

Supporting Information for

Exploring Structural Trends for Complexes of Me₂E(OSO₂CF₃)₂ (E = Si, Ge, Sn) with Pyridine Derivatives

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(a) Experimental

All reactions and manipulations were performed under an atmosphere of nitrogen using either standard Schlenk techniques, or within an MBraun or Innovative Technology glovebox. All non-deuterated solvents were initially dried *via* a Grubbs solvent purification system, and subsequently distilled from CaH₂. Me₂SiCl₂, Me₂GeCl₂, Me₂SnCl₂, MeOTf, AlCl₃, GaCl₃, 4-(dimethylamino)pyridine (*dmap*), 2,2'-bipyridine (*bipy*) were purchased from Sigma Aldrich Ltd. and used without further purification, with the exception of *dmap* and *bipy*, which were sublimed under high vacuum and recrystallised from CH₂Cl₂, respectively. Me₂CCl₂ and Me₂CBr₂ was purchased from Sigma Aldrich Ltd. and Acros Organics, respectively, and distilled from CaCl₂ prior to use. AgOTf was purchased from Strem Chemicals and used as received. Deuterated solvents were purchased from Sigma Aldrich Ltd. as single unit ampoules, and used without further purification.

NMR spectra were recorded using either Bruker Avance 500, 360 or 300 MHz spectrometers. Chemical shifts are reported relative to residual protonated solvent peaks (¹H, ¹³C), or to external H₃PO₄ (³¹P); CFCl₃ (¹⁹F); Me₄Sn (¹¹⁹Sn); Me₄Si (²⁹Si). IR spectra were recorded on a Perkin Elmer Spectrum 1000 FT-IR spectroscopy as Nujol mulls on KBr plates.

X-ray crystallographic data were collected at the MAX Diffraction Facility at McMaster University. Suitable crystals were selected and mounted in Paratone oil on a MiTeGen loop, then placed in the cold stream of the diffractometer (173 K). Data were collected using 0.5 degree omega and phi scans on a Bruker Apex2 diffractometer using MoK(alpha) radiation, or on a Bruker Smart6000 CCD detector / Bruker D8 3-circle goniometer / Rigaku Cu rotating anode X-ray generator with Göbel cross-coupled parallel focussing mirrors, using 0.5 degree omega scans. Unit cell parameters were determined from three consecutive scans at different orientations. The data were integrated using SAINT and then corrected for absorption with SADABS (face-indexing and redundancy). Software: Bruker APEX2 v2013.10.0: Bruker AXS Inc., Madison, WI. For full crystallographic details, see Section (iii) below. Molecular structures presented in the manuscript were plotted using ORTEP-3 V2.02, with thermal ellipsoids at the 50% probability level. CCDC depositions 977497-977502 contain the supplementary crystallographic data for this paper.

Elemental analyses were performed by Canadian Microanalytical Service Ltd., Delta British Columbia, Canada.

