Syntheses and ^{1}H-, ^{13}C- and ^{15}N-NMR Spectra of Ethynyl Isocyanide, $H{-}C{\equiv}C{-}N{\equiv}C$, $D{-}C{\equiv}C{-}N{\equiv}C$ and Prop-1-ynyl Isocyanide, $H_3C{-}C{\equiv}C{-}N{\equiv}C$, $D_3C{-}C{\equiv}C{-}N{\equiv}C$: High Resolution Infrared Spectrum of Prop-1-ynyl Isocyanide

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Abstract: Ethynyl isocyanide, $H{-}C{\equiv}C{-}N{\equiv}C$ (**1a**), deuteroethynyl isocyanide, $D{-}C{\equiv}C{-}N{\equiv}C$ (**1b**), prop-1-ynyl isocyanide, $H_3C{-}C{\equiv}C{-}N{\equiv}C$ (**1c**), and trideuteroprop-1-ynyl isocyanide, $D_3C{-}C{\equiv}C{-}N{\equiv}C$ (**1d**) are synthesized by flash vacuum pyrolysis of suitable organometallic precursor molecules $(CO)_5Cr(CN{-}CCl{=}CClH)$ (**5a**), $(CO)_5Cr(CN{-}CCl{=}CClD)$ (**5b**), $(CO)_5Cr(CN{-}CCl{=}CCl{-}CH_3)$ (**5c**) and $(CO)_5Cr(CN{-}CCl{=}CCl{-}CD_3)$ (**5d**), respectively. Compounds **5a–d** are formed in two steps by radical alkylation of tetraethylammonium pentacarbonyl(cyano)chromate, $NEt_4[Cr(CO)_5(CN)]$ (**2**) by 1,1,2,2,-tetrachloroethane (**3a**), 1,1,2,2-tetrachloro-1,2-dideuteroethane (**3b**), 1,1,2,2,-tetrachloropropane (**3c**), and 1,1,2,2-tetrachloro-1,3,3,3-tetradeuteropropane (**3d**) yielding $[(CO)_5Cr(CN{-}CCl_2{-}CCl_2{-}H)]$ (**4a**), $[(CO)_5Cr(CN{-}CCl_2{-}CCl_2D)]$ (**4b**), $[(CO)_5Cr(CN{-}CCl_2{-}CCl_2{-}CH_3)]$ (**4c**), and $[(CO)_5Cr(CN{-}CCl_2{-}CCl_2{-}CD_3)]$ (**4d**). Dehalogenation of **4a–d** using zinc in diethylether/acetic acid gives **5a–d**, respectively. A multinuclear NMR study revealed the ^{1}H-, ^{13}C- and ^{15}N-NMR data of **1a** and **1c**. Molecular spectroscopic data of **1c** were determined by high resolution infrared spectroscopy. The by-products of the pyrolysis are the *E* and *Z* isomers of the halogenated ethenyl isocyanides $H(Cl)C{=}CCl{-}NC$ (**6a**) and $H_3C(Cl)C{=}CCl{-}NC$ (**6c**) which have been characterized by IR, MS and NMR spectroscopy.

Keywords: alkynes • chromium • high resolution IR spectroscopy • interstellar molecules • isocyanides

Introduction

More than 100 years after the synthesis of the first isocyanides, ethyl isocyanide by Gautier[1] and phenyl isocyanide by Hofmann[2] we reported on the preparation, microwave spectroscopic study and structure of the first alkynyl isocyanide, ethynyl isocyanide, $H{-}C{\equiv}C{-}NC$.[3] This has been studied by HeI and HeII photoelectron spectroscopy,[4] millimeter-wave spectroscopy,[5] and high-resolution FT-IR spectroscopy.[6] Recently the very unstable $CN{-}C{\equiv}C{-}CN$ molecule which had only been obtained before in an argon matrix and characterized by IR spectroscopy[7] could be synthesized, and a broad study has been performed by a group of connected laboratories.[8] Fehlhammer et al. succeeded in synthesizing and stabilizing $H{-}C{\equiv}C{-}NC$, $Me_3Si{-}C{\equiv}C{-}NC$ and $C_6H_5{-}C{\equiv}C{-}NC$ on a transition metal complex.[9] However, no attempt has been made to obtain the free isocyanide.

Furthermore, alkynyl isocyanides are molecules of astrochemical interest. Soon after the discovery of $H{-}NC$[10] and $H{-}C{\equiv}C{-}CN$[11] in interstellar molecular clouds Wilson proposed that the isomer $H{-}C{\equiv}C{-}NC$ might be an interstellar molecule, too, and calculated the rotational constant by ab initio methods.[12] Additional theoretical work including related molecules like propynyl isocyanide has been published by various groups.[13, 14] Immediately after the laboratory data of $H{-}C{\equiv}C{-}NC$ were known Kawaguchi et al. reported on the detection of ethynyl isocyanide in the interstellar molecular cloud TMC-1.[15] In 1997 there a was second report about its identification in IRC + 10216.[16] In 1992 the missing third isomer HNCCC was also found in TMC-1 by the same group[17] mainly based on theoretical

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0947-6539/00/0618-3377 $ 17.50+.50/0

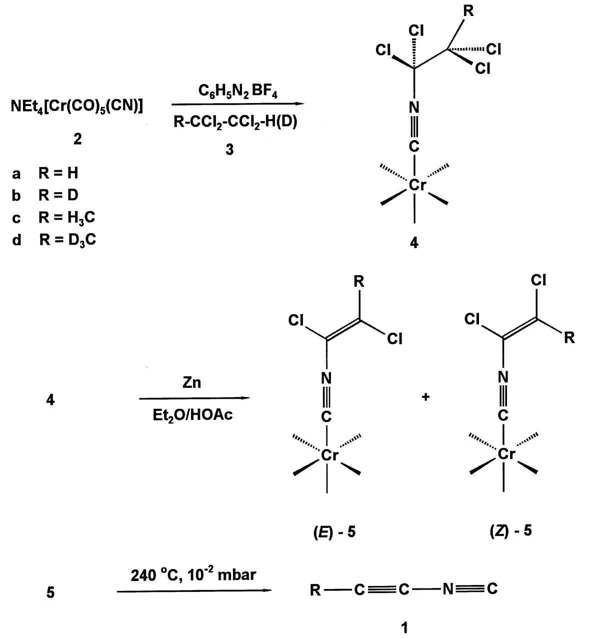
calculations by Botschwina et al.,[18] and laboratory millimeter wave spectroscopic work of Hirahara et al.[19] Interestingly the interstellar chemistry of cyano alkynes is not limited to $H-C\equiv C-CN$. A whole series of cyano polyynes $H-(C\equiv C)_n-CN$ has been detected and the question of the carbon source of these molecules has led to the discovery of C_{60}, buckminster fullerene.[20] Recently, Thaddeus et al. succeeded in generating $H-(C\equiv C)_n-NC$ ($n = 2,3$) (approximately 0.1 to 1 pmole) by electrical discharge in a molecular beam of butadiyne, propynenitrile or others seeded in Ne, besides large amounts of other compounds.[21, 22] The detection of the isocyanopolyyne molecules is based solely on Fourier transform microwave spectroscopy in combination with ab initio calculations.

As propynyl cyanide (butyronitrile), $H_3C-CC-CN$, could also be idendified in the interstellar space, the existence of propynyl isocyanide in dark molecular clouds may be expected.[23] In continuation of our work on alkynyl isocyanides, organometallic pathways to unstable isocyanides and molecules of radioastronomical interest we report in detail on the synthesis and NMR spectroscopic data of ethynyl isocyanide and propynyl isocyanide and the high resolution infrared spectrum of propynyl isocyanide.

