$[Hg(CO)_2][Sb_2F_{11}]_2$

$[Pt(CO)_4][Sb_2F_{11}]_2$

$[Os(CO)_6][Sb_2F_{11}]_2$

Predominantly σ-Bonded Metal Carbonyl Cations (σ-Carbonyls): New Synthetic, Structural, and Bonding Concepts in Metal Carbonyl Chemistry

Helge Willner*[a] and Friedhelm Aubke[b]

Abstract: Predominantly σ-bonded metal carbonyl cations (σ-carbonyls) are conveniently generated in the Lewis superacid SbF_5 or the conjugate Brønsted–Lewis superacid $HF-SbF_5$, primarily by solvolytic or reductive carbonylations. Thermally stable salts are formed with the fluoroantimonate(v) ions $[SbF_6]^-$ and $[Sb_2F_{11}]^-$. The salts are characterised by analytical, structural, spectroscopic and computational methods. Most homoleptic carbonyl cations have very regular geometries, comensurate with their d-electron configurations: linear (d^{10}), square planar (d^8) or octahedral(d^6). The cations with metals in oxidation states of $+2$ or $+3$ are termed "superelectrophilic". Extended molecular structures form by significant interionic C−F contacts with electrophilic carbon as acceptor. To account for all experimental observations, a conceptually simple synergetic bonding model is proposed. An outlook at anticipated future developments based on very recent results is provided.

Keywords: carbonyl ligands · cations · fluoro antimonates · solid-state structures · superacidic systems

Introduction

Homoleptic metal carbonyl cations, after pioneering studies by E. O. Fischer and W. Hieber in the 1960s, have remained restricted to cations of the type $[M(CO)_6]^+$ formed by Group 7 metals.[1, 2] All attempts to extend the synthetic approach, for example, halide abstraction by the Lewis acids $M'X_3$, $M' = Al$, Fe, $X = Cl$, Br at high temperatures and CO pressures from

[a] Prof. Dr. H. Willner
    Fakultät 4, Anorganische Chemie
    Gerhard Mercator Universität
    Lotharstr. 1, 47048 Duisburg (Germany)
    Fax: (+49) 203-379-2231
    E-mail: willner@uni-duisburg.de

[b] Prof. Dr. F. Aubke
    Department of Chemistry
    The University of British Columbia
    2036 Main Mall, Vancouver, B.C. V6T 1Z1 (Canada)
    Fax: (+1) 604-822-2847
    E-mail: aubke@chem.ubc.ca

$M(CO)_5X$, $M = Mn$, Tc, Re to other metal carbonyl halides, have been without success.[1, 2] The generation of [Au-$(CO)_2]^+_{(solv)}$[3] in the Brønstedt superacid HSO_3F[4, 5] in 1990, and the subsequent isolation of $[Au(CO)_2][Sb_2F_{11}]$ has provided a break-through. An early success of our new synthetic strategy has been the synthesis of $[Hg(CO)_2][Sb_2F_{11}]_2$,[6] which has remained the only thermally stable and fully characterised carbonyl compound formed by a post-transition metal.

The replacement of HSO_3F[5] and magic acid, HSO_3F-SbF_5,[4] first by SbF_5, the strongest molecular Lewis acid,[7, 8] and then by $HF-SbF_5$,[9, 10] has allowed an extension of the existence range of σ-metal carbonyl cations and their derivatives.[11–13] As seen in Figure 1, there are at present
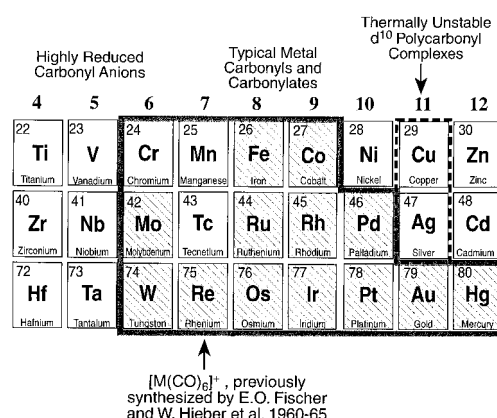

Figure 1. The distribution of thermally stable homoleptic metal carbonyls and their derivatives. Metals that form σ-carbonyl cations are highlighted; shading indicates structurally characterised compounds.

sixteen metals, ranging from Group 6 to 12, that form thermally stable cationic metal carbonyl derivatives. As seen in Table 1, most of the metal carbonyl cations are, following a suggestion by G. A. Olah, termed "superelectrophiles",[14] with the central metals in oxidation states of $+2$ and $+3$. In addition to homoleptic metal carbonyl cations of the general type $[M(CO)_n]^{m+}$, with $n = 2$ (linear), 4 (square planar) and 6 (octahedral) and $m = 1$, 2, or 3, a number of derivatives are known. They are formed by substitution of one or more CO ligands of a homoleptic metal carbonyl cation by anions (Cl^-, SO_3F^-, SbF_6^-, etc.).

Table 1. Thermally stable homoleptic σ-metal carbonyl cations[a,b] and their derivatives[a,b] generated in/with superacids.

