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Studies on the Properties of Organoselenium(IV) Fluorides and Azides

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The reaction of organoselenides and -diselenides (R_2Se and $(RSe)_2$) with XeF_2 furnished the corresponding organoselenium(IV) difluorides R_2SeF_2 (R = Me (**1**), Et (**2**), *i*Pr (**3**), Ph (**4**), Mes (=2,4,6-$(Me)_3C_6H_2$) (**5**), Tipp (=2,4,6-$(iPr)_3C_6H_2$) (**6**), 2-$Me_2NCH_2C_6H_4$ (**7**)), and trifluorides $RSeF_3$ (R = Me (**8**), *i*Pr (**9**), Ph (**10**), Mes (**11**), Tipp (**12**), Mes* (=2,4,6-$(tBu)_3C_6H_2$) (**13**), 2-$Me_2NCH_2C_6H_4$ (**14**)), respectively. In addition to characterization by multinuclear NMR spectroscopy, the first molecular structure of an organoselenium(IV) difluoride as well as the molecular structures of subsequent decomposition products have been determined. The substitution of fluorine atoms with Me_3SiN_3 leads to the corresponding organoselenium(IV) diazides $R_2Se(N_3)_2$ (R = Me (**15**), Et (**16**), *i*Pr (**17**), Ph (**18**), Mes (**19**), 2-$Me_2NCH_2C_6H_4$ (**20**)) and triazides $RSe(N_3)_3$ (R = Me (**21**), *i*Pr (**22**), Ph (**23**), Mes (**24**), Tipp (**25**), Mes* (**26**), 2-$Me_2NCH_2C_6H_4$ (**27**)), respectively. The organoselenium azides are extremely temperature-sensitive materials and can only be handled at low temperatures.

Introduction

Whereas the chemistry of tellurium halides as precursors for the corresponding tellurium azides has been well investigated over the past years,[1–8] the field of selenium azide compounds is less studied. The selenium azides known prior to this study are the ionic selenonium azides of the type $[R_3Se]N_3$ (R = Me, Ph),[9] the organoselenium(II) azides $RSeN_3$ (R = Ph, C_6F_5, Mes, 2,4,6-$(CF_3)_3C_6H_2$, Mes*, 2,6-$(Mes)_2C_6H_3$, 2-$Me_2NCH_2C_6H_4$),[10] of which only 2-$Me_2NCH_2C_6H_4SeN_3$ could be isolated at ambient temperature, and recently, also reported by us and others, the binary selenium(IV) azides $Se(N_3)_4$, $Se(N_3)_5^-$, and $Se(N_3)_6^{2-}$.[11] In the area of selenium(IV) fluorides of the type R_2SeF_2 and $RSeF_3$, several compounds were reported,[12–23] but up to now the only reported crystal structures are of the binary species SeF_4,[24] SeF_5^-,[25] and SeF_6^{2-},[26] as well as of an organoselenium(VI) difluoride.[27] In this contribution, we present a detailed study of organoselenium(IV) fluorides and azides with different substituents.

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Experimental Section

General procedures. All manipulation of air- and moisture-sensitive materials were performed under an inert atmosphere of dry argon using flame-dried glass vessels or oven-dried plastic equipment and Schlenk techniques.[28] The selenium fluorides were handled in PFA-vessels (perfluoralkoxy-copolymer) due to the extreme sensitivity toward glass. For all NMR measurements of those compounds, a 4 mm PFA-tube was used, which was placed into a standard 5 mm NMR glass tube. The solvents dichloromethane and acetonitrile were dried by standard methods and freshly distilled prior to use. The $(RSe)_2$ compounds were prepared according to literature procedures.[29–31] 2,4,6-trimethylbromobenzene, *iso*-propylmagnesium chloride, *tert*-butyllithium, phenyllithium, trimethylsilyl azide, dimethyl diselenide (all Sigma Aldrich), dimethyl selenide (Avocado), and xenon difluoride (ABCR) were used as received. Infrared spectra were recorded on PerkinElmer Spektrum One FTIR or Nicolet 520 FTIR spectrometers (as neat liquids/solids or Nujol mulls), Raman spectra on a PerkinElmer 2000 NIR FT spectrometer fitted with a Nd:YAG laser (1064 nm) as neat solids or liquids. The Raman spectra of **15** and **21** were recorded at about −110 °C in a nitrogen-cooled Dewar sample container. NMR spectra were recorded on a JEOL Eclipse 400 instrument, and chemical shifts were determined with respect to external Me_4Si (^{1}H, 399.8 MHz; ^{13}C, 100.5 MHz), $MeNO_2$ (^{14}N, 28.9 MHz), $CFCl_3$ (^{19}F, 376.1 MHz), and Me_2Se (^{77}Se, 76.3 MHz). Because of the temperature dependence of the ^{77}Se NMR resonances, all samples were recorded at 25 °C except all selenium azide compounds (at −50 °C) and where otherwise indicated. Because of the high sensitivity of the compounds, elemental analyses could not be performed satisfactorily and are therefore not reported.

Caution. *Covalent selenium azides are potentially explosive, although no hazards were observed during our studies. This necessitates meticulous safety precautions during their preparation and handling; please see ref 11.*

X-ray Crystallography. For all compounds, an Oxford Xcalibur3 diffractometer with a CCD area detector was employed for data collection using Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved using direct methods (*SHELXS*[32] or *SIR97*[33]) and refined by full-matrix least-squares on F^2 (*SHELXL*[32]). All non-hydrogen atoms were refined anisotropically. The HF hydrogen atoms were located in a difference Fourier map and placed with a H−F distance of 0.92 Å. ORTEP plots are shown with thermal ellipsoids at the 50% probability level.

Preparation of the Diorgano Monoselenides R_2Se. All monoselenides were prepared using $Se(dtc)_2$ as Se^{2+} equivalent and reacted with the corresponding metal organic reagent (either the Grignard reagent or the organolithium compound) analogous to ref 34.

Diethyl Selenide, Et_2Se. Colorless, malodorous liquid (35% yield). ^{1}H NMR ($CDCl_3$): δ 2.58 (q, CH_2, $^{3}J_{\mathrm{H-H}} = 7.6$ Hz, $^{2}J_{\mathrm{H-77Se}} = 140.7$ Hz, 2H), 1.39 (t, CH_3, $^{3}J_{\mathrm{H-H}} = 7.6$ Hz, $^{3}J_{\mathrm{H-77Se}} = 127.0$ Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 16.5 (CH_2, $^{1}J_{\mathrm{C-77Se}} = 59.2$ Hz), 15.7 (CH_3, $^{2}J_{\mathrm{C-77Se}} = 8.5$ Hz). ^{77}Se NMR ($CDCl_3$): δ 239.

Diisopropyl Selenide, *i*Pr_2Se. Colorless, malodorous liquid (40% yield). ^{1}H NMR ($CDCl_3$): δ 3.13 (sept, CH, $^{3}J_{\mathrm{H-H}} = 6.9$ Hz, $^{2}J_{\mathrm{H-77Se}} = 141.5$ Hz, 2H), 1.39 (d, CH_3, $^{3}J_{\mathrm{H-H}} = 6.9$ Hz, $^{3}J_{\mathrm{H-77Se}} = 126.5$ Hz, 12H). ^{13}C NMR ($CDCl_3$): δ 28.3 (CH, $^{1}J_{\mathrm{C-77Se}} = 60.0$ Hz), 24.8 (CH_3, $^{2}J_{\mathrm{C-77Se}} = 12.7$ Hz). ^{77}Se NMR ($CDCl_3$): δ 422.

Ditertiarybutyl Selenide, *t*Bu_2Se. Pale-yellow, malodorous liquid (18% yield). ^{1}H NMR ($CDCl_3$): δ 1.50 (s). ^{13}C NMR ($CDCl_3$): δ 42.4 (CSe), 33.9 (CH_3, $^{2}J_{\mathrm{C-77Se}} = 13.1$ Hz). ^{77}Se NMR ($CDCl_3$): δ 600.

Diphenyl Selenide, Ph_2Se. Yellow, malodorous liquid (27% yield). ^{1}H NMR ($CDCl_3$): δ 7.49−7.28 (m). ^{13}C NMR ($CDCl_3$): δ 132.9 (*o*-C), 131.1 (*p*-C), 129.3 (C−Se), 127.3 (*m*-C). ^{77}Se NMR ($CDCl_3$): δ 416.

Bis(2,4,6-trimethylphenyl) Selenide, Mes_2Se. Yellow solid (44% yield). ^{1}H NMR ($CDCl_3$): δ 6.81 (s, *m*-CH, 4H), 2.23 (s, *o*-CCH_3, 12H), 2.21 (s, *p*-CCH_3, 6H). ^{13}C NMR ($CDCl_3$): δ 141.3 (*o*-C), 136.9 (*p*-C), 129.4 (C−Se), 128.9 (*m*-C), 23.5 (*o*-CH_3), 20.8 (*p*-CH_3). ^{77}Se NMR ($CDCl_3$): δ 225.

Bis(2,4,6-triisopropylphenyl) Selenide, $Tipp_2Se$. Pale-yellow solid (60% yield). ^{1}H NMR ($CDCl_3$): δ 6.88 (s, H_{arom}, 4H), 3.63 (sept, *o*-CH, $^{3}J_{\mathrm{H-H}} = 6.9$ Hz, 4H), 2.80 (sept, *p*-CH, $^{3}J_{\mathrm{H-H}} = 6.9$ Hz, 2H), 1.17 (d, *p*-CH_3, $^{3}J_{\mathrm{H-H}} = 6.9$ Hz, 12H), 0.96 (d, *o*-CH_3, $^{3}J_{\mathrm{H-H}} = 6.9$ Hz, 24H). ^{13}C NMR ($CDCl_3$): δ 151.4/148.7/131.0/122.0 (C_{arom}), 34.1/33.9 (CH), 24.1/24.0 (CH_3). ^{77}Se NMR ($CDCl_3$): δ 162.

