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C–C Coupling Reactions of Pentacarbonyl(trifluoroethenyl isocyanide)-chromium with Cyclopentadienyl Complexes

Dieter Lentz,*[a] Monika Mujkic,[a] and Stefanie Roth[a]

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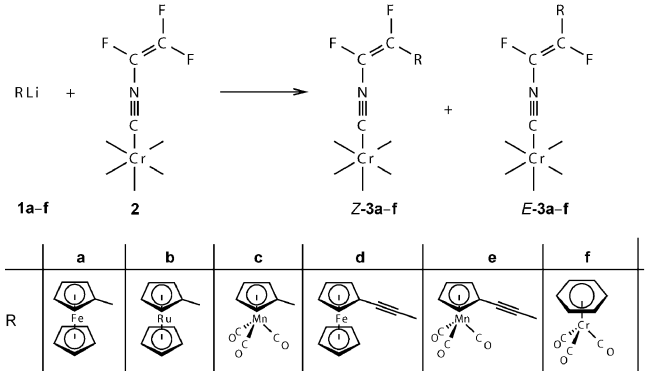
The nucleophic attack of the trifluoroethenyl group of pentacarbonyl(trifluoroethenyl isocyanide)chromium **2** by various cyclopentadienyl ligand containing nucleophiles **1a–f** allow an efficient synthesis of functionalized cyclopentadienyl complexes **3a–f**. Extension of this method to 1,1′-dilithioferrocene (**4a**) and 1,1′-dilithioruthenocene (**4b**) yields the difunctionalized derivatives **5a** and **b**, respectively. In general compounds of type **3** and **5** are obtained as mixtures of the *E* and *Z* isomers. The crystal and molecular structures of *Z*-**3a**, *Z*-**3b**, *Z*-**3c** and *E*,*Z*-**5a** were elucidated by X-ray diffraction.

Introduction

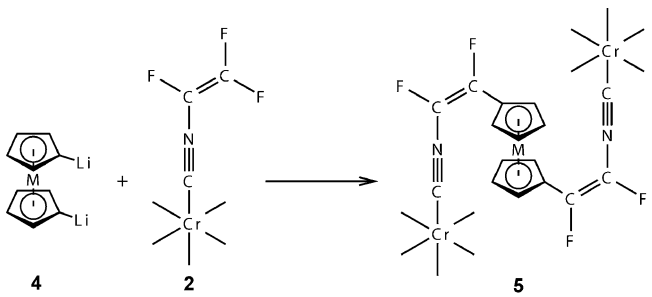
The synthesis of alkenyl and alkynyl isocyanides is still challenging due to the limits of classical synthetic methods. While ethenyl isocyanide can be synthesized classically,[1] ethynyl isocyanide[2] and propynyl isocyanide[3] are accessible by pyrolysis of suitable organometallic precursors. 1-Cyano-2-isocyanoacetylene[4] can prepared by the selective replacement of an activated fluorine substituent of the CF_2 group of pentacarbonyl(trifluoroethenyl isocyanide)chromium and pyrolysis of the resulting isocyanide complex. Herein we report on an effective, simple synthesis of alkenyl isocyanides with organometallic substituents as outlined in Scheme 1 stabilized at the pentacarbonyl chromium fragment.



Scheme 1.

As long as the organolithium compounds of type **1a–f** and **4a–b** can be prepared there seem to be no limitations in the utility of this method leading to cyclopentadienyl complexes with fluorinated functionalised side chains that are otherwise difficult to obtain. Only a few cyclopentadienyl complexes with unsaturated fluorinated side chains are known so far,[5] and none of these have been characterized by X-ray crystallography. Of the two possible isomers of **3** the *Z* isomer is always the prevailing one and the only one observed for the cymantrene derivative **3c**.

In the reaction of ferrocenyllithium **1a** with **2** always a small amount of **5a** is formed as mixtures of the *E*,*Z*-, *Z*,*Z*- and *E*,*E*-isomers, respectively. **5a** and the analogous ruthenium compound **5b** can be prepared more efficiently from 1,1′-dilithioferrocene and -ruthenocene, **4a** and **b**, respectively (Scheme 2). The isomeric ratio can be easily determined by integration of the signals in the ^{19}F NMR spectra as the *cis* and *trans* arrangement of the fluoro substituents in 1,2-difluoro alkenes results in very different $^3J(^{19}F\text{-}^{19}F)$ coupling constants.[6] Attempts to separate the isomers by chromatography failed but small amounts of the prevailing isomers could be obtained by crystallization from *n*-pentane.



