normal range. The structural results show that the bonding of these new rigid chiral ligands to Mo(0) is typical of bidentate and tridentate phosphines in five-membered chelate rings.

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Registry No. **1**, 74363-92-1; **2a**, 123642-42-2; **2b**, 123749-01-9; **3**, 123642-43-3; **4**, 123642-44-4; **5**, 123642-45-5; **6**, 123642-46-6; **7**, 123642-47-7; **8**, 123642-48-8; **9**, 72868-88-3; **10**, 74364-03-7; DMPP, 30540-36-4; Et_2VyP, 13652-21-6; $Ph_2P(CH{=}CH_2)$, 2155-96-6; $PhP(CH{=}CH_2)_2$, 26681-88-9; Ph_2PH, 829-85-6; Ph_2AsH, 829-83-4; molybdenum hexacarbonyl, 13939-06-5; [2-(phenylvinylphosphino)-5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]hept-5-ene (isomer a), 123642-41-1.

Supplementary Material Available: For the two structure studies, listings of crystal and refinement data, bond distances and angles, H atom coordinates, and thermal parameters (*U*) (12 pages); listings of observed and calculated structure factors (×10) (24 pages). Ordering information is given on any current masthead page.

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Synthetic and Mechanistic Investigations of the Reactions of Organic Nitriles with Thiazyl Chloride and the Thermolysis of 1,3-Dichloro-1,3,2,4,6-dithiatriazines

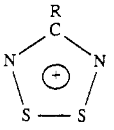
Allen Apblett and Tristram Chivers*

Received April 25, 1989

The reaction of organic nitriles with $(NSCl)_3$ at 23 °C produces good yields of the six-membered rings $RCN_3S_2Cl_2$ (**2**, R = ^{t}Bu, CCl_3, Ph) in the absence of a solvent or **2** (R = Me_2N, Et_2N, $^iPr_2N$) in chloroform. The reaction is complete in a few days for R = R'_2N, but it requires several weeks for the other derivatives. For R = Ph and ^{t}Bu the formation of **2** is accompanied by smaller amounts of the five-membered ring $RCN_2S_2^+Cl^-$ (**1**). The reaction rate is accelerated by UV irradiation, although the yields of **2** are lower. A red intermediate in the reaction of Me_2NCN with 2 mol of NSCl is tentatively identified as $Me_2NCNS(Cl)N$ on the basis of ^1H, ^{13}C, and ^{14}N NMR spectroscopy. The thermolysis of **2** (R = ^{t}Bu, CCl_3, Ph, Me_2N, Et_2N, $^iPr_2N$) generates **1** in excellent yields. This ring contraction is shown by ^{14}N NMR spectroscopy to occur at temperatures ranging from 40 °C (R = ^{t}Bu) to 110 °C (R = Me_2N) and by ^1H NMR spectroscopy to be second-order. A mechanism for the conversion of **2** into **1** is proposed. The reaction of Me_2NCN with NSCl in a 1:1 molar ratio at 23 °C in CCl_4 produces the eight-membered ring $1,3\text{-}(Me_2NC)_2N_4S_2Cl_2$ (**8**, R = NMe_2), in 80% yield, whereas a mixture of **8** and $Me_2NCN_4S_3Cl$ is obtained in nitromethane.

Introduction

The first investigations of the reactions of organic nitriles RCN (R = ^{t}Bu, CCl_3, Ph) with $(NSCl)_3$ were carried out at ⩾60 °C and led to the isolation of the corresponding 1,2,3,5-dithiadiazolium chloride (**1**) in ⩽50% yields.[1] Subsequently, the reaction of CF_3CN with $(NSCl)_3$ at 50 °C in an autoclave was reported to give **1** (R = CF_3) as the major product (45%) with the 1,3-dichloro-1,3,2,4,6-dithiatriazine (**2**, R = CF_3), as a minor product (21%).[2] By contrast, we found that **2** (R = Me_2N, Et_2N, $^iPr_2N$) is obtained in >80% yields by the cycloaddition reaction of the corresponding dialkylcyanamide, R_2NCN, with two NSCl units generated from dilute solutions of $(NSCl)_3$ in CCl_4 at 60 °C.[3] It is not clear from these results whether the difference in the identity of the products from the RCN–$(NSCl)_3$ reaction is determined by variations in the reaction conditions or by the nature of the R group (or both).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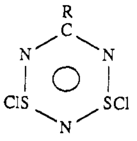
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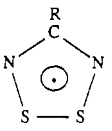
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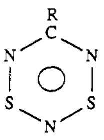
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The synthesis, structures, and properties of the seven-π-electron 1,2,3,5-dithiadiazolyl radicals (**3**)[4-7] and the eight-π-electron 1,3,2,4,6-dithiatriazines (**4**)[2,8-12] are of current interest, and these ring systems are usually prepared by the reduction of **1** and **2**, respectively.[13] Consequently, we have examined several RCN–$(NSCl)_3$ systems in detail in order to (a) determine the effect of the R group on the outcome of the reaction, (b) establish the appropriate reaction conditions for the synthesis of **1** and **2**, (c) elucidate the mechanism of the RCN–$(NSCl)_x$ cycloaddition reaction, and (d) identify any other products that may be formed

Table I. ^{14}N NMR Chemical Shifts for $RCN_3S_2Cl_2$ (**2**)[a]

R	δ(N)[b]	δ(N)[c]	δ(R_2N)
Me_2N	-211	-263	-211
Et_2N	-213	-240	-213
$^iPr_2N$	-205	-241	-220
Cl_3C	-181	-248	
^{t}Bu	-191	-242	
Ph	-196	-237	

[a] In CH_2Cl_2. Chemical shifts are relative to $MeNO_2$(l). [b] The two equivalent ring nitrogen atoms. [c] The unique ring nitrogen atom.

