New Homoleptic Metal Carbonyl Cations: the Syntheses, Vibrational and ^{13}C MAS NMR Spectra of Hexacarbonyl-ruthenium(II) and -osmium(II) Undecafluorodiantimonate(V), $[Ru(CO)_6][Sb_2F_{11}]_2$ and $[Os(CO)_6][Sb_2F_{11}]_2$

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The new homoleptic carbonyl cations $[Ru(CO)_6]^{2+}$ and $[Os(CO)_6]^{2+}$ are obtained as $[Sb_2F_{11}]^-$ salts by the reductive carbonylation of $M(SO_3F)_3$ (M = Ru, Os), under very mild conditions (60–90 °C, 1 atm CO), in liquid SbF_5 in a simple, one-step procedure, and are characterized by FT Raman, FTIR and ^{13}C MAS NMR spectroscopy.

Among homoleptic transition metal carbonyls, mononuclear and octahedral species like the carbonylate anions of the type $[M(CO)_6]^-$ (M = V, Nb or Ta),[1] neutral molecules like $M(CO)_6$ (M = Cr, Mo or W),[2] and the cations $[M(CO)_6]^+$ (M = Mn, Tc or Re),[3] have been known for some time.[1–3] A more recent addition are the highly reduced carbonylates $[M(CO)_6]^{2-}$ (M = Ti, Zr or Hf).[4]

The existence of the dications $[M(CO)_6]^{2+}$ (M = Fe, Ru or Os), has long been anticipated, and there have been early claims of the identification of $[Fe(CO)_6]^{2+}$[5,6] and of $[Os(CO)_6]^{2+}$[5] as $[AlCl_4]^-$ salts,[5] or as products of an amine-catalysed disproportionation of $Fe(CO)_5$.[6] However, these claims have been subsequently repudiated,[7] and it was accepted that none of the three cations exists in isolable, thermally stable compounds.[3,8] It appears that the Lewis acids used ($AlCl_3$, $FeCl_3$) were inadequate, and the resulting conjugate anions ($AlCl_4^-$, $FeCl_4^-$) were incapable of stabilizing dipositive cations.[3]

We have recently reported a new synthetic approach to homoleptic carbonyl cations of electron-rich metals, which has allowed for the first time the isolation and characterization of two types of homoleptic dications, linear $[Hg(CO)_2]^{2+}$,[9] and square-planar $[M(CO)_4]^{2+}$ (M = Pd or Pt).[10] Thermally stable salts are in all instances formed with $[Sb_2F_{11}]^-$ as counter anion.[8–10] Of these, $[Hg(CO)_2][Sb_2F_{11}]_2$ has recently been structurally characterized,[9b] where it has been found that secondary SbF···CO contacts are stabilizing the resulting salts in the solid state.

The synthetic method used, the solvolysis of $Hg(SO_3F)_2$ in liquid SbF_5 in a CO atmosphere,[9a] is now adopted to the syntheses of $[Ru(CO)_6][Sb_2F_{11}]_2$ and $[Os(CO)_6][Sb_2F_{11}]_2$ from $Ru(SO_3F)_3$[11] or $Os(SO_3F)_3$,[12] respectively. In a simple, one-step process according to eqn. (1), the new homoleptic metal

$$2\,M(SO_3F)_3 + 16\,SbF_5 + 13\,CO \xrightarrow[60\text{–}90\ ^\circ C,\ 2\text{–}4\ d]{SbF_5(l),\ ca.\ 1\ atm\ CO} 2\,[M(CO)_6][Sb_2F_{11}]_2 + CO_2 + S_2O_5F_2 + 4\,Sb_2F_9(SO_3F) \quad (1)$$
(M = Ru or Os)

carbonyl salts form as white, moisture-sensitive solids. They are identified by microanalysis, the mass balance of the reaction and CO uptake measurements. Reductive carbonylation in a strongly acidic medium, first employed in the generation of $[Au(CO)_2]^+$ in HSO_3F,[13] is also found to be very effective in liquid SbF_5 as reaction medium. The reactions proceed quantitatively under rather mild conditions. The temperature of the reaction should be held below 100 °C to avoid reduction to Os or Ru metal. All attempts to extend our approach to the synthesis of $[Fe(CO)_6][Sb_2F_{11}]_2$ have so far failed, and the known compound $Fe[SbF_6]_2$[14] is formed instead. It is, however, possible to generate the cations $[M(CO)_6]^+$ (M = Mn, Re), in liquid SbF_5 from their $M(CO)_5Cl$ precursors, and to isolate the compounds $[M(CO)_6][Sb_2F_{11}]$ (M = Mn, Re), again under mild conditions (60–80 °C, 0.5–0.8 atm CO), which differ markedly from those of the original high-pressure syntheses with $AlCl_3$ as Lewis acid.[3,15] Attempts to obtain metal carbonyl fluorosulfates of Ru and Os were successful. Both $Ru(SO_3F)_3$ and $Os(SO_3F)_3$ were reduced in HSO_3F at *ca.* 25 °C to brown M^{II} carbonyl fluorosulfates that have not been identified fully. In liquid SbF_5 in a CO atmosphere the compounds convert to $[M(CO)_6][Sb_2F_{11}]_2$.

