The Synthesis, Vibrational Spectra, and Molecular Structure of [Ir(CO)$_6$][SbF$_6$]$_3$·4HF − The First Structurally Characterized Salt with a Tripositive, Homoleptic Metal Carbonyl Cation and the First Example of a Tetrahedral Hydrogen-Bonded (HF)$_4$ Cluster

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Abstract: The reductive carbonylation of IrF$_6$ in a dilute solution of SbF$_5$ in anhydrous HF (1:6 by volume) produces surprisingly at 25 °C and 1.5 atm CO the complex salt [Ir(CO)$_6$][SbF$_6$]$_3$·4HF, while [Ir(CO)$_6$][Sb$_2$F$_{11}$]$_3$ is obtained in liquid SbF$_5$ under similar conditions. Vibrational spectra in the CO stretching range for both salts and [Ir(CO)$_6$]$^{3+}$$_{(solv)}$ are identical within error limits, and ν(CO)$_{av}$ is with 2269 cm^{-1} the highest average stretching frequency so far observed for octahedral metal carbonyl cations. A vibrational assignment supported by DFT calculations is presented, and the vibrational fundamentals are compared to those of [Os(CO)$_6$]$^{2+}$. The molecular structure of [Ir(CO)$_6$][SbF$_6$]$_3$·4HF is determined by single-crystal X-ray diffraction. Crystal data for [Ir(CO)$_6$][SbF$_6$]$_3$·4HF: rhombohedral, R3c (No. 161), a = 14.630(4) Å, c = 18.377(7) Å, V = 3406.4(18) Å^3, Z = 6, T = 150 K, R_1 = 0.0338 [I > 2σ (I)], wR_2 = 0.0797). The average Ir–C bond length in the octahedral [Ir(CO)$_6$]$^{3+}$ cation is with 2.029(10) the longest observed for iridium carbonyl derivatives, consistent with the absence of Ir → CO π-back-bonding. The four solvate HF molecules form a tetrahedron via long, asymmetric, and partly delocalized hydrogen bonds with F−F edge lengths of 2.857 (3x) and 2.914 (3x) Å. There is no precedent for a polyhedral (HF)$_n$ cluster in the gas, liquid, or solid phase. The four F atoms of the (HF)$_4$ cluster are coordinated to the C atoms of the six CO ligands of the cation, which again is without precedent. The coordination of one of the F atoms to three C atoms in a iso-tridentate mode with contact distances C−F(8) of 2.641(10) Å is most unusual. The observed tight C−F coordination in [Ir(CO)$_6$][SbF$_6$]$_3$·4HF provides conclusive evidence for the presence of electrophilic carbon in the cation and illustrates how superelectrophilic cations such as [Ir(CO)$_6$]$^{3+}$ are solvent stabilized in the conjugate Brønsted−Lewis superacid HF−SbF$_5$.

Introduction

The use of the Lewis superacid SbF$_5$[1,2] and, more recently, of the conjugate Brønsted−Lewis superacid HF−SbF$_5$[3,4] as reaction media has allowed the generation of a substantial number of new metal carbonyl cations and their derivatives.[5,6] Thermally stable, crystalline salts are formed with the superacid anion [Sb$_2$F$_{11}$]$^{-}$,[7] while the simpler [SbF$_6$]$^{-}$ anion is so far found only in salts with the octahedral cations [M(CO)$_6$]$^{2+}$, M = Fe,

Ru, Os.[8,9] Many of the cations, with the metals in oxidation states of +2 and +3, following a suggestion by G. A. Olah,[10] are termed "superelectrophilic". Metals forming these cations range from group 12 (Hg) to group 6 (Mo, W) and have CO σ-bonded to the central metal ion.[6,11] A substantial number of fluoroantimonate(V) salts with superelectrophilic[10] metal carbonyl cations have recently been structurally characterized,[6,11] and metal carbonyl cations[5,6,8,9,11,12] have become established members of the large and diverse metal carbonyl family.

In this publication, we want to report on the synthesis and structural characterization of [Ir(CO)$_6$][SbF$_6$]$_3$·4HF. The com-

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(1) Fabré, P. L.; Devynk, J.; Tremillon, B. *Chem. Rev.* **1982**, *82*, 591.
(2) Christe, K. O.; Dixon, D. A.; McLemore, D.; Wilson, W. W.; Sheehy, J. A.; Boatz, J. A. *J. Fluorine Chem.* **2000**, *101*, 151.
(3) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley: New York, 1985.
(4) O'Donnell, T. A. *Superacids and Acidic Melts as Inorganic Reaction Media*; V. C. H.: Weinheim, Germany, 1993.
(5) Willner, H.; Aubke, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2402.
(6) Willner, H.; Aubke, F. *Inorganic Chemistry Highlights*; Wiley−V.C.H.: Weinheim, Germany, 2001.

(7) Zhang, D.; Rettig, S. J.; Trotter, J.; Aubke, F. *Inorg. Chem.* **1996**, *35*, 6113.
(8) Bernhardt, E.; Bley, B.; Wartchow, R.; Willner, H.; Bill, E.; Kuhn, P.; Sham, I. H. T.; Bodenbinder, M.; Bröchler, R.; Aubke, F. *J. Am. Chem. Soc.* **1999**, *121*, 7188.
(9) Bernhardt, E.; Bach, C.; Wartchow, R.; Willner, H.; Aubke, F. *Inorg. Chem.*, to be submitted.
(10) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767.
(11) Willner, H.; Aubke, F. *Angew. Chem.*, submitted for publication.
(12) Willner, H.; Bodenbinder, M.; Bröchler, R.; Hwang, G.; Rettig, S. J.; Trotter, J.; von Ahsen, B.; Westphal, U.; Jonas, V.; Thiel, W.; Aubke, F. *J. Am. Chem. Soc.* **2001**, *123*, 588.

pound is unprecedented on four accounts: (i) The regular octahedral $[Ir(CO)_6]^{3+}$ cation is the only known tripositive homoleptic metal carbonyl cation; (ii) $[Ir(CO)_6][SbF_6]_3 \cdot 4HF$ is the first HF solvate among metal carbonyl fluoroantimonates;[5,6] (iii) the solvate HF interacts with the $[Ir(CO)_6]^{3+}$ cation by iso-tridentate and aniso-bidentate intermolecular C–F contacts and with the $[SbF_6]^-$ anions by weak hydrogen bonds. The molecular structure shows how superelectrophilic metal carbonyl cations are solvent stabilized in HF–SbF$_5$; (iv) the F-coordinated HF-ligands are associated by weak, asymmetric, and delocalized hydrogen bonds to form tetrahedral $(HF)_4$ clusters.

The structural and spectroscopic data reported by us here and in previous studies on σ-bonded metal carbonyl cations[5,6,8,11,12] (σ-carbonyls) are supported by DFT calculations[13] which allow an understanding of the nature of metal–CO bonding in thermally stable, fully characterized solid-state compounds.[11]

Experimental Section

General Procedures and Reagents. (a) Apparatus. Volatile materials were manipulated in a glass or a stainless steel vacuum line of known volume, equipped with a capacitance pressure gauge (Type 280E, Setra Instruments, Acton, MA) and valves with PTFE stems (Young, London) or stainless steel needle valves (3762H46Y Hoke, Creskill, NJ), respectively. Anhydrous HF or DF, both containing a few percent of SbF$_5$, were stored in PFA tubes (12 mm o.d., 300 mm long), heat gun sealed at the bottom, and connected on top to a stainless steel needle valve (3762H46Y Hoke, Creskill, NJ). All other volatile compounds were stored in glass containers equipped with a valve with PTFE stem (Young, London). In the case of ^{13}CO, the storage vessel contained a molecular sieve (5 Å, Merck) to recover the excess of ^{13}-CO after use by cooling with liquid nitrogen. For synthetic reactions in HF/SbF$_5$ solutions, a two part V-shaped reactor consisting of two PFA tubes (12 mm o.d., 100 mm length) and a PFA needle valve (Fluoroware, MN) with an approximate volume of 25 mL were used. A figure of the reactor is presented in the Supporting Information.

(b) Chemicals and Synthetic Procedures. Iridium powder (99.9% pure) was obtained as a gift from the Degussa-Hüls Company. Antimony(V) fluoride (Atochem North America, formerly Ozark-Mahoning) was purified by atmospheric pressure distillation, followed by a vacuum distillation as described recently.[8,12] To remove moisture from anhydrous HF (Solvay AG, Hannover, Germany) as $[H_3O]$-$[Sb_2F_{11}]$,[7] a small amount of SbF$_5$ was added, and the mixture was stored in a PFA vial. CO (99%, Linde Gas) and ^{13}CO (99% enriched, IC Chemicals) were obtained from commercial sources. Iridium hexafluoride, IrF$_6$, was obtained by direct fluorination of Ir with F$_2$ (Solvay AG, Hannover, Germany) as described previously.[14,15] The reductive carbonylation of IrF$_6$ in SbF$_5$ had been reported by us previously[16,17] to yield $[Ir(CO)_6][Sb_2F_{11}]_3$.

Warning: Of the reagents used in this study, HF, F$_2$, CO, SbF$_5$, and IrF$_6$ are either highly corrosive, strongly oxidizing, or toxic. Vacuum lines, used for the handling of these reagents, are contained inside well-ventilated fume hoods. Safety equipment should be worn, and available safety information sheets should be consulted, together with the original literature, when attempting to repeat the reactions described here.