Bis(2-dimethylaminomethylphenyl) Selenide, $(2\text{-}Me_2NCH_2\text{-}C_6H_4)_2Se$. Light-brown solid (55% yield). ^{1}H NMR ($CDCl_3$): δ 7.38−7.06 (m, H_{arom}), 3.55 (s, CH_2, 4H), 2.23 (s, CH_3, 12H). ^{13}C NMR ($CDCl_3$): δ 140.3/134.4/134.2/129.8/127.9/127.0 (C_{arom}), 63.9 (CH_2), 44.9 (CH_3). ^{77}Se NMR ($CDCl_3$): δ 344.

General Procedure for the Preparation of the Diorganoselenium(IV) Difluorides R_2SeF_2. Into a solution of 0.9 mmol of the monoselenide in 3 mL of CH_2Cl_2 was added 1.0 mmol XeF_2 at 0 °C. After the solution was stirred for 2 h at 0 °C and 1 h at ambient temperature, the color of the solution changed from pale yellow to colorless. Evaporation of the solvent yielded the diorganoselenium(IV) difluorides as colorless or pale-yellow liquids (**1**–**3**) and colorless solids (**4**–**7**), respectively.

Dimethylselenium Difluoride, Me_2SeF_2 (1). ^{19}F NMR (CD_2Cl_2): δ −71.0 (s, $^{1}J_{\mathrm{F-77Se}} = 646.3$ Hz). ^{77}Se NMR (CD_2Cl_2): δ 790 (t, $^{1}J_{\mathrm{Se-19F}} = 646.3$ Hz). Identified byproduct $CH_2F(CH_3)SeF_2$: ^{19}F NMR (CD_2Cl_2): δ −83.4 (m, $^{1}J_{\mathrm{F-77Se}} = 603.4$ Hz, SeF_2, 2F), −209.5 (tm, $^{2}J_{\mathrm{F-1H}} = 46.8$ Hz, CH_2F, 1F).

Diethylselenium Difluoride, Et_2SeF_2 (2). ^{19}F NMR (CD_2Cl_2): δ −94.8 (s, $^{1}J_{\mathrm{F-77Se}} = 638.1$ Hz). ^{77}Se NMR (CD_2Cl_2): δ 865 (t, $^{1}J_{\mathrm{Se-19F}} = 638.1$ Hz).

Diisopropylselenium Difluoride, *i*Pr_2SeF_2 (3). ^{19}F NMR (CH_2Cl_2): δ −110.4 (s, $^{1}J_{\mathrm{F-77Se}} = 632.0$ Hz). ^{77}Se NMR (CH_2Cl_2): δ 929 (t, $^{1}J_{\mathrm{Se-19F}} = 632.0$ Hz).

Diphenylselenium Difluoride, Ph_2SeF_2 (4). Raman: 3737 (16), 3069 (30), 2902 (16), 1577 (22), 1381 (44), 1298 (31), 1213 (25), 1002 (39), 892 (24), 862 (24), 733 (100, νSeC), 483 (40, νSeF), 386 (58), 293 (51) cm^{-1}. ^{19}F NMR (CH_2Cl_2): δ −67.0 (s, $^{1}J_{\mathrm{F-77Se}} = 531.5$ Hz). ^{77}Se NMR (CH_2Cl_2): δ 783 (t, $^{1}J_{\mathrm{Se-19F}} = 531.5$ Hz).

Bis(2,4,6-trimethylphenyl)selenium Difluoride, Mes_2SeF_2 (5). Raman: 3023 (41), 2978 (42), 2928 (85), 1599 (46), 1580 (24), 1461 (26), 1448 (26), 1384 (62), 1296 (63), 1252 (16), 1040 (18), 1020 (28), 956 (16), 734 (40), 591 (35), 565 (100, νSeC), 549 (73), 517 (31), 476 (77, νSeF), 413 (26), 382 (52), 350 (32), 290 (41), 230 (38), 205 (44), 184 (51) cm^{-1}. IR (KBr): 3432 br, 3021 w, 2967 m, 2924 s, 2854 w, 2732 w, 1732 w, 1689 w, 1639 w, 1597 s,

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1573 m, 1456 vs, 1407 m, 1397 s, 1293 s, 1258 w, 1175 w, 1011 s, 952 w, 884 w, 852 vs, 732 w, 702 s, 587 m, 562 m, 545 m, 501 w, 457 (νSeF) vs, cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.95 (s, *m*-CH, 4H), 2.30 (s, *o*-CCH_3, 12H), 2.25 (s, *p*-CCH_3, 6H). ^{13}C NMR ($CDCl_3$): δ 140.0 (*o*-*C*CH_3), 138.3 (C−Se), 136.7 (*p*-*C*CH_3), 130.6 (*m*-CH), 21.5 (*o*-C*C*H_3), 20.7 (*p*-C*C*H_3). ^{19}F NMR ($CDCl_3$): δ −68.5 (s, $^{1}J_{\text{F}-77\text{Se}} = 597.8$ Hz). ^{77}Se NMR ($CDCl_3$): δ 804 (t, $^{1}J_{\text{Se}-19\text{F}} = 597.8$ Hz) ppm. Anal. Calcd for $C_{18}H_{22}SeF_2$: C, 60.8; H, 6.2. Found: C, 60.6; H, 6.3.

Bis(2,4,6-triisopropylphenyl)selenium Difluoride, $Tipp_2SeF_2$ (6). Raman: 3051 (14), 2986 (45), 2964 (59), 2910 (49), 2869 (41), 1594 (31), 1570 (12), 1462 (28), 1446 (27), 1382 (39), 1333 (16), 1303 (28), 1264 (29), 1236 (18), 1105 (20), 1062 (12), 1015 (21), 960 (15), 939 (11), 885 (37), 842 (13), 817 (11), 733 (100, νSeC), 650 (14), 606 (26), 520 (21), 488 (34, νSeF), 451 (21), 385 (43), 292 (45) cm^{-1}. IR (KBr): 3440 br, 2960 vs, 2928 s, 2868 s, 2378 w, 2346 w, 2103 w, 1593 m, 1566 m, 1526 w, 1461 s, 1420 w, 1384 s, 1362 s, 1314 w, 1257 w, 1166 w, 1155 w, 1102 m, 1069 m, 1055 m, 1008 w, 936 w, 877 s, 827 w, 788 w, 743 m, 648 w, 516 w, 459 (νSeF) vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.13 (s, *m*-CH), 1.25−1.05(m). ^{13}C NMR ($CDCl_3$): δ 139.9 (*o*-*C*$CH(CH_3)_2$), 131.1 (C−Se), 125.4 (*p*-*C*CH_3), 121.9 (*m*-CH), 34.0, 32.4, 23.6. ^{19}F NMR ($CDCl_3$): δ −50.9 (s, $^{1}J_{\text{F}-77\text{Se}} = 608.2$ Hz). ^{77}Se NMR ($CDCl_3$): δ 819 (t, $^{1}J_{\text{Se}-19\text{F}} = 608.2$ Hz).

Bis(2-dimethylaminomethylphenyl)selenium Difluoride, (2-$Me_2NCH_2C_6H_4)_2SeF_2$ (7). Raman: 3062 (29), 2953 (72), 2885 (100), 2841 (53), 1591 (23), 1459 (54), 1362 (26), 1330 (32), 1252 (18), 1218 (18), 1169 (26), 1153 (28), 1030 (27), 974 (20), 843 (33), 809 (41), 661 (27), 630 (19), 487 (30), 399 (33), 368 (40), 316 (25), 208 (27) cm^{-1}. IR (KBr): 3415 br, 3054 w, 2953 s, 2867 s, 2829 s, 2787 m, 2632 br, 2464 w, 2431 w, 2043 br, 1834 s, 1468 br, 1301 w, 1237 vs, 1174 w, 1120 w, 1097 w, 1017 s, 977 w, 951 w, 877 m, 839 m, 763 s, 617 m, 511 w, 472 m cm^{-1}. ^{19}F NMR (CH_2Cl_2): δ −71.4 (s, $^{1}J_{\text{F}-77\text{Se}} = 657.2$ Hz). ^{77}Se NMR (CH_2Cl_2): δ 835 (t, $^{1}J_{\text{Se}-19\text{F}} = 657.2$ Hz).

General Procedure for the Preparation of the Diorganoselenium(IV) Diazides $R_2Se(N_3)_2$. Into a solution of 1.0 mmol of the selenium(IV) difluorides (**1**−**7**) in 1 mL CH_2Cl_2 was added 2.2 mmol Me_3SiN_3 at −50 °C. After stirring the solution at −50 °C for 20 min, a sample for NMR spectroscopy was prepared and measured at −50 °C. After those NMR experiments, the compounds were stored in a freezer at −32 °C. Only **18** is stable for about 2 weeks at −32 °C, all other diazides showed a more or less rapid decomposition to the corresponding monoselenides, partially even at −50 °C after a few hours.

Dimethylselenium Diazide, $Me_2Se(N_3)_2$ (15). The compound is stable for hours at −50 °C, and slow decomposition occurs at −32 °C. For the Raman measurement, a solution (about 1 mL within three steps) was transferred into a glass NMR tube, and all volatile materials were removed in vacuo at −40 °C, yielding a colorless solid, which quickly decomposes upon warming to ambient temperature. Raman: 2941 (17), 2097 (16)/ 2026 (22, $\nu_{\text{as,N3}}$), 1216 (15), 1189 (9), 761 (5), 569 (3)/ 564 (6, ν_{SeC}), 403 (100, ν_{SeN}), 374 (18), 252 (27), 189 (35), 98 (20) cm^{-1}. ^{14}N NMR (CD_2Cl_2): δ −136 (N_β), −190 (N_γ), −248 (N_α, br). ^{77}Se NMR (CD_2Cl_2): δ 574.

