



# Synthesis of fluorinated geminal diisocyanides stabilized on a transition metal

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## ARTICLE INFO

### Article history:

Received 30 March 2011  
Received in revised form 26 April 2011  
Accepted 26 April 2011  
Available online 4 May 2011

### Keywords:

Fluorine  
Isocyanides  
Chromium  
Complexes  
Crystal structure

## ABSTRACT

Chromium complexes of the geminal diisocyanides bis(pentacarbonyl)- $\mu$ -2,2-diisocyano-1,1,1,3,3,3-hexafluoropropane)dichromium **1a** and bis(pentacarbonyl)- $\mu$ -2,2-diisocyano-1,1,1,3,3-pentafluorobutane)dichromium **1b** were obtained by radical alkylation of pentacarbonylcyanochromate besides pentacarbonyl(2-isocyano-1,1,1,3,3,3-hexafluoropropane)chromium **2a** and pentacarbonyl(2-isocyano-1,1,1,3,3-pentafluorobutane)chromium **2b**, respectively. Pentacarbonyl(2-isocyano-1,1,1,2,3,3,3-heptafluoropropane)chromium **2c** was prepared analogously. The crystal and molecular structures of **1a** and **b** were determined by X-ray diffraction.

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## 1. Introduction

Diisocyanomethane, the least stable isomer of malonodinitrile, although prepared by Neidlein [1] in 1964 and fully characterized more than thirty years later including a X-ray crystal structure determination [2] and an experimental electron density study [3] remained the only geminal diisocyanide isolated in substance probably due its extreme instability. Crystals of diisocyanomethane melt at  $-15^\circ\text{C}$  turning brown due to beginning decomposition and decompose explosively at  $-10^\circ\text{C}$  to give a brown black insoluble polymer. Nevertheless it was possible to study its coordination chemistry [2] and isolate several mono- and dinuclear complexes.  $[(\text{CO})_5\text{W}-\text{CN}]_2\text{C}(\text{t-Bu})_2$  the only further transition metal complex of a geminal diisocyanide was prepared using an organometallic pathway [4].

A similar situation can be found for fluorinated isocyanides. Prior to our own work trifluoromethyl isocyanide [5–7] and pentafluorophenyl isocyanide [8,9] obtained in poorly reproducible syntheses and sometimes with by-products which are hard to remove were the only fluorinated isocyanides. The chemistry of fluorinated isocyanides is summarized in a review article [10]. Fehlhammer et al. have developed an organometallic pathway for functionalized isocyanides [11] including fluorinated isocyanides like *n*-heptafluoropropyl isocyanide stabilized at a pentacarbonylchromium fragment which fulfils two tasks at once: first introduction of the isocyano function by radical alkylation; second to stabilize the very reactive isocyanide by coordination. In some

special cases the isocyanide complex can be decomposed by flash vacuum pyrolysis. These strategies have been used by us to synthesize isocyanides which cannot be obtained by the usual routes like trifluoroethenyl isocyanide [12], difluoromethyl isocyanide [13] and isocyano ethyne (isocyano acetylene) [14] and 3-isocyano-2-propynenitrile (cyano-isocyano acetylene) [15].

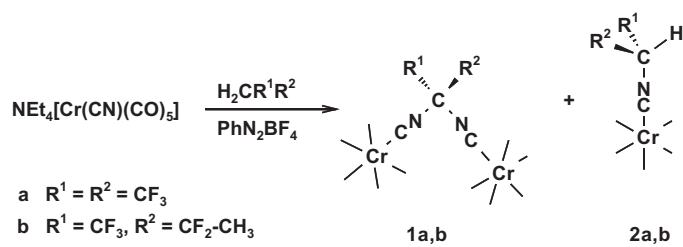
Herein we report on an extension of this work yielding fluorinated geminal diisocyanides stabilized at pentacarbonylchromium fragments.

## 2. Results and discussion

As established by Fehlhammer et al. [11] pentacarbonylcyanochromate reacts with haloalkanes in the presence of phenyldiazonium tetrafluoroborate yielding the corresponding  $\alpha$ -halogenoalkyl isocyanide complexes. A radical mechanism was proposed by the authors. Geminal diisocyanide ligands could not be detected among the reaction products.

