**Sulfur Dications**

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# Dicationic Sulfur Analogues of N-Heterocyclic Silylenes and Phosphenium Cations**

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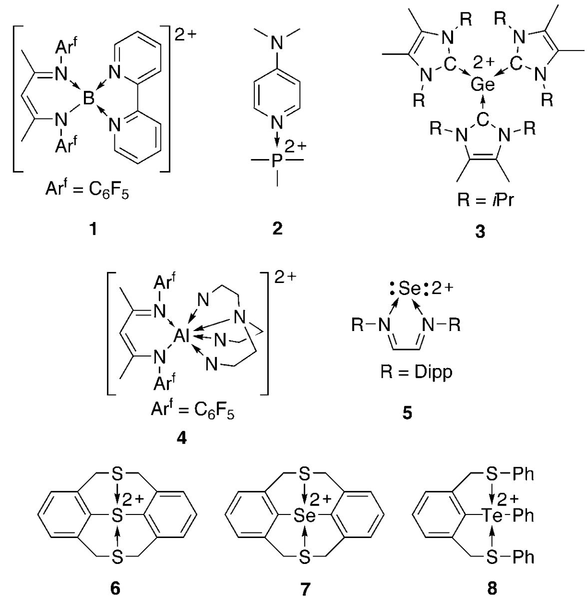
The isolation of multicationic compounds centered around main-group elements is a new frontier of p-block chemistry that has been developing rapidly in recent years. Although such molecules have been targeted for several decades, the task of sequestering such species in a storable form is immense; furthermore, structural characterization of the corresponding salts is exceedingly rare. The difficulty associated with synthesizing these compounds is likely a result of forcing elements with high electronegativity to be deficient in their electron count, thus making them highly electrophilic and susceptible to vigorous reaction in solution, rendering their isolation a formidable challenge. There has been some success in this area over the past two years, with reports of dicationic complexes centered around boron(III), phosphorus(V), germanium(II), aluminum(III), and selenium(II) (**1**–**5**, Scheme 1).[1–5] Early developments in the dicationic chemistry of sulfur, selenium, and tellurium are underscored by the pioneering results of Furukawa and co-workers. However, these are restricted to rare examples of annulated derivatives (e.g. **6**–**8**) with covalent linkages to the main-group element of interest.[6] This particular arrangement imposes a close proximity of the central element to the electron-rich donor atoms, thus stabilizing the dicationic chalcogen center.



*Scheme 1.* Examples of main-group-centered dications. Dipp = 2,6-diisopropylphenyl.

The most common method for stabilizing main-group-centered dications is by coordination of a Lewis base to the formally positively charged atom, thus allowing for a delocalization of the dicationic charge and rendering the salts isolable. Our approach to conquering this challenge has been to construct bonding arrangements that mimic those of N-heterocyclic carbenes and can be seen as main-group-element carbene analogues.[5] One such compound has been reported for selenium, yet the extension of the methodology to the far right-hand side of the periodic table, specifically for the remaining elements of Group 16, has remained elusive. Our work on the selenium analogue and an in-depth computational study of these systems have demonstrated that, although the electronic structure of Group 16 analogues are vastly different from classic N-heterocyclic carbenes or their known p-block congeners, the bonding arrangements are a minimum on the potential energy surface; therefore, tangible examples should be attainable.[7]

In this context, we report the high-yielding synthesis and comprehensive characterization of sulfur(II) dications (**9**-[OTf]$_2$) from the direct reaction of $SCl_2$, TMS-OTf, and $R_2$DAB (Scheme 2; TMS-OTf = trimethylsilyltrifluoromethanesulfonate, DAB = diazabutadiene). Furthermore, the triflate (OTf) anions are easily exchanged in a quantitative fashion by salt metathesis for the weakly coordinating $[B(C_6F_5)_4]^-$ ion, yielding a dicationic $S^{II}$ core that is essentially free of any substantial cation–anion interactions at the sulfur center (Scheme 2). These species represent the first structural mimics of the classic N-heterocyclic silylene species (NHSi) and phosphenium cations (NHP) and a further extension of such a bonding arrangement to the chalcogens.[8,9]

