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Salts of the Cobalt(I) Complexes $[Co(CO)_5]^+$ and $[Co(CO)_2(NO)_2]^+$ and the Lewis Acid–Base Adduct $[Co_2(CO)_7CO{-}B(CF_3)_3]$

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Abstract: The reaction of $[Co_2(CO)_8]$ with $(CF_3)_3BCO$ in hexane leads to the Lewis acid–base adduct $[Co_2(CO)_7CO{-}B(CF_3)_3]$ in high yield. When the reaction is performed in anhydrous HF solution $[Co(CO)_5][(CF_3)_3BF]$ is isolated. The product contains the first example of a homoleptic metal pentacarbonyl cation with 18 valence electrons and a trigonal-bipyramidal structure. Treatment of $[Co_2(CO)_8]$ or $[Co(CO)_3NO]$ with NO^+ salts of weakly coordinating anions results in mixed crystals containing the $[Co(CO)_5]^+$/$[Co(CO)_2(NO)_2]^+$ ions or pure novel $[Co(CO)_2(NO)_2]^+$ salts, respectively. This is a promising route to other new metal carbonyl nitrosyl cations or even homoleptic metal nitrosyl cations. All compounds were characterized by vibrational spectroscopy and by single-crystal X-ray diffraction.

Keywords: carbonyl ligands · cobalt · density functional calculations · nitrosyl ligands · vibrational spectroscopy

Introduction

Homoleptic metal carbonyl cations have a number of unique features that set them apart from other metal carbonyls:[1–6] 1) The cations, many of which are superelectrophilic,[7] are conveniently generated in conjugate Brønsted–Lewis superacids[8,9] such as HF–SbF_5;[1–6] 2) Salts of high thermal stability are formed with $[Sb_2F_{11}]^-$ or less frequently $[SbF_6]^-$ or $[BF_4]^-$ as counteranions;[1–6,10] 3) These salts have been extensively characterized by single-crystal X-ray diffraction, as well as by spectroscopic (IR, Raman, ^{13}C NMR), thermochemical (DSC), and computational methods;[1–6] 4) The geometries of the cations are octahedral (d^6), square-planar (d^8), or linear (d^{10}), whereby the last two geometries had been previously unknown for metal carbonyl complexes;[1–6] 5) The vast majority of metal carbonyl cations are formed by metals from the second (4d) and third (5d) transition series.[1–6]

Due to the considerable oxidizing ability of SbF_5, many feasible carbonyl monocations, such as $[Co(CO)_5]^+$, $[Cr(CO)_6]^+$, and $[Ta(CO)_7]^+$, are not obtainable in HF–SbF_5, and other synthetic pathways are required, which employ Lewis acids incapable of oxidizing side reactions.

Here we report on recent results for Co^I, which are at variance with most of the general aspects summarized above: 1) Treatment of $[Co_2(CO)_8]$ with the new conjugate Brønsted–Lewis superacid HF–$(CF_3)_3BCO$ allows the synthesis of $[Co(CO)_5][(CF_3)_3BF]$, which contains the first example of a trigonal-bipyramidal metal carbonyl cation, as reported in a preliminary communication.[11] 2) In hexane solution $[Co_2(CO)_8]$ forms with $(CF_3)_3BCO$ a Lewis acid-base adduct $[Co_2(CO)_7CO{-}B(CF_3)_3]$, which has been structurally characterized. 3) $[Co(CO)_3NO]$ reacts with nitrosyl salts such as $NO[B(CF_3)_4]$ to give new cationic mixed carbonyl nitrosyl complexes, for example, $[Co(CO)_2(NO)_2][B(CF_3)_4]$. 4) DFT calculations on $[Co(CO)_5]^+$, its isoelectronic species $[Mn(CO)_5]^-$ and $Fe(CO)_5$, as well as on $[Co(NO)_2(CO)_2]^+$ support the vibrational assignments and predict some bonding properties.

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Results and Discussion

Synthetic aspects: The aim of this study was the syntheses of thermally stable salts of cobalt(I) carbonyl cations from $[Co_2(CO)_8]$ as precursor. Since cobalt(I) is expected to be electrophilic and sensitive to oxidation, the counterion in the salt must be nonoxidizing, weakly coordinating, and chemically robust. Promising in this respect are perfluoroalkyl borates such as $[B(CF_3)_4]^-$[12] and $[(C_2F_5)_3BF]^-$,[13] which are readily available. Appropriate precursors for oxidative carbonylations such as $M[B(CF_3)_4]$ ($M^+ = Ag^+$,[12] NO^+,[14] Ph_3C^+,[15] $[H(Et_2O)_2]^+$,[15] etc.) are known, and the borane carbonyl $(CF_3)_3BCO$[16,17] a precursor for the nonoxidizing Lewis superacid $B(CF_3)_3$, is available. However, $B(CF_3)_3$ is a short-lived, transient species.[18] On dissolving $(CF_3)_3BCO$ in anhydrous HF loss of CO occurs and the system behaves like a conjugate Brønsted–Lewis superacid with H_2F^+ and $[(CF_3)_3BF]^-$ as components.[18]

Initially, $[Co_2(CO)_8]$ was treated with $(CF_3)_3BCO$ in an inert solvent such as hexane in the absence of any oxidizing agent, and the Lewis acid–base adduct $[Co_2(CO)_7CO{-}B(CF_3)_3]$ was formed in nearly quantitative yield [Eq. (1)].

$$[Co_2(CO)_8] + (CF_3)_3BCO \rightarrow [Co_2(CO)_7CO{-}B(CF_3)_3] + CO \tag{1}$$

Similar adducts, such as $[Co_2(CO)_7CO{-}AlBr_3]$ and $[Co_2(CO)_7CO{-}BX_3]$ (X = Cl, Br, I),[19–23] have been described but not structurally characterized. Other Lewis acids (e.g., $GaBr_3$ and $TlCl_3$) form further reaction products with $[Co_2(CO)_8]$.[23,24] Nitriles in place of $[Co_2(CO)_8]$ react with $(CF_3)_3BCO$ in an analogous manner yielding $XCN{\cdot}B(CF_3)_3$ ($X = CH_3$, H).[16,17,25]

