

Syntheses, Molecular Structures, and Vibrational Spectra of Chloropentacarbonylrhodium(III) and -iridium(III) Undecafluorodiantimonate(V), $[\text{Rh}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$ and $[\text{Ir}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$: An Experimental and Density Functional Study

Helge Willner,^{†,‡} Christian Bach,[†] Rudolf Wartchow,[†] Changqing Wang,[§] Steven J. Rettig,[§] James Trotter,[§] Volker Jonas,^{||} Walter Thiel,[⊥] and Friedhelm Aubke*^{*,§}

Institut für Anorganische Chemie der Universität, Callinstrasse 9, D-30167 Hannover, Germany, Department of Chemistry, The University of British Columbia, 2036 Main Mall, Vancouver, BC V6T 1Z1, Canada, San Diego Supercomputer Center, MC 0505, 9500 Gilman Drive, San Diego, California 92093-0505, and Max Planck Institut für Kohlenforschung, Kaiser Wilhelm Platz 1, D-45470 Mülheim an der Ruhr, Germany

Received October 8, 1999

The reactions of either bis(μ -chloro)tetracarbonyldirhodium(I), $[\text{Rh}(\text{CO})_2(\mu\text{-Cl})_2]$, or chlorotricarbonyliridium(I), $[\text{Ir}(\text{CO})_3\text{Cl}]_n$, in the conjugate Brønsted–Lewis superacid $\text{HF}\text{--}\text{SbF}_5$ and in a CO atmosphere, produce $[\text{Rh}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$ or $[\text{Ir}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$, respectively. In these oxidative carbonylation reactions, antimony(V) fluoride functions as an oxidizing agent. The reduced product is identified as $6\text{SbF}_3 \cdot 5\text{SbF}_5$. $[\text{Rh}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$ is obtained in the form of single crystals. Crystal data: monoclinic, space group $P2_1$ (No. 4); $a = 9.721(1)$, $b = 12.602(1)$, $c = 10.538(1)$ Å; $\beta = 106.51(1)^\circ$; $V = 1237.7(2)$ Å³; $Z = 2$; $T = 300$ K; $R_1 [I > 3\sigma(I)] = 0.0367$, $wR_2 = 0.0739$. Single crystals of $[\text{Ir}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$ are produced in small amounts from a solution of *mer*- $\text{Ir}(\text{CO})_3(\text{SO}_3\text{F})_3$ in magic acid, $\text{HSO}_3\text{F}\text{--}\text{SbF}_5$. The possible source of chlorine will be discussed. Crystal data for $[\text{Ir}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$: monoclinic, space group $P2_1$ (No. 4); $a = 9.686(2)$, $b = 12.585(2)$, $c = 10.499(2)$ Å; $\beta = 106.59(2)^\circ$; $V = 1226.5(4)$ Å³; $Z = 2$; $T = 294$ K; $R_1 [I > 3\sigma(I)] = 0.032$, $R_w = 0.031$. The bond lengths and bond angles are nearly identical in the two isostructural salts; however, the cell volume of $[\text{Ir}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$ is slightly smaller than that of $[\text{Rh}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$. The cations (point group C_{4v}) feature unusually long M–C bonds (M = Rh, Ir) and correspondingly short CO bonds, as well as high CO stretching wavenumbers and high CO stretching force constants. The $[\text{Sb}_2\text{F}_{11}]^-$ anions are not symmetry related, and their dihedral and bridge angles differ slightly in both salts. There are significant interionic contacts in $[\text{Ir}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$ exclusively of the C–F type (about 2 for each C atom of the five carbonyl groups) resulting in extended structures. The vibrational spectra for both $[\text{M}(\text{CO})_5\text{Cl}]^{2+}$ cations (M = Rh, Ir) are assigned with the help of density functional calculations, which also provide intensities for IR and Raman bands. While $[\text{Rh}(\text{CO})_5\text{Cl}]^{2+}$ is the first cationic carbonyl derivative of Rh(III), the vibrational and structural parameters for $[\text{Ir}(\text{CO})_5\text{Cl}]^{2+}$ are compared to data for $[\text{Ir}(\text{CO})_6]^{3+}$ and *mer*- $\text{Ir}(\text{CO})_3(\text{SO}_3\text{F})_3$.

Introduction

Homoleptic metal carbonyl cations of the type $[\text{M}(\text{CO})_6]^+$ (M = Mn,^{1,2} Tc,³ and Re^{4,5}) have been known since 1961. In their pioneering studies Fischer et al.^{1,2} and Hieber et al.^{3–5} have utilized the halide abstraction from the corresponding metal carbonyl halides by molecular Lewis acids of the type $\text{M}'\text{X}_3$ (M' = Al, Fe; X = Cl, Br) at elevated temperatures and high CO pressures to generate $[\text{M}(\text{CO})_6]^+$ (M = Mn, Tc, Re) cations

as $[\text{M}'\text{X}_4]^-$ salts (M' = Al, Fe; X = Cl, Br), which were previously thought to be incapable of existence.⁶ This view is based on a superficial understanding of the prevailing bonding concept, the Dewar–Chatt–Duncanson model,^{7–9} as well as on unsuccessful attempts, to extend the synthetic methodology^{1–5} to other metal carbonyl halides.^{10,11} Consequently no further progress in the field of homoleptic metal carbonyl cations had occurred for the next 25 years.^{12–14}

A change was initiated in 1990 with the unexpected generation of the dicarbonylgold(I) cation, $[\text{Au}(\text{CO})_2]^+$,¹⁵ by the

* Corresponding author. Phone: (604) 822-3817. Fax: (604) 822-2847. E-mail: aubke@chem.ubc.ca.

[†] Institute für Anorganische Chemie der Universität.

[‡] New address: Fachbereich 6, Anorganische Chemie, Gerhard Mercator Universität GH Duisburg, Lotharstr. 1, D-47048 Duisburg, Germany.

[§] The University of British Columbia.

^{||} San Diego Supercomputer Center.

[⊥] Max Planck Institut für Kohlenforschung.

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reductive carbonylation of $\text{Au}(\text{SO}_3\text{F})_3^{16}$ in the protonic superacid HSO_3F .¹⁷ Shortly thereafter conversion into thermally stable, solid $[\text{Au}(\text{CO})_2][\text{Sb}_2\text{F}_{11}]^{18}$ by solvolysis of the intermediate $\text{Au}(\text{CO})\text{SO}_3\text{F}^{15}$ in the Lewis superacid SbF_5^{19-21} was reported.

