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Fluorinated isocyanonitriles

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Abstract

Pentacarbonyl(fluoroisocyanoacetonitrile)chromium **4** is obtained from the reaction of pentacarbonyl(trifluoroethenyl isocyanide)chromium **3** with ammonia. Pentacarbonyl(2,3,3,3-tetrafluoro-2-isocyanopropionitrile)chromium **5** is prepared by radical alkylation of tetraethylammonium[pentacarbonyl(cyano)chromate **1**. The structure of **4** has been elucidated by X-ray crystallography. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Our studies have shown that the introduction of fluorine into isocyanides has strong effects on their reactivity and ligand behavior [1]. Thus, trifluoromethyl isocyanide proved to be a strong π acceptor ligand, even stronger than the carbonyl or thiocarbonyl ligands [1]. Due to their high reactivity, instability and the lack of a general synthetic methods fluorinated isocyanides are difficult to prepare and to handle. Only a few isocyanides with nitrile substituents in α-position to the isocyano group have been prepared so far [2]. The parent compound isocyanoacetonitrile was fully characterized only recently [3]. During our work on the chemistry of isocyanoacetonitrile [3] and diisocyanomethane [4], we became interested in the chemistry and ligand behavior of their fluorinated derivatives.

2. Results and discussion

As there exists no obvious fluoroorganic starting material for the synthesis of these type of compounds using conventional isocyanide synthesis methods like the Ugi, Hofmann or Gautier synthesis [5], we had to develop different synthetic strategies. Fluorinated nitriles can be synthesized in high yield by reaction of a suitable fluoroalkene with ammonia [6], e.g. 2,3,3,3-tetrafluoropropionitrile from hexafluoropropene. Pentacarbonyl(trifluoroethenyl isocyanide)chromium [7] **3** reacts similarly to fluorinated alkenes. For example, **3** dimerizes to form metal-stabilized 1,2,3,3,4,4-hexafluoro-1,2-diisocyanocyclobutane [8] and is easily attacked by nucleophiles at the β-carbon atom yielding complexes of the type $(CO)_5Cr(CN–CF{=}CF–Nu)$ (Nu = CN, CCH, CCPh), which can be used to prepare otherwise inaccessible isocyanides like cyanoisocyanoacetylene by vacuum pyrolysis [9] (Scheme 1).

The fluoroisocyanoacetonitrile chromium complex **4** is obtained in the reaction of **3** with ammonia. The pentacarbonyl chromium fragment fulfills several tasks. First of all, it enables the synthesis of **3** in two steps by radical alkylation of tetraethylammonium pentacarbonyl(cyano)chromate **1** to form the halogenated ethyl isocyanide complex **2**, and subsequent dehalogenation with zinc in diethyl ether–acetic acid. Secondly, the $[(CO)_5Cr]$ fragment serves as a protecting group preventing the otherwise facile polymerization of the halogenated isocyanides. Unfortunately this high-yield synthesis by reaction of **3** with ammonia is limited to compound **4**. Hence we were looking for a more general method. Fehlhammer and co-workers have developed the radical alkylation of tetraethylammonium pentacarbonyl(cyano)chromate **1** in the presence of diazonium salts for the synthesis of α-halogeno isocyanides

