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Article

Synthesis and Reactivity of Sulfur(II) Dications Stabilized Using Monodentate Ligands

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The stoichiometric 1:2:2 reaction of SCl_2, trimethylsilyl trifluoromethanesulfonate, and pyridine produced sulfur(II) dications featuring two pyridine donors. The complexes were reacted with unsaturated organic substrates, which displayed addition with carbon−carbon and carbon−nitrogen double bonds. The substitution on the para position of the ligand was varied by using electron donating, electron withdrawing, and neutral groups. The electronics at this position were determined to have a substantial effect on the outcome of the reaction. The presence of an electron donating group increased the Lewis basicity sufficiently to completely stop the reaction, whereas an electron withdrawing group decreased the reaction time. These observations are unique to the chemistry of sulfur(II) dications and main group polycations as a whole.

Introduction

The activation of small molecules is an important area in the fields of organic and inorganic chemistry especially for the transformation of abundant chemical feedstocks into more complex molecules or for targeted synthesis.[1] In the past, transition metal catalysts have been the dominant players in this field. Recently, nonmetal reagents have shown utility in this area, spurring further developments within the p-block. Most noteworthy has been the development of the "Frustrated Lewis Pair" by the Stephan and Erker groups, which is derived from the combination of a sterically encumbered Lewis acid and Lewis base, precluding the formation of a classical adduct.[2,3] Certain carbenes, specifically the cyclic alkyl amino and diamido derivatives, have also shown the ability to transform several unreactive substrates and have proven useful in the activation of a variety of molecules,

such as dihydrogen, alkynes, alkenes, carbon dioxide, ammonia, and nitrous oxide.[4−13] Aside from these reagents, other nonmetal examples for performing such tasks are minimal.[14−20]

Main group complexes have also shown a rich chemistry in addition reactions across the double bond in unsaturated organic substrates. Notable examples include hydroborations and, in the presence of a catalyst, hydrostannation and hydrosilylation reactions.[21−23] With respect to the reactivity of sulfur compounds with alkenes, sulfur homopolyatomic cations form novel heterocycles with nitriles though cycloaddition reactions and sulfur chlorides have shown

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(1) Tolman, W. B. *Activation of Small Molecules*; Wiley-VCH: New York, 2006.
(2) Stephan, D. W. *Dalton Trans.* **2009**, 3129–3136.
(3) Stephan, D. W.; Erker, G. *Angew. Chem., Int. Ed.* **2010**, *49*, 46–76.
(4) Frey, G.; Lavallo, V.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. *Science* **2007**, *316*, 439–441.
(5) Kuchenbeiser, G.; Soleilhavoup, M.; Donnadieu, B.; Bertrand, G. *Chem. Asian J.* **2009**, *4*, 1745–1750.
(6) Welch, G. C.; San Juan, R. R.; Masuda, J.; Stephan, D. W. *Science* **2006**, *314*, 1124–1126.
(7) McCahill, J. S. J.; Welch, G. C.; Stephan, D. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 4968–4971.
(8) Dureen, M. A.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 8396–8397.
(9) Otten, E.; Neu, R. C.; Stephan, D. W. *J. Am. Chem. Soc.* **2009**, *131*, 9918–9919.
(10) Ashley, A. E.; Thompson, A. L.; O'Hare, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 9839–9843.
(11) Menard, G.; Stephan, D. W. *J. Am. Chem. Soc.* **2010**, *132*, 1796–1797.
(12) Hudnall, T. W.; Bielawski, C. W. *J. Am. Chem. Soc.* **2009**, *131*, 16039–16041.
(13) Hudnall, T. W.; Moerdyk, J. P.; Bielawski, C. W. *Chem. Commun.* **2010**, *46*, 4288–4290.
(14) Li, B.; Xu, Z. *J. Am. Chem. Soc.* **2009**, *131*, 16380–16382.
(15) Spikes, G. H.; Fettinger, J. C.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 12232–12233.
(16) Meltzer, A.; Innoue, S.; Prasang, C.; Dreiss, M. *J. Am. Chem. Soc.* **2010**, *132*, 3038–3046.
(17) Jana, A.; Schulzke, C.; Roesky, H. W. *J. Am. Chem. Soc.* **2009**, *131*, 4600–4601.
(18) Yao, S.; Xiong, Y.; Brym, M.; Driess, M. *J. Am. Chem. Soc.* **2007**, *129*, 7268–7269.
(19) Jana, A.; Objartel, I.; Roesky, H. W.; Stalke, D. *Inorg. Chem.* **2009**, *48*, 798–800.
(20) Xiong, Y.; Yao, S.; Muller, R.; Kaupp, M.; Driess, M. *J. Am. Chem. Soc.* **2010**, *132*, 6912–6913.
(21) Dhillon, R. S. *Hydroboration and Organic Synthesis*; Springer: New York, 2007; Vol. *14*.
(22) Smith, N. D.; Mancuso, J.; Lautens, M. *Chem. Rev.* **2000**, *100*, 3257–3282.
(23) Roy, A. K. *Adv. Organomet. Chem.* **2008**, *55*, 1–59.

Scheme 1. The Reaction of Sulfur Chlorides with Olefins in Thioether Synthesis

additions to olefins.[24,25] A reaction of interest early in the 20th century was in the production of sulfur mustard.[26] This chemical warfare agent was first synthesized in 1822 by Despretz, which was accomplished by the direct reaction of SCl_2 with ethylene to produce the toxin.[27] The reaction has been studied extensively since that time, and the proposed mechanism involves the formation of a cationic thiiranium intermediate (**1a**), followed by attack of the halide to a carbon atom in the three-membered ring to yield the desired thioether (**1b**, Scheme 1).[28] Although these reactions have been known for a number of years, developments are still being made today, and most noteworthy is the work by Denmark.[29,30] These reactions have been useful in organic synthesis but toxicity is a concern.

A class of molecules that is predicted to have interesting reactivity toward small molecules is main group polycations, which carry a formal charge of 2+ or larger on the central atom as they possess a highly electropositive moiety. The development of such molecules has flourished in recent years;

however, there have been no examples that take advantage of the reactive center in onward chemistry.[31−57]

In this context, our lab has developed a series of sulfur(II) dications utilizing multidentate ligands to stabilize the highly charged atom.[35−37] The reported examples feature bi- and tridentate (**2**, **3**, and **4**) ligands about the sulfur atom (Figure 1). Preliminary reactivity studies have thus far been unsuccessful as the tridentate derivatives are too stable, and the bidentate species react uncontrollably. Herein we report an extension of the previous work, synthesizing the first monodentate sequestered sulfur(II) dications featuring monodentate pyridine ligands (**5**). These species readily undergo addition with carbon−carbon and carbon−nitrogen double bonds into the sulfur−nitrogen dative bond displaying new reactivity for main goup polycations. Pyridine ligands are of interest as the substitution on the pyridine ring has a distinct influence on the donor properties at the nitrogen atom, and this provides a means of tuning the electronic properties of the dication. This study focuses on the synthesis, characterization, and reactivity of these new sulfur(II) dications, with electron donating, neutral, and withdrawing substituents on the ligand.