By using a similar synthetic methodology, the field of homoleptic metal carbonyl cations and their derivatives has expanded rapidly²² to include at present examples from metals in groups 6 to 12. Liquid SbF_5 , the strongest molecular Lewis acid,²¹ and more recently the conjugate Brønsted–Lewis superacid $\text{HF}–\text{SbF}_5^{19-21}$ have emerged as ideal reaction media and convenient sources for the counterion, the superacid anion $[\text{Sb}_2\text{F}_{11}]^-$.²³ Reductive and solvolytic conversions of transition metal fluorosulfates²⁴ in homoleptic metal carbonyl cation salts²² are the principal synthetic methods. The growing group of homoleptic metal carbonyl cation complexes, synthesized in this manner, includes many “superelectrophilic” species.²⁵ Structurally characterized superelectrophilic cations represent three major structural types: linear $[\text{Hg}(\text{CO})_2]^{2+}$,²⁶ square planar $[\text{M}(\text{CO})_4]^{2+}$ ($\text{M} = \text{Pd}, \text{Pt}^{27}$), and octahedral $[\text{M}(\text{CO})_6]^{2+}$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}^{22,28,29}$). In almost all salts $[\text{Sb}_2\text{F}_{11}]^-$ is found as a counteranion with $[\text{Fe}(\text{CO})_6][\text{SbF}_6]_2^{28}$ a notable exception.

While in general carbonylation reactions have been very effective and widely applicable,²² there have been some difficulties with the metals in group 9. At present, cationic carbonyl species of rhodium and cobalt are unknown. For iridium, problems center around the starting material $\text{Ir}(\text{SO}_3\text{F})_3$,^{24,30} which is obtained by the reaction of iridium with bis(fluoro-sulfonyl)peroxide,^{31,32} $\text{S}_2\text{O}_6\text{F}_2$, in HSO_3F at 110 °C. This reaction is very slow, often incomplete, and accompanied by extensive corrosion and the evolution of O_2 from the decomposition of $\text{S}_2\text{O}_6\text{F}_2$.³⁰ Hence $\text{Ir}(\text{SO}_3\text{F})_3$ is only available in small quantities. Despite these limitations, there has been some progress: CO addition to $\text{Ir}(\text{SO}_3\text{F})_3$ results in the formation of $\text{Ir}(\text{CO})_3(\text{SO}_3\text{F})_3$.

Of the two geometrical isomers, *mer*- $\text{Ir}(\text{CO})_3(\text{SO}_3\text{F})_3$ was isolated and structurally characterized.³³ Dissolution of this species in $\text{HSO}_3\text{F}–\text{SbF}_5$ (magic acid)^{19,20} produces after a total reaction time of 8 weeks at room temperature very small amounts of crystalline $[\text{Ir}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$, which was only characterized by a crystal structure determination.³⁴ Finally, the reductive carbonylation of IrF_6 in liquid SbF_5 allows the synthesis of $[\text{Ir}(\text{CO})_6][\text{Sb}_2\text{F}_{11}]_3$.^{34,35}

In this publication we want to report: (a) a new synthetic route to $[\text{Ir}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$, its vibrational spectra, and a detailed discussion of the molecular structure; (b) the synthesis and the molecular structure of $[\text{Rh}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$; (c) a comparison of the vibrational spectra of $[\text{M}(\text{CO})_5\text{Cl}]^{2+}$ ($\text{M} = \text{Rh}, \text{Ir}$) supported by density functional calculations.

Experimental Section

(i) Chemicals. $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (99% purity) and $[\text{Ir}(\text{CO})_3\text{Cl}]_n$ (95% purity) were obtained from Chempur, Karlsruhe, Germany, and used without further purification. *mer*- $\text{Ir}(\text{CO})_3(\text{SO}_3\text{F})_3$,³³ $\text{Ir}(\text{SO}_3\text{F})_3$,³⁰ and $\text{S}_2\text{O}_6\text{F}_2$,³² were synthesized as described previously. F_2 (technical grade, Air Products) and SO_3 (Dupont, Wilmington, DE) were obtained from commercial sources. HSO_3F (technical grade, Bayer AG, Leverkusen, Germany) was purified by double distillation at atmospheric pressure as described previously.^{17d} Anhydrous HF (99% purity, Allied Signal, Seelze, Germany) was used without further purification and stored over a small amount of SbF_5 to remove traces of water as $[\text{H}_3\text{O}][\text{Sb}_2\text{F}_{11}]$.²³ Technical grade SbF_5 (Elf Atochem, North America) was purified by distillation, first at atmospheric pressure and then in vacuo. Carbon monoxide (99% purity) was obtained from Linde Gases Hannover, Germany and condensed in a glass trap cooled with liquid nitrogen and reevaporated, to retain moisture and other impurities.

(ii) Instrumentation. Raman spectra were recorded on a Bruker FRA 106 Raman accessory mounted on the optical bench of a Bruker IFS 66 FTIR spectrometer. The solid samples were filled into glass capillaries (2 mm o.d.) under a dry argon atmosphere (glovebox). The tubes were plugged with a small amount of halocarbon grease and flame sealed outside the glovebox. Infrared spectra were recorded on a Bruker IFS 66v FT-IR spectrometer. The solid samples were crushed and spread in an argon atmosphere as fine powders between AgBr plates (Korte, Kiel, Germany).

(iii) Apparatus. Volatile materials were manipulated in glass or stainless steel vacuum lines of known volume, equipped with capacitance pressure gauges (Type 280 E, Setra Instruments, Acton, MA) and valves with PTFE stems (Young, London, U.K.) or stainless steel needle valves (3762H46Y, Hoke, Creskill, NJ). Anhydrous HF with some SbF_5 was stored in PFA tubes (300 mm long, 12 mm o.d.) fitted on top with a stainless steel needle valve. Solid materials were manipulated inside a drybox (Braun, Munich, Germany), filled with dry argon, with a residual moisture of less than 0.1 ppm.

