

Organometallic Lewis Acids, Part LVIII [1]. Directed Synthesis of Dinuclear Metal Carbonyl Complexes of Rhenium, Iron, Chromium, and Tungsten with a Single Unsupported Halide or Pseudohalide Bridge (Cl⁻, Br⁻, I⁻, CN⁻, C(CN)₃⁻, NCS⁻, PPh₂⁻, SH⁻) by Use of Re(CO)₅FBF₃

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 80th birthday

By use of Re(CO)₅FBF₃ the complexes with a single unsupported halide or pseudohalide bridge [Cp(OC)₂Fe–X–Re(CO)₅]⁺ BF₄⁻ (X = Cl, I, PPh₂), (OC)₅M–X–Re(CO)₅ (M = Cr, W; X = Br, I, CN, NCS, SH), (OC)₅W–N≡C–C[–C≡N–Re(CO)₅]₂⁺ BF₄⁻, Cp(OC)(NC)Fe–C≡N–Re(CO)₅, and [(OC)₅Re–N₃–Re(CO)₅]⁺ BF₄⁻ have been synthesized.

Key words: Rhenium, Iron, Chromium, Tungsten, Carbonyl Metal Complexes, Halide- and Pseudohalide-bridged Complexes, Pentacarbonylrheniumtetrafluoroborate

Introduction

Pentacarbonylrheniumtetrafluoroborate has been proven as a highly reactive complex for the addition of the “organometallic Lewis acid” Re(CO)₅⁺ to nucleophilic donor atoms. The various reactions of Re(CO)₅FBF₃, performed in our group, have been reviewed [2–5].

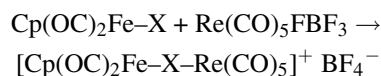
In the following we report on the synthesis of a series of heterodinuclear cationic and neutral complexes of the type



with X = halide, pseudohalide, PPh₂⁻, SH⁻.

Results and Discussion

The cationic complexes **1–3** have been obtained by reaction of Re(CO)₅FBF₃ with Cp(OC)₂Fe–X [6, 7]:



1–3

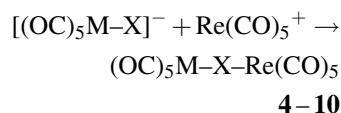
1: X = Cl

2: X = I

3: X = PPh₂

Similarly, the mercaptide-bridged complex [Cp(OC)₂Re–S(R)–Re(CO)₅]⁺ BF₄⁻ has been prepared from Cp(OC)₂Fe–SR and Re(CO)₅FBF₃ (R = Me, Ph) [8]. From the reaction of Cp(OC)₂Fe–PPh₂ [4] with Re(CO)₅FBF₃ two products could be isolated (yellow cubes and red needles). For the yellow complex the experimental data support the phosphide-bridged structure **3** (see Experimental Part). Only a few complexes with a single phosphide bridge are known [9–13].

Neutral complexes **4–10** are formed from (OC)₅ReFBF₃ and the anions [M(CO)₅X]⁻ [14–23]:



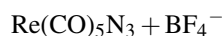
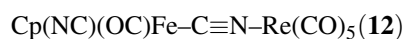
	4	5	6	7	8	9	10
M	Cr	Cr	Cr	Cr	Cr	W	W
X	Br	I	CN	NCS	SH	NCS	SH

The pentacarbonylcyanochromate(0), [(OC)₅Cr CN]⁻, has been proven as ideal and very often used building block (and as ligand) for the synthesis of cyanide-bridged complexes (OC)₅Cr–

CN-ML_n [24–33] with Fehlhhammer's super complexes [34, 35] (e. g. $[(\text{OC})_5\text{Cr-CN}]_6\text{Cr}^{3-}$ as one of the highlights. The synthesis of $(\text{OC})_5\text{Cr-CN-Re}(\text{CO})_5$ (**6**) is a new example.

The organometallic Lewis acid $\text{Re}(\text{CO})_5^+$ could be added to each of the cyanide ligands in $[\text{Pt}(\text{CN})_4]^{2-}$ and $[\text{Au}(\text{CN})_2]^-$ [36] to afford CN-bridged metal compounds.

