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Reactions of α-Diimine Ligands with the in Situ Generated "S(OTf)$_2$" Synthon

Caleb D. Martin and Paul J. Ragogna*

*Department of Chemistry, The University of Western Ontario, The Chemistry Building, 1151 Richmond Street,
London, Ontario N6A 5B7, Canada*

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A series of reactions of α-diimine ligands with a 2:1 mixture of SCl$_2$ and trimethylsilyltrifluormethanesulfonate(TMS-OTf), which behaves as an S(OTf)$_2$ synthon, were performed. The reactivity was shown to differ based on the substitution at the nitrogen atoms of the ligand as aromatic groups yielded dicationic sulfur nitrogen heterocycles whereas alkyl groups resulted in the loss of one of the organic substituents at nitrogen giving monocationic 1,2,5-thiadiazolium rings. The substitution on the backbone carbon being a hydrogen atom, phenyl group (diazabutadiene; DAB) or acenaphthene (bisiminoacenaphthene, BIAN) proved not to be influential on the outcome of the reaction as both systems resulted in N,N′-chelated dications. These are rare examples of sulfur structural mimics of the N-heterocyclic silylene, and the BIAN species represent the first complexes of sulfur with this ubiquitous ligand.

Introduction

The reactivity of α-diimine ligands (e.g., R$_2$DAB, R$_2$BIAN; Figure 1) with the majority of the elements on the periodic table has been widely explored. The bulk of these studies have been conducted on metals, whereas non-metallic elements have, for the most part, been ignored.[1] One explanation for the lack of experimentation on the non-metals is that they generally have higher electronegativities, are electron rich (lone pair bearing), and consequently have a lower affinity for nitrogen based ligand systems. This is reflected in the number of reports for such chemistry in the open literature; however, boron and phosphorus have been extensively studied with Schiff-base ligand systems, and have revealed highly novel outcomes.[2]

For example, boron trichloride reacts in a 1:1 stoichiometry with aryl BIAN derivatives with the displacement of a halide resulting in the diimine sequestered boron cation with a chloride anion (**1**). If the same reaction is conducted with a second equivalent of BCl$_3$ or 2 equiv of BBr$_3$, the halide binds to the second BX$_3$ molecule resulting in a BX$_4^-$ anion.[3,4] Similarly, an alkyl DAB ligand reacts stoichiometrically with BBr$_3$ producing an analogous cationic diimine BBr$_2$ complex with a Br$^-$ counterion (**2**).[5] The reaction of an aryl DAB with BCl$_3$ in a 1:1 stoichiometry in hexanes gives rise to covalent N−B bonds with a loss of the diimine framework giving a neutral diazaborolidine with double-halogenation of the backbone carbon atoms (**3**).[6,7] Switching the solvent to CH$_2$Cl$_2$ produces a different outcome as the elimination of HCl occurs generating a carbon−carbon double bond in the ligand framework (**4**).[7]

Reactions of DAB or BIAN ligands with PBr$_3$ proceed cleanly in the presence of a halide trap (e.g., cyclohexene) and undergo a charge-transfer giving the corresponding bromophosphines (**5**, **6**).[8] The reaction proceeds by generating a P(I) intermediate which is then oxidized to P(III) by the ligand in a subsequent step; hence, a charge-transfer from the phosphorus center to the ligand occurs. These halophosphorus compounds are precursors to N-heterocyclic phosphenium cations (**7**, **8**) via halide abstraction. The phosphenium cations can also be made directly with a 1:1 mixture of SnCl$_2$ and PCl$_3$ or PI$_3$ alone with either DAB or BIAN ligands.[9−11] The reactivity proved consistent in all cases regardless of the substitution on the α-carbon.

Over the past several years, there has been a surge in interest in the chemistry between diimine ligands and the p-block elements. Our research group has been interested in the interactions of these ligands with the chalcogens and have

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*To whom correspondence should be addressed. E-mail: pragogna@uwo.ca. Phone: 1-519-661-2111, ext: 87048. Fax: 1-519-661-3022.

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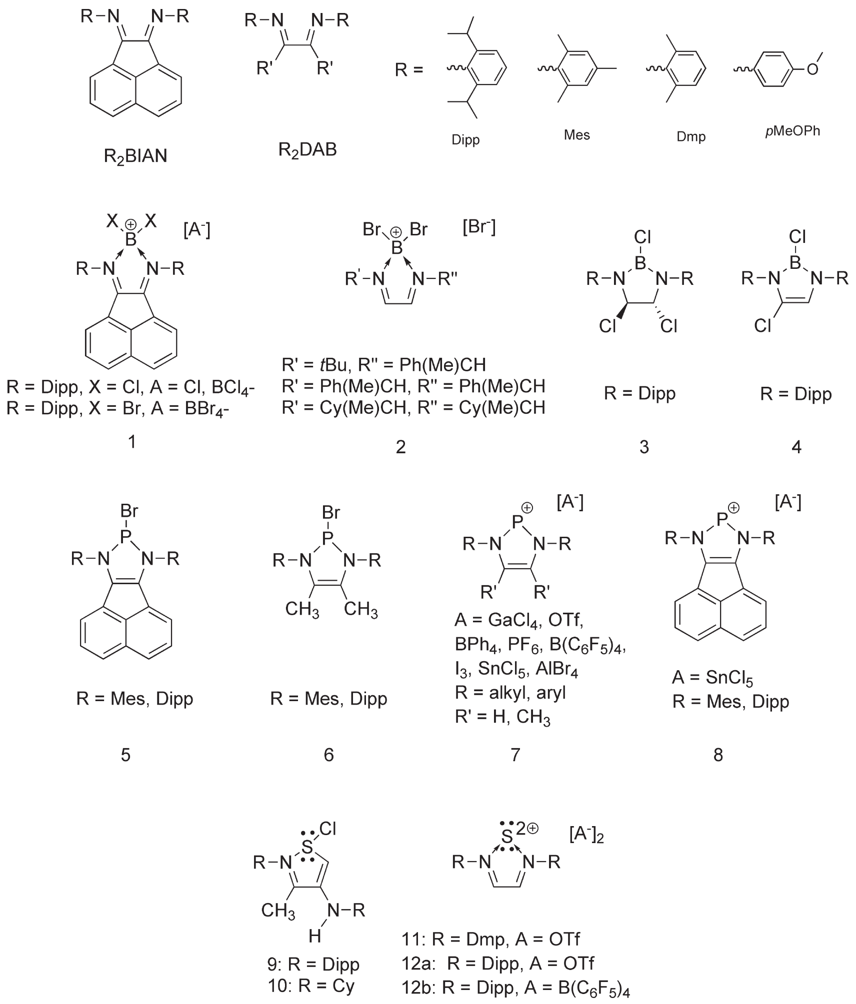

