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PAPER

Syntheses of highly unsaturated isocyanides via organometallic pathways†

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The carbon coupling reaction by nucleophilic attack of $(CO)_5Cr(CN-CF=CF_3)$ 1 by lithium or Grignard compounds 2a-i yields the isocyanide complexes (CO)₅Cr(CN-CF=CF-R) 3a-i (a R = CH=CH₂, **b** R = CH=CF₂, **c** R = C=CH, **d** R = C=C-SiMe₃, **e** R = C=C-Ph, **f** R = C=C-C₆F₄OMe, $\mathbf{g} \mathbf{R} = \mathbf{C} = \mathbf{C} - \mathbf{C}_6 \mathbf{H}_3 (\mathbf{C} \mathbf{F}_3)_2$, $\mathbf{h} \mathbf{R} = \mathbf{C}_6 \mathbf{F}_5$, $\mathbf{i} \mathbf{R} = \mathbf{C}_6 \mathbf{H}_3 (\mathbf{C} \mathbf{F}_3)_2$) as mixtures of *E* and *Z* isomers. The dinuclear complexes **5a–c** are obtained from the reaction of **1** with the dilithio or dimagnesium compound **4a–c** as the Z,Z-, E,Z- and E,E-isomers, respectively. $(CO)_5Cr(CN-CF=CF-CEC-CF=CF-NC)$ - $Cr(CO)_5$ 7 is obtained as a mixture of Z,Z-, Z,E- and E,E-isomers from (CO)₅Cr(CN-CF= CF-C≡C-H 3d by Eglington-Glaser coupling. (CO)₅Cr(CN-CF=CF-C≡C-CF=CF-NC)Cr(CO)₅ 6 and (CO)₅Cr(CN-CF=CF-C=C-C=C-CF=CF-NC)Cr(CO)₅ 7 react with octacarbonyldicobalt forming the cluster compounds Z,Z-[{η²-µ₂-(CO)₅Cr(CN-CF=CF-CECF-NC)Cr- $(CO)_{5}$ $Co_{2}(CO)_{6}$ $Z, Z-8, E, Z-[{\eta^{2}-\mu_{2}-(CO)_{5}Cr(CN-CF=CF-CEC-CF=CF-NC)Cr(CO)_{5}}-CF=CF-NC)Cr(CO)_{5}$ $Co_2(CO)_6] E,Z-8 \text{ and } E,E-[\{\eta^2-\mu_2-(CO)_5Cr(CN-CF=CF-CF=CF-NC)Cr(CO)_5\}$ $Co_2(CO)_6$] *E*,*E*-8 and *Z*,*Z*-[{ η^2 - μ_2 -(CO)₅Cr(CN-CF=CF-CEC-C=C-CF=CF-NC)Cr(CO)₅}- $\{Co_2(CO)_6\}_2\}$ Z,Z-9, E,Z- $[\{\eta^2 + \mu_2 - (CO)_5 Cr(CN - CF = CF - C = C - CF = CF - NC)Cr(CO)_5\}$ $\{Co_2(CO)_6\}_2\} E, Z-9 \text{ and } E, E-[\{\eta^2-\mu_2-(CO)_5Cr(CN-CF=CF-CEC-CEC-CF=CF-NC)-CF=CF-CEC-CF=CF-NC\}$ $Cr(CO)_{5}$ { $Co_{2}(CO)_{6}$ } Z,Z-9, respectively. The crystal and molecular structures of *E*-3d, *Z*-3h, Z,Z-8, E,Z-8 and Z,Z-9 were elucidated by single-crystal X-ray crystallography.

Introduction

Ethenyl isocyanide was prepared by Matteson and Bailey¹ almost 100 years after the synthesis of the first isocyanides, ethyl isocyanide by Gautier² and phenyl isocyanide by Hofmann.³ Despite the high potential in multicomponent reactions⁴ further examples of alkenyl isocyanides like CH3-CH=CH-NC,5 H5C6-CH=CH-NC,6 1-isocyano-2-dimethylamino-alkenes7 or 1(S)-camphor-2cis-methylidene-isocyanide⁸ are still rare and CH₃CH=C(CH₃)-CH=CH-NC⁹ is the only one of these having conjugated double bonds. Some of these have been used in polymerization experiments forming poly(vinyliminomethylenes)¹⁰ and in the synthesis of heterocycles.11 1-isocyano-2-dimethylamino-alkenes7 or 1(S)-camphor-2-cis-methylidene-isocyanide8 have been successfully used as isocyanide in multicomponent reactions. The first fluorinated ethenyl isoycanide, F2C=CF-NC, was synthesized in 1992¹² and its structure was elucidated by low temperature single-crystal X-ray crystallography.13 Fehlhammer et al. reported

on chloroethenyl isocyanides synthesized and stabilized at a pentacarbonyl chromium fragment in 1989.¹⁴

In 1991 we reported on the preparation, microwave spectroscopic study, and structure of the first alkynyl isocyanide, ethynyl isocyanide, H-C=C-NC, by vacuum pyrolysis of a suitable organometallic precursor molecule, (CO)₅Cr(CN-CCl=CCl(H).15 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.16 H-C=C-NC has been subsequently studied by HeI and HeII photoelectron spectroscopy,¹⁷ millimetre wave spectroscopy,18 high-resolution FTIR spectroscopy,19 and NMR spectroscopy.²⁰ Recently the very unstable CN-C=C-CN molecule, which had only been obtained before in an argon matrix and characterised by IR spectroscopy,²¹ was synthesised, and a broad study has been performed by a collaborative effort.²² Propynyl isocyanide is the only further alkynyl isocyanide that had been obtained thus far in preparative quantities and studied by various spectroscopic methods.^{20,23} Recently, Thaddeus et al. succeeded in generating H–(C=C)_n–NC (n = 2,3) (approximately 0.1 to 1 picomol) along with large amounts of other compounds by electrical discharge in a molecular beam of butadiyne, propynenitrile or others seeded in Ne.24,25 The detection of the isocyanopolyyne molecules was based solely on Fourier transform microwave spectroscopy in combination with ab initio calculations. Fehlhammer et al. succeeded in synthesising and stabilising

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H–C==C–NC, Me₃Si–C==C–NC and C₆H₅–C==C–NC in a transition metal complex.²⁶ However, no attempt has been made to obtain the free isocyanides.

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 halogenated alkanes and therefore is limited to molecules with relatively small chain length. Consequently, only a few alkenyl and alkynyl isocyanides could be prepared by the pyrolysis of (1,2-dichloroalkenyl isocyanide)(pentacarbonyl)chromium complexes. Although Fehlhammer's method for the synthesis of metal complex stabilised alkynyl isocyanides is promising it has been demonstrated only on three examples and failed in an attempt to synthesise (CO)₅Cr(CN–C==C–t-Bu)²⁶ or (CO)₅Cr(CN–C=C–CF₃).²⁷ Furthermore, it requires alkynyl(phenyl)iodonium salts, which are not generally available.²⁸

Pentacarbonyl(trifluoroethenyl isocyanide)chromium behaves like a fluoroalkene. For example, it dimerizes on heating forming a four membered ring.²⁹ 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.³⁰

In principal there are several different possibilities for a nucleophilic attack of pentacarbonyl(trifluoroethenyl isocyanide)chromium (Scheme 1) including the carbonyl or isocyanide carbon atoms, which would lead to carbene complexes³¹ or the metal atom, forming substitution products. In recent publications^{22,32} we have shown that the nucleophilic attack occurs solely at the CF₂ group of pentacarbonyl(trifluoroethenyl isocyanide)chromium and related compounds, allowing a systematic variation of the substituent in the β position to the isocyano group. In continuation of our work on unsaturated isocyanides we report in detail on the synthesis and structural determination of highly unsaturated halogenated alkenyl isocyanide complexes with conjugated double and triple bonds.



Results and discussion

Synthesis

Our synthetic strategy is based on the systematic modification of trifluoroethenyl isocyanide. As very electrophilic systems, highly fluorinated alkenes can be easily attacked by nucleophiles.³⁰ The

nucleophilic attack of the complex 1 occurs exclusively at the difluoromethylene group in the β position to the isocyanide nitrogen atom, as observed earlier.^{22,32} No by-products from the other possible reaction channels were observed so far although pentacarbonyl(trifluoromethyl isocyanide)chromium is easily attacked by nucleophiles resulting in the formation of carbene complexes.³³

The trifluoroethenyl isocyanide complex 1 reacts readily with Grignard and lithium compounds **2a–i** yielding the isocyanide complexes **3a–i**, respectively. (Scheme 2) As expected, mixtures of the two possible constitutional isomers *E*-**3a–i** and *Z*-**3a–i** were formed. As the ${}^{3}J({}^{19}F-{}^{19}F)$ coupling constants of *cis* and *trans* configurated fluoro alkenes differ by at least one to two orders of magnitude, $|{}^{3}J_{cis}| < |{}^{3}J_{trans}|$,³⁴ the constitution and the isomeric ratio can be easily deduced from the ${}^{19}F$ NMR spectra.



Selected NMR spectroscopic data of 3a-i are listed in Table 1 together with the isomeric ratio. In most cases the Z isomer is the expected prevailing one. This is in accordance with the so called *cis* effect³⁵ observed for example in the higher thermodynamical stability of Z-1,2-diffuoro ethene compared to the *E* isomer. In general the *E* isomer is formed in slightly larger amounts if the Grignard reagent is used as the nucleophile suggesting that the isomeric ratio depends more strongly on kinetic effects than thermodynamic stability. As observed earlier, the Z isomer is the dominating one if organo lithium compounds are used.^{32,36}

Reaction of 1 with the dilithio or dimagnesio compounds 4a–c yields an isomeric mixture, ZZ, EZ and EE, of the disocyanide complexes 5a–c, as depicted in Scheme 3. The isomeric ratios have been determined as ZZ : EZ : EE = 51 : 15 : 1 and 5 : 9 : 2 for 5a and 5b, respectively, but can cannot be determined reliably for 5c as the signals of the isomers could not be resolved in the ¹⁹F NMR spectrum. This fact is probably due to the large distances between the two ethenyl groups.