Scheme 2.

[a] Institut für Chemie und Biochemie / Anorganische Chemie, Freie Universität Berlin,
Fabeckstr. 34–36, 14195 Berlin, Germany
Fax: +49-30-838-53310
E-mail: lentz@chemie.fu-berlin.de

The crystal and molecular structures of *Z*-**3a** (Figure 1), *Z*-**3b** (two polymorphous crystals) (Figure 2), *Z*-**3c** (Figure 3) and *E*,*Z*-**5a** (Figure 4) were elucidated by X-ray crystallography.[7] In all of the compounds the alkene plane is slightly turned out of the plane of the cyclopentadienyl ring with C–C–C–C dihedral angles of –23.9 **3a**, –21.6 **3b** (polymorph I), 29.8 **3b** (polymorph II), –33.0 **3c** and 0.2/8.6° **5a**, respectively. Quite unexpected the two bulky substituents of **4a** are almost in an eclipsed position with an dihedral angle C28 C1R C6R C18 of 13.1°. An almost eclipsed arrangement of the cyclopentadienyl substituents is also observed in **3a**, **3b** (polymorph I) and the low-temperature structure of ferrocene.[9a] The eclipsed D_{5h} symmetry structure is the minimum for ferrocene at 98 K[9b] in the gaseous phase.[10] However, the energy barriers for the rotation of the cyclopentadienyl ligands are extremely small. This is in accordance with the crystallization of a second polymorphous form of **3b** which differs mainly by the almost staggered conformation of the cyclopentadienyl ligands and the different C–C–C–C dihedral angle of the vinyl substituent. This results in a little smaller cell volume and a higher density of the polymorph (II).

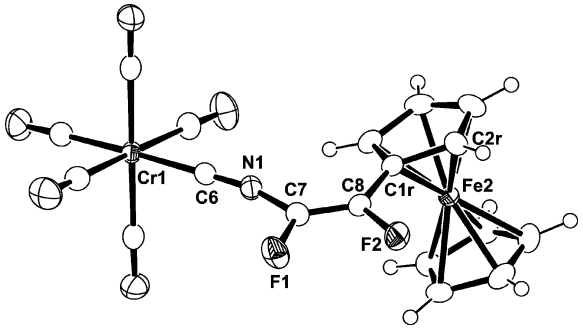


Figure 1. Molecular structure (ORTEP[8]) of *Z*-**3a**.

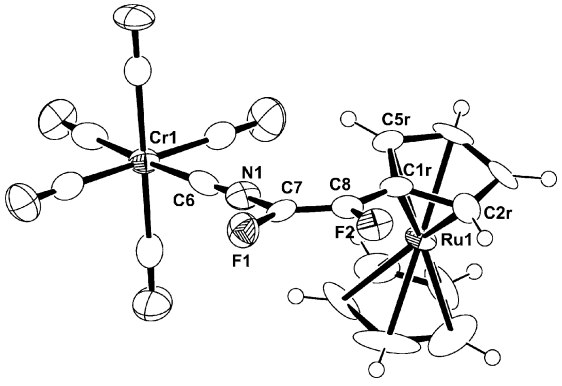


Figure 2. Molecular structure (ORTEP[8]) of *Z*-**3b II**.

Introduction of an electron-withdrawing substituent in **3a** shifts the redox potential 0.3 V in comparison to ferrocene.

In summary the trifluoroethenyl group of **2** can be used as a functional group and synthetic tool for the synthesis of new isocyanide complexes for which other synthetic methods are unavailable.

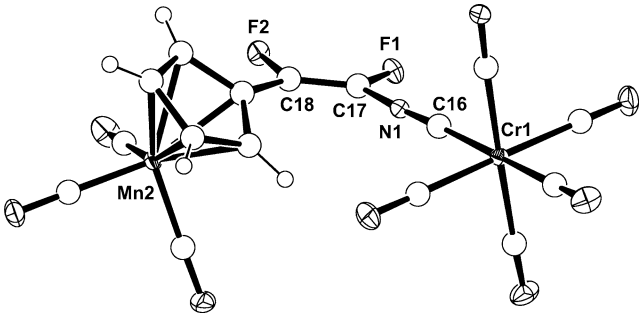


Figure 3. Molecular structure (ORTEP[8]) of *Z*-**3c**.