Figure 1. α-Diimine complexes of non-metals.

mainly focused on Se and Te.[12−21] Initial reports featuring sulfur identified reactivity differing from boron and phosphorus. In reactions of SCl_2 with an aryl or alkyl-substitued diazabutadiene ligand featuring methyl groups on the backbone carbon, an unexpected N,C-bound hetercycle is obtained (**9**, **10**).[15] The mechanism is believed to occur by attack of the eneamine tautomer of the ligand to the chalcogen center, which is supported by analogy to the selenium congener. The reaction of SCl_2 with an aryl-DAB ligand possessing hydrogen atoms on the backbone carbon, in the presence of TMS-OTf (triflouromethanesulfonate, OTf = triflate), results in the formation of an N,N′-chelated dicationic sulfur center (**11**, **12a**), where the anion could be exchanged with the weakly coordinating $B(C_6F_5)_4^-$ counterion (**12b**).[18]

Aside from these preliminary examples, the chemistry of sulfur with α-diimine ligands remains virtually undeveloped. In this context, we have conducted a more comprehensive study to include varied ligand sets to better understand the effect of varying the substitution at nitrogen and on the backbone carbon atoms.

Through these experiments it has been determined that the BIAN framework, or phenyl groups on the backbone carbon atoms, have little effect, giving rise to N,N′-chelated heterocycles, analogous to the DAB chemistry. Interestingly the substitution at nitrogen on the DAB ligands plays a critical role in the outcome of the reaction. In alkyl derivatives, an alkyl group is lost in the course of the reaction yielding 1,2,5-thiadiazolium ring systems in stark contrast to the aryl substituted derivatives.

Experimental Section

General Procedures. 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 *p*MeOPh$_2$DAB, *p*MeOPh$_2$BIAN, Dipp$_2$BIAN, *t*Bu$_2$DAB, and Cy$_2$DAB were synthesized using

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literature procedures.[22−26] The Ph_2DABPh_2 ligand was made by the procedure described by Gibson substituting aniline as the amine.[27] Dichloromethane, CH_3CN, Et_2O, and *n*-pentane were obtained from Caledon Laboratories and dried using an MBraun Controlled Atmospheres Solvent Purification System. The dried solvents were stored in Strauss flasks under an N_2 atmosphere, or over 4 Å molecular sieves in the glovebox. Solvents for ^1H NMR spectroscopy ($CDCl_3$, CD_3CN) were purchased from Cambridge Isotope Laboratories, and dried by stirring for 3 days over CaH_2, distilled prior to use and stored in the glovebox over 4 Å molecular sieves. Trimethylsilyltriflouromethanesulfonate (TMS-OTf) was purchased from Alfa Aesar and used as received. Multinuclear NMR data are listed in parts per million (ppm), relative to Me_4Si (^{13}C and ^1H) and $CFCl_3$ (^{19}F), coupling constants are in hertz, and all NMR spectra were recorded on an INOVA 400 MHz spectrometer (^1H = 399.76 MHz, ^{13}C = 100.52 MHz, ^{19}F = 376.15 MHz). X-ray diffraction data were collected on a Nonius Kappa-CCD area detector using Mo−K_α radiation (λ = 0.71073 Å). Crystals were selected under oil, mounted on glass fibers then 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.

Samples for FT-Raman spectroscopy were packed in capillary tubes and flame-sealed. Data were collected using a Bruker RFS 100/S spectrometer, with a resolution of 4 cm^{-1}. FT-IR spectra were collected on samples as KBr pellets using a Bruker Tensor 27 spectrometer, with a resolution of 4 cm^{-1}. Decomposition points were recorded in flame-sealed capillary tubes using a Gallenkamp Variable Heater. UV−visible absorption spectra were acquired using a Varian Cary 300 spectrophotometer in CH_3CN, at 25 °C in 1 cm quartz cells. Elemental analyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada.

General Synthesis of 13−18. Trimethylsilyltrifluoromethane sulfonate in CH_2Cl_2 (1.5 mL) was added dropwise to a solution of SCl_2 in CH_2Cl_2 (10 mL) at −78 °C and stirred for 15 min. A solution of DAB or BIAN in CH_2Cl_2 (8 mL) was added dropwise to the mixture yielding orange/red (**15**, **18**), purple (**13, 14**), colorless with a white precipitate (**16**) or light brown (**17**) solutions.