(c) The Synthesis of $[Ir(CO)_6][SbF_6]_3 \cdot 4HF$ and Crystal Growth. The PFA reactor, fitted with a PTFE coated magnetic stirring bar, was passivated for about 3 h with 0.2 atm of F$_2$ at room temperature. Using

a stainless steel vacuum line for transfer and liquid N$_2$ as coolant, 0.3 mmol of IrF$_6$ was condensed into one of the sidearms (A) together with about 3 mL of HF and 0.5 mL of SbF$_5$. Subsequently, CO was introduced into the reactor to give a pressure of about 1.5 atm at room temperature. On warming to room temperature and stirring, IrF$_6$ formed within a few minutes a clear yellow solution which quickly turned colorless. To ensure a complete reaction, the CO atmosphere was renewed after 16 h, and the solution was left stirring for another 12 h at room temperature. For crystal growth and a subsequent single-crystal X-ray diffraction analysis, the tube containing the HF solution (A) was immersed in an ethanol bath, which was kept at −24 °C with the help of a cryostat. Since crystallization had not started after 24 h, the second arm (B) of the reactor was cooled to −78 °C (ethanol/dry ice) to remove HF slowly from the reaction mixture. After approximately 16 h, a small amount of colorless crystals had formed. The mixture was left standing for an additional 3 days. After decanting the supernatant solution from arm (A) into arm (B), all volatiles were removed in vacuo, while arm (A) was kept at −78 °C and arm (B) at room temperature. Under these conditions, some HF condensed into arm (A), which was used to wash the crystals repeatedly. Subsequently, dry argon was admitted to the reactor. Crystals suitable for an X-ray analysis were selected at −70 °C in a protecting atmosphere of dry N$_2$ to prevent decomposition. A small sample was placed on the cold copper trough and flushed with dry nitrogen. Suitable crystals were selected under a microscope and fitted into Lindemann glass capillaries with an o.d. of 0.1–0.3 mm and a wall thickness of 0.01 mm. The capillaries were sealed off at both ends in a stream of cold N$_2$ to give a glass cylinder of approximately 20 mm length. To prevent thermal degradation of the crystals, the glass cylinder containing the crystals was picked up with cooled forceps and fixed with wax in the goniometer head.

(d) Instrumentation. (I) Vibrational Spectroscopy. Infrared spectra were recorded at room temperature on a IFS-66v FT spectrometer (Bruker, Karlsruhe, Germany). Two different detectors together with a Ge/KBr or a 6 μm Mylar beam splitter operating in the region 5000–400 or 550–80 cm^{-1}, respectively, were used. One hundred and twenty-eight scans were co-added for each spectrum, using an apodized resolution of 2 or 4 cm^{-1}. The samples were crushed between CaF$_2$, AgBr (Korth, Kiel, Germany), or polyethylene (Cadillac, Hannover, Germany) disks inside the drybox. Raman spectra were recorded at room temperature with a Bruker RFS 100/S FT Raman instrument in the region 5000–80 cm^{-1} with a spectral resolution of 2 cm^{-1} using the 1064 nm exciting line (~500 mW) of a Nd:YAG laser (Adlas, DPY 301, Lübeck, Germany). Spectra of crystalline samples of $[Ir(CO)_6]$-$[SbF_6]_3 \cdot 4HF$ either in solution or in the solid state were obtained through the walls of the PFA reactor, which caused some interference from bands due to PFA and limited the spectral interpretation to the CO stretching range.

(II) NMR Spectroscopy. ^{13}C NMR spectra were obtained at room temperature on a Bruker MSL-200 FT spectrometer operating at 50.33 MHz.

(III) Single-Crystal X-ray Diffraction. Diffraction data were collected at 150 K on a Siemens P4R4 four circle diffractometer with Mo Kα radiation. The structure was solved by direct methods and refined by least-squares F^2 as a racemic twin (61:39). Experimental details are given in Tables 1 and S1 in the Supporting Information section.

Results and Discussion

Synthetic Aspects. Over the last six years, there have been a number of attempts to generate $[Ir(CO)_6]^{3+}$ that have resulted in the syntheses and structural characterizations of various Ir-(III) carbonyl derivatives. These attempts are briefly reviewed here. The addition of CO to $Ir(SO_3F)_3$[18] in HSO$_3$F at room temperature has produced an isomer mixture of *fac-* and *mer-*

(13) Jonas, V.; Thiel, W. *Organometallics* **1998**, *17*, 353.
(14) Ruff, O.; Fischer, J. *Z. Anorg. Allg. Chem.* **1929**, *179*, 166.
(15) Hargreaves, G. B.; Peacock, R. D. *Proc. Chem. Soc., London* **1959**.
(16) Bach, C.; Willner, H.; Wang, C.; Rettig, S. J.; Trotter, J.; Aubke, F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1974.
(17) von Ahsen, B.; Bach, C.; Pernice, H.; Willner, H.; Aubke, F. *J. Fluorine Chem.* **2000**, *102*, 243.

(18) Lee, K. C.; Aubke, F. *J. Fluorine Chem.* **1982**, *19*, 501.

Table 1. Crystallographic Data for [Ir(CO)$_6$][SbF$_6$]$_3$·4HF

compound	[Ir(CO)$_6$][SbF$_6$]$_3$·4HF
empirical formula	C$_6$H$_4$F$_{22}$IrO$_6$Sb$_3$
formula weight	1147.35
crystal system	rhombohedral
space group	$R3c$ (No. 161)
unit cell dimensions: a [Å]	14.630(4)
c [Å]	18.377(7)
unit cell volume: V [Å^3]	3406.4(18)
Z value	6
ρ_{calcd} [g cm^{-3}]	3.356
T [K]	150
radiation, Mo Kα λ [Å]	0.71069
reflections collected/unique	3020/1643
θ range [deg]	2.74–27.00
R [$I > 2\sigma(I)$]: R_1	0.0338
wR_2	0.0797

Ir(CO)$_3$(SO$_3$F)$_3$, of which the latter isomer is structurally characterized by single-crystal X-ray diffraction.[19] In closely related work, the oxidation of Ir$_4$(CO)$_{12}$ by XeF$_2$ in anhydrous HF produces a mixture of *fac*- and *mer*-Ir(CO)$_3$F$_3$[20,21] with the *fac* isomer characterized by EXAFS.[21]

Attempts at a subsequent solvolytic carbonylation of Ir(CO)$_3$-(SO$_3$F)$_3$ in SbF$_5$ are only partly successful. While, according to spectroscopic evidence, [Ir(CO)$_6$]$^{3+}$ is formed, attempts to isolate a salt in pure form fail.[22] Instead, a small amount of crystalline [Ir(CO)$_5$Cl][Sb$_2$F$_{11}$]$_2$ forms and is structurally characterized.[16,23] Fluoro chloro carbon lubricant is seen as the source of chlorine in the final product.[23] A more direct and reproducible route to [Ir(CO)$_5$Cl][Sb$_2$F$_{11}$]$_2$ is subsequently found in the oxidative carbonylation of [Ir(CO)$_3$Cl]$_x$ where SbF$_5$ also functions as oxidizing agent.[23] However, this complex, as well as the isostructural salt [Rh(CO)$_5$Cl][Sb$_2$F$_{11}$]$_2$,[23] obtained from [Rh(CO)$_2$(μ-Cl)]$_2$ in an analogous manner and the related compound [W(CO)$_6$(FSbF$_5$)][Sb$_2$F$_{11}$][24] are found to be unsuited as precursors to salts of the homoleptic cations [M(CO)$_6$]$^{3+}$, M = Rh, Ir, or [W(CO)$_7$]$^{2+}$, because, according to the molecular structures,[16,23,24] the anionic ligands Cl^{-} [23] or (FSbF$_5$)$^{-}$ [24] are tightly bonded to the respective metal ion, and their substitution by CO has so far not been possible.[23,24]

In summary, of the major carbonylation methods, neither the solvolysis in HSO$_3$F[19] or SbF$_5$[16,23] nor the oxidative methods in HF[20,21] or SbF$_5$[23] are suitable routes to the [Ir(CO)$_6$]$^{3+}$ cation.[6,11] However, with *mer*-Ir(CO)$_3$(SO$_3$F)$_3$,[19] [Ir(CO)$_5$Cl]-[Sb$_2$F$_{11}$]$_2$,[16,23] and *fac*-Ir(CO)$_3$F$_3$[20,21] three structurally characterized Ir(III) carbonyl complexes are obtained. Structural and spectroscopic data for the first two complexes are included in Table 2 and are supported by DFT calculations for [Ir-(CO)$_5$Cl]$^{2+}$.[23] The EXAFS data for *fac*-Ir(CO)$_3$F$_3$ allow a limited comparison. The Ir–C distances are with 2.030(8) Å comparable to the corresponding data in Table 2. The Ir–O distances of 3.040(4) Å would suggest C–O bond lengths of ~1.01 Å, and ν(CO) at 2213 and 2165 cm^{-1} is comparable to CO stretching wavenumbers reported for *fac*-Ir(CO)$_3$(SO$_3$F)$_3$ (2233 and 2157 cm^{-1}).[19]