Group	Cation	Point group	Method of generation and reaction medium	Derivative	Point group	Method of synthesis and reaction medium
12	$[Hg(CO)_2]^{2+}$ $[Hg_2(CO)_2]^{2+}$	$D_{\infty h}$	solvolytic carbonylation in SbF_5 or $HF-SbF_5$			
11	$[Au(CO)_2]^{2+}$	$D_{\infty h}$	reductive carbonylation in SbF_5	$[Au(CO)SO_3F]$	$\sim C_1$	reductive carbonylation in HSO_3F
10	$[Pd(CO)_4]^{2+}$ $[Pt(CO)_4]^{2+}$	D_{4h}	reductive carbonylation in SbF_5 or $HF-SbF_5$	cis-$[Pd(CO)_2(SO_3F)_2]$ cis-$[Pt(CO)_2(SO_3F)_2]$ cis-$[Pd_2(\mu\text{-}CO)_2]^{2+}$ [c]	$\sim C_{2v}$ $\sim C_{2v}$ D_{2h}	reductive carbonylation in HSO_3F recryst. from HSO_3F
9	$[Ir(CO)_6]^{3+}$	O_h [d]	reductive carbonylation in $HF-SbF_5$	mer-$[Ir(CO)_3(SO_3F)_3]$ fac-$[Ir(CO)_3F_3]$ [f]	$\sim C_{2v}$ $\sim C_{3v}$	CO addition in HSO_3F oxidation in HF with XeF_2
	$[Rh(CO)_4]^{+}$ $[Ir(CO)_4]^{+}$	D_{4h} [e]	Cl abstraction with MCl_3 (M: Ga, Al)	$[Rh(CO)_5Cl]^{2+}$ $[Ir(CO)_5Cl]^{2+}$	C_{4v} C_{4v}	oxidative carbonylation in SbF_5
8	$[Fe(CO)_6]^{2+}$ [g]	O_h	oxidative carbonylation in SbF_5 or $HF-SbF_5$			
	$[Ru(CO)_6]^{2+}$ [g]	O_h	reductive carbonylation in SbF_5 or $HF-SbF_5$			
	$[Os(CO)_6]^{2+}$ [g]			$trans$-$[OsO_2(CO)_4]^{2+}$	D_{4h}	reductive carbonylation in SbF_5
7	$[M(CO)_6]^{+}$ (M = Mn, Tc, Re[h])	O_h	halide abstraction with MX_3 (M = Al, Fe; X = Cl, Br) at high T, high p_{CO}			
6				polym-$[\{Mo(CO)_4\}_2(\mu\text{-}F_2SbF_4)_3]^{+}$	C_1	oxidation of $M(CO)_6$ (M = Mo, W)
				$[W(CO)_6(FSbF_5)]^{+}$	C_1	by SbF_5 in $HF-SbF_5$

[a] Structurally characterised species in bold. [b] With $[Sb_2F_{11}]^{-}$ ion unless stated otherwise. [c] With SO_3F^{-} as counterion. [d] Characterised as $[Ir(CO)_6][SbF_6]_3 \cdot 4HF$. [e] $M_2Cl_7^{-}$ (M = Ga, Al) as counterion. [f] Characterised by EXAFS. [g] Also obtained and structurally characterised with $[SbF_6]^{-}$. [h] $[Re(CO)_6][Re_2F_{11}]$ has been structurally characterised.

As in the early examples cited,[3, 6, 15] the superacid ion $[Sb_2F_{11}]^{-}$,[16] formed by self-assembly in liquid SbF_5 as well as in $HF-SbF_5$,[16] is frequently found as a counterion. The resulting salts have high thermal stabilities, with decomposition points usually well beyond 100 °C. They are generally obtained in very high purity. As a consequence, most salts are fully characterised by various analytical, physical, spectroscopic and structural methods.[11–13] In summary, metal carbonyl cations and their derivatives[11–13] have in the short time of their existence become important members of the large and diverse metal carbonyl family[17–20] and a classification of all CO complexes into three groups: metal carbonylates,[20] neutral metal carbonyls[17–19] and metal carbonyl cations[11–13] is fully justified and useful (see Figure 1).

We want to discuss here the concepts behind the individual synthetic methods and the bonding situation for σ-carbonyls, based on mostly recent structure determinations, spectroscopic analyses and the use of computational methods[11–13, 21]

Synthetic Concepts

The reaction medium: The use of the Lewis superacid SbF_5[4, 7, 8] as reaction medium in carbonylation reactions[6, 11–13, 15] is viewed as both an extension and an improvement over the use of AlX_3, X = Cl, Br in the early studies[1, 2] on four accounts:

1) SbF_5 is a stronger Lewis acid[7, 8] and at ambient conditions a liquid. Reactions proceed with reactants and products in a suspension.

2) The reaction conditions are milder ($T \sim 60$ °C, $p \sim 1$ atm CO) and carbonylations can be performed in glass bulbs.

3) A range of starting materials like medium- to high-valent metal fluorides or fluorosulfates can be used,[11] in addition to metal carbonyls or their derivatives.[12, 13]

4) The reaction products and excess SbF_5 can be easily separated.[6, 11–13, 15]

There are, however, limitations: SbF_5 is a good oxidizing and fluorinating agent. This has three implications:

1) Low-valent metal carbonyl cations like $[M(CO)_4]^{+}$, M = Rh, Ir cannot be generated in the presence of SbF_5. Here the use of nonoxidizing Lewis acids like MCl_3, M = Al, Ga is advantageous (see Table 1).

2) The deliberate use of SbF_5 in oxidative carbonylations for example, of $[M(CO)_6]$ M = Mo, W[12] results in the formation of a reduced byproduct (SbF_3 or the adduct $6SbF_3 \cdot 5SbF_5$[22]), which needs to be separated from the product and results in reduced yields.