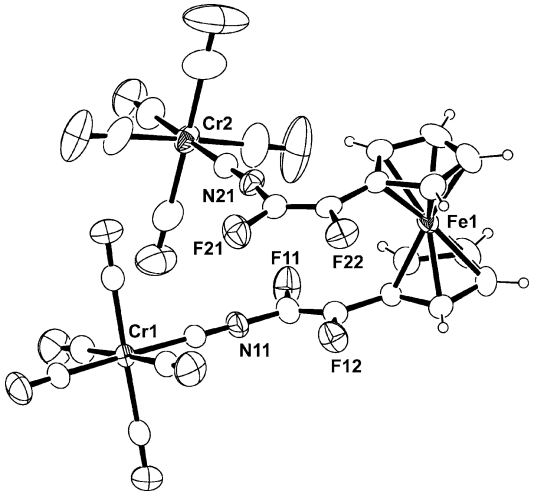


Figure 4. Molecular structure (ORTEP[8]) of *E*,*Z*-**5a**.

Experimental Section

In a typical experiment the organolithium compounds **1a**, **1c**–**f** and **4a**,**b** were prepared according to literature methods using *n*BuLi or *t*BuLi.[11] The resulting solution were diluted by *n*-pentane to avoid decomposition of the product by fluoride ions in solution. A solution of **2** was added at –78 °C and the mixture was warmed to ambient temperature. After filtration through silica the solvent was evaporated under vacuum and the residue was purified by chromatography on silica. Crystallization from *n*-pentane yielded **3a** (175 mg, 19%, *Z*/*E* = 10:1), red crystals, m.p. 88–89 °C; **3b** (110 mg, 20%, *Z*/*E* = 4:1) yellow crystals, **3c** (445 mg, 46%, *Z*), yellow crystals, m.p. 94–95 °C; **3d** (280 mg, 57%, *Z*/*E* = 3:1), red crystals, m.p. 104–105 °C; **3e** (48 mg, 16%, *Z*/*E* = 20:3), red brown crystals; **3f** (205 mg, 83%, *Z*/*E* = 10:1), m.p. 152 °C (dec.), **5a** (387 mg, 52%, *E*,*Z*/*Z*,*Z*/*E*,*E* = 8:5:1), red crystals, m.p. (*E*/*Z*-**5a**) 123 °C; **5b** (360 mg, 46%, *E*,*Z*/*Z*,*Z*/*E*,*E* = 3:2:1), yellow crystals.

3a: MS (EI, 80 eV, 80 °C): *m*/*z* (%) = 465 (33) [M^+] 437 (6) [M^+ – CO], 409 (2) [M^+ – 2 CO], 381 (10) [M^+ – 3 CO], 353 (16) [M^+ – 4 CO], 325 (100) [M^+ – 5 CO], 305 (3), 269 (5), 235 (14) [M^+ – CCN – $Cr(CO)_5$], 231 (12), 204 (10), 136 (6) [$^{52}Cr(CO)_3$], 121 (4) [FeCp], 52 (3) [^{52}Cr], 28 (3) [CO]; high resolution MS: (M^+) calcd. 464.92032, found 464.92155. ^{19}F NMR ($CDCl_3$): *Z*-**3a**: δ = –123.7 (s, 1 F, C*F*=CF–C), –130.9 (s, 1 F, CF=C*F*–C) ppm. *E*-**3a**: δ = –141.9 (d, $^3J_{FF}$ = 122.5 Hz, 1 F, C*F*=CF–C), –144.3 (d, 1 F, CF=C*F*–C) ppm. ^1H NMR ($CDCl_3$): *Z*-**3a**: δ = 4.27 (s, 5 H, Cp), 4.46 (s, 2 H, Cp), 4.58 (s, 2 H, Cp) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): *Z*-**3a**: δ = 214.9 (s, 1 C, CO_{trans}), 213.3 (s, 4 C, CO_{cis}), 191.7 (s, 1 C, CN), 147.4 (dd, $^1J_{CF}$ = 250, $^2J_{CF}$ = 24 Hz; 1 C, Cp–CF), 125.5

