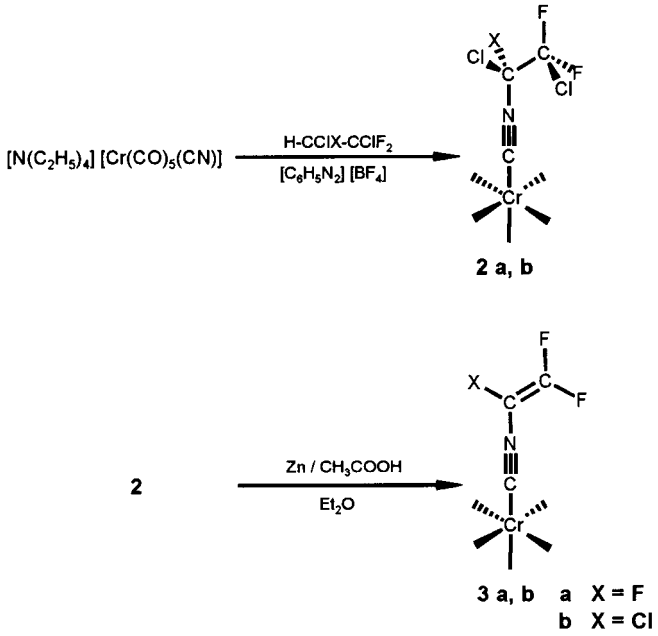
Cyanoisocyanoacetylene, N≡C–C≡C–N≡C**

Christoph Bartel, Peter Botschwina,* Hans Bürger,* Antonio Guarnieri,* Änne Heyl, Aiko Huckauf, Dieter Lentz,* Tatjana Merzliak, and El Bachir Mkadmi

More than 100 years after the synthesis of the first isocyanides, ethyl isocyanide by Gautier[1] and phenyl isocyanide by Hofmann,[2] we reported the synthesis, microwave study, and structure of the only known alkynyl isocyanide compound HC≡C–NC,[3] which was subsequently detected by Kawaguchi et al.[4] in the interstellar molecular cloud TMC1. Cyano- and isocyanopolyynes are of great interest due to their presence in interstellar space. Fehlhammer and Kunz[5] synthesized the alkynyl isocyanides as ligands on the metal complex fragment $[(CO)_5Cr(CN–C\equiv C–R)]$ (R = H, $SiMe_3$, C_6H_5). Ethynyl isocyanide (R = H) is the parent compound of the isocyanopolyynes, the isomers of cyanopolyynes that have been intensively studied by Kroto and et al.[6] The simplest cyanoisocyanopolyyne, $CN–(C\equiv C)_n–CN$ ($n = 1$), was obtained photochemically in an argon matrix at 16 K, and identified by IR spectroscopy[7] by comparison with the results from ab initio calculations.[8] However, a synthesis that would yield sufficient material for the measurement of rotation and high-resolution IR spectra was hitherto unavailable.

Our synthesis strategy for the preparation of CN–C≡C–CN (**1**) and $CN–(C\equiv C)_n–H$ ($n = 2$) begins with the 2,2-difluoro substituted ethenyl isocyanide complexes **3a**[9] and **3b**, which can be synthesized in good yields and whose substituents can be varied by nucleophilic substitution. The metal complex fragment fulfills several functions at once. First it enables the synthesis of the complex in two steps by radical alkylation of tetraethylammonium pentacarbonyl(cyano)chromate(0) to form the halogenated ethyl isocyanide complexes **2a** and **2b**, and subsequent dehalogenation with zinc in diethyl ether/acetic acid (Scheme 1). Second the $[(CO)_5Cr]$ fragment serves as a protecting group preventing the otherwise facile polymerization of the halogenated isocyanides.[10] Third the finely dispersed metal that is released during the vacuum pyrolysis is used to generate the C–C triple bond by dehalogenation, a reaction which appears to be particularly problematic due to the strength of the C–F bond.



Scheme 1. Synthesis of **2a**, **2b** and **3a**, **3b**.

Nucleophilic substitution of a β-fluorine atom proceeds under remarkably mild conditions with various nucleophiles. Reaction of **3a** and **3b** with potassium cyanide or the alkynyl Grignard reagents RC≡CMgBr (R = H, $SiMe_3$, C_6H_5) yields the complexes **4a** and **4b**, and **5a**–**e**, respectively. Isotope labeling to yield ^{13}CN-**4b** and C^{15}N-**4b**, which are important for spectroscopic investigations, can be readily performed (Scheme 2). Only the β-carbon atom is attacked by the nucleophile.