(iv) Synthetic Reactions. (a) Synthesis of $[\text{Rh}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$ and Formation of Single Crystals. A sample of 0.155 g (0.4 mmol) of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was placed in a 100 mL round-bottomed PFA flask with a 29 socket standard taper (Bohlender, Lauda, Germany) fitted with a 29 stainless steel cone and a needle valve (3762H46Y Hoke, Creskill, NJ). The evacuated flask was cooled with liquid nitrogen. Approximately 2 mL each of SbF_5 and anhydrous HF were added by distillation. Gaseous carbon monoxide was admitted, and the pressure was adjusted to 2 atm of CO at room temperature. After warming of the reactor to -40 °C the color of the stirred reaction mixture changed from dark red to yellow within 2 h. At a temperature of 50 °C a pale yellow precipitate was formed, and after 4 days all volatile materials were pumped off. The extremely reactive and moisture sensitive solid mixture contained $[\text{Rh}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$ in the form of pale yellow,

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Table 1. Summary of Crystal Data and Refinement Results for [Rh(CO)₅Cl][Sb₂F₁₁]₂ and [Ir(CO)₅Cl][Sb₂F₁₁]₂

data	[Rh(CO) ₅ Cl][Sb ₂ F ₁₁] ₂	[Ir(CO) ₅ Cl][Sb ₂ F ₁₁] ₂ ^a
empirical formula	C ₅ ClF ₂₂ O ₅ RhSb ₄	C ₅ ClF ₂₂ IrO ₅ Sb ₄
fw	1183.4	1272.7
color of crystal	pale yellow	pale yellow
cryst system	monoclinic	monoclinic
space group (No.)	P2 ₁ (4)	P2 ₁ (4)
a/Å	9.721(1)	9.686(2)
b/Å	12.602(1)	12.585(2)
c/Å	10.538(1)	10.499(2)
β/deg	106.51(1)	106.59(2)
V/Å ³	1237.7(2)	1226.5(4)
Z	2	2
T/°C	27	21
ρ _{calc} /g cm ⁻³	3.175	3.446
wavelength/Å	0.710 73	0.710 73
μ/cm ⁻¹	52.5	100.5
2θ _{min/max} /deg	5.0/56.5	6.0/65
residuals	R ₁ ^b = 0.0367 [I > 2 σ(I)] wR ₂ ^c = 0.0739	R ₁ ^b = 0.032 [I > 3σ(I)] R _w ^d = 0.031

^a Reference 34. ^b R₁ = ∑||F_o - |F_c|| / ∑|F_o|. ^c wR₂ = ∑w(F_o² - F_c²) / ∑w(F_o²) × fd^{1/2}. ^d R_w = [(∑w(|F_o - |F_c||)² / ∑w(F_o²)²)^{1/2}.

irregular crystals and the byproduct 6SbF₃·5SbF₅⁵⁶ as a light gray powder. In a drybox, a suitable crystal was picked from the mixture and gently wedged into a Lindemann glass capillary. The tube was sealed inside the drybox with a small amount of halocarbon grease and then flame sealed outside the box.

(b) Synthesis of [Ir(CO)₅Cl][Sb₂F₁₁]₂. In a round-bottom PFA flask of approximately 100 mL volume, fitted with a magnetic stirring bar, a 29 socket and a fitting stainless steel cone with needle valve (3762H46Y Hoke, Cresskill NJ), 0.155 g (0.5 mmol) of [Ir(CO)₅Cl]_n was added. The evacuated flask was cooled to liquid nitrogen temperature, and 2 mL of SbF₅ and an equal amount of HF were added in vacuo. The CO pressure was adjusted to about 2 atm at room temperature. The reaction mixture, initially a black suspension, became lighter as the suspension was stirred vigorously for 2 days at 50 °C. Removal of all volatiles in vacuo produced a mixture of a gray-white solid and highly moisture sensitive, pale yellow crystals, which were identified by Raman and IR spectroscopy.

(c) Formation of Single Crystals of [Ir(CO)₅Cl][Sb₂F₁₁]₂. To 40 mg of crystalline *mer*-Ir(CO)₃(SO₃F)₃ contained in a one part glass reactor of about 50 mL volume, slightly less than 1 mL of HSO₃F was added in vacuo to give at room temperature a very pale yellow solution. Subsequently 2 mL of SbF₅ was added in vacuo. On warming of the contents to 40 °C, a slightly viscous solution formed. The CO pressure was adjusted to about 2 atm and the mixture was left standing at room temperature. After 6 weeks the formation of a crystal on the bottom of the reactor was noted. The solution was allowed to remain at room temperature for further 2 weeks. It was noted that no other crystals had formed and the original crystal did not grow larger. The crystal was then carefully picked from solution, cut into several pieces inside a drybox, and mounted in X-ray capillaries. The experiment was repeated, but no crystals formed this time. The amount obtained was too small for microanalysis and vibrational studies.

(d) Partial Characterization of [Rh(CO)₅Cl][Sb₂F₁₁]₂ and [Ir(CO)₅Cl][Sb₂F₁₁]₂ by Vibrational Spectroscopy. The IR and Raman spectra of both [Rh(CO)₅Cl][Sb₂F₁₁]₂ and [Ir(CO)₅Cl][Sb₂F₁₁]₂ obtained from [Rh(CO)₂Cl]₂ and [Ir(CO)₃Cl]_n, respectively, contain a number of bands which are attributed either to the anion [Sb₂F₁₁]⁻ or the byproduct 6 SbF₃·5SbF₅. Compared to the cation bands, they have variable relative intensities, and their positions in both salts are in cm⁻¹: Raman, 698 m, 670 vs, 650 s, 633 ms, 600 m, 580 w, 295 s, and 285 m, sh; IR, 710 s, sh, 695 vs, 660 s, 543 ms, sh, 526 s, 495 m, sh.

(v) X-ray crystallography. A summary of crystal data and structure refinement for both compounds are collected in Table 1.

(a) [Ir(CO)₅Cl][Sb₂F₁₁]₂. Details on the structure determination have been published in a preliminary publication.³⁴ Further details on the structure may be obtained from Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshofen, Germany, ordering number CSD-

405106. The structure was solved by heavy atom Patterson methods and expanded using Fourier techniques. All calculations were carried out with teXsan (Molecular Structure Corp., The Woodlands, TX, 1995).

(b) [Rh(CO)₅Cl][Sb₂F₁₁]₂. Data were recorded at room temperature with a Stoe IPDS (Imaging Plate) diffractometer. The structure was solved in P2₁ by direct methods (SHELXS-86),³⁶ and the final full-matrix least-squares refinements of all atomic parameters (SHELXL-93)³⁷ were carried out on a DECα Vax computer. The figures were drawn using the PLATON program.³⁸

(vi) Theoretical Methods. Gradient-corrected density functional calculations were carried out by using the Gaussian94³⁹ and Gaussian98⁴⁰ program systems. Gradient corrections for exchange and for correlation were taken from the work of Becke⁴¹ and Perdew,⁴² respectively (usually abbreviated as BP or BP86). Two basis sets were employed, labeled ECP1 and ECP2. Both use a quasi-relativistic effective core potential at the transition metal together with the corresponding (8s,7p,5d)/[6s,5p,3d] valence basis set.⁴³ For carbon, oxygen, and chlorine, ECP1 employs the 6-31G(d) basis,⁴⁴ whereas ECP2 uses a (10s,6p)/[5s,3p] triplezeta basis for C and O⁴⁵ and (13s9p)/[6s5p] for Cl,⁴⁶ supplemented by two sets of d polarization functions each.⁴⁷ Spherical d functions were applied throughout. Using analytic energy gradients, the molecular geometries were optimized within the constraint of C_{4v} point group symmetry. Second derivatives were obtained analytically with Gaussian98, which also provides Raman intensities at the BP86/ECP2 level. The present computational approach is the same as in our previous studies.^{48,49} In most tables of this publication, we only report BP86/ECP2 data which should generally be more reliable, because they employ a larger basis. Therefore, comparisons with experiment will normally refer to BP86/ECP2. The calculated frequencies at the BP86/ECP1 level are given in the Supporting Information.