The highly unsaturated diisocyanide complex **6**, in which two difluoroethenyl isocyanide units are connected by one carbon carbon triple bond, has already been obtained earlier by reaction of **1** with tributylstannylethyne and butyllithium.³⁶ In order to create longer chain molecules a different synthetic strategy has to employed. (CO)₅Cr(CN-CF=CF-C=C-C=C-CF=CF-NC)Cr(CO)₅ **7** is formed in high yields by an *Eglington-Glaser* coupling reaction using Hay conditions,³⁷ as presented in Scheme 4.

According to the ¹⁹F NMR spectrum the ZZ-, EZ- and EEisomers are formed in a ratio of 9:3:1. Interestingly, the isomeric ratio is independent from the one of **3c**, even if pure Z-**3c**, which

Table 1 ¹⁹F NMR data of 3a-i

Compound	$\delta(\text{F1})/\delta(\text{F2})$	${}^{3}J({}^{19}\mathrm{F1}{}^{-19}\mathrm{F2})$	Ratio Z/E reagent	Further data
Z-3a	-121.2/-148.2	0	1:2	
E-3a	-138.1/-156.1	117	grignard reagent	
Z-3b	-120.3/-144.0	29.5	20:1	-72.62/-74.29 (CF ₂)
E-3b	-137.45/-153.54	122	lithium reagent	-73.37/-75.53 (CF ₂)
Z-3c	-108 3/-137 8	127	8	
E-3c	-127 4/-147 5			
Z-3d	-112 1/-134 8	3	11.9/9.1	
E-3d	-1282/-1443	127	grignard/lithium	
Z-3e	-110 7/-133 6	0	4.6/9.1	
E-30	_128 4/_143 4	126.0	grignard/lithium	
Z-3f	-126.47 - 145.4 -106.1/-137.9	0	16·1	
E 3f	-100.17 - 137.9 -124.67 - 147.1	126.0	lithium	
Ζ-31	-124.07 - 147.1 -106.67 - 137.8	0	$1 \cdot 5 / 0 \cdot 1$	-64.2 (CE)
Z-3g	-100.07 - 137.8 124.07 - 141.5	126.0	arian ard /lithium	-64.2 (CF ₃)
2-5g	-124.97 - 141.3 108 5 / 120 4	120.0		-04.2 (CF ₃)
Z-3n	-108.37-139.4	0	15.1	$-155.5(\Gamma_0)$
				-137.0 (F _m)
F 31	104 (4, 141 5	100 7	11-1	-144.7 (F _p)
<i>E</i> -3h	-124.6/-141.5	129.7	lithium	$-133.9(F_{o})$
				$-158.2(F_m)$
				$-145.4(F_p)$
Z-3i	-109.6/-142.9	0	36:1	$-63.9 (CF_3)$
E-3i	-128.5/-151.3	122.5	lithium	-63.9 (CF ₃)



Scheme 3



can be obtained by multiple sublimation of 3c, is used as a starting material. Thus, we can conclude that the intermediate compounds formed during the coupling reaction can undergo isomerization of the C–C double bond. All attempts to separate the isomers by chromatography using different eluents and stationary phases failed. In order to stabilize the highly reactive alkynes,

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and to allow a separation of the isomers, **6** and **7** were treated with octacarbonyl dicobalt forming the expected alkyne cluster compounds [$\{\eta^2-\mu_2-(CO)_5Cr(CN-CF=CF-CF=CF-NC)Cr(CO)_5\}Co_2(CO)_6\}$ **8** and [$\{\eta^2-\mu_2-\eta^2-\mu_2-(CO)_5Cr(CN-CF=CF-CC)Cr(CO)_5\}Co_2(CO)_6\}$] **9**, respectively. As can be seen from the ¹⁹F NMR spectra the isomeric ratios are maintained during the reaction and **8** and **9** are again formed as mixture of isomers. Column chromatography on silica allowed at least the enrichment and crystallization of the most abundant *Z*,*Z* isomers of **8** and **9** and the *E*,*Z* isomer of **8**. Again the different isomers can be easily distinguished by the very different ³J(¹⁹F-¹⁹F) coupling constant of the constitutional isomers.

Crystal structures

The crystal and molecular structures of E-3d, Z-3h, Z,Z-8, E,Z-8 and Z,Z-9 were elucidated by single-crystal X-ray diffraction. Selected bond lengths and angles are listed in Table 2 for comparison. ORTEP drawings of the molecules with the atomic numbering scheme are given in Fig. 1, 2, 3 and 4. The crystallographic data for E-3d, Z-3h, Z,Z-11, E,Z-11 and Z,Z-12 are summarised in Table 3.

In all of the complexes studied by single-crystal X-ray crystallography the chromium atom is coordinated almost octahedrally by the five carbonyl ligands and the isocyanide ligand. The Cr–C distances to the carbonyl ligands show only small variations and

Bond/angle	<i>E</i> -3d	Z-3h	<i>Z</i> , <i>Z</i> -8	<i>E</i> , <i>Z</i>-8	Z,Z-9
Cr-C _{trans}	1.909(4)	1.912(3)	1.910(2), 1.904(2)	1.882(6), 1.884(6)	1.905(10)
Cr–C _{cis}	1.900-1.922(4)	1.903-1.926(3)	1.906(2)-1.925(2)	1.883(6)-1.903(6)	1.901(10)-1.911(10)
Cr-C _{isocvanide}	1.931(4)	1.925(3)	1.924(2), 1.931(2)	1.907(6), 1.913(6)	1.936(10)
C=C	1.315(5))	1.313(5)	1.341(2), 1.338(2)	1.309(7), 1.325(7)	1.315(11)
C–F	1.327(5), 1.341(4)	1.338(4), 1.349(4)	1.340(2), 1.342(2), 1.340(2), 1.343(2)	1.325(6), 1.345(6), 1.359(5), 1.352(5)	1.356(9)
C-N-C	176.1(3)	174.8(3)	167.0(2), 168.0(2)	169.5(6), 170.5(5)	158.1(9)
F1-C-N	114.3(3)	113.9(3)	114.7(2), 114.3(1)	114.2(5), 113.2(5)	115.3(8)
F2–C–C	117.8(3)	115.4(3)	116.3(1), 116.8(1)	117.0(4), 116.0(4)	113.7(7)
Co–C			1.934(2), 1.978(2), 1.932(2), 1.980(2)	1.928(5), 1.933(5), 1.931(5), 1.963(5)	1.915(8), 1.975(8),
					1.950(8), 1.963(8)
η^2 -C=C			1.362(2)	1.370(6)	1.353(11)

Table 2 Selected bond lengths (Å) and angles (°) of E-3d, Z-3h, Z,Z-8, E,Z-8, 9

Table 3 Crystallographic data for E-3d, Z-3h, Z,Z-8, E,Z-8, 9

	<i>E</i> -3d	Z-3h	<i>Z</i> , <i>Z</i> -8	<i>E</i> , <i>Z</i> -8	9
Chemical formula	C ₁₃ H ₉ CrF ₂ NO ₅ Si	C ₁₄ CrF ₇ NO ₅	$C_{24}Co_2Cr_2F_4N_2O_{16}$	$C_{24}Co_2Cr_2F_4N_2O_{16}$	$C_{32}Co_4Cr_2F_4N_2O_{22}$
Formula mass	377.30	447.15	870.12	870.12	1180.06
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic	Orthorhombic
a/Å	6.1314(18)	21.850(5)	10.0587(6)	13.6560(10)	13.994(3)
b/Å	11.701(2)	6.184(2)	12.0685(7)	12.1796(9)	11.837(3)
c/Å	23.613(6)	11.752(4)	13.6716(8)	36.970(3)	24.944(6)
$\alpha /^{\circ}$	90.00	90.00	107.4920(10)	90.00	90.00
β/°	93.923(5)	98.566(10)	93.9400(10)	90.00	90.00
$\gamma /^{\circ}$	90.00	90.00	103.9440(10)	90.00	90.00
Unit cell volume/Å ³	1690.1(8)	1570.2(9)	1518.29(15)	6149.0(8)	4131.9(16)
T/K	173(2)	173(2)	193(2)	193(2)	193(2)
Space group	$P2_1/n$	$P2_1/c$	$P\overline{1}$	Pbca	Pbca
No. of formula units per unit cell, Z	4	4	2	8	4
Radiation type	Μο-Κα	Μο-Κα	Μο-Κα	Μο-Κα	Μο-Κα
Absorption coefficient, μ/mm^{-1}	0.788	0.837	1.873	1.850	2.181
No. of reflections measured	19 666	16978	21 046	51 431	32 362
No. of independent reflections	3458	3220	10 576	5439	3671
R _{int}	0.0491	0.0477	0.0214	0.1272	0.0420
Final R_1 values $(I > 2\sigma(I))$	0.0463	0.0405	0.0288	0.0387	0.0666
Final w $R(F^2)$ values $(I > 2\sigma(I))$	0.1094	0.0966	0.0780	0.0606	0.1720
Final R_1 values (all data)	0.0700	0.0634	0.0357	0.0987	0.0772
Final w $R(F^2)$ values (all data)	0.1219	0.1080	0.0821	0.0679	0.1783
Goodness of fit on F^2	1.054	1.021	1.033	1.034	1.224



Fig. 1 Molecular structure (ORTEP⁴⁰) of *E*-3d. Ellipsoids drawn at 50% probability scale.

most importantly the distances show no significant dependence on the position *cis* or *trans* to the isocyanide ligand. The Cr–C distances to the isocyanide carbon atom vary from 1.907 to 1.936



Fig. 2 Molecular structure (ORTEP⁴⁰) of *Z*-**3h**. Ellipsoids drawn at 50% probability scale.

Å with the shortest distances observed for E,Z-8, which also has the shortest Cr–CO distances, probably due to libration effects. The C–C bond lengths of the ethenyl units are in a range observed for C–C double bonds. In all of the cobalt clusters the C–C bond of the coordinated triple bond is lengthened to between 1.353 and 1.370 Å. As in other isocyanide complexes the isocyanide moiety exhibits small deviations from linearity, which are probably due to crystal packing effects.



Fig. 3 Molecular structure (ORTEP⁴⁰) of ZZ-8 and EZ-8. Ellipsoids drawn at 50% probability scale.



Fig. 4 Molecular structure (ORTEP⁴⁰) of *Z*,*Z*-9. Ellipsoids drawn at 50% probability scale. Atom C4i is created by the crystallographic inversion center by the symmetry operation 1 - x, -y, 1 - z.

