Syntheses of Halogenated Ethenyl Isocyanide Chromium Complexes as Organometallic Precursor Molecules for Ethenyl and Ethynyl Isocyanides

Marco Balbo-Block, Christoph Bartel, Dieter Lentz,* and Dagmar Preugschat[a]

Abstract: The radical alkylation of tetraethylammonium pentacarbonyl(cyano)chromate **1** yielded the halogenated ethyl isocyanide complexes [(CO)$_5$Cr(CN−CClX−CClYF)] **3** (**a**, X = Cl, Y = F; **b** , X = F, Y = F and **c**, X = Y = Cl). Dehalogenation of **3** using zinc in diethyl ether gave [(CO)$_5$Cr(CN−CX=CFY)] **4**. The compounds **4a, b** reacted with various nucleophiles exclusively at the difluoromethylene group. The unstable phosphorane **5**, which is formed on reaction of **4b** with trimethylphosphane, decomposed thermally and on hydrolysis yielding pentacarbonyl(1,2-difluoroethenyl isocyanide)chromium (**6**). The cyano substituent can be introduced in the β position of the isocyanide function by reaction of **4a**, **b** with potassium cyanide, leading to the formation of [(CO)$_5$Cr(CN−CX=CF−CN)] (**7**). Reactions of **4a, b** with organolithium or organomagnesium compounds yielded [(CO)$_5$Cr(CN−CX=CF−R)] (**8**) and [(CO)$_5$Cr(CN−CF=CF−C≡C−CF=CF−NC)Cr(CO)$_5$] (**10**). The trimethylsilyl group in **8a**, **b**, **d** could be removed by a solution of potassium carbonate in methanol leading to [(CO)$_5$Cr(CN−CX=CF−C$_n$−H)] (**11**) (n = 2, 4). Octacarbonyldicobalt reacted with **8e** under coordination of the C−C triple bond to the hexacarbonyldicobalt fragment, resulting in the cluster compound **12**. The crystal and molecular structure of **8i**, **11a**, **b**, and **12** were elucidated by X-ray crystallography. The alkenyl and alkynyl isocyanides CN−CCl=CF$_2$ (**13a**), CN−CF=CF$_2$ (**13b**), CN−CCl=CClF (**13c**), CN−CF=CFH (**14**), CN−CC−H (**15**), CN−CC−CN (**16**), and CN−CCl=CF−CN (**17**) were obtained by flash vacuum pyrolysis of **4a**, **4b**, **4c**, **6**, and **7a**, respectively.

Keywords: alkenes • alkynes • chromium • isocyanides • interstellar molecules

Introduction

Ethenyl isocyanide was prepared by Matteson and Bailey[1] almost 100 years after the synthesis of the first isocyanides, ethyl isocyanide by Gautier[2] and phenyl isocyanide by Hofmann.[3] The first fluorinated ethenyl isoycanide, F_2C=CF−NC, was synthesized in 1992[4] and its structure was recently elucidated by low-temperature X-ray crystallography.[5] Fehlhammer et al. reported on chloroethenyl isocyanides synthesized and stabilized by a pentacarbonylchromium fragment in 1989.[6] Nevertheless, methods for the synthesis of halogenated ethenyl isocyanides are still rare.

In 1991 we reported on the preparation, microwave spectroscopic study, and structure of the the first alkynyl isocyanide, ethynyl isocyanide, H−C≡C−NC, by vacuum pyrolysis of a suitable organometallic precursor molecule, [(CO)$_5$Cr(CN−CCl=CCl(H)].[7] Shortly after the rotational constants of this molecule were published, Kawaguchi et al. succeeded in detecting H−C≡C−NC in TMC-1 (taurus molecular cloud) by radioastronomy.[8] H−C≡C−NC has been subsequently studied by HeI and HeII photoelectron spectroscopy,[9] millimeter-wave spectroscopy,[10] high-resolution FTIR spectroscopy,[11] and NMR spectroscopy.[12] Recently the very unstable CN−C≡C−CN molecule which had only been obtained before in an argon matrix and characterized by IR spectroscopy[13] was synthesized, and a broad study has been performed by a collaborative effort.[14] Propynyl isocyanide is the only other alkynyl isocyanide which has been obtained thus far in preparative quantities and studied by various spectroscopic methods.[12, 15] Recently, Thaddeus et al. succeeded in generating H−(C≡C)$_n$−NC (n = 2,3) (approximately 0.1 to 1 picomole) along with large amounts of other compounds by electrical discharge in a molecular beam of butadiyne, propynenitrile, or others seeded in Ne.[16, 17] The detection of the isocyanopolyyne molecules was based solely on Fourier transform microwave spectroscopy in combination with ab initio calculations. Fehlhammer et al. successfully synthesized and stabilized H−C≡C−NC, Me$_3$Si−C≡C−NC, and C$_6$H$_5$−C≡C−NC in a transition metal complex.[18] However, no attempt has been made to obtain the free isocyanides.

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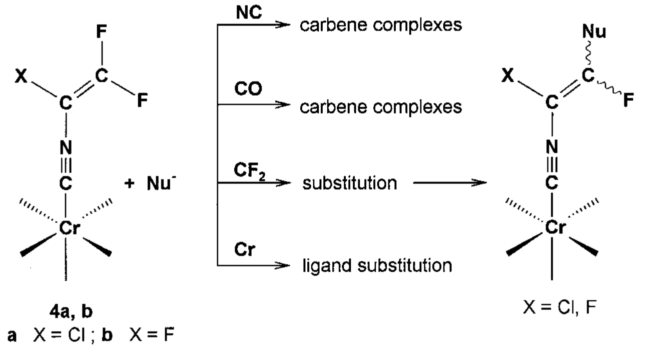
[a] Priv.-Doz. Dr. D. Lentz, M. Balbo-Block, Dr. C. Bartel,
Dr. D. Preugschat
Fachbereich Chemie
Institut für Chemie - Anorganische und Analytische Chemie
Freie Universität Berlin
Fabeckstrasse 34–36, 14195 Berlin (Germany)
Fax: (+49)30-83852424
E-mail: lentz@chemie.fu-berlin.de

Thus far all methods for the preparation of halogenated alkenyl isocyanides were based on the radical halogenation of tetraethylammonium(pentacarbonyl)chromate in a suitable halogenated alkane. This method requires suitable halogenated alkanes and therefore is limited to molecules with a relatively short chain length. Consequently only a few alkenyl and alkynyl isocyanides could be prepared by pyrolysis of (1,2-dichloroalkenyl isocyanide)(pentacarbonyl)chromium complexes. Although Fehlhammer's method for the synthesis of metal complex stabilized alkynyl isocyanides is promising it has been demonstrated on three examples only and was not successful in an attempt to synthesize $[(CO)_5Cr(CN{-}C{\equiv}C{-}t\text{Bu})]$[18] or $[(CO)_5Cr(CN{-}C{\equiv}C{-}CF_3)]$.[19] Furthermore, it requires alkynyl(phenyl)iodonium salts which are not generally available.[20]

Recently, we observed that pentacarbonyl(trifluoroethenyl isocyanide)chromium behaves like a fluoroalkene. For example, it dimerizes on heating leading to a four-membered ring.[21] Highly fluorinated alkenes are very electrophilic systems. Therefore they can be easily attacked by nucleophiles resulting in an intermediate carbanion which can undergo further reactions to the final products.[22] In principle there are several different possibilities for nucleophilic attack on pentacarbonyl(trifluoroethenyl isocyanide)chromium (see Scheme 1) such as at the carbonyl or isocyanide carbon atoms, which would lead to carbene complexes,[23] or at the metal atom, which would give substitution products. In a recent communication[14] we have shown that the nucleophilic attack occurs solely at the CF_2 group of pentacarbonyl(trifluoroethenyl isocyanide)chromium and related compounds, which allows a systematic variation of the substituent in the β position to the isocyano group. In continuation of our work on alkynyl isocyanides as molecules of radioastronomical interest, we report herein in detail on the synthesis and structure determination of halogenated alkenyl isocyanide complexes as organometallic precursor molecules for the synthesis of alkenyl and alkynyl isocyanides.

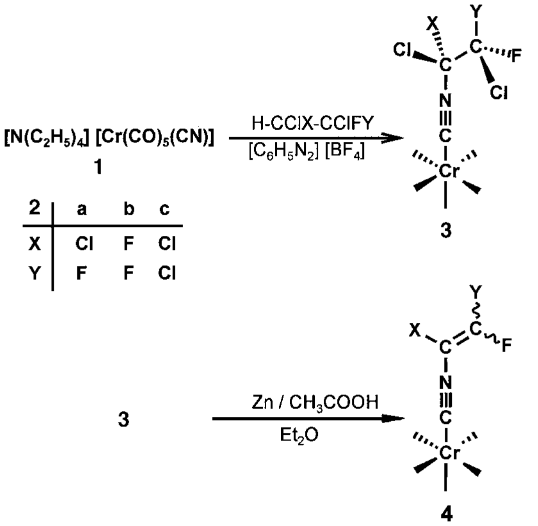


Scheme 1. Different possible sites for nucleophilic attack on pentacarbonyl(trifluoroethenyl isocyanide)chromium and their outcome.

Results and Discussion

Our synthetic strategy based on the systematic modification of halogenated ethenyl isocyanides requires their synthesis on a metal complex framework as outlined in Scheme 2. The pentacarbonyl chromium fragment fulfils several purposes:

1) It allows the synthesis of the halogenated pentacarbonyl(isocyanide)chromium complexes based on the radical alkylation of pentacarbonyl(cyano)chromate discovered by Fehlhammer et al.[24]
2) It serves as a protecting group stabilising the halogenated isocyanides which otherwise tend to polymerize even at low temperatures,[25] making it possible to modify the organic moiety.
3) It serves for the dehalogenation of the alkenyl isocyanide during the pyrolysis.



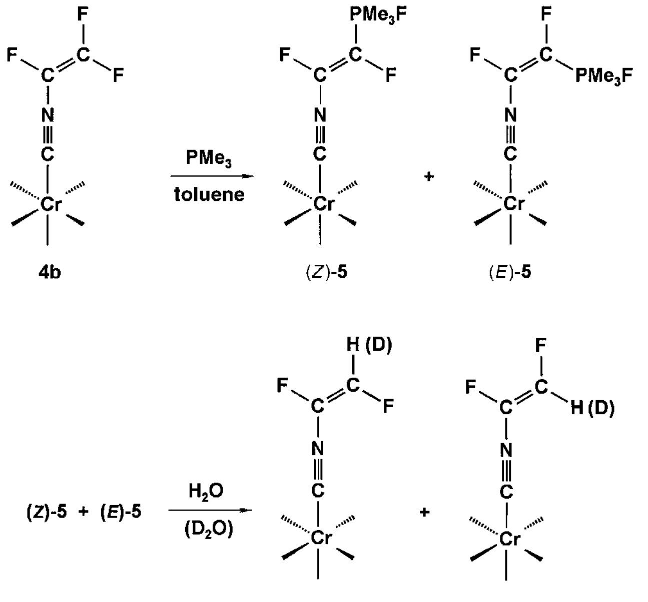
Scheme 2. The synthesis of halogenated ethenyl isocyanides on a metal complex framework.

Reaction of tetraethylammonium(pentacarbonyl)(cyano)chromate **1** with phenyldiazonium tetrafluoroborate in the solvents 1,2,2-trichloro-1,1-difluoroethane (**2a**), 1,2-dichloro-1,1,2-trifluoroethane (**2b**), and 1,1,2,2-tetrachloro-1-fluoroethane (**2c**) yields the perhalogenated ethyl isocyanide complexes **3** (Scheme 2) which can be converted to the corresponding ethenyl isocyanide complexes **4** by dehalogenation using zinc.

As very electrophilic systems highly fluorinated alkenes can be easily attacked by nucleophiles.[22] On the other hand carbonyl and isocyanide complexes have other electrophilic centers such as the carbonyl and isocyanide carbon atoms and the metal center which might give raise to by-products as outlined in Scheme 1.

The nucleophilic attack on the complexes **4** occurs exclusively at the difluoromethylene group in the β position to the isocyanide nitrogen atom. No by-products from the other possible reaction channels were observed so far, although pentacarbonyl(trifluoromethyl isocyanide)chromium is readily attacked by nucleophiles resulting in the formation of carbene complexes.[26]

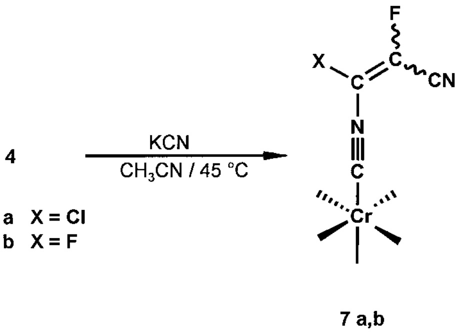
Reaction of **4b** with trimethylphosphane results in the formation of a thermally unstable phosphorane **5** via nucleophilic attack of the β-carbon atom followed by fluoride migration to the phosphorus center (Scheme 3). Similar to the



Scheme 3. Reaction of **4b** to give **5** and the subsequent reaction to give **6**.

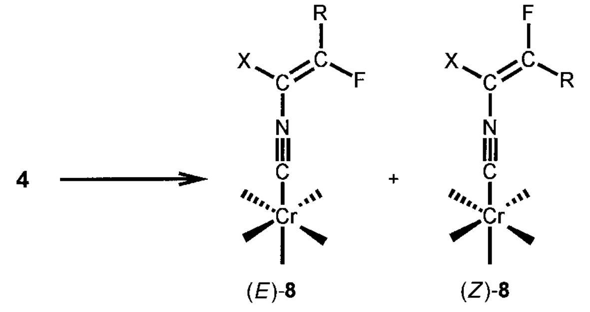
previously described phosphoranes $F_3C-CF=CF-PFR_3$[27] and $F_5S-CF=CF-PFR_3$,[28] **5** could not be isolated but it could be characterized by low-temperature ^{19}F and ^{31}P NMR spectroscopy of the reaction mixture. The $^{31}P\{^1H\}$ NMR spectrum exhibits three resonances at $\delta = -14.7$ (t, $^1J(^{19}F,^{31}P) = 536$ Hz; $PF_2(CH_3)_3$), -61.4 (s; $P(CH_3)_3$), and -77.8 (d, $^1J(^{19}F,^{31}P) = 555$ Hz, **5**). The ^{19}F NMR spectrum shows three resonances in at $\delta = 19.3$ (d, PF), 138.2 ($^3J(^{19}F,^{19}F) = 128$ Hz; CF), and -141.8 which can be assigned to the product **5** besides the signals of starting material and decomposition products. As both spectra recorded at -50 °C exhibit signals of the starting materials, **5**, and the decomposition product **6**, no attempts were made to isolate the phosphorane **5**. Thermal decomposition and hydrolysis with H_2O or D_2O yields the 1,2-difluoroethenyl isocyanide complexes **6** and [D]-**6**, respectively.

(*E*/*Z*)-Pentacarbonyl(1-chloro-2-cyano-2-difluoroethenyl isocyanide)chromium (**7a**) and (*E*/*Z*)-pentacarbonyl(2-cyano-1,2-difluoroethenyl isocyanide)chromium (**7b**) were obtained from **4a** and **4b**, respectively, and potassium cyanide in acetonitrile; this route also provided a facile route to ^{13}C- and ^{15}N-labeled compounds (Scheme 4).



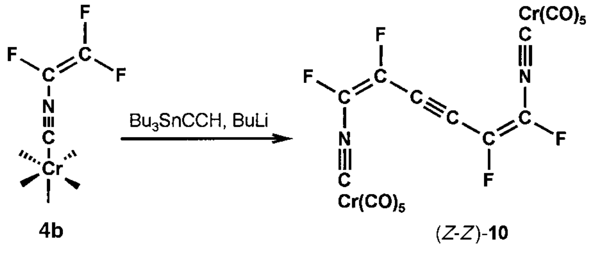
Scheme 4. Reaction of **4a, b** with KCN to give **7a, b**.

Several organic substituents could be introduced in the β position to the isocyanide nitrogen atom (Scheme 5) in complexes **8** by using various organolithium or -magnesium compounds as nucleophiles. The organic substituents range from methyl to trimethylsilylbutadiynyl and it appears that this reaction is a quite general and depends only on the availability of the organolithium or Grignard compound. Consequently, attempts to prepare $[(CO)_5Cr(CN-CF=CF-C\equiv C-CN)]$ and $[(CO)_5Cr(CN-CF=CF-C\equiv C-COOMe)]$ from $HC\equiv C-CN$ and $HC\equiv C-COOMe$ failed. $[(CO)_5Cr(CN-CF=CFOMe)]$ (**8i**) was the only product isolated from the reaction of $HC\equiv C-COOMe$ with lithium diisopropylamide (LDA) and **4b**. However, **4b** reacts with methanol in the presence of potassium carbonate forming the addition product $[(CO)_5Cr(CN-CHF-CF_2OMe)]$ (**9**). Organomagnesium compounds give higher yields than organolithium compounds. This might be due to lower fluoride concentrations in the reaction mixture, as high fluoride concentrations lead to a complete decomposition of **4a** and **b** to unidentified products. Deprotonation of ethynyltributylstannane with butyllithium and subsequent reaction with **4b** yields the dinuclear chromium complex **10** (Scheme 6). Removal of the trimethylsilyl protecting groups in **8a–d** by using potassium carbonate in methanol (Scheme 7) yields **11a–c**. However, it is extremely difficult to control the desilylation by using tetrabutylammonium fluoride in THF. After a reaction time of a few minutes



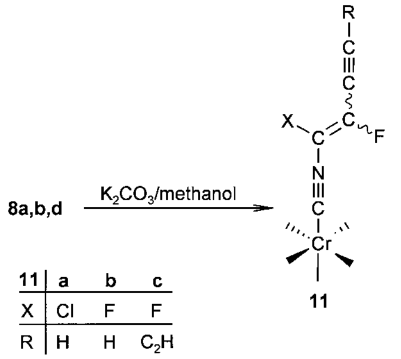
8	a	b	c	d	e	f	g	h	i
X	Cl	F	Cl	F	Cl	F	Cl	F	F
R	C_2SiMe_3	C_2SiMe_3	C_4SiMe_3	C_4SiMe_3	C_2Me	C_2Ph	Me	Me	OMe

Scheme 5. Introduction of organic substituents into the β position to the isocyanide nitrogen atom give rise to complexes **8**.