(19) Wang, C.; Lewis, A. R.; Batchelor, R. J.; Einstein, F. W. B.; Willner, H.; Aubke, F. *Inorg. Chem.* **1996**, *35*, 1279.
(20) Brewer, S. A.; Holloway, J. H.; Hope, E. G.; Watson, P. G. *J. Chem. Soc., Chem. Commun.* **1992**, 1577.
(21) Brewer, S. A.; Brisdon, A. K.; Holloway, J. H.; Hope, E. G.; Peck, L. A.; Watson, P. G. **1995**, 2945.
(22) Wang, C. Ph.D. thesis, University of British Columbia, 1996.
(23) Willner, H.; Bach, C.; Wartchow, R.; Wang, C.; Rettig, S. J.; Trotter, J.; Jonas, V.; Thiel, W.; Aubke, F. *Inorg. Chem.* **2000**, *39*, 1933.
(24) Bröchler, R.; Sham, I. H. T.; Bodenbinder, M.; Schmitz, V.; Rettig, S. J.; Trotter, J.; Willner, H.; Aubke, F. *Inorg. Chem.* **2000**, *39*, 2172.
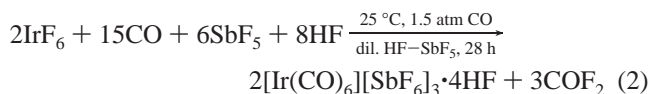
The remaining third major synthetic approach to metal carbonyl cations, reductive carbonylation,[5,6,11] provides a promising avenue to the [Ir(CO)$_6$]$^{3+}$ cation. From the discussion above, it appears unlikely that the protonic superacids[3,4] HF or HSO$_3$F are suitable reaction media. It has previously been possible to generate linear [Au(CO)$_2$]$^{+}$ [25,26] or square planar [M(CO)$_4$]$^{2+}$, M = Pd, Pt,[27,28] in HSO$_3$F; however, on account of the relatively high nucleophilicity of the self-ionization ion SO$_3$F^{-}, only the fluorosulfates Au(CO)SO$_3$F[25] and *cis*-M(CO)$_2$-(SO$_3$F)$_2$, M = Pd,[27] Pt,[12] are formed by nucleophilic substitution and isolated from solution. [Au(CO)$_2$][Sb$_2$F$_{11}$][26] or [M(CO)$_4$]-[Sb$_2$F$_{11}$]$_2$,[12] M = Pd, Pt, is then obtained by subsequent solvolytic carbonylation in SbF$_5$ or in HF–SbF$_5$.

Since there is no evidence for the transitory existence of [Ir-(CO)$_6$]$^{3+}$ in either HSO$_3$F or HF and neither *mer*-Ir(CO)$_3$-(SO$_3$F)$_3$[19] nor *fac*-Ir(CO)$_3$F$_3$[20,21] is easily obtainable as precursors, the reductive carbonylation of IrF$_6$ in SbF$_5$ is the only feasible route to a [Ir(CO)$_6$]$^{3+}$ salt. The formation and isolation of [Ir(CO)$_6$][Sb$_2$F$_{11}$]$_3$ in a 3e^{-} reduction proceed according to[16,17]

$$2IrF_6 + 15CO + 12SbF_5 \xrightarrow[\text{SbF}_5,\ 4\ \text{h}]{50\ °C,\ 1\ \text{atm CO}} 2[Ir(CO)_6][Sb_2F_{11}]_3 + 3COF_2 \quad (1)$$

In an equally facile manner, OsF$_6$ or PtF$_6$[17] undergoes a 4e^{-} reduction to [Os(CO)$_6$][Sb$_2$F$_{11}$]$_2$[9] or [Pt(CO)$_4$][Sb$_2$F$_{11}$]$_2$,[12] respectively, in HF–SbF$_5$. The resulting crystalline materials have allowed the structural characterization of the [Os(CO)$_6$]$^{2+}$ [9] and the [Pt(CO)$_4$]$^{2+}$ [12] cations, the former with both [Sb$_2$F$_{11}$]$^{-}$ and [SbF$_6$]$^{-}$ as counteranions.[9] In all instances, a complete exchange of F^{-} against CO ligands takes place in an elegant and facile manner. In the case of MF$_6$, M= Os, Ir, the regular octahedral coordination geometries of Os(II) and Ir(III) are retained. In the case of [Ir(CO)$_6$][Sb$_2$F$_{11}$]$_3$, suitable single crystals are not obtained. The microcrystalline powder formed allows, with the help of DFT calculations,[13] complete vibrational analysis of the cation, which will be discussed below.

To obtain crystalline [Ir(CO)$_6$][Sb$_2$F$_{11}$]$_3$, the synthesis of the salt is performed in a dilute solution of SbF$_5$ in HF (about 1:6 by volume) and a CO atmosphere of about 1.5 atm. The dilute HF–SbF$_5$ solution is chosen instead of anhydrous HF to prevent nucleophilic substitution of CO by F^{-}. This could conceivably lead to the cation [Ir(CO)$_5$F]$^{2+}$ or previously reported Ir-(CO)$_3$F$_3$.[20,21] With the reaction mixture kept at room temperature for 28 h, a Raman spectrum of the clear solution in a PFA cell shows two intense lines in the CO stretching region at 2295 and 2275 cm^{-1}. Surprisingly, colorless crystals of [Ir(CO)$_6$]-[SbF$_6$]$_3$·4HF are obtained at -78 °C, which are suitable for a molecular structure determination by single-crystal X-ray diffraction (vide infra). The formation reaction is formulated as

$$2IrF_6 + 15CO + 6SbF_5 + 8HF \xrightarrow[\text{dil. HF–SbF}_5,\ 28\ \text{h}]{25\ °C,\ 1.5\ \text{atm CO}} 2[Ir(CO)_6][SbF_6]_3·4HF + 3COF_2 \quad (2)$$

(25) Willner, H.; Aubke, F. *Inorg. Chem.* **1990**, *29*, 2195.
(26) Willner, H.; Schaebs, J.; Hwang, G.; Mistry, F.; Jones, R.; Trotter, J.; Aubke, F. *J. Am. Chem. Soc.* **1992**, *114*, 8972.
(27) von Ahsen, B.; Wartchow, R.; Willner, H.; Jonas, V.; Aubke, F. *Inorg. Chem.* **2000**, *39*, 4424.
(28) Bodenbinder, M.; Balzer-Jöllenbeck, G.; Willner, H.; Batchelor, R.; Einstein, F. W. B.; Wang, C.; Aubke, F. *Inorg. Chem.* **1996**, *35*, 82.

Table 2. Octahedral Metal Carbonyl Salts of Ir(III), Os(II), and Re(I) Experimental and Calculated[a] Data
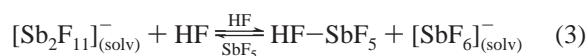
compound		structural parameter		spectroscopic inf.		
		d(M–C)$_{av}$ [Å]	d(C–O)$_{av}$ [Å]	ν(CO)$_{av}$ [cm^{-1}]	$f_{(CO)} \times 10^2$ N m^{-1}	ref
[Ir(CO)$_6$][SbF$_6$]$_3$·4HF		2.029(10)	1.090(10)	2268	20.8	this work
		{2.063}	{1.124}	{2241}	{19.91}	13
[Ir(CO)$_5$Cl][Sb$_2$F$_{11}$]$_2$	ax.:	2.05(1)	1.07(1)	2246	20.39	16, 23
		{2.016}	{1.130}	{2212}	{19.09}	13
	eq.:	2.02(1)	1.09(1)			16, 23
		{2.021}	{1.127}		{19.58}	13
mer-Ir(CO)$_3$(SO$_3$F)$_3$	trans:	2.003(6)	1.111(8)	2218	19.90	19
	cis:	1.937(7)	1.094(8)			
[Os(CO)$_6$][Sb$_2$F$_{11}$]$_2$		2.027(5)	1.102(1)	2209	19.7	9
		{2.045}	{1.130}	{2185}	{19.13}	13
[Re(CO)$_6$][Re$_2$F$_{11}$]		2.01(4)	1.13(3)	2116	18.01	29, 32
		{2.047}	{1.141}	{2102}	{17.82}	13

[a] Calculated values in parentheses. For details, see ref 13.

The CO stretching vibrations at 2297 (A$_{1g}$), 2278 (E$_g$), and 2254 (T$_{1u}$) cm^{-1} are identical within error limits to those of solid [Ir(CO)$_6$][Sb$_2$F$_{11}$]$_3$[16,17] and the solution data quoted above. Calculated[13] band positions are with 2272, 2245, and 2228 cm^{-1} lower by 25–32 cm^{-1}. While the presence of [Ir(CO)$_6$]$^{3+}$ in both solid compounds as well as in solution is clearly established, the invariance of ν(CO) in all three environments is surprising. The high solubility of tripositive [Ir(CO)$_6$]$^{3+}$ in HF–SbF$_5$ is equally surprising. It appears that the expected high lattice energy of the salts is compensated for by the high solvation energy for the cation.

