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The Synthesis and the Molecular Structure of Hexakis(carbonyl)hexafluoroantimonato(V)tungsten(II) Undecafluorodiantimonate(V), $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$

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The reaction of tungsten hexacarbonyl, $W(CO)_6$, with antimony(V) fluoride, SbF_5, in the conjugate Brønsted−Lewis superacid $HF-SbF_5$ at 40 °C produces quantitatively the salt $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ as the main product. The observed $2e^-$ oxidation without any loss of CO is unprecedented. The cation $[W(CO)_6(FSbF_5)]^+$ is seven coordinated with a distorted C_{2v} capped trigonal prismatic structure. $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ crystallizes in the monoclinic space group $P2_1$ (No. 4). $a = 8.2051(12)$ Å, $b = 16.511(3)$ Å, $c = 8.1432(2)$ Å, $\beta = 111.5967(6)°$, $V = 1025.8(2)$ Å^3, $Z = 2$. Number of reflections measured = 9112, unique 4410. Residuals on F, $I > 3\sigma(I)$: R (R_w) = 0.023 (0.023). In the $[W(CO)_6(FSbF_5)]^+$ cation the $FSbF_5$ group is very tightly coordinated to tungsten with the bridging fluorine nearly equidistant from W and Sb. The details of the molecular structure are compared to those of polymeric $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$ reported by us very recently.

Introduction

The hexacarbonyls $Mo(CO)_6$ and $W(CO)_6$ are very useful precursors for the synthesis of a wide range of organometallic and coordination compounds.[1] This is in particular true for their use in the formation of the large family of halo carbonyl complexes of molybdenum(II) and tungsten(II).[2,3] In addition to oxidation, the partial substitution of CO by halides and/or by a wide range of donor ligands leads to a large number of frequently oligomeric mono-, di-, tri-, and tetracarbonyl derivatives with interesting structural properties.[2,3] During attempts to extend the range of known, thermally stable homoleptic metal carbonyl cations[4] to the group 6 metals, we have studied the reaction of $Mo(CO)_6$, with the mild oxidizing and fluorinating agent and Lewis superacid SbF_5.[5,6] The main product of the resulting oxidation and partial decarbonylation reaction, polymeric $[\{Mo(CO)_4\}_2(F_2SbF_4)_3]_x[Sb_2F_{11}]_x$, is characterized by X-ray diffraction. The results of this study have been published recently in this journal.[7] We have subsequently studied the reaction of $W(CO)_6$ with SbF_5 and report the results, the formation, and the structural characterization of $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ at this time.

Experimental Section

Chemicals. The metal hexacarbonyl $W(CO)_6$ (Pressure Chemicals) was purified by vacuum sublimation prior to use. Antimony(V) fluoride (Atochem North America) was doubly distilled, first at atmospheric pressure and then in vacuo. Anhydrous hydrogen fluoride (Air Products) was treated with elemental fluorine (Air Products) shortly before use and stored in a Kel-F storage vessel. Removal of remaining water was achieved by the addition of small amounts of SbF_5 to produce crystalline $[H_3O][Sb_2F_{11}]$,[8] which was removed by decanting. Carbon monoxide (99.9% pure) was obtained from Medigas.

Instrumentation. Standard vacuum line techniques were employed to manipulate volatile materials. For the handling of HF, manifolds were constructed from Monel and stainless steel and fitted with stainless steel Whitey valves. A Vacuum Atmosphere Corporation DRI-LAB model D1-001-S-G drybox, filled with dry nitrogen and fitted with a HE-493 DriTrain, was used to manipulate solid and nonvolatile liquid samples. Infrared spectra were recorded on a Bomen MB-102 FT-IR spectrometer. Solid samples were finely ground and pressed between AgCl or AgBr windows. Raman spectra were recorded with a Bruker RFS100 FT-Raman accessory, mounted on an optical bench of a Bruker IFS-66v FT-IR instrument. Solid samples were contained in melting point capillaries. X-ray diffraction measurements were made on a Rigaku/ADSC CCD area detector with graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). Data were collected at -93 ± 1 °C to a maximum 2θ value of 60.0°. The structure was solved by heavy-atom Patterson methods[9] and Fourier techniques.[10] All calculations were performed using the teXsan[11] crystallographic software package of the Molecular Structure Corporation. Crystal data are collected in Table 1.

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(1) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1998; p 1046.
(2) Baker, P. K. *Adv. Organomet. Chem.* **1996**, *40*, 45.
(3) Baker, P. K. *Chem. Soc. Rev.* **1998**, 125.
(4) Willner, H.; Aubke, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2402.
(5) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; J. Wiley: New York, 1985.
(6) O'Donnell, T. A. *Superacids and Acidic Melts as Inorganic Chemical Reaction Media*; VCH Publishers: Weinheim, Germany, 1993 and references therein.
(7) Bröchler, R.; Freidank, D.; Bodenbinder, M.; Sham, I. H. T.; Willner, H.; Rettig, S. J.; Trotter, J.; Aubke, F. *Inorg. Chem.* **1999**, *38*, 3684.
(8) Zhang, D.; Rettig, S. J.; Trotter, J.; Aubke, F. *Inorg. Chem.* **1996**, *35*, 6113.
(9) PATTY: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Garibay, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system. Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1992.
(10) DIRDIF94: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-94 program system. Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1994.