Conclusion

Using the carbon carbon bond formation at the C–F activated carbon fluorine bond of pentacarbonylchromium stabilized trifluorethenyl isocyanide allows the straightforward synthesis of numerous highly unsaturated isocyanides. If lithium organic compounds are used as nucleophiles the isomers with the fluorine substituents in *cis* position at the double bond are the prevailing one whereas the use of Grignard reagents results in a greater amount of the *trans* configurated compound. There seem to be no limitations in the nature of the nucleophilic reagent. However,

due to the high reactivity of fluorine substituted isocyanides the compounds can only be handled if stabilized at the metal centre. In order to use them, for example, as reagents for multicomponent reactions *in situ*, deprotection strategies need to be developed.

Experimental

General

All reactions were carried out under dry argon by using standard Schlenk 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, ¹⁹F and ¹³C NMR spectra were recorded using a JEOL LAMBDA 400 instrument with TMS or solvent signals (¹H, ¹³C) and CFCl₃ (¹⁹F) as the standards. Infrared spectra were taken on a Shimadzu, Nicolet 5SXC or a Bruker Vector 22 instrument. Raman spectra were obtained on a Varian MAT 711 (80 eV) instrument. Pentacarbonyl(trifluoroethenyl isocyanide)chrom¹² **1**, pentafluorophenyltrimethylsilylethyne,³⁸ 4methoxytetrafluorophenylethyne³⁹ and **3c–e³⁶** were prepared following the literature procedure.

Caution: Some fluoro alkenes like octafluoro-*iso*-butene or hexafluorocyclobutene are extremely toxic.⁴¹ As the toxicity of the compounds described below is unknown one should take care to avoid contact with skin or incorporation of the materials. They should be handled under a well ventilated hood.

3,5-Bis(trifluoromethyl)phenylethynyltrimethylsilane

3,5-Bis(trifluoromethyl)bromobenzene 5.86 g (20 mmol) and triphenylphosphine 100 mg (0.4 mmol) were dissolved in 60 mL of triethylamine and 40 mL of toluene. The reaction mixture was degassed by several freezing, pumping and argon venting cycles. Trimethylsilylethyne 2.16 g (22 mmol), palladium acetate 20 mg (0.09 mmol) and copper iodide 20 mg (0.1 mmol) were added under a stream of argon. The reaction mixture was heated to 80 °C for 12 h. After cooling to ambient temperature the reaction mixture was filtered to remove insoluble by-products. The solvent was removed under vacuum, the residue was dissolved in 100 mL of diethylether, extracted with 100 mL of hydrochloric acid (10%), 100 mL of water, 100 mL of saturated sodium carbonate solution and finally 100 mL of water. The organic phase was dried using magnesium sulfate and the ether was removed under vacuum leaving a yellow oil. Column chromatography on silica using pentane as eluent yielded 3,5-bistrifluoromethylphenylethynyltrimethylsilane (6.05 g, 97%) after removal of the solvent under vacuum as a colourless oil, which solidified to colourless needle shaped crystals after standing for a while, m.p. 44 °C. Further purification is possible by vacuum sublimation (25 °C, 10⁻² mbar) onto a cold finger kept at -20 °C.

¹⁹F NMR (376 MHz, CDCl₃, CFCl₃ intern): δ = -64.0 (s, 6 F, CF₃); ¹H-NMR (CDCl₃, 399.65 MHz): δ = 7.88 (s, 2 H, ArH), 7.79 (s, 1 H, ArH), 0.27 (s, 9 H, Si(CH₃)₃). ¹³C{¹H}-NMR (CDCl₃, 100.4 MHz): δ = 132.0 (qua, ²*J*_{CF} = 34 Hz, 2 C, *i*-*C*_{Ar}-CF₃), 131.9 (qua, ³*J*_{CF} = 3.7 Hz, 2 C, C_{Ar}-H), 125.6 (s, 1 C, *i*-*C*_{Ar}-C≡C), 123.1 (qua, ¹*J*_{CF} = 273 Hz, 2 C, CF₃), 121.8 (qua, ³*J*_{CF} = 3.7 Hz, 1 C,

C_{Ar}-H), 101.5 (s, 1 C, Ar-C≡C), 98.7 (s, 1 C, C≡C-TMS), -0.46 (s, 3 C, Si(CH₃)₃). IR (KBr): v (cm⁻¹) = 3812 w, 3748 w, 3660 w, 3091 m, 3064 w, 2967 s, 2903 m, 2857 w, 2798 w, 2652 w, 2308 w, 2268 w, 2233 w, 2174 m, 2128 w, 2109 w, 2069 m, 2016 w, 1981 w, 1950 w, 1906 w, 1866 w, 1835 w, 1807 w, 1787 w, 1711 w, 1617 m, 1610 m, 1593 w, 1562 w, 1529 w, 1514 w, 1497 vw, 1460 m, 1411 m, 116 s, 1332 w, 1315 w, 1279 s, 1253 s, 1172 vs, 1143 vs, 1108 s, 1068 m, 1001 w, 979 w, 929 s, 914 s, 896 s, 844 vs, 762 s, 732 m, 700 s, 684 s, 654 m, 632 w, 623 w, 598 vw, 571 w, 559 w, 532 w, 509 vw, 431 m, 416 m, 406 w. IR (Pentan): $v (cm^{-1}) = 1463 s, 1377 m$, 1279 s, 1148 s, 930 m, 899 w, 846 m, 733 w, 700 w, 684 m, 668 m; Raman: v_{shift} (cm⁻¹) = 3090 w, 2965 w, 2902 m, 2173 vs, 2129 w, 1611 m, 1412 w, 1376 m, 1265 w, 1211 m, 1186 w, 1132 w, 1107 w, 1000 s, 844 w, 760 w, 732 m, 701 w, 655 s, 630 m, 598 m, 531 w, 417 m, 348 w, 311 w, 295 w, 277 m, 212 m, 182 m, 152 s, 107 vs. MS (EI, 80 eV): m/z = 310 (M⁺, 10.7%), 297 (M⁺ – CH, 5.1%), 296 $(M^+ - CH_2, 18.6\%), 295 (M^+ - CH_3, 100\%), 291 (M^+ - F, 4.6\%),$ $265 (M^{+} - 3 CH_3, 4.3\%), 219 (4.3\%), 214 (5.6\%), 155 (4.6\%), 147$ (5.1%), 138 (4.0%), 113 (4.0%), 77 (5.5%), 73 (Si(CH₃)₃, 9.4%), 43 (SiCH₃, 5.6%), 28 (²⁸Si, 12.0%).

3,5-Bis(trifluoromethyl)phenylethyne 2g

A solution of 3,5-bistrifluoromethylphenylethynyltrimethyl-silane in a 1:1 mixture of THF and methanol was treated with a 0.1 M aqueous sodium hydroxide solution in water. The progress of the reaction was followed by TLC. The reaction was complete after about 1 h. After addition of about the same amount of water the product was extracted into diethylether. After drying of the organic phase with MgSO₄ the solvent was removed under vacuum leaving 3,5-bis(tri-fluoromethyl)phenylethyne as a colourless oil in almost quantative yield. The product turned red after a short period of time at ambient temperature due to decomposition and was used immediately without further characterization.

Pentacarbonyl(1,2-difluorobuta-1,3-dienylisocyanide)-chromium (3a)

Ethenylmagnesiumbromide (1 M in THF) 2 mL (2 mmol) were diluted by 30 mL of THF, the solution was cooled to -10 °C and pentacarbonyl(trifluoroethenyl isocyanide)chromium 1 was added. The reaction mixture was allowed to warm to ambient temperature with stirring. After an additional 30 min 50 mL of *n*-pentane was added to the brown clear solution, which was filtered through a thin pad of silica. ¹⁹F NMR analysis indicated a quantitative conversion and an isomeric ratio of E/Z = 2/1. The solvent volume was reduced to about 10 mL under vacuum keeping the solution below -10 °C. The residue was transferred into sublimation apparatus, remaining solvent was removed under vacuum (10^{-3} mbar) at ambient temperature yielded **3a** as a pale yellow solid (75–80%), which melts above -20 °C forming a yellow oil. The product readily polymerizes on further warming.

¹⁹F NMR (376 MHz, CDCl₃, CFCl₃ intern): (*E*)-Isomer: δ = -138.1 (d, ³*J*_{FF} = 117 Hz, 1F, (*E*)-CF=CF-CH=CH₂), -156.1 (dd, ³*J*_{HF} = 25 Hz, ³*J*_{FF} = 117 Hz, 1F, (*E*)-CF=CF-CH=CH₂); (*Z*)-Isomer: δ = -121.2 (s, 1F, (*Z*)-CF=CF-CH=CH₂), -148.2 (d, ³*J*_{HF} = 25 Hz, 1F, (*Z*)-CF=CF-CH=CH₂); ¹H NMR (400 MHz, CDCl₃): (*E*)-Isomer: δ = 6.53–6.38 (dddd, ⁴*J*_{HF} = 3.6 Hz,