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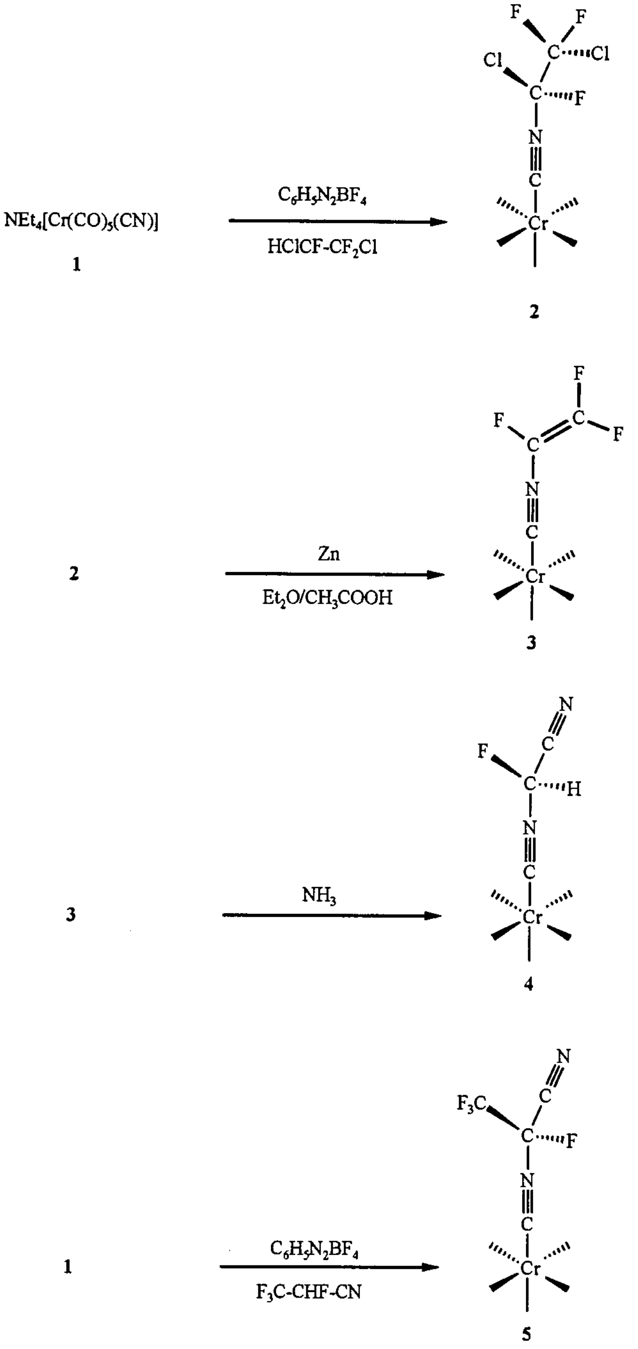

Scheme 1.

and *O*-heterocyclic isocyanides [10]. Attempts to use this procedure for the synthesis of metal complex stabilized isocyanonitriles failed using acetonitrile or chloroacetonitrile as solvent and alkylation agent [10]. Both with difluoroacetonitrile and dichloroacetonitrile we could only confirm the results of Fehlhammer and co-workers and could not isolate an isocyanide complex in substantial amounts. However, the radical alkylation of **1** using 2,3,3,3-tetrafluoropropionitrile as a solvent yields the tetrafluoroisocyanopropionitrile complex **5** in 10% yield besides other unidentified products.

Complexes **4** and **5** have been fully characterized by spectroscopic methods. The ^{1}H- and ^{19}F-NMR spectra of **4** exhibit doublets at 6.19 and -137.2 ppm ($^2J_{HF} = 48$ Hz) for the CHF group, respectively. The ^{19}F-NMR spectrum of **5** consists out of a doublet and a quartet at -81.2 and -117.8 ppm ($^3J_{FF} = 10$ Hz).

The ^{13}C-NMR data of **4** and **5** are summarized in Table 1 exhibiting signals with the expected signal multiplicity for the methylene and cyano carbon atoms due to coupling with the fluorine substituents. Signals between 196 and 218 ppm can be assigned to the carbonyl and isocyanide carbon atoms, respectively. In general, the ^{13}C-NMR spectra of pentacarbonylchromium complexes with various ligands all show more or less the same pattern of two signals in an approximate intensity of 4:1 with the signal for the *trans* carbonyl ligand at higher frequency (low field). The only exceptions to this rule so far have been $(CO)_5Cr(CS)$ [11], $(CO)_5Cr(CSe)$ [11] and $(CO)_5Cr(CNCF_3)$ [12], which all contain very powerful π acceptor ligands. In agreement with earlier observations, the assignment of the resonances for compound **4** as given in Table 1 is straightforward. Remarkable, however, is the small difference in chemical shift values (0.4 ppm) for the *cis* and *trans* carbonyl carbon atoms. As a difference in the ^{13}C chemical shift values of the *cis* and *trans* carbonyl carbon atoms of **5** of more than 7 ppm seems to be very unlikely, the resonance at 217.5 ppm has to be assigned to the isocyanide carbon atom, leaving the remaining signals at 211.1 and 210.5 ppm for the *cis* and *trans* carbonyl carbon atoms. The low-frequency signal at 210.5 ppm is assigned to the *trans* CO ligand due to its intensity. The replacement of a hydrogen substituent by the strong electron-withdrawing CF_3 group seems to

Table 1
^{13}C-NMR data of **4** and **5** [a]

Compound [a]	CN	CFX	NC	CO_{cis}	CO_{trans}
4	110.0 $^2J_{CF} = 38$ Hz	75.2 $^1J_{CF} = 215$ Hz	196.3	212.6	213.0
5	108.2 $^2J_{CF} = 41$ Hz	82.8 $^1J_{CF} = 227$ Hz $^2J_{CF} = 42$ Hz	217.8	211.1	210.5

[a] Solution in $CDCl_3$.