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Table 1. Crystal Data of $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$

formula: $C_6F_{17}O_6Sb_3W$
fw: 1040.14
lattice params
$a = 8.2051(12)$ Å
$b = 16.511(3)$ Å
$c = 8.1432$ Å
$\beta = 111.5967(6)°$
$V = 1025.8(2)$ Å^3
$Z = 2$, $D_c = 3.367$ g/cm^3
$F_{000} = 928.00$
space group: P_{2_1} (No. 4), monoclinic
crystal dimens: 0.35 × 0.30 × 0.25 mm
2θ max: 60.0°
no. of reflns measd: 9112
unique (incl Friedel pairs): 4410 ($R_{int} = 0.029$)
residuals (on F, $I > 3\sigma(I)$): R,[a] R_w[b] = 0.023, 0.023

[a] $R = \sum||F_o^2| - |F_c^2||/\sum|F_o^2|$. [b] $R_w = \sum w(|F_o^2| - |F_c^2|)^2/\sum wF_o^4)]^{1/2}$.

Synthesis and Crystal Growth of $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$. To 1 mmol (352 mg) of freshly sublimed $W(CO)_6$ were added about 5 mL of freshly distilled SbF_5 and about 10 mL of anhydrous HF by vacuum line transfer using Monel and stainless steel equipment. The mixture was contained in a Kel-F reactor of ~35 mL volume, fitted with a Monel adaptor. The CO pressure was adjusted to 2 atm. On warming to 40 °C the mixture turned yellow immediately. The temperature was maintained for 24 h and then gradually lowered at a rate of ~1 °C/h. This produced yellow crystals on the reactor wall which grew to ~0.3−5.0 mm in length. The yield of isolated crystalline product is ~320 mg or 30%. After removal of all volatiles, the crystals were picked under a polarizing microscope and loaded inside the drybox into Lindemann glass capillaries. The crystalline, extremely moisture sensitive material is thermally stable up to 100 °C. Beyond this temperature a slow, gradual release of CO is noted together with the formation of a colorless, viscous liquid (SbF_5) and a yellowish residue, tentatively identified as $[\{W(CO)_4\}_2(F_2SbF_4)_3]_x[Sb_2F_{11}]_x$. The residue of the crystallization described above was dissolved in HF and yielded a batch of colorless crystals. These were identified by their cell constants as $6SbF_3{\cdot}5SbF_5$, whose structure is known[12] (see Results and Discussion). The reaction was repeated in a glass reactor of about 50 mL contents fitted with a Teflon stem stopcock. Only SbF_5 was used as reaction medium, and no additional CO was added. After 1 week at 40 °C 179.5 mg (0.51 mmol) of $W(CO)_6$ was converted to 774.4 mg of a yellow solid (expected: 730.4 mg) with the difference due to small amounts of residual SbF_5. No release of CO during the reaction was noticed. The solid residue was identified by vibrational spectroscopy as a mixture of $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ and the adduct $6SbF_3{\cdot}5SbF_5$.[12]

Results and Discussion

(a) Synthesis. It is found in the course of this study that tungsten hexacarbonyls $W(CO)_6$ will undergo a facile 2e$^-$ oxidation when reacted with antimony(V) fluoride, SbF_5, under rather mild conditions (40 °C), described in the Experimental Section. The oxidation may be performed in an excess of SbF_5 or in the conjugate Brønsted−Lewis superacid HF−SbF_5,[5,6] where crystalline products are obtained. Unlike other formation reactions of homoleptic metal carbonyl cations and their derivatives in liquid SbF_5 as reaction medium,[4] where a single, solid product is obtained, the use of SbF_5 as oxidizing agent will result in a solid product mixture. In this case, the main product is obtained from HF−SbF_5 with about 20 mol % SbF_5 in the form of yellow crystals and is identified by single-crystal X-ray diffraction as $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$. The IR and Raman spectra of the bulk, crystalline material are consistent with the results from the molecular structure determination, even though a meaningful interpretation of the vibrational spectra is only possible in the CO-stretching range.

The reduced byproduct is identified also by single-crystal X-ray diffraction after recrystallization from anhydrous HF. The cell constants of the colorless crystals obtained are identical to those of a structurally characterized adduct, formulated as $6SbF_3{\cdot}5SbF_5$.[12] The Raman spectrum of the adduct has also been reported previously,[13] which allows additional characterization of the byproduct. However due to similar solubilities in both HF and HF−SbF_5 a clean, quantitative separation of main product and byproduct is not possible. A reaction balance for the formation of $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ is obtained, by using a glass reactor of about 50 mL volume, which is more accurately weighed than the Kel-F/Monel reactor described in the Experimental Section, and liquid SbF_5 is used as reaction medium. The balance of the reaction is obtained in this manner (see Experimental Section). Attempts to obtain estimates of the carbon contents for the yellow crystals are unsatisfactory. Values obtained fall between 5.5% and 6.0%, well below the theoretical value of 6.92%. A similar situation is found for $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$[7] and is probably due to the high fluorine contents of the samples, producing small amounts of CF_4 as byproduct during combustion.