Results and Discussion

Syntheses: The syntheses of eth-1-ynyl isocyanide (**1a**), its isotopomer $D-C\equiv C-NC$ (**1b**), and prop-1-ynyl isocyanide **1c** and the deuterated compound **1d** are outlined in Scheme 1. Radical alkylation of tetraethylammonium-pentacarbonyl(cyano)chromate (**2**) in the presence of stoichiometric amounts of benzenediazonium tetrafluoroborate following a procedure described by Fehlhammer et al.[24] using 1,1,2,2-tetrachloroethane (**3a**), 1,1,2,2-tetrachloro-1,2-dideuteroethane (**3b**) or 1,1,2,2,-tetrachloropropane (**3c**), and 1,1,2,2-tetrachloro-1,3,3,3-tetradeuteropropane (**3d**) as solvents yields pentacarbonyl(1,1,2,2-tetrachloroethyl isocyanide)chromium (**4a**), its deuterated isotopomer **4b**, pentacarbonyl(1,1,2,2-tetrachloropropyl isocyanide)chromium (**4c**), and its deuterated analogue **4d**, respectively. Dehalogenation of **4** using zinc powder in diethylether in the presence of acetic acid yields **5a–d** as a mixture of the *E* and *Z* isomers. No attempts have been made to separate the isomers as TLC using different eluents indicates similar R_f values for the isomers.

Abstract in German: *Ethinylisocyanid, $H-C\equiv C-N\equiv C$ (**1a**), Deuteroethinylisocyanid, $D-C\equiv C-N\equiv C$ (**1b**), Prop-1-inylisocyanid, $H_3C-C\equiv C-N\equiv C$ (**1c**) und Trideuteroprop-1-inylisocyanid, $D_3C-C\equiv C-N\equiv C$ (**1d**) konnten durch Vakuumpyrolyse geeigneter Organometall-Precursor-Moleküle wie $[(CO)_5Cr(CN-CCl{=}CClH)]$ (**5a**), $[(CO)_5Cr(CN-CCl{=}CClD)]$ (**5b**), $[(CO)_5Cr(CN-CCl{=}CCl-CH_3)]$ (**5c**) und $[(CO)_5Cr(CN-CCl{=}CCl-CD_3)]$ (**5d**) erhalten werden. Die Verbindungen **5a–d** werden jeweils in zwei Stufen synthetisiert. Durch radikalische Alkylierung von Tetraethylammoniumpentacarbonyl-(cyano)chromat, $NEt_4[Cr(CO)_5(CN)]$ (**2**) in 1,1,2,2,-Tetrachlorethan (**3a**), 1,1,2,2-Tetrachlor-1,2-dideuteroethan (**3b**), 1,1,2,2,-Tetrachlorpropan (**3c**) und 1,1,2,2-Tetrachlor-1,3,3,3-tetradeuteropropan (**3d**) erhält man $[(CO)_5Cr(CN-CCl_2-CCl_2-H)]$ (**4a**), $[(CO)_5Cr(CN-CCl_2-CCl_2D)]$ (**4b**), $[(CO)_5Cr(CN-CCl_2-CCl_2-CH_3)]$ (**4c**) und $[(CO)_5Cr(CN-CCl_2-CCl_2-CD_3)]$ (**4d**). Dehalogenierung von **4a–d** mit Zink in Diethylether/Eisessig ergibt **5a–d**. Aus ein- und zwei-dimensionalen NMR Spektren konnten die ^1H-, ^{13}C- und ^{15}N-NMR spektroskopischen Daten von **1a** and **1c** erhalten werden. Molekülspektroskopische Daten von **1c** wurden mittels hochaufgelöster IR Spektroskopie bestimmt. Die Nebenprodukte der Pyrolysereaktionen sind die E und Z Isomere der halogenierten Ethenylisocyanide $H(Cl)C{=}CCl-NC$ (**6a**) und $H_3C(Cl)C{=}CCl-NC$ (**6c**), die durch IR, MS und NMR Spektroskopie charakterisiert wurden.*



Scheme 1.

The spectroscopic data of **4a** and **5a** are in perfect agreement with those published by Fehlhammer et al.[24] The purity of the deuterated isotopomers **4b** and **5b** was checked by ^{2}D-NMR spectroscopy. The characterization of **4c–d** and **5c–d** is based on spectroscopic methods. The ^{1}H-NMR (^{2}D-NMR) spectrum of **4c** in $CDCl_3$ and **4d** in diethylether shows a single resonance at $\delta = 2.44$ ($\delta = 2.53$). The $^{13}C\{^1H\}$ NMR spectrum of **4c** consists of eight signals which are assigned as follows: $\delta = 32.3$ (CH_3), 91.7 (CCl_2-NC), 92.8 (H_3C-CCl_2), 192.8 (N*C*), 212.7 (CO_{cis}), 213.8 (CO_{trans}). As **5c** is obtained as a mixture of the *E* and *Z* isomer, two sets of resonances are observed both in the ^{1}H- and ^{13}C-NMR spectra. Integration of the signals in the ^{1}H-NMR spectrum allowed an estimation of the isomer ratio of 2.4:1. However, the spectra did not allow an unambiguous assignment of the resonances to the *E* or *Z* isomer.

Flash vacuum pyrolysis of **5a–b** at 240 °C yielded **1a–b** which were trapped at −196 °C, purified by fractional condensation in vacuo (10^{-3} Pa) through traps kept at −196, −125, and −78 °C, and analyzed by NMR, IR, and mass spectra. According to the mass spectroscopic analysis almost pure **1a** is collected in the trap kept at −125 °C. The −196 °C trap contains **1a** besides chloroethyne and HCN; this indicates that the elimination of ClCN is the second, less favored reaction channel of the pyrolysis of **5a**. 1,2-Dichloroethenyl isocyanide (**6a**) is collected in the trap kept at −78 °C and characterized by spectroscopic methods.

The mass spectrum of **1a** exhibits the molecular ions at $m/z = 51$ as well as fragment ions due to loss of H ($m/z = 50$) or HC_2 ($m/z = 26$). As long as the pyrolysis temperature is kept at 240 °C no evidence for the formation of the isomeric propynenitrile can be found in the IR spectrum in which **1a** exhibits strong absorptions at 3339, 2219, 2037, 1228, and 621 cm^{-1}. High resolution IR data, MW and MMW spectra of **1a** and **1b** were reported elsewhere.[3, 5, 6]

Figure 1 compares the structural data of **1a** and **1c** obtained from the rotational constants of several isotopomers [3, 25] with those of the related nitriles[26, 27] and cyanoisocyanoacetylene.[8] As expected, related C−C bond lengths exhibit only small variations and the nitrile C≡N bond is shorter than the isocyanide N≡C bond. Although **1a** polymerizes readily in the condensed phase, **1a** is perfectly stable in the gas phase at low pressure even at ambient temperature or in dilute solutions at −65 °C. This fact allowed us to obtain NMR spectroscopic data of **1a** by a combination of one- and two-dimensional methods. The ^{1}H-NMR spectrum of **1a** in CD_2Cl_2 exhibits a resonance at $\delta = 2.29$ which shows a correlation due to scalar coupling to the nitrogen isotope ^{15}N in the gradient selected HMQC spectrum. This results in a chemical shift value of $\delta = -227.5$ relative to nitromethane in a region typical of isocyanides.[28] The ^{13}C{^{1}H} NMR spectrum exhibits two resonances at $\delta = 47.9$ (H−*C*≡C−N≡C) and 160.2 (H−C≡C−N≡*C*) besides a very broad, but weak signal at $\delta = 61.6$ (H−C≡*C*−N≡C) which could not be unambiguously detected in the one-dimensional spectrum due to the poor signal-to-noise ratio. However, an unambiguous result was obtained by a gradient selected correlation spectrum shown in Figure 2 which further allowed the determination of $^1J(^1H,^{13}C) = 273$ Hz and $^2J(^1H,^{13}C) = 59$ Hz.