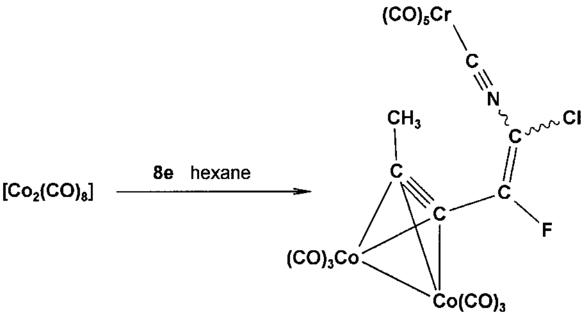
+ small amounts of the (*E-Z*) and (*E-E*) isomers

Scheme 6. Reaction of **4b** and ethynyltributylstannane and butyllithium to give **10**.



11	a	b	c
X	Cl	F	F
R	H	H	C$_2$H

Scheme 7. Removal of the protecting groups on **8a, b, d** to give **11**.



12

Scheme 8. Reaction of [Co$_2$(CO)$_8$] with **8e** to give **12**.

only traces of the starting materials or products could be detected by ^{19}F NMR spectroscopy. This observation again demonstrates the sensitivity of the ethenyl isocyanide complexes towards fluoride ions. Complexes **11a** and **b** can also be prepared directly from **4a** and **b**, respectively, and HCCMgBr, however, it is difficult to control the yields and purity of the products. All nucleophilic substitution reactions of **4a** and **b** result in mixtures of the *E* and *Z* isomers.

The chromium complexes **3**–**10** are crystalline materials with low melting points and high volatility. They are very soluble in most organic solvents. Both the solutions and the crystals can be handled in air without significant decomposition for short periods of time. However, they should be kept under argon in a cold place for longer term storage. The unprotected alkynyl compounds **11** are much more sensitive and should be handled in an inert gas atmosphere. (*E*/*Z*)-Pentacarbonyl(1-chloro-2-fluoropent-1-en-3-ynyl isocyanide)chromium [(CO)$_5$Cr(CNCClCFC$_2$CH$_3$)] (**8e**) reacts with octacarbonyldicobalt to give a typical alkyne complex **12** with the expected dimetallatetrahedrane structure (Scheme 8) in the form of dark red air-stable crystals.

All complexes were fully characterized by spectroscopic methods. Mass spectra usually exhibit the molecular ion as well as fragment ions assigned to the successive loss of the five carbonyl ligands together with those of smaller fragments. Although the pentacarbonylchromium fragment possesses local C_{4v} symmetry, the assignment of the CO vibrations is not easy due to strong coupling with the CN stretching mode.

NMR spectra are an effective analytical tool in characterizing these compounds. The $^3J(^{19}F,^{19}F)$ coupling constants of the compounds **4b**, **6**, **7b**, **8b**, **d**, **f**, **h**, **i**, **11a, b** allow an easy assignment of the resonances of the *E* and *Z* isomer, respectively. Selected chemical shift values and $^1J(^{13}C,^{19}F)$ and $^2J(^{13}C,^{19}F)$ coupling constants are listed in Table 1. From these values a general trend can be found:

The resonance of the β-fluorine atom of the *E* isomer with the fluorine atoms in *trans* position is observed at about 10 ppm higher field than that of the *Z* isomer. ^{13}C chemical shift values of the alkene carbon atoms of the *E* isomer are observed at lower field than that of the *Z* isomer. $^1J(^{13}C,^{19}F)$ coupling constants of the β-fluorine atom vary but those of the *E* isomer are about 10 Hz smaller than those of the *Z* isomer for the same compound. The opposite trend is observed for the $^2J(^{13}C,^{19}F)$ coupling constants of the β-fluorine atom. A similar trend is observed for the chloro-substituted compounds **4a**, **7a**, **8a**, **c**, **e**, **g** and **11a** (Table 1 bottom part); this allows an assignment of the resonances to the *E* and *Z* isomer, respectively. The correctness of this assignment is proven by

Table 1. Selected chemical shift values [ppm] and ^{13}C,^{19}F coupling constants [Hz]. β-Fluorine substituents *trans* to a halogen substituent are labeled *E*. The assignment of the resonances in the upper part of this table is unambiguous due to the ^{19}F,^{19}F coupling constant.

	δ ^{19}F(β)			δ ^{13}C(β)			$^1J_{CF}$			δ ^{13}C(α)			$^2J_{C,F}$		
	(*E*)	(*Z*)	**Δ**	(*E*)	(*Z*)	**Δ**	(*E*)	(*Z*)	**Δ**	(*E*)	(*Z*)	**Δ**	(*E*)	(*Z*)	**Δ**
4b	–112.5	–101.0	**–11.5**												
6	–170.6	–160.2	**–10.4**	138.3			259			133.9			39		
7b	–165.8	–156.9	**–9.9**	123.7	121.3	**2.4**	240	251	**11**	137.5	135.8	**1.7**	45	38	**7**
8b	–144.3	–134.8	**–9.5**	132.3	130.6	**1.7**	237	246	**9**	134.8	133.1	**1.7**	54	45	**9**
8d	–146.9	–137.2	**–9.7**	132.3	130.7	**1.6**		247		136.3	134.3	**2.0**		45	
8f	–143.4	–133.6	**–9.8**	132.8	131.0	**1.8**	236	245	**9**	134.0	132.5	**1.5**	55	46	**9**
8h	–134.3	–126.1	**–8.3**	147.8	144.7	**3.1**	255	260	**5**						
8i	–155.8	–150.2	**–5.6**	151.5	150.8	**0.7**	277	286	**9**	119.0	118.5	**0.5**	67	58	**9**
11b	–147.5	–137.8	**–9.7**	132.2	130.5	**1.7**	237	246	**9**	135.9	133.7	**2.2**	53	43	**10**
11c	–148.5	–138.6	**–9.9**												
4a	–89.6	–82.3	**–7.3**				294	300	**6**				51	39	**12**
7a	–131.7	–123.8	**–7.9**	131.9	131.3	**0.6**	256	259	**3**	117.5	115.2	**2.3**	46	33	**13**
8a	–109.6	–105.2	**–4.6**	142.2	140.7	**1.5**	250	254	**4**	109.5	108.8	**0.7**	56	43	**13**
8c	–112.3	–107.3	**–5.0**	142.2	140.6	**1.6**	250	252	**2**	111.6	110.6	**1.0**	55	42	**13**
8e	–106.4	–101.9	**–4.5**	143.4	141.4	**2.0**	251	253	**2**	108.2	107.7	**0.5**	57	46	**11**
8g	–97.9	–93.4	**–4.5**	159.3	158.1	**1.2**	267	271	**4**	102.7	102.2	**0.5**			
11a	–110.5	–93.4	**–5.0**	142.2	140.4	**1.8**	251	254	**3**	110.8	109.9	**0.9**	52	40	**12**

the X-ray crystal structure determination of (*E*)-**8a** (see below). The alkyne proton of **11a** and **b** are observed at $\delta = 4.00$ ((*E*)-**11a**), 3.97 ((*Z*)-**11a**) and 4.11 ((*E*)-**11b**), 3.92 ((*Z*)-**11b**), respectively. The signals are split into a doublet and a doublet of doublets due to scalar coupling with fluorine ((*E*)-**11a**, $^4J_{\mathrm{H,F}} = 3$ Hz; (*Z*)-**11a**, $^4J_{\mathrm{H,F}} = 4$ Hz; (*E*)-**11b**, $^4J_{\mathrm{H,F}} = 3$ Hz, $^5J_{\mathrm{H,F}} = 3$ Hz; (*Z*)-**11b**, $^4J_{\mathrm{H,F}} = 3$ Hz, $^5J_{\mathrm{H,F}} = 1$ Hz), respectively. In **11d** even a $^6J_{\mathrm{H,F}}$ coupling is observed.

The ^{13}C NMR spectra give further information, especially on the ligand properties of the halogenated isocyanides. The interpretation of the spectra is usually straightforward due to scalar coupling with fluorine or proton substituents. In the case of the ^{13}C- or ^{15}N-labeled compounds additional ^{13}C,^{13}C, ^{15}N,^{19}F, and ^{13}C,^{15}N coupling constants can be determined. Missing information is derived from two-dimensional ^{19}F,^{13}C and ^{1}H,^{13}C HMQC spectra.

In complexes of the type [(CO)$_5$CrL] the resonances of the carbonyl ligands give rise to signals around $\delta = 200$ in the ^{13}C NMR spectra in an intensity ratio of 4:1. With a few exceptions the signal of the *trans* carbonyl carbon atom is registered at higher frequency than that of the *cis* carbonyl ligands. Only for very strong π-acceptor ligands like CS,[29] CSe,[29] CNCN,[30] and CF$_3$NC,[31] is the resonance of the *trans* carbonyl ligand observed at the same frequency or at lower frequency than the *cis* carbonyl ligand. The difference in chemical shift values of the halogenated ethyl isocyanide complexes **3a–c** decreases with the number of fluorine substituents (for **3b** it is only 0.1 ppm). Thus the π-acceptor ability of the 1,2-dichloro-1,2,2-trifluoroethyl isocyanide ligand approaches that of the carbonyl ligand. The differences in chemical shift values between *cis* and *trans* carbonyl ligands is much larger for all of the alkenyl isocyanide complexes studied, which is in agreement with structural data that show these isocyanides are weaker π-acceptor ligands.

In most cases the ratio of the *E* and *Z* isomers is very close to one (Table 2). Depending on the reaction conditions the 1,2-difluorethenyl complex **6** is formed predominantly as the *E* isomer. This may be due to the almost exclusive formation of (*Z*)-**5** which has the fluorine substituents in *trans* position. The excess (*E*)-**6** in the thermal decomposition of **5** seems to be greater than that obtained by hydrolysis of **5**. Unexpectedly, reaction of **4b** with 4-trimethylsilylbutadiynyllithium results in an at least sixfold excess of the *Z* isomer. Even more striking is the almost exclusive formation of decacarbonyl[(*Z,Z*)-1,2,5,6-tetrafluoro-1,6-isocyano-hexa-1,5-dien-3-yne]dichromium ((*Z,Z*)-**10**) which makes it difficult to determine the spectroscopic data of the other two isomers although the *E,Z* isomer should be statistically favored. As the R_f values of the isomers using different eluents turned out to be very similar, no attempts were made to separate the isomers by chromatography. However, in some cases the difference in solubility and volatility of the *E* and *Z* isomer allowed a separation by fractional crystallization or sublimation.

X-ray crystal structure determinations

The crystallographic data of **11a**, **11b**, **8i**, and **12** are summarized in Table 3. Selected bond lengths and angles are compared in Table 4. ORTEP drawings of the molecules are given in Figure 1, Figure 2, and Figure 3, respectively. In all of the complexes studied by X-ray crystallography the chromium atom is coordinated almost octahedrally by the five carbonyl ligands and the isocyanide ligand. The chromium–carbon bond lengths to the carbonyl ligands vary slightly ranging from 1.895 to 1.918 Å with no significant shortening of the bond *trans* to the isocyanide ligand. Cr–C bond lengths to

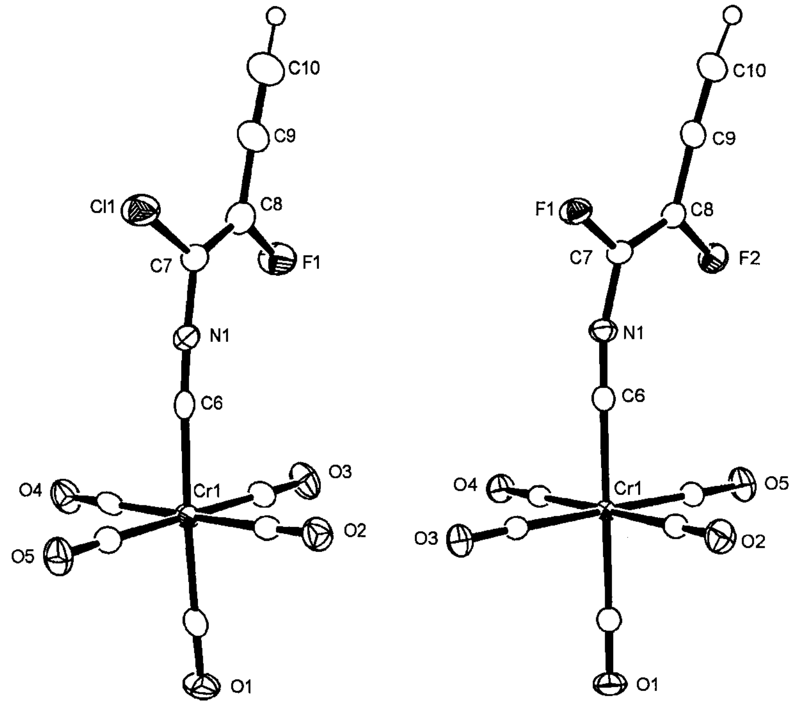


Figure 1. Molecular structure (ORTEP[40]) of **11a** (left) and **11b** (right).

Table 2. Ratio of the *E* and *Z* isomers formed as determined by integration of the ^{19}F NMR spectra of the reaction mixtures.

	6	**6**	**7a**	**7b**	**8a**	**8b**	**8c**	**8d**	**8e**	**8f**	**8g**	**8h**	**8i**
E/*Z*	50[a]	6[b]	0.77	0.77	0.8	0.8	2.0	0.15	1.3	0.8	1.4	0.8	0.71

[a] Obtained by thermal decomposition of **5**. [b] Obtained by hydrolysis of **5**.

Table 3. Crystal data and structure refinement for **11a**, **11b**, **8i**, and **12**.

	11a	**11b**	**8i**	**12**
empirical formula	$C_{10}HClCrFNO_5$	$C_{10}HCrF_2NO_5$	$C_9H_3CrF_2NO_6$	$C_{17}H_3ClCo_2CrFNO_{11}$
M_r	321.57	305.12	311.12	621.51
T [K]	163(2)	123(2)	153(2)	293(2)
λ [Å]	0.71073	0.71073	0.71073	0.71069
crystal system	monoclinic	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$C2/c$
a [Å]	6.7242(12)	7.0088(4)	6.4969(4)	24.063(5)
b [Å]	11.730(2)	6.2563(4)	9.6269(6)	9.693(2)
c [Å]	15.359(3)	25.7584(15)	10.2481(6)	20.680(4)
α [°]	90	90	81.1150(10)	90
β [°]	91.615(4)	94.5440(10)	78.0610(10)°	105.650(16)
γ [°]	90	90	73.3140(10)	90
V [Å^3]	1210.9(4)	1125.93(12)	597.60(6)	4644.8(17)
Z	4	4	2	8
ρ_{calcd} [Mg m^{-3}]	1.764	1.800	1.729	1.778
μ [mm^{-1}]	1.192	1.059	1.005	2.050
$F(000)$	632	600	308	2432
Crystal size [mm^3]	$0.40 \times 0.30 \times 0.15$	$0.30 \times 0.21 \times 0.08$	$0.5 \times 0.3 \times 0.3$	$0.38 \times 0.30 \times 0.15$
θ_{max} [°]	27.53	31.03	31.46	25.00
index ranges	$-8 \leq h \leq 8$, $0 \leq k \leq 15$, $0 \leq l \leq 19$	$-9 \leq h \leq 9$, $0 \leq k \leq 9$, $0 \leq l \leq 36$	$-9 \leq h \leq 9$, $-13 \leq k \leq 14$, $-14 \leq l \leq 14$	$-24 \leq h \leq 28$, $-6 \leq k \leq 11$, $-24 \leq l \leq 9$
reflections collected	11481	13436	7107	4666
independent reflections/R_{int}	2792/0.1023	3445/0.0304	3524/0.0144	4107/0.0107]
completeness to θ_{max} [%]	99.9	96.0	89.0	100.0
absorption correction	empirical SADABS	empirical SADABS	empirical SADABS	empirical PSI scan
T_{max}/T_{min}	0.96/0.81	0.9422/0.7440	0.695/0.554	0.970/0.805
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/parameters	2792/0/176	3445/0/176	3524/0/184	4107/0/307
goodness-of-fit on F^2	0.935	1.034	1.033	1.018
R_1/wR_2 [$I > 2\sigma(I)$]	0.0400/0.0623	0.0257/0.0677	0.0235/0.0673	0.0284/0.0753
R_1/wR_2 (all data)	0.0853/0.0692	0.0362/0.0717	0.0254/0.0684	0.0619/0.0848
$\Delta\rho_{max}/\Delta\rho_{min}$ [e Å^{-3}]	0.320 and −0.329	0.379/−0.532	0.396/−0.527	0.263/−0.248

Table 4. Selected bond lengths [Å] and angles [°] for **11a**, **11b**, **8i**, **12.**

