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Article

Homoleptic, σ-Bonded Octahedral Superelectrophilic Metal Carbonyl Cations of Iron(II), Ruthenium(II), and Osmium(II). Part 2: Syntheses and Characterizations of $[M(CO)_6][BF_4]_2$ (M = Fe, Ru, Os)

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As the first examples of homoleptic, σ-bonded superelectrophilic metal carbonyl cations with tetrafluoroborate $[BF_4]^-$ as the counter anions three thermally stable salts of the composition $[M(CO)_6][BF_4]_2$ (M = Fe, Ru, Os) have been synthesized and extensively characterized by thermochemical, structural, and spectroscopic methods. A common synthetic route, the oxidative carbonylation of either $Fe(CO)_5$ (XeF_2 as the oxidizer) or $M_3(CO)_{12}$ (M = Ru, Os) (F_2 as the oxidizer) in the conjugate Brønsted–Lewis superacid HF/BF_3, was employed. The thermal behavior of the three salts, studied by differential scanning calorimetry (DSC) and gas-phase IR spectroscopy of the decomposition products, has been compared to that of the corresponding $[SbF_6]^-$ salts. The molecular structures of $[M(CO)_6][BF_4]_2$ (M = Fe, Os) were obtained by single-crystal X-ray diffraction at 100 K. X-ray powder diffraction data for $[M(CO)_6][BF_4]_2$ (M = Ru, Os) were obtained between 100 and 300 K in intervals of 50 K. All three salts are isostructural and crystallized in the tetragonal space group *I*4/*m* (No. 87). As for the corresponding $[M(CO)_6][SbF_6]_2$ salts (M = Fe, Ru, Os), similar unit cell parameters and vibrational fundamentals were also found for the three $[BF_4]^-$ compounds. For the structurally characterized salts $[M(CO)_6][BF_4]_2$ (M = Fe, Os), very similar bond parameters for both cations and anions were found. Hence, the invariance of structural and spectroscopic properties of $[M(CO)_6]^{2+}$ cations (M = Fe, Ru, Os) extended from the fluoroantimonates $[Sb_2F_{11}]^-$ and $[SbF_6]^-$ as counteranions also to $[BF_4]^-$.

Introduction

Among superelectrophilic,[1] homoleptic metal carbonyl cations with metals in oxidation states of 2+ or 3+ reported by us in recent years,[2−4] the regular octahedral cations $[M(CO)_6]^{2+}$ (M = Fe, Ru, Os)[5−7] formed by the group 8 metals are unique on several accounts, as discussed in the preceding paper.[7] Both experimental and calculated data for square-planar[8] and linear[9] superelectrophilic,[1] homoleptic metal carbonyl cations and various derivatives[2−4] differ in many respects from those of their octahedral counterparts and are available only for $[Sb_2F_{11}]^-$ salts so far.[2−4,8,9]

The high intrinsic stability of the octahedral $M(CO)_6$ coordination geometry is manifested in the existence of metal hexacarbonylate anions $[M(CO)_6]^{n-}$ ($n = 2, 1$) in groups 4 and 5,[10,11] neutral $M(CO)_6$ in group 6,[12−14] cations of the

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type $[M(CO)_6]^+$ in group 7,[15,16] and recently reported $[Ir(CO)_6]^{3+}$ in $[Ir(CO)_6][SbF_6]_3 \cdot 4HF$.[17] Because of the intrinsic stability of superelectrophilic[1] $[M(CO)_6]^{2+}$ (M = Fe, Ru, Os),[5−7] it should be possible to generate the solvated cations in superacidic media, other than HF/SbF_5,[18,19] and stabilize these cations by anions other than $[Sb_2F_{11}]^-$ or $[SbF_6]^-$.[2−7]

Alternate synthetic methods such as halide abstraction from precursors of the form $M(CO)_4X_2$ (M = Fe, Os, X = Cl, Br) by the Lewis acids AlX_3 (X = Cl, Br) at elevated temperatures and CO pressures, a methodology that allowed the synthesis of the group 7 cations $[M(CO)_6]^+$ (M = Mn, Tc, Re) as $[AlX_4]^-$ salts, had failed, reportedly resulting in erroneous claims.[15,16]

A promising approach is suggested by the recent synthesis of $[Co(CO)_5][(CF_3)_3BF]$,[20] according to eq 1

$$Co_2(CO)_8 + 2(CF_3)_3BCO + 2HF \xrightarrow[25\ °C]{aHF,CO} 2[Co(CO)_5][(CF_3)_3BF] + H_2 \quad (1)$$

which contains the first trigonal-bipyramidal metal carbonyl cation.[4,20] In the synthesis, the elusive Lewis acid $(CF_3)_3B$ is replaced by $(CF_3)_3BCO$,[21,22] and the acidium ion $[H_2F]^+$(solv) is found to act as an oxidizing reagent in an oxidative carbonylation.[2−4] However, as more fully investigated subsequently,[23] slow degradation of $[(CF_3)_3BF]^-$ in aHF occurs, resulting in the formation of $[C_2F_5BF_3]^-$(solv) and HCF_3, which limits the use of this novel reaction system.

In addition to the degradation and rearrangement reactions of the anion in the conjugate superacid $HF/(CF_3)_3BCO$,[20] oxidation by $[H_2F]^+$ is found to be difficult. Protonation of substrates such as $Fe(CO)_5$, observed some time ago in liquid HCl,[24] becomes a competing process as found in preliminary experiments, which will be discussed elsewhere.[25]

In this study, the use of the conjugate Brønsted−Lewis superacid HF/BF_3[26,27] as the reaction medium in carbonylation reactions will be explored. Despite its lower Brønsted acidity,[26,27] the system offers two clear advantages over the HF/SbF_5[18,19,26,27] superacid used in the preceding study[7] and elsewhere:[2−5,8,9,17] (i) oxidative side reactions as observed for SbF_5[5,7] are not feasible and (ii) oligomerization of the anions, observed in the HF/SbF_5 system[18,19,28] and responsible for the formation of two types of salts,[5−7] is highly improbable in HF/BF_3.[26,27]

Oxidative carbonylation[2−4,29] becomes the method of choice. Suitable precursors such as $Fe(CO)_5$ or $M_3(CO)_{12}$ (M = Ru, Os) are commercially available, and it is anticipated that all three $[M(CO)_6]^{2+}$ salts (M = Fe, Ru, Os) can be synthesized by a common route. Both XeF_2, used previously by us in this role,[5,7] and F_2 will be employed as external oxidizing agents. In addition, an attempt will be made to synthesize the related salt $[Fe(CO)_6][AsF_6]_2$, which would permit a comparison to the corresponding $[Sb_2F_{11}]^-$, $[SbF_6]^-$,[5,7] and $[BF_4]^-$ salts.