Reaction (1) proceeds in anhydrous HF (aHF) solution in a different way, whereby the proton acts as oxidizing agent [Eq. (2)] and $[Co(CO)_5][(CF_3)_3BF]$ was isolated in 72% yield.[11]

$$\begin{aligned}&[Co_2(CO)_8] + 2\,(CF_3)_3BCO + 2\,HF \xrightarrow[\text{aHF}]{\text{2 bar CO, RT}}\\&2\,[Co(CO)_5][(CF_3)_3BF] + H_2\end{aligned} \tag{2}$$

An earlier claim for $[Co(CO)_5]^+$ in $[Co(CO)_5][Co(CO)_4]$[26] was found to be in error.[27] In the gas phase, electron-impact studies demonstrated the existence of the series of cations $[Co(CO)_n]^+(g)$ ($n = 1$–5) and the Co–CO bonding energies were determined.[28] Laser ablation of cobalt in a CO atmosphere and isolation of the products in low-temperature matrices provided evidence for $[Co(CO)_n]^+$ ($n = 1$, 2).[29] A report on the synthesis of $[Co(CO)_4]^+(solv)$ in HSO_3F and HSO_3F/SbF_5 starting from $[Co_2(CO)_8]$ was recently published.[30] According to the vibrational data it was concluded that one solvent molecule is coordinated at the cobalt center.

An alternative oxidative carbonylation of $[Co_2(CO)_8]$ was found to be possible by using nitrosyl salts of weakly coordinating anions[11] [Eq. (3)].

$$\begin{aligned}&[Co_2(CO)_8] + 2\,NO[B(CF_3)_4] \xrightarrow[\text{C}_6\text{H}_{14}\text{ or CH}_2\text{Cl}_2]{\text{2 bar CO, RT}}\\&[Co(CO)_5][B(CF_3)_4] + [Co(NO)_2(CO)_2][B(CF_3)_4] + CO\end{aligned} \tag{3}$$

The reaction can be rationalized as follows: in a first step NO^+ oxidizes one Co^0 center in $[Co_2(CO)_8]$ to Co^I. In the presence of CO the $[Co(CO)_5]^+$ ion is formed. Both NO and NO^+ replace two CO molecules at the other Co^0 center, and subsequently the $[Co(NO)_2(CO)_2]^+$ cation is formed. This result is not unexpected, because similar reactions of NO^+ salts are known in organometallic chemistry.[31–33]

The equimolar mixture of $[Co(CO)_5]^+$ and $[Co(NO)_2(CO)_2]^+$ salts could not be separated and therefore a direct synthesis of a $[Co(NO)_2(CO)_2]^+$ salt was performed by treating $[Co(CO)_3NO]$[31–34] with $NO[B(CF_3)_4]$[14] [Eq. (4)].

$$\begin{aligned}&[Co(CO)_3NO] + NO[B(CF_3)_4] \xrightarrow{\text{CH}_2\text{Cl}_2}\\&[Co(CO)_2(NO)_2][B(CF_3)_4] + CO\end{aligned} \tag{4}$$

With the exception of $[Fe(CO)_5NO]Cl$,[35] metal carbonyl nitrosyl cations with linear M–NO groups seem to be unknown. However, many 18e molecules of the type $[M(CO)_{4-n}(NO)_n]$ (M = Cr, Mn, Fe, Co, Ni; $n = 0$–4) are known, some of which have been structurally characterized by gas-phase electron diffraction.[31–33]

Characterization of the products: The Lewis acid–base adduct $[Co_2(CO)_7CO{-}B(CF_3)_3]$ is a yellow thermally stable solid. Its formation according to Equation (1) can be followed by Raman spectroscopy. In comparison to the CO vibrations of $[Co_2(CO)_8]$ (2111 (s), 2029 (vs), 2015 (vs), 1866 (w), 1847 (w), 1830 cm^{-1} (w)) all ν(CO) band positions of the adduct are shifted to higher wavenumbers (2144 (s), 2093 (vs), 2081 (vs), 1880 cm^{-1} (w)) as a result of the strong electron withdrawing ability of the Lewis acid $B(CF_3)_3$. The Raman scattering of the $B(CF_3)_3$ fragment is low, and therefore only two weak bands of this moiety at 727 and 606 cm^{-1} were visible. Because the pattern in the ν(CO) region is similar in both the precursor and the adduct (Figure 1), the structure should be little changed. The boron atom is bonded to one of the bridging CO ligands, as was confirmed by a single-crystal X-ray diffraction study. One of the two independent molecular units in the solid state is depicted in Figure 2. Crystallographic data are listed in Table 1, and selected internal bond parameters in Table 2. The $B(CF_3)_3$ fragment is strongly bound to one oxygen lone pair of one of the bridging CO ligands and the resulting bond length O5–B1 is 1.535(12) Å in both independent molecules, but significantly longer than 1.4583(12) Å found for the O–B bond in the anion $[(CF_3)_3BOMe]^-$.[36] The possibility that $(CF_3)_3BCO$ has replaced a carbonyl ligand from $[Co_2(CO)_8]$ to give a B-C-O arrangement has been ruled out unambiguously. Exchange of the atom-type assignment for atoms C5 and O5 as well as C5′ and O5′ in the crystal struc-

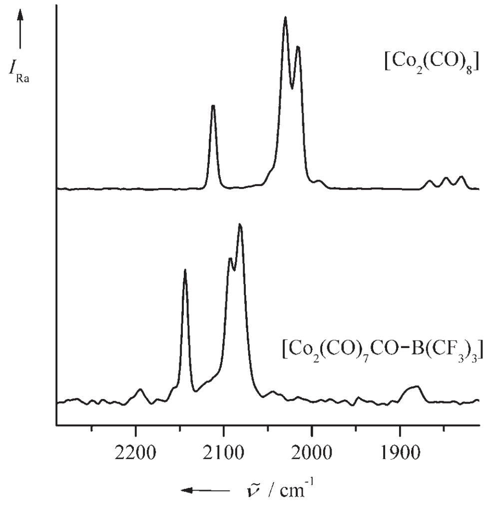

Figure 1. CO stretching region in the Raman spectra of $[Co_2(CO)_8]$ (top) and $[Co_2(CO)_7CO{-}B(CF_3)_3]$ (bottom).

