HD/Ar) and 0.5:1:100 ($M/H_2+D_2/Ar$). The deposition rates were about 2 mmol of matrix gas per hour.

Reagents used: H_2 (Air Liquide, 99.995%), D_2 (Isotec, 99.5%), Ar (Messer, purity 4.8). HD was prepared by reaction of $LiAlH_4$ with D_2O and passed through a liquid N_2 trap (ca. 90% HD and 10% H_2).

Photolysis: high-pressure Xe/Hg arc or a medium-pressure Hg lamp (Philips LP 125, 200 or 125 W, respectively); heating effects of the matrix by IR radiation were minimized by a water filter. Light of the desired wavelengths was delivered by appropriate interference or Pyrex filters.

IR spectra of the matrix samples were recorded mostly in the reflection mode at resolutions ranging from 0.5 to 0.05 cm^{-1} and with a wavenumber accuracy of ± 0.1 cm^{-1}. FTIR spectrometers: Nicolet Magna-IR 560 (in Oxford), Bruker 113v (in Karlsruhe), and Bruker 120 (in Paris).

DFT calculations were performed with the GAUSSIAN 98 program package.[13] The results reported here are those delivered by the B3PW91 method, with a 6–311G(d) basis set for Ga and a LANL2DZ basis set with additional d-polarization functions (exponent 0.5) for In.

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Carbonyltris(trifluoromethyl)borane, $(CF_3)_3BCO$, An Unusual Boron Carbonyl[**]

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Helge Willner,[*] and Friedhelm Aubke[*]

Dedicated to Professor Hans Bürger
on the occasion of his 65th birthday

Since the discovery of carbonylborane, $H_3B(CO)$, by Burg and Schlesinger[1] in 1937, approximately twenty further boron carbonyl derivatives have been reported and for the most part extensively characterized.[2,3] These boron carbonyls are isolable under ambient conditions, and were synthesized primarily by the addition of CO to suitable boranes and subhalogenides of boron.[2] We report here a new mononuclear boron carbonyl compound that was synthesized in an unusual manner: carbonyltris(trifluoromethyl)borane, $(CF_3)_3B(CO)$ (**1**).

The unexpected formation of **1** was observed during attempts to explore the limits of stability of salts of the new tetrakis(trifluoromethyl)borate ion $[B(CF_3)_4]^-$.[4] $K[B(CF_3)_4]$ slowly decomposes at room temperature in concentrated sulfuric acid (96%) to give a volatile product. The gas-phase IR spectrum of this product is shown in Figure 1. A preliminary identification of this material as $(CF_3)_3B(CO)$ is

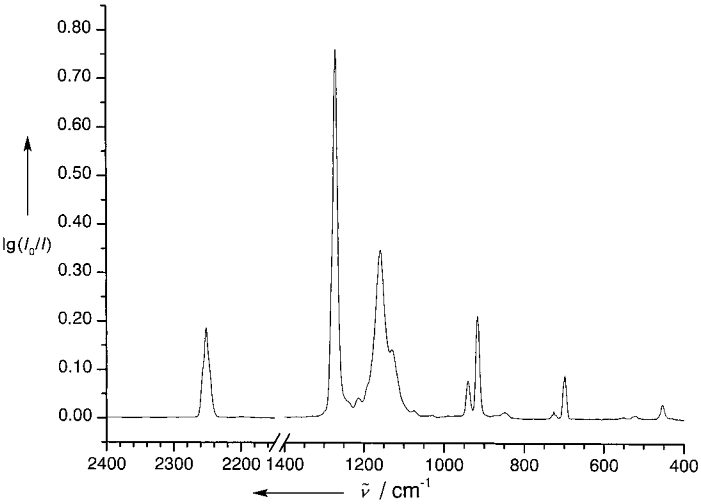

Figure 1. The gas-phase IR spectrum of **1** (0.59 mbar) at 28 °C (optical path length 19.5 cm).

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Table 1. NMR data of **1** and related compounds.[a]

Compound	$\delta(^{11}B)$	$\delta(^{13}C)$ (CF_3)	$\delta(^{13}C)$	$\delta(^{19}F)$	$^1J(^{11}B,^{13}C)$ (CF_3)	$^1J(^{11}B,^{13}C)$	$^1J(^{13}C,^{19}F)$	$^2J(^{11}B,^{19}F)$	$^3J(^{13}C,^{19}F)$ (CF_3)	$^3J(^{13}C,^{19}F)$	$^4J(^{19}F,^{19}F)$	Ref.
$[(CF_3)_3BC(O)OD]^-$[b]	– 19.0	135.0	192.5	– 60.6	72.8	67.0	305.1	25.8	4.0	3.4	6.3	[c]
$[B(CF_3)_4]^-$	– 18.9	132.9	–	– 61.6	73.4	–	304.3	25.9	3.9	–	5.8	[4]
1, CD_2Cl_2[c]	– 17.9	126.2	159.8	– 58.7	80 ± 5	30 ± 5	298 ± 3	36 ± 2	n.o.[e]	n.o.[e]	n.o.[e]	[d]
1, SO_2[b]	– 17.8	126.7	158.9	– 58.3	75 ± 10	30 ± 10	298 ± 3	32 ± 2	n.o.[e]	n.o.[e]	n.o.[e]	[d]
$[(CF_3)_3B(OH)]^-$	– 10.6	134.7	–	– 68.0	75.8	–	311.4	26.8	2.7	–	n.o.[e]	[7]