The well-characterized $[M(CO)_6]^{2+}$ salts[5,7] with both $[Sb_2F_{11}]^-$ and $[SbF_6]^-$ provide an excellent opportunity for a comparison, which will include (i) structural aspects of $[Fe(CO)_6][BF_4]_2$ and $[Os(CO)_6][BF_4]_2$, (ii) thermal stabilities and thermal decomposition modes, (iii) estimated lattice energies using a recently reported approach,[30,31] and (iv) vibrational spectra supported by DFT calculations for the $[BF_4]^-$ anion and published data for the $[M(CO)_6]^{2+}$ cations (M = Fe, Ru, Os).[32]

Experimental Procedures

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 were fitted with bellow valves (Balzers type BPV 25004 and Nupro type SS4BG) as well as Gyrolok and Cajon fittings. For synthetic reactions in aHF, 100-mL reactors were used, consisting of PFA bulbs with an NS 29 socket standard taper (Bohlender, Lauda, Germany) in connection with a PTFE NS 29 cone standard taper top and a PFA needle valve (type 204-30 Galtek, fluoroware, Chaska, MN). The parts were held together by a metal compression flange, and the reactor was leak-tight ($<10^{-5}$ mbar L s^{-1}) without use of grease. Solid materials were manipulated inside an inert atmosphere box (Braun, Munich, Germany) filled with argon, with a residual moisture content of less than 0.1 ppm.

Chemicals. Anhydrous HF (used as received) and F_2 (both gifts from Solvay AG, Hannover, Germany), CO (standard grade, Messer GmbH, Krefeld, Germany), $Fe(CO)_5$ (purity not stated, BASF AG, Ludwigshafen, Germany), $M_3(CO)_{12}$ (M = Fe, Ru, Os) (Strem Chemicals), $Fe_3(CO)_{12}$ (Aldrich), and all standard chemicals were obtained from commercial sources.

Vibrational Spectroscopy. Infrared spectra were recorded at room temperature on an IFS-66v FT spectrometer (Bruker, Karlsru-

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Table 1. Crystallographic Data for $[M(CO)_6][BF_4]_2$ (M = Fe, Os) at 100 K

empirical formula	$C_6B_2F_8FeO_6$	$C_6B_2F_8O_6Os$
formula weight (g mol^{-1})	397.53	531.88
color	colorless	colorless
crystal system,	tetragonal,	tetragonal,
space group	*I*4/*m*, (No. 87)	*I*4/*m*, (No. 87)
a (Å)	7.4114(3)	7.4802(1)
c (Å)	10.8790(3)	10.9445(3)
V (Å^3)	597.58(3)	612.38(2)
Z value	2	2
ρ_{calc} (Mg m^{-3})	2.209	2.885
θ range (deg)	3.75−33.14	3.30−27.73
R1 [$I > 2\sigma(I)$][a]	0.0267	0.0379
wR2 (all data)[b]	0.0705	0.0952
goodness-of-fit on F^2	1.083	0.770

[a] $R1 = (\sum||F_o| - |F_c||)/\sum|F_o|$. [b] $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^2]^{1/2}$.

he, Germany). For each spectrum, 64 scans were co-added with an apodized resolution of 2 cm^{-1}. Solid samples were measured either as powders, crushed between AgBr disks, or as Nujol mulls between AgBr disks in the region 5000−400 cm^{-1}. Raman spectra were recorded at room temperature with a Bruker RFS100/S FT Raman spectrometer using the 1064 nm exciting line of a Nd:YAG laser. Crystalline samples contained in large melting point capillaries (2 mm o.d.) were used for recording spectra in the region of 3500−80 cm^{-1} with a resolution of 1 cm^{-1}. For each spectrum, 256 scans were co-added, and the Raman intensities were corrected by calibration of the spectrometer with a tungsten halogen lamp.

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. Portions of about 5−10 mg of the solid samples were weighed and contained in sealed aluminum crucibles. They were studied in the temperature range of 20−500 °C with a heating rate of 10 K min^{-1}; throughout this process, the furnace was flushed with dry nitrogen. For the evaluation of the output, the Netzsch Proteus 4.0 software was employed.

Single-Crystal X-ray Diffraction. Crystals suitable for X-ray diffraction were obtained from HF solutions. Diffraction data were collected at 100 K on a KappaCCD diffractometer (Bruker AXS) using Mo Kα radiation ($\lambda = 0.71073$ Å) and a graphite monochromator. Crystal structures were determined using SHELXS-97,[33] and full-matrix least-squares refinement based on F^2 was performed using SHELXL-97.[34] No absorption corrections were applied. Molecular structure diagrams were drawn using the program Diamond.[35] A summary of experimental details and crystal data is presented in Tables 1 and S1.

Powder X-ray Diffraction. Samples of $[M(CO)_6][BF_4]_2$ (M = Fe, Ru, Os) were filled into thin-walled glass capillaries of 0.5-mm diameter inside a glovebox. Data for M = Fe and Ru were collected at room temperature using Cu Kα radiation ($\lambda = 1.54056$ Å) on a PANalytical X′Pert MPD using a hybrid monochromator and, in the case of M = Fe, an additional secondary monochromator to suppress iron fluorescence. Data for M = Os were collected using an STOE STADI P powder diffractometer equipped with a Ge primary monochromator, also using Cu Kα radiation. Graphics, lattice constant refinements, and structure calculations were all carried out using the STOE WinX^{Pow} suite of programs.[36]

Synthetic Reactions. (a) $[Fe(CO)_6][BF_4]_2$. A 100-mL PFA reactor, fitted with a PTFE-coated magnetic stirring bar, was charged with 250 mg of XeF_2 (1.2 mmol) in a drybox. At −196 °C, 220 mg of $Fe(CO)_5$ (1.1 mmol) was transferred in vacuo into the reaction vessel, followed by 5 mL of anhydrous HF and 4.5 mmol of BF_3. After the addition of CO (4.5 mmol) at −196 °C, the reactor was allowed to warm to room temperature, giving a clear colorless solution. The mixture was stirred vigorously for 1 h and then kept at room temperature without stirring. After 3 days, a white precipitate had formed. The reaction mixture was stored for one additional week, to ensure completion of the reaction. All volatile compounds were removed in vacuo, leaving a white solid material. The reactor was brought into a drybox, and 320 mg of $[Fe(CO)_6][BF_4]_2$ (0.8 mmol, 73%) was isolated. During recording of the IR spectra, the formation of $Fe(CO)_5$ was observed. Anal. Calcd. for $C_6B_2F_8FeO_6$: C, 18.13%. Found: C, 13.19%; H, ca. 0.3%. The low carbon content is probably due to partial hydrolysis of $[Fe(CO)_6][BF_4]_2$ in agreement with problems that arose during recording of the IR spectra. The compound was found to be thermally stable to about 95 °C (80 °C, DSC), where decomposition with gas evolution (BF_3, CO, and traces of SiF_4 and CO_2) began. A light gray residue was obtained.

(b) $[Ru(CO)_6][BF_4]_2$. In a drybox, 300 mg of $Ru_3(CO)_{12}$ (0.5 mmol) was placed into a 100-mL PFA reactor fitted with a PTFE-coated magnetic stirring bar. Five milliliters of anhydrous HF and fluorine (3.6 mmol) was condensed into the reactor while being cooled with liquid N_2. Subsequently, the reaction mixture was held at −78 °C and slowly warmed to room temperature while being stirred for 5 h. Then, at −196 °C, all volatile compounds were removed in vacuo, and F_2 (1.4 mmol) was added again. The reaction mixture was slowly brought to room temperature and stirred overnight. A light gray solution was obtained. The reactor was recooled, using liquid N_2, and all volatile compounds were removed under reduced pressure. At −196 °C, BF_3 (5.6 mmol) and CO (5.6 mmol) were transferred into the reactor. The reaction mixture was warmed to room temperature, and an off-white solid precipitated immediately. After the reaction mixture had been kept at ambient temperature for 1 day, all volatiles were pumped off, giving an off-white solid. The reactor was transferred into a drybox, and 415 mg of $[Ru(CO)_6][BF_4]_2$ (0.9 mmol, 66%) was isolated. Anal. Calcd. for $C_6B_2F_8O_6Ru$: C, 16.28%. Found: C, 16.14%. Despite the good agreement between the calculated and observed carbon content, an unknown impurity was detected by X-ray powder diffraction. A yellow-colored sample was found to be thermally stable to ~115 °C (most likely because of the impurity), and on further heating to 190 °C (195 °C, DSC), vigorous gas evolution (BF_3, CO) was noted, and a black residue was produced.