	11a	**11b**	**8i**	**12**
Cr1–C1	1.897(3)	1.9108(13)	1.9048(11)	1.895(3)
Cr1–C_{cis}	1.897(3)–1.917(3)	1.9082(13)–1.9184(13)	1.9058(12)–1.9158(12)	1.901(3)–1.916(4)
Cr1–C6	1.942(3)	1.9338(13)	1.9466(11)	1.959(3)
N1–C6	1.170(3)	1.1753(16)	1.1683(15)	1.165(4)
N1–C7	1.374(3)	1.3562(16)	1.3603(14)	1.369(3)
Cl1–C7	1.719(3)			1.725(3)
F1–C7		1.3376(14)	1.3449(13)	
F1–C8	1.365(3)			1.349(3)
F2–C8		1.3503(15)	1.3352(14)	
C7–C8	1.318(4)	1.3356(18)	1.3225(16)	1.332(4)
C8–C9	1.415(4)	1.4181(18)		1.421(4)
C8–O6			1.3222(13)	
C9–C10	1.173(4)	1.1859(19)		1.339(4)
Co2–Co3				2.4573(7)
Co–C9(10)				1.949(3)–1.966(3)
C6-N1-C7	175.3(3)	167.66(13)	176.91(12)	165.0(3)
N1-C7-Cl1	116.3(2)			114.9(2)
N1-C7-F1		114.90(11)	114.40(10)	
F1-C8-C9	116.8(3)			115.6(3)
F2-C8-C9		116.47(11)		
C10-C9-C8	178.1(4)	177.74(15)		

the isocyanide ligand range from 1.934 to 1.959 Å. The substituent at the isocyanide nitrogen atoms are in an almost eclipsed position to one of the carbonyl ligands; the C-Cr-C7-X (X = Cl, F) torsion angles lie between 5.4 and 16.4°. This is the only conformation that allows an effective π back bonding to the isocyanide carbon atom, since the C–N bond is part of a conjugated system. However, the conjugation effects on the bond lengths are very small and seem to be most pronounced for **11b**. As found for most isocyanide complexes[32] the C6-N1-C7 bond angles deviate less than 20° from 180°. Owing to the coordination to the two cobalt atoms the C9–C10 bond in **12** is significantly longer than the C–C triple bond in **11a** and **11b**. The C8-C9-C10 and C9-C10-C11 bond angles in **12** are significantly smaller than 180°. The Co–Co bond length of 2.4573(7) Å compares well with other hexacarbonyl(μ_2-η^2-alkyne)dicobalt complexes structurally studied.[33]

Pyrolysis experiments

Pyrolysis experiments in which the compounds **4a**, **b**, **c**, **6**, **7a**, **8e**, and **11a** were used to obtain the free isocyanides were

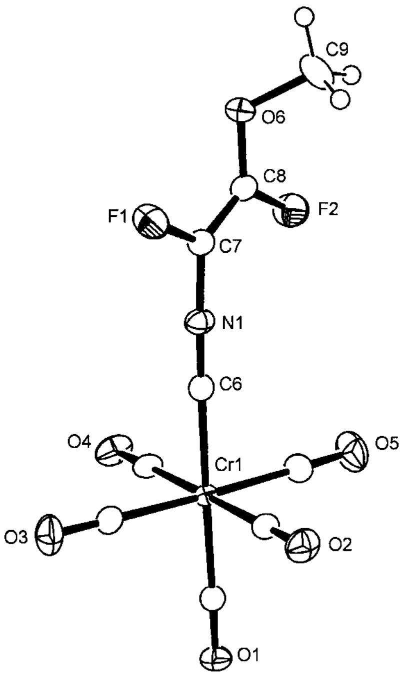


Figure 2. Molecular structure (ORTEP[40]) of **8i**.

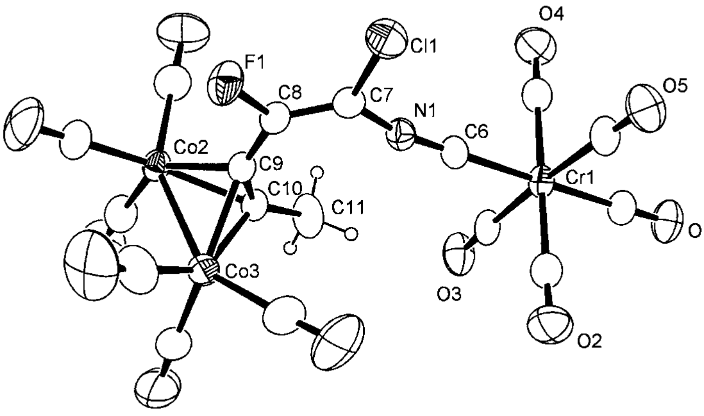
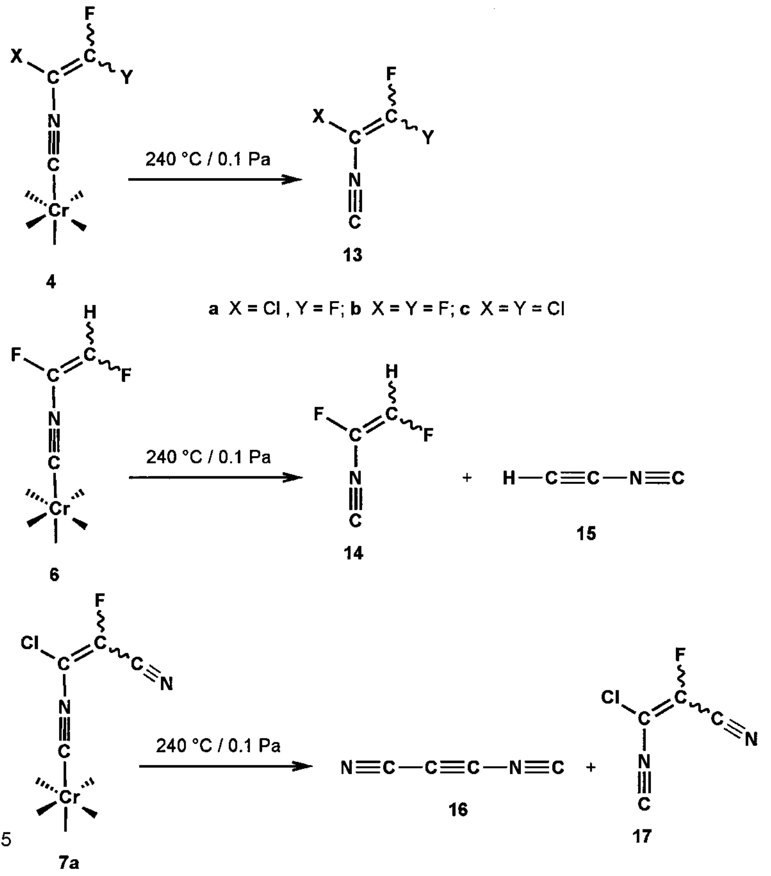


Figure 3. Molecular structure (ORTEP[40]) of **12**.

partially successful. Flash vacuum pyrolysis of **4b** yields the first perfluorinated alkenyl isocyanide **13b** as a colorless gas (Scheme 9). Compound **13b** is stable at low temperature, in the gaseous phase at low pressure, or in dilute solution. It decomposes readily even below 0 °C in concentrated solution or as a neat substance. Vapor pressure measurements between 189 K and 225 K result in $\ln p = -24736/RT + 17.13$ and an extrapolated boiling point of 18 °C.

The mass spectrum of **13b** exhibits the molecular ion and smaller fragment ions. The IR spectrum shows absorption at 2111 and 1801 cm^{-1} due to NC and C=C stretching modes. The ^{19}F NMR spectrum of **13b** (Figure 4) consists of an ABC pattern similar to **4**. However, an additional splitting into 1:1:1 triplet is observed for the resonance of the fluorine atom in the geminal position to the nitrogen atom. Generally, free isocyanides although quite unsymmetrical can have small electric field gradients at the nitrogen atom which allows the observation of the $^{1}H,^{14}N$ or $^{19}F,^{14}N$ coupling and results in small line width in the ^{14}N NMR spectra.[34] The structures of trifluoroethenyl isocyanide **13b** and its isomer trifluoroacrylonitrile were determined recently by X-ray crystallography.[5] All attempts to obtain fluoroethynyl isocyanide by pyrolysis of **4a**, **4b**, or **4c** failed. According to the IR spectra (ν(NC) 2111 vs, ν(C=C) 1744 vs and ν(NC) 2104 vs, ν(C=C) 1654 s cm^{-1}) CN–CCl=CF_2 (**13a**) and CN–CCl=CClF (**13c**) are formed on pyrolysis of **4a** and **4c** at 250 °C, respectively.



Scheme 9.

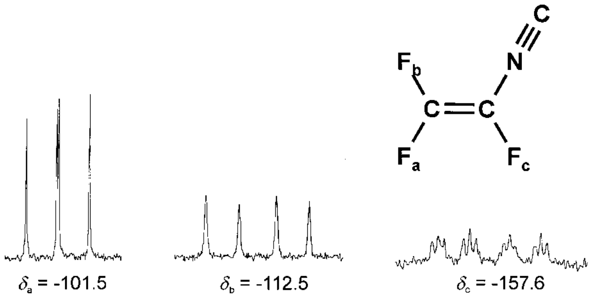


Figure 4. ^{19}F NMR spectrum of **13**. $^{2}J(^{19}F_a,^{19}F_b) = 53$ Hz, $^{3}J(^{19}F_a,^{19}F_c) = 50$ Hz, $^{3}J(^{19}F_b,^{19}F_c) = 113$ Hz, $^{2}J(^{14}N,^{19}F_c) = 10$ Hz.

As expected pyrolysis of **6** yields the ethenyl isocyanide **14** as a mixture of the *E* and *Z* isomers. The ratio of the isomers is equivalent to that of the precursor complex **6**. All spectroscopic data are consistent with **6**. The ^{19}F NMR spectrum exhibits additional splitting due to coupling to the nitrogen isotope ^{14}N. Nevertheless the product contained a more volatile material which was easily identified as ethynyl isocyanide **15** by comparing the mass and IR spectra with those of previously prepared samples (Scheme 9).[7] Although this undesired side reaction made the purification of **6** difficult, this result was important because it clearly demonstrated the possibility of alkyne formation by a defluorination reaction.

Consequently, we have synthesized **7**, **8**, and **11** as potential precursor molecules for cyanoisocyanoacetylene and isocyanopolyynes. However, the results of the pyrolysis experiments of **7**, **8**, and **11** are different. Apart from the fact that the pyrolysis of **7** is less efficient than that of $[(CO)_5Cr(CN{-}CCl{=}CClH)]$ it yields cyanoisocyanoacetylene **16** in amounts sufficient to record all necessary spectroscopic data (Scheme 9). As the cyano group is introduced in the final step, isotopic labeling of the cyano group by ^{15}N or ^{13}C can be performed easily, and this provides a sufficient number of rotational constants of the isotopomers for a reliable structure determination.[14] The expected by-product 1-chloro-2-cyano-2-fluoroethenyl isocyanide (2-chloro-3-fluoro-3-isocyanopropennitrile) (**17**) was purified by fractional condensation under vacuum and identified by mass, IR, and NMR spectra. Again a mixture of the *E* and *Z* isomers was obtained. In almost all pyrolysis experiments using **11a** an explosive decomposition of the chromium complex was observed, leading to the formation of a dark brown material which filled the complete vacuum line. Occasionally $HC\equiv C{-}C\equiv C{-}C\equiv N$ could be detected by comparison of the IR spectrum with literature values[35] and by millimeter-wave spectroscopy.[36] Attempts using **8e** were equally unsuccessful.

Conclusion

The cross-coupling reaction of pentacarbonylchromium-protected halogenated ethenyl isocyanides with various carbon nucleophiles is a very effective method for the synthesis of various isocyanides. Vacuum pyrolysis of some of these complexes is still the only preparative route for alkynyl isocyanides. To generalize our synthesis strategy it is necessary to develop more facial dehalogenation methods as well as easier methods for the removal of the pentacarbonylchromium protecting group.

Experimental Section

General: All reactions were carried out under dry argon by using standard Schlenck 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. ^1H, ^2D, ^{13}C, and ^{15}N NMR spectra were recorded by using a JEOL FX 90Q or JEOL LAMBDA 400 instrument with TMS or solvent signals (^1H, ^2D, ^{13}C), nitromethane (^{15}N) and $CFCl_3$ (^{19}F) as standards. Infrared spectra were taken on a Perkin Elmer 883, Nicolet 5SXC or a Bruker Vector 22 instrument. Raman spectra were recorded by using a Bruker RFS 100 or SPEX1403 instrument. Mass spectra were obtained on a Varian MAT 711 (80 eV) or a Balzers QMS 200 instrument. Tetraethylammonium pentacarbonyl(cyano) chromate **1** was prepared following the literature procedure;[37] however, sublimed hexacarbonyl chromium and freshly sublimed sodium bis(trimethylsilyl)amide were used to get a maximum yield of 95% and to avoid the formation of pyrophoric by-products. $K[Cr(CO)_5(C^{15}N)]$ was prepared according to literature procedures.[38] 1,2-Dichlorotrifluoroethane (Hoechst and DuPont), 1,1,2-trichlorodifluoroethane (Hoechst and DuPont), and 1,1,2,2-tetrachlorofluoroethane (PCR) were used as received. The chlorofluoroethanes employed were purified by distillation using a spinning band column for reuse.

Pentacarbonyl(1,1,2-trichloro-2,2-difluoroethyl isocyanide)chromium (3a): Tetraethylammonium pentacarbonyl(cyano)chromate (9.40 g, 27.0 mmol) was suspended in 1,1,2-trichloro-2,2-difluoroethane (80 mL). Phenyldiazonium tetrafluoroborate (25 mmol) was added at −78 °C. On warming to ambient temperature the light yellow suspension turned to dark brown, while nitrogen gas was evolved. After 2 h at ambient temperature the solvent was removed in vacuum into a trap kept at −196 °C for reuse. The residue was extracted several times with pentane. The solvent was removed in vacuum. The remaining product was purified by column chromatography (silica/pentane). Sublimation in vacuum (35 °C/0.1 Pa) yielded **3a** as a yellow solid. Yield: 5.52 g (14.3 mmol, 53%); m.p. 62 °C; elemental analysis for $C_8Cl_3CrF_2NO_5$ (%): calcd: C 24.86, N 3.62; found: C 24.94, N 3.94; MS (EI, 80 eV): *m/z*: 385, 329, 301, 273, 245 (100%), 210, 175, 52; IR (pentane): $\tilde{\nu} = 2005$ sh, 1985 vs, 1956 sh cm^{-1}; IR (KBr): $\tilde{\nu} = 2185$ m, 2120 s, 1955 vs, 1190 s, 1160 s, 1100 s, 1018 s, 1002 m, 841 s, 773 s, 676 vs, 648 vs, 545 s, 522 w, 441 s cm^{-1}; Raman: $\tilde{\nu} = 2184$ vw, 2110 w, 2002 vs, 1942 w, 1101 w, 1018 w, 1001 vw, 841 vw, 774 vw, 679 vw, 648 vw, 625 vw, 545 vw, 526 vw, 500 vw, 454 w, 442 w, 388m, 551 w, 312 vw, 293 vw, 252vw, 229 vw, 169 vw, 105 m cm^{-1}; ^{13}C NMR: $\delta = 84.8$ (t, $^2J_{C,F} = 37$ Hz; CCl_2), 124.6 (t, $^1J_{C,F} = 303$ Hz; $CClF_2$), 202.5 (s; NC), 212.1 (s; CO_{cis}), 212.6 (s; CO_{trans}); ^{19}F NMR: $\delta = -66.82$ (s; $CClF_2$).

Pentacarbonyl(1,2-dichloro-1,2,2-trifluoroethyl isocyanide)chromium (3b): The compound **3b** was prepared similarly to **3a** using 1,2-dichloro-1,2,2-trifluoroethane (100 mL). Yield: 4.3 g (11.6 mmol, 46.4%) as a yellow solid; m.p. 39 °C; elemental analysis for $C_8Cl_2CrF_3NO_5$ (%): calcd C 25.97, N 3.79; found C 27.28, N 3.77; MS (EI, 80 eV): *m/z*: 369, 306, 257, 229, 194 (100%), 52; IR (pentane): $\tilde{\nu} = 2010$ w, 1983 vs, 1952 m cm^{-1}; ^{13}C NMR: $\delta = 101.5$ (dt, $^1J_{C,F} = 270$ Hz, $^2J_{C,F} = 38$ Hz; CClF), 122.7 (dt, $^1J_{C,F} = 303$ Hz, $^2J_{C,F} = 38$ Hz; $CClF_2$), 208.1 (s; NC), 211.8 (s; CO_{cis}), 211.9 (s; CO_{trans}); ^{19}F NMR : $\delta = -83.0$ (dd, $^3J_{C,F} = 9$ Hz, $^3J_{C,F} = 10$ Hz; CFCl), −70.1 (dd, $^2J_{C,F} = 165$ Hz, $^3J_{C,F} = 10$ Hz; CF_2Cl), −69.3 (dd, $^2J_{C,F} = 165$ Hz, $^3J_{C,F} = 9$ Hz; CF_2Cl).

Pentacarbonyl(1,1,2,2-tetrachloro-2-fluoroethyl isocyanide)chromium (3c): The compound **3c** was prepared similarly to **3a** using 1,1,2,2-tetrachloro-2-fluoroethane (100 mL). Yield: 0.79 g (2.0 mmol, 34%) as a yellow solid; m.p. 71 °C; elemental analysis for $C_8Cl_4CrFNO_5$ (%): calcd: C 23.85, N 3.48; found: C 23.86, N 3.38; MS (EI, 80 eV): *m/z*: 403, 291, 263, 191, 52; IR (pentane): $\tilde{\nu} = 1978$ vs br cm^{-1}; ^{13}C NMR: $\delta = 88.95$ (d, $^2J_{C,F} = 35$ Hz; CCl_2), 120.6 (d, $^1J_{C,F} = 310$ Hz; CCl_2F, major conformer), 121.6 (d, $^1J_{C,F} = 311$ Hz; CCl_2F, minor conformer), 199.9 (s; NC), 212.3 (s; CO_{cis}), 212.9 (s; CO_{trans}); ^{19}F NMR : $\delta = -64.4$ (major conformer), −52.9 (minor conformer).