[a] Coupling constants J in Hz. [b] Linewidth 1 – 2 Hz. [c] Linewidth 30 – 60 Hz. [d] This work. [e] n.o. = not observed.

based on the observation of a band at 2252 cm^{-1} (characteristic of ν_{CO} in σ-bonded carbonyls),[5] a band pattern in the range of 1300 – 400 cm^{-1}(characteristic of a $B(CF_3)_x$ group),[4, 6] and the absence of vibrational-rotational fine structure (indicative for high moments of inertia due to a large molecular mass). A comparison of the ^{19}F, ^{11}B, and ^{13}C NMR spectra with those of related species (Table 1) provides additional evidence. However the NMR spectroscopic evidence is not unambiguous, since all NMR signals, independent of solvents (CD_2Cl_2, SO_2) and temperature (– 40 to 0 °C) are broadened up to 40 Hz so that coupling patterns are not clearly recognizable.

In the EI mass spectrum (70 eV), the ion of highest mass occurs at m/z 227, which is consistent with the ion $(CF_3)_2{}^{11}B(CF_2)CO^+$. From vapour density measurements a molecular mass of 246 ± 2 $g\,mol^{-1}$ is obtained which agrees well with the calculated value of 245.85 $g\,mol^{-1}$. The reaction with CH_3CN at room temperature produces in addition to CO a product, whose Raman spectrum is identical with that of $(CF_3)_3B(NCCH_3)$.[7]

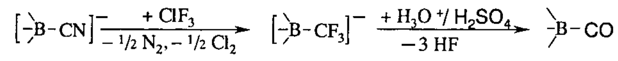
Selected characteristic data for **1**, the CO adduct $F_3B \cdot CO$, $H_3B(CO)$, and other typical, thermally stable boron carbonyls are summarized in Table 2. The characteristic feature of all boron carbonyls is the higher wavenumber of the CO stretch than that of free CO (2143 cm^{-1}). This is due mainly to the bond polarization of the CO ligand at the boron atom,[18] which is also found for thermally stable metal carbonyl cations and their derivatives,[5, 19] in which CO is σ-bonded to metal cations. Among the boron carbonyls, **1** has the highest wavenumber so far for the CO stretch (2252 cm^{-1}).

In sharp contrast to the synthesis of all other boron carbonyls, where CO is added to suitable starting materials,[2] in the synthesis of **1** the CO group is generated in situ by the hydrolysis of a single CF_3 group. The reaction step described is thus part of a series of transformations, in which starting from $[B(CN)_4]^-$,[20] the B–C bond remains intact, while the nature of the ligand is altered (Scheme 1).

Table 2. Characteristic data of selected carbonyl derivatives.

Compound	ν_{CO} [cm^{-1}]	r(B–C) [Å]	D(B–C) [$kJ\,mol^{-1}$]	T_{decomp} [°C][a]
$F_3B \cdot CO$	2151[8]	2.89[9]	7.6[17]	– 200[2]
$H_3B(CO)$	2165[11]	1.54,[12] (1.51)[10]	141[12]	20[2]
1	2252[b]	(1.58)[b]	(112)[b]	0[b]
1,10-$B_{10}H_8(CO)_2$	2147[13]			200[13]
1,12-$B_{12}H_{10}(CO)_2$	2210[13]	1.54[14]		400[13]
$(BF_2)_3B(CO)$	2162[15]	1.52[16]		20[16]
$(BCl_2)_3B(CO)$	2176[16]	1.54[16]		20[16]

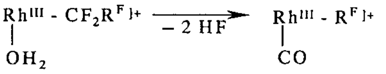
[a] Estimated by behavior described in literature. [b] This work; in parentheses: calculated data.



Scheme 1.

In a vacuum, **1** evolves from the suspension as a gas, which is isolated in a cold trap at – 110 °C as a colorless, partly crystalline solid in about 95 % yield by fractional condensation, using a series of traps held at – 30, – 110, and – 196 °C. Even though the C–F bond dissociation energy of 485 $kJ\,mol^{-1}$ is the highest of all carbon – element single bonds, the hydrolysis reaction, which results in the formation of a strong C–O bond, is expected to be exothermic on account of the formation of 3 moles of HF (3 × 567 $kJ\,mol^{-1}$).