With both $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ and $6SbF_3{\cdot}5SbF_5$[12] clearly identified, the oxidation of $W(CO)_6$ by SbF_5 in the superacid HF−SbF_5 can be formulated as follows:

$$6W(CO)_6 + 29SbF_5 \xrightarrow[\text{HF}-\text{SbF}_5\text{, 1 day}]{40\ °\text{C, 2 atm of CO}} 6[W(CO)_6(FSbF_5)][Sb_2F_{11}] + 6SbF_3{\cdot}5SbF_5 \quad (1)$$

The reaction and the resulting product $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ are unusual on two accounts: (i) There is no net loss of CO during the 2e$^-$ oxidation of $W(CO)_6$ to the cation $[W(CO)_6(FSbF_5)]^+$. As in other homoleptic metal carbonyl cations[4] of the type $[M(CO)_n]^{m+}$, with M from groups 8−12, $n = 2$, 4, or 6, and $m = 1$, 2, or 3, CO binds strongly to the W(II) center. The only nucleophiles present in HF−SbF_5,[5] the fluoroantimonate(V) anions $[SbF_6]^-$ and $[Sb_2F_{11}]^-$, are evidently very weak and not able to displace CO from the coordination sphere of tungsten(II). (ii) The simultaneous presence of $(FSbF_5)^-$ as ligand and $[Sb_2F_{11}]^-$ as counteranion in the same compound is very uncommon. A precedent is found in the product of the reaction of $Mo(CO)_6$ with SbF_5, polymeric $[\{Mo(CO)_4\}_2(F_2SbF_4)_3]_x[Sb_2F_{11}]_x$,[7] where $[SbF_6]^-$ functions as *cis*-F-bridging bidentate ligand according to the molecular structure reported by us previously.[7] A remote precedent for the cation $[W(CO)_6(FSbF_5)]^+$ is seen in $[Ir(CO)_5Cl]^{2+}$,[14,15] where Cl$^-$ completes the octahedral configuration of Ir(III). In all instances[7,14,15] $[Sb_2F_{11}]^-$ functions as counteranion.

Two structurally characterized contrasting examples for the $[W(CO)_6(FSbF_5)]^+$ cation of the type $[W(CO)_3(NO)(L)(FSbF_5)]$,

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(11) teXsan: Crystal Structure Analysis Package, Molecular Structure Corporation (1985 and 1992).
(12) Nandana, W. A. S.; Passmore, J.; White, P. S. *J. Chem. Soc., Dalton Trans.* **1985**, 1623.
(13) Birchall, T.; Dean, P. A. W.; Valle, B. D.; Gillespie, R. J. *Can. J. Chem.* **1973**, *51*, 667.
(14) Bach, C. H.; Willner, H.; Wang, C.; Rettig, S. J.; Trotter, J.; Aubke, F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1974.
(15) Willner, H.; Bach, C.; Wartchow, R.; Wang, C.; Rettig, S. J.; Trotter, J.; Jonas, V.; Thiel, W.; Aubke F. *Inorg. Chem.*, submitted for publication.

L = Me_2PhP or Cy_3P, Cy = cyclo hexyl, have been reported previously by Hersh et al.[16,17] They are formed by the reaction of $LW(CO)_5$ with $[NO][SbF_6]$ in CH_2Cl_2 with loss of 2 mol of CO. Even though the coordination around tungsten is distorted octahedral, with a d^6 electron configuration, there are remote structural and spectroscopic similarities involving the *mer*-$W(CO)_3$ moieties and the monodentate $FSbF_5$ group, to permit a useful comparison with $[W(CO)_6(FSbF_5)]^+$, which will be done below.

The reaction product $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ is a bright yellow, moisture-sensitive crystalline solid. The salt is thermally stable up to 100 °C. On further heating partial elimination of CO and SbF_5 is noted. Changes observed in the vibrational spectra suggest a condensation reaction according to

$$2x[W(CO)_6(FSbF_5)][Sb_2F_{11}] \xrightarrow{T > 100\ °C} [\{W(CO)_4\}_2(F_2SbF_4)_3]_x[Sb_2F_{11}]_x + 4xCO + xSbF_5 \quad (2)$$

The decomposition is followed by weighing and by monitoring the CO evolution by manometry. The decomposition product has in the CO stretching range a band distribution very similar to that reported for the molybdenum(II) complex.[7]

While it has not been possible to isolate the product of the thermal decomposition in a pure state, it appears that the reactions of $M(CO)_6$, M = Mo, W, with SbF_5 differ only in the relative thermal stabilities of the reaction products, which allow in one instance[7] the isolation of polymeric $[\{Mo(CO)_4\}_2(F_2SbF_4)_3]_x[Sb_2F_{11}]_x$ and, in the case of $W(CO)_6$, that of the salt $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ as the main products. To prevent some partial decomposition of this salt, the reaction of $W(CO)_6$ with SbF_5 is best performed in a CO atmosphere. The use of $HF-SbF_5$ as reaction medium or for recrystallization[7] produces in both cases single crystals suitable for molecular determinations as seen in eqs 1 and 3. The reduced byproduct is in both

$$12xMo(CO)_6 + 41xSbF_5 \xrightarrow[SbF_5(l),\ 1\ day]{60\ °C,\ 24\ h} 6[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x + 4xCO + x(6SbF_3{\cdot}5SbF_5) \quad (3)$$

instances $6SbF_3{\cdot}5SbF_5$,[12,13] which explains that antimony(V) fluoride functions as oxidizing agent.

