

# Preparation of the First Fluorinated Alkenyl Isocyanide $F_2C=CF-NC$ by Flash Vacuum Pyrolysis of $[Cr(CO)_5(CN-CF=CF_2)]$ . Crystal and Molecular Structure of $[Cr(CO)_5(CN-CF=CF_2)]$ at 125 K

Dieter Lentz\* and Dagmar Preugschat

Institut für Anorganische und Analytische Chemie, Freie Universität Berlin, Fabeckstr. 34-36, W-1000 Berlin 33, Germany

Trifluorovinyl isocyanide,  $F_2C=CF-NC$ , is obtained by flash vacuum pyrolysis of  $[Cr(CO)_5(CN-CF=CF_2)]$  at 240 °C and identified by spectroscopic methods; the structure of the chromium complex  $[Cr(CO)_5(CN-CF=CF_2)]$  has been elucidated by X-ray crystallography.

The only fluorinated isocyanides known thus far are trifluoromethyl isocyanide<sup>1</sup> and pentafluorophenyl isocyanide<sup>2</sup> which exhibit a chemistry very different from common isocyanides.<sup>3</sup> However, they cannot be obtained by the well established methods for the synthesis of isocyanides.<sup>4</sup> Recently flash vacuum pyrolysis has been used for the synthesis of unstable isocyanides such as  $CN-CN$ <sup>5</sup> and  $HC\equiv C-N\equiv C$ <sup>6</sup> from suitable organic and organometallic precursors.

Functionalized isocyanides can be built up by radical alkylation of pentacarbonylcyanochromate.<sup>7</sup> Using the pentacarbonyl fragment as a protecting group these complexed isocyanides can be modified by standard organic reactions. However, only a few attempts have been made thus far to obtain the free isocyanides from these complexes.<sup>6</sup> In continuation of our studies on fluorinated isocyanides we report the synthesis of trifluorovinyl isocyanide at a pentacarbonyl chromium fragment and its flash vacuum pyrolysis to yield the first fluorinated alkenyl isocyanide.

Reaction of tetraethylammonium[pentacarbonyl(cyano)chromate] **1** with benzenediazonium tetrafluoroborate in 1,2-dichloro-1,2,2-trifluoroethane yields the 1,2-dichloro-1,2,2-trifluoroethane isocyanide complex **2**. Dechlorination of **2** by zinc in diethyl ether in the presence of acetic acid yields

the desired trifluorovinyl isocyanide complex **3**. Compounds **2** and **3** have been fully characterized by spectroscopic methods.<sup>†</sup> In the <sup>19</sup>F NMR spectrum of **3** one observes the typical abc spectrum of a trifluorovinyl group. In addition the structure of **3** has been elucidated by an X-ray crystal structure analysis at 125 °C.<sup>‡</sup> The chromium atom is almost octahedral

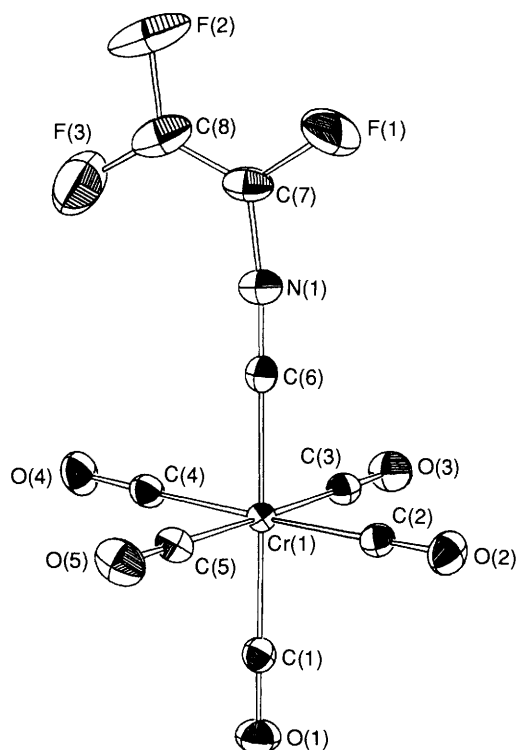
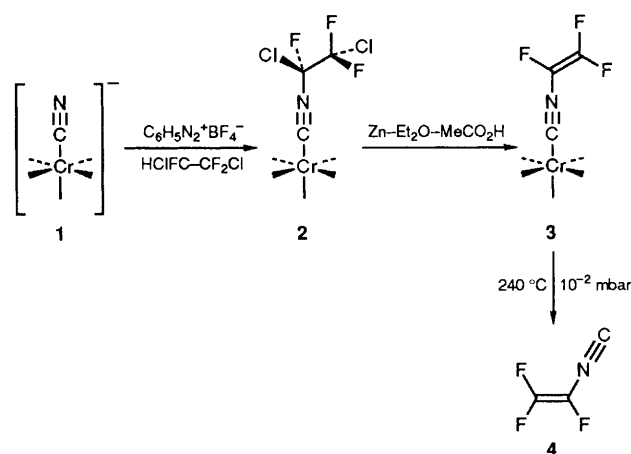