(c) $[Os(CO)_6][BF_4]_2$. A PFA reactor, fitted with a PTFE-coated magnetic stirring bar, was charged with 306 mg of $Os_3(CO)_{12}$ (0.34 mmol) inside a drybox. At −196 °C, 5 mL of anhydrous HF and 2.7 mmol of fluorine were condensed into the PFA vessel. At room temperature, the reaction mixture was stirred for 3 h. Subsequently, more fluorine (1 mmol) was added at −196 °C, and the reaction mixture was slowly warmed to room temperature. After 3 h, all volatiles were removed in vacuo at −196 °C, and BF_3 (4.1 mmol) and CO (4.1 mmol) were added. The reaction mixture was warmed to room temperature, and within 20 min, a clear light yellow solution was obtained. After 1 h, colorless crystals began to form.

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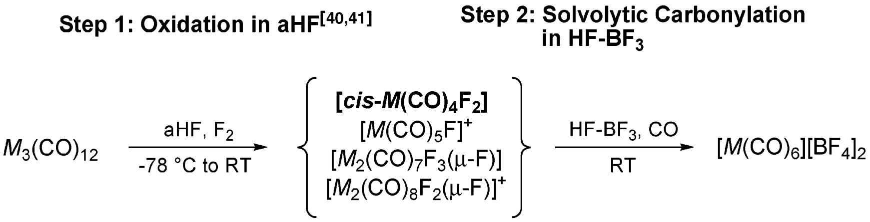
Scheme 1. Two-Step Oxidative Carbonylation of $M_3(CO)_{12}$ (M = Ru, Os) in HF/BF$_3$ and aHF



Within 1 day, the solution had turned from light yellow to light gray. After 5 days, all volatiles were removed in vacuo, and the reaction vessel was transferred into a drybox. A total of 388 mg of [Os(CO)$_6$][BF$_4$]$_2$ (0.72 mmol, 72%) was obtained as a white crystalline solid. Anal. Calcd. for $C_6B_2F_8O_6Os$: C, 13.55%. Found: C, 13.23%. The compound was thermally stable up to ~300 °C (280 °C, DSC). The gaseous decomposition products consisted of CO and BF$_3$, as well as some CO$_2$ and SiF$_4$. The residue was black, and a film of metallic Os had formed inside the reactor.

(d) Attempted Synthesis of [Fe(CO)$_6$][AsF$_6$]$_2$. Into a 250-mL flask, fitted with a PTFE valve and a magnetic stirring bar were added 0.390 g (1.99 mmol) of Fe(CO)$_5$, ca. 8 mL of $C_4F_9SO_2F$ (in further attempts, CH_2Cl_2 or CF_2ClCCl_2F), 7.0 mmol of AsF$_5$, and 2.3 mmol of CO by condensation. Upon warming of the reaction mixture to room temperature, the initial green color changed to yellow within 30 min. After 3 days, all volatiles were removed in vacuo with the reactor kept at room temperature. The residue of 0.687 g or 1.14 mmol would suggest a yield of ~57%, but the thermally unstable material was found to be inhomogeneous: according to its Raman spectrum, it contained, in addition to [Fe(CO)$_6$][AsF$_6$]$_2$, some [Fe(CO)$_6$][As$_2$F$_{11}$]$_2$, Fe[AsF$_6$]$_2$, FeF[AsF$_6$], FeF$_2$, and possibly FeF$_3$.

Results and Discussion

Synthetic Aspects. Oxidative carbonylation[2−4,29] was used by us recently for the synthesis of [(Co(CO)$_5$][(CF)$_3$BF],[20] starting from Co$_2$(CO)$_8$ in the new superacid HF/(CF$_3$)$_3$-BCO.[21,22] As discussed in the Introduction, the acidium ion [H$_2$F]$^+$ acts as an internal oxidant, an approach first described by Souma et al.[37]

An attempt to adapt this method to the generation of [Fe(CO)$_6$]$^{2+}$ by oxidation of Fe$_3$(CO)$_{12}$ in HF/BF$_3$ results in protonation instead, according to eq 2

$$Fe_3(CO)_{12} + 3HF + 3BF_3 + 3CO \xrightarrow[-196 \text{ to } 25\ °C]{HF/BF_3,\ CO} 3\,[HFe(CO)_5][BF_4] \quad (2)$$

The isolated product is of limited thermal stability and is identified by its Raman spectrum.[25]

In analogy to the generation of [Fe(CO)$_6$]$^{2+}$ in HF/SbF$_5$,[5,7] the oxidation of Fe(CO)$_5$ by XeF$_2$ in HF/BF$_3$ proceeds according to

$$Fe(CO)_5 + XeF_2 + CO + 2BF_3 \xrightarrow[-196 \text{ to } 25\ °C]{HF/BF_3,CO} [Fe(CO)_6][BF_4]_2 + Xe \quad (3)$$

After removal of all volatiles in vacuo, the new salt is obtained as a colorless, crystalline powder in an isolated yield of 73%. [Fe(CO)$_6$][BF$_4$]$_2$ is thermally stable to 95 °C (80 °C, DSC). It was found that the iron compound is the most moisture sensitive within the series [M(CO)$_6$][BF$_4$]$_2$ (M = Fe, Ru, Os). During recording of the IR spectra, the formation of Fe(CO)$_5$ was observed, whereas the Ru and Os compounds are stable under the same conditions.

The formation of [Fe(CO)$_6$][BF$_4$]$_2$ is much simpler than that of [Fe(CO)$_6$][Sb$_2$F$_{11}$]$_2$, which is obtained in ~50% yield.[5] Identified byproducts include [Fe(CO)$_6$][SbF$_6$]$_2$, which is also structurally characterized;[5] paramagnetic Fe[SbF$_6$]$_2$, which has been reported previously,[38] detected by magnetic susceptibility measurements;[5] and 6SbF$_3$·5SbF$_5$,[39] which indicates that SbF$_5$ functions as a co-oxidizer.[7] None of these byproducts or their equivalents are formed in HF/BF$_3$.

In contrast, the cations [M(CO)$_6$]$^{2+}$(solv) (M = Ru, Os) are generated in this study from the precursors M$_3$(CO)$_{12}$ in two distinct steps: oxidation by F$_2$ in aHF, followed by carbonylation of the product in HF/BF$_3$.[26,27]

As illustrated in Scheme 1, the first step, the oxidation of M$_3$(CO)$_{12}$ (M = Ru, Os)[40,41] by XeF$_2$[40,41] or F$_2$[42] in aHF, has been studied previously by ^{13}C and ^{19}F NMR spectroscopy,[40,41] and several products have been identified: *cis*-M(CO)$_4$F$_2$ (M = Ru, Os)[40,41] is the main product. The observation of [M(CO)$_5$F]$^+$ (M = Ru, Os)[40,41] suggests some CO redistribution. The minor constituents [M$_2$(CO)$_7$F$_3$(μ-F)], [M$_2$(CO)$_8$F$_2$(μ-F)]$^+$, and [{M(CO)$_3$F(μ-F)}$_4$] (M = Ru, Os)[40,41] and the anions *mer*- and *fac*-[Ru(CO)$_3$F$_3$]$^-$ [40] are not expected to persist in HF/BF$_3$.