Other SH-bridged complexes $[(\text{OC})_5\text{M-S(H)-M}(\text{CO})_5]^-$ (M = Cr, W) have been reported from the reaction of $[\text{M}(\text{CO})_5\text{SH}]^-$ with $\text{M}(\text{CO})_5\text{THF}$ [21, 23], and $[\text{Cp}(\text{OC})_3\text{W-S(H)-W}(\text{CO})_3\text{Cp}]^+$ was obtained from $\text{Cp}(\text{CO})_3\text{WSH}$ and $\text{Cp}(\text{OC})_3\text{W}^+$ [37]. The cation $\text{Re}(\text{CO})_5^+$ could be added twice to the tricyanomethanide ligand in $[(\text{OC})_5\text{W-N}\equiv\text{C-C}(\text{CN})_2]^-$ [38] to afford complex **11**, whereas only one equivalent of $\text{Re}(\text{CO})_5^+$ was added to $[\text{Cp}(\text{OC})(\text{NC})\text{Fe}(\text{CN})]^-$ [39] to give **12**.



Previously, the synthesis and crystal structure of the tricyanomethanido complex $(\text{OC})_5\text{Re-N}\equiv\text{C-C}(\text{CN})_2$ [40] were reported. By addition of another equivalent of $\text{Re}(\text{CO})_5^+$ to this complex an insoluble product was obtained which could not be purified.

From $\text{Re}(\text{CO})_5\text{FBF}_3$ and NaN_3 the cationic azide-bridged complex $[(\text{OC})_5\text{Re-N}_3\text{-Re}(\text{CO})_5]^+ \text{BF}_4^-$ (**13**) could be isolated, whereby $\text{Re}(\text{CO})_5\text{N}_3$ may be formed as an intermediate. The analogous dirhenium complexes $[(\text{OC})_5\text{Re-X-Re}(\text{CO})_5]^+$ (X = F, Cl, Br) bridged by a single halide have been synthesized by Mews [41] and Raab [36]. Other examples for complexes bridged by a single azide are $[(\text{OC})_5\text{Cr-N}_3\text{-Cr}(\text{CO})_5]^-$ [42], $[\text{bipy}(\text{OC})_3\text{M-N}_3\text{-M}(\text{CO})_3\text{bipy}]^-$ (M = Cr, Mo, W) [42] and $[(\text{Ph}_3\text{P})_2(\text{OC})\text{M-N}_3\text{-M}(\text{CO})(\text{PPh}_3)_2]^+$ (M = Rh, Ir) [43].

Further complexes bridged by a single anion include, e. g., $[(\text{OC})_5\text{Mn-NCS-Mn}(\text{CO})_5]^+$ [41], $(\text{OC})_5\text{M-X-M}(\text{CO})_5^-$ (M = Cr, Mo, W), (X = I, SCN, CN) [44–47], $[\text{Cp}(\text{OC})_2\text{Fe-X-Fe}(\text{CO})_2\text{Cp}]^+$ [48, 49], $[\text{Cp}(\text{ON})_2\text{Cr-Cl-Cr}(\text{NO})_2\text{Cp}]^+$ [50], $[\text{Cp}(\text{OC})_3\text{M-I-M}(\text{CO})_3\text{Cp}]^+$ (M = Mo, W) [51, 52],

$[(\text{dppe})(\text{OC})_2\text{Mo-F-Mo}(\text{CO})_2(\text{dppe})]^+$ [53], $(\text{OC})_2(\text{Cl})\text{Rh-Cl-Rh}(\text{CO})(\text{aminophosphorane})$ [54], and $[(\text{Ph}_3\text{P})\text{Au-Cl-Au}(\text{PPh}_3)]^+$ [55].

Nickel [56, 57], palladium [58–63] and platinum [58–65] complexes with a single unsupported halide bridge and with various other ligands have attracted the interest of various research groups until recent times.