(dd, $^1J_{CF}$ = 254, $^2J_{CF}$ = 43 Hz, 1 C, *C*F–NC), 70.8 (s,2 C, *o*-C_{Cp}H), 70.3 (s, 1 C, *i*-C_{Cp}), 70.0 (s, 5 C, C_5H_5), 67.1 (s, 2 C, *m*-C_{Cp}H) ppm. IR (KBr): $\tilde{\nu}$ = (2126 m), 2034 (s), 2009 (m), 1938 (vs), 1691 (m), 1470 (w), 1412 (w), 1387 (w), 1303 (w), 1248 (s), 1144 (m), 1108 (w), 1055 (m), 1032 (w), 1003 (w), 976 (w), 870 (w), 829 (w), 674 (s), 659 (s), 647 (s), 500 (m), 484 (w), 434 (m) cm^{-1}. IR (hexane): $\tilde{\nu}$ = 2029 (m), 2007 (w), 1973 (s), 1945 (w); Raman: $\tilde{\nu}_{shift}$ = 3120 (w), 2112 (m), 2026 (vs), 1996 (s), 1971 (m), 1946 (w), 1691 (s), 1470 (m), 1412 (w), 1387 (w), 1304 (w), 1243 (s), 1215 (w), 1142 (w), 1108 (m), 1060 (w), 1034 (w), 892 (w), 858 (w), 826 (w), 675 (w), 664 (m), 638 (w), 441 (w), 419 (w), 406 (w), 387 (s), 314 (s), 212 (w), 171 (w), 118 (s) cm^{-1}.

5a: MS (EI, 80eV, 130 °C): *m*/*z* (%) = 744 (77) [M$^+$], 604 (52) [M$^+$ – 5 CO], 548 (54) [M$^+$ – 7 CO], 520 (20) [M$^+$ – 8 CO], 492 (100) [M$^+$ – 9 CO], 464 (79) [M$^+$ – CFCFNCCr(CO)$_5$], 440 (17), 412 (10), 331 (14), 273 (18), 232 (33), 52 (8) [^{52}Cr], 28 (7) [CO]. High resolution MS: (M$^+$) calcd. 743.82745, found 743.82644. ^{19}F NMR ($CDCl_3$): *Z*,*Z*-**5a**: δ = –120.2 (s, 2 F, C*F*=CF–C), –135.3 (s, 2 F, CF=C*F*–C); *E*,*Z*-**5a**: δ = –121.1 [s, 1 F, (*Z*)-C*F*=CF–C], –136.2 [s, 1 F, (*Z*)-CF=C*F*–C], –137.4 [d, $^3J_{FF}$ = 122.5 Hz, 1 F, (*E*)-C*F*=CF–C], –146.8 [d, 1 F, (*E*)–CF=C*F*–C]; *E*,*E*-**5a**: δ = –139.0 [d, $^3J_{FF}$ = 122.5 Hz, 2 F, (*E*)-C*F*=CF–C], –146.0 [d, 1 F, (*E*)-CF=C*F*–C] ppm. ^{1}H NMR ($CDCl_3$): *E*,*Z*-**5a**: δ = 4.68 (s, 4 H, Cp), 4.56 (s, 4 H, Cp) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 214.89, 214.40 (CO_{trans}), 213.12, 213.07 (CO_{cis}), 195.99, 194.14 (CN), 147.21, 145.02 (Cp–CF), 127.30, 114.85 (*C*F–NC), 72.71, 72.32, 72.19, 72.0, 68.46, 68.00 (C_{Cp}) ppm. IR (KBr): $\tilde{\nu}$ = 3432 (w), 2963 (w), 2124 (w), 2018 (w), 2006 (w), 1944 (s), 1684 (w), 1384 (w), 1262 (m), 1096 (m), 1022 (m), 868 (w), 802 (m), 671 (w), 646 (m), 440 (w) cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 3056 (w), 2027 (m), 1968 (s), 1269 (vs), 1260 (vs), 1096 (m), 1060 (w), 1012 (m), 809 (m) Raman: ν_{shift} = 2964 (w), 2904 (w), 2109 (m), 2028 (s), 2000 (s), 1963 (w), 1683 (vs), 1471 (m), 1383 (w), 1345 (w), 1308 (w), 1242 (s), 1218 (w), 1059 (w), 707 (w), 661 (m), 639 (w), 568 (w), 468 (w), 440 (m), 387 (vs), 318 (s), 227 (w), 197 (w), 165 (w), 108 (vs) cm^{-1}.

