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Reviews

σ-Bonded Metal Carbonyl Cations and Their Derivatives: Syntheses and Structural, Spectroscopic, and Bonding Principles[†]

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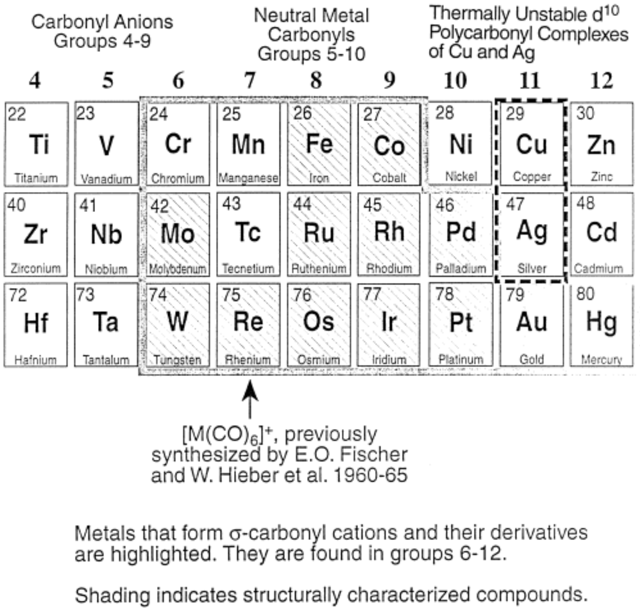
Homoleptic σ-bonded metal carbonyl cations (σ-carbonyls) and their derivatives have grown in recent years into a large subgroup of mononuclear metal carbonyl complexes. They are at present formed by 17 elements, including the post transition metal mercury. Most are generated in superacids: the Lewis superacid SbF_5 and the conjugate Brønsted−Lewis superacid $HF-SbF_5$. Thermally stable salts are formed with the superacid anions $[Sb_2F_{11}]^-$ and $[SbF_6]^-$. Many of the cations are superelectrophilic, with metals in oxidation states of +2 or +3. Three different synthetic routes are developed: reductive (A) or solvolytic carbonylations (B) and oxidative methods (C). Considerable progress has been made by replacing the Lewis superacid SbF_5 as reaction medium by the conjugate Brønsted−Lewis superacid $HF-SbF_5$. This allows reactions to proceed faster in a homogeneous phase and to produce crystalline materials. In total 27 mostly recent molecular structures have been obtained, including that of $[Ir(CO)_6][SbF_6]_3{\cdot}4HF$, the first HF solvate with one of the HF molecules coordinated in an isotridentate mode to three carbon atoms of the cation. Due to the electrophilic nature of the carbonyl carbon in fluoroantimonate salts of metal carbonyl cations, extended structures are formed via significant interionic C- - - F contacts. A new σ-bonded carbonyl, $(CF_3)_3BCO$, which has been fully characterized, expands the existence range of metal carbonyl cations to group 13. The large amount of spectroscopic and structural information accumulated is used to present a conceptually simple bonding model.

1. Introduction

Homoleptic metal carbonyl cations and their derivatives[1,2] are a recent addition to the large and diverse family of metal carbonyl compounds. The homoleptic cations are of the general type $[M(CO)_n]^{m+}$, with M ranging from group 12 (Hg) to group 6 (Mo, W) (see Figure 1). The principal coordination numbers and geometries are $n = 2$, linear ($D_{\infty h}$), $n = 4$, square planar (D_{4h}), and $n = 6$, octahedral (O_h). Metal oxidation states and, in the case of homoleptic carbonyl cations, the ionic charge m range from +1 to +3. Derivatives are formed generally by substitution of CO by anionic monodentate ligands (SO_3F^-, SbF_6^-, and Cl^-). This has allowed also the expansion to cationic complexes with coordination



Metals that form σ-carbonyl cations and their derivatives are highlighted. They are found in groups 6-12.

Shading indicates structurally characterized compounds.

Figure 1. Distribution of thermally stable homoleptic metal carbonyls.

[†] Dedicated to Professor Emeritus Ronald J. Gillespie—prolific researcher, inspiring teacher, and esteemed friend.

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number 7.[2−4] Following a suggestion by G. A. Olah,[5] those cations with metals in oxidation states of +2 and +3 are termed *superelectrophiles*. At present the majority of the metal carbonyl cations known are superelectrophilic.[2]

Thermally stable salts, with decomposition temperatures frequently higher than 200 °C, are invariably formed with the fluoroantimonate anions $[Sb_2F_{11}]^-$ and $[SbF_6]^-$. The latter anion is so far found only in salts with octahedral cations such as $[M(CO)_6]^{2+}$ (M = Fe, Ru, Os)[2,6,7] and $[Ir(CO)_6]^{3+}$.[8] The cations are exclusively generated in superacids.[5,9] Most prominent among these are liquid SbF_5, the strongest molecular superacid,[10,11] and the conjugate Brønsted−Lewis superacid $HF-SbF_5$, the strongest protonic superacid.[5,9] A number of synthetic routes have been developed by us,[1] which will be summarized in the following section. While SbF_5 and $HF-SbF_5$ can be used interchangeably, the use of the latter has produced crystalline salts, which have allowed us to determine a substantial number of accurate molecular structures.[2,8,12] These structures together with complete vibrational analyses, supported by DFT calculations,[12,13] have afforded a detailed insight into metal ion−CO bonding in cationic, thermally stable solid-state compounds, as will be outlined in this review.

Early pioneering studies by E. O. Fischer et al. and W. Hieber et al. in the early 1960s[1,14,15] have produced the monocations $[M(CO)_6]^+$ (M = Mn, Tc, Re) as AlX_4^- salts (X = Cl, Br), but all attempts to extend the synthetic approach (halide abstractions by AlX_3 (X = Cl, Br) at ∼90 °C and CO pressures of ∼300 atm) have been unsuccessful.[16] It should be emphasized that the classical approach used by Fischer et al. and Hieber et al. differs from our methodology described below only in the choice of Lewis acids and precursors, requiring consequently milder reaction conditions ($T = 25-60$ °C, $p(CO) \approx 1$ atm).[1] The failure of these and other attempts[14,15] and a superficial understanding of the synergic bonding concept has resulted in the view that di- and tripositive homoleptic metal carbonyl cations should be incapable of existence.[16]

The generation of $[Au(CO)_2]^+_{solv}$ in HSO_3F and the subsequent isolation and extensive spectroscopic characterization of $[Au(CO)_2][Sb_2F_{11}]$[17] in 1992 marked the start of a rapid development, which has been reviewed by us.[1,2] At present 16 metals from groups 6 to 12 form stable cationic metal carbonyl complexes (see Figure 1). Support for an understanding of the bonding in metal carbonyl cations has come from a number of recent theoretical studies.[12,13,18]

Most of the metal carbonyl cations, described here, have no precedents and their existence as a substantial group has been neither predicted nor anticipated in earlier studies.

In this publication we want to summarize the underlying synthetic concepts and principal structural, spectroscopic, and bonding features[2] that have emerged in recent years. Because the CO ligands are mainly σ-bonded to the metal cations, they are termed "σ-carbonyls".

To focus strictly on basic aspects, we refer for more general information and detailed referencing to recent reviews by us.[1,2] We consider this overview a continuation of our detailed earlier account, which also provides a historical perspective.[1] This sequel is made necessary by many new developments, allowing a deeper insight into the nature of M−CO bonding in solid-state complexes. We will therefore not repeat here a number of basic aspects and general concepts which had been previously presented.[1]

2. Discussion

2.1. General Synthetic Concepts. The first documented use of strong protonic acids with the intention to generate metal carbonyl complexes appears to have been an attempt by Manchot and König[19] to generate silver(I) carbonyls in concentrated H_2SO_4. The same solvent, as well as stronger protonic acids, have subsequently been used very successfully by Y. Souma and her students[20] over many years, to study in situ carbonyls of copper(I), silver(I), and, more recently, gold(I), palladium(I), and platinum(I) as active catalysts.[21] A recent major achievement of her group has been the generation and spectroscopic identification of dinuclear $[Pt_2(CO)_6]^{2+}$ in H_2SO_4.[22] Closely related to our work are extensive studies in acid halide solvents such as $SOCl_2$ by F. Calderazzo et al., directed at the syntheses of carbonyl halides of gold, palladium, and platinum.[23] These metal carbonyl halides show a strong resemblance to metal carbonyl fluorosulfates, obtained by us much later from fluorosulfuric acid as the reaction medium.[1,2]

Our own entry in this field was accidental. Attempts to generate in the condensed phase the formyl cation $[HCO]^+$, initially discovered as an interstellar species,[24,25] by protonation of CO in the conjugate Brønsted−Lewis superacid $HSO_3F-Au(SO_3F)_3$,[26,27] resulted

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Table 1. Synthetic Routes to σ-Metal Carbonyl Fluoroantimonates and Derivatives with SbF_5(K) or $HF-SbF_5$(L) as Reaction Media[a]

Method (A): Reductive Carbonylation	**Ref.**
i) $Pt(SO_3F)_4 + 5CO + 8SbF_5 \xrightarrow[1\ d]{L,\ 25^\circ C} [Pt(CO)_4][Sb_2F_{11}]_2 + 2Sb_2F_9(SO_3F) + CO_2 + S_2O_5F_2$	[12]
ii) $PtF_6 + 6CO + 4SbF_5 \xrightarrow[1\ d]{K,\ 50^\circ C} [Pt(CO)_4][Sb_2F_{11}]_2 + 3COF_2$	[30,31]
iii) $2IrF_6 + 15CO + 6SbF_5 + 8HF \xrightarrow[28h]{L,\ 25^\circ C} 2[Ir(CO)_6][SbF_6]_3 \cdot 4HF + 3COF_2$	[8]
Method (B): Solvolytic Carbonylation	
i) $Hg(SO_3F)_2 + 2CO + 8SbF_5 \xrightarrow[1\ h]{K,\ 100^\circ C} [Hg(CO)_2][Sb_2F_{11}]_2 + 2Sb_2F_9(SO_3F)$	[37]
ii) *cis*-$M(CO)_2(SO_3F)_2 + 8SbF_5 + 2CO \xrightarrow[1\ d]{L,\ 25^\circ C} [M(CO)_4][Sb_2F_{11}]_2 + 2Sb_2F_9(SO_3F)$	[12]
M = Pd or Pt	
Method (C): Oxidative Reactions	
i) $2Fe(CO)_5 + 2CO + XeF_2 + 4SbF_5 \xrightarrow[2\ d]{K,\ 50^\circ C} 2[Fe(CO)_6][Sb_2F_{11}]_2 + Xe$	[7]
ii) $[Rh(CO)_2\mu\text{-}Cl]_2 + 6CO + 4SbF_5 \xrightarrow[1\ d]{L,\ 50^\circ C} 2[Rh(CO)_5Cl][Sb_2F_{11}] + 2SbF_3{}^{[b]}$	[39]
iii) $W(CO)_6 + 4SbF_5 \xrightarrow[1\ d]{L,\ 40^\circ C} [W(CO)_6(FSbF_5)][Sb_2F_{11}] + SbF_3{}^{b)}$	[4]
Method (D): Extrusion of SbF_5 by Anhydrous HF	
i) $[M(CO)_6][Sb_2F_{11}]_2 + 2HF \xrightarrow[2\ d]{HF,\ 25^\circ C} [M(CO)_6][SbF_6]_2 + 2HF\text{-}SbF_5$	[6,7]
M = Fe, Ru, Os	

[a] CO pressure 1−2 atm. [b] With an excess of SbF_5 the adduct $6SbF_3{\cdot}5SbF_5$ will form.

instead in the discovery of $[Au(CO)_2]^+$ and the subsequent isolation of $[Au(CO)_2][Sb_2F_{11}]$.[17] While we never got any conclusive evidence for protonated CO at that time—the protonation has been accomplished subsequently in $HF-SbF_5$ by others[28]—a rapid expansion into cationic metal carbonyl chemistry took place in a short period of time.[1,2]

2.2. Reaction Types. The four general reaction types are illustrated in Table 1 by mainly recent examples.

2.2.1. Reductive Carbonylation Reductive carbonylation (method A) of metal fluorosulfates and fluorides is both elegant and versatile. The byproducts COF_2, CO_2, and $S_2O_5F_2$ and the solvolysis product identified as $Sb_2F_9(SO_3F)$[1,29] are sufficiently volatile and will not interfere in the product isolation. This is not the case with metal chlorides, where in addition to $COCl_2$ a mixed fluoride−chloride of antimony(V) forms, which has limited volatility.[29] Five platinum-group metals (Pd, Pt, Ir, Os, Ru)[8,12,30,31] form thermally stable, homoleptic, superelectrophilic metal carbonyl cations from high-valence fluoride or fluorosulfate precursors. In the case of rhodium the potential precursors RhF_6 and $Rh(SO_3F)_3$[32] are exceedingly difficult to prepare and are not available in sufficiently large quantities for meaningful studies.

Of the coinage metals, only $[Au(CO)_2]^+$ is obtained from superacid media and isolated as a stable[17] $[Sb_2F_{11}]^-$ salt from either $Au(SO_3F)_3$[17,26,27] or AuF_3[17] as precursor.[1,17] All attempts to obtain $[Ag(CO)_2]^+$ in thermally stable salts by the reductive carbonylation of either $Ag(SO_3F)_2$ or AgF_2 in various superacids or by CO addition to $Ag[Sb_2F_{11}]$ have failed.[33] This is altogether not surprising, because calculated bond energies $D(M-CO)$ for hypothetical $[M(CO)_2]^+{}_g$ are for $M = Au$ at 45.0 kcal mol^{-1} about 20 kcal mol^{-1} higher than those for $[Ag(CO)_2]^+{}_g$;[34] relativistic effects, which are found for $[Au(CO)_2]^+$,[17] are not expected to be important for $[Ag(CO)_2]^+$ and will not contribute to the strength of the Ag−C bond.

The reductive carbonylation of either $Pd[Pd(SO_3F)_6]$ or $Pt(SO_3F)_4$[32] in HSO_3F allows the synthesis of *cis*-

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Table 2. Synthetic Routes to Univalent Metal Carbonyl Cation Salts and Derivatives

a) Halide Abstraction by Group 13 Lewis Acids: **Ref.**

i) $M(CO)_5X + AlX_3 + CO \xrightarrow[\sim 300\text{ atm CO}]{85\text{-}100°C} [M(CO)_6][AlX_4]$ [14,15]

M = Mn, Tc, Re; X = Cl, Br

ii) $[Rh(CO)_2Cl]_2 + 2M_2Cl_6 + 4CO \xrightarrow[1\text{ atm CO}]{25°C} 2[Rh(CO)_4][M_2Cl_7]$ M = Al, Ga [55]

b) Arene Displacement by CO:

$[(\eta^6\text{-}C_6H_6)Rh(CO)_2][1\text{-Et-}CB_{11}F_{11}] + 2CO \longrightarrow [Rh(CO)_4][1\text{-Et-}CB_{11}F_{11}] + C_6H_6$ [84]

c) Hydrolysis of $[B(CF_3)_4]^-$ in conc. H_2SO_4:

$[B(CF_3)_4]^-_{(solv.)} + H_3O^+ \xrightarrow[\text{conc. } H_2SO_4]{25°C} (CF_3)_3BCO_{(g)} + 3HF_{(solv.)}$ [57,58]

d) Oxidation of a Metal Carbonyl Cluster by H_2X^+ X = F, SO_3F

$Co_2(CO)_{8(s)} + 2(CF_3)_3BCO_{(solv.)} + 2HF \xrightarrow[2\text{ atm CO}]{25°C} 2[Co(CO)_5][(CF_3)_3BF] + H_2$ [59]

$M(CO)_2(SO_3F)_2$ (M = Pd, Pt) as final products. They are converted by solvolytic carbonylation quantitatively to $[M(CO)_4][Sb_2F_{11}]_2$ (M = Pd, Pt).[1,2,12] The reductive carbonylation of PtF_6 in HF[2] results in the formation of $[Pt(CO)_4][PtF_6]$,[12,31] so far the only known carbonyl fluoride of platinum.[35,36]

2.2.2. Solvolytic Carbonylations. The uses of solvolytic carbonylations (method B), where the oxidation state of the metal atom in the precursor remains unchanged, are limited (see Tables 1 and 2). However, prominent among the examples is the conversion of $Hg(SO_3F)_2$[32] into $[Hg(CO)_2][Sb_2F_{11}]_2$,[1,2,37] which is thermally stable up to 160 °C and has remained the only known, isolable CO derivative of a post transition metal.[1,2]

In summary, solvolytic carbonylations allow for simple and facile product isolation and have quantitative yields. Where fluorosulfates are used as precursors, as for example in the synthesis of $[Hg(CO)_2][Sb_2F_{11}]_2$,[1,2,37] the byproduct $Sb_2F_9(SO_3F)$ is sufficiently volatile as discussed above. In CO additions, as in the formation of *mer*-$Ir(CO)_3(SO_3F)$[1,2,38] from $Ir(SO_3F)_3$,[32] there are no byproducts but the reaction is rather slow.