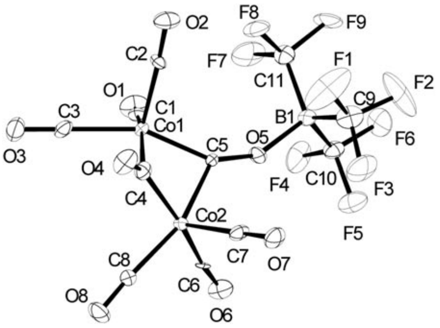

Figure 2. One of the two independent formula units (molecule 1) in the unit cell of $[Co_2(CO)_7CO{-}B(CF_3)_3]$ (anisotropic displacement parameter ellipsoids are set to 25 % probability).

Table 1. Crystallographic data of $[Co_2(CO)_7CO]{-}B(CF_3)_3]$ and $[Co(CO)_5][(CF_3)_3BF]$.

	$[Co_2(CO)_7CO{-}B(CF_3)_3]$	$[Co(CO)_5][(CF_3)_3BF]$
empirical formula	$C_{11}BCo_2F_9O_8$	$C_8BCoF_{10}O_5$
color	yellow	orange
size [mm]	0.53 × 0.07 × 0.07	0.16 × 0.10 × 0.10
crystal system,	triclinic	monoclinic
space group	$P1$ (no. 1)	$P2_1/c$ (no. 14)
a [Å]	7.0513(2)	7.9858(1)
b [Å]	8.6352(2)	13.9485(1)
c [Å]	14.9936(5)	12.5826(1)
α [°]	86.787(1)	90
β [°]	79.896(1)	98.91
γ [°]	77.418(2)	90
V [Å^3]	877.06(4)	1384.67(2)
Z	2	4
ρ_{calcd} [g cm^{-3}]	2.120	2.091
μ [mm^{-1}]	2.024	1.383
$F(000)$ [e]	540	840
data collection range [°]	$6.64 < \theta < 33.31$	$3.85 < \theta < 30.56$
no. of reflns collected/ unique	12 892/7981	25 226/4219
no. of reflns obsd $[I > 2\sigma(I)]$	6297	3847
R_1 $(I > 2\sigma(I))$[a]	0.064	0.030
wR_2 (all data)[b] [%]	0.180	0.076

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; weighting scheme $w = [\sigma^2(F_o)+(aP)^2+bP]^{-1}$, $P = [\max(0,F_o^2)+2F_c^2)/3]$; $[Co(CO)_5][(CF_3)_3BF]$: $a = 0.0325$, $b = 1.1691$; $[Co_2(CO)_7CO{-}B(CF_3)_3]$: $a = 0.0345$, $b = 8.9016$.

ture refinement yields unrealistic isotropic displacement parameters and R values that are 0.5 percentage points higher. The nonlinear geometry of the B-O-C fragment is a further strong indication for the correct assignment of the atom types.

Due to repulsion of one CF_3 group (C11), the bond angle O5-C5-Co1 (av 145°) is wider than O5-C5-Co2 (av 129°), and the C5-O5-B1 bond angle (av 148.5°) is much greater than the 120°, expected for the oxygen lone pair at the bridged C=O group. In addition, lengthening of the C5–O5 bond by 0.07 Å compared to C4–O4 and distortion of the Co1-C5-Co2 bridge is noted. The electron-withdrawing effect of $B(CF_3)_3$ decreases the bond lengths in Co1-C5-Co2 by about 0.1 Å in comparison to those in Co1-C4-Co2 and leads to a diametrically unsymmetrical carbonyl bridge. The structural differences between $[Co_2(CO)_7CO{-}B(CF_3)_3]$ and $[Co_2(CO)_8]$[37] are small and not very significant (Table 2) except for the asymmetric carbonyl bridges. The bond lengths of the terminal

Table 2. Experimental and calculated bond lengths [Å] and angles [°] of $[Co_2(CO)_7CO{-}B(CF_3)_3]$ and experimental bond parameters of $[Co_2(CO)_8]$.[b]

Parameter	$[Co_2(CO)_7CO{-}B(CF_3)_3]$ molecule 1	molecule 2	calcd[a]	calcd[b]	$[Co_2(CO)_8]$[c] molecule 1	molecule 2
Co–Co	2.518(2)	2.511(2)	2.537	2.510	2.5301(8)	2.5278(8)
Co–$CO_{terminal}$	1.850[d]	1.848[d]	1.848	1.824	1.826[d]	1.829[d]
Co–CO_{bridge}	1.951[d]	1.961[d]	1.965	1.939	1.939[d]	1.941[d]
Co–COB	1.860[d]	1.860[d]	1.891	1.872		
C–$O_{terminal}$	1.127[d]	1.126[d]	1.133	1.142	1.135[d]	1.134[d]
C–O_{bridge}	1.176(13)	1.148(13)	1.160	1.170	1.166[d]	1.163[d]
C–OB	1.232(12)	1.234(12)	1.217	1.220		
O–B	1.535(13)	1.535(13)	1.580	1.575		
B–CF_3	1.619[d]	1.605[d]	1.633	1.622		
C–F	1.343[d]	1.340[d]	1.360	1.361		
Co-CO_{bridge}-Co	80.3(3)	79.5(3)	80.4	80.7	81.5[d]	81.3[d]
Co-COB-Co	85.2(3)	84.9(4)	84.3	84.2		
Co-C-$O_{terminal}$	177.2[d]	177.7[d]	177.4	176.2	177.7[d]	177.3[d]
Co-C-O_{bridge}	139.8[d]	140.1[d]	139.8	139.6	139.2[d]	139.3[d]
Co-C-OB	136.9[d]	137.4[d]	137.8	137.9		
C-O-B	149.2(8)	148.3(8)	148.2	144.2		
O-B-CF_3	106.4[d]	106.7[d]	105.5	105.4		

[a] B3LYP/6-31G(d). [b] B3LYP/6-311+G(d) without frequency calculation. [c] Approximate C_{2v} symmetry.[37] [d] Averaged values.