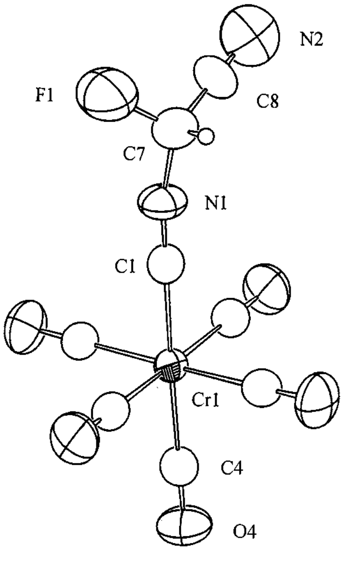

Fig. 1. ORTEP diagram of complex **4**.

result in an enhancement of the π acceptor ability of the isocyanide and a low-frequency shift of the *trans* carbonyl ligand.

The structure of **4** has been elucidated by X-ray crystallography. The molecular structure of **4** is depicted in Fig. 1. **4** is coordinated almost octahedrally by 5 carbonyl and the isocyanide ligand. The metal carbonyl carbon distances vary from 188.7(5) to 191.0(4) pm with the Cr–C_{trans} distance of 190.1(5) pm almost at the center of this distribution. The chromium carbon distance to the isocyanide ligand of 192.7(4) pm lies at the lower end of the values found in X-ray crystal-structure determinations of pentacarbonyl(isocyanide)chromium complexes (Table 2), demonstrating a significant contribution of backbonding in the metal carbon bond to the isocyanide ligand. Consequently the chromium carbon distance to the *trans* carbonyl ligand is not lengthened as observed for weak π acceptor ligands in the *trans* position. As in most isocyanide complexes, the isocyanide moiety is weakly bent (C1–N1–C2 168.0(5)°), whereas the nitrile moiety is almost linear (C2–C3–N2 176.3(8)°).

Attempts to synthesize the free isocyanide molecules by vacuum pyrolysis were unsuccessful, however. HCN and $Cr(CO)_6$ were the only pyrolysis products of **4** that could be identified by mass and IR spectroscopy. Pyrolysis of **5** yields a colorless substance in a trap kept at −196°C. Fractional condensation under vacuum (10^{-5} mbar) through traps kept at −110 and −196°C yields two fractions. IR, mass and ^{19}F-NMR spectra proved that the more volatile component contains trifluoroacrylonitrile by comparison with the data of a sample prepared by independent methods [19]. The material collected at −110°C consists out of a mixture of compounds. The mass spectrum exhibits a peak at

Table 2
Important bond lengths (pm) and angles (°) of **4** in comparison with pentacarbonyl(isocyanide)chromium complexes

$(CO)_5Cr(CNR)$	Cr–CN	Cr–CO_{trans}	Cr–CO_{cis}	C–N–C
–$(CH_2NC)_2$ [17]	000.0(0)	000.0(0)	– 000.0(0)	000.0(0)
–CN [13]	188.3(3)	191.3(4)	190.3 ∅	168.5(4)
–C≡C–C_6H_5 [14]	192.6(4)	189.6(4)	189.1 ∅	175.1(4)
–CHF–CN **4**	192.7(4)	190.1(5)	188.7(5) –191.0(4)	168.0(5)
–CO–C_6H_5 [15]	192.8(3)	189.9(3)	189.0(4) –190.8(4)	173.9(3)
–CF=CF_2 [7]	194.2(2)	190.9(2)	190.2(2) –191.4(2)	173.6(2)
–CHF_2 [16]	195.6(2)	190.0(2)	190.9(2) –191.5(2)	169.7(2)
–CH_2–NC [4]	197.4(4)	188.6(4)	188.7(4) –190.9(4)	166.8(4)
–CH_2–CN [3]	198.2(2)	187.6(2)	189.9(2) –191.1(2)	168.9(2)
–CH_2–$C(CH_3)$	198.8(2)	188.2(2)	190.1(2) –190.9(2)	178.2(2)
–$(CH_2NC)_2$ [17]				
–NH_2 [18]	200.0(3)	186.1(3)	187.9(3) –189.8(4)	170.3(3)

$m/z = 114$. The IR spectrum in the gaseous phase shows absorptions at 2123 and 1727 cm^{-1} indicating the presence of an isocyanide moiety and a C–C double bond. The ^{19}F-NMR spectrum exhibits two doublets at −68.0 and −54.9 ppm ($J_{FF} = 46$ Hz) with a relative intensity of 1: 1 which most likely result from a CF_2 group besides further smaller signals. Summarizing the available information on the major compound **6**, it is most likely to be 3,3-difluoro-2-isocyanoacrylnitrile. Unfortunately a further characterization of **6** was prevented by the small amounts of **6** that can be synthesized.