3) In oxidative carbonylations of chloride containing precursors (e.g., $[Ir(CO)_3Cl]$[23]), the M−Cl interaction becomes stronger on oxidation. Hence chloride abstraction is no longer feasible and, in the example cited above, $[Ir(CO)_5Cl]^{2+}$ is obtained rather than $[Ir(CO)_6]^{3+}$.[23]
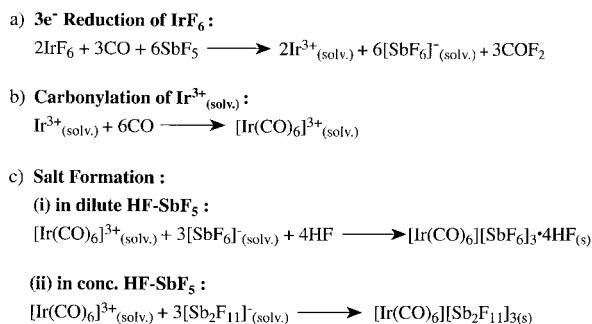
The use of $HF-SbF_5$[9, 10] again brings advantages: the higher ionizing ability of the protonic superacid and the reduced viscosity of the medium, allow reactions to proceed faster, at lower temperatures and in homogenous phase. It is found, that CO is modestly soluble in superacids, with CO uptake from the gas phase possible at low CO pressures of ~ 1 atm.[11–13] The reaction products are crystalline. As a result a substantial number of crystal structures are obtained (see Table 1).[12, 13, 21, 23] In the syntheses of $[M(CO)_6]^{2+}$ salts, M = Fe, Ru, Os,[11–13] both $[Sb_2F_{11}]^{-}$ and $[SbF_6]^{-}$ are possible

counterions, on account of equilibria such as that given in Equation (1).[24]

$$[SbF_6]^-_{(solv)} + SbF_{5(solv)} \underset{}{\overset{HF-SbF_5}{\rightleftharpoons}} [Sb_2F_{11}]^-_{(solv)} \qquad (1)$$
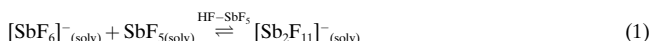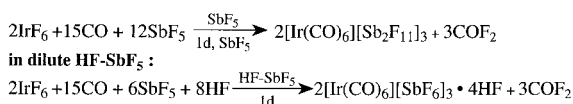
It is anticipated that use of new superacids containing nonoxidizing, weakly coordinating anions[25, 26] will extend the existence range of metal carbonyl cations. A promising anion in this respect is $[B(CF_3)_4]^-$.[27]

Carbonylation reactions in HF–SbF₅ or SbF₅: For the generation of homoleptic metal carbonyl cations, reductive or solvolytic carbonylation reactions are elegant methods that produce the new compounds in quantitative yields.[11–13] When metal fluorides or fluorosulfates are used as starting materials, the byproducts COF_2 or a 1:1 mixture of CO_2 and $S_2O_5F_2$ are volatile and easily removed in vacuo from the reaction mixture. In reduction reactions the potential counterions $[SbF_6]^-$ or $[Sb_2F_{11}]^-$ are generated. An illustration of the reductive carbonylation of IrF_6 in liquid SbF_5 is shown in Scheme 1. 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

a) **3e⁻ Reduction of IrF₆ :**

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

b) **Carbonylation of Ir³⁺(solv.) :**

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

c) **Salt Formation :**

   (i) in dilute HF-SbF₅ :

$$[Ir(CO)_6]^{3+}_{(solv.)} + 3[SbF_6]^-_{(solv.)} + 4HF \longrightarrow [Ir(CO)_6][SbF_6]_3 \cdot 4HF_{(s)}$$

   (ii) in conc. HF-SbF₅ :

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

Overall Reaction in SbF₅ :

$$2IrF_6 + 15CO + 12SbF_5 \xrightarrow[\text{1d, SbF}_5]{\text{SbF}_5} 2[Ir(CO)_6][Sb_2F_{11}]_3 + 3COF_2$$

in dilute HF-SbF₅ :

$$2IrF_6 + 15CO + 6SbF_5 + 8HF \xrightarrow[\text{1d}]{\text{HF-SbF}_5} 2[Ir(CO)_6][SbF_6]_3 \cdot 4HF + 3COF_2$$

Scheme 1. The reductive carbonylation of IrF_6 in HF–SbF₅ at 50 °C and 1 atm CO.

the $[Ir(CO)_6]^{3+}$ ion, with volatile COF_2 as sole byproduct. The product from the reaction in SbF_5 is identified as [Ir-(CO)₆][Sb₂F₁₁]₃, while in dilute HF–SbF₅ the solvate [Ir-(CO)₆][SbF₆]₃ · 4 HF forms instead.[21]

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,[3, 11–13, 15, 21] indicates a general reaction pathway, which is illustrated in Scheme 2. It is assumed in this rationale, that the initial step involves the generation of so called "naked" (or very weakly coordinated) metal cations by reduction and/or solvolysis; these ions are found in a superacid "matrix" together with two types of very weak Lewis bases: gaseous carbon monoxide (CO) and the fluoroantimonate(v) ions $[SbF_6]^-$, $[Sb_2F_{11}]^-$, $[Sb_3F_{16}]^-$ etc.[24]

1) **Components of the Superacid Matrix at ~50°C, 1 atm. CO**
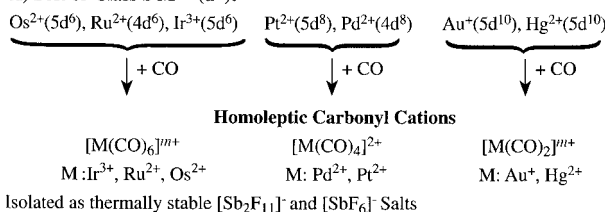Equilibrium Species:

a) $[SbF_6]^-_{(solv.)} + SbF_{5(solv.)} \rightleftharpoons [Sb_2F_{11}]^-_{(solv.)}$;

b) $CO_{(g)} \rightleftharpoons CO_{(solv.)}$
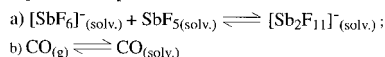
2) **Metal Ions Formed by Reduction and/or Solvolysis:**

