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Preparation of 1,3,2,4,6-Dithiatriazines with Substituted Aryl Groups and the X-ray Crystal Structure of the (4-Chlorophenyl)dithiatriazine Dimer

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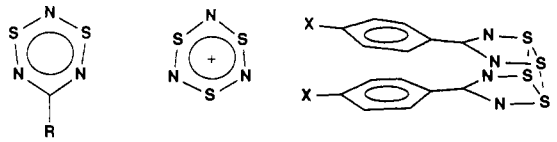
The synthesis of $XC_6H_4CN_5S_3$, $XC_6H_4CN_3S_2Cl_2$, $\{XC_6H_4CN_3S_2\}_2$, and $XC_6H_4CN_3S_2{\cdot}C_7H_{10}$ (X = 4-CH_3, 4-Cl, 3-CF_3, 4-CF_3, 4-CH_3O, 4-C_6H_5) is reported. The crystal structure of $\{4\text{-}ClC_6H_4CN_3S_2\}_2$ was determined by a single-crystal X-ray diffraction study. The compound crystallizes in the triclinic space group $P\bar{1}$ with $Z = 2$ in a cell of dimensions $a = 6.107$ (1) Å, $b = 12.070$ (2) Å, $c = 13.206$ Å, $\alpha = 113.73$ (1)°, $\beta = 99.04$ (2)°, and $\gamma = 97.53$ (2)°. The least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms converged at $R = 0.084$ for 1480 unique reflections. The structure is a cofacial dimer of $4\text{-}ClC_6H_4CN_3S_2$ units, with short S···S contacts of 2.509 (4) and 2.534 (4) Å. Dimer units are stacked head-to-tail in the crystal along the *bc* diagonal. ^{1}H-NMR studies of the more soluble compounds show significant shielding of the aromatic protons (0.3–0.6 ppm) attributable to ring currents of adjacent aromatic rings. This is consistent with the preservation in solution of the wedge-shaped dimeric structure found in the solid state.

Introduction

Dithiatriazines **1** with two-coordinate sulfur and nitrogen atoms and a variety of substituents R are an important but elusive class of thiazyl heterocycle.[1-4] Formally these planar rings are 8π



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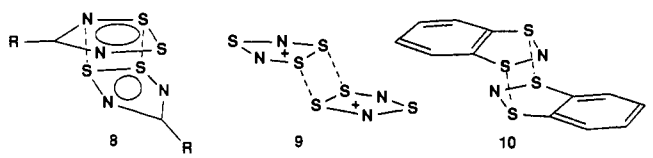
electron systems and thus antiaromatic. They are isoelectronic with the (unknown) $S_3N_3^+$ cation **2**. A variety of them have been reported, where R = CF_3 or NR_2.[1] The materials obtained have been successfully derivatized by halogens or olefins, but little is known about the parent compounds. In our initial paper on the preparation of the free dithiatriazine ring, we demonstrated that the reduction of dichloride **4a** led to a stable, insoluble, cofacial dimer, **5a**.[2]

The observed dimerization was attributed to the coupling of triplet ground states in **1** to achieve a singlet ground state. The key theoretical questions regarding the electronic structure of the gas-phase structure of a free dithiatriazine have been addressed in a recent paper by Goddard and Oakley.[3] Ab initio calculations indicate that the ground state of the model compound (**1**, R = H) is in fact a structurally distorted singlet species with C_s symmetry. However, the process observed in nature is not one of distortion but rather association. This more complex process has not yet been amenable to theoretical treatment.

An interesting alternative route to **5a** and to the closely related derivative with a *p*-chlorophenyl substituent **5c** has been reported by Banister and co-workers.[4] They obtained these dithiatriazines from the corresponding 1,2,3,5-dithiadiazolium dimers **7** in a direct-current nitrogen glow discharge. The fixation of atomic nitrogen by a main-group compound is quite unusual. The Durham group used infrared spectroscopy and X-ray powder diffraction to verify the formation of **5a**.

The cofacial arrangement of the dithiatriazines in dimeric **5a** is not the only structure imaginable. Twisted structures, **8**, exist



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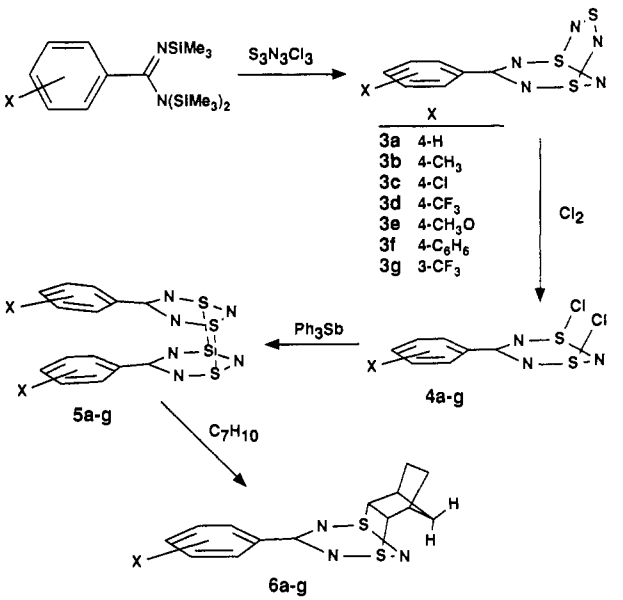
for some 1,2,3,5-dithiadiazolium dimers,[5,4b] and an opposed structure, **9**, is known for several salts of the $S_3N_2^+$ dimer[6] and also for the dimer of 1,3,2-benzodithiadiazole, **10**.[7] Even more

Scheme I



interesting is the relative arrangement of the dimer units in the crystal, which under suitable circumstances could lead to stacks with short interdimer contacts. We report here the single-crystal X-ray structure of **5c**. It was found to be isostructural with **5a**. Although disappointing to our goal of extended structures, this

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result provides support for the mechanism hypothesized by the Durham group for the nitrogen fixation reaction.

An important outstanding question is the structure of dithiatriazines in solution. **5a** was found to be extremely insoluble, and all attempts to dissolve it in a variety of solvents were accompanied by extensive decomposition and the appearance of an ESR signal due to the NSN^- radical anion,[2] a well-known decomposition product of binary sulfur nitrides. Our goal in this work has been to extend the number of fully-characterized dithiatriazines by substituent modification at the para and meta positions of the aryl ring in type **5** compounds. Both electron-donating and electron-withdrawing groups[8] have been employed in order to probe electronic effects on dithiatriazine structure. We report on the synthesis and characterization of six new derivatives, **5b–g**. NMR studies on the more soluble ones provide clear evidence that the dimeric structure found in the solid state is preserved in solution.

Results and Discussion

Synthesis of Dithiatriazines. The synthetic route to the dithiatriazines **5b–g** is given in Scheme I. The electron-withdrawing substituents X = Cl and CF_3 and the electron-donating substituents X = CH_3 and CH_3O were employed. **5f**, where X = Ph, was also prepared, but not unexpectedly turned out to be extremely insoluble. We have not succeeded in preparing this compound in crystalline form, though its structure in the solid state could be very interesting.

The required persilylated amidines were prepared by the literature method. The addition of such amidines to trimeric thiazyl chloride under mild conditions seems to be a general reaction. The bicyclic derivatives of type **3** were obtained in all cases, as evidenced by the mass spectral and elemental analysis. The similarity in the IR spectra of **3a–g** strongly suggests they have a similar cage structure to that of **3a**, the structure of which has been obtained by X-ray crystallography.[9] The crystal structure of $CF_3CN_5S_3$ has been reported, and this is also very similar to **3a**.[1e] Incidentally, the amidine coupling reaction works equally well for the preparation of phosphorus-containing bicyclic compounds using $R_2P(NSiMe_3)N(SiMe_3)_2$.[10]

Oxidative cleavage of the –N=S=N– bridge with elemental chlorine has also proved to be applicable to all our type **3** compounds. The electronic influence of the substituents X was quite marked on the rate of reaction of the type **3** compounds with chlorine. With X = CF_3 or Cl, completion of the chlorination reaction typically took 1–2 h at 20 °C on the scale reported. Where X = CH_3 or CH_3O, reaction was complete after 20 min at 0 °C. In summary, electron-withdrawing substituents on the C_6H_4 ring retard the reaction of Cl_2 with the bicyclic cage, whereas electron-donating groups are activating. It is interesting to note that the directly-bound trifluoromethyl group in $CF_3CN_5S_3$ renders this cage totally resistant to chlorine or neat SO_2Cl_2.[11]

Dithiatriazine dichlorides **4b–g** are readily reduced by the action of Ph_3Sb (1 equiv) to form the "free" dithiatriazine compounds. These were all found to be thermally stable, buff-colored solids. Careful mixing of the reagents with a minimum of agitation leads to the precipitation of fine crystalline solids. These crystals range in color from yellow-bronze for the CH_3O substituent to a dark amber for the two CF_3-containing compounds. In this manner, small plates of **5c** were grown, which were suitable for X-ray diffraction. Despite many attempts, X-ray-quality crystals have not yet been obtained for the other dithiatriazines.