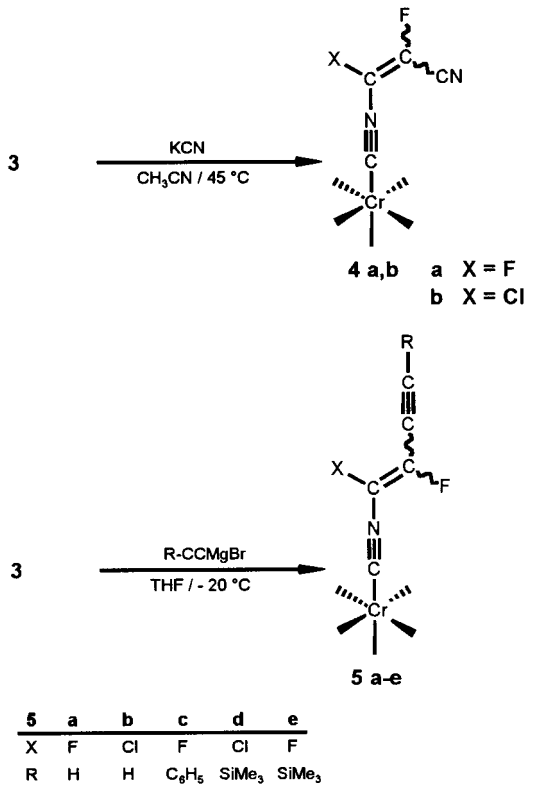
The pyrolysis of **4b** to yield cyanoisocyanoacetylene (3-isocyano-2-propyne nitrile) (**1**) proceeds in a far more complex fashion than the pyrolysis of $[(CO)_5Cr(CN–CCl=CClH)]$ to give HC≡C–NC (Scheme 3).[4] The pyrolysis products identified consist mainly of unconverted **4b**, carbon monoxide, 1-chloro-2-cyano-2-fluoroethenyl isocyanide (**6**), and **1**. The latter condenses during vacuum pyrolysis in a trap cooled to $-196\,^{\circ}C$ and can be separated from **6** by fractional condensation under vacuum. The unequivocal identification of the binary carbon–nitrogen compound **1** was confirmed experimentally by mass spectrometry, high-resolution IR spectroscopy in the frequency range 2000–2400 cm^{-1} and, above all, by millimeter (MMW) wave spectroscopy, which is particularly informative for linear molecules. In addition, MS, IR, and one- and two-dimensional

[*] Prof. P. Botschwina, Ä. Heyl, T. Merzliak
Institut für Physikalische Chemie der Universität
Tammannstrasse 6, D-37077 Göttingen (Germany)
Fax: (+49) 551-39-3144
E-mail: pbotsch@gwdg.de
Prof. H. Bürger, Dr. El B. Mkadmi
Anorganische Chemie der Universität
Gaussstrasse 20, D-42097 Wuppertal (Germany)
Fax: (+49) 202-4392901
E-mail: buerger1@uni-wuppertal.de
Prof. A. Guarnieri, A. Huckauf
Lehrstuhl für Hochfrequenztechnik
Technische Fakultät der Universität
Kaiserstrasse 2, D-24143 Kiel (Germany)
Fax: (+49) 431-77572-453
E-mail: ag@techfak.uni-kiel.de
Dr. D. Lentz, C. Bartel
Institut für Anorganische und Analytische Chemie
der Freien Universität
Fabeckstrasse 34–36, D-14195 Berlin (Germany)
Fax: (+49) 30-838-2424
E-mail: lentz@chemie.fu-berlin.de

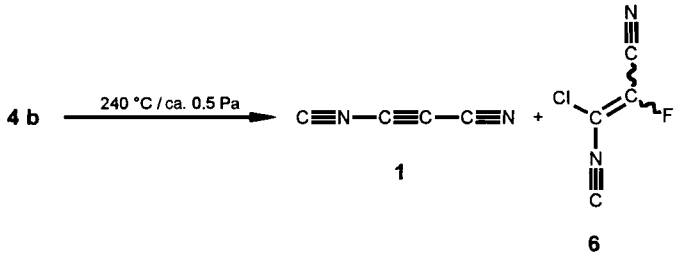
[**] This work was supported by the Fonds der Chemischen Industrie and by the Deutschen Forschungsgemeinschaft (DFG). According to IUPAC the title compound should be named 3-isocyano-2-propyne nitrile.

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/angewandte/ or from the author.

  1433-7851/98/3720-2879 $ 17.50+.50/0



Scheme 2. Synthesis of **4a**, **4b** and **5a–e**.



Scheme 3. Synthesis of **1** and **6**.

^{19}F and ^{13}C NMR spectroscopy enabled the identification of the two isomeric ethenyl isocyanide compounds **6**.