2.1. Conclusions

Fluoroisocyanoacetonitrile and tetrafluoroisocyanopropionitrile could be obtained stabilized at a pentacarbonylchromium fragment by organometallic pathways. These isocyanide ligands turned out be powerful π acceptor ligands. However, synthetic pathways for fluorinated isocyanonitriles are still limited. Thus far there exists no general procedure. The synthetic use in organic chemistry even of those examples which could be synthesized on the pentacarbonylchromium fragment is limited by low yields and the lack of a method to get the isocyanides as free molecules.

3. Experimental

All reactions were carried out under dry argon by using standard Schlenck tube and vacuum techniques. ^{1}H-, ^{19}F-, and ^{13}C-NMR spectra were recorded by using a Jeol Lambda 400 instrument using TMS, $CFCl_3$, and TMS or solvent signals as reference standards. IR spectra were taken on a Perkin–Elmer 883 instrument. Mass spectra were obtained on Varian 711 spectrometer (80 eV). Tetraethylammonium pentacarbonyl(cyano)chromate [20] **1** using toluene instead of benzene as solvent, pentacarbonyl(trifluoroethenyl isocyanide)chromium **3** [7], tetrafluoropropionitrile [6], and difluoroacetonitrile [21] were prepared according to literature methods. The hexacarbonylchromium and sodiumbis(trimethylsilyl)amide used in the synthesis of **1** should be sublimed before use as impurities will have large effects on the yield of **1**.

*3.1. Pentacarbonyl(fluoroisocyanoacetonitrile)chromium (**4**)*

Pentacarbonyl(trifluoroethenyl isocyanide)chromium (299 mg (1 mmol)) was dissolved into 15 ml diethylether. 3 mmol of ammonia was condensed onto the reaction-mixture using a conventional glass vacuum line system and pVT techniques. The reaction was allowed to warm to ambient temperature and stirred for 1 h. The mixture was filtered at silica, all solvent was removed under vacuum and the resulting residue sublimed at 50°C (0.1 Pa), yielding 220 mg (79.7%) of **4** as pale yellow crystals. M.p. 87°C. Calc. for $C_8HCrFN_2O_5$%: 34.78 C, 10.14 N, 0.36 H; Found%: 35.45 C, 10.24 N, 1.01 H. ^{19}F-NMR ($CDCl_3$): $\delta = -137.2$ (d, $^1J_{HF} = 48$ Hz) ppm. ^{1}H-NMR ($CDCl_3$): $\delta = 6.19$ (d, $^1J_{HF} = 48$ Hz) ppm. $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta = 75.2$ (d, CHF, $^1J_{CF} = 215$ Hz), 110.0 (d, CN, $^2J_{CF} = 38$ Hz), 196.3 (NC), 212.6 (CO_{cis}), 213.0 (CO_{trans}) ppm. $^{13}C\{^{19}F\}$-NMR ($CDCl_3$): $\delta = 75.2$ (d, CHF, $^1J_{CH} = 189$ Hz), 110.0 (s, CN), 196.3 (NC), 212.6 (CO_{cis}), 213.0 (CO_{trans}) ppm. IR(KBr): $\tilde{\nu} = 2922$ w, 2855 w, 2266 w, 2140 m, 1936 s, 1331 m, 1317 m, 1189 w, 1065 m, 1044 m, 900 m, 673 s, 651 s, 598 w, 563 w, 536 w, 490 w, 473 w, 444 m, 353 w cm^{-1}. IR(pentane): $\tilde{\nu} = 2130$ w, 2023 w, 1971 s cm^{-1}. MS (80 eV): $m/z =$ 276 [M^+], 164 [M^+–4CO], 136 [$(CrCNCHFCN)^+$], 78 [$(CrCN)^+$], 52 [Cr^+].

