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.

Acknowledgment. We thank Dr. J. Evans and Mr. S. Jenny for help with the mass spectrometric and matrix-isolation studies, respectively.

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

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Contribution from the Anorganisch-Chemisches Institut der Universität, Göttingen, West Germany

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

O. Glemser and Jean'ne M. Shreeve*[1]

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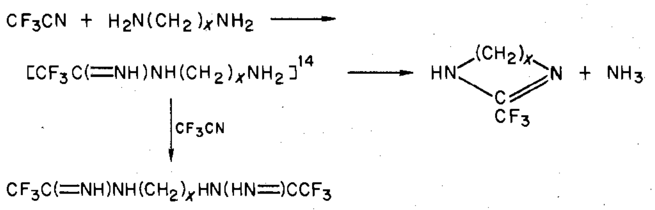
The high susceptibility of perfluoroalkyl nitriles to attack by nucleophiles, such as ammonia,[2-4] hydrazine,[5] hydrogen sulfide,[3,6-8] alcohols,[9-11] hydroxylamines,[10,12] thiols,[13] and amines,[3,14,15] results from the strong electron-withdrawing effect of the perfluoroalkyl group which enhances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

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

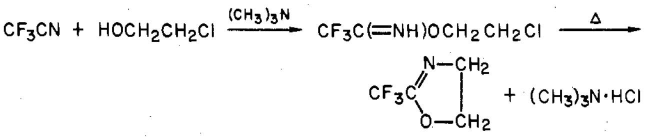
$$CF_3CN + RSH \xrightarrow{K_2CO_3} CF_3C({=}NH)SR^{13}$$

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



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]

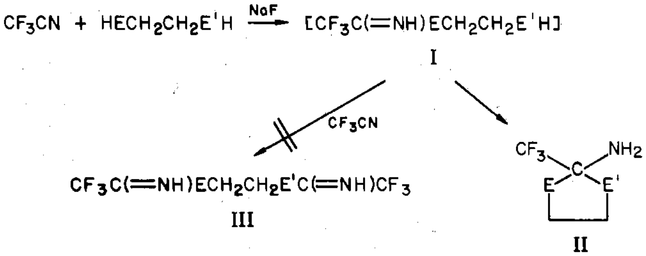


With cyanogen, a variety of interesting bicyclic compounds are obtained when the reactants are diamines[18] or amino mercaptans.[19] However, cyclization does not occur with amino alcohols[20] or with diols.[21] Cyanogen with $H_2NCH_2CH_2OH$ gives $[HOCH_2CH_2N(H)C({=}NH)]_2$ or $[H_2NCH_2CH_2OC({=}NH)]_2$ (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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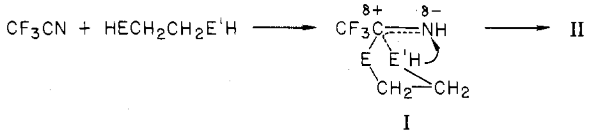
sulfur-containing compounds have an unpleasant odor.

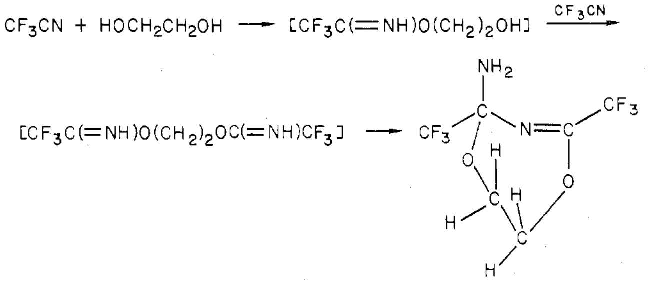
The formation of 2-amino-2-(trifluoromethyl)-substituted compounds must result from nucleophilic attack (enhanced by the fluorine ion) at the nitrile carbon to form the unisolable intermediate I which undergoes further nucleophilic attack with concomitant ring closure, viz.



I

No reaction occurs under the conditions used if NaF is not present. The yields range between 98% for E = O and E′ = S and 30% for E = E′ = S.