A) **Soft or Class b $M^{m+}(d^n)$:**

$Os^{2+}(5d^6), Ru^{2+}(4d^6), Ir^{3+}(5d^6)$ $Pt^{2+}(5d^8), Pd^{2+}(4d^8)$ $Au^+(5d^{10}), Hg^{2+}(5d^{10})$

$\downarrow + CO$ $\downarrow + CO$ $\downarrow + CO$

Homoleptic Carbonyl Cations

$[M(CO)_6]^{m+}$ $[M(CO)_4]^{2+}$ $[M(CO)_2]^{m+}$

M :$Ir^{3+}, Ru^{2+}, Os^{2+}$ M: Pd^{2+}, Pt^{2+} M: Au^+, Hg^{2+}

Isolated as thermally stable $[Sb_2F_{11}]^-$ and $[SbF_6]^-$ Salts

B) **Hard or Class a $M^{2+}(d^n)$ $n = 4, 10$**

M = $Cr(3d^4)$, $Mn(3d^5)$, $Fe(3d^6)$, $Co(3d^7)$, $Ni(3d^8)$, $Cu(3d^9)$, $Zn(3d^{10})$, $Ag(4d^{10})$, $Cd(4d^{10})$

React with $[SbF_6]^-$ $\longrightarrow$ $M[SbF_6]_{2(s)}$

C) **Soft M^+, M = Cu, $3d^{10}$, Ag, $4d^{10}$ in Strong Protonic Acids**

Form solvated polycarbonyls $[Cu(CO)_n]^+_{solv.}$, $n = 1-4$, and $[Ag(CO)_n]^+_{solv.}$, $n = 1-3$

No isolable products are obtained from these solutions.

Scheme 2. Reaction chemistry of "naked" metal ions in CO/HF · SbF₅ and other protonic acids.

The generated cations consist of the 5d species Hg^{2+},[6] Au^+,[15] Pt^{2+}, Ir^{3+} and Os^{2+}[12] as well as the 4d ions Pd^{2+} and Ru^{2+}.[12] All seven cations are strongly polarizing transients that require stabilisation by suitable donor ligands in order to give isolable salts with complex cations. As illustrated in Scheme 2, all cations in this group, termed **A**, are viewed as soft to borderline acids, in terms of Pearson's soft and hard acid and base (SHAB) concept,[28] or, according to a classification proposed earlier by Ahrland, Chatt and Davies, as class b metal ions.[29] These soft acids will react preferentially with the soft Lewis base CO in SbF₅ or HF–SbF₅,[28] to form thermally stable homoleptic, frequently superelectrophilic,[14] metal carbonyl cations.[11–13] The resulting metal carbonyl cations are all diamagnetic and have unique compositions, just like neutral mononuclear metal carbonyls[17–19] or metal carbonylates.[17–20] The metal carbonyl ions $[M(CO)_n]^{m+}$ crystallise with $[Sb_2F_{11}]^-$ or $[SbF_6]^-$ and most of the resulting salts have been structurally characterised by single-crystal X-ray diffraction[6, 11–13, 21, 30] (see Table 1).

The composition of the homoleptic metal carbonyl cations and their molecular structures fall into three groups in accordance with their d-electron configurations: 1) linear (d^{10}) $D_{\infty h}$, found for $[Hg(CO)_2]^{2+}$[6] and $[Au(CO)_2]^+$;[3, 15] 2) square planar (d^8), D_{4h} for $[Pd(CO)_4]^{2+}$ and $[Pt(CO)_4]^{2+}$;[30] and 3) octahedral, (d^6) O_h for $[Os(CO)_6]^{2+}$, $[Ru(CO)_6]^{2+}$[12] and $[Ir(CO)_6]^{3+}$.[21]

Linear and square-planar geometries have previously been unknown in metal carbonyl chemistry,[17–20] and the effective atomic number (EAN) rule is obeyed only for the $[M(CO)_6]^{m+}$ ions. The regular octahedral geometry is also found for metal carbonylates in Groups 4 and 5,[20] neutral homoleptic molecules in Group 6[17–19] and as discussed for cations in Groups 7,[1, 2] 8 and 9.[11–13, 31] This structural similarity allows an extensive, systematic correlation of their structural and

spectroscopic properties,[11, 12] supported by density functional theory (DFT) calculations[30, 31] on sixteen isostructural molecules or ions. According to DFT calculations,[31] all $[M(CO)_6]$ species have partial atomic charges q_C that are more positive (or less negative) than q_M; hence, the difference $q_C - q_M$ is a positive entity,[30, 31] as is found in the case for metal carbonylates[20] and neutral metal carbonyls.[17–19] In summary all $[M(CO)_6]^{m+}$ ions with $m = 2, 3$ have electrophilic carbon centres, as do the $[M(CO)_4]^{2+}$ ions M = Pd, Pt.[30]

In addition a number of cations (type **B** in Scheme 2), mostly from the 3d series and generally 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.[32] 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.[33] The formation of $M[SbF_6]_2$ complexes rather than $[M(CO)_n]^{m+}$ species is not unexpected, since the M^{2+} ions are viewed as hard-to-border-line, according the SHAB concept[28] or predominantly as class a metals[29] (see Scheme 2).

