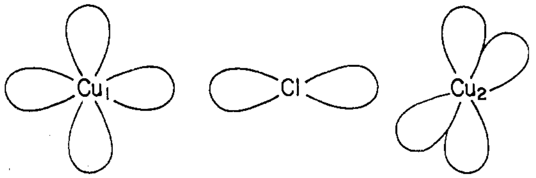

Figure 3. Orbital overlap scheme for the chloride bridging in $(RNH_3)_2CuCl_4$.

exchange coupling is vitiated here in contrast to the four other cyanide-bridged species.

The magnetic behavior of $[Cu(terpy)CN]NO_3$ may also be compared with that in the linear halide bridged, two-dimensional, ferromagnetic $(RNH_3)_2CuCl_4$ and $(RNH_3)_2CuBr_4$ salts[11] (Figure 3). The similarity here is that the bridging angle in both cases ideally should be 180°. In these latter salts, the unpaired electron density on Cu_1 is delocalized onto a p orbital on the bridging halide.[12] Thus, as in $[Cu(terpy)CN]NO_3 \cdot H_2O$, it is in an orbital orthogonal to the $d_{x^2-y^2}$ orbital on Cu_2 and Hund's rule leads to the prediction of the observed, ferromagnetic interaction ($J \sim +10\ cm^{-1}$) via this one-atom bridge. A similar bridging mechanism can be proposed for $[Cu(terpy)CN]NO_3 \cdot H_2O$ wherein unpaired electron density is delocalized into a σ^* molecular orbital resulting from the interaction of $d_{x^2-y^2}$ on Cu_1 with the highest filled σ orbital on cyanide. Were the resulting molecular orbital strictly orthogonal to $d_{x^2-y^2}$ on Cu_2, ferromagnetic exchange coupling would result. However, bending of the Cu_2NC angle away from 180° could produce slight antiferromagnetism. Since the angle in question is 164°,[4] the observed weak antiferromagnetism of $[Cu(terpy)CN]NO_3 \cdot H_2O$ may very well be a consequence of the nonlinear bridge.

Evidence as to the weakness of cyanide bridge can be found from the infrared spectrum of $[Cu(terpy)CN]NO_3 \cdot H_2O$. Whereas the Nujol mull spectrum shows a CN stretching mode at 2171 cm^{-1} as expected for bridging cyanide,[10] the same band shifts to 2143 cm^{-1} when pelleted in KBr. In the latter instance the CN bridge is surely broken under high pressure to give a terminal cyanide linkage. This underscores the danger of relying solely on KBr pelleting as a means of deducing structural information from infrared spectra.

Although one might expect $[Cu(terpy)CN]ClO_4$, to be analogous in structure and magnetic properties to the NO_3^- complex, this seems not to be the case. The infrared spectrum shows a cyanide stretching band at 2145 cm^{-1} (Nujol mull) and a somewhat split ν_3 band for ClO_4^- at 1084 and 1112 cm^{-1}. Also, the complex exhibits linear Curie–Weiss behavior in the temperature range 1.7–100 K with $\Theta = -0.026$ K. With this small value for the Weiss constant, no further analysis was made on this basically paramagnetic salt. Hence both the infrared and magnetic data combined imply monomeric copper(II) with terminal cyanide and possible weak interaction of copper(II) with ClO_4^-. Quite likely, the cyanide bridging found in $[Cu(terpy)CN]NO_3 \cdot H_2O$ but absent in the ClO_4^- salt, may be due to a difference in lattice forces within the two salts.

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Registry No. $[Cu(terpy)CN]ClO_4$, 70235-90-4; $[Cu(terpy)CN]NO_3$, 70235-91-5.

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Contribution from the Department of Chemistry,
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Methyltrioxorhenium. An Air-Stable Compound Containing a Carbon–Rhenium Bond

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During the preparation of trimethyldioxorhenium (using literature methods[1]), we observed the growth of needle crystals in tubes containing residues and which had been left open to the atmosphere. Purification of the product by sublimation in vacuo resulted in the isolation of a colorless crystalline material which melted sharply. Elemental analysis suggested the compound to be methyltrioxorhenium. The compound could be synthesized by exposure of either tetramethyloxorhenium[2] or trimethyldioxorhenium[1] to dry air in a closed system. The mass spectrum showed parent-ion peaks $CH_3ReO_3^+$ at 250 and 248 mass units corresponding to species containing ^{187}Re and ^{185}Re, respectively. The two peaks did not have the expected intensity ratio based on the relative isotopic abundances, due to the overlap of the lower mass unit peak with that of the species $CH^{187}ReO_3^+$.