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(13) The synthesis of **4** by the direct insertion of plasma-generated nitrogen atoms into the S–S bond of **3** has been reported, but this reaction appears to be limited to aryl derivatives.[10]

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Table II. ^{14}N NMR Chemical Shifts for [RCN$_2$S$_2$]Cl (**1**)[a]

R	δ(N)[b]	δ(R$_2$N)	R	δ(N)[b]
Me$_2$N	−69	−318	^{t}Bu	−4
Et$_2$N	−62	−250	Cl$_3$C	−181
^{i}Pr$_2$N	−59	−244	Ph	−122

[a] In CH$_2$Cl$_2$. Chemical shifts are relative to MeNO$_2$(l). [b] The two equivalent ring nitrogen atoms.

by varying the conditions of these reactions.[14]

Experimental Section

Reagents and General Procedures. All experimental procedures were performed under an atmosphere of dry nitrogen. The following solvents were dried by heating at reflux with the appropriate drying agent and then distilled before use: *n*-pentane (Na), *n*-hexane (Na), toluene (Na), carbon tetrachloride (P$_2$O$_5$), methylene dichloride (P$_2$O$_5$), 1,2-dichloroethane (P$_2$O$_5$), MeNO$_2$ (molecular sieves).

The following reagents were commercial products used as received: Me$_2$NCN, Et$_2$NCN, ^{i}Pr$_2$NCN, CCl$_3$CN, ^{t}BuCN, and SO$_2$Cl$_2$ (Aldrich); PhCN, S$_2$Cl$_2$, and NH$_4$Cl (Fisher). (NSCl)$_3$ was prepared from S$_3$N$_2$Cl$_2$ by a modification of the literature procedure.[15] After the second chlorination of S$_3$N$_2$Cl$_2$, the crude (NSCl)$_3$ was ground to a powder and a third chlorination with Cl$_2$ was followed by the addition of sufficient SO$_2$Cl$_2$ to cover the solid product. This mixture was stirred for 12 h, and then volatile products were removed in vacuo to give pure (NSCl)$_3$, mp 91 °C (cf. lit. mp 92 °C).[16]

Instrumentation. Infrared spectra (4000–400 cm^{-1}) were recorded as Nujol or Fluorolube mulls (CsI windows) on a Nicolet 5DX FT-IR spectrophotometer. UV–visible spectra were obtained by using a Cary 219 spectrophotometer and cuvettes that were sealed with rubber septa. Mass spectra were measured on a Kratos MS80RFA instrument (EI/70 eV). ^{14}N NMR spectra were recorded on a Bruker AM-400 spectrometer and chemical shifts are reported relative to MeNO$_2$(l). ^{1}H and ^{13}C NMR spectra were obtained on a Bruker ACE 200 spectrometer, and chemical shifts are reported relative to Me$_4$Si in CDCl$_3$.

Chemical analyses were performed by the Analytical Services Division, Department of Chemistry, The University of Calgary, and by Canadian Microanalytical Service, New Westminster, BC, Canada.

Preparation of ^{t}BuCN$_3$S$_2$Cl$_2$ (2, R = ^{t}Bu). (a) A mixture of ^{t}BuCN (1.0 g, 12.0 mmol) and (NSCl)$_3$ (1.62 g, 6.7 mmol) was placed in a 10 mm o.d. Pyrex tube sealed with a Teflon-lined screw cap. After 12 weeks at 23 °C this mixture had become a yellow, crystalline mass. The excess of ^{t}BuCN was removed in vacuo, and the solid residue was extracted with *n*-pentane (50 mL). Removal of *n*-pentane gave **2** (R = ^{t}Bu) (1.10 g, 4.5 mmol). IR (cm^{-1}): 1390 s, 1366 s, 1325 m, 1221 vs, 1093 m, 1031 s, 944 m, 912 vs, 794 s, 591 m, 511 s, 478 s, 396 s. ^{1}H NMR (in CDCl$_3$): δ 1.22. ^{13}C NMR (in CDCl$_3$): δ 26.9 (*C*H$_3$), 43.5 (*C*Me$_3$), 180.0 (*C*N$_3$S$_2$). The purity of the product was established by ^{14}N NMR spectroscopy (Table I), which revealed the absence of **1** (R = ^{t}Bu) (Table II), but satisfactory analytical data could not be obtained due to the thermal and moisture sensitivity of **2** (R = ^{t}Bu). The insoluble residue was shown to be **1** (R = ^{t}Bu) by comparison of the IR spectrum with that reported in the literature.[1]

(b) A mixture of ^{t}BuCN (1.0 g, 12.0 mmol) and (NSCl)$_3$ (1.62 g, 6.7 mmol) was placed in a 16 mm o.d. quartz tube sealed with a rubber septum. The tube was cooled with a water jacket and irradiated with a 250-W sum lamp for 1 week. Volatile materials were removed in vacuo to give **2** (R = ^{t}Bu) (0.81 g, 3.3 mmol) after extraction with *n*-pentane. The insoluble residue was shown to be a mixture of **1** (R = ^{t}Bu) and S$_4$N$_3$Cl (IR spectrum).