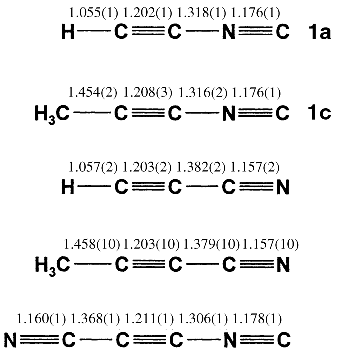


Figure 1. Structural data (r_0/Å) of **1a**[3] and **1c**[25] in comparison to H−C≡C−CN,[27] H_3C−C≡C−CN,[26] and CN−C≡C−CN.[8]

As expected, 1,2-dichloroethenyl isocyanide (**6a**) is formed as a mixture of *E* and *Z* isomers. The mass spectrum exhibits the molecular ion at $m/z = 121$ besides fragment ions by loss of Cl, ClCN, and Cl_2. The infrared spectrum of gaseous **6a** is dominated by a very strong absorption at 2101 cm^{-1} which can be assigned to the N≡C vibration. A band due to the C−C double bond is observed at 1601 cm^{-1}. Gradient selected ^{1}H,^{13}C correlation spectra allow the determination of the chemical shift values and coupling constants of the alkene proton and carbon atoms. Due to the lack of a scalar coupling no correlation to the isocyanide carbon atom could be observed. At first sight no direct assignment of the *E* and *Z* isomers to the two different signal sets seems to be possible. However, in 1,2-difluoro derivatives such as 1,2-difluoroethene,[29] 1,2-difluoroethenyl isocyanide and pentacarbonyl(1,2-difluoroethenyl isocyanide)[30] the proton resonance of the *Z* isomer is observed at higher field than that of the *E* isomer. Thus, one might assume that the major isomer of **5a** and **6a** can be assigned to the *Z* isomer, too. However, the difference in ^{1}H chemical shift values in *E*- and *Z*-1,2-dichloroethene is very small with the *E* isomer about 0.04 ppm at higher field[31] which makes the above mentioned assignment ambiguous.

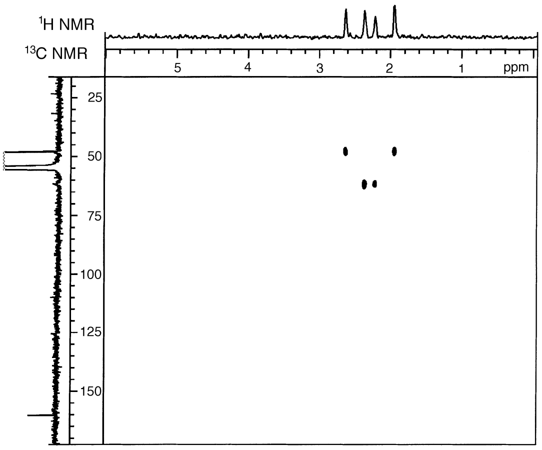


Figure 2. Gradient selected heteronuclear bond correlation experiment (^{1}H{^{13}C}-HMBC) of ethynyl isocyanide **1a**.

The mass spectrum of **1c** exhibits the molecular ion $m/z = 65$ as most abundant ion and smaller fragment ions due to successive loss of protons, CH_2 and CH_3. Signals at $m/z = 100$ and 135 indicate the presence of small amounts of 1,2-dichloroprop-1-enyl isocyanide as an impurity. The ^{1}H-NMR spectrum at −65 °C shows a singlet at $\delta = 1.88$ corresponding to the methyl protons and signals at $\delta = 2.24$ and 2.33, which can be assigned to the *E* and *Z* isomers of 1,2-dichloroprop-1-enyl isocyanide. The ^{13}C-NMR data of **1c** could be obtained and assigned by a combination of one- and two-dimensional techniques. The methyl carbon atom is observed as a quartet at $\delta = 2.57$, $^1J_{HC} = 134$ Hz. Whereas the methyl bonded alkyne carbon atom exhibits a well resolved quartet at $\delta = 55.57$, $^2J_{CH} = 11$ Hz, the nitrogen bonded alkyne carbon atom can hardly be recognized in the one dimensional ^{13}C-NMR spectrum due to line broadening by unresolved coupling to the nitrogen isotope ^{14}N. A gradient selected heteronuclear bond correlation experiment (HMBC) allowed the unambiguous assignment of this resonance at $\delta = 59.1$. The isocyanide carbon atom shows a resonance at $\delta = 155.24$ typical of isocyanide carbon atoms. Two weak signals at $\delta = 21.0$ and 23.0 are due to the *E* and *Z* isomer of 1,2-dichloroprop-1-enyl isocyanide, respectively. Finally a gradient selected heteronuclear bond correlation experiment (HMBC) revealed the ^{15}N chemical shift of the isocyanide nitrogen atom at $\delta = -225$ (CH_3NO_2, external standard).

The low resolution IR spectrum of **1c** in the gaseous phase is dominated by one very strong band (2083 cm^{-1}) besides several weak bands which will be discussed below. The results of an independent millimeterwave and microwave study by Guarnieri et al. are published elsewhere.[25] Ab initio calculations of **1c** and **1d** by Botschwina et al.[32] will be reported independently.

High resolution infrared spectrum of propynyl isocyanide: CH_3CCNC has C_{3v} symmetry and possesses 6 A_1 and 6 E vibrational fundamentals. We have observed the A_1 fundamentals $\tilde{\nu}_1 - \tilde{\nu}_3$ which reveal typical compact PQR structure, and the E fundamentals $\tilde{\nu}_7 - \tilde{\nu}_9$ showing pronounced and widely spread $^{P,R}Q_K$ branches. A search for $\tilde{\nu}_4$ and $\tilde{\nu}_5$ in the appropriate ranges was only of little success, in agreement with the predicted low intensities,[32] while $\tilde{\nu}_6$ and $\tilde{\nu}_{10} - \tilde{\nu}_{12}$ were outside the spectral range covered by the present investigation. Table 1 gives the presently best experimental wavenumbers of the vibrational fundamentals.

Compound **1c** is a prolate symmetric top with an extremely large A:B ratio of about 74. It is therefore not surprising that the energy levels of **1c** offer many possibilities for anharmonic and rotational perturbations. Furthermore, Q branches of parallel bands are very weak and therefore difficult to detect. The low wavenumbers of $\tilde{\nu}_{11}$ and $\tilde{\nu}_{12}$, 285 and 143 cm^{-1},[32] cause very strong hot bands, Boltzmann factors at room temperature (to be multiplied by 2 for $(\tilde{\nu}_i + \tilde{\nu}_t) - \tilde{\nu}_t$, $i = 1-3$ and $7-9$; $t = 11$ and 12, respectively, to get relative intensities) being 0.25 ($t = 11$) and 0.50 ($t = 12$). Consequently hot bands with $\tilde{\nu}_{12}$ as lower level may be as strong as the cold band (for a detailed evaluation of hot band intensities see ref. [33]). It is therefore crucial to have a tool enabling discrimination of cold and hot bands. Since, however, only few lines were resolved this cannot be easily done in the usual fashion by means of combination differences of P and R lines sharing a common upper level.