There is a disadvantage to the use of methods A and B: the most suitable precursors are not commercially available, but routes to their syntheses are well documented.[32]

2.2.3. Oxidative Methods. For the generation of metal carbonyl cations from groups 9, 8 and 6, oxidative methods (method C) become more important.[2] We differentiate here between those reactions that require an external oxidizer and those where SbF_5 has a 3-fold role: as reaction medium, with or without HF, as oxidizer and as a source for the counteranion $[Sb_2F_{11}]^-$. In these reactions the CO content of the precursor may increase,[7,39] decrease,[3] or remain the same[4] (see also Table 1). In group 9 the species $[M(CO)_5Cl][Sb_2F_{11}]_2$ (M = Rh, Ir)[39] are formed by oxidation of the precursors $[Rh(CO)_2(\mu\text{-}Cl)]_2$ and $[Ir(CO)_3Cl]_n$, respectively, with SbF_5 in the presence of CO. In group 8 both $[Os(CO)_6]^{2+}$ and $[Ru(CO)_6]^{2+}$ [6] are generated by reductive carbonylations of the precursors $M(SO_3F)_3$ (M = Ru, Os)[32] and OsF_6 in SbF_5[6,31,40] and isolated as $[Sb_2F_{11}]^-$ salts. However, this approach fails when FeX_3 (X = Cl, SO_3F) are used as reagents and $Fe[SbF_6]_2$[7] with a layered structure[41] forms instead.

The oxidative carbonylations of $[Rh(CO)_2Cl]_2$ and $[Ir(CO)_3Cl]_n$ in SbF_5[39] illustrate another important limitation: during the two-electron oxidation of M (M = Rh, Ir) the M−Cl bonds become stronger and shorter. Hence, removal of Cl^- and replacement by CO does not occur and the homoleptic cations $[M(CO)_6]^{3+}$ (M = Rh, Ir) are not obtained in this manner.

As seen in Table 1, the use of SbF_5 as oxidizing agent entails formation of a reduced byproduct, formulated as SbF_3. In the presence of SbF_5 in excess, an adduct of the composition $6SbF_3 \cdot 5SbF_5$ forms, which has a complicated structure.[42] It will be necessary to separate the product by crystallization from $HF-SbF_5$. Alternatively, in the case of $[Fe(CO)_6][Sb_2F_{11}]_2$,[2,43] which is resistant toward oxidizing agents, it is possible to convert SbF_3

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or $6SbF_3{\cdot}5SbF_5$ quantitatively to SbF_5 by reaction with fluorine at 25 °C in HF.

Even though oxidative methods require, in contrast to methods A and B, separation of the product from the nonvolatile byproduct, recrystallization from $HF-SbF_5$ produces crystalline materials in modest yields, which have allowed in all instances a complete characterization, including molecular structure determinations by single-crystal X-ray diffraction.[3,4,7,39] Common to all three methods (A–C) is the exclusive formation of $[Sb_2F_{11}]^-$ salts from either of the superacids SbF_5 and $HF-SbF_5$. An advantage of method C is the use of commercially available precursors; however, this advantage is partly offset by the use of unusual reagents (XeF_2, AsF_5), the need of product isolation by crystallization, and difficulties associated with working in SbF_5 or $HF-SbF_5$.

2.2.4. Extrusion of SbF_5. The final method listed in Table 1, the extrusion of SbF_5 (method D) from $[Sb_2F_{11}]^-$ salts to form the corresponding $[SbF_6]^-$ salts, is at present limited to group 8.[2,6,7] Here interionic interactions between the $[M(CO)_6]^{2+}$ cations (M = Fe,[7] Ru,[6] Os[6]) and the $[Sb_2F_{11}]^-$ anions are weaker and less numerous than in salts with linear $[Hg(CO)_2]^{2+}$ [37] or square-planar $[M(CO)_4]^{2+}$cations (M = Pd, Pt).[12] Replacement of $[Sb_2F_{11}]^-$ anions, usually of C_1 symmetry, by octahedral $[SbF_6]^-$ facilitates the complete vibrational analyses of the octahedral $[M(CO)_6]^{2+}$ (M = Fe,[7] Ru,[6] Os[6]) cations and allows the direct observation of all 13 fundamentals.[2,6,7] At the core of this approach lies the well-studied[44] solution equilibrium in the superacid $HF-SbF_5$

$$[Sb_2F_{11}]_{solv}^{\ -} + HF \rightleftharpoons HF\text{-}SbF_5 + [SbF_6]_{solv}^{\ -} \quad (1)$$

which with increasing SbF_5 concentrations will shift to the left and in dilute solution will increase the concentration of $[SbF_6]^-_{solv}$. It is assumed that both types of $[M(CO)_6]$–fluoroantimonates (M = Fe,[7] Ru,[6] Os[6]) will be somewhat soluble in $HF-SbF_5$. A recent unexpected finding, made during the reductive carbonylation of IrF_6 in a dilute solution of SbF_5 in HF (~1:6 by volume), may serve as an illustration, where an unusual solvate of the composition $[Ir(CO)_6][SbF_6]_3{\cdot}4HF$[8] forms instead of $[Ir(CO)_6][Sb_2F_{11}]_3$ (see Table 1):

$$2IrF_6 + 15CO + 6SbF_5 + 8HF \xrightarrow[\text{dil HF}-SbF_5]{25\ °C,\ 1.5\ \text{atm CO}} 2[Ir(CO)_6][SbF_6]_3{\cdot}4HF + 3COF_2 \quad (2)$$

The structure of this solvate will be discussed in the next section.

2.2.5. Carbonylation Reactions in $HF-SbF_5$ or SbF_5: A Rationale. For the generation of homoleptic metal carbonyl cations, reductive and solvolytic carbonylations are elegant methods that produce the new compounds in quantitative yields.[1,2] An illustration of the reductive carbonylation of IrF_6 in liquid SbF_5 is shown in Scheme 1A in detail. As can be seen, a complete exchange (F^- against CO) of all six ligands occurs in a remarkably simple 3e reduction. In the reaction, IrF_6 is quantitatively converted to the cation $[Ir(CO)_6]^{3+}$, with volatile COF_2 as the sole byproduct. The product from the reaction in SbF_5 is identified as $[Ir(CO)_6][Sb_2F_{11}]_3$, while in dilute $HF-SbF_5$ the solvate $[Ir(CO)_6][SbF_6]_3{\cdot}4HF$ forms instead.[8]

Scheme 1

(A) Reductive Carbonylation of IrF_6 in $HF\text{-}SbF_5$ at 50 °C and 1 atm of CO

(a) 3e Reduction of IrF_6

$$2IrF_6 + 3CO + 6SbF_5 \rightarrow 2Ir^{3+}{}_{solv} + 6[SbF_6]^- + 3COF_2$$

(b) Carbonylation of $Ir^{3+}{}_{solv}$

$$Ir^{3+}{}_{solv} + 6CO \rightarrow [Ir(CO)_6]^{3+}{}_{solv}$$

(c) Salt Formation

(i) In Dilute $HF-SbF_5$

$$[Ir(CO)_6]^{3+}{}_{solv} + 3[SbF_6]^-{}_{solv} + 4HF \rightarrow [Ir(CO)_6][SbF_6]_3{\cdot}4HF_s$$

(ii) In Concentrated $HF-SbF_5$ or Liquid SbF_5

$$[Ir(CO)_6]^{3+}{}_{solv} + 3[Sb_2F_{11}]^-{}_{solv} \rightarrow [Ir(CO)_6][Sb_2F_{11}]_{3\ s}$$

Overall Reaction

In SbF_5[30,31]

$$2IrF_6 + 15CO + 12SbF_5 \xrightarrow[1\ \text{day}]{SbF_5} 2[Ir(CO)_6][Sb_2F_{11}]_3 + 3COF_2$$

In Dilute $HF-SbF_5$[8]

$$2IrF_6 + 15CO + 6SbF_5 + 8HF \xrightarrow[1\ \text{day}]{HF-SbF_5} 2[Ir(CO)_6][SbF_6]_3{\cdot}4HF + 3COF_2$$

(B) Oxidation of $W(CO)_6$ in $HF-SbF_5$[4]

(i) 2e Oxidation

$$W(CO)_6 + 3SbF_5 \rightarrow [W(CO)_6]^{2+}{}_{solv} + 2[SbF_6]^- + SbF_3$$

(ii) Hard Acid–Base Interaction

$$[W(CO)_6]^{2+}{}_{solv} + [SbF_6]^- \rightarrow [W(CO)_6(FSbF_5)]^+{}_s$$

(iii) Salt Formation

$$[W(CO)_6(FSbF_5)]^+{}_{solv} + [Sb_2F_{11}]^- \rightarrow [W(CO)_6(FSbF_5)][Sb_2F_{11}]_s$$

Overall Reaction

$$W(CO)_6 + 4SbF_5 \xrightarrow{HF-SbF_5} [W(CO)_6(FSbF_5)][Sb_2F_{11}]_s + SbF_3$$

A similar illustration of method C, the oxidation of $W(CO)_6$ by SbF_5 in $HF-SbF_5$ to $[W(CO)_6(FSbF_5)]$-

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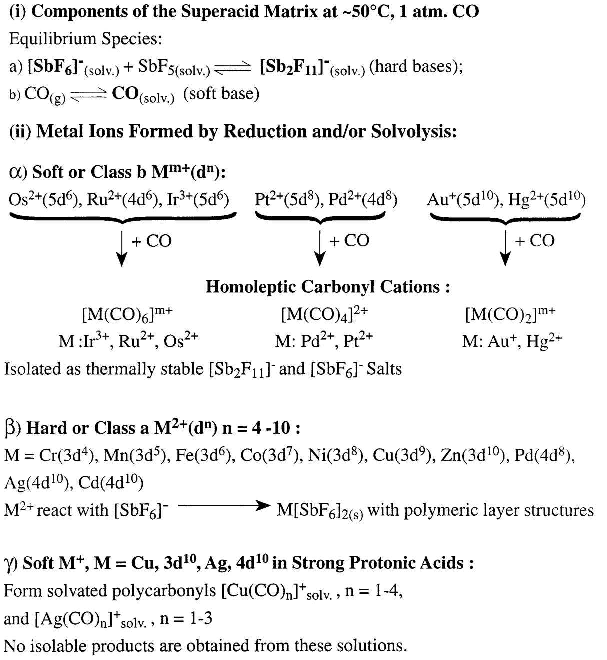
Scheme 2. Reaction Chemistry of "Naked" Metal Ions in CO/HF−SbF_5 and Other Protonic Acids



$[Sb_2F_{11}]$,[4] is shown in Scheme 1B. Details will be discussed in section 3.1.

The complete absence of isolable or spectroscopically detectable intermediates or byproducts (other than volatile COF_2, CO_2, or $S_2O_5F_2$) in all reductive or solvolytic carbonylation reactions studied by us[1,2,6,8,12,17] suggests a general reaction pathway, which is illustrated in Scheme 2. It is assumed in this rationale that the generation of so-called "naked" (or very weakly coordinated) metal cations by reduction and or solvolysis occurs, which are found in a superacid "matrix" together with two types of very weak Lewis bases: gaseous solvated carbon monoxide, CO_{solv}, and the fluoroantimonate(V) anions $[SbF_6]^-$, $[Sb_2F_{11}]^-$, $[Sb_3F_{16}]^-$, etc.[44,45]

The generated cations consist of the 5d species Hg^{2+},[37] Au^+,[17] Pt^{2+},[12] Ir^{3+},[17] and Os^{2+} [6] as well as the 4d ions Pd^{2+} [12] and Ru^{2+}.[6] All seven cations are strongly polarizing transients, which require stabilization by suitable donor ligands, to give isolable salts with complex cations. As illustrated in Scheme 2, all cations in this group, termed α, are viewed as soft to borderline acids, in terms of Pearson's[46] soft and hard acid and base (SHAB) concept, or, according to a classification proposed earlier by Ahrland, Chatt, and Davies,[47] as class b metal ions. These soft acids will in SbF_5 or HF−SbF_5 react preferentially with the soft Lewis base CO,[46] to form thermally stable, homoleptic, frequently superelectrophilic[5] metal carbonyl cations.[1,2] The resulting metal carbonyl cations are all diamagnetic and have unique and precise compositions, just like neutral mononuclear metal carbonyls[48−50] or metal carbonylates.[48−51] Their molecular structures fall into three groups in accordance with their d-electron configurations: (i) linear (d^{10}) $D_{\infty h}$, found for $[Hg(CO)_2]^{2+}$ [37] and $[Au(CO)_2]^+$;[17,21] square-planar (d^8) D_{4h}, for $[Pd(CO)_4]^{2+}$ and $[Pt(CO)_4]^{2+}$;[12] (iii) octahedral (d^6) O_h, for $[Os(CO)_6]^{2+}$, $[Ru(CO)_6]^{2+}$,[6] and$[Ir(CO)_6]^{3+}$.[8]

Linear and square-planar geometries have previously been unknown in metal carbonyl chemistry,[48−51] and the effective atomic number (EAN) rule is obeyed only for the octahedral $[M(CO)_6]^{m+}$ cations. The regular octahedral geometry is also found for metal carbonylates in groups 4 and 5,[51] neutral homoleptic molecules in group 6,[48−50] and as discussed for cations in groups 7,[14,15] 8, and 9.[1,2,6−8] This structural similarity allows an extensive, systematic correlation of their structural and spectroscopic properties,[1,2] supported by DFT calculations[13] on 16 isostructural molecules or ions. According to DFT calculations,[13] all $M(CO)_6$ species have partial atomic charges q_C that are more positive (or less negative) than q_M and the difference $q_C - q_M$ is a positive entity,[12,13] as is the case for metal carbonylates[51] and neutral metal carbonyls.[48−50] Accordingly, all σ-carbonyls have electrophilic carbon centers.[12]

In addition, a group of cations, termed β, mostly from the 3d series and of the type M^{2+} (M = Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd) can be generated in HF−SbF_5, as well as in a wide range of ionizing solvents either by reduction or solvolysis. However, even at high CO pressures, there is no CO uptake and layered materials of the type $M[SbF_6]_2$ form.[41] The M^{2+} ions, with the exception of the d^{10} ions Zn^{2+} and Cd^{2+}, are all paramagnetic and have magnetic susceptibilities and moments, commensurate with high-spin cations in weak octahedral ligand fields.[43] The formation of $M[SbF_6]_2$ complexes rather than $[M(CO)_n]^{m+}$ species is not unexpected, since the M^{2+} cations are viewed as hard to borderline, according to the SHAB concept[46] or predominantly as class a metals[47] (see Scheme 2).

In addition, the soft acids[46] Cu^+ and Ag^+, labeled type γ in Scheme 2, form in strong protonic acids solvated polycarbonyl cations of the type $[M(CO)_n]^+$ (M = Cu, Ag; $n = 1{-}4$), but no isolable products result. However, the solvated polycarbonyl cations have found extensive use in catalysis.[21]

Correspondingly, Cu^+ and Ag^+ salts with weakly coordinating anions will in aprotic solvents readily add CO stepwise.[52,53] There are, however, two important differences (i) The formation of polycarbonyls occurs, which is without precedent in metal carbonyl chemistry.[49,50] The composition of these polycarbonyls is controlled by temperature and CO pressure. Up to four CO ligands can be coordinated to M^+ (M = Cu, Ag) by increasing the CO pressure. (ii) The CO addition is reversible, and stepwise loss of CO occurs with either increasing temperature or decreasing CO pressure.

In summary, the role of superacids as reaction media in reductive or solvolytic carbonylation reactions is seen in (i) the formation of "naked" cations, (ii) the dissolution of CO, and (iii) the formation of the ions $[SbF_6]^-$ and

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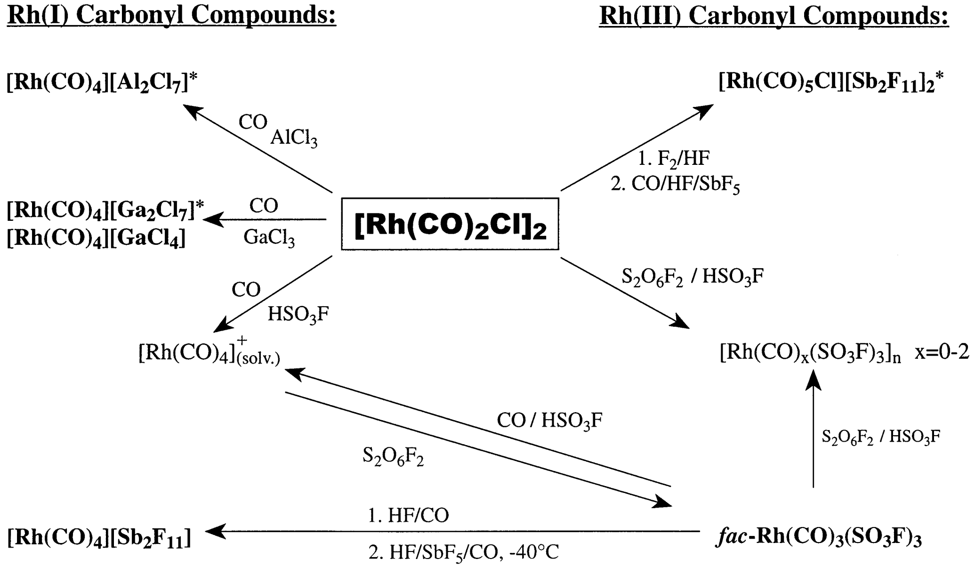
Scheme 3. Syntheses of Carbonyl Compounds[a] of Rh^{I} and Rh^{III} Starting from $[Rh(CO)_2Cl]_2$[55]



[a] Isolated compounds are shown in boldface type. Asterisks indicate structurally characterized compounds.