(i) Preparative Procedures

The compounds $[\text{Me}_2\text{E}(\text{dmap})_2][\text{OTf}]_2$ (E = Si or Ge), were prepared *via* analogous methodologies. The preparation of $[\text{Me}_2\text{Si}(\text{dmap})_2][\text{OTf}]_2$ is, therefore, described in detail as a representative example. **$[\text{Me}_2\text{Si}(\text{dmap})_2][\text{OTf}]_2$** : To a solution of Me_2SiCl_2 (75.3 mg, 0.58 mmol) in CH_2Cl_2 (6 mL) was added solid AgOTf (300 mg, 1.17 mmol), and the mixture stirred at ambient temperature for 1 h in the dark. The mixture was then filtered to remove AgCl , and cooled to $-30\text{ }^\circ\text{C}$ before the addition of solid *dmap* (142.6 mg, 1.17 mmol). The clear, colourless reaction mixture was then stirred for a further 1 h at ambient temperature, before removing all volatiles under high vacuum, yielding the product as a colourless solid. *X*-ray quality crystals were grown from a $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ mixture at $-30\text{ }^\circ\text{C}$. Yield: 0.31 g, 88%; ^1H NMR (300 MHz, CD_2Cl_2): δ_{H} 8.24-8.18 (4H, m, Ar-H), 6.94-6.88 (4H, m, Ar-H), 3.24 (12H, s, $\text{N}(\text{CH}_3)_2$), 1.29 (6H, s [$w/^{29}\text{Si}$ satellites, $J_{\text{HSi}} = 124\text{ Hz}$], $\text{Si}(\text{CH}_3)_2$); ^{19}F NMR (283 MHz, CD_2Cl_2): δ_{F} -78.74 (s, CF_3); ^{13}C NMR (76 MHz, CD_2Cl_2): δ_{C} 158.0 (s), 143.2(s), 121.3 (q, $J_{\text{CF}} = 322\text{ Hz}$, CF_3), 109.23(s), 40.8(s), -3.3 (s); ^{29}Si NMR (72 MHz, CD_2Cl_2): δ_{Si} 25.8 (s, SiMe_2); FT-IR (Nujol Mull, ranked intensities): 1642(5), 1577(4), 1270(1), 1219(9), 1145(7), 1088(8), 1068(4), 1027(2), 822(6), 633(3), 517(10); Melting Range: 192-194 $^\circ\text{C}$; Elemental Analysis: Calculated (%): C: 35.99, H: 4.36, N: 9.33, Found (%): C: 35.17, H: 4.51, N: 9.51.

$[\text{Me}_2\text{Ge}(\text{dmap})_2][\text{OTf}]_2$: Colourless solid. In this case the product was only sparingly soluble in CH_2Cl_2 , thus *X*-ray quality crystals were obtained from a $\text{MeCN}/\text{Et}_2\text{O}$ mixture at $-30\text{ }^\circ\text{C}$. Yield: 0.45 g, 86%, ^1H NMR (300 MHz, CD_2Cl_2): δ_{H} 8.07-8.01 (4H, m, Ar-H), 6.81-6.75 (4H, m, Ar-H), 3.19 (12H, s, $\text{N}(\text{CH}_3)_2$), 1.63 (6H, s, $\text{Ge}(\text{CH}_3)_2$); ^{19}F NMR (283 MHz, CD_2Cl_2): δ_{F} -78.73 (s, CF_3). ^{13}C NMR (91 MHz, CD_2Cl_2): δ_{C} 156.6 (s, Ar-H), 143.8 (s, Ar-H), 120.8 (q, $J_{\text{CF}} = 321\text{ Hz}$, CF_3), 108.2 (s, Ar-H), 39.8 (s, $\text{N}(\text{CH}_3)_2$), 3.6 (s, $\text{Ge}(\text{CH}_3)_2$); FT-IR (Nujol Mull, ranked intensities): 1632(5), 1573(9), 12765(2), 1252(1), 1223(7), 1160(6), 1059(8), 1031(3), 836(10), 638(4); Melting Range: 206-208 $^\circ\text{C}$; Elemental Analysis: Calculated (%): C: 33.51, H: 4.06, N: 8.68, Found (%): C: 33.19, H: 4.26, N: 8.88.

$\text{Me}_2\text{Sn}(\text{dmap})_2(\text{OTf})_2$: To a solution of Me_2SnCl_2 (85.9 mg, 0.39 mmol) in MeCN (4 mL) was added solid *dmap* (95.4 mg, 0.78 mmol), and the resulting cloudy mixture was stirred at ambient temperature for 1 h. Solid AgOTf (200 mg, 0.78 mmol) was then added, and the mixture stirred for a further 1 h before filtering to remove AgCl . All volatiles were then removed under high vacuum, yielding a white powder, from which *X*-ray quality crystals were grown *via*