New ab initio calculations have been carried out with the CCSD(T) method[11] and Dunning's cc-pVTZ basis set,[12] the results of which have already been reported in part.[13] The CCSD(T) equilibrium structure is given in Figure 1a together with a recommended equilibrium structure (Figure 1b) which

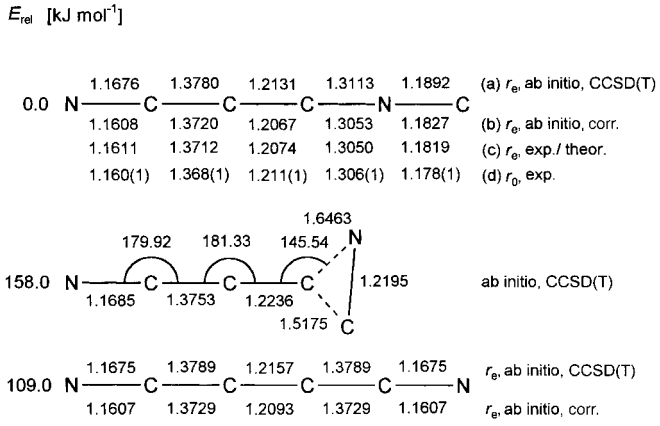


Figure 1. Structure data for **1** (top) and dicyanoacetylene (bottom), and for a planar transition structure that appears during isomerization and corresponds to a saddle point on the potential hypersurface (middle). Energies are given relative to **1** (left). The bond lengths [Å] and angles [°] were obtained by various methods (right). CCSD(T) = coupled cluster single, double and triple excitations.

involves corrections for systematic errors, taken over from HC_5N[14] and HC_2NC.[15] Structure (b) yields an equilibrium rotational constant B_e (NC_3NC) of 1408.58 MHz. Combining it with the CCSD(T) value for the difference $B_0 - B_e$ of 1.05 MHz as obtained from vibration–rotation coupling constants calculated by second-order perturbation theory in normal coordinate space,[16] we arrive at a B_0 prediction of 1409.63 MHz, which proved to be very useful in the search for the MMW spectrum of **1**.

A total of ten isotopomers, which originated from the complexes **4b** and C^{15}N-**4b**, were investigated by MMW spectroscopy. Accurate B_e values (Table 1) were obtained by combination of experimental ground-state values B_0 and theoretical values for the difference $B_e - B_0$. Therefrom, a numerically very stable equilibrium structure (Figure 1c) was obtained through least-squares fit. It agrees with the corrected CCSD(T) equilibrium structure within the joint estimated error bars (ca. 0.0005 Å). Besides C_5O,[17] **1** is the largest linear

Table 1. Rotation and centrifugal-distortion constants for different isotopomers of **1**.

Isotopomer	B_0 [MHz][a]	B_e [MHz][b]	D_0 [Hz][a]	D_e [Hz][c]	N	σ_{Fit} [kHz]
NCCCNC	1409.975270(26)[d]	1408.923	34.5472(37)[d]	31.8	46	6[d]
N^{13}CCCNC	1395.68724(30)	1394.655	34.20(12)	31.4	12	16
NC^{13}CCNC	1408.75194(19)	1407.729	34.483(79)	31.8	14	11
NCC^{13}CNC	1408.30202(19)	1407.262	34.320(86)	31.8	12	9
NCCCN^{13}C	1372.62445(20)	1371.575	32.432(73)	30.0	12	9
^{15}NCCCNC	1374.080484(75)	1373.047	32.805(31)	30.2	10	3
^{15}N^{13}CCCNC	1361.05560(56)	1360.042	31.93(23)	29.7	6	15
^{15}NC^{13}CCNC	1373.07526(38)	1372.070	32.85(16)	30.1	8	11
^{15}NCC^{13}CNC	1372.29168(41)	1371.271	32.27(16)	30.1	7	12
^{15}NCCCN^{13}C	1337.69348(25)	1336.663	31.262(97)	28.4	7	7

[a] Experimental values obtained from millimeter wave spectroscopy. [b] Calculated according to $B_e \approx B_0(\text{exp.}) + \sum_i \alpha_i(\text{theor.}) d_i/2$, where α_i is the vibration–rotation coupling constant and d_i is the degeneracy factor for vibration mode i (d_i: 1 for stretching vibrations, 2 for bending vibrations). [c] Calculated from the corrected equilibrium structure (see Figure 1) and the quadratic force constants for the stretching vibrations (CCSD(T)/cc-pVTZ). [d] The experimental constants for the main isotopomer in the table refer to an adjustment in which the sixth-order centrifugal distortion constant was included; the adjustment yielded $H_0 = 2.08 \times 10^{-6}$ Hz. H_0 could not be determined from the available data for the other isotopomers and was set to zero. N = number of common lines.