As the molecular structure indicates, polymer formation involves exclusively cis-bidentate bridging μ-$F_2SbF_4^-$ ligands. The superacid anion $[Sb_2F_{11}]^-$ [8] found here and in $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ is also present as counteranion for the vast majority of the known thermally stable, homoleptic metal carbonyl cations.[4] In addition to the main reaction product, $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$, small amounts of $[Mo(CO)_6(FSbF_5)][Sb_2F_{11}]$ form as byproduct according to the vibrational spectra. It has not been possible to obtain this compound in pure form.[7]

It hence appears that both $W(CO)_6$ and $Mo(CO)_6$ react with SbF_5 in a rather similar manner: initial oxidation to $[M(CO)_6(FSbF_5)][Sb_2F_{11}]$, M = Mo, W, is followed by a condensation reaction with partial elimination of CO and SbF_5 and the formation of *cis*-μ-$F_2SbF_4^-$ bridges to produce polymeric $[\{M(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$, M = Mo, W. The polymerization and elimination of CO appears to be more facile for molybdenum, while the $M(CO)_6$-moiety has a greater thermal stability in the case of tungsten and heating to 100 °C is required to effect condensation.

Table 2. Vibrational Spectra of $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ and $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$ in the CO Stretching Region

$[W(CO)_6(FSbF_5)][Sb_2F_{11}]$		$[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$[7]	
IR (cm^{-1}) int	Raman (cm^{-1}) int	IR (cm^{-1}) int	Raman (cm^{-1}) int
2205 vw	2206 s		
2170 w, sh	2170 s		
2157 w, sh[a]	2157 vw[a]	2156 ms	2156 vs
2147 s	2146 s		
2102 vw, sh[a]	2098 vw[a]	2105 m, sh	2105 vs
2088 s	2084 m, sh	2092 vs	2088 m, sh
2075 s, sh	2078 s	2086 vs	2085 m
2064 s	2060 s		
$\bar{\nu}$(CO) av (cm^{-1}):			
2125	2124	2110	2109
$f_{CO} \times 10^2$ 18.2 N m^{-1}:		18.0	

[a] Attributed to $[\{W(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$.

In summary, while oxidation reactions with SbF_5 described here and elsewhere[7,15] lack the elegance and simplicity of reductive and solvolytic carbonylation reactions, previously employed in the synthesis of homoleptic carbonyl cation salts,[4] the use of $HF-SbF_5$ produces in all instances crystalline materials,[7,15] which are characterized by single-crystal X-ray diffraction.

(b) Vibrational Spectra. As can be seen in Table 2, all vibrational bands observed in the CO stretching range are both IR and Raman active. In addition all degeneracies are removed, which implies that the local symmetry of the $W(CO)_6$ group and the $Mo(CO)_4$ moiety is C_i in each instance. Hence six or four fundamentals are respectively observed. This point is confirmed by the molecular structures of both compounds[7] to be discussed below. The observed average CO stretching frequencies ~2125 cm^{-1} for the tungsten compound and of ~2110 cm^{-1} for the molybdenum compound are about 100 cm^{-1} higher than the $\bar{\nu}(CO)_{av}$ values for $Mo(CO)_6$ and $W(CO)_6$ of 2003 and 2010 cm^{-1},[18,19] respectively, and slightly below 2143 cm^{-1} for free CO,[20] which indicates significantly reduced π-back-bonding in the two cationic derivatives. Even though $\bar{\nu}$(CO) values are not as high as in most homoleptic metal carbonyl cations, they are, to our knowledge, the highest reported for Mo(II) and W(II) carbonyl derivatives.[2,3,21,22]

For $[W(Me_2PhP)\text{-}mer\text{-}(CO)_3(NO)(FSbF_5)]$[16,17] two $\bar{\nu}$(CO) IR bands at 2102 and 2012 cm^{-1} are reported with the latter band doubly degenerate. The $\bar{\nu}(CO)_{avg}$ value is 2042 cm^{-1}, 83 cm^{-1} lower than in $[W(CO)_6(FSbF_5)]^+$, but very slightly higher than in $W(CO)_6$,[18,19] more in line with previous reports for typical carbonyls.[21,22] The band spacing reflects a more regular, symmetrical arrangement within the *mer*-$W(CO)_3$ moiety than is observed for the $W(CO)_6$- and $Mo(CO)_4$-moieties[7] in the corresponding cations discussed here.

In the region below 750 cm^{-1}, the vibrational spectrum of $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ is uninterpretable. We have a near coincidence of bands due to the $[Sb_2F_{11}]^-$ anion, which has C_i

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(16) Hersh, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 4599.

(17) Honeychuk, R. V.; Hersh, W. H. *Inorg. Chem.* **1989**, *28*, 2889.

(18) Jones, L. H.; McDowell, R. S.; Goldblatt, M. *Inorg. Chem.* **1969**, *8*, 34.

(19) Jones, L. H. *Inorganic Vibrational Spectroscopy*; Marcel Dekker: New York, 1971; Vol. 1.

(20) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986.

(21) (a) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: New York, 1975. (b) Kettle, S. F. A. *Top. Curr. Chem.* **1977**, *71*, 111.

(22) (a) De La Cruce, C.; Sheppard, N. *J. Mol. Struct.* **1990**, *224*, 141. (b) Adams, D. M. *Metal Ligand and Related Vibrations*; Arnold: London, 1967.