Preparation of CCl$_3$CN$_3$S$_2$Cl$_2$ (2, R = CCl$_3$). The procedures were essentially the same as those described above for the preparation of **2** (R = ^{t}Bu) except that the reaction times were 3 weeks for method a and 2 days for method b. The crude product was extracted with CH$_2$Cl$_2$/*n*-hexane (1:1) and recrystallized from the same solvent mixture to give **2** (R = CCl$_3$) in 71% and 77% yields, respectively. Anal. Calcd for C$_2$Cl$_5$N$_3$S$_2$: C, 7.81; Cl, 57.70; N, 13.66; S, 20.84. Found: C, 7.94; Cl, 57.88; N, 13.93; S, 21.11. EI mass spectrum [*m*/*e* (ion, relative intensity)]: 272 (CCl$_3$N$_3$S$_2$Cl$^+$, 5), 237 (CCl$_3$N$_3$S$_2^+$, 20), 118 (CS$_2$N$_3^+$, 10), 92 (S$_2$N$_2^+$, 15), 78 (S$_2$N$^+$, 40), 64 (S$_2^+$, 20), 46 (NS$^+$, 100). IR (cm^{-1}): 1302 vs, 930 vs, 845 s, 801 vs, 723 m, 684 s, 553 m, 535 s, 484 vs, 470 s, 411 s. ^{13}C NMR (in CDCl$_3$): δ 95.3 (*C*Cl$_3$), 165.4 (*C*N$_3$S$_2$). ^{14}N NMR data are given in Table I.

Preparation of PhCN$_3$S$_2$Cl$_2$ (2, R = Ph). A mixture of PhCN (1.10 g, 10.6 mmol) and (NSCl)$_3$ (1.62 g, 6.7 mmol) at 23 °C for 16 weeks produced large, yellow hexagonal crystals and an orange powder, which were separated manually. The yellow crystals were identified as **2** (R = Ph) (1.09 g, 4.1 mmol) by comparison of an IR spectrum with that reported in the literature.[8] In a similar manner, the orange powder was shown to be **1** (R = Ph).[1]

Preparation of R$_2$NCN$_3$S$_2$Cl$_2$ (2, R = Me, Et, ^{i}Pr). The dialkylcyanamide R$_2$NCN (10 mmol) was added by syringe to a solution of (NSCl)$_3$ (6.7 mmol) in chloroform (30 mL). The progress of the reactions was monitored by ^{14}N NMR spectroscopy, and upon completion [12 h (R = Me), 48 h (R = Et), 1 week (R = ^{i}Pr)], *n*-pentane (15 mL) was added to the solutions until they became cloudy. These solutions were then cooled to −30 °C to give yellow crystals of **2** (R = Me, Et, ^{i}Pr) in ca. 90% yield. The products were identified by comparison of their IR spectra with those reported in the literature.[3] ^{14}N NMR data are given in Table I.

Thermolysis of R$_2$NCN$_3$S$_2$Cl$_2$ (2, R = Me, Et, ^{i}Pr). A solution of **2** (R = Me, Et, ^{i}Pr) in toluene (10 mL) was heated at reflux for 24 h. The solution was cooled to 23 °C to give purple crystals of **1** in 91%, 74%, and 71% yields for R = Me, Et, and ^{i}Pr, respectively. Anal. for **1** (R = Me). Calcd for C$_3$H$_6$ClN$_3$S$_2$: C, 19.62; H, 3.29; N, 22.88. Found: C, 19.37; H, 3.53; N, 23.17. Anal. for **1** (R = ^{i}Pr). Calcd for C$_7$H$_{14}$ClN$_3$S$_2$: C, 35.06; H, 5.88; N, 17.52. Found: C, 35.38; H, 6.01; N, 17.34. The product **1** (R = Et) was identified by comparison of IR spectroscopic data with the literature values.[9] NMR data for **1** (R = Me, Et, ^{i}Pr) are given in Table II. IR (cm^{-1}): **1** (R = Me), 1568 s, 1406 m, 1245 s, 1179 m, 1082 s, 1022 m, 930 s, 899 s, 802 s, 706 s, 668 m, 570 vs, 457 m; **1** (R = ^{i}Pr), 1560 vs, 1366 s, 1242 m, 1181 m, 1162 m, 1095 s, 1044 s, 791 m, 577 m, 529 m.

Thermolysis of RCN$_3$S$_2$Cl$_2$ (2, R = Ph, ^{t}Bu, CCl$_3$). A solution of **2** (R = Ph, ^{t}Bu, CCl$_3$) (1 mmol) in 1,2-dichloroethane (3 mL) in a 10-mm NMR tube sealed with a Teflon-lined screw cap was placed in the cavity of a Bruker AM 400 spectrometer. The temperature of the sample was increased in increments of 5 °C, and ^{14}N NMR spectra were recorded at each temperature by using the absolute intensity mode. When the concentration of **2** began to decrease, the temperature was held constant until the concentration of **2** reached zero. The solutions were then allowed to cool to 23 °C to give yellow crystals of **1** (R = Ph, ^{t}Bu, CCl$_3$), identified by their IR spectra,[1] in almost quantitative yields.