Diethylselenium Diazide, $Et_2Se(N_3)_2$ (16). The compound is stable for hours at −50 °C and about 1 day at −32 °C. ^{1}H NMR (CD_2Cl_2): δ 3.29 (q, CH_2), 1.63 (t, CH_3). ^{13}C NMR (CD_2Cl_2): δ 49.0 ($^{1}J_{\text{C}-77\text{Se}} = 53.8$ Hz, CH_2), 10.8 ($^{2}J_{\text{C}-77\text{Se}} = 13.1$ Hz, CH_3). ^{14}N NMR (CD_2Cl_2): δ −134 (N_β), −189 (N_γ), −250 (N_α, br). ^{77}Se NMR (CD_2Cl_2): δ 692.

Diisopropylselenium Diazide, *i*$Pr_2Se(N_3)_2$ (17). The compound is stable for hours at −50 °C and about 2 d at −32 °C but decomposes completely overnight at + 4 °C. ^{14}N NMR (CH_2Cl_2): δ −135 (N_β), −195 (N_γ), −307 (N_α, br). ^{77}Se NMR (CH_2Cl_2): δ 816.

Diphenylselenium Diazide, $Ph_2Se(N_3)_2$ (18). The compound is stable for about 2 weeks at −32 °C and shows only slow decomposition when slowly warming up to ambient temperature. ^{14}N NMR (CH_2Cl_2): δ −136 (N_β), −181 (N_γ), −251 (N_α, br). ^{77}Se NMR (CH_2Cl_2): δ 662.

Bis(2,4,6-trimethylphenyl)selenium Diazide, $Mes_2Se(N_3)_2$ (19). The compound decomposes even during the NMR measurement at −50 °C within a few hours. As a result, no ^{14}N NMR data could be obtained. ^{77}Se NMR (CH_2Cl_2): δ 635.

Bis(2-dimethylaminomethylphenyl)selenium Diazide, (2-$Me_2NCH_2C_6H_4)_2Se(N_3)_2$ (20). The compound shows slow decomposition by storing a solution over 3 days at −32°, storing a solution at + 4 °C resulted in complete decomposition within a few hours. ^{14}N NMR (CH_2Cl_2): δ −144 (N_β), −217 (N_γ), −313 (N_α, br). ^{77}Se NMR (CH_2Cl_2): δ 769.

General Procedure for the Preparation of the Organoselenium(IV) Trifluorides $RSeF_3$. Into a solution of 0.25 mmol of the diselenide in 1.5 mL of CH_2Cl_2 was added 0.75 mmol XeF_2 in small quantities at 0 °C. After the solution was stirred for 20 min at 0 °C, the pale-yellow solutions of the organoselenium(IV) trifluorides (**8**−**14**) were analyzed by multinuclear NMR spectroscopy. Evaporation of all volatile materials in vacuo yielded colorless solids. At least after 2 days according to ^{19}F NMR spectroscopy, decomposition to several products, which could not be identified further, was noticeable.

Methylselenium Trifluoride, $MeSeF_3$ (8). ^{19}F NMR (CH_2Cl_2): δ −37.8 (br). ^{77}Se NMR (CH_2Cl_2): δ 1257.

Isopropylselenium Trifluoride, *i*$PrSeF_3$ (9). ^{19}F NMR (CH_2Cl_2): δ −57.7 (br). ^{77}Se NMR (CH_2Cl_2): δ 1276.

Phenylselenium Trifluoride, $PhSeF_3$ (10). ^{19}F NMR (CH_2Cl_2): δ −28.0 (F_{ax}), −70.6 (F_{eq}). ^{77}Se NMR (CH_2Cl_2): δ 1162. Decomposition product noticeable after 1d at +4 °C: PhSeOF ^{19}F NMR (CH_2Cl_2): δ +45.4 ($^{1}J_{\text{F}-77\text{Se}} = 1170$ Hz). ^{77}Se NMR (CH_2Cl_2): δ 1078 (d, $^{1}J_{\text{Se}-19\text{F}} = 1170$ Hz).

2,4,6-Trimethylphenylselenium Trifluoride, $MesSeF_3$ (11). ^{19}F NMR (CH_2Cl_2): δ −3.8 (F_{ax}), −78.5 (F_{eq}). ^{77}Se NMR (CH_2Cl_2): δ 1230.

2,4,6-Triisopropylphenylselenium Trifluoride, $TippSeF_3$ (12). ^{19}F NMR (CH_2Cl_2): δ +2.8 (F_{ax}), −74.4 (F_{eq}). ^{77}Se NMR (CH_2Cl_2): δ 1232.

2,4,6-Tritertiarybutylphenylselenium Trifluoride, Mes*SeF_3 (13). ^{19}F NMR ($CDCl_3$): δ −12.3 (F_{ax}), −49.9 (F_{eq}). ^{77}Se NMR ($CDCl_3$): δ 1249.

2-Dimethylaminomethylphenylselenium Trifluoride, 2-$Me_2NCH_2C_6H_4SeF_3$ (14). ^{19}F NMR (CH_2Cl_2): δ −26.3 (F_{ax}), −46.5 (F_{eq}). ^{77}Se NMR (CH_2Cl_2): δ 996.

General Procedure for the Preparation of the Organoselenium(IV) Triazides $RSe(N_3)_3$. Into a solution of 0.50 mmol of the trifluorides (**8**–**14**) in 1 mL CH_2Cl_2 was added 1.5 mmol Me_3SiN_3 at −50 °C. The reaction immediately proceeded, observable by the arising deep yellow color of the solution. After stirring the solution at −50 °C for 10 min, a sample for the NMR spectroscopy was prepared and measured at −50 °C. Decomposition to the corresponding diselenides at −50 °C occurred already after a few hours. In the case of **21**, the triazide precipitated due to its poor solubility in CH_2Cl_2. The decomposition of the triazides resulted in the formation of the corresponding diselenide and dinitrogen with the organoselenium(II) azides, $RSeN_3$, as intermediates.

Methylselenium Triazide, $MeSe(N_3)_3$ (21). For the Raman measurement, a solution (about 1 mL within three steps) was transferred into a glass NMR tube and all of the volatile materials were removed in vacuo at −40 °C, yielding a colorless solid, which quickly decomposes upon warming to ambient temperature. Raman: 2985 (17), 2123 (18)/ 2098 (8)/ 2059 (19,$\nu_{as,N3}$), 1226 (7), 1145 (12), 1099 (8), 991 (6), 671 (8)/ 587 (11, ν_{SeC}), 368 (100, ν_{SeN}), 335 (32), 275 (31), 88 (24) cm^{-1}. ^{14}N NMR (CH_2Cl_2): δ −137 (N_β). ^{77}Se NMR (CH_2Cl_2): δ 951. Decomposition product: $MeSeN_3$ ^{77}Se NMR (CH_2Cl_2): δ 1015.

Isopropylselenium Triazide, *i*PrSe(N_3)$_3$ (22). ^{14}N NMR (CH_2Cl_2): δ −139 (N_β). ^{77}Se NMR (CH_2Cl_2): δ 1014. Decomposition product: *i*PrSeN$_3$ ^{77}Se NMR (CH_2Cl_2): δ 1185.

Phenylselenium Triazide, $PhSe(N_3)_3$ (23). ^{77}Se NMR (CH_2Cl_2): δ 899. Decomposition product: $PhSeN_3$ ^{77}Se NMR (CH_2Cl_2): δ 1130.

2,4,6-Trimethylphenylselenium Triazide, $MesSe(N_3)_3$ (24). ^{14}N NMR (CH_2Cl_2): δ −137 (N_β), −174 (N_γ). ^{77}Se NMR (CH_2Cl_2): δ 884. Decomposition product: $MesSeN_3$ ^{77}Se NMR (CH_2Cl_2): δ 1012.

2,4,6-Triisopropylphenylselenium Triazide, $TippSe(N_3)_3$ (25). ^{14}N NMR (CH_2Cl_2): δ −138 (N_β), −175 (N_γ). ^{77}Se NMR (CH_2Cl_2): δ 900. Decomposition product: $TippSeN_3$ ^{77}Se NMR (CH_2Cl_2): δ 982.

2,4,6-Tritertiarybutylphenylselenium Triazide, $Mes^*Se(N_3)_3$ (26). Only decomposition product could be detected: Mes^*SeN_3 ^{77}Se NMR (CH_2Cl_2): δ 1002.

2-Dimethylaminomethylphenylselenium Triazide, $2\text{-}Me_2NCH_2C_6H_4Se(N_3)_3$ (27). ^{14}N NMR (CH_2Cl_2): δ −136 (N_β), −225 (N_γ). ^{77}Se NMR (CH_2Cl_2): δ 920. Decomposition product: $2\text{-}Me_2NCH_2C_6H_4SeN_3$ ^{77}Se NMR (CH_2Cl_2): δ 1046 ppm.