CO ligands are slightly shorter in $[Co_2(CO)_7CO{-}B(CF_3)_3]$, in accordance with the higher wavenumbers of ν(CO). Independent of the basis sets, the bonding parameters are quite well reproduced by DFT calculations.

The reaction product $[Co(CO)_5][(CF_3)_3BF]$, formed according to Equation (2), is an orange, moisture-sensitive solid. Consistent with differential scanning calorimetry (DSC) measurements and thermal decomposition studies in a glass capillary, the salt is thermally stable up to 110 °C, above which decomposition with gas evolution occurs. The compound is only slightly soluble in anhydrous HF and decomposes within a few hours. It was not possible to record the ^{13}C NMR spectrum of the cation, either in anhydrous HF solution or in the solid state by the magic-angle spinning (MAS) method, presumably due to line broadening. In the MAS ^{13}C NMR spectrum only the signal of the CF_3 groups at 134 ppm was observed.

In the ν(CO) stretching region three Raman (2197, 2155, 2120 cm^{-1}) and two IR bands (2146, 2120 cm^{-1}) were observed, and the band at 2120 cm^{-1} is both Raman- and IR-active (Figure 3). According to the selection rules, the band pattern is only consistent with $[Co(CO)_5]^+$ in D_{3h} symmetry. Therefore, the irreducible representation of all fundamentals and their activities is given by Equation (5).

$$\Gamma_{\mathrm{vib}} = 4\,A_1'\ (\mathrm{Ra}) + A_2'\ (-) + 4\,A_2''\ (\mathrm{IR}) + 6E'\ (\mathrm{IR, Ra}) + 3\,E''\ (\mathrm{Ra}) \quad (5)$$

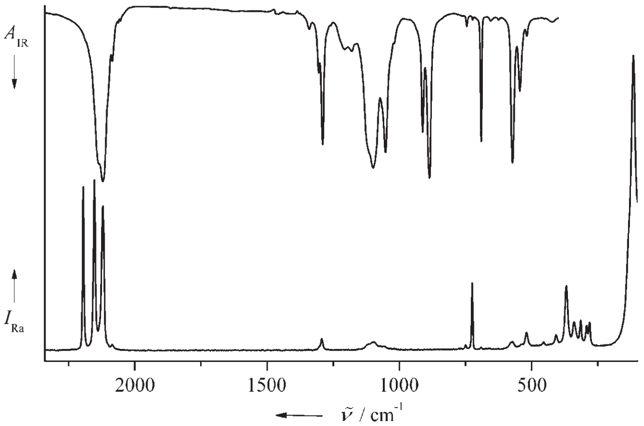

Figure 3. IR and Raman spectrum of $[Co(CO)_5][(CF_3)_3BF]$.

Of the 17 possible IR or Raman active fundamentals 12 were obtained experimentally (Table 3). The other, missing bands are either too weak, overlapping, or obscured by anion bands.[38] As can be seen in Table 3 the agreement between experimental and calculated band positions as well as IR and Raman intensities is reasonable. This allows an unambiguous assignment of the observed fundamentals. A comparison of the ν(CO) bands with data reported for unstable $[Co(CO)_4L]^+$ in HSO_3F solution leads to the conclusion that $[Co(CO)_5]^+$(solv) was probably present.[30] Furthermore, in Table 3 the vibrational data of $[Co(CO)_5]^+$ are compared with those of the isoelectronic species $[Fe(CO)_5]$ and $[Mn(CO)_5]^-$. For $[Mn(CO)_5]^-$ complete experimental data have not yet been obtained. In this triad with increasing positive charge of the metal center, all ν(CO) bands shift to higher wavenumbers and the separation between the different stretching fundamentals decreases. On the other hand the skeletal motions show the opposite trend. This phenomenon is attributed to decreasing M−CO π backdonation in this series, as described for the hexacarbonyls $[M(CO)_6]$ (M = W, Re^+, Os^{2+}, Ir^{3+}).[4–6,39]

The structure of $[Co(CO)_5][(CF_3)_3BF]$ was confirmed by single-crystal X-ray diffraction. The crystallographic data are listed in Table 1, a formula unit of the compound is shown in Figure 4, and selected bond parameters are collected in Table 4. There are no significant interactions between

Table 3. Vibrational data of the isoelectronic metal carbonyls $[Mn(CO)_5]^-$, $[Fe(CO)_5]$, and $[Co(CO)_5]^+$.

	$[Mn(CO)_5]^{-}$ [a]			$[Fe(CO)_5]$ [b]			$[Co(CO_5]^{+}$ [c]			Assignment according to
obsd	calcd[d]	I_{IR}/I_{Raman}[e]	obsd	calcd[d]	I_{IR}/I_{Raman}[e]	obsd	I_{IR}/I_{Raman}	calcd[d]	I_{IR}/I_{Raman}[e]	D_{3h} symmetry
	2059	35/0	2121	2175	89/0	2197	–/vs	2269	0/174	A_1' $\nu_s(CO)_{ax}$
	1949	213/0	2042	2095	234/0	2155	–/vs	2226	0/208	A_1' $\nu_s(CO)_{eq}$
1899	1959	0/2341	2034	2098	0/1562	2146	vs/–	2224	781/0	A_2'' $\nu_{as}(CO)_{ax}$
1862	1922	193/3962	2013	2070	219/2722	2120	vs/vs	2208	1321/220	E' $\nu_{as}(CO)_{eq}$
	709	1.8/332	645	655	0.02/273	571	s/–	573	143/0.02	E' $\delta_{as}(CoCO)$
	668	0/178	619	615	0/132	544	m/–	530	69/0	A_2'' $\delta_{as}(CoCO)$
	580	1.6/0	553	566	1.0/0	–		521	0/0.14	E'' $\delta_{as}(CoCO)$
	513	6.0/4.5	493	479	2.5/4.7	422	w/–	426	0.74/0.42	E' $\delta_{as}(CoCO)$
	505	0/5.2	475	467	0/9.6	422	w/–	402	3.3/0	A_2'' $\nu_{as}(CoC)_{ax}$
	461	20/0	443	433	6.0/0	407	–/w	386	0/2.9	A_1' $\nu_s(CoC)_{ax}$
	433	65/0	413	409	38/0	369	–/s	341	0/8.2	A_1' $\nu_s(CoC)_{eq}$
	460	0.26/11	429	436	0.0/29	339	m–s/w	329	27/1.2	E' $\nu_{as}(CoC)_{eq}$
	396	0.02/0	375	367	0.27/0	–		328	0/0.76	E'' $\delta_{as}(CoCO)$
	400	0/0	383	365	0/0	–		314	0/0	A_2' $\delta(CoCO)$
	96	5.7/0.09	105	104	4.0/0.77	–		107	1.0/1.7	E' $\delta(CCoC)$
	103	0/0.65	100	107	0/1.0	–		104	1.0/0	A_2'' $\delta(CCoC)$
	92	19/0	97	97	15/0	115	–/vs	94	0/11	E'' $\delta(CCoC)$
	49	4.7/0.01	74	53	5.6/0.02	–		51	0.00/5.0	E' $\delta(CCoC)$