Kinetic Study of the Thermolysis of Me$_2$NCN$_3$S$_2$Cl$_2$ (2, R = Me$_2$N). Me$_2$NCN$_3$S$_2$Cl$_2$ (0.141 g, 0.605 mmol) was introduced into an NMR tube (10 mm × 10 cm), which was then sealed with a rubber septum. Dry CDCl$_3$ (1 mL) was added to the NMR tube by syringe. The contents of the tube were cooled to 77 K, and the tube was flame-sealed at the 8-cm mark. The NMR tube was inserted completely into a temperature-controlled oven at 120 °C. At regular time intervals the tube was removed from the oven and quickly immersed in an ice-water bath, and then the ^{1}H NMR spectrum was recorded. In this way the concentration of **2** (R = Me$_2$N) as a function of time was measured. The data are given in the supplementary material and in Figure 3.

Preparation of 1,3-(Me$_2$NC)$_2$N$_4$S$_2$Cl$_2$ (8). Me$_2$NCN (0.70 g, 10 mmol) was added by syringe to a solution of (NSCl)$_3$ (0.80 g, 3.3 mol) in CCl$_4$ (20 mL). The reaction mixture was stirred for 20 h at 23 °C and then cooled to −20 °C to give a yellow precipitate of 1,3-(Me$_2$NC)$_2$N$_4$S$_2$Cl$_2$ (1.21 g, 4.0 mmol), identified by IR spectroscopy.[3]

Reaction of Me$_2$NCN and NSCl (1:1) in Nitromethane. Me$_2$NCN (0.70 g, 10 mmol) was added to a solution of (NSCl)$_3$ (0.80 g, 3.3 mmol) in nitromethane (3 mL) at 23 °C. An immediate reaction occurred to give a red solution and an orange precipitate of S$_4$N$_4$ (0.29 g, 1.6 mmol) (IR spectrum). The supernatant solution was removed via a transfer needle, and slow evaporation of MeNO$_2$ produced a mixture of 1,3-(Me$_2$NC)$_2$N$_4$S$_2$Cl$_2$ (yellow powder) and Me$_2$NCN$_4$S$_3$Cl (colorless rectangular crystals) in comparable amounts (IR spectrum). The crystals of Me$_2$NCN$_4$S$_3$Cl were separated manually and exhibited an IR spectrum identical with that reported in the literature.[17]

Results and Discussion

Preparation of 1,3-Dichloro-1,3,2,4,6-dithiatriazines (2). The six-membered rings **2** (R = ^{t}Bu, CCl$_3$, Ph) can be prepared from the appropriate nitrile and (NSCl)$_3$ by employing milder reaction conditions (23 °C in the absence of a solvent) than those used by Banister et al.[1] For example, trichloroacetonitrile reacts very slowly with (NSCl)$_3$ to give **2** (R = CCl$_3$) in 77% yield after 3

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(14) For a preliminary communication, see: Apblett, A.; Chivers, T. *J. Chem. Soc., Chem. Commun.* **1989**, 88.

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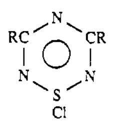
weeks. The reaction of *tert*-butyl cyanide with $(NSCl)_3$ required 12 weeks to go to completion and according to ^1H NMR spectroscopy gave a mixture of **1** (R = ^tBu, 29%) and **2** (R = ^tBu, 71%), from which the six-membered ring was obtained in an overall yield of 45% (based on NSCl). Similarly, the reaction of benzonitrile with $(NSCl)_3$ yields **2** (R = Ph) in 41% yield after 12 weeks together with a considerable amount of **1** (R = Ph). This route to **2** (R = Ph) is not superior to the chlorination of the bicyclic compound $PhCS_3N_5$ described by Oakley et al.[8] Relatively short reaction times are necessary for the preparation of **2** (R = R'_2N) from R'_2NCN (R' = Me, Et, ^iPr) and $(NSCl)_3$ at 23 °C in chloroform. The progress of these reactions was monitored by ^{14}N NMR spectroscopy and shown to depend on the steric bulk of the R' group; the reaction is complete in 12 h, 48 h, and 1 week for R = Me, Et, and ^iPr, respectively.

These reactions can be accelerated by ultraviolet irradiation, but the yields of **2** are lower for long reaction times due to the production of some S_4N_3Cl from the photolysis of $(NSCl)_3$. For example, irradiation of a mixture of CCl_3CN (10% excess) and $(NSCl)_3$ in a water-cooled quartz tube with a 250-W sun lamp for 2 days produced **2** (R = CCl_3) in 77% yield. However, **2** (R = ^tBu) was obtained in only 33% yield together with substantial amounts of **1** (R = ^tBu) after irradiation for 1 week.

The ^{14}N NMR spectra of **2** exhibit well-separated signals in the region −181 to −213 ppm for the two equivalent ring nitrogen atoms and at higher field (−237 to −263 ppm) for the unique ring nitrogen atom (Table I). The resonance for the R'_2N group in the dialkylamino derivatives overlaps the former signal.

Mechanism of the RCN–NSCl Cycloaddition Reaction. A mechanism for the cycloaddition reaction of organic nitriles with NSCl units must take into account (a) the unique effect of R'_2N substituents on the reaction rate, (b) the failure of this reaction for the preparation of **2** for R groups that contain α-protons,[1,19] and (c) the absence of the ring systems **5**[20] and **6**[3,21] among the reaction products.