Computational Details. All calculations were carried out using the program package *G03W*.[35] The structure and frequency calculations were performed with Becke's B3 three parameter hybrid functional using the LYP correlation functional (B3LYP).[36] For carbon, hydrogen, and nitrogen, a correlation consistent double-ζ basis set was used (cc-pVDZ).[37–40] The core electrons of selenium were treated with an ECP28MWB Stuttgart/Dresden pseudopotential,[41] for the valence electrons a double-ζ basis augmented with one set of d functions (d_{exp} = 0.338) was used: (4s5p1d)/[2s3p1d].[41,42]

Scheme 1. Synthesis of the diorgano selenides

$$\text{R–Met} + \text{Se(dtc)}_2 \cdot \text{C}_6\text{H}_6 \xrightarrow[\text{Et}_2\text{O}]{-50\ °\text{C}} \text{R–Se–R} + 2\ \text{Met(dtc)} + \text{C}_6\text{H}_6$$

R = Me, Et, *i*-Pr, *t*-Bu, Ph, Mes, Tipp, $2\text{-}Me_2NCH_2C_6H_4$

Met = MgBr, Li

Results and Discussion

Diorgano Selenides. The diorgano selenides were prepared from the corresponding Grignard reagent or the organolithium reagent, respectively, with the convenient Se^{2+} synthon, Se(dtc)$_2$ (dtc = diethyldithiocarbamate)[43,44] according to Scheme 1. This Se^{2+} equivalent is stable and storable at ambient temperature in contrast to unstable $SeCl_2$, which has to be generated in situ prior to use and disproportionates in less than 24 h.[45]

The reagent selenium(II) bis(diethyldithiocarbamate) crystallized as yellow platelets in the monoclinic crystal system, space group *C*2/*c*, with $Z = 4$ (Figure 1) as benzene solvate.

The solvate-free compound has been reported previously[46,47] but no sufficient discussion of the compound has been carried out and also no ORTEP plot has been published due to high thermal vibration in one of the ethyl groups. During our investigations, we also obtained solvate-free crystals, and the previously reported cell parameters could be confirmed as orthorhombic with the cell axes a = 6.5670(5), b = 9.6110(5), c = 25.1800(5) Å, and also one ethyl group is disordered, in contrast to the benzene solvate of Se(dtc)$_2$, crystallizing in the monoclinic crystal system with no disorder. The selenium atom is coordinated by four sulfur atoms with two different Se−S distances (Se1−S1 2.3078(5) Å and Se1−S2 2.7660(5) Å). The carbamate moiety is nearly planar with torsion angles of 178.40(7)° (S1(i)−Se1−S1−C1) and 178.94(15)° (Se1−S1−C1−N1) and two ethyl groups are pointing up, whereas the opposite ethyl groups are pointing down with respect to that plane. This results in a layered structure with benzene molecules between those layers (Figure 2).

Organoselenium Difluorides and Diazides. The reaction of the organoselenides R_2Se with 1 equiv of XeF_2 furnished the corresponding organoselenium(IV) difluorides Me_2SeF_2 (**1**), Et_2SeF_2 (**2**), *i*Pr$_2$SeF$_2$ (**3**), Ph_2SeF_2 (**4**), Mes_2SeF_2 (**5**), $Tipp_2SeF_2$ (**6**), and $(2\text{-}Me_2NCH_2C_6H_4)_2SeF_2$ (**7**) (Scheme 2). The selenium fluorides are, as observed previously, extremely sensitive toward moisture and were therefore handled under an inert atmosphere of dry argon.

Because of the reaction of HF, which was according to ^{19}F NMR spectroscopy always present in small amounts in the reaction mixtures, with glass and subsequent formation of

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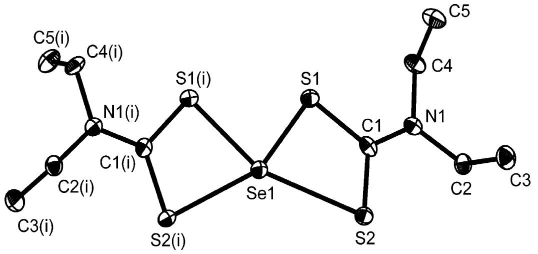


Figure 1. Molecular structure of $Se(dtc)_2 \cdot C_6H_6$, solvent molecule omitted. Selected bond lengths (Å) and angles (°): Se1−S1 2.3078(5), Se1−S2 2.7660(5), S1−C1 1.759(2), S2−C1 1.686(2), C1−N1 1.334(2), S1−Se1−S2 70.61(2), S1−C1−S2 118.17(12), with $i = 2 - x, y, 1½ - z$.

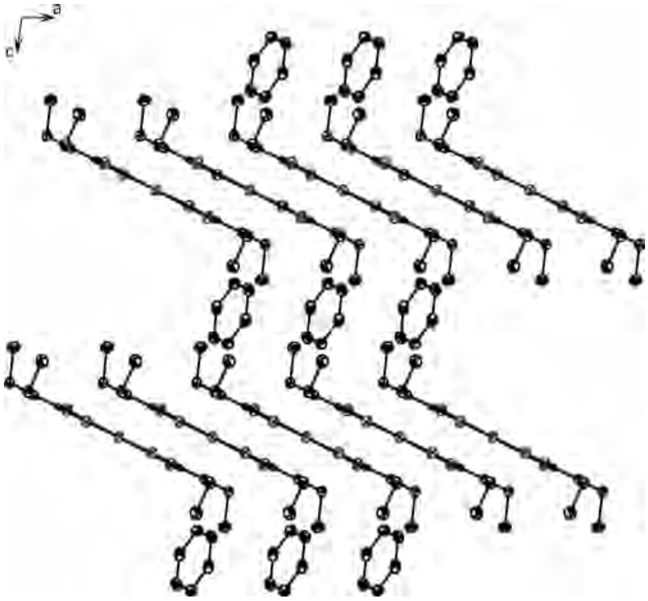
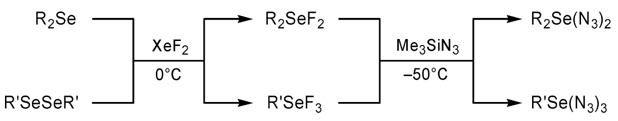


Figure 2. Crystal packing of $Se(dtc)_2$ as benzene solvate, view along [010].

Scheme 2. Synthesis of selenium(IV) fluorides and azides



R = Me, Et, *i*Pr, Ph, Mes, Tipp, $2\text{-}Me_2NCH_2C_6H_4$

R' = Me, *i*Pr, Ph, Mes, Tipp, Mes*, $2\text{-}Me_2NCH_2C_6H_4$

Scheme 3. Reaction of HF with glass and subsequent reaction of Mes_2SeF_2 (**5**) with traces of moisture

$$4\,HF + SiO_2 \longrightarrow SiF_4 + 2\,H_2O$$

$$SiF_4 + 2\,HF \longrightarrow H_2SiF_6$$

$$Mes_2SeF_2\ (\mathbf{5}) + H_2O \longrightarrow Mes_2SeO + 2\,HF$$

$$Mes_2SeO + HF \longrightarrow Mes_2SeO \cdot HF\ (\mathbf{5a})$$

$$2\,Mes_2SeO + H_2SiF_6 \longrightarrow (Mes_2SeOH)_2(SiF_6)\ (\mathbf{5b})$$

traces of water (Scheme 3), all selenium−fluorine compounds have to be handled in PFA vessels. The selenium difluorides were obtained as pale-yellow liquids (**1**−**3**) and colorless solids (**4**−**7**), respectively, and are storable at +4 °C over a period of about 2 weeks at maximum, before, according to ^{19}F NMR spectroscopy, decomposition to various unidentified products occurred. The intended product of the reaction of *t*Bu_2Se with XeF_2 did not yield the desired unknown *t*Bu_2SeF_2, but red selenium and *t*BuF were formed, which was identified by ^{19}F NMR spectroscopy. Because of the electronegative fluorine atoms, the selenium atom is deshielded and therefore the resonances of the difluorides in the ^{77}Se NMR spectra are shifted toward a lower field compared to the corresponding monoselenides, and appear as triplets in the range between $\delta = 780$ and 930 ppm (Table 1). The resonances in the ^{19}F NMR spectra of the difluorides are in the range of $\delta = -110$ to -55 ppm with $^{19}F-^{77}Se$ coupling constants of 530−660 Hz, in accordance with the observed couplings (triplet) in the corresponding ^{77}Se NMR spectra. The ^{77}Se NMR resonance of **1** is shifted slightly to a lower field compared to the previously reported value ($\delta = 776$ ppm in $CDCl_3$),[17] and the Se−F coupling constant with a value of 646 Hz falls in between the reported values of 634[17] and 650 Hz[22], respectively. The ^{19}F NMR resonance of this compound was detected at higher field ($\delta = -71.0$ vs -64.1 ppm in $CDCl_3$[17]/-66.6 ppm in C_6D_6[22]). The obtained byproduct of the reaction could be identified as $CH_2F(CH_3)SeF_2$ due to two resonances in the ^{19}F NMR spectrum at $\delta = -83.4$ ($^1J_{F\text{-}77Se} = 603$ Hz) and -209.5 ppm with a ratio 2:1.

Storing a solution of **5** in a closed PFA vessel at +4 °C over a period of a few days yielded colorless crystals. The compound crystallizes in the monoclinic crystal system, space group *C*2/*c* with $Z = 8$ (Figure 3). The asymmetric unit consists of two molecules, of which only one is discussed in detail due to only marginal differences between them. The selenium atom is pseudo-trigonal bipyramidal coordinated with both fluorine atoms occupying the axial positions and the free lone-pair of selenium in one equatorial position. The Se−F distances were refined to 1.876(2) (Se1−F1) and 1.887(2) Å (Se1−F2) and are slightly longer compared to the bond lengths in the selenium(VI) difluoride, $(biphen)_2SeF_2$ (1.853(4) Å[27]). The Se−C bond lengths are practically identical (Se1−C1 1.944(4)/Se1−C10 1.945(4) Å) and in the range of typical selenium−carbon bonds (di*p*-tolylselenium dichloride 1.93(3)/dibromide 1.95(3) Å[48]). The bond angle F1−Se1−F2 (174.13(10)°) is more bent compared to the angles in di*p*-tolylselenium dichloride/dibromide (177.5(1)/177(1)°).