The formation of [SbF$_6$]$^-$ as a counteranion during a carbonylation reaction, where SbF$_5$ is present in an excess,[5,6,11] is also surprising, because all carbonylations in SbF$_5$ or HF–SbF$_5$ lead to [Sb$_2$F$_{11}$]$^-$ salts only. The anions [SbF$_6$]$^-$ and [Sb$_2$F$_{11}$]$^{-}$ [8,9] are both found in salts with group 8 cations [M(CO)$_6$]$^{2+}$, M = Fe, Ru, Os. The [M(CO)$_6$][Sb$_2$F$_{11}$]$_2$, M = Fe, Ru, Os,[8,9] salts are the primary products, which are converted into the corresponding [SbF$_6$]$^-$ salts by repeated washing with anhydrous HF.[8,9] On the other hand, square planar [M(CO)$_4$]$^{2+}$, M = Pd, Pt,[5,6,12] or linear [Hg(CO)$_2$]$^{2+}$ [28] is formed exclusively as [Sb$_2$F$_{11}$]$^-$ salts. Both types of salts with square planar[5,6,12] or linear[28] cations show up to five significant interionic C–F contacts per CO ligand, which are involved in the formation of extended structures.[12,28] This seems to prevent removal of SbF$_5$ from the [Sb$_2$F$_{11}$]$^-$ anions in anhydrous HF.

It is evident, on the basis of the reported molecular and extended structures,[6,8,9,12,28] that stabilization of the superelectrophilic metal carbonyl cations by interionic C–F contacts is less important for salts with octahedral [M(CO)$_6$]$^{2+}$, M = Fe, Ru, Os,[8,9] and not observed for [Re(CO)$_6$]$^+$.[29] The formation of interionic C–F contacts is facilitated by the [Sb$_2$F$_{11}$]$^-$ anion, which is frequently distorted from D_{4h} symmetry by bending and rotational processes.[6–9,12,28] The formation of [SbF$_6$]$^-$ in HF–SbF$_5$[3,4] is explained by the well-established equilibrium:[30]

$$[Sb_2F_{11}]^-_{(solv)} + HF \underset{SbF_5}{\overset{HF}{\rightleftharpoons}} HF-SbF_5 + [SbF_6]^-_{(solv)} \quad (3)$$

The equilibrium is shifted to the right in dilute HF–SbF$_5$, and according to a recent ^{19}F NMR study,[30] [SbF$_6$]$^-$ is now the dominant species and will hence form the counteranion. Not unexpectedly, as will be discussed below, the molecular structure of [Ir(CO)$_6$][SbF$_6$]$_3$·4HF shows the absence of any significant interionic C–F contacts. This is due to the presence of HF in the lattice, which act as spacers and bridges between cations and anions, resulting in an extended structure, as will be discussed later.

At present, all attempts to synthesize [Rh(CO)$_6$]$^{3+}$ salts have so far been without success despite repeated efforts, as discussed recently.[6,11,23] Consequently, [Ir(CO)$_6$]$^{3+}$ either in [Ir(CO)$_6$]-[Sb$_2$F$_{11}$]$_3$[16,17] or in [Ir(CO)$_6$][SbF$_6$]$_3$·4HF is the sole example of a tripositive, superelectrophilic[10] homoleptic metal carbonyl cation. Hence, an extensive and careful characterization by structural, spectroscopic, and computational methods is important and will be presented below.

Vibrational Spectra of the [Ir(CO)$_6$]$^{3+}$ Cation. Vibrational wavenumbers for [Ir(CO)$_6$]$^{3+}$ and its ^{13}C isotopomer down to 100 cm^{-1} have previously been reported for the [Sb$_2$F$_{11}$]$^-$ salt.[17] As discussed already, the CO stretching wavenumbers of [Ir(CO)$_6$]$^{3+}$$_{(solv)}$ in HF–SbF$_5$ and in the two solid complexes [Ir(CO)$_6$][Sb$_2$F$_{11}$]$_3$[16,17] and [Ir(CO)$_6$][SbF$_6$]$_3$·4HF, the subject of this study, are all identical within the customary error limits. It appears plausible that this similarity extends also to the remaining 10 observable fundamentals, as is the case for the members of the two isostructural triads [M(CO)$_6$][Sb$_2$F$_{11}$]$_2$ and [M(CO)$_6$][SbF$_6$]$_2$ for M = Fe,[8] Ru,[9] Os,[9] which have very similar bond parameters.[8,9]

In addition to [Os(CO)$_6$]$^{2+}$,[9] there are among neutral and cationic metal hexa-carbonyls two additional isoelectronic and isosteric species that are useful in the vibrational characterization of [Ir(CO)$_6$]$^{3+}$, [Re(CO)$_6$]$^+$,[29] and W(CO)$_6$,[31] which are both structurally characterized by X-ray diffraction as [Re(CO)$_6$]-[Re$_2$F$_{11}$][29] and in the case of W(CO)$_6$ by electron diffraction in the gas phase.[31] More importantly, there are detailed vibrational analyses for [Re(CO)$_6$]$^+$ [32] and W(CO)$_6$[33,34] reported, and the vibrational spectra for all M(CO)$_6$ species, M = W, Re, Os, Ir, have been modeled by DFT methods.[13,35] There is clearly a substantial amount of structural,[9,29,31] spectroscopic,[8,9,32–34] and supporting computational[13,35] work available to conduct a

(29) Bruce, D.; Holloway, J. H.; Russel, D. R. *J. Chem. Soc., Dalton Trans.* **1978**, 1627.

(30) Culman, J.-C.; Fauconet, M.; Jost, R.; Sommer, J. *New J. Chem.* **1999**, *23*, 863.

(31) Arnesen, S. P.; Seip, M. M. *Acta Chem. Scand.* **1986**, *20*, 2711.

(32) Abel, E. W.; McLean, R. A. N.; Tyfield, S. P.; Braterman, P. S.; Walker, A. P.; Hendra, P. J. *J. Mol. Spectrosc.* **1969**, *30*, 29.

(33) Jones, L. H.; McDowell, R. S.; Goldblatt, M. *Inorg. Chem.* **1988**, *27*, 2349.

(34) Jones, L. H. *Inorganic Vibrational Spectroscopy*; Marcel Dekker: New York, 1971.

(35) Jonas, V.; Thiel, W. *J. Chem. Phys.* **1995**, *102*, 8474.

Table 3. Spectroscopic and Computational Data of the Superelectrophilic Cations $[Os(CO)_6]^{2+}$ and $[Ir(CO)_6]^{3+}$

			$[Os(CO)_6]^{2+\ a}$		$[Ir(CO)_6]^{3+\ b}$	
			exp	calc[c]	exp	calc[c]
(i) vibrational data [cm^{-1}]						
ν_1	ν(CO)	A_{1g}	2258	2237	2295	2272
ν_3	ν(CO)	E_g	2214	2188	2278	2245
ν_6	ν(CO)	T_{1u}	2189	2166	2254	2228
ν_7	δ(MCO)	T_{1u}	560	567	531	528
ν_{12}	δ(MCO)	T_{2u}	509	509	480	477
ν_{10}	δ(MCO)	T_{2g}	480	471		449
ν_2	ν(MC)	A_{1g}	429	428	422	402
ν_4	ν(MC)	E_g	409	401		373
ν_8	ν(MC)	T_{1u}	344	336		319
ν_5	δ(MCO)	T_{1g}	345	339		326
ν_9	δ(MCO)	T_{1u}	145	101	138	107
ν_{11}	δ(CMC)	T_{2g}	142	93		95
ν_{13}	δ(CMC)	T_{2u}	96	77		83
ν(M−C)$_{av}$			380	373		351
ν(C−O)$_{av}$			2209	2185	2269	2241
(ii) vibrational force constants [$\times 10^2$ N m^{-1}]						
f_{CO}			19.7	19.1	20.8	19.9
f_{MC}				2.16		1.92
(iii) atomic charges [e$^-$]						
qM				−0.35		0.11
qC				0.66		0.59
qO				−0.20		−0.11
(iv) ^{13}C NMR[b]						
δ ^{13}C [ppm]			147		121	

[a] Reference 9. [b] References 16, 17. [c] Reference 13.

Figure 1. A plot of the CO stretching fundamentals for octahedral $[M(CO)_6]^{m+}$. M = W, Re, Os, Ir, m = 0, 1, 2, 3 versus the nuclear charge Z.

spectroscopic characterization of $[Ir(CO)_6]^{3+}$, which is followed in the next section by the structural characterization of $[Ir(CO)_6]$-$[SbF_6]_3$·4HF.

Vibrational assignments for $[Ir(CO)_6]^{3+}$ and $[Os(CO)_6]^{2+}$,[9] which have not been published, are shown in Table 3 together with calculated wavenumbers,[13] experimental and calculated[13] vibrational force constants (f_{CO} and f_{MC}), partial atomic charges q for the M−C−O moiety obtained from a natural population analysis,[13] and ^{13}C NMR chemical shifts[5] for both cations. Figure 1 shows a plot of the three CO stretching fundamentals versus the nuclear charge for the isoelectronic species W(CO)₆,[33,34] $[Re(CO)_6]^+$,[32] $[Os(CO)_6]^{2+}$,[9] and $[Ir(CO)_6]^{3+}$.