Experimental Section

General Procedures. All manipulations were performed under an inert atmosphere in a nitrogen filled MBraun Labmaster dp glovebox or using standard Schlenk techniques unless specified. Sulfur dichloride was synthesized using a literature procedure.[58] Trimethylsilyltrifluoromethanesulfonate (TMS-OTf), 4-dimethylaminopyridine (DMAP), 4-trifluoromethylpyridine, and *N*, *N'*-diisopropylcarbodiimide (DIC) were purchased from Alfa Aesar. Ethylene (Polymer 3.0 grade, 99.9% pure) was obtained from PRAXAIR Specialty Gases and Equipment and 4-phenylpyridine from Fisher Scientific. All reagents were used without further purification. Dichloromethane, CH_3CN, *n*-pentane, and Et_2O were obtained from Caledon Laboratories and dried using an MBraun Controlled Atmospheres Solvent Purification system. Acetone and THF were used as received from Caledon. The dried solvents were stored in Strauss flasks under an N_2 atmosphere or over 4 Å molecular sieves in the glovebox. Solvents used for ^1H NMR spectroscopy [CD_3CN and $(CD_3)_2$-CO] were purchased from Sigma-Aldrich and dried by storing in the glovebox over 4 Å molecular sieves. Multinuclear NMR data are listed in 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 (^1H = 399.76 MHz, ^{13}C = 100.52 MHz, ^{19}F = 376.15 MHz) spectrometer or INOVA 600 MHz spectrometer. Single crystal X-ray diffraction data were collected on a Nonius Kappa-CCD area detector or a Bruker Apex II-CCD detector using Mo−K_α radiation (λ = 0.71073 Å). Crystals were selected under N-paratone oil,

(24) Cameron, T. S.; Haddon, R. C.; Mattar, S. M.; Parsons, S.; Passmore, J.; Ramirez, A. P. *Inorg. Chem.* **1992**, *31*, 2274–2279.

(25) Cameron, T. S.; Decken, A.; Fang, M.; Parsons, S.; Passmore, J.; Wood, D. J. *Chem. Commun.* **1999**, 1801–1802.

(26) Duchovic, R. J.; Vilensky, J. A. *J. Chem. Educ.* **2007**, *84*, 944–948.

(27) Despretz, M. *Ann. Chim. Phys.* **1822**, *21*, 437–438.

(28) Mueller, W. H. *Angew. Chem., Int. Ed.* **1969**, *8*, 482–492.

(29) Denmark, S. E.; Vogler, T. *Chem.—Eur. J.* **2009**, *15*, 11737–11745.

(30) Denmark, S. E.; Collins, W. R.; Cullen, M. D. *J. Am. Chem. Soc.* **2009**, *131*, 3490–3492.

(31) Bandyopadhyay, R.; Cooper, B. F. T.; Rossini, A. J.; Schurko, R. W. *J. Organomet. Chem.* **2010**, *695*, 1012–1018.

(32) Rupar, P. A.; Bandyopadhyay, R.; Cooper, B. F. T.; Stinchcombe, M. R.; Ragogna, P. J.; MacDonald, C. L. B.; Baines, K. M. *Angew. Chem., Int. Ed.* **2009**, *48*, 5155–5158.

(33) Cheng, F.; Hector, A. L.; Levason, W.; Reid, G.; Webster, M.; Zhang, W. *Angew. Chem., Int. Ed.* **2009**, *48*, 5152–5154.

(34) Rupar, P. A.; Staroverov, V. N.; Baines, K. M. *Science* **2008**, *322*, 1360–1363.

(35) Martin, C. D.; Ragogna, P. J. *Inorg. Chem.* **2010**, *49*, 4324–4330.

(36) Martin, C. D.; Le, C. M.; Ragogna, P. J. *J. Am. Chem. Soc.* **2009**, *131*, 15126–15127.

(37) Martin, C. D.; Jennings, M. C.; Ferguson, M. J.; Ragogna, P. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 2210–2213.

(38) Dutton, J. L.; Tuononen, H. M.; Ragogna, P. J. *Angew. Chem., Int. Ed.* **2009**, *48*, 4409–4413.

(39) Weigand, J. J.; Burford, N.; Decken, A.; Schulz, A. *Eur. J. Inorg. Chem.* **2007**, 4868–4872.

(40) Dutton, J. L.; Tuononen, H. M.; Jennings, M. C.; Ragogna, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 12624–12625.

(41) Vidovic, D.; Findlater, M.; Cowley, A. H. *J. Am. Chem. Soc.* **2007**, *129*, 8436–8437.

(42) Vidovic, D.; Findlater, M.; Reeske, G.; Cowley, A. H. *J. Organomet. Chem.* **2007**, *692*, 5683–5686.

(43) Vargas-Baca, I.; Findlater, M.; Powell, A.; Vasudevan, K. V.; Cowley, A. H. *Dalton Trans.* **2008**, 6421–6426.

(44) Braunschweig, H.; Kaupp, M.; Lambert, C.; Nowak, D.; Radacki, K.; Schinzel, S.; Uttinger, K. *Inorg. Chem.* **2008**, *47*, 7456–7458.

(45) Mathur, M. A.; Ryschkewitsch, G. E. *Inorg. Chem.* **1980**, *19*, 3054–3057.

(46) Bergholdt, A. B.; Kobayashi, K.; Horn, E.; Takahashu, O.; Sato, S.; Furukawa, N.; Yokoyama, M.; Yamaguchi, K. *J. Am. Chem. Soc.* **1998**, *120*, 1230–1236.

(47) Foss, O.; Hauge, S. *Acta Chem. Scand.* **1959**, *13*, 1252–1253.

(48) Foss, O.; Hauge, S. *Acta Chem. Scand.* **1961**, *15*, 1616–1617.

(49) Foss, O.; Husebye, S.; Tornroos, K. W.; Fanwick, P. E. *Polyhedron* **2004**, *23*, 3021–3032.

(50) Schmidbaur, H., H.; Wimmer, T.; Reber, G.; Muller, G. *Angew. Chem., Int. Ed.* **1988**, *27*, 1071–1074.

(51) Schmidpeter, A.; Lochschmidt, S.; Karaghiosoff; Sheldrick, W. S. *J. Chem. Soc., Chem Commun* **1985**, 1447–1448.

(52) Hensen, K.; Stumpf, T.; Bolte, M.; Nather, C.; Fleischer, H. *J. Am. Chem. Soc.* **1998**, *120*, 10402–10408.

(53) Folkerts, H.; Hiller, W.; Herker, M.; Vyboishchikov, S. F.; Frenking, G.; Dehnicke, K. *Angew. Chem., Int. Ed.* **1995**, *34*, 1362–1363.

(54) Fujihara, H.; Mima, H.; Erata, T.; Furukawa, N. *J. Am. Chem. Soc.* **1992**, *114*, 3117–3118.

(55) Sato, S.; Ameta, H.; Horn, E.; Takahashi, O.; Furukawa, N. *J. Am. Chem. Soc.* **1997**, *119*, 12374–12375.

(56) Dutton, J. L.; Battista, T. L.; Sgro, M. J.; Ragogna, P. J. *Chem. Commun.* **2010**, *46*, 1041–1043.

(57) Dutton, J. L.; Ragogna, P. J. *Chem. Eur. J.* **2010**, *16*, in press, DOI: 10.1002/chem.201001447.