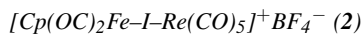
The carbonyl metal complexes **1–13** have been characterized by their CO absorptions in the IR spectra (see Experimental Part). The IR absorptions of the azide bridge in **13** appears at 2138 cm^{-1} ($\nu_{\text{as}}(\text{N}_3)$) and 1270 cm^{-1} ($\nu_{\text{s}}(\text{N}_3)$) and are very similar to those of $[(\text{Ph}_3\text{P})_2(\text{OC})\text{Rh-N}_3\text{-Rh}(\text{CO})(\text{PPh}_3)_2]^+$ (2163 and 1280 cm^{-1}) [43]. A $\mu_{1,1}\text{-N}_3$ bridge is assumed for **13** as it is found in most of the carbonyl complexes with N_3 bridges [66, 67]. The properties of **10** (similar to those of $[\text{Cr}(\text{CO})_5\text{SH}]^-$ [21] or $\text{CpCr}(\text{CO})_3\text{SH}$ [68]) point to a relatively high acidity of the SH ligand. Indeed, the ^1H NMR signal of **10** disappears immediately after addition of CD_3OD , and **10** can be deprotonated by NaH.

Experimental Part

$\text{Re}(\text{CO})_5\text{FBF}_3$ was prepared immediately before use from $\text{CH}_3\text{Re}(\text{CO})_5$ and tetrafluoroboric acid etherate [69–71]. NMR spectra: Varian FT 80A and Jeol FX 90 Q spectrometers.



To a suspension of $\text{Re}(\text{CO})_5\text{FBF}_3$ (382 mg, 0.93 mmol) in 10 mL of dichloromethane $\text{CpFe}(\text{CO})_2\text{Cl}$ (200 mg, 0.94 mmol) [6] was added. After 30 min 30 mL of diethyl ether were added to the clear red solution, and a red-brown oily product precipitated. The suspension was stirred for 1 h at -78°C to give a dark-red powder which was washed several times with diethyl ether and dried *in vacuo*. To the product dichloromethane (10 mL) was added, the solid was filtered off, and the solution was layered with 20 mL of diethyl ether. After 12 h a deep-red powder was obtained which was washed several times with diethyl ether and dried *in vacuo*. Yield 40%. – $\text{C}_{12}\text{H}_5\text{BClFeRe}$ (625.5): calcd. C 23.05, H 0.81; found C 22.86, H 1.48. – IR (CH_2Cl_2 , cm^{-1}): $\nu = 2156\text{ w}$, 2070 m , 2047 m , 2024 m , 1987 m (CO). – ^1H NMR (90 MHz, CD_2Cl_2): $\delta = 5.06\text{ ppm}$ (s, C_5H_5).



To a suspension of $\text{Re}(\text{CO})_5\text{FBF}_3$ (360 mg, 0.87 mmol) in 5 mL of dichloromethane $\text{CpFe}(\text{CO})_2\text{I}$ (250 mg, 0.82 mmol) [6] was added, whereby a deep-red solution

was formed. The mixture was stirred for 1 h. Then, 10 mL of diethyl ether were added. The deep-red precipitate was washed three times with diethyl ether and dried *in vacuo*. Yield 90%. – $C_{12}H_5BF_4FeIRe$ (716.9): calcd. C 20.10, H 0.70; found C 20.78, H 1.76. – IR (CH_2Cl_2 , cm^{-1}): $\nu = 2154$ w, 2126 w, 2061 m, 2045 s, 2015 m, 1996 m (CO). – 1H NMR (90 MHz, CD_2Cl_2): $\delta = 5.32$ ppm (s, C_5H_5).