[a] Ref. [53]. [b] This work and ref. [54]. [c] This work, $[(CF_3)_3BF]^-$ salt. [d] B3LYP/6-311+G(d). [e] IR intensities in km mol^{-1}, Raman activities in Å^4 amu^{-1}.

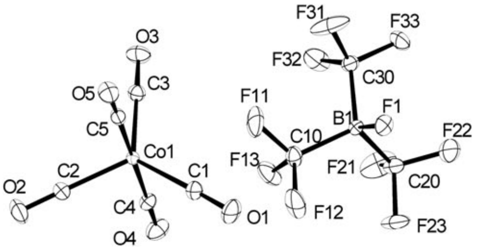

Figure 4. Formula unit of $[Co(CO)_5][(CF_3)_3BF]$ in the solid state (anisotropic displacement parameter ellipsoids are set to 40 % probability).

Table 4. Experimental and calculated bond lengths [Å] and angles [°] of $[Co(CO)_5]^+$ and the isoelectronic complexes $[Fe(CO)_5]$and $[Mn(CO)_5]^-$.

	$[Mn(CO)_5]^{-}$[a]		$[Fe(CO)_5]$[b]		$[Co(CO)_5]^{+}$[c]	
	exptl	calcd[d]	exptl	calcd[d]	exptl	calcd[d]
$(M-C_{ax})-(M-C_{eq})$	0.022	0.024	0.008	0.007	−0.027	−0.040
$M-C_{ax}$	1.820(11)	1.835	1.811(2)	1.828	1.826(2)	1.845
$M-C_{eq}$	1.798(11)	1.811	1.803(2)	1.821	1.853(2)	1.885
$(C-O)_{ax}$	1.148(9)	1.158	1.117(2)	1.139	1.117(2)	1.124
$(C-O)_{eq}$	1.156(9)	1.164	1.133(2)	1.143	1.117(2)	1.126
C_{ax}-M-C_{ax}	178.4(4)	180	178.9(1)	180	177.83(6)	180
C_{eq}-M-C_{eq}	120.0(4)	120	120.0(1)	120	119.99(7)	120
C_{ax}-M-C_{eq}	90.0(4)	90	90.1(1)	90	90.01(7)	90
M-$(C\text{-}O)_{ax}$	179.4(8)	180	179.4(2)	180	178.62(14)	180
M-$(C\text{-}O)_{eq}$	178.8(8)	180	179.6(2)	180	178.54(15)	180

[a] Cation: $[Ni(1,10\text{-}phen)_3]^{2+}$.[55] [b] Ref. [56]. [c] This work; anion: $[(CF_3)_3BF]^-$. [d] B3LYP/6-311+G(d).

anions and cations. Representative bond lengths and angles for the cation are compared in Table 4 to the corresponding data of the isoelectronic complexes $[Fe(CO)_5]$ and $[Mn(CO)_5]^-$. The structure of $[Co(CO)_5]^+$ is regular trigonal-bipyramidal (D_{3h}) with maximal deviations of C-Co-C bond angles from the ideal values of 4°. The axial Co−C bond lengths are shorter than the equatorial ones, whereas in $[Mn(CO)_5]^-$ the axial Mn−C bonds are longer, and in $[Fe(CO)_5]$ no significant differences between Fe−C_{ax} and Fe−C_{eq} bonds are found.

In the isoelectronic series $[Mn(CO)_5]^-$, $Fe(CO)_5$, and $[Co(CO)_5]^+$, M−C bond lengths increase and C−O bond lengths decrease in agreement with changes in the skeleton and ν(CO) wavenumbers. All observations are reproduced by DFT calculations. A qualitative molecular orbital model for pentacoordinated transition metal complexes with D_{3h} symmetry has been published.[40] According to this model the axial M−C bond should be stronger than equatorial ones for d^8 low-spin complexes if the σ effect of the CO ligands dominates over the π effect. (The strong M−CO_{ax} σ bonds are involved in the empty d_{z^2} orbital, while the M−CO_{eq} π bonds are weak).

Salts of the $[(CF_3)_3BF]^-$ ion are well known but the vibrational spectrum and structure of this anion had not been studied.[41] Therefore, Table 5 lists vibrational data of the $[(CF_3)_3BF]^-$ ion of the $[Co(CO)_5]^+$ and the Cs^+ salts and compares them to calculated values. The proposed assignment of modes is in accordance with C_3 symmetry. The structural parameters are listed in Table 6 and allow a comparison of those of $[(CF_3)_3BCl]^-$,[41] $[(CF_3)_3BBr]^-$,[41] and $[B(CF_3)_4]^-$.[12] The $[(CF_3)_3BCl]^-$ and $[(CF_3)_3BBr]^-$ anion exhibit C_3 symmetry in their Cs^+ salts, and the structure of the $[(CF_3)_3BF]^-$ anion shows only small deviations from C_3 symmetry, in agreement with the calculated structures (Table 6). A reduction of the symmetry is also noted for $[B(CF_3)_4]^-$, which has T rather than T_d symmetry.[12] As expected, the B−Hal bond length in the borate anions increases from Hal = F to Br. The structural parameters of the $(CF_3)_3B$ fragments in all four anions are similar and the differences are not significant.