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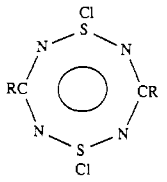

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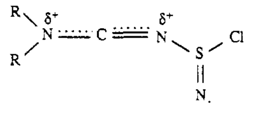

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The reaction of Me_2NCN with $(NSCl)_3$ occurs on a convenient time scale to be studied in detail by ^1H and ^{14}N NMR spectroscopy. The addition of Me_2NCN to a yellow solution of $(NSCl)_3$ in $CDCl_3$ produces a mint green solution, indicating the formation of NSCl monomer.[22] After 15 min the solution becomes red and then slowly fades to the yellow-orange color of **2** (R = Me_2N). The methyl groups of the red species are anisochronous and give rise to two signals in the ^1H NMR spectrum at 3.42 and 3.56 ppm and in the ^{13}C NMR spectrum at 40.6 and 41.0 ppm. The signal for the nitrile carbon atom of the red intermediate occurs at 149.8 ppm. Three signals are observed in the ^{14}N NMR spectrum at 209, −154, and −340 ppm, and these are assigned to the ClS*N*, C*N*, and Me_2*N* nitrogen atoms, respectively. Thus, the NMR spectroscopic results suggest a zwitterion **7** (R = Me), with restricted rotation about the C=NR_2 bond, as the most likely structure for the red intermediate. The intermediate **7** was isolated as a red oil by carrying out the Me_2NCN–NSCl reaction in hexane, but an IR spectrum showed that it was contaminated with Me_2NCN and a pure sample could not be obtained.

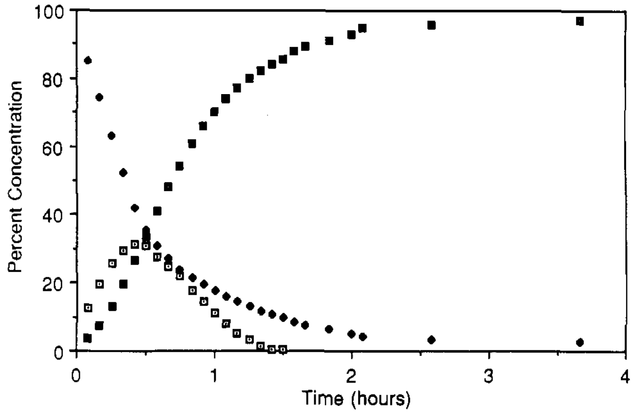

Figure 1. Changes in the concentrations of Me_2NCN (◆), **2** (R = Me_2N) (■), and **7** (R = Me) (▣) as a function of time in the Me_2NCN–$(NSCl)_3$ reaction.

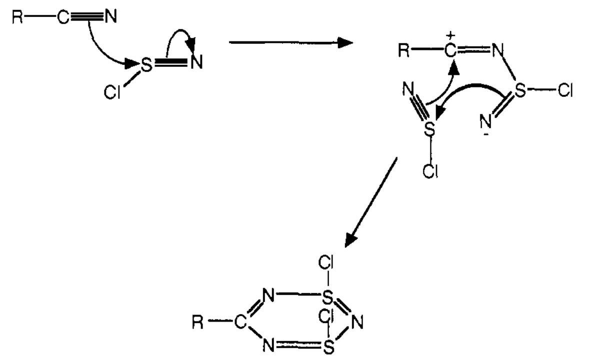

Figure 2. Proposed mechanism for the formation of **2** (R = Me_2N).

The concentrations of the reactants, intermediate, and product of the reaction of Me_2NCN with 2 mol of NSCl were monitored by ^1H and by ^{14}N NMR spectroscopy. After 5 min, **2** (R = Me_2N) can be detected in addition to Me_2NCN and **7** (R = Me) in the ^1H NMR spectrum. In the early part of the reaction the ^{14}N NMR signals for NSCl monomer (+328 ppm)[16] and the NSCl unit of **7** (R = Me) coalesce into one exchange-broadened peak whose chemical shift varies with time as NSCl monomer is consumed until a sharp singlet at +209 ppm, assigned to the NSCl unit of **7** (R = Me), is observed. The concentrations of Me_2NCN, **7** (R = Me), and **2** (R = Me_2N) obtained from integration of the ^1H NMR spectra are plotted as a function of time in Figure 1. The concentration of **2** (R = Me_2N) increases steadily as Me_2NCN is consumed, and the concentration of the intermediate quickly reaches a constant value that is maintained until the reaction is nearly complete. The results indicate that the cycloaddition of Me_2NCN with two NSCl units involves the sequential addition of NSCl units to the nitrile, i.e. initial nucleophilic attack of the nitrile on NSCl, followed by a 2 + 4 cycloaddition of a second NSCl moiety to the intermediate (Figure 2). An earlier suggestion[3] that the reaction involves cycloaddition of the nitrile with $(NSCl)_2$ can now be ruled out as the major reaction pathway.[24,25] The participation of $(NSCl)_2$ was originally proposed to account for the absence of **5** and **6** among the isolated reaction products.[3] However, the fact that **7** (R = Me) can be isolated suggests that the dimerization of **7** (R = Me) to give **6** is very much slower than its reaction with NSCl to give **2**. The

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(19) In this study the reaction of malononitrile (2.5 mmol) with $(NSCl)_3$ (3.3 mmol) in CH_2Cl_2 at 23 °C produced a yellow precipitate of S_4N_3Cl (1.7 mmol) and a complex mixture of soluble products (IR and ^{14}N NMR spectroscopy).

(20) Hayes, P. J.; Oakley, R. T.; Cordes, A. W.; Pennington, W. T. *J. Am. Chem. Soc.* **1985**, *107*, 1346 and references cited therein.