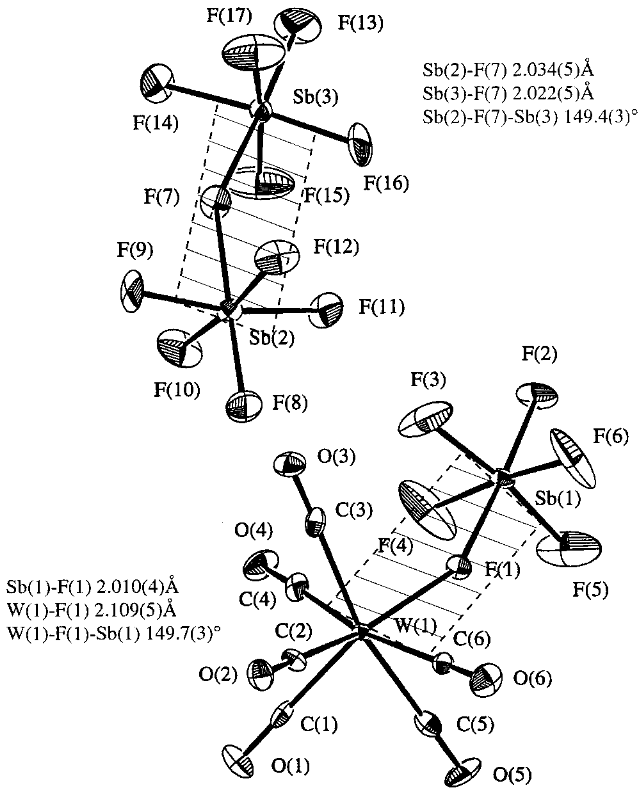

Figure 1. 1. A formula unit of $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$. ORTEP plot, 50% probability thermal ellipsoids. The bridging groups of the cation and anion are highlighted.

Table 3. Selected Bond Lengths and Angles for $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$

(a) Bond Distances (Å)

atom	atom	distance	atom	atom	distance
W(1)	F(1)	2.109(5)	W(1)	C(1)	1.996(9)
W(1)	C(2)	2.021(7)	W(1)	C(3)	2.139(9)
W(1)	C(4)	2.150(9)	W(1)	C(5)	2.130(10)
W(1)	C(6)	2.131(9)	Sb(1)	F(1)	2.010(4)
Sb(1)	F(2)	1.868(5)	Sb(1)	F(3)	1.839(6)
Sb(1)	F(4)	1.829(6)	Sb(1)	F(5)	1.812(7)
Sb(1)	F(6)	1.801(6)	Sb(2)	F(7)	2.034(5)
Sb(2)	F(8)	1.818(6)	Sb(2)	F(9)	1.841(5)
Sb(2)	F(10)	1.840(6)	Sb(2)	F(11)	1.846(5)
Sb(2)	F(12)	1.864(6)	Sb(3)	F(7)	2.022(5)
Sb(3)	F(13)	1.851(6)	Sb(3)	F(14)	1.848(6)
Sb(3)	F(15)	1.833(7)	Sb(3)	F(16)	1.849(6)
Sb(3)	F(17)	1.811(6)	O(1)	C(1)	1.160(10)
O(2)	C(2)	1.155(8)	O(3)	C(3)	1.128(10)
O(4)	C(4)	1.109(10)	O(5)	C(5)	1.118(10)
O(6)	C(6)	1.111(10)			

(b) Bond Angles (deg)

atom	atom	atom	angle	atom	atom	atom	angle
F(1)	W(1)	C(1)	143.3(3)	F(1)	W(1)	C(2)	147.2(3)
F(1)	W(1)	C(3)	87.7(3)	F(1)	W(1)	C(4)	86.5(3)
F(1)	W(1)	C(5)	79.4(3)	F(1)	W(1)	C(6)	82.7(3)
C(1)	W(1)	C(2)	69.3(4)	C(1)	W(1)	C(3)	116.4(3)
C(1)	W(1)	C(4)	73.6(3)	C(1)	W(1)	C(5)	74.9(3)
C(1)	W(1)	C(6)	115.5(3)	C(2)	W(1)	C(3)	74.3(3)
C(2)	W(1)	C(4)	114.8(4)	C(2)	W(1)	C(5)	117.1(3)
C(2)	W(1)	C(6)	79.4(4)	C(3)	W(1)	C(4)	77.2(3)
C(3)	W(1)	C(5)	167.1(3)	C(3)	W(1)	C(6)	102.3(3)
C(4)	W(1)	C(5)	101.5(3)	C(4)	W(1)	C(6)	169.2(3)
C(5)	W(10)	C(6)	76.5(3)				

symmetry and the $-FSbF_5$ ligand. In addition W−C stretching and W−C−O deformation modes are expected here. The low symmetry of the $W(CO)_6$-moiety is expected to result in extensive band proliferation. In sharp contrast, for the highly symmetrical $[Fe(CO)_6]^{2+}$ cation in $[Fe(CO)_6][Sb_2F_{11}]_2$ and $[Fe(CO)_6][SbF_6]_2$ all 13 fundamentals have been detected experimentally.[23]