recrystallization from a MeCN/Et₂O mixture at -30 °C. Yield: 0.21 g, 77%; ¹H NMR (300 MHz, CD₃CN): δ_H 7.89 - 7.85 (4H, m, Ar-H), 6.74 - 6.69 (4H, m, Ar-H), 3.07 (12H, s, N(CH₃)₂), 1.42 (6H, s [w/Sn satellites, *J*_{H_{Sn}} = 87 and 91 Hz], Sn(CH₃)₂); ¹⁹F NMR (283 MHz, CD₃CN): δ_F -79.22 (s, CF₃); ¹³C NMR (76 MHz, CD₃CN): δ_C 156.1 (s, Ar-H), 144.6 (s, Ar-H), 107.3 (s, Ar-H), 38.7 (s, N(CH₃)₂), 7.3 (s, Sn(CH₃)₂); ¹¹⁹Sn NMR (134 MHz, CD₃CN): δ_{Sn} -175.0 (br. s); FT-IR (Nujol Mull, ranked intensities): 1633(7), 1309(3), 1247(1), 1206(5), 1173(2), 1060(8), 1025(4), 721(10), 638(6), 517(9); Melting Range: 219-221 °C; Elemental Analysis: Calculated (%): C: 31.28, H: 3.79, N: 8.11, Found (%) C: 31.41, H: 3.91, N: 8.24.

Products of the form [Me₂E(2,2'-*bipy*)(OTf)][OTf] (E = Si or Ge), were prepared *via* analogous methodologies. The preparation of [Me₂Si(2,2'-*bipy*)(OTf)][OTf] will, therefore, be described in detail as a representative example. **[Me₂Si(2,2'-*bipy*)(OTf)][OTf]**: To a solution of Me₂SiCl₂ (50.2 mg, 0.39 mmol) in CH₂Cl₂ (6 mL) was added solid AgOTf (200 mg, 0.79 mmol), and the mixture stirred for 1 h at ambient temperature in the dark. The resulting mixture was then filtered to remove AgCl, and the resulting clear colourless solution cooled to -30 °C before the addition of solid 2,2'-*bipy* (60.8 mg, 0.39 mmol). Over 1 h at ambient temperature a colourless solid was observed to precipitate. All volatiles were subsequently removed under high vacuum, and the resulting colourless solid recrystallised from MeCN/Et₂O at -30 °C to furnish X-ray quality crystals of the desired product. Yield: 0.18 g, 89%, ¹H NMR (360 MHz, CD₃CN): δ_H 9.19-9.07 (2H, m, Ar-H), 8.87-8.75 (2H, m, Ar-H), 8.74-8.62 (2H, m, Ar-H), 8.22-8.11 (2H, m, Ar-H), 0.96 (6H, s, Si(CH₃)₂); ¹⁹F NMR (283 MHz, CD₃CN): δ_F -78.99 (s); ¹³C NMR (91 MHz, CD₃CN): δ_C 148.3 (s), 148.2 (s), 146.9 (s), 131.0 (s), 125.0 (s), 120.9 (q, ¹*J*_{CF} = 320 Hz, CF₃), 6.7 (s); ²⁹Si NMR (72 MHz, CD₃CN): δ_{Si} -47.0 (s); FT-IR (Nujol Mull, ranked intensities): 1259(1), 1193(5), 1157(3), 1073(10), 1032(4), 984(6), 782(7), 771(9), 722(2), 637(8); Melting Range: >180 °C (decomposes); Elemental Analysis: Calculated (%): C: 32.81, H: 2.75, N: 5.46, Found (%) C: 32.34, H: 2.76, N: 5.57.

[Me₂Ge(2,2'-*bipy*)(OTf)][OTf]: Colourless solid. X-ray quality crystals grown from MeCN/Et₂O at -30 °C. Yield: 0.37 g, 83%, ¹H NMR (300 MHz, CD₃CN): δ_H 9.33-9.27 (2H, m, Ar-H), 8.87-8.81 (2H, m, Ar-H), 8.72-8.65 (2H, m, Ar-H), 8.21-8.15 (2H, m, Ar-H), 1.61 (6H, s, Ge(CH₃)₂); ¹⁹F NMR (282 MHz, CD₃CN): δ_F -78.76 (s); ¹³C NMR (76 MHz, CD₃CN): δ_C 148.5 (s), 148.3 (s), 147.7 (s), 131.5 (s), 126.0 (s), 124.4 (s), 121.7 (q, ¹*J*_{CF} = 320 Hz, CF₃), 12.6 (s); FT-IR (Nujol Mull, ranked intensities): 1339(8), 1283(1), 1224(2), 1184(7), 1149(3), 1032(6),

1022(4), 783(9), 637(5), 573(10), 516(6); Melting Range: 214-216 °C; Elemental Analysis: Calculated (%): C: 30.18, H: 2.53, N: 5.03, Found (%) C: 30.07, H: 2.46, N: 5.02.