Although in no case is I or III isolated in these systems, it is interesting to note that in the reaction of a large excess of CF_3CN with $HOCH_2CH_2OH$ (NaF) it seems reasonable to suggest that III may be an intermediate since the product obtained in addition to II could result from an intramolecular condensation.



This compound is not formed under the conditions used, where CF_3CN was added in small aliquots until it was in excess relative to $HOCH_2CH_2OH$. However, when the CF_3CN was added in excess initially, the white, sublimable solid was also formed in about 20% yield with an accompanying reduction in the quantity of the 1,3-dioxolane.

Spectral data were very useful in assigning the correct structures for these new heterocycles. For the 2-amino-2-(trifluoromethyl)-1,3-dioxo(oxathio, dithio)lanes, ν_{NH_2} occurred between 3415 and 3315 cm^{-1} and δ_{NH_2} as a broadened band at about 1610 cm^{-1}. No strong, sharp bands were observed in the 1675-cm^{-1} region where $\nu_{C=N}$ should appear. Molecular ions were found for the dithio and the oxathio compounds with $M - NH_2^+$ ($M - O^+$?) the largest m/e for the dioxo compound. Other fragments are as expected for the proposed structures. Fluorine NMR spectra show CF_3 at ϕ −84.8, −81.7, and −77.4 as oxygen is replaced stepwise by sulfur in the ring. In the case of the proton spectra not only do the chemical shifts for CH_2O, CH_2S, and NH_2 occur in the appropriate region but the area ratios are invariably 1:1:1. The elemental analyses are in excellent agreement with theoretical values.

In the case of $CF_3C(NH_2)\overline{N{=}C(CF_3)OCH_2CH_2O}$, elemental analyses confirm the empirical formula only. However, from the infrared spectrum, bands can be assigned to ν_{NH_2}, δ_{NH_2}, and $\nu_{C=N}$ (1675 cm^{-1}). In the ^{19}F spectrum, two resonances of equal area at ϕ −74.7 and −83.6 can be attributed to CF_3 groups in different chemical environments. That is, ϕ −83.6 agrees with our assignment of the resonance at ϕ −84.8 in $CF_3\overline{C(NH_2)OCH_2CH_2O}$ above and ϕ −74.7 with that of ϕ −74.4 for $CF_3\overline{C{=}NSCH_2CH_2O}$ where CF_3 is bonded to the imido carbon.[23] The NH_2 resonance occurs at δ 6.0 and the area ratio of $CH_2{:}NH_2$ = 2:1. In the mass spectrum, peaks at m/e 208 assigned to $(M - C_2H_4O)^+$ [or $(M - C_2H_6N)^+$] and at 192 to $(M - C_2H_4O_2)^+$ [or $(M - C_2H_6NO)^+$] are possible for the proposed cycle but impossible for the acyclic molecule $(CF_3C(NH)OCH_2)_2$.

Experimental Section

Starting Materials. Trifluoroacetonitrile was prepared by a standard literature method. The other reagents were standard shelf reagents and were used after drying over molecular sieves in the case of liquids and at 150 °C for NaF.

Reactions were carried out by using standard vacuum line techniques. Compounds were purified by sublimation, trap-to-trap separation, or prolonged exposure to dynamic vacuum. Infrared spectra were obtained by using a liquid film between KBr plates or solids as KBr disks. The ^{19}F and ^1H NMR spectra were measured at 60 MHz with CCl_3F or $(CH_3)_4Si$ as internal references. Mass spectra were obtained at 70 eV. Elemental analyses were completed by Beller Mikroanalytisches Laboratorium, Göttingen.

General Procedure. To a 50-mL Pyrex glass vessel equipped with a Teflon stopcock and containing 30–40 mmol of anhydrous NaF was added 5–15 mmol of the diol, mercaptoethanol, or dithiol and then CF_3CN was introduced in 1–2-mmol aliquots over a period of several hours. This mixture was warmed to 20 °C and was stirred for several hours. More of the CF_3CN was added until a 1 or 2 mmol excess was in the reaction vessel. The rate of reaction was moderate at room temperature as indicated by a slow decrease in the pressure of CF_3CN in the vessel. The product was removed with difficulty under dynamic vacuum (10^{-2} torr) and easily separated from the excess CF_3CN by fractional condensation.