Compound 13. TMS-OTf (0.372 g, 1.68 mmol), SCl_2 (0.086 g, 0.84 mmol), *p*$MeOPh_2DAB$ (0.150 g, 0.558 mmol). Despite numerous efforts **13** could only be isolated in small quantities (less than 10 mg) by vapor diffusion of Et_2O into CH_3CN.; d.p. 185−187 °C; ^1H NMR (CD_3CN, δ) 9.69 (d, 2H, $SN_2C_2H_2$), 7.86 (d, 4H, ^3J = 6.0 Hz, *ortho*-$PhOCH_3$), 7.32 (d, 4H, ^3J = 4.8 Hz, *meta*-$PhOCH_3$), 3.99 (s, 6H, $PhOCH_3$); $^{19}F\{^1H\}$ NMR (CH_3CN, δ) −78.7; FT-IR (cm^{-1}(ranked intensity)) 518(11), 575(14), 639(8), 760(12), 833(7), 977(15), 1033(3), 1161(2), 1272(1), 1438(9), 1465(6), 1509(5), 1577(13), 1591(4), 3076(10); FT-Raman (cm^{-1}(ranked intensity)) 415(14), 702(11), 795(13), 1005(9), 1091(5), 1146(7), 1171(8), 1300(1), 1341(2), 1434(3), 1451(4), 1505(10), 1563(12), 1596(6), 1650(15). Elemental Analysis (%) calcd for $S_3O_6F_6C_{18}H_{16}N_2$: C 36.12, H 2.69, N 4.65; found C 36.12, H 3.12, N 4.65.

Compound 14. TMS-OTf (0.169 g, 0.76 mmol), SCl_2 (0.039 g, 0.38 mmol), *p*-$MeOPh_2BIAN$ (0.150 g, 0.38 mmol). The volatiles were removed in vacuo, the powder was redissolved in CH_3CN (4 mL) and Et_2O was added (4 mL), and the solution was stored at −30 °C for 2 h giving a deep red microcrystalline material. This was recrystallized from a 1:1 CH_3CN:Et_2O mixture yielding pure material; 0.140 g, 51%; d.p. 160−161 °C. ^1H NMR (CD_3CN, δ) 8.73 (d, 2H, ^3J = 8.4 Hz, *aryl*-H), 8.12 (d, 2H, ^3J = 7.2 Hz, *aryl-H*), 8.08−8.02 (m, 6H, *aryl-H*), 7.42 (d, 2H, ^3J = 8.8 Hz, *aryl*-H), 4.03 (s, 6H, $PhOCH_3$); $^{13}C\{^1H\}$ NMR (CH_3CN, δ) 165.7, 162.1, 148.5, 139.3, 131.6, 131.4, 128.6, 125.4, 120.2, 117.6, 57.3; $^{19}F\{^1H\}$ NMR (CH_3CN, δ) −78.6; UV−vis (CH_3CN) λ_{max}, nm (ε, M^{-1}, cm^{-1}) 276 (700), 312 (450), 459 (200), 535 (sh); FT-IR (cm^{-1}(ranked intensity)) 472(10), 521(7), 571(12), 637(2), 778(9), 837(4), 1030(3), 1154(8), 1218(13), 1276(1), 1374(15), 1419(14), 1445(11), 1507(5), 1601(6); FT-Raman (cm^{-1}-(ranked intensity)) 358(13), 432(5), 472(11), 792(14), 977(15), 1158(3), 1184(7), 1210(4), 1261(8), 1334(6), 1372(10), 1441(9), 1508(1), 1569(12), 1598(2).

Compound 15. TMS-OTf (0.167 g, 0.600 mmol), SCl_2 (0.031 g, 0.300 mmol), $Dipp_2BIAN$ (0.150 g, 0.300 mmol). The volatiles were removed in vacuo, the powder was redissolved in CH_2Cl_2 (4 mL), and *n*-pentane was added (6 mL); the solution was stored at −30 °C overnight giving a red crystalline material. The crystals were collected, and *n*-pentane (2 mL) was added to the mother liquor yielding a second crop of crystals; 0.171 g, 73%; d.p. 154−156 °C; ^1H NMR (CD_3CN, δ) 8.56 (d, 2H, ^3J = 8.0 Hz, *aryl-H*), 7.91 (t, 2H, ^3J = 8.0 Hz, *aryl-H*), 7.84 (t, 2H, ^3J = 8.0 Hz, *aryl-H*), 7.60 (d, 4H, ^3J = 8.0 Hz, *aryl-H*), 7.47 (d, 2H, ^3J = 7.2 Hz, *aryl-H*), 2.94 (sept, 4H, ^3J = 6.8 Hz, $CH(CH_3)_2$), 1.40 (d, 12 H, ^3J = 6.8 Hz, $CH(CH_3)_2$), 1.15 (d, 12H, ^3J = 6.4 Hz, $CH(CH_3)_2$); $^{13}C\{^1H\}$ NMR (CH_3CN, δ) 165.5, 146.0, 140.5, 136.0, 132.2, 132.1, 131.9, 130.6, 129.8, 127.6, 120.7, 30.2, 24.4, 24.3; $^{19}F\{^1H\}$ NMR ($CHCl_3$, δ) −78.3; UV−vis (CH_3CN) λ_{max}, nm (ε, M^{-1}, cm^{-1}) 281 (2250), 439 (450); FT-IR (cm^{-1}(ranked intensity)) 353(15), 474(9), 524(6), 577(10), 637(2), 771(5), 810(12), 832(13), 1031(3), 1165(10), 1230(11), 1275(1), 1511(14), 1611(8), 2968(7); FT-Raman (cm^{-1}(ranked intensity)) 85(5), 136(12), 352(6), 474(3), 562(4), 977(7), 1020(10), 1030(8), 1102(15), 1217(9), 1249(8), 1368(14), 1506(1), 1586(13), 1603(2).