Me₂Sn(2,2'-*bipy*)(OTf)₂: To a solution of Me₂SnCl₂ (85.9 mg, 0.39 mmol) in MeCN (4 mL) was added solid 2,2'-*bipy* (61.0 mg, 0.78 mmol), and the resulting cloudy mixture was stirred at ambient temperature for 1 h. Solid AgOTf (200 mg, 0.78 mmol) was then added, and the mixture stirred for a further 1 h before filtering to remove AgCl. All volatiles were then removed under high vacuum, yielding a white powder, from which X-ray quality crystals were grown *via* recrystallisation from a MeCN/Et₂O mixture at -30 °C. Yield: 0.21 g, 90%, ¹H NMR (300 MHz, CD₃CN): δ_H 9.23-9.11 (2H, m, Ar-H), 8.76-8.63 (2H, m, Ar-H), 8.59-8.46 (2H, m, Ar-H), 8.11-7.98 (2H, m, Ar-H), 1.35 (6H, s [w/Sn satellites, 96 and 100 Hz], Sn(CH₃)₂); ¹⁹F NMR (283 MHz, CD₃CN): δ_F -79.07; ¹³C NMR (91 MHz, CD₃CN): δ_C 149.2 (s), 149.1 (s), 145.6 (s), 130.2 (s), 125.7 (s), 14.2 (s); ¹¹⁹Sn NMR (134 MHz, CD₃CN): δ_{Sn} -216.9 (s), FT-IR (Nujol Mull, ranked intensities): 1327(6), 1314(4), 1249(2), 1234(3), 1200(7), 1171(1), 1018(5), 780(10), 730(9), 633(8); Melting Range: 206-208 °C; Elemental Analysis: Calculated (%): C: 27.88, H: 2.34, N: 4.64, Found (%) C: 27.65, H: 2.40, N: 4.63.

(ii) Attempted Syntheses of [Me₂C(*dmap*)₂][[OTf]₂] and [Me₂C(*bipy*)][[OTf]₂]

Syntheses of [Me₂C(*dmap*)₂][[OTf]₂] and [Me₂C(*bipy*)][[OTf]₂], respectively were attempted unsuccessfully by a variety of methods as discussed below. Attempts to synthesise [Me₂C(*dmap*)₂][[OTf]₂] are described as representative examples.

As for the analogous Si, Ge and Sn compounds, synthetic investigations were initiated using Me₂CCl₂ (2,2-dichloropropane) as a precursor. Upon the treatment of this compound with two equivalents of AgOTf in CH₂Cl₂ solution a darkening of the reaction mixture was observed over 1 h, with a deep maroon solution attained following filtration. The addition of two equivalents of *dmap* to the mixture led to the loss of maroon colour, and the immediate development of a light yellow solution with the precipitation of a colourless solid. Upon removal of all volatiles under high vacuum, however, ¹H NMR in d₃-MeCN indicated that the desired complex had not been formed, with the only involatile species in fact consistent with [H-*dmap*][[OTf]], although the mechanism of the formation of this species remains unclear. Identical behavior was observed upon repeating this experiment with the dibromoalkane Me₂CBr₂. Repeating reactions of

Me_2CX_2 (X = Cl or Br) in C_6D_6 and CD_3CN produced no evidence of halide abstraction by AgOTf over 1 h at ambient temperature, with only Me_2CX_2 remaining in solution.