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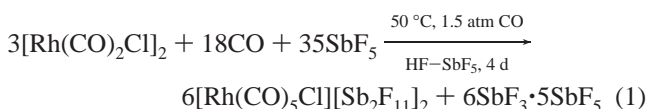
The force field transformations into internal and symmetry coordinates were performed with the program Intder.⁵⁰ All force constants are given in 10^2 N m^{-1} for stretches and stretch–stretch interactions and $10^2 \text{ N m}^{-1} \text{ rad}^{-2}$ for bending modes.

Results and Discussion

(a) Synthetic Aspects. The reported carbonylation reactions of $\text{Ir}(\text{SO}_3\text{F})_3$,³⁰ which have resulted in the formation of $\text{Ir}(\text{CO})_3(\text{SO}_3\text{F})_3$, with the *mer*-isomer structurally characterized,³³ and the subsequent accidental formation of single crystals of $[\text{Ir}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$ ³⁴ cannot be adopted for the synthesis of the analogous rhodium(III) carbonyl compounds for two reasons: (i) Rhodium(III) fluorosulfate, $\text{Rh}(\text{SO}_3\text{F})_3$ is even more difficult to synthesize than $\text{Ir}(\text{SO}_3\text{F})_3$.³⁰ The oxidation of Rh metal by $\text{S}_2\text{O}_6\text{F}_2$ ^{31,32} in HSO_3F takes about 2 weeks at about 120 °C. The reaction is accompanied by extensive corrosion of the glass reactor and O_2 evolution, giving an impure product.⁵¹ (ii) Attempted carbonylation reactions with small amounts of $\text{Rh}(\text{SO}_3\text{F})_3$ in superacids suggest a different reactivity; neither $\text{Rh}(\text{CO})_3(\text{SO}_3\text{F})_3$, $[\text{Rh}(\text{CO})_6][\text{Sb}_2\text{F}_{11}]_3$, nor $[\text{Rh}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$ is obtained by this route. Instead the solvated cation $[\text{Rh}(\text{CO})_4]^+_{\text{solv}}$ is formed in HSO_3F solution; however, a solid is not isolated.⁵² Likewise, the reductive carbonylation of IrF_6 to give $[\text{Ir}(\text{CO})_6][\text{Sb}_2\text{F}_{11}]_3$ ³⁴ has so far not been adopted to the generation of $[\text{Rh}(\text{CO})_6]^{3+}$, because RhF_6 ⁵³ is extremely difficult to prepare. It therefore seems that neither solvolytic nor reductive carbonylation²² will lead readily to rhodium(III) carbonyl derivatives.

This leaves the oxidative carbonylation of suitable substrates in superacids²² as a potentially useful synthetic approach. Two relevant precedents have been reported by us recently. They involve the $2 e^-$ oxidations of commercially available $\text{W}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ to produce in SbF_5 or HF-SbF_5 the cation $[\text{W}(\text{CO})_6(\text{FSbF}_5)]^+$ ⁵⁴ and the polymeric cation $[\{\text{Mo}(\text{CO})_4\}_2(\text{cis-}\mu\text{-F}_2\text{SbF}_4)_3]^+$,⁵⁵ both with $[\text{Sb}_2\text{F}_{11}]^-$ as counteranion. The salts are structurally characterized by single-crystal X-ray diffraction. SbF_5 functions in both oxidations as oxidizing agent, as reaction medium, and as source of the $[\text{Sb}_2\text{F}_{11}]^-$ anion. During oxidation with SbF_5 the adduct $6\text{SbF}_3 \cdot 5\text{SbF}_5$ forms, which has a known molecular structure.⁵⁶ We have identified this adduct by the determination of its cell constants after recrystallization from anhydrous HF ^{54,55} and by its Raman spectrum.⁵⁷

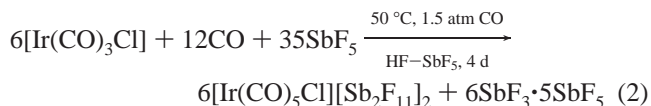
The same approach, oxidative carbonylation with SbF_5 as oxidizing agent, is used here as a successful synthetic route to the first cationic rhodium(III) carbonyl complex, $[\text{Rh}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$. In the formation reaction



rhodium(I) dicarbonyl chloride dimer, $[\text{Rh}(\text{CO})_2(\mu\text{-Cl})_2]$, is used

as starting material. This compound is commercially available. It may be prepared from $\text{RhCl}_3(\text{H}_2\text{O})_n$ and CO .⁵⁸ Its crystal structure is known,⁵⁹ and the compound serves as precursor for many organometallic rhodium(I) compounds.^{12,14,60}

Equally straightforward is the synthesis of $[\text{Ir}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$, where only the crystal structure is known,³⁴ but a reproducible synthetic route has so far been lacking. Here commercially available $[\text{Ir}(\text{CO})_3\text{Cl}]_n$ ⁶¹ is used as starting material



The main products in both reactions are pale yellow crystals, which may be picked under a microscope. They may be separated from the gray-white, powdery byproduct, formulated as $6\text{SbF}_3 \cdot 5\text{SbF}_5$,⁵⁶ in amounts sufficient to determine the molecular structure of $[\text{Rh}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$. However, a clean separation of the main product from the byproduct in bulk quantities is not possible, because neither material is sublimable without decomposition and solubilities in HF-SbF_5 are comparably low for main and byproduct.

Washing with anhydrous HF , where the adduct $6\text{SbF}_3 \cdot 5\text{SbF}_5$ is sufficiently soluble to allow recrystallization,^{54,55} permits the formation of enriched samples of $[\text{M}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$ ($\text{M} = \text{Rh}, \text{Ir}$) for the recording of Raman spectra. IR spectra are obtained on the product mixture and are only interpretable in the CO-stretching region.