Pentacarbonyl(1-chloro-2-difluoroethenyl isocyanide)chromium (4a): A solution of **3a** (3.80 g, 9.8 mmol) in diethyl ether was cooled to 0 °C and zinc powder (6.40 g, 98.0 mmol) and acetic acid (2 mL) were added. The reaction mixture was stirred for 6 h at ambient temperature. After filtration the solvent was removed in vacuum at −20 °C. The residue was purified by column chromatography (silica, pentane). Sublimation in vacuum (35 °C/0.1 Pa) yielded **4a** as yellow crystals. Yield: 2.47 g (7.8 mmol, 80%); m.p. 60 °C; elemental analysis for $C_8ClCrF_2NO_5$ (%): calcd: C 30.45, N 4.44; found: C 30.58, N 4.68; MS (EI, 80 eV): *m/z*: 315, 287, 259, 231, 203, 175 (100%), 78, 52; IR (KBr): $\tilde{\nu} = 2125$ m, 2051 s, 1942 br, vs, 1733 s, 1336 s, 1187 m, 1145 vw, 1029 s, 685 s, 650 vs, 572 vw, 539 w, 507 vw, 490 vw, 464 w, 445 m cm^{-1}; IR(pentane): $\tilde{\nu} = 2116$ w, 2029 m, 1977 vs, 1946 w, 1902 vw, 1731 m cm^{-1}; Raman (solid): $\tilde{\nu} = 2370$ vw, 2119 m, 2027 s, 1997 s, 1968 w, 1942 vw, 1734 w, 1188 m, 1145 vw 1029 vw, 683 m, 647 vw, 572 m, 537 w, 506 vw, 464 vw, 435 w, 390 vs, 345 vw, 326, vw, 270 w, 191 w, 166 m cm^{-1}; ^{13}C NMR: $\delta = 86.3$ (dd, $^2J_{CF} = 51$ Hz, $^2J_{C,F} = 39$ Hz; CCl), 156.8 (dd, $^1J_{C,F} = 300$ Hz, $^1J_{C,F} = 294$ Hz; CCF_2), 191.2 (s; NC), 213.2 (s; CO_{cis}), 214.6 (s; CO_{trans}); ^{19}F NMR: $\delta = -89.63$ (d, $^2J_{F,F} = 11$ Hz), −82.31 (d, $^2J_{F,F} = 11$ Hz).

Pentacarbonyl(trifluoroethenyl isocyanide)chromium (4b): The compound **4b** was prepared similarly to **4a** using **3b** (Yield: 0.78 g (2.6 mmol, 89%) as yellow crystals; m.p. 38 °C; elemental analysis for $C_8CrF_3NO_5$ (%): calcd: C 32.12, N 4.68; found: C 33.41, N 4.55; MS (EI, 80 eV): *m/z*: 299, 271, 243, 215, 187, 159 (100%), 52; IR (pentane): $\tilde{\nu} = 2114$ w, 2020 m, 1973 vs, 1944 m, 1774m cm^{-1}; ^{13}C NMR: $\delta = 117.1$ (dt, $^1J_{C,F} = 297$ Hz, $^2J_{C,F} = 49$ Hz; CF), 152.3 ($^1J_{C,F} = 286$ Hz, $^1J_{C,F} = 293$ Hz, $^2J_{C,F} = 49$ Hz; CF_2), 199.3 (s; NC), 213.0 (s; CO_{cis}), 214.2 (s; CO_{trans}); ^{19}F NMR: $\delta = -152.9$ (dd, $^{2}J_{\mathrm{C,F}} = 46.4$ Hz, $^{3}J_{\mathrm{C,F}} = 112$ Hz; CClF), -111.6 (dd, $^{2}J_{\mathrm{C,F}} = 46$ Hz, $^{3}J_{\mathrm{C,F}} = 53.7$ Hz; CF_2), -100.5 (dd, $^{3}J_{\mathrm{C,F}} = 112$ Hz, $^{3}J_{\mathrm{C,F}} = 53.7$ Hz; CF_2).

Pentacarbonyl(1,2-chloro-2-fluoroethenyl isocyanide)chromium (4c): The compound **2c** was prepared similarly to **4a** using **3c** (1.03 g, 2.6 mmol). Yield: 0.65 g (2.9 mmol, 75 %) as yellow crystals containing both isomers; m.p. 55 °C; elemental analysis for $C_8Cl_2CrFNO_5$ (%) calcd: C 28.94, N 4.22; found: C 29.62, N 4.27; MS (EI, 80 eV): *m/z*: 331, 303, 275, 245, 219, 191, 52; IR (pentane): $\tilde{\nu} = 2023$ m, 1972 s, 1940 w,sh cm^{-1}; ^{13}C NMR: $\delta = 101.25$ (d, $^{2}J_{\mathrm{C,F}} = 49$ Hz; CCl), 102.83 (d, $^{2}J_{\mathrm{C,F}} = 38$ Hz; CCl), 146.08 ($^{1}J_{\mathrm{C,F}} = 309$ Hz; CClF), 147.98 ($^{1}J_{\mathrm{C,F}} = 312$ Hz; CClF), 190.3, 191.12 (s; NC), 213.11, 213.12 (s;CO_{cis}), 214.46, 214.64 (s; CO_{trans}); ^{19}F NMR: $\delta = -77.8$ (s), -84.3 (s).

(*E*/*Z*)-Pentacarbonyl(1,2-difluoro-2-λ^5-fluorotrimethylphospharanylethenyl isocyanide)chromium (5): Compound **4b** (60 mg, 0.2 mmol) was dissolved in [D_8]toluene (1 mL) in a 5 mm NMR tube and cooled to -78 °C. Trimethylphosphane (0.2 mmol) was condensed onto the solution. After mixing at -78 °C the tube was brought into the NMR spectrometer and allowed to warm to -50 °C. ^{19}F and ^{31}P NMR spectra were recorded at -50 °C and exhibited signals of trimethylphosphane, **3b**, **5**, **6**, and difluorotrimethylphosphorane. ^{31}P NMR: $\delta = -77.1$ (d, $^{1}J_{\mathrm{P,F}} = 552$ Hz) **5;** -61.4 (s), PMe_3; -14.7 (t, $^{1}J_{\mathrm{P,F}} = 536$ Hz) PF_2Me_3; ^{19}F NMR: $\delta = -97.7$ (dd), -109.8 (dd), -150.7 (dd) **4b;** -166.6 (dd), -142.7 (d) (*E*)-**6**; -137.77 (dd, $^{2}J_{\mathrm{P,F}} = 12$ Hz, $^{1}J_{\mathrm{F,F}}$ 128 Hz), -134.26 (d, $^{1}J_{\mathrm{P,F}}$ 128 Hz), 23.26 (d, $^{1}J_{\mathrm{P,F}} = 552$ Hz) **5**; -4.0 (d, $^{1}J_{\mathrm{P,F}} = 536$ Hz) PF_2Me_3.

Pentacarbonyl(1,2-difluoroethenyl isocyanide)chromium (6): Trimethylphosphane (4 mmol) was added by vaccum transfer to a solution of **4b** (450 mg, 1.5 mmol) in pentane (5 mL) at-78 °C. After stirring for three hours the yellow suspension was allowed to warm to -40 °C and water (0.36 mL, 20 mmol) was added. After stirring for an additional two hours the solvent was removed in vacuum at -10 °C and the residue was extracted with pentane. The pentane extract was purified by PTLC (silica, pentane, first fraction, $R_F = 0.42$). Sublimation in vacuum (25 °C, 0.1 Pa) yielded **6** as a colorless crystalline solid of both isomers. Yield: 172 mg (0.6 mmol, 40 %) m.p. 35 °C; elemental analysis for $C_8HCrF_2NO_5$ (%): calcd: C 34.18, H 0.36, N 4.98; found: C 34.35, H 0.80, N 4.76; MS (EI, 80 eV): *m/z*: 281, 253, 225, 197, 169, 141, 52; IR (pentane): $\tilde{\nu} = 2116$ m, 2020 s, 1975 vs, 1944 scm^{-1}; IR (KBr): $\tilde{\nu} = 3128$ w, 2122 m, 2036 s, 1951 vs, 1864 m, 1701 w, 1325 m, 1221 m, 1159 m, 880 m, 796 w, 653 s, 441 m cm^{-1}; (*E*)-**6**: ^{1}H NMR: $\delta = 7.30$ (dd, $^{2}J_{\mathrm{H,F}} = 72$ Hz, $^{3}J_{\mathrm{H,F}} = 4$ Hz, 1 H; CHF); ^{13}C{^{1}H} NMR: $\delta = 133.9$ (dd, $^{1}J_{\mathrm{C,F}} = 244$ Hz, $^{2}J_{\mathrm{C,F}} = 39$ Hz; CF), 138.3 (dd, $^{1}J_{\mathrm{C,F}} = 259$ Hz, $^{2}J_{\mathrm{C,F}} = 69$ Hz; CHF), 197.7 (s; NC), 213.0 (s; CO_{cis}), 214.3 (s; CO_{trans}); ^{19}F NMR: $\delta = -170.6$ (dd, $^{2}J_{\mathrm{F,H}} = 72$ Hz, $^{3}J_{\mathrm{F,F}} = 130$ Hz; CHF), -143.4 (d, $^{3}J_{\mathrm{F,F}} = 130$ Hz; CF); (*Z*)-**6**: ^{1}H NMR: $\delta = 6.80$ (dd, $^{2}J_{\mathrm{H,F}} = 70$ Hz, $^{3}J_{\mathrm{H,F}} = 12$ Hz, 1 H, CHF); ^{19}F NMR: $\delta = -160.2$ (d, $^{2}J_{\mathrm{F,H}} = 70$ Hz; CHF), -116.6 (d, $^{2}J_{\mathrm{F,H}} = 13$ Hz; CF). [D]-**6**: D_2O was used in the hydrolysis step. (*E*)-[D]-**6**: ^{2}D NMR: $\delta = 7.13$ (d, $^{2}J_{\mathrm{D,F}} = 11$ Hz), ^{19}F NMR: $\delta = -143.6$ (d, CF, $^{3}J_{\mathrm{F,F}} = 130$ Hz), -171.1 (dt, CDF, $^{3}J_{\mathrm{F,F}} = 130$ Hz, $^{2}J_{\mathrm{D,F}} = 11$ Hz); (*Z*)-[D]-**6**: ^{2}D NMR: $\delta = 6.58$ (dd, $^{2}J_{\mathrm{D,F}} = 11$ Hz, $^{3}J_{\mathrm{D,F}} = 1.9$ Hz), ^{19}F NMR: $\delta = -116.9$ (s; CF), -160.6 (t, CDF, $^{2}J_{\mathrm{D,F}} = 11$ Hz).

(*E*/*Z*)-Pentacarbonyl(1-chloro-2-cyano-2-fluoroethenyl isocyanide)chromium (7a): Complex **4a** (966 mg, 3.1 mmol) was dissolved in acetonitrile (20 mL) and heated to 45 °C. Potassium cyanide (586 mg, 9.0 mmol) was added. The progress of the reaction was monitored by ^{19}F NMR spectroscopy. After about 45 min the mixture was placed on a silica column and eluted with pentane. This resulted in two fractions, the first of which contained **4a** the second the product ($R_F = 0.10$) **7a**. Sublimation in vacuum (35 °C, 0.1 Pa) yielded **7a** as an orange solid composed of both isomers. Yield: 706 mg (2.2 mmol, 71 %); m.p. 64 °C; elemental analysis for $C_9ClCrFN_2O_5$ (%): calcd: C 33.51, N 8.68; found: C 33.80, N 8.51; MS (EI, 80 eV): *m/z*: 322, 294, 266, 238, 210, 182 (100 %), 78, 52; IR (KBr): $\tilde{\nu} = 2235$ vw, 2222 vw, 2117 s, 2025 s sh, 1950 vs br, 1626 vs, 1272 s, 1190 s, 1163 m, 1076 vw, 1015 vw, 980 m, 931 w, 865 vw, 682 s, 649 vs, 577 w, 539 w 437 m, 386 w, 338 vw cm^{-1}; IR (pentane): $\tilde{\nu} = 1987$ vs, 1977 m sh, 1955 sh cm^{-1}; Raman (solid): $\tilde{\nu} = 2254$ vw, 2235 w, 2222 w, 2115 w, 2002 vs, 1984 m 1959 w, 1949 w, 1628 s, 1600 vw, 1271 m, 1191 m, 1160 w, 980 vw, 931 vw, 730 vw, 678 w, 664 w, 625 w, 539 w, 510 w, 432 m, 387 vs, 338 vw, 209 vw, 195 vw, 171 vw 110 vs cm^{-1}; (*E*)-**7a**: ^{13}C NMR: $\delta = 108.9$ (d, $^{2}J_{\mathrm{C,F}} = 40$ Hz; CN), 117.5 (d, $^{2}J_{\mathrm{C,F}} = 46$ Hz; CCl), 131.9 (d, $^{1}J_{\mathrm{C,F}} = 256$ Hz; CF), 202.4 (d, $^{4}J_{\mathrm{C,F}} = 5$ Hz NC), 212.0 (s; CO_{cis}), 212.6 (s; CO_{trans}); ^{19}F NMR: $\delta = -131.73$ (s; CF); (*Z*)-**7a**: ^{13}C NMR: $\delta = 109.4$ (d, $^{2}J_{\mathrm{C,F}} = 40$ Hz; CN), 115.2 (d, $^{2}J_{\mathrm{C,F}} = 33$ Hz; CCl), 131.3 (d, $^{1}J_{\mathrm{C,F}} = 259$ Hz; CF), 203.8 (d, $^{4}J_{\mathrm{C,F}} = 6$ Hz, NC), 212.0 (s; CO_{cis}), 212.8 (s; CO_{trans}); ^{19}F NMR : $\delta = -123.80$ (s; CF).

(*E*/*Z*)-Pentacarbonyl(1,2-difluoro-2-cyanoethenyl isocyanide)chromium (7b): The compound **7b** was prepared similarly to **7a** using **4b**. Yield: 16 mg (0.05 mmol, 20 %); m.p. 35 °C; elemental analysis for $C_9CrF_2N_2O_5$ (%): calcd: C 35.31, N 9.15; found: C 35.02, N 8.76; MS (EI, 80 eV): *m/z*: 306, 278, 250, 222, 194, 166 (100 %), 52; IR (hexane): $\tilde{\nu} = 2015$ w, 1986 vs, 1964 sh m cm^{-1}; IR (KBr): $\tilde{\nu} = 2227$ w, 2115 w, 1966 vs, 1684 w, 1311 m, 1264 m, 1240 m, 1110 w, 1079 m, 1022 w, 865, vw, 804 w, 728 m, 650 s, 613 vw, 599 vw, 522 w, 436 m, 382 vw, 305 vw cm^{-1}; Raman (solid): $\tilde{\nu} = 2229$ w, 2115 vw, 2024 w, 2004 m 1978 vw 1961 vw, 1691 w, 1677 sh, 1314 m 1262 w, 727 vw, 615 vw, 527 vw, 431 w, 387 vs, 395 vw, 323 vw, 305 vw, 297 vw, 244 w, 175 vw, 146 vw, 115 vs cm^{-1}. (*E*)-**7b**: ^{13}C NMR: $\delta = 108.1$ (dd, $^{2}J_{\mathrm{C,F}} = 37$ Hz, $^{3}J_{\mathrm{C,F}} = 10$ Hz; CN), 123.7 (dd, $^{1}J_{\mathrm{C,F}} = 240$ Hz, $^{2}J_{\mathrm{C,F}} = 62$ Hz; CF–CN), 137.5 (dd, $^{1}J_{\mathrm{C,F}} = 264$ Hz, $^{2}J_{\mathrm{C,F}} = 45$ Hz; CN-CF), 209.2 (s; NC), 211.5 (s; CO_{cis}), 211.6 (s; CO_{trans}); ^{19}F NMR : $\delta = -165.8$ (d, $^{3}J_{\mathrm{F,F}} = 128$ Hz; CF–CN), -114.8 (d, $^{3}J_{\mathrm{F,F}} = 128$ Hz; CN–CF); (*Z*)-**5b**: ^{13}C NMR: $\delta = 109.0$ (dd, $^{2}J_{\mathrm{C,F}} = 36$ Hz, $^{3}J_{\mathrm{C,F}} = 3$ Hz; CN), 121.3 (dd, $^{1}J_{\mathrm{C,F}} = 251$ Hz, $^{2}J_{\mathrm{C,F}} = 38$ Hz; CF–CN), 135.8 (dd, $^{1}J_{\mathrm{C,F}} = 282$ Hz, $^{2}J_{\mathrm{C,F}} = 37$ Hz; CN–*C*F), 212.9 (s; NC), 211.6 (s; CO_{cis}), 211.6 (s; CO_{trans}); ^{19}F NMR : $\delta = -156.7$ (d, $^{3}J_{\mathrm{F,F}} = 3$ Hz; C*F*-CN), -90.0 (d, $^{3}J_{\mathrm{F,F}} = 3$ Hz; CN–C*F*).

[$(CO)_5Cr(CNCClCF^{13}CN)$] (7c) and [$(CO)_5Cr(CNCClCFC^{15}N)$] (7d): The compounds **7c** and **7d** were prepared similarly to **7a** by using ^{13}C-KCN and ^{15}N-KCN. Additional spectroscopic data, only those vibrationational spectroscopic data are listed which show significant changes: **7c**: IR (KBr): $\tilde{\nu} = 2175$ w cm^{-1}; Raman (solid): $\tilde{\nu} = 2175$ w, 926 vw, 531 w cm^{-1}, (*E*)-**7c**: $^{1}J_{\mathrm{C,C}} = 113$ Hz, $^{2}J_{\mathrm{C,C}} = 11$ Hz; (*Z*)-**7c**: $^{1}J_{\mathrm{C,C}} = 116$ Hz, $^{2}J_{\mathrm{C,C}} = 13$ Hz. **7d:** IR (KBr): $\tilde{\nu} = 2214$ vw, 2200 vw cm^{-1}; Raman (solid): $\tilde{\nu} = 2214$ vw, 2198 w cm^{-1}; ^{15}N-NMR: δ {second isomer} $= -90.54\{-91.86\}$ (s; $C^{15}N$).