As can been seen from the oxidative carbonylation of $[Fe(CO)_5]$ according to the overall reaction given in Equation (2), relatively hard metals[28, 29] like Fe^{2+} can also form homoleptic, superelectrophilic[14] metal carbonyl cations.

$$[Fe(CO)_5] + CO + XeF_2 + 4 SbF_5 \xrightarrow[\text{or SbF}_5]{\text{HF–SbF}_5} [Fe(CO)_6][Sb_2F_{11}]_2 + Xe \qquad (2)$$
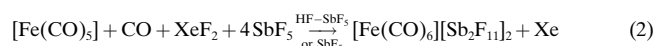
With both $[Sb_2F_{11}]^-$ and $[SbF_6]^-$ as counterions, salts of high thermal stability up to 190 °C[34] are formed. The irreversible thermal decomposition studied by DSC, leads to Fe$[SbF_6]_2$, with simultaneous loss of all six CO ligands.[33, 34] In a similar manner, $[M(CO)_6]$ (M = Mo, W) undergoes $2e^-$ oxidation in HF–SbF$_5$ by SbF$_5$. In case of tungsten, $[W(CO)_6(FSbF_5)][Sb_2F_{11}]$ is isolated,[35] while for Mo condensation produces polymeric $[\{Mo(CO)_4\}_2(F_2SbF_4)_3][Sb_2F_{11}]$.[36]

In addition the soft acids[28] Cu$^+$ and Ag$^+$ (labelled type **C** in Scheme 2) form solvated polycarbonyl ions of the type $[M(CO)_n]^+$ (M = Cu, Ag, n = 1 to 4) in strong protonic acids; however, no isolable products result. In spite of this the solvated polycarbonyl cations have found extensive use in catalysis.[37]

Correspondingly, Cu$^+$ and Ag$^+$ salts with weakly coordinating anions will readily add CO stepwise in aprotic solvents.[38, 39] There are, however, two important differences:

1) The formation of polycarbonyls occurs; this is without precedent in metal carbonyl chemistry.[10–12, 16–20] 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.
2) The CO addition is reversible and stepwise loss of CO occurs either with increasing temperature or decreasing CO pressure.

In summary, the role of superacids as reaction media in reductive or solvolytic carbonylation reactions is seen 1) in the formation of "naked" cations, 2) dissolution of CO and 3) formation of the ions $[SbF_6]^-$ and $[Sb_2F_{11}]^-$. The metal cations will either take up the soft donor CO,[28, 29] irreversibly or reversibly in case of Cu$^+$ and Ag$^+$, or react with $[SbF_6]^-$ to form $M[SbF_6]_2$. The diverging behaviour of the "naked" M^{n+} ions can be rationalised in terms of the SHAB concept[28] and the metal ion classification according to Ahrland, Chatt and Davies.[29] No other synthetic method has so far produced a super-electrophilic metal carbonyl cation in a thermally stable salt.

Structural Aspects of σ-Bonded Metal Carbonyl Cations and Their Derivatives

All 22 molecular structures mentioned in Table 1 involve metal carbonyl cations of very high electrophilicity. The $[Sb_2F_{11}]^-$ ion, formed by self assembly in the superacids, is the most common counterion. In Group 8 complexes, $[SbF_6]^-$ is encountered also, whereby both $[Sb_2F_{11}]^-$ and $[SbF_6]^-$ are found. The structural parameters and vibrational spectra for both sets of $[M(CO)_6]^{2+}$ ions (M = Fe, Ru, Os) are identical within esd values and independent of the anion.[12, 13] This is also the case for the isostructural pair $[Rh(CO)_4][M'_2Cl_7]$ (M' = Al, Ga).[12]

Among the salts in Table 1, additional isostructural pairs are listed, formed by 4d and 5d metals: $[M(CO)_4][Sb_2F_{11}]_2$, M = Pd, Pt;[30] $[M(CO)_5Cl][Sb_2F_{11}]_2$, M = Rh, Ir;[23] $[M(CO)_6][Sb_2F_{11}]_2$, M = Ru, Os[12] and $[M(CO)_6][SbF_6]_2$, M = Ru, Os,[12, 13]. In these complexes the unit cell volumes V, of the 5d metal salts are very slightly smaller (by about 0.3 to 0.8 %) than those of the corresponding salts formed by 4d metals,[12, 13] on account of relativistic effects.[40]

In addition to the noted contraction of the unit cell volumes V, for salts formed by 5d metals of isostructural pairs[23, 30] and triads $[M(CO)_6]^{2+}$ (M = Fe, Ru, Os)[12, 13, 34] with either $[SbF_6]^-$ or $[Sb_2F_{11}]^-$ as counterions, the principal internal bond parameters d_{M-C}, d_{C-O}, $\nu(CO)_{av}$ and f_{CO} for the cations are identical within error limits, again due to relativistic effects.[40] Hence interionic C–F contacts are for isostructural salts comparable in numbers and the strength of these contacts.[12, 13]

Consistent with the near absence of M→CO π back-bonding, two interrelated effects are noted: a) M–C bond lengths increase with increasing oxidation states of M and are, for superelectrophilic[14] cations, with ~2.0(1) Å[12, 13] among the longest M–C distances listed for the various metals in the Cambridge data index;[41] b) correspondingly C–O distances are very short, among the shortest listed in the Cambridge data index.[41] However, as discussed,[11–13] the strength of the C–O bond is better expressed in terms of $\nu(CO)_{av}$ or f_{CO} and measured values are as high as ~2280 cm^{-1}. According to a theoretical study,[42] these very high $\nu(CO)_{av}$ values are, primarily, due to a polarisation of the C–O bond. With increasing positive charge of the central metal atom an increasing positive charge on the C atoms of the CO ligands is induced. This results in an increasing Coulomb contribution on the CO bond, with the O atom negatively charged. Its strength will depend directly on the oxidation state of M and inversely on the number of CO ligands in the coordination

sphere of the cation. Consequently for a homoleptic metal carbonyl ion of the type $[M(CO)_n]^{m+}$, the strength of the C–O bond, measured as $d_{C–O}$, $\nu(CO)$ or f_{CO}, is found to be directly proportional to the complex charge m and inversely proportional to the coordination number n.