Treatment of $[Co_2(CO)_8]$ in different solvents with the nitrosonium salt $NO[B(CF_3)_4]$[14] leads on one hand to $[Co(CO)_5]^+$ and on the other to $[Co(CO)_2(NO)_2]^+$. Pure $[Co(CO)_2(NO)_2][B(CF_3)_4]$ was obtained by treatment of $[Co(CO)_3NO]$[34] with $NO[B(CF_3)_4]$. The product is a brown, very moisture sensitive solid, which decomposes exothermically at 80 °C according to DSC measurements. As gaseous decomposition products, CO, NO, and $(CF_3)_3BCO$ were detected. The IR and Raman spectra in the CO and NO stretching range are displayed in Figure 5. Because the profiles of the respective bands in the pure salt differ considerably from that in the mixture, it appears that the mixture actually consists of mixed crystals. All observed band positions and intensities for the $[Co(CO)_2(NO)_2]^+$ ion are listed in Table 7. They are in good agreement with the calculated values [B3LYP/6-311+G(d)], which confirms the existence of this novel nitrosyl carbonyl cation.

Experimental Section

Apparatus: Volatile materials were manipulated in stainless steel or glass vacuum lines of known volume, equipped with capacitance pressure gauges (Type 280E, Setra Instruments, Acton, MA). The glass lines were equipped with PTFE-stem valves (Young, London), and the stainless steel lines with bellow valves (Balzers type BPV 25004 and Nupro type SS4BG), as well as with Gyrolok and Cajon fittings. For synthetic reactions in aHF reactors of perfluoroalkoxy copolymer (PFA) were used, consisting of 100 mL PFA bulbs with a standard-taper NS 29 socket (Bohlender, Lauda, Germany) in connection with a PTFE NS 29 standard-taper cone top and a PFA needle valve (type 204-30 Galtek, Fluoroware, Chaska, Minnesota). The parts were held together with a metal compression flange and the reactor was tight (leak rate $<10^{-5}$ mbar L s^{-1}) without using grease. Solid materials were manipulated inside an inert-atmosphere box (Braun, Munich, Germany) filled with argon, with a residual moisture content of less than 1 ppm.

Chemicals: Anhydrous HF (used as received, a gift from Solvay AG, Hannover, Germany), CO (standard grade, Messer GmbH, Krefeld, Germany), $[Co_2(CO)_8]$ (Strem Chemicals), and all standard chemicals were obtained from commercial sources. The borane carbonyl $(CF_3)_3BCO$ was prepared according to the literature procedure from $K[B(CF_3)_4]$ and sul-

Table 5. Experimental and calculated[a] band positions [cm^{-1}] and intensities of the $[(CF_3)_3BF]^-$ ion.

Calcd			$[Co(CO)_5][(CF_3)_3BF]$		$Cs[(CF_3)_3BF]$[b]		Assignment[c]		
$\tilde{\nu}$[d]	I_{IR}[e]	I_{Ra}[f]	IR[d]	Raman[d]	IR[d]	Raman[d]			
1267	3.4	3.6		1305w		1306w	A	ν_1	$\nu_s(CF_3)$
1259	297	5	1290m	1294w	1295s	1296w	E	ν_{13}	$\nu_s(CF_3)$
1089	643	5	1150–1070vs, br	1180–1040m, vbr	1110vs, br	1180–1040m, vbr	A	ν_2	$\nu_{as}(CF_3)$
1071	507	7					E	ν_{14}	$\nu_{as}(CF_3)$
1044	243	0.4					A	ν_3	$\nu(BF)$
1028	92	2.1	1052s				E	ν_{15}	$\nu_{as}(CF_3)$
985	0.03	0.6					A	ν_4	$\nu_{as}(CF_3)$
874	465	0.1	887s		887s		E	ν_{16}	$\nu_{as}(BC)$
712	0.4	10	723w	724s	720m	725s	A	ν_5	$\delta_s(CF_3)$
682	80	0.3	691m	691vw	690vs	691vw	E	ν_{17}	$\delta_s(CF_3)$
566	0.4	2.4		576w		573w	A	ν_6	$\delta_{as}(CF_3)$
530	0.1	0.9		539vw		539vw	E	ν_{18}	$\delta_{as}(CF_3)$
511	0.02	0.3	519w	519w	519w	520w	A	ν_7	$\delta_{as}(CF_3)$
509	7	2.9					E	ν_{19}	$\delta_{as}(CF_3)$
445	1.5	0.4		454w		454w	A	ν_8	$\rho(CF_3)$
307	0.6	3.2		315m		316m	E	ν_{20}	$\rho(CF_3)$
280	0.6	1.8		292m		294m	E	ν_{21}	$\rho(CF_3)$
265	0.4	1.6		281m		284m	A	ν_9	$\nu_s(BC)$
240	0.02	0.01					A	ν_{10}	$\rho(CF_3)$
206	3.6	0.02					E	ν_{22}	$\delta(CBF)$
141	0.2	0.03					A	ν_{11}	$\delta(CBC)$
116	0.04	0.01					E	ν_{23}	$\delta(CBC)$
55	0.1	0.01					E	ν_{24}	$\tau(CF_3)$
41	0.01	0.01					A	ν_{12}	$\tau(CF_3)$

[a] B3LYP/6-311+G(d). [b] Ref. [38]. [c] According to C_3 symmetry. [d] Wavenumbers in cm^{-1}. [e] IR intensities in $km\,mol^{-1}$. [f] Raman activities in $Å^4\,amu^{-1}$.

Table 6. Experimental and calculated bond lengths [Å] and angles [°] of $[(CF_3)_3BF]^-$ and related borate anions.