  1433-7851/98/3720-2880 $ 17.50+.50/0

molecule for which an equilibrium structure could be determined by these joint experimental and theoretical methods. We also determined a r_0 structure of **1** (Figure 1 d) by least-squares fit to the B_0 values of all ten isotopomers investigated. Comparison with the structures of HCCNC[3] and HCCCN[18] shows that all triple bonds in **1** are somewhat elongated due to increased conjugation, whereas the single bonds are shortened.

The high-resolution IR spectra are very dense due to the presence of "hot" bands that have not yet been analyzed. However the three very intense vibrations ν_1, ν_2, and ν_3, which have estimated relative intensities of 1.5:1:2, were well resolved. The spectroscopic constants for **1** obtained by high-resolution IR spectroscopy are presented in Table 2. They are in excellent agreement with the predictions made from ab initio calculations.[8]

Table 2. Spectroscopic constants for **1**[a] obtained with high-resolution IR spectroscopy.

	$\tilde{\nu}_1$	$\tilde{\nu}_2$	$\tilde{\nu}_3$
$\tilde{\nu}_0$ [cm^{-1}][b]	2295.72337(9)	2209.62521(4)	2052.98160(7)
$(B''-B')\times 10^4$ [cm^{-1}][c]	1.7223(13)	1.16163(13)	0.8413(9)
$(D''-D')\times 10^{10}$ [cm^{-1}]	6.8(3)	0.115(8)	4.95(23)
J_{max}	67	145	66
number of data	110	233	126
$\sigma_{Fit}\times 10^4$ [cm^{-1}]	4.1	3.6	3.7

[a] Millimeter wave data (Table 1) was used to determine B'' and D''. The values in parentheses are the standard deviations. [b] Results from ab initio calculations with the CEPA-1-method: $\tilde{\nu}_1 = 2320.7$, $\tilde{\nu}_2 = 2231.1$, $\tilde{\nu}_3 = 2061.3$ cm^{-1}.[8] [c] Theoretical predictions: 1.69, 1.19, and 0.90×10^{-4} [cm^{-1}].[8]

The energy difference between the potential minima of the isomers N≡C−C≡C−N≡C and N≡C−C≡C−C≡N is 109.0 kJ mol^{-1} (Figure 1). This value is reduced to 107.6 kJ mol^{-1} after inclusion of the zero-point energy. The planar saddle point of the associated isomerization reaction lies 158.0 kJ mol^{-1} above the energy minimum of **1**. The triple bonds remain almost unchanged along the energetically most favorable isomerization pathway; only the N−C bond in the three-membered ring at the saddle point is slightly extended by 0.031 Å.[19]

Due to the modular construction of the precursor complexes from the easily synthesized starting compound **3**, it appears likely that it will be possible to synthesize further alkynyl isocyanides, which might also exist in interstellar space. These compounds might also be detectable by radio astronomy after extensive investigations with various spectroscopic methods. For the chemist, these multifunctional alkynyl and alkenyl isocyanide compounds could be interesting synthesis building blocks and complex ligands. However, extensive investigation of their chemical properties is limited by the fact that only small quantities can be synthesized.

Experimental Section

High-resolution IR spectroscopy: A high-resolution IR spectrum of **1** was recorded at room temperature between 1800 and 2400 cm^{-1} with a Bruker-120HR interferometer. This was equipped with a Globar IR light source, a KBr beam splitter, and an InSb detector cooled by liquid nitrogen. A band-pass filter was used, and the resolution (reciprocal maximum optical path difference) was set at 2.3×10^{-3} cm^{-1}. Peaks from OCS were used for calibration.[20] By using a 28 cm long IR gas cell at a pressure of about 200 Pa, a total of 320 single scans were coadded. Under these conditions, the strongest line had a transmission of about 75 %. The lines were assigned interactively with Loomis – Wood program.[21]

Millimeter wave spectroscopy: The rotation spectra were recorded according to the source double modulation procedure with the MMW spectrometer extensively described in ref. [21]. A Ku band backward wave oscillator (BWO) (HP-8695-A) and a klystron (OKI-20V10) (in combination with an active frequency multiplier) were used as the radiation source in the frequency range 40 to 120 GHz. The higher frequency range (240 to 315 GHz) was covered without further multiplication by a Russian BWO (Istok-OB-30). The measurements were carried out in a 2.40 m long, glass free-absorption cell at a temperature of 28 °C and a pressure of 1 Pa. A liquid-helium-cooled InSb bolometer (Putley detector) was used as the detector. The maximum errors for frequency measurements carried out in this way are about ±5 kHz.

In order to analyze the spectra, the measured absorption frequencies were adjusted according to the least squares method with the expression $\nu = 2B_0(J+1) - 4D_0(J+1)^3 + H_0(J+1)^3[(J+2)^3 - J^3]$ which is valid for a transition of the type $J+1 \leftarrow J$.

Ab initio calculations: The ab initio calculations were performed with the MOLPRO96 program.[23] The CCSD(T) implementation is described in ref. [24, 25].