Characterization of Dithiatriazines. All the dithiatriazines have the correct chemical analysis. Their mass spectra contain strong peaks for the parent ion; for **5c** this is the 100% peak, reflecting the greater volatility imparted by the CF_3 group. The fragmentation patterns for all six compounds are similar but vary in the intensity of each of the fragments produced. Olefin derivatives have also been prepared using norbornene. The adducts **6b–g** have been characterized by microchemical analysis and high-field ^{1}H-NMR spectroscopy. The spectra of all the norbornene adducts are extremely similar and are consistent with the structure indicated in Scheme I. The norbornene adduct of **2**, i.e. $S_3N_3 \cdot C_7H_{10}^+$, adopts a similar structure in the solid state, but ^{1}H NMR data are not available for comparison with our compounds.[12] The similarity among the spectra of **6b–g** suggests that the adducts are quite rigid in solution.

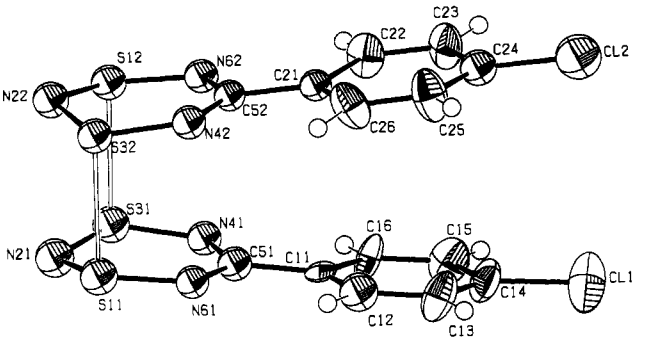

Figure 1. ORTEP drawing of **5c**, showing the atom-numbering scheme and the "wedge" shape of the dimer unit. The closest inter-ring contacts occur at the S atoms (2.509 and 2.534 Å), the rings sloping gently so that the Cl atoms are furthest apart. The (calculated) hydrogen atoms have been included with artificially small temperature coefficients.

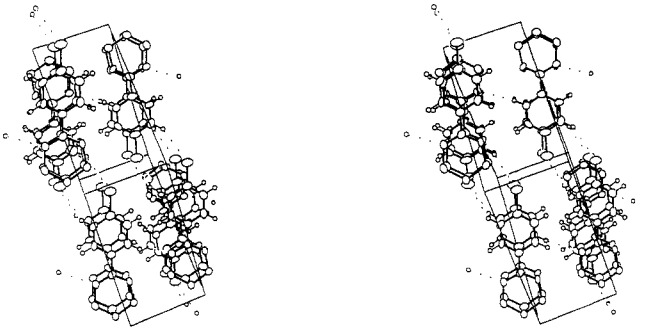

Figure 2. Crystal packing diagram of **5c** viewed perpendicular to the *bc* diagonal. The internuclear contacts mentioned in the text are indicated by dashed lines.

Crystal and Molecular Structure of 5c. This compound crystallizes as a head-to-head dimer which is very similar to the solid-state structure of the phenyl analogue[2] (Figure 1). The two unique molecules in the asymmetric unit form a discrete dimer with very close nonbonded contacts between the sulfur atoms of 2.509 (4) and 2.534 (4) Å for S(11)–S(32) and S(12)–(31), respectively. The 2.509 (4) Å value is somewhat shorter than the distances (2.526 and 2.532 Å) observed in the structure of **5a**. The structure of **5c** is thus slightly more skewed than **5a**. For comparison, the sum of the van der Waals radii for sulfur is 3.60 Å,[13] while a typical S–S single bond is 2.04 Å.[14] The transannular S···S contact in S_4N_4 is 2.586 Å.[15]

The dimer units are stacked head-to-tail, giving the pattern of two dithiatriazine rings stacked above two phenyl rings in infinite columns running along the *bc* diagonal (Figure 2). The interdimer structure of **5c** bears a striking resemblance to that of **5a**.[2] Both compounds crystallize in the same space group, and they have very similar solid-state structures. The cell volume of **5c** is slightly

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Table I. ^{1}H NMR Data (δ) for Dithiatriazines, **5**, and Olefin Adducts, **6**[a]

compd	H_2	H_3	H_4	H_5	H_6
5b	7.13 d (8)	6.63 d (8)			
6b	7.73 d (8)	7.12 d (8)			
$\Delta\delta$[b]	+0.65	+0.49			
5d	7.45 d (7)	7.16 d (7)			
6d	7.95 d (8)	7.57 d (8)			
$\Delta\delta$	+0.50	+0.41			
5e	7.26 d (9)	6.42 d (9)			
6e	7.80 d (9)	6.81 d (9)			
$\Delta\delta$	+0.54	+0.39			
5g	7.56 s		7.32 d (8)	7.02 t (8)	7.51 d (8)
6g	8.05 s		7.63 d (8)	7.43 t (8)	8.04 d (8)
$\Delta\delta$	+0.59		+0.31	+0.41	+0.53

[a] The protons attached to the aromatic ring are numbered sequentially, with the dithiatriazine ring as a substituent at position 1. The protons ortho to the latter are always found at lowest field; assignments are based on ^{1}H–^{13}C heteronuclear correlation experiments on **6**. $CDCl_3$ was used throughout as solvent and internal reference, $\delta(CHCl_3) = 7.25$ ppm. Spectra for **5** were obtained in 10-mm sample tubes under vacuum using a broad-band probe; those for **6** were acquired under aerobic conditions in a 5-mm high-resolution probe. Nonaromatic proton signals for **6** are reported in the Experimental Section. [b] $\Delta\delta = \delta(\mathbf{6}) - \delta(\mathbf{5})$.

expanded to accommodate the larger 4-Cl substituent. There are weak contacts between the columns of dimers, as indicated in Figure 2. The contact from H(12) to N(62) at 3.025 (9) Å connects adjacent stacks of dimers in the *a* direction, while the contacts Cl(1)–H(23) and Cl(2)–H(15) connect to a second centrosymmetrically related dimer pair across the *bc* diagonal with distances 3.165 (5) and 3.027 (5) Å. None of these contacts appear to be responsible for the reversed orientation of subsequent dimer pairs along the infinite stacks. In fact it is almost certainly the efficient packing of the wedge-shaped dimer units in a "dovetail alignment" that accounts for the observed sequence.

By comparing the published infrared spectrum of **5c** with our own, we are now able to confirm the preparation of this compound by the nitrogen plasma route of Banister et al. They are identical in peak positions and general appearance. Banister et al. have emphasized that the plasma route is severely constrained by structural considerations, on the basis of the known crystal structures of **5a** and **7** (X = H). The dithiadiazolium substrate must be of low volatility and have a crystal structure which is open to infusing N atoms. A driving force for the conversion is undoubtedly the stronger interannular bonding in the dithiatriazine dimers (S···S contacts are 3.11 Å in **7** (X = H) and ca. 2.5 Å in **5a,c**). In this context, although the crystal structure of the corresponding **7** (X = Cl) is not known, the fact that **5a** and **5c** are isostructural is significant. Certainly whatever mechanism is responsible for the nitrogen fixation reaction is common to both compounds.

Apparently the nitrogen fixation route to the synthesis of dithiatriazines does not lead to single crystals. From our experience, recrystallization of these aryldithiatriazines is next to impossible. We were only able to obtain pristine crystalline material by growing the crystals directly from the reduction of the dichlorides under carefully controlled conditions. For this reason, the chemical sequence outlined here still seems a better and more general route for the preparation of dithiatriazines.

Electronic Structure of Dithiatriazines. Goddard and Oakley have recently analyzed the electronic structures of the two model compounds **1** (R = H, NH_2).[3] There has been considerable controversy regarding the ground-state electronic structure of this heterocyclic system, which could be a triplet by accidental equivalence of the electronegativity of R–C and S.[1b,d] Their calculations show that a distorted (C_s) geometry singlet state is more stable than the symmetric triplet (C_{2v}) by about 60 kJ mol^{-1}. Nature takes a different distortion coordinate in the solid state, and the properties of all the dithiatriazines reported here are consistent with a dimeric solid-state structure.

Solution NMR Studies. We have now managed to obtain proton NMR spectra for several of the more soluble derivatives, and the data are summarized in Table I. The most soluble compound is **5g**, but even this one is limited in $CHCl_3$ to about 5 mg mL^{-1}. Solubility in all the other common NMR solvents was even lower

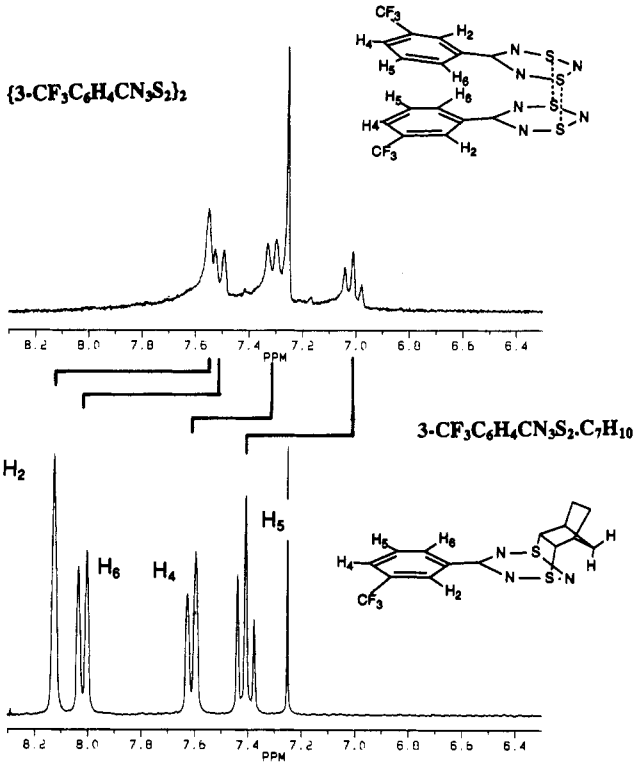

Figure 3. ^{1}H-NMR spectra of **5g** and **6g** (aromatic region only). The singlet at 7.25 ppm in both spectra is due to residual $CHCl_3$ in the solvent.