$[Sb_2F_{11}]^-$. The metal cations will either take up the soft donor CO,[46,47] irreversibly or reversibly in case of Cu^+ and Ag^+, or react with $[SbF_6]^-$ to give $M[SbF_6]_2$. The diverging behavior of "naked" M^{n+} cations is rationalized in terms of the SHAB concept[46] and the metal ion classification according to Ahrland, Chatt, and Davies.[47] No other synthetic method has produced so far a superelectrophilic metal carbonyl cation in a thermally stable salt.

In a similar manner, oxidative methods C are viewed to produce transient metal carbonyl[3,4,7] or carbonyl chloro[30,39] cations in $HF-SbF_5$ or SbF_5 which are stabilized by $[Sb_2F_{11}]^-$ (see Scheme 1B).

2.2.6. Alternate Synthetic Routes to Homoleptic Metal Carbonyl Cations and Their Derivatives. A number of univalent metal carbonyl cations of the general type $[M(CO)_n]^+$ (M = Cr, Co, Rh, Ir, etc.; n = 4−6) are not obtainable in SbF_5 or $HF-SbF_5$,[9−11,54] because these cations are sensitive toward oxidation by SbF_5. Alternate routes are summarized in Table 2.

The use of group 13 Lewis acids AlX_3[9,54] (X = Cl, Br) in halide abstraction reactions is exemplified by the generation of the group 7 cations $[M(CO)_6]^+$ (M = Mn, Tc, Re) in early studies,[14,15] as discussed in the Introduction. This approach is adopted in the generation of the salts $[Rh(CO)_4][M_2Cl_7]$ (M = Al, Ga) by solvolytic carbonylation of $[Rh(CO)_2Cl]_2$ under mild conditions (25 °C, 1 atm of CO).[55] As can be seen in Scheme 3, starting from either $[Rh(CO)_2Cl]_2$ or $[Rh(CO)_4]^+_{solv}$, a number of redox reactions in Brønsted superacids[9,54] have been utilized, which allow the synthesis and isolation of *fac*-$Rh(CO)_3(SO_3F)_3$ and previously structurally characterized $[Rh(CO)_5Cl][Sb_2F_{11}]_2$[39] in high yields and provide an indirect route to $[Rh(CO)_4][Sb_2F_{11}]$, which is characterized by vibrational methods, supported by DFT calculations. Hence, rhodium becomes the only metal so far to form thermally stable, fully characterized σ-carbonyl complexes, with rhodium in two different oxidation states and coordination geometries: square-planar Rh(I) d^8 and octahedral Rh(III) d^6.[55]

Another reaction sequence revolves around the recently reported anion $[B(CF_3)_4]^-$.[56] Its partial hydrolysis in concentrated H_2SO_4[57] according to

$$[B(CF_3)_4]^-_{solv} + H_3O^+_{solv} \xrightarrow[\text{conc } H_2SO_4]{25\ °C} (CF_3)_3BCO_g + 3HF \quad (3)$$

produces the extensively characterized σ-carbonyl $(CF_3)_3BCO$,[58] with ν(CO) at 2267 cm^{-1}, the highest CO stretching wavenumber found for a borane monocarbonyl[53] and identical with $\nu(CO)_{av}$ for $[Ir(CO)_6]^{3+}$.[8,30] The molecular structure of $(CF_3)_3BCO$ is obtained both in the gas phase and in the solid state and will be discussed in the next section.

Equally intriguing is its chemistry. Since the Lewis acid $B(CF_3)_3$ is nonexistent,[58] solutions of $(CF_3)_3BCO$ in anhydrous HF constitute a strong conjugate Brønsted−Lewis superacid, which is capable of oxidizing $Co_2(CO)_8$ according to[59]

$$2HF + Co_2(CO)_8 + 2(CF_3)_3BCO \xrightarrow[HF\cdot(CF_3)_3BCO]{25\ °C,\ 2\ atm\ of\ CO} 2[Co(CO)_5][(CF_3)_3BF] + H_2 \quad (4)$$

The reaction, given as a net, overall equation, and the structurally characterized salt $[Co(CO)_5][(CF_3)_3BF]$[58] are remarkable on three accounts. (i) The acidium ion H_2F^+ functions as an oxidizer. The reduced product H_2 has been detected previously[60] by mass spectrometry, following the generation of $[Co(CO)_5]^+_{solv}$ from $Co_2(CO)_8$

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Table 3. Structurally Characterized Superelectrophilic Metal Carbonyl Fluoroantimonate(V) Salts

					struct param		spectrosc properties		
group	no.	compd	synth[a] method	mol struct of cation	$d(\mathrm{M-C})_{\mathrm{av}}$ (Å)	$d(\mathrm{C-O})_{\mathrm{av}}$ (Å)	$\bar{\nu}(\mathrm{CO})_{\mathrm{av}}$ ($\mathrm{cm^{-1}}$)	f_{CO} (10^2 $\mathrm{N\ m^{-1}}$)	ref
12	1	$[\mathrm{Hg(CO)_2}][\mathrm{Sb_2F_{11}}]_2$	B	linear $D_{\infty h}$	2.083(10)	1.104(12)	2281	21.0	37
10	2	$[\mathrm{Pd(CO)_4}][\mathrm{Sb_2F_{11}}]_2$	A, B	sq planar D_{4h}	1.992(6)	1.106(6)	2259	20.63	12
	3	$[\mathrm{Pt(CO)_4}][\mathrm{Sb_2F_{11}}]_2$	A, B	sq planar D_{4h}	1.982(9)	1.110(9)	2261	20.64	12
9	4	$[\mathrm{Ir(CO)_6}][\mathrm{SbF_6}]_3\cdot 4\mathrm{HF}^{c}$	A, D	oct O_h	2.031(9)	1.090(9)	2268	20.8	8
	5	$[\mathrm{Rh(CO)_5Cl}][\mathrm{Sb_2F_{11}}]_2$	C	dist oct C_{4v}	2.011(10)	1.102(10)	2247	20.41	39
	6	$[\mathrm{Ir(CO)_5Cl}][\mathrm{Sb_2F_{11}}]_2$	B, C	dist oct C_{4v}	2.026(10)	1.086(20)	2246	20.39	39
8	7	$[\mathrm{Fe(CO)_6}][\mathrm{Sb_2F_{11}}]_2$	C	oct O_h	1.911(5)	1.104(6)	2215	19.82	7
	8	$[\mathrm{Fe(CO)_6}][\mathrm{SbF_6}]_2$	C, D	oct O_h	1.908(7)	1.108(9)			
	9	$[\mathrm{Ru(CO)_6}][\mathrm{Sb_2F_{11}}]_2$	A	oct O_h	2.039(5)	1.094(10)	2214	19.80	6
	10	$[\mathrm{Ru(CO)_6}][\mathrm{SbF_6}]_2$	A, D	oct O_h	2.024(5)	1.101(7)			
	11	$[\mathrm{Os(CO)_6}][\mathrm{Sb_2F_{11}}]_2$	A	oct O_h	2.027(5)	1.102(7)	2209	19.71	6
	12	$[\mathrm{Os(CO)_6}][\mathrm{SbF_6}]_2$	A, D	oct O_h	2.022(10)	1.104(7)			
6	13	$[\{\mathrm{Mo(CO)_4}\}_2(\mathrm{F_2SbF_4})_3]_x[\mathrm{Sb_2F_{11}}]_x$	C	7-coord C_1	2.036(10)	1.113(10)	2110	18.7	3
	14	$[\mathrm{W(CO)_6(FSbF_5)}][\mathrm{Sb_2F_{11}}]$	C	7-coord C_1	2.095(6)	1.130(10)	2124	18.2	4

[a] See Table 1.

in various Brønsted acids. (ii) The cation $[\mathrm{Co(CO)_5}]^+$ is the first example of a trigonal-bipyramidal metal carbonyl cation. Its structure will be discussed in the next section. (iii) The anion $[(\mathrm{CF_3})_3\mathrm{BF}]^-$, which is found in a number of simple salts,[61] is, together with $[\mathrm{B(CF_3)_4}]^-$, a promising weakly coordinating anion, in many respects superior to currently used WCA's.[62]

In summary, the mostly recent synthetic methods listed in Table 2 complement the existing methods summarized in Table 1 very well and add new and unique impulses to the group of known σ-carbonyls[1,2] on five accounts. (i) They allow with the synthesis of $(\mathrm{CF_3})_3\mathrm{BCO}$[57,58] and its characterization an expansion of the field into group 13. (ii) They add to the existing conjugate Brønsted−Lewis superacid systems[9,54] a new member, where the Lewis acid is in aHF generated in situ from the precursor $(\mathrm{CF_3})_3\mathrm{BCO}$.[57,58] This new system and the new superacid anion $[(\mathrm{CF_3})_3\mathrm{BF}]^-$ [59] are expected to find further use in ongoing work. (iii) Trigonal-bipyramidal $[\mathrm{Co(CO)_5}]^+$ (D_{3h})[59] is, on account of its 18e count, viewed as an "organometallic" metal carbonyl cation, while $[\mathrm{Rh(CO)_4}]^+$ (D_{4h})[55] is regarded as a 16e "coordination complex" just like $[\mathrm{M(CO)_4}]^{2+}$ (M = Pd, Pt),[12] with all four cations having d^8 electron configurations. (iv) A recently reported outline of the chemical reactions of $(\mathrm{CF_3})_3\mathrm{BCO}$[58] and the redox chemistry of Rh(I) and Rh(III) in Scheme 3[55] are first steps in exploring what promises to be a fascinating reaction chemistry of σ-carbonyls. (v) The syntheses of $[\mathrm{Rh(CO)_4}][\mathrm{M_2Cl_7}]$ (M = Al, Ga[55]) and of $[\mathrm{Co(CO)_5}][(\mathrm{CF_3})_3\mathrm{BF}]$[59] and their subsequent characterization by analytical, spectroscopic and structural methods show that thermally stable salts can form in the absence of extended structure formation. Strong M−CO bonds for M = Rh^+, Co^+ form without significant contributions from relativistic effects.[63]

2.2.7. Synthetic Aspects: Summary and Conclusions. The synthetic routes summarized in Tables 1 and 2 have produced a substantial number of previously unknown σ-carbonyls.[1,2] The group consists primarily of salts with homoleptic and frequently superelectrophilic[5] metal carbonyl cations and their derivatives.[1,2] All are generated either in strong Brønsted acids and superacids[9,54] (Table 1) or with the help of Lewis acids,[9,54] as shown in Tables 1 and 2. To illustrate the great versatility of our principal approach, generation of cations in HF−$\mathrm{SbF_5}$ followed by isolation and characterization as $[\mathrm{Sb_2F_{11}}]^-$ salts, two recent examples are cited: the xenon−gold cations of Seppelt et al.[64] and the polynitrogen cation $[\mathrm{N_5}]^+$ of Christe et al.[65]

The σ-carbonyls form stable salts which permit their full characterization by analytical (microanalysis, mass balance of reactions), spectroscopic (IR, Raman, NMR), thermochemical (DSC and thermal decomposition), and structural methods. There are at present almost 30 accurate molecular structure determinations by single-crystal X-ray diffraction, 24 of these by us. They will be discussed in the next section.

2.3. σ-Carbonyls: Structural Aspects. 2.3.1. General Comments. Selected structural parameters, $d(\mathrm{M-C})_{\mathrm{av}}$ and $d(\mathrm{C-O})_{\mathrm{av}}$, and spectroscopic features, $\nu(\mathrm{C-O})_{\mathrm{av}}$ and f_{CO} (Cotton−Kraihanzel method),[66] for well-characterized salts (see preceding section) are listed in Tables 3 and 4. Vibrational data are included, because in compounds with very high C−O bond orders, ν(C−O) and f_{CO} allow a more precise estimate of the C−O bond strength and permit a better differentiation between related carbonyl compounds than do C−O internuclear distances.[1,2] Also included for each salt are the best synthetic methods, using the notation A−D introduced in the preceding section that is also employed in Table 2, and the symmetry point group of the cation or molecule.

It is found to be convenient to list in Table 3 only data on superelectrophilic metal carbonyl fluoroantimonates, while information on salts with univalent metal carbonyl cations and related metal carbonyl fluorosulfates and *cis*-$\mathrm{Pt(CO)_2Cl_2}$[67] is collected in Table 4. Not included

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Table 4. Structurally Characterized Compounds with Unipositive Metal Carbonyl Cations and Various Related Derivatives

					struct param		spectrosc properties		
group	no.	compd	synth method	mol struct of cation	d(M−C)$_{av}$ (Å)	d(C−O)$_{av}$ (Å)	$\bar{\nu}$(CO)$_{av}$ (cm^{-1})	f_{CO} (10^2 N m^{-1})	ref
13	15	$(CF_3)_3BCO$	B	pyramidal C_{3v}	1.69(2)	1.110(10)	2269	20.8	58
11	16	$[Au(CO)_2][Sb_2F_{11}]$	A, B	linear $D_{\infty h}$	1.98(3)	1.11(5)	2236	20.1	1, 121
	17	$[Au(CO)_2]_2[Sb_2F_{11}][SbF_6]$	A	linear $D_{\infty h}$	1.972(15)	1.123(5)			120
10	18	*cyclo*-$[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$	A	sq planar D_{4h}	1.975(4)	1.133(6)	2002	16.6	72
	19	*cis*-$Pd(CO)_2(SO_3F)_2$	A	sq planar C_{2v}	1.932(5)	1.108(6)	2218	19.87	70
	20	*cis*-$Pt(CO)_2(SO_3F)_2$	A	sq planar C_{2v}	1.882(3)	1.116(6)	2202	19.56	71
	21	*cis*-$Pt(CO)_2C1_2$	B	sq planar C_{2v}	1.897(5)	1.115(6)	2171	18.7	67
9	22	$[Co(CO)_5][(CF_3)_3BF]$	C	trig bipyr D_{3h}	1.826(2)^a 1.853(2)^b	1.117(2)^a 1.117(2)^b	2146	18.3	59
	23	$Rh(CO)_4][1\text{-}EtCB_{11}F_{11}]$	B	sq planar D_{4h}	1.951(6)	1.116(6)	2167	18.9	84
	24	$[Rh(CO)_4][Al_2Cl_7]$	B	sq planar D_{4h}	1.950(6)	1.117(10)	2163	18.9	55
	25	$[Rh(CO)_4][Ga_2Cl_7]$	B	sq planar D_{4h}	1.964(7)	1.123(6)	2162	19.0	55
	26	*mer*-$Ir(CO)_3(SO_3F)_3$	B	oct C_{2v}	2.003(6)^c 1.937(7)^d	1.111(7)^c 1.094(8)^d	2218	19.9	38
7	27	$[Re(CO)_6][Re_2F_{11}]$	C	oct O_h	2.01(4)	1.094(10)	2116	18.1	78

[a] Axial. [b] Equatorial. [c] Trans. [d] Cis.