Compound 16. TMS-OTf (0.264 g, 1.19 mmol), SCl_2 (0.058 g, 0.595 mmol), *t*Bu_2DAB (0.100 g, 0.595 mmol). Normal pentane was added to the reaction mixture, resulting in the formation of more white precipitate. The supernatant was decanted, and the solid dried in vacuo giving a white powder. The material was found to be unstable in solution for periods greater than 15 min and as a solid for periods greater than 30 min; therefore, ^{13}C NMR data and elemental analysis could not be obtained. 0.136 g, 88%; d.p. 95−101 °C; ^1H NMR ($CDCl_3$, δ 10.13 (s, 1H, backbone *H*), 9.03 (s, 1H, backbone *H*), 2.01 (s, 9H, *t*Bu); $^{19}F\{^1H\}$ NMR (CH_3CN, δ −78.4; FT-IR (cm^{-1}(ranked intensity)); 518(6), 553(14), 574(11), 638(4), 846(7), 1001(13), 1027(3), 1169(5), 1248(1), 1278(2), 1382(10), 1418(9), 1480(15), 3073(8), 3089(12); FT-Raman (cm^{-1}(ranked intensity)) 314(5), 349(3), 575(12), 706(2), 758(8), 783(11), 846(6), 1030(1), 1151(14), 1226(13), 1448(15), 2920(10), 2997(4), 3088(9).

Compound 17. TMS-OTf (0.202 g, 0.907 mmol), SCl_2 (0.047 g, 0.454 mmol), Cy_2DAB (0.100 g, 0.454 mmol). Normal pentane was added to the reaction mixture, resulting in the formation of a beige precipitate. The supernatant was decanted, and the solid dried in vacuo giving a beige powder. The material was found to be unstable in solution for periods longer than 10 min and as a solid for periods greater than 20 min; therefore, ^{13}C NMR data and elemental analysis could not be obtained. 0.099 g, 69%; d.p. 48 °C; ^1H NMR ($CDCl_3$, δ 10.09 (s, 1H, backbone *H*), 8.93 (s, 1H, backbone *H*), 5.33 (m, 1H, *ispo-H*-Cy), 2.39−1.28 (m, 10H, Cy); $^{19}F\{^1H\}$ NMR (CH_3CN, δ) −78.4; FT-IR (cm^{-1}(ranked intensity)) 517(12), 556(4), 575(9), 731(6), 760(5), 812(1), 841(3), 897(2), 1029(15), 1168(13), 1251(14), 1459(11), 2866(8), 2943(10), 3064(7); FT-Raman (cm^{-1}(ranked intensity)) 121(8), 316(7), 349(6), 575(12), 626(15), 760(3), 805(11), 1034(1), 1147(9), 1247(13), 1273(10), 1354(14) 1451(3), 2866(4), 2949(2).

Compound 18. TMS-OTf (0.195 g, 0.878 mmol), SCl_2 (0.045 g, 0.439 mmol), Ph_2DABPh_2 (0.160 g, 0.439 mmol). The volatiles were removed in vacuo, and the powder was redissolved in

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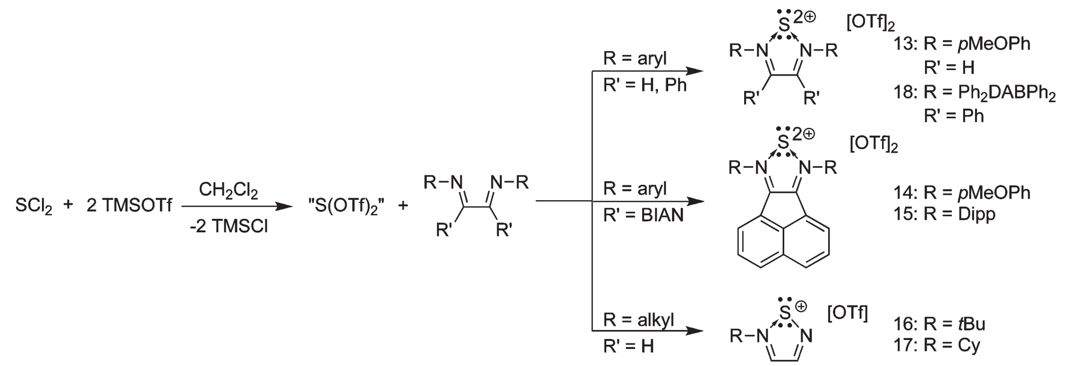
Scheme 1. Reactions of α-Diimines with "S(OTf)$_2$"



CH_2Cl_2 (4 mL), and *n*-pentane was added (4 mL), the solution was then stored at −30 °C overnight giving an orange powder. The supernatant was decanted, and the solids were washed with *n*-pentane (3 × 5 mL). 0.184 g, 60%; d.p. 111−113 °C; ^{1}H NMR ($CDCl_3$, δ) 8.08 (d, 4 H, ^3J = 8.4 Hz, *aryl-H*), 7.73 (t, 2H, ^3J = 7.6 Hz, *aryl-H*), 7.67−7.55 (m, 10H, *aryl-H*) 7. 37 (t, 4H, ^3J = 8.0 Hz, *aryl-H*); $^{13}C\{^1H\}$ NMR (CH_3CN, δ) 165.9, 135.5, 132.8, 132.1, 131.6, 130.4, 128.1, 124.0; $^{19}F\{^1H\}$ NMR (CH_3CN, δ) −78.4; UV−vis (CH_3CN) λ_{max}, nm (ε, M^{-1}, cm^{-1}) 278 (1450), 316 (sh); FT-IR (cm^{-1}(ranked intensity)) 1596(9), 1485(10), 1457(14), 1433(8), 1296(13), 1250(1), 1162(5), 1025(2), 788(15), 758(4), 729(11), 694(6), 637(3), 574(12), 519(7) ; FT-Raman (cm^{-1}(ranked intensity)) 3074(11), 1596(2), 1505(8), 1484(15), 1433(6), 1365(1), 1318(13), 1117(4), 1026(7), 1002(3), 627(14), 464(9), 404(10), 356(12), 102(5).