or else resulted in immediate hydrolysis of the compound. When these compounds are made up in $CDCl_3$ from a freshly-opened bottle, and the spectrum is acquired immediately, two sets of aromatic signals are invariably observed. One has the anomalously shielded values as reported in Table I. The other has more normal shifts for analogous monomeric compounds. (The ^{1}H NMR shifts of the monomeric olefin adducts of type **6** are included in Table I for the purpose of comparison.) However, after 10 min, the upfield set of signals decay away while the downfield set persists, until complete hydrolysis sets in. We therefore prepared samples in 10-mm NMR tubes equipped with Teflon Young valves and vacuum transferred degassed $CDCl_3$ dried over molecular sieves. Despite these precautions, small signals of the downfield set of signals persisted from some samples of dithiatriazines. However, picking and dissolving only single crystals for the NMR studies causes the downfield signals to disappear completely, leaving only the anomalously shielded set of aromatic proton resonances in the spectra. We conclude that the downfield signals are due to residual impurities introduced probably during the synthesis of the dimers. We attribute the anomalous shielding in the upfield set to aromatic ring-current effects between the two eclipsed aromatic rings in the dimeric dithiatriazine.

Figure 3 compares the spectra obtained for the meta-substituted dithiatriazine **5g** with that of the monomeric norbornene adduct **6g**. Note that only a single signal is seen for each of the ring protons in **5g**, consistent with C_2 symmetry for the dimer. The line broadening in the upper spectrum is due to the lower magnetic field homogeneity in the 10-mm probe. The extent of the aromatic shielding experienced by each proton in the ring is clearly dependent on the inter-ring separation at that point. The size of the shielding effect, if we take **6g** as an unperturbed system, varies with the position on the aryl ring: greatest for H_2 and H_6, less for H_5, and least for H_4. This provides striking evidence that the "wedge"-shaped dimeric structure seen in the solid state for **5a** and **5c** (Figure 1) is also found in solutions of **5g**. Similarly, for the para-substituted compounds in Table I, $\Delta\delta$ for the ortho protons is consistently greater than that for the meta ones. It seems that these also have the dimeric wedge structure in solution.

These simple ^{1}H NMR studies therefore suggest that, at least in slightly polar solvents, dithiatriazines dissolve as intact dimers.

We feel this is consistent with the very low solubility of these compounds. We have also conducted variable-temperature NMR studies on **5g**. Up to 70 °C, there is no evidence from NMR for dissociation of the dimer. No new signals were observed, nor was there any evidence of further line broadening which would be expected if dissociation to a diradical monomer occurred.

A preliminary ^{13}C NMR study of **5g** has also been undertaken. Prohibitively long data acquisition (i.e. 75 h) was required to obtain passable S/N. The ^{13}C chemical shifts do not differ markedly from those of **6g**. So far we have not been able to detect an effect on the structure or solution behavior of the various para and meta substituents, other than on solubility. Further studies (electronic spectral and electrochemistry) are under way. All solution work with dithiatriazines must use ultrapure material (preferably macroscopic crystals) and be performed under vacuum for the complete exclusion of air and moisture.

Summary

We have demonstrated the general utility of the synthetic method first developed for the preparation of $PhCN_3S_2$ in the synthesis of related aryl-substituted dithiatriazines. The products are generally more crystalline than the products Banister et al. achieve by the plasma nitrogen route, and we have been able to obtain the single-crystal X-ray structures of **5a** and **5c**. In view of the isostructural character of these two compounds, it will be interesting to obtain more crystal structures of dithiatriazines, and efforts to grow suitable crystals are continuing. The solution studies here have demonstrated that aryldithiatriazines dissolve as intact dimers with the same wedge structures observed in the solid state. The strong influence of this shape on the interdimer packing augurs against the realization of extended stacking of dithiatriazines with free aryl substituents.

Experimental Section

Starting Materials and General Procedures. Silylated amidines[16] and $S_3N_3Cl_3$[17] were prepared by the literature methods. Cl_2 (Matheson), triphenylantimony, 1,4-norbornadiene, and 1-norbornene (Aldrich) were obtained commercially and used as received. Solvents were Fisher reagent grade, or better, and were distilled from P_2O_5 (CCl_4, $CHCl_3$, CH_2Cl_2) or $LiAlH_4$ (pentane). CH_3CN was double-distilled from P_2O_5 and CaH_2. Unless otherwise indicated, all procedures were performed under an atmosphere of purified N_2 using a drybox, Schlenkware, and vacuum-line techniques. Infrared spectra were recorded on Perkin-Elmer 1330 grating and Bomem MB102 Fourier transform spectrometers. High-resolution mass spectra were recorded at the Mass Spectrometry Centre, University of Alberta. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ. The 250- and 400-MHz ^1H and 63-MHz ^{13}C NMR spectra were recorded on Bruker instruments.

Preparation of 3-$CF_3C_6H_4C\{NSi(CH_3)_3\}N\{Si(CH_3)_3\}_2$. A solution of 3-$CF_3C_6H_4CN$ (25.0 g, 146 mmol) in 25 mL of ether was added dropwise to a slurry of $(Me_3Si)_2NLi\cdot Et_2O$ (35.3 g, 146 mmol) in 200 mL of ether. The ^1H NMR spectrum of the solution showed complete conversion to 3-$CF_3C_6H_4C\{NSi(CH_3)_3\}NSi(CH_3)_3^-Li^+$ after 21 h ($\delta(SiMe_3)$ = –0.296 ppm in ether). A 175-mL volume of ether was distilled off, and 175 mL of toluene was added to the reaction mixture. A 17.5-g (160-mmol) amount of $ClSiMe_3$ in 25 mL of toluene was added dropwise, and the solution was refluxed. After 19 h the ^1H NMR spectrum of the solution indicated that the formation of the 3-CF_3 amidine was complete ($\delta(SiMe_3)$ = 0.09 ppm, $\delta(ClSiMe_3)$ = 0.21 ppm in toluene/ether). After cooling, LiCl was separated from the purple solution by filtration through glass wool. The solvent was distilled off, and the dark residue was subjected to vacuum distillation using an air condenser. The first fraction was a little *p*-$CF_3C_6H_4CN$. Product distilled as the second fraction, a dark yellow liquid, bp 89 °C (33.48 g, 57%). Anal. Calcd for $C_{17}H_{31}F_3N_2Si_3$: C, 50.45; H, 7.72; N, 6.92. Found: C, 50.58; H, 7.74; N, 6.74. IR (neat, 1650–200-cm^{-1} region): 1632 (s), 1431 (w), 1333 (s), 1248 (s), 1167 (s), 1134 (s), 1072 (m), 1001 (m), 882 (s), 843 (s, br), 756 (m), 723 (w), 704 (m), 685 (m), 650 (w), 629 (w), 520 (w), 471 (w), 424 (w), 330 (w), 248 (w). ^1H NMR: 7.60–7.39 (m, 4 H), 0.06 (s, 29 H) ppm. Mass spectrum: *m/z* 404 (M^+, 13%), 389 (M^+ – Me, 10%), 245 ($(Me_3Si)_2CNSiMe_3^+$, 14%), 75 ($H_2SiMe_3^+$, 100%).

Preparation of 4-$CH_3C_6H_4CN_5S_3$ (3b). A solution of 4-$CH_3C_6H_4CN(SiMe_3)_2NSiMe_3$ (16.8 g, 48 mmol) in 40 mL of methylene chloride was added without stirring to a solution of $S_3N_3Cl_3$ (11.98 g, 48 mmol) in 150 mL of methylene chloride over 30 min. The solvent was removed in vacuo, and the crude product was recrystallized from hot acetonitrile to give yellow-orange moisture-sensitive plates (11.36 g, 42 mmol, 87.5%), mp 149–150 °C. Anal. Calcd. for $C_8H_7N_5S_3$: C, 35.67; H, 2.62; N, 26.00; S, 35.71. Found: C, 35.82; H, 2.69; N, 26.26; S, 35.49%. IR (1600–250-cm^{-1} region): 1562 (w), 1415 (m), 1334 (s), 1292 (w), 1259 (m), 1182 (m), 1153 (w), 1091 (s), 1047 (sh), 1018 (vs), 927 (m), 833 (m), 796 (m), 773 (m), 717 (w), 671 (m), 595 (w), 576 (m), 549 (m), 505 (m), 489 (m), 474 (m), 393 (m), 347 (m), 254 (w). Mass spectrum: *m/z* 209 ($CH_3C_6H_4CN_3S_2^+$, 16%), 195 ($CH_3C_6H_4CN_2S_2^+$, 43%), 163 ($CH_3C_6H_4CN_2S^+$, 19%), 149 ($CH_3C_6H_4CNS^+$, 20%), 117 ($CH_3C_6H_4CN^+$, 100%).