(c) The Molecular Structure of $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$. A formula unit of $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ is shown in Figure 1, which also illustrates the numbering system for individual atoms. Selected bond distances and angles are listed in Table 3. The seven-coordinate cation is best described as a distorted, C_{2v} capped trigonal prism, with the prism formed by the six CO ligands, and the quadrilateral face capped by fluorine of the monodentate $FSbF_5^-$ ligand. Structural analogues are found in isocyanide complexes of Mo(II) and W(II) of the type $[M(CNR)_7]^{2+}$ or $[M(CNR)_6X]^+$ where M = Mo or W, R = *tert*-butyl, and X = Cl, Br, or I.[24] As described for $[Mo(CNR)_6Br]Br$, there are in $[W(CO)_6(FSbF_5)]^+$ two short W−C distances of 1.996(9) and 2.021(7) Å, respectively, to the ligands C(1)O(1) and C(2)O(2), located on the unique edge of the prism. The two corresponding CO distances 1.160(10) and 1.155(8) Å are rather long. The remaining four W−C bond distances involve the four CO ligands in the quadrilateral plane and are longer. They range from 2.130(10) to 2.150(9) Å. Conversely the four CO distances are short and fall between 1.109(10) and 1.128(10) Å. There appears to be strongly reduced π-back-bonding within the distorted quadrilateral plane. The four W−C distances in this plane are longer than the q_u (upper quartile) value of 2.034 Å from the Cambridge data index,[25] while the corresponding C−O bond lengths are at the shorter end of reported CO distances and fall below the q_l value of 1.132 Å.[24] The remaining two short W−C distances are comparable to the average value of 2.002 Å based on 508 entries in the index.[25] The low symmetry (C_i) of the $W(CO)_6$-moiety and the observed spread of W−C and C−O distances are reflected in the IR and Raman spectra, where in the CO stretching region six bands are observed between 2207 and 2064 cm^{-1}.

There are also significant distortions of bond angles in the $[W(CO)_6(FSbF_5)]^+$ cation. The C−W−C angles for CO groups cis to each other fall into three groups of ∼75°, ∼102°, and ∼115° and W−C−O angles depart from linearity by up to 5°. Similar angular distortions are found for $[\{Mo(CO)_4\}_2(F_2SbF_4)_3]^+$.[7] The strictly octahedral molecule $W(CO)_6$ with W−C and C−O distances[26] of 2.058(3) and 1.148(30) Å provides a strong contrast to the highly distorted $W(CO)_6$-moiety of the $[W(CO)_6(FSbF_5)]^+$ cation.

For the two octahedral complexes $[W(L)(CO)_3(NO)(FSbF_5)]$, L = Me_2PhP, Cy_3P,[16,17] W−C distances between 2.052(21) and 2.095(6) Å are observed for the $W(CO)_3$ group. The spread is much narrower and the distances are slightly longer than q_u of 2.034 Å from the Cambridge data index[25] but shorter than the four long M−C distances in $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ which have an average value of 2.137(9) Å. All bond angles around tungsten are close to 90°.

An intriguing similarity is noted for the Sb−F−Sb bridge in the anion and the W−F−Sb bridge in the cation. Both groups

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(23) 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.

(24) Lam, C. T.; Novotny, M.; Lewis, D. L.; Lippard, S. J. *Inorg. Chem.* **1978**, *17*, 2127.

(25) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton. Trans.* **1989**, Suppl., S1.

(26) Arnesen, S. P.; Seip, H. M. *Acta Chem. Scand.* **1966**, *20*, 2711.

Table 4. Internal Bond Parameters for $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ and $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$

$[W(CO)_6(FSbF_5)][Sb_2F_{11}]$	$[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$[a]
(a) Bond Distances (Å)	
W−C: 1.996(9)−2.150(9)	Mo−C: 2.021(1)−2.052(10)
W−C av: 2.095(6)	Mo−C av: 2.036(10)
C−O: 1.109(10)−1.160(1)	C−O: 1.089(11)−1.136(11)
C−O av: 1.130(10)	C−O av: 1.113(10)
W−μ-F: 2.109(5)	Mo−μ-F: 2.140(5)−2.196(5)
Sb−μ-F−(W): 2.010(4)	Sb−μ-F−(Mo): 1.933(6)−1.988(5)
anion, Sb−μ-Sb: 2.034(5) and 2.022(5)	Sb−μ-F−Sb: 2.051(6) and 2.014(6)
W−CO[b]	Mo−CO[b]
d_m: 2.007	d_m: 1.973
q_u: 2.034	q_u: 2.007
(b) Bond Angles (deg)[c]	
C−W−C:	C−Mo−C:
69.3(4) to 77.2(3)	70.2(4) and 75.3(4)
101.5(3) 117.1(3)	111.6(4) and 113.9(4)
Sb−F−W: 149.7(3)	Sb−F−Mo: 142.1(3)−162.8(13)
W−C−O: 174.8(8)−179.3(8)	Mo−C−O: 174.8(9)−178.7(9)
anion, Sb−F−Sb: 149.4(3)	Sb−F−Sb: 150.0(3)

[a] Data taken from ref 7. [b] Data on average bond distances (d_m) and upper quartile (q_u) are taken from ref 25. [c] For adjacent CO groups.

are highlighted in Figure 1. The bridge angle for the cation is 149.7(3)°, identical within the esd values quoted to 149.4(3)° found for the anion. If allowance is made for a slightly larger effective radius of W(II), the distances within the two bridging units are nearly identical. The $Sb-F_b$ distances of 2.034(5) and 2.022(5) Å in the anion are only marginally longer than in the cation (2.010(4) Å).