Results and Discussion

Synthesis. To explore the chemistry of sulfur with α-diimine ligands, an in situ "S(OTf)$_2$" synthon was prepared by reaction of TMS-OTf and SCl_2 in a 2:1 stoichiometry in CH_2Cl_2 at −78 °C yielding a light orange solution.[18,28] To the solution of "S(OTf)$_2$", 1 equiv of a DAB or BIAN ligand in CH_2Cl_2 was added dropwise generating crimson (Dipp$_2$BIAN, **15**; Ph$_2$DABPh$_2$, **18**) or purple (*p*MeOPh$_2$DAB, **13**; *p*MeOPh$_2$BIAN, **14**) solutions, or beige precipitates (*t*Bu$_2$DAB, **16**; Cy$_2$DAB, **17**) (Scheme 1). Removal of the volatiles in vacuo for Dipp$_2$BIAN, Ph$_2$DABPh$_2$, *p*MeOPh$_2$DAB, and *p*MeOPh$_2$BIAN gave rise to red or purple powders. Normal pentane was added to the solutions of the alkyl derivatives resulting in the further precipitation of material; the supernatant was then decanted, and the powder dried in vacuo.

Proton NMR spectroscopy of the redissolved crude powder from the *p*MeOPh$_2$DAB reaction in CD_3CN revealed a major product (~70% purity) with a diagnostic downfield shift of the backbone protons on the DAB ligand (δ = 9.77 ppm cf. free ligand δ = 8.42 ppm) reminiscent of **11** and **12a** (δ = 10.23−10.21 ppm cf. free ligand δ = 8.13 ppm).[18,23] The major product in the spectrum consisted of one set of resonances indicative of a symmetric bonding environment. The backbone protons integrated to two, with respect the six methoxy protons. A single resonance at −78.7 ppm was observed in the $^{19}F\{^1H\}$ NMR spectrum consistent with ionic triflate in solution ([NOct$_4$][OTf] δ = −78.5 ppm). On the basis of these data, the bonding was assigned as the N,N′-chelated dicationic chalcogen complex (**13**).

Upon increasing the stoichiometry of "S(OTf)$_2$" to 1.5 stoichiometric equivalents, the yield in the crude mixture increased to approximately 85%. We postulate that the imine nitrogen atoms are sufficiently basic to deprotonate the backbone protons on the dicationic heterocycle which are acidic upon the coordination of the ligand to the highly charged sulfur center. This ultimately results in decomposition of the desired product, as protonated ligand became more prevalent in the crude ^{1}H NMR sprectrum. Decreasing the amount of free ligand in solution hinders this process and allows the reaction to proceed more cleanly. Increasing the stoichiometry of "S(OTf)$_2$" did not result in a greater yield in the R$_2$BIAN (**14** and **15**) or the Ph$_2$DABPh$_2$ (**18**) complexes, which do not possess the acidic backbone protons. A related observation has been made with the heterocyclic nitrenium cation (nitrogen analogue of **7**) as the proton on these systems can also be abstracted.[29] Despite extensive efforts to develop a high yielding purification procedure, the highest isolated yield of a pure product for the *para*-methoxy derivative was on the order of 5%, despite the reaction going to 85% as indicated by ^{1}H NMR spectroscopy. The difficulties in purifying this material can be attributed to the high insolubility of **13** in organic solvents and adding to this problem, **13** also has the same solubility as the impurities. Single crystals were grown from the small amount of purified material by vapor diffusion of Et_2O into acetonitrile, which were suitable for X-ray diffraction experiments, confirming the structural assignment of **13**.

To examine an analogous ligand framework lacking these reactive backbone protons, the chemistry was extended to the BIAN ligand system and the DAB ligand featuring phenyl groups on the backbone carbon atoms. Crude powders from the reactions of "S(OTf)$_2$" with Dipp$_2$BIAN, *p*MeOPh$_2$BIAN, and Ph$_2$DABPh$_2$ displayed enhanced solubilities in organic solvents making the isolation of larger quantities of pure material possible. The *p*MeOPh$_2$BIAN derivative (**14**) was purified as deep

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(28) In an attempt to characterize this "S(OTf)$_2$" species, the mixture was probed by ^{19}F NMR spectroscopy. The ^{19}F NMR spectrum at room temperature gave a singlet shifted to lower field, indicating a more ionic triflate. However, despite extensive attempts to identify a single, pure product, nothing definitive could be ascertained. Furthermore, if the chemistry (reported in this manuscript) is carried out in the absence of OTf$^-$, only starting material and decomposition products are observed in the ^{1}H NMR spectrum. Therefore, we assign the S(OTf)$_2$ as an in situ preparation.