Unexpectedly we observed the formation of fluorinated diisocyanides on reaction of tetraethylammonium pentacarbonylcyanochromate with phenyldiazonium tetrafluoroborate in 1,1,1,3,3,3-hexafluoropropane and 1,1,1,3,3-pentafluorobutane, respectively, as depicted in Scheme 1. The complexes bis(pentacarbonyl)- $\mu$ -2,2-diisocyano-1,1,1,3,3,3-hexafluoropropane)dichromium **1a** and bis(pentacarbonyl)- $\mu$ -2,2-diisocyano-1,1,1,3,3-pentafluorobutane)dichromium **1b** were obtained as needle shaped crystals by crystallization from *n*-pentane. The expected isocyanide complexes pentacarbonyl(2-isocyano-1,1,1,3,3,3-hexafluoropropane)chromium **2a** and pentacarbonyl(2-isocyano-1,1,1,3,3-pentafluorobutane)chromium **2b** were isolated by chromatographic work up in similar or lower yield. An analogous

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Scheme 1.

reaction using 1,1,1,2,3,3,3-heptafluoropropane as solvent yielded pentacarbonyl(2-isocyano-1,1,1,2,3,3,3-heptafluoropropane)chromium **2c**.

Astonishingly, the diisocyanide complexes **1a** and **b** are formed in similar or even higher yields than the monoisocyanide complexes **2a** and **b** although their formation by radical alkylation requires the reaction with a reactant whose concentration is much lower than the concentration of the solvent.

The  $^{19}\text{F}$  NMR spectra of **1a** and **2a** exhibit a singlet and a doublet ( $^3J(^1\text{H}-^{19}\text{F}) = 5.3$  Hz) at  $-78.4$  and  $-70.9$  ppm for the trifluoromethyl group, respectively. The corresponding  $^1\text{H}$  NMR spectrum of **2a** consists of the expected septet at 4.78 ppm. **1b** exhibits a triplet at  $-75.6$  and a multiplet at  $-98.8$  in the  $^{19}\text{F}$  NMR spectrum with coupling constants of  $^4J(^{19}\text{F}-^{19}\text{F}) = 10$  Hz and  $^3J(^1\text{H}-^{19}\text{F}) = 19$  Hz, respectively and a triplet at 1.97 ppm in the  $^1\text{H}$  NMR spectrum. Due to the  $\text{C}_1$  symmetry of **2b** the fluorine atoms of the difluoro methylene group get chemically inequivalent and give rise to AB pattern at  $-94.4$  and  $-95.7$  ppm ( $^2J(^{19}\text{F}-^{19}\text{F}) = 258$  Hz) showing additional splitting due to coupling with the  $\text{CH}_3$  ( $^3J(^1\text{H}-^{19}\text{F}) = 19$  Hz),  $\text{CH}$  ( $^3J(^1\text{H}-^{19}\text{F}) = 7$  Hz) and  $\text{CF}_3$  ( $^4J(^{19}\text{F}-^{19}\text{F}) = 10$  Hz) groups. Resonances at 1.87 (tr) and 4.54 (sext.) ppm can be observed in the  $^1\text{H}$  NMR spectrum. The  $^{19}\text{F}$  NMR spectrum of **2c** consists out of the expected doublet and septet at  $-81.7$  (d, 6F,  $^3J(^{19}\text{F}-^{19}\text{F}) = 6.8$  Hz),  $-142.8$  (septet, 1F) ppm.

Important differences can be observed in the  $^{13}\text{C}$  NMR spectra of **1a** compared to **1b**, **2a** and **2b**. Whereas **1b**, **2a** and **2b** show the expected low field shift of the  $^{13}\text{C}$  resonance of the *trans* carbonyl group compared to the *cis* carbonyl group the opposite trend is observed for **1a** similar to pentacarbonyl(trifluoromethylisocyanide)chromium [10].

All complexes **1a**, **1b**, **2a** and **2b** exhibit a strong broad absorption around  $1905\text{--}1910\text{ cm}^{-1}$  due to the carbonyl stretching.

Both **1a** and **1b** form very thin needle shape crystals which allowed the determination of the crystal and molecular structures by X-ray diffraction. Due to the very poor quality of the crystal of **1b** only low resolution data could be obtained which allowed only verifying the identity of the compound but no further details. The molecular structures are depicted in Fig. 1. Figs. 2 and 3 display packing diagrams of the compounds.