For homoleptic, superelectrophilic metal carbonyl ions $[M(CO)_n]^{m+}$ of the 5d series, the observed order of increasing CO bond strength, with $\nu(CO)_{av}$ in cm^{-1} for $[Sb_2F_{11}]^-$ salts[11, 12] is: $[Os(CO)_6]^{2+}$ (2209) < $[Pt(CO)_4]^{2+}$ (2259) < $[Ir(CO)_6]^{3+}$ (2268) < $[Hg(CO)_2]^{2+}$ (2280). It is apparent that M–CO bonding for all species involves mainly M ← CO σ donation.

Substitution of one or more CO groups in a homoleptic cation by anions (Cl$^-$, SOF$^-$, FSbF$_5^-$) will reduce the effective oxidation sate of M and consequently f_{CO} or $\nu(CO)_{av}$ for the $\{M(CO)_n\}$ moiety of the resulting derivative will decrease.[11–13, 21] The validity of the empirical relationship is apparent also from the observed range of $\nu(CO)_{av}$, f_{CO}, $d_{C–O}$ and $d_{M–C}$ for the currently known metal carbonyl cations and their derivatives[11–13] listed in Table 1. For example, $\nu(CO)_{av}$ extends from 2280 cm^{-1} for linear $[Hg(CO)_2]^{2+}$ to low values of 2116 and 2124 cm^{-1} for octahedral $[Re(CO)_6]^+$ or seven-coordinate $[W(CO)_6(FSbF_5)]^+$, respectively.[11–13]

Finally for isostructural, octahedral $[M(CO)_6]$ species, the relationship extends also to neutral metal carbonyls and metal carbonylates.[17–20] Even though the bond parameters ($\nu(CO)$, f_{CO}, $d_{C–O}$, $d_{M–C}$) vary widely for the σ metal–carbonyl cations on the one hand[11–13] and the reduced metal carbonylates $[M(CO)_6]^{2-}$ (M = Ti, Zr, Hf)[20] on the other. A careful analysis of the four bond parameters, including also ^{13}C chemical shifts[11–13] for octahedral $[M(CO)_6]$ species, reveals that all variations in bond parameter with increasing oxidation state of M are gradual and can be explained readily by a wider variation in σ donation and π backbonding, the two main components of synergetic M–CO bonding.[12, 43, 44] These conclusions are fully confirmed by DFT calculations.[31]

In summary it is apparent, that CO is a far more versatile ligand than had been assumed previously.[17–19] The use of powerful reducing agents in basic solvents[20] on the one hand and strong oxidisers in superacidic reaction media on the other[11–13] has widened the observed range of $\nu(CO)$ from ~1500 to 2300 cm^{-1}. The resulting complexes range from supernucleophiles[20] to superelectrophiles.[15, 34] There is no need for the use of a classification into "classical" ($\nu(CO)$ < 2143 cm^{-1}) and "nonclassical" ($\nu(CO)$ > 2143 cm^{-1}) metal carbonyls,[38] because M–CO bonding remains synergetic[12, 33, 43] over the entire range, and the two different bonding modes of CO claimed[38] do not exist in metal carbonyls.[11–13, 17–20]

Two interesting observations are not readily explained by the proposed relationship between CO bond strength, the oxidation state of M and the coordination number of the $\{M(CO)_n\}$ species, discussed previously:

1) For the three CO stretching fundamentals (A$_{1g}$, E$_g$, T$_{1u}$) of isoelectronic octahedral $[M(CO)_6]$ complexes (5d metals) the increase in $\nu(CO)$ is no longer linear and increments of $\Delta\nu(CO)$ between different species decrease for the ions $[Os(CO)_6]^{2+}$ and $[Ir(CO)_6]^{3+}$[11–13, 21] (see Figure 2).
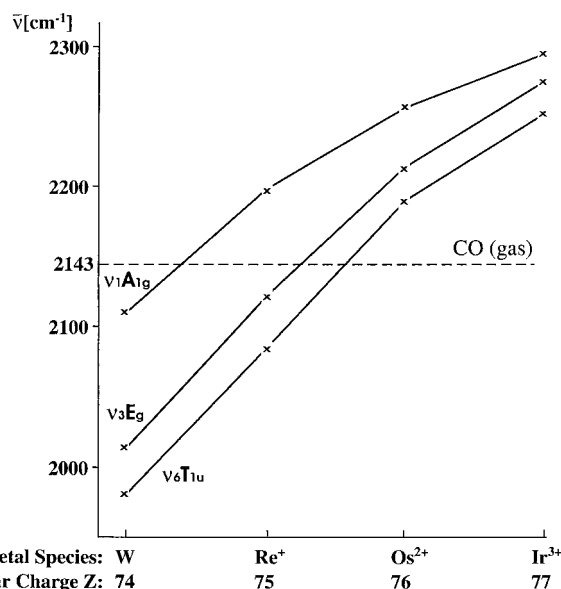
Figure 2. A plot of the CO-stretching fundamentals [cm^{-1}] for octahedral $[M(CO)_6]^{m+}$ (M = W, Re, Os, Ir; m = 0, 1, 2, 3) versus the nuclear charge.