Ground state constants available from microwave measurements[25] were most useful for the analyses. That in reality hot band J clusters in the ^{Q}P and ^{Q}R branches of the parallel bands $\tilde{\nu}_1 - \tilde{\nu}_3$ are not always as prominent as those of the cold bands is due to differences in the K-dependent parameters of the lower and upper E states involving $\tilde{\nu}_{11}$ and $\tilde{\nu}_{12}$ on the one hand, and to perturbations of the upper states on the other hand.

We have observed the parallel bands $\tilde{\nu}_1 - \tilde{\nu}_3$ of CH_3CCNC located at 2941.01, 2289.15, and 2082.99 cm^{-1}, respectively and resolved their J clusters. These bands are illustrated by Figure 3A – C. As is evident from Figure 3A the parallel band $\tilde{\nu}_1$ is superimposed on a perpendicular band ($\tilde{\nu}_7$), $^{P}Q_4$, $^{P}Q_5$, and $^{P}Q_6$ branches of $\tilde{\nu}_7$ standing out of the P, Q, R-type structure of $\tilde{\nu}_1$. The Q branch of $\tilde{\nu}_1$ is weak but discernible, and J clusters are sharp and were followed up to $J' = 52$.

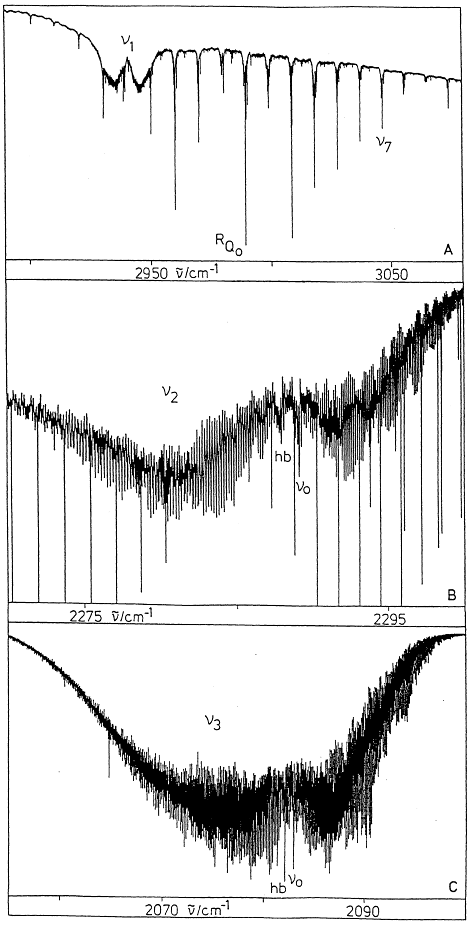


Figure 3. $\tilde{\nu}_1/\tilde{\nu}_7$ (A), $\tilde{\nu}_2$ (B) and $\tilde{\nu}_3$ band (C) of CH_3CCNC. For experimental details see Table 4.

The next parallel band $\tilde{\nu}_2$ is weak and overlapped by lines of residual $^{13}CO_2$, Figure 3B. The strongest hot band, presumably $(\tilde{\nu}_2 + \tilde{\nu}_{12}) - \tilde{\nu}_{12}$, is displaced by $x_{2,12} = -1.10$ cm^{-1}. On the contrary, $\tilde{\nu}_3$ is very strong, in fact by far the strongest band of all, and well resolved into J clusters, Figure 3C. Here, the Q branches of the cold and of the strongest of the hot bands are quite sharp, and the anharmonicity constant, $x_{3,12} = -0.90$ cm^{-1}, has been determined.

Since the ^{Q}P and ^{Q}R clusters of $\tilde{\nu}_1 - \tilde{\nu}_3$, although sharp, could not be resolved into K compo-

Table 1. Molecular parameters of CH_3CCNC; ground state [cm^{-1}].[a]

$\tilde{\nu}_i$	$\tilde{\nu}_0$ [cm^{-1}]	$(A_0 - A')$	$(B_0 - B')$ [10^{-4} cm^{-1}]	$(A\zeta^z)$ [cm^{-1}]	No. data	J [K_{max}]	σ [10^{-3} cm^{-1}]
$\tilde{\nu}_1$	2941.0122(4)		– 0.027(3)		68	52[b]	1.7
$\tilde{\nu}_2$	2289.14847(18)		3.3244(4)		122	99[b]	1.3
$\tilde{\nu}_3$	2082.98788(5)		1.83636(10)		179	107[b]	0.45
$\tilde{\nu}_4$	1395(5)[c]						
$\tilde{\nu}_7$	2984.91(10)[d]			0.373(21)	–		[e]
$\tilde{\nu}_8$	1447.9(14)[d]			– 1.6(4)	–		[e]
$\tilde{\nu}_9$	1032.500(5)[d]	– 3.137(29)	0.267(30)	2.150 8 (4)	35	28	4.3

[a] Ref. [25] $A = 5.297$; $B = 7.3261823 \times 10^{-2}$; $D_J = 3.4854 \times 10^{-9}$; $D_{JK} = 7.2193 \times 10^{-7}$; $D_K = 0$ (constrained); this work $B = 7.32609(5) \times 10^{-2}$, $D_J = 3.44(3) \times 10^{-9}$. [b] See text. [c] Estimated from Coriolis effects and low resolution spectrum. [d] For A_0 fixed to 5.297 cm^{-1}. [e] See Tables 2 and 3.

nents, we had to fit the peak maxima. The constant D_{JK} has a very small value and we do not know exactly the K values associated with the peak maxima. Therefore, no K correction could be applied.

First, a polynomial fit was performed according to:

$$\tilde{\nu}_{obs} = a + bm + cm^2 + dm^3 \tag{1}$$

with the approximations $a = \tilde{\nu}_0$, $b = (B' + B'')$, $c = (B' - B'')$, $d = -4D_{J''}$ and $m = -J$ in the P and J+1 in the R branch. The results of this fit and their standard deviations are consistent with those of a fit using a conventional model in which the peaks were assigned to $K = 0$. Ground state and $\tilde{\nu}_s$ energies ($s = 1-3$) were taken as:

$$\begin{aligned} E(v, J, K) &= \tilde{\nu}_s^0 + B_s J(J{+}1) + (A_s - B_s)K^2 \\ &- D_J^s J^2(J{+}1)^2 - D_{JK}^s J(J{+}1)K^2 - D_K^s K^4 \end{aligned} \tag{2}$$

and D_J^s and D_{JK}^s constrained to their ground state values obtained from the rotational spectra, Table 1. A_0 was adopted from the ab initio calculation and D_K^0 fixed to zero.

Now $\tilde{\nu}_s^0$ and $\alpha_i^B = (B_0 - B')$ are physically more meaningful because B' is no longer correlated with the ground state parameter B_0. The values of the former parameters are set out in Table 1. The difference $(D_{J''} - D_J')$, when calculated, was almost zero which is a proof of the absence of rotational perturbations in the $\tilde{\nu}_1 - \tilde{\nu}_3$ states. Such perturbations would supposedly exert effects on the sharpness of the J clusters and/or on the value of $(D_{J''} - D_J')$.