3b: ^{19}F NMR ($CDCl_3$): *Z*-**3b**: δ = –124.1 (d, $^3J_{FF}$ = 4.2 Hz 1 F, C*F*=CF–C), –130.5 (d, t, $^4J_{HF}$ = 1.6 Hz 1 F, CF=C*F*–C); *E*-**3b**: δ = –140.6 (d, $^3J_{FF}$ = 123.5 Hz, 1 F, C*F*=CF–C), –143.9 (d, t, $^4J_{HF}$ = 1.6 Hz, 1 F, CF=C*F*–C) ppm. ^{1}H NMR ($CDCl_3$): *Z*-**3b**: δ = 4.64 (s, 5 H, Cp), 4.75 (m, 2 H, Cp), 4.92 (m, 2 H, Cp); *E*-**3a**: δ = 4.63 (s, 5 H, Cp), 4.73 (m, 2 H, Cp), 4.92 (m, 2 H, Cp) ppm. IR (ATR-FT): $\tilde{\nu}$ = *Z*-**3b**: $\tilde{\nu}$ = 2114 (w), 2028 (m), 1914 (vs) (CO) cm^{-1}.

5b: M.p. 106–107 °C. MS (EI, 80 eV): *m*/*z* (%) = 789 (18.8) [M$^+$], 649 (12.3) [M$^+$ – 5 CO], 597 (7.9) [M$^+$ – ^{52}Cr(CO)$_5$], 593 (13.9) [M$^+$ – 7 CO], 565 (11.4) [M$^+$ – 8 CO], 537 (33.3) [M$^+$ – 9 CO], 509 (18.4) [M$^+$ – 10 CO], 458 (10.3), 330 (20.7), 301 (10.5), 253 (16.0), 220 (38.1), 108 (44.7), 80 (60.2), 52 (100).

High resolution (M$^+$) calcd. 789.79688, found 789.79744. ^{19}F NMR ($CDCl_3$, $CFCl_3$): *Z*,*Z*-**5b**: δ = –121.6 (s, 1 F, C*F*=CF–C), –133.9 (s, 1 F, CF=C*F*–C), *E*,*Z*-**5b**: δ = –123.0 [s, 1 F, (*Z*)-C*F*=CF–C], –135.8 [s, 1 F, (*Z*)-CF=C*F*–C], –137.8 [d, $^3J_{FF}$ = 123.5 Hz, 1 F, (*E*)-C*F*=CF–C], –147.0 [d, 1 F, (*E*)-CF=C*F*–C]; *E*,*E*-**5b**: δ = –138.9 (d, $^3J_{FF}$ = 123.5 Hz, 1 F, C*F*=CF–C), –145.2 (d, 1 F, CF=C*F*–C) ppm. ^{1}H NMR ($CDCl_3$, 399.65 MHz): **5b**: δ = 5.05, 5.01 (m, 2 H, Cp), 4.85, 4.83, 4.82 (m, 2 H, Cp) ppm.