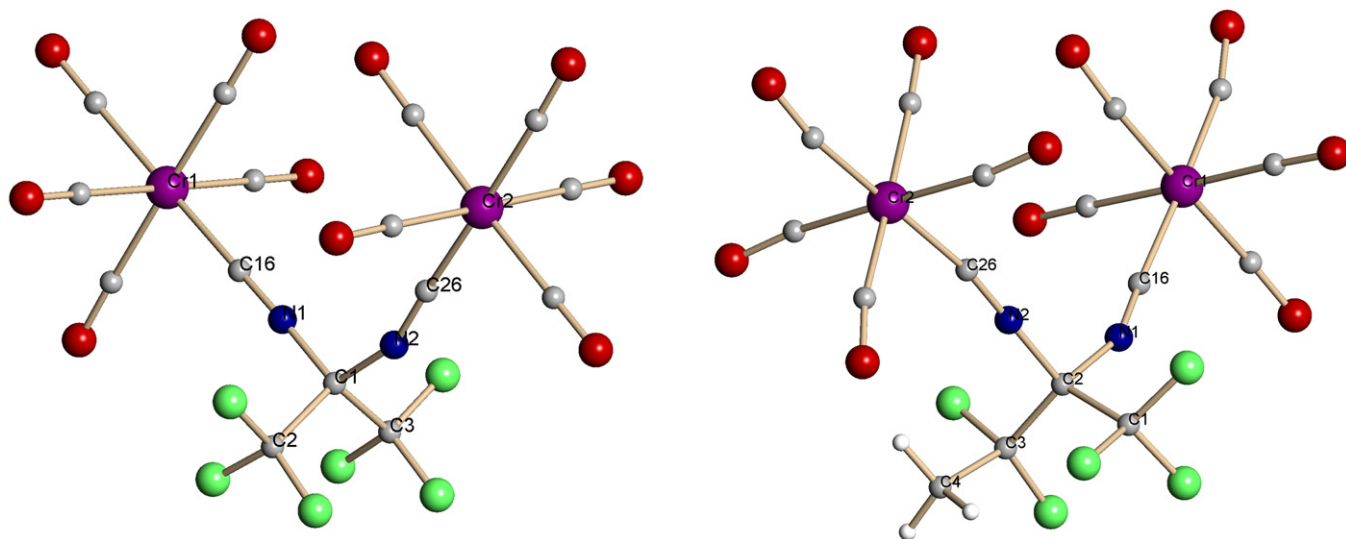
In both complexes the chromium atoms are octahedral coordinated by five carbonyl ligands and the bridging geminal diisocyanide ligand. In **1a** the metal carbon distances vary slightly between 1.903(9) and 1.936(10) Å. All bond angles at the chromium atoms are close to  $90^\circ$  and  $180^\circ$ , respectively. The carbon nitrogen distances C1 N1 1.411(9), C1 N2 1.427(8), C16 N1 1.152(8) and C26 N2 1.189(9) Å as well as the carbon distances C1 C2 1.558(9) and C1 C3 1.560(10) Å lie within the expected ranges. Whereas one isocyanide function C26 N2 C1  $159.0(6)^\circ$  is slightly bent the other one C16 N1 C1  $176.2(6)^\circ$  is almost linear.

The differences in bond angles are probably due to crystal packing effects as C–N–C bond angles in isocyanide complexes vary in broad range [16]. As can be seen from the packing diagrams the carbonyl groups and  $\text{CF}_3$  groups of **1a** are segregated as far as possible resulting in double layers which are stacked along the crystallographic *c* axis.

Due to the crystal quality of **1b** all bond lengths had to be restrained during the least squares refinement. Therefore a discussion of bond lengths and angles is impossible. Nevertheless a close similarity in the packing diagram of **1b** to **1a** can be found. Again double layers are formed in way that the pentacarbonyl chromium fragments are opposing each other whereas the fluorine substituents and protic substituents are arranged in pairs allowing a maximum distance from each other.

### 3. Experimental

All reactions were carried out under argon, using standard Schlenk and vacuum line techniques. Tetraethylammonium-pentacarbonyl(cyano)chromate **2** was prepared following the literature procedure [17], however, using sublimed hexacarbonyl chromium and freshly sublimed sodium-bis(trimethylsilyl)amide to get a maximum yield of 95% and to avoid pyrophoric by-products. Phenyl diazonium tetrafluoroborate was prepared according to literature methods [18]. 1,1,1,3,3,3-Hexafluoropropane (DUPONT), 1,1,1,2,3,3,3-heptafluoropropane (Linde) and 1,1,1,3,3-pentafluorobutane (Solvay Fluor GmbH) were used as received.