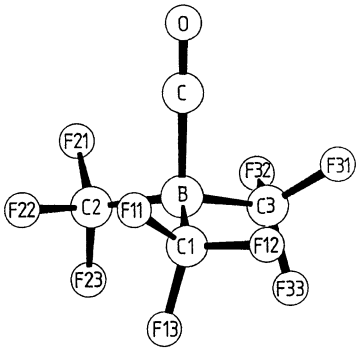

Figure 2. Molecular structure of $(CF_3)_3BCO$.[58]

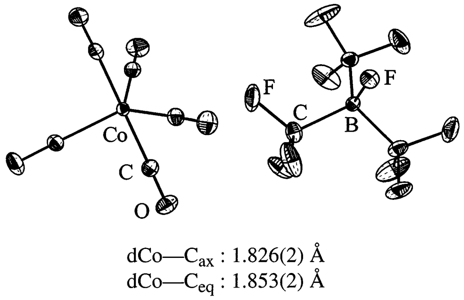

Figure 3. Solid-state structure of $[Co(CO)_5](CF_3)_3BF]$.[59]

here are older structural data on ClAuCO.[68] Most of our structural work has recently been summarized.[2]

The solid-state structures of $(CF_3)_3BCO$[58] and $[Co(CO)_5][(CF_3)_3BF]$[59] are shown in Figures 2 and 3, respectively, and the relevant structural data are included in Table 4. Both structures will not be discussed in detail here. An extensive discussion of $(CF_3)_3BCO$, which departs from the general thrust of this review, has appeared very recently.[58] The molecular structure of the $[Co(CO)_5]^+$ salt[59] is even more recent, and a full paper should be completed before inclusion of the details in a review is contemplated. The extended structures of $[Hg(CO)_2][Sb_2F_{11}]_2$,[37] $[Pt(CO)_4][Sb_2F_{11}]_2$,[12] and $[Os(CO)_6][Sb_2F_{11}]_2$,[6] all formed by 5d-block metals, are shown in Figure 4. Identical structures are found for $[Pd(CO)_4][Sb_2F_{11}]_2$[12] and $[M(CO)_6][Sb_2F_{11}]_2$ (M = Fe,[7] Ru[6]). A formula unit of $[M(CO)_6][SbF_6]_2$ (M = Fe,[7] Ru,[6] Os[6]) is shown in Figure 5. In Figure 6 the “solvated” $[Ir(CO)_6]^{3+}$ in $[Ir(CO)_6][SbF_6]_3{\cdot}4HF$[8] is shown, emphasizing isotridentate and anisobidentate C- - -FH con-

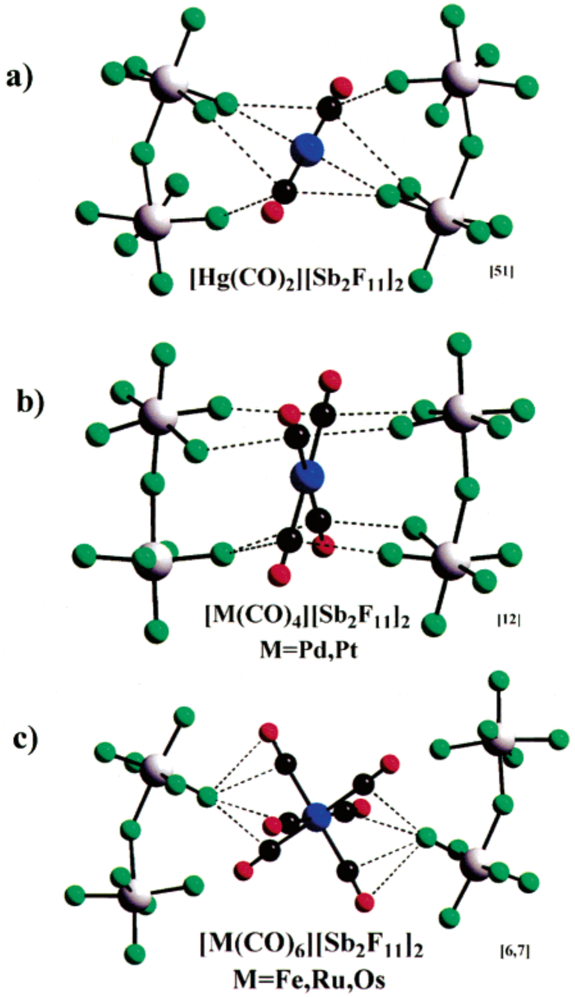

Figure 4. Extended molecular structures of (a) $[Hg(CO)_2][Sb_2F_{11}]_2$, (b) $[M(CO)_4][Sb_2F_{11}]_2$ (M = Pd, Pt), and (c) $[M(CO)_6][Sb_2F_{11}]_2$ (M = Fe, Ru, Os). Only significant F−C contacts are shown.

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(68) Jones, P. G. *Z. Naturforsch., B* **1982**, *37*, 823.

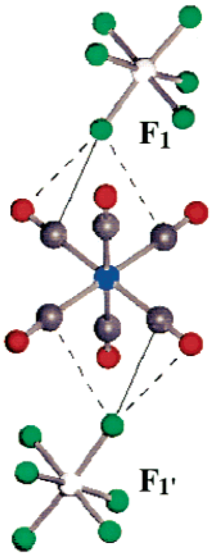

Figure 5. Formula unit of $[M(CO)_6][SbF_6]_2$ (M = Fe, Ru, Os).[6,7]

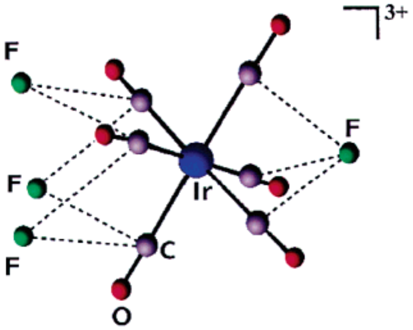

Figure 6. Molecular structure of the solvated cation in $[Ir(CO)_6][SbF_6]_3 \cdot 4HF$.[8]

tacts.[8] Finally the cation $[W(CO)_6(FSbF_5)]^{+}$ [4] and a repeat unit of the polymeric $[\{Mo(CO)_4\}_2(F_2SbF_4)_3]^{+}$ [3] are combined into Figure 7.

To focus on the metal carbonyl cations and the nature of metal–CO bonding in solid-state compounds, we have omitted any discussion on the structures and conformations of the $[Sb_2F_{11}]^-$ anions, which have been discussed by us very recently.[2,12] The structural data, all but four from our laboratories, are supplemented by detailed vibrational assignments and DFT calculations,[12,13,34] to be discussed below.

The data in Tables 3 and 4 are arranged to discuss in order crystallographic details, coordination geometries of the cations, internal bond parameters combined with vibrational data, and finally extended structures, formed by significant interionic or intermolecular interactions.

2.3.2. Crystal Data. Four isostructural series are listed in Table 3: the pairs $[M(CO)_4][Sb_2F_{11}]_2$ (M = Pd, Pt,[2,12] and $[M(CO)_5Cl][Sb_2F_{11}]_2$ (M = Rh, Ir)[39] and the triads $[M(CO)_6][Sb_2F_{11}]_2$ and $[M(CO)_6][SbF_6]_2$ (M = Fe,[7] Ru,[6] Os[6]). The unit cell volumes *V* of the four salts formed by the 5d metals Pt, Ir, and Os are only slightly smaller by 0.4–0.9% than are the volumes of the salts formed by the 4d metals Pd, Rh, and Ru, while bond parameters and spectroscopic properties within each pair[12,39] or triad[6,7] are very similar. The observed "lanthanide contraction" is attributed to relativistic effects[63,69] and stronger interionic contacts found for the 5d complexes. For a fifth isostructural pair listed in Table 4, *cis*-$M(CO)_2(SO_3F)_2$ (M = Pd, Pt[70,71]), the volume of the Pt compound is larger by about 4.1% and the structural and spectroscopic data differ slightly. In both compounds comparatively weak inter- and intramolecular C- - -O interactions are observed.[37,71] The pair $[Rh(CO)_4][M_2Cl_7]$ (M = Al, Ga[55]) is also isostructural. The smaller unit cell volume for the Ga salt is in part due to the different temperatures of the X-ray studies, 143 K for the Ga species and 293 K for the Al compound.[55]

2.3.3. Coordination Geometries. Except for the binuclear cation $[c\text{-}Pd_2(\mu\text{-}CO)_2]^{2+}$,[72] the only cation of those listed in Tables 3 and 4 with bidentate bridging (η^2) CO groups and strong metal–metal bonding reported by us, and the dinuclear cation $[\{Mo(CO)_4\}_2(\mu\text{-}F_2SbF_4)_3]^+$ (Figure 7) as a repeat unit in polymeric $[\{Mo(CO)_4\}_2(\mu\text{-}F_2SbF_4)_3]_x[Sb_2F_{11}]_x$[3] with bidentate bridging $(F_2SbF_4)^-$ ligands, all cations or molecular species listed in Tables 3 and 4 are essentially mononuclear with regular coordination geometries. Exceptions are both seven-coordinated moieties in group 6, which are extensively distorted.[3,4] This is not unexpected for seven-coordinated species, as the carbonyl bromides and iodides of tungsten(II) and molybdenum(II) indicate.[73] The cation $[W(CO)_6(FSbF_5)]^{+}$ [4] shown in Figure 7 has a distorted C_{2v}-capped trigonal-prismatic structure with a variation in W–C distances of 0.16 Å and very irregular bond angles. The $Mo(CO)_4F_3$ moiety, found within the polymeric framework, is more regular with a 4:3 geometry.[3] Judging by the number of IR and Raman bands in the CO stretching range, both metal carbonyl moieties have C_1 symmetry.

All remaining geometries are regular, and all homoleptic species are centrosymmetric (O_h, D_{3h}, D_{4h}, $D_{\infty h}$). Only for $[M(CO)_4]^{2+}$ (M = Pd, Pt) are very slight indications for small distortions and a breakdown of the mutual exclusion rule for Raman- and IR-active vibrations noted.[12] The approximate point groups are listed in Tables 3 and 4. The coordination geometries and d^n-electron configurations (EAN) encountered are as follows. (i) Octahedral d^6 with an EAN of 18 is found in 11 examples. (ii) Square planar d^8 with an EAN of 16 is found in 7 examples as well as in *cis*-$Pt(CO)_2Cl_2$[67] and a limited number of structurally characterized halo carbonyl anions and complexes of palladium(II) and platinum(II).[23] (iii) Linear d^{10} with a valence electron count of 14 is limited to 3 examples and Au(CO)Cl.[68] For a recent addition, trigonal-bipyramidal $[Co(CO)_5]^+$, a d^8 configuration is found with 18e in the valence shell of Co(I).[59]

Both linear and square-planar geometries have not been observed previously in homoleptic metal carbonyl compounds, where any departure from an effective atomic number of 18 is usually associated with strongly oxidizing or reducing characteristics. However, in many coordination compounds, in particular in isoelectronic cyano metalate anions,[74] linear (d^{10}) and square-planar

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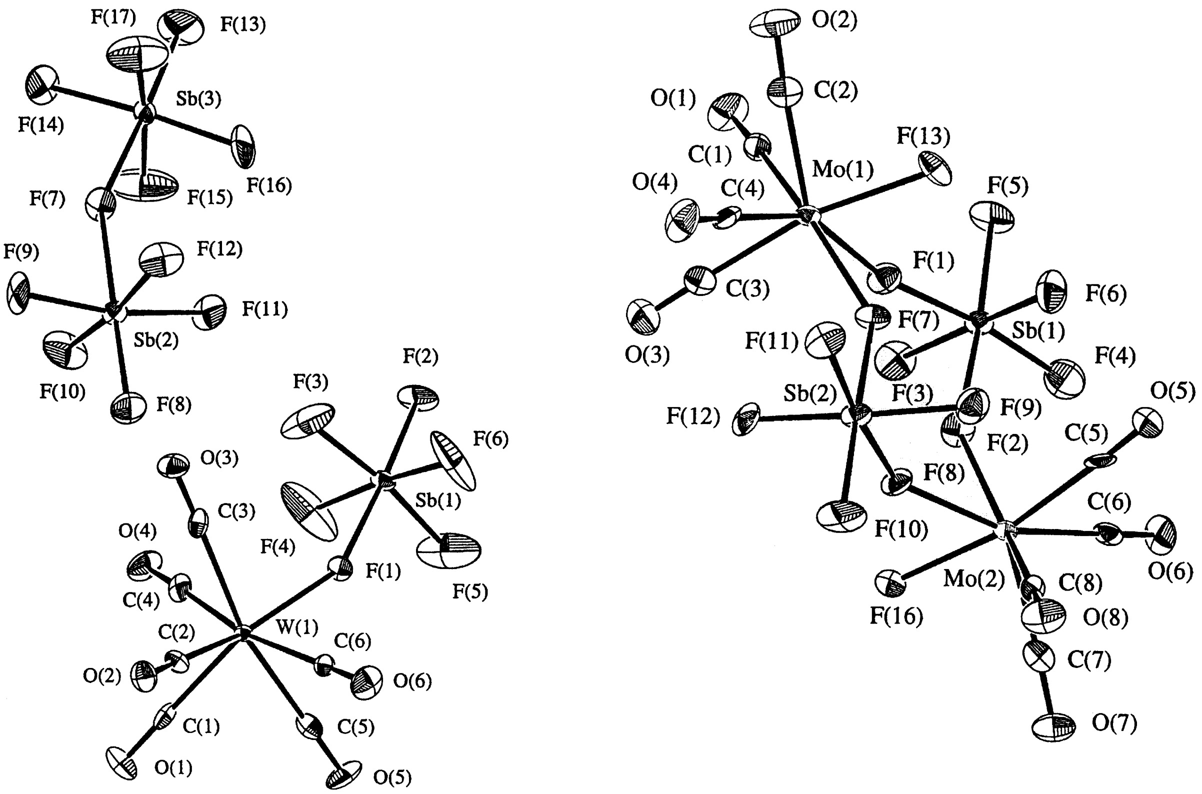

Figure 7. (a, left) Molecular structure of $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$.[4] (b, right) Repeat unit of the polymeric $[\{Mo^{II}(CO)_4\}_2[F_2SbF_4)_3]^+{}_x$ cation.[3]

(d^8) configurations are quite common, together with octahedrally coordinated complexes.

On the other hand, tetrahedral or trigonal geometries, odd-numbered d-electron configurations (d^5, d^7, d^9), and complexes or cations with paramagnetic ground states have so far not been encountered among metal carbonyl cations and their derivatives.[1,2] The $[Co(CO)_5]^+$ ion[59] shown in Figure 3 is the first five-coordinate (trigonal-bipyramidal) metal carbonyl cation. As the data in Table 4 show, axial Co−C bond lengths are shorter than equatorial ones.[59] Furthermore, none of these complexes with lower coordination numbers can be formed by controlled thermal decomposition of octahedral, square planar, or linear precursors, as discussed above.

In summary, all metal carbonyl cations have, in agreement with theoretical calculations,[13,18,34] simple undistorted coordination geometries for d^{10}, d^8, and d^6 configurations. The d^4 ions or moieties in group 6 are extensively distorted, as discussed. All attempts to synthesize with $[Fe(CO)_6]^{3+}$ a cation with a d^5 configuration have been unsuccessful.[1,2] It is interesting to note that $[Fe(CO)_6]^{2+}$ can withstand oxidation attempts by powerful oxidizers such as F_2 and NiF_4.[7] It is apparent that CO in σ-bonded compounds remains an intermediate to strong field ligand,[75] which induces in octahedral d^6 complexes spin pairing and does not allow formation of complexes with odd d-electron counts.

2.3.4. Internal Bond Parameters and Spectroscopic Properties. The internal bond parameters ($d(M-C)_{av}$, $d(C-O)_{av}$) and the vibrational properties ($\nu(CO)_{av}$, f_{CO}) for metal carbonyl salts and their derivatives are listed in Tables 3 and 4. They provide a direct and, for the most part, accurate measure of the strength of metal−carbon and carbon−oxygen bonds in the cations and their derivatives.[2] While a direct comparison of the vibrational properties ($\nu(CO)$, f_{CO}) for all species listed is possible, M−C and C−O distances are judged by comparison to data for M−CO complexes listed for each metal in the Cambridge data collection.[76] Such a comparison is not possible for Hg and Pd, where $[Hg(CO)_2]^{2+}$ [37] and the Pd(II) compounds with terminal CO groups reported here have no precedents.[76] The interpretation of the data is clear. Long M−C bonds indicate in thermally stable metal carbonyl cations the absence of metal to CO π back-bonding. The observed short C−O bonds, as seen in Table 3, are almost indistinguishable for the 14 structures listed. High $\nu(CO)_{av}$ and f_{CO} values are in metal carbonyl cations attributed to a polarization of the C−O bond, an electrostatic effect induced by the M^{m+} cation rather than to a covalent effect, arising from electron donation from the 5σ orbital of CO to the metal center.[77]

As can be seen from the data in Tables 3 and 4, all M−C internuclear distances fall into a narrow range of 2.0 ± 0.1 Å. They are for each individual metal among the longest M−C bond lengths listed.[76] The C−O internuclear distances listed are at the shorter end of the data found in the Cambridge data collection,[76] shorter than a q_l value of 1.132 Å on the basis of 10 022 examples. The observed "bunching" of C−O bond lengths,

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[74] Sharpe, A. G.; Chadwick, B. M. *Adv. Inorg. Chem. Radiochem.* **1966**, *8*, 83.

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[77] Goldman, A. S.; Krogh-Jesperson, K. *J. Am. Chem. Soc.* **1996**, *118*, 12159.

different esd values, and thermal motions make an interpretation uncertain and unreliable.

A much clearer differentiation between individual carbonyl complexes listed in Tables 3 and 4 is possible by using vibrational data. The CO stretching wavenumbers can be measured easily with an accuracy of ± 2 cm^{-1}. For homoleptic metal carbonyl cations with terminal CO ligands, $\nu(\mathrm{CO})_{\mathrm{av}}$ falls between 2280 cm^{-1} (for $[\mathrm{Hg(CO)_2}]^{2+}$)[37] and 2116 cm^{-1} (for $[\mathrm{Re(CO)_6}]^{+}$),[78] a value slightly lower than 2143 cm^{-1} for free CO. The corresponding f_{CO} values for both cations span a range of about 2.0×10^2 N m^{-1}, while $d(\mathrm{CO})_{\mathrm{av}}$ values for compounds listed in Tables 3 and 4 are nearly identical.

When vibrational data in Tables 3 and 4 are compared, three clear trends emerge. (i) $\nu(\mathrm{CO})_{\mathrm{av}}$ and f_{CO} are, in complexes with a common geometry, directly proportional to the oxidation state of the central metal. (ii) In complexes with metals in identical oxidation states, $\nu(\mathrm{CO})_{\mathrm{av}}$ and f_{CO} are inversely proportional to the coordination number. (iii) Substitution of CO in homoleptic cations by anionic monodentate ligands ($\mathrm{Cl^-}$, $\mathrm{SO_3F^-}$, $\mathrm{SbF_6^-}$) will reduce both $\nu(\mathrm{CO})_{\mathrm{av}}$ and f_{CO}.