Preparation of 4-$ClC_6H_4CN_5S_3$ (3c). A solution of 4-$ClC_6H_4CN(SiMe_3)_2NSiMe_3$ (22.2 g, 59.9 mmol) in 40 mL of warm CH_3CN was added without stirring to a solution of $S_3N_3Cl_3$ (14.66 g, 59.9 mmol) in 150 mL of acetonitrile. Golden platelets of product form as the mixture is placed on ice. After filtering under N_2, rinsing with small portions of acetonitrile, and drying in vacuo, the crude product (12.71 g, 43.9 mmol, 73.2%) was recrystallized from hot acetonitrile as orange plates, mp 131–132 °C. Anal. Calcd for $C_7H_4ClN_5S_3$: C, 29.01; H, 1.39; N, 24.17; S, 33.20. Found: C, 28.83; H, 1.59; N, 23.60; S, 32.53. IR (1600–250-cm^{-1} region): 1591 (m), 1483 (sh), 1414 (s), 1337 (s), 1234 (w), 1173 (w), 1155 (w), 1105 (sh), 1088 (s), 1028 (s), 1012 (vs), 989 (s), 925 (m), 841 (m), 788 (m), 742 (s), 709 (m), 686 (w), 661 (w), 555 (s), 540 (m), 507 (m), 466 (sh), 451 (s), 381 (w), 341 (w). Mass spectrum: *m/z* (reporting ^{35}Cl) 229 ($ClC_6H_4CN_3S_2^+$, 4%), 215 ($ClC_6H_4CN_2S_2^+$, 18%), 183 ($ClC_6H_4CN_2S^+$, 4%), 169 ($ClC_6H_4CNS^+$, 10%), 137 ($ClC_6H_4CN^+$, 100%).

Preparation of 4-$CF_3C_6H_4CN_5S_3$ (3d). **3d** was prepared by the method of **3c** using 4-$CF_3C_6H_4CN(SiMe_3)_2NSiMe_3$ (10.0 g, 25 mmol) and $S_3N_3Cl_3$ (6.1 g, 25 mmol). Yield: 6.37 g (20 mmol, 80%). **3d** was recrystallized from hot CH_3CN as large golden plates, mp 154–156 °C. Anal. Calcd for $C_8H_4F_3N_5S_3$: C, 29.72; H, 1.25; N, 21.66; S, 29.75. Found: C. 29.66; H, 1.36; N, 21.59; S, 29.75. IR (1600–250-cm^{-1} region): 1537 (w), 1512 (w), 1423 (m), 1323 (m), 1261 (m), 1145 (w), 1111 (w), 1091 (m), 1062 (w), 1016 (s), 925 (w), 854 (m), 796 (s), 785 (m), 771 (sh), 721 (w), 700 (w), 682 (w), 574 (m), 553 (w), 524 (m), 505 (m), 480 (m), 410 (m), 395 (m), 333 (m), 279 (w). Mass spectrum: *m/z* 263 ($CF_3C_6H_4CN_3S_2^+$, 9%), 249 ($CF_3C_6H_4CN_2S_2^+$, 59%), 217 ($CF_3C_6H_4CN_2S^+$, 6%), 203 ($CF_3C_6H_4CNS^+$, 18%), 171 ($CF_3C_6H_4CN^+$, 100%).

Preparation of 4-$CH_3OC_6H_4CN_5S_3$ (3e). **3e** was prepared by the method of **3b** from 4-$CH_3OC_6H_4CN(SiMe_3)_2NSiMe_3$ (6.74 g, 18.4 mmol) and $S_3N_3Cl_3$ (4.52 g, 18.4 mmol). Yield: 3.65 g (12.7 mmol, 69%). **3e** was recrystallized from hot acetonitrile as yellow-orange plates, mp 138–141 °C. Anal. Calcd for $C_8H_7N_5OS_3$: C, 33.17; H, 2.47; N, 24.54; S, 33.71. Found: C, 33.67; H, 2.58; N, 24.45; S, 33.47. IR (1600–250-cm^{-1} region): 1510 (w), 1361 (w), 1334 (m), 1259 (s), 1176 (m), 1091 (sh), 1047 (m), 1024 (s), 927 (w), 842 (m), 777 (m), 756 (m), 694 (w), 669 (m), 574 (m), 553 (w), 513 (m), 470 (m), 424 (w), 381 (w), 322 (w), 300 (w), 279 (w). Mass spectrum: *m/z* 285 ($CH_3OC_6H_4CN_5S_3^+$, 3%), 257 ($CH_3OC_6H_4CN_3S_3^+$, 3%), 225 ($CH_3OC_6H_4CN_3S_2^+$, 26%), 212 ($CH_3OC_6H_4CN_2S_2^+$, 96%), 133 ($CH_3OC_6H_4CN^+$, 100%).

Preparation of 4-$C_6H_5C_6H_4CN_5S_3$ (3f). **3f** was prepared by the method of **3b** using 4-$C_6H_5C_6H_4CN(SiMe_3)_2NSiMe_3$ (2.4 g, 5.8 mmol) and $S_3N_3Cl_3$ (1.42 g, 5.8 mmol). Yield: 1.2 g (3.6 mmol, 72%). **3f** was recrystallized from methylene chloride at low temperature as yellow-orange plates, mp 139–140 °C. Anal. Calcd for $C_{13}H_9N_5S_3$: C, 47.11; H, 2.74; N, 21.13; S, 29.02. Found: C, 47.27; H, 3.00; N, 20.91; S, 29.23. IR (1600–250-cm^{-1} region): 1599 (m), 1558 (w), 1413 (s), 1363 (s), 1340 (vs), 1261 (s), 1199 (s), 1199 (w), 1176 (w), 1091 (s), 1020 (s), 912 (m), 854 (w), 796 (vs), 694 (m), 644 (w), 530 (w), 495 (w), 476 (m), 426 (w), 383 (w), 324 (m). Mass spectrum: *m/z* (reporting ^{35}Cl) 271 ($C_6H_5C_6H_4CN_3S_2^+$, 3%), 257 ($C_6H_5C_6H_4CN_2S_2^+$, 93%), 211 ($C_6H_5C_6H_4CNS^+$, 26%), 179 ($C_6H_5C_6H_4CN^+$, 100%).

Preparation of 3-$CF_3C_6H_4CN_5S_3$ (3g). **3g** was prepared by the method of **3b** using 3-$CF_3C_6H_4CN(SiMe_3)_2NSiMe_3$ (5.0 g, 12 mmol) and $S_3N_3Cl_3$ (3.0 g, 12 mmol). Yield: 3.3 g (10 mmol, 83%). **3g** was recrystallized from hot CH_3CN as orange moisture-sensitive needles, mp 113–114 °C. Anal. Calcd for $C_8H_4F_3N_5S_3$: C, 29.72; H, 1.25; N, 21.66. Found: 29.84; H, 1.51; N, 21.83. IR (1600–250-cm^{-1} region): 1591 (w), 1462 (s), 1371 (s, br), 1317 (s, br), 1280 (s, br), 1165 (s, br), 1117 (s, br), 1072 (s), 1028 (s), 999 (s), 953 (s), 936 (s), 820 (s), 775 (s), 739 (s), 721 (s), 694 (s), 689 (s), 665 (s), 646 (w), 617 (s), 561 (s), 515 (s), 505 (s), 480 (s), 434 (w), 380 (w), 369 (w), 203 (w). Mass spectrum: *m/z* 304 ($CF_2C_6H_4CN_5S_3^+$, 14%), 263 ($CF_3C_6H_4CN_3S_2^+$, 49%), 249

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($CF_3C_6H_4CN_2S_2^+$, 83%), 217 ($CF_3C_6H_4CN_2S^+$, 32%), 203 ($CF_3C_6H_4CNS^+$, 63%), 171 ($CF_3C_6H_4CN^+$, 79%), 46 (SN^+, 100%).

Preparation of 4-$CH_3C_6H_4CN_3S_2Cl_2$ (4b). Chlorine gas was passed over a slurry of **3b** (7.00 g, 25.9 mmol) in 100 mL of CCl_4 cooled to 0 °C for approximately 5 min. The mixture was stirred at this temperature until all the solids reacted and then filtered under nitrogen to remove a small portion of $RCN_2S_2^+Cl^-$, and the filtrate was evaporated to dryness in vacuo. The residual solid was recrystallized from toluene/methylene chloride as yellow moisture-sensitive plates (4.41 g, 15.7 mmol, 60.6%), mp 117–120 °C. Anal. Calcd for $C_8H_7Cl_2N_3S_2$: C, 34.29; H, 2.52; N, 15.00; Cl, 25.31. Found: C, 34.19; H, 2.41; N, 14.95; Cl, 25.31. IR (1600–250-cm^{-1} region): 1599 (m), 1506 (w), 1421 (m), 1346 (s), 1180 (m), 1117 (m), 1016 (m), 916 (s), 837 (s), 790 (s), 702 (m), 686 (s), 636 (m), 605 (s), 516 (s), 495 (s), 476 (s), 443 (vs), 380 (vs), 318 (vs), 275 (m). Mass spectrum: m/z (reporting ^{35}Cl) 280 ($\{CH_3C_6H_4Cl_2N_3S^+$, 4%), 244 ($CH_3C_6H_4CN_3S_2Cl^+$, 2%), 209 ($CH_3C_6H_4CN_3S_2^+$, 72%), 195 ($CH_3C_6H_4CN_2S_2^+$, 10%), 163 ($CH_3C_6H_4CN_2S^+$, 69%), 149 ($CH_3C_6H_4CNS^+$, 6%), 117 ($CH_3C_6H_4CN^+$, 63%), 46 (NS^+, 100%).