There are very few reported precedents for the hydrolysis of a CF_3 group in an acidic environment. In a mechanistic study by Hughes et al.[21] of a cationic Rh^{III} complex, the α-CF_2 group of a perfluorobenzyl or C_3F_7 ligand was hydrolyzed by coordinated H_2O to a CO group with evolution of HF; in this reaction the C_6F_5 or C_2F_5 ligands, respectively, remain coordinated to the Rh center [Eq. (1), $R^F = C_6F_5$, C_2F_5]. Also in arenes CF_3 substituents are converted in concentrated H_2SO_4 under more severe conditions (> 100 °C, > 6 h) to carboxy groups.[22]



$$\underset{\displaystyle OH_2}{\overset{}{Rh^{III}}} - CF_2R^F]^+ \xrightarrow{-2\,HF} \underset{\displaystyle CO}{Rh^{III}} - R^F]^+ \qquad (1)$$

Compound **1** is a clear, colorless liquid at room temperature with a melting point of 9 ± 1 °C. At this temperature the vapor pressure is 38 mbar; the sublimation vapor pressure curve is given by the expression $\ln p = -6162/T + 25.5$ (p in mbar, T in K). Above its melting point, **1** decomposes so quickly that a reliable vapor pressure curve cannot be obtained. In the gas phase, the thermal decomposition appears to be first order with $t_{1/2} = 50$ min at 28 °C. CO and BF_3 are observed among the decomposition products. In the presence of an excess of ^{13}CO or $C^{18}O$, the CO ligand in **1** is exhanged, which can be monitored by the increase in intensity of the IR bands at 2200 or 2201 cm^{-1}, respectively. As the observed band positions for the ^{13}C and ^{18}O isotopomers agree well with bands at 2202 and 2198 cm^{-1}, calculated according to the two-mass model, appreciable vibrational mixing for the CO group in **1** is ruled out.

As reported previously for 1,12-$B_{12}H_{10}(CO)_2$;[14] **1** is not degraded hydrolytically with water. Instead reversible equilibria (2) and (3) are suggested.

$$(CF_3)_3B(CO) + H_2O \rightleftharpoons (CF_3)_3BC(OH)_2 \qquad (2)$$

$$(CF_3)_3BC(OH)_2 + H_2O \rightleftharpoons [(CF_3)_3BCOOH]^- + [H_3O]^+ \qquad (3)$$

The acidic aqueous solution is stable for several weeks at room temperature. The observed chemical shifts and spin coupling patterns (see Table 1) strongly suggest the presence of a $(CF_3)_3BC$ fragment. The exact nature of these species and their concentrations in equilibria (2) and (3) will be the subject of a subsequent investigation. As reported for metal carbonyl cations,[5, 19] the carbonyl carbon atom in **1** is the electrophilic center. However, unlike in **1** traces of water induce irreversible hydrolysis in metal carbonyl cations.

To support the interpretation of **1**, we carried out calculations using the Gaussian 98 program package[23] B3LYP/6-31G*. According to these calculations, an equilibrium structure with C_3 symmetry is expected, in which the CF_3 groups are rotated by 13° relative to each other and the B−CO bond length is about 1.58 Å. A rather high value of 3.27 D is predicted for the dipole moment; hence the broad linewidth of the NMR signals is explained by the interaction with the quadrupolar nuclei ^{10}B and ^{11}B. The recorded IR spectrum of **1** agrees well with the calculated one. Using the same basis set to calculate the energies of CO and $B(CF_3)_3$, we obtain a bond dissociation energy of 112 kJ mol^{-1} for **1**, which is consistent with the observed low thermal stability of **1**. Finally, calculated partial atomic charges of $q_B = -0.002$, $q_C = +0.404$, and $q_O = -0.166\ e^-$ are obtained for the B-C-O group, which support our claim that the C(O) atom is the electrophilic center in **1**.

Since the free Lewis acid $B(CF_3)_3$ is not stable, a dissociation equilibrium between the primary dissociation products is not observed. The calculated F^- ion affinity for the hypothetical $B(CF_3)_3$ molecule is similar to the so far strongest Lewis acids SbF_5 (502 kJ mol^{-1})[24] and AuF_5 (591 kJ mol^{-1}).[25]

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Unexpected Carbonyl Mobility in Aminoketoses: The Key to Major Maillard Crosslinks**

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Markus O. Lederer*

Covalently crosslinked proteins are among the major modifications caused by Maillard processes (reactions of reducing sugars with amines) and belong to the so-called 'advanced glycation end products' (AGEs). Most AGEs are formed from aminoketoses **1** via highly reactive dicarbonyl intermediates such as **2**–**4** (Scheme 1).[1–3] In long-lived connective tissue and matrix components, AGEs accumulate with age and are generated to a greater extent in diabetes.[4] AGEs can activate cellular receptors[5] and contribute to pathophysiology associated with ageing in general as well as

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