Fig. 1. Molecular structures of **1a** (left) and **1b** (right).

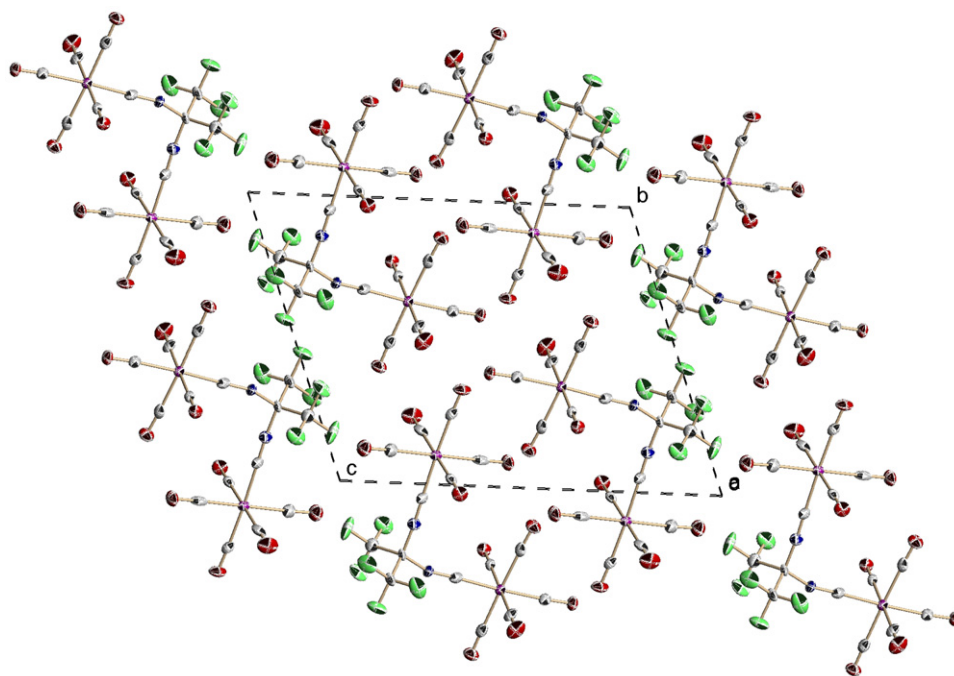


Fig. 2. Packing diagram of **1a**.

Other substances were obtained commercially and used as received, without further purification. NMR spectra were recorded on a JEOL Lambda 400.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were referenced to solvent signals,  $^{19}\text{F}$  NMR spectra were referenced externally to  $\text{CFCl}_3$ . IR spectra were recorded on a Nicolet iS10 spectrometer with ATR Smart Dura Sample/IR device. Mass spectra were recorded on a MAT 711 spectrometer in electron impact mode (EI).

3.1. Bis(pentacarbonyl)- $\mu$ -2,2-diisocyano-1,1,1,3,3,3-hexafluoropropane)dichromium **1a** and pentacarbonyl(2-isocyano-1,1,1,3,3,3-hexafluoropropane)chromium **2a**

About 50 mL of 1,1,1,3,3,3-hexafluoropropane were condensed to 2.0 g (5.8 mmol) of tetraethylammonium pentacarbonylcyano-

chromate in a 100 mL Schlenk flask cooled by dry ice/ethanol and fitted with a reflux condenser cooled to  $-25\text{ }^\circ\text{C}$ . 0.93 g phenyldiazonium tetrafluoroborate were added and the magnetically stirred reaction mixture was allowed to warm to ambient temperature and kept under reflux for 3 h. The solvent was removed under vacuum and the residue was extracted with five 50 mL portions of n-pentane. The solution was concentrated using a rotary evaporator to about 5 mL. Crystallization afforded 0.9 g (26.5%) yellow needle shaped crystals of bis(pentacarbonyl)- $\mu$ -2,2-diisocyano-1,1,1,3,3,3-hexafluoropropane)dichromium **1a**, m.p.  $94\text{ }^\circ\text{C}$ . The  $^{19}\text{F}$  NMR spectrum of the pentane solution exhibits resonances of pentacarbonyl(2-isocyano-1,1,1,3,3,3-hexafluoropropane)chromium **2a** ( $\delta = -74.0\text{ ppm}$  (d, 6F,  $^3J(^1\text{H}-^{19}\text{F}) = 5.3\text{ Hz}$ )) and bis(pentacarbonyl)- $\mu$ -2,2-diisocyano-1,1,1,3,3,3-hexafluoropropane)di-