In order to independently determine the ground state parameters B_0 and D_J^0 of **1c** from the infrared spectra we have merged the data of $\tilde{\nu}_1 - \tilde{\nu}_3$ and fitted 106 ground state combination differences (GSCD) with σ(Fit) = 5 × 10⁻⁴ cm⁻¹. The following ground state values were obtained:

$$B_0 = 0.0732609(5)\ \text{cm}^{-1},\ D_J^0 = 3.44(3) \times 10^{-9}\ \text{cm}^{-1}$$

These parameters do not differ by more than two of their standard deviations from the more accurate ones determined by pure rotational spectroscopy.[25] The inevitable presence of systematic errors due to omission of K-dependent contributions (D_{JK}) should, however, be mentioned. Regretably, combination differences could not be formed from individual J, K lines belonging to the perpendicular bands.

The perpendicular bands $\tilde{\nu}_7 - \tilde{\nu}_9$ consist of strong and sharp Q branches revealing strong–weak–weak intensity alternation for the $K = 3p$ and $K = 3p \pm 1$, Q branches, respectively, with $p = 0, 1, 2$. Each of these Q branches, which altogether span a spectral region of more than 100 cm⁻¹, consist of a bunch of components whose shifts from the strongest ("cold") Q branch vary in an irregular fashion. The different, rather sharp components represent mostly the entire unresolved J manifold of cold and hot band Q branch transitions although splittings by J crossings with unknown perturbers occur as well. The separation of different components is < 1 cm⁻¹ and small in relation to that of successive Q branches, which is given by $2(A - A\varsigma^z - B)$, about 10 cm⁻¹.

The assignment of the strongest of the Q branch components to the cold band is not unambiguous since this assignment cannot be checked by GSCD. In view of the presumably mostly anharmonic perturbations, with K level crossings, this is, however, of no importance for the admittingly somewhat coarse conclusions that we can draw for the perpendicular bands. For several $K\Delta K$ series of $\tilde{\nu}_7$ and $\tilde{\nu}_8$ and the ${}^RR_3$ series of $\tilde{\nu}_9$, it was possible to relate individual lines to respective Q branches and to determine a J-dependent parameter, $(B_0 - B_{t,k})$. In all other cases only Q branch maxima were subjected to fits which were based, for the most general case, on the energy expression:

$$\begin{aligned} E(v, l, J, k) &= \tilde{\nu}_t^0 + B_t J(J{+}1) + (A_t - B_t)k^2 \\ &- D_J^t J^2(J{+}1)^2 - D_{JK}^t J(J{+}1)k^2 - D_K^t k^4 - [2A\zeta_t^z - \eta_{tJ} J(J{+}1) - \eta_{tK} k^2\ ]kl \end{aligned} \tag{3}$$

The K assignment of Q branches followed from their intensity alternation, the symmetric intensity distribution within the band, the slightly different shapes of ${}^RQ_0$ branches owing to l(2,2) resonance, and in some cases the observation of first ${}^RR$ and ${}^PP$ lines with $J = K$. Whenever reasonable fits could be made, a least-squares program was used.[34]

The $\tilde{\nu}_7$ band associated with the degenerate CH$_3$ stretch is shown in Figure 3A. Q branches were followed from $K\Delta K = -9$ to $+9$. The displacement of ${}^PQ_5$ is obvious at first glance. Series of individual $\Delta J \pm 1$ lines were assigned as set out in Table 2. Their fits matched the positions of the related Q branches perfectly. The fit of the subband origins ${}^PQ_K(K)$ and ${}^RQ_K(K{+}1)$ either given by the Q branch maxima and weighted 0.1, or by extrapolation from $\Delta J \pm 1$ series and unit-weighted, is set out in Table 3. The meaning of the parameters of the polynomial:

Table 2. Subband fits [cm⁻¹] of the $\tilde{\nu}_7$ and $\tilde{\nu}_8$ bands.[a]

	Subband $K\Delta K$ ×	Band origin	$(B_0 - B')$ 10⁴	$J_{max.}'$	No. of data	$\sigma \times 10^3$
$\tilde{\nu}_7$	−1	2979.9783 (8)	0.333(17)	30	24	2.2
	0	2989.1806(24)	−0.06(10)	19	11	2.3
	+1	2999.0228(12)	0.218(24)	30	22	2.8
	+3	3017.9659(6)	−0.148(12)	31	25	1.8
	+4	3027.6982(16)	−0.073(34)	29	18	3.2
	+5	3037.2312(16)	−0.04(5)	23	13	2.4
	+6	3046.5642(22)	1.22(20)	14	8	3.1
$\tilde{\nu}_8$	−6	1373.2231(8)	1.441(7)	46	40	3.0
	−3	1417.9229(10)	−1.180(21)	29	24	2.9
	0	1455.3110(5)	−1.023(4)	59	82	2.8
	+3	1496.9224(7)	−0.512(6)	49	40	2.8

[a] Dimensionless.

$$\tilde{\nu}_K = a + b(K\Delta K) + c(K\Delta K)^2$$

is

$$\begin{aligned} a &= \tilde{\nu}_0 + (A' - B') - 2A\varsigma^z \\ b &= 2\,(A' - A\varsigma^z - B') \\ c &= (A' - A_0) - (B' - B_0) \end{aligned} \tag{4}$$

This fit disclosed many more systematic shifts of subband origins due to perturbations.

Table 3. Fit of subband origins $\tilde{\nu}_K$ [cm^{-1}] of $\tilde{\nu}_7$ and $\tilde{\nu}_8$.[a]

$K\Delta K$	$\tilde{\nu}_7$, $\tilde{\nu}_K$	obs. – calcd	weight	$K\Delta K$	$\tilde{\nu}_8$, $\tilde{\nu}_K$	obs. – calcd	weight
−9	2901.04	0.38	0.1	−9	1330.45	−1.63	0.1
−8	2910.58	−0.11	0.1	−8	1344.62	−1.37	0.1
−7	2920.44	−0.24	0.1	−7	1358.90	−0.97	0.1
−6	2930.31	−0.32	0.1	−6	1373.22	−0.52	1.0
−5	2938.69	−1.84	0.0	−5	(1387.57)[b]	–	0.0
−4	2950.24	−0.14	0.1	−4	1402.11	0.72	0.1
−3	2960.03	−0.16	0.1	−3	1417.92	2.74	1.0
−2	2969.80	−0.16	0.1	−2	1425.96	−2.99	0.1
−1	2979.98	0.29	1.0	−1	1441.13	−1.56	0.1
0	2989.18	−0.19	1.0	0	1455.31	−1.09	1.0
1	2999.02	0.01	1.0	1	1469.16	−0.94	0.1
2	3008.56	−0.04	0.1	2	1481.56	−2.20	0.1
				2	1484.67	0.91	0.1
3	3017.97	−0.18	1.0	3	1496.92	−0.49	1.0
4	3027.70	0.04	1.0	4	1509.14	−1.89	0.1
5	3037.23	0.11	1.0	5	1523.23	−1.39	0.1
6	3046.56	0.02	1.0	6	1541.26	3.07	0.1
7	3055.79	0.12	0.1	7	1553.83	2.09	0.1
8	3065.26	0.02	0.1	8	1566.99	1.73	0.1
9	3074.24	0.28	0.1				

[a] $\tilde{\nu}_K = a + b(K\Delta K) + c(K\Delta K)^2$ [cm^{-1}]; a ($\tilde{\nu}_7$) = 2989.37(10), a ($\tilde{\nu}_8$) = 1456.4(14); b ($\tilde{\nu}_7$) = 9.659(21), b ($\tilde{\nu}_8$) = 13.70(27); c ($\tilde{\nu}_7$) = −0.022(4), c ($\tilde{\nu}_7$) = −0.01(6); σ ($\tilde{\nu}_7$) = 0.17, σ ($\tilde{\nu}_7$) = 1.6. [b] Calculated.