To continue the generation of [M(CO)$_6$]$^{2+}$(solv) (M = Ru, Os) as described here, all excess F$_2$ is removed in vacuo after the completed oxidation. For the carbonylation step, CO and BF$_3$ are added. The latter increases the Brønsted acidity of the reaction medium[26,27] and enhances its ionizing ability.

As seen in Scheme 1, all four major components of the mixture[40,41] are cleanly converted by solvolytic carbonylation into [M(CO)$_6$]$^{2+}$(solv) (M = Ru, Os) just as the initial oxidation products of Fe(CO)$_5$, the transients Fe(CO)$_4$F$_2$, and [Fe(CO)$_5$F]$^+$ are carbonylated either in HF/SbF$_5$[7] or in HF/BF$_3$ to [Fe(CO)$_6$]$^{2+}$. The substitution of fluoride by CO is suggested to involve ionic dissociation in superacids[26,27] to

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Table 2. Selected Structural and Thermochemical Properties of $[Fe(CO)_6]^{2+}$ Salts

compound	$V_{\mathrm{formula\ unit}}$ ($Å^3$)	U_{Pot}[a] ($kJ\ mol^{-1}$)	F^- affinity[b] ($kJ\ mol^{-1}$)	$T_{\mathrm{decomposition}}$ (°C)	major volatile decomposition products
$[Fe(CO)_6][BF_4]_2$	299[c]	1564	348	90	$2BF_3 + 6CO$
$[Fe(CO)_6][AsF_6]_2$	403[d]	1450	433	25	$2AsF_5 + 6CO$
$[Fe(CO)_6][SbF_6]_2$	425[e]	1431	504	190	6CO

[a] Reference 30. [b] Of the respective Lewis acid.[49] [c] This Article. [d] Estimated value, see text. [e] Ref 5.

form short-lived transients of the type $[M(CO)_n]^{2+}$ (M = Fe, Ru, Os; $n = 4, 5$), which act as soft acids[43] or class b acceptors[44] toward CO to form stable d^6 $[M(CO)_6]^{2+}(solv)$ (M = Fe, Ru, Os) and then salts with $[Sb_2F_{11}]^-$, $[SbF_6]^-$,[7] or $[BF_4]^-$ as counteranions.

Hence, the soft and hard acid and base concept of Pearson[43] or the metal ion classification of Ahrland et al.[44] that had previously been invoked to rationalize the formation of superelectrophilic metal carbonyl cations[2−4,29] by reductive solvolytic carbonylation[29] is found useful here, to rationalize their formation by oxidative carbonylation as well.

In summary, the use of alternate conjugate Brønsted−Lewis superacids[26,27] such as HF/BF_3, discussed here, or of $HF/(CF_3)_3BCO$, reported elsewhere,[20,25] results in an enhanced importance of oxidative carbonylation as a synthetic method for the generation of homoleptic metal carbonyl cations.[2−4,29] The synthesis of the triad $[M(CO)_6][BF_4]_2$ (M = Fe, Ru, Os) provides the basis for a comparison to the corresponding triad of $[SbF_6]^-$ salts,[5,7] in regard to their thermochemical properties and thermal decomposition modes, which are discussed next.

Thermochemical Properties and Thermal Decomposition Modes of Various $[Fe(CO)_6]^{2+}$ Salts. Little attention has been paid in the past to thermochemical properties of superelectrophilic homoleptic metal carbonyl cation salts,[2−4,29] and only occasionally[7,8] have thermal decomposition studies, using differential scanning calorimetry (DSC), been reported.[7,8] The extensively characterized $[M(CO)_6]^{2+}$ salts (M = Fe, Ru, Os) with $[Sb_2F_{11}]^-$, $[SbF_6]^-$,[4−7] or $[BF_4]^-$ as counteranions provide the basis for an exploratory investigation of their thermochemical properties and the observed thermal decomposition modes.

For this study, the $[Fe(CO)_6]^{2+}$ salts are chosen for the following reasons: (i) reliably determined molecular structures for $[Fe(CO)_6][SbF_6]_2$[5,7] and $[Fe(CO)_6][BF_4]_2$ are known, and their unit cell volumes per formula unit allow an estimate of their lattice energies, U_{pot}, as reported by Jenkins et al.;[30,31] (ii) a detailed DSC study of $[Fe(CO)_6][SbF_6]_2$, complemented by gas-phase IR spectra of the decomposition products, is found in part I of this study;[7] and (iii) a reason for the lack of thermal stability of elusive $[Fe(CO)_6][AsF_6]_2$ and our failure to isolate this compound (see Experimental Procedures) must be provided.

For the estimate of lattice energies U_{pot},[30] experimentally determined unit cell volumes V for $[Fe(CO)_6][SbF_6]_2$[5,7] and $[Fe(CO)_6][BF_4]_2$ are used. Because the unit cell volumes in the triad $[M(CO)_6][SbF_6]_2$ (M = Fe, Ru, Os) are identical[5,7] and the V values for the three $[BF_4]^-$ salts are very similar (vide infra), it follows that the U_{pot} values within each triad agree closely. For the U_{pot} of $[Fe(CO)_6][AsF_6]_2$, the estimate is based on the calculated or published[30] partial volumes of $[Fe(CO)_6]^{2+}$ and $[AsF_6]^-$.

The volume per formula unit and U_{pot} values are listed in Table 2. The lattice energies increase from 1431 kJ mol^{-1} for $[Fe(CO)_6][SbF_6]_2$ to 1564 kJ mol^{-1} for $[Fe(CO)_6][BF_4]_2$. This is not surprising given that, in $[Fe(CO)_6]^{2+}$ salts, U_{pot} is found to be inversely proportional to the anion radius.[45] An intermediate U_{pot} value of 1450 kJ mol^{-1} for $[Fe(CO)_6][AsF_6]_2$ provides no indication that this salt does not exist at ambient temperature because it loses CO at room temperature.

For $[Fe(CO)_6][SbF_6]_2$, the following thermal decomposition sequence is observed upon heating

$$[Fe(CO)_6][SbF_6]_2 \xrightarrow[-6CO]{T > 190\ °C} Fe[SbF_6]_2 \xrightarrow[-2SbF_5]{T > 350\ °C} FeF_2 \quad (4)$$

Decarbonylation produces paramagnetic $Fe[SbF_6]_2$,[38] which has a layer structure and is identified by temperature-dependent magnetic susceptibility measurements.[5] In the triad $[M(CO)_6][SbF_6]$ (M = Fe, Ru, Os), increasing onset temperatures for the decarbonylation process of 190, 280, and 350 °C, respectively, reflect the increasing strength of the M−C bonds in the $[M(CO)_6]^{2+}$ cations (M = Fe, Ru, Os) due to relativistic effects[46,47]and polar contributions to the M−C bond due to polarization of the C≡O bond by M^{2+}.[48] The nature of the residues from the thermolysis of $[M(CO)_6][SbF_6]_2$ (M = Ru, Os) is unclear.[7]

In the triad $[M(CO)_6][BF_4]_2$ (M = Fe, Ru, Os), the thermal stability, with onset temperatures of 80, 195, and 300 °C, respectively, is lower than that of the $[SbF_6]^-$ salts. The thermal decompositions, formulated for $[Fe(CO)_6][BF_4]_2$ as

$$[Fe(CO)_6][BF_4]_2 \xrightarrow{T > 80\ °C} FeF_2 + 2BF_3 + 6CO \quad (5)$$

indicate the simultaneous loss of CO and BF_3 in a single thermal event. DSC studies for $[M(CO)_6][BF_4]_2$ (M = Ru, Os) involve as yet unidentified intermediates. In all instances, the simultaneous evolution of CO and BF_3, together with traces of CO_2 and SiF_4, is observed.