Preparation of 4-$ClC_6H_4CN_3S_2Cl_2$ (4c). **4c** was prepared as **4b** from **3c** (8.01 g, 27.7 mmol) at room temperature. **4c** was recrystallized from methylene chloride/pentane as moisture-sensitive yellow-orange needles (6.3 g, 21 mmol, 75.8% yield), mp 79 °C. Anal. Calcd for $C_7H_4ClN_3S_2$: C, 27.97; H, 1.34; N, 13.98. Found: C, 28.05; H, 1.52; N, 13.81. IR (1600–250-cm^{-1} region): 1591 (m), 1560 (sh), 1420 (s), 1344 (s), 1294 (s), 1262 (m), 1170 (m), 1107 (sh), 1092 (s), 1047 (w), 1028 (w), 1012 (m), 914 (m), 849 (m), 787 (m), 743 (s), 694 (sh), 683 (s), 669 (s), 628 (w), 592 (w), 551 (m), 527 (w), 509 (s), 470 (vs), 445 (vs), 387 (s), 326 (s), 245 (m). Mass spectrum: m/z (reporting ^{35}Cl) 229 ($ClC_6H_4CN_3S_2^+$, 27%), 215 ($ClC_6H_4CN_2S_2^+$, 21%), 183 ($ClC_6H_4CN_2S^+$, 23%), 169 ($ClC_6H_4CNS^+$, 14%), 137 ($ClC_6H_4CN^+$, 100%).

Preparation of 4-$CF_3C_6H_4CN_3S_2Cl_2$ (4d). **4d** was prepared as **4b** from **3d** (5.0 g, 15 mmol) at 0 °C. **4d** was recrystallized from *n*-pentane by dissolving at room temperature and cooling to −35 °C. The golden, moisture-sensitive needles were collected on a cooled filter stick (3.44 g, 10.3 mmol, 68.6% yield), mp 87–89 °C. The solid slowly decomposes at room temperature. IR (1600–250-cm^{-1} region): 1512 (w), 1427 (m), 1315 (s), 1261 (m), 1138 (s), 1111 (s), 1095 (s), 1068 (vs), 1016 (vs), 914 (m), 862 (m), 794 (s), 761 (m), 707 (m), 696 (s), 592 (w), 542 (w), 509 (m), 472 (m), 389 (m), 370 (m), 322 (m), 287 (w). Mass spectrum: m/z (reporting ^{35}Cl) 333 ($CF_3C_6H_4CN_3S_2Cl_2^+$, 1%), 298 ($CF_3C_6H_4CN_3S_2Cl^+$, 1%), 263 ($CF_3C_6H_4CN_3S_2^+$, 44%), 249 ($CF_3C_6H_4CN_2S_2^+$, 55%), 217 ($CF_3C_6H_4CN_2S^+$, 37%), 203 ($CF_3C_6H_4CNS^+$, 19%), 171 ($CF_3C_6H_4CN^+$, 100%). A satisfactory analysis could not be obtained.

Preparation of 4-$CH_3OC_6H_4CN_3S_2Cl_2$ (4e). **4e** was prepared as **4b** from **3e** (3.2 g, 11.2 mmol) in 125 mL of CCl_4 at 0 °C. The yield was 2.9 g (9.7 mmol, 88%) as a bright yellow solid after removal of the solvent. The solid material decomposes rapidly at room temperature. IR (1600–250-cm^{-1} region): 1558 (w), 1541 (w), 1507 (w), 1377 (s), 1346 (m), 1314 (sh), 1261 (vs), 1169 (m), 1145 (sh), 1092 (s), 1022 (s), 934 (w), 914 (w), 842 (w), 798 (vs), 752 (w), 723 (w), 690 (w), 582 (w), 546 (w), 459 (m), 395 (m), 341 (m), 300 (m), 279 (m), 248 (m).

Preparation of 4-$C_6H_5C_6H_4CN_3S_2Cl_2$ (4f). **4f** was prepared as **4b** from **3f** (0.6 g, 1.8 mmol) at 0 °C, using 75 mL of CCl_4. **4f** was recrystallized from CH_2Cl_2 as small moisture-sensitive needles (0.37 g, 1.1 mmol, 61.1% yield, mp 101 °C dec). Anal. Calcd for $C_{13}H_9N_3S_2Cl_2$: C, 45.62; H, 2.65; N, 12.28; Cl, 20.72. Found: C, 45.73; H, 2.81; N, 12.33; Cl, 20.58. IR (1600–250-cm^{-1} region): 1599 (m), 1413 (m), 1363 (s), 1342 (s), 1261 (m), 1199 (w), 1176 (w), 1093 (w), 1020 (w), 972 (w), 918 (m), 852 (w), 794 (m), 775 (w), 694 (m), 644 (w), 549 (w), 530 (w), 495 (w), 476 (m), 428 (w), 383 (m), 322 (w), 291 (w), 266 (m). Mass spectrum: m/z 271 ($C_6H_5C_6H_4CN_3S_2^+$, 13%), 257 ($C_6H_5C_6H_4CN_2S_2^+$, 39%), 225 ($C_6H_5C_6H_4CN_2S^+$, 3%), 211 ($C_6H_5C_6H_4CNS^+$, 10%), 193 ($C_6H_5C_6H_4CN_2^+$, 6%), 179 ($C_6H_5C_6H_4CN^+$, 100%).

Preparation of 3-$CF_3C_6H_4CN_3S_2Cl_2$ (4g). **4g** was prepared as **4b** from **3g** (2.5 g, 7.7 mmol) at 0 °C. **4g** was recrystallized from CH_2Cl_2 by dissolving at room temperature and cooling to −35 °C. The amber, moisture-sensitive needles were collected on a cooled filter stick (2.1 g, 6.2 mmol, 79.9% yield), mp 110–112 °C. The solid material decomposes rapidly at room temperature. IR (1600–250-cm^{-1} region): 1591 (w), 1487 (m), 1452 (s, br), 1333 (vs, br), 1167 (s, br), 1107 (s, br), 1028 (s, br), 997 (s, br), 949 (s), 937 (s), 820 (s), 777 (s), 741 (s), 720 (s), 691 (s), 666 (m), 646 (m), 617 (s), 561 (s), 507 (s), 480 (s), 434 (w), 380 (m), 332 (w), 270 (w), 201 (w). Mass spectrum: m/z (reporting ^{35}Cl) 263 ($CF_3C_6H_4CN_3S_2^+$, 10%), 249 ($CF_3C_6H_4CN_2S_2^+$, 45%), 217 ($CF_3C_6H_4CN_2S^+$, 9%), 203 ($CF_3C_6H_4CNS^+$, 16%), 171 ($CF_3C_6H_4CN^+$, 46%), 46 (SN^+, 100%).

Preparation of (4-$CH_3C_6H_4CN_3S_2$)$_2$ (5b). A solution of triphenylantimony (0.64 g, 1.8 mmol) in 15 mL of $CHCl_3$ was added dropwise to **4b** (0.5 g, 1.8 mmol) dissolved in 20 mL of $CHCl_3$ without agitation. Small brown crystals appeared about halfway through the addition. When the addition was complete, the mixture was allowed to sit at room temperature for about 1 h. The crystals were filtered in air, rinsed with a small amount of $CHCl_3$, and allowed to dry. Yield: (0.198 g, 0.95 mmol, 52.5%), mp 117–118 °C. Anal. Calcd for $C_{16}H_{14}N_6S_4$: C, 45.91; H, 3.37; N, 20.08; S, 30.64. Found: C, 45.78; H, 3.48; N, 20.16; S, 30.56. IR (1600–250-cm^{-1} region): 1558 (w), 1539 (w), 1506 (w), 1423 (s), 1377 (s), 1338 (vs), 1294 (w), 1186 (m), 1161 (w), 1115 (m), 1018 (m), 896 (m), 823 (m), 787 (m), 771 (m), 721 (m), 690 (m), 671 (m), 470 (m), 455 (m), 418 (w), 383 (m), 302 (m), 279 (m), 252 (w). Mass spectrum: m/z 209 ($CH_3C_6H_4CN_3S_2^+$, 18.6%), 195 ($CH_3C_6H_4CN_2S_2^+$, 11%), 163 ($CH_3C_6H_4CN_2S^+$, 17%), 149 ($CH_3C_6H_4CNS^+$, 5%), 117 ($CH_3C_6H_4CN^+$, 36%), 46 (NS^+, 100%).

Preparation of (4-$ClC_6H_4CN_3S_2$)$_2$ (5c). **5c** was prepared as **5b** from **4c** (0.5 g, 1.66 mmol) and triphenylantimony (0.59 g, 1.66 mmol). Small brown platelets formed (0.27 g, 1.2 mmol, 72% yield), mp 112.5–114 °C. Anal. Calcd for $C_{14}H_8C_{12}N_6S_4$: C, 36.60; H, 1.76; N, 18.29; S, 27.92. Found: C, 36.67; H, 1.55; N, 18.23; S, 27.78. IR (1600–250-cm^{-1} region): 1589 (m), 1558 (w), 1485 (m), 1456 (s), 1419 (vs), 1342 (vs), 1282 (w), 1175 (m), 1165 (m), 1105 (m), 1091 (s), 1010 (s), 901 (m), 833 (s), 787 (m), 772 (m), 731 (s), 675 (s), 453 (m), 444 (m), 378 (m), 322 (w), 281 (w). Mass spectrum: m/z (reporting ^{35}Cl) 229 ($ClC_6H_4CN_3S_2^+$, 51%), 215 ($ClC_6H_4CN_2S_2^+$, 70%), 183 ($ClC_6H_4CN_2S^+$, 44%), 151 ($ClC_6H_4CN_2^+$, 22%), 137 ($ClC_6H_4CN^+$, 69%), 78 (N_2S^+, 100%).