2) For a new, fully characterised borane carbonyl, $(CF_3)_3BCO$,[45] values of $\nu(CO) = 2267$ cm^{-1} and $f_{CO} = 21.80 \times 10^2$ N m^{-1} are observed; these are much higher than in any other borane carbonyl[37, 45] and identical to the $\nu(CO)_{av}$ value for $[Ir(CO)_6]^{3+}$.[11–13, 21]

A plausible cause for a reduction in C–O bond strength for superelectrophilic metal carbonyl cation is seen in an interionic charge transfer from the fluoroantimonate(v) anions into the π* molecular orbitals of the CO ligands in $[M(CO)_n]^{m+}$ in which n = 2, 4 or 6 and m = 2, 3.

Direct evidence for such an interionic electron transfer is twofold:

1) There are several significant interionic C–F interactions and considerably weaker, imposed O–F contacts found in the solid-state structures[12, 13] (see Table 1). The observed C–F contacts are up to 0.7 Å shorter than the sum of the van der Waals radii for C and F of 3.19 Å[46] and decrease both in number and strength with increasing coordination number in the order: 2 (linear) ~4 (square planar) > 6 octahedral > 7 coordinate species due to increasing electrophilicity of the carbonyl C atom (vide supra) (see frontispiece).

2) To facilitate the formation of extended structures through C–F interionic contacts, the conformation of the ubiquitous $[Sb_2F_{11}]^-$ is distorted, in salts with superelectrophilic metal carbonyl cations, from its D_{4h} equilibrium symmetry[47] by bending and rotational processes[12, 13] towards C_1. In salts with unipositive ions like $[Au(CO)_2]^+$ and $[Rh(CO)_4]^+$, the D_{4h} symmetry of $[Sb_2F_{11}]^-$ is retained and significant C–F contacts are absent.

Convincing proof for the electrophilic nature of carbon comes from the recently reported molecular structure of $[Ir(CO)_6][SbF_6]_3 \cdot 4\,HF$[21] (see Figure 3). The F atoms of the HF solvate molecules are strongly coordinated in isotridentate and anisobidentate modes to the six C atoms of a regular octahedral $[Ir(CO)_6]^{3+}$ ion.[21] The structure of

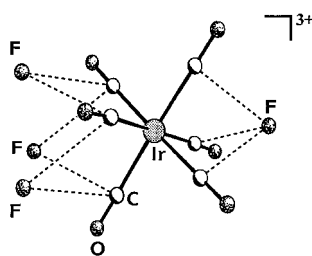Figure 3. The colecular structure of the solvated cation in $[Ir(CO)_6]$-$[SbF_6]_3 \cdot 4\,HF$.

$[Ir(CO)_6][SbF_6]_3 \cdot 4\,HF$[21] provides a realistic model for the solvation of superelectrophilic metal carbonyl cations in $HF-SbF_5$[9, 10] and other superacids.[4] Additional evidence for the electrophilic nature of the carbonyl C atoms comes from an emerging chemistry[48] and the growing use of $[M(CO)_n]^{m+}$ species in catalysis.[37]

A limited number of molecular structures have been reported for the polycarbonyl complexes of Cu^I and Ag^I and reviewed recently.[39] The structural features reported, differ from those of σ-carbonyl cations[11–13] on five counts:

1) Any interionic or intermolecular contacts to the C atoms of the CO ligands are absent.

2) Relatively short, covalent contacts between anions and M$^+$ (M = Cu, Ag) are found in a number of monocarbonyl complexes.

3) In addition to anion–cation contacts, bent $\{Cu(CO)_2\}$ moieties with C-Cu-C bond angles of about $120°$ are found.[39]

4) In CO complexes of Cu^I and Ag^I, $\nu(CO)$ is found to be anion dependent with wide variations noted.[39]

5) Some Ag–F contacts of ~ 3 Å found in $Ag[B(OTeF_5)_4]$[49] are retained on CO addition to give $[Ag(CO)_n][B(O-TeF_5)_4]$,[50] $n = 1, 2$ with Ag–F contacts of similar strength also found in $Ag[Al(OR_F)_4]$ complexes.[51]

These observations set the polycarbonyl ions of Cu^I and Ag^I apart from the σ-carbonyl cations[11–13] and other metal carbonyls[17–20] and allow three conclusions:

1) 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.[38, 39]

2) This polarity is retained on coordination to CO and multiple, reversible CO addition to the metal centre is possible.

3) In addition, relativistic effects for Au$^+$ and Hg^{2+} strengthen the σ-bonds to CO formed by these metals and thermally stable salts can be prepared with the 5d^{10} species.

A comparison between σ-carbonyls and the polycarbonyl complexes of Cu^I and Ag^I is found in Table 2. The proposed subdivision into σ-metal carbonyl and polycarbonyl complexes is confirmed by "perturbation" calculations for linear d^{10} dicarbonyl species.[52]

The presence of electrophilic carbon centres in σ-metal carbonyl cations[11–13] establishes a link to the large family of stable carbocations,[53] which can also be generated in superacids.[4] With NMR spectroscopy widely used in their study in solution, a limited number of reliably determined molecular structures have become available.[54, 55] They feature similar superacid ions to $[SbF_6]^-$ and $[Sb_2F_{11}]^-$. The presence of fewer electrophilic carbon centres results frequently in ion pairing, but extended structures are encountered as well.[54, 55]

Bonding Aspects in σ-Carbonyls

To summarise the bonding interactions encountered in salts formed by metal carbonyl cations ($[M(CO)_n]^{m+}$ $n = 2, 4, 6$; $m = 1-3$) and fluoroantimonate(v) anions ($[Sb_2F_{11}]^-$, $[SbF_6]^-$) in the solid state, a model is presented in Figure 4. The model