Reversible phase transitions, observed for all three $[M(CO)_6][SbF_6]_2$ salts (M = Fe, Ru, Os) in the range of 150−170 °C in their DSC plots, are not detected for any of the three

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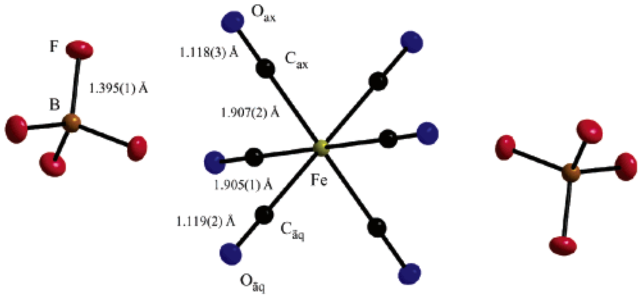

Figure 1. Formula unit of $[Fe(CO)_6][BF_4]_2$ in the crystal structure (50% probability).

$[BF_4]^-$ salts. There is also no evidence for an intermediate of the type $Fe[BF_4]_2$, either after the synthesis or during the thermal decomposition of $[Fe(CO)_6][BF_4]_2$.

A measure for the thermal stability of fluoroanions is found in the calculated fluoride ion affinities of the respective molecular fluro Lewis acids.[49] Data relevant to this study are listed in Table 2 and follow the order SbF_5 (504 kJ mol^{-1}) > AsF_5 (433 kJ mol^{-1}) > BF_3 (348 kJ mol^{-1}). As shown in this Article, $[M(CO)_6][BF_4]_2$ (M = Fe, Ru, Os) and the elusive $[Fe(CO)_6][AsF_6]_2$ have higher lattice energies at 25 °C than the three $[SbF_6]^-$ salts. Upon heating, the thermal instabilities of the constituent $[BF_4]^-$ and $[AsF_6]^-$ anions provide a facile dissociation pathway for the thermolyses of the $[BF_4]^-$ and $[AsF_6]^-$ salts. Hence, it is not surprising that the vast majority of all superelectrophilic[1] metal carbonyl cations[2−4,29] are generated in SbF_5 or HF/SbF_5 and form salts of high thermal stability, with either $[Sb_2F_{11}]^-$ or $[SbF_6]^-$ as counteranions.

Structural Aspects. (a) General Comments. Whereas for the triads $[M(CO)_6][Sb_2F_{11}]_2$[5,7] and $[M(CO)_6][SbF_6]_2$[5,7] (M = Fe, Ru, Os) reliable and accurate molecular structures are obtained for all six salts by single-crystal X-ray diffraction,[5,7] this is not the case for the tetrafluoroborates $[M(CO)_6][BF_4]_2$ (M = Fe, Ru, Os). Single-crystal data are obtained only for $[Fe(CO)_6][BF_4]_2$ and $[Os(CO)_6][BF_4]_2$ as summarized in Table 1. More detailed listings of crystal data, their acquisition, and structure solutions are found as Supporting Information in Table S1.

A satisfactory structure solution is possible for $[Fe(CO)_6][BF_4]_2$ (Figure 1). The accuracy of the data for $[Os(CO)_6][BF_4]_2$ is reduced by twinning (Figure S1). To establish a structural similarity of the crystal data for the triad $[M(CO)_6][BF_4]_2$ (M = Fe, Ru, Os) and to permit a comparison to those for the corresponding $[SbF_6]^-$ salts,[5,7] the unit cell parameters are obtained from powder diffraction data for $[M(CO)_6][BF_4]_2$ (M = Ru, Os); for M = Ru, see Figure 2. A new dimension is added by determining the temperature dependency of the unit cell parameters *a* and *c* and the unit cell volume *V* in the temperature range of 100−300 K, with measurements made in 50 K increments for $[M(CO)_6][BF_4]_2$ (M = Ru, Os). The results are presented in Figure 3 and are discussed next.

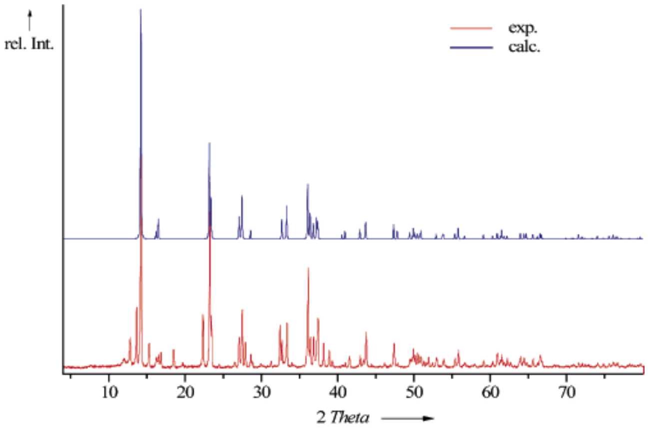

Figure 2. Measured (lower trace) and simulated (upper trace) powder diffractogram of $[Ru(CO)_6][BF_4]_2$. An unknown impurity can be seen in the lower trace.

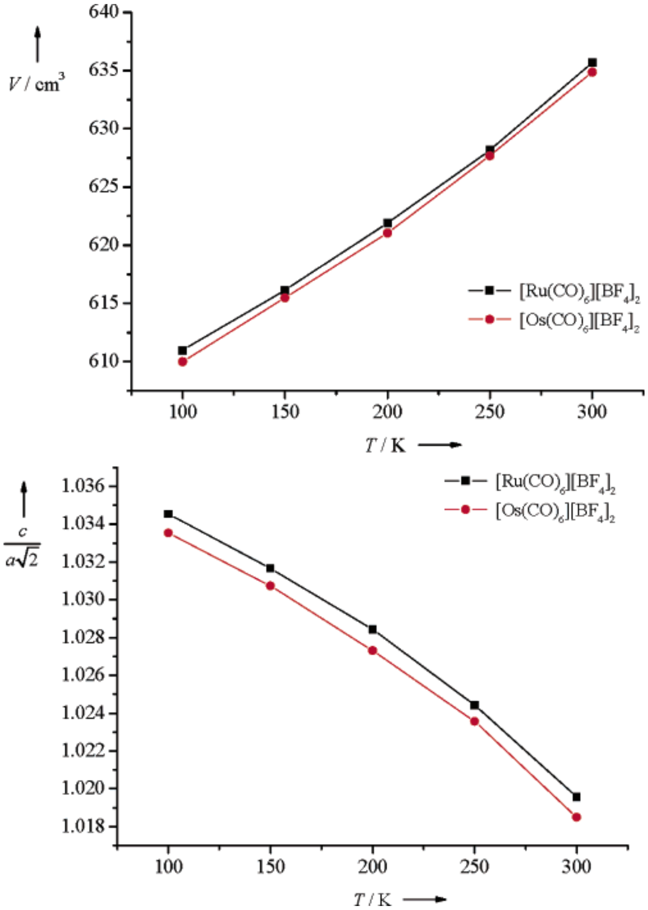

Figure 3. Temperature dependence of the unit cell volume and of the deviation of the cell constants from a cubic meter in $[Ru(CO)_6][BF_4]_2$ and $[Os(CO)_6][BF_4]_2$. For data, see Supporting Information.