The $\tilde{\nu}_8$ band associated with the asymmetric CH$_3$ bending mode and extending from 1330–1570 cm^{-1} was followed by means of broad but unresolved Q branches with $-9 < K\Delta K < +9$. Of these Q branches, $^PQ_5$ is missing while $^RQ_2$ and $^RQ_5$ are split into several components, those belonging to $^RQ_2$ being quite sharp. $^RQ_0$ is most pronounced. While $^PQ_9$ to $^PQ_6$ are J-degraded to low wavenumber, $^PQ_4$ to $^RQ_8$ are oppositely degraded to high wavenumber. This is indicative of an x,y Coriolis rotational perturbation by an A_1 type band coming to resonance with $\tilde{\nu}_8$ at $kl = -4$ and in agreement with the absence of any discernible feature attributable to $^PQ_5$. The perturber is certainly the fundamental $\tilde{\nu}_4$ (δ_s CH$_3$) that is clearer visible in the low resolution spectrum, Figure 4. Several series of $\Delta J = \pm 1$ lines attached to the respective Q branches have been observed: $^PP_6$, $^PP_3$, $^RP_0$, $^RR_0$, $^RR_3$, and $^RR_6$. Some of these series have been fitted as outlined for $\tilde{\nu}_7$. The results of these fits of individual $K\Delta K$ series are set out in Table 2.

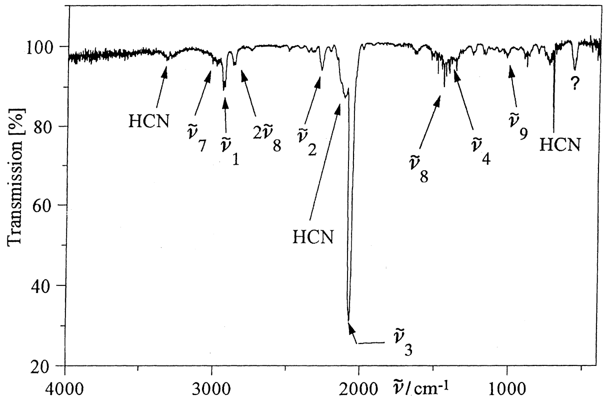


Figure 4. Low resolution infrared spectrum of CH$_3$CCNC.

The separation between subband origins of $\tilde{\nu}_8$ varies in an irregular fashion from 8 to 14 cm^{-1}, and strong anharmonic perturbations in addition to the above mentioned Coriolis resonance are indicated. Although any fit of subband origins $\tilde{\nu}_K$ is physically not meaningful, the differences (obs. – calcd), Table 3, reveal some interesting insight. Apparently two anharmonic level crossings occur near $kl = -2$ (mostly affecting $^P(PQR)_3$) and near $kl = 7$ (mostly affecting $^R(PQR)_6$). Anharmonic constants are estimated to be of the order of 3–4 cm^{-1} in the former and 2–3 cm^{-1} in the latter case. Nothing is known on the nature of the perturber and the mechanism involved. The perturbations of the $kl = 3$ and 6 sublevels as evident from $^RQ_2$ and $^RQ_5$ seem to be local. The subband origins are set out in Table 3.

The CH$_3$ rocking fundamental $\tilde{\nu}_9$ centered at 1032.5 cm^{-1} and displayed in Figure 5 is apparently less perturbed. Q branches were followed from $-9 < K\Delta K < +9$, and $^RR_3$ lines could be identified up to $J'' = 28$. Q branches are quite sharp, half widths not exceeding 0.5 cm^{-1}, and are mostly J-degraded to low wavenumber. $^RQ_5$ reveals an irregular shape, which is accompanied by a displacement from the expected position by about +0.2 cm^{-1}. Likewise also $^PQ_8$ is displaced by about +0.1 cm^{-1} from the expected position.

Since the majority of the Q branches behave as if they were unperturbed, subband origins can be fitted refining $\tilde{\nu}_0$, $A\zeta^z$ and $(A_0 - A')$. A merge with the $^RR_3$ lines, from which $(B_0 - B')$ may be deduced, yields the results reported in Table 1.

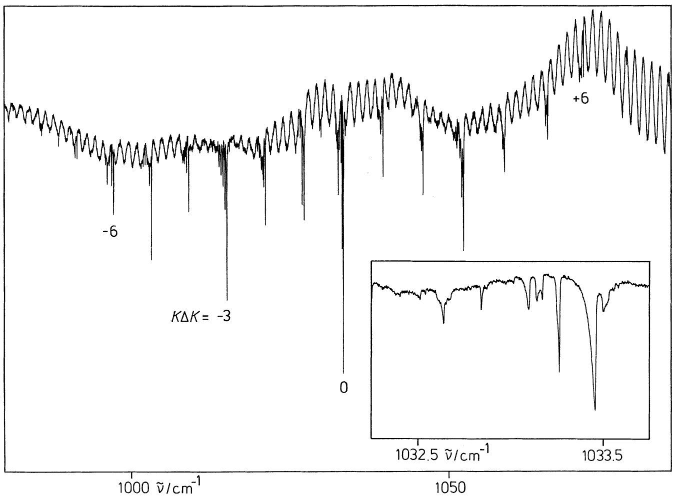


Figure 5. $\tilde{\nu}_9$ band of CH$_3$CCNC. The insert shows the $^RQ_0$ branch region.

Table 1 contains all numerical information deduced from the high resolution study that may also be suitable for comparison with predictions from ab initio calculations.

Conclusion

Our studies have shown that alkynyl isocyanides and halogenated ethenyl isocyanides can be synthesized by flash vacuum pyrolysis of halogenated ethenyl isocyanide complexes. NMR studies of **1a** and **1c** have demonstrated that the alkynyl isocyanides possess a stability in dilute solution high enough to allow a study of their interesting reactivity which might result from the small energy difference between the lone pair at the isocyanide carbon atom and the HOMO which is situated at the C≡C triple bond.[4] However, these studies will be limited to a few examples as our method is not suitable for the preparation of large amounts.

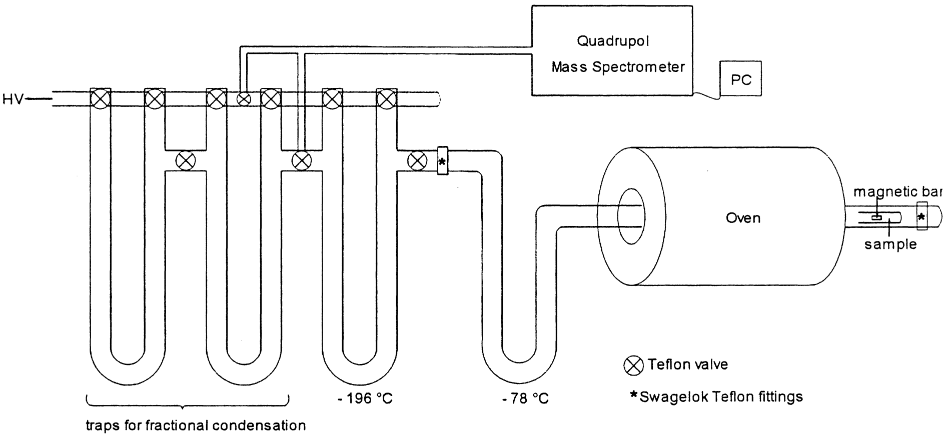


Figure 6. Schematic representation of the pyrolysis apparatus.