Z-3c: MS (EI, 80 eV, 100 °C): *m*/*z* (%) = 483 (100) [M$^+$], 455 (3) [M$^+$ – CO], 399 (14) [M$^+$ – 3 CO], 371 (25) [M$^+$ – 4 CO], 343 (63) [M$^+$ – 5 CO], 315 (30) [M$^+$ – 6 CO], 287 (11) [M$^+$ – 7 CO], 259 (30) [M$^+$ – 8 CO], 204 (6), 114 (4), 52 (3) [^{52}Cr], 28 (3) [CO]. High resolution MS: (M$^+$) calcd. 482.86905, found 482.86859. ^{19}F NMR ($CDCl_3$): δ = –116.2 (s, 1 F, C*F*=CF–C), –136.4 (s, 1 F, CF=C*F*–C) ppm. ^{1}H NMR ($CDCl_3$): δ = 4.82 (s, 2 H, Cp), 5.15 (s, 2 H, Cp) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 222.9 (s, 3 C, Mn–CO), 213.8 (s, 1 C, Cr–CO_{trans}), 212.8 (s, 4 C, Cr–CO_{cis}), 197.7 (s, 1 C, CN), 140.6 (dd, $^1J_{CF}$ = 248, $^2J_{CF}$ = 24 Hz; 1 C, C_{Ar}–CF), 126.5 (d, $^1J_{CF}$ = 248 Hz, 1 C, CF=*C*F–NC), 85.2 (d, $^2J_{CF}$ = 24 Hz, 1 C, C_{Cp}), 82.8 (s, 2 C, C_{Cp}), 82.7 (s, 2 C, C_{Cp}) ppm. IR (KBr): $\tilde{\nu}$ = 3424 (w), 2118 (w), 2022 (s), 1993 (m), 1958 (s), 1937 (vs), 1918 (s), 1699 (w), 1487 (w), 1383 (w), 1316 (vw), 1260 (m), 1154 (w), 1068 (w), 1056 (w), 984 (w), 915 (vw), 867 (w), 831 (w), 685 (m), 669 (m), 648 (s), 631 (m), 538 (w), 497 (vw), 444 (w) cm^{-1}. IR (hexane): $\tilde{\nu}$ = 2038 (s), 2017 (m), 1980 (vs), 1960 (s) cm^{-1}. Raman: $\tilde{\nu}_{shift}$ = 3126 (w), 2114 (m), 2040 (m), 2031 (m), 2010 (vs), 1999 (m), 1986 (w), 1956 (w), 1939 (w), 1925 (w), 1696 s, 1487 (m), 1382 (w), 1316 (w), 1248 s, 1226 (w), 677 (w), 651 (w), 641 (w), 491 (m), 437 (w), 424 (w), 415 (w), 389 (vs), 368 (w), 346 (m), 321 (w), 189 (m) cm^{-1}.

3d: MS (EI, 80 eV, 100 °C): *m*/*z* (%) = 489 (47) [M$^+$], 433 (17) [M$^+$ – 2 CO], 405 (9) [M$^+$ – 3 CO], 377 (17) [M$^+$ – 4 CO], 349 (100) [M$^+$ – 5 CO], 293 (– F, – Cp, 30) [M$^+$ – 4 CO], 259 (20), 255 (20), 252 (36), 248 (20), 176 (7), 138 (6), 121 (6), 52 (4) [^{52}Cr], 28 (8) [CO]. High resultion MS: (M$^+$) calcd. 488.92033, found 488.92012. ^{19}F NMR ($CDCl_3$): *Z*-**3d**: δ = –113.0 (d, $^3J_{FF}$ = 4.8 Hz, *Z*-C*F*=CF–C), –131.7 (d, CF=C*F*–C), *E*-**3d**: δ = –130.5 (d, $^3J_{FF}$ = 127.8 Hz, C*F*=CF–C), –141.1 (d, CF=C*F*–C) ppm. IR (KBr): $\tilde{\nu}$ = 3420 (w), 2960 (w), 2924 (w), 2854 (w), 2225 (w), 2198 (m), 2115 (m), 2024 (s), 2000 (vs) cm^{-1}. 1944 (vs), 1673 (w), 1464 (w), 1384 (w), 1279 (w), 1263 (w), 1196 (m), 1107 (w), 1087 (w), 1029 (w), 823 (w), 757 (w), 669 (m), 647 s, 606 (w), 487 (w), 445 (w) cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 2197 (m), 2114 (w), 2017 (m), 1969 (vs) cm^{-1}. Raman: $\tilde{\nu}_{shift}$ = 3123 (w), 2963 (w), 2906 (w), 2109 (m), 2027 (vs), 2000 s, 1964 (w), 1683 (vs), 1471 (m), 1384 (w), 1343 (w), 1308 (w), 1242 s, 1218 (w), 1059 (w), 661 (m), 575 (w), 481 (w), 442 (w), 387 (vs), 351 (w), 318 (m), 227 (w), 165 (w) cm^{-1}.

3e: MS (EI, 80 eV, 150 °C): *m*/*z* (%) = 507 (100) [M$^+$], 479 (6) [M$^+$ – CO], 423 (25) [M$^+$ – 3 CO], 395 (46) [M$^+$ – 4 CO], 367 (94) [M$^+$ – 5 CO], 339 (25) [M$^+$ – 6 CO], 311 (55) [M$^+$ – 7 CO], 283 (75) [M$^+$ – 8 CO], 228 (24), 190 (36), 183 (17), 151 (12), 141 (12), 139 (13) [^{55}Mn(CO)$_3$], 138 (26), 125 (21), 123 (16), 111 (26) [^{55}Mn(CO)$_2$], 99 (29), 97 (63), 85 (48), 83 (40) [^{55}MnCO], 71 (55), 69 (58), 57 (91), 55 (64) [^{55}Mn], 52 (28) [^{52}Cr]. ^{19}F NMR ($CDCl_3$): *Z*-**3d**: δ = –108.1 (s, 1 F, C*F*=CF–C), –135.6 [s, 1 F, (CF=C*F*–C)]; *E*-**3d**: δ = –127.1 (d, $^3J_{FF}$ = 128 Hz, 1 F, C*F*=CF–C), –145.2 (d, 1 F, CF=C*F*–C) ppm.