*3.2. Pentacarbonyl(tetrafluoroisocyanopropionitrile) chromium (**5**)*

A 2 g (5.8 mmol) sample of $[(C_2H_5)_4N][(CO)_5CrCN]$ (**1**) was dissolved in 9 g CF_3CHF–CN at −78°C. Phenyldiazoniumtetrafluoroborate (930 mg (5.7 mmol)) was added at −78°C and the reaction mixture was allowed to warm to ambient temperature. Formation of nitrogen was observed beginning at −30°C, which intensifies. At −10°C the reaction mixture turned reddish–brown. The reaction mixture was stirred for 30 min at ambient temperature. The solvent was removed under vacuum at −10°C. The residue was extracted with *n*-pentane. Column chromatography on silica using pentane–dichloromethane as eluant yielded **5** in the first fraction. 210 mg (10.5%) yellow crystals were isolated by removing the solvent under vacuum. M.p. 18 °C. The other two fractions were discarded as they exhibited no signal in the ^{19}F-NMR spectra. ^{19}F-NMR ($CDCl_3$): $\delta = -81.2$ (d, CF_3, $J = 10$ Hz), −117.8 (d, CF, $J = 10$ Hz) ppm. $^{13}C\{^1H\}$-NMR ($CDCl_3$): $\delta = 82.8$ (dq, CF, $^1J_{CF} = 227$ Hz; $^2J_{CF} = 42$ Hz), 108.2 (d, CN, $^2J_{CF} = 41$ Hz), 117.5 (dq, CF_3, $^1J_{CF} = 289$ Hz, $^2J_{CF} = 33$ Hz), 210.5 (CO_{trans}), 211.1 (CO_{cis}), 217.8 (CO_{trans}) ppm. IR(pentane): $\tilde{\nu} = 2053$ m, 2019 s, 1991 vs, 1960 s, 1913 m, sb cm^{-1}. MS (80 eV) $m/z = 344$ [M^+], 232 [M^+ –4CO], 204 [$\{CrCN–CF(CF_3)–CN\}^+$], 52 [Cr^+].

*3.3. Vacuum pyrolysis of **4** and **5***

In a typical experiment 200 mg of **4** or **5** are placed into the open end of a glass tube ($l = 500$ mm, $d = 15$ mm), which is connected to a trap system of a conventional glass vacuum line with Teflon valves by a $\frac{1}{2}$ inch Swagelok Teflon fitting. After closing the rear end of the glass tube with a 0.5 inch Swagelok Teflon fitting, the tube is evacuated to about 10^{-5} mbar and 30 cm of the glass tube is heated to 240 to 270°C. The starting material sublimes through the heating zone. Volatile materials are collected in traps kept at −78 and −196°C. The vacuum line is connected to the inlet valve of a Pfeiffer QMS 200M3 quadrupole mass spectrometer, which allows online analysis of the pyrolysis products. During the pyrolysis experiment the pressure increases to about 10^{-3} mbar due to CO formation. Further purification of the products is achieved by fractional condensation. To record IR spectra the products are allowed to expand in a IR cell (100 mm) fitted with KBr windows. Samples for NMR measurements are obtained by condensing the volatile material into a conventional 5 mm NMR tube connected to the vacuum line by a Swagelok Teflon fitting and diluting the sample with a deuterated solvent.

3.4. X-ray crystallographic study

Suitable crystals of **4** were obtained by crystallization from *n*-pentane–diethylether at −20°C. A platelet shaped crystal was mounted on the top of a glass fiber. Crystal data: $C_8HCrFN_2O_5$, $M = 276.11$, monoclinic, $P2_1/a$ No. 14, $a = 1190.0(3)$, $b = 632.9(3)$, $c = 1448.7(3)$ pm, $\beta = 97.18(2)°$, $V = 1.0825(6) \times 10^9$ pm^3, $Z = 4$, $d_{calc} = 1.694$ Mg m^{-3}, Data collection: STOE 4-circle diffractometer, Mo–K$_\alpha$ crystal size $0.4 \times 0.3 \times 0.025$ mm^3, ω-scan, $2.83 \leq \theta \leq 25.01°$, $-14 \leq h \leq 13$, $-2 \leq k \leq 7$, $-16 \leq l \leq 17$, 3925 measured reflections, 1912 unique reflections ($R_{int} = 0.0585$), 1183 reflections with $I > 2\sigma(I)$, $\mu = 1.081$ mm^{-1}, no absorption correction, structure solution direct methods (SHELXS-90 [22]), structure refinement, full-matrix least-squares on F_o^2

(SHELXL-97 [23]) using anisotropic thermal parameters for non-hydrogen atoms, hydrogen atom on calculated position with $r(\text{C–H}) = 98$ pm and $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})$, $R_1(\text{obs}) = 0.041$, $wR_2(\text{all}) = 0.1097$ for 154 refined parameters. XPMA and ZORTEP [24] were used for molecular drawings.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-117227. Copies of the data can be obtained free from charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: 44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk.

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