While cationic iridium(III) carbonyl derivatives have been reported previously by us^{33,34} as discussed above, $[\text{Rh}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$ is the first cationic carbonyl salt of rhodium(III). Hence rhodium, together with iridium, molybdenum, and tungsten, are so far the only transition metals where, in addition to the recently discovered cationic carbonyl derivatives,^{33,34,54,55} also typical metal carbonyls^{12–14} and highly reduced metal carbonylates⁶² have become known. For rhodium and iridium the oxidation state of the metals in thermally stable CO derivatives ranges from +3 to –3.

The chloropentacarbonyl cation $[\text{Ir}(\text{CO})_5\text{Cl}]^{2+}$ ³⁴ is related to the homoleptic carbonyl cation $[\text{Ir}(\text{CO})_6]^{3+}$,³⁴ with one CO ligand replaced by the Cl^- anion. In both salts, $[\text{Sb}_2\text{F}_{11}]^-$ is found as counteranion.³⁴ The corresponding homoleptic carbonyl cation $[\text{Rh}(\text{CO})_6]^{3+}$ is so far unknown, and all attempts to achieve substitution of Cl^- in $[\text{Rh}(\text{CO})_5\text{Cl}]^{2+}$ by CO under more forcing conditions (elevated temperatures, higher CO pressures) have been unsuccessful. Similarly the conversion of $[\text{W}(\text{CO})_6(\text{FSbF}_5)]^+$ into $[\text{W}(\text{CO})_7]^{2+}$ has not been accomplished so far.⁵⁴ It appears that, in both complex cations, the single anionic ligand, Cl^- or $(\text{FSbF}_5)^-$, is very tightly bonded to the central metal and is not readily substituted by the neutral CO ligand. Direct evidence for the strong coordination of $(\text{FSbF}_5)^-$ to the

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W(CO)₆ fragment is found in the molecular structure of [W(CO)₆(FSbF₅)]₂[Sb₂F₁₁].⁵⁴ In both [Ir(CO)₅Cl]²⁺ and [Rh(CO)₅Cl]²⁺, the M–Cl (M = Rh, Ir) bond lengths are unusually short, as will be discussed below.

Hence, both [M(CO)₅Cl]²⁺ cations (M = Rh, Ir) cannot be viewed as suitable precursors for the generation of the homoleptic carbonyl cations [M(CO)₆]³⁺ (M = Rh, Ir). This is evident also from the observation that, during the oxidative carbonylation of either [Rh(CO)₂Cl]₂ or [Ir(CO)₃Cl]_n in HF–SbF₅ (eqs 1 and 2), the chloro ligand remains coordinated to the central atom and the M–Cl bond appears to be strengthened by the 2 e[−] oxidation. On the other hand, during reductive or solvolytic carbonylations in superacids,²² where the oxidation state of the metal ion is either reduced or remains unchanged, anionic ligands such as SO₃F[−], Cl[−], or F[−] are labile toward substitution by CO and a substantial number of homoleptic metal carbonyl cations are formed from MX_n precursors with X = SO₃F, Cl, or F.²² In the oxidative carbonylations described here, the Cl[−] ligands are found to be substitution inert toward CO.

The accidental formation of [Ir(CO)₅Cl][Sb₂F₁₁]₂³⁴ during the attempted solvolytic carbonylation of *mer*-Ir(CO)₃(SO₃F)₃³³ in HSO₃F–SbF₅, which gives impure [Ir(CO)₆]³⁺ as the main product, appears to be a slow substitutional process, where a CO ligand is exchanged for Cl[−]. The most probable source of Cl[−] appears to be the chloro–fluorocarbon (Kel-F) grease used, since all other reagents and reactants are reportedly free of chlorine.^{34,52} The active species in magic acid^{19,20} (HSO₃F–SbF₅) appears to be protonated HCl. All attempts to prepare larger amounts of [Ir(CO)₅Cl][Sb₂F₁₁]₂ by deliberate addition of various chlorides to the reaction mixture have failed. Only small amounts of *mer*-Ir(CO)₃(SO₃F)₃ are available for reactions as already discussed above.

There are a number of known chloropentacarbonylmetal complexes, which are isoelectronic or valence isoelectronic with the cations [M(CO)₅Cl]²⁺ (M = Rh, Ir). They include carbonylate anions of the type [M(CO)₅Cl][−] (M = Cr, Mo, W⁶³), neutral species of the composition M(CO)₅Cl (M = Mn, Re^{64–67}), and the cation [Fe(CO)₅Cl]⁺.⁶⁸ However, as the vibrational spectra^{69–71} indicate, contribution from π-backbonding to the synergic M–CO bonding^{7–9} becomes increasingly dominant with decreasing the oxidation state of the central atom from +1 to −1.

In summary, while a simple synthetic route to both [Rh(CO)₅Cl][Sb₂F₁₁]₂ and [Ir(CO)₅Cl][Sb₂F₁₁]₂ is found in the oxidative carbonylation with SbF₅ as oxidizing agent (see eqs 1 and 2), there remain serious problems with the clean separation of the products in bulk quantities. This detracts from the effectiveness of the synthetic method. Despite these problems single crystals of both complex salts have been isolated. The molecular structures of [Rh(CO)₅Cl][Sb₂F₁₁]₂ and of [Ir(CO)₅Cl]-

Table 2. Selected Interatomic Distances and Bond Angles for [Rh(CO)₅Cl][Sb₂F₁₁]₂

Bond Lengths (Å)			
Rh(1)–Cl(1)	2.294(3)	Rh(1)–C(1)	1.999(12)
Rh(1)–C(2)	2.032(12)	Rh(1)–C(3)	2.015(10)
Rh(1)–C(4)	2.008(11)	Rh(1)–C(6)	2.000(10)
Sb(1)–F(1)	2.023(9)	Sb(2)–F(1)	1.977(10)
Sb(3)–F(12)	2.038(9)	Sb(4)–F(12)	1.982(9)
O(1)–C(1)	1.107(14)	O(2)–C(2)	1.087(15)
O(3)–C(3)	1.107(13)	O(4)–C(4)	1.102(14)
O(6)–C(6)	1.103(12)		
Bond Angles (deg)			
Cl(1)–Rh(1)–C(1)	88.3(3)	Cl(1)–Rh(1)–C(2)	178.9(3)
Cl(1)–Rh(1)–C(3)	88.3(3)	Cl(1)–Rh(1)–C(4)	85.1(3)
Cl(1)–Rh(1)–C(6)	86.0(3)	C(1)–Rh(1)–C(2)	92.6(4)
C(1)–Rh(1)–C(3)	90.3(4)	C(1)–Rh(1)–C(4)	173.5(5)
C(1)–Rh(1)–C(6)	90.1(4)	C(2)–Rh(1)–C(3)	91.1(4)
C(2)–Rh(1)–C(4)	94.0(4)	C(2)–Rh(1)–C(6)	94.7(4)
C(3)–Rh(1)–C(4)	89.3(4)	C(3)–Rh(1)–C(6)	174.2(5)
C(4)–Rh(1)–C(6)	89.6(4)	Sb(3)–F(12)–Sb(4)	156.3(5)
Rh(1)–C(1)–O(1)	179.5(8)	Rh(1)–C(2)–O(2)	179.3(9)
Rh(1)–C(3)–O(3)	179.7(10)	Rh(1)–C(4)–O(4)	176.9(10)
Rh(1)–C(6)–O(6)	179.0(10)	Sb(1)–F(1)–Sb(2)	154.7(6)