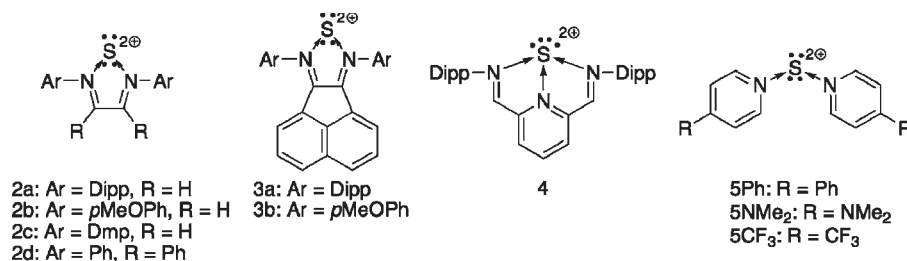(58) Steudel, R.; Jensen, D.; Plinke, B. *Z. Naturforsch.* **1987**, *42b*, 163–168.

Figure 1. Bi- and tridentate supported sulfur(II) dications (**2**, **3**, and **4**) and the new monodentate derivatives (**5**); Dipp = 2,6-diisopropylphenyl, *p*MeOPh = *para*-methoxyphenyl, Dmp = 2,6-dimethylphenyl.

mounted on nylon loops then immediately placed in a cold stream of N_2. Structures were solved and refined using SHELXTL.

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. Elemental analyses were performed by Columbia Analytical Services in Tucson, AZ.

Synthesis. 5Ph. A solution of SCl_2 (0.032 g, 0.315 mmol) and TMSOTf (0.140 g, 0.629 mmol) in CH_2Cl_2 (5 mL) was prepared at −78 °C. To this mixture 4-phenylpyridine (0.098 g, 6.29 mmol) in CH_2Cl_2 (5 mL) was added immediately generating a white precipitate. The supernatant was decanted and the solids were dried in vacuo. 0.180 g, 89%; d.p. 170−172 °C; ^1H NMR (CD_3CN, δ) 9.33 (d, 4H, ^3J = 6.6 Hz), 8.45 (d, 4H, ^3J = 6.6 Hz), 8.01 (d, 4H, ^3J = 8.4 Hz), 7.74 (t, 2H, ^3J = 7.8 Hz), 7.68−7.65 (m, 4H); ^{13}C (CH_3CN, δ) 155.2 152.0, 136.6, 136.4, 133.1, 131.8, 128.8; $^{19}F\{^1H\}$ NMR (CH_3CN, δ) −78.6.

5NMe₂. The analogous procedure for **5Ph** was utilized with the same quantities substituting DMAP (0.077 g, 0.629 mmol) for 4-phenylpyridine 0.168 g, 93%; d.p. 136−138 °C; ^1H NMR (CD_3CN, δ) 8.34 (d, 4H, ^3J = 8.0 Hz), 6.90 (d, 4H, ^3J = 8.4 Hz), 3.24 (s, 12H); ^{13}C (CH_3CN, δ) 158.1, 147.1, 110.0, 41.4; $^{19}F\{^1H\}$ NMR (CH_3CN, δ) −78.6. Elemental analysis: Calc for $C_{16}H_{20}F_6N_4O_6S_3$ C 33.45, H 3.51, N 9.76; found C 33.45, H 3.22, N, 9.56.

5CF₃. A solution of SCl_2 (0.032 g, 0.315 mmol) and TMSOTf (0.140 g, 0.629 mmol) in CH_2Cl_2 (5 mL) was prepared at −78 °C. To this mixture 4-trifluoromethylpyridine (0.093 g, 0.629 mmol) in CH_2Cl_2 (5 mL) was added generating a white precipitate. Normal pentane (5 mL) was added resulting in more solids precipitating from solution. The supernatant was decanted and the solids were dried in vacuo. 0.171 g, 87%, d.p. 179−181 °C; ^1H NMR (CD_3CN, δ) 9.65 (d, 4H, ^3J = 6.4 Hz), 8.50 (d, 4H, ^3J = 6.4 Hz); ^{13}C NMR (CH_3CN, δ) 153.8, 127.8, 123.1; $^{19}F\{^1H\}$ NMR (CH_3CN, δ) −65.5 (s, 6F), −78.6 (s, 6F).

6Ph. A solution of **5Ph** (0.150 g, 0.234 mmol) in CH_3CN (10 mL) was prepared in a Schlenk round bottomed flask in a dinitrogen atmosphere. The flask was immersed in a liquid nitrogen bath and the solution was frozen. The nitrogen was removed in vacuo and the flask was warmed to room temperature allowing the solvent to thaw. The flask was filled with one atmosphere of ethylene and stirred overnight. The solvent was removed in vacuo resulting in a yellow paste. The desired material was crystallized in the open atmosphere by vapor diffusion of ether into acetone. 0.112 g, 69%; mp 138−141 °C; ^1H NMR (CD_3CN, δ) 8.75 (d, 4H, ^3J = 7.2 Hz), 8.29 (d, 4H, ^3J = 6.6 Hz), 7.95−7.93 (m, 4H), 7.69−7.62 (m, 6H), 4.73 (t, 6.6 Hz, 4H), 3.19 (t, 6.6 Hz, 4H); ^{13}C (($CD_3)_2CO$, δ): 157.3, 146.2, 134.8, 133.1, 130.7, 129.0, 125.7, 60.4, 32.4; $^{19}F\{^1H\}$ NMR (CH_3CN, δ) −78.6; elemental analysis: Calc for $C_{31}H_{32}F_6N_2O_7S_3$ C 48.27, H 3.76, N 4.02; Found C 48.79, H 3.65, N, 3.84. ESI-MS *m/z* 547 [M^{2+}][OTf$^-$].

6CF₃. The analogous procedure for **6Ph** was used substituting **5CF₃** (0.200 g, 3.21 mmol) in place of **5Ph**. The resulting yellow paste was dissolved in THF (3 mL) and pentane (3 mL) was added in the open atmosphere. The solution was stored at −30 °C overnight generating a white solid. The supernatant was decanted and the solids were dried in vacuo. 0.089 g, 41%; mp 146−148 °C; ^1H NMR (($CD_3)_2CO$, δ) 9.61 (d, 4H, ^3J = 6.4 Hz), 8.67 (d, 4H, ^3J = 6.4 Hz), 5.26 (t, 4H, ^3J = 7.2 Hz), 3.56 (t, 4H, ^3J = 6.8 Hz); ^{13}C (($CD_3)_2CO$, δ): 148.8, 126.1, 126.0, 62.2, 32.4; $^{19}F\{^1H\}$ NMR (($CD_3)_2CO$, δ) −65.0, (6F), −78.2 (6F).