3f: $C_{17}H_5Cr_2F_2NO_8$ (493.2): calcd./found C 41.40/40.95 H 1.02/1.50 N 2.84/2.83%. MS (EI, 80 eV): *m*/*z* (%) = 493 (^{52}Cr, 61) [M$^+$], 437 (1.3) [M$^+$ – 2 CO], 409 (36) [M$^+$ – 3 CO], 353 (51) [M$^+$ – 5 CO], 325 (100) [M$^+$ – 6 CO], 297 (67) [M$^+$ – 7 CO], 269 (54) [M$^+$ – 8 CO], 217 (9), 179 (6), 127 (2.5). ^{19}F NMR ($CDCl_3$): *Z*-**3f**: δ = –112.1 (s, 1 F, C*F*=CF–C), –137.3 (s, 1 F, CF=C*F*–C); *E*-**3f**: δ = –131.4 (d, $^3J_{FF}$ = 123 Hz, 1 F, C*F*=CF–C), –149.3 (d, 1 F, CF=C*F*–C) ppm. ^{1}H NMR ($CDCl_3$): δ = 5.64 (s, 2 H), 5.46 (s, 1 H), 5.35 (s, 2 H) ppm. ^{13}C{^{19}F} NMR ($CDCl_3$, 100.4 MHz): δ = 232.8, 230.6 [s, 3 C, Cr($CO)_3$], 213.5 (s, 1 C, Cr–CO_{trans}), 212.7 (s, 4 C, Cr–CO_{cis}), 198.7 (s, 1 C, CN), 141.9 (s, 1 C, C_{Ar}–CF=CF), 127.7 (s, 1 C, CF=*C*F–NC), 93.5 (s, 1 C, C_{Ar}–CF=CF), 91.8 (s, 2 C, *o*-C_{Ar}H), 90.4 (s, 2 C, *m*-C_{Ar}H), 88.7 (s, 1 C, *p*-C_{Ar}H) ppm. IR (KBr): $\tilde{\nu}$ = 3430 (m), 3099 (w), 2363 (vw), 2114 (m), 2030 (s), 2001 (s), 1964 (vs), 1940 (vs), 1907 (vs), 1685 (m), 1528 (w), 1502 (w), 1458 (w), 1411 (w), 1384 (w), 1326 (w), 1297 (w), 1255 (s), 1162 (w), 1138 (m), 1059 (w), 999 (w), 958 (m), 922 (vw), 816 (w), 719 (m), 669 (m), 647 (s), 631 (m), 615 (m), 530 (m), 475 (w), 444 (m) cm^{-1}. IR (CH_2Cl_2): $\tilde{\nu}$ = 1970 (s), 1910 (m) cm^{-1}. Raman: $\tilde{\nu}_{shift}$ = 3099 (w), 2112 (m), 2027 s, 2019 (vs), 1999 s, 1960 (m), 1936 (w), 1902 (w), 1889 (m), 1682 s, 1528 (m), 1502 (w), 1458 (w), 1325 (m), 1297

(w), 1243 s, 1163 (w), 999 (w), 681 (m), 648 (m), 608 (m), 532 (w), 476 (m), 437 (w), 427 (w), 387 (vs), 356 (w), 315 (w), 301 (m), 185 (m) cm^{-1}.