The reaction of one equivalent $SCl_2$ with two equivalents of TMS-OTf at −78 °C in $CH_2Cl_2$ produced a light orange solution. After stirring for 15 minutes, the addition of a substoichiometric amount of aryl α-diimine ($R_2$DAB; R = Dipp, Dmp) in $CH_2Cl_2$ resulted in an intense orange solution,

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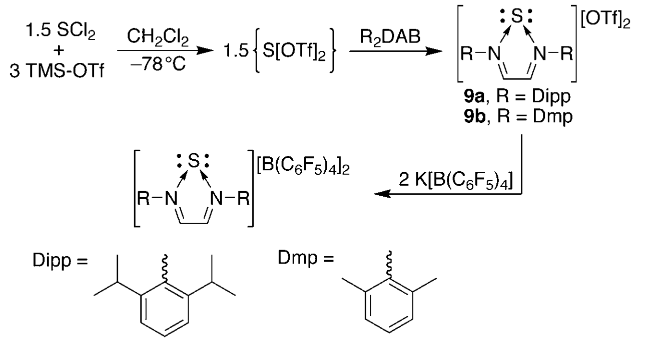

*Scheme 2.* Synthetic pathway to the α-diimine sulfur(II) complexes **9**[OTf]$_2$ and **9a**[B(C$_6$F$_5$)$_4$]$_2$.

and removal of volatile components gave orange–red powders.[*] $^1$H NMR spectroscopy of the redissolved solids in CD$_3$CN revealed highly pure products. The most striking feature in the $^1$H NMR spectra is the significantly deshielded signals for the N$_2$C$_2$ backbone protons (**9a**[OTf]$_2$ $\delta = 10.23$ ppm, **9b**[OTf]$_2$ $\delta = 10.17$ ppm vs. $\delta = 8.13$ ppm in the free ligands) and is reminiscent of the dicationic selenium analogue ($\delta = 10.58$ ppm).[5] $^{19}$F NMR spectroscopy on the same samples revealed a single resonance indicative of ionic triflate in solution (**9b**[OTf]$_2$ $\delta = -78.6$, **9a**[OTf]$_2$ $\delta = -78.7$ ppm, cf. [Bu$_4$N][OTf] $\delta = -78.7$ ppm).[10] On the basis of the NMR data, the compounds were assigned as the triflate salts of the dicationic SN$_2$C$_2$ heterocycles **9a**[OTf]$_2$ and **9b**[OTf]$_2$.

Both derivatives of **9**[OTf]$_2$ are stable under inert atmosphere in the solid state at room temperature and in solution below −25 °C. However, in solution at room temperature, samples show appreciable decomposition within two hours, as indicated by $^1$H NMR spectroscopy, and all samples undergo violent decomposition upon exposure to the open atmosphere.

Crystalline materials suitable for X-ray diffraction studies of **9**[OTf]$_2$ were grown by vapor diffusion of Et$_2$O into concentrated acetonitrile solutions of the bulk powder at −30 °C. The diffraction data confirmed the proposed identity of the dicationic heterocycles, each of which was isolated in approximately 80 % yield (Figure 1 and Figure 2).[11]

A facile anion exchange reaction can be performed by the addition of two equivalents of K[B(C$_6$F$_5$)$_4$] in CH$_2$Cl$_2$ at room temperature to **9a**[OTf]$_2$, yielding **9a**[B(C$_5$F$_5$)$_4$]$_2$. Filtration of the KOTf by-product and subsequent precipitation with *n*-pentane and removal of volatile components gave a highly pure red powder. A redissolved sample of the washed product shows an $^1$H NMR spectrum that is virtually unchanged from that of the OTf$^-$ analogue. The $^{19}$F{$^1$H} NMR spectrum revealed the expected pattern for the B(C$_6$F$_5$)$_4^-$ ion and the absence of the OTf$^-$ ion. Single crystals of **9a**[B(C$_6$F$_5$)$_4$]$_2$ were grown by the vapor diffusion of *n*-pentane into a concentrated CH$_2$Cl$_2$ solution of **9a**[B(C$_6$F$_5$)$_4$]$_2$ at −30 °C and analyzed by X-ray diffraction, the results of which confirm the new cation–anion pairing (Figure 3).[11]