The NMR spectroscopic investigations were performed with a 400 MHz (^{1}H) multinuclear NMR spectrometer at 22 °C. Unless otherwise stated, $CDCl_3$ was the solvent. The chemical shifts are relative to tetramethylsilane (^{1}H, ^{13}C) and trichlorofluoromethane (^{19}F).

2b: Tetraethylammonium pentacarbonyl(cyano)chromate(0) (5.37 g, 15.4 mmol) was suspended in 1,1,2-trichloro-2,2-difluoroethane (56 g) and the suspension cooled to −78 °C. Phenyldiazonium tetrafluoroborate (3.45 g, 18.0 mmol) was added whilst cooling under reflux (−5 °C) under an inert atmosphere, and the suspension was slowly warmed to 20 °C. After 4 h the solvent was removed at −20 °C and 0.1 Pa. The residue was extracted with pentane. The extract was purified over silica gel with pentane. The first fraction was sublimed on a cold finger (−25 °C) at 30 °C and 0.1 Pa. M.p. 62 °C; ^{13}C NMR: $\delta = 212.6$ (s, CO_{trans}), 212.1 (s, CO_{cis}), 202.8 (s, NC), 124.7 (t, $^1J(C,F) = 303$ Hz, $CClF_2$), 84.9 (t, $^2J(C,F) = 38$ Hz, CCl_2); ^{19}F NMR: $\delta = -65.07$ (s, $CClF_2$); IR (pentane): $\tilde{\nu} = 1986$ (vs), 1955 (m), 1899 (w) cm^{-1}; MS (80 eV): m/z: 385 [M^+], 329 [$M^+ - 2CO$], 301 [$M^+ - 3CO$], 273 [$M^+ - 4CO$], 245 [$M^+ - 5CO$], 210 [$M^+ - 5CO - Cl$], 175 [$M^+ - 5CO - 2Cl$], 78 [$CrCN^+$], 52 [Cr^+].

3b: Compound **2b** (3.8 g, 9.8 mmol) was dissolved in diethyl ether (50 mL) and treated with zinc powder (6.4 g, 98.0 mmol) and acetic acid (2 mL). After stirring for 12 h, the suspension was filtered. The filtrate was purified over silica gel with pentane. The product was isolated from the second fraction. A yellow solid (2.47 g, 7.8 mmol, 80 %) was obtained by sublimation at 35 °C and 0.1 Pa on a cold finger (−25 °C). M.p. 58 °C; ^{13}C NMR: $\delta = 214.6$ (s, CO_{trans}), 213.2 (s, CO_{cis}), 191.2 (s, NC), 156.8 (dd, $^1J(C,F) = 300$, $^1J(C,F) = 294$ Hz, CF_2), 86.3 (dd, $^2J(C,F) = 51$, $^2J(C,F) = 39$ Hz, CCl); ^{19}F NMR: $\delta = -80.64$ (d, $^2J(F,F) = 11.4$ Hz, 1 F, CF_2), −87.97 (d, $^2J(F,F) = 11.4$ Hz, 1 F, CF_2); IR (pentane): $\tilde{\nu} = 2116$ (w), 2029 (s), 1977 (vs), 1946 (m), 1902 (vw), 1731 (m) cm^{-1}; MS (70 eV): m/z: 315 [M^+], 287 [$M^+ - CO$], 259 [$M^+ - 2CO$], 231 [$M^+ - 3CO$], 203 [$M^+ - 4CO$], 175 [$M^+ - 5CO$], 78 [$CrCN^+$], 52 [Cr^+].

4b: Compound **3b** (966 mg, 3.1 mmol) was dissolved in anhydrous acetonitrile (20 mL) and the solution was warmed to 45 °C. Potassium cyanide (586 mg, 9.0 mmol) was added. After stirring for 45 min, the suspension was placed on a silica gel column and eluted with pentane. Two fractions were obtained. Unconverted **3b** was recovered from the first fraction, the second fraction contained the product. A yellow solid (706 mg, 71 %) was obtained by sublimation at 35 °C and 0.1 Pa on a cold finger (−25 °C). M.p. 64 °C; ^{13}C NMR: δ {2nd isomer} = 212.8 {212.6} (s, CO_{trans}), 212.0 (s, CO_{cis}), 203.8 {202.4} (d, $^4J(C,F) = 6$ {5} Hz, NC), 131.3 {131.9} (d, $^1J(C,F) = 259$ {256} Hz, CF), 115.2 {117.4} (d, $^2J(C,F) = 33$ {46} Hz, CCl), 109.4 {108.9} (d, $^2J(C,F) = 40$ {40} Hz, CN); ^{19}F NMR: δ {2nd isomer} = −122.06 {−129.99} (s, 1 F, CF); IR (pentane): $\tilde{\nu} = 1987$ (vs), 1977 (m), 1955

  1433-7851/98/3720-2881 $ 17.50+.50/0

(w), 1900 (vw) cm^{-1}; MS (80 eV): *m/z*: 322 [M^+], 294 [$M^+ - CO$], 266 [$M^+ - 2CO$], 238 [$M^+ - 3CO$], 210 [$M^+ - 4CO$], 182 [$M^+ - 5CO$], 78 [$CrCN^+ - 5CO$], 52 [Cr^+].