 ${}^{3}J_{\rm HH} = 11.5$ Hz, ${}^{3}J_{\rm HH} = 17.4$ Hz, ${}^{3}J_{\rm HF} = 26.1$ Hz, 1 H, CH= CH₂), $5.73 (dd, {}^{2}J_{HH} = 1.8 Hz, {}^{3}J_{HH} = 17.4 Hz, 1 H, CH = CH_{2}), 5.47 (ddd,$ ${}^{2}J_{\rm HH} = 1.8$ Hz, ${}^{4}J_{\rm HF} = 3.6$ Hz, ${}^{3}J_{\rm HH} = 11.5$ Hz, 1 H, CH=CH₂); (Z)-Isomer: $\delta = 6.36-6.22$ (dddd, ${}^{4}J_{\rm HF} = 1.8$ Hz, ${}^{3}J_{\rm HH} = 11.4$ Hz, ${}^{3}J_{\rm HH} = 17.2$ Hz, ${}^{3}J_{\rm HF} = 24.6$ Hz, 1 H, CH=CH₂), 5.83 (dd, ${}^{2}J_{\rm HH} =$ 1.8 Hz, ${}^{3}J_{HH} = 17.2$ Hz, 1 H, CH=CH₂), 5.58 (dd, ${}^{2}J_{HH} = 1.8$ Hz, ${}^{3}J_{\text{HH}} = 11.4$ Hz, 1 H, CH=CH₂); ${}^{13}C{}^{1}H$ -NMR (100.4 MHz, $CDCl_3$): (E)-Isomer: $\delta = 214.6$ (s, 1 C, CO_{trans}), 213.1 (s, 4 C, CO_{cis}), 197.3 (s, 1 C, CN), 146.6 (dd, ${}^{1}J_{CF} = 248$ Hz, ${}^{2}J_{CF} = 51$ Hz; 1 C, CF=CF-CH=CH₂), 128.7 (dd, ${}^{1}J_{CF} = 254$ Hz, ${}^{2}J_{CF} = 43$ Hz, 1 C, CF=CF-CH=CH₂), 121.1 (dd, ${}^{2}J_{CF} = 19.0$ Hz, ${}^{3}J_{CF} = 5.4$ Hz, 1 C, CH=CH₂), 118.6 (dd, ${}^{3}J_{CF} = 5.3$ Hz, ${}^{4}J_{CF} = 3.7$ Hz, 1 C, CH= CH_2); (Z)-Isomer: $\delta = 214.3$ (s, 1 C, CO_{trans}), 213.0 (s, 4 C, CO_{cis}), 195.9 (s, 1 C, CN), 144.0 (dd, ${}^{1}J_{CF} = 254$ Hz, ${}^{2}J_{CF} = 25$ Hz; 1 C, CF=CF-CH=CH₂), 127.2 (dd, ${}^{1}J_{CF} = 254$ Hz, ${}^{2}J_{CF} = 43$ Hz, 1 C, CF=CF-CH=CH₂), 121.3 (dd, ${}^{2}J_{CF} = 19.2$ Hz, ${}^{3}J_{CF} = 2.7$ Hz, 1 C, CF=CF-CH=CH₂), 120.4 (dd, ${}^{3}J_{CF} = 12.8$ Hz, ${}^{4}J_{CF} =$ 3.7 Hz, 1 C, CF=CF-CH= CH_2); IR (Pentan): v (cm⁻¹) = 657 m, 1379 m, 1946 w, 1977 vs, 2019 m.

Pentacarbonyl(1,2,4,4-tetrafluorobuta-1,3-dienyl isocyanide)chromium (3b)

A 250 mL Schlenk flask was charged with 10 mL of diethylether and 10 mL of THF. After several freezing and pumping cycles under cooling with liquid nitrogen 1.2 mmol of 1,1-difluoroethene were condensed to this mixture. After warming to -100 °C the flask was flushed with argon. 1 mL of *t*-butyllithium (1.5 M in hexane) was added dropwise using a syringe. The colourless solution turned yellow. After 0.5 h 300 mg (1 mmol) of **1** was added and the reaction mixture was allowed to warm to ambient temperature within 1 h. After filtration through a thin layer of silica the solvent was removed of under vacuum at -20 °C. Preparative thin layer chromatography on silica using pentane as an eluent yielded **3b** in the first fraction. After removal of the solvent 200 mg (58%) of **3b** (isomeric mixture Z: E = 20:1) is obtained as viscous yellow oil, which can be further purified by distillation under vacuum (10^{-2} mbar) at ambient temperature onto a cold finger cooled to -20 °C.

¹⁹F-NMR (376 MHz, CDCl₃, CFCl₃ intern): (Z)-Isomer: δ = -72.35 (dddd, ${}^{2}J_{FF} = 30.6$ Hz, ${}^{3}J_{HF} = 22.1$ Hz, ${}^{5}J_{FF} = 8.8$ Hz, ${}^{4}J_{FF} =$ 2.0 Hz, 1 F, CF=CF-CH=CF₂), -73.70 (d, ${}^{2}J_{FF}$ = 29.6 Hz, 1 F, CF=CF-CH=CF₂), $-120.31(dd, {}^{3}J_{FF} = 29.5 Hz, {}^{5}J_{FF} = 8.8 Hz,$ 1 F, CF=CF-CH=CF₂), -143.95 (ddd, ${}^{3}J_{FF} = 29.5$ Hz, ${}^{3}J_{HF} =$ 19.5 Hz, ${}^{4}J_{FF} = 2.0$ Hz, 1 F, CF=CF-CH=CF₂); (*E*)-Isomer: $\delta =$ -73.01 (dddd, ${}^{2}J_{FF} = 32.9$ Hz, ${}^{3}J_{HF} = 22.3$ Hz, ${}^{5}J_{FF} = 11.5$ Hz, ${}^{4}J_{FF} = 1.8$ Hz, 1 F, CF=CF-CH=CF₂), -74.72 (d, ${}^{2}J_{FF} = 32.9$ Hz, 1 F, CF=CF-CH=CF₂), -137.45 (dddd, ${}^{3}J_{FF} = 122.0$ Hz, $J_{FF} =$ 22.4 Hz, ${}^{5}J_{FF} = 11.6$ Hz, ${}^{4}J_{HF} = 2.3$ Hz, 1 F, CF=CF-CH=CF₂), -153.54 (dddd, ${}^{3}J_{FF} = 122.0$ Hz, $J_{FF} = 31.4$ Hz, ${}^{3}J_{HF} = 23.7$ Hz, ${}^{4}J_{\text{FF}} = 1.8$ Hz, 1 F, CF=CF-CH=CF₂). ¹H-NMR (400 MHz, CDCl₃): (Z)-Isomer: δ = 5.04 (m, J_{HF} = 20.8 Hz, J_{HF} = 1.2 Hz, 1 H); (*E*)-Isomer: $\delta = 5.20$ (m, $J_{\rm HF} = 21.3$ Hz, 1 H); ${}^{13}C{}^{19}F{}-NMR$ $(100.4 \text{ MHz}, \text{CDCl}_3)$: (Z)-Isomer: $\delta = 214.0 \text{ (s, 1 C, CO}_{trans}), 212.9$ (s, 4 C, CO_{cis}), 197.0 (s, 1 C, CN), 138.5 (CF=CF-CH=CF₂), 128.1 (CF=CF-CH=CF₂), 72.6 (CF=CF-CH=CF₂), 70.90 (CF=CF-CH=CF₂); IR (CH₂Cl₂): v (cm⁻¹) = 2115 w, 2023 m, 1970 vs, 1781 w, 1733 m, 1390 w, 1149 w, 841 w, 657 s. Raman: v_{shift} (cm⁻¹) = 198 w, 260 w, 385 vs, 433 m, 550 w, 580 w, 614 w, 666 w, 762 w, 841 w, 930 w, 1062 w, 1149 w, 1236 w, 1261 m, 1311

w, 1374 w, 1621 w, 1672 m, 1733 m, 2008 s, 2114 m. MS (EI, 80 eV, 30 °C): m/z (%) = 343 (12) [M⁺], 315 (1.3) [M⁺ – CO], 287 (4) [M⁺ – 2 CO], 259 (2) [M⁺ – 3 CO], 247 (4), 231 (12) [M⁺ – 4 CO], 203 (58) [M⁺ – 5 CO], 106 (10), 90 (4), 81 (15), 79 (15), 75 (10), 71 (26), 63 (11), 53 (11) [⁵³Cr], 52 (100) [⁵²Cr], 50 (6). Elemental analysis calcd for C₁₀HCrF₄NO₅ (342.9): C 35.01, H 0.29, N 4.08; found: C 34.72, H 0.00, N 5.07%.

Pentacarbonyl(2,3,5,6-tetrafluoro-4-methoxyphenyl)but-1-en-3ynylisocyanid)chromium (3f)

204 mg (1.0 mmol) *para*-Methoxytetrafluorophenyl-acetylen **2f** were dissolved in 10 mL of diethylether. 0.4 mL (1.0 mmol) of nbutyllithium (2.5 M in n-hexane) were added at -78 °C. After one hour at -78 °C 300 mg (1.0 mmol) of **1** dissolved in a minimum amount of diethylether was added and the solution was allowed to warm to ambient temperature and stirred for additional 15 min. After filtration over a plug of silica an intense yellow solution was obtained, which was concentrated and purified by TLC yielding 220 mg (46%) of **3f** as a yellow, microcrystalline solid, mp. 52–53 °C and an isomeric ratio of **3f** (*Z*): **3f** (*E*) = 16:1.

¹⁹F-NMR (CDCl₃, CFCl₃ intern, 376.0 MHz): (Z)-Isomer: δ = -106.07 (s, 1 F, (Z)-CF=CF), -137.86 (s, 1 F, (Z)-CF=CF), -136.14 (m, 2 F, Ar–F), -157.63 (m, 2 F, Ar–F); (E)-Isomer: $\delta =$ -124.59 (d, ${}^{3}J_{FF} = 126$ Hz, 1 F, (E)-CF=CF-C), -147.12 (d, ${}^{3}J_{FF} =$ 126 Hz, 1 F, (E)-CF=CF-C), -136.28 (m, 2 F, Ar-F), -157.70 (m, 2 F, Ar–F). ¹H-NMR (CDCl₃, 399.65 MHz): $\delta = 4.10$ (s, 3 H, CH₃– O). IR (Lösung): v (CH₂Cl₂) = 1498 m, 1506 m, 1972 vs, 2015 m. Raman: v_{shift} (cm⁻¹) = 2214 s, 2112 m, 2017 s, 2008 m, 1971 m, 1950 w, 1662 m, 1644 s, 1456 w, 1428 w, 1339 w, 1290 m, 1257 s, 1197 w, 1148 w, 1096 w, 981 w, 907 w, 731 w, 657 w, 601 m, 564 w, 529 w, 425 m, 385 vs, 233 w, 159 m, 111 s. MS (EI, 80 eV, 50 °C): m/z = 483 (M⁺, 65.3%), 427 (M⁺ - 2 CO, 11.7%), 399 (M⁺ - 3 CO, 30.5%), 371 (M⁺ - 4 CO, 39.9%), 343 (M⁺ - 5 CO, 100%), 291 (M⁺ – ⁵²Cr(CO)₅, 1.2%), 253 (CH₃O–C₆F₄–C=C–NC, 31.2%), 238 ([253]⁺ - CH₃, 8.2%)), 225 ([253]⁺ - CO, 13.4%), 223 $([253]^+ - CH_2O, 11.5\%), 210 ([238]^+ - CO, 7.6\%), 204 (5.0\%), 69$ (3.0%), 52 (52 Cr, 11.5%). High resolution MS; calcd: 482.92697, found: 482.92477.