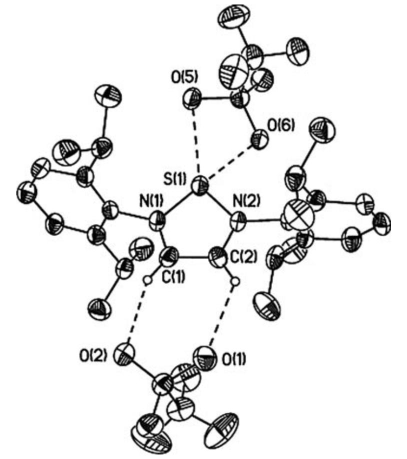

*Figure 1.* Solid-state structures of **9a**[OTf]$_2$. Thermal ellipsoids are set at the 50 % probability level; hydrogen atoms not interacting with the anion are omitted for clarity. Selected bond lengths [Å] and angles [°]: S(1)–N(1) 1.699(6), S(1)–N(2) 1.696(6), N(1)–C(1) 1.293(9), N(2)–C(2) 1.324(9), C(1)–C(2) 1.407(10), O(6)···S(1) 2.313(5), O(5)···S(1) 2.850(5), O(2)···H(1A) 2.265, O(1)···H(2A) 2.544; N(1)-S(1)-N(2) 87.8(3).

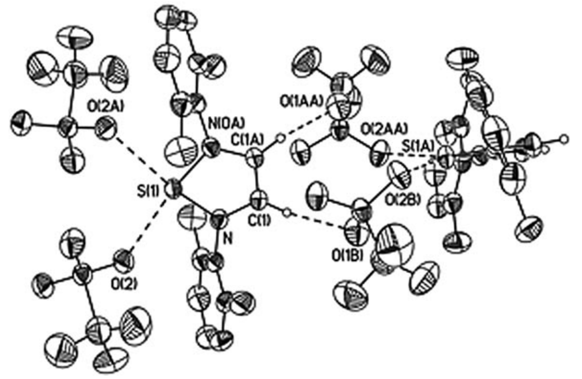

*Figure 2.* Solid-state structures of **9b**[OTf]$_2$. Thermal ellipsoids are set at the 50 % probability level; hydrogen atoms not interacting with the anion and solvate molecules are omitted for clarity. Selected bond lengths [Å] and angles [°]: S(1)–N 1.695(3), N–C(1) 1.305(5), C(1)–C(1A) 1.390(8), O(2)···S(1) 2.615(3), O(1B)···H(1) 2.309, O-(1AA)···H(1A); N-S(1)-N(0A) 88.0(2).

The structures of the sulfur(II) dications are similar and display planar five-membered C$_2$N$_2$S rings (largest deviation from planarity 0.011 Å). The bond lengths within the C$_2$N$_2$S ring for all derivatives of **9** support the retention of two C=N double bonds and a C–C single bond (Av: C=N 1.309 Å; C–C 1.398 Å). The S–N bonds are slightly shorter than typical sulfur–nitrogen single bonds (1.655(2)–1.699(6) Å vs. 1.76 Å), which can be explained by binding of the ligand to the electron-poor sulfur(II) center.[12] These endocyclic bond

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[*] If one equivalent of α-diimine is used, yields are significantly lower (by about 20 %). Although we do not have conclusive evidence, it appears that the highly acidic backbone protons in the formed dication are deprotonated by unreacted ligand as the cation is formed in solution. Keeping a significant excess of intermediate SOTf$_2$ present helps to mitigate the effect of this decomposition pathway.