Crystal Data and Unit Cell Dimensions for $[M(CO)_6][BF_4]_2$ (M = Fe, Ru, Os). The $[M(CO)_6][BF_4]_2$ salts (M = Fe, Ru, Os) crystallize in the tetragonal system, as do the previously reported $[M(CO)_6][SbF_6]_2$ salts.[5,7] The structure can be derived from the CaF_2 prototype, with the anions in all tetrahedral holes. Because the local site symmetry for the $[BF_4]^-$ ions is $\bar{4}$ and that of $[SbF_6]^-$ is 222, different space groups for the two triads are found: *I*4/*m* (No. 87) for $[M(CO)_6][BF_4]_2$ and *P*4/*mnc* (No. 128) for the corresponding $[SbF_6]^-$ salts,[7] with a common *Z* value of 2 for both space groups.

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Table 3. Unit Cell Dimensions and Volumes for the Complex Salts $[M(CO)_6][BF_4]_2$ and $[M(CO)_6][SbF_6]_2$ (M = Fe, Ru, Os)

$[M(CO)_6]^{2+}$		M: Fe	M: Ru	M: Os
$[BF_4]^-$ [a]	a (Å)	7.4114(3)	7.4745(4)[b]	7.4802(1)
T = 100 K	c (Å)	10.8790(3)	10.9364(10)	10.9445(3)
	V (Å^3)	597.58(3)	610.99(4)	612.38(2)
	V_{calc} (Å^3)[c]	(152.8)	(159.5)	(160.0)
$[BF_4]^-$ [a]	a (Å)		7.6114(5)[b]	7.6103(10)[b]
T = 300 K	c (Å)		10.9733(9)	10.9617(7)
	V (Å^3)		635.71(5)	634.87(19)
	V_{calc} (Å^3)[c]		(171.8)	(171.5)
$[SbF_6]^-$ [d]	a (Å)	8.258(1)	8.278(1)	8.274(1)
T = 300 K	c (Å)	12.471(2)	12.449(2)	12.421(2)
	V (Å^3)	850.5(2)	853.1(2)	850.3(2)
	V_{calc} (Å^3)[c]	(183.3)	(184.6)	(183.2)

[a] This Article. [b] Powder diffraction. [c] V_{calc} denotes partial volume of the $[M(CO)_6]^{2+}$ cation (M = Fe, Ru, Os). [d] References 5 and 7.

Table 4. Structural Data $[M(CO)_6][BF_4]_2$ (M = Fe, Os) and $[M(CO)_6][SbF_6]_2$ (M = Fe, Ru, Os)

	$[BF_4]^-$		$[SbF_6]^-$		
	Fe	Os	Fe	Ru	Os
Bond Lengths (Å)					
$M-C_{ax}$	1.907(2)	1.996(19)	1.917(7)	2.020(6)	2.013(8)
$M-C_{eq}$	1.905(1)	2.00(3)	1.903(6)	2.026(6)	2.026(6)
$C-O_{ax}$	1.118(3)	1.162(91)	1.096(9)	1.100(8)	1.109(11)
$C-O_{eq}$	1.119(2)	1.155(54)	1.114(8)	1.101(6)	1.101(7)
Bond Angles (deg)					
$M-C-O_{ax}$	180	180	180	180	180
$M-C-O_{eq}$	180.00(11)	178.88(355)	178.9(5)	179.3(4)	179.4(5)
$C_{ax}-M-C_{ax}$	180	180	180	180	180
$C_{eq}-M-C_{eq}$	180	180	180	180	180
$C_{ax}-M-C_{eq}$	90	90	90	90	90
$C_{eq}-M-C_{eq}$	90	90	90	90	90

A comparison of the unit cell dimensions for the two triads is presented in Table 3. Single-crystal data at 100 K are used for $[M(CO)_6][BF_4]_2$ (M = Fe, Os) (also see Table 1), and powder data at 100 K are listed for $[Ru(CO)_6][BF_4]_2$. To facilitate a comparison to the single-crystal data for $[M(CO)_6][SbF_6]_2$ (M = Fe, Ru, Os), obtained at room temperature,[5,7] unit cell parameters derived from powder diffraction data at 300 K for $[M(CO)_6][BF_4]_2$ (M = Ru, Os) are included in Table 3.

The unit cell parameters a and c as well as the unit cell volumes V are remarkably constant for the $[M(CO)_6]^{2+}$ salts (M = Fe, Ru, Os) with either $[BF_4]^-$ or $[SbF_6]^-$ as counteranions.[5,7] Because the bond parameters and vibrational properties of the two anions $[BF_4]^-$ and $[SbF_6]^-$ in the respective triads are identical,[7] differences in unit cell volumes reflect differences in cation size and, implicitly, differences in the relative strength of the M−C bonds in these cations.

With the partial volumes of both $[BF_4]^-$ and $[SbF_6]^-$ known,[31] it is possible to calculate partial volumes for the $[M(CO)_6]^{2+}$ cations (M = Fe, Ru, Os) from experimental V values and $Z = 2$ in all instances. In the $[SbF_6]^-$ triad, the partial volumes of $[M(CO)_6]^{2+}$ (M = Fe, Ru, Os) are at ∼300 K estimated as 184(1) Å^3. The calculated partial volumes V_{cal} are included in Table 3 in brackets. The partial volumes calculated in this manner for all $[M(CO)_6]^{2+}$ salts (M = Fe, Ru, Os) listed in Table 3 are included in parentheses in the listing.

The following comments are made: (i) Whereas the unit cell dimensions (a and c) and volumes (V and V_{cal}) are invariant of M in the group $[M(CO)_6][SbF_6]_2$ (M = Fe, Ru, Os), they increase for the $[BF_4]^-$ complexes slightly from Fe to Ru and then remain constant for $[Os(CO)_6][BF_4]_2$. A similar pattern is observed for the triad $[M(CO)_6][Sb_2F_{11}]_2$ (M = Fe, Ru, Os).[7] This reflects increasing M−C bond strength. Evidence for such an increase was discussed in the previous section. (ii) The calculated V_{cal} values for the $[BF_4]^-$ salts at ∼300 K are smaller than the corresponding values for $[M(CO)_6][SbF_6]_2$ (M = Fe, Ru, Os). This suggests a more efficient packing of the tetrahedral $[BF_4]^-$ ions into tetrahedral holes. This is reflected in higher lattice energies for $[M(CO)_6][BF_4]_2$ (M = Fe, Ru, Os), as discussed previously (see Table 2). (iii) As the temperature is increased from 100 to 300 K, the unit cells appear to expand, and the values (a, V, and V_{cal}) increase slightly. Conversely, the partial volumes of $[BF_4]^-$ and $[SbF_6]^-$ are also expected to decrease when going from 300 to 100 K. Hence, the V_{cal} values at 100 K are somewhat underestimated. A detailed study of the temperature dependence of unit cell parameters for the pair $[M(CO)_6][BF_4]_2$ (M = Ru, Os) is shown in Figure 3 and discussed next.