7Ph. To a solution of **5Ph** (0.200 g, 0.313 mmol) in acetonitrile (5 mL), neat cyclohexene (0.039 g, 0.625 mmol) was added and the reaction was stirred overnight resulting in a light brown solution. The volatiles were removed in vacuo giving a brown paste. The material was purified by two recrystallizations by vapor diffusion of Et_2O into a concentrated acetone solution in the open atmosphere. 0.106 g, 42%; mp 249−251 °C; ^1H NMR (($CD_3)_2CO$, δ): 9.28 (d, 4H, ^3J = 5.6 Hz), 8.63 (d, 4H, ^3J = 6.4 Hz), 8.13−8.11 (m, 4H), 7.73−7.67 (m, 6H), 4.59 (td, ^3J = 8.0 Hz, ^3J = 4.0 Hz, 2H), 3.28 (td, ^3J = 7.6 Hz, ^3J = 4.0 Hz, 2H), 2.42−2.39 (m, 2H), 2.21−1.15 (m, 16H); ^{13}C (($CD_3)_2CO$, δ): 157.9, 134.8, 133.3, 130.8, 129.1, 128.8, 126.0, 76.1, 51.4, 36.0, 34.1, 25.9, 25.3; $^{19}F\{^1H\}$ NMR (($CH_3)_2CO$, δ) −78.0. Elemental analysis: Calc for $C_{36}H_{38}F_6N_2O_6S_3$ C 53.72, H 4.76, N 3.48; Found C 53.53, H 4.59, N, 3.73. ESI-MS *m/z* 655 [M^{2+}][OTf$^-$].

8Ph. A solution of **5Ph** (0.100 g, 0.156 mmol) in acetonitrile (4 mL) was prepared in a vial and neat DIC (0.020 g, 0.156 mmol) was added. The solution was stirred for 10 h acquiring a light brown color. The volatiles were removed in vacuo producing a brown oil. The oil was dissolved in a minimal amount of acetonitrile (1 mL) and diethylether (2 mL) was added dropwise. The vial was stored at −35 °C for 1 h which caused the precipitation of a white powder. The supernatant was removed and the solids were dried in vacuo. 0.49 g, 41%; d.p. 155−157 °C; ^1H NMR (CD_3CN, δ) 9.10 (br, 2H), 8.85 (br, 2H), 8.56 (d, 2H, ^3J = 5.4 Hz), 8.34 (dd, 2H, ^3J = 7.2 Hz, ^4J = 1.8 Hz), 8.07 (d, 2H, ^3J = 7.8 Hz), 7.99 (d, 2H, ^3J = 7.8 Hz), 7.76 (t, 1H, ^3J = 7.2 Hz), 7.73−7.65 (m, 5H), 3.99 (br, 1H), 3.19 (br, 1H), 1.35 (br, 6H), 1.27, (d, 6H, ^3J = 6.0 Hz). ^{13}C (CD_3CN, δ): 161.1, 158.9, 143.4, 134.7, 133.4, 134.3, 133.7, 133.5, 130.8, 130.7, 129.8, 129.2, 127.3, 127.2, 126.0, 59.5, 53.4, 23.7, 21.8; $^{19}F\{^1H\}$ NMR (CH_3CN, δ) −78.6. ESI-MS *m/z* 766 [M^{3+}][2OTf$^-$].

Results and Discussion

Synthesis. The addition of two stoichometric equivalents of TMS-OTf to SCl_2 in CH_2Cl_2 at −78 °C generated an orange solution, to which a para-substituted pyridine (**5Ph**, R = Ph; **5NMe₂**, R = NMe₂; **5CF₃**, R = CF₃) in CH_2Cl_2 was added resulting in the immediate generation of a copious amount of white precipitate (Scheme 2). The supernatant was removed by decantation or filtration and the white solids were dried in vacuo. Proton NMR spectroscopy of the bulk materials in CD_3CN displayed a single set of signals consistent with only one pyridine

Scheme 2. Synthetic Route to Pyridine Stabilized Sulfur(II) Dications (**5Ph**, **5NMe$_2$**, and **5CF$_3$**)

5Ph: R = Ph
5NMe$_2$: R = NMe$_2$
5CF$_3$: R = CF$_3$
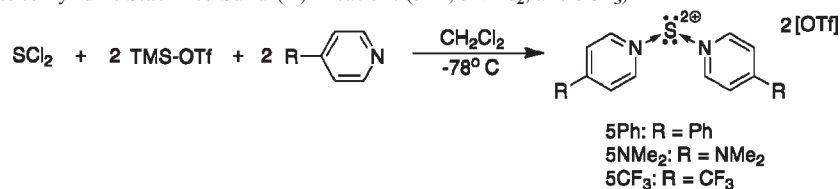
Scheme 3. Reactivity of the Dicationic Systems with Organic Substrates
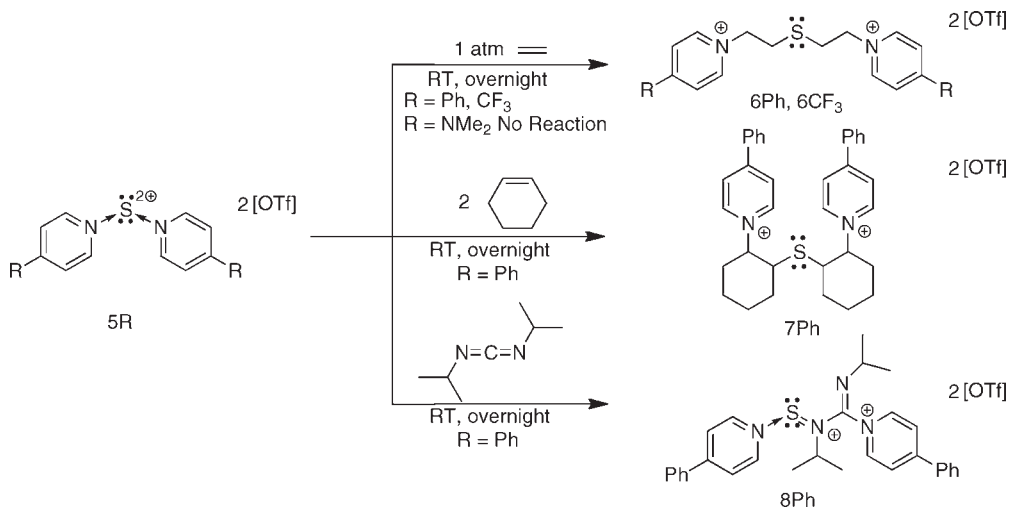
species present for all three derivatives. Diagnostic features were downfield shifts of the pyridine signals with respect to the free ligands, which is consistent with the bidentate and tridentate derivatives and is indicative of binding to an electron deficient center. The $^{19}F\{^1H\}$ NMR spectra of **5Ph**, **5NMe$_2$**, and **5CF$_3$** revealed signals for ionic triflate in solution ($\delta = -78.6$ ppm c.f. [NOct$_4$]- [OTf] $\delta = -78.5$ ppm) and **5CF$_3$** contained a second signal at -68.5 ppm for the trifluoromethyl group, also shifted downfield with respect to the free pyridine. X-ray diffraction experiments of **5Ph** and **5NMe$_2$** confirmed the identity of the compounds, two pyridine ligands coordinating to a dicationic sulfur center, consistent with the multinuclear NMR spectroscopic data. All three compounds were prepared in high yields (**5Ph**: 89%; **5NMe$_2$**: 93%; **5CF$_3$**: 87%) and were all extremely air/moisture sensitive, decomposing rapidly upon exposure to the open atmosphere.