Preparation of (4-$CF_3C_6H_4CN_3S_2$)$_2$ (5d). **5d** was prepared as **5b** from **4d** (0.5 g, 1.49 mmol) and triphenylantimony (0.52 g, 1.49 mmol). Tiny reddish-brown crystals formed (0.308 g, 1.17 mmol, 78.5% yield), mp 110–112 °C. Anal. Calcd for $C_{16}H_8F_6N_6S_4$: C, 36.50; H, 1.53; N, 15.96; S, 24.36. Found: C, 36.66; H, 1.68; N, 15.98; S, 24.12. IR (1600–250-cm^{-1} region): 1427 (s), 1342 (sh), 1321 (vs), 1169 (s), 1126 (vs), 1109 (vs), 1064 (vs), 1012 (m), 929 (w), 904 (m), 846 (m), 808 (w), 787 (m), 779 (m), 767 (m), 750 (w), 700 (m), 677 (m), 590 (w), 457 (m), 426 (w), 407 (m), 343 (m). Mass spectrum: m/z 263 ($CF_3C_6H_4CN_3S_2^+$, 100%), 249 ($CF_3C_6H_4CN_2S_2^+$, 50%), 217 ($CF_3C_6H_4CN_2S^+$, 74%), 171 ($CF_3C_6H_4CN^+$, 35%), 152 ($CF_2C_6H_4CN^+$, 68%), 92 ($N_2S_2^+$, 74%), 78 (N_2S^+, 52%).

Preparation of (4-$CH_3OC_6H_4CN_3S_2$)$_2$ (5e). **5e** was prepared as **5b** from freshly prepared **4e** (1.2 g, 4.0 mmol) and Ph_3Sb (1.4 g, 4.0 mmol). Coppery flakes formed (0.28 g, 1.2 mmol, 30% yield). Anal. Calcd for $C_{16}H_{14}N_6O_2S_4$: C, 42.65; H, 3.13; N, 18.65; S, 28.46. Found: C, 41.90; H, 3.52; N, 18.27; S, 28.00. IR (1600–250-cm^{-1} region): 1581 (w), 1510 (m), 1429 (s), 1377 (s), 1346 (vs), 1303 (m), 1255 (vs), 1178 (vs), 1111 (m), 1064 (w), 1033 (m), 929 (w), 895 (m), 833 (m), 812 (m), 785 (m), 769 (m), 734 (m), 690 (w), 671 (s), 632 (w), 603 (w), 503 (w), 478 (w), 447 (m), 395 (m), 335 (m), 291 (w). Mass spectrum: m/z 225 ($CH_3OC_6H_4CN_3S_2^+$, 30%), 211 ($CH_3OC_6H_4CN_2S_2^+$, 16%), 179 ($CH_3OC_6H_4CN_2S^+$, 22%), 165 ($CH_3OC_6H_4CNS^+$, 6%), 154 (hydrolysis, 48%), 133 ($CH_3OC_6H_4CN^+$, 100%).

Preparation of (4-$C_6H_5C_6H_4CN_3S_2$)$_2$ (5f). **5f** was prepared as **5b** from **4f** (0.25 g, 0.73 mmol) and triphenylantimony (0.26 g, 0.73 mmol). Crystals were very small and buff in color (0.12 g, 0.43 mmol, 59% yield), mp 130 °C dec. Anal. Calcd for $C_{13}H_9N_3S_2$: C, 57.54; H, 3.34; N, 15.48; S, 23.63. Found: C, 57.29; H, 3.57; N, 15.27; S, 23.44. IR (1600–250-cm^{-1} region): 1599 (w), 1415 (m), 1344 (m), 1338 (m), 1178 (w), 1159 (w), 1112 (w), 1006 (m), 931 (w), 893 (w), 841 (w), 814 (w), 765 (m), 727 (m), 686 (m), 677 (m), 636 (w), 451 (m), 374 (m), 279 (w). Mass spectrum: m/z 271 ($C_6H_5C_6H_4CN_3S_2^+$, 14%), 257 ($C_6H_5C_6H_4CN_2S_2^+$, 70%), 211 ($C_6H_5C_6H_4CNS^+$, 17%), 179 ($C_6H_5C_6H_4CN^+$, 100%), 78 ($S_2N_2^+$, 36%).

Preparation of (3-$CF_3C_6H_4CN_3S_2$)$_2$ (5g). **5g** was prepared as **5b** from freshly prepared **4g** (2.1 g, 6.2 mmol) and triphenylantimony (2.2 g, 6.2 mmol) with the added precaution of first degassing the solution of **4g** by repeated freeze–thaw cycles. Dark-amber to red plates formed (0.35 g, 1.3 mmol, 11% yield), mp 117–119 °C. Anal. Calcd for $C_{16}H_8F_6N_6S_4$: C, 36.50; H, 1.53; N, 15.96. Found: C, 36.75; H, 1.51; N, 15.86. IR (1600–250-cm^{-1} region): 1454 (s), 1385 (s), 1350 (s), 1316 (m), 1277 (m), 1179 (s), 1121 (s), 1092 (m), 1074 (m), 999 (w), 988 (w), 955 (m), 916 (m), 897 (m), 801 (s), 777 (m), 764 (m), 714 (m), 702 (m), 693 (m), 671 (m), 665 (m), 646 (w), 611 (w), 488 (w), 461 (w), 446 (w), 436 (w), 386 (w), 366 (m). Mass spectrum: m/z 263 ($CF_3C_6H_4CN_3S_2^+$, 19%), 249 ($CF_3C_6H_4CN_2S_2^+$, 58%), 217 ($CF_3C_6H_4CN_2S^+$, 11%), 171 ($CF_3C_6H_4CN^+$, 38%), 78 (N_2S^+, 84%), 46 (SN^+, 100%). ^{13}C NMR: 146.44 (s), 135.35 (s), 130.20 (q, 32 Hz), 128.58 (s), 128.36 (s), 127.5 (q, 4 Hz), 123.44 (q, 273 Hz), 122.3 ppm (q, 4 Hz).

Preparation of 4-$CH_3C_6H_4CN_3S_2{\cdot}C_7H_{10}$ (6b). To a suspension of **5b** (75 mg, 0.35 mmol) in 3 mL of CH_3CN was added 99 mg (1.0 mmol) of norbornene. After several hours of stirring, the brown color faded to give a clear solution. Removal of solvent in vacuo followed by recrys-

tallization from a minimum of hot CH_3CN and cooling to 0 °C gave colorless needles (80 mg, 0.26 mmol, 75%), mp 165–166 °C. Anal. Calcd for $C_{15}H_{17}N_3S_2$: C, 59.37; H, 5.64; N, 13.85; S, 21.13. Found: C, 59.20; H, 5.79; N, 13.82; S, 21.41. IR (1600–250-cm^{-1} region): 1423 (m), 1323 (vs), 1296 (m), 1254 (w), 1215 (w), 1180 (w), 1169 (m), 1138 (m), 1111 (w), 1024 (w), 920 (m), 873 (w), 835 (w), 794 (m), 775 (m), 748 (s), 694 (m), 607 (m), 557 (w), 517 (w), 497 (w), 459 (m), 435 (w), 378 (m), 326 (w), 266 (w). ^1H NMR: 7.73 and 7.12 AB doublet (C_6H_4), 4.63 d ($H_{2,3}$), 2.64 m ($H_{1,4}$), 2.34 s (CH_3), 1.88 and 0.95 AB doublet ($H_{9,10}$), 1.57 and 1.37 m (H_{5-8}) ppm.[18]

Preparation of 4-$ClC_6H_4CN_3S_2$·C_7H_{10} (6c). **6c** was prepared by the method of **6b** from 75 mg of **5c** and 120 mg of norbornene to yield colorless plates (68 mg, 65%), mp 183–185 °C. Anal. Calcd for $C_{14}H_{14}ClN_3S_2$: C, 51.92; H, 4.36; N, 12.97; S, 19.80. Found: C, 51.85; H, 4.51; N, 12.89; S, 19.72. IR (1600–250-cm^{-1} region): 1591 (w), 1425 (w), 1418 (s), 1319 (vs), 1296 (w), 1219 (w), 1157 (w), 1134 (w), 1092 (m), 1011 (m), 916 (w), 878 (w), 855 (w), 795 (m), 779 (m), 745 (s), 745 (s), 714 (m), 694 (w), 540 (w), 521 (w), 446 (m), 365 (w), 314 (w), 283 (w), 260 (w). ^1H NMR: 7.77 and 7.29 AB doublet (C_6H_4), 4.63 d ($H_{2,3}$), 2.64 m ($H_{1,4}$), 1.87 and 0.96 AB doublet ($H_{9,10}$), 1.59 and 1.38 m (H_{5-8}) ppm.[18]