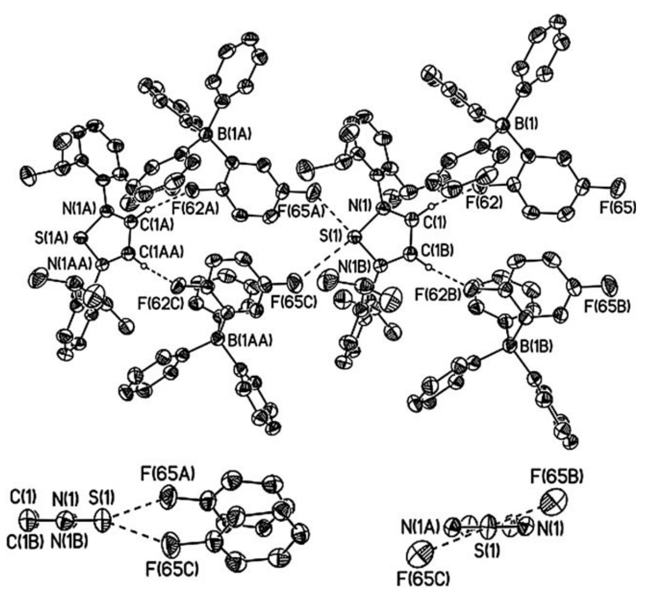

***Figure 3.*** Solid-state structure of **9a**$[B(C_6F_5)_4]_2$. Thermal ellipsoids are set at the 50% probability level; hydrogen atoms not in the backbone, solvate molecules, and fluorine atoms not interacting with the dication are removed for clarity. Selected bond lengths [Å] and angles [°]: S(1)–N(1) 1.655(3), N(1)–C(1) 1.313(4), C(1)–C(1B) 1.396(7), F(65A)···S(1) 3.079(3), F(62)···H(1A) 2.084, F62···H(1A) 2.442; N(1)-S(1)-N(1B) 90.9(2).

lengths are in close agreement with computed results for these derivatives (C–N 1.331, C–C 1.389, S–N 1.705 Å). Although a Lewis representation properly delocalizes the dicationic charge on the peripheral nitrogen atoms, given the previously published computational data and solid-state structural features, the bonding in these compounds can be best described by a N,N-chelated sulfur center bearing two lone pairs with a formal charge of +2.[7] This dative model is further underscored by the relative ease with which the sulfur atom can be displaced from the chelate ring by the addition of strong Lewis bases such as phosphine.[13]

Sulfur–oxygen contacts between the cations and anions in **9**[OTf]$_2$ within the sum of the van der Waals radii (3.25 Å) are found in both species. However, no distortion of the corresponding sulfur–oxygen bond in the triflate ions is detected, which indicates that there is no covalent interaction between the cation and the anion.[14]

Compound **9a**$[B(C_6F_5)_4]_2$ also displays detectable cation–anion contacts in the solid state. The closest contact occurs between the backbone proton of the ligand and a fluorine atom from a $C_6F_5$ ring, which lies within the sum of the van der Waals radii (2.080 vs. 2.60 Å).[14] One long S···F contact on the very edge of the sum of the van der Waals radii (3.077(3) vs. 3.20 Å) is also found.[14] However, the corresponding C–F bond in the anion displays no tendency towards elongation as observed in other main-group compounds (1.351(4) vs. 1.414(6) Å).[15] The two anions are symmetry related, and an $AX_4E_2$ electron-pair configuration might be expected about sulfur, which would exhibit a clear square-planar geometry common to 12-electron chalcogen centers.[16] However, the angle between the N-S-N and F···S···F planes is not consistent with a square-planar geometry (deviation from planarity is 20.4°; Figure 3, bottom). These combined observations lead to the conclusion that no substantial S···F cation–anion interactions are present.

The α-diimine sequestered sulfur(II) dicationic triflate salts **9**[OTf]$_2$ were synthesized and structurally characterized. Bonding in these compounds is best described by a N,N-chelated sulfur(II) dication; these compounds represent the first sulfur-containing structural mimics of N-heterocyclic silylene species and phosphenium cations.