If we combine the trends summarized above and include also $\mathrm{(CF_3)_3BCO}$[58] and the formyl cation $\mathrm{HCO^+}$,[4,25] for which accurate structural[79] and vibrational data[80] are known, it is possible to identify the homoleptic, superelectrophilic metal carbonyl cations for each coordination geometry, where π back-bonding is absent and CO is bound to the metal ion by σ bonding only. Since for $\mathrm{HCO^+}$, due to vibrational coupling, $\nu(\mathrm{CO})$ is at 2184 cm^{-1} rather low, the CO stretching force constant f_{CO} (10^2 N m^{-1}) is used. The internuclear C−O distances in Å are included in parentheses. The following order of decreasing f_{CO} values (in 10^2 N m^{-1} emerges: $\mathrm{HCO^+}$ 21.3 (1.105)[79,80] > $[\mathrm{Hg(CO)_2}]^{2+}$ 21.0 (1.104(12))[37] > $[\mathrm{Ir(CO)_6}]^{3+}$ 20.8 (1.090(9))[8,30,31] > $\mathrm{(CF_3)_3BCO}$ 20.8(1.11(2))[58] > $[\mathrm{Pt(CO)_4}]^{2+}$ 20.6 (1.110(9))[12] > $[\mathrm{Os(CO)_6}]^{2+}$ 19.71 (1.102(7))[6] > $[\mathrm{Re(CO)_6}]^{+}$ 18.1 (1094-(10)).[78,81]

With all metals from the third transition series, where relativistic effects are high, f_{CO} values gradually decrease in small increments with increasing coordination number. It is noted that octahedral $[\mathrm{Ir(CO)_6}]^{3+}$ [8] and square-planar $[\mathrm{Pt(CO)_4}]^{2+}$ [12] have traded positions in the above ordering on account of the higher oxidation state of the former.

There are a number of plausible explanations for the observed decrease in CO bond strength with increasing coordination number. Among these are a reduced s orbital contribution to the metal orbitals of σ symmetry or a reduced C−O bond polarization[77] for each M−CO moiety as the number of CO ligands increases. A third explanation involves what may be called solid-state effects, which involve the observed formation of extended structures for superelectrophilic carbonyl cations and their derivatives, which affect $\nu(\mathrm{CO})$. These effects will be discussed in the following sections.

2.3.5. Extended Molecular Structures. All superelectrophilic metal carbonyl fluoroantimonates listed in Table 3 form extended structures, mostly via significant, mainly interionic secondary[82] C- - -F interactions (see Figures 4−6). In these interactions, the carbon atoms of the CO ligands act as electrophilic acceptor sites. The electrophilicity of carbon is seemingly directly proportional to the oxidation state of the metal. The C- - -F interactions are detected by a careful analysis of the structural data for the compounds shown in Tables 3 and 4.[2,12]

The results are summarized briefly as follows. (i) While the molecular geometries for octahedral, trigonal-bipyramidal, square-planar, and linear metal carbonyl cations are very regular (see Figures 3−6) as discussed before, only the M−C−O bond angles will invariably depart from linearity by about 2−4°.[2] This is explained by secondary interactions[82] of C atoms of the cations with F atoms of the anions.[2,12] (ii) The $[\mathrm{Sb_2F_{11}}]^-$ anions are extensively distorted from the D_{4h} ground-state conformation,[83] by bending and rotation of the equatorial $\mathrm{SbF_4}$ groups in the dioctahedral anion. The distortions are expressed in terms of the Sb−F−Sb bridge angle α and the dihedral angle ψ.[12,78] In $[\mathrm{Sb_2F_{11}}]^-$ salts with unipositive cations such as $[\mathrm{Au(CO)_2}]^{+}$ [17] and $[\mathrm{Rh(CO)_4}]^{+}$,[55] with the latter studied only by vibrational spectroscopy,[12] the anion is undistorted and has D_{4h} symmetry. The same is reported for the anion in $[\mathrm{Re(CO)_6}][\mathrm{Re_2F_{11}}]$.[78] We have suggested that the $[\mathrm{Sb_2F_{11}}]^-$ anion will distort, usually toward C_1 symmetry, to facilitate the formation of stronger C- - -F contacts only in salts with superelectrophilic metal carbonyl cations. The anion $[\mathrm{SbF_6}]^-$ has so far only been found in salts with octahedral cations (see Table 3). Only slight distortions are found for $[\mathrm{SbF_6}]^-$, most noticeably in the very recent molecular structure of $[\mathrm{Ir(CO)_6}][\mathrm{SbF_6}]\cdot 4\mathrm{HF}$,[8] which will be discussed more fully below. (iii) In the molecular structures depicted in Figure 4, significant C- - -F contacts between both constituent ions are directly observed. Their significance is judged by comparison to the sum of the van der Waals radii as listed by Bondi[84] (3.17 Å for C and F). Both the strength and number of these C- -F interionic contacts depend, as stated, on the oxidation state of the metal and the geometry of the cation. The strongest contacts are found for linear $[\mathrm{Hg(CO)_2}]^{2+}$ [37] (2.653(9) Å) and square-planar $[\mathrm{M(CO)_4}]^{2+}$ (M = Pd, Pt),[12] with the shortest contacts at 2.592(10) Å (Pt) and 2.613(7) Å (Pd), respectively. Limited accessibility to the C atoms in salts with octahedral metal carbonyl cations is a contributing factor for the observation of fewer and weaker interionic interactions in salts with octahedral cations.

The failure to observe any meaningful interionic M- - -F interactions in the recently reported structures of $[\mathrm{M(CO)_4}][\mathrm{Sb_2F_{11}}]_2$ (M = Pd, Pt)[12] clearly indicates that partial positive charges are higher on carbon than they are on the metal, consistent with DFT calculations,[12] because in the square-planar cations both M and C are equally well accessible. This is illustrated here by the extended molecular structures of $[\mathrm{M(CO)_4}][\mathrm{Sb_2F_{11}}]_2$ (M = Pt, Pd) (Figure 4).

In addition to weak interionic C- - -F contacts, there are also for the group 6 salts intercationic C- -F contacts

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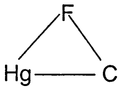
involving the $[SbF_6]^-$ ligands coordinated to W or Mo,[3,4] respectively. In the fluorosulfato derivates *cis*-$M(CO)_2(SO_3F)_2$ (M = Pd, Pt)[70,71] and *mer*-$Ir(CO)_3(SO_3F_3)_3$[38] both inter- as well as intramolecular C- - -O contacts are detected.

A confusing situation is encountered for the $[Rh(CO)_4]$ salts listed in Table 4: for the $[Ga_2Cl_7]^-$ and $[Al_2Cl_7]^-$ salts, there are only a few weak, insignificant C- - -Cl contacts.[55] For $[Rh(CO)_4][Et-CB_{11}F_{11}]$,[85] which is claimed by the authors to be "nonclassical", five reportedly significant Rh- - -F contacts between 3.220 and 3.588 Å are cited. However, all are longer than the sum of the van der Waals radii,[84] estimated to be 3.10 Å. A reevaluation of the deposited structural data by us has revealed 14 C- - -F contacts in the range of 2.926−3.155 Å, all very slightly shorter than Σ(vdW) of 3.17 Å[84] and all omitted by the authors. It hence appears that the claim of "nonclassical"[85] behavior is clearly not in harmony with observable facts.[85]

It should also be mentioned that in *cis*-$Pt(CO)_2Cl_2$[67] the formation of "supramolecular" columns, formed from square-planar molecules by weak C- - -Cl contacts, is reported and that the antiparallel alignment of linear $Au(CO)Cl$[68] molecules in the lattice suggests very weak C- - -Cl contacts as well. Both are strong indications for the presence of electropositive carbon in the molecules.[67,68]

In summary, as we have stated recently,[12] in the molecular structures of thermally stable metal carbonyl fluoroantimonates and their derivatives which are summarized here in Tables 3 and 4, there is no evidence for meaningful single M- - -F interionic contacts shorter than the sum of the van der Waals radii.[84] In $[Hg(CO)_2][Sb_2F_{11}]_2$[1,2,37] for each cation four bifurcated



contacts are found, which help to complete a distorted-octahedral coordination polyhedron for Hg. However, there are more numerous (six) additional C- - -F contacts down to 2.653(9) Å for the cation.[1,2]

Strong support for the observed preference of C- - -F over M- - -F interactions in square-planar and octahedral metal carbonyl cations and derivatives comes from calculated partial charges obtained from a natural population analysis.[2,12,13] In all instances higher positive charges reside on C than on M, while O carries a negative partial charge in the di- and tripositive cations studied here.[2] However, in $[Rh(CO)_4]^+$ rhodium is negatively charged,[12] and the "significant" Rh- - -F contacts claimed by Lupinetti et al.[85] are better interpreted as weak, repulsive interactions.

A very unusual extended structure is found very recently[8] for $[Ir(CO)_6][SbF_6]_3\cdot 4HF$. The cation is shown in Figure 6. While the cation has a regular octahedral structure, vibrational spectra in the CO stretching region are identical with solution data for the compound dissolved in dilute $HF-SbF_5$ and those for $[Ir(CO)_6][Sb_2F_{11}]_3$ (see Table 4), which have been known for some time now.[30,31] The presence of HF solvate molecules in a lattice of a metal carbonyl fluoroantimonate is unprecedented.[1,2] The four HF molecules are in the first instance connected by asymmetric hydrogen bonds and form a tetrahedral $(HF)_4$ cluster. The cluster formation of HF is unusual. In the gas, liquid, or solid phase only H-bonded chains or cycles are encountered.[86] Three of the four F atoms in the cluster form pairs of weak C- - -F contacts of 2.988(10) and 2.971(10) Å, respectively, with the CO groups of the cation.

More unusual is the coordination of the fourth HF molecule in the $(HF)_4$ cluster. The HF molecule is placed along a C_3 axis of the cation and binds in an isotridentate fashion to the adjacent three C atoms. The contact distances of 2.654 Å are surprisingly short and are only surpassed by a single interionic C- - -F contact each in $[Hg(CO)_2][Sb_2F_{11}]_2$[37] and $[M(CO)_4][Sb_2F_{11}]_2$ (M = Pd, Pt),[12] as already discussed. It appears that interionic C- - -F contacts are not found, but the HF molecules, as seen in Figure 2, act as bridges between both constituent ions in the lattice.

There have been two structurally characterized HF solvates reported previously. Both in $La(HF)_2[AsF_6]_3$[87] and in $Pb(HF)[AsF_6]_2$,[88] HF is coordinated over fluorine to La or Pb, respectively, in a monodentate fashion. Bi- or tridentate coordination of HF to C, as found in $[Ir(CO)_6][SbF_6]_3\cdot 4HF$,[8] confirms experimentally the calculated partial charge distribution from natural population analysis.[13] There is further experimental evidence for an electrophilic carbon in $[Ir(CO)_6]^{3+}$. Observations made while recording the IR spectrum of $[Ir(CO)_6][SbF_6]_3\cdot 4HF$ suggest nucleophilic attack of F^- on one of the six CO ligands, resulting in its transformation in a fluoroacyl ligand[89,90] according to

$$[Ir(CO)_6]^{3+} + F^- \rightarrow [Ir(CO)_5(C(O)F)]^{2+} \qquad (5)$$

$[Ir(CO)_6]^{3+}$ is the only tripositive metal carbonyl cation known,[1,2] which has now been structurally characterized.[8] The molecular structure of the salt provides an insight into the way superelectrophilic cations are solvent stabilized at the carbon of the CO ligands in $HF-SbF_5$, where they exist and have fair solubilities.[2] It seems that the high lattice energies, expected for di- and tripositive cations, are compensated for by high solvation energies. It also becomes clear why superelectrophilic metal carbonyl cations, just like the related group of carbocations,[91] are only stable in superacids as solvents, where they are generated and obtained as fluoroantimonates.[1,2]

2.3.6. Solid-State Structures of Molecular CO Adducts of Copper(I) and Silver(I). A number of molecular structures have been reported for the polycarbonyl complexes of Cu(I) and Ag(I) and reviewed recently.[52,53] The structural features reported differ from those of σ-carbonyl cations[1,2] on five accounts: (i) any

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(86) *Gmelins Handbook of Inorganic Chemistry*; Springer-Verlag: Berlin, 1982; Vol. Suppl. 3, p 79.

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Table 5. Summary and Comparison between Metal Carbonyl Cations and Complexes of Cu(I) and Ag(I)

features and properties	homoleptic metal carbonyl cations: $[M(CO)_n]^{m+}$	Cu(I) and Ag(I) CO complexes $M(CO)_nY$ ($n = 1-4$)
distribn	5d: Hg, Au, Pt, Ir, Os, Re 4d: Pd, Rh, Ru, Tc 3d: Mn, Fe, Co	4d: Ag 3d: Cu
metal oxidn state	+1 to +3	+1
reacn media	superacids (SbF5, HF−SbFs, etc.)	aprotic solvents
synth methods	(i) irreversible CO addn to transient, soft M^{n+} ($n = 1-3$) (ii) oxidative carbonylation of metal carbonyls and derivs	reversible, pressure- and temp-controlled CO addition to M^+ salts with weakly coord anions, Y^-
composition	3 types of $[M(CO)_n]^{m+}$: $n = 2$, $D_{\infty h}$, d^{10}; $n = 4$, D_{4h}, d^8; $n = 6$, O_h, d^6	polycarbonyl complexes $M(CO)_nY$, $n = 1-3, 4$; depending on P_{CO}, T
characterizn	extensively characterized by analytical, spectroscopic (IR, Raman, NMR) methods and X-ray diffraction and supported by DFT calculations	characterized by computational methods; limited no. of molecular structures; vibrational spectra in the CO stretching region only
thermal stability	stable between 100 and 250 °C as $[Sb_2F_{11}]^-$ or $[SbF_6]^-$ salts	unstable under ambient conditions
thermal decomposition	complex, irrev complete loss of CO, M and COF_2 formed	stepwise rev loss of CO
strength of CO bond ($\bar{\nu}_{CO}$, f_{CO}, d_{CO})	proportional to (oxidn state of M)/(coord no. of M)	strong anion dependence of ν_{CO}
extended struct	formed via C−F contacts	M- - -F contacts M- - -Y covalent bonds
partial atomic charges	$q_C > q_M \gg q_O$ $q_C - q_M$ is positive	$q_M > q_C \gg q_O$ $q_C - q_M$ is negative

interionic or intermolecular contacts to the C atoms of the CO ligands are absent; (ii) relatively short, covalent contacts between anions and M^+, M = Cu, Ag are found in a number of monocarbonyl complexes; (iii) in addition to anion−cation contacts, bent $Cu(CO)_2$ moieties with C−Cu−C bond angles of about 120° are found;[53] (iv) in complexes of Cu(I) and Ag(I), ν(CO) is found to be anion dependent with wide variations noted;[53] (v) some Ag- - -F contacts of ~3 Å found in $Ag[B(OTeF_5)_4]$[92] are retained on CO addition to give $[Ag(CO)_n][B(OTeF_5)_4]$[93] ($n = 1, 2$) with Ag- - -F contacts of similar strength also being found in $Ag[Al(OR_F)_4]$ complexes.[94]

These observations set the polycarbonyl complexes of Cu(I) and Ag(I) clearly apart from the σ-carbonyl cations[1,2] and other metal carbonyls[48−51] and allow three conclusions: (i) the partial charge distribution in the M−C−O moiety (M = Ag, Cu) is different with q_M more positive than q_C, consistent with theoretical calculations;[34,53] (ii) this polarity is retained on coordination to CO, and multiple, reversible CO addition to the metal center is possible; (iii) on the other hand, relativistic effects for Au^+ and Hg^{2+} strengthen the σ bonds to CO formed by these metals and thermally stable salts can be obtained.[17,37] A comparison between σ-carbonyls and the polycarbonyl complexes of Cu(I) and Ag(I) is found in Table 5. The proposed subdivision into σ-metal carbonyl and polycarbonyl complexes is confirmed by "perturbation" calculations for linear d^{10} dicarbonyl species.[95]

The observation that Ag- - -F contacts of ~3.0 Å are found for $Ag[B(OTeF_5)_4]$[92] and various $Ag[Al(OR_F)_4]$ species[94] casts serious doubt on the frequently stated claim[52,53,93,95] that such M- - -F contacts, which are not found for σ-carbonyls[1,2] (see Table 5), are an "essential feature in nonclassical cationic CO salt with F-containing anions".[53]

2.3.7. Comparison Between σ-Carbonyls and Carbocations: Structural Aspects.

Secondary interionic contacts of the type C- - -X (X = F, Cl, O) are also observed in the solid-state structures of stable carbocations[91] with counteranions such as $[EF_6]^-$ and $[E_2F_{11}]^-$ (E = As, Sb), $[SbCl_6]$, and $[AlCl_4]$.[96−98] With NMR as the principal technique for the study of carbocations,[91,96] the number of reliably determined molecular structures is quite small. On the basis of the limited information[96−98] available, it appears that C- - -F contacts are less numerous, about 1 or 2 per carbon, and are relatively weak. Contact distances are usually 0.1−0.4 Å shorter than 3.17 Å, the sum of the van der Waals radii.[84] Differences in superelectrophilic metal carbonyl fluoroantimonates[2] described here are largely 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 last species, where up to five C- - -F contacts per CO ligand are observed.[2]

Since there is only a single electrophilic carbon in most carbocations,[91] ion pairing is more common than the formation of one-dimensional extended structures.[96−98] Despite these differences, the presence of electrophilic carbon in carbocations[91] and in σ-metal carbonyl cations provides a strong link between the two groups. Both form extended structures with carbon as acceptor. Both groups are generated exclusively in superacids such as $HF-SbF_5$ as discussed above, are only existent in solutions of superacid, and form stable, isolable salts with superacid anions such as the fluoroantimonates. Solvent stabilization in $HF-SbF_5$ should also be very similar for both types of cations, even though equally conclusive evidence for C- - -F(H) contacts, as provided by the recent structure of $[Ir(CO)_6][SbF_6]_3 \cdot 4HF$, appears to be lacking for the carbocations.[91,96−99]

In summary, metal σ-carbonyls[1,2] and stable carbocations[5,54,91] are both generated exclusively in superacids,[9,54] have electrophilic carbon centers, are stabilized in the solid state by very similar superacid anions,[45] and form extended structures. For these reasons we strongly object to any classification of the σ-carbonyls as "clas-

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sical" or "nonclassical" CO complexes, which for carbocations is in violation of IUPAC recommendations[100] as discussed by us previously.[1]

Since the chemistry of metal carbonyl cations is just beginning to emerge, there will certainly be many examples of similar reactivities established in the future. It should be remembered that carbocation chemistry has recently celebrated its 100th birthday[99] while metal carbonyl cations generated in superacids date back to 1990.[101]

2.4. Spectroscopic Studies of σ-Carbonyl Cations and Their Derivatives. 2.4.1. General Comments. The discussion in this section will be limited, because all σ-carbonyl cations and their derivatives have been routinely characterized by IR and Raman spectroscopy, with the results supported by DFT calculations as well as by ^{13}C NMR spectroscopy, included in our earlier review.[1] A more detailed ^{13}C NMR study on the dynamics of Rh(I), Ag(I), and Au(I) carbonyls in HSO_3F[102] is in preparation.