Experimental Section

Approximately 100 mg of Me_4ReO[2] (Me = methyl) or Me_3ReO_2[1] was transferred into a 1-L bulb. Dry air was admitted up to atmospheric pressure. The growth of long needles could be seen in a few days, and after 4 weeks yields in excess of 50% were obtained. The product was purified by sublimation in vacuo. $MeReO_3$ is soluble in CH_3CN, C_6H_6, $CHCl_3$, EtOH, or Et_2O (Et = ethyl). It is also sparingly soluble in CS_2 or C_6H_{14}. The proton magnetic resonance spectrum in $CDCl_3$ showed one sharp resonance at τ 7.4. (This value is close to that found for related methylrhenium compounds.[1,2]) Elemental analysis for C and H gave the following. Anal. Calcd for CH_3O_3Re: C, 4.82; H, 1.20. Found: C, 4.94, 4.98; H, 1.26, 1.25. The melting point was 110 °C.

Results and Discussion

The vibrational spectra under a variety of conditions are summarized in Table I. The assignments are based on a "tetrahedral" monomeric species with a direct rhenium–carbon bond. The results are comparable to those obtained for ReO_3Cl[3] and (monomeric) ReO_3F.[4] The rhenium–carbon bond stretching mode is expected to occur in the region of 500 cm^{-1}.

Two features of this compound are of particular interest: the presence of a rhenium–carbon bond in an air-stable compound and the stabilization of a rhenium–carbon bond by the oxo ligands. The possibility that this material might be methyl perrhenate is eliminated by its stability to water. In 1974 it was pointed out[5] that the only known ester of perrhenic acid is the trimethylsilyl derivative, and this is (as expected) very sensitive to hydrolysis.[6] Finally, we note that the preparation of this compound suggests that suitable preparative

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Table I. Vibrational Spectra of Methyltrioxorhenium[a]

Raman		infrared[b]			
solid	soln[c]	soln[c]	gas (70 °C)	Ar matrix	assignt
999 s[d]	999 s, p[e]	999 w	1003 w	1000 ms	ReO_3 sym str
			985	970 vs	ReO_3 antisym str
964 m		960 s	975 vs		
			962	966 m	
			743 mw		CH_3 rock
530 m			574 w	566 w	Re–C
330 m			324 w		ReO_3 def
242 m					

[a] Reported range 1100–250 cm^{-1} (gas and matrix infrared) or to 100 cm^{-1} (solid Raman). [b] A hexachlorobutadiene mull of the solid showed weak IR bands at 2895 and 2980 cm^{-1} (C–H stretching modes); in addition, there was a further slightly stronger band at 1360 cm^{-1} (C–H deformation). Corresponding bands were seen in the matrix infrared spectrum. [c] Solutions (in CS_2) were examined only in the region of 1000 cm^{-1}. [d] s = strong, m = medium, w = weak, v = very. [e] p = polarized.

routes could lead to Me_2WO_2, $MeReS_3$, and possibly $HReO_3$ for example. We do not propose to attempt these syntheses.

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Registry No. $MeReO_3$, 70197-13-6; Me_4ReO, 53022-70-1; Me_3ReO_2, 56090-01-8.

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Fluoride Ion Induced Cyclization of Trifluoroacetonitrile with Oxygen- and Sulfur(II)-Containing Nucleophiles

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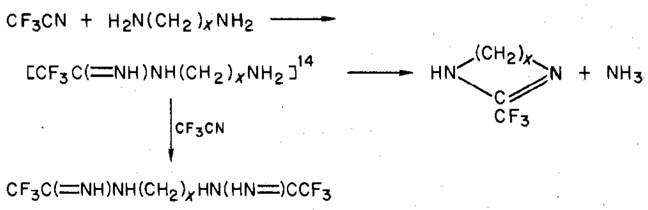
The high susceptibility of perfluoroalkyl nitriles to attack by nucleophiles, such as ammonia,[2-4] hydrazine,[5] hydrogen sulfide,[3,6-8] alcohols,[9-11] hydroxylamines,[10,12] thiols,[13] and amines,[3,14,15] results from the strong electron-withdrawing effect of the perfluoroalkyl group which enhances the electrophilicity of the nitrile carbon. For example