Similar abstraction reactions were subsequently attempted using alternative sources of the OTf anion, namely MeOTf and Me_3SiOTf , with no evidence of halide abstraction apparent at ambient temperature upon the treatment of CH_2Cl_2 solution of Me_2CX_2 with either abstractor. In these cases addition of solid *dmap* to a mixture of the abstractor and haloalkane led only to the formation of adducts the *dmap* adducts $[\text{Me-}dmap][\text{OTf}]$ and $[\text{Me}_3\text{Si-}dmap][\text{OTf}]$, respectively, the identity of which was confirmed by independent synthesis.

Thermolytic synthesis of $[\text{Me}_2\text{C}(dmap)_2][\text{X}]_2$ (X = Cl or Br), from which halide exchange could finally yield the desired triflate salt, was also attempted, but heating a mixture of Me_2CX_2 and two equivalents of *dmap* in toluene at 100 °C over 42 h did not yield the desired product, with only unreacted *dmap* recovered following removal of all volatiles under high vacuum. Similarly, the addition of *dmap* to an excess of neat Me_2CCl_2 led to no reaction over 100 h at either ambient temperature or 75 °C.

Attempted synthesis of $[\text{Me}_2\text{C}(dmap)_2][\text{OTf}]_2$ using AgOTf: To a solution of Me_2CX_2 (X = Cl or Br) (0.15 mmol) in CD_2Cl_2 (1 mL) at ambient temperature was added solid AgOTf (78.6 mg, 0.30 mmol) and the mixture stirred for 1 h before filtering becoming a dark brown in colour. The mixture was then filtered and analyzed by ^1H NMR spectroscopy which indicated the formation of >10 new products, with no species particularly prevalent. The ^{19}F NMR spectrum also displayed 3 resonances, all consistent with triflate anions. Solid *dmap* (36.6 mg, 0.30 mmol) was added to the mixtures leading to immediate formation of a white precipitate and loss of the brown colour. Removal of all volatiles from the reaction mixture and dissolution of the residual solids in $\text{d}_3\text{-MeCN}$ evidenced the clean formation of a species consistent with $[\text{H-}dmap][\text{OTf}]$ for both Me_2CCl_2 and Me_2CBr_2 . ^1H NMR (300 MHz, $\text{d}_3\text{-MeCN}$): δ_{H} 11.64 (1H, s, $[\underline{\text{H}}\text{-}dmap]$), 8.01-7.95 (2H, m, Ar-H), 6.80-6.75 (2H, m, Ar-H), 3.10 (6H, s, NMe_2); ^{19}F NMR (283 MHz, $\text{d}_3\text{-MeCN}$): δ_{F} -79.28 (s, CF_3).

C_6D_6 : The reaction of Me_2CX_2 (X = Cl or Br) with two equivalents of AgOTf in C_6D_6 led to no abstraction over 2 h at ambient temperature by ^1H NMR, with only unreacted dihaloalkane present in solution [δ_{H} 1.76 or 2.10 for X = Cl or Br, respectively].

CD_3CN : The reaction of Me_2CX_2 ($X = Cl$ or Br) with two equivalents of $AgOTf$ in CD_3CN led to no abstraction over 2 h at ambient temperature by 1H NMR, with only unreacted dihaloalkane present in solution [δ_H 2.16 or 2.59 for $X = Cl$ or Br , respectively].

Attempted synthesis of $[Me_2C(dmap)_2][OTf]_2$ using Me_3SiOTf or $MeOTf$: To a solution of Me_2CX_2 ($X = Cl$ or Br) (0.15 mmol) in CD_2Cl_2 (1 mL) at ambient temperature was added neat Me_3SiOTf (66.6 mg, 0.30 mmol) or $MeOTf$ (49.2 mg, 0.30 mmol) and the mixture stirred for 1 h. The mixture was then cooled to $-30\text{ }^\circ C$, and solid *dmap* then added before warming to ambient temperature and stirring for a further 1 h. The mixture was then analyzed by 1H NMR spectroscopy (CD_2Cl_2), which indicated the formation of products consistent with $[Me_3Si(dmap)][OTf]$ and $[Me(dmap)][OTf]$, respectively (see below for independent preparation), with unreacted Me_2CX_2 also apparent (δ_H 2.18 or 2.54 for $X = Cl$ or Br , respectively).