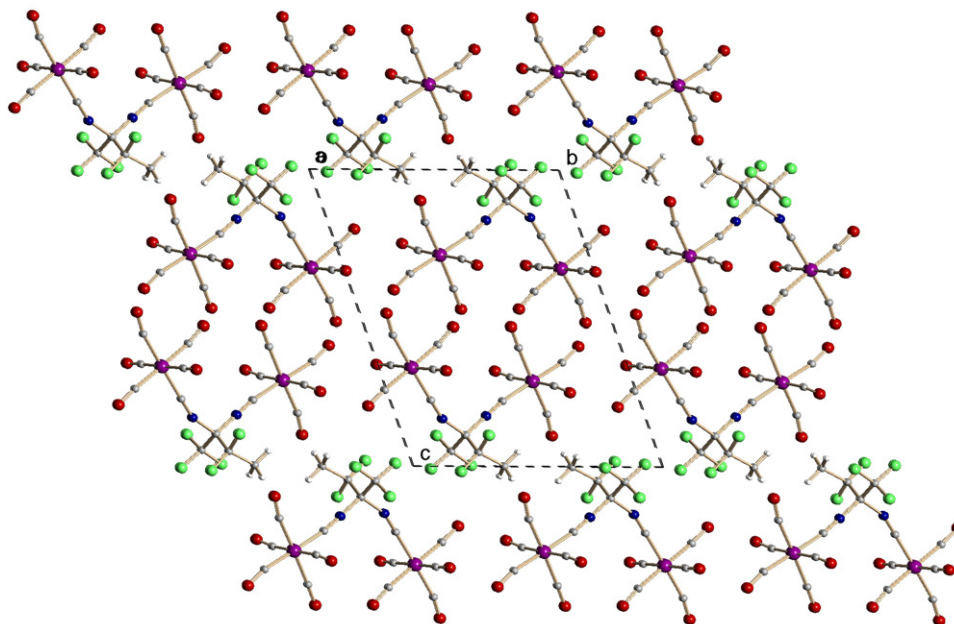


Fig. 3. Packing diagram of **1b**.

chromium **1a** ( $\delta = -79.9$  ppm) and unidentified by-products at  $-68.4$  and  $-75.9$  ppm, respectively. Purification of the filtrate by preparative TLC on silica yield pentacarbonyl(2-isocyano-1,1,1,3,3,3-hexafluoropropane)chromium **2a** as yellow crystals, m.p.  $54$  °C.

### 3.2. Bis(pentacarbonyl)- $\mu$ -2,2-diisocyano-1,1,1,3,3,3-hexafluoropropane)dichromium **1a**

$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -78.4$  ppm;  $^{13}\text{C}$ - $\{^{19}\text{F}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 72.9$  C( $\text{CF}_3$ )<sub>2</sub>, 118.5 CF<sub>3</sub>, 208.6 NC, 211.7 CO<sub>trans</sub>, 211.8 CO<sub>cis</sub> ppm; IR (neat):  $\nu = 2196$  (m), 2119 (sh), 1975 (s) 1939 (vs), 1296 (w), 1238 (w), 1226 (w), 1125 (w), 1076 (w), 962 (w), 730 (w), 646 (w)  $\text{cm}^{-1}$ ; MS (EI, 80 eV):  $m/z = 586$  ( $\text{M}^+$ ), 502 ( $\text{M}^+ - 3\text{CO}$ ), 446 ( $\text{M}^+ - 5\text{CO}$ ), 306 ( $\text{M}^+ - 10\text{CO}$ ), and smaller fragment ions.

#### 3.2.1. Pentacarbonyl(2-isocyano-1,1,1,3,3,3-hexafluoropropane)chromium **2a**

$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -70.9$  ppm (d, 6F,  $^3J(^{1}\text{H}-^{19}\text{F}) = 5.3$  Hz);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 4.81$  (septet,  $^3J(^{1}\text{H}-^{19}\text{F}) = 5.3$  Hz) ppm;  $^{13}\text{C}$ - $\{^1\text{H}, ^{19}\text{F}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 59.1$  CH( $\text{CF}_3$ )<sub>2</sub>, 119.4 CF<sub>3</sub>, 190.1 NC, 213.0 CO<sub>cis</sub>, 214.0 CO<sub>trans</sub> ppm; IR (neat):  $\nu = 2965$  (s), 2162 (m), 2126 (m), 2054 (m), 2011 (w), 2005 (w), 1986 (w), 1905 (br, vs), 1351 (s), 641 (br, s)  $\text{cm}^{-1}$ ; MS (EI, 80 eV):  $m/z = 369$  ( $\text{M}^+$ ), 313 ( $\text{M}^+ - 2\text{CO}$ ), 257 ( $\text{M}^+ - 4\text{CO}$ ), 229 ( $\text{M}^+ - 5\text{CO}$ ) and smaller fragment ions.