	$[(CF_3)_3BF]^-$[a]		$[(CF_3)_3BCl]^-$[b]		$[(CF_3)_3BBr]^-$[b]		$[B(CF_3)_4]^-$[c]	
	exptl	calcd[d]	exptl	calcd[d]	exptl	calcd[d]	exptl	calcd[d]
B−Hal[e]	1.407(2)	1.419	1.861(6)	1.889	2.029(17)	2.068		
$B{-}CF_3$	1.628[f]	1.652	1.627(4)	1.645	1.657(1)	1.642	1.625(3)	1.647
C−F	1.350[f]	1.370	1.340[f]	1.368	1.314[f]	1.368	1.355(3)	1.368
CF_3-B-Hal[e]	109.1[f]	108.5	108.1(2)	108.3	108.7(7)	108.0		
CF_3-B-CF_3	109.9[f]	110.4	110.8(2)	110.6	110.2(6)	110.9	109.5(3)	109.5
τ[g]	11.8[f]	11.8	6.1	0.4	5.9	3.8	7.3	14.3
symmetry	C_1 (approx. C_3)	C_3	C_3	C_3	C_3	C_3	C_3	T

[a] This work; cation: $[Co(CO)_5]^+$. [b] Ref. [41]; cation: Cs^+. [c] Ref. [12]; cation: Cs^+. [d] B3LYP/6-311+G(d). [e] Hal = F, Cl, Br. [f] Averaged values. [g] τ = torsional angle for rotation of the CF_3 groups from the staggered orientation.

furic acid.[16,17] The nitrosyl salt $NO[B(CF_3)_4]$ was synthesized by treating $[C(NH_2)_3][B(CF_3)_4]$ with liquid NO_2.[14] $[Co(CO)_3(NO)]$ was obtained by reaction of $[Co_2(CO)_8]$ with NO.[34] Volatile products were stored in glass ampoules which were opened and flame-sealed again using an ampoule key.[42]

Vibrational spectroscopy: Infrared spectra were recorded at room temperature on an IFS-66v FT spectrometer (Bruker, Karlsruhe, Germany). A DTGS detector together with a KBr/Ge beam splitter was used in the region of 5000–400 cm^{-1} and the salts were measured as neat solids or as Nujol mulls between AgBr disks. In this region 64 scans were co-added for each spectrum with an apodized resolution of 2 cm^{-1}. A Ge-coated 6 μm Mylar beam splitter and a far-IR DTGS detector were used in the region of 650–80 cm^{-1} and the salts were measured as neat solids or as Nujol mulls between polyethylene disks. In this region, 128 scans were co-added for each spectrum, with an apodized resolution of 2 cm^{-1}. Raman spectra were recorded at room temperature with a Bruker RFS100/S FT Raman spectrometer using the 1064 nm exciting line of an Nd/YAG laser in melting-point capillaries or through the wall of the reaction vessel in the region 3500–80 cm^{-1} with a resolution of 1 cm^{-1}. For each spectrum 256 scans were co-added.

Differential scanning calorimetry: Thermoanalytical measurements were made with a Netzsch DSC204 instrument. Temperature and sensitivity calibrations in the temperature range of 20–500 °C were carried out with naphthalene, benzoic acid, KNO_3, $AgNO_3$, $LiNO_3$, and CsCl. About 5–10 mg of the solid samples were weighed and contained in sealed aluminum crucibles. They were studied in the temperature range of 20–600 °C with a heating rate of 5 $K\,min^{-1}$; throughout this process the furnace was flushed with dry nitrogen. For the evaluation of the output, the Netzsch Protens4.0 software was employed.

Single-crystal X-ray diffraction: Suitable crystals of $[Co_2(CO)_7CO{-}B(CF_3)_3]$ and $[Co(CO)_5][(CF_3)_3BF]$ were obtained for X-ray diffraction studies as described in the synthetic procedures. Diffraction data were collected at 100 K on a KappaCCD diffractometer (Bruker AXS) using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. The crystal structure was determined by using SHELXS-97,[43] and full-matrix least-squares refinement based on F^2 was performed with SHELXL-97.[44] Integration and empirical absorption corrections (DENZO scalepack)[45] were applied. Molecular structures were drawn with the program Diamond.[46] Experimental details and crystal data are collected in Table 1.

CCDC-252159 ($[Co_2(CO)_7CO{-}B(CF_3)_3]$) and CCDC-199269 ($[Co(CO)_5]$-$[(CF_3)_3BF]$) contain the supplementary crystallographic data for this

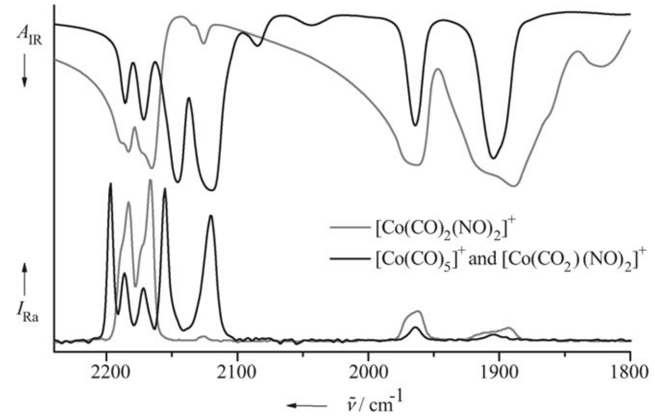

Figure 5. CO and NO stretching region in the IR and Raman spectra of $[Co(CO)_2(NO)_2][B(CF_3)_4]$ (gray) as well as mixed crystals of $[Co(CO)_2(NO)_2][B(CF_3)_4]$ and $[Co(CO)_5][B(CF_3)_4]$ (black).

Table 7. Experimental and calculated vibrational data of $[Co(CO)_2(NO)_2]^+$.