We then carried out benchmark reactions of these new complexes using a series of organic substrates (Scheme 3). The reaction of **5Ph** with the simplest olefin, ethylene, was monitored by ^1H NMR spectroscopy and after 15 min elapsed, the reaction mixture began turning light brown. The ^1H NMR spectrum showed the emergence of a signal at $\delta = 5.41$ ppm for free ethylene, two overlapping triplets as well as four sets of triplets ranging between 2.9 and 5 ppm (Figure 2). After allowing the reaction to proceed for 2.5 h, there was a predominant set of resonances indicating the reaction was proceeding to a single product. It is also noteworthy that throughout the course of the reaction the $\{^1H\}^{19}F$ NMR spectrum displayed a peak characteristic of covalent triflate ($\delta = -75.0$ ppm). The reaction was left to stir overnight, allowing for complete conversion.

Single crystals of sufficient quality for X-ray diffraction experiments were grown from the bulk powder by vapor diffusion of Et$_2$O into a saturated acetone solution in the open atmosphere. The redissolved crystals in acetonitrile-d_6 gave two triplets at 4.73 and 3.19 ppm, which each integrated to four with respect to the ligand indicative of an equal number of pyridine ligands to ethylene groups in the product. These signals were shifted upfield from ethylene consistent with a change in hybridization from sp^2 to sp^3 at the carbon center. On the basis of these data the structure was assigned as **6Ph**, with the ethylene moiety inserted into the sulfur−nitrogen dative bond, which was confirmed by X-ray diffraction studies.

A proposed mechanism for this insertion is outlined in Figure 3. The first step likely involves dissociation of one of the pyridine ligands from **5R** giving **A**, which undergoes a cyclization with ethylene to produce the thiiranium ring **B**. Although a weak nucleophile, a triflate counterion ring opens to give **C**, where free pyridine in solution easily displaces the triflate (**D**). Although it is more intuitive to have the free pyridine act as the nucleophile in this step, covalent triflate signals are clearly present in the $^{19}F\{^1H\}$ NMR spectra (consistent with **C** and **G**), which subsequently disappear as the reaction proceeds (Supporting Information).[59] This process then occurs a second time (through **E**, **F**, and **G**) to yield the final product **6R**. In total 10 sets of triplets are expected; however, only six are clearly observed; the intermediates **A** and **E** are likely consumed very quickly, thus not observable on the NMR time scale and the overlapping signals are assigned to species **B** and **F** as they resemble peaks reminiscent of

(59) Huang, L.; Huang, X. *Electronic Encyclopedia of Reagents in Organic Synthesis*; John Wiley & Sons: New York, **2005**, RM226M.
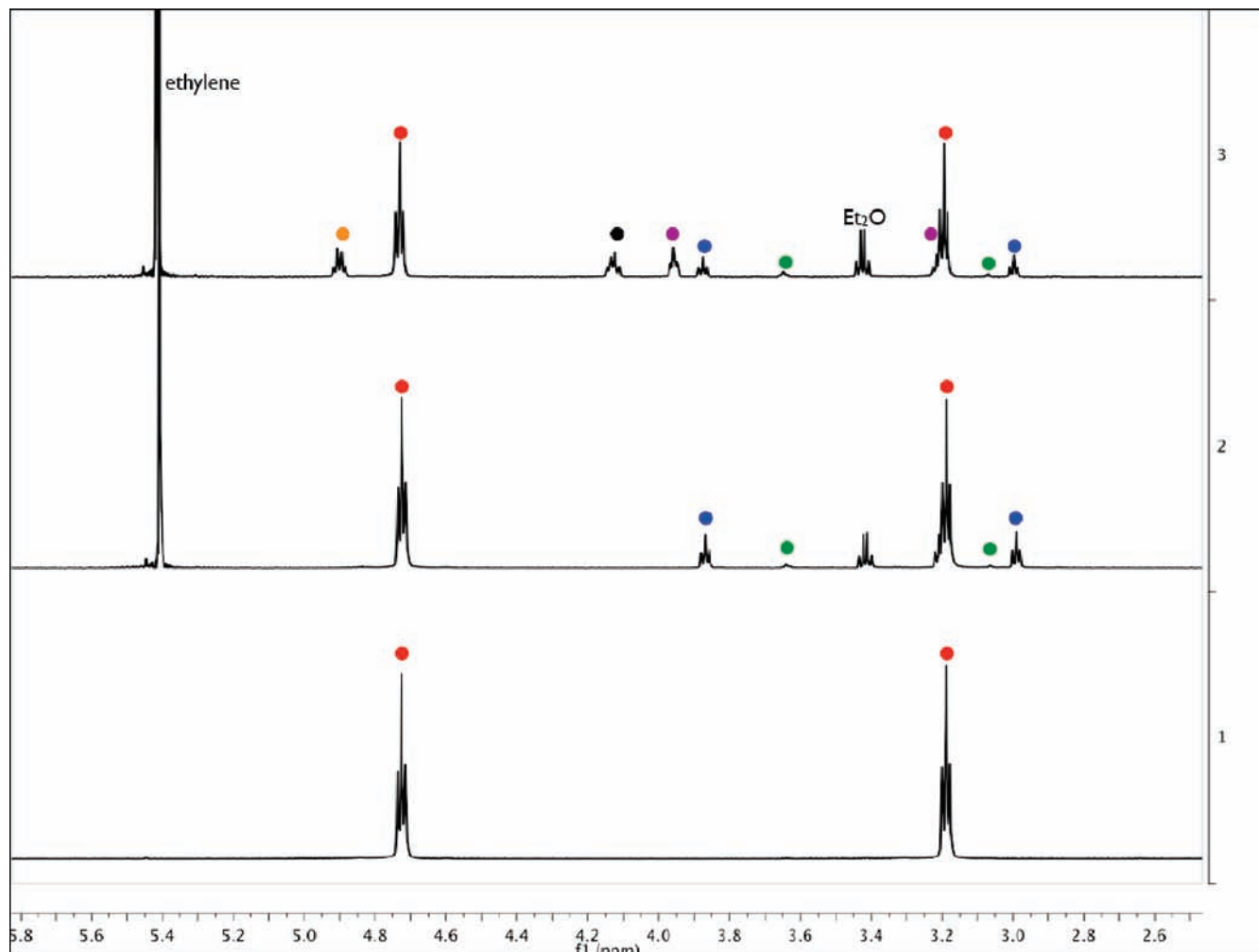
Figure 2. Stacked ^{1}H NMR plot of the reaction progress of **5Ph** with ethylene in CD$_3$CN zoomed in on the ethylene region; for the full sweep window refer to the Supporting Information. (3) Spectrum 15 min after the solution was exposed to ethylene; (2) spectrum after 2.5 h; (1) spectrum of purified **6Ph**. Orange and black dots denote thiiranium intermediates; purple, green, and blue dots denote other intermediates; red dot denotes product.

protons within a thiiranium ring.[30] Intermediates **C**, **D**, and **F** would each produce an additional two sets of signals and the asymmetric **G** two more set of triplets, to produce five pairs of triplets (total of 10). This mechanism is only a hypothesis but an in-depth kinetic study is necessary to clearly elucidate the definitive steps.