[$(CO)_5Cr(C^{15}NCClCFCN)$] (7e): The compound **7e** was prepared from $NEt_4[Cr(CO)_5(C^{15}N)]$. Additional spectroscopic data: (*E*)-**5e**: ^{15}N NMR : $\delta = -204.4$ (d, $^{3}J_{\mathrm{F,N}} = 3$ Hz); ^{13}C NMR: $^{1}J_{\mathrm{C,N}}$(N-C) $= 30$ Hz, $^{1}J_{\mathrm{C,N}}$(CN) $= 22$ Hz, $^{2}J_{\mathrm{C,N}} = 7$ Hz; ^{19}F NMR : $\delta = -131.79$ (d, $^{3}J_{\mathrm{F,N}} = 3$ Hz; CF); **(Z)-7e**: ^{15}N NMR: $\delta = -202.1$ (d, $^{3}J_{\mathrm{F,N}} = 3$ Hz); ^{13}C NMR: $^{1}J_{\mathrm{C,N}}$(N-C) $= 30$ Hz, $^{1}J_{\mathrm{C,N}}$(CN) $= 22$ Hz, $^{2}J_{\mathrm{C,N}} = 2$ Hz; ^{19}F NMR: $\delta = -123.89$ (d, $^{3}J_{\mathrm{F,N}} = 3$ Hz; CF).

(*E*/*Z*)-Pentacarbonyl(1-chloro-2-fluoro-4-trimethylsilyl-but-1-en-3-ynyl isocyanide)chromium [$(CO)_5Cr\{CNCClCFC_2Si(CH_3)_3\}$] (8a): Ethynyl(trimethyl)silane (2.1 mL, 15 mmol) was slowly added to a solution of methylmagnesium bromide (10 mmol, 4.2 mL of a 2.4 M solution in diethyl ether) in THF (20 mL) at 0 °C forming a colorless precipitate. The suspension was allowed to warm to ambient temperature and stirred for 2 h. Complex **4a** (1.028 g, 3.3 mmol) was added and the solution turned dark brown. After 20 min pentane (50 mL) was added and the reaction mixture was filtered through a silica pad ($l = 3$ cm, $d = 1$ cm) and eluted with pentane. The solvent was removed in vacuum at -20 °C. The residue was sublimed in vacuum (35 °C, 0.1 Pa). Yield: 862 mg (2.2 mmol, 64 %) of both isomers. Elemental analysis for $C_{13}H_9ClCrFNO_5Si$ (%): calcd: C 39.66, H 2.30, N 3.56; found: C 39.78, H 2.93, N 3.74; MS (EI, 80 eV): *m/z*: 393, 337, 309, 281, 253, 73, 52; IR (pentane): $\tilde{\nu} = 2117$ m, 2026 s, 1976 vs, 1945 m cm^{-1}; IR (KBr): $\tilde{\nu} = 2963$ w, 2923 w, 2852 vw, 2159 vw, 2116 m, 2042 s, 1961 vs, 1940 vs, 1616 w, 1251 m, 1154 w, 990 m, 850 s, 763 w, 727 m, 705 vw, 659 s, 648 s, 567 vw, 533 vw, 486 m cm^{-1}; Raman (solid): $\tilde{\nu} = 2967$ w, 2904 w, 2299 vw, 2242 vw, 2159 m, 2113 m, 2015 vs, 1997 s, 1972 w, 1938 vw, 1622 s, 1617 s, 1259 m, 1153 m, 854 vw, 765 vw, 725w, 705 vw, 665 w, 644 vw, 628 w, 616 w, 567 vw, 512 vw, 490 vw, 437 m, 387 vs, 275 w, 212 vw, 167 w cm^{-1}. (*E*)-**8a**: ^{1}H NMR: $\delta = 0.27$ (s, 9 H; CH_3); ^{13}C NMR: $\delta = -0.5$ (qh, $^{1}J_{\mathrm{C,H}} = 122$ Hz, $^{3}J_{\mathrm{C,H}} = 2$ Hz; CH_3), 90.2 (d, $^{2}J_{\mathrm{C,F}} = 35$ Hz; CF–*C*), 109.5 (d, $^{2}J_{\mathrm{C,F}} = 56$ Hz; CCl), 113.8 (m, $^{3}J_{\mathrm{C,F}} = 1$ Hz, $^{3}J_{\mathrm{C,H}} = 3$ Hz; C–Si), 142.2 (d, $^{1}J_{\mathrm{C,F}} = 250$ Hz; CF), 186.9 (s; CN), 213.3 (s; CO_{cis}), 214.8 (s; CO_{trans}); ^{19}F NMR: $\delta = -109.63$ (s); (*Z*)-**8a**: ^{1}H NMR: $\delta = 0.27$ (s, 9 H; CH_3); ^{13}C{^{1}H} NMR: $\delta = -0.9$ (s; CH_3), 90.7 (d, $^{2}J_{\mathrm{C,F}} = 34$ Hz; CF–*C*), 108.8 (d, $^{2}J_{\mathrm{C,F}} = 43$ Hz; CCl), 115.3 (dd, $^{3}J_{\mathrm{C,F}} = 4$ Hz; C–Si), 140.7 (d, $^{1}J_{\mathrm{C,F}} = 254$ Hz; CF), 192.4 (s; CN), 213.1 (s; CO_{cis}), 214.9 (s; CO_{trans}); ^{19}F NMR: $\delta = -104.99$ (s).

(*E*/*Z*)-Pentacarbonyl(1,2-difluoro-4-trimethylsilyl-but-1-en-3-ynyl isocyanide)chromium [$(CO)_5Cr\{CNCFCFC_2Si(CH_3)_3\}$] (8b): The compound **8b** was prepared similarly to **8a** by using the Grignard reagent of ethynyl(trimethyl)silane (10.0 mmol) and **4b** (1495 mg, 5.0 mmol). The product was purified by sublimation in vacuum (35 °C/ 0.1 Pa). Yield: 1610 mg (4.3 mmol, 85 %) of both isomers as a yellow solid. Elemental analysis for $C_{13}H_9CrF_2NO_5Si$ (%): calcd: C 41.38, H 2.40, N 3.71; found: C 41.60, H 2.63, N 3.71; MS (EI, 80 eV): *m/z*: 377, 321, 293, 265, 237, 203 (100%), 73, 52; IR (KBr): $\tilde{\nu}$ = 2969 w, 2159 w, 2115 s, 2037 vs, 1982 vs, 1960 vs, 1939 vs, 1414 w, 1289 w, 1250 m, 1234 s, 1094 m, 1071 w, 1019 vw, 860 s, 847 s, 774 m, 762 w, 668 s, 657 vs, 647 vs, 584 w, 497 vw, 437 m cm^{-1}; IR (pentane): $\tilde{\nu}$ = 2113 vw, 2014 w, 1981 vs, 1950 m cm^{-1}; Raman (solid): $\tilde{\nu}$ = 2971 vw, 2908 w, 2328 vw, 2158 m, 2113 s, 2017 vs, 2002 s, 1984 w, 1958 vw, 1945 w, 1968 m, 1416 vw, 1288 s, 1259 vw, 1093, vw, 850 vw, 774 vw, 639 w, 610 w, 598 vw, 584 vw, 433 w, 385 m, 271 vw, 223 vw, 178 vw 108 m cm^{-1}. (*E*)-**8b**: ^{1}H NMR: δ = 0.24 (s, 9H; CH$_3$); ^{13}C NMR: δ = 1.0 (q, $^{1}J_{C,H}$ = 120 Hz; CH$_3$), 88.5 (dd, $^{2}J_{C,F}$ = 32 Hz, $^{3}J_{C,F}$ = 10 Hz; CF−*C*C), 117.0 (s; C*C*−Si), 132.3 (dd, $^{1}J_{C,F}$ = 237 Hz, $^{2}J_{C,F}$ = 58 Hz; CF−C), 134.8 (dd, $^{1}J_{C,F}$ = 252 Hz, $^{2}J_{C,F}$ = 54 Hz, N−CF), 201.6 (d, $^{3}J_{C,F}$ = 9 Hz, NC), 212.8 (s; CO$_{cis}$), 214.2 (s; CO$_{trans}$); ^{19}F NMR: δ = −144.27 (d, $^{3}J_{F,F}$ = 127 Hz; CF−CC), −128.23 (d, $^{3}J_{F,F}$ = 127 Hz, N−CF); (*Z*)-**8b**: ^{1}H NMR: δ = 0.24 (s, 9H; CH$_3$); ^{13}C NMR: δ = −1.0 (q, $^{1}J_{C,H}$ = 120 Hz; CH$_3$), 89.2 (d, $^{2}J_{C,F}$ = 31 Hz; CF−*C*C), 113.3 (s; C*C*−Si), 130.6 (dd, $^{1}J_{C,F}$ = 246 Hz, $^{2}J_{C,F}$ = 33 Hz; CF−C), 133.1 (dd, $^{1}J_{C,F}$ = 266 Hz, $^{2}J_{C,F}$ = 45 Hz, N−CF), 195.0 (s; NC), 213.0 (s; CO$_{cis}$), 214.1 (s; CO$_{trans}$); ^{19}F NMR: δ = −134.80 (d, $^{3}J_{F,F}$ = 3 Hz; CF-CC), −110.12 (d, $^{3}J_{F,F}$ = 3 Hz, N-CF).

(*E/Z*)-Pentacarbonyl(1-chloro-2-fluoro-6-trimethylsilyl-hex-1-en-3,5-diynyl isocyanide)chromium [(CO)$_5$Cr{CNCClCFC$_4$Si(CH$_3$)$_3$}] (8c): Methyllithium (1.5 mL of a 1.6 M solution in diethyl ether) was added to a solution of 1,4-bis(trimethylsilyl)butadiyne (585 mg, 3 mmol) in diethyl ether (10 mL) and stirred for 1 h at ambient temperature. Complex **4a** (505 mg, 1.6 mmol) was added. After 5 min the reaction mixture was cooled with liquid nitrogen. The reaction mixture was allowed to warm to ambient temperature and the solvent was removed under vacuum. The dark brown residue was extracted with pentane to give a dark orange-brown solution. The solvent and volatile by-products were pumped off under vacuum at 30 °C. The residue was dissolved in pentane and filtered through a pad of silica yielding a orange solution. After the solvent had been removed under vacuum, **8c** (335 mg, 50%) was isolated as a dark yellow solid (m.p. 50 °C) containing a mixture of both isomers. MS (EI, 80 eV): *m/z*: 417, 374, 361, 333, 305, 277 (100%), 179, 156, 73, 52; IR (KBr): $\tilde{\nu}$ = 2962 m, 2900 vw, 2116 vw, 2099 vw, 2067 m 2023 w, 1967 s, 1735 w 1636 w 1413 w, 1335 vw, 1249 s, 1176 w, 1101 vw, 1036 vw, 846 s, 765 m, 704 w, 648 s, 554 m, 446 w, 380 m cm^{-1}; IR (*n*-hexane): $\tilde{\nu}$ = 2114 vw, 2102 vw, 2018 w, 1977 s, 1946 vw cm^{-1}; (*E*)-**8c**: ^{1}H NMR: δ = 0.22 (s, 9H; CH$_3$); ^{13}C{^{19}F} NMR: δ = −0.91 (q, $^{1}J_{C,H}$ = 121 Hz; CH$_3$), 61.99 (d, $^{2}J_{C,F}$ = 38 Hz; CF−*C*C), 85.20 (d, $^{4}J_{C,F}$ = 3 Hz; CC−Si), 89.58 (d, $^{3}J_{C,F}$ = 6 Hz; CF−C*C*), 101.74 (m, $^{3}J_{C,H}$ = 2.5 Hz, $^{5}J_{C,F}$ = 0.8 Hz; C*C*−Si), 111.61 (d, $^{2}J_{C,F}$ = 55 Hz, N−*C*Cl), 142.19 (d, $^{1}J_{C,F}$ = 250 Hz; CF), 189.44 (d, $^{4}J_{C,F}$ = 4 Hz; CN), 213.00 (s; CO$_{cis}$), 214.61 (s; CO$_{trans}$); ^{19}F NMR: δ = −112.27; (*Z*)-**8c**: ^{1}H NMR: δ = 0.24 (s, 9H; CH$_3$); ^{13}C NMR: δ = −0.84 (q, $^{1}J_{C,H}$ = 121 Hz; CH$_3$), 62.46 (d, $^{2}J_{C,F}$ = 35 Hz; CF−*C*C), 85.48 (d, $^{4}J_{C,F}$ = 4 Hz; CC−Si), 90.40 (d, $^{3}J_{C,F}$ = 5 Hz; CF−C*C*), 101.47 (m, $^{3}J_{C,H}$ = 2.8 Hz, $^{5}J_{C,F}$ = 1.3 Hz; C*C*−Si), 110.64 (d, $^{2}J_{C,F}$ = 42 Hz, N−*C*Cl), 140.60 (d, $^{1}J_{C,F}$ = 252 Hz; CF), 194.23.7 (d, $^{4}J_{C,F}$ = 7 Hz; CN), 212.94 (s; CO$_{cis}$), 214.63 (s; CO$_{trans}$); ^{19}F NMR: δ = −107.32 (s).

(*E/Z*)-Pentacarbonyl(1,2-difluoro-6-trimethylsilyl-hex-1-en-3,5-diynyl isocyanide)chromium [(CO)$_5$Cr{CNCFCFC$_4$Si(CH$_3$)$_3$}] (8d): Methyllithium (6.0 mmol, 1.5 M in diethyl ether) was added to a solution of bis(trimethyl silyl)butadiyne (1552 mg, 8.0 mmol) in diethyl ether (30 mL). After the solution had been stirred for 3 h at ambient temperature, **4b** (1495 mg, 5.0 mmol) was added. After 15 min water (0.2 mL) was added to stop the reaction. The remaining suspension was diluted with pentane (30 mL) and filtered through a pad (5 cm) of silica. The solvent was removed in vacuum at −20 °C and the residue purified by column chromatography (silica/pentane) and sublimation in vacuum (45 °C, 0.1 Pa). Yield: 2113 mg (5.8 mmol, 72%) of both isomers as a yellow solid. M.p. 43 °C; elemental analysis for $C_{15}H_9CrF_2NO_5Si$ (%): calcd: C 44.89, H 2.26, N 3.49; found: C 45.01, H 2.59, N 4.02; MS (EI, 80 eV): *m/z*: 401, 345, 289, 261(100%), 73, 52; IR (KBr): $\tilde{\nu}$ = 2963 vw, 2195 w, 2114 m, 2105 m, 2023 vs, 2004 vs, 1948 vs, 1704 vw, 1653 m, 1345 w, 1274 s, 1252 m, 1132 m, 1004 w, 985 w, 958 m, 848 s, 762 w, 706 m, 648 s, 540 w, 436 m cm^{-1}; IR (pentane): $\tilde{\nu}$ = 2199 vw, 2113 sh, 2106 vw, 2012 w, 1982 vs, 1951 sh m cm^{-1}; Raman (solid): $\tilde{\nu}$ = 2965 vw, 2903 vw, 2194 vs, 2112 w, 2016 m, 1997 s, 1945 w, 1653 s, 1342 w, 1332 w, 1267 m, 1132 w, 985 vw, 957 vw, 849 vw, 762 vw, 703 w, 631 m, 604 m, 574 vw, 540, vw, 507 vw, 485 w, 432 m, 385 s, 331 vw, 272 vw, 237 vw, 219 vw, 178 vw cm^{-1}. (*E*)-**8d**: ^{1}H NMR: δ = 0.24 (s, 9H; CH$_3$); ^{13}C{^{19}F} NMR: δ = −0.9 (q, $^{1}J_{C,H}$ = 121 Hz; CH$_3$), 60.2 (s; CF−*C*C), 85.5 (s; *C*C−Si), 92.8 (s; CF−C*C*), 101.7 (s; C*C*−Si), 132.3 (s; CF−C), 136.3 (s; N−CF), 203.9 (s; CN), 212.5 (s; CO$_{cis}$), 213.8 (s; CO$_{trans}$); ^{19}F NMR: δ = −146.94 (d, $^{3}J_{F,F}$ = 127 Hz; CF−CC), −125.30 (d, $^{3}J_{F,F}$ = 127 Hz, N−CF); (*Z*)-**8d**: ^{1}H NMR: δ = 0.22 (s, 9H; CH$_3$); ^{13}C NMR: δ = −0.9 (q, $^{1}J_{C,H}$ = 121 Hz; CH$_3$), 61.2 (d, $^{2}J_{C,F}$ = 34 Hz; CF−*C*C), 85.4 (s; *C*C−Si), 89.2 (s; CF−C*C*), 100.5 (s; C*C*−Si), 130.7 (dd, $^{1}J_{C,F}$ = 247 Hz, $^{2}J_{C,F}$ = 35 Hz CF−C), 134.3 (dd, $^{1}J_{C,F}$ = 270 Hz, $^{1}J_{C,F}$ = 45 Hz, N−CF), 198.7 (s; CN), 212.6 (s; CO$_{cis}$), 213.7 (s; CO$_{trans}$); ^{19}F NMR: δ = −137.22 (s; CF−CC), −104.18 (s; N−CF).