(21) Boeré, R. T.; Cordes, A. W.; Craig, S. L.; Oakley, R. T.; Reed, R. W. *J. Am. Chem. Soc.* **1987**, *109*, 868.

(22) Heal, H. G. *The Inorganic Heterocyclic Chemistry of Sulfur, Nitrogen and Phosphorus*; Academic Press: New York, 1980; p 135.

(23) Witanowski, W.; Stefaniak, L.; Webb, G. A. *Nitrogen NMR Spectroscopy*; Annual Reports of NMR Spectroscopy, Vol. 18; Academic Press: London, 1986.

(24) ^{14}N NMR studies of the $(NSCl)_3 \rightleftharpoons 3NSCl$ equilibrium provide no evidence for detectable amounts of $(NSCl)_2$.[16]

(25) SCF calculations for *cyclic* forms of $(NSCl)_2$ indicate that the dimer is thermodynamically unstable with respect to 2NSCl but should be kinetically stable at low temperatures. *Acyclic* structures for $(NSCl)_2$ were not considered. Ahlrichs, R.; Ehrhardt, C. *Chem. Phys.* **1986**, *107*, 1.

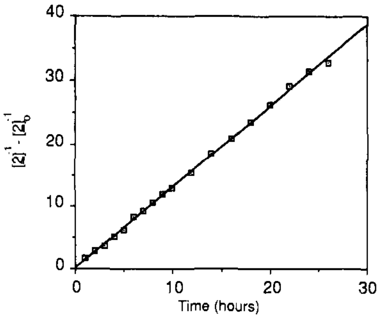


Figure 3. Plot of $[2]^{-1} - [2]_0^{-1}$ vs time for the thermolysis of **2** (R = Me_2N).

lack of **5** presumably indicates that the reaction of **7** (R = Me) with NSCl is much faster than the reaction of **7** (R = Me) with Me_2NCN.

The stabilization of the intermediate **7** (R = Me, Et, ${}^iPr$) in reactions of R'_2NCN with $(NSCl)_3$ is attributed to electron donation from the amino nitrogen to the electron-deficient carbon center ($p\pi$–$p\pi$ bonding), as indicated by the observed inequivalence of the methyl groups in **7** (R = Me). For other nitriles this stabilization either cannot occur (R = CCl_3, ${}^tBu$) or is ineffective (R = Ph), with the result that **7** is undetectable and the reactions are very slow. In the case of nitriles with α-protons, e.g. CH_3CN,[1b] $C_6H_5CH_2CN$,[1b] or $CH_2(CN)_2$,[19] the rapid loss of HCl from the corresponding intermediate could account for the lack of success of the cycloaddition reaction. The intermediate **7** is of particular significance as a possible precursor for polymers of the type $[(R)CNSN]_x$, which are expected to exhibit one-dimensional conductivity.[26]

Thermal Conversion of 2 into 1. The preparation of **2** from organic nitriles and $(NSCl)_3$ at room temperature and earlier reports that such reactions produce **1** when conducted at higher temperatures suggest that **1** may be formed by thermal degradation of **2**.[1] Therefore, we have investigated the thermal decomposition of various derivatives of **2** in order to assess the influence of the exocyclic substituent R on the ring contraction process.

All derivatives of **2** are yellow or yellow-orange, moisture-sensitive solids. The thermolysis of **2** (R = Me_2N, Et_2N, ${}^iPr_2N$) occurs in toluene at reflux to give the corresponding derivatives of **1** as purple crystals in >70% yields. This route to **1** (R = Me_2N) represents a significant improvement over the previous synthesis (in ca. 20% yield) from **2** (R = Me_2N) and sodium azide.[9] The thermolysis of other derivatives of **2** was monitored by ^{14}N NMR spectroscopy. The two signals for the ring nitrogen atoms of **2** (Table I) are gradually replaced by a downfield singlet for the two equivalent nitrogen atoms of **1** (Table II). The thermal decomposition of **2** occurs at 80 °C (R = CCl_3, Ph) and 40 °C (R = ${}^tBu$) to give the corresponding five-membered rings, **1**, in almost quantitative yields.[27] Thus, the approximate order of thermal stability for the various derivatives of **2** is $R'_2N > CCl_3 \sim Ph > {}^tBu$. There is no obvious correlation between the thermal stability of **2** and either the electronic properties or size of the exocyclic substituent.

The transformation of **2** (R = Me_2N) into **1** (R = Me_2N) was monitored by UV–visible and ^1H NMR spectroscopies in an attempt to detect an intermediate and to determine the reaction order. A red intermediate (λ_{max} 500 nm, $\delta(^1H)$ 3.51), which could not be isolated, was observed, and the reaction was found to be second order in **2** (R = Me_2N) (Figure 3). This indicates that the ring contraction occurs via initial dimerization of **2** (R = Me_2N) to give a twelve-membered ring (Figure 4), a process that has been observed for other six-membered heterocyclothiazenes.[28,29] The subsequent extrusion of N_2 and Cl_2, possibly via the formation of a diazo linkage, would account for the high yields of **1** formed in this process.