The analogous reactions were carried out with **5NMe$_2$** and **5CF$_3$**, examining a more electron donating group (NMe$_2$) at the para position as well as a more electron withdrawing group (CF$_3$) with respect to the phenyl substituted species to determine the effect of varying the donor strength of the ligand. The dimethylamino sub-stituted dication did not react at all with ethylene even at elevated pressures and temperatures (200 psi, 90 °C), whereas a faster reaction was observed for **5CF$_3$**. The proton NMR spectrum of the redissolved solids revealed similar resonances for the ethylene moiety, reminiscent of **6Ph**, consistent with the formation of the ethylene in-serted product **6CF$_3$**. This indicates the potential for tuning the system by taking advantage of the variability at the para position.

To see if the reactivity could be extended to other olefins, neat cyclohexene was added to an acetonitrile solution of **5Ph**. The solution slowly transformed to a light

brown color. After stirring overnight, the volatiles were removed in vacuo giving a brown paste. Proton NMR spectroscopy of the unpurified material indicated the pre-sence of primarily one cyclohexene containing product. Two successive recrystallizations of the material by vapor diffusion of Et$_2$O into acetone gave colorless crystals. The integrations in the ^{1}H NMR spectrum of the redissolved crystals in acetone-d_6 indicated the presence of an equiva-lent number of cyclohexyl groups and pyridine ligands. The two signals of the alkene protons were shifted to higher field with respect to cyclohexene. By analogy to the ethylene reaction, the product was assigned as **7Ph**, the product resulting from the addition of two cyclohexyl units into the S—N bonds. It is noteworthy that the pro-duct contains four chiral centers giving the possibility of several enantiomers. However, only a single diastereomer was observed by proton NMR spectroscopy.

To investigate the reactivity of these complexes with heteroatomic olefins, carbon—nitrogen bonds were stu-died using N,N′-diisopropylcarbodiimide (DIC). One equivalent of DIC was added to a solution of **5Ph** in CH$_3$CN, and the solution was stirred for 10 h resulting in a light brown color. The volatiles were removed in vacuo leaving a brown paste. The paste was redissolved in
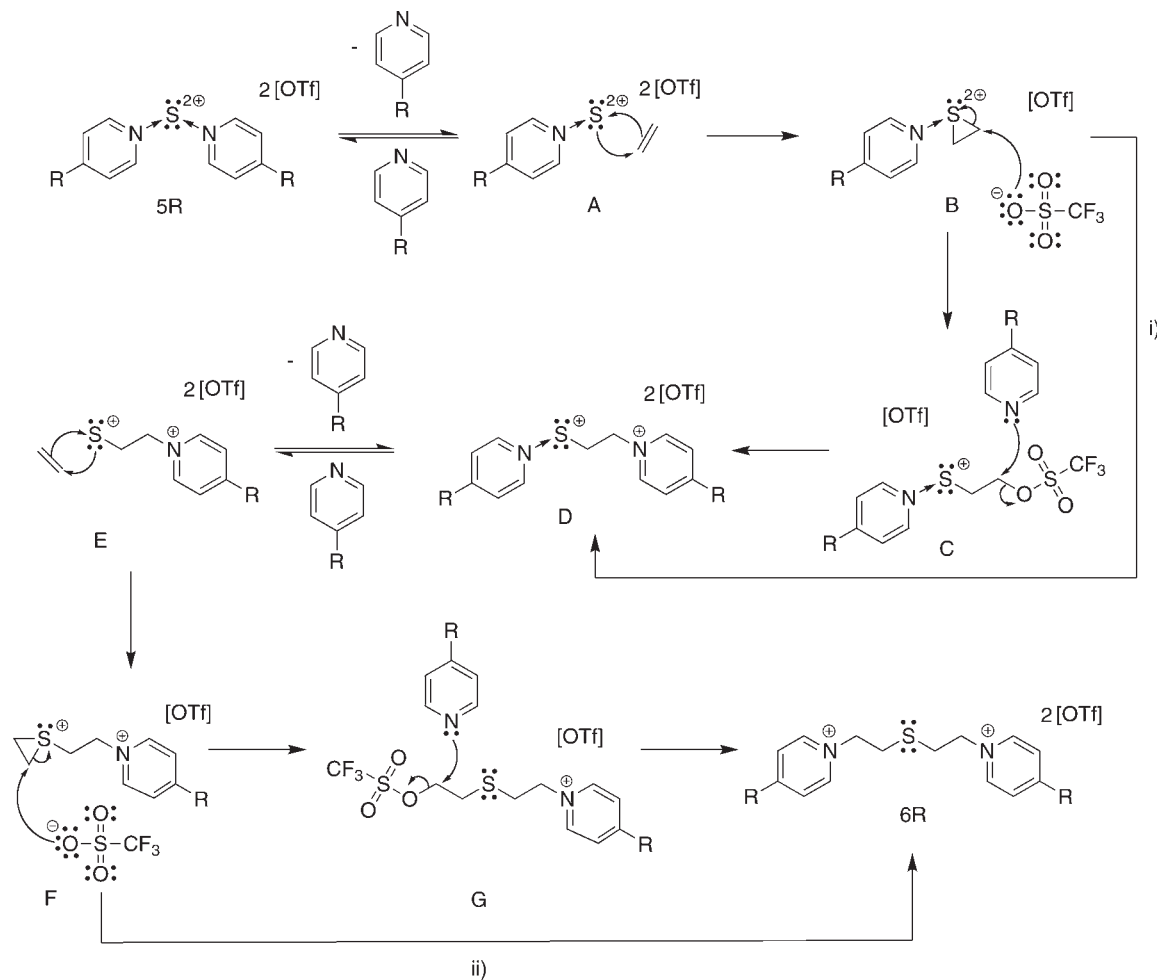
Figure 3. Proposed mechanism of the conversion of **5R** to **6R**. In steps (i) and (ii) pyridine could also ring open the thiiranium intermediate.
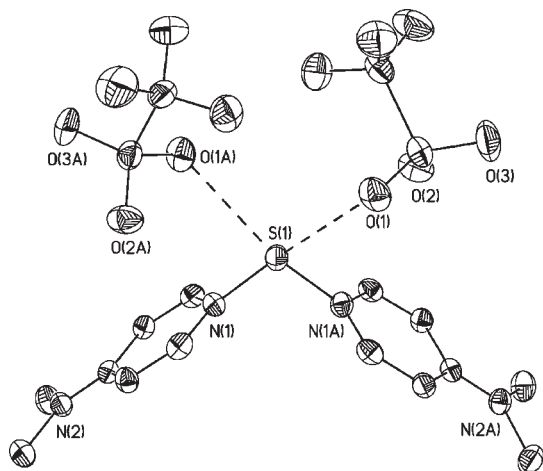

Figure 4. Solid-state structure of **5NMe₂**. Ellipsoids are drawn to 50% probability and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): S(1)−N(1) 1.717(3), S(1)···O(3) 2.888(3), N(1)−S(1)−N(1A) 101.1(2).

acetonitrile and diethylether was added. Upon storing the solution at −35 °C, a white precipitate was obtained. Redissolving the solids in CD_3CN and obtaining a ^1H NMR spectrum, a loss of symmetry in the DIC moiety was apparent. Two sets of resonances for the pyridine protons indicated two chemically inequivalent pyridines
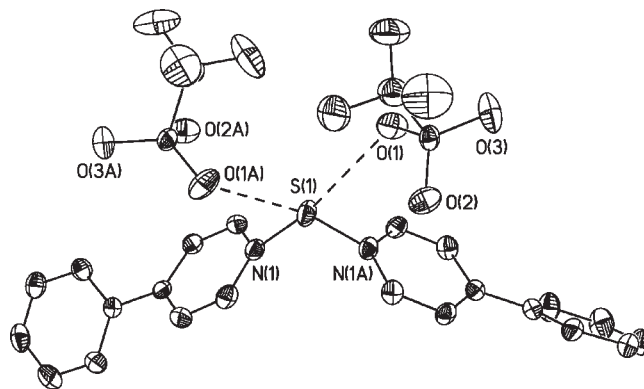