(*E/Z*)-Pentacarbonyl(1-chloro-2-fluoro-pent-1-en-3-ynyl isocyanide)chromium [(CO)$_5$Cr(CNCClCFC$_2$CH$_3$)] (8e): The complex **8e** was prepared similarly to **8a** using the Grignard reagent of propyne (4.5 mmol) and **4a** (500 mg, 1.6 mmol). After filtration through a pad of silica (2 cm) and elution with pentane the solvent was removed in vacuum and the residue was distilled under vacuum (0.1 Pa) at 30 to 40 °C using a microdistillation apparatus with a small cup at the bottom of the condensation finger. Compound **8e** was isolated as yellow orange oil containing a mixture of the *E* and *Z* isomer. Yield: 350 mg (66%). MS (EI, 70 eV) : *m/z*: 335, 279, 251, 223, 195 (100%), 160, 89, 71, 52; IR (KBr): $\tilde{\nu}$ = 2954 vw, 2913 vw, 2118 m, 2102 s, 2070 s, 2026 s, 2011s, 1950 vs, 1633 m, 1575 w, 1439 vw, 1426 w, 1366 vw, 1263 vw, 1188 vw, 1159 m, 1056 m, 1040 m,10113 m, 885 w, 713 w, 651 s, 626 m, 515 s, 494 m, 468 m 442 m cm^{-1}; IR (pentane): $\tilde{\nu}$ = 2234 vw, 2216 w, 2029 m, 1976 vs, 1944 w cm^{-1}; Raman (solid): $\tilde{\nu}$ = 2924 w, 2847 vw, 2331 vw, 2230 m, 2116 s, 2028 s, 2005 s, 2946 w sh, 1620 s, 1427 vw, 1375 w, 1297 w, 1169 s, 1062 vw, 1039 vw, 1022 vw, 880 w, 826 vw, 732 vw, 664 w, 632 vw, 611 w, 572 vw, 546 w, 521 w, 438 w, 386 vs, 343 vw, 326 vw, 302 vw, 254 vw, 183 vw cm^{-1}; ^{1}H NMR: δ = 2.157 (d, $^{5}J_{H,F}$ = 4.6 Hz), 2.164 (d, $^{5}J_{H,F}$ = 4.8 Hz); the assignment of the ^{13}C resonance is based on ^{19}F,^{13}C correlation spectra (HMQC and HMBC); (*E*)-**8e**: ^{13}C NMR: δ = 4.98 (q, $^{1}J_{C,H}$ = 133 Hz), 68.06 (dq, $^{3}J_{C,H}$ = 5 Hz, $^{2}J_{C,F}$ = 37 Hz; CF−*C*C), 105.24 (q, $^{2}J_{C,H}$ = 11 Hz; CF−C*C*), 108.22 (d, $^{2}J_{C,F}$ = 57 Hz; CCl), 143.42 (d, $^{1}J_{C,F}$ = 251 Hz; CF), 185 (s; CN), 213.58 (s; CO$_{cis}$), 215.12 (s; CO$_{trans}$); ^{19}F NMR: δ = −106.39 (qua, $^{5}J_{H,F}$ = 4.6 Hz); (*Z*)-**8e**: ^{13}C NMR: δ = 5.26 (q, $^{1}J_{C,H}$ = 133 Hz), 68.41 (dq, $^{3}J_{C,H}$ = 5 Hz, $^{2}J_{C,F}$ = 35 Hz; CF−*C*C), 104.17 (q, $^{2}J_{C,H}$ = 11 Hz; CF−C*C*), 107.72 (d, $^{2}J_{C,F}$ = 46 Hz; CCl), 141.41 (d, $^{1}J_{C,F}$ = 253 Hz; CF), 190.8 (s; CN), 213.39 (s; CO$_{cis}$), 215.25 (s; CO$_{trans}$); ^{19}F NMR : δ = −101.94 (q, $^{5}J_{H,F}$ = 4.8 Hz).

(*E/Z*)-Pentacarbonyl(1,2-difluoro-4-phenyl-but-1-en-3-ynyl isocyanide)-chromium [(CO)$_5$Cr(CNCFCFC$_2$C$_6$H$_5$)] (8f): Methylmagnesium bromide (2 mmol, 3 M solution in diethyl ether) was slowly added to a solution of ethynylbenzene in THF (10 mL) at 0 °C leading to a colorless suspension which was allowed to warm to ambient temperature and stirred for 90 min. Addition of complex **2b** (300 mg, 1.0 mmol) resulted in a brown reaction mixture. After the mixture had been stirred for 30 min, pentane (100 mL) was added to the dark brown suspension. After filtration through a pad of silica the product was purified by crystallization from pentane at −30 °C. The less soluble *E* isomer crystallized first as orange crystals (m.p. 105 °C). Almost pure *Z* isomer was obtained as yellow crystals (m.p. 62 °C) by sublimation of the compound that remained in solution in vacuum (35 °C, 0.1 Pa). Elemental analysis for $C_{16}H_5CrF_2NO_5$ (%): calcd: C 50.41, H 1.32, N 3.67; found: C 50.27, H 1.67, N 3.79; MS (EI, 80 eV): *m/z*: 381, 353, 325, 297, 269, 241 (100%), 189, 151, 52; IR (KBr): $\tilde{\nu}$ = 2211 w, 2113 w, 2000 sh, 1941 vs br, 1489 w, 1444 vw, 1341 vw, 1267 m, 1184 m, 1168 m, 1074 m, 1024 vw, 820 w, 756 m, 685 s, 647 vs, 586 w, 522 w, 496 vw, 435 m cm^{-1}; Raman (solid): $\tilde{\nu}$ = 3067 vw, 2208 s, 2157 vw, 2111 m, 2041 s, 1993 vs, 1946 w, 1670 vs, 1596 m, 1489 w, 1341 w, 1270s, 1167 m, 1074 w, 1025 vw, 998 w, 821 vw, 755 vw, 688vw, 647 w, 598 m, 522 w, 432 m, 388 vs, 365 w, 334 vw, 250 vw, 177 w, 116 vs cm^{-1}; ^{1}H NMR: δ = 7.52–7.32 (m, 5H; Ph); (*E*)-**8f**: IR (pentane): $\tilde{\nu}$ = 2212 w, 2114 vw, 2014 m, 1981 vs, 1950 m cm^{-1}; ^{13}C{^{1}H} NMR: δ = 74.5 (dd, $^{2}J_{C,F}$ = 33 Hz, $^{3}J_{C,F}$ = 11 Hz; CF−*C*C), 108.1 (dd, $^{3}J_{C,F}$ = 12 Hz, $^{4}J_{C,F}$ = 6 Hz; CF−C*C*), 120.3 (s; Ph−C1), 128.6 (s; Ph−C2), 130.4 (s; Ph−C4), 131.7 (s; Ph−C3), 132.8 (dd, $^{1}J_{C,F}$ = 236 Hz, $^{2}J_{C,F}$ = 58 Hz; CF−CC), 134.0 (dd, $^{1}J_{C,F}$ = 251 Hz, $^{2}J_{C,F}$ = 55 Hz, N−CF), 201.3 (s; NC), 212.8 (s; CO$_{cis}$), 214.2 (s; CO$_{trans}$); ^{13}C {^{19}F} NMR: ($^{3}J_{C,H}$ = 5 Hz; CF−C*C*), ($^{2}J_{C,H}$ = 8 Hz, Ph−C1), ($^{1}J_{C,H}$ = 163 Hz, $^{2}J_{C,H}$ = 7 Hz, Ph−C2), ($^{1}J_{C,H}$ = 163 Hz, $^{2}J_{C,H}$ = 7 Hz, Ph−C4), ($^{1}J_{C,H}$ = 164 Hz, $^{2}J_{C,H}$ = 7 Hz, Ph−C3); ^{19}F NMR: δ = −143.42 (d, $^{3}J_{F,F}$ = 126 Hz; CF-CC), -128.35 (d, $^{3}J_{F,F}$ = 126 Hz, N−CF); (*Z*)-**8f**: IR (pentane): $\tilde{\nu}$ = 2212 w, 2115 w, 2018 m, 1981 vs, 1950 w cm^{-1}; ^{13}C{^{1}H} NMR: δ = 75.0 (d, $^{2}J_{C,F}$ = 33 Hz; CF−*C*C), 104.5 (dd, $^{3}J_{C,F}$ = 7 Hz, $^{4}J_{C,F}$ = 6 Hz; CF−C*C*), 119.9 (s; Ph−C1), 128.7 (s; Ph−C2), 130.5 (s; Ph−C4), 131.0 (dd, $^{1}J_{C,F}$ = 245 Hz, $^{2}J_{C,F}$ = 58 Hz; CF−CC), 131.9 (s; Ph−C3), 132.5 (dd, $^{1}\mathrm{J}_{\mathrm{CF}}$ = 266 Hz, $^{2}J_{C,F}$ = 46 Hz, N−CF), 195.7 (s; NC), 212.9 (s; CO$_{cis}$), 214.1 (s; CO$_{trans}$); ^{13}C{^{19}F} NMR: ($^{3}J_{C,H}$ = 5 Hz; CF−C*C*), ($^{2}J_{C,H}$ = 8 Hz, Ph−C1), ($^{1}J_{C,H}$ = 161 Hz,

$^{2}J_{C,H}=7$ Hz, Ph–C2), ($^{1}J_{C,H}=162$ Hz, $^{2}J_{C,H}=8$ Hz, Ph–C4); ^{19}F NMR : $\delta = -133.62$ (s; CF–CC), -110.73 (s; N–CF).

(*E*/*Z*)-Pentacarbonyl(1-chloro-2-fluoro-prop-1-enyl isocyanide)chromium $[(CO)_5Cr(CNCClCFCH_3)]$ (8g): Methylmagnesium bromide (1.5 mL, 3.0 mmol, 2 M in THF) was added to a solution of **4a** (630 mg, 2.0 mmol) in diethyl ether (30 mL) and heated to reflux. After 15 min pentane (100 mL) was added and the solution was filtered through a pad of silica. The solvent was removed in vacuum at −20 °C and the residue was purified by PTLC. The first fraction contained **4a**, the second the product **8g**, which was eluted with dichloromethane and sublimed in vacuum (25 °C, 0.1 Pa) yielding both isomers as a light yellow solid (443 mg, 1.4 mmol; 71 %). M.p. 43 °C; elemental analysis for $C_9H_3CrClFNO_5$ (%): calcd: C 34.69, H 0.97, N 4.50; found: C 34.92, H 1.80, N 4.94; MS (EI, 80 eV): *m/z*: 311, 255, 227, 199, 171 (100 %), 78, 71, 52; IR (KBr): $\tilde{\nu}=2129$ s, 2058 vs, 1945 vs, 1666 m, 1428 w, 1384 m, 1267 m, 1260 m, 1166 s, 1143 m, 1036 s, 952 m, 943 m, 918 m, 678 s, 653 vs, 633 m, 535 vw, 517 vw, 489 vw, 446 s cm^{-1}; IR (pentane): $\tilde{\nu}=2118$ m, 2037 s, 2007 m, 1975 vs, 1942 m cm^{-1}; Raman (solid): $\tilde{\nu}=2974$ vw, 2934 w, 2325 vw, 2123 m, 2035 s, 1993 m, 1988 m, 1972 m, 1927 w, 1667 w, 1434 vw, 1384 w, 1259 w, 1166 m. 1141 w, 1036 vw, 916 vw, 671 m, 651 vw, 633 m, 562 vw, 547 w, 535 vw, 517 vw, 501 vw, 444 m, 390 vs, 326 vw, 262 w, 179 w cm^{-1}. (*E*)-**8g**: ^{1}H NMR: $\delta=2.24$ (d, $^{3}J_{H,F}=16$ Hz, 3H; CH$_3$); ^{13}C NMR: $\delta=15.8$ (dq, $^{1}J_{C,F}=131$ Hz, $^{2}J_{C,F}=24$ Hz; CH$_3$), 102.7 (not resolved, CCl), 159.3 (dq, $^{1}J_{C,F}=267$ Hz, $^{2}J_{C,H}=8$ Hz; CF), 184.9 (s; CN), 213.5 (s; CO$_{cis}$), 215.2 (s; CO$_{trans}$);^{19}F NMR: $\delta=-97.91$ (q, $^{3}J_{F,H}=16$ Hz; CF); (*Z*)-**8g**: ^{1}H NMR: $\delta=2.17$ (d, $^{3}J_{H,F}=16$ Hz, 3H; CH$_3$); ^{13}C NMR: $\delta=15.1$ (dq, $^{1}J_{C,F}=131$ Hz, $^{2}J_{C,F}=24$ Hz; CH$_3$), 102.2 (not resolved, CCl), 158.1 (dq, $^{1}J_{C,F}=271$ Hz, $^{2}J_{C,H}=8$ Hz; CF), 184.8 (s; CN), 213.6 (s; CO$_{cis}$), 215.6 (s; CO$_{trans}$); ^{19}F NMR: $\delta=-93.35$ (q, $^{3}J_{F,H}=16$ Hz; CF).

(*E*/*Z*)-Pentacarbonyl(1,2-difluoro-prop-1-enyl isocyanide)chromium $[(CO)_5Cr(CNCFCFCH_3)]$ (8h): Compound **8h** was prepared similarly to **8g** by using **4b** (600 mg, 2.0 mmol).Yield: 524 mg (1.8 mmol, 89 %) of both isomers as a colorless solid. M.p. 46 °C; elemental analysis for $C_9H_3CrF_2NO_5$ (%): calcd: C 36.63, H 1.03, N 4.75; found: C 36.82, H 1.56, N 5.12; MS (EI, 80 eV): *m/z*: 295, 267, 239, 211, 183, 155 (100 %), 78, 71, 52; IR (KBr): $\tilde{\nu}=2927$ vw, 2126 s, 2055 vs, 1939 vs, 1729 s, 1431 w, 1388 m, 1278 w, 1239 s, 1228 m, 1119 m, 1035 vw, 966 w, 734 m, 649 vs, 562 w, 525 vw, 489 w, 443 m, 386 vw cm^{-1}; IR (pentane): $\tilde{\nu}=2116$ w, 2055 w, 2031 m, 2009 w, 1976 vs, 1945 w cm^{-1}; Raman (solid). $\tilde{\nu}=2931$ vw, 2121 m, 2035 s, 1998 s, 1966 w, 1935 vw, 1730 w, 1443 vw, 1388 w, 1279 w, 1238 w, 1121 vw, 1032 vw, 732 w, 669 w, 647 vw, 562 w, 533 vw, 440 w, 390 vs, 346 vw, 265 vw, 209 w cm^{-1}. ^{1}H NMR: δ {2nd isomer} = 2.16 {2.12} (s; 3H, CH$_3$); (*E*)-**8h**: ^{13}C {^{19}F} NMR: $\delta=13.0$ (q, $^{1}J_{C,H}=130$ Hz; CH$_3$), 130.0 (s; CN–*C*F), 147.8 (q, $^{2}J_{C,H}=8$ Hz; CF–CH$_3$), 193.3 (s; CN), 213.3 (s; CO$_{cis}$), 215.0 (s; CO$_{trans}$); ^{13}C {^{1}H} NMR: $\delta=13.0$ (dd, $^{2}J_{C,F}=23$ Hz, $^{3}J_{C,F}=3$ Hz; CH$_3$), 147.8 (dd, $^{1}J_{C,F}=255$ Hz, $^{2}J_{C,F}=56$ Hz; CF–CH$_3$); ^{19}F NMR: $\delta=-143.09$ (q, $^{3}J_{F,F}=126$ Hz, N–CF), -134.44 (dq, $^{3}J_{F,F}=126$ Hz, $^{3}J_{F,H}=16$ Hz, CF-CH$_3$); (*Z*)-**8h**: ^{13}C{^{19}F} NMR: $\delta=13.0$ (q, $^{1}J_{C,H}=130$ Hz; CH$_3$), 128.8 (s; CN–*C*F),144.7 (q, $^{2}J_{C,H}=8$ Hz; CF–CH$_3$),191.7 (s; CN), 213.3 (s; CO$_{cis}$), 214.7 (s; CO$_{trans}$); ^{13}C {^{1}H} NMR: $\delta=13.0$ (d, $^{2}J_{C,F}=23$ Hz; CH$_3$), 144.7 (dd, $^{1}J_{C,F}=260$, $^{2}J_{C,F}=21$, CF–CH$_3$); ^{19}F NMR: $\delta=-126.05$ (q, $^{3}J_{F,H}=16$ Hz; CF-CH$_3$), -124.88 (s; N – CF).

$[(CO)_5Cr(CNCFCFOCH_3)]$ (8i): Complex **8i** was the only isolated product in experiments to deprotonate propiolic acid methyl ester with LDA and reaction with **4b**. Propiolic acid methyl ester (0.9 mL, 10.0 mmol) was dissolved in diethyl ether (30 mL) at 0 °C and lithium diisopropylamide (4 mL, 8.0 mmol, 2 M in THF) was added. After five minutes **4b** (1495 mg, 5.0 mmol) was added. The reaction mixture was filtered through a pad of silica after 10 min. The solvent was removed in vacuum at −20 °C and the residue purified by column chromatography (silica, pentane) and crystallized from pentane at −30 °C. Yield: 701 mg (2.3 mmol, 45 %) of both isomers as a white solid. M.p. 57 °C; elemental analysis for $C_9H_3CrF_2NO_6$ (%): calcd: C 34.75, H 0.97, N 4.50; found: C 34.81, H 1.57, N 5.04; MS (EI, 80 eV) : *m/z*: 311, 283, 255, 227, 199, 171 (100 %), 78, 52; IR (KBr): $\tilde{\nu}=2960$ w, 2864 vw, 2123 s, 2046 vs, 1944 vs, 1745 m, 1453 m, 1384 vw, 1290 m, 1266 s, 1178 w, 1124 s, 950 m, 757 m, 653 vs, 576 w, 544 w, 494 vw, 441 m cm^{-1}; IR (pentane): $\tilde{\nu}=2116$ w, 2036 m, 1999 vw, 1975 vs, 1944 w, 1746 w cm^{-1}; Raman (solid): $\tilde{\nu}=2960$ vw, 2119 s, 2035 s, 1999 m, 1970 w, 1938 vw, 1744 w, 1260 m. 1126 vw, 949 vw, 755 w, 668 w, 650 vw, 634 vw, 574 vw, 544 vw, 495 vw, 440 w, 391 vs, 265 vw, 210 vw cm^{-1}. (*E*)-**8i**: ^{1}H NMR: $\delta=3.93$ (s, 3H; OCH$_3$); ^{13}C NMR: $\delta=59.8$ (q, $^{1}J_{C,H}=149$ Hz, OCH$_3$), 119.0 (dd, $^{1}J_{C,F}=236$ Hz, $^{2}J_{C,F}=67$ Hz, N–CF), 151.5 (dd, $^{1}J_{C,F}=277$ Hz, $^{2}J_{C,F}=48$ Hz; CF–O), 193.2 (NC), 213.4 (s; CO$_{cis}$), 215.3 (s; CO$_{trans}$); ^{19}F NMR: $\delta=-155.82$ (d, $^{3}J_{F,F}=114$ Hz), -114.44 (d, $^{3}J_{F,F}=114$ Hz); (*Z*)-**8i**: ^{1}H NMR: $\delta=3.92$ (s, 3H; OCH$_3$); ^{13}C NMR: $\delta=59.7$ (q, $^{1}J_{C,H}=149$ Hz; OCH$_3$), 118.5 (dd, $^{1}J_{CF}=241$ Hz, $^{2}J_{CF}=58$ Hz; N–CF), 150.8 (dd, $^{1}J_{C,F}=286$ Hz, $^{2}J_{C,F}=42$ Hz; CF–O), 193.0 (NC), 213.4 (s; CO$_{cis}$), 215.1 (s; CO$_{trans}$); ^{19}F NMR: $\delta=-150.20$ (d, $^{3}J_{F,F}=18$ Hz), -103.93 (d, $^{3}J_{F,F}=18$ Hz).