### 3.3. Bis(pentacarbonyl)- $\mu$ -2,2-diisocyano-1,1,1,3,3-pentafluorobutane)dichromium **1b** and pentacarbonyl(2-isocyano-1,1,1,3,3-pentafluorobutane)chromium **2b**

A suspension of 3 g (8.6 mmol) tetraethylammonium pentacarbonylcyanochromate in 30 mL 1,1,1,3,3-pentafluorobutane in a 100 mL Schlenk flask was cooled to  $-78$  °C using a dry ice ethanol bath. 2.3 g (8.3 mmol) phenyldiazonium tetrafluoroborate were added. The reaction mixture was allowed to warm to ambient temperature with magnetically stirring. The supernatant solution was decanted and the residue extracted four times with 30 mL portions of n-pentane. The combined solutions were concentrated using a rotary evaporator and filtered over a plug of silica. The filtrate was concentrated to a few millilitres. Crystallization at  $-30$  °C yielded bis(pentacarbonyl)- $\mu$ -2,2-diisocyano-1,1,1,3,3-pentafluorobutane)dichromium, 50 mg (2%) as colourless needle shaped crystals, m.p.  $89$  °C. The remaining solution was purified by TLC on silica yielding 30 mg (1%) of pentacarbonyl(2-isocyano-1,1,1,3,3-pentafluorobutane)chromium as colourless oil.

### 3.4. Bis(pentacarbonyl)- $\mu$ -2,2-diisocyano-1,1,1,3,3-pentafluorobutane)dichromium **1b**

$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -75.6$  (tr, 3 F,  $^4J(^{19}\text{F}-^{19}\text{F}) = 10$  Hz),  $-98.8$  (m, 2F,  $^3J(^{1}\text{H}-^{19}\text{F}) = 19$  Hz,  $^4J(^{19}\text{F}-^{19}\text{F}) = 10$  Hz);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.97$  (tr,  $^3J(^{1}\text{H}-^{19}\text{F}) = 19$  Hz) ppm;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 212.3$  CO<sub>cis</sub>, 212.5 CO<sub>trans</sub> ppm; IR (neat):  $\nu = 2182$  (w), 2120 (m), 2050 (m), 1910 (vs), 1724 (w), 1624 (w), 1446 (m), 1394 (w), 1272 (m), 1225 (m), 1199 (m), 1109 (w), 1070 (w), 974 (w), 958 (w) 906 (w), 757 (w), 641 (s)  $\text{cm}^{-1}$ ; MS (EI, 80 eV):  $m/z = 582$  ( $\text{M}^+$ ), 442 ( $\text{M}^+ - 5\text{CO}$ ), 302 ( $\text{M}^+ - 10\text{CO}$ ), and smaller fragment ions.

### 3.5. Pentacarbonyl(2-isocyano-1,1,1,3,3-pentafluorobutane)chromium **2b**

$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -71.4$  (CF<sub>3</sub>,  $^3J(^{1}\text{H}-^{19}\text{F}) = 7$  Hz,  $^4J(^{19}\text{F}-^{19}\text{F}) = 10$  Hz),  $-94.4$  (CF<sub>2</sub>,  $^2J(^{19}\text{F}-^{19}\text{F}) = 258$  Hz,  $J(^{1}\text{H}-^{19}\text{F}) = 19$  Hz,  $^4J(^{19}\text{F}-^{19}\text{F}) = 10$  Hz),  $-95.7$  (CF<sub>2</sub>,  $^2J(^{19}\text{F}-^{19}\text{F}) = 258$  Hz,  $J(^{1}\text{H}-^{19}\text{F}) = 19$  Hz,  $^4J(^{19}\text{F}-^{19}\text{F}) = 10$  Hz) ppm;