Preparation of 4-$CF_3C_6H_4CN_3S_2$·C_7H_{10} (6d). **6d** was prepared by the method of **6b** from 75 mg of **5d** and 80 mg of norbornene to yield colorless plates (71 mg, 71%), mp 188–191 °C. Anal. Calcd for $C_{15}H_{14}F_3N_3S_2$: C, 50.41; H, 3.95; N, 11.76; S, 17.94. Found: C, 50.30; H, 4.00; N, 11.81; S, 18.12. IR (1600–250-cm^{-1} region): 1518 (w), 1429 (s), 1329 (vs), 1302 (s), 1257 (w), 1257 (w), 1226 (w), 1180 (w), 1161 (s), 1134 (vs), 1066 (s), 1024 (m), 1001 (w), 943 (w), 916 (m), 869 (m), 854 (m), 819 (w), 798 (m), 783 (m), 767 (s), 721 (m), 702 (m), 690 (m), 679 (m), 633 (w), 594 (w), 570 (w), 528 (m), 505 (w), 474 (w), 428 (w), 395 (w), 368 (m), 337 (w), 310 (w), 260 (w). ^1H NMR: 7.95 and 7.57 AB doublet (C_6H_4), 4.66 d ($H_{2,3}$), 2.66 m ($H_{1,4}$), 1.87 and 0.98 AB doublet ($H_{9,10}$), 1.60 and 1.39 m (H_{5-8}) ppm.[18]

Preparation of 4-$CH_3OC_6H_4CN_3S_2$·C_7H_{10} (6e). **6e** was prepared by the method of **6b** from **5e** (75 mg) and norbornene (0.45 g, excess). **6e** was recrystallized from CH_3CN to yield colorless blocks (50 mg, 45%), mp 146–148 °C. Anal. Calcd for $C_{15}H_{17}ON_3S_2$: C, 56.40; H, 5.36; N, 13.15; S, 20.07. Found: C, 55.58; H, 5.46; N, 13.27; S, 19.38. IR (1600–200-cm^{-1} region): 1583 (w), 1508 (m), 1377 (s), 1329 (s), 1305 (w), 1294 (m), 1273 (w), 1249 (vs), 1168 (m), 1140 (m), 1107 (m), 1060 (w), 1030 (m), 995 (w), 914 (m), 869 (m), 844 (m), 794 (m), 756 (m), 736 (m), 698 (m), 634 (w), 607 (w), 559 (w), 532 (w), 505 (w), 466 (m), 422 (w), 383 (w), 352 (w), 318 (w), 281 (w), 248 (w). Mass spectrum: m/z 225 ($CH_3OC_6H_4CN_3S_2^+$, 69%), 211 ($CH_3OC_6H_4CN_2S_2^+$, 14%), 179 ($CH_3OC_6H_4CN_2S^+$, 28%), 165 ($CH_3OC_6H_4CNS^+$, 5%), 133 ($CH_3OC_6H_4CN^+$, 100%), 66 ($C_5H_6^+$, 62%). ^1H NMR: 7.80 and 6.81 AB doublet (C_6H_4), 4.62 d ($H_{2,3}$), 3.80 s (CH_3O), 2.62 m ($H_{1,4}$), 1.87 and 0.94 AB doublet ($H_{9,10}$), 1.58 and 1.36 m (H_{5-8}) ppm.[18]

Preparation of 4-$C_6H_5C_6H_4CN_3S_2$·C_7H_{10} (6f). **6f** was prepared by the method of **6b** from 75 mg of **5f** and norbornene (460 mg) to yield pale yellow blocks (54 mg, 55%), mp 175–176 °C. Anal. Calcd for $C_{20}H_{19}N_3S_2$: C, 65.72; H, 5.24; N, 11.50; S, 17.54. Found: C, 63.98; H, 5.36; N, 11.21; S, 16.81. IR (1600–250-cm^{-1} region): 1562 (w), 1412 (s), 1346 (vs), 1300 (m), 1261 (w), 1250 (w), 1188 (w), 1138 (w), 1118 (w), 1082 (w), 1024 (m), 1010 (m), 970 (w), 922 (w), 875 (w), 856 (s), 794 (m), 783 (m), 763 (m), 748 (vs), 729 (w), 702 (w), 642 (m), 561 (w), 530 (m), 522 (m), 499 (w), 480 (w), 405 (w), 360 (w), 310 (w), 280 (w), 266 (w). ^1H NMR: 7.3–8.0 m ($C_6H_5C_6H_4$), 4.67 d ($H_{2,3}$), 2.66 m ($H_{1,4}$), 2.34 s (CH_3), 1.88 and 0.97 AB doublet ($H_{9,10}$), 1.59 and 1.38 m (H_{5-8}) ppm.[18]

Preparation of 3-$CF_3C_6H_4CN_3S_2$·C_7H_{10} (6g). **6g** was prepared by the method of **6b** from 0.30 g of **5g** and 0.54 g of norbornene to yield colorless plates (0.25 g, 62%), mp 193 °C. Anal. Calcd for $C_{15}H_{14}F_3N_3S_2$: C, 50.41; H, 3.95; N, 11.76. Found: C, 50.43; H, 4.01; N, 11.80. IR (1600–250-cm^{-1} region): 1454 (s), 1385 (s), 1344 (s), 1304 (s), 1265 (s), 1223 (m), 1184 (m), 1159 (s), 1121 (vs), 1086 (s), 1069 (s), 936 (s), 916 (s), 882 (m), 808 (s), 795 (s), 766 (s), 741 (s), 696 (s), 675 (m), 646 (m), 615 (m), 565 (w), 523 (s), 503 (m), 469 (w), 453 (w), 436 (w), 399 (w), 378 (m), 361 (m), 332 (w), 247 (w). ^1H NMR: aromatic, Table I; 4.56 d ($H_{2,3}$), 2.64 m ($H_{1,4}$), 1.86 and 0.96 AB doublet ($H_{9,10}$), 1.56 and 1.38 m (H_{5-8}) ppm.[18] ^{13}C NMR: 158.07 (s), 139.40 (s), 130.31 (q, 33 Hz), 129.98 (s), 128.32 (s), 127.36 (q, 4 Hz), 124.04 (q, 272 Hz), 123.86 (q, 4 Hz), 87.93 (s), 38.13 (s), 33.07 (s), 27.99 ppm.

X-ray Measurements. A small opaque black plate of **5c** was mounted with epoxy on a glass fiber and mounted on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters and their standard deviations were derived from the setting angles of 25 reflections in the range $9.99 < \theta < 13.94°$. Reduced cell calculations did not indicate any higher metric symmetry. Crystal and instrumental instability were monitored through the measurement of three standard reflections every 1 h of X-ray exposure time; there was no indication of crystal decomposition. The net intensities of the data were corrected for reflection width, scale variation, Lorentz, and polarization effects. Variance $\sigma^2(I)$ was calculated on the basis of counting statistics. Crystal data and experimental details of the structure determination are compiled in Table II.

All non-hydrogen atoms were located in an E map with phases derived from symbolic addition.[19] After isotropic refinement all of the hydrogen

Table II. Summary of Crystal Data, Intensity Collection, and Structure Refinement for $\{S_2N_3C_7H_4Cl\}_2$ (**5c**)

formula	$\{S_2N_3C_7H_4Cl\}_2$
cell dimens	
a	6.107 (1) Å
b	12.070 (2) Å
c	13.206 (2) Å
α	113.73 (1)°
β	99.04 (2)°
γ	97.53 (2)°
V	859.52 Å^3
D_m	1.75 (4) g cm^3
D_c	1.775 g cm^3
cryst dimens	0.188 × 0.125 × 0.129 mm
radiation (λ)	Mo Kα (graphite monochromator) (0.710 69 Å)
$(\sin R)/\lambda_{max}$	0.64 Å^{-1}
range	
h	0/7
k	−15/15
l	−9/9
tot. no. of reflcns	7616
no. of unique reflcns	6461
no. of obsd reflcns	1480 ($6.0\sigma(F)$ cutoff)
no. of variables	235
least-squares function	$\sum(\|\|F_o\| - \|F_c\|\|)w$
$R = \sum(\|\|F_o\| - \|F_c\|\|)/\sum\|F_o\|$	0.084
$R_w = \sum(\|\|F_o\| - \|F_c\|\|)w/\sum\|F_o\|w$	0.067
$S = [(\sum(\|\|F_o\| - \|F_c\|\|)w)/(m - n)]^{1/2}$	3.358
w	$1/\sigma(F)^2$
μ	7.96 cm^{-1}
$F(000)$	464 electrons