Acknowledgments

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[7] Crystal structures: Crystals of **3a**, **3b**, **3c** and **5a** were grown from *n*-pentane solution at –30 °C. **3a**: $C_{18}CrF_2FeH_9NO_5$, M = 465.1, triclinic, $P\bar{1}$, a = 6.847(2), b = 11.385(3), c = 12.013(4) Å, α = 101.03(2), β = 101.37(3), γ = 99.62(3) °, V = 880.54(4) $Å^3$, Z = 2, $\rho_{calcd.}$ = 1.754 $g\,cm^{-3}$, T = 193 K, structure solution by direct methods and full-matrix least-squares refinement,[12] 11009 measured reflexions, 5318 crystallographic unique reflexions (R_{int} = 0.051) and 4332 reflexions with $F_o > 4\sigma(F_o)$, Mo-K_α, λ = 0.71073 Å, $2\theta_{max}$ = 61.10°, R_1 = 0.0294, wR_2 = 0.0843, 253 parameters, anisotropic displacement parameters, H-atoms isotropic, riding model. **3b** (polymorph I): $C_{18}CrF_2H_9NO_5Ru$, M = 510.3, triclinic, $P\bar{1}$, a = 7.132(1), b = 11.346(2), c = 11.941(1) Å, α = 101.29(1), β = 100.12(1), γ = 100.50(1) °, V = 909.07(25) $Å^3$, Z = 2, $\rho_{calcd.}$ = 1.864 $g\,cm^{-3}$, T = 173 K, structure solution by direct methods and full-matrix least-squares refinement,[12] 22510 measured reflexions, 5547 crystallographic unique reflexions (R_{int} = 0.014) and 5130 reflexions with $F_o > 4\sigma(F_o)$, Mo-K_α, λ = 0.71073 Å, $2\theta_{max}$ = 61.10°, R_1 = 0.0172, wR_2 = 0.0460, 253 parameters, anisotropic displacement parameters, H-atoms isotropic, riding model. **3b** (polymorph II): $C_{18}H_9CrF_2NO_5Ru$, M = 510.3, triclinic, $P\bar{1}$, a = 5.898(4), b = 11.550(7), c = 13.852(8) Å, α = 73.38(1), β = 84.72(1), γ = 83.09(1) °, V = 895.9(9) $Å^3$, Z = 2, $\rho_{calcd.}$ = 1.892 $g\,cm^{-3}$, T = 173 K, structure solution by direct methods and full-matrix least-squares refinement as twinned crystal,[9] 6916 measured reflexions, 5514 reflexions used for twin refinement and 3410 reflexions with $F_o > 4\sigma(F_o)$, Mo-K_α, λ = 0.71073 Å, $2\theta_{max}$ = 50.9°, R_1 = 0.065, wR_2 = 0.161, 254 parameters, BASF 0.380, anisotropic displacement parameters, H-atoms isotropic, riding model. **3c**: $C_{16}H_4CrF_2MnNO_8$, M = 483.1, triclinic, $P\bar{1}$, a = 6.509(2), b = 14.200(2), c = 19.460(4) Å, α = 87.931(4), β = 80.595(4), γ = 79.607(4) °, V = 1745.63(4) $Å^3$, Z = 4, $\rho_{calcd.}$ = 1.838 $g\,cm^{-3}$, T = 100 K, structure solution by direct methods and full-matrix least-squares refinement (SHELX-97),[12] 20469 measured reflexions, 10270 crystallographic unique reflexions (R_{int} = 0.0990) and 4880 reflexions with $F_o > 4\sigma(F_o)$, Mo-K_α, λ = 0.71073 Å, $2\theta_{max}$ = 61.2°, R_1 = 0.0505, wR_2 = 0.1158, 523 parameters, anisotropic displacement parameters, H-atoms isotropic, riding model. **5a**: $C_{26}H_8Cr_2F_4FeN_2O_{10}$, M = 774.2, triclinic, $P\bar{1}$, a = 7.112(2), b = 13.854(4), c = 14.609(4) Å, α = 83.40(2), β = 89.23(2), γ = 86.39(2) °, V = 1427.0(7) $Å^3$, Z = 2, $\rho_{calcd.}$ = 1.732 $g\,cm^{-3}$, T = 293 K, structure solution by direct methods and full-matrix least-squares refinement,[12] 5264 measured reflexions, 4741 crystallographic unique reflexions (R_{int} = 0.032) and 3298 reflexions with $F_o > 4\sigma(F_o)$, Mo-K_α, λ = 0.71073 Å, $2\theta_{max}$ = 50,0°, R_1 = 0.042, wR_2 = 0.118, 406 parameters, anisotropic displacement parameters, H-atoms isotropic, riding model. CCDC-660006 (for **3a**), -660004 (for **3b**, **I**), -660005 (for **3b**, **II**), -660002 (for **3c**), and -660003 (**5a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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