^{15}N-**4b**: ^{15}N NMR ($CDCl_3$,CH_3NO_2 ext.): δ {2nd isomer} = −90.5 {−91.9} (s, CF-CN); ^{13}C NMR {2nd isomer}: ^1J(N,C) = 18 {17}, ^2J(N,C) = 3 {4} Hz; ^{13}C-**4b**: ^{13}C NMR {2nd isomer}: ^1J(C,C) = 116 {113}, ^2J(C,C) = 13 {11} Hz.

4a: Synthesis analogous to **4b**. M.p. 35 °C; ^{13}C NMR: δ (*E*{*Z*} isomer) = 211.6 {211.6} (s, CO_{trans}), 211.51 {211.58} (s, CO_{cis}), 209.2 (s, NC), 137.5 {135.8} (dd, ^1J(C,F) = 265 {278}, ^2J(C,F) = 44 {37} Hz, CN*C*F), 123.7 {121.3} (dd, ^1J(C,F) = 240 {251}, ^2J(C,F) = 62 {38} Hz, *C*FCN), 108.1 {109.0} (dd, ^2J(C,F) = 37 {36}, ^3J(C,F) = 10 {3} Hz, CN); ^{19}F NMR: δ (*E*{*Z*} isomer) = −114.8 {−90.0} (d, ^3J(F,F) = 128 {3} Hz, 1F, NCCF), −165.8 {−156.7} (d, ^3J(F,F) = 128 {3} Hz, 1F, CFCN); IR (hexane): $\tilde{\nu}$ = 2015 (w), 1999 (vw), 1986 (vs), 1964 (br) cm^{-1}; MS (70 eV): *m/z*: 306 [M^+], 278 [$M^+ - CO$], 250 [$M^+ - 2CO$], 222 [$M^+ - 3CO$], 194 [$M^+ - 4CO$], 166 [$M^+ - 5CO$], 78 [$CrCN^+$], 52 [Cr^+].

5a–e: General method: The Grignard reagents of the ethyne derivatives (2 equiv) were synthesized according to standard methods[26] in THF and then added to **2** (1 equiv). After 2 h, three times the amount of pentane was added and the suspension was filtered. The product was then purified by sublimation at 0.1 Pa on a cold finger (−20 °C).

5a: ^{1}H NMR: δ(*E*{*Z*} isomer) = 4.10 {3.92} (dd, ^4J(H,F) = 3 {3}, ^5J(H,F) = 1 {3} Hz, 1H, CCH); ^{19}F NMR: δ (*E*{*Z*} isomer) = −127.4 {−108.3} (d {s}, ^3J(F,F) = 127 Hz, 1F, CNCF), −147.5 {−137.8} (dd {d}, ^3J(F,F) = 127, ^4J(H,F) = 3 {3} Hz, 1F, CFCCH); MS (70 eV): *m/z*: 305 [M^+], 277 [$M^+ - CO$], 249 [$M^+ - 2CO$], 221 [$M^+ - 3CO$], 193 [$M^+ - 4CO$], 165 [$M^+ - 5CO$], 52 [Cr^+].

5b: M.p. 32 °C; ^{1}H NMR: δ {2nd isomer} = 4.00 {3.97} (d, ^4J(H,F) = 3 {4} Hz, 1H, CH); ^{13}C NMR: δ {2nd isomer} = 214.5 {214.6} (s, CO_{trans}), 213.2 {213.0} (s, CO_{cis}), 189.0 {193.8} (s, NC), 142.2 {140.4} (dd, ^1J(C,F) = 251 {254}, ^3J(C,H) = 5 {6} Hz, CF), 110.8 {109.9} (d, ^2J(C,F) = 52 {40} Hz, CCl), 93.2 {94.2} (dd, ^1J(C,H) = 261 {261}, ^3J(C,F) = 5 {5} Hz, *C*CH), 70.9 {71.3} (dd, ^2J(C,H) = 51 {51}, ^2J(C,F) = 27 {25} Hz, *C*CH); ^{19}F NMR: δ {2nd isomer} = −110.54 {−105.50} (d, ^4J(F,H) = 3 {4} Hz, 1F, CF).