## *Experimental Section*

Caution: Exposing solid samples of the compounds reported below to the open air results in vigorous decomposition. Although we have had no difficulties synthesizing and handling the reported compounds in varying amounts under inert conditions, it is recommended that large amounts of sample (greater than 0.200 g) not be exposed to the open atmosphere.

All manipulations were performed under an inert atmosphere in a nitrogen-filled MBraun Labmaster 130 glovebox or using standard Schlenk techniques. Sulfur dichloride and the α-diimine ligands were synthesized using literature procedures.[17,18] All solvents were dried using an MBraun controlled-atmosphere solvent purification system and stored in Straus flasks under an $N_2$ atmosphere or over 4 Å molecular sieves in the glovebox. [D$_3$]Acetonitrile was dried by stirring for three days over $CaH_2$, distilled prior to use, and stored in the glovebox over 4 Å molecular sieves. All NMR spectra were recorded on a Varian INOVA 400 MHz spectrometer ($^1H$ = 399.76 MHz, $^{13}C$ = 100.52 MHz, $^{19}F$ = 376.15 MHz) in $CD_3CN$ at room temperature. X-ray diffraction data were collected on a Nonius Kappa-CCD area detector using $Mo_{K\alpha}$ radiation ($\lambda$ = 0.71073 Å). Crystals were selected under oil, mounted on glass fibers, and immediately placed in a cold stream of $N_2$. Structures were solved by direct methods and refined using full matrix least squares on $F^2$. Hydrogen-atom positions were calculated. Elemental analyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada or by Columbia Analytical Services, Tucson, Arizona, USA.

General Procedure for **9**[OTf]$_2$: TMS-OTf in $CH_2Cl_2$ (1.5 mL) was added dropwise to $SCl_2$ in $CH_2Cl_2$ (10 mL) at −78 °C and stirred for 15 min. A solution of $R_2$DAB in $CH_2Cl_2$ (8 mL) was added dropwise to the mixture yielding an orange/red solution. Volatile components were removed in vacuo.

**9a**[OTf]$_2$: TMS-OTf (0.266 g, 1.20 mmol), $SCl_2$ (0.062 g, 0.60 mmol), Dipp$_2$DAB (0.150 g, 0.399 mmol). The solids were washed with $Et_2O$ (4×5 mL) giving a light orange powder. Yield: 0.185 g, 78%; m.p. 147–149 °C (dec). $^1H$ NMR ($CD_3CN$), $\delta$ = 10.23 (s, 2 H), 7.81 (t, 2 H, $^3J$(H-H) = 7.6 Hz), 7.60 (d, 4 H, $^3J$(H-H) = 7.6 Hz), 2.45 (sept, 4 H, $^3J$(H-H) = 6.8 Hz), 1.33 (d, 12 H, $^3J$(H-H) = 6.4 Hz), 1.30 ppm (d, 12 H, $^3J$(H-H) = 6.8 Hz); $^{13}C\{^1H\}$ NMR ($CH_3CN$), $\delta$ = 163.0, 145.9, 135.9, 131.5, 126.9, 30.4, 24.6, 24.4 ppm; $^{19}F\{^1H\}$ NMR ($CH_3CN$), $\delta$ = −78.7 ppm. FTIR (relative intensity) $\tilde{\nu}$ = 519(8), 577(12), 638(3), 762(13), 810(10), 1007(5), 1028(1), 1170(6), 1201(4), 1230(7), 1270(2), 1317(14), 1371(15), 1468(9), 2975(11) cm$^{-1}$. FT Raman (relative intensity) $\tilde{\nu}$ = 126(4), 316(15), 673(2), 762(7), 1007(13), 1028(6), 1047(8), 1068(14), 1244(5), 1351(3), 1445(1), 1583(12), 2914(9), 2942(10), 2982(11) cm$^{-1}$. UV/Vis ($CH_3CN$): $\lambda_{max}$ = 362 nm. Elemental analysis (%) calcd for $C_{28}H_{36}F_6N_2O_6S_3$: C 47.58, H 5.14, N 3.97; found C 47.24, H 5.52, N 3.94. ESI-MS: *m/z* 408 ([*M*]$^+$, [$C_{26}H_{36}N_2S$]$^+$).