Pentacarbonyl(1,2,2-trifluoro-2-methoxyethen-1-yl isocyanide)chromium $[(CO)_5Cr(CNCHFCF_2OCH_3)]$ (9): Potassium carbonate (28 mg, 0.2 mmol) was added to a suspension of **4b** (415 mg, 1.5 mmol) in methanol (4 mL). Within a few minutes the yellow suspension turned into dark brown. After 15 min the mixture was placed on a pad of silica and the product fraction was eluted with dichloromethane. The solvent was removed in vacuum at 20 °C leaving **9** as a yellow oil. Yield: 387 mg (1.2mmol, 84 %); m.p. 14 °C; $C_9H_4CrF_2NO_6$ (%): calcd C 32.65, H 1.22, N 4.23; found: C 32.64, H 1.52, N 4.73; MS (EI, 80 eV): *m/z* = 331, 303, 275, 247, 219, 191 (100 %), 78, 52; IR (KBr): $\tilde{\nu}=2970$ w, 2871 vw, 2145 s, 2045 vs, 1946 b, 1457 m, 1375 w, 1335 s, 1303 m, 1259 s, 1235 s, 1161 s, 1124 m, 1091 vs, 1051 s, 1021 m, 974 m, 826 m, 737 m, 723 m, 653 vs, 590 m, 567 w, 531 w, 496 w, 443s cm^{-1}; Raman (solid): $\tilde{\nu}=2971$ vw, 2872 vw, 2145 w sh, 2127 w, 2040 m, 2005 s, 1943 w sh, 1458 vw, 1376 vw, 1335 w, 1259 vw, 1090 vw, 973 vw, 826 vw, 804 vw, 736 vw, 722 vw, 665, vw, 590 vw, 568 vw, 534 vw, 497 vw, 441 w, 386 vs, 321 vw, 259 vw cm^{-1}; ^{1}H NMR: $\delta=3.72$ (s; 3H, CH$_3$), 5.53 (d, $^{2}J_{H,F}=50$ Hz, 1H; CHF); ^{13}C{^{1}H} NMR: $\delta=51.5$ (t, $^{3}J_{C,F}=7$ Hz; CH$_3$), 86.8 (dt, $^{1}J_{C,F}=221$ Hz, $^{2}J_{C,F}=42$ Hz; CFH), 118.2 (dt, $^{1}J_{C,F}=270$ Hz, $^{2}J_{C,F}=27$ Hz; CF$_2$), 188.5 (s; CN), 213.4 (s; CO$_{cis}$), 214.5 (s; CO$_{trans}$); ^{13}C{^{19}F} NMR: $\delta=51.5$ (q, $^{1}J_{C,F}=149$ Hz; CH$_3$), 86.8 (d, $^{1}J_{C,H}=179$ Hz; CFH), 118.2 (s; CF$_2$), 188.5 (s; CN), 213.4 (s; CO$_{cis}$), 214.5 (s; CO$_{trans}$); ^{19}F NMR: $\delta=-159.70$ (dt, $^{2}J_{F,H}=50$ Hz, $^{3}J_{F,F}=12$ Hz; CHF), -92.19 (ddd, $^{2}J_{F,F}=138$ Hz, $^{3}J_{F,F}=12$ Hz, $^{3}J_{F,H}=3$ Hz; CF$_2$), -90.81 (dd, $^{2}J_{F,F}=138$ Hz, $^{3}J_{F,F}=12$ Hz; CF$_2$).

$[(CO)_5Cr(CNCFCFC_2CFCFNC)Cr(CO)_5]$ (10): *n*-Butyllithium (1.5 mL, 3.0 mmol, 2 M in pentane) was slowly added to tributyl(ethynyl)stannane (945 mg, 3.0 mmol) dissolved in diethyl ether (40 mL) at −50 °C. After 1 h the solution was allowed to warm to −20 °C and **4b** (900 mg, 3.0 mmol) was added. The solution was allowed to warm to ambient temperature over 30 min, pentane (20 mL) was added, and the reaction mixture filtered through pad of silica. Crystallization from pentane yielded the *Z*,*Z* isomer as an orange solid, while **4b** and small amounts of the other isomers were still dissolved. Yield: 100 mg (0.2 mmol, 11 %); elemental analysis for $C_{18}Cr_2F_4N_2O_{10}$ (%): calcd: C 37.01, N 4.80; found: C 37.76, N 5.32; MS (EI, 80 eV) : *m/z*: 584, 472, 444, 416, 388, 360, 332, 304 (100 %), 71, 52; (*Z*,*Z*)-**10**: m.p. 121 °C; IR (KBr): $\tilde{\nu}=2115$ m, 2040 vs, 2005 vs, 1943 vs, 1666 m, 1373 w, 1275 s, 1219 s, 1108 m, 862 vw, 797 m, 695 m, 645 vs, 586 w, 565 w, 499 vw, 472 vw, 440 m, 424 m, 386 vw, 349 vw cm^{-1}; IR (pentane): $\tilde{\nu}=2114$ vw, 2017 w sh, 2008 w, 1987 vs, 1970 s cm^{-1}; Raman (solid): $\tilde{\nu}=2207$ w, 2114 w, 2040 vw, 1998 vs, 1975 vw, 1948 m, 1668 m, 1658 m, 1290 m, 1201 m, 1109 vw, 1046 vw, 795 vw, 701 vw, 651 vw, 586 w, 564 vw, 527 vw, 499 vw, 470 vw, 429 w, 387 vs, 360 vw, 288 vw, 237 w, 163 w cm^{-1}; ^{13}C NMR: $\delta=89.6$ (d, $^{2}J_{C,F}=36$ Hz; CF–*CC*), 129.6 (dd, $^{1}J_{C,F}=245$ Hz, $^{2}J_{C,F}=35$ Hz; CF–CC), 134.5 (dd, $^{1}J_{C,F}=272$ Hz, $^{2}J_{C,F}=43$ Hz, N–CF), 201.7 (s; CN), 213.0 (s; CO$_{cis}$), 213.6 (s; CO$_{trans}$); ^{19}F NMR: $\delta=-140.95$ (s; CF–CC), -100.56 (s; N–CF); (*E*,*E*)-**10**: ^{19}F NMR: $\delta=-140.04$ (d, $^{3}J_{F,F}=124$ Hz; CF–CC), -120.50 (d, $^{3}J_{F,F}=124$ Hz, N–CF); (*E*,*Z*)-**10**: ^{19}F NMR: $\delta=-151.31$ (d, $^{3}J_{C,F}=126$ Hz,(*E*)-CF=C*F*–C), -141.97 (s; (*Z*)-CF=C*F*–C), -140.04 (d, $^{3}J_{C,F}=126$ Hz, (*E*)-C*F*=CF–C), -101.95 (s; (*Z*)-C*F*=CF–C).

(*E*/*Z*)-Pentacarbonyl(1-chloro-2-fluoro-but-1-en-3-ynyl isocyanide)chromium $[(CO)_5Cr(CNCClCFC_2H)]$ (11a): Potassium carbonate (40 mg, 0.3 mmol) was added to a suspension of **8a** (709 mg, 1.8 mmol) in methanol (4 mL) at ambient temperature. The desilylation was completed within a few minutes and the black solution was purified by PTLC (silica 1mm, pentane). The first fraction was eluted with dichloromethane. The solvent was evaporated in vacuum at −20 °C and the residue sublimed in vacuum to yield 426 mg (1.3 mmol, 74 %) of both isomers as a yellow, air- and light-sensitive solid. Elemental analysis for $C_{10}HCrClFNO_5$ (%): calcd: C 37.35, H 0.31, N 4.36; found: C 37.20, H 1.58, N 4.60; MS (EI, 80 eV): *m/z*: 321, 293, 265, 237, 209, 181 (100 %), 78, 52; IR (KBr): $\tilde{\nu}=3295$ m, 2119 m, 2035 vs, 1945 br, 1609 w, 1264 w, 1176 m, 1034 vw, 977 w, 936 w, 678 s, 651 vs, 557 vw, 526 m, 497 vw, 442 m cm^{-1}; IR (pentane): $\tilde{\nu}=2117$ w, 2021 m, 1978 vs, 1947 w cm^{-1}; Raman (solid): $\tilde{\nu}=2335$ vw, 2105 m, 2029 m 2015 s, 2004 s, 1941 w, 1671 vw, 1624 m, 1271 w, 1170 m, 976 vw, 933 vw, 684 sh, 673 w, 606 vw, 558 m, 528 vw, 437 w, 388 m, 335 vs, 288 vw, 272 vw, 208 vw, 140 m cm^{-1}; (*E*)-**11a**: ^{1}H NMR: $\delta=4.00$ (d, $^{4}J_{H,F}=3$ Hz, 1H; CC–H); ^{13}C NMR: $\delta=70.9$

(dd, $^{2}J_{C,H}=51$ Hz, $^{2}J_{C,F}=27$ Hz; *C*CH), 93.2 (dd, $^{1}J_{C,H}=261$ Hz, $^{3}J_{C,F}=5$ Hz; CH), 110.8 (d, $^{2}J_{C,F}=52$ Hz; CCl), 142.2 (dd, $^{1}J_{C,F}=251$ Hz, $^{3}J_{C,H}=5$ Hz; CF), 189.0 (s; CN), 213.2 (s; CO_{cis}), 214.5 (s; CO_{trans}); ^{19}F NMR: $\delta=-110.54$ (d, $^{4}J_{F,H}=3$ Hz; CF); (*Z*)-**11a**: ^{1}H NMR: $\delta=3.97$ (d, $^{4}J_{H,F}=4$ Hz, 1H, CC−H); ^{13}C NMR: $\delta=71.3$ (dd, $^{2}J_{C,H}=51$ Hz, $^{2}J_{C,F}=25$ Hz , *C*CH), 94.2 (dd, $^{1}J_{C,H}=261$ Hz, $^{3}J_{C,F}=5$ Hz; CH), 109.9 (d, $^{2}J_{C,F}=40$ Hz; CCl), 140.4 (dd, $^{1}J_{C,F}=254$ Hz, $^{3}J_{C,H}=6$ Hz , CF), 193.7 (s; CN), 213.0 (s; CO_{cis}), 214.6 (s; CO_{trans}); ^{19}F NMR: $\delta=-105.50$ (d, $^{4}J_{F,H}=4$ Hz; CF).

(*E*/*Z*)-Pentacarbonyl(1,2-difluoro-but-1-en-3-ynyl isocyanide)chromium [$(CO)_5Cr(CNCFCFC_2H)$] (11b): Compound **11b** was prepared similarly to **11a** by using **8b** (755 mg, 2.0 mmol). Yield: 531 mg (1.7 mmol, 87%) of both isomers as a air- and light-sensitive brown solid. Elemental analysis for $C_{10}HCrF_2NO_5$ (%): calcd: C 39.35, H 0.33, N 4.59; found: C 39.62, H 0.78, N 4.59; MS (EI, 80 eV) : *m/z*: 305, 277, 249, 221, 193, 165 (100%), 90, 71, 52; IR (pentane): $\tilde{\nu}=$ 3309 m, 2119 w, 2110 w, 2014 m, 1981 vs, 1951 s cm^{-1}; Raman (solid): $\tilde{\nu}=$ 2105 s, 2038 m, 2028 m, 1998 s, 1989 s, 1948 w, 1667 m, 1292 m, 1249 vw, 1227 w, 1083 vw, 730 vw, 650 vw, 604 w, 527 vw, 433 w, 388 s, 285 vw, 232 vw, 190 w, 154 w, 116 vs cm^{-1}; (*E*)-**11b**: ^{1}H NMR: $\delta=4.11$ (dd, $^{4}J_{H,F}=3$ Hz, $^{5}J_{H,F}=3$ Hz, 1H, CC-H); ^{13}C NMR: $\delta=69.2$ (ddd, $^{2}J_{C,H}=51$ Hz, $^{2}J_{C,F}=35$ Hz, $^{3}J_{C,F}=10$ Hz; CCH), 96.2 (ddd, $^{1}J_{C,H}=260$ Hz, $^{2}J_{C,F}=12$ Hz, $^{3}J_{C,F}=6$ Hz; CH), 132.2 (ddd, $^{1}J_{C,F}=237$ Hz, $^{2}J_{C,F}=58$ Hz, $^{3}J_{C,H}=5$ Hz; CF−C), 135.9 (dd, $^{1}J_{C,F}=254$ Hz, $^{2}J_{C,F}=53$ Hz, N−CF), 202.7 (d, $^{3}J_{C,F}=9$ Hz, NC), 212.7 (s; CO_{cis}), 213,9 (s; CO_{trans}); ^{19}F NMR: $\delta=-147.53$ (dd, $^{3}J_{F,F}=127$ Hz, $^{4}J_{F,H}=3$ Hz; CF−CC), −127.41 (d, $^{3}J_{F,F}=127$ Hz, N−CF); (*Z*)-**11b**: ^{1}H NMR: $\delta=3.92$ (dd, $^{4}J_{H,F}=3$ Hz, $^{5}J_{H,F}=1$ Hz, 1H, CC-H); ^{13}C NMR: $\delta=70.1$ (dd, $^{2}J_{C,H}=51$ Hz, $^{2}J_{C,F}=34$ Hz; CCH), 92.8 (ddd, $^{1}J_{C,H}=261$ Hz, $^{3}J_{C,F}=6$ Hz, $^{4}J_{C,F}=6$ Hz; CH), 130.5 (ddd, $^{1}J_{C,F}=246$ Hz, $^{2}J_{C,F}=34$ Hz, $^{3}J_{C,H}=5$ Hz; CF−C), 133.7 (dd, $^{1}J_{C,F}=265$ Hz, $^{2}J_{C,F}=43$ Hz, N−CF), 197.8 (s; NC), 212.9 (s; CO_{cis}), 213.8 (s; CO_{trans}), ^{19}F NMR: $\delta=-137.82$ (d, $^{4}J_{F,H}=3$ Hz; CF−CC), −108.32 (s; N−CF).

(*E*/*Z*)-Pentacarbonyl(1,2-difluoro-hex-1-en-3,5-diynyl isocyanide)chromium [$(CO)_5Cr(CNCFCFC_4H)$] (11d): Compound **11d** was prepared similarly to **11a** by using **8d** (160 mg, 0.4 mmol) but was obtained in small yields. (*E*)-**11d**: ^{1}H NMR: $\delta=3.01$ (d, $J_{H,F}=2$ Hz, 1H; C−H); ^{1}H ^{13}C NMR(HMQC): $\delta=80$ ($^{1}J_{C,H}=245$ Hz; C*C*−H); ^{19}F NMR: $\delta=-148.50$ (dd, $^{3}J_{F,F}=126$ Hz; CF−CC), −124.43 (d, $^{3}J_{F,F}=126$ Hz, N−CF); (*Z*)-**11d**: ^{1}H NMR: $\delta=2.91$ (dd, $J_{H,F}=1$ Hz, $J_{H,F}=2$ Hz, 1H, C−H); ^{1}H ^{13}C NMR(HMQC, HMBC): $\delta=66$ ($^{2}J_{C,H}=44$ Hz; CC−H), 79 ($^{1}J_{C,H}=245$ Hz; C*C*−H), 89 (*C*CC−H); ^{19}F ^{13}C NMR(HMQC): $\delta=60.5$ (CF−*C*C), 130.3 (*C*F−CC), 134.4 (N−*C*F); ^{19}F NMR: $\delta=-138.64$ (s; CF−CC), −103.00 (s; N−CF).