$[Cp(OC)_2Fe-PPh_2-Re(CO)_5]^+BF_4^-$ (3)

To $(OC)_5ReFBF_3$ (540 mg, 1.3 mmol) in 5 mL of dichloromethane a solution of $CpFe(CO)_2PPh_2$ (433 mg, 1.2 mmol) [7] in 5 mL of dichloromethane was added. After 10 min an almost clear red solution was formed to which 5 mL of dichloromethane were added. After filtration diethyl ether (30 mL) was added to the filtrate, whereby a dark oil precipitated. The mixture was stirred for 48 h. The formed orange powder was washed several times with diethyl ether, dried *in vacuo* and dissolved in 10 mL of dichloromethane. A small amount of a solid was filtered off, and the filtrate was layered with 20 mL of diethyl ether. After 2 d yellow cubes and red needles were isolated, which were recrystallized from CH_2Cl_2/Et_2O . The solvent was decanted off, and the solid was washed with diethyl ether and dried *in vacuo*. – Elemental analysis of the yellow cubes: $C_{24}H_{15}BF_4FeO_7PRE$ (777.2): calcd. C 37.19, H 1.95; found C 39.52, H 2.70. – IR (nujol, cm^{-1}): $\nu = 2152$ w, 2043 s, 2039 s, 2029 s, 1908 w (CO). – Crystal data: monoclinic space group $P2_1/n$, $a = 1379.3$, $b = 1380.0$, $c = 1387.0$ pm, $\beta = 98.97^\circ$, $V = 2.608$ nm 3 , $Z = 4$. The single-crystal data set ascertained the connectivity but did not allow a satisfactory refinement of the crystal structure.

$(OC)_5Cr-Br-Re(CO)_5$ (4)

To a suspension of $Re(CO)_5FBF_3$ (344 mg, 0.84 mmol) in 10 mL of THF the complex $NEt_4[Cr(CO)_5Br]$ (305 mg, 0.82 mmol) [14] was added. After 2 h the precipitate was filtered off, and from the solution the solvent was removed *in vacuo* until the product precipitated. The mixture was cooled to $-78^\circ C$, and the yellow-orange product was filtered off and dried *in vacuo* for 12 h. The solid complex decomposes easily to give a brown powder. Yield 50%. – $C_{10}BrCrO_{10}Re$ (598.5): calcd. C 20.07; found C 20.42. – IR (THF, cm^{-1}): $\nu = 2152$ w, 2041 s, 1982 s, 1938 s, 1894 s (CO).

$(OC)_5Cr-I-Re(CO)_5$ (5)

A suspension of $Re(CO)_5FBF_3$ (366 mg, 0.88 mmol) in 10 mL of THF was cooled to $-78^\circ C$, and $NEt_4[Cr(CO)_5I]$ [14] (380 mg, 0.85 mmol) was added in small portions. The mixture was allowed to warm to room temperature and stirred for 1 h. The precipitate was filtered off, and from the filtrate the solvent was removed *in vacuo*. The deep-red residue was dissolved in 20 mL of diethyl ether

with some drops of THF, and then the mixture was cooled to $-20^\circ C$ for 12 h. After filtration the product was precipitated from the solution by addition of *n*-hexane and dried *in vacuo* with exclusion of light. Yield 60%. – $C_{10}CrIO_{10}Re$ (645.2): calcd. C 18.82; found C 18.86. – IR (THF, cm^{-1}): $\nu = 2148$ w, 2108 vw, 2038 s, 2011 w, 1981 s, 1938 s, 1894 m (CO). – ^{13}C NMR ($[D_6]THF$): $\delta = 221.5$, 213.6, 181.5, 177.9 ppm.

$(OC)_5Cr-CN-Re(CO)_5$ (6)

$Re(CO)_5FBF_3$ (306 mg, 0.75 mmol) and $NEt_4[Cr(CO)_5CN]$ (229 mg, 0.65 mmol) [16–18] were stirred in 10 mL of THF for 12 h at room temperature. The THF solution was decanted off, and the solid was extracted with 10 mL of THF. Both THF solutions were combined, and the solvent was removed *in vacuo*. The colorless residue was two times purified from THF/*n*-pentane solution. Yield 60%. – $C_{11}CrNO_{11}Re$ (544.6): calcd. C 24.26, N 2.57; found C 24.46, N 2.53. – IR (THF, cm^{-1}): $\nu = 2161$ vw, 2127 w, 2095 vw, 2050, 2007 m, 1979 m, 1939 s, 1925 sh (CO, CN).