Fig. 1 ORTEP<sup>11</sup> Plot of **3** with 50% thermal ellipsoids. Selected bond distances (pm) and angles (°). Cr(1)–C(6) 194.2(2), Cr(1)–C(1) 190.9(2), Cr–CO<sub>cis</sub> 190.2(2)–191.4(2), C(6)–N(1) 116.2(2), C(7)–N(1) 135.7(2), C(7)–C(8) 131.1(3), Cr(1)–C(6)–N(1) 177.8(1), C(6)–N(1)–C(7) 173.6(2), N(1)–C(7)–C(8) 123.8(2).

<sup>†</sup> Spectroscopic and physical data for **2**: yellow crystals, m.p. 39 °C, sublimed 25 °C/10<sup>−2</sup> mbar. MS (80 eV): *m/z* 369 (M<sup>+</sup>), 306 (M<sup>+</sup> – CO – Cl), 257 (M<sup>+</sup> – 4CO), 229 (M<sup>+</sup> – 5CO), 194 (M<sup>+</sup> – Cl – 5CO) and smaller fragment ions. The molecular ion exhibits the correct isotopic pattern. IR (pentane)  $\nu/cm^{-1}$ : 2010w, sh, 1983vs, 1952m, vbr. <sup>19</sup>F NMR (CDCl<sub>3</sub>, CFCl<sub>3</sub> ref.):  $\delta_a$  –68.5 (<sup>2</sup>J 165, <sup>3</sup>J 9.3 Hz),  $\delta_b$  –70.8 (<sup>2</sup>J 165, <sup>3</sup>J 9.8 Hz),  $\delta_c$  –93.0 (<sup>3</sup>J 9.3, <sup>3</sup>J 9.8 Hz). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 102.1 [<sup>1</sup>J(<sup>19</sup>F, <sup>13</sup>C) 270, <sup>2</sup>J(<sup>19</sup>F, <sup>13</sup>C) 38 Hz], 122.9 [<sup>1</sup>J(<sup>19</sup>F, <sup>13</sup>C) 303, <sup>2</sup>J(<sup>19</sup>F, <sup>13</sup>C) 38 Hz], 208.2 (CN), 212.0 (CO).

For **3**: pale yellow crystals, m.p. 38 °C, sublimed 25 °C/10<sup>−2</sup> mbar. MS (80 eV): *m/z* 299 (M<sup>+</sup>), 271 (M<sup>+</sup> – CO), 243 (M<sup>+</sup> – 2CO), 215 (M<sup>+</sup> – 3CO), 187 (M<sup>+</sup> – 4CO), 159 (M<sup>+</sup> – 5CO) and smaller fragment ions. IR (pentane)  $\nu/cm^{-1}$ : 2114w, 2020m, 1973vs, 1944m, 1774m. <sup>19</sup>F NMR (CDCl<sub>3</sub>, CFCl<sub>3</sub> ref.):  $\delta_a$  –101.0,  $\delta_b$  –112.5,  $\delta_c$  –153.0, <sup>3</sup>J<sub>bc</sub> 112, <sup>3</sup>J<sub>ac</sub> 53, <sup>2</sup>J<sub>ab</sub> 46 Hz. <sup>13</sup>C NMR (CDCl<sub>3</sub>): 117.1 [CF, <sup>1</sup>J(<sup>13</sup>C, <sup>19</sup>F) 297, <sup>2</sup>J(<sup>13</sup>C, <sup>19</sup>F) 49 Hz], 152.3 [CF<sub>2</sub>, <sup>1</sup>J(<sup>13</sup>C, <sup>19</sup>F) 285.6, 293.0, <sup>2</sup>J(<sup>13</sup>C, <sup>19</sup>F) 49 Hz], 199.3 (CN), 213.0 (CO, *cis*), 214.2 (CO, *trans*).