Table III. Positional Parameters for Non-Hydrogen Atoms and Equivalent Isotropic Thermal Parameters

atom	x	y	z	$1000U$, Å^2
S(11)	0.1199 (5)	−0.0317 (3)	0.8057 (3)	47.7
N(21)	−0.145 (1)	−0.0969 (8)	0.7856 (8)	48.5
S(31)	−0.3349 (5)	−0.0433 (3)	0.7289 (3)	42.5
N(41)	−0.239 (1)	0.0358 (8)	0.6676 (8)	38.1
C(51)	−0.011 (2)	0.073 (1)	0.678 (1)	36.5
N(61)	0.155 (1)	0.0465 (8)	0.7368 (8)	37.4
C(11)	0.045 (2)	0.147 (1)	0.6182 (9)	32.8
C(12)	0.272 (2)	0.197 (1)	0.629 (1)	50.5
C(13)	0.327 (2)	0.271 (1)	0.577 (1)	57.8
C(14)	0.163 (2)	0.298 (1)	0.514 (1)	54.5
C(15)	−0.062 (2)	0.248 (1)	0.501 (1)	59.1
C(16)	−0.117 (2)	0.174 (1)	0.551 (1)	51.2
Cl(1)	0.2416 (6)	0.3967 (4)	0.4556 (3)	84.5
S(12)	0.3244 (5)	0.8604 (3)	1.0861 (3)	41.9
N(22)	0.133 (1)	0.8945 (8)	1.0075 (8)	44.3
S(32)	−0.1301 (5)	0.8523 (3)	1.0099 (3)	39.4
N(42)	−0.166 (1)	0.7485 (8)	1.0549 (8)	37.7
C(52)	0.005 (2)	0.7131 (9)	1.1026 (9)	30.9
N(62)	0.229 (1)	0.7555 (8)	1.1214 (8)	38.9
C(21)	−0.068 (2)	0.6126 (9)	1.135 (1)	31.5
C(22)	0.088 (2)	0.562 (1)	1.181 (1)	54.1
C(23)	0.020 (2)	0.469 (1)	1.211 (1)	60.9
C(24)	−0.209 (2)	0.425 (1)	1.197 (1)	44.4
C(25)	−0.362 (2)	0.471 (1)	1.149 (1)	62.7
C(26)	−0.296 (2)	0.565 (1)	1.121 (1)	53.1
Cl(2)	−0.3010 (6)	0.3076 (3)	1.2334 (3)	70.3

(18) Numbering scheme for norbornene NMR: bridgehead, $H_{1,4}$; gem to the S, $H_{2,3}$; ring methylenes, H_{5-8}; bridge methylene, $H_{9,10}$.

(19) Schenk, H.; Hall, S. R. SIMPEL, XTAL2.4 User's Manual. Hall, S. R., Stewart, J. M., Eds.; Universities of Western Australia and Maryland, 1988.

Table IV. Selected Interatomic Distances (Å) and Angles (deg)

N(21)-S(11)	1.635 (9)	N(22)-S(12)	1.64 (1)
N(21)-S(31)	1.62 (1)	N(22)-S(32)	1.631 (9)
N(41)-S(31)	1.59 (1)	N(42)-S(32)	1.59 (1)
C(51)-N(41)	1.37 (2)	C(52)-N(42)	1.34 (2)
C(51)-N(61)	1.33 (2)	C(52)-N(62)	1.34 (1)
N(61)-S(11)	1.57 (1)	N(62)-S(12)	1.59 (1)
C(11)-C(51)	1.46 (2)	C(21)-C(52)	1.48 (2)
S(11)-S(32)	2.509 (4)	S(12)-S(31)	2.534 (4)
N(21)-S(11)-N(61)	113.8 (6)	N(42)-C(52)-N(62)	128 (1)
S(11)-N(21)-S(31)	116.3 (7)	N(42)-C(52)-C(21)	114 (1)
N(21)-S(31)-N(41)	114.2 (5)	N(62)-C(52)-C(21)	118 (1)
S(31)-N(41)-C(51)	123 (1)	S(12)-N(62)-C(52)	121.4 (9)
N(41)-C(51)-N(61)	126 (1)	C(52)-C(21)-C(22)	121 (1)
N(41)-C(51)-C(11)	115 (1)	C(52)-C(21)-C(26)	122 (1)
N(61)-C(51)-C(11)	119 (1)	C(51)-C(11)-C(12)	120 (1)
S(11)-N(61)-C(51)	124.9 (9)	C(51)-C(11)-C(16)	123 (1)

atoms were located in difference Fourier maps. The data were corrected for absorption by DIFABS after isotropic refinement.[20] All non-hydrogen atoms were refined anisotropically, with the hydrogens calculated in idealized positions with fixed isotropic temperature factors, which were not refined. The refinement did not converge until the data were limited to the sphere with $(\sin\theta)/\lambda$ less than 0.64. Convergence was reached at $R = 0.084$. The final values of the refined positional parameters are presented in Table III, and important bond lengths are in Table IV. Neutral-atom scattering factors were used with anomalous dispersion corrections applied.[21] No corrections for extinction were made. All calculations were carried out on a Zenith 386 running UNIX V.3 computer at the University of Calgary with the program package XTAL.[22]

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Registry No. **3b**, 139100-95-1; **3c**, 139100-96-2; **3d**, 139100-97-3; **3e**, 139100-98-4; **3f**, 139100-99-5; **3g**, 139101-00-1; **4b**, 139101-01-2; **4c**, 139101-02-3; **4d**, 139101-03-4; **4e**, 139101-04-5; **4f**, 139101-05-6; **4g**, 139101-06-7; **5b**, 139101-07-8; **5c**, 110654-28-9; **5d**, 139101-08-9; **5e**, 139101-09-0; **5f**, 139101-10-3; **5g**, 139101-11-4; **6b**, 139101-12-5; **6c**, 139101-13-6; **6d**, 139101-14-7; **6e**, 139101-15-8; **6f**, 139101-16-9; **6g**, 139101-17-0; $S_3N_3Cl_3$, 18428-81-4; $4\text{-}CH_3C_6H_4CN(SiMe_3)_2NSiMe_3$, 117357-77-4; $4\text{-}ClC_6H_4CN(SiMe_3)_2NSiMe_3$, 117357-78-5; $4\text{-}CF_3C_6H_4CN(SiMe_3)_2NSiMe_3$, 117357-81-0; $4\text{-}CH_3OC_6H_4CN(SiMe_3)_2NSiMe_3$, 117357-79-6; $4\text{-}C_6H_5C_6H_4CN(SiMe_3)_2NSiMe_3$, 117357-82-1; $3\text{-}CF_3C_6H_4CN(SiMe_3)_2NSiMe_3$, 139101-18-1; 1-norbornene, 21810-44-6.

Supplementary Material Available: Tables of hydrogen atom positions and thermal parameters, comprehensive lists of bond distances and angles, and a table of significant contact distances (8 pages); a table of F_o, F_c, and $\sigma(F)$ values (23 pages). Ordering information is given on any current masthead page.

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Tetrakis(pentafluorooxotellurato)borate(1-): Coordinating Ability and Reactivity of a Very Large Weakly Coordinating Anion

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The suitability of $B(OTeF_5)_4^-$ as a counterion for the generation of "coordinatively unsaturated" or weakly solvated metal and metalloid cations has been studied by IR and NMR spectroscopy and by single-crystal X-ray diffraction. Addition of $B(OTeF_5)_3$ to $MOTeF_5$ (M = Ag, Tl) in the weakly coordinating solvents mesitylene, dichloromethane, 1,2-dichloroethane, and 1,1,2-trichlorotrifluoroethane produces solutions of $[M(solv)_x]^+[B(OTeF_5)_4]^-$. In the case of Ag^+ and 1,1,2-trichlorotrifluoroethane, the unsolvated compound $AgB(OTeF_5)_4$ was isolated as crystals belonging to the monoclinic system ($P2_1/n$, a = 11.419 (7) Å, b = 10.329 (4) Å, c = 15.31 (1) Å, β = 91.53 (5)°, Z = 4, T = -127 °C). The Ag^+ ion is bonded weakly to three $B(OTeF_5)_4^-$ ions, with three Ag-O contacts (2.500 (5)-2.756 (5) Å) and six Ag-F interactions (2.644 (5)-3.017 (5) Å). In the case of Tl^+ and either dichloromethane or 1,1,2-trichlorotrifluoroethane, the unsolvated salt $TlB(OTeF_5)_4$ is formed. Both $AgB(OTeF_5)_4$ and $TlB(OTeF_5)_4$ are thermally unstable, slowly forming $MOTeF_5$ and volatile $B(OTeF_5)_3$. This decomposition is slower for Tl^+ (days) than for Ag^+ (hours). Oxygen-17 NMR experiments demonstrate that the $OTeF_5^-$ substituents in $B(OTeF_5)_4^-$ do not exchange rapidly with free $OTeF_5^-$ but are rapidly exchanged in the presence of Lewis acids such as H^+, Ag^+, and $B(OTeF_5)_3$. Reactions of $AgB(OTeF_5)_4$ or $TlB(OTeF_5)_4$ with Fe(Por)Cl (Por = tetraphenylporphyrinate dianion or octaethylporphyrinate dianion) or Ph_3SiCl in dichloromethane or mesitylene produce $B(OTeF_5)_3$ and $Fe(Por)OTeF_5$ or $Ph_3SiOTeF_5$, respectively—the putative unsaturated cations $Fe(Por)^+$ or Ph_3Si^+ were not observed. In the case of Ph_3SiCl, the unsaturated cation Ph_3Si^+ or some similar species may be an intermediate, since Ph_3SiCl does not react directly with $N(n\text{-}Bu)_4B(OTeF_5)_4$. The reaction of $Ph_3CB(OTeF_5)_4$ with Ph_3SiH in dichloromethane also produces $Ph_3SiOTeF_5$.

Introduction

It has been nearly 20 years since Rosenthal published his brief review titled "The Myth of the Non-Coordinating Anion".[1] With the advent of modern techniques for eliminating water from reaction mixtures[2] and of automated X-ray diffraction equipment, the classical "noncoordinating" anions ClO_4^-,[3] $CF_3SO_3^-$,[4] FSO_3^-,[4] BF_4^-,[5] PF_6^-,[6] SbF_6^-,[7] and BPh_4^-[8] have been shown to coordinate

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