The list of experimentally determined fundamentals is incomplete for $[Ir(CO)_6]^{3+}$ for two reasons: (i) both $[Ir(CO)_6]$-$[Sb_2F_{11}]_3$[16,17] and $[Ir(CO)_6][SbF_6]_3$·4HF are extremely reactive, and IR spectra are of poor quality. Hence, a reasonably complete number of overtones and combination bands is not available and cannot be used to estimate the positions of missing fundamentals. This approach has been useful in the vibrational analyses of $[M(CO)_6]^{2+}$, M = Fe, Ru, Os.[8,9] (ii) Raman data for $[Ir(CO)_6][SbF_6]_3$·4HF are only obtained in PFA tubes. For $[Ir(CO)_6][Sb_2F_{11}]_3$, there is also some overlap with bands due to the anion. For a vibrational analysis of $[M(CO)_6]^{2+}$, M = Fe, Ru, Os,[8,9] both the $[Sb_2F_{11}]^-$ and the $[SbF_6]^-$ salts are available, while vibrational data for $[Re(CO)_6]^+$ are obtained using octahedral $[AsF_6]^-$ as a counteranion.[32]

Despite these experimental limitations, a reasonable vibrational assignment for $[Ir(CO)_6]^{3+}$ is achieved with the help of DFT calculations.[13,35] A meaningful comparison of all 13 fundamentals for both isoelectronic $[M(CO)_6]$ species, M = Os, Ir, is possible. As can be seen in Table 3, agreement between experimental and calculated wavenumbers is generally very good. As observed previously,[8,12] values for the CO stretching fundamentals ν_1, ν_3, and ν_6 are underestimated by 20−30 cm^{-1},
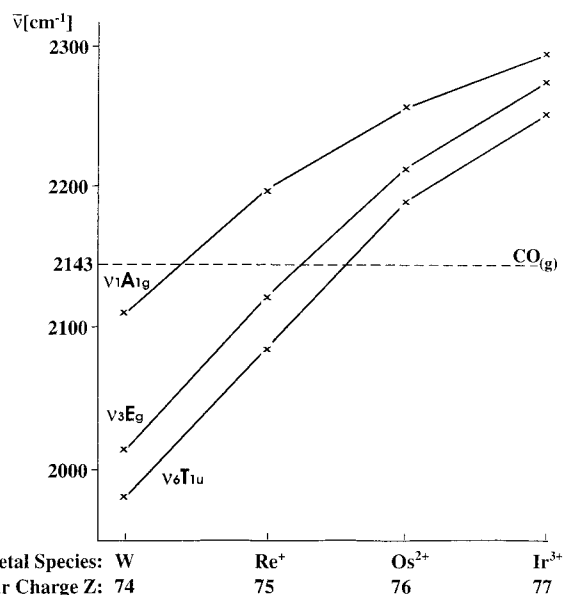
while experimental M−C stretching fundamentals ν_2, ν_4, and ν_8 are usually lower by about 10 cm^{-1}. Similar discrepancies are found for the bending modes.

The following conclusions are reached: (i) both $[Ir(CO)_6]^{3+}$ and $[Os(CO)_6]^{2+}$[9] are strictly octahedral. There is no breakdown of the mutual exclusion rule for IR and Raman active fundamentals, most noticeably in the CO stretching range. This implies that distortions of the octahedral environment of the metal in the solid state are either absent or relatively symmetrical, resulting in the retention of the inversion center. This is in contrast to observations for $[M(CO)_4][Sb_2F_{11}]_2$, M = Pd, Pt,[12] where, on account of significant interionic C−F interactions in the solid state, the mutual exclusion rule is invalidated.

(ii) In the isosteric and isoelectronic series $[M(CO)_6]^{m+}$ with M^m = W^0, Re$^+$, Os^{2+}, Ir^{3+}, the strength of the C−O bond, measured in terms of ν(CO), increases with increasing oxidation state of M (Figure 1). This is apparent from the increase for each one of the three stretching fundamentals, $\nu_1(A_{1g})$, ν_3 (E_g), and ν_6 (T_{1u}), as well as of ν (CO)$_{av}$.[5] The latter has for $[Ir(CO)_6]^{3+}$ with 2269 cm^{-1} the highest ν(CO)$_{av}$ value for any octahedral M(CO)₆ species.[5,6,11] With the highest value for square planar ($[Pt(CO)_4]^{2+}$ 2261 cm^{-1})[12] and linear metal carbonyl cations ($[Hg(CO)_2]^{2+}$ 2280 cm^{-1})[28] in close proximity, these data serve as a good illustration of a relationship we have established recently,[11] where the strength of the CO bond in metal carbonyl complexes (cationic, neutral, or anionic) expressed in terms of d_{CO} or better ν(CO) and f_{CO} is directly proportional to the formal oxidation state of the metal and inversely proportional to the coordination number of the complex.[11]

(iii) As the ν(CO)$_{av}$, f_{CO}, and d_{CO} values for the octahedral species $[Ir(CO)_5Cl]^{2+}$[23] and *mer*-Ir(CO)₃(SO₃F)₃[19] listed in Table 2 indicate, replacement of one or more CO ligands by anions (Cl$^-$, SO₃F$^-$) will decrease the effective oxidation state of Ir, resulting in a slight lengthening of d_{CO} and a decrease of ν(CO)$_{av}$ and f_{CO}. Vibrational data for *fac*-Ir(CO)₃F₃[20,21] and *fac*-Ir(CO)₃(SO₃F)₃[19] follow the same trend.[20,21]

(iv) As seen in Figure 1 and Table 3, the increase in $\nu(CO)$ with increasing oxidation state of M for $\nu(CO)_{av}$ and for each fundamental is not linear but appears to level off for [Os-$(CO)_6]^{2+ \, 9}$ and more so for [Ir(CO)$_6$]$^{3+}$. This is most noticeable for ν_1 (A$_{1g}$). As a consequence, the band separation between all three fundamentals expressed as ν_1 (A$_{1g}$) $-$ ν_6 (T$_{1u}$) decreases for both cations to 69[9] and 41 cm^{-1}, respectively, with increasing nuclear charge.

The apparent slight decrease in CO bond strength at high oxidation states for M = Os^{2+}, Ir^{3+} has been explained recently[6,11] by increased electron delocalization from the fluoroantimonate anion,[9,16,17] or in case of [Ir(CO)$_6$][Sb$_2$F$_{11}$]$_3$·4HF from coordinated HF, into π^* mo's of the CO ligands. Extended structure formation via such an external F $\rightarrow$ π^* dative interaction is not observed for [Re(CO)$_6$][Re$_2$F$_{11}$][29] and not evident from the vibrational spectra of [Re(CO)$_6$]$^{+ \, 32}$ for a simple reason: the above electron delocalization from anions ([Sb$_2$F$_{11}$]$^-$) or from HF into π^* mo's of CO and the M $\rightarrow$ CO back-donation component of synergetic bonding[36,37] are seen as competing processes. At high oxidation states of M, π-back-donation becomes improbable, while external F $\rightarrow$ π^* electron donation increases in effectiveness.

While it is easy to interpret high CO stretching wavenumbers − for example, in [Ir(CO)$_6$]$^{3+}$ $\nu(CO)_{av}$ is 126 cm^{-1} higher than that in free CO (2143 cm^{-1})[38] − in terms of diminished or strongly reduced π-back-bonding and consequently increased σ-bonding and CO bond polarization by M^{m+}, there are other vibrational criteria that should be taken into consideration when judging M−CO bonding in metal carbonyl complexes. These criteria include ν(M−C) and f_{MC}, which should be low, and values listed in Table 3 for [Os(CO)$_6$]$^{2+ \, 9}$ and [Ir(CO)$_6$]$^{3+}$ support this view. Differences in interaction force constants $f_{CO/CO}$ or $f_{CO/MC}$ for isoelectronic species as discussed recently for [Fe(CO)$_6$]$^{2+ \, 8}$ and Cr(CO)$_6$ are equally important.[33,34] This would require a normal coordinate analysis (NCA) and calculation of a general valence force field (GVFF) which are at present not possible for the [Ir(CO)$_6$]$^{3+}$ cation.

(v) The relative intensities of the Raman active fundamentals ν_1 (A$_{1g}$) and ν_3 (E$_g$) are of interest to spectroscopists. For anionic [V(CO)$_6$]$^{-}$,[32] neutral M(CO)$_6$, M = Cr, Mo, W,[33,34] and the cations [Re (CO)$_6$]$^{+ \, 32}$ and [M(CO)$_6$]$^{2+}$, M = Ru, Os,[9] ν_3 (E$_g$) is considerably more intense than the totally symmetrical ν_1 (A$_{1g}$). As the band separation between ν_1 and ν_3 decreases with increasing oxidation state of M from 136 cm^{-1} for [V(CO)$_6$]$^{- \, 32}$ to 17 cm^{-1} for [Ir(CO)$_6$]$^{3+}$, the intensity of ν_1 (A$_{1g}$) increases gradually and becomes for [Fe(CO)$_6$]$^{2+ \, 8}$ and [Ir(CO)$_6$]$^{3+}$ comparably or slightly higher than the intensity of ν_3 (E$_g$). The implication is that the bonding in M(CO)$_6$ complexes becomes more ionic with increasing oxidation state of M. It should be recalled that in octahedral hexahalide complexes of the type EX$_6$ of metals and nonmetals, the A$_{1g}$ E−X stretching vibration is always considerably more intense than the E$_g$ stretching mode.[38]

As will be seen below, the conclusions regarding metal−CO bonding based on the vibrational spectra of [Ir(CO)$_6$]$^{3+}$, [Os-(CO)$_6$]$^{2+}$,[9] and related M(CO)$_6$ complexes are fully confirmed by the molecular structure of [Ir(CO)$_6$][SbF$_6$]$_3$·4HF.
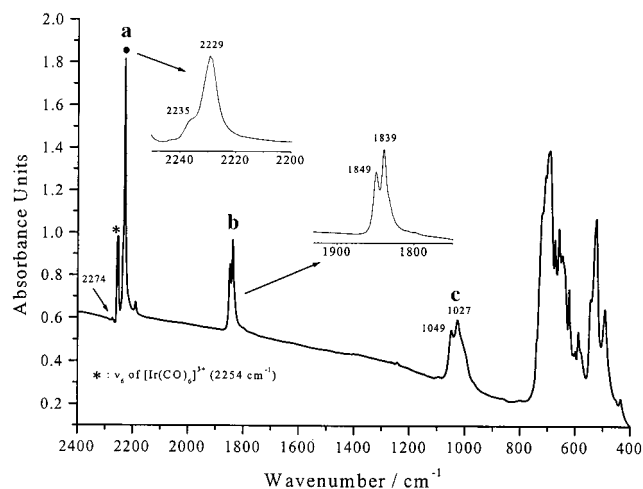
Figure 2. The IR spectrum of [Ir(CO)$_5$(C(O)F)][SbF$_6$]$_2$.