Synthesis of $[Me_3Si(dmap)][OTf]$: To a solution of Me_3SiOTf (54.6 mg, 0.25 mmol) in CH_2Cl_2 (4 mL) at $-30\text{ }^\circ C$ was added solid *dmap* (30 mg, 0.25 mmol), and the mixture warmed to ambient temperature and stirred for 1 h before the removal of all volatiles under high vacuum to yield a colourless solid. 1H NMR (300 MHz, CD_2Cl_2): δ_H 8.02 (2H, m, Ar-H), 6.93 (2H, m, Ar-H), 3.22 (6H, s, NMe_2), 0.58 (9H, s, $SiMe_3$); ^{19}F NMR (283 MHz, CD_2Cl_2): δ_F -78.78 (s, CF_3); ^{13}C NMR (76 MHz, CD_2Cl_2): δ_C 157.5 (s, Ar), 143.3 (s, Ar), 121.4 (q, $J_{CF} = 322$ Hz, CF_3), 108.9 (s, Ar), 40.45 (s, Me), 0.8 (s, $SiMe_3$); ^{29}Si NMR (71.6 MHz, CD_2Cl_2): δ_{Si} 31.9 (s, $SiMe_3$).

Synthesis of $[Me(dmap)][OTf]$: To a solution of $MeOTf$ 47.7 mg, 0.25 mmol) in CH_2Cl_2 (4 mL) at $-30\text{ }^\circ C$ was added solid *dmap* (30 mg, 0.25 mmol), and the mixture warmed to ambient temperature and stirred for 1 h before the removal of all volatiles under high vacuum. 1H NMR (300 MHz, CD_2Cl_2): δ_H 8.0 (2H, m, Ar-H), 6.83 (2H, m, Ar-H), 3.94 (3H, s, Me-dmap), ^{19}F NMR (283 MHz, CD_2Cl_2): δ_F -78.90 (s, CF_3), ^{13}C NMR (76 MHz, CD_2Cl_2): δ_C 156.7 (s, Ar), 143.1 (s, Ar), 121.4 (q, $J_{CF} = 321$ Hz, CF_3), 108.4 (s, Ar), 45.3 (s, Me), 40.6 (s, NMe_2).

Attempted synthesis of $[Me_2C(dmap)_2][OTf]_2$ (Toluene thermolysis): To a solution of Me_2CX_2 ($X = Cl$ or Br) (0.41 mmol) in toluene (4 mL) was added solid *dmap* (100 mg, 0.82 mmol), and the reaction heated to $100\text{ }^\circ C$ over 42 h in a sealed reaction tube. All volatiles were then subsequently removed from the clear, colourless solution, and the resulting colourless solids

analyzed by ^1H NMR, indicating the presence of only unreacted *dmap*. ^1H NMR (300 MHz, CD_2Cl_2): δ_{H} 8.19-8.13 (2H, m, Ar-H), 6.49-6.45 (2H, m, Ar-H), 2.94 (6H, s, NMe_2).

Attempted synthesis of $[\text{Me}_2\text{C}(\textit{dmap})_2][\text{OTf}]_2$ (Neat Me_2CCl_2 as solvent): To solid *dmap* (50 mg, 0.41 mmol) was added neat Me_2CCl_2 (0.5 mL, 5.1 mmol) and the resulting mixture stirred at ambient temperature over 100 h. All volatiles were then removed under high vacuum, and the resulting solids analyzed by ^1H NMR in CD_2Cl_2 indicating only unreacted *dmap*. An identical result was recorded on repeating this experiment at 75 °C over the same time period.