In a typical reaction, to $HSCH_2CH_2SH$ (8.6 mmol) and NaF (35 mmol) was added CF_3CN (11 mmol). After 1 or 2 days at ambient temperature, the very slightly volatile of $CF_3\overline{C(NH_2)SCH_2CH_2S}$ was removed after extended exposure to dynamic vacuum (30% yield). No reaction occurred under the same conditions without NaF.

New Compounds. $CF_3\overline{C(NH_2)OCH_2CH_2O}$. An 85% yield was found when 15 mmol of $HOCH_2CH_2OH$ was reacted with 18 mmol of CF_3CN (excess NaF). The colorless slightly volatile liquid was purified by removing the product under dynamic vacuum at 0 °C after the excess CF_3CN was pulled off at −78 °C. IR (capillary film): 3420 (w), 3350 (w), 3000 (w), 2918 (w), 1687 (vw), 1610 (w), 1480 (vw), 1250 (sh), 1170 (s), 1060 (s), 1030 (m), 1013 (m), 955 (w), 780 (w), 718 (w), 627 (w), 572 (vw), 538 (vw), 440 (w) cm^{-1}. Mass spectrum: $M - NH_2^+$, 141; $M - OCH_2^+$, $M - NH_2CH_2^+$, 127; CF_3CO^+, 97; $M - CF_3^+$, 88; CF_3^+, 69; $CH_2CH_2O^+$, 44. NMR: $\phi(CF_3)$ −84.8, $\delta(CH_2)$ 4.10 (mult), $\delta(NH_2)$ 2.42 (br). Anal. Calcd: C, 30.84; H, 3.87; N, 9.08; F, 36.7. Found: C, 30.57; H, 3.82; N, 8.92; F, 36.3.

$CF_3C(NH_2)\overline{N{=}C(CF_3)OCH_2CH_2O}$. When CF_3CN was added in excess in one aliquot to $HOCH_2CH_2OH$ (excess NaF), in addition to the cyclic compound II, $CF_3C(NH_2)\overline{N{=}C(CF_3)OCH_2CH_2O}$ was formed in 20–25% yield. This colorless sublimable solid melts at 72 °C. IR (KBr disk): 3450 (m), 3315 (w), 3270 (w), 3180 (m), 3015 (vw), 2920 (w), 1675 (s), 1610 (vw), 1475 (vw), 1433 (m), 1205 (s), 1150 (s), 1165 (s), 1177 (s), 1110 (m), 1050 (m), 1025 (m), 985 (m), 943 (m), 810 (w), 730 (w), 718 (w), 640 (w), 568 (w), 557 (w), 540 (w) cm^{-1}. Mass spectrum: $M - C_2H_4O^+$, 208; $M - C_2H_4O_2^+$, 192; $M - CF_3^+$, 183; $CF_3COCH_2CH_2O^+$, 141; $CF_3CNOCH_2CH_2^+$, 139; CF_3CO^+, 97. NMR: $\phi(CF_3)$ − 74.7, −83.6; $\delta(CH_2)$ 4.10; $\delta(NH)$ 6.0 (br). Anal. Calcd: C, 28.40; H, 2.55; N, 11.00; F, 45.3. Found: C, 28.57; H, 2.38; N, 11.11; F, 45.2.

$CF_3\overline{C(NH_2)OCH_2CH_2S}$. A nearly quantitative yield (>98%) was obtained when 6 mmol of $HOCH_2CH_2SH$ (excess NaF) was reacted with 7.5 mmol of CF_3CN. The slightly volatile liquid was purified by fractional condensation. IR (capillary film): 3415 (m), 3340 (m), 2960 (m), 2895 (m), 1745 (w), 1613 (m, br), 1472 (w), 1440 (w), 1362 (m), 1343 (m), 1275 (m), 1175 (sh), 1150 (vs), 1048 (s), 1028 (s), 978 (s), 938 (m), 895 (s), 856 (s), 728 (s), 610 (m), 593 (m), 560 (w), 540 (w), 482 (w). Mass spectrum: M^+, 173; $M - CH_2NH_2^+$, $M - CH_2O^+$, 143; $M - CH_2CH_2S^+$, 113; CH_2CH_2S, 60; $CH_2CH_2O^+$, 44. NMR: $\phi(CF_3)$ −81.7 pentet (J_{H-F} = 0.7 Hz), $\delta(NH_2)$ 2.53 (br), $\delta(CH_2O)$ 4.28 (tr of mult), $\delta(CH_2S)$ 3.10 (tr of mult) ($J_{SCH_2-OCH_2}$ = 6 Hz). Anal. Calcd: C, 27.55; H, 3.56; N, 8.03; S, 18.29. Found: C, 27.75; H, 3.45; N, 8.09; S, 18.50.