Only one of the two independent molecules exhibits intermolecular Se···F contacts (3.230(7) Å, Figure 3), slightly shorter than the sum of their van der Waals radii (vdWr SeF, 3.37 Å[49]), forming dimeric units. This leads to a layered structure parallel to the *ab* plane with secondary contacts between the layers.

Furthermore, the molecular structures of subsequent hydrolysis products due to a reaction with traces of moisture could be determined. The selenium(IV) difluoride **5** was stored at low temperature in a closed PFA vessel inside a glass vessel. In contrast to this method, the previous attempts to crystallize **5** did not yield the desired difluoride, however, oxygen containing compounds were isolated. Due to meticulous avoidance of traces of moisture, the water was likely formed inside the reaction

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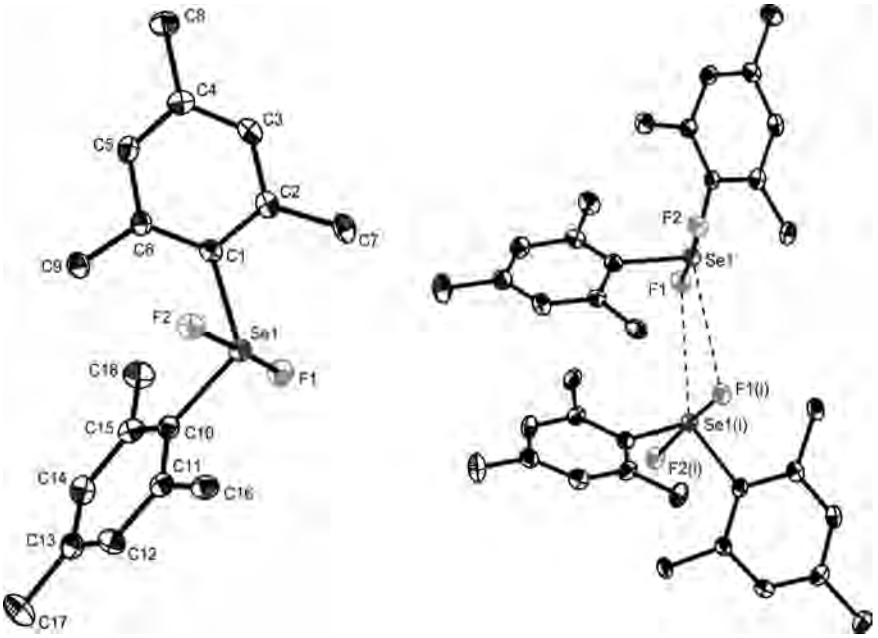

Figure 3. Molecular structure of Mes_2SeF_2 (**5**) (left, only one molecule of the asymmetric unit displayed) and Se···F interactions shown (right). Selected distances (Å) and angles (°): Se−F1 1.876(2), Se1−F2 1.887(2), Se1−C1 1.944 (4), Se1−C10 1.945(4), F1−Se1−F2 174.13(10), C1−Se1−C10 110.67(16), Se1···F1(*i*) 3.230(7) with $i = 1 - x, y, {}^1/_2 - z$.

Table 1. NMR Resonances (δ in ppm) of the Organoselenium(IV) Difluorides/Azides and Trifluorides/Azides (Fluorides 25 °C, Azides −50 °C)

compound	solvent	^{77}Se	^{19}F	^{14}N ($N_\beta/N_\gamma/N_\alpha$)
Me_2SeF_2 (**1**)	CD_2Cl_2	790	−71.0	
Et_2SeF_2 (**2**)	CD_2Cl_2	865	−94.8	
$i Pr_2SeF_2$ (**3**)	CH_2Cl_2	929	−110.4	
Ph_2SeF_2 (**4**)	CH_2Cl_2	783	−67.0	
Mes_2SeF_2 (**5**)	$CDCl_3$	804	−68.5	
$Tipp_2SeF_2$ (**6**)	$CDCl_3$	819	−50.9	
$(2\text{-}Me_2NCH_2C_6H_4)_2SeF_2$ (**7**)	CH_2Cl_2	835	−71.4	
$MeSeF_3$ (**8**)	CH_2Cl_2	1257	−37.8(br)	
$i PrSeF_3$ (**9**)	CH_2Cl_2	1276	−57.7(br)	
$PhSeF_3$ (**10**)	CH_2Cl_2	1162	−28.0/−70.6	
$MesSeF_3$ (**11**)	CH_2Cl_2	1230	−3.8/−78.5	
$TippSeF_3$ (**12**)	CH_2Cl_2	1232	+2.8/−74.4	
Mes^*SeF_3 (**13**)	$CDCl_3$	1249	−12.3/−49.9	
$2\text{-}Me_2NCH_2C_6H_4SeF_3$ (**14**)	CH_2Cl_2	996	−26.3/−46.5	
$Me_2Se(N_3)_2$ (**15**)	CD_2Cl_2	574		−136/−190/−248(br)
$Et_2Se(N_3)_2$ (**16**)	CD_2Cl_2	692		−134/−189/−250(br)
$i Pr_2Se(N_3)_2$ (**17**)	CH_2Cl_2	816		−135/−150/−307(br)
$Ph_2Se(N_3)_2$ (**18**)	CH_2Cl_2	662		−136/−181/−251(br)
$Mes_2Se(N_3)_2$ (**19**)	CH_2Cl_2	635		-
$(2\text{-}Me_2NCH_2C_6H_4)_2Se(N_3)_2$ (**20**)	CH_2Cl_2	769		−144/−217/−313(br)
$MeSe(N_3)_3$ (**21**)	CH_2Cl_2	951 (1015)[a]		−137/−/−
$i PrSe(N_3)_3$ (**22**)	CH_2Cl_2	1014 (1185)[a]		−139/−/−
$PhSe(N_3)_3$ (**23**)	CD_2Cl_2	899 (1130)[a]		−138/−/−
$MesSe(N_3)_3$ (**24**)	CH_2Cl_2	884 (1012)[a]		−138/−174/−
$TippSe(N_3)_3$ (**25**)	CH_2Cl_2	900 (982)[a]		−138/−175/−
$Mes^*Se(N_3)_3$ (**26**)	CH_2Cl_2	− (1002)[a]		-
$2\text{-}Me_2NCH_2C_6H_4Se(N_3)_3$ (**27**)	CD_2Cl_2	920 (1046)[a]		−136/−225/−

[a] Resonances for the intermediate decomposition product $RSeN_3$ in parentheses.

vessel. The compounds were stored at temperatures below +4 °C for several weeks, and initially the glass wall became colder than the PFA vessel inside. Traces of the solvent (with some dissolved HF) might have condensed at the colder glass wall reacted with the glass and, because of the tilted storage of the vessel, could have trickled back in the reaction mixture into the open PFA vessel. This might explain the formation of the oxygen-containing species **5a**, **5b**, and also **7a**, according to Scheme 3.

The reaction of the extremely reactive selenium difluoride with moisture furnishes the corresponding selenium oxide. An alternative route for the formation of the selenium oxide might be a mixed hydroxofluoride $Mes_2Se(OH)F$ as intermediate, formed by a stepwise hydrolysis, followed by an intramolecular HF elimination. The presence of additional HF in the reaction mixture leads to an HF adduct $Mes_2SeO{\cdot}HF$ (**5a**). Because of the greater acidity of the hexafluorosilicic acid compared to HF, H_2SiF_6 protonates

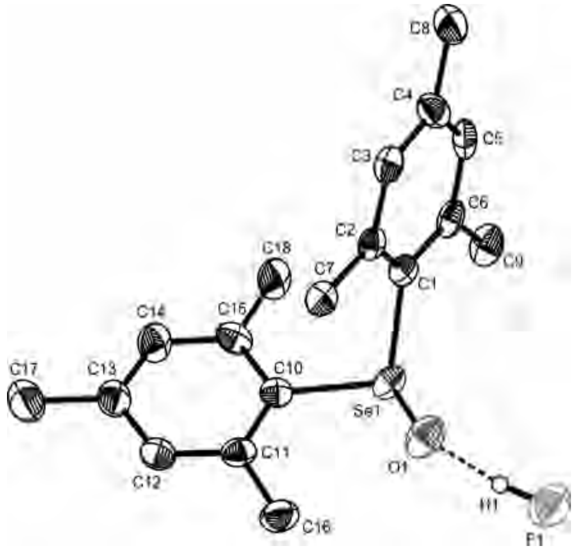

Figure 4. Molecular structure of $Mes_2SeO \cdot HF$ (**5a**). Selected distances (Å) and angles (°): Se1−O1 1.674(4), Se1−C1 1.941(4), Se1−C10 1.953(5), O1···H1 1.52(1), H1−F1 0.92(11), C1−Se1−C10 100.7(2), C1−Se1−O1 101.1(2), C10−Se1−O1 106.3(2), Se1−O1···H1 116.4(4), O1···H1−F1 162(1).

the selenium oxide and leads to the cationic species $[Mes_2SeOH]_2[SiF_6] \cdot 2CH_2Cl_2$ (**5b**) with the hexafluorosilicate anion as dichloromethane disolvate. **5a** crystallized in the orthorhombic crystal system, space group *Pbcn* with $Z = 8$ (Figure 4). The selenium atom is pseudo-tetrahedral coordinated and exhibits similar bond lengths compared to the molecular structure of $(p\text{-}MeOC_6H_4)_2SeO \cdot H_2O$[50] with respect to Se−O (1.674(4) vs 1.665(2) Å) and Se−C (1.941(4)/1.953(5) vs 1.937(4)/1.939(4) Å) distances. The Se−O distance is also nearly the same as that in the selenium analogue of DMSO, DMSeO, which exhibits an Se−O distance of 1.6756(16) Å[51] and therefore clearly indicates that in **5a** a selenium−oxygen double bond is present.