Pentacarbonyl(1,2-difluoro-4-(3,5-bis(trifluoromethyl)-phenyl)but-1-en-3-ynylisocyanid)chromium (3g)

(a) using the Grignard reagent:

240 mg (1.0 mmol) of 3,5-bis(trifluormethyl)phenylacetylen **2g** were dissolved in 10 mL of THF and 0.4 mL (1.0 mmol) of a methylmagnesiumbromide solution (2.5 M in THF) was added at ambient temperature. After 3 h 300 mg (1.0 mmol) of **1** dissolved in diethylether was added and stirred for 15 min at ambient temperature. After filtration over a plug of silica the solvent was removed under vacuum The compound was purified by TLC on silica yielding 300 mg (58%) of **3g** as a yellow oil with an isomeric ratio of **3g** (*Z*): **3g** (*E*) = 1:05.

b) using the lithium reagent:

240 mg (1.0 mmol) of **2g** was dissolved in 10 mL of diethylether and 0.4 mL (1.0 mmol) of n-butyl lithium (2.5 M in n-hexane) was added at -78 °C. After 1h 300 mg (1.0 mmol) of **1** in diethylether was added. The reaction mixture was allowed to warm to ambient temperature. A work-up as decribed above yielded 340 mg (66%) of **3g** with an isomeric ratio of **3g** (*Z*): **3g** (*E*) = 9:1.

¹⁹F-NMR (CDCl₃, CFCl₃ intern, 376.0 MHz): (Z)-Isomer: δ = -64.19 (s, 6 F, CF₃), -106.37 (s, 1 F, (Z)-CF=CF-C), -137.76 (s, 1 F, (Z)-CF=CF-C); (E)-Isomer: $\delta = -64.11$ (s, 6 F, CF₃), -124.92 (d, ${}^{3}J_{\text{FF}} = 126$ Hz, 1 F, (E)-CF=CF-C), -147.42 (d, ${}^{3}J_{\text{FF}} = 126$ Hz, 1 F, (E)-CF=CF-C). ¹H-NMR (CDCl₃, 399.65 MHz): (Z)-Isomer: $\delta = 7.97$ (s, 2 H, *o*-ArH), 7.94 (s, 1 H, *p*-ArH); (*E*)-Isomer: $\delta = 8.00$ (s, 2 H, *o*-ArH), 7.95 (s, 1 H, *p*-ArH). ¹³C{¹H, ¹⁹F}-NMR (CDCl₃, 100.4 MHz): (Z)-Isomer: $\delta = 213.43$ (s, 1 C, CO_{trans}), 212.85 (s, 4 C, CO_{cir}), 197.74 (s, 1 C, CN), 134.54, 132.65, 131.64, 128.87, 124.06, 123.76, 122.46, 121.34, 100.43; (E)-Isomer: δ = 213.75 (s, 1 C, CO_{trans}), 212.66 (s, 4 C, CO_{cis}), 191.19 (s, 1 C, CN), 136.1, 132.65, 131.36, 125.61, 123.73, 122.81, 104.01. IR (CH₂Cl₂): $v (\text{cm}^{-1}) = 1085 \text{ m}, 1145 \text{ s}, 1177 \text{ s}, 1392 \text{ m}, 1960 \text{ vs}, 2015 \text{ m}.$ Raman: v_{shift} (cm⁻¹) = 2216 s, 2114 m, 2021 m, 2006 m, 1999 m, 1967 w, 1674 m, 1615 w, 1391 w, 1317 w, 1271 m, 1181 m, 1082 w, 999 m, 906 w, 742 w, 702 w, 656 w, 626 w, 610 m, 579 w, 562 w, 530 w, 499 w, 455 w, 430 m, 389 vs, 326 w, 302 w, 278 w, 235 m, 150 m, 127 s, 109 vs. MS (EI, 80 eV): m/z = 517 (M⁺, 19.3%), 474 (61.3%), 461 (M⁺ - 2 CO, 5.4%), 433 (M⁺ - 3 CO, 9.3%), 405 (M⁺ -4 CO, 20.7%), 377 (M⁺ -5 CO, 89.3%), 325 (M⁺ -5^{2} Cr(CO)₅, 5.9%), 287 (66.4%), 268 (22.1%), 237 ((CF_3)₂C₆H₃C₂, 13.8%), 218 (16.0%), 213 ((CF₃)₂C₆H₃, 3.4%), 192 (⁵²Cr(CO)₅, 3.8%), 159 (22.0%), 155 (22.1%), 108 (⁵²Cr(CO)₂, 6.8%), 80 (⁵²Cr(CO), 21.0%), 78 (15.9%), 71 (16.7%), 52 (⁵²Cr, 100%), 43 (10.3%), 28 (56.9%). High resolution MS; calcd: 516.92883, found: 516.92749.

Pentacarbonyl(1,2-difluor-2-pentafluorophenyl)ethenylisocyanide)chromium (3h)

170 mg (0.7 mmol) of pentafluorbrombenzol were dissolved in 20 mL of diethylether and cooled to -78 °C and 0.45 mL (0.7 mmol) of *n*-Butyllithium (1.6 M in hexane) were added. After stirring for 1 h at -78 °C 200 mg (0.67 mmol) of **1** dissolved in a minimum amount of diethylether was added. The reaction mixture was allowed to warm to ambient temperature and stirred for 1h. After filtration over a plug of silica the solvent was removed under vacuum at -20 °C. The yellow residue was purified by chromatography on silica using pentane as eluent. Yield 230 mg (73%) of **3h** with an isomeric ratio of **3h** (*Z*): **3h** (*E*) = 13:1. Crystallization from n-pentane gave pure **Z**-**3h** as yellow platelet crystals, mp. 48–49 °C.

¹⁹F-NMR (CDCl₃, CFCl₃ intern, 376.0 MHz): (Z)-Isomer: δ = -108.5 (s, 1 F, (Z)-CF=CF-C), -130.4 (dt, 1 F, ${}^{4}J_{FF} = 8.5$ Hz, ${}^{6}J_{\text{FF}} = 2.5 \text{ Hz}, (Z)\text{-CF}=CF-C), -133.5 (m, 2 \text{ F}, {}^{4}J_{\text{FF}} = 8.5 \text{ Hz},$ ${}^{4}J_{FF} = 3.1$ Hz, Ar–F_{ortho}), -144.7 (dt, 1 F, ${}^{3}J_{FF} = 21.0$ Hz, ${}^{6}J_{FF} =$ 2.5 Hz, Ar-F_{para}), -157.6 (m, 2 F, ${}^{3}J_{FF} = 21.0$ Hz, ${}^{3}J_{FF} = 8.7$ Hz, Ar– F_{meta}); (E)-Isomer: $\delta = -124.6$ (dt, ${}^{3}J_{FF} = 129.7$ Hz, ${}^{5}J_{FF} = 14.0$ Hz, 1 F, (*E*)-CF=CF-C), -133.9 (m, ${}^{5}J_{FF} = 14.0$ Hz, ${}^{4}J_{FF} = 8.3$ Hz, 2 F, Ar– F_{ortho}), -141.5 (ddt, ${}^{3}J_{FF} = 129.7$ Hz, ${}^{4}J_{FF} = 8.3$ Hz, ${}^{5}J_{FF} = 2.5 \text{ Hz}, 1 \text{ F}, (E) \text{-CF} = CF - C), -145.4 (dt, {}^{3}J_{FF} = 20.8 \text{ Hz}, 1 \text{ F},$ Ar– F_{para}), –158.2 (m, ${}^{3}J_{FF}$ = 20.8 Hz, ${}^{3}J_{FF}$ = 9.5 Hz, ${}^{5}J_{FF}$ = 2.5 Hz, 2 F, Ar- F_{meta}). ¹³C{¹⁹F}-NMR (CDCl₃, 100.4 MHz): (Z)-Isomer: $\delta = 212.6$ (s, 1 C, CO_{trans}), 212.5 (s, 4 C, CO_{cis}), 197.4 (s, 1 C, CN), 144.7, 143.8, 138.0, 133.3, 130.8, 102.8; (*E*)-Isomer: $\delta = 213.6$ (s, 1 C, CO_{trans}), 213.2 (s, 4 C, CO_{cis}), 201.0 (s, 1 C, CN), 144.3, 143.6, 137.9, 135.3, 130.9, 102.6. IR (KBr): v (cm⁻¹) = 3423 w, 2970 vw, 2930 w, 2120 m, 2041 s, 2007 m, 1997 m, 1931 vs, 1696 m, 1651

w, 1526 m, 1499 m, 1437 w, 1388 vw, 1344 w, 1278 m, 1233 m, 1153 w, 1128 m, 1045 w, 1033 vw, 1021 vw, 990 m, 830 m, 783 w, 737 vw, 683 m, 645 s, 593 w, 581 w, 534 w, 497 w, 444 m, 430 m. IR (CH₂Cl₂): v (cm⁻¹) = 2120 w, 2019 m, 1972 vs, 1708 w, 1651 w, 1524 m, 1505 m, 1439 w, 1348 w, 1281 w, 1269 vs, 1260 vs, 1232 m, 1126 m, 995 m, 828 m. Raman: v_{shift} (cm⁻¹) = 2118 m, 2051 m, 2016 m, 1997 vs, 1953 m, 1695 m, 1651 w, 1526 vw, 1435 w, 1342 vw, 1275 m, 1231 w, 829 vw, 651 w, 637 w, 592 w, 581 w, 527 w, 497 w, 452 w, 431 w, 388 s, 366 w, 297 w, 228 w, 211 w, 196 w, 171 w, 110 vs. MS: (80 eV, EI, 60 °C): m/z = 447 (M⁺, ⁵²Cr, 15.5%), 419 (M⁺ - CO, ⁵²Cr, 2.0%), 391 (M⁺ - 2 CO, ⁵²Cr, 6.3%), 363 (M⁺ - 3 CO, ⁵²Cr, 9.6%), 335 (M⁺ - 4 CO, ⁵²Cr, 21.1%), 308 (M⁺ - 5 CO, ⁵³Cr, 20.6%), 307 (M⁺ - 5 CO, ⁵²Cr, 100%), 255 (M⁺ - ⁵²CrCO₅, 7.5%), 186 (C₇F₄CN, 6.4%), 160 (C₇F₄, 6.0%), 148 (C₆F₄, 9.2%), 80 (52 CrCO, 8.7%), 78 (7.0%), 53 (53 Cr, 7.9%), 52 (52 Cr, 76.5%), 32 (7.9%). High resolution MS: calcd: 446.90698, found: 446.90733.