$CF_3\overline{C(NH_2)SCH_2CH_2S}$. A 30% yield was obtained when an excess of CF_3CN was reacted with 8.6 mmol of $HSCH_2CH_2SH$ (excess NaF). The colorless viscous liquid was purified by holding the reaction vessel at −15 °C, removing all volatile materials, and then at 22 °C removing the product by extended pumping. IR (capillary film): 3390 (w), 3315 (w), 2930 (w), 1610 (w, br), 1425 (w), 1310 (m), 1273 (w), 1248 (w), 1215 (sh), 1165 (sh), 1148 (vs), 1108 (sh), 953 (w), 890 (m), 855 (m), 828 (m), 770 (w, br), 705 (m), 680 (w), 581 (w), 480 (w) cm^{-1}. Mass spectrum: M^+, 189; $M - C_2H_4^+$, 161; $M - CF_3^+$, 120; $CH_2CH_2S^+$, 60. NMR: $\phi(CF_3)$ −77.4 (pentet, $J_{F\text{-}CH} \simeq 1$ Hz); $\delta(NH_2)$ 2.47; $\delta(CH_2S)$ 3.45 ($J_{NH\text{-}CH} \simeq 1$ Hz). Anal. Calcd: C, 25.49; H, 3.15; N, 7.37; S, 33.96. Found: C, 25.40; H, 3.17; N, 7.41; S, 33.86.

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Registry No. $CF_3C(NH_2)OCH_2CH_2O$, 70247-62-0; $CF_3C(NH_2)N{=}C(CF_3)OCH_2CH_2O$, 70247-63-1; $CF_3C(NH_2)OCH_2CH_2S$, 70247-64-2; $CF_3C(NH_2)SCH_2CH_2S$, 70247-65-3; $HOCH_2CH_2OH$, 107-21-1; $HOCH_2CH_2SH$, 60-24-2; $HSCH_2CH_2SH$, 540-63-6; CF_3CN, 353-85-5; NaF, 7681-49-4.

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(1) To whom correspondence should be addressed at the Department of Chemistry, University of Idaho, Moscow, Idaho 83843.
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Contribution from the Department of Chemistry,
Indiana University, Bloomington, Indiana 47405

Addition of Dimethylcyanamide to Hexakis(alkoxy)dimolybdenum Compounds

Malcolm H. Chisholm* and Raymond L. Kelly

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Prior work has established that the triple bond $(M\equiv M)$ in $Cp_2Mo_2(CO)_4$ forms 1:1 adducts with a number of unsaturated molecules. The latter act as four electron donor ligands and span the Mo–Mo bonds in the manner shown schematically in Figure 1. The Mo-to-Mo distance increases from 2.448 (1) Å in $Cp_2Mo_2(CO)_4$ $(M\equiv M)$[1] to 2.974 (1), 3.015 (1), and 3.117 (1) Å in the adducts $Cp_2Mo_2(CO)_4{\cdot}(un)$, when un = $HC\equiv CH$,[2] Me_2NCN,[3] and $CH_2{=}C{=}CH_2$,[4] respectively. This is tantamount to a M–M triple to single bond transformation[5] and is in keeping with the maintenance of an 18-valence-shell electron count per molybdenum atom.