When using published[31] partial anion volumes for $[BF_4]^-$ and $[SbF_6]^-$, some caution is required. Because of the limited number of structures used for their determinations, error limits are quoted[30] that might affect some of the conclusions made here.

As seen in Figure 3, when the temperature is raised gradually from 100 to 300 K, the unit cell volume V increases steadily, and both a and c increase as well. The increase of a is stronger than that of c. As a consequence, the deviation from the cubic metric given by $c/a\sqrt{2}$ decreases slowly, and a phase transition from the tetragonal to the cubic system at temperatures well above 450 K is probable (Figure 3).

Internal Bond Parameter for the $[M(CO)_6][BF_4]_2$ Salts (M = Fe, Os). Whereas the preceding discussion of unit cell dimensions for the triad $[M(CO)_6][BF_4]_2$ (M = Fe, Ru, Os) is based on both single-crystal and powder X-ray diffraction data (Tables 3 and S15), a meaningful discussion of internal bond parameters (bond lengths and angles) is possible only for $[Fe(CO)_6][BF_4]_2$ because the quality of data for the $[Os(CO)_6]^{2+}$ salt is limited as a result of twinning.

Selected bond data for $[M(CO)_6][BF_4]_2$ (M = Fe, Os), obtained at 100 K, are listed in Tables 4 and 5. A formula unit of $[Fe(CO)_6][BF_4]_2$ is depicted in Figure 1, and selected interionic contacts are shown for this salt in Figure 4.

Calculated[50] and experimental bond lengths and angles for the $[BF_4]^-$ anion in the two salts are compared in Table 6. As can be seen, any departure from T_d symmetry for the $[BF_4]^-$ anion is for $[Fe(CO)_6][BF_4]_2$ insignificant and for $[Os(CO)_6][BF_4]_2$ unclear.

A comparison of selected bond parameters of $[M(CO)_6][BF_4]_2$ (M = Fe, Os) with those of the triad $[M(CO)_6][SbF_6]_2$ (data obtained at 300 K) is shown in Table 4. Except for $[Fe(CO)_6][SbF_6]_2$, where very small tetragonal distortions for

Table 5. CO Stretching Fundamentals of [M(CO)$_6$]$^{2+}$ (M = Fe, Ru, Os) in Different Salts with Fluoro Anions

cation	[BF$_4$]$^-$ [a]	[SbF$_6$]$^-$ [b]	[Sb$_2$F$_{11}$]$^-$ [b]	calc[c]	assignment
[Fe(CO)$_6$]$^{2+}$	2238	2242	2241	2221	A_{1g} ν_1 ν(CO)
	2211	2219	2220	2188	E_g ν_3 ν(CO)
	2197	2205	2204	2173	T_{1u} ν_6 ν(CO)
	2209	2216	2216	2186	ν(CO)$_{avg}$
[Ru(CO)$_6$]$^{2+}$	2250	2252	2254	2235	A_{1g} ν_1 ν(CO)
	2211	2219	2222	2192	E_g ν_3 ν(CO)
	2191	2198	2199	2172	T_{1u} ν_6 ν(CO)
	2208	2214	2216	2189	ν(CO)$_{avg}$
[Os(CO)$_6$]$^{2+}$	2255	2258	2259	2237	A_{1g} ν_1 ν(CO)
	2205	2214	2218	2188	E_g ν_3 ν(CO)
	2180	2189	2190	2166	T_{1u} ν_6 ν(CO)
	2201	2210	2211	2185	ν(CO)$_{avg}$

[a] This Article. [b] References 5 and 7. [c] Reference 32.

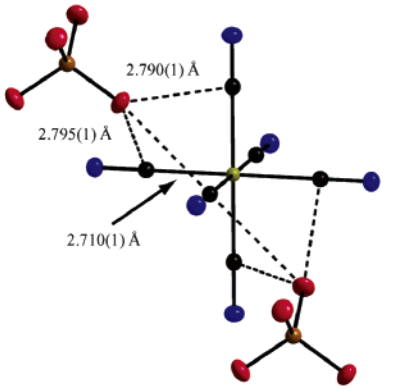

Figure 4. Selected interionic contacts in [Fe(CO)$_6$][BF$_4$]$_2$.

Table 6. Experimental and Calculated[a] Structural Data for the [BF$_4$]$^-$ Anion in [M(CO)$_6$][BF$_4$]$_2$ (M = Fe, Os)

		metal	
	calc[a]	Fe	Os
B−F (Å)	1.417	1.395(1)	1.389(10)−1.401(11)
F−B−F (2x) (deg)	109.47	109.73(5)	108.1(5)−110.1(5)
F−B−F (4x) (deg)	109.47	109.34(5)	

[a] B3LYP/6-311+G(d).[50]

both constituent ions are reported,[5] all [M(CO)$_6$]$^{2+}$ cations (M = Fe, Ru, Os) are best interpreted as regular octahedral in both groups. This is particularly evident from the bond angles, which rarely depart from 180° or 90°. The Fe−C bond lengths in the two [Fe(CO)$_6$]$^{2+}$ salts are identical within esd values.

A final point of interest concerns the interionic C···F contacts shown in Figure 4. The contact distances in the range of 2.710(1)−2.795(1) Å are very slightly shorter than C···F distances of 2.842(5)−3.061 Å reported for [Fe(CO)$_6$][SbF$_6$]$_2$[5] that involve only four of the six C atoms of the cation. These observations provide experimental confirmation for the more efficient packing of [BF$_4$]$^-$ in tetrahedral holes we proposed in the previous section, based on unit cell dimensions (see Table 3).

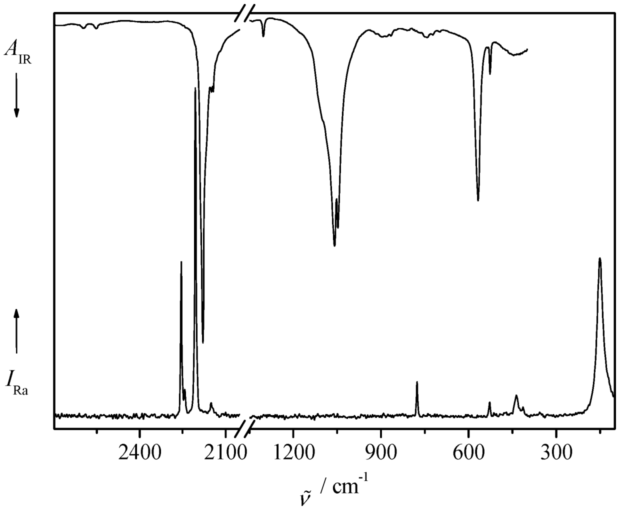

Figure 5. IR (Nujol) and Raman spectrum of [Os(CO)$_6$][BF$_4$]$_2$.