Table 3. Selected Interatomic Distances and Bond Angles for [Ir(CO)₅Cl][Sb₂F₁₁]₂^a

Bond Lengths (Å)			
Ir(1)–Cl(1)	2.321(3)	Ir(1)–C(1)	2.05(1)
Ir(1)–C(2)	2.01(1)	Ir(1)–C(3)	2.04(2)
Ir(1)–C(4)	2.00(2)	Ir(1)–C(5)	2.02(2)
Sb(1)–F(1)	1.946(9)	Sb(2)–F(1)	2.089(10)
Sb(3)–F(12)	1.980(10)	Sb(4)–F(12)	2.007(9)
O(1)–C(1)	1.07(1)	O(2)–C(2)	1.08(2)
O(3)–C(3)	1.08(2)	O(4)–C(4)	1.08(2)
O(5)–C(5)	1.12(2)		
Bond Angles (deg)			
Cl(1)–Ir(1)–C(1)	178.6(5)	Cl(1)–Ir(1)–C(2)	85.8(4)
Cl(1)–Ir(1)–C(3)	88.4(3)	Cl(1)–Ir(1)–C(4)	88.6(4)
Cl(1)–Ir(1)–C(5)	85.4(4)	C(1)–Ir(1)–C(2)	94.2(5)
C(1)–Ir(1)–C(3)	91.6(5)	C(1)–Ir(1)–C(4)	92.8(5)
C(1)–Ir(1)–C(5)	93.2(5)	C(2)–Ir(1)–C(3)	174.2(6)
C(2)–Ir(1)–C(4)	89.9(6)	C(2)–Ir(1)–C(5)	90.1(5)
C(3)–Ir(1)–C(4)	90.0(6)	C(3)–Ir(1)–C(5)	89.3(5)
C(4)–Ir(1)–C(5)	174.0(6)	Sb(1)–F(1)–Sb(2)	153.2(6)
Sb(3)–F(12)–Sb(4)	156.5(6)	Ir(1)–C(1)–O(1)	176(1)
Ir(1)–C(2)–O(2)	179(1)	Ir(1)–C(3)–O(3)	179(1)
Ir(1)–C(4)–O(4)	177(1)	Ir(1)–C(5)–O(5)	178(1)

^a The originally published³⁴ numbering of atoms in the [Ir(CO)₅Cl]²⁺ cation has been retained.

[Sb₂F₁₁]₂, reported in a preliminary communication,³⁴ obtained by single-crystals X-ray diffraction will be discussed in the next section.

(b) The Molecular Structures of [Rh(CO)₅Cl][Sb₂F₁₁]₂ and [Ir(CO)₅Cl][Sb₂F₁₁]₂. The relevant crystal data together with details on structure solutions and refinements for both complex salts are summarized in Table 1. As described in the Experimental Section, two different methods of structure solution and refinement are used. Selected bond parameters (interatomic distances and bond angles) for both salts are compiled in Tables 2 and 3. The data for the cations are compared to values from density functional calculations in Table 4. The molecular structure of [Rh(CO)₅Cl][Sb₂F₁₁]₂ is shown in Figure 1, while the corresponding structure of [Ir(CO)₅Cl][Sb₂F₁₁]₂ may be found in ref 34. A stereoview of the unit cell of [Ir(CO)₅Cl][Sb₂F₁₁]₂ is reproduced in Figure 2, to illustrate the packing of anions and cations.

As can be seen from the data in Table 1, [Rh(CO)₅Cl][Sb₂F₁₁]₂ and [Ir(CO)₅Cl][Sb₂F₁₁]₂ are isostructural. Both salts crystallize in the monoclinic space group *P*2₁ (No. 4). The

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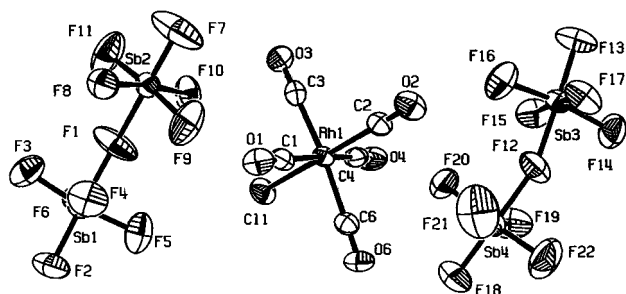
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Table 4. A Summary of Calculated and Experimental Bond Parameters^a for [M(CO)₅Cl]²⁺ (M = Rh, Ir)

	[Rh(CO) ₅ Cl] ²⁺			[Ir(CO) ₅ Cl] ²⁺		
	BP86/ECP1 ^b	BP86/ECP2 ^b	expt	BP86/ECP1 ^b	BP86/ECP2 ^b	expt ^c
(a) Bond Lengths in Å						
<i>d</i> (M–Cl)	2.377	2.368	2.294(3)	2.406	2.396	2.321(3)
<i>d</i> (M–C) _{ax}	2.035	2.035	2.03 (1)	2.017	2.016	2.05 (1)
<i>d</i> (M–C) _{eq}	2.019	2.020	2.006 ^a	2.026	2.027	2.02 ^a
<i>d</i> (C–O) _{ax}	1.139	1.128	1.09 (2)	1.141	1.130	1.07 (1)
<i>d</i> (C–O) _{eq}	1.138	1.126	1.105 ^a	1.138	1.127	1.09 ^a
(b) Averaged Bond Angles in Deg						
∠(C _{ax} –M–C _{eq})	94.5	94.6	94	94.3	94.3	93
∠(M–C–O) _{eq}	177.5	177.4	179	177.4	177.4	178

^a Averaged data. ^b The acronyms BP or BP 86 refer to reviews by Becke⁴¹ and Perdew.⁴² ECP1 and ECP2 refer to levels of theory, where quasi-relativistic effective core potentials are used at the transition metal with the corresponding 8s, 7p,5d or 6s, 5p3d are used. For C, O, and Cl, different basis sets are used (see Experimental Section). ^c Reference 34.