Hence, the discussion here is concerned (a) with vibrational spectra of octahedral metal carbonyl complexes and (b) with a brief discussion of the results of FT microwave spectroscopy obtained by M. C. L. Gerry and his group[103−105] on nine linear four atomic species of the type XMCO (M = Cu, Ag, Au; X = F, Cl, Br) in the gas phase.

2.4.2. Vibrational Spectra of Metal Carbonyl Cations and Related Species. The use of vibrational spectroscopy is presented here in order to (i) support our view of bonding in σ-metal carbonyl cations with extended structures in the solid state,[1,2] (ii) illustrate the prudent use of ab initio calculations in support of vibrational assignments, and (iii) extend vibrational assignment of octahedral metal carbonyl cations also to neutral[48−50] and anionic species with octahedral geometries.[51]

We have chosen a series of four structurally characterized isoelectronic and isosteric octahedral metal carbonyl complexes: neutral $W(CO)_6$[106] and the three cations $[Re(CO)_6]^+$,[78] $[Os(CO)_6]^{2+}$,[6] and $[Ir(CO)_6]^{3+}$.[8] Very detailed vibrational studies of $W(CO)_6$ (as well as of $Mo(CO)_6$ and $Cr(CO)_6$)[107,108] and of $[Re(CO)_6]^+$ (as well as of $[V(CO)_6]^-$)[81] have been known for some time. Vibrational assignments for $[Os(CO)_6]^{2+}$ [6] and $[Ru(CO)_6]^{2+}$[6] have so far not been published. The vibrational analysis of $[Ir(CO)_6]^{3+}$ has been completed recently.[8] A detailed vibrational analysis for $[Fe(CO)_6]^{2+}$ [7] has also been reported by us. A density functional study of the vibrational spectra for all known octahedral $M(CO)_6$ species in groups 5−9 is available,[13,109] which includes intensities of IR bands, stretching force constants (f_{CO} and f_{MC}), and calculated partial atomic charges. The molecular structures of the anions $[M(CO)_6]^-$ [110] (M = Nb, Ta) complement an extensive body of accurate structural, vibrational, and computational information.

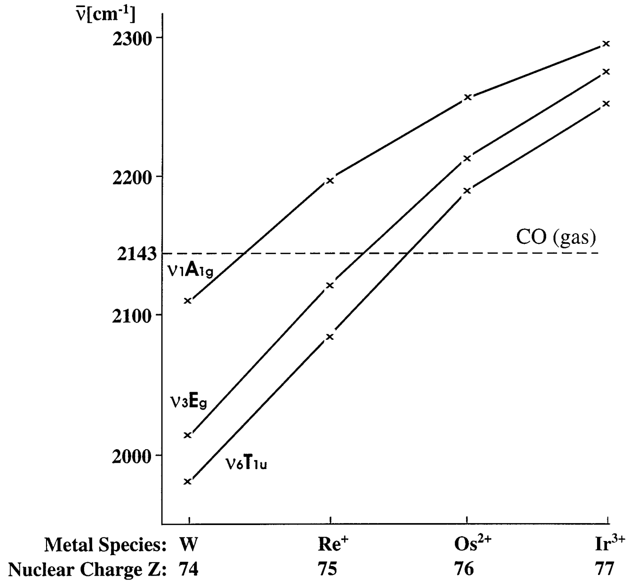

Figure 8. Plot of the CO stretching fundamentals for octahedral $[M(CO)_6]^{m+}$ (M = W^0, Re$^+$, Os^{2+}, Ir^{3+}; in cm^{-1}) versus the nuclear charge *Z*.[8]

The fundamental vibrational frequencies for isoelectronic and isosteric $[M(CO)_6]^{m+}$ (M = W, Re, Os, Ir; $m = 0-3$) are collected in Table 6 in order of increasing wavenumbers, together with the corresponding calculated values. Also listed are experimental and calculated CO stretching force constants, f_{CO}, and calculated M−C stretching force constants, f_{MC}. Also included are calculated atomic charges from a natural population analysis[13] for the M−C−O group (M = W, Re$^+$, Os^{2+}, Ir^{3+}), which have been cited and discussed in the preceding section.

Inclusion of $[Ta(CO)_6]^-$ in this comparison is not possible, on account of the incomplete vibrational information, even though structural[110] ($d_{Ta-C} = 2.083(6)$ Å, d_{C-O} 1.149(8) Å) and computational data[13] correlate very well. A plot of the three CO stretching fundamentals $\nu_1(A_{1g})$, $\nu_3(E_g)$, and $\nu_6(T_{1u})$ against their nuclear charge *Z* for all four $M(CO)_6$ species is shown in Figure 8.

As can be seen in Table 6, agreement between experimental and calculated wavenumbers is generally very good. As observed previously,[6,7] calculated values for the CO stretching fundamentals ν_1, ν_3, and ν_6 are overestimated 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.

Differences in M−C stretching modes ν_2, ν_4, and ν_8 as well as in the bending fundamentals ν_7, ν_{12}, and ν_{10} are very small for $W(CO)_6$ and $[Re(CO)_6]^+$, reflected in $\nu(M-C)_{av}$ values of 395 and 393 cm^{-1}, respectively, and f_{MC} values of 2.43×10^2 and 2.40×10^2 N m^{-1}. An increase of the ionic charge to 2+ and 3+ results in a

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Table 6. Vibrational Fundamentals, Force Constants, and Partial Charges for $[M(CO)_6]^{n+}$ (M = W, Re, Os, Ir; n = 0−3)

(i) Vibrational Fundamentals (cm^{-1})

	$W(CO)_6$		$[Re(CO)_6]^+$		$[Os(CO)_6]^{2+}$		$[Ir(CO)_6]^{3+}$	
assignment	obsd[a]	calcd[b]	obsd[c]	calcd[d]	obsd[e]	calcd[d]	obsd[f]	calcd[d]
$\nu_1\ \nu_{CO}(A_{1g})$	2126	2095	2197	2171	2258	2237	2295	2272
$\nu_3\ \nu_{CO}(E_g)$	2021	1999	2122	2103	2214	2188	2278	2245
$\nu_6\ \nu_{CO}(T_{1u})$	1998	1977	2085	2080	2189	2166	2254	2228
$\nu_7\ \delta_{MCO}(T_{1u})$	587	581	584	594	560	567	531	528
$\nu_{12}\ \delta_{MCO}(T_{2u})$	522	520	522	525	509	509	480	477
$\nu_{10}\ \delta_{MCO}(T_{2g})$	482	468	486	480	480	471		449
$\nu_2\ \nu_{MC}(A_{1g})$	426	430	441	440	429	428	422	402
$\nu_4\ \nu_{MC}(E_g)$	410	415	426	418	409	401		373
$\nu_8\ \nu_{MC}(T_{1u})$	374	382	356	366	344	336		319
$\nu_5\ \delta_{MCO}(T_{1g})$	362	350	354	350	345	339		326
$\nu_9\ \delta_{MCO}(T_{1u})$	82	78	82	92	145	101	138	107
$\nu_{11}\ \delta_{CMC}(T_{2g})$	81	81	82	89	142	93		95
$\nu_{13}\ \delta_{CMC}(T_{2u})$	61	56		69	96	77		83
$\nu_{M-C(av)}$	395	398	393	396	380	373		351
$\nu_{C-O(av)}$	2025	2004	2116	2103	2209	2185	2269	2241

(ii) Force Constants (10^2 N m^{-1})

	$W(CO)_6$		$[Re(CO)_6]^+$		$[Os(CO)_6]^{2+}$		$[Ir(CO)_6]^{3+}$	
	obsd[a]	calcd[d]	obsd[c]	calcd[d]	obsd[e]	calcd[d]	obsd[f]	calcd[d]
f_{CO}	16.6	16.2	18.1	17.8	19.7	19.1	20.8	19.9
f_{MC}		2.43		2.40		2.16		1.92

(iii) Partial Atomic Charges (1/e)[d]

	$W(CO)_6$	$[Re(CO)_6]^+$	$[Os(CO)_6]^{2+}$	$[Ir(CO)_6]^{3+}$
q_M	−0.95	−0.69	−0.35	0.11
q_C	0.56	0.58	0.60	0.59
q_O	−0.40	−0.30	−0.20	−0.11

[a] References 106 and 107. [b] Reference 109. [c] Reference 108. [d] Reference 13. [e] Reference 6. [f] Reference 8.

marked decrease of both $\nu(M-C)_{av}$ and f_{MC} for $[Os(CO)_6]^{2+}$ and $[Ir(CO)_6]^{3+}$, based on the positions of ν_2, ν_4, and ν_8 for the latter species. It hence appears that the initial increase of the ionic charge from 0 to 3+ results initially in a very slight lengthening of the M−CO bond, which becomes more pronounced for $[Os(CO)_6]^{2+}$ and even more so for $[Ir(CO)_6]^{3+}$. The observed lengthening of the M−C bond is explained by decreasing π back-bonding as the oxidation state of the metal increases.

While the M−C bonds lengthen initially very slightly within the isoelectronic $M(CO)_6$ series with increasing nuclear charge and then increase more noticeably, the opposite is true when $\nu(CO)$ is monitored for the three CO stretching fundamentals $\nu_1(A_{1g})$, $\nu_3(E_g)$, and $\nu_6(T_{1u})$, as the ionic charge increases from 0 to 3+ as seen in Figure 8. This is particularly true for $\nu_1(A_{1g})$, the totally symmetric "breathing" vibrations, which initially increase steeply, followed by a leveling off for $[Os(CO)_6]^{2+}$ and $[Ir(CO)_6]^{3+}$. For both ν_3 and ν_6 the curvature at the end is less pronounced, as is the case for $\nu(CO)_{av}$, reported by us previously[1] for $[M(CO)_6]$ species ranging from $[Hf(CO)_6]^{2-}$ to $[Ir(CO)_6]^{3+}$.

In addition the overall band separation $\nu_6-\nu_1$ for all three fundamentals decreases with increasing ionic charge from 141 cm^{-1} for $W(CO)_6$[107,108] over 112 cm^{-1} for $[Re(CO)_6]^+$ [81] and 69 cm^{-1} for $[Os(CO)_6]^{2+}$ [6] to 41 cm^{-1} for $[Ir(CO)_6]^{3+}$.[8,30,31] The observed increase in $\nu(CO)$ for all fundamentals with increasing oxidation state of M suggests increased σ bonding with a concomitant polarization of the C−O bond.[77]

The close correspondence of observed and calculated wavenumbers for all 13 fundamentals for the four $[M(CO)_6]$ species in Table 6 with $\nu(CO)_{av}$ increasing from 2025 cm^{-1} for $W(CO)_6$ to 2269 cm^{-1} for $[Ir(CO)_6]^{3+}$, including the smooth trends for all three fundamentals in Figure 8, provide a convincing argument against the view[52,53,93] that there are two types of carbonyls, "nonclassical" and "classical" with $\nu(CO)$ of free CO at 2143 cm^{-1} as dividing line.

With the recent developments in regard to σ-bonded metal carbonyl cations reviewed here and elsewhere[1,2] and the highly reduced metal carbonylates which are complementary to the metal carbonyl cations,[51,111] CO must be viewed as a far more versatile ligand than had been assumed previously.[48] Consequently, the range of $\nu(CO)$ for terminal CO ligands extends now from about 1450 to 2300 cm^{-1}, roughly 3 times as wide than previously assumed (1850−2125 cm^{-1}).[48] Equally wide is the spectrum of chemical reactivity, with metal carbonyls ranging from powerful nucleophiles[51,111] to superelectrophiles.[1,2,5]

The synergic bonding description[112,113] in its modified form, proposed by us,[1] is sufficiently adequate to describe metal−CO bonding in this wide range of carbonyl complexes by invoking a wider variation in bonding contributions made by σ donation and π back-donation. As discussed in this review, for superelectrophilic σ-bonded metal carbonyl cations,[1,2] the strength of the C−O bond, expressed in terms of $\nu(CO)$, is in all metal CO compounds inversely proportional to the coordination number of the complex (molecule or ion) and directly proportional to the oxidation state of the

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(113) Chatt, J.; Duncanson, J. A. *J. Chem. Soc. A* **1953**, 2939.

central metal. The presence of ancillary, anionic ligands in the complex may reduce ν(CO) again, as discussed.

Hence, in any group of metal carbonyl compounds ν(CO) may be found on either side of 2143 cm^{-1}, ν(CO) of free CO, as selected examples will illustrate. For homoleptic, superelectrophilic metal carbonyl cations linear $[Hg(CO)_2]^{2+}$ [37] has at 2281 cm^{-1} the highest $\nu(CO)_{av}$ wavenumber of any metal carbonyl complex.[1,2] In the seven-coordinated tungsten(II) cation $[W(CO)_6(FSbF_5)]^+$ [1,2,4] $\nu(CO)_{av}$ is at 2124 cm^{-1}, below 2143 cm^{-1}. On the other side, metal carbonylate anions usually have bands well below 2000 cm^{-1} (e.g. $[V(CO)_6]^-$ at 1897 cm^{-1} [81]); however, in the anionic platinum(IV) derivate $[PtCl_5(CO)]^-$ ν(CO) is at 2191 cm^{-1}.[114]

For σ-bonded metal carbonyl cations,[1,2] ν(CO) may be as high as 2295 cm^{-1} ($\nu_1(A_{1g})$ of $[Ir(CO)_6]^{3+}$;[8,31,33] see Table 6) or, as discussed above, for $[Re(CO)_6]^+$ [81] and $[W(CO)_6(FSbF_5)]^+$,[4] lower than 2143 cm^{-1}.

2.4.3. Use of Computational Techniques. We have used in the characterization of σ-bonded metal carbonyl cations DFT calculations by our collaborators V. Jonas and W. Thiel to confirm, support, and supplement experimental findings.[12,13,39] This is illustrated in Table 6, where calculations provide vibrational wavenumbers, intensities of Raman lines and IR bands, force constants (f_{CO} and f_{MC}), partial atomic charges (q_M, q_C, q_O) and also internuclear distances (d(M−C) and d(C−O)).[12,13] Differences between experimental and calculated data, arising from solid-state compounds being compared to hypothetical cations in the gas phase, have been analyzed in each case.[2,12,13,39] They have been in part attributed to the extended structures found in solid-state complexes.[2] In summary, there has been a sound experimental basis for theoretical calculations.

With the increased use of DFT calculations, vibrational spectroscopy has become a very powerful tool. We have used vibrational spectroscopy in conjunction with DFT calculations in two general ways: (i) to establish, together with analytical methods, the bulk composition of a compound whose molecular structure we have obtained and (ii) to infer from vibrational, DFT, and analytical data a probable molecular structure in cases where single X-ray diffraction has not been successful.

2.4.4. Group 11 Linear Metal Carbonyl Halides. Metal−CO Bonding in Coinage Metal Carbonyl Derivates. Gaseous linear metal carbonyl halides of the type XMCO (M = Cu,[103] Ag,[104] Au;[105] X = F, Cl, Br) have very recently come into prominence. They are generated by laser ablation of the three metals, in the presence of CO and a halide precursor, inside a microwave cavity and have been studied by Fourier transform microwave spectroscopy (FTMW).[103−105] The nine transient molecules are unambiguously characterized by their rotational constants, centrifugal distortion constants, and nuclear quadrupole constants, which are obtained for the various isotopomers.[103−105] In addition, very precise internuclear M−C (M = Cu, Ag, Au), C−O, and M−X (X = F, Cl, Br) distances are obtained, which are corroborated by ab initio calculations at the second-order Møller−Plesset (MP2)[114] level of theory. MP2 calculations are also used to calculate vibrational wavenumbers, Mulliken orbital populations, and partial atomic charges[103−105] for the XMCO molecules.