Both sets of values are shorter than the sum of the van der Waals radii of 3.17 Å.[51] In recent publications,[3,4,7,29] we have interpreted the observed C···F contacts in σ metal carbonyl fluoroantimonates in terms of electron transfer from F of the anions into π^* MOs of the CO ligands[3,4,29] on the cations. The slightly more extensive electron transfer suggested for [Fe(CO)$_6$][BF$_4$]$_2$ relative to that in [Fe(CO)$_6$][SbF$_6$]$_2$[5] is expected to affect the positions of ν(CO) for both salts in their vibrational spectra, discussed next.

Vibrational Spectra. The IR and Raman spectra of [Os(CO)$_6$][BF$_4$]$_2$ are depicted in Figure 5, and the respective spectra of [M(CO)$_6$][BF$_4$]$_2$ (M = Fe, Ru) are shown in Figures S2 and S3. To identify effects attributable to the counteranion, the CO stretching fundamentals, ν_1 (A_{1g}), ν_3 (E_g), and ν_6 (T_{1u}) of [M(CO)$_6$]$^{2+}$ (M = Fe, Ru, Os) with [BF$_4$]$^-$, [SbF$_6$]$^-$,[5,7] and [Sb$_2$F$_{11}$]$^-$ [5,7] as counteranions, together with calculated band positions,[32] are summarized in Table 5. Also included are ν(CO)$_{avg}$ values. Two effects are discernible: (i) dependency of the band position on the metal and (ii) dependency of ν(CO) on the counteranion.

In the first part of this study,[7] we observed that ν_1 (A_{1g}) increases in the order Fe < Ru < Os whereas ν_3 (E_g) remains constant or decreases slightly and ν_6 (T_{1u}) decreases more steeply for the [SbF$_6$]$^-$ and [Sb$_2$F$_{11}$]$^-$ salts. As can be seen in Table 5, for [M(CO)$_6$][BF$_4$]$_2$ (M = Fe, Ru, Os), the band positions of the three fundamentals ν_1 (A_{1g}), ν_3 (E_g), and ν_6 (T_{1u}) follow the same pattern.

A comprehensive vibrational assignment including a normal coordinate analysis and force field calculations is reported for [Fe(CO)$_6$][SbF$_6$]$_2$,[5] and all 13 fundamentals of [M(CO)$_6$]$^{2+}$ (M = Ru, Os) with [SbF$_6$]$^-$ as the anion have recently been identified.[7] The observed fundamental vibrations for [M(CO)$_6$]$^{2+}$ (M = Fe, Ru, Os) in their respective

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$[BF_4]^-$ and $[SbF_6]^-$ [5,7] salts are listed in Table S16, where they are compared to calculated data.[32] As can be seen, all $[M(CO)_6]^{2+}$ cations (M = Fe, Ru, Os) are clearly identified, and most fundamentals are assigned. There are some gaps, in particular, in the region below 500 cm^{-1}, where for the $[SbF_6]^-$ salts, band positions are occasionally obtained from overtones and combination bands rather than being directly observed. This procedure is more difficult and ambiguous on account of the increased number of $[BF_4]^-$ bands in important regions (Table S9).

The band positions for each fundamental in the three triads show a very slight dependency on the counteranion: for the $[SbF_6]^-$ and $[Sb_2F_{11}]^-$ salts, the ν(CO) values are identical within ±2 cm^{-1}, whereas for the three $[BF_4]^-$ salts, ν(CO) is consistently lower by about 4−9 cm^{-1}. This small margin is consistent with the more efficient packing of $[BF_4]^-$ into the tetrahedral hole, expressed in shorter C···F contacts, due to slightly stronger $F \rightarrow \pi^*_{(CO)}$ interionic electron transfer,[4,29] as discussed in the preceding section.

These admittedly small but noticeable differences not withstanding, it is apparent that, in the three triads $[M(CO)][Sb_2F_{11}]$, $[M(CO)_6][SbF_6]_2$, and $[M(CO)_6][BF_4]_2$ (M = Fe, Ru, Os), the structural and vibrational properties of both cations and anions are independent of M and do not vary with counteranion. This intrinsic stability of the octahedral coordination in superelectrophilic σ metal carbonyl cations sets the group 8 $[M(CO)_6]^{2+}$ cations (M = Fe, Ru, Os) clearly apart from other metal carbonyl cations[2−4,8,9,15,16,20,29] but also from other homoleptic, octahedral metal carbonyl complexes.[10−14]

Conclusion

The three isostructural salts of the composition $[M(CO)_6][BF_4]_2$ (M = Fe, Ru, Os) reported here are the first fully characterized examples of homoleptic superelectrophilic[1] σ-bonded metal carbonyl cations[2−4,29] stabilized by an anion other than $[Sb_2F_{11}]^-$ or $[SbF_6]^-$ [2−4,29] to form isolable salts of relatively high thermal stability.

A common synthetic route, the oxidative (F_2, XeF_2) carbonylation of commercially available precursors [$Fe(CO)_5$, $M_3(CO)_{12}$ (M = Ru, Os)] in the Brønsted superacids[26,27] aHF or HF/BF_3 produces the isostructural $[M(CO)_6][BF_4]_2$ salts (M = Fe, Ru, Os) in high yields. Whereas their lattice potential energies U_{pot}[30,31] are higher than those of $[M(CO)_6][SbF_6]_2$[5,7] (M = Fe, Ru, Os), their thermal stabilities are lower, on account of the lower fluoride ion affinity of BF_3 as compared to that of SbF_5.[49]

Structural studies reported here consist of the molecular structure determinations of $[M(CO)_6][BF_4]_2$ (M = Fe, Os) by single-crystal X-ray diffraction and powder X-ray diffraction of the corresponding Ru and Os complex salts. The unit cells are found to expand in the temperature range of 100−300 K, and the different changes of the cell lengths a and c suggest a phase transition from tetragonal to cubic above their decomposition temperatures.

The structural and vibrational studies reported here allow the following conclusions: (i) the $[M(CO)_6]^{2+}$ cations (M = Fe, Ru, Os) have structural and vibrational properties that are nearly independent of the anion, $[BF_4]^-$ studied here and $[SbF_6]^-$ or $[Sb_2F_{11}]^-$ featured in part I;[7] (ii) the anions have identical structures and vibrational properties in the three groups of $[M(CO)_6]^{2+}$ salts (M = Fe, Ru, Os); (iii) in each triad, the structural and vibrational features of both $[M(CO)_6]^{2+}$ cations and anions ($[BF_4]^-$, $[SbF_6]^-$, $[Sb_2F_{11}]^-$) are nearly independent of M (Fe, Ru, Os); and (iv) these features, summarized previously, and the near absence of significant interionic contacts illustrate the intrinsic stability of the octahedral coordination geometry.

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Supporting Information Available: Tables of atomic coordinates, anisotropic displacement factors, cell parameters at different temperatures, and bond lengths in the crystal structures of the observed and calculated vibrational frequencies of $[BF_4]^-$ and $[M(CO)_6]^{2+}$ (M = Fe, Ru, Os). Figures of the IR spectrum of $[Ru(CO)_6][BF_4]_2$, the IR and Raman spectra of $[Fe(CO)_6][BF_4]_2$, and a view of $[Os(CO)_6][BF_4]_2$ in the crystal structure. X-ray crystallographic files in CIF format have been deposited at the Cambridge Crystallographic Center under the deposition numbers CCDC-232217 for $[Fe(CO)_6][BF_4]_2$ and CCDC-232216 for $[Os(CO)_6][BF_4]_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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