Pentacarbonyl(1,2-difluor-2-(3,5-bistrifluoromethylphenyl)ethenylisocyanid)chromium (3i)

3i was prepared analogously to **3h**. The product was purified by TLC on silica using pentane as eluent. Yield 230 mg (58%) as a yellow oil with an isomeric ratio of **3i** (Z) : **3i** (E) = 36 : 1.

¹⁹F-NMR (CDCl₃, CFCl₃ intern, 376.0 MHz): (Z)-Isomer: δ = -63.9 (s, -CF₃, 6 F), -109.6 (s, 1 F, (Z)-CF=CF-C), -142.9 (s, 1 F, (Z)-CF=CF-C), (E)-Isomer: $\delta = -63.9$ (s, -CF₃, 6 F), -128.5 (d, ${}^{3}J_{\text{FF}} = 122.5 \text{ Hz}, 1 \text{ F}, (E)-CF=CF-C), -151.3 \text{ (d, }{}^{3}J_{\text{FF}} = 122.5 \text{ Hz},$ 1 F, (E)-CF=CF-C). ¹H-NMR (CDCl₃): (Z)-Isomer: $\delta = 8.10$ (s, 2 H, *o*-Ar–H), 7.95 (s, 1 H, *p*-Ar–H); (*E*)-Isomer: δ = 8.19 (s, 2 H, o-Ar-H), 8.02 (s, 1 H, p-Ar-H). ¹³C{¹H, ¹⁹F}-NMR (CDCl₃, 100.4 MHz): (Z)-Isomer: δ = 212.8 (s, 1 C, CO_{trans}), 212.4 (s, 4 C, CO_{cis}), 201.3 (s, 1 C, CN), 141.5, 133.4, 132.9, 129.2, 123.5, 121.4, 118.7; (E)-Isomer: $\delta = 213.8$ (s, 1 C, CO_{trans}), 213.2 (s, 4 C, CO_{cis}), 201.3 (s, 1 C, CN), 144.6, 132.8, 129.5, 121.8, 118.5. IR (KBr): v $(cm^{-1}) = 3965 w, 3441 w, 3102 w, 2964 m, 2928 w, 2857 vw, 2778$ vw, 2670 w, 2548 w, 2440 w, 2361 w, 2267 w, 2242 vw, 2117 m, 2026 s, 1981 vs, 1947 vs, 1681 m, 1621 m, 1532 vw, 1514 w, 1470 m, 1452 w, 1434 vw, 1392 s, 1347 w, 1324 w, 1280 vs, 1255 vs, 1187 s, 1141 s, 1110 m, 1018 m, 947 w, 901 s, 848 m, 806 s, 757 vw, 740 w, 719 s, 700 m, 684 s, 653 vs, 622 s, 588 w, 561 vw, 531 w, 517 w, 498 w, 440 s, 420 m. Raman: v_{shift} (cm⁻¹) = 2114 w, 2011 m, 1955 w, 1680 m, 1620 w, 1390 m, 1299 w, 1250 m, 1001 w, 718 w, 657 w, 621 w, 433 w, 383 vs, 314 w, 213 w, 154 m. MS (EI, 80 eV): m/z =493 (M⁺, 3.8%), 437 (M⁺ - 2 CO, 5.1%), 409 (M⁺ - 3 CO, 6.2%), $381 (M^+ - 4 CO, 17.5\%), 353 (M^+ - 5 CO, 60.8\%), 333 (12.3\%),$ 301 (5.0%), 282 (3.7%), 263 (100%), 244 (10.2%), 194 (12.3%), 80 (5.1%), 52 (⁵²Cr, 24.3%). High resolution MS; calcd: 492.92886, found: 492.92799.

Decacarbonyl(1,4-bis(1,2-difluoro-2-isocyanoethenyl)benzene)dichromium (5a)

To 240 mg (1.0 mmol) of 1,4-Dibrombenzol 4a in 10 mL of diethylether were added 2 equivalents of n-butyllithium (2.6 mL, 1.6 M in hexane) at -78 °C. After 1 h 600 mg (2.0 mmol) of 1 dissolved in diethylether was added. The reaction mixture was allowed to warm to ambient temperature. After filtration through a plug of silica and purification by TLC 5a was obtained as a mixture of the possible isomers in a ratio of 5a (ZZ): 5a (EZ): 5a

(EE) = 51:15:1. Yield 413 mg. (63%) as a yellow solid, mp. 86–87 $^{\circ}\mathrm{C}.$

¹⁹F-NMR (CDCl₃, CFCl₃ intern, 376.0 MHz): (ZZ)-Isomer: δ = -119.7 (s, 2 F, (Z)-CF=CF-C), -139.1 (s, 2 F, (Z)-CF=CF-C); (EZ)-Isomer: $\delta = -119.8$ (s, 1 F, (Z)-CF=CF-C), -134.8 (d, ${}^{3}J_{FF} =$ 126 Hz, 1 F, (E)-CF=CF-C), -139.1 (s, 1 F, (Z)-CF=CF-C), -150.7 (d, ${}^{3}J_{FF} = 126$ Hz, 1 F, (*E*)-CF=C*F*-C); (*EE*)-Isomer: $\delta =$ -112.6 (d, ${}^{3}J_{FF} = 126$ Hz, 2 F, (E)-CF=CF-C), -157.6 (d, ${}^{3}J_{FF} =$ 126 Hz, 2 F, (E)-CF=CF-C). ¹H-NMR (CDCl₃, 399.65 MHz): $\delta = 7.75 - 7.50$ (m, 4 H, Ar-H). ¹³C{¹H, ¹⁹F}-NMR (CDCl₃, 100.4 MHz): $\delta = 216.02, 214.31 (CO_{trans}), 214.07, 212.81 (CO_{cis}), 179.60$ (CN), 158.47, 155.99 (CF=CF-C), 132.32, 130.75 (CF=CF-C), 127.99, 127.30, 126. 69, 126.62, 114.75, 114.24 (C_{Ar}). IR (KBr): v (cm⁻¹) = 3420 w, 2967 w, 2935 w, 2867 w, 2133 m, 2116 w, 2048 s, 2030 w, 2003 w, 1947 vs, 1934 vs, 1667 w, 1511 w, 1460 w, 1435 w, 1409 w, 1379 w, 1320 w, 1304 w, 1275 w, 1254 m, 1218 w, 1159 w, 1149 w, 1131 w, 1117 w, 1082 w 1018 vw, 968 w, 946 vw, 894 w, 841 m, 832 w, 788 w, 752 w, 680 m, 651 s, 620 w, 599 w, 511 w, 479 w, 446 m. IR (CH₂Cl₂): v (cm⁻¹) = 2115 w, 2050 m, 2023 w, 1963 s, 655 m. Raman: v_{shift} (cm⁻¹) = 109 vs, 165 w, 224 w, 257 w, 287 w, 343 w, 389 s, 417 w, 450 m, 473 w, 502 w, 534 w, 581 w, 607 w, 628 w, 666 w, 730 w, 741 w, 828 w, 973 w, 1074 w, 1128 w, 1189 s, 1203 m, 1217 w, 1257 m, 1285 w, 1298 w, 1306 m, 1332 w, 2936 w.

MS (EI, 80 eV, 90 °C): m/z = 636 (M⁺, 11%), 572 (26%), 534 (7%), 524 (M⁺ - 4 CO, 3%), 516 (11%), 496 (M⁺ - 5 CO, 19%), 488 (9%), 460 (15%), 440 (M⁺ - 7 CO, 8%), 432 (20%), 412 (M⁺ - 8 CO, 23%), 384 (M⁺ - 9 CO, 20%), 380 (31%), 356 (M⁺ - 10 CO, 25%), 304 (11%), 220 (11%), 178 (8%), 145 (12%), 108 (18%), 80 (34%), 53 (12%), 52 (100%), 41 (8%).

Decacarbonyl(1,4-bis(1,2-difluoro-2-isocyanoethenyl)-2,3,5,6-tetrafluorobenzene)dichromium (5b)

Using **4b** in a procedure as described above yields **5b**, 404 mg (57%) as a yellow microcrystalline solid in an isomeric ratio of **5b** (*ZZ*): **5b** (*EZ*): **5b** (*EE*) = 5:9:2, mp. 166 °C (dec.).

¹⁹F-NMR (CDCl₃, CFCl₃ intern, 376.0 MHz): (ZZ)-Isomer: $\delta =$ -107.9 (s, 2 F, (Z)-CF=CF-C), -133.7 (s, 4 F, Ar-F), -134.7 (s, 2 F, (Z)-CF=CF-C); (EZ)-Isomer: $\delta = -108.5$ (s, 1 F, (Z)-CF=CF-C), -123.6 (dt, ${}^{5}J_{FF} = 15$ Hz, ${}^{3}J_{FF} = 128$ Hz, 1 F, (*E*)-CF=CF-C), -134.1 (s, 1 F, (Z)-CF=CF-C), -145.7 (dt, ${}^{4}J_{FF} = 9$ Hz, ${}^{3}J_{FF} = 128$ Hz, 1 F, (E)-CF=CF-C), -134.0 (m, 4 F, Ar-F); (EE)-Isomer: $\delta = -123.8 \,(dt, {}^{5}J_{FF} = 16 \,\text{Hz}, {}^{3}J_{FF} = 128 \,\text{Hz}, 2 \,\text{F}, (E) - CF = CF - C),$ -145.4 (d, ${}^{3}J_{FF} = 128$ Hz, 2 F, (*E*)-CF=CF-C), -134.2 (s, 4 F, Ar-F). ¹³C{¹⁹F}-NMR (CDCl₃, 100.4 MHz): (ZZ)-Isomer: δ = 213.3 (s, 2 C, CO_{trans}), 212.5 (s, 8 C, CO_{cis}), 198.9 (s, 2 C, CN), 144.3 (s, 2 C, (Z)-CF=CF-C), 133.4 (s, 2 C, (Z)-CF=CF-C), 110.7 (s, 4 C, C_{Ar}–F), 110.2 (s, 2 C, *i*-C); (*EZ*)-Isomer: δ = 213.0, 212.9 (s, 1 C, CO_{trans}), 212.4, 212.3 (s, 4 C, CO_{cis}), 202.4, 198.4 (s, 1 C, CN), 144.0, 143.8, 133.0, 130.9, (s, 1 C, CF=*C*F–C), 110.6, 110.3 (s, 2 C, C_{Ar}–F), 110.0, 109.8 (s, 1 C, *i*-C). IR (KBr): v (cm⁻¹) = 3421 m, 3220 w, 2961 vw, 2924 w, 2853 w, 2117 m, 2008 s, 1945 vs, 1698 w, 1496 m, 1473 m, 1346 w, 1274 m, 1186 m, 1119 w, 1066 w, 984 m, 874 w, 797 m, 651 s, 531 w, 444 m, 427 w. IR (CH_2Cl_2) : v (cm⁻¹) = 2017 w, 1974 s, 1604 w, 1495 w, 1425 w, 897 w. Raman: v_{shift} (cm⁻¹) = 1580 w, 1649 s, 1695 s, 1943 w, 1956 m, 1999 s, 2015 m, 2047 w, 2115 m. MS (EI, 80 eV, 80 °C): m/z = 708 $(M^+, 18\%), 624 (M^+ - 3 CO, 1.2\%), 596 (M^+ - 4 CO, 7\%), 568 (M^+)$ - 5 CO, 29%), 540 (M⁺ - 6 CO, 6%), 512 (M⁺ - 7 CO, 18%), 484