The bond angles C1−Se1−C10 (100.7(2)°), C1−Se1−O1 (101.1(2)°), and C10−Se1−O1 (106.3(2)°) lead to the expected distorted tetrahedral coordination of the selenium atom with bond angles slightly smaller than the ideal tetrahedral angle. The oxygen atom is further coordinated by a hydrogen bridge O1···H1−F1 with a donor−acceptor distance of 2.413(5) Å (O1···H1 1.5(1) Å) and an angle of 162(1)°.

The second decomposition product of **5**, $[Mes_2SeOH]_2[SiF_6]$ (**5b**), crystallized in the monoclinic crystal system, space group $P2_1/n$ with $Z = 4$ (Figure 5). The selenium atom is still tetrahedrally coordinated, but the selenium−oxygen distance (1.741(3) Å) is, because a double bond is no longer present, elongated compared to that in **5b**. Calculations of the gas-phase structures of R_2SeO, $R_2SeO \cdots HX$, and R_2SeOH^+ compounds,[50] which have been performed earlier at the B3LYP/LANL2DZdp level of theory, support our findings. According to these calculations for R = Ph the bond lengths increase in this row from 1.660 Å (R_2SeO) to 1.669 Å ($R_2SeO \cdots HX$) and 1.795 Å (R_2SeOH^+). According to these calculations, the computed Se−O single bond distance in $R_2Se(OH)_2$ is according to these calculations 1.967 Å and therefore rather long compared to the distance in **5b**. Therefore it can be concluded that the cationic species Mes_2SeOH^+ is formed, also confirmed by the proton, which could be located during the refinement at the oxygen atom O1.

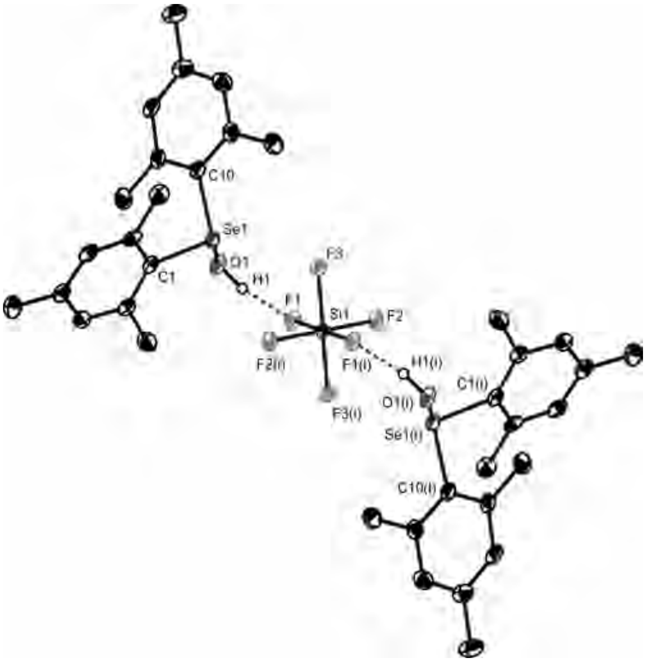

Figure 5. Molecular structure of $[Mes_2SeOH]_2[SiF_6] \cdot 2CH_2Cl_2$ (**5b**), solvate molecules not shown, and only selected atoms labeled for clarity. Selected distances (Å) and angles (°): Se1−O1 1.741(3), Se1−C1 1.944(4), Se1−C10 1.933(4), O1−H1 0.84, H1···F1 1.66(5), Si1−F1 1.711(2), Si1−F2 1.679(2), Si1−F3 1.677(2), C1−Se1−C10 102.4(2), Se1−O1−H1 112(5), O1−H1···F1 166.3(5) with $i = 1 - x, -y, 1 - z$.

The comparable molecular structure of $[Ph_2SeOH][O_3S(p\text{-}(Me)C_6H_4)]$[52] exhibits with 1.768(8) Å a slightly longer Se−O distance than that found in **5b**. The cations in **5b** are linked to the SiF_6^{2-} counterions via hydrogen bridges, which are only between H1···F1 and a donor−acceptor distance of 2.545(7) Å and an angle of 166.3(5)°.

As observed with Mes_2SeF_2 (**5**), in the case of $(2\text{-}Me_2NCH_2C_6H_4)_2SeF_2$ (**7**) traces of water also lead to the formation of the selenium oxide, $(2\text{-}Me_2NCH_2C_6H_4)_2SeO \cdot HF$ (**7a**), as HF adduct (Figure 6). The selenium atom is pseudo-octahedrally coordinated with two virtually equal intramolecular Se···N contacts of 2.749(8) Å (Se1···N1) and 2.748(7) Å (Se1···N2) respectively. These intramolecular contacts are considerably elongated compared to the reported molecular structure of $2\text{-}Me_2NCH_2C_6H_4SeN_3$.[10]

The Se−O distance (1.701(3) Å) is elongated compared to the distance in **5a** (1.674(4) Å), and the hydrogen bridge O1···H1−F1 shows nearly the same values (donor−acceptor distance 2.405(5) Å, F1−H1···O1 160(7)°) as observed previously for **5a**.

From the selenium(IV) difluorides **1**−**7** as precursors, the corresponding selenium(IV) diazides $Me_2Se(N_3)_2$ (**15**), Et

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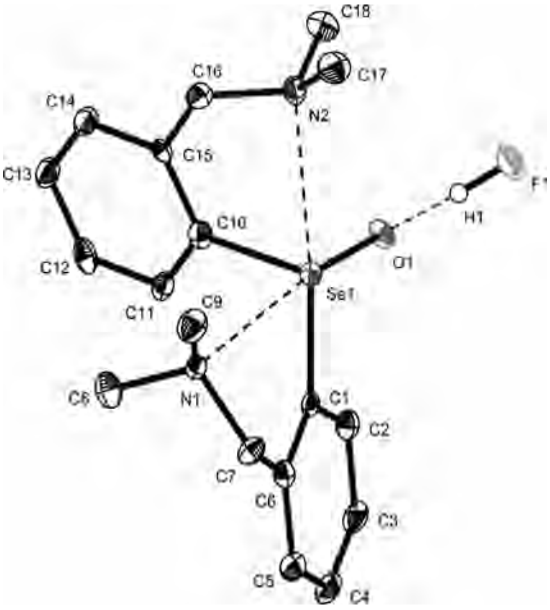

Figure 6. Molecular structure of (2-$Me_2NCH_2C_6H_4)_2SeO \cdot HF$ (**7a**). Selected distances (Å) and angles (°): Se1−O1 1.701(3), Se1−C1 1.965(5), Se1−C10 1.951(5), O1···H1 1.518(5), H1−F1 0.92(5), Se1···N1 2.749(8), Se1···N2 2.748(7), C1−Se1−C10 98.8(2), N2···Se1−C1 174.19(1), N2···Se1−C10 75.36(1), N2···Se1···N1 104.87(1), N1···Se1−O1 169.98(1), N1···Se1−C1 73.42(1), N1···Se1−C10 80.32(1), Se1−O1···H1 106.30(1), O1···H1−F1 160(7).

Scheme 4. Decomposition of the selenium(IV) diazides

$$R_2Se(N_3)_2 \longrightarrow R_2Se + 3\,N_2$$

Scheme 5. Decomposition of the selenium(IV) triazides

$$2\,R'Se(N_3)_3 \longrightarrow 2\,[R'SeN_3] + 6\,N_2 \longrightarrow R'SeSeR' + 3\,N_2$$

$Se(N_3)_2$ (**16**), *i*$Pr_2Se(N_3)_2$ (**17**), $Ph_2Se(N_3)_2$ (**18**), $Mes_2Se(N_3)_2$ (**19**), and (2-$Me_2NCH_2C_6H_4)_2Se(N_3)_2$ (**20**) were obtained by the reaction with 2 equiv of Me_3SiN_3 at −50 °C according to Scheme 2. The selenium(IV) azides are stable only at temperatures around −50 °C and according to ^{77}Se NMR spectra decompose at increased temperatures under vigorous formation of dinitrogen to the corresponding monoselenides (Scheme 4).

Depending on the organic substituent, some selenium(IV) diazides have not been observed, such as $Tipp_2Se(N_3)_2$, or start to decompose even at −50 °C (**19**), or are still detected in small amounts besides monoselenide and traces of diselenide after one month at −30 °C (**18**). In the ^{77}Se NMR spectra, the resonances of the selenium(IV) diazides (Table 1) occur in the range between $\delta = 574$ (**15**) and 816 ppm (**17**) and, as expected, are shifted toward higher field compared to the corresponding difluorides. In the ^{14}N NMR spectra, the resonances for N_β and N_γ can readily be detected, whereas the resonance for N_α is often very broad. In the case of **19**, the resonances in the ^{14}N NMR spectra could not be detected due to the rapid decomposition of this diazide. Interestingly, in contrast to the organotellurium azides, the organoselenium azides cannot be stabilized by sterically more demanding substituents, likely affected by the smaller selenium atom compared to a tellurium atom. Apart from the intramolecular donor stabilized selenium azide **20**, the most stable azides in solution are the methyl (**15**) and phenyl (**18**) substituted diazides. In case of the reaction of $Tipp_2SeF_2$ with Me_3SiN_3, the resonance of the corresponding diazide could not be observed; instead only the decomposition product (monoselenide) was observed in the ^{77}Se NMR spectrum after a short reaction time at −50 °C. The Raman spectrum for **15** (Figure 7) was obtained at low temperatures. The antisymmetric stretching vibration ($\nu_{as,N3}$) is found as medium intense peaks at 2097−2056 cm^{-1}, whereas the SeN stretching vibration is detected at 403 cm^{-1} and shifted to a higher wavenumber compared to the corresponding tellurium compound (346 cm^{-1})[6] due to the lighter element selenium. The SeC stretching vibration (564 cm^{-1}) is also shifted to a higher wavenumber compared to $Me_2Te(N_3)_2$ (540 cm^{-1}).[6]