The thermal stabilities of $[Ru(CO)_6][Sb_2F_{11}]_2$ and $[Os(CO)_6][Sb_2F_{11}]_2$ were comparable. On heating in a sealed capillary, both solids shrank at *ca.* 170 °C and decomposed at 300 °C to black residues. Solutions of $[M(CO)_6][Sb_2F_{11}]_2$ in HSO_3F or in HSO_3F–SbF_5 were unstable and decomposed slowly with CO evolution. Both compounds were insoluble in SO_2 and we were not able to obtain single crystals. Characterization of the cations hence rests on vibrational and ^{13}C MAS NMR spectra.

The vibrational analysis is facilitated by the syntheses of the ^{13}C isotopomers from ^{13}CO. Vibrational bands attributed to the $[Sb_2F_{11}]^-$ anions are readily identified by comparison to precedents.[9,10,16] This allows the identification of five out of six Raman active and three of four IR active fundamentals of $[M(CO)_6]^{2+}$ (M = Ru, Os), by their ^{12}C–^{13}C shifts. Raman and IR bands due to the cation are mutually exclusive, which indicates that $[M(CO)_6]^{2+}$ is octahedral.

As observed in the Raman spectra of other $M(CO)_6$ species,[17,18] the A_{1g} CO stretching vibrations are found at higher wavenumbers, but are of lower intensity, than the E_g vibrations at lower wavenumbers. As summarized in Table 1, the CO stretching vibrations of the two homoleptic carbonyl cations $[M(CO)_6]^{2+}$ (M = Ru, Os) occur at considerably higher wavenumbers than for the other isoelectronic $M(CO)_6$ species, and the stretching force constants are 19.82 and 19.74 × 10^2

Table 1 Vibrational spectra (ν_{CO} region) and ^{13}C chemical shifts for octahedral, isoelectronic $[M(CO)_6]$ species

	ν_1 A_{1g}/cm^{-1}	ν_3 E_g/cm^{-1}	ν_6 F_{1u}/cm^{-1}	$\bar{\nu}$ CO_{av}/cm^{-1}	f_{CO} × 10^2/N m^{-1}	^{13}C NMR/δ
$[Ru(CO)_6]^{2+}$[a]	2254 (2203)	2222 (2172)	2199 (2149)	2216 (2166)	19.82 (19.81)[d]	166.1
$[Os(CO)_6]^{2+}$[a]	2259 (2206)	2218 (2166)	2190 (2141)	2211 (2160)	19.76 (19.78)[d]	147.3
$[Re(CO)_6]^{+}$[b]	2197	2122	2085	2116	18.67	
$Mo(CO)_6(s)$[c]	2113 (2064)	2005 (1960)	1986 (1943)	2014 (1969)	17.15	204[e]
$W(CO)_6(s)$[c]	2115 (2066)	1998 (1953)	1977 (1933)	2007 (1962)	17.02	192[e]

[a] Wavenumbers in parentheses refer to the ^{13}C isotopomer bands. [b] Ref. 17. [c] Ref. 18. [d] Obtained by using the Cotton–Kraihanzel method (see *e.g.* F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, 1962, **84**, 4432. [e] B. E. Mann, *J. Chem. Soc., Dalton Trans.*, 1973, 2012.

N m^{-1} respectively, compared to 17.15 and 17.02 × 10^2 N m^{-1} for $Mo(CO)_6$ and $W(CO)_6$.[18]

^{13}C NMR chemical shifts are found at δ 166.1 and 147.3 for the ruthenium(II) and osmium(II) hexacarbonyl cations. As the oxidation state of the metal increases, π-back bonding gradually appears to diminish. This is reflected in an increase of both $\bar{\nu}$ CO_{av}, the stretching force constants f_r, and a shift of the ^{13}C resonance to lower frequencies, as seen in Table 1. Recently reported ^{13}C NMR δ values of 179 and 176.9 for $[Ru(CO)_5H]^+$ and of δ 159 for $[Os(CO)_5H]^{2+}$ in anhydrous HF[19] correlate well, as do chemical shifts of δ 217 and 211 reported for the carbonylate anions $[Nb(CO)_6]^-$ and $[Ta(CO)_6]^-$ [1] on the other end of the range.

In summary, a new synthetic methodology, the solvolysis in liquid antimony(V) fluoride in a CO atmosphere is, for the first time, extended to the binary fluorosulfates $Ru(SO_3F)_3$[11] and $Os(SO_3F)_3$.[12] In a simple one-step procedure the new, thermally stable salts $[M(CO)_6][Sb_2F_{11}]_2$ (M = Ru, Os), form readily. The $[M(CO)_6]^{2+}$ cations are strictly octahedral. The ability of the $[Sb_2F_{11}]^-$ anion to stabilize highly electrophilic, dipositive cations by interionic secondary contacts between F and the electrophilic C atom of the carbonyl group is confirmed by the molecular structures of $[Hg(CO)_2][Sb_2F_{11}]_2$[9b] and $[Ir(CO)_5Cl][Sb_2F_{11}]_2$,[20] where an octahedrally coordinated cation, $[Ir(CO)_5Cl]^{2+}$ is found, and significant F···C interionic contacts are observed.

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