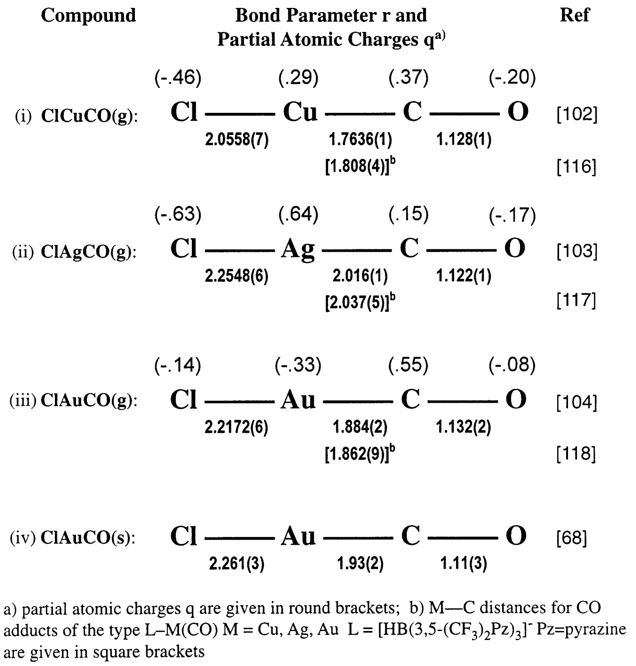

Figure 9. Internuclear distances r (Å) and partial atomic charge q (e) for linear group 11 metal carbonyl chlorides ClMCO (M = Cu, Ag, Au): schematic representation and comparison to related solid-state complexes.

Of the nine sets of data,[103−105] the three bond distances r(Cl−M), r(M−C), and r(C−O) for the triad ClMCO (M = Cu, Ag, Au) are shown in Figure 9. Also listed as superscripts in parentheses are the partial atomic charges q_{Cl}, q_M, q_C, and q_O for the transients. For comparison purposes, the corresponding structural data for linear $ClAuCO_s$ obtained some time ago by single-crystal X-ray diffraction[68] are also listed in Figure 9. Finally, d(M−C) (M = Cu, Ag, Au) data from a series of structural CO addition complexes of the type LMCO (M = Cu,[115] Ag,[116] Au[117]), where L is the tris(pyrazolyl)borate anion $[HB((3.5-CF_3)_2Pz)_3]^-$, are included in the comparison in Figure 9.

The following comments apply. (i) Agreement between X-ray data[68,115,116] listed in Figure 9 and FTMW data is good. Disrepancies between both sets of data arise from the low accuracy of the ClAuCO structure,[68] the effects of weak C- - -Cl contacts in the solid state, and differences in the coordination environment of M (Cu, Ag, Au), which is linear for ClMCO[103−105] and C_{3v} for LMCO.[115−117] (ii) Agreement in C−M (M = Cu, Ag, Au) bond lengths extends also to other solid-state complexes such as ClCuCO (1.82(2) Å),[118] which has a polymeric structure with tridentate bridging Cl^-, linear $[Au(CO)_2]^+$ (1.972(15) Å),[119,120] and the nearly linear $Ag(CO)_2$ moieties in $Ag(CO)_2(B(OTeF_5)_4)$[93] (2.06(4)−2.20(4) Å). (iii) Hence, it becomes clear that the internuclear distances obtained by FTMW are realistic and useful in the discussion of structural data for solid-state CO complexes formed by the coinage metals. (iv) Observed C−O distances for the ClM(CO) molecules[103−105] deviate very little from r_{CO} = 1.1219 Å[121] for CO_g. Similarly,

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ν(CO) values for all XMCO (X = F, Cl, Br; M = Cu,[103] Ag,[104] Au[105]) transients are found in proximity to the stretching wavenumber for CO_g of 2143 cm^{-1}; however, vibrational data for the transients are calculated as discussed and are not obtainable by FTMW spectroscopy,[103−105] which precludes a meaningful comparison. (v) Discrepancies of the Ag−C and Cu−C distances may be explained by differences in the appropriate effective ionic radii[122,123] for Ag^+ and Cu^+, which for coordination number 2 are 0.81 and 0.60 Å, respectively, since in both series of metal carbonyl halides[103,104] the M−X (X = F, Cl, Br) distances differ for M = Ag, Cu by a similar margin of ∼0.2 Å. (vi) It is tempting to attribute the shorter *r*(Au−Cl) and *r*(Au−C) values relative to *r*(Ag−Cl) and *r*(Ag−C) to relativistic effects,[63,69] causing a contraction of the effective radius of Au(I). However, the observed shortening of the Au−C bond by about 0.132 Å is much larger than for *r*(Au−Cl) (0.038 Å). A similar substantial contraction by 0.175 Å for the two isostructural adducts LMCO (M = Ag, Au[116,117]) is found (see Figure 9), and *d*(Ag−C) distances for the three crystallographically different $Ag(CO)_2$ moieties in $Ag(CO)_2[B(OTeF_5)_4]$[93] are at 2.06(4)−2.20(4) Å longer than Au−C distances in $[Au(CO)_2]^+$ [119,120] (1.972(15) Å) or in ClAuCO (1.93 Å).

When the partial atomic charges of q_M and q_C, obtained from MP2 calculations and listed in Figure 9, are taken into account, it becomes clear that we are looking at two, substantially different metal−CO bond types. (i) The Ag−CO bond in transient $ClAg{-}CO_g$[104] as well as in the solid-state complexes LAg−CO[116] and the $Ag(CO)_2$ groups of $Ag(CO)_2[B(OTeF_5)_4]$[93] is seen as a weak, dative bond, with CO acting as Lewis base and AgCl or Ag^+ salts as acceptors, either in the gas phase[104] or in precursor salts[92,93,116] with weakly coordinating anions. (ii) The Au−CO bond results from an interaction of the soft acid[46,47] Au^+_g[105] or Au^+_{solv}[17] with the soft base CO, followed by an extensive bond polarization,[77] with the carbonyl carbon the electrophilic acidic center, just as in other predominantly σ-bonded metal carbonyl cations. The stronger polarizing ability of Au^+, reflecting the higher nuclear charge of gold, augmented by relativistic contributions[63,69] is the cause of the different bond types, and manifestations of this difference are summarized in Table 5.

It becomes clear that the weak dative bond OC→Ag found in XAgCO,[104] the pyrazolyl AgCO adduct LAg-CO,[116] and in structurally characterized $Ag(CO)_n[B(OTeF_5)_4]$ (*n* = 1, 2[93]) reflects in all instances the inability of Ag^+ to polarize CO sufficiently,[77] to generate a sizable positive charge on C of the carbonyl ligand.

Weak dative M←CO bonding in the polycarbonyl complexes of Cu(I) and Ag(I) provides a satisfactory explanation for the various manifestations listed in Table 5, which set them clearly apart from the σ-carbonyls.

2.5. Synergetic Bonding in σ-Carbonyl Cations in the Solid State. While the identification of electrophilic carbon in transient XAuCO[104] (X = F, Cl, Br) molecules by FTMW spectroscopy, discussed in the preceding section, provides an interesting perspective, there is both direct and indirect evidence for electrophilic carbonyl carbon in σ-carbonyls in the solid state.[2] This evidence is obtained by more conventional techniques, such as single-crystal X-ray diffraction and vibrational spectroscopy, both supported by DFT calculations[2] as discussed in sections 2.3 and 2.4.

Direct evidence is 3-fold.

(i) There are significant interionic C- - -F contacts and somewhat weaker imposed O- - -F interactions found among the nonbonding contacts in solid-state structures of salts, formed by superelectrophilic[5] metal carbonyl cations and the fluoroantimonate (V) anions $[Sb_2F_{11}]^-$ and to a lesser extent $[SbF_6]^-$, as discussed in section 2.3.5 and shown in Figures 4 and 5. Our contention is that these interactions involve the antibonding π_3 and π_4 MO's of CO as acceptor orbitals. The strength and number of these interactions decrease with increasing coordination number and follows the approximate order 2 (linear) ≈ 4 (square planar) > 6 (octahedral) > 7, which is explainable by a combination of the decreasing electrophilicity of carbon and the accessibility of the CO ligand to interionic contacts.[2,125] In the group 6 cations,[3,4] which have coordinated $[SbF_6]^-$ anions, intraionic C- - -F contacts are found, and in the fluorosulfato derivatives *cis*-$M(CO)_2(SO_3F)_2$ (M = Pd, Pt[70,71]) and *mer*-$Ir(CO)_3(SO_3F)_3$,[38] both inter- and intramolecular C- - -O contacts are observed.

(ii) As discussed previously,[2,12] in $[Sb_2F_{11}]^-$ salts with superelectrophilic[5] σ-carbonyl cations,[3,4,6,7,12,30,37,39,55] the $[Sb_2F_{11}]^-$ is distorted from its equilibrium D_{4h} conformation[83] by bending and rotational processes toward C_1 symmetry, which are measured in terms of the bridge angle α and the dihedral angle ψ.[78] In salts with unipositive cations such as $[Au(CO)_2]^+$ [17,83] and $[Rh(CO)_4]^+$,[55,83] the D_{4h} conformation of $[Sb_2F_{11}]^-$ is retained. Also in $[Re(CO)_6][Re_2F_{11}]$,[78] the related $[Re_2F_{11}]^-$ anion has D_{4h} symmetry. This means C- - -F contacts are either absent or too weak to cause distortion of the $[E_2F_{11}]^-$ anion (E = Sb,[17,55] Re[78]).

In addition, the comparison of structural data for $[M(CO)_5Cl][Sb_2F_{11}]_2$[2,30,39,55] (M = Rh, Ir) to those of $[M(CO)_6][Sb_2F_{11}]$ (M = Ru, Os[2,6]) support our claim that C- - -F interactions increase with increasing oxidation state of M, in cases where the cations have the same coordination geometries.

(iii) As discussed above, conclusive proof for the presence of electrophilic carbon comes from the recently reported structure of $[Ir(CO)_6][SbF_6]\cdot 4HF$.[8] While interionic C- - -F contacts are absent, HF is coordinated via F to all six C atoms of $[Ir(CO)_6]^{3+}$ [8] (see Figure 6 and discussion in section 2.3.5). The observation reported by us[8] that ν(CO) bands in $[Ir(CO)_6][SbF_6]_3\cdot 4HF$, $[Ir(CO)_6][Sb_2F_{11}]_3$,[30,31] and $HF{-}SbF_5$ solutions of $[Ir(CO)_6]^{3+}{}_{solv}$[8] are identical strongly suggests that σ-metal carbonyl cations in superacids are solvated at the C atom.

Indirect evidence for the presence of electrophilic carbon comes from two observations we have discussed previously in this review.

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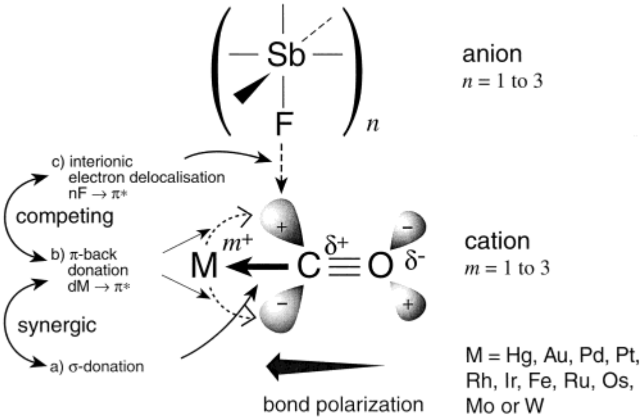

Figure 10. Bonding interactions in metal carbonyl cations with fluoroantimonate anions in the solid state.

(i) In section 2.3.4 evidence is presented that the strength of CO bonds in σ-carbonyls expressed in $\nu(\mathrm{CO})_{\mathrm{av}}$, f_{CO}, or $d(\mathrm{CO})$ is proportional to the oxidation state of M and inversely proportional to its coordination number.[125] An empirical order is proposed. In this order, two nonmetallic carbonyls, $[\mathrm{HCO}]^{+}$ [79] and uncharged $(\mathrm{CF_3})_3\mathrm{BCO}$,[58] rank extremely high, despite the low oxidation states of the central atoms.

(ii) As discussed in section 2.4.2 and shown in Figure 8 and Table 6, a plot of the three CO stretching fundamentals A_{1g}, E_g, T_{1u} in octahedral $[\mathrm{M(CO)_6}]$ complexes ($\mathrm{M} = \mathrm{W}^0$, Re^+, Os^{2+}, Ir^{3+}) against the oxidation state of M is no longer linear and increments of $\Delta\nu(\mathrm{CO})$ for $[\mathrm{Os(CO)_6}]^{2+}$ [6] and $[\mathrm{Ir(CO)_6}]^{3+}$ [8] decrease as discussed. A similar observation is made when $\nu(\mathrm{CO})_{\mathrm{av}}$ for $\mathrm{M(CO)_6}$ ($\mathrm{M} = \mathrm{Hf}^{2-}$, Ta^-, W, Re^+, Os^{2+}, Ir^{3+}) is plotted in order of increasing atomic number.[1,30]

To summarize the bonding interactions encountered in salts formed by metal carbonyl cations ($[\mathrm{M(CO)}_n]^{m+}$: $n = 2, 4, 6$; $m = 1-3$) and fluoroantimonate(V) anions ($[\mathrm{Sb_2F_{11}}]^-$, $[\mathrm{SbF_6}]^-$) in the solid state, a model is presented in Figure 10. In addition to the classical components of synergetic bonding, σ donation and π back-donation,[112,113,126] two new components are added: (i) bond polarization of CO bonds[77] by M^{m+}, which contributes to the strengths of CO bonds, and (ii) $\mathrm{F}\rightarrow\pi^*$ interionic electron delocalization, which includes also the anion of the extended structures.

σ donation and bond polarization are complementary and will effectively strengthen the C−O bond. In contrast, π back-donation and interionic electron delocalization are competing processes, which will weaken the C−O bond by electron release into π^* MOs of the CO ligands. At high oxidation states of M (+2, +3), π back-bonding becomes improbable, and $\mathrm{M}\leftarrow\mathrm{CO}$ σ-bonding dominates. We have chosen the term "metal σ-carbonyl cation" or σ-carbonyl for this situation, which describes the principal $\mathrm{M}\leftarrow\mathrm{CO}$ bonding mode. Hence, in the absence of π back-bonding, $\nu(\mathrm{CO})_{\mathrm{av}}$ in the $[\mathrm{Os(CO)_6}]^{2+}$ and $[\mathrm{Ir(CO)_6}]^{3+}$ salts decreases on account of $\mathrm{F}\rightarrow\pi^*$ electron donation,[1,2,125] but in the molecular σ-carbonyl $(\mathrm{CF_3})_3\mathrm{BCO}$,[58] $\nu(\mathrm{CO})$ is unexpectedly high because no external π donation occurs.

3. Summary, Conclusion, and Outlook: Where Are We and Where Do We Go From Here?

As in case of the well-established and related (see section 2.3.7) stable carbocations,[91,99] the use of superacids such as $\mathrm{SbF_5}$[9−11,54] and $\mathrm{HF{-}SbF_5}$[9,54] as reaction media in various types of carbonylation reactions[1,2,125] (Table 1) has allowed in recent years the generation of a substantial number of mostly "superelectrophilic"[5] metal σ-carbonyl cations and their derivatives,[1,2] formed by metals ranging from group 6 to 12 (Figure 1), in oxidation states up to +3. Salts of surprisingly high thermal stability[2] form, with the superacid anions $[\mathrm{Sb_2F_{11}}]^-$ [127] and less frequently $[\mathrm{SbF_6}]^-$ [44,127] as counteranion.

Many of these salts have been structurally characterized by single-crystal X-ray diffraction[2] (see Table 3), and most of the cations have been the subject of a complete vibrational analysis (see e.g. section 2.4.2, Figure 8, Table 6). The solvated superelectrophilic[5] metal carbonyl cations exist only in the conjugate Brønsted−Lewis superacids $\mathrm{HF{-}SbF_5}$[9,44,54] and $\mathrm{HSO_3F{-}SbF_5}$.[9,54,128,129] An example for solvation at the electrophilic C atoms of the CO ligands by HF is found in the solid-state structure of $[\mathrm{Ir(CO)_6}][\mathrm{SbF_6}]_3\cdot 4\mathrm{HF}$[8] (see Figure 6).

In the very strong Brønsted superacids HF[130] and $\mathrm{HSO_3F}$,[9,54] most homoleptic σ-carbonyl cations undergo nucleophilic displacement of CO by the autoprotolysis ions F^-[9,54] and $\mathrm{SO_3F}^-$,[131,132] respectively. A number of the resulting fluorosulfato derivatives have been structurally characterized[38,71] and are listed in Table 4.