The IR spectrum of [Ir(CO)$_6$][SbF$_6$]$_3$·4HF is found to change with time; the consistent observation of three sets of IR bands shown in Figure 2, labeled a−c with (a) at 2274 (w), 2235 (m, sh), and 2229 (vs) cm^{-1}, (b) 1849 (m) and 1839 (s) cm^{-1}, and (c) 1049 (m) and 1027 (s) cm^{-1}, in addition to ν_6 of [Ir(CO)$_6$]$^{3+}$ at 2254 (vs) cm^{-1} in the IR spectrum of [Ir(CO)$_6$][SbF$_6$]$_3$·4HF, suggests the transformation of the cation to a species tentatively identified as [Ir(CO)$_5$(C(O)F)]$^{2+}$ for two reasons: (i) the observed band positions in the CO stretching region are very similar to those for [Ir(CO)$_5$Cl]$^{2+}$ (2279 (w), 2232 (vs), and 2227 (s) cm^{-1});[23] (ii) coordinated −C(O)F has been found[39,40] and structurally characterized in the salt [IrF(PEt$_3$)$_2$(CO)$_2$-(C(O)F)][BF$_4$] with ν(CO) at 2163, 2110 cm^{-1} (due to *cis*-Ir-(CO)$_2$) and 1815, 1752 cm^{-1} (attributed to Ir−C(O)F). The lower band positions in this salt reflect the lower oxidation state of iridium in the cation.[39,40] The doublet (c) bands are tentatively interpreted as ν(C−F) vibrations. The observation of two bands in both the C−O and the C−F stretching region is thought to be due to two different orientations of the fluoroacyl ligand in the complex cation. Formation of the fluoroacyl group is thought to occur via nucleophilic attack of F$^-$ according to

$$[Ir(CO)_6]^{3+} + F^- \rightarrow [Ir(CO)_5(C(O)F)]^{2+} \qquad (4)$$
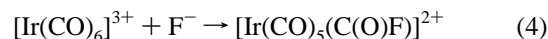
which is consistent with the electrophilic character of carbon in [Ir(CO)$_6$]$^{3+}$.

The Molecular Structure of [Ir(CO)$_6$][SbF$_6$]$_3$·4HF. The internal distances and angles for [Ir(CO)$_6$][SbF$_6$]$_3$·4HF are listed in Table 4. The averaged Ir−C and C−O distances as well as $\nu(CO)_{av}$ and f_{CO} for the [Ir(CO)$_6$]$^{3+}$ cation are listed in Table 2 together with calculated data[13] and are compared to the corresponding data for [Ir(CO)$_5$Cl]$^{2+}$,[23] *mer*-Ir(CO)$_3$(SO$_3$F)$_3$,[19] [Os(CO)$_6$]$^{2+}$,[9] and [Re(CO)$_6$]$^{+}$.[29]

There are four points of interest which will be discussed in sequence: (i) the [SbF$_6$]$^-$ anion, (ii) the [Ir(CO)$_6$]$^{3+}$ cation, (iii) the coordination of HF to the six C atoms of [Ir(CO)$_6$]$^{3+}$ in a solvated cation of the type {[Ir(CO)$_6$](F$_{(8)}$H)(F$_{(7)}$H)$_3$}$^{3+}$, and (iv) the association of F-coordinated HF to form a tetrahedral (HF)$_4$ cluster via asymmetric, delocalized F−H−F hydrogen bonds.

(36) Dewar, J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71.
(37) Chatt, J.; Duncanson, J. A. *J. Chem. Soc. A* **1953**, 2939.
(38) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986.

(39) Blake, A. J.; Cockman, R. W.; Ebsworth, E. A. V.; Holloway, J. H. *J. Chem. Soc., Chem. Commun.* **1988**, 529.
(40) Ebsworth, E. A. V.; Robertson, N. L.; Yellowlees, J. *J. Chem. Soc., Dalton Trans.* **1993**, 1031.

Table 4. Selected Internal Bond Parameters for [Ir(CO)$_6$][SbF$_6$]$_3$·4HF[a]

Bond Lengths [Å]			
Ir−C(2)	2.023(10)	Sb−F(2)	1.849(6)
Ir−C(2)#1	2.023(10)	Sb−F(5)	1.864(6)
Ir−C(2)#2	2.023(10)	Sb−F(1)	1.863(7)
Ir−C(1)	2.035(10)	Sb−F(3)	1.878(7)
Ir−C(1)#1	2.035(10)	Sb−F(4)	1.878(6)
Ir−C(1)#2	2.035(10)	Sb−F(6)	1.910(6)
C(1)−O(1)	1.074(12)		
C(2)−O(2)	1.107(13)		

Bond Angles [deg]			
C(2)−Ir−C(2)#1	89.1(4)	F(2)−Sb−F(5)	91.9(3)
C(2)−Ir−C(2)#2	89.1(4)	F(2)−Sb−F(1)	92.7(3)
C(2)#1−Ir−C(2)#2	89.1(4)	F(5)−Sb−F(1)	92.2(4)
C(2)−Ir−C(1)#2	89.6(4)	F(2)−Sb−F(3)	90.8(3)
C(2)#1−Ir−C(1)#2	90.6(4)	F(5)−Sb−F(3)	175.5(3)
C(2)#2−Ir−C(1)#2	178.6(4)	F(1)−Sb−F(3)	91.3(4)
C(2)−Ir−C(1)	178.6(4)	F(2)−Sb−F(4)	178.0(3)
C(2)#1−Ir−C(1)	89.6(4)	F(5)−Sb−F(4)	90.0(3)
C(2)#2−Ir−C(1)	90.6(4)	F(1)−Sb−F(4)	86.6(3)
C(1)#2−Ir−C(1)	90.8(4)	F(3)−Sb−F(4)	87.3(3)
C(2)−Ir−C(1)#1	90.6(4)	F(2)−Sb−F(6)	89.7(3)
C(2)#1−Ir−C(1)#1	178.6(4)	F(5)−Sb−F(6)	87.2(3)
C(2)#2−Ir−C(1)#1	89.6(4)	F(1)−Sb−F(6)	177.5(3)
C(1)#2−Ir−C(1)#1	90.8(4)	F(3)−Sb−F(6)	89.2(3)
C(1)−Ir−C(1)#1	90.8(4)	F(4)−Sb−F(6)	91.0(3)
O(1)−C(1)−Ir	177.1(9)		
O(2)−C(2)−Ir	177.3(8)		

[a] Symmetry transformations used to generate equivalent atoms: #1, −x + y, −x, z; #2, −y, x − y, z.

(i) The three [SbF$_6$]$^-$ anions in the formula unit are symmetry related and are distorted from octahedral symmetry toward C_{4v}, by lengthening one of the six Sb−F distances from an average value of 1.866 to 1.910(6) Å. The F−Sb−F bond angles deviate from 90° by approximately 2−3°. These slight distortions from O_h symmetry might be induced by weak, delocalized hydrogen-bonding interactions of the [SbF$_6$]$^-$ anion with some of the HF molecules in the lattice. An alternative cause, significant C−F interionic interactions, which are frequently observed in super electrophilic metal carbonyl hexafluoroantimonates[6,11] like [M(CO)$_6$][SbF$_6$]$_2$,[8,9] M = Fe, Ru, Os, can be ruled out.

(ii) The [Ir(CO)$_6$]$^{3+}$ cation is essentially octahedral, thus confirming conclusions based on the vibrational analysis of the cation, discussed in the preceding section. The two sets of three Ir−C distances of 2.023(10) and 2.035(10) Å are identical within esd limits, and the C−Ir−C angles deviate from 90° by ~1°. As is commonly observed for metal carbonyl cations in the solid state,[6,11] bond angles of the M−C−O moiety deviate from linearity by about 2−3°. The probable cause of this distortion will be discussed below. The observed Ir−C bonds of [Ir(CO)$_6$]$^{3+}$ are comparable or very slightly longer than Ir−C distances listed in Table 2 for CO in equatorial positions in [Ir(CO)$_5$Cl]$^{2+}$,[16,23] *mer*-Ir(CO)$_3$(SO$_3$F)$_3$,[19] and *fac*-Ir(CO)$_3$F$_3$[20,21] obtained from EXAFS data. They are among the longest Ir−C bond lengths so far reported for iridium carbonyl complexes (see, e.g., q_u of 1.898 Å in the Cambridge data compilation[41]).