Octacarbonyl{μ_2-pentacarbonyl[(*E*/*Z*)-1-chloro-2-fluoropent-1-en-3-ynyl isocyanide]chromium}dicobalt [$Co_2(CO)_6\{\mu_2$-$(CO)_5Cr(CNCClCFC_2CH_3)\}$] (12): Octacarbonyldicobalt (150 mg, 0.44 mmol) and **8e** (150 mg, 0.45 mmol) were dissolved in *n*-hexane (5 mL) and stirred at ambient temperature for 12 h. The solution was filtered through thin pad of silica using hexane as eluent. Most of the solvent was removed under vacuum. Crystallization at −30 °C yielded **12** (180 mg, 66%) as dark red crystals (m.p. 102 °C) as a mixture of the *E* and *Z* isomer. Elemental analysis for $C_{17}H_3ClCo_2CrFNO_{11}$ (%): calcd: C 32.85, H 0.49, N 2.25; found: C 32.79, H 1.34, N 2.71, MS (EI, 80 eV) : *m/z*: 621, 593, 565, 537, 509, 481, 453, 425, 397, 369, 341, 313, 279, 220, 195, 108, 80, 52; IR (KBr): $\tilde{\nu}=2920$ vw, 22852 vw, 2117 w, 2101 s, 2027 s, 1951 vs, 1633 w, 1575 vw, 1439 vw, 1426 vw, 1264 vw 1159 w, 1057 w, 1040 vw, 1014 vw, 851 vw, 714 vw, 653, s, 627 w, 516 m, 495 m, 468 w, 445 m cm^{-1}; IR (hexane): $\tilde{\nu}=2102$ w, 2066 w, 2045 m, 2035 m, 2020 vw, 1974 s cm^{-1}; ^{1}H-NMR: δ (major/minor isomer) = 2.772/2.854; the assignment of the ^{13}C resonance is based on ^{19}F,^{13}C correlation spectra (HMQC and HMBC) and signal intensities; ^{13}C NMR: δ (major/minor isomer) = 22.35 (q, $^{1}J_{C,H}=131$ Hz)/21.79 (q, $^{1}J_{C,H}=131$ Hz), 69.10 (d, $^{2}J_{C,F}=45$ Hz; CF−*C*C)/68.84 (d, $^{2}J_{C,F}=48$ Hz; CF−*C*C), 94.89 (m, $^{2}J_{C,H}=9$ Hz, $^{3}J_{C,F}=9$ Hz; CF−C*C*)/ 93.74 (m, $^{2}J_{C,H}=9$ Hz, $^{3}J_{C,F}=9$ Hz; CF−C*C*), 102.05 (d, $^{2}J_{C,F}=48$ Hz; CCl)/101.38 (d, $^{2}J_{C,F}=61$ Hz; CCl), 156.61 (d, $^{1}J_{C,F}=254$ Hz; CF)/155.76 (d, $^{1}J_{C,F}=249$ Hz; CF), 187.44/194.53 (s; CN), 197.89 (br, Co(*C*O)), 213.41/213.06 (s; CO_{cis}), 215.27/214.66 (s; CO_{trans}); ^{19}F NMR: δ (major/minor isomer) = −90.42/ −96.82 (s).

Trifluoroethenyl isocyanide (13b): The pyrolysis tube ($l=500$ mm, $od=16$ mm) of an apparatus as shown in Figure 5 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 was cooled to −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(trifluoroethenyl isocyanide)chromium (**4b**; 1.9 g, 6.4 mmol) and placed into the pyrolysis tube by opening the Teflon fitting at the rear end. The apparatus was then evacuated immediately. Unreacted **4b** was trapped at −78 °C. An optimum pyrolysis temperature (250 °C) and pressure (0.1 to 1 Pa) was obtained by adjusting the position of the sample using a magnet. After a few hours all of **4b** had sublimed. The product **13b** was collected in a trap cooled to −196 °C. The amount of **13b** (2 to 4 mmol) obtained in the −196 °C trap was sufficient for vapor pressure determination measurements, which gave an extrapolated boiling point of 18(6) °C. The data fit the linear equation $\ln p=-24736(442)/RT+17.1301(2562)$ giving an enthalpy of vaporization of 24.7(5) kJ mol^{-1}. An IR spectrum was recorded in a 100 mm infrared gas cell. To record the NMR spectra the compound was condensed into an ordinary glass NMR tube containing deuterochloroform (0.7 mL) and sealed under vacuum. NMR spectra were recorded at ambient temperature. ^{19}F NMR ($CDCl_3$): $\delta=-101.5$ (dd, $^{2}J_{F,F}=53$ Hz, $^{3}J_{F,F}=50$ Hz), −112.5 (dd, $^{2}J_{F,F}=53$ Hz, $^{3}J_{F,F}=113$ Hz), −157.6 (dd, $^{3}J_{F,F}=50$ Hz, $^{3}J_{F,F}=113$ Hz, $^{1}J_{N,F}=10$ Hz); IR (gaseous): $\tilde{\nu}=$ 2111 s (CN), 1801 s (C=C), 1363 s, 1279 vs, 1212 m, 1147 vs, 936 w cm^{-1}; MS (80 eV, EI): *m/z*: 107 $[M]^+$, 88 $[C_3F_2N]^+$, 76 $[C_2F_2N]^+$ and smaller fragment ions; high-resolution MS: $[M]^+$ calcd: 106.99829, found: 106.99827.

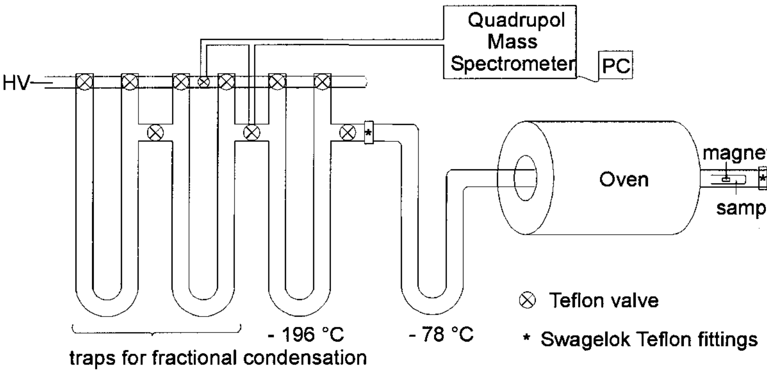


Figure 5. Schematic representation of the pyrolysis apparatus.

(*E*/*Z*)-1,2-Dichloro-2-fluoroethenyl isocyanide [CN−CCl=CFCl] (13c): Experimental conditions were as described above, using precursor **4c** and a pyrolysis temperature of 250 °C. The pyrolysis products were trapped at −196 °C. IR (gaseous): $\tilde{\nu}=2104$ vs (CN), 1654 s (C=C), 1280 w, 1215 s, 1207 s, 1153 m, 1147 m, 1120 s, 1111 s, 962 w, 931 m, 876 s, 786 w, 780 w, 729 w cm^{-1}; MS (80 eV, EI): *m/z*: 139 $[M]^+$, 104 $[C_3ClFN]^+$ and smaller fragment ions; high-resolution MS: $[M]^+$ calcd: 138.93913, found: 138.93919.

1-Chloro-2,2-difluroethenyl isocyanide (13a): Experimental conditions were as described above, using precursor **4a** and a pyrolysis temperature of 250 °C. The pyrolysis products were trapped at −196 °C. IR (gaseous): $\tilde{\nu}=2111$ vs (CN), 1744 vs (C=C), 1354 s, 1346 s, 1173 s, 1056 vs, 1051 vs cm^{-1}; ^{19}F NMR (CD_2Cl_2, −50 °C): $\delta=-79.9$ (d, $^{2}J_{F,F}=7$ Hz), −86.6 (d, $^{2}J_{F,F}=7$ Hz); ^{13}C NMR (CD_2Cl_2, −50 °C): $\delta=157.1$ (dd, $^{1}J_{C,F}=292$ Hz, $^{1}J_{C,F}=301$ Hz), 175.5 (s; CN).

(*E*/*Z*)-1,2-Difluoroethenyl isocyanide [CN−CF=CFH] (14): Experimental conditions were as described above, using precursor **6** (250 mg, 0.9 mmol) and a pyrolysis temperature of 230 °C. The pyrolysis products were purified by fractional condensation and trapped at −196 °C. MS (EI, 80 eV): *m/z*: 89 (100%), 70, 51; IR (gas): $\tilde{\nu}=3128$ w, 2106 vs, 1720 w, 1558 w, 1332 m, 1322 m, 1243 vs, 1230 vs, 1186 vs, 1179 vs, 1171 vs, 903 vw, 831 w, 795 m cm^{-1}, additional absorption due to HCCNC **15** were observed at 3339, 2219, 2037,

0947-6539/01/0704-0892 $ 17.50+.50/0

1229, 621 cm^{-1}; (*E*)-**4**: ^{1}H NMR: $\delta = 7.26$ (dd, $^2J_{H,F} = 72$ Hz, $^3J_{H,F} = 3$ Hz, 1 H; CHF); ^{19}F NMR : $\delta = -167.0$ (dd, $^2J_{F,H} = 71$ Hz, $^3J_{F,F} = 129$ Hz; CHF), -143.4 (dd, $^3J_{F,F} = 129$ Hz, $^3J_{F,H} = 3$ Hz, $^2J_{F,N} = 10$ Hz; CF); (*Z*)-**4**: ^{1}H NMR: $\delta = 6.83$ (dd, $^2J_{H,F} = 69$ Hz, $^3J_{H,F} = 12$ Hz, 1 H; CHF); ^{19}F NMR : $\delta = -155.2$ (ddt, $^2J_{F,H} = 69$ Hz, $^2J_{F,N} = 5$ Hz, $^3J_{F,F} = 2$ Hz; CHF), -121.7 (dt, vbr, $^2J_{F,N} = 10$ Hz, $^3J_{F,H} = 12$ Hz; CF).

Isocyanopropynenitrile (16) and (*E*)/(*Z*)-3-Chloro-2-fluoro-3-isocyanopropenenitrile (17): Experimental conditions were as described above, using precursor **7a** and a pyrolysis temperature of 240 °C. The pyrolysis products were collected in a trap kept at −196 °C and purified by fractional condensation under vacuum (0.001 Pa) through traps cooled to −78 °C, −100 °C, and −196 °C. Compounds **16** and **17** were collected in the trap kept at −196 °C and −100 °C, respectively.(*E*)-**17**: ^{13}C{^{19}F} NMR (CD_2Cl_2) : $\delta = 108.9$ (d, $^2J_{C,F} = 39$ Hz; CN), 134.7 (d, $^1J_{C,F} = 261$ Hz; CF), 181.1 (s; NC); ^{19}F NMR: $\delta = -121.13$ (s; CF); (*Z*)-**17**: ^{13}C{^{19}F} NMR: $\delta = 109.1$ (d, $^2J_{C,F} = 39$ Hz; CN), 133.2 (d, $^1J_{C,F} = 271$ Hz; CF); ^{19}F NMR : $\delta = -114.47$ (s; CF). **16:** IR (gas): $\tilde{\nu} = 2296$ w, 2210 s and 2053 cm^{-1}; MS: *m/z*: 76 $[M]^+$, 50 $[C_3N]^+$ and smaller fragment ions.

Crystallography: Crystal data and details of the structure determinations are presented in Table 4. The intensity data were collected using a Bruker AXS Smart (**11a, 11b**, **8i**) and a STOE (**12**) diffractometer, respectively. Corrections for Lorentz polarization and absorption effects were applied to the data. The structures were solved by Patterson and direct methods (SHELXS-97),[39] respectively. Hydrogen atoms were found in subsequent difference maps **11a**, **b** and refined isotropically and refined in calculated positions **8i** and **12** with isotropic thermal parameters. Anisotropic thermal parameters were applied to all non-hydrogen atoms. Refinement for all structures on F^2 were achieved by using the SHELXL-97 system.[39]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC-145286 (**11a**), CCDC-115287 (**11b**), CCDC-145288 (**8i**) and CCDC-145289 (**12**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44)1223-336-033; e-mail:deposit@ccdc.cam.ac.uk).

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[1] D. S. Matteson, R. A. Bailey, *J. Am. Chem. Soc.* **1968**, *90*, 3761.
[2] A. Gautier, *Justus Liebigs Ann. Chem.* **1867**, *142*, 289; A. Gautier, *Justus Liebigs Ann. Chem.* **1868**, *146*, 124.
[3] A. W. Hofmann, *Justus Liebigs Ann. Chem.* **1867**, *144*, 114; A. W. Hofmann, *Justus Liebigs Ann. Chem.* **1868**, *146*, 107.
[4] D. Lentz, D. Preugschat, *J. Chem. Soc. Chem. Commun.* **1992**, 1523.
[5] J. Buschmann, S. Kleinhenz, D. Lentz, P. Luger, K. V. Madappat, D. Preugschat, J. S. Thrasher, *Inorg. Chem.* **2000**, *39*, 2807.
[6] W. P. Fehlhammer, G. Beck, *J. Organomet. Chem.* **1989**, *379*, 97.
[7] M. Krüger, H. Dreizler, D. Preugschat, D. Lentz, *Angew. Chem.* **1991**, *103*, 1674; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1644.
[8] K. Kawaguchi, M. Ohishi, S.-I. Ishikawa, N. Kaifu, *Astrophys. J.* **1992**, *386*, L51.
[9] L. Zanathy, H. Bock, D. Lentz, D. Preugschat, P. Botschwina, *J. Chem. Soc. Chem. Commun.* **1992**, 403.
[10] A. Guarnieri, R. Hinze, M. Krüger, H. Zerbe-Foese, D. Lentz, D. Preugschat, *J. Mol. Spectrosc.* **1992**, *156*, 39; A. Huckauf, A. Guarnieri, D. Lentz, A. Fayt, *J. Mol. Spectrosc.* **1998**, *188*, 109.
[11] H. Bürger, S. Sommer, D. Lentz, D. Preugschat, *J. Mol. Spectrosc.* **1992**, *156*, 360.
[12] H. Bürger, D. Lentz, B. Meisner, N. Nickelt, D. Preugschat, M. Senzlober, *Chem. Eur. J.* **2000**, *6*, 3377.
[13] A. M. Smith, G. Schallmoser, A. Thoma, V. E. Bondybey, *J. Chem. Phys.* **1993**, *98*, 1776.
[14] C. Bartel, P. Botschwina, H. Bürger, A. Guarnieri, Ä. Heyl, A. Huckauf, D. Lentz, T. Merzliak, El B. Mkadmi, *Angew. Chem.* **1998**, *110*, 3036; *Angew. Chem. Int. Ed.* **1998**, *37*, 2879.
[15] J. Gripp, A. Guarnieri, W. Stahl, D. Lentz, *J. Mol. Struct.* **2000**, *526*, 81.
[16] P. Thaddeus, M. C. McCarthy, M. J. Travers, C. A. Gottlieb, W. Chen, *Faraday Discuss.* **1998**, *109*, 121.
[17] P. Botschwina, Ä. Heyl, W. Chen, M. C. McCarthy, J.-U. Grabow, M. J. Travers, P. Thaddeus, *J. Chem. Phys.* **1998**, *109*, 3108.
[18] R. Kunz, W. P. Fehlhammer, *Angew. Chem.* **1994**, *106*, 331; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 330.
[19] D. Bergemann, Diplomarbeit, Freie Universität Berlin.
[20] P. J. Stang in *Modern Acetylene Chemistry* (Eds. P. J. Stang, F. Diederich), VCH, Weinheim, **1995**, p. 67.
[21] D. Lentz, F. Nowak, D. Preugschat, M. Wasgindt, *Angew. Chem.* **1993**, *105*, 1547; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1456.
[22] R. D. Chambers in *Synthetic Fluorine Chemistry*, Eds. G. A. Olah, R. D. Chambers, G. K. S. Prakash, Wiley-Interscience, New York, **1992**; R. D. Chambers, J. F. S. Vaughan, *Topics in Current Chem.* **1997**, *192*, 1.
[23] K. H. Dötz in *Reactions of Coordinated Ligands* (Ed. P. S. Bratermann), Plenum Press, New York, **1986**; B. Crociani in *Reactions of Coordinated Ligands* (Ed. P. S. Bratermann), Plenum Press, New York, **1986**.
[24] W. P. Fehlhammer, F. Degel, G. Beck, *Chem. Ber.* **1987**, *120*, 461.
[25] D. Lentz, *Angew. Chem.* **1994**, *106*, 1377; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1315.
[26] D. Lentz, R. Marschall, *Chem. Ber.* **1990**, *123*, 751.
[27] D. J. Burton, S. Shinya, R. D. Howells, *J. Am. Chem. Soc.* **1979**, *101*, 3689.
[28] H. Wessolowsky, G.-V. Röschenthaler, R. Winter, G. Gard, *Z. Naturforsch. B* **1991**, *46*, 123.
[29] A. M. English, K. R. Plowman, I. M. Baibich, J. P. Hickey, I. S. Butler, G. Jaouen, P. Lemoux, *J. Organomet. Chem.* **1981**, *205*, 177.
[30] G. Christian, H. Stolzenberg, W. P. Fehlhammer, *J. Chem. Soc. Chem. Commun.* **1992**, 184.
[31] D. Lentz, *Chem. Ber.* **1984**, *117*, 415.
[32] E. Singleton, H. E. Oosthuizen, *Adv. Organomet. Chem.* **1983**, *22*, 209.
[33] R. S. Dickson, P. J. Fraser, *Adv. Organomet. Chem.* **1974**, *12*, 323; M. J. Went, *Adv. Organomet. Chem.* **1997**, *41*, 69.
[34] J. Mason in *Multinuclear NMR*, (Ed. J. Mason), Plenum, New York, London **1987**, p. 335–362.
[35] K. Yamada, G. Winnewisser, *Z. Naturforsch. A* **1981**, *36*, 1052; S. Haas, G. Winnewisser, K. Yamada, *Can. J. Chem.* **1994**, *72*, 1165.
[36] A. Guarnieri, A. Huckauf, personal communication.
[37] *Handbuch der präparativen Anorganischen Chemie* (Ed. G. Brauer), Bd. 3, F. Enke, Stuttgart **1981**.
[38] M. Höfler, H. Löwenich, *J. Organometal. Chem.* **226** (1982) 229.
[39] SHELX97 [Includes SHELXS97, SHELXL97, CIFTAB] Programs for Crystal Structure Analysis (Release 97–2), G. M. Sheldrick, Universität Göttingen, Germany, **1998**.
[40] ORTEP3 for Windows, L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.

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