5c: M.p. (*E*{*Z*} isomer}: 62 {105} °C; ^{19}F NMR: δ (*E*{*Z*} isomer} = −128.4 {−110.7} (d {s}, ^3J(F,F) = 127 Hz, CNCF), −143.4 {−133.6} (d {s}, ^3J(F,F) = 127 Hz, CFCC); MS (70 eV): *m/z*: 381 [M^+], 353 [$M^+ - CO$], 325 [$M^+ - 2CO$], 297 [$M^+ - 3CO$], 269 [$M^+ - 4CO$], 241 [$M^+ - 5CO$], 52 [Cr^+].

5d: M.p. (1st isomer) 83 °C; ^{1}H NMR: δ {2nd isomer} = 0.27 {0.27} (s, 9H, CH_3); ^{13}C{^{1}H} NMR (1st isomer): δ = 214.9 (CO_{trans}), 213.1 (CO_{cis}), 192.4 (NC), 140.7 (d, ^1J(C,F) = 254 Hz, CF), 115.2 (d, ^3J(C,F) = 4 Hz, *C*CSi), 108.8 (d, ^2J(C,F) = 43 Hz, CCl), 90.7 (d, ^2J(C,F) = 34 Hz, *C*CSi), −0.8 (s, CH_3); ^{13}C NMR (2nd isomer): δ = 214.8 (s, CO_{trans}), 213.3 (s, CO_{cis}), 186.9 (s, NC), 142.2 (d, ^1J(C,F) = 250 Hz, CF), 113.8 (m, *C*CSi), 109.5 (d, ^2J(C,F) = 56 Hz, CCl), 90.2 (d, ^2J(C,F) = 35 Hz, *C*CSi), −1.0 (^1J(C,H) = 122, ^3J(C,H) = 2 Hz, CH_3); ^{19}F NMR : δ {2nd isomer} = −109.63 {−104.99} (s); IR (pentane, 2nd isomer): $\tilde{\nu}$ = 2130 (vw), 2112 (w), 2020 (s), 1974 (vs), 1945 (s), 1843 (vw), 1652 (vw) cm^{-1}; MS (70 eV): *m/z*: 393 [M^+], 337 [$M^+ - 2CO$], 309 [$M^+ - 3CO$], 281 [$M^+ - 4CO$], 253 [$M^+ - 5CO$], 132 [$M^+ - Cr(CO)_5 - SiMe_3$], 52 [Cr^+].

5e: ^{1}H NMR: δ (*E* isomer) = 0.24 (s, 9H, CH_3); ^{13}C NMR: δ (*E* isomer) = 214.1 (s, CO_{trans}), 212.7 (s, CO_{cis}), 201.6 (d, ^3J(C,F) = 8 Hz, NC), 136.0 (dd, ^1J(C,F) = 254, ^2J(C,F) = 54 Hz, CNCF), 132.3 (dd, ^1J(C,H) = 237, ^2J(C,F) = 56 Hz, CFCC), 117.1 (m, *C*CSi), 88.5 (dd, ^2J(C,F) = 32, ^3J(C,F) = 10 Hz, *C*CSi), −0.9 (q, ^1J(C,H) = 121 Hz); ^{19}F NMR: δ (*E*{*Z*} isomer) = −128.24 {−110.13} (d {s}, ^3J(F,F) = 127 Hz, NCCF), −144.28 {−134.81} (d, ^3J(F,F) = 127 {3} Hz, CFCC); MS (70 eV): *m/z*: 377 [M^+], 321 [$M^+ - 2CO$], 293 [$M^+ - 3CO$], 265 [$M^+ - 4CO$], 237 [$M^+ - 5CO$], 52 [Cr^+].

1,6: Compound **4b** (526 mg) was pumped at 0.1 Pa through a 20 cm long pyrolysis zone heated to 240 °C. The pyrolysis gas was fed through a grease-free system of cold traps at −78 °C and −196 °C. During pyrolysis, finely dispersed chromium deposited in the heating zone. Five equivalents of carbon monoxide were released. The rate of pyrolysis was adjusted so that the apparatus was under a pressure of about 0.5 Pa.

Unconverted **4b** sublimed in the −78 °C cold trap. The pyrolysis gases condensed at −196 °C were purified by fractional condensation at 0.1 Pa and −100 °C in a −196 °C cold trap. The receiving flask contained essentially only **6**. ^{13}C NMR (CD_2Cl_2, −45 °C): δ {2nd isomer} = {181.1} (s, *C*NC), 133.2 {134.6} (d, ^1J(C,F) = 271 {261} Hz, CF), 109.1 {108.7} (d, ^2J(C,F) = 39 {39} Hz, CCl); ^{19}F NMR (CD_2Cl_2, −45 °C): δ {2. isomer} = −114.47 {−121.13} (s). Compound **1** was condensed at −196 °C together with a small amount of as-yet unidentified gases. IR (gas): $\tilde{\nu}_1$ = 2296, $\tilde{\nu}_2$ = 2210 and $\tilde{\nu}_3$ = 2053 cm^{-1}.