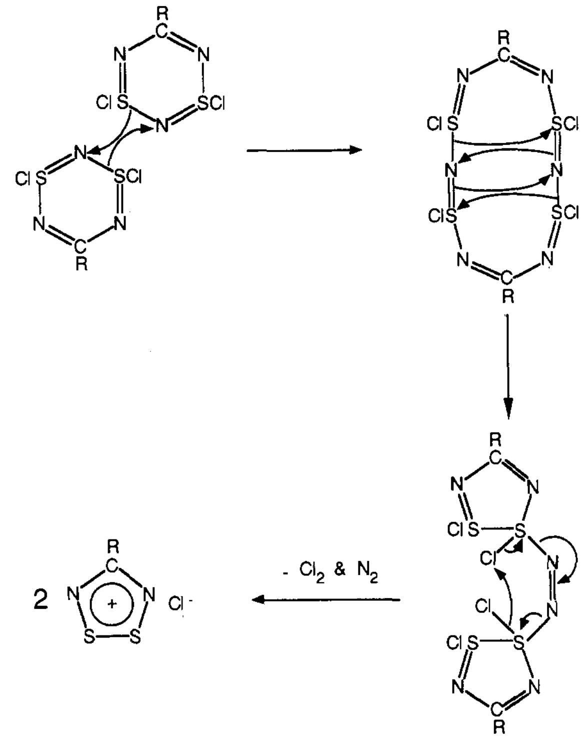
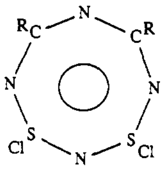


Figure 4. Proposed mechanism for the ring contraction reaction **2** → **1**.

Formation of Eight-Membered Rings from RCN and (NSCl)₃. In an earlier study, the eight-membered ring **8** (R = Me_2N) was isolated in high yield when a solution of $(NSCl)_3$ in CCl_4 at 60 °C was treated with a *large excess* of Me_2NCN.[3] The heterocycle



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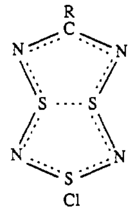

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8 (R = Me_2N) is unstable with respect to loss of Me_2NCN *in solution* to give **2** (R = Me_2N). The preparation of other derivatives of **8** from R'_2NCN and $(NSCl)_3$ and the effect of varying the reaction conditions on the formation of **8** (R = Me_2N) have now been investigated. It was found that **8** (R = Me_2N) can be obtained in 80% yield by the reaction of Me_2NCN with NSCl *in a 1:1 molar ratio* at room temperature in CCl_4. Attempts to prepare **8** (R = Et_2N, ${}^iPr_2N$) under similar conditions gave only **2** (R = Et_2N, ${}^iPr_2N$). The reaction of **2** (R = Me_2N) with Me_2NCN in CCl_4 also produces **8** (R = Me_2N), presumably via the reversible insertion of the nitrile into the six-membered ring (eq 1). The instability of **8** (R = Me_2N) in solution has prevented an investigation of its chemistry.

$$Me_2NCN_3S_2Cl_2 + Me_2NCN \rightleftharpoons 1,3\text{-}(Me_2NC)_2N_4S_2Cl_2 \qquad (1)$$

When the reaction of Me_2NCN with NSCl in a 1:1 molar ratio was carried out in nitromethane, the known bicyclic ring system **9** (R = NMe_2)[17] was obtained as a mixture with **8** (R = NMe_2). The crystals of **9** (R = NMe_2) can be separated by hand, and this reaction provides a better source of **9** (R = NMe_2) than the slow and low-yield synthesis from **2** (R = NMe_2) and Me_3SiNSO.[17] The planar cation of **9** (R = CF_3), 1,3,5,2,4,6,8-trithiatetrazocine,

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(26) Whangbo, M. H.; Hoffmann, R.; Woodward, R. B. *Proc. R. Soc. London, A* **1979**, *366*, 23.

(27) The thermal conversion of **2** (R = CF_3) into **1** (R = CF_3) at 120 °C is mentioned without details in ref 2.

(28) (a) Chivers, T.; Rao, M. N. S.; Richardson, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 186. (b) Burford, N.; Chivers, T.; Rao, M. N. S.; Richardson, J. F. *Inorg. Chem.* **1984**, *23*, 1946.

(29) Chivers, T.; Rao, M. N. S.; Richardson, J. F. *J. Chem. Soc., Chem. Commun.* **1983**, 702.

has been obtained in 4% yield from the reaction of CF_3CN with $(NSCl)_3$ in SO_2 at 55 °C in a Teflon autoclave,[30] and **9** (R = ^{t}Bu) has been isolated in unspecified yield from the reaction of trimethylacetamidine and $(NSCl)_3$.[31]

Summary and Conclusions. The initial product of the reaction of organic nitriles with $(NSCl)_3$ in carbon tetrachloride is the six-membered ring **2**. This direct synthesis of **2** should expedite investigations of the corresponding eitht-π-electron systems, **4**. The rate of formation of **2** is much faster for R = R'_2N than for R = ^{t}Bu, Ph, and CCl_3. This difference is attributed to the stabilization of the intermediate **7** by electron donation from the R'_2N group to the electron-deficient carbon ($p\pi$–$p\pi$ bonding). The isolation of **7** (R = Me) offers the possibility of preparing polymers of the type $[(R)CNSN]_x$ via reduction. The thermal conversion of **2** into **1** upon thermolysis explains previous reports of the formation of **1** from the reaction of organic nitriles with $(NSCl)_3$ at elevated temperatures and provides a good synthesis of dialkylamino derivatives of the five-membered ring. The reaction of Me_2NCN with $(NSCl)_3$ in *nitromethane* is an improved route to the trithiatetrazocine ring system **9** (R = Me_2N) that will facilitate studies of this eight-membered ring.

