 5, indicating the same selenium species in each of the products. The proton NMR spectra of the products in Table I exhibit N–H resonances in the range δ 9.3–9.8 in addition to the expected alkyl resonances. These $[R_2NH_2]_2[Se_2O_5]$ salts are reasonably soluble in chlorinated organic solvents such as CH_2Cl_2 and $CHCl_3$ undoubtedly owing to the effects of the two organic cations as well as the weak dissociation of these salts of weak acids with weak bases.

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Registry No. $SeOCl_2$, 7791-23-3; SeO_2, 7446-08-4; Me_3SiCl, 75-77-4; Me_2NH, 124-40-3; $(Me_2N)_2SeO$, 2424-09-1; $(Me_2N)_2S$, 2424-06-8; $(Ph_2P)_2Se$, 109243-13-2; $(Bu_2P)_2Se$, 109243-14-3; $((Me_2N)_2P)_2Se$, 109243-15-4; *i*-$Pr_2Se(O)Cl$, 109243-16-5; (*i*-$Pr)_2NH$, 108-18-9; *i*-Pr_2NSiMe_3, 17425-88-6; *meso*-[*i*-$Pr_2NSe(O)]_2O$, 109243-17-6; (±)-[*i*-$Pr_2NSe(O)]_2O$, 109243-18-7; (*i*-$PrN)_2Se$, 109243-19-8; $(OC_4H_8N)_2Se$, 109243-20-1; $SeCl_4$, 10026-03-6; $(Me_2N)_3SeCl$, 109243-23-4; $(Me_2N)_2SeCl_2$, 109243-24-5; $[Me_2NH_2][Se_2O_5]$, 2881-47-2; $[Et_2NH_2]_2[Se_2O_5]$, 44594-94-7; [*n*-$Pr_2NH_2]_2[Se_2O_5]$, 109243-21-2; [*i*-$Pr_2NH_2]_2[Se_2O_5]$, 109243-22-3; Et_2NH, 109-89-7; Pr_2NH, 142-84-7; morpholinotrimethylsilane, 13368-42-8; (dimethylamino)trimethylsilane, 2083-91-2.

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Contribution from the Fachbereich Chemie,
Anorganische Chemie, Universität Dortmund,
D-4600 Dortmund 50, FRG, and Institut für Physikalische
und Theoretische Chemie, Universität Tübingen,
7400 Tübingen 1, FRG

Gas-Phase Structure of $AsCl_2F_3$ and a Vibrational Analysis of $AsCl_nF_{5-n}$ (n = 1–5)

R. Minkwitz,[†] H. Prenzel,[†] A. Schardey,[†] and H. Oberhammer*[‡]

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After preparing the very unstable $AsCl_5$ by photolytic low-temperature chlorination of $AsCl_3$,[1] we recently succeeded in synthesizing the entire series of mixed chlorofluoroarsoranes from $AsCl_4^+AsF_6^-$.[2–6] These arsoranes are significantly less stable than the homologous phosphoranes, whose gas-phase structures and force fields have been reported recently in this journal.[7] An independent electron diffraction study has also recently been reported for PCl_2F_3.[8] $AsCl_4F$ forms upon the pyrolysis of $AsCl_4^+AsF_6^-$ and can be solidified on cooled surfaces below −196 °C, after a short distance of flight. Because of its thermal instability the compound is not condensable.[5] The byproduct AsF_5 is separated in a reaction with activated KF.[9]

The primary pyrolysis products undergo halogen-exchange reactions during longer times of flight to form $AsCl_2F_3$ and $AsClF_4$.[2,3] There are no indications that the postulated intermediary species $AsCl_3F_2$ forms. This arsorane is accessible, however, by a gas-phase/solid reaction of $AsCl_2F_3$ and $CaCl_2$ and may be characterized by vibrational spectroscopy below −196 °C.[4] $AsCl_2F_3$ and $AsClF_4$ decompose in their liquid phases at temperatures above −75 and −90 °C, respectively, to give mainly $AsCl_4^+AsF_6^-$,[2] but $AsCl_2F_3$ is recondensable at its melting point, thus allowing an investigation of its gas-phase structure by electron diffraction. Analysis of the radial distribution curve (Figure 1) confirms the conformation predicted by the VSEPR theory[10] or the electronegativity rule,[11] i.e., C_{2v} symmetry with equatorial positions of the two chlorine atoms. The geometry of $AsCl_2F_3$ is characterized by five geometric parameters that are well-determined by the six "characteristic features" (peaks or shoulders) of the radial distribution curve. A diagonal-weight matrix has been applied to the intensities in the least-squares analysis, and the scattering amplitudes and phases of Haase[12] are used. The ratio of axial and equatorial As–F vibrational amplitudes is constrained to the spectroscopic value. The five independent geometric parameters and seven vibrational amplitudes have been refined simultaneously. Four correlation coefficients have values larger than $|0.6|$: AsF_{eq}/AsF_{ax}, 0.89; $AsF_{eq}/F_{ax}AsF_{eq}$, −0.66; $AsF_{ax}/l(AsF)$, −0.80; $AsF_{eq}/l(AsF)$, 0.90. The results of the least-squares analysis are summarized in Table I. The r_a distances have been converted to r_g values by using the experimental vibrational amplitudes.

The angular distortions from the ideal trigonal bipyramid are small. The angles $F_{ax}AsF_{eq}$ and $Cl_{eq}AsCl_{eq}$ deviate by less than 1° from the ideal angles of 90 and 120°, respectively. The equatorial As–F bond in $AsCl_2F_3$ (As–F_{eq} = 166.3 (7) pm) appears to be slightly longer than in AsF_5 (As–F_{eq} = 165.6 (4) pm),[13] but the difference (Δ(As–F_{eq}) = 0.7 (8) pm) is within the combined experimental uncertainties. The axial As–F bonds lengthen by 1.2 (7) pm upon substitution of two equatorial fluorines by chlorines (As–F_{ax} = 171.1 (5) and 172.3 (4) pm in AsF_5[13] and $AsCl_2F_3$, respectively). These trends in the As–F bond lengths are equal to those observed in the analogous phosphoranes: Δ(P–F_{eq}) = 0.6 (7) pm and Δ(P–F_{ax}) = 1.3 (5) pm.[7] No gas-phase values for As(V)–Cl bond lengths are known in the literature for comparison.

Valence force fields for the chlorofluoroarsoranes $AsCl_nF_{5-n}$ with n = 1–5 were determined with the program NORCOR[14] from

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[†] Universität Dortmund.

[‡] Universität Tübingen.

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