$(OC)_5Cr-NCS-Re(CO)_5$ (7)

Under exclusion of light $Re(CO)_5FBF_3$ (351 mg, 0.86 mmol) and $NEt_4[Cr(CO)_5NCS]$ (315 mg, 0.82 mmol) [19] were stirred in 10 mL of THF at $-78^\circ C$ for 30 min. The mixture was allowed to warm and was stirred for 2 h at room temperature. The solution was decanted off, and the solvent was removed *in vacuo*. The yellow residue was dissolved in THF, and *n*-pentane was added until the solution became dim yellow; thin needles crystallized at $-20^\circ C$. Yield 60%. – $C_{11}CrNO_{10}Re$ (576.4): calcd. C 22.92, N 2.43, S 5.56; found C 23.51, N 2.71, S 5.94. – IR (THF, cm^{-1}): $\nu = 2152$ m, 2092 w, 2071 m, 2046 vs, 2009 s, 1941 vs, 1902 s, 577 m.

$(OC)_5Cr-S(H)-Re(CO)_5$ (8)

To $(OC)_5ReFBF_3$ (276 mg, 0.67 mmol) in 15 mL of dichloromethane $AsPh_4[Cr(CO)_5SH]$ (349 mg, 0.57 mmol) [21] was added at $-78^\circ C$. After 1 h the mixture was allowed to warm to room temperature. When the suspension became clear the solvent was removed *in vacuo*. The yellow resinous residue was extracted twice with 10 mL of THF, and the THF solution was concentrated to dryness. The oily product was stirred with 5 mL of diethyl ether until it became crystalline, washed twice with 3 mL of diethyl ether and dried *in vacuo*. Recrystallization from $CH_2Cl_2-Et_2O$ afforded yellow needles. Yield 70%. – $C_{10}HCrO_{10}ReS$ (551.4): calcd. C 21.78, H 0.18; found C 21.50, H 0.51. – IR (nujol, cm^{-1}): $\nu = 2153$ m, 2029 vs, 1975 s, 1914 vs, 1895 s, 1869 s, 1854 s, 1842 s (CO). – 1H NMR (90 MHz, $[D_6]THF$): $\delta = 2.53$ ppm (s).

$(OC)_5W-NCS-Re(CO)_5$ (**9**)

To $Re(CO)_5FBF_3$ (386 mg, 0.94 mmol) in 10 mL of dichloromethane $NEt_4[W(CO)_5NCS]$ (440 mg, 0.75 mmol) [19] was added at $-78^\circ C$. The green-yellow mixture was allowed to warm up to give a yellow suspension which was stirred for 1 h at room temperature. Then, the solvent was removed *in vacuo*, and the residue was stirred with 10 mL of THF. The yellow THF solution was decanted off and concentrated to dryness. The pale-yellow product was washed several times with a small amount of diethyl ether and dried *in vacuo*. Through slow diffusion of petroleum ether into a saturated THF solution small yellow plates were obtained. Yield 70%. – $C_{11}NO_{10}ReSW$ (576.4): calcd. C 18.66, N 1.98, S 4.53; found C 19.33, N 2.10, S 4.49. – IR (THF, cm^{-1}): $\nu = 2148$ m, 2048 s, 2010 m, 1934 s, 1899 s (CO), 597 m.

 $(OC)_5W-S(H)-Re(CO)_5$ (**10**)

To $Re(CO)_5FBF_3$ (348 mg, 0.85 mmol) in 10 mL of THF the complex $AsPh_4[W(CO)_5SH]$ (510 mg, 0.7 mmol) [21] was added in portions at $-78^\circ C$. After 30 min the mixture was allowed to warm up to give a yellow suspension, which was stirred for 30 min at room temperature. The solvent was removed *in vacuo*, and the residue was extracted with 10 mL of THF. The THF solution was concentrated to dryness, and the resulting yellow resin was washed several times with diethyl ether until it became crystalline. The ocker-yellow product was dried *in vacuo*. Yield 80%. – $C_{10}HO_{10}ReSW$ (683.2): calcd. C 17.58, H 0.15, S 4.69; found C 17.78, H 0.42, S 4.65. – IR (CH_2Cl_2 , cm^{-1}): $\nu = 2151$ w, 2097 w, 2063 w, 2016 m, 2008 m, 1981 s, 1933 vs, 1901 sh (CO).