(b) X-ray Crystallographic Information

[Me₂Si(*dmap*)₂][OTf]₂ (CCDC Number: 977497)

Empirical formula	C ₂₀ H ₃₀ Cl ₄ F ₆ N ₄ O ₆ S ₂ Si
Formula weight	770.49
Temperature	173(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 8.1122(4) Å b = 11.4867(6) Å c = 18.7960(9) Å α = 95.057(2)° β = 98.939(2)° γ = 108.631(2)°
Volume	1621.66(14) Å ³
Z	2
Density (calculated)	1.578 Mg/m ³
Absorption coefficient	5.574 mm ⁻¹
F(000)	788
Crystal size	0.724 x 0.571 x 0.312 mm ³
Theta range for data collection	2.406 to 68.244°
Index ranges	-9 ≤ h ≤ 9, -13 ≤ k ≤ 13, -22 ≤ l ≤ 22
Reflections collected	17672
Independent reflections	5782 [R(int) = 0.0357]
Completeness to theta = 67.679°	97.7 %
Absorption correction	Numerical
Max. and min. transmission	0.4629 and 0.1285
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5782 / 9 / 398
Goodness-of-fit on F ²	1.451
Final R indices [I > 2σ(I)]	R ₁ = 0.0571, wR ₂ = 0.1757
R indices (all data)	R ₁ = 0.0636, wR ₂ = 0.1836
Extinction coefficient	n/a
Largest diff. peak and hole	0.980 and -1.048 e.Å ⁻³

[Me₂Ge(*dmap*)₂][OTf]₂ (CCDC Number: 977499)

Empirical formula	C ₂₀ H ₂₆ F ₆ Ge N ₅ O ₆ S ₂
Formula weight	677.12
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 2 ₁ /c
Unit cell dimensions	a = 10.6701(13) Å b = 11.5348(14) Å c = 23.336(3) Å α = 90°. β = 93.922(2)°. γ = 90°.
Volume	2865.5(6) Å ³
Z	4
Density (calculated)	1.570 Mg/m ³
Absorption coefficient	1.297 mm ⁻¹
F(000)	1364
Crystal size	0.273 x 0.137 x 0.135 mm ³
Theta range for data collection	1.749 to 29.673°.
Index ranges	-14 ≤ h ≤ 14, -16 ≤ k ≤ 16, -32 ≤ l ≤ 32
Reflections collected	45770
Independent reflections	8101 [R(int) = 0.0449]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Numerical
Max. and min. transmission	0.9026 and 0.8264
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8101 / 0 / 371
Goodness-of-fit on F ²	0.970
Final R indices [I > 2σ(I)]	R1 = 0.0370, wR2 = 0.0962
R indices (all data)	R1 = 0.0584, wR2 = 0.1061
Extinction coefficient	n/a
Largest diff. peak and hole	0.670 and -0.619 e.Å ⁻³

Me₂Sn(*dmap*)₂(OTf)₂ (CCDC Number: 977501)

Empirical formula	C ₁₈ H ₂₆ F ₆ N ₄ O ₆ S ₂ Sn
Formula weight	691.24
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C 2/c
Unit cell dimensions	a = 9.4758(5) Å b = 13.6913(6) Å c = 21.1332(12) Å α = 90°. β = 100.452(2)°. γ = 90°.
Volume	2696.2(2) Å ³
Z	4
Density (calculated)	1.703 Mg/m ³
Absorption coefficient	1.184 mm ⁻¹
F(000)	1384
Crystal size	0.166 x 0.141 x 0.078 mm ³
Theta range for data collection	1.960 to 34.308°.
Index ranges	-14 ≤ h ≤ 15, -21 ≤ k ≤ 21, -33 ≤ l ≤ 33
Reflections collected	32769
Independent reflections	5618 [R(int) = 0.0323]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Numerical
Max. and min. transmission	0.9525 and 0.8654
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5618 / 0 / 168
Goodness-of-fit on F ²	1.040
Final R indices [I > 2σ(I)]	R1 = 0.0251, wR2 = 0.0553
R indices (all data)	R1 = 0.0359, wR2 = 0.0570
Extinction coefficient	n/a
Largest diff. peak and hole	0.422 and -0.367 e.Å ⁻³

[Me₂Si(*bipy*)(OTf)][OTf] (CCDC Number: 977498)