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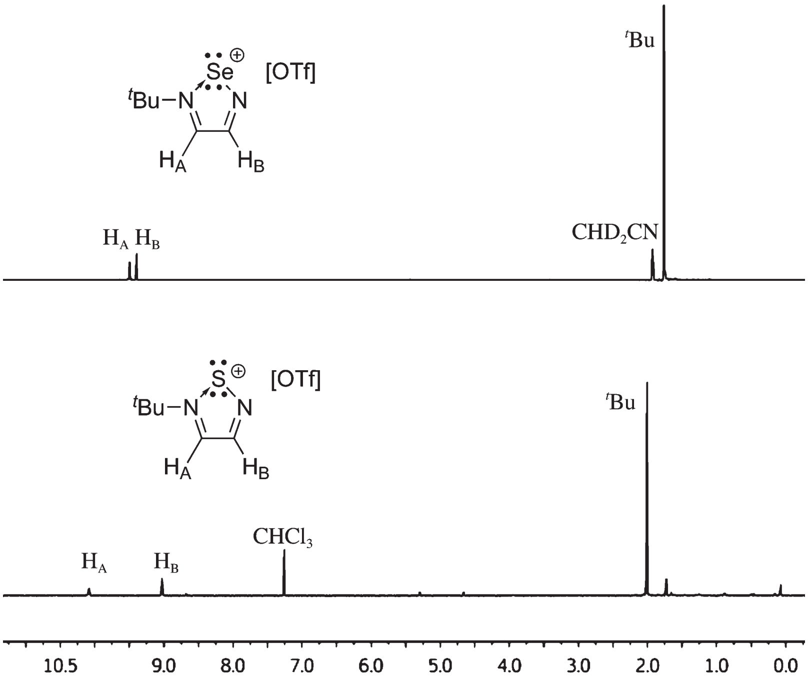

Figure 2. Stacked plot of ^1H NMR spectra of **16** bottom in $CDCl_3$ and the selenium congener top in CD_3CN.

red crystals in 51% yield by two subsequent recrystallizations of a 1:1 mixture of CH_3CN and Et_2O of the bulk powder at −30 °C as confirmed by ^1H NMR spectroscopy. Crystals suitable for X-ray crystallographic studies were grown by vapor diffusion of Et_2O into acetonitrile confirming the structure of **14**. The $Dipp_2BIAN$ analogue (**15**) and Ph_2DABPh_2 (**18**) derivative were purified by recrystallization of the bulk powder from a saturated solution of CH_2Cl_2 and pentane stored at −30 °C overnight, which generated orange X-ray quality crystals of **15** and **18** in good yield (**15**, 73%; **16**, 60%). In all cases ^1H NMR spectroscopy revealed a symmetric bonding environment regarding the ligand framework. The ^1H NMR spectra displayed downfield shifts of the BIAN (**14** and **15**) and phenyl protons (**18**) on the backbone carbon atoms in the products consistent with the coordination of the ligand to a highly charged center. Single resonances in the $^{19}F\{^1H\}$ NMR spectra were indicative of ionic triflate (**14** $\delta = -78.6$ ppm; **15** $\delta = -78.3$ ppm, **18** $\delta = -78.4$ ppm). These data supported the synthesis of a dicationic SC_2N_2 heterocycle (**14**, **15**, and **18**).

The connectivity of **14**, **15**, and **18** was analogous to the R_2DAB complexes confirming that the acenaphthene or the phenyl groups on the backbone does not change the outcome of the reaction but improves the solubility of the products allowing for the isolation of the *para*-methoxy derivative. The dicationic salts (**13**−**15**) all were unstable in solution at room temperature (periods greater than 2 h), but solid samples could be stored for weeks in an inert atmosphere at room temperature. Compounds **13**−**15** and **18** represent dicationic structural mimics of the N-Heterocyclic silylene, and **14** and **15** are the first sulfur BIAN complexes reported.[30]

To examine the effect of alkyl substitution on the nitrogen atom, the reactions of "$S(OTf)_2$" with tBu_2DAB and Cy_2DAB ligands were carried out. The ^1H NMR spectrum of the solids revealed pure products (tBu_2DAB, **16**; Cy_2DAB, **17**). A break in symmetry of the backbone protons, contrary to that in **13**−**15** and **18** (*t*Bu, **16**, δ = 10.13, 9.03 ppm; Cy, **17**, δ = 10.09, 8.93 ppm), was observed in both cases, indicative of a different reaction. Also noteworthy, was a reduction of the integration values of the *tert*-butyl or cyclohexyl protons by half suggesting the loss of an alkyl group contrary to what occurs in the aryl DAB and BIAN species. An in situ ^1H NMR spectroscopy experiment in $CDCl_3$ of the reaction of tBu_2DAB with "$S(OTf)_2$" clearly indicated the formation of *tert*-butyl chloride (δ = 1.62 ppm) as a reaction byproduct. The ^1H NMR spectra were reminiscent of the related selenium system with tBu_2DAB (δ = 9.49, 9.40 ppm) showing a break in symmetry of the ligand framework (Figure 2).[14] The $^{19}F\{^1H\}$ spectra displayed one signal diagnostic of ionic triflate ($\delta = -78.4$ ppm). On the basis of these data the compounds were assigned the same connectivity as the selenium derivative, as the thiadiazolium triflate salts **16** and **17**. This 1,2,5-chalcadiazolium ring system is not unusual for the heavy chalcogens (S, Se, Te).[12,14,20,31−33] Unfortunately these compounds were highly unstable in solution with **17** decomposing within 10 min of being synthesized. Even as a powder at room temperature, decomposition was observed within 20 min. Given this instability, crystallization attempts were unsuccessful. However, on the basis of the similarity of the data with those obtained for selenium and tellurium, the structures were assigned as **16** and **17**.[14,20]

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Table 1. X-ray Details of **13**−**15**, **18**