Figure 5. Solid-state structure of **5Ph**. Ellipsoids are drawn to 50% probability and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): S(1)−N(1) 1.737(3), S(1)···O(1) 2.829(3), N(1)−S(1)−N(1A) 100.3(2).

were present and in total, integrated in a 2:1 ratio with respect to the DIC molecule, indicative of the incorporation of a single diimide into the product. The $^{19}F\{^1H\}$ NMR spectrum displayed a single peak consistent with ionic triflate in solution ($\delta = -78.5$ ppm). On the basis of these data, the product was tentatively assigned as the addition product of the sulfur dication into one of the C=N bonds in DIC (**8Ph**) with the formation of a new S−N bond and a new N−C bond with the diimide. X-ray
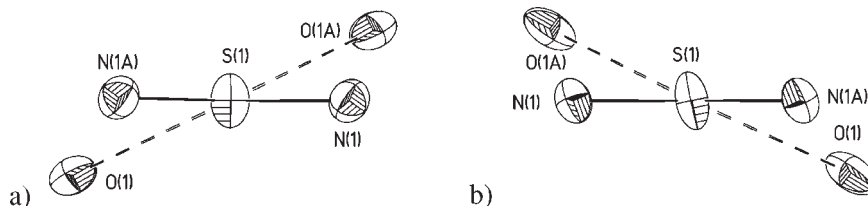
Figure 6. View of the dicationic sulfur center in (a) **5NMe$_2$** and (b) **5Ph**, interplanar O−S−O and N−S−N angles: **5Ph**: 25.5° and **5NMe$_2$**: 26.4°.
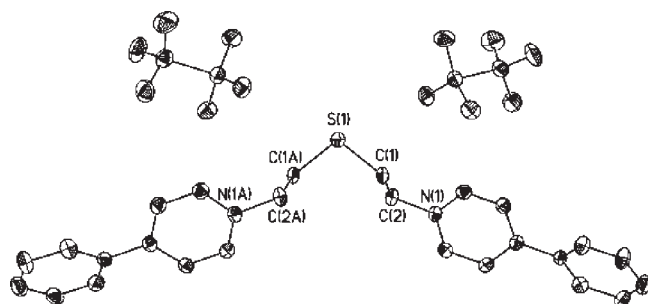

Figure 7. Solid-state structure of **6Ph**. Ellipsoids are drawn to 50% probability, and all hydrogen atoms and solvates are omitted for clarity. Selected bond lengths (Å) and angles (°): S(1)−C(1) 1.805(2), N(1)−C(2) 1.487(3), C(1)−C(2) 1.518(3), C(1)−S(1)−C(1A) 103.28(16).
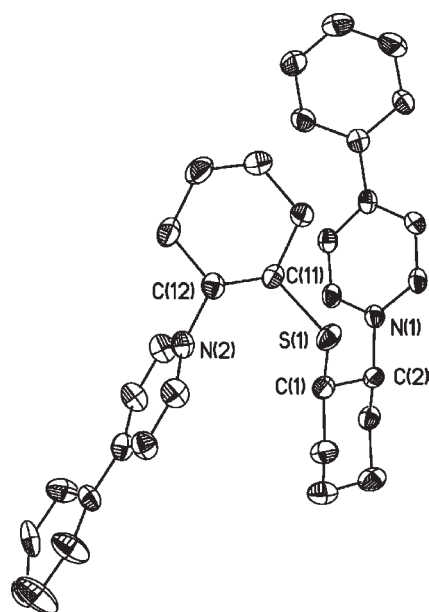

Figure 8. Solid-state structure of **7Ph** displaying the molecule in the *R, R, R, R* − configuration within the unit cell; only one position of the disordered phenyl group is shown. Ellipsoids are drawn to 50% probability and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): S(1)−C(1) 1.824(4), S(1)−C(11) 1.824(4), C(1)−C(2) 1.530(5), C(11)−C(12) 1.519(5), C(2)−N(1) 1.490(5), C-(12)−N(2) 1.496(5), C(1)−S(1)−C(11) 106.92(18).

diffraction experiments confirmed the identity of this reaction product.

X-ray Crystallographic Studies. Compounds **5Ph** and **5NMe$_2$** were crystallized by vapor diffusion of Et$_2$O into acetonitrile yielding colorless crystals. The two compounds are isostructural, and are both in the *C2/c* space group with the molecule lying on a center of symmetry (Figures 4 and 5). Both pyridine ligands are bound to the dicationic sulfur center with bond lengths slightly shorter than typical nitrogen−sulfur single bonds, which is
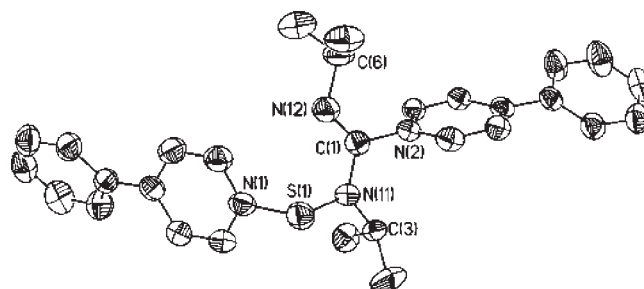

Figure 9. Solid-state structure of **8Ph**. Ellipsoids are drawn to 50% probability and all hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): S(1)−N(11) 1.664(4), S(1)−N(1) 1.801(4), N(11)−C(1) 1.379(5), C(1)−N(12) 1.254(5), N(2)−C(1) 1.477(5), N-(1)−S(1)−N(11) 105.37(17), S(1)−N(11)−C(3) 121.4(3), C(1)−N-(11)−C(3) 122.8(3), S(1)−N(11)−C(1) 115.8(3).

attributed to their attraction to the electropositive center (1.737(3), **5Ph** and 1.717(3), **5NMe$_2$** c.f. 1.76 Å).[60] The difference in these bond lengths is subtle but surprisingly; this has a large influence in the reactivity. The N−S−N bond angles are 101.1(2)° and 100.3(2)°, consistent with two ligands and two lone pairs or an AX$_2$E$_2$ electron pair configuration. The oxygen atoms of the triflate anions do lie within the sum of the van der Waals radii for O and S (closest contact S···O 2.829(3), **5Ph**; S···O 2.888(3), **5NMe$_2$**; c.f. 3.25 Å); however, they do not complete a square planar geometry about the sulfur center (Figure 6) which would be consistent with covalently bound triflate to a chalcogen center.[60,61] In fact, the interplanar bond angles show a significant deviation from an ideal square planar geometry (25.5° for **5Ph**, 26.4° for **5NMe$_2$** c.f. 0°). Furthermore, there is no elongation in the corresponding sulfur−oxygen bond length with respect to the other sulfur−oxygen bonds in the triflate anions, which would be observed if a covalent interaction were present [**5Ph**: S(2)−O(1) 1.430(3), c.f. 1.424(3) and 1.434(3); **5NMe$_2$**: S(2)−O(1) 1.435(3) c.f. 1.430(3) and 1.442(3)].[38] On the basis of these data, the molecules were assigned the structures of a dicationic sulfur(II) center stabilized by two pyridine ligands with two triflate counterions. Despite numerous attempts, unfortunately we were unable to grow crystals of suitable quality for X-ray diffraction experiments for **5CF$_3$**. However, on the basis of the analogous spectroscopic data, the structure was assigned to **5CF$_3$**.