Empirical formula	C ₁₄ H ₁₄ F ₆ N ₂ O ₆ S ₂ Si
Formula weight	512.48
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C c
Unit cell dimensions	a = 14.1596(18) Å b = 22.794(3) Å c = 7.3679(9) Å α = 90°. β = 118.801(2)°. γ = 90°.
Volume	2083.9(5) Å ³
Z	4
Density (calculated)	1.633 Mg/m ³
Absorption coefficient	0.401 mm ⁻¹
F(000)	1040
Crystal size	0.310 x 0.271 x 0.155 mm ³
Theta range for data collection	1.787 to 29.758°.
Index ranges	-19 ≤ h ≤ 19, -31 ≤ k ≤ 31, -10 ≤ l ≤ 10
Reflections collected	20167
Independent reflections	5944 [R(int) = 0.0219]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Numerical
Max. and min. transmission	0.9716 and 0.9087
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5944 / 2 / 280
Goodness-of-fit on F ²	1.134
Final R indices [I > 2σ(I)]	R ₁ = 0.0310, wR ₂ = 0.0759
R indices (all data)	R ₁ = 0.0380, wR ₂ = 0.0783
Absolute structure parameter	0.005(18)
Extinction coefficient	n/a
Largest diff. peak and hole	0.288 and -0.265 e.Å ⁻³

[Me₂Ge(*bipy*)(OTf)][OTf] (CCDC Number: 977500)

Empirical formula	C14 H14 F6 Ge N2 O6 S2
Formula weight	556.98
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 7.7487(2) Å b = 11.1678(3) Å c = 12.4220(3) Å α = 110.4190(10)° β = 95.6880(10)° γ = 95.4360(10)°
Volume	992.76(4) Å ³
Z	2
Density (calculated)	1.863 Mg/m ³
Absorption coefficient	1.845 mm ⁻¹
F(000)	556
Crystal size	0.329 x 0.292 x 0.174 mm ³
Theta range for data collection	1.767 to 32.500°
Index ranges	-11 ≤ h ≤ 11, -16 ≤ k ≤ 16, -18 ≤ l ≤ 18
Reflections collected	25958
Independent reflections	7179 [R(int) = 0.0154]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Numerical
Max. and min. transmission	0.7825 and 0.6508
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7179 / 0 / 280
Goodness-of-fit on F ²	1.032
Final R indices [I > 2σ(I)]	R1 = 0.0255, wR2 = 0.0708
R indices (all data)	R1 = 0.0290, wR2 = 0.0725
Extinction coefficient	n/a
Largest diff. peak and hole	0.789 and -0.708 e.Å ⁻³

Me₂Sn(*bipy*)(OTf)₂ (CCDC Number: 977502)

Empirical formula	C ₁₄ H ₁₄ F ₆ N ₂ O ₆ S ₂ Sn
Formula weight	603.08
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P 2 ₁ /c
Unit cell dimensions	a = 10.623(3) Å b = 15.281(4) Å c = 13.418(3) Å α = 90°. β = 113.235(4)°. γ = 90°.
Volume	2001.6(8) Å ³
Z	4
Density (calculated)	2.001 Mg/m ³
Absorption coefficient	1.576 mm ⁻¹
F(000)	1184
Crystal size	0.232 x 0.201 x 0.094 mm ³
Theta range for data collection	2.122 to 33.281°.
Index ranges	-16 ≤ h ≤ 13, -23 ≤ k ≤ 21, -20 ≤ l ≤ 20
Reflections collected	34376
Independent reflections	7581 [R(int) = 0.0304]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Numerical
Max. and min. transmission	0.9157 and 0.7783
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	7581 / 0 / 282
Goodness-of-fit on F ²	1.042
Final R indices [I > 2σ(I)]	R1 = 0.0207, wR2 = 0.0503
R indices (all data)	R1 = 0.0285, wR2 = 0.0514
Extinction coefficient	n/a
Largest diff. peak and hole	0.599 and -0.442 e.Å ⁻³