The $W-F_b$ bond length of 2.109(5) Å is unusually short and comparable to a reported tungsten−fluorine distance to a terminal F atom of 2.081(1) Å found in $W^{III}(PMe_3)_4H_2(OH_2)F$.[29] The remaining $Sb-F_t$ distances fall in the range 1.801(6)−1.868(5) Å for the cation $[Sb_2F_{11}]^-$. For the anion a comparable range 1.811(6)−1.864(6) Å is observed. Variations within both ranges are small, and lengthening of the terminal Sb−F bonds appears to involve F atoms engaged in intraionic F(2) or interionic F(12), F(14), and F(16) interactions with C atoms of the CO ligands. If we view the fluorine bridges arising from an interaction of $[SbF_6]^-$ with a strong Lewis acid as F^- acceptor, SbF_5 in the case of the anion and the 16e$^-$ moiety $[W(CO)_6]^{2+}$ in the case of the cation, we conclude that the latter must have a Lewis acidity comparable to that of SbF_5, which is commonly viewed as the strongest molecular Lewis acid.[5,6]

In the complexes of the type $WL(CO)_3(NO)(FSbF_5)$, L = Me_2PhP or Cy_3P,[16,17] the W−F−Sb bridges are more unsymmetrical than in $[W(CO)_6(FSbF_5)]^+$. Both $W-F_b$ distances are with 2.169(11) and 2.186(3) Å slightly longer, while the $Sb-F_b$ distances of 1.954(11) and 1.979(3) Å are shorter than in the cation described here. Formation of the F bridges in the ion pairs of the complexes $[W(L)(CO)_3(NO)(FSbF_5)]$ can be viewed as arising from an interaction of $[SbF_6]^-$ with the five-coordinated cations $[W(L)(CO)_3(NO)]^+$ which should be a weaker fluoride ion acceptor than either $[W(CO)_6]^{2+}$ or SbF_5. The W−F−Sb bridge angles are with 147.15(59)° and 138.9(15)° more acute than in $[W(CO)_6(FSbF_5)]^+$. There are in addition to the two complexes[16,17] discussed here several other precedents where monodentate ligands of the type FEF_5, E = P, As, Sb, or $F-BF_3$, are found in transition metal complexes and structurally characterized.[30] There are, however, to our knowledge no cationic complexes known which would be considered as precedents for $[W(CO)_6(FSbF_5)]^+$.[30,31]

(d) A Comparison of Structural Features of $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ and $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$. As discussed in the section on synthesis both complexes are formed during the interaction of $M(CO)_6$, M = Mo, W, with SbF_5, as the main products and are structurally characterized.

The resulting coordination geometries for W(II) and Mo(II) differ. The former, as discussed above, is best described as a C_{2v} capped trigonal prism, while the $Mo(CO)_4F_3^-$ segment may be described as a square antiprism or a 4:3 geometry. There are precedents for both geometries among structurally characterized halocarbarbonyl complexes of molybdenum(II) and tungsten(II);[2,3] however, the 4:3 geometry appears to be somewhat rare for Mo(II) coordination compounds.[32]

Despite the different structure types and diverse coordination geometries of the two cations, there are two areas where a useful comparison between both complexes can be made: (i) the internal bond parameter (bond distances and bond angles) for both molecular cations and (ii) the conformation of the $[Sb_2F_{11}]^-$ anion in both salts, which provides a link to other structurally characterized metal carbonyl cation salts with the same anion.[4,14,15,23,27]

Some selected internal bond parameters for both salts are listed in Table 4. As can be seen from the wide spread in M−C and, to a lesser extent CO-bond distances, as well as from the wide variations in C−M−C angles, the $M(CO)_n$ moieties, M = Mo, W, $n = 4, 6$, are highly distorted. Distortions are expected for the C_{2v} capped trigonal prismatic structure and have been observed previously.[24,32] However in both metal carbonyl moieties, the local symmetry is reduced to C_i, in agreement with the observation of four and six CO stretching vibrations which are IR and Raman active (see Table 2). The observed spread in M−C distances and CO stretching vibrations is more pronounced for the $W(CO)_6$-group than for the $Mo(CO)_4$-moiety.

For both the molybdenum and the tungsten carbonyl cation, the average M−C, M = Mo, W, distances are very slightly longer than the corresponding upper quartile q_u values from the Cambridge index,[25] while the averaged CO distances for both complexes are slightly shorter than the lower quartile q_l value

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(27) Bodenbinder, M.; Balzer-Jöllenbeck, G.; Willner, H.; Batchelor, R. J.; Einsten, F. W. B.; Wang, C.; Aubke, F. *Inorg. Chem.* **1996**, *35*, 82.

(28) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(29) Green, M. L. H.; Parkin, G.; Mingquin, C.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1984**, 1400.

(30) Beck, W.; Sünkel, K. *Chem. Rev.* **1988**, *88*, 1405.

(31) Abel, E. W.; Tyfield, S. P. *Adv. Organomet. Chem.* **1970**, *8*, 117.

(32) Melnik, M.; Sharrock, P. *Coord. Chem. Rev.* **1985**, *65*, 49.

of 1.132 Å. The latter observation is consistent with the observed average CO stretching wavenumbers of 2125 and 2110 cm^{-1} for the tungsten and molybdenum cation, respectively, which are both slightly below $\bar{\nu}(CO)$ in gaseous CO (2143 cm^{-1}).[20] There appears to be a modest reduction in π-back donation in both cations when compared to the synergic bonding situation found for $M(CO)_6$, M = Mo, W,[18,19,26] or for the complexes $[W(L)(CO)_3(NO)(FSbF_5)]$.[16,17]

Considerably longer M−C distances, higher $\bar{\nu}(CO)_{av}$ values, and higher CO stretching force constants are found for the structurally characterized $[Sb_2F_{11}]^-$ salts with the metal carbonyl cations $[Hg(CO)_2]^{2+}$ (ref 27), $[Ir(CO)_5Cl]^{2+}$ (refs 14, 15), and $[Fe(CO)_6]^{2+}$ (ref 23) with $\bar{\nu}(CO)_{av}$ as high as 2280 cm^{-1} in $[Hg(CO)_2]^{2+}$ and f_{CO} 21.0 × 10^2 N m^{-1} (ref 27). Here the extent of π-back-bonding is affected by the formal charge of the central metal, which is +2 in all three cases,[14,15,23,27] compared to +1 in $[W(CO)_6(FSbF_5)]^+$ and $+^1/_2$ in $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]^+$.