**Figure 1.** Molecular structure of [Rh(CO)₅Cl][Sb₂F₁₁]₂, with 50% probability thermal ellipsoids shown.

molecular structures for both [M(CO)₅Cl][Sb₂F₁₁]₂ salts (M = Rh, Ir) are topologically nearly identical to those of the isostructural triad [M(CO)₆][Sb₂F₁₁]₂ (M = Fe,²⁸ Ru,²⁹ Os²⁹); however, the [M(CO)₆]²⁺ cations are octahedral (point group *O_h*) and hence have an inversion center. As a consequence, the space group is *P2₁/n* (No. 14). Unlike in [M(CO)₆][Sb₂F₁₁]₂^{28,29} and in [Hg(CO)₂][Sb₂F₁₁]₂,²⁶ which also crystallizes in the same space group (*P2₁/n*), the two [Sb₂F₁₁][−] anions in [M(CO)₅Cl][Sb₂F₁₁]₂ (M = Rh, Ir) are no longer symmetry related and identical. Differences are noted for the Sb–F–Sb bridge angle and the dihedral angles, formed by rotation of the two SbF₄ moieties, but these differences are rather small (see Tables 2 and 3) and will be discussed below.

To compare the structures of [M(CO)₆][Sb₂F₁₁]₂ (M = Fe, Ru, Os^{28,29}) and [Rh(CO)₅Cl][Sb₂F₁₁]₂, an unconventional presentation for the latter in *P2₁* is used: the origin remains as in space group *P2₁/n* and does not fall on the 2₁ axis, as is commonly the case. Consequently the metal atom is very slightly displaced from the position 0, 0, 0, which indicates the “missing” center of symmetry. The same is true for the second metal atom in the unit cell, which is now in close proximity to 1/2, 1/2. A more conventional presentation and a different labeling of the atom is reported for [Ir(CO)₅Cl][Sb₂F₁₁]₂,³⁴ which we have retained here.

An interesting observation concerns the cell constants for the two [M(CO)₅Cl][Sb₂F₁₁]₂ (M = Rh, Ir) salts: the cell lengths *a*, *b*, and *c* are very slightly smaller for the iridium salt, compared with the rhodium congener. Consequently, the cell volume of [Ir(CO)₅Cl][Sb₂F₁₁]₂ is less than that of [Rh(CO)₅Cl][Sb₂F₁₁]₂ by about 0.9%. Similar contractions in unit cell volume are found in the isostructural pairs [M(CO)₄][Sb₂F₁₁]₂ (M = Pd, Pt²⁷) and [M(CO)₆][Sb₂F₁₁]₂ (M = Ru, Os²⁹). It is tempting to invoke relativistic effects,^{72,73} which should cause shorter and

stronger metal–ligand bonds for the 5d metal cations in these respective isostructural pairs. While relativistic effects are doubtlessly responsible for the short bonds found in [Pt(CO)₄]²⁺,²⁷ [Os(CO)₆]²⁺,²⁹ and [Ir(CO)₅Cl]²⁺, the reduced unit cell volume observed here cannot be explained in this manner. As can be seen in Tables 2–4, all M–C and M–Cl bonds are actually comparable or very slightly longer in [Ir(CO)₅Cl]²⁺ than they are in [Rh(CO)₅Cl]²⁺. With anion dimensions and volumes nearly identical in both salts, it appears that tighter packing of the constituent ions in [Ir(CO)₅Cl][Sb₂F₁₁]₂, due to stronger secondary⁷⁴ interionic contacts, must be the cause of the observed reduction in unit cell volume.

The secondary interionic contacts observed in [Ir(CO)₅Cl][Sb₂F₁₁]₂ involve mainly equatorial fluorine atoms of the dioctahedral [Sb₂F₁₁][−] anion and the C atoms of the carbonyl group of the complex cation. The strength of these contacts is judged by comparison to the sum of the van der Waals radii, which according to Bondi⁷⁵ is 3.17 Å for C–F interactions. Contractions from this sum by 10% or more are viewed as significant, with the upper limit for significant contacts at 2.85 Å for C–F contacts.

For [Ir(CO)₅Cl][Sb₂F₁₁]₂, we observe approximately two significant contacts per CO group, with the shortest distance at 2.69(2) Å. In addition there is about one “marginal” contact per carbonyl group with distances between 2.85 and 3.17 Å. In case of [Rh(CO)₅Cl][Sb₂F₁₁]₂ there are apparently fewer and weaker secondary contacts with the shortest distance of 2.89 Å. There are no significant O–F contacts in either salt. A similar preponderance of interionic C–F contacts is reported for [Hg(CO)₂][Sb₂F₁₁]₂,²⁶ [M(CO)₄][Sb₂F₁₁]₂ (M = Pd, Pt²⁷), [Fe(CO)₆][Sb₂F₁₁]₂,²⁸ [W(CO)₆(FSbF₅)]₂[Sb₂F₁₁]₂,⁵⁴ and [Mo(CO)₄]₂(F₂–SbF₄)₃[Sb₂F₁₁]₂,⁵⁵ where in all instances extended or polymeric⁵⁵ structures are found.

To facilitate the formation of secondary C–F contacts, the [Sb₂F₁₁][−] anion is bent and expressed in terms of a Sb–F–Sb bridge angle and the two SbF₄ planes are frequently rotated into a staggered conformation, which is expressed in terms of a dihedral angle. For [Ir(CO)₅Cl][Sb₂F₁₁]₂, the bridge angles are 153.2(6) and 156.5(6)° and the dihedral angles are 34 and −41°. Comparable bridge angles of 154.7(6) and 156.3(5)° and dihedral angles of 31 and −41° are found for the anions in [Rh(CO)₅Cl][Sb₂F₁₁]₂. A rather unusual bridge asymmetry is noted for both sets of anions. The two Sb atoms are usually equidistant to the bridging F atom with distances of about 2.03 Å.^{26–28,54,55} For [Rh(CO)₅Cl][Sb₂F₁₁]₂, two pairs at 1.977(10) and 2.023(9) Å or 1.982(10) and 2.038(9) Å are found. For [Ir(CO)₅Cl][Sb₂F₁₁]₂,