Received: May 28, 1998 [Z 11909 IE]
German version: *Angew. Chem.* **1998**, *110*, 3036–3040

Keywords: alkynes · chromium · isocyanides · nitriles · structure elucidation

[1] A. Gautier, *Justus Liebigs Ann. Chem.* **1867**, *142*, 289; A. Gautier, *Justus Liebigs Ann. Chem.* **1868**, *146*, 124.
[2] A. W. Hofmann, *Justus Liebigs Ann. Chem.* **1867**, *144*, 114; A. W. Hofmann, *Justus Liebigs Ann. Chem.* **1868**, *146*, 107.
[3] M. Krüger, H. Dreizler, D. Preugschat, D. Lentz, *Angew. Chem.* **1991**, *113*, 1674; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1644.
[4] K. Kawaguchi, M. Ohishi, S.-I. Ishikawa, N. Kaifu, *Astrophys. J.* **1992**, *386*, L51.
[5] R. Kunz, W. P. Fehlhammer, *Angew. Chem.* **1994**, *106*, 331; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 330.
[6] See for example: H. W. Kroto, *Angew. Chem.* **1992**, *104*, 113; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 111; R. F. Curl, *Angew. Chem.* **1997**, *109*, 1636; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1566; H. W. Kroto, *Angew. Chem.* **1997**, *109*, 1649; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1578; R. E. Smalley, *Angew. Chem.* **1997**, *109*, 1667; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1594, and references therein.
[7] A. Smith, G. Schallmoser, A. Thoma, V. Bondybey, *J. Chem. Phys.* **1993**, *98*, 1776.
[8] P. Botschwina, M. Horn, J. Flügge, S. Seeger, *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 2219; M. Horn, P. Botschwina, J. Flügge, *Theoret. Chim. Acta* **1994**, *88*, 1.
[9] D. Lentz, D. Preugschat, *J. Chem. Soc. Chem. Commun.* **1992**, 1523.
[10] D. Lentz, *Angew. Chem.* **1994**, *106*, 1377; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1315.
[11] K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479.
[12] T. H. Dunning, *J. Chem. Phys.* **1989**, *90*, 1007.
[13] P. Botschwina, Ä. Heyl, M. Horn, presented at the 15th Colloquium on High Resolution Molecular Spectroscopy, Glasgow, Great Britain, **1997** (Poster F17).
[14] P. Botschwina, Ä. Heyl, M. Oswald, T. Hirano, *Spectrochim. Acta A* **1997**, *53*, 1079.
[15] P. Botschwina, M. Horn, S. Seeger, J. Flügge, *Chem. Phys. Lett.* **1992**, *195*, 427, **1992**, *200*, 651.
[16] I. M. Mills in *Molecular Spectroscopy: Modern research* (Eds.: K. N. Rao, C. W. Matthews), Academic Press, New York, **1972**, pp. 115–140.
[17] P. Botschwina, J. Flügge, P. Sebald, *J. Phys. Chem.* **1995**, *99*, 9755.
[18] M. D. Harmony, V. W. Laurie, R. L. Kuezkowski, R. E. Schwendeman, D. A. Ramsay, F. J. Lovas, W. J. Lafferty, A. G. Maki, *J. Phys. Chem. Ref. Data* **1979**, *9*, 619.
[19] An extensive discussion of the potential hypersurface in the region of the saddle point and a comparison with results obtained from various other methods will be given elsewhere: P. Botschwina, V. Dyczmons, T. Merzliak, unpublished results.
[20] Wavenumber calibration tables from heterodyne frequency measurements: A. G. Maki, J. S. Wells, *NIST Spec. Publ.* **1991**, 821.
[21] J. Doose, A. Guarnieri, W. Neustock, R. Schwarz, F. Winther, F. Hegelund, *Z. Naturforsch. A* **1989**, *44*, 538.
[22] B. P. Winnewisser, J. Reinstädtler, K. M. T. Yamada, J. Behrend, *J. Mol. Spectrosc.* **1989**, *136*, 12.
[23] MOLPRO96 is an ab initio program package from H.-J. Werner and P. J. Knowles with contributions from J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. A. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, R. Lindh, M. E. Mura, T. Thorsteinson.
[24] C. Hampel, K. Peterson, H.-J. Werner, *Chem. Phys. Lett.* **1992**, *190*, 1.
[25] M. J. O. Deegan, P. J. Knowles, *Chem. Phys. Lett.* **1994**, *227*, 321.
[26] L. Brandsma, *Preparative Acetylenic Chemistry*, 2nd ed., Elsevier, Amsterdam, **1988**.

  1433-7851/98/3720-2882 $ 17.50+.50/0