Upon the examination of the solid-state structure of the reaction product with ethylene, **6Ph**, an ethyl group is now found between the pyridine nitrogen and the formerly dicationic sulfur center from **5Ph**, meaning a new N−C bond with the pyridine ligand and a S−C bond with the

(60) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, 1960.

(61) Krebs, B.; Ahlers, F. P. *Adv. Inorg. Chem.* **1990**, *35*, 235–317.

Table 1. X-ray details for **5Ph**, **5NMe$_2$**, **6Ph·(CH$_3$)$_2$CO**, **7Ph**, and **8Ph**

compound	5Ph	5NMe$_2$	6Ph·(CH$_3$)$_2$CO	7Ph	8Ph
empirical formula	C$_{24}$H$_{18}$F$_6$N$_2$O$_6$S$_3$	C$_{16}$H$_{20}$F$_6$N$_4$O$_6$S$_3$	C$_{31}$H$_{32}$F$_6$N$_2$O$_7$S$_3$	C$_{36}$H$_{38}$F$_6$N$_2$O$_6$S$_3$	C$_{31}$H$_{32}$F$_6$N$_4$O$_6$ S$_3$
FW (g/mol)	640.58	574.54	754.77	804.86	766.79
crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic
space group	$C2/c$	$C2/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	25.234(3)	20.142(4)	30.303(6)	11.287(2)	8.3050(5)
b (Å)	9.8706(13)	10.009(2)	10.033(2)	12.121(2)	15.0203(10)
c (Å)	11.2571(15)	11.392(2)	11.027(2)	14.544(3)	15.1251(10)
α (deg)	90	90	90	83.80(3)	107.243(4)
β (deg)	104.2900(10)	90.17(3)	92.44(3)	89.35(3)	95.421(4)
γ (deg)	90	90	90	72.99(3)	98.949(3)
V (Å^3)	2717.1(6)	2296.5(8)	3349.4(12)	1891.1(7)	1760.2(2)
Z	4	4	4	2	2
D_c (mg m^{-3})	1.566	1.662	1.497	1.413	1.447
radiation, λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
temp (K)	173(2)	150(2)	150(2)	150(2)	150(2)
$R_1 [I > 2\sigma I]^a$	0.0596	0.0583	0.0505	0.0664	0.0759
$wR_2 (F^2)^a$	0.1657	0.1323	0.1375	0.1914	0.2325
GOF $(S)^a$	1.283	1.065	1.042	1.013	1.043

^{a} $R_1(F[I > 2(I)]) = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR_2(F^2 [\text{all data}]) = [w(F_o^2 - F_c^2)^2]^{1/2}$; $S(\text{all data}) = [w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = no. of data; p = no. of parameters varied; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ and a and b are constants suggested by the refinement program.

dicationic center were generated (Figure 7). The carbon–carbon bond length has elongated significantly from that of ethylene (1.33–1.518(3) Å) consistent with the conversion from a double to a single bond. The newly formed N–C bond and S–C bonds are also consistent with single bonds confirming the structure as **6Ph**.

The addition reaction product with cyclohexene showed a related solid-state structure (Figure 8). However, the fact that the carbon atoms bear an additional group in comparison to ethylene gives the potential for multiple products, as there are four chiral centers in the molecule. On the basis of the ^{1}H NMR data, only one species was observed. Compound **6Ph** crystallized in the triclinic space group $P\bar{1}$, with two molecules lying within the unit cell related to one another by a center of symmetry. The asymmetric unit revealed a molecule in the R, R, R, R − configuration; however, given the centrosymmetric space group, the other molecule in the unit cell is its mirror image (S, S, S, S − configuration). This means the crystal is a 50:50 racemic mixture of the two enantiomers. This is consistent with the ^{1}H NMR spectroscopic data as both species would produce identical spectra. It can be concluded that the pyridine and sulfur in all cases are positioned anti to one another, which is reasonable as this arrangement imposes more favorable steric interactions.

Examination of the solid-state structure of **8Ph** (Figure 9) shows that another addition reaction has occurred. One pyridine group remains bound to the sulfur center, and the other has migrated to the central carbon atom in the diimide unit. The sulfur is now bound to a nitrogen atom from the DIC species. The sulfur–nitrogen bond lengths are 1.664(4) and 1.801(4) Å for the newly formed bond to the diimide and for the pyridine ligand, respectively. The latter is longer than that in the dication, which could be attributed to the reduced cationic character at sulfur. The newly formed S–N bond is shorter than a single bond, indicating a strong interation with the DIC moiety. The nitrogen–carbon bond lengths from the DIC unit are 1.379(5) and 1.254(5) Å, consistent with the retention of one double bond and the elongation of the other to a single bond. The geometry about the nitrogen atom is trigonal planar (sum of angles = 360.0°). The

most accurate structural representation would have the positive charge on the nitrogen atom from the DIC moiety and a double bond to the sulfur center. The elongated pyridine sulfur interaction from the dication is a result of the pyridine being bound to a neutral sulfur atom (Table 1).

Conclusion

Through these studies, a new series of sulfur(II) dications were synthesized by utilizing monodentate pyridine ligands to stabilize the sulfur center. These compounds may be described as pyridinium salts, but based on the lability of the sulfur–nitrogen bond in the chemistry of the molecules, the dative model is more accurate, and these species represent the first monodentate stabilized sulfur(II) dications. The substitution at the para position on the pyridine ring could be altered, which was influential on the reactivity at the sulfur center. This proved to be useful in reacting the dications with olefins as the strong donor ligand dimethylaminopyridine prevented any reaction from occurring, while the phenyl and trifluoromethyl substituted pyridine readily reacted inserting the olefin into the sulfur–nitrogen bond. The reaction is very similar to that of sulfur dichloride with ethylene in the production of sulfur mustard. The reaction products possess a carbon atom bound to a pyridinium center, which represents an excellent leaving group and should be useful in the onward synthesis of new organic molecules. The system was extended from ethylene to cyclohexene showing the analogous reactivity producing only products with substituents anti to one another. Moreover, the addition chemistry was also transferable to carbon–nitrogen bonds. The 1:1 stoichiometric reaction with N,N'-diisopropylcarbodiimide resulted in the pyridine bonding to the central carbon in the diimide and a covalent sulfur nitrogen bond. Current efforts are focused on modifying the current system in hopes of activating other small molecules with sulfur reagents.

Supporting Information Available: CIF files for **5Ph**, **5NMe₂**, **6Ph**, **7Ph**, and **8Ph**, FT-IR, and FT-Raman characterization data and stacked plot NMR spectra for the reaction of **5Ph** and ethylene. This material is available free of charge via the Internet at http://pubs.acs.org.