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Note Added in Proof. The synthesis of **1** (R = NMe_2) in 54% yield from the reaction of *N,N*-dimethylguanidinium hydrochloride with excess sulfur dichloride in acetonitrile has been reported recently.[32]

Supplementary Material Available: A table of kinetic data for the thermolysis of **2** (R = Me_2N) (1 page). Ordering information is given on any current masthead page.

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(30) Höfs, H. V.; Hartman, G.; Mews, R.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 988.

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(32) Cordes, A. W.; Goddard, J. D.; Oakley, R. T.; Westwood, N. P. C. *J. Am. Chem. Soc.* **1989**, *111*, 6147.

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Chromium(II) and Vanadium(II) Reduction of Pentacyanocobaltate(III) Complexes

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The chromium(II) and vanadium(II) reductions of the pentacyanocobaltate(III) complexes of pyrazine (pyz), isonicotinamide (isn), 4-cyanopyridine (4-CN-py), and pyridine (py) have been studied. For chromium(II), the reductions are first order in Cr(II) and cobalt(III) complex and independent of hydrogen ion concentration. At 25 °C, I = 1.0 M ($LiClO_4$), $k_{Cr} = 1.5 \times 10^3$, 19, 28, and 1.2 $M^{-1}\ s^{-1}$ for pyz, isn, 4-CN-py, and py, respectively. A radical-ion mechanism is proposed for the reduction of the first three complexes. For V(II), two reactions are observed with rate laws $k_{obs1} = k_1[V^{2+}] + k_{-1}$ and $k_{obs2} = k[V^{2+}]/(1 + K_1[V^{2+}])$. The first reaction is the formation of a binuclear intermediate precursor complex bridged by a cyanide from the oxidant. Values of k_1 ($M^{-1}\ s^{-1}$), k_{-1} (s^{-1}) for pyz, isn, 4-CN-py, py: 65, 1.1; 55, 1.0; 46, 1.2; 49, 1.0. The saturation type kinetics observed in the second reaction are consistent with formation of a precursor complex that is a "dead end" on the reduction pathway and a subsequent outer-sphere reduction between monomeric reactants.

Introduction

The chemistry of pentacyanocobaltate(III) complexes has provided a wealth of information concerning thermal and photochemical substitution reactions in octahedral systems.[1] Comparison of UV-vis and ^{13}C NMR spectra for these complexes with those for analogous pentacyanoferrate(II) systems has been important in the study of π-back-bonding interactions between the metal center and coordinated ligands.[2] Surprisingly, however, few investigations of the reduction of pentacyanocobaltate(III) complexes have been made.

Espenson and Davies[3] reported the first studies on the vanadium(II) reductions of $[(CN)_5Co^{III}L]$ complexes where L = Cl^-, Br^-, I^-, SCN^-, N_3^-, and H_2O. For the N_3^- and NCS^- complexes, an inner-sphere redox pathway was proposed. The reaction was postulated to proceed via ion-pair formation followed by a V(II) substitution-controlled electron transfer as illustrated for the azide complex.

$$[V(OH_2)_6]^{2+} + [Co(CN)_5N_3]^{3-} \rightleftarrows [V(OH_2)_6,Co(CN)_5N_3]^- \quad K$$

$$[V(OH_2)_6,Co(CN)_5N_3]^- \rightarrow [Co(CN)_5]^{3-} + [V(OH_2)_5N_3]^{2+} \quad k$$

In order to investigate the generality of the above mechanism and because of the paucity of data on the redox reactions of $(CN)_5Co^{III}$ complexes, we report here the kinetics of the chromium(II) and vanadium(II) redox reactions with pentacyanocobaltate(III) complexes possessing potential organic bridging ligands. We also report the results of a reinvestigation of the vanadium(II) reduction of $[Co(CN)_5N_3]^{3-}$ and $[Co(CN)_5SCN]^{3-}$.[3]

Experimental Section

All reagent solutions were prepared in water that had been passed through a Milli-Q Water purification system. Perchloric acid solutions were prepared by dilution of 70% doubly distilled perchloric acid (G. F. Smith Chemical Co.) and standardized with standard sodium hydroxide. Lithium perchlorate stock solutions were prepared from G. F. Smith anhydrous reagent grade $LiClO_4$ and filtered through a 0.5-μm Millipore filter. The solutions were standardized by charging aliquots on an ion-exchange column of Amberlite IR 120(H) resin and determining the acid released by titration with standard sodium hydroxide.

Chromium(II) perchlorate solutions were prepared by reduction of solutions of G. F. Smith chromium(III) perchlorate with zinc amalgam. Chromium(II) concentrations were determined as described previously.[4]

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(1) Abou-El-Wafe, M. H.; Burnett, M. G. *J. Chem. Soc., Chem. Commun.* **1983**, 833. Borea, R.; Ellis, J.; Tsao, M.; Wilmarth, W. K. *Inorg. Chem.* **1967**, *6*, 243.

(2) Figard, J. E.; Paeekstelis, J. V.; Byrne, E. F.; Petersen, J. D. *J. Am. Chem. Soc.* **1977**, *99*, 8417.

(3) Davies, K. M.; Espenson, J. H. *J. Chem. Soc. Chem. Commun.* **1969**, 111. Davies, K. M.; Espenson, J. H. *J. Am. Chem. Soc.* **1969**, *91*, 3093.

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