	$[Co(CO)_2(NO)_2]^+$			Assignment according	
Raman[a]	IR[a]	calcd[b]	I_{IR}/I_{Raman}[c]	to C_{2v} symmetry	
2183s	2183s	2254	183/149	A_1	ν(CO)
2167s	2165s	2232	461/165	B_2	ν(CO)
1962m	1960vs	2078	729/56	A_1	ν(NO)
1893m	1886vs	2018	1749/33	B_1	ν(NO)
606sh	606m	622	27/0.39	A_1	δ(CoNO)
588m	585m	606	47/11	B_1	ν(CoN)
	554sh	589	34/1.1	B_2	δ(CoNO)
531s[e]	542m	546	26/42	A_1	ν(CoN)
		459	0/0.11	A_2	δ(CoNO)
415w	415m	447	15/1.8	A_1	δ(CoCO)
415w	415m	437	57/0.60	B_1	δ(CoNO)
	386m	383	17/1.3	B_2	ν(CoC)
327sh[e]		351	7.7/3.7	A_1	ν(CoC)
		292	0.69/0.08	B_2	δ(CoCO)
		291	0/0.13	A_2	δ(CoCO)
		257	0.00/0.15	B_1	δ(CoCO)
92vs		86	0.03/3.3	A_1	δ(NCoN)
92vs		85	0.13/5.5	B_1	δ(CCoN)
		70	0.03/2.6	B_2	δ(CCoN)
		63	0.15/8.6	A_1	δ(CCoC)
		62	0/8.4	A_2	δ(CCoN)

[a] This work; anion: $[B(CF_3)_4]^-$. [b] B3LYP/6-311+G(d). [c] IR intensities in km mol^{-1}, Raman activities in Å^4 amu^{-1}.

paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Quantum-chemical calculations: DFT calculations[47] were carried out by using Becke's three-parameter hybrid functional and the Lee–Yang–Parr correlation functional (B3LYP)[48–50] with the Gaussian 98 program suite.[51] Geometries were optimized and energies calculated with the 6-311+G(d) or 6-31G(d) basis set, and all structures represent true minima on the respective hypersurface (no imaginary frequency). Diffuse functions were incorporated because improved energies are obtained for anions.[52] All energies presented herein are zero-point-corrected, and for enthalpies and free energies the thermal contributions are included for 298 K.

$[Co_2(CO)_7CO{-}B(CF_3)_3]$: $[Co_2(CO)_8]$ (106 mg, 0.3 mmol) was placed in a cylindrical glass reaction vessel (l=10 cm, V=10 mL) fitted with a PTFE valve and a magnetic stirring bar. $(CF_3)_3BCO$ (120 mg, 0.5 mmol) and hexane (3 mL) were condensed into the flask at −196 °C. After addition of 0.4 mmol of CO, the reaction mixture was warmed to room temperature and vigorously stirred for a short time. After one day a yellow solid and traces of a yellow crystalline solid formed. The reaction mixture was kept at room temperature for two weeks. Raman spectroscopy identified the yellow main product as $[Co_2(CO)_7CO{-}B(CF_3)_3]$, and the yellow side product as a $[Co(CO)_5]^+$ salt with an unidentified counteranion. The identity of $[Co_2(CO)_7CO{-}B(CF_3)_3]$ was confirmed by single-crystal X-ray diffraction.

Reaction of $[Co_2(CO)_8]$ with $NO[B(CF_3)_4]$: In a dry box $NO[B(CF_3)_4]$[14] (300 mg 0.9 mmol) was weighed into a 50-mL round-bottom flask fitted with a PTFE valve and a magnetic stirring bar. Hexane or dichloromethane (14 mL) was added to the nitrosyl salt under reduced pressure. After the reaction mixture was warmed to room temperature, $[Co_2(CO)_8]$ (400 mg 1.2 mmol) was added in a stream of dry nitrogen. The reaction mixture was cooled to −196 °C and CO (4 mmol) was condensed into the flask. The reaction mixture was stirred at room temperature for one week. Then all volatile substances were removed in vacuo. $[Co_4(CO)_{12}]$ was formed as side product and removed by washing with hexane. A mixture of solids was isolated (590 mg). According to the Raman spectrum the mixture contained about 50 % $[Co(CO)_5][B(CF_3)_4]$, about 50 % $[Co(CO)_2(NO)_2][B(CF_3)_4]$, and traces of the starting material $NO[B(CF_3)_4]$.

$[Co(CO)_5][(CF_3)_3BF]$: A 50-mL PFA round-bottom flask fitted with a PFA valve and a magnetic stirring bar was charged in a dry nitrogen gas stream with $[Co_2(CO)_8]$ (300 mg, 0.9 mmol), and subsequently aHF (2 mL), $(CF_3)_3BCO$ (533 mg, 2.2 mmol), and CO (2.8 mmol) were added by condensation in vacuo. During slow warming to room temperature and stirring a light yellow solid precipitated from the HF solution. The reaction mixture was left without stirring overnight at room temperature, which resulted in the formation of orange crystals. After removal of all volatile substances in vacuo an additional brown residue was formed and removed by washing with CH_2Cl_2. The orange crystals were dried in vacuo and stored in an inert atmosphere. Yield of isolated product: 550 mg (1.3 mmol, 72 %).

$[Co(CO)_2(NO)_2][B(CF_3)_4]$: In a dry box $NO[B(CF_3)_4]$ (300 mg, 0.9 mmol) was weighed into a 50-mL round-bottom flask fitted with a PTFE valve and a magnetic stirring bar. $[Co(CO)_3(NO)]$ (173 mg, 1.0 mmol) hexane or dichloromethane (16 mL) and CO (4 mmol) were added to the nitrosyl salt at −196 °C. The reaction mixture was stirred at room temperature for two days. All volatile substances were removed in vacuo. Yield of isolated product: 416 mg (0.9 mmol, 98 %). Cobalt analysis calcd for $BC_6CoF_{12}N_2O_4$: 12.8 %; found = 13.1 %. In a similar way some $[Co(CO)_2(NO)_2][(CF_3)_3BF)]$ was obtained by treating 1 mmol of $NO[(CF_3)_3BF]$ in aHF (2 mL) with $[Co(CO)_3NO]$ (1 mmol) at room temperature for 2 h.

Several attempts to grow single crystals of $[Co(CO)_2(NO)_2][B(CF_3)_4)]$ and $[Co(CO)_2(NO)_2][(CF_3)_3BF)]$ from aHF or dichloromethane solution failed.

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