	13·CH$_3$CN	**14**	**15·0.5CH$_2$Cl$_2$**	**18**
empirical formula	$C_{20}H_{19}F_6N_3O_8S_3$	$C_{28}H_{20}F_6N_2O_8S_3$	$C_{38.5}H_{40}Cl_{0.70}F_6N_2O_6S_3$	$C_{28}H_{20}F_6N_2O_6S_3$
FW (g/mol)	639.56	722.64	872.36	690.64
crystal system	orthorhombic	orthorhombic	monoclinic	triclinic
space group	*Pna*2(1)	*Pbca*	*P*2(1)/*c*	$P\bar{1}$
a (Å)	7.2453(9)	18.324(4)	20.459(4)	10.446(2)
b (Å)	16.174(2)	13.677(3)	12.219(2)	11.972(2)
c (Å)	22.279(3)	23.463(5)	17.293(4)	13.970(3)
α (deg)	90	90	90	113.30(3)
β (deg)	90	90	110.96(3)	94.40(3)
γ (deg)	90	90	90	108.73(3)
V (Å^3)	2610.8(6)	5880(2)	4036.8(14)	1477.4(5)
Z	4	8	4	2
D_c (mg m^{-3})	1.627	1.633	1.435	1.553
radiation, λ (Å)	0.71073	0.71073	0.71073	0.71073
temp (K)	193(2)	150(2)	150(2)	150(2)
$R1[I > 2\sigma(I)]^a$	0.0597	0.0601	0.0717	0.0481
$wR2(F^2)^a$	0.1476	0.1749	0.1982	0.1377
GOF $(S)^a$	1.055	1.017	1.0200	1.089

[a] $R1(F[I > 2\sigma(I)]) = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2(F^2\,[\text{all data}]) = [w(F_o{}^2 - F_c{}^2)^2]^{1/2}$; $S(\text{all data}) = [w(F_o{}^2 - F_c{}^2)^2/(n-p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = 1/[^2(F_o{}^2) + (aP)^2 + bP]$ where $P = (F_o{}^2 + 2F_c{}^2)/3$ and a and b are constants suggested by the refinement program.

Table 2. Selected Metrical Parameters for Compounds **11**, **12a**, **13**, **14**, **15**, and **18**[a]

	11[18]	**12a**[18]	**13**	**14**	**15**	**18**	[c]calculated[35]
[b]S−N	1.695(3)	1.696(6) 1.699(6)	1.658(5) 1.682(4)	1.697(3) 1.708(3)	1.705(3) 1.704(3)	1.676(2) 1.679(2)	1.705
[b]N−C	1.305(5)	1.293(9) 1.324(9)	1.323(7) 1.339(6)	1.312(5) 1.316(5)	1.323(4) 1.325(4)	1.325(3) 1.329(3)	1.331
[b]C−C	1.390(8)	1.407(10)	1.379(8)	1.439(5)	1.412(4)	1.421(4)	1.389
O···S	2.615(3)	2.313(5)	2.997(6)	2.654(4)	2.454(2)	2.638(2)	
O···H	2.309	2.265	2.290				
N−S−N	88.0(2)	87.8(3)	90.3(2)	90.38(15)	90.15(12)	88.80(11)	90.3
[b]SN_2C_2 deviation from planarity	0.005(8)	0.011(10)	0.020(9)	0.019(5)	0.005(4)	0.0039(5)	
Aryl/SC_2N_2 angle	76.1	80.7, 97.2	26.8, 37.9	76.2, 81.3	46.3, 80.5	86.2, 90.5	

[a] Bond lengths are in angstroms (Å) and angles in degrees (deg). [b] All metrical parameters refer to endocyclic E-E bonds. [c] Calculated optimized geometries are for the *N*-Ph substituted derivatives featuring protons on the backbone carbon atoms.

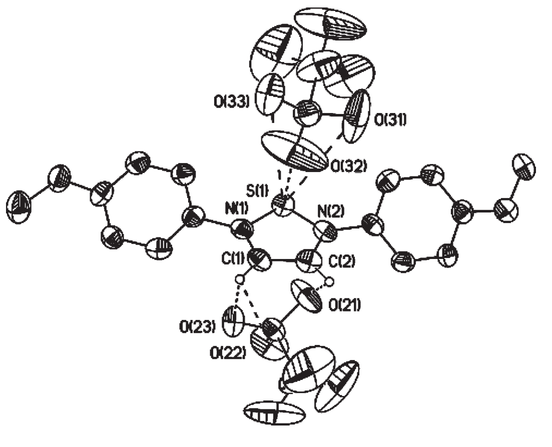

Figure 3. Solid-state structure of **13**. Ellipsoids are drawn to 50% probability, all hydrogen atoms excluding hydrogen atoms interacting with the anion and solvates are omitted for clarity.

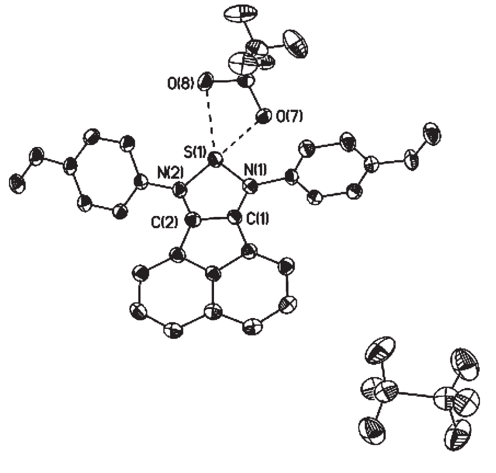

Figure 4. Solid-state structure of **14**. Ellipsoids are drawn to 50% probability and all hydrogen atoms are omitted for clarity.