Experimental Section

General: All reactions were carried out under dry argon by using standard Schlenk and vacuum techniques. Volatile materials were handled in a conventional glass vacuum line and amounts were determined by PVT techniques. Moisture sensitive compounds were handled in an automatic dry box (Braun) under dry argon. ^{1}H-, ^{2}D-, ^{13}C-, and ^{15}N-NMR spectra were recorded using a JEOL FX 90Q or JEOL LAMBDA 400 instrument with TMS or solvent signals, and nitromethane (^{15}N) as standards. Low resolution infrared spectra were taken on a Perkin–Elmer 883 instrument; for high-resolution spectra see below. Mass spectra were obtained on a Varian MAT 711 (80 eV). Tetraethylammonium-pentacarbonyl(cyano)-chromate (**2**) was prepared following the literature procedure,[35] however, using sublimed hexacarbonyl chromium and freshly sublimed sodium-bis(trimethylsilyl)amide to get a maximum yield of 95 % and to avoid pyrophoric by-products. 1,1,2,2-Tetrachloropropane was prepared from dichloroacetone and phosphorous pentachloride in accordance to a literature procedure,[36] distilled from the reaction vessel under high vacuum and purified by distillation on a spinning band column under vacuum (b.p. 80–88 °C, 21 mbar); nevertheless traces of an impurity could not be removed. 1,1,2,2,-Tetrachloro-1,3,3,3-tetradeuteropropane was prepared by chlorination of deutero propyne (containing approx. 6 % tetradeutero allene)[37] obtained by deuterolysis of Mg_2C_3 prepared from magnesium powder and pentane.[37, 38] Pentacarbonyl(*E*/*Z*-dichloroethenyl isocyanide)chromium and its deuterated isotopomer were prepared by literature methods.[24]

Ethynyl isocyanide (1a): The pyrolysis tube ($l = 500$ mm, $\varnothing = 16$ mm) of an apparatus as shown in Figure 6 was heated to 350 °C without cooling the traps and evacuated for 2 h. Then the oven temperature was lowered to about 200 to 240 °C, the first trap is cooled −78 °C, and a test tube containing a small magnetic stirring bar (which allowed the adjustment of the sample tube within the pyrolysis tube) was charged with pentacarbonyl(dichloroethenyl isocyanide)chromium **5a** (300 to 600 mg) and placed into the pyrolysis tube by opening the teflon fitting at the rear end. After closing the apparatus was evacuated immediately. Unreacted **5a** was trapped at −78 °C. An optimum pyrolysis temperature (240 °C) and pressure (0.1 to 1 Pa) was obtained by adjusting the position of the sample using a magnet and monitoring the products using the quadrupole mass spectrometer. When the desired products were detected the second trap was cooled using liquid nitrogen. After couple of hours all **5a** had been sublimed. Crude **1a** was purified by fractional condensation from a trap kept at −78 °C into traps kept at −125 °C and −196 °C, respectively. The trap kept at −78 °C contained **6a** as shown by mass, IR and NMR spectroscopy. The trap kept at −196 °C contained small amounts of **1a**, HCN, and chloroethyne, whereas almost pure **1a** was collected in the trap kept at −125 °C.

The amount of **1a** (0.1 to 0.5 mmol) obtained in the −125 °C trap was sufficient to record a IR spectrum in a 100 mm infrared gas cell. To record the NMR spectra the compound was condensed into an ordinary glass NMR tube containing [D_2]dichloromethane (0.7 mL) and sealed under vacuum. NMR spectra were recorded at −65 °C to avoid decomposition.

Compound **1a**: ^{1}H NMR (399.78 MHz, CD_2Cl_2): $\delta = 2.29$; $^{13}C\{^1H\}$ NMR (100.54 MHz, CD_2Cl_2): $\delta = 47.9$ (CN–*C*CH), 61.6 (CN–C*C*H), 160.2 (*C*N–CCH); gradient selected ^{1}H/^{15}N HMBC: $\delta = -227.5$ (C*N*–CCH); IR (gaseous): $\tilde{\nu} = 3339, 2219, 2037, 1228, 621$ cm^{-1}; MS (80 eV, EI): m/z: 51 $[M]^+$, 50 $[M-H]^+$, 26 $[CN]^+$.

Compound **6a:** ^{1}H NMR (399.78 MHz, CD_2Cl_2): $\delta = 6.54$ (*Z*), 6.90 (*E*); gradient selected $^1H\{^{13}C\}$ HMBC (CD_2Cl_2): $\delta = 113$ (CN–*C*(Cl) =C(Cl)H, *Z*), 115 (CN–*C*(Cl)=C(Cl)H, *E*), 120 (CN–C(Cl)=*C*(Cl)H, $^1J_{CH} = 256$ Hz, *Z*), 124 (CN–C(Cl)=C(Cl)H, $^1J_{CH} = 256$ Hz, *E*); IR(gaseous): $\tilde{\nu} = 3100$ (w), 2101 (vs, NC), 1601 (w, C=C), 1102 (w), 1052 (m), 968 (vw), 900 (w), 856 (s), 799 (m), 760 (w), 621 (w) cm^{-1}.

Deuteroethynyl isocyanide (1b) was prepared as described above using **5b** as starting material and identified by microwave,[3] millimeterwave,[5] and high resolution IR spectroscopy.[6]

Pentacarbonyl(1,1,2,2-tetrachloropropyl isocyanide)chromium (4c): $NEt_4[Cr(CO)_5(CN)]$ (6.96 g, 20 mmol) was dissolved in 1,1,2,2-tetrachloropropane (**3a**) (80 g) in a 250 mL Schlenk flask equipped with a magnetic stirring bar and slowly cooled to −35 °C. After the addition of $C_6H_5N_2 \cdot BF_4$ (4.03 g, 21 mmol) the reaction mixture was allowed to warm to ambient temperature and stirred for 12 h. The precipitate was filtered on a sintered glass fritt and washed with pentane. The solvent was removed in vacuum (0.1 Pa) at ambient temperature and the solid residue was sublimed at 40 to 50 °C in vacuum (0.1 Pa) yielding **4c** (2.25 g, 21 %) as pale yellow crystals which decompose on heating to 103 °C.

^{1}H NMR (89.6 MHz, $CDCl_3$): $\delta = 2.44$; $^{13}C\{^1H\}$ NMR (23.04 MHz, $CDCl_3$): $\delta = 32.3$ (CH_3), 91.7 ($\mathit{C}Cl_2$–NC), 92.8 (H_3C–$\mathit{C}Cl_2$), 192.8 (NC), 212.7 (CO_{cis}), 213.8 (CO_{trans}); IR (*n*-hexane): $\tilde{\nu} = 2115$ (vw), 2012 (w), 1979 (vs), 1948 (m) cm^{-1}; Raman (solid): $\tilde{\nu} = 2953$ (vw), 2152 (vw), 2119 (w), 2019 (m), 2000 (m), 1961 (w), 1947 (vw), 1103 (w), 1054 (w), 915 (w), 903 (w), 806 (w), 684 (w), 665 (w), 658 (w), 574 (w), 524 (m), 499 (w), 458 (w), 436 (w), 390 (vs), 360 (w), 338 (vw), 300 (w), 225 (w), 199 (vw), 174 (w), 103 (vvs) cm^{-1}; MS (80 eV, EI): m/z: 397 $[M]^+$, 362 $[M-Cl]^+$, and smaller fragment ions; m/z: 396.81780 ($[M]^+$ found), 396.81705 ($[M]^+$ calcd), the experimental and calculated isotopic patterns of the molecular ion are in good agreement.