$$CF_3CN + ROH \xrightarrow{R_3N} CF_3C({=}NH)OR^{10}$$

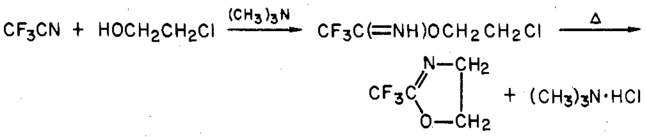
$$CF_3CN + RSH \xrightarrow{K_2CO_3} CF_3C({=}NH)SR^{13}$$

$$CF_3CN + R_2NH \longrightarrow CF_3C({=}NH)NR_2^{15}$$



In this paper, we wish to report a route to a 1,3-dioxolane, a 1,3-oxathiolane, and a 1,3-dithiolane in which fluoride ion catalyzes the cyclization reactions of CF_3CN with 1,2-ethanediol, 2-mercaptoethanol, and 1,2-ethanedithiol. While these syntheses may not be surprising, we believe this is a facile way to these interesting compound types which heretofore has not been explored. In addition, a seven-member heterocycle is also obtained.

Previously, unfluorinated nitriles (RCN; R = Ph, *n*-C_7H_{15}, *o*-, *m*-, *p*-tolyl, *p*-$NO_2C_6H_4$) when refluxed at length with 1,2-ethanediol produced hydroxyalkyl esters, $RC(O)O(CH_2)_2OH$.[16] However, 2-oxazolines result when amino alcohols $H_2N(CH_2)_nCHROH$ (R = H, CH_3; n = 1 or 2) are reacted with a wide range of alkyl and aryl nitriles in the presence of catalytic amounts of metal salts, e.g., $ZnSO_4$, $ZnCl_2$, or $(CH_3C(O)O)_2Cd$.[17] With excess base, $(CH_3)_3N$, a 2-oxazoline is also formed in the reaction of trifluoroacetonitrile and 2-chloroethanol.[11]

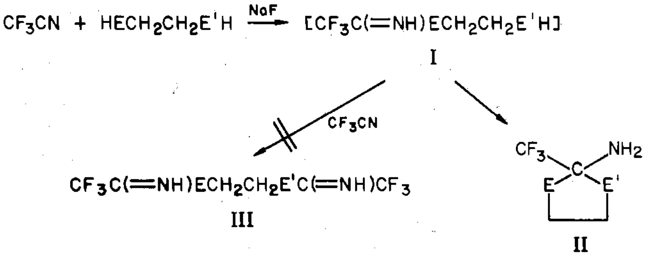


With cyanogen, a variety of interesting bicyclic compounds are obtained when the reactants are diamines[18] or amino mercaptans.[19] However, cyclization does not occur with amino alcohols[20] or with diols.[21] Cyanogen with $H_2NCH_2CH_2OH$ gives $[HOCH_2CH_2N(H)C({=}NH)]_2$ or $[H_2NCH_2CH_2OC({=}NH)]_2$ (depending on the base catalyst used), and with $HO(CH_2)_xOH$ and HCl, oxaldiimidate dihydrochlorides, $[HO(CH_2)_xOCNH_2Cl]_2$, result.

Results and Discussion

While there are large numbers of 1,3-oxathiolanes, C_3OS, 1,3-dithiolanes, C_3S_2, and 1,3-dioxolanes, C_3O_2, described in the literature,[22] these are usually synthesized from 2-mercapto alcohols with ketones or aldehydes or methyl vinyl ethers in the presence of an acid catalyst, from aldehydes or ketones and 1,2-alkanethiols with anhydrous HCl, or from aldehydes or ketones or acetylene and 1,2-glycols or ethylene oxides. The ring closure reactions of CF_3CN in the literature are limited to those with diamines, e.g., $H_2NCH_2CH_2NH_2$, with concomitant loss of ammonia[14] and with 2-chloroethanol[11] with loss of hydrogen chloride as $(CH_3)_3N{\cdot}HCl$. In these cases, the cyclic products are an imidoazoline and an oxazoline; that is, each contains an imido (>C=N–) grouping. This is true also for the bicyclic compounds formed between cyanogen and diamines[18] or amino mercaptans.[19]

However, in the reactions examined in this study, with sodium fluoride as the base, cyclization to form a substituted 1,3-dioxolane, a 1,3-oxathiolane, and a 1,3-dithiolane (II) occurs readily at room temperature when an excess of CF_3CN is used.



E = E′ = O, S
E = O, E′ = S

These compounds (II) are slightly volatile, colorless liquids which can be manipulated by using standard vacuum line techniques and are neither air nor moisture sensitive. The

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