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 1.87$  (CH<sub>3</sub>, tr,  $J(^{1}\text{H}-^{19}\text{F}) = 19$  Hz), 4.54 (CH, sext.,  $^3J(^{1}\text{H}-^{19}\text{F}) = 7$  Hz) ppm;  $^{13}\text{C}$ - $\{^1\text{H}, ^{19}\text{F}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 20.5$  CH<sub>3</sub>, 62.0 CH, 118.1 CF<sub>2</sub>, 120.3 CF<sub>3</sub>, 183.2 NC, 213.4 CO<sub>trans</sub>, 214.6 CO<sub>cis</sub> ppm; IR (KBr):  $\nu = 2196$  (m), 2119 (sh), 1975 (s) 1939 (vs), 1296 (w), 1238 (w), 1226 (w), 1125 (w), 1076 (w), 962 (w), 730 (w), 646 (w)  $\text{cm}^{-1}$ .

### 3.6. Pentacarbonyl(2-isocyano-1,1,1,2,3,3,3-heptafluoropropane)chromium **2c**

Reaction similar to that described above using 1,1,1,2,3,3,3-heptafluoropropane as solvent yielded 0.19 g pentacarbonyl(2-isocyano-1,1,1,2,3,3,3-heptafluoropropane)chromium as yellow crystals after crystallization from pentane.

$^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -81.7$  (d, 6 F,  $^3J(^{19}\text{F}-^{19}\text{F}) = 6.8$  Hz),  $-142.8$  (septet, 1F); IR (KBr):  $\nu = 2000$  (s), 1969 (s), 1250 (w), 1160 (w), 1101 (m), 985 (w), 671 (s)  $\text{cm}^{-1}$ .

## Crystallography

Crystal data and details of the structure determinations are presented in Table 1. The intensity data were collected using a Bruker AXS SMART CCD diffractometer.

Corrections for Lorentz polarisation and absorption effects were applied to the data. The structures were solved by Patterson and direct methods (SHELXS-97) [19], respectively. Hydrogen atoms (**1b**) were refined in calculated positions with isotropic thermal parameter. Anisotropic thermal parameters were applied to all non-hydrogen atoms of compound **1a**. All atoms of **1b** were refined isotropically and chemical equal bond distances were restraint using the SADI instruction of SHELXL. Refinement for all structures on  $F^2$  was achieved using the SHELXL-97 system [19].

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-819313 **1a**, CCDC 819314 **1b**. 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).

**Table 1**  
Crystallographic data of **1a** and **1b**.

Compound reference	<b>1a</b>	<b>1b</b>
Chemical formula	C <sub>15</sub> Cr <sub>2</sub> F <sub>6</sub> N <sub>2</sub> O <sub>10</sub>	C <sub>16</sub> H <sub>3</sub> Cr <sub>2</sub> F <sub>5</sub> N <sub>2</sub> O <sub>10</sub>
Formula mass	586.17	582.20
Crystal system	Triclinic	Triclinic
<i>a</i> /Å	6.274(3)	6.429(7)
<i>b</i> /Å	11.705(5)	12.056(13)
<i>c</i> /Å	14.929(6)	15.347(18)
$\alpha$ /°	70.047(9)	70.35(3)
$\beta$ /°	80.438(8)	82.02(3)
$\gamma$ /°	86.964(8)	88.62(3)
Unit cell volume/Å <sup>3</sup>	1016.3(7)	1109(2)
Temperature/K	173(2)	133(2)
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
No. of formula units per unit cell, <i>Z</i>	2	2
Radiation type	MoK $\alpha$	MoK $\alpha$
Absorption coefficient, $\mu$ /mm <sup>-1</sup>	1.182	1.076
No. of reflections measured	7898	2465
No. of independent reflections	3597	672
<i>R</i> <sub>int</sub>	0.0740	0.1537
Final <i>R</i> <sub>1</sub> values ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0542	0.1555
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.1134	0.3621
Final <i>R</i> <sub>1</sub> values (all data)	0.1228	0.2223
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values (all data)	0.1389	0.4041
Goodness of fit on <i>F</i> <sup>2</sup>	1.001	1.349
CCDC number	819,313	819,314

## Acknowledgments

We appreciate the support from the Deutsche Forschungsgemeinschaft (DFG) and the Graduate School (GK1582) "Fluorine as a Key Element". We thank DUPONT for hexafluoropropane and Solvay Fluor GmbH for 1,1,1,3,3-pentafluorobutane.

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