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 $\begin{array}{l} (M^{+} - 8\ CO,\ 35\%),\ 456\ (M^{+} - 9\ CO,\ 38\%),\ 428\ (M^{+} - 10\ CO,\ 43\%), \\ 376\ (M^{+} - 10\ CO,\ -\ ^{52}Cr,\ 14\%),\ 338\ (M^{+} - 10\ CO,\ -\ ^{52}Cr,\ -\ 2\ F, \\ 10\%),\ 214\ (7\%),\ 149\ (16\%),\ 142\ (15\%),\ 130\ (7\%),\ 108\ (^{52}Cr(CO)_2, \\ 7\%),\ 80\ (^{52}CrCO,\ 24\%),\ 78\ (10\%),\ 71\ (17\%),\ 53\ (^{53}Cr,\ 11\%),\ 52 \\ (^{52}Cr,\ 100\%).\ Elemental\ analysis\ calcd\ C\ 37.31,\ N\ 3.96\%;\ found: \\ C\ 36,57,\ N\ 3.53\%. \end{array}$

Decacarbonyl(1,4-bis(3,4-difluoro-4-isocyanobut-3en-4-yne-1-yl)benzene)dichromium (5a)

130 mg (1.0 mmol) of 1,4-bis(ethynyl)benzene **4c** were dissolved in 30 mL of tetrahydrofuran and two equivalents of methylmagnesiumbromide (0.8 mL, 2.5 M) were added at ambient temperature. After 3h 600 mg (2.0 mmol) of **1** dissolved in diethylether was added and the reaction mixture was stirred for 15 min. Chromatographic work up as described above yielded 294 mg (43%) of a yellow oil. Due to the small separation of the resonances of the different isomers only a overall ratio of (E): (Z) = 11:9 could be determined.

¹⁹F-NMR (CDCl₃, CFCl₃ intern, 376.0 MHz): (ZZ)-Isomer: δ = -109.6 (s, 2 F, (Z)-CF=CF-C), -134.4 (s, 2 F, (Z)-CF=CF-C); (*EZ*)-Isomer: $\delta = -109.5$ (s, 1 F, (*Z*)-CF=CF-C), -127.4 (d, ${}^{3}J_{FF} =$ 126.0 Hz, 1 F, (E)-CF=CF-C), -134.4 (s, 1 F, (Z)-CF=CF-C), -144.2 (d, ${}^{3}J_{FF} = 126.0$ Hz, 1 F, (*E*)-CF=C*F*-C); (*EE*)-Isomer: $\delta = -126.5$ (d, ${}^{3}J_{FF} = 126.0$ Hz, 2 F, (E)-CF=CF-C), -144.9 (d, ${}^{3}J_{\text{FF}} = 126.0 \text{ Hz}, 2 \text{ F}, (E)-\text{CF}=\text{CF}-\text{C}). \text{ IR (KBr): } v (\text{cm}^{-1}) = 3921$ vw, 3414 w, 3306 w, 3293 m, 2960 w, 2925 m, 2854 w, 2543 vw, 2447 vw, 2343 vw, 2205 m, 2117 m, 2015 s, 1956 vs, 1668 m, 1505 w, 1494 w, 1463 w, 1404 w, 1384 w, 1350 w, 1274 s, 1263 s, 1184 m, 1161 m, 1103 w, 1083 vw, 1067 m, 1017 w, 953 w, 862 w, 835 s, 803 m, 752 m, 647 vs, 582 m, 544 m, 492 w, 445 m, 433 m. Raman: v_{shift} $(cm^{-1}) = 3068 vw, 2849 vw, 2530 w, 2432 vw, 2203 vs, 2157 w, 2111$ m, 2039 m, 1992 m, 1952 w, 1671 s, 1599 vs, 1496 vw, 1334 w, 1275 m, 1168 m, 1067 w, 601 w, 531 vw, 481 w, 431 w, 388 m, 108 m. MS (EI, 80 eV): m/z = 684 (M⁺, ⁵²Cr, 2.4%), 628 (M⁺ - 2 CO, ⁵²Cr, 0.5%), 600 (M⁺ - 3 CO, ⁵²Cr, 0.7%), 572 (M⁺ - 4 CO, ⁵²Cr, 2.5%), 544 (M⁺ - 5 CO, ⁵²Cr, 7.3%), 516 (M⁺ - 6 CO, ⁵²Cr, 1.9%), 488 $(M^{+} - 7 CO, {}^{52}Cr, 3.6\%), 460 (M^{+} - 8 CO, {}^{52}Cr, 5.3\%), 432 (M^{+} - 9)$ CO, 52Cr, 4.6%), 405 (M+ - 10 CO, 53Cr, 17.1%), 404 (M+ - 10 CO, ⁵²Cr, 10.5%), 349, (12.0%), 321 (8.7%), 293 (28.2%), 266 (21.1%), 265 (100%), 175 (26.9%), 168 (26.3%), 109 (⁵³Cr(CO)₂, 3.4%), 81 (53CrCO, 3.7%), 80 (52CrCO, 3.1%), 78 (Ph, 2.7%), 57 (10.8%), 52 (⁵²Cr, 30.7%).

Decacarbonyl(1,2,7,8-tetrafluoroocta-1,7-dien-3,5diynyldiisocyanide)-dichromium (7)

10 mg of CuBr, one drop of triethylamine and TMEDA were added to 175 mg (0.57 mmol) of pentacarbonyl(1,2-difluorobut-1en-3-inylisocyanide)chromium ((CO)₅Cr(CNCFCFC₂H) **3c** in 10 mL of acetone. The suspension was vigorously stirred at ambient temperature in an open flask allowing air contact. After 1 h no reactant could be detected by TLC. The reaction mixture was filtered through a thin pad of silica to remove insoluble materials. After column chromatography on silica and pentane as eluent and crystallization 140 mg (81%) **5** were obtained as a mixture of the three possible isomers in a ratio of (*ZZ*) : (*EZ*) = 6 : 3 : 1. The isomeric mixture forms a microcrystalline solid with mp. 105 °C (dec).

¹⁹F-NMR (376.0 MHz, CDCl₃, CFCl₃ intern): (ZZ)-Isomer: $\delta = -98.3$ (s, 2 F, (Z)-CF=CF-C), -140.9 (s, 2 F, (Z)-CF=CF-C); (EZ)-Isomer: $\delta = -99.4$ (s, 1 F, (Z)-CF=CF-C), -120.3 (d, ${}^{3}J_{FF} = 126$ Hz, 1 F, (E)-CF=CF-C), -140.5 (s, 1 F, (Z)-CF=CF-C), -150.7 (d, ${}^{3}J_{FF} = 126$ Hz, 1 F, (*E*)-CF=C*F*-C); (*EE*)-Isomer: $\delta = -120.3$ (d, ${}^{3}J_{FF} = 126$ Hz, 2 F, (*E*)-CF=CF-C), -150.4 (d, ${}^{3}J_{FF} = 126 \text{ Hz}, 2 \text{ F}, (E)-CF = CF-C). {}^{13}C{}^{19}F{-NMR} (100.4 \text{ MHz},$ $CDCl_3$): $\delta = 213.3, 213.2, 213.0, 212.9 (CO_{trans}), 212.4, 212.3, 212.2$ (CO_{civ}), 206.3, 202.5, 201.2, 195.4 (CN), 141.2, 136.6, 136.3, 134.6, 130.4, 129.9, 129.6, 129.5 (CF), 90.3, 90.1, 74.3, 73.9 (CF-C=C-). IR (CH₂Cl₂): v (cm⁻¹) = 2120 w, 2038 m, 1966 s, 1269 vs, 1260 vs. Raman: v_{shift} (cm⁻¹) = 2194 s, 2112 w, 2013 m, 2004 m, 1990 m, 1979 m, 1946 w, 1655 s, 1392 w, 1275 m, 1140 w, 935 w, 603 w, 425 w, 385 s, 326 w, 117 w; MS (EI, 80 eV): m/z = 609 (30) [M⁺, ⁵³Cr], 608 (63) [M⁺, ⁵²Cr], 496 (13) [M⁺ - 4 CO], 469 (19) [M⁺ - 5 CO, ⁵³Cr], 468 (46) [M⁺ - 5 CO, ⁵²Cr], 412 (21) [M⁺ - 7 CO, ⁵²Cr], 385 (27) [M⁺ - 8 CO, ⁵³Cr], 384 (100) [M⁺ - 8 CO, ⁵²Cr], 357 (47), 356 (99.6) [M⁺ – 9 CO, ⁵²Cr], 329 (30) [M⁺ – 10 CO, ⁵³Cr], 328 (94.5) [M⁺ - 10 CO, ⁵²Cr], 238 (43) [M⁺ - (CO)₅CrCNCFCF, ⁵²Cr], 149 (15), 148 (30), 142 (26), 141 (23), 52 (27) [52 Cr], 28 (58). Elemental analysis calcd for C₂₀Cr₂F₄N₂O₁₀ (608.2): C 39.50, N 4.61; found: C 40.12, N 3.37%.