The compounds Mo_2X_6,[6] where X = R (alkyl), NR_2, and OR, also contain Mo-to-Mo triple bonds. However, in these compounds the molybdenum atoms do not attain 18-valence-shell configurations and have been shown to be capable of undergoing reactions which lead to a net donation of four electrons to the central $(M\equiv M)^{6+}$ moiety without disruption of the M–M multiple bond. The previously reported preparations of $Mo_2(OSiMe_3)_6{\cdot}2HNMe_2$[7] and $Mo_2(OBu\text{-}t)_4(O_2COBu\text{-}t)_2$[8] from $Mo_2(OR)_6$ compounds provide two examples of structurally characterized compounds having triple bonds $(M\equiv M)$ between four-coordinated molybdenum atoms.[9] We are currently extending our studies of the reactions of $Mo_2(OR)_6$ compounds to include reactions involving small unsaturated molecules of the type known to form adducts with $Cp_2Mo_2(CO)_4$ and report here studies involving dimethylcyanamide, Me_2NCN.

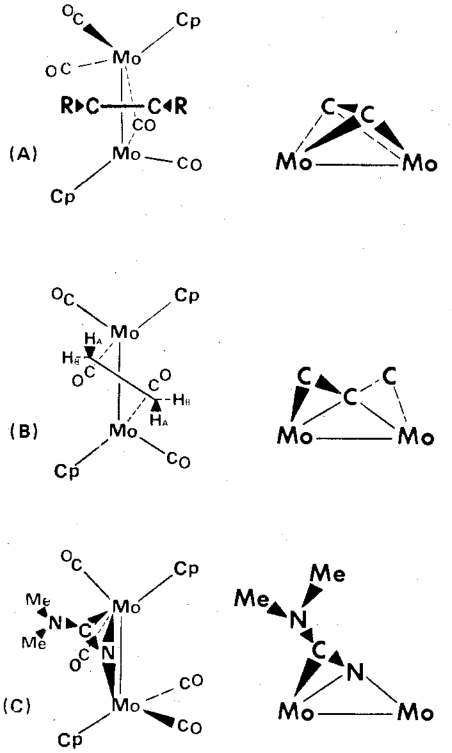

Figure 1. Schematic representations of the $Cp_2Mo_2(CO)_4{\cdot}un$ molecules (A, un = $RC\equiv CR$; B, un = allene; C, un = Me_2NCN) emphasizing the coordination of the central Mo_2un group.

Results and Discussion

Hydrocarbon solutions of $Mo_2(OR)_6$ compounds (R = Bu-*t* and Pr-*i*) react with Me_2NCN to give intense purple solutions from which dark crystals can be obtained by careful crystallizations. (Regrettably no crystals have proved suitable for detailed X-ray studies thus far.[10]) The dark, air- and moisture-sensitive crystals are formulated as 1:1 adducts $Mo_2(OR)_6{\cdot}NCNMe_2$ on the basis of analytical and spectroscopic data (vide supra).

Formation of these adducts is reversible and, the Me_2NCN ligand is readily lost when these compounds are heated in vacuo: only $Mo_2(OR)_6$ compounds sublime. However, in the mass spectrometer weak molecular ions are observed, $Mo_2(OR)_6{\cdot}NCNMe_2^+$, followed by loss of Me_2NCN to give $Mo_2(OR)_6^+$ which are the most intense ions in the spectra. In solution $Mo_2(OBu\text{-}t)_6{\cdot}NCNMe_2$ exists in equilibrium with $Mo_2(OBu\text{-}t)_6$ and the free cyanamide whereas $Mo_2(OPr\text{-}i)_6{\cdot}NCNMe_2$ appears stable with respect to this type of ligand loss. This difference we attribute to the greater steric bulk of the *tert*-butyl group and parallels previous observations on the formation of amine adducts of $Mo_2(OR)_6$ compounds.[11]

In the IR spectrum of $Mo_2(OPr\text{-}i)_6{\cdot}NCNMe_2$ there is an intense band at 1582 cm^{-1} assignable to a stretching mode of the coordinated Me_2NCN molecule. This is reduced from a free ligand value for $\nu(C\equiv N)$ of 2205 cm^{-1}. There is also a strong broad asymmetric band at 634 cm^{-1} which we assign to $\nu(Mo\text{–}O)$ of terminal Mo–OPr-*i* ligands. We find no evidence in the IR spectrum for bridging OPr-*i* ligands.

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