**9b**[OTf]$_2$: TMS-OTf (0.378 g, 1.70 mmol), $SCl_2$ (0.088 g, 0.851 mmol), Dmp$_2$DAB (0.150 g, 0.567 mmol). The solids were redissolved in $CH_3CN$ (6 mL), and the product was selectively precipitated with $Et_2O$ (6 mL) to yield a light orange powder. Yield:

0.277 g, 82 %; m.p. 148–151 °C (dec). $^{1}$H NMR ($CD_3CN$), $\delta = 10.17$ (s, 2H), 7.66 (t, 2H, $^{3}J$(H-H) = 5.6 Hz), 7.47 (d, 4H, $^{3}J$(H-H) = 5.2 Hz), 2.32 ppm (s, 12H); $^{13}$C{$^{1}$H} NMR ($CH_3CN$), $\delta = 162.2$, 136.0, 135.7, 135.4, 131.2, 18.3 ppm; $^{19}$F{$^{1}$H} NMR ($CD_3CN$), $\delta = -78.6$ ppm. FTIR (relative intensity) $\tilde{\nu} = 518(5)$, 578(8), 638(3), 762(13), 784(6), 1030(2), 1095(12), 1169(4), 1231(11), 1276(1), 1393(15), 1479(7), 1523(9), 1604(10), 3113(14) cm$^{-1}$. FT Raman (relative intensity) $\tilde{\nu} = 123(1)$, 318(14), 349(15), 505(6), 552(13), 681(8), 761(12), 1028(9), 1068(4), 1156(7), 1258(11), 1336(2), 1406(10), 1436(3), 1583(5) cm$^{-1}$. UV/Vis ($CH_3CN$): $\lambda_{max} = 452$ nm. Elemental analysis (%) calcd for $C_{20}H_{20}F_6N_2O_6S_3$: C 40.40, H 3.39, N 4.71; found C 40.59, H 3.51, N 4.78.

Synthesis of **9a**[B($C_6F_5$)$_4$]$_2$: K(B($C_6F_5$)$_4$) (0.204 g, 0.284 mmol) in $CH_2Cl_2$ (5 mL) was combined with **9a**[OTf]$_2$ (0.100 g, 0.142 mmol) in $CH_2Cl_2$ (5 mL) at room temperature and stirred for 15 min. The mixture was filtered, and *n*-pentane (8 mL) was added to the supernatant, resulting in the precipitation of a deep red powder. The powder was dried in vacuo. Yield: 0.208 g, 83 %; m.p. 124–126 °C (dec). $^{1}$H NMR ($CD_3CN$) $\delta = 10.21$ (s, 2H), 7.83 (t, 2H, $^{3}J$(H-H) = 7.8 Hz), 7.61 (d, 4H, $^{3}J$(H-H) = 8.4 Hz), 2.42 (sept, 4H, $^{3}J$(H-H) = 7.2 Hz), 1.33 (d, 12H, $^{3}J$(H-H) = 7.8 Hz), 1.29 ppm (d, 12H, $^{3}J$(H-H) = 6.0 Hz); $^{13}$C{$^{1}$H} NMR ($CH_3CN$) $\delta = 163.5$, 149.5 (d, $^{1}J$(C-F) = 244.7 Hz), 146.1, 139.7 (d, $^{1}J$(C-F) = 246.5 Hz), 137.7 (d, $^{1}J$(C-F) = 247.0 Hz), 136.5, 131.7, 127.2, 125.8, 30.7, 24.7, 24.5 ppm; $^{19}$F{$^{1}$H} NMR ($CD_3CN$) $\delta = -133.1$, $-163.3$, $-167.8$ ppm. FTIR (relative intensity) $\tilde{\nu} = 575(14)$, 637(12), 663(6), 685(7), 757(5), 776(8), 805(15), 981(2), 1093(3), 1206(11), 1279(10), 1375(13), 1465(1), 1517(4), 1646(9) cm$^{-1}$. FT Raman (relative intensity) $\tilde{\nu} = 144(1)$, 394(11), 422(12), 449(7), 476(9), 492(6), 587(8), 693(10), 1044(4), 1056(5), 1238(13), 1313(2), 1415(3), 1337(14), 1580(15) cm$^{-1}$. UV/Vis ($CH_3CN$): $\lambda_{max} = 439$ nm. Elemental analysis (%) calcd for $C_{74}H_{36}B_2F_{40}N_2S$: C 50.28, H 2.05, N 1.81; found C 50.27, H 1.83, N 1.60.