$\label{eq:loss} Decacarbonyl(1,2,7,8-tetrafluoroocta-1,7-dien-3,5-(dodecacarbonyl[\mu-(3,4-\eta:3,4-\eta:5,6-\eta:5,6-\eta-diinyl]]tetracobalt)diisocyanide)-dichromium (9)$

To a solution of 700 mg (1.1 mmol) of $(CO)_5 \text{Cr}(\text{CNCFCFC}_2\text{C}_2\text{CF-CFNC})\text{Cr}(\text{CO})_5$ 7 in 10 mL of a pentane/dichloromethane mixture (1:1) 980 mg (2.9 mmol) of octacarbonyldicobalt was added under argon atmosphere. During stirring of the solution the reaction was observed by TLC. After there was no remaining 7 detectable the solution was filtered, the solvent and surplus octacarbonyldicobalt were removed in vacuum. The residue was recrystallized in a pentane/dichloromethane mixture. At -30 °C 710 mg (55% yield) of dark brown crystals of **9** were obtained, m.p. 166 °C (dec.).

¹⁹F-NMR (376.0 MHz, CDCl₃, CFCl₃ intern): (ZZ)-Isomer: $\delta = -101.8$ (s, 2 F, (Z)-CF=CF-C), -120.9 (s, 2 F, (Z)-CF=CF-C); (EZ)-Isomer: $\delta = -102.1$ (s, 1 F, (Z)-CF=CF-C), -120.9 (s, 1 F, (Z)-CF=CF-C), -123.8 (d, ${}^{3}J_{FF} = 126$ Hz, 1 F, (E)-CF = CF - C), -126.2 (d, ${}^{3}J_{FF} = 126$ Hz, 1 F, (*E*)-CF = CF - C); (*EE*)-Isomer: $\delta = -124.0$ (d, ${}^{3}J_{FF} = 125$ Hz, 2 F, (*E*)-CF=CF-C), -126.4 (d, ${}^{3}J_{FF} = 125$ Hz, 2 F, (*E*)-CF=CF-C). ${}^{13}C{}^{19}F{}$ -NMR (100.4 MHz, CDCl₃): (ZZ)-Isomer: $\delta = 212.8$ (CO_{trans}), 212.5 (CO_{cis}), 200.4 (CN), 196.9 (Co(CO)₃), 142.7, 129.8 (CF), 93.6, 73.1 (C=C); (*EZ*)-Isomer: $\delta = 214.2$ (CO_{trans}), 213.7 (CO_{cis}), 203.0 (CN), 196.9 (Co(CO)₃), 147.2, 129.5 (CF), 91.1, 72.0 (C=C). IR (CH₂Cl₂): v (cm⁻¹) = 2093 w, 2074 m, 2064 s, 2054 s, 1971 m, 1858 m. MS (EI, 80 eV, 70 °C): m/z (%) = 960 (0.1) [M⁺ - ${}^{52}Cr(CO)_6$, 932 (0.5) [M⁺ - ${}^{52}Cr(CO)_7$], 820 (0.1) [M⁺ - ${}^{52}Cr(CO)_{11}$], 792 (0.5) $[M^+ - {}^{52}Cr(CO)_{12}]$, 764 (0.4) $[M^+ - {}^{52}Cr(CO)_{13}]$, 736 $(0.5) [M^+ - {}^{52}Cr(CO)_{14}], 708 (0.4) [M^+ - {}^{52}Cr(CO)_{15}], 680 (0.2)$ $[M^{+} - {}^{52}Cr(CO)_{16}], 652 (0.4) [M^{+} - {}^{52}Cr(CO)_{17}], 624 (0.4) [M^{+} -$ ⁵²Cr(CO)₁₈], 572 (53) [⁵⁹Co₄(CO)₁₂], 544 (55) [⁵⁹Co₄(CO)₁₁], 516 (9) [⁵⁹Co₄(CO)₁₀], 488 (8) [⁵⁹Co₄(CO)₉], 460 (45) [⁵⁹Co₄(CO)₈], 432 (89) $[{}^{59}Co_4(CO)_7], 404 (31) [{}^{59}Co_4(CO)_6], 376 (18) [{}^{59}Co_4(CO)_5], 348$ (22) [⁵⁹Co₄(CO)₄], 320 (38) [⁵⁹Co₄(CO)₃], 292 (28) [⁵⁹Co₄(CO)₂], 264 (25) [59Co4CO], 236 (33) [59Co4], 220 (69) [52Cr(CO)6], 192 (11) $\begin{bmatrix} {}^{52}Cr(CO)_5 \end{bmatrix}, 177 (20), 164 (6) \begin{bmatrix} {}^{52}Cr(CO)_4 \end{bmatrix}, 136 (7) \begin{bmatrix} {}^{52}Cr(CO)_3 \end{bmatrix}, 118 \\ (12), 115 (3) \begin{bmatrix} {}^{59}Co(CO)_2 \end{bmatrix}, 108 (97) \begin{bmatrix} {}^{52}Cr(CO)_2 \end{bmatrix}, 87 (6) \begin{bmatrix} {}^{59}CoCO \end{bmatrix}, 81 \\ (19) \begin{bmatrix} {}^{53}CrCO \end{bmatrix}, 80 (100) \begin{bmatrix} {}^{52}CrCO \end{bmatrix}, 59 (11), 53 (7), 52 (78).$

$Decacarbonyl(1,2,5,6-tetrafluorohex-1,5-dien-3-(hexacarbonyl[\mu_2-(3,4-\eta^2: 3,4-\eta^2-inyl)]dicobalt)-diisocyanide)dichromium (8)$

Analogously to the syntheses of **9**, 108 mg (0.18 mmol) of $(CO)_5Cr(CNCFCFC_2CFCFNC)Cr(CO)_5$ **6** was dissolved in 10 mL of a pentane/dichloromethane mixture (1:1) under argon atmosphere at ambient temperature. After addition of 210 mg (0.61 mmol) of octacarbonyldicobalt the solution was stirred for 1.5 h. After filtration and removal of the solvents the isomers **8** were isolated by fractionated column chromatography and fractionated crystallization from petrolether at -30 °C. The yield was 74 mg (47%) of dark red crystals of **8**, m.p. (*ZZ*)-**8**: 138–139 °C; (*EZ*)-**8**: 119–121 °C.

¹⁹F-NMR (376.0 MHz, CDCl₃, CFCl₃ intern): (ZZ)-Isomer: $\delta = -104.4$ (s, 2 F, (Z)-CF=CF-C), -120.9 (s, 2 F, (Z)-CF=CF-C); (EZ)-Isomer: $\delta = -105.3$ (s, 1 F, (Z)-CF=CF-C), -120.9 (d, ${}^{3}J_{FF} = 125$ Hz, 1 F, (E)-CF=CF-C), -121.5 (s, 1 F, (Z)-CF=CF-C), -128.4 (d, ${}^{3}J_{FF} = 125$ Hz, 1 F, (E)-CF=CF-C); (*EE*)-Isomer: $\delta = -122.2$ (d, ${}^{3}J_{FF} = 125$ Hz, 2 F, (*E*)-CF=CF-C), -129.3 (d, ${}^{3}J_{FF} = 125$ Hz, 2 F, (E)-CF=CF-C). ${}^{13}C{}^{19}F{}$ -NMR (CDCl₃, 100.4 MHz): (ZZ)-Isomer: $\delta = 213.0$ (CO_{trans}), 211.9 (CO_{cis}), 206.6 (Co(CO)₃), 202.5 (CN), 141.8, 125.9 (CF), 96.2 (C=); (EZ)-Isomer: $\delta = 213.6, 212.9$ (CO_{trans}), 212.3, 212.2 (CO_{cis}), 201.9, 198.3 (CN), 195.7 (Co(CO)₃), 145.4, 141.6, 128.1, 125.8 (CF), 96.3, 85.0 (C \equiv). IR (CH₂Cl₂): (ZZ)-Isomer: v (cm⁻¹) = 2111 s, 2080 s, 2065 s, 2045 s, 2028 m, 2002 s, 1969 vs. (CO), 1945 vs, 1644 w (C=C), 1250 m (CF), 835 w, 660 s, 647 s; (EZ)-Isomer: v $(cm^{-1}) = 2110 s, 2075 s, 2046 s, 2037 m, 2019 m, 1954 vs.$ (CO), 1660 w, 1571 w (C=C), 1259 m (CF), 1172 m, 1107 w, 657 s. Raman: (ZZ)-Isomer: v_{shift} (cm⁻¹) = 2109 w, 2074 vw, 2055 vw, 2038 vw, 2030 vw, 2016 w, 2004 vs, 1967 w, 1951 vw, 1938 w, 1660 s, 1646 m, 1592 vw, 1262 m, 1245 m, 1195 w, 1044 vw, 655 vw, 612 w, 434 w, 384 s, 197 w, 106 s; (*EZ*)-Isomer: v_{shift} (cm⁻¹) = 2107 w, 2049 vw, 2017 m, 2002 m, 1946 w, 2016 w, 1665 vs, 1571 w, 1301 m, 1272 m, 1249 w, 1168 vw, 852 vw, 683 vw, 655 vw, 619 w, 527 vw, 433 w, 386 m, 275 vw. MS (EI, 80 eV): m/z (%) = 870 (6) [M⁺, ⁵²Cr], 842 (14) [M⁺ - CO], 786 (5) [M⁺ - 3 CO], 702 (10) [M⁺ - 6 CO], 646(9) [M⁺ - 8 CO], 618(7) [M⁺ - 9 CO], 590(11) [M⁺ - 10 CO], 534 (10) [M⁺ - 12 CO], 506 (12) [M⁺ - 13 CO], 478 (13) [M⁺ -14 CO], 220 (100) [52Cr(CO)6], 28 (32). Elemental analysis calcd for C₂₄Co₂Cr₂F₄N₂O₁₆ (870.1): C 33.13, N 3.22; found: C 33.83, N 3.39%.

Crystallography

Crystal data and details of the structure determinations are presented in Table 3. The intensity data were collected using a Bruker AXS Smart CCD diffractometer: corrections for Lorentz polarisation and absorption effects $(SADABS)^{42}$ were applied to the data. The structures were solved by Patterson and direct methods $(SHELXS-97)^{43}$ Anisotropic thermal parameters were applied to all non-hydrogen atoms. Refinement for all structures on F^2 were achieved using the SHELXL-97 system.⁴² Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre and are available as ESI.†

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