Organoselenium Trifluorides and Triazides. Starting from the diselenides, the reaction with 3 equiv XeF_2 furnished

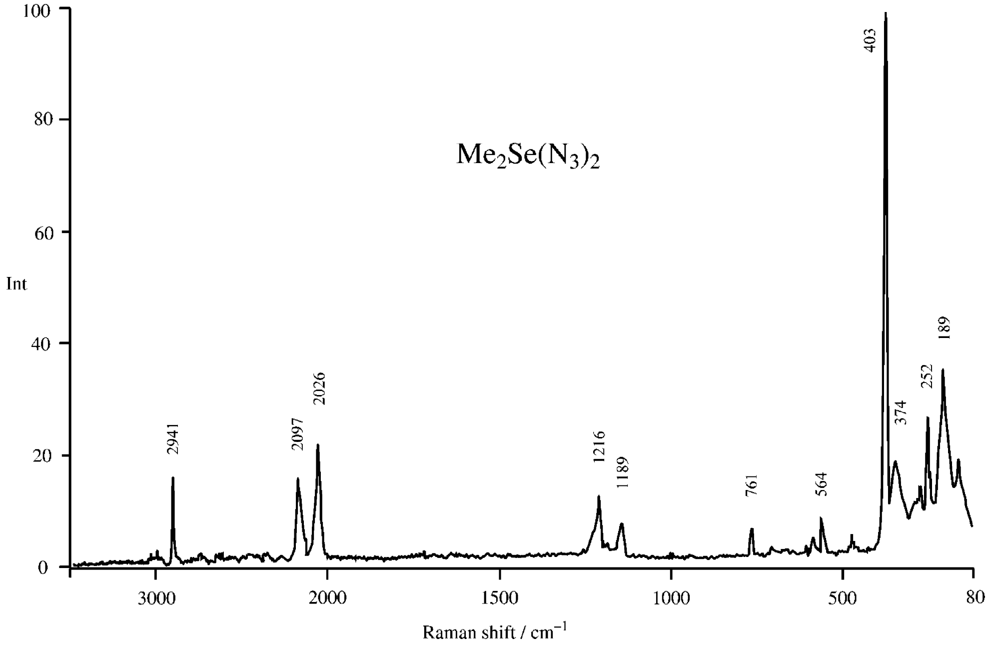

Figure 7. Low-temperature Raman spectrum of $Me_2Se(N_3)_2$ **15**.

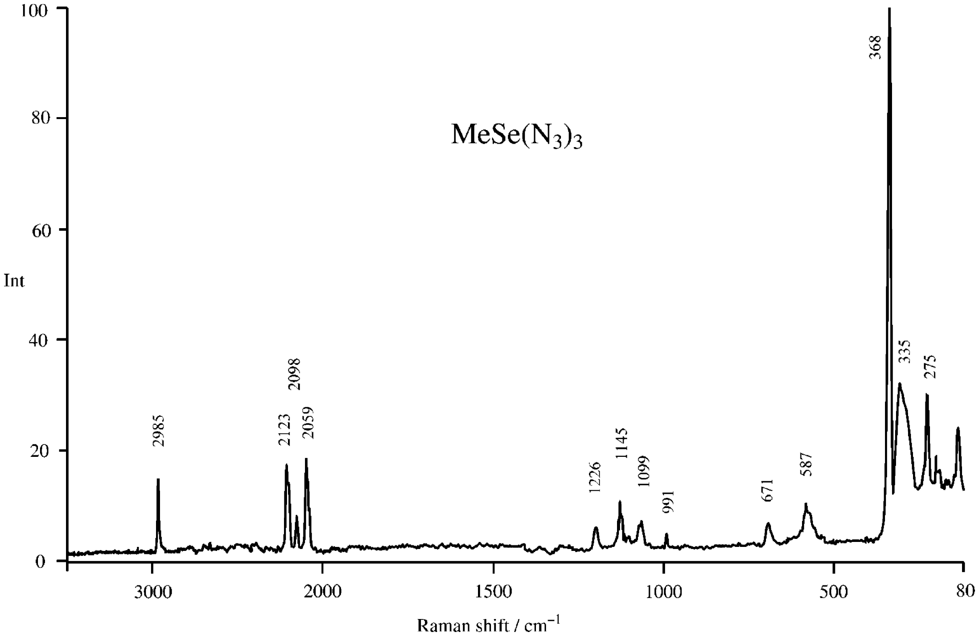

Figure 8. Low-temperature Raman spectrum of $MeSe(N_3)_3$ **21**.

Table 2. Computational results for $Me_2Se(N_3)_2$ and $MeSe(N_3)_3$ at B3LYP/cc-pVDZ level of theory (ECP28MWB for Se)

	$Me_2Se(N_3)_2$ (**15**)		$MeSe(N_3)_3$ (**21**)
point group	C_2	C_{2v}	C_1
$-E$/a.u.	417.556034	417.564072	541.813812
ΔE/kcal mol^{-1}	+5.0	0.0	
NIMAG	0	0	0
dipole moment/D	0.4	4.7	3.2
zpe/kcal mol^{-1}	63.0	62.9	47.3
d(Se−N)/Å	2.124	2.113	eq. 1.949 ax. 2.077
$d(N_\alpha–N_\beta)$/Å	1.222	1.227	eq. 1.244 ax. 1.230
$d(N_\beta–N_\gamma)$/Å	1.153	1.149	eq. 1.137 ax. 1.147
<(NSeN)/°	173.9	173.1	ax−ax 171.1 ax−eq 89.7
<(SeNN)/°	114.5	111.6	eq. 113.9 ax. 112.8
<(NNN)/°	179.4	177.3	eq. 174.6 ax. 176.9
$\nu(Se-N)_{ip}$/cm^{-1a}	315 (0/107)	335 (0/78)	346 (302/8)
$\nu(Se-N)_{oop}$/cm^{-1a}	348 (90/1)	318 (310/1)	323 (51/15) 378 (10/97)
$\nu_{sym}(N_3)_{oop}$/cm^{-1a}	1321 (28/9)	1314 (220/2)	ax. 1301 (272/2)
$\nu_{sym}(N_3)_{ip}$/cm^{-1a}	1324 (39/19)	1324 (106/13)	eq. 1245 (143/2) ax. 1313 (104/9)
$\nu_{asym}(N_3)_{oop}$/cm^{-1a}	2153 (892/68)	2174 (1153/90)	2180 (1015/99) 2206 (729/86)
$\nu_{asym}(N_3)_{ip}$/cm^{-1a}	2169 (501/112)	2202 (709/146)	2219 (370/200)
natural charge on Se (NBO)	+1.17	+1.14	+1.35

[a] ip = in phase, oop = out of phase, (IR/Raman) intensities in parentheses, IR intensities are given in km mol^{-1}, Raman scattering activities are given in Å^4 amu^{-1}.

the corresponding organoselenium(IV) trifluorides: $MeSeF_3$ (**8**), *i*$PrSeF_3$ (**9**), $PhSeF_3$ (**10**), $MesSeF_3$ (**11**), $TippSeF_3$ (**12**), Mes^*SeF_3 (**13**), and 2-$Me_2NCH_2C_6H_4SeF_3$ (**14**) (Scheme 2). The selenium trifluorides are less stable than the difluorides, and decomposition starts at +4 °C within days. All compounds are characterized by multinuclear NMR spectroscopy (Table 1) and exhibit resonances in the ^{77}Se NMR spectra in the region between $\delta = 1257$ (**8**) and 996 ppm (**14**), some of them which are extremely broadened. Compared to the previously discussed selenium difluorides, all resonances are shifted toward lower field as a result of an additional electronegative fluorine atom being present. In the ^{19}F NMR spectra for **10**−**14**, both resonances for the axial and equatorial fluorine atoms, derived from the expected pseudo-trigonal bipyramidal coordination of the selenium atom, could be observed and are between $\delta = -28$ and +2.8 ppm (axial) and $\delta = -46$ and −79 ppm (equatorial), respectively. For **8** ($\delta = -37.8$ ppm) and **9** ($\delta = -57.7$ ppm), only one broad resonance could be observed in the ^{19}F NMR spectra, due to a fast equatorial-axial fluorine exchange process. **14** is expected to exhibit a pseudo-tetragonal bipyramidal coordination of the central atom similar to 2-$Me_2NCH_2C_6H_4TeF_3$,[1] due to the presence of an intramo-

Figure 9. Calculated structures of $Me_2Se(N_3)_2$ (**15**) (C_2 isomer left, C_{2v} isomer center) and $MeSe(N_3)_3$ (**21**) (right).

lecular coordination of the nitrogen atom. Because of the broadness of the signals, no $^2J_{F-F}$ coupling could be observed. The previously reported single ^{19}F NMR resonance for **10** (CH_2Cl_2 solution, $\delta = -24.0$ ppm[19]) is quite different from our results because we observed two resonances at $\delta = -28.0$ and -70.6 ppm in the same solvent. If the reported resonance displays the resonance for the axial fluorine atoms and the resonance for the equatorial fluorine atom was too broad to be observed, the resonance is only slightly different from our resonance of the axial fluorine atom. If this is not the case and only one broad resonance represents both magnetically different fluorine atoms as stated in the article, one would expect a broad resonance in between our two values. According to NMR spectroscopy, a decomposition product of **10** could be identified as the partially hydrolyzed compound PhSeOF (^{77}Se NMR $\delta = 1078$ (d) ppm; ^{19}F NMR $\delta = +45.4$ ppm; $^1J_{Se-F} = 1170$ Hz), previously characterized by its melting point and elemental analysis.[19]