The even weaker nucleophiles $[\mathrm{Sb_2F_{11}}]^-$ and $[\mathrm{SbF_6}]^-$ [133] in the solvent system $\mathrm{HF{-}SbF_5}$[9,54] pose limitations as well (see Scheme 1B). During the attempted oxidative carbonylation of $\mathrm{M(CO)_6}$ (M = Mo, W[3,4]) with $\mathrm{SbF_5}$ as oxidizer, 2e oxidation is followed by addition of the stronger nucleophile $[\mathrm{SbF_6}]^-$ rather than CO and $[\mathrm{M(CO)_6(FSbF_5)}][\mathrm{Sb_2F_{11}}]$ is found in the case of the tungsten salt.[4] Condensation leads to the formation of $[\{\mathrm{M(CO)_4}\}_2[\mathrm{F_2SbF_4}]_3]_x[\mathrm{Sb_2F_{11}}]_x$ with the Mo salt.[3] The implication is that homoleptic metal carbonyl cations such as $[\mathrm{M(CO)_7}]^{2+}$ (M = Mo, W) and $[\mathrm{M(CO)_7}]^{+}$ (M = Nb, Ta) are not obtainable by oxidative carbonylation in $\mathrm{HF{-}SbF_5}$. On the other hand, the reductive carbonylation of $\mathrm{WF_6}$ in $\mathrm{HF{-}SbF_5}$ reportedly[31] does not succeed, because $\mathrm{WF_6}$, unlike $\mathrm{IrF_6}$ (see Scheme 1A), is not a good oxidizing agent toward CO. Hence, an expansion toward homoleptic σ-carbonyl cations of groups 5 and 6 using currently known synthetic methodologies and $\mathrm{HF{-}SbF_5}$ as reaction medium is not promising.

As also discussed recently[55] and shown in Scheme 3, $[\mathrm{Rh(CO)_6}]^{3+}$ is not obtained for two reasons. (a) $\mathrm{RhF_6}$[134,135]

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is difficult to synthesize and seems to be reduced by CO in HF−SbF_5 to Rh(I). This view is supported by the observation[55] that reductive carbonylation of $Rh(SO_3F)_3$ in HSO_3F results in $[Rh(CO)_4]^+_{solv}$. (b) Oxidation of commercially available $[Rh(CO)_2Cl]_2$, even with F_2 in HF,[55] will produce $[Rh(CO)_5Cl][Sb_2F_{11}]_2$[39] as the final product.

Despite these limitations arising from the solvent characteristics of HF−SbF_5,[9,54] the nucleophilicity of $[SbF_6]^-$ and $[Sb_2F_{11}]^-$,[133] the availability of suitable precursors to generate solvated cations and side reactions, as the formation of polymeric $M[SbF_6]_2$ (M = Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd[41]), discussed in Scheme 2, HF−SbF_5[9,54] and SbF_5[10,11] are the only reaction media that have produced superelectrophilic[5] σ-carbonyl cations[2,125] and the superacid anions $[Sb_2F_{11}]^-$ [127] and $[SbF_6]^-$ [44,127] are uniquely suited to form extended structures[2] (section 2.3.5) via the formation of significant C- - -F contacts to the electrophilic carbonyl atoms. There is at present no alternative method known that can produce even a single homoleptic metal carbonyl cation with the metal in oxidation states of +2 and +3 in thermally stable compounds.

An additional limitation to the generation of metal carbonyl cations is posed by the oxidizing ability of SbF_5, which has prevented the generation of univalent cations of the type $[M(CO)_n]^+$ (M = Cr, Mn, Co, Rh, Ir, and others; $n = 4-6$).[125] For this reason, alternate synthetic methods have been developed and are summarized in Table 2. They involve the use of nonoxidizing Lewis acids. The generation of $[Rh(CO)_4][M_2Cl_7]$ (M = Al, Ga[55]) is adopted from the syntheses of $[M(CO)_6]^+$ (M = Mn, Re, Tc) salts in the pioneering studies by E. O. Fischer et al. and W. Hieber et al.[14,15] The discovery[57] and extensive characterization[58] of $(CF_3)_3BCO$ (see Figure 2) provides both a new σ-carbonyl with unusual structural and spectroscopic properties[58] and a Lewis acid precursor in the new conjugate superacid system HF/$(CF_3)_3BCO$. Its use has allowed the synthesis of $[Co(CO)_5][(CF_3)_3BF]$,[59] the first example of a salt with a trigonal-bipyramidal cation (see Figure 3). The formation reaction, oxidation of $Co_2(CO)_8$ by the acidium species H_2F^+, previously used by Souma et al.[60] should prove to be useful. Likewise, the superacid anion $[(CF_3)_3BF]^-$ [59] together with the "parent ion" $[B(CF_3)_4]^-$ [56] should, on account of their small size and their weak coordination ability, find use as weakly coordinating nonoxidizing anions.

Current efforts are directed toward the synthesis of $[B(CF_3)_4]^-$ salts with oxidizing cations. They could be used in aprotic solvents to synthesize other unipositive or low-valent metal carbonyl cations. Promising candidates are (i) $[Cr(CO)_6]^+$, which could conceivably be the first paramagnetic metal carbonyl cation, isoelectronic with $V(CO)_6$, (ii) the isoelectronic 18e cation $[Ni(CO)_5]^{2+}$, which could provide a contrast to the D_{4h} cations $[M(CO)_4]^{2+}$ (M = Pd, Pt[12]) and fill a gap in Table 1, since carbonyl cations of nickel are unknown, (iii) $[Cu(CO)_4]^+$, which could be tetrahedral. A salt of the type $[Cu(CO)_4][1\text{-Et-}CB_{11}F_{11}]$ has been reported recently in a preliminary communication[136] and will hopefully be fully characterized soon.

A number of known homoleptic carbonyl cations should be structurally characterized. The list includes octahedral $[Mn(CO)_6]^+$,[137] square-planar $[Ir(CO)_4]^+$,[55] and linear, dinuclear $[Hg_2(CO)_2]^{2+}$.[37] The crystal growth may have to involve nonoxidizing Lewis acids, since the metals involved are sensitive toward oxidation by SbF_5. On the other hand, exploratory synthetic efforts toward selected lanthanide carbonyl cations[138] and a theoretical study into the existence of $[Tl(CO)_2]^{3+}$ [139] are somewhat discouraging.

Very few chemical applications of metal σ-carbonyl cations and their derivatives have been reported for three reasons. (i) The field is new. The systematic generation of metal carbonyl cations and the isolation of salts in and from superacids started in 1990.[1,101] (ii) The synthetic methods described here are unconventional, and starting materials are rarely commercially available. Furthermore, the cost of basic supplies (HSO_3F, SbF_5, F_2, noble metals, etc.) has risen sharply in recent years. (iii) Our approach aimed at understanding the nature of the metal−carbonyl bond is clearly demonstrated in this review and involves the development of viable, sound synthetic routes,[1,2] the complete identification of products by analytical and physical methods,[1,2] an extensive characterization of new compounds by structural[2] and spectroscopic[1,2] techniques and theoretical methods as a finishing touch.[12,13,39]

Consequently, our synthetic efforts have been limited to the development of new synthetic routes (see e.g. Scheme 3) and to effect substitution of CO by other donor ligands such as PF_3 and $NCCH_3$, as discussed recently.[1] Another more recent example is the use of $(CF_3)_3BCO$ as a synthon to give a number of new $(CF_3)_3B$ compounds.[58]

However, a promising start in the synthetic use of metal carbonyl cations has been made by others,[140,141] in particular by Y. Souma and her group,[21,22,60,142,143] who have studied the catalytic use of solvated carbonyl cations of group 10 and 11 in strong protonic acids. A very useful contribution has been made by H. V. R. Dias with the synthesis of three coinage metal adducts of the type $[HB(3,5\text{-}(CF_3)_2Pz)_3]M{-}CO$ (M = Cu,[115] Ag,[116] Au[117]), which have been structurally characterized and have been discussed in section 2.4.4.

To provide both a final summary and a limited historical perspective we have listed in Table 7 the known thermally stable (decomposition points between 100 and 300 °C), fully characterized (known bulk composition, complete vibrational analyses, molecular structure determination, and DFT calculations[12,13,139]) salts with homoleptic, mononuclear metal σ-carbonyl cations, together with the year of publication of the reference cited.

As seen in Table 7, linear cations are only formed by the 5d metals Hg and Au with $5d^{10}$ configurations and

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Table 7. Thermally Stable, Fully Characterized Salts with Homoleptic σ-Metal Carbonyl Cations:[a] Historical Summary

compd	year
(i) Coordination Carbonyl Compounds	
(a) Linear Cations, $D_{\infty h}$, EAN = 14, $5d^{10}$	
$[Au(CO)_2][Sb_2F_{11}]$[17]	1992[b]
$[Au(CO)_2]_2[Sb_2F_{11}][SbF_6]$[120]	2000[c]
$[Hg(CO)_2][Sb_2F_{11}]_2$[37]	1996
(b) Square Planar, D_4h, EAN = 16, $4d^8$ and $5d^8$	
$[Rh(CO)_4][Al_2Cl_7]$[55]	2003
$[Rh(CO)_4][Ga_2Cl_7]$[55]	2003
$[Pd(CO)_4][Sb_2F_{11}]_2$[12]	2001
$[Pt(CO)_4][Sb_2F_{11}]_2$[12]	2001
(ii) Organometallic Carbonyl Compounds, EAN = 18	
(a) Trigonal Bipyramidal, D_3h, d^8	
$[Co(CO)_5][(CF_3)_3BF]$[59]	2003
(b) Octahedral, O_h, $3d^6$, $4d^6$, $5d^6$	
$[Re(CO)_6][Re_2F_{11}]$[78]	1978[c]
$[Re(CO)_6][AsF_6]$[108]	1969[b]
$[Fe(CO)_6][Sb_2F_{11}]_2$[7]	1999
$[Fe(CO)_6][SbF_6]_2$[7]	1999
$[Ru(CO)_6][Sb_2F_{11}]_2$[6]	2003[d]
$[Ru(CO)_6][SbF_6]_2$[6]	2003[d]
$[Os(CO)_6][Sb_2F_{11}]_2$[6]	2003[d]
$[Os(CO)_6][SbF_6]_2$[6]	2003[d]
$[Ir(CO)_6][SbF_6]_3\cdot 4HF$[8]	2002

[a] Salts with superelectrophilic cations are shown in boldface type. [b] Synthesis and vibrational analysis. [c] Synthesis and molecular structure determination. [d] To be submitted for publication.

an EAN of 14, while Ag(I) and Cu(I) form polycarbonyl complexes[21,52] (see Table 5), in complete analogy to the structures of metal cyanide anions.[74] Both $4d^8$ and $5d^8$ ions form square-planar carbonyl cations[12,55] with an EAN of 16, again in analogy to the isoelectric and isosteric cyanide anions of Rh(I), Pd(II), and Pt(II).[74] The trigonal-bipyramidal structure of $[Co(CO)_5]^+$ [59] is also found for the group 8 uncharged $M(CO)_5$ (M = Fe, Ru, Os) species[48−50] and the metal anions $[M(CO)_5]^-$ (M = Mn, Tc, Re) and $[M(CO)_5]^{3-}$ (M = V, Nb, Ta),[51,111] all with an EAN of 18.

With regard to the metal σ-carbonyl cation salts listed in Table 7, the following concluding comments apply. (i) Enormous progress in our understanding of the metal−carbonyl bond in metal σ-carbonyl cations[2,125] has been made in recent years. This is evident from the 11 unique homoleptic metal σ-carbonyl cations found in 17 fully characterized salts listed in Table 7. By comparison, in 1997, when our first review[1] was published, only two of these homoleptic cations, $[Hg(CO)_2]^{2+}$ [37] and $[Re(CO)_6]^+$,[78,81] were fully characterized. (ii) Structural and spectroscopic information, supported by DFT calculations[12,13,139] on these cations and derivatives such as $[M(CO)_5Cl][Sb_2F_{11}]_2$ (M = Rh, Ir[39]), $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$,[4] and polymeric $[\{Mo(CO)_4\}_2(F_2SbF_4)_3][Sb_2F_{11}]$,[3] listed in Table 3 underscore the preeminent role the superacid anion $[Sb_2F_{11}]^-$ [45] plays on account of its low nucleophilicity,[133] its structural fluxionality[83] in forming extended structures,[2] and its facile in situ formation by self-assembly in HF−SbF_5.[44] (iii) With the help of structural, spectroscopic, and relevant computational evidence[12,13,39,139] presented in this review, a bonding model is presented in section 2.5 to account for our observations. In this model, the classical components of synergetic M−CO bonding,[112,113,126] σ-donation, and metal (d)→π^* back-donation are complemented by contributions from CO bond polarization, first proposed by Goldman and Krogh-Jesperson[77] and external F→π^* back-donation. (iv) Strong evidence for the presence of electrophilic carbon in the σ-carbonyls establishes a strong link to the large family of carbocations[54,91,99] on account of their generation in superacids[9] and strong structural similarities,[104−106] as discussed in section 2.3.7. (v) The distribution of fully characterized salts in Table 7 and crystallographic data for isostructural pairs (Tables 3 and 4) formed by 4d and 5d metals attest to the contribution made by relativistic effects.[63,69] (vi) The assumption made in Schemes 1 and 2 that solvated cations of borderline to soft[46] or class b metal ions[47] such as Au^+, Hg^{2+}, Pd^{2+}, Pt^{2+}, Ru^{2+}, Os^{2+}, and Ir^{3+}, formed by either solvolysis or reduction (methods A and B) in HF−SbF_5 and their subsequent carbonylation, produce well-defined metal carbonyl cations is confirmed by the listing in Table 7: all seven class b[47] metal ions form fully characterized salts with $[Sb_2F_{11}]^-$ or $[SbF_6]$. $[Re(CO)_6]^+$, first made by Hieber and Kruck,[144] may be added to this list, because it can also be generated by reductive carbonylation of ReF_6.[31] $[Rh(CO)_4]^+_{solv}$ is formed, as discussed, by reductive carbonylation of $[Rh(SO_3F)_3]$ in HSO_3F. (vii) $[Rh(CO)_4][M_2Cl_7]$ (M = Al, Ga[55]), synthesized from $[Rh(CO)_2Cl]_2$ and $[Co(CO)_5][(CF_3)_3BF]$,[59] both listed in Table 7 as very recent additions, and the synthesis of the σ-carbonyl $(CF_3)_3BCO$[57,58] demonstrate that fruitful new synthetic avenues are available and that the show will go on.

The nonclassical metal−CO bonding concept[52,53,93,95] by Strauss et al. fails to be a valid approach to describe metal−carbonyl bonding on three accounts. (i) The concept was first proposed on limited evidence in 1994, when the molecular structures of $Ag(CO)_n[B(OTeF_5)_4]_4$ ($n = 1, 2$) were interpreted as "$[Ag(CO)]^+$ and $[Ag(CO)_2]^+$ nonclassical (σ-only)".[93] Since that time, well over 20 molecular structures of genuine metal carbonyl cations have been reported[2] (see Tables 3, 4, and 7) which are not in harmony with the nonclassical concept. (ii) The reoccurring observation that the carbonyl carbons are electrophilic (see Figures 4−6) has been ignored in recent reviews[52,54] and calculations by Frenking et al.,[18,34] which limits their usefulness. (iii) The characterization of metal carbonyl cations in otherwise ill-defined material largely by "computational means"[52,53] is in stark contrast to our fact-based approach[1,2] used in this review.

Acknowledgment. Our sincere thanks go to Professor Dietmar Seyferth for his kind invitation to write this review and Professor John E. Ellis for a copy of his manuscript. We are somewhat reluctant in telling our side of the metal carbonyl story in *Organometallics*, since it involves heavy doses of superacid chemistry and fluorine chemistry and a heavy reliance on structural and spectroscopic methods. While this is probably good reading for organometallic chemists, it is worthwhile to remember that the syntheses of three Pt(II) carbonyl chlorides, among them the σ-carbonyl *cis*-$Pt(CO)_2Cl_2$, by the organic chemist P. Schützenberger[145,146] in 1868

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[144] Hieber, W.; Kruck, T. *Angew. Chem.* **1961**, *73*, 580.
[145] Schützenberger, P. *Bull. Soc. Chim. Fr.* **1868**, *10*, 188.
[146] Schützenberger, P. *C.R. Hebd. Sciences Acad. Sci.* **1870**, *70*, 1134.

mark the beginning of metal carbonyl chemistry, well before the discovery of $Ni(CO)_4$ in 1890. The pioneering studies by E. O. Fischer and W. Hieber around 1960, resulting in the discovery of $[M(CO)_6]^+$ ($M = Mn, Tc, Re$[14,15,144]), are classic studies in organometallic chemistry. With the syntheses of $(CF_3)_3BCO$[57,58] and of $[Co(CO)_5]^+$ [59] described here, a return to organometallic chemistry is indicated. Hence all that ends well is well,[147] or so we hope. On a more serious note, we wish to express our sincere appreciation and gratitude to our diploma, masters, and doctoral students, postdoctoral fellows, and research associates for their dedicated efforts over the last 10 years, which have allowed us to convert a serendipitous discovery into a substantial, fully characterized group of new metal carbonyl compounds. Equally important has been the contribution made by theoreticians, the collaboration with crystallographers from Simon Fraser University, The University of British Columbia, Max-Planck-Institut für Kohlenforschung, Universität Hannover, and Gerhard-Mercator-Universität Duisburg, and the encouragement of and fruitful discussions with many colleagues and friends.

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(147) Shakespeare, W., around 1600.