Like the $M(CO)_n$, M = Mo, W, $n = 4, 6$, the pyramidal Mo−(μ-F)$_3$ group is significantly distorted from C_{3v} local symmetry. Mo−μ-F distances vary between 2.140(5) and 2.196(5) Å while F−Mo−F bond angles are rather acute and range from 73.2(2)° to 77.6(2)°.[7] The bidentate $F_2SbF_4^-$ ligand coordinates less strongly to Mo than the monodentate $FSbF_5^-$ group in $[W(CO)_6(FSbF_5)]^+$. This is reflected in the observed Sb−μ-F−(Mo) distances between 1.933(6) and 1.969(5) Å, whereas in $[W(CO)_6(FSbF_5)]^+$ a Sb−μ-F−(W) distance of 2.00(4) Å is found (see Figure 1).

There are a number of strong similarities between the structurally characterized metal carbonyl−$[Sb_2F_{11}]^-$ salts[4,14,15,23,27] and the two complexes discussed here: (i) M−C−O bond angles depart from linearity and fall between 174.8(8)° and 179.3(8)°, as seen in Table 3. (ii) The dioctahedral anion $[Sb_2F_{11}]^-$ is distorted with Sb−F−Sb bridge angles of 150.0(3)° and 149.4(3)° and dihedral angles of 19° and 30°, respectively. In addition, both SbF_4^- groups are in a staggered conformation. Very similar bridge angles and rotational distortions are found for the anions in $[Hg(CO)_2][Sb_2F_{11}]_2$,[27] $[Ir(CO)_5Cl][Sb_2F_{11}]_2$,[14,15] $[Fe(CO)_6][Sb_2F_{11}]_2$,[23] and $[H_3O][Sb_2F_{11}]$.[8] These anion distortions are attributed to significant interionic contacts[4] or to asymmetric O−H···F hydrogen bonds.[8] (iii) There are a number of significant secondary interionic contacts[33] which involve primarily C atoms of the carbonyl groups and equatorial F atoms of the $[Sb_2F_{11}]^-$ anion.[4,14,15,23,27] In the case of the Mo(II) and W(II) complexes, there are fewer such contacts but in addition there are intracationic C···F contacts, which involve F atoms of the $F_2SbF_4^-$ [7] and $FSbF_5^-$ ligands. In total there is about one significant C···F contact per carbonyl group. For $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ the secondary contacts are between 0.45 and 0.20 Å shorter than the sum of the van der Waals radii.[28] In $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$ weaker contacts are noted which fall between 0.2 and 0.1 Å shorter than the sum of the van der Waals radii.[28] The differences in the number of secondary C···F contacts and their strength between $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$[7] and $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ on one hand and metal carbonyl $[Sb_2F_{11}]^-$ salts[4,14,15,23,27] on the other hand reflect differences in formal charges of the central metal. In addition, in open, less crowded cations like linear $[Hg(CO)_2]^{2+}$ [27] or square planar $[M(CO)_4]^{2+}$, M = Pd, Pt,[34] secondary interionic contacts with the $[Sb_2F_{11}]^-$ anions are more numerous and stronger[27,34] than in the seven-coordinated Mo(II) and W(II) salts discussed here.

Summary and Conclusions

The results presented here and elsewhere[7,14,15] describe a new synthetic approach to thermally stable, predominantly σ-bonded cationic metal carbonyl derivatives of W and Mo with $[Sb_2F_{11}]^-$ as counteranion. The Lewis superacid antimony(V) fluoride[5,6] either by itself or as component of the Brønsted−Lewis superacid HF−SbF_5[5,6] functions as reaction medium and source for the counteranion, bioctahedral $[Sb_2F_{11}]^-$ as well as oxidizing agent toward the group 6 hexacarbonyls $M(CO)_6$, M = Cr, Mo, W. While the target of this study, the seven-coordinate homoleptic carbonyl cation $[M(CO)_7]^{2+}$ M = Mo, W, has remained elusive, two derivatives $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ and polymeric $[\{Mo(CO)_4\}_2(cis\text{-}\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$[7] have been isolated and structurally characterized by single-crystal X-ray diffraction. Both complexes are unprecedented in the coordination chemistry of Mo(II) and W(II)[2,3,32] as well as among metal carbonyl cations and their derivatives.[4,30,31]

With this study the existence range of homoleptic metal carbonyl cations and their derivatives,[4] all generated in superacid media[5,6] and stabilized by the anion $[Sb_2F_{11}]^-$, is extended from group 12 to the early transition metals Mo and W in group 6.

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Supporting Information Available: An X-ray crystallographic file in CIF format for the complex $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(33) Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 1.

(34) Bodenbinder, M.; Bröchler, R.; Sham, I. H. T.; Rettig, S. J.; Trotter, J.; v. Ahsen, B.; Willner, H.; Jonas, V.; Thiel, W.; Aubke, F. *J. Am. Chem. Soc.*, to be submitted.