Pentacarbonyl(1,1,2,2-tetrachloro-3,3,3-trideuteropropyl isocyanide)chromium (4d): Compound **4d** was prepared as described above using 1,1,2,2-tetrachloro-1,3,3,3-tetradeutero-propane (**3d**) (36.7 g) as a solvent and **2**

(3.51 g, 10 mmol) and $C_6H_5N_2 \cdot BF_4$ (2.06 g, 11 mmol). Yield **4d**: 650 mg, 16%; ^{2}D NMR (Et$_2$O, TMS): $\delta = 2.53$.

(*E*/*Z*)-Pentacarbonyl(1,2-dichloropropenyl isocyanide)chromium (*E*/*Z*-5c): Compound **4c** (2.25 g, 5.5 mmol) were dissolved in diethyl ether (50 mL). After the addition of zinc powder (2 g) and acetic acid (3 mL), the mixture was stirred for 3.5 h at ambient temperature. After filtration the solvent was removed under vacuum and the residue was sublimed in vacuum at 40 °C yielding **5c** (1.8 g, 80%) as pale yellow crystals; m.p. 77–83 °C; ^{1}H NMR (399.78 MHz, CDCl$_3$): $\delta =$ 2.30 (2.37, CH$_3$), 2.36 (1.0, CH$_3$); ^{13}C NMR (100.54 MHz, CDCl$_3$): $\delta =$ 22.16 (CH$_3$, $^1J_{CH} = 130$ Hz, major isomer), 22.94 (CH$_3$, $^1J_{CH} = 132$ Hz, minor isomer), 110.19 (CCl, major isomer), 111.82 (CCl, minor isomer), 130.91 (CCl, $^2J_{CH} = 7.9$ Hz), 134.41 (CCl, $^2J_{CH} = 7.9$ Hz), 183.67 (CN, major isomer), 184.16 (CN, minor isomer), 213.47 (CO$_{cis}$, minor isomer), 213.56 (CO$_{cis}$, major isomer), 215.07 (CO$_{trans}$, minor isomer), 215.30 (CO$_{trans}$, minor isomer); IR (*n*-hexane): $\tilde{\nu} = 2114$ (vw), 2027 (m), 1972 (vs), 1941 (vw), 1718 (s) cm^{-1}; MS (80 eV, EI): *m*/*z*: 327 $[M]^+$, 299 $[M - CO]^+$, 271 $[M - 2CO]^+$, 243 $[M - 3CO]^+$, 215 $[M - 4CO]^+$, 187 $[M - 5CO]^+$ and smaller fragment ions.

(*E*/*Z*)-Pentacarbonyl(1,2-dichloro-3,3,3-trideuteropropenyl isocyanide)-chromium (*E*/*Z*-5d): **(*E*/*Z*)-5d** was prepared as described above using **4d** (650 mg, 1.6 mmol), zinc (1 g), acetic acid (1.6 mL), and diethylether (5 mL) yielding **5d** as pale yellow crystals (300 mg, 56%). ^{2}D NMR (13.71 MHz, Et$_2$O): $\delta = 2.32$ (CH$_3$, major isomer), 2.40 (CH$_3$, minor isomer); MS (80 eV, EI): *m*/*z*: 330 $[M]^+$, 302 $[M - CO]^+$, 274 $[M - 2CO]^+$, 246 $[M - 3CO]^+$, 218 $[M - 4CO]^+$, 190 $[M - 5CO]^+$ and smaller fragment ions.

Prop-1-ynyl isocyanide (1c): In a typical experiment **5c** (300 mg) was placed in a small test tube containing a magnetic stirring bar. A glass tube ($\varnothing = 16$ mm, $l = 500$ mm) was connected to a high vacuum glass line by two U-traps, placed into an oven ($l = 300$ mm), closed by a stopper, and evacuated while heating to 350 °C to remove volatile impurities from the glass surface. After 1 h the oven was cooled to 240 °C, the traps were cooled to −196 °C and −78 °C, the glass tube was opened and the test tube was placed into the glass tube. The position of the test tube within the glass tube was varied by using a magnet until an optimized evaporation rate of **5c** was reached which corresponded to an increase of the pressure to 0.1 to 1 Pa due to carbon monoxide formed during the pyrolysis. Under these conditions the pyrolysis was complete within 8 to 12 h. The amount of **1c** (0.1 to 0.2 mmol) obtained in the −196 °C trap was sufficient to record an IR spectrum in a 100 mm gas cell. To record the NMR spectra the compound was condensed into an ordinary glass NMR tube containing [D$_2$]dichloromethane (0.7 mL) and sealed under vacuum. NMR spectra were recorded at −65 °C to avoid decomposition. Compound **1c**: ^{1}H NMR (399.78 MHz, CD$_2$Cl$_2$): $\delta = 1.86$; ^{13}C{^{1}H} NMR (100.54 MHz, CD$_2$Cl$_2$): $\delta =$ 2.57 (CN−CC−*C*H$_3$), 55.57 (CN−C*C*−CH$_3$), 59.0 (CN−*C*C−CH$_3$), 155.26 (*C*N−CC−CH$_3$); gradient selected ^{1}H{^{15}N} HMBC: $\delta = -225$ (C*N*−CC−CH$_3$); IR (gaseous): see Table 1; MS (80 eV, EI): *m*/*z*: 65 $[M]^+$, 64 $[M - H]^+$, 63 $[M - 2H]^+$, 62 $[M - 3H]^+$, and smaller fragment ions, as well as two peaks due to the impurity **6c** $m/z = 136$ $[CN{-}CCl{=}CCl{-}CH_3]^+$, 100 $[CN{-}C_2Cl{-}CH_3]^+$.

High resolution IR spectrum of propynyl isocyanide: Although purified by fractional condensation in vacuo, **1c** collected in a −126 °C trap still contained some impurities, in particular HCN, part of which might have been formed in the absorption cell. This may explain in part why the spectrum is rather weak. A survey spectrum is shown in Figure 4. Five high resolution spectra ①–⑤ in the 450–3340 cm^{-1} region were recorded; details are set out in Table 4. Owing to the thermal instability of **1c** most measurements were carried out with the cell cooled to −20 to −25 °C. A Bruker 120 HR interferometer was employed and calibration of spectra performed with standard reference lines of CO$_2$ and H$_2$O.[39] Wavenumber accuracy of sharp features is better than 1×10^{-3} cm^{-1}. Optical filters were used to eliminate low and high wavenumber radiation.

Table 4. Experimental details.

Spectrum No.	①	②	③	④	⑤
Wavenumber range [cm^{-1}]	450–1150	970–1670	1750–2400	2000–2950	2500–3340
bands studied	$\tilde{\nu}_9$	$\tilde{\nu}_8$	$\tilde{\nu}_3$	$\tilde{\nu}_2$	$\tilde{\nu}_1$, $\tilde{\nu}_7$
path length [cm]	28	28	28	28	28
pressure [mbar]	10	10	3	10	10
temperature [°C]	−25	−23	+22	−20	−23
windows	CsBr	CsBr	KBr	CsBr	CsBr
beam splitter	KBr	KBr	KBr	KBr	CaF$_2$
detector	Cu/Ge	MCT 800	InSb	InSb	InSb
resolution (1/MOPD[a]) [10^{-3} cm^{-1}]	3.8	2.7	3.3	4.4	4.4
no. of scans	500	30	150	80	130
signal/noise of power spectrum	200	80	700	500	100

[a] MOPD = maximum optical path difference.

Acknowledgements

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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Received: January 14, 2000 [F2240]