Table 2. 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 $[M(CO)_n]Y$ ($n = 1-4$)
distribution	5d: Hg, Au, Pt, Ir, Os, Re; 4d: Pd, Rh, Ru, Tc; 3d: Mn, Fe, Co	4d: Ag; 3d:Cu
metal oxidation state	$+1$ to $+3$	$+1$
reaction media	superacids (SbF$_5$, HF−SbF$_5$, etc.)	aprotic solvents
synthetic methods	1) irreversible CO addition to transient, soft M^{n+} ($n = 1-3$) 2) oxidative carbonylation of metal carbonyls and derivatives	reversible, pressure- and temperature-controlled CO addition to M$^+$ salts with weakly coordinating 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 $[M(CO_n Y]$ $n = 1-4$; depending on p_{CO}, T
characterization	extensively characterized by analytical, spectroscopic (IR, Raman, NMR) methods and X-ray diffraction, and supported by DFT calculations	characterized by computational methods; limited number of molecular structures; vibrational spectra in the CO stretching region only
thermal stability	stable between 100 to 250 °C as $[Sb_2F_{11}]^-$ or $[SbF_6]^-$ salts	unstable at ambient conditions
thermal decomposition	complex, irreversible complete loss of CO; M and COF$_2$ formed	stepwise, reversible loss of CO
strength of CO bond (ν_{CO}, f_{CO}, d_{C-O})	proportional to (oxidation state of M/ coordination number of M)	strong anion dependance of $\nu(CO)$
extended structures	formed through C−F contacts	M−F contacts and M−Y covalent bonds
partial atomic charges:	$qC > qM \gg qO$ $qC - qM$ is positive	$qM > qC \gg qO$ $qC - qM$ is negative
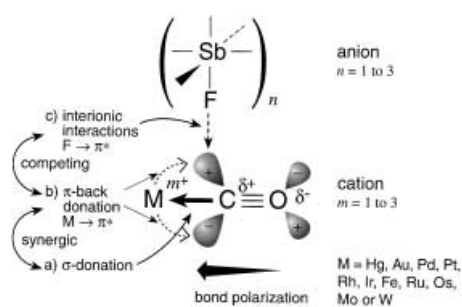
Figure 4. Bonding interactions in metal carbonyl cations with fluorantim-onate anions in the solid state.

is derived from a description of synergetic bonding,[43, 44] introduced by us previously.[11] The metals include, in addition to the "soft"[28] or class b metals,[29] also Fe, Rh, Mo and W, whereby carbonyl cations are synthesised by oxidative methods.[11–13] In addition to the classical components of synergetic bonding, σ-donation and π-back-donation,[43, 44] two new components are added: 1) bond polarisation of the CO bond[42] by M^{m+}—this contributes to the very strong CO bonds—and 2) $F \rightarrow \pi^*$ back-donation, which includes in the discussion also the anion of the extended structures.

σ-Donation and bond polarisation are complementary and will effectively strengthen the C–O bond. In contrast, π-back-donation and interionic electron delocalisation 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 M–CO σ bonding dominates. We have chosen the term "σ metal carbonyl cation" or σ-carbonyl for this situation, which describes the principal M ← CO bonding mode. Hence, in the absence of π-backbonding, $\nu(CO)_{av}$ in the $[Os(CO)_6]^{2+}$ and $[Ir(CO)_6]^{3+}$ salts decreases through $F \rightarrow \pi^*$ back-dona-tion,[11–13] but in the molecular σ-carbonyl $(CF_3)_3BCO$,[45] $\nu(CO)$ is unexpectedly high.

Summary, Conclusions and Outlook

In a relatively short period of time since the first detection of $[Au(CO)_2]^{+[3]}$ in a superacidic media,[4] thermally stable σ-bonded metal carbonyl cations and their derivatives[11–13] have grown into a substantial, well-characterised group. Through new, imaginative synthetic methodology, well over twenty molecular structures,[11–13, 21, 22, 30, 34] complete vibrational anal-yses[11, 12, 15, 30, 34] and supporting DFT calculations[30, 31] are available and form a sound experimental basis for a bonding description. In this description, the traditional components of synergetic bonding,[43, 44] that is, σ-donation and M →CO π-back-donation, are supplemented by CO bond polarisation[42] and external electron delocalisation into π* MO's on CO to account for the high electrophilicity of the carbonyl carbon atom.[21, 23]

There are four recent indications that the rapid develop-ments of the last 12 years,[11–13] summarised above, have not come to an end yet and that our synthetic methodology can be expanded beyond carbonylations in HF–SbF_5:

1) The abstraction of chloride from $[Rh(CO)_2Cl]_2$ by the Lewis acids MCl_3 (M = Al, Ga) in the gas phase has, in the presence of CO, produced $[Rh(CO)_4][M_2Cl_7]$ (M = Al, Ga), both of which are structurally characterised.[56]
2) The oxidation of $[\{Rh(CO)_2Cl\}_2]$ or $[Rh(CO)_4]^+_{(solv)}$ in HF or HSO_3F by F_2 or $S_2O_6F_2$ has produced $[Rh(CO)_5Cl][Sb_2F_{11}]_2$ (previously structurally character-ised)[23] and fac-$[Rh(CO)_3(SO_3F)_3]$, respectively.[56] 3) The partial hydrolysis of $[B(CF_3)_4]^{-[27]}$ in concentrated H_2SO_4 has produced surprisingly the new borane carbonyl $(CF_3)_3BCO$,[57] which has been structurally characterised both in the gas phase and in the solid state.[45]
4) The reaction of $(CF_3)_3BCO$ with $Co_2(CO)_8$ in HF in the presence of CO has produced $[Co(CO)_5][B(CF_3)_3F)]$.[58] The structural analysis reveals the presence of the first trigonal bipyramidal (D_{3h}) metal carbonyl cation.[58]

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