The reaction of the organoselenium trifluorides **8**−**14** with 3 equiv of Me_3SiN_3 at low temperatures furnished the corresponding organoselenium(IV) triazides $MeSe(N_3)_3$ (**21**), *i*$PrSe(N_3)_3$ (**22**), $PhSe(N_3)_3$ (**23**), $MesSe(N_3)_3$ (**24**), $TippSe(N_3)_3$ (**25**), "$Mes^*Se(N_3)_3$" (**26**), and $2\text{-}Me_2NCH_2C_6H_4Se(N_3)_3$ (**27**). The ^{77}Se NMR resonance of the selenium(IV) triazides are shifted to a higher field compared to the corresponding trifluorides and are in the range $\delta = 951-884$ ppm, whereas the ^{14}N NMR resonances could only be observed incompletely due to the instability of the compounds (Table 1). The triazides are unstable even at −50 °C and, when slowly warmed up, decompose immediately to the corresponding diselenide and dinitrogen (Scheme 5). After recording a low temperature Raman spectrum, the colorless solid of **21** deflagrated with a cloud of red selenium upon warming to ambient temperature. In contrast, a solution of **21** slowly decomposes. In the low-temperature Raman spectrum of **21** (Figure 8), the antisymmetric N_3 stretching vibration ($\nu_{as,N3}$) is found as several medium intense peaks at 2123−2059 cm^{-1}, whereas the SeN stretching vibration is detected at 368 cm^{-1} and shifted to a lower wavenumber compared to the corresponding diazide **15**. The comparison between the SeC (587 cm^{-1}) and TeC (559 cm^{-1})[6] vibrations in the corresponding tellurium(IV) triazide $MeTe(N_3)_3$ fits to the expected trends, such that peaks of the selenium compounds are shifted to higher wavenumbers compared to the corresponding tellurium compounds.

The decomposition products were identified by ^{77}Se NMR spectroscopy. As intermediates the corresponding selenium(II) azides were detected, which could be isolated in one case with the intramolecular donor-stabilizing substituent $2\text{-}Me_2NCH_2C_6H_4$. This compound has been previously reported by us and represents the only known molecular

Table 3. Crystal and structure refinement data

	$Se(dtc)_2 \cdot C_6H_6$	Mes_2SeF_2 (**5**)	$Mes_2SeO \cdot HF$ (**5a**)	$(Mes_2SeOH)_2(SiF_6) \cdot 2\ CH_2Cl_2$ (**5b**)	$(2\text{-}Me_2NCH_2C_6H_4)_2SeO \cdot 2\ HF$ (**7a**)
empirical formula	$C_{16}H_{26}N_2S_4Se$	$C_{36}H_{44}F_4Se_2$	$C_{18}H_{23}FOSe$	$C_{19}H_{25}Cl_2F_3OSeSi_{0.5}$	$C_{18}H_{24}FN_2OSe$
formula mass	453.63	710.64	353.33	490.30	383.36
temperature (K)	100	100	100	200	100
crystal size (mm)	0.32 × 0.17 × 0.09	0.32 × 0.24 × 0.16	0.27 × 0.15 × 0.07	0.57 × 0.48 × 0.28	0.25 × 0.22 × 0.13
crystal description	yellow platelet	colorless block	colorless block	colorless block	colorless block
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic	monoclinic
space group	*C2/c*	*C2/c*	*Pbcn*	$P2_1/n$	*C2/c*
a (Å)	8.2071(2)	28.800(6)	24.185(5)	11.345(16)	19.390(5)
b (Å)	12.0351(3)	15.571(3)	7.722(5)	14.013(2)	16.059(5)
c (Å)	20.7122(7)	14.146(3)	17.391(5)	13.655(2)	12.961(5)
β (deg)	99.053(3)	97.228(2)		98.4973(14)	118.703(5)
V (Å^3)	2020.33(10)	6293.2(3)	3248(2)	2147.04(8)	3540(2)
Z	4	8	8	4	8
ρ_{calcd} (g cm^{-3})	1.491	1.500	1.445	1.517	1.4387
μ (mm^{-1})	2.272	2.398	2.319	2.057	2.137
$F(000)$	936	2912	1456	996	1584
θ range (deg)	3.8−26.0	3.8−26.0	3.8−26.0	3.9−26.0	3.8−26.0
index ranges	$-10 \le h \le 10$ $-13 \le k \le 14$ $-25 \le l \le 25$	$-35 \le h \le 35$ $-19 \le k \le 19$ $-17 \le l \le 17$	$-29 \le h \le 27$ $-9 \le k \le 7$ $-21 \le l \le 20$	$-13 \le h \le 13$ $-17 \le k \le 17$ $-16 \le l \le 16$	$-23 \le h \le 13$ $-19 \le k \le 18$ $-15 \le l \le 15$
reflns collected	6527	31196	11117	22731	9106
reflns observed	1535	4305	1546	3381	1989
reflns unique	1964 ($R_{int} = 0.0351$)	6168 ($R_{int} = 0.0459$)	3186 ($R_{int} = 0.0675$)	4186 ($R_{int} = 0.0237$)	3470 ($R_{int} = 0.0552$)
$R1$, wR2 (2σ data)	0.0235, 0.0524	0.0384, 0.1003	0.0444, 0.0985	0.0403, 0.1088	0.0438, 0.1173
$R1$, wR2 (all data)	0.0333, 0.0555	0.0637, 0.1188	0.1011, 0.1134	0.0543, 0.1215	0.0732, 0.1224
max./min. transm.	0.810/0.648	0.680/0.446	0.850/0.627	0.560/0.394	0.760/0.590
data/restr./params	1964/0/105	6168/0/379	3186/1/194	4186/1/246	3470/1/212
GOF on F^2	1.03	1.11	0.92	1.06	0.99
larg. diff. peak/hole (e/Å^3)	0.51/−0.33	0.77/−0.65	0.91/−0.49	1.46/−1.12	0.83/−1.48

structure of an organoselenium azide.[10] In case of the other substituents, the selenium(II) azides are unstable, but can be detected, and decompose further to the diselenides and vigorous formation of dinitrogen even at low temperature. The resonances of the selenium(II) azides could be observed in the ^{77}Se NMR spectra and are shifted to lower field compared to the corresponding selenium(IV) triazides. The resonances of the decomposition products of **23**, **26**, and **27** are consistent with our previously reported resonances ($PhSeN_3$: $\delta = 1130$ vs 1128 ppm, Mes*SeN_3: $\delta = 1002$ vs 1001 ppm, 2-$Me_2NCH_2C_6H_4SeN_3$: $\delta = 1046$ vs 1048 ppm).[10] In the ^{77}Se NMR spectrum of the most sterical demanding substituent used in this study (Mes*, **26**), only the resonance for the selenium(II) azide was observed at $\delta = 1002$ ppm and no resonance for the selenium(IV) triazide was detected. For compounds **21** ($\delta = 1015$ ppm), **22** ($\delta = 1185$ ppm), **24** ($\delta = 1012$ ppm), and **25** ($\delta = 982$ ppm) the resonances for the intermediate selenium(II) azide were detected after a short reaction time.

Calculated Structures of $Me_2Se(N_3)_2$ (15) and $MeSe(N_3)_3$ (21). Calculations for **15** and **21** have been performed at the B3LYP level of theory, and the computational results are summarized in Table 2. For **15**, two isomers were located that are both based on a pseudo-trigonal bipyramidal structure with the two azide groups occupying the axial positions and the two methyl groups and the lone pair being in the equatorial position (Figure 9). One isomer has the azide groups pointing toward the methyl groups (C_2 symmetry), and the other isomer has the azide groups pointing away from the methyl groups (C_{2v} symmetry), similar to the calculated structure of $Me_2Te(N_3)_2$.[6] Whereas both isomers are true minima on their potential energy surface (PES, NIMAG = 0), the isomer with the azide groups pointing away from the methyl groups (C_{2v}) is thermodynamically favored by 5 kcal mol^{-1}. The computed vibrational frequencies for **15** are in reasonable agreement with the experimental Raman data (Supporting Information) but allow no distinction between the two isomers as a result of only marginal differences in the computed frequencies. For **21**, one isomer was located on its PES. The structure is again based on a pseudo-trigonal bipyramidal arrangement with two azide groups occupying the axial positions and the methyl group, one azide group, and the lone pair in the equatorial position (Figure 9), similar to the analogous computed structure of the tellurium compound $MeTe(N_3)_3$.[6]

Conclusion

The extremely moisture-sensitive organoselenium(IV) difluorides and trifluorides have been prepared from the corresponding mono- and diselenides, obtained with the aid of the Se^{2+} synthon $Se(dtc)_2$, and studied spectroscopically. The first crystal structures of organoselenium(IV) difluorides and subsequent decomposition products are presented. Furthermore, the first organoselenium(IV) diazides and triazides, which are only stable at low temperatures and decompose on warm up under vigorous formation of dinitrogen, are reported. Therefore, the characterization of the new organoselenium(IV) azides of the type $R_2Se(N_3)_2$ and $RSe(N_3)_3$ was limited to low-temperature NMR and Raman spectroscopy.

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Supporting Information Available: X-ray crystallographic files (CIF) of crystal data collection and refinement parameters, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for compounds $Se(dtc)_2 \cdot C_6H_6$, **5**, **5a**, **5b**, and **7a**. Complete listing of observed and calculated Raman bands for **15** and **21**. This material is available free of charge via the Internet at http://pubs.acs.org.

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