The C−O bond lengths are very short, and the ν(CO)$_{av}$ values for Ir(III) carbonyls are the highest observed for octahedral metal carbonyl complexes. As discussed elsewhere,[6,11] the structural and spectroscopic data for octahedral [Ir(CO)$_6$]$^{3+}$, square planar [Pt(CO)$_4$]$^{2+}$,[12] and linear [Hg(CO)$_2$]$^{2+}$[28] provide compelling

(41) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, P. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, 91.
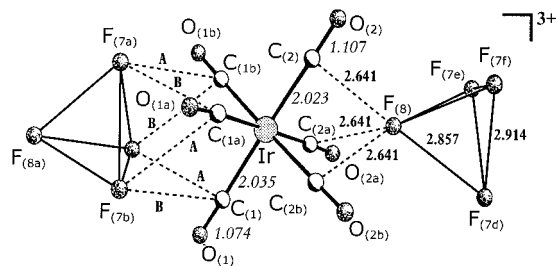
Figure 3. The solvated {[Ir(CO)$_6$](HF)$_4$}$^{3+}$ cation in [Ir(CO)$_6$][SbF$_6$]$_3$·4HF. Contact distances (bold) and bond lengths (italics) are in Å. Hydrogen atoms are omitted. For esd values, see text. F$_{(7)}$−C contacts: *A* = 2.968, *B* = 2.991.

evidence for the absence of π-back-bonding in these σ-bonded metal carbonyl cations, or "σ-carbonyls".[11] However, in contrast to findings for linear [Hg(CO)$_2$][Sb$_2$F$_{11}$]$_2$,[28] square planar [M(CO)$_4$][Sb$_2$F$_{11}$]$_2$,[12] M = Pd, Pt, and to a lesser extend octahedral [M(CO)$_5$Cl][Sb$_2$F$_{11}$]$_2$, M = Ir, Rh,[16,23] or [M(CO)$_6$]-[Sb$_2$F$_{11}$] and [M(CO)$_6$][SbF$_6$]$_2$, M = Fe,[8] Ru,[9] Os,[9] where a limited number of significant interionic C−F contacts are observed,[6,9] similar interionic interactions are missing in the structure of [Ir(CO)$_6$][SbF$_6$]$_3$·4HF. Instead, significant C−F(H) interactions involving the HF solvate molecules are observed and will be discussed next.

(iii) HF coordination to [Ir(CO)$_6$]$^{3+}$: As seen in Figure 3, one F atom of the four HF molecules (F(8)) in the formula unit of [Ir(CO)$_6$][SbF$_6$]$_3$·4HF occupies the C_3 axis passing through the [Ir(CO)$_6$]$^{3+}$ cation. This results in significant contacts of 2.641(10) Å to three carbon atoms (C(2)) of a *fac*-Ir(CO)$_3$ moiety. The resulting Ir−F(8) and O−F(8) contacts are with 3.258(10) and 2.893(10) Å comparable or slightly shorter than the respective sums of the van der Waals radii[42] of ~3.25 and 2.99 Å. The three C−F(8) contacts are considerably shorter than the sums of the van der Waals radii (3.17 Å) and rank among the shortest interionic single C−F contacts, found in [Pt(CO)$_4$]-[Sb$_2$F$_{11}$]$_2$[12] (2.591(10) Å) and [Hg(CO)$_2$][Sb$_2$F$_{11}$]$_2$[28] (2.595(5) Å). As seen in Figure 3, three pairs of longer C−F contacts of 2.968(10) and 2.991(10) Å are found between the remaining three symmetry-related H−F(7) molecules and three C(1) atoms of neighboring [Ir(CO)$_6$]$^{3+}$ cations, resulting in the formation of a "solvated" {[Ir(CO)$_6$](F$_{(8)}$H)(F$_{(7)}$H)$_3$}$^{3+}$ cation. The formulation chosen reflects two types of C−F interactions observed in the structure: (a) significant C(2)−F(8) iso-tridentate contacts to a single [Ir(CO)$_6$]$^{3+}$ as shown in Figure 3 and (b) marginal C$_{(1)}$−F$_{(7)}$ aniso-bidentate contacts to another [Ir(CO)$_6$]$^{3+}$ cation in the unit cell, thus linking (HF)$_4$ tetrahedra to [Ir(CO)$_6$]$^{3+}$ cations resulting in a one-dimensional polymeric chain. A short segment of this chain is shown in Figure 3.

The presence of coordinated HF in structurally characterized metal complexes is extremely rare. Only recently two examples, La(HF)$_2$(AsF$_6$)$_3$[43] and Pb(HF)(AsF$_6$)$_2$,[44] have been reported. In both instances,[43,44] the F atom is coordinated to the metal, with HF as a monodentate ligand. The coordination to carbon of metal carbonyl complexes as observed here is so far unprecedented. The observed iso-tridentate and aniso-bidentate modes of HF bonding are equally unprecedented.

(42) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.
(43) Mazej, Z.; Borrmann, H.; Lutar, K.; Zemva, B. *Inorg. Chem.* **1998**, *37*, 5912.
(44) Tramsek, M.; Lork, E.; Mews, R.; Zemva, B. *J. Fluorine Chem.* **2001**, *110*, 123.

The structure of the "solvated" cation $\{[Ir(CO)_6](F_{(8)}H)-(F_{(7)}H)_3\}^{3+}$ in Figure 3 provides a plausible model, how $[Ir(CO)_6]^{3+}$ and other superelectrophilic metal carbonyl cations[6,11] are solvent stabilized in the conjugate Brønsted–Lewis superacid HF–SbF$_5$,[3,4] the only medium they exist in. In all instances, electrophilic carbon of the CO ligands functions as acceptor; however, the denticity in presumably monomeric $\{[M(CO)_n]-(HF)_{n'}\}^{m+}$ may differ from the one observed in $[Ir(CO)_6][SbF_6]_3\cdot$4HF reported here. An octa solvate of the type $\{[Ir(CO)_6]-(HF)_8\}^{3+}_{(solv)}$ with HF placed above all eight octahedral faces along all C_3 axes of $[Ir(CO)_6]^{3+}$ and coordinated by iso-tridentate contacts to the six C atoms is an attractive but so far unproven possibility.

The expected high solvation energies appear to overcome the anticipated high lattice energies of superelectrophilic metal carbonyl fluoroantimonate salts. This explains the solubility of such salts in superacid media.[3,4]

The tight coordination of HF to two or three CO groups simultaneously is attributed to its small size, which allows a close approach to the C atoms of the carbonyl ligands. In sharp contrast, the much bulkier superacid anion $[Sb_2F_{11}]^{-7}$ must distort in salts with superelectrophilic metal carbonyl cations[6,11] from its D_{4h} equilibrium structure[45] to facilitate significant interionic C–F contacts. This observation suggests a possibility to stabilize other possible high valent metal carbonyl cations such as octahedral $[Pt(CO)_6]^{4+}$ or square planar $[Au(CO)_4]^{3+}$, whose existence has been suggested by DFT calculations.[12,13] The use of HF as coordinating ligand together with $[SbF_6]^-$ as counteranion appears to offer an advantage over the bulkier $[Sb_2F_{11}]^-$ anion.[7]

In view of the structure of $[Ir(CO)_6][SbF_6]_3\cdot$4HF, the observed coordination of HF to the six carbonyl carbon atoms of the cation provides conclusive evidence that the carbon atoms and not the metal have the higher positive partial charge in the $[Ir(CO)_6]^{3+}$ cation. This view is consistent with the vibrational analysis of $[Ir(CO)_6][Sb_2F_{11}]_3$ discussed in the preceding section. Support comes also from well over 20 molecular structures on salts and derivatives of σ-metal carbonyl cations, which we have reviewed recently.[6,11]

There is also a strong similarity between superelectrophilic σ-metal carbonyl cations[5,6,11] and the large family of stable carbocations[46] discovered by G. A. Olah and his group,[47] on account of the presence of electrophilic carbon as a common feature in both groups, σ-metal carbonyl cations[5,6,11] and carbocations.[10] In addition to their generation in superacid media,[3,4,10,47] the carbonyl cations have also structural similarities to the σ-metal carbonyl cations.[5,6,11] Secondary interionic contacts of the type C–X, X = F, Cl, O, are also observed in the solid-state structures of stable carbocations[46,47] with counteranions such as $[EF_6]^-$, $[E_2F_{11}]^-$, E = As, Sb, $[SbCl_6]^-$, or $[AlCl_4]^-$.[48–50]

With NMR, the principle technique for the study of carbocations,[46] the number of reliably determined molecular structures

is quite small. On the basis of the limited information[48–50] available, it appears that C–F contacts are less numerous, about one or two per carbon, and relatively weak, with C–F contacts usually 0.1–0.4 Å shorter than 3.17 Å, the sum of the van der Waals radii.[42] Differences between carbocation salts[48–50] and superelectrophilic metal carbonyl fluoroantimonates[6,11] are due to the presence of several electrophilic carbon centers (two, four, or six) per cation and to higher ionic charges (+2 or +3) in the latter, where up to five interionic C–F contacts per CO ligand are observed.[6,11,12,28]

Since there is only a single electrophilic carbon in most carbocations, ion pairing is more common than the formation of one-dimensional extended structures.[48–50] Despite these differences, the presence of electrophilic carbon in carbocations and in σ-metal carbonyl cations[9,11] provides a strong common link between both groups, which both form extended structures with carbon as the acceptor.