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**Keywords:** anions · carbene analogues · cations · sulfur

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[11] Crystal data for **9a**[OTf]$_2$: $C_{28}H_{36}F_6N_2O_6S_3$, $T = 150(2)$ K, $M_r = 706.77$ g mol$^{-1}$, crystal size: 0.18 × 0.05 × 0.05 mm, triclinic, space group $P\bar{1}$, $a = 10.488(2)$, $b = 10.941(2)$, $c = 15.231(3)$ Å, $\alpha = 77.92(3)$, $\beta = 82.44(3)$, $\gamma = 73.50°$, $V = 1633.8(6)$ Å$^3$, $Z = 2$, $\rho_{calcd} = 1.437$ g cm$^{-3}$, $\mu = 0.304$ mm$^{-1}$, $2\theta_{max} = 24.47°$, 7852 reflections measured, 5262 unique ($R_{int} = 0.0597$), 406 refined parameters, $R_1[(I) > 2\sigma(I)] = 0.0856$, w$R_2(F^2) = 0.2095$, $R_1$(all data) = 0.1357, w$R_2$(all data) = 0.2300, $\rho$(e)(min/max) = −0.360/0.528 e Å$^{-3}$. Crystal data for **9b**[OTf]$_2$·Et$_2$O: $C_{24}H_{30}F_6N_2O_7S_3$, $T = 193(2)$ K, $M_r = 668.68$ g mol$^{-1}$, crystal size: 0.29 × 0.14 × 0.12 mm, orthorhombic, space group *Ibca*, $a = 16.0424(14)$, $b = 16.6859(15)$, $c = 22.960(2)$ Å, $V = 6146.1(10)$ Å$^3$, $Z = 8$, $\rho_{calcd} = 1.445$ g cm$^{-3}$, $\mu = 0.321$ mm$^{-1}$, $2\theta_{max} = 25.36°$, 21 056 reflections measured, 2830 unique ($R_{int} = 0.0646$), 186 refined parameters, $R_1[(I) > 2\sigma(I)] = 0.0674$, w$R_2(F^2) = 0.1814$, $R_1$(all data) = 0.0950, w$R_2$(all data) = 0.2042, $\rho$(e)(min/max) = −0.591/1.399 e Å$^{-3}$. Crystal data for **9a**[B($C_6F_5$)$_4$]$_2$·2 $CH_2Cl_2$: $C_{76}H_{40}B_2Cl_4F_{40}N_2S$, $T = 150(2)$ K, $M_r = 1936.58$ g mol$^{-1}$, orthorhombic, space group *Pbcn*, $a = 18.958(4)$, $b = 12.585(3)$, $c = 32.661(7)$ Å, $V = 7792(3)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.651$, $\mu = 0.321$ mm$^{-1}$, $2\theta_{max} = 25.03°$, 12 983 reflections measured, 6864 unique ($R_{int} = 0.0263$), 578 refined parameters, $R_1[(I) > 2\sigma(I)] = 0.0645$, w$R_2(F^2) = 0.1824$, $R_1$(all data) = 0.0845, w$R_2$(all data) = 0.1988, $\rho$(e)(min/max) = −0.935/0.915 e Å$^{-3}$. CCDC-705646, 705647, 705648 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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