 $(OC)_5W-NC-C[CNRe(CO)_5]_2^+BF_4^-$ (**11**)

$Re(CO)_5FBF_3$ (660 mg, 1.6 mmol) and $NEt_4[W(CO)_5NCC(CN)_2]$ (500 mg, 0.9 mmol) [38] in 20 mL of THF were stirred at $-78^\circ C$ for 12 h and slowly allowed to warm up. The yellow solution was decanted off, and the residue was extracted with 20 mL of THF. The combined THF solutions were concentrated to dryness, and the residue was purified from THF-diethyl ether and then from acetone-diethyl ether. The product was washed with diethyl ether and dried *in vacuo*. Yield 90%. – $C_{19}BF_4N_3O_{15}Re_2W$

(740.2): calcd. C 19.79, N 5.64; found C 20.29, N 3.73. – IR (nujol, cm^{-1}): $\nu = 2234$ w, 2221 w (CN), 2167 w, 2059 vs, 2022 m, 1977 m, 1939 vs, 1900 m (CO).

 $Cp(OC)(NC)Fe-CN-Re(CO)_5$ (**12**)

To a clear solution of $(OC)_5ReFBF_3$ (361 mg, 0.88 mmol) in 15 mL of water $K[CpFe(CO)(CN)_2]$ (255 mg, 1.06 mmol) [39] was added in portions. From the resulting slightly dim, pale-yellow solution a yellow precipitate was obtained within 12 h. The now green solution was decanted off, and the residue was washed several times with water and dried *in vacuo*. The solid was dissolved in 10 mL of CH_2Cl_2 , and the solution was layered with 20 mL of diethyl ether. The pale-yellow crystalline product was washed with diethyl ether and dried *in vacuo*. From the CH_2Cl_2 solution another portion of **12** was obtained by precipitation with diethyl ether. Yield 70%. – $C_{13}H_5FeN_2O_6Re$ (527.2): calcd. C 29.62, H 0.96, N 5.31; found C 29.74, H 0.96, N 5.55. – IR (nujol, cm^{-1}): $\nu = 2163$ w, 2129 m, 2104 m, 2046 s, 2017 s, 2005 m, 1969 m, 1954 m, 1941 m (CO). – 1H NMR (90 MHz, CD_2Cl_2): $\delta = 4.75$ ppm (s, C_5H_5).

 $[(OC)_5Re-N_3-Re(CO)_5]^+BF_4^-$ (**13**)

A suspension of $Re(CO)_5FBF_3$ (320 mg, 0.77 mmol) and NaN_3 (50 mg, 0.77 mmol) in 5 mL of dichloromethane was stirred for 4 h at room temperature. The residue was centrifuged off, and the solution was dropped into 20 mL of diethyl ether, whereby **13** precipitated. The yield could be improved by extraction of the residue twice with 3 mL of CH_2Cl_2 . The precipitate was then centrifuged off, washed twice with 3 mL of diethyl ether and dried *in vacuo*. Complex **13** does not explode upon heating. Yield 80%; m. p. 112–125 $^\circ C$. – $C_{10}BF_4N_3O_{10}Re_2$ (781.4): calcd. C 15.35, N 5.37; found C 15.47, N 5.32. – IR (nujol, cm^{-1}): $\nu = 2170$ w, 2100 w, 2050 vs, 2000 s, 1960s (CO); 2132 m ($\nu_{as}(N_3)$), 1270 vw ($\nu_s(N_3)$). – IR (CH_2Cl_2 , cm^{-1}): $\nu = 2179$ w, 2106 w, 2062 vs, 2003 s (CO); 2138 m (N_3).

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