There is strong support for the presence of electrophilic carbon in octahedral metal hexacarbonyl species from theoretical calculation.[13,23,51,52] In addition to calculated vibrational spectra including IR and Raman intensities,[13,23] force constants, structural parameters,[13,23,51] and ^{13}C NMR parameters,[52] calculated partial atomic charges for the M–C–O moieties of the M(CO)$_6$ species[13,23,51,52] have been very useful and are listed[23] for the cations $[Os(CO)_6]^{2+}$[9] and $[Ir(CO)_6]^{3+}$ in Table 3. While numerical values for q_M, q_C, and q_O differ on account of the basis sets used, in all instances higher positive charges are obtained for C than for M,[13,23,51,52] while oxygen has usually a negative partial charge.[13,23,51,52]

A recent theoretical study,[53] entitled "The Nature of the Transition Metal–Carbonyl Bond...", differs because the authors fail to recognize the electrophilic nature of the carbonyl carbon for $[Os(CO)_6]^{2+}_{(g)}$, $[Ir(CO)_6]^{3+}_{(g)}$, or other $[M(CO)_6]$ species, and suggest higher partial charges on M(Os, Ir) than on C. This is at variance with all experimental observations, reported here or elsewhere,[6,8,9,11] and other more relevant and less opinionated theoretical studies.[13,23,51,52]

(iv) The (HF)$_4$ cluster: In the preceding section (iii), we have emphasized the C–FH interactions in the molecular structure of $[Ir(CO)_6][SbF_6]_3\cdot$4HF, which involve fluorine as the donor of electronic charge toward the C atoms of the carbonyl ligands. The discussion has ignored the four hydrogen atoms of the four HF solvate molecules; however, Figure 3 shows that there is an unprecedented tetrahedral aggregation of these four HF molecules.

The four HF molecules in the formula unit form a distorted tetrahedron shown in Figure S4 with F···F edges ranging from 2.857 (3x) to 2.914 (3x) Å in length. The hydrogen atom belonging to F(7) has been located by difference Fourier methods. It forms a slightly bent hydrogen bridge within the triangular plane of the tetrahedron defined by F(7). The hydrogen atom bound to F(8) is also expected to be involved in hydrogen bonding. Because of the regular shape of the (HF)$_4$ tetrahedron, a 3-fold disorder is assumed, resulting in nearly linear F–H···F bonds statistically distributed over the three sites.

(45) Sham, I. H. T.; Patrick, B.; von Ahsen, B.; von Ahsen, S.; Willner, H.; Thompson, R. C.; Aubke, F. *J. Fluorine Chem.*, submitted for publication.

(46) Olah, G. A.; Schleyer, P. v. R. *Carbenium Ions*; Wiley-Interscience: New York, 1968, 1970, 1972, 1973, 1976; Vols. I–V.

(47) (a) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1393. (b) Olah, G. A. *J. Org. Chem.* **2001**, *66*, 5943.

(48) Laube, T. In *Stable Carbocation Chemistry*; Prakash, G. K. S.; Schleyer, P. v. R., Eds.; J. Wiley: New York, 1997; p 453.

(49) Laube, T. *Chem. Rev.* **1998**, *98*, 1277.

(50) Christe, K. O.; Zhang, D.; Bau, R.; Hegge, J.; Olah, G. A.; Prakash, G. K. S.; Sheehy, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 481.

(51) Szillagy, R. K.; Frenking, G. *Organometallics* **1997**, *16*, 4807.

(52) Ehlers, A. W.; Ruiz-Morales, Y.; Baerends, E. J.; Ziegler, T. *Inorg. Chem.* **1997**, *36*, 5031.

(53) Diefenbach, A.; Bickelhaupt, F. M.; Frenking, G. *J. Am. Chem. Soc.* **2000**, *122*, 6449.

The assumed H atom position has been included in the final structural model.

These observations differ from extensive earlier studies of HF polymers[54] in the gas,[55,56] liquid, and solid state,[57] because head-to-tail polymerization of HF via asymmetric hydrogen bond results in complex mixtures of either zigzag chains or cyclic (HF)$_n$, n = 6, oligomers with F−F distances between 2.57[56] and 2.49 Å.[57]

In [Ir(CO)$_6$][SbF$_6$]$_3$·4HF, there is a much looser aggregation of F-coordinated HF via delocalized hydrogen bonds, reflected in longer F−F distances. The constituent ions [Ir(CO)$_6$]$^{3+}$ and [SbF$_6$]$^−$ appear to serve as templates for the tetrahedral (HF)$_4$ cluster, which has not been encountered previously.[54]

Summary and Conclusion

An altered synthetic approach, the use of dilute solutions of SbF$_5$ in anhydrous HF in the previously reported reductive carbonylation of IrF$_6$,[16,17] has resulted in the isolation and structural characterization of the solvate [Ir(CO)$_6$][SbF$_6$]$_3$·4HF. The molecular structure determination has revealed a number of unprecedented features: (i) The octahedral [Ir(CO)$_6$]$^{3+}$ cation, characterized also by vibrational spectra and DFT calculations,[13] is the first tripositive homoleptic metal carbonyl cation; (ii) Ir−CO bonding is exclusively of the σ-bond type; (iii) iso-tridentate and aniso-bidentate coordination of HF via fluorine to the carbon atoms of the [Ir(CO)$_6$]$^{3+}$ cation; (iv) the structure of the "solvated" cation {[Ir(CO)$_6$](F$_{(8)}$H)(F$_{(7)}$H)}$^{3+}$ provides a model for the solvation of superelectrophilic cations in superacids such as HF−SbF$_5$; and (v) the aggregation of F-coordinated HF molecules via delocalized hydrogen bonds to form a weakly bound tetrahedral (HF)$_4$ cluster.

The structural and vibrational characterization of [Ir(CO)$_6$]$^{3+}$ reported here complements our studies on fully characterized,

mostly superelectrophilic, and σ-bonded homoleptic metal carbonyl cations, that form thermally stable salts exclusively with the fluoroantimonate anions [Sb$_2$F$_{11}$]$^−$ and [SbF$_6$]$^{−5,6,11}$ and are generated only in superacids.[3,4]

The cations include linear [Au(CO)$_2$]$^{+25,26}$ and [Hg(CO)$_2$]$^{2+}$,[28] square planar [M(CO)$_4$]$^{2+}$, M = Pd, Pt,[12] and octahedral [M(CO)$_6$]$^{2+}$, M = Fe, Ru, Os,[8,9] and [Ir(CO)$_6$]$^{3+}$, as well as the derivatives [M(CO)$_5$Cl]$^{2+}$, M = Rh, Ir,[23] [W(CO)$_6$-(FSbF$_5$)]$^+$,[24] and polymeric [{Mo(CO)$_4$}$_2$(F$_2$SbF$_4$)$_3$]$^+$,[58] with the latter two examples of seven-coordination. So far, [Ir(CO)$_6$]-[SbF$_6$]$_3$·4HF described here is the only HF solvate in this group of compounds.[5,6,12]

Evidence for the cations [Ir(CO)$_5$(C(O)F)]$^{2+}$ (presented in the vibrational section) and [Ir(CO)$_5$F]$^{2+}$ (not discussed here) presents a challenge for future work and provides an indication that the fascinating developments of Ir(III) carbonyl cations[16,17,23] and their derivatives[19−21] may not have come to an end yet.

Supporting Information Available: A figure of the PFA reactor, the solvated [SbF$_6$]$^−$ anion, various views of the [Ir-(CO))$_6$]$^{3+}$ cation and the (HF)]$_4$ cluster, the Raman spectrum of [Ir(CO)$_6$][SbF$_6$]$_3$· 4HF in a PFA reactor, a complete table of crystallographic data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org. An X-ray crystallographic file in CIF format of [Ir(CO)$_6$][SbF$_6$]$_3$· 4HF has been deposited at the Cambridge Crystallographic Data Center under deposition number 177895.

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(54) Gmelin. *Handbook of Inorganic Chemistry, Fluorine*; Springer Verlag: Berlin, 1982; Vol. 3, pp 79−91.
(55) Janzen, J.; Bartell, L. S. *J. Chem. Phys.* **1969**, *50*, 3611.
(56) Reichert, U. V.; Hartmann, *Z. Naturforsch., A: Phys. Sci.* **1972**, *27*, 983.
(57) Atoji, M.; Lipscomb, W. N. *Acta Crystallogr., Sect. A* **1954**, *7*, 173.
(58) Bröchler, R.; Freidank, D.; Bodenbinder, M.; Sham, I. H. T.; Willner, H.; Rettig, S. J.; Trotter, J.; Aubke, F. *Inorg. Chem.* **1999**, *38*, 3684.