For **4**: MS (80 eV): *m/z* 107 (M<sup>+</sup>), 88 (C<sub>3</sub>F<sub>2</sub>N<sup>+</sup>), 76 (C<sub>2</sub>F<sub>2</sub>N<sup>+</sup>) and smaller fragment ions. IR (gaseous)  $\nu/cm^{-1}$ : 2111s (NC), 1801s (C=C), 1363s, 1279vs, 1212m, 1147vs, 936w. <sup>19</sup>F NMR (CDCl<sub>3</sub>):  $\delta_a$  –101.5,  $\delta_b$  –112.5,  $\delta_c$  –157.6, <sup>3</sup>J<sub>bc</sub> 113, <sup>3</sup>J<sub>ac</sub> 50, <sup>2</sup>J<sub>ab</sub> 53, <sup>2</sup>J(<sup>14</sup>N, <sup>19</sup>F<sub>c</sub>) 10 Hz.

<sup>‡</sup> Crystal data for **3**: C<sub>8</sub>CrF<sub>3</sub>NO<sub>5</sub>, *M* = 299.08, pale yellow crystal 0.2 × 0.2 × 0.6 mm<sup>3</sup>; triclinic, space group *PT* (No. 2), *a* = 563.39(4), *b* = 1008.51(8), *c* = 1009.67(8) pm,  $\alpha$  = 105.750(7),  $\beta$  = 98.115(6),  $\gamma$  = 95.866(8)°, *V* = 5.4062 × 10<sup>8</sup> pm<sup>3</sup>, *Z* = 2, *D<sub>c</sub>* = 1.837 g cm<sup>−3</sup>, Enraf-Nonius, CAD4 four circle diffractometer Mo-K $\alpha$  radiation,  $\lambda$  = 71.069 pm,  $\mu$  = 10.8 cm<sup>−1</sup>, *T* = 125 K, *F*(000) = 291.99,  $\omega$ –2 $\theta$  scan, 2 ≤  $\theta$  ≤ 30°; 3311 measured reflections, 3132 unique reflections, 2514 observed reflections with *F<sub>o</sub>* > 4 $\sigma$ (*F<sub>o</sub>*), anisotropic temperature factors, 163 refined parameters, *R* = 0.29, *R<sub>w</sub>* = 0.031, *w* = 1.50[ $\sigma^2(F_o)$  + 0.0004 *F<sub>o</sub>*<sup>2</sup>]<sup>−1</sup>. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

coordinated by five carbonyl groups and the trifluorovinyl isocyanide ligand, with chromium carbon bond lengths between 190.2(2) and 191.4(2) pm to the carbonyl. The longer chromium carbon bond of 194.2(2) pm to the isocyanide ligand indicates that this ligand is less strongly bound than the trifluoromethyl isocyanide ligand in  $[\text{Cr}(\text{CO})_5(\text{CNCF}_3)]^8$  or *trans*- $[\text{Cr}(\text{CO})_4(\text{CNCF}_3)(\text{CNCH}_3)]^9$ . The isocyano function is close to linear both on the isocyanide carbon atom [Cr(1)–C(6)–N(1) 177.8(1)°] and the nitrogen atom [C(6)–N(1)–C(7) 173.6(2)°].

Flash vacuum pyrolysis of **3** at 240°C results in the formation of the free isocyanide **4** which has been characterized by  $^{19}\text{F}$  NMR, IR and mass spectroscopy. The isocyanide function can be unambiguously detected by a strong IR absorption at 2111  $\text{cm}^{-1}$  and the coupling of the *geminal* fluorine atom with the nitrogen isotope  $^{14}\text{N}$  (nuclear spin 1) of about 10 Hz.

Trifluorovinyl isocyanide is a colourless gas b.p. 11°C (extrapolated from vapour pressure measurements) and m.p. –122°C. As for other isocyanide–cyanide pairs the boiling point of the isocyanide is lower than that of the nitrile, b.p. ( $\text{F}_2\text{C}=\text{CF}-\text{CN}$ ) 16.4–16.5°C.<sup>10</sup> Liquid trifluorovinyl isocyanide turns yellow on warming to –50°C owing to slow decomposition.

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