X-ray Crystallographic Studies. Upon examination of the crystal structures of **13**−**15** and **18** the bonding motif is congruent to those reported previously (**11** and **12**; see Tables 1 and 2 for details, Figures 3, 4, 5, and 6).[18] The structures display planar 5-membered C_2N_2S rings [largest deviation from planarity 0.020(9)Å]. The color of compound **13** in the solid state and in solution is deep purple, contrary to **11** and **12**, which are orange. This high coloration is likely a result of the oxygen atoms *para* to the DAB ligand donating into the DAB π-system extending the conjugation. The metrical parameters indicate that the interplanar aryl/C_2N_2S ring angles are significantly smaller than those of **13**. The angles are on the order of 30° whereas in **11** and **12**, the aryl rings are much closer to being orthogonal to the sulfur heterocycle (**13**: 26.8°, 37.9° cf. **11**: 80.7°, 97.2°; **12a** 76.1°). This

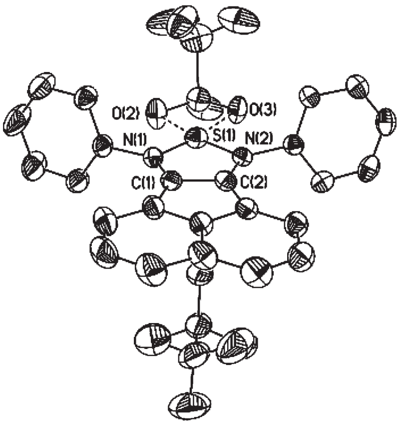

Figure 5. Solid-state structure of **15**. Ellipsoids are drawn to 50% probability, all hydrogen atoms, isopropyl groups and solvates are omitted for clarity.

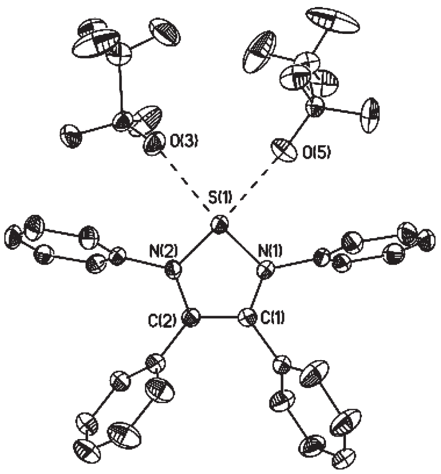

Figure 6. Solid-state structure of **18**. Ellipsoids are drawn to 50% probability and all hydrogen atoms are omitted for clarity.

phenomenon also could be present as **13** does not present bulky substituents on the *ortho* positions of the aryl ring permitting the ring to orient itself with the C_2N_2S plane.

The BIAN and Ph_2DABPh_2 complexes are essentially isostructural to the DAB derivatives bearing protons on the backbone carbons **11**−**13**. The bulkier BIAN and phenyl substituted backbone orient the aryl rings more out of the plane than the DAB ligands. With respect to the BIAN complexes, **14**, as it bears *para*-methoxy groups is highly colored as with **13** and orients the aryl rings more in plane than the bulkier Dipp derivative, **15** (interplanar angles: **14** = 46.3, 80.5 cf. **15** = 76.2°, 81.3°). The endocyclic bonds in all structures within the C_2N_2S ring [C−N 1.312(5)−1.339(6); C−C 1.379(8)−1.439(5) Å] support the retention of two C=N double bonds and a C−C single bond consistent with the free ligand. Sulfur−nitrogen bonds slightly shorter than typical sulfur−nitrogen single bonds [1.658(5)−1.708(3) Å cf. 1.74 Å] are observed, which can be rationalized by the binding of the ligand to the electron deficient sulfur(II) center.[34] These endocyclic bond lengths are in close agreement with computational results [C−C 1.389, C−N 1.331, S−N 1.705 Å].[35] The bonding of these compounds can be best described as a N,N′-chelated sulfur center bearing two lone pairs with a formal charge of +2.

Sulfur−oxygen contacts between the cations and anions in all species within the sum of the van der Waals radii (3.25 Å) are observed.[33] However, there is no distortion of the corresponding sulfur−oxygen bond in the triflate ions, contrary to what is observed in covalently bound substituents. In these covalent species, the corresponding S−O bond length for the coordinated oxygen atom is significantly elongated with respect to the other two S−O bonds within the triflate.[17] In compound **13**, the closest cation−anion interactions lie between the oxygen atom and the acidic backbone proton. The contact is well within the sum of the van der Waals radii (shortest contact 2.290 Å cf. 2.60 Å).

In spite of the oxygen contacts with the dicationic sulfur center, these species are distinct dication−anion pairs. Spectroscopic solution data and the metrical parameters are consistent of a dicationic species as they are in agreement with the computational results.

Conclusion

By reacting SCl_2 with TMS-OTf, a "$S(OTf)_2$" synthon was generated, which was effective in the synthesis of new sulfur nitrogen heterocycles by reactions with diimine ligands. If aryl DAB or BIAN ligands were used N,N′-chelated sulfur dications were obtained. These complexes represent the first sulfur BIAN complexes reported and are structural mimics of the N-heterocyclic silylene or phosphenium cation. If an alkyl DAB ligand is used, the loss of an alkyl group on the nitrogen atom is observed resulting in thiadiazolium complexes. This differs from the reactivity of the other non-metals which are prone to undergo charge transfer with the ligand. This is new reactivity for sulfur and these BIAN compounds show promise as S^{2+} delivery reagents which is currently under exploration in our laboratory.

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Supporting Information Available: Crystallographic data in CIF format and Figures S1−S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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