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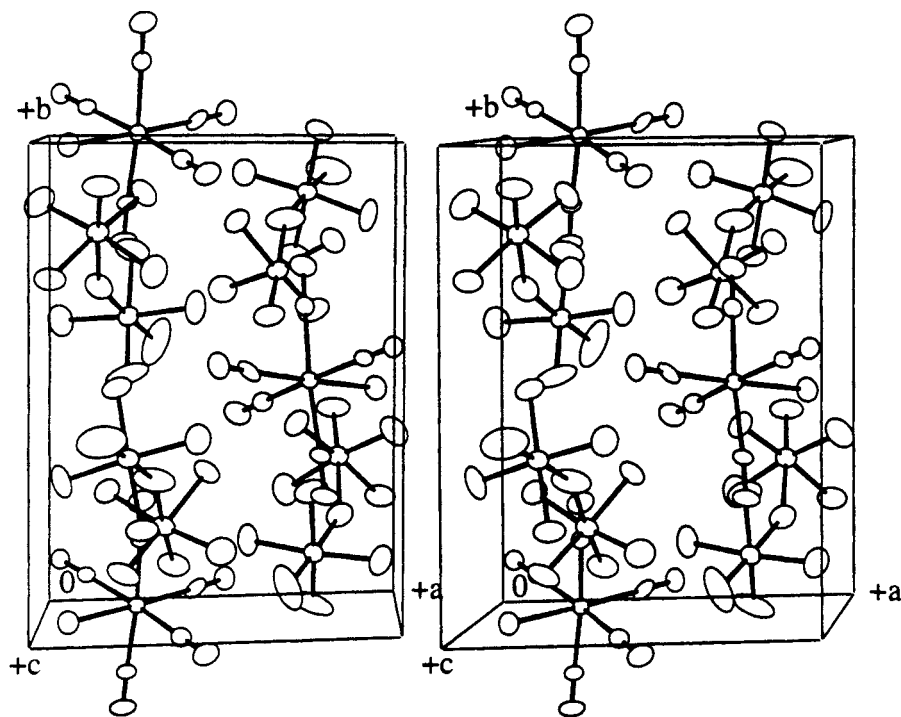


Figure 2. Stereoview of the unit cell of [Ir(CO)₅Cl][Sb₂F₁₁]₂.

similar pairs of distances at 1.946(9) and 2.089(10) Å or 1.980(10) and 2.007(9) Å are observed. The remaining SbF distances for the anions in both salts are comparable and range from 1.80 to 1.86 Å with differences due to the involvement of some fluorine atoms in secondary interactions as discussed above.

For the two [M(CO)₅Cl]²⁺ cations (M = Rh, Ir) the relevant bond lengths are listed in Tables 2 and 3. The Rh–Cl and Ir–Cl distances of 2.294(3) and 2.321(3) Å are shorter than the *q_l* values of 2.335 and 2.353 Å, respectively, from the Cambridge data collection.⁷⁶ The tabulated data refer to octahedrally coordinated complexes and are based on 76 and 65 examples, respectively.⁷⁶ The CO groups trans to Cl are in both cations relatively weakly bonded with Rh–C and Ir–C distances of 2.032(12) and 2.05(1) Å. The average M–C_{eq} bond lengths *d*(Rh–C) of 2.005 (11) and *d*(Ir–C) of 2.018(10) Å are considerably longer than the upper quarter *q_u* values of 1.869 and 1.898 Å from the Cambridge data compilation, which are based on 238 and 148 examples, respectively. The iridium–carbon distances reported for *mer*-Ir(CO)₃(SO₃F)₃³³ provide an interesting comparison. In the *trans*-OC-Ir-CO segment, iridium carbon distances of 2.006(6) and 1.999(6) Å are still longer than *q_l*. A shorter Ir–C distance of 1.937 (7) Å and a slightly shorter CO bond length of 1.094(8) Å are found for the CO group trans to the fluorosulfate anion, which implies that the *trans* CO group is more tightly bound to iridium. The opposite is true for the cations [M(CO)₅Cl]²⁺ (M = Rh, Ir) with Cl[−] in *trans* position to CO as discussed above. It is not obvious why Cl[−] should weaken while SO₃F[−] strengthens the bond to the CO group trans to itself.

All interatomic C–O distances in [M(CO)₅Cl]²⁺ (M = Rh, Ir) are short and fall below the *q_l* value of 1.132 Å from the Cambridge data collection.⁷⁶ The shortest C–O bond lengths are found for the axial CO groups trans to Cl[−] in both complex cations. The close correspondence between *d*(C–O) and *d*(M–C) (M = Rh, Ir) suggests insignificant contributions from

π -back-bonding to M–CO bonding just like in other homoleptic metal carbonyl cations.²² A more accurate measure of the strength of the CO bond in [M(CO)₅Cl]²⁺ will be provided by the vibrational spectra, which will be discussed in the next section.

As can be seen in Table 4, agreement between experimental interatomic distances and calculated values for [M(CO)₅Cl]²⁺ is generally fair. In the DFT calculations the lengths of the M–Cl (M = Rh, Ir) and the CO bonds are overestimated. In free CO(g), the calculations^{49a} also overestimate the experimental bond length,⁷⁷ so that the observed trend to shorter CO bond lengths in the carbonyl cations is reproduced. Experimentally, the axial M–C bonds are longer than the equatorial ones (Table 4) which is found by DFT only for M = Rh but not for M = Ir. Despite such shortcomings, the structural data from DFT calculation provide a good check for the experimental data with differences frequently attributable to solid-state effects and interionic interactions.

The observed bond angles for the [M(CO)₅Cl]²⁺ cations are consistent and as expected for octahedrally coordinated species. All C_{eq}–M–C_{eq} angles are very close to 90 or 180°. The C_{eq}–M–C_{ax} angles are slightly larger than 90° while C_{eq}–M–Cl angles are smaller than 90° by about 2–3°. This implies in terms of the VSEPR theory of molecular geometry,^{78–80} that in predominantly σ -bonded metal carbonyl cations with unusually long M–C bonds, the bonding pairs in these bonds require more space than the bonding pair in the rather short M–Cl bonds with M = Rh and Ir. As is frequently observed in homoleptic metal carbonyl cations^{22,26–28} and their derivatives, the M–C–O groups depart slightly from linearity, usually by 2–3°. ^{33,54,55} This is frequently caused by interionic or intermolecular contacts

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Table 5. Experimental and Calculated Vibrational Wavenumbers (cm^{-1}) for $[\text{Rh}(\text{CO})_5\text{Cl}]^{2+}$

vib mode	exptl		calcd BP86/ECP2				
	IR	Raman	ν	$\Delta\nu^a$	IR int ^b	Raman int ^c	
A ₁ ν_1 $\nu(\text{CO})$	2273 (vw)	2272 (vs)	2245	-27	4.8	187.8	
A ₁ ν_2 $\nu(\text{CO})$	2240 (m, sh)	2240 (s)	2195	-45	128.1	151.9	
A ₁ ν_3 $\delta(\text{RhCO})$	528 (m)		527		74.6	0.2	
A ₁ ν_4 $\nu(\text{RhC})$		398 (m)	394	-4	0.0	22.1	
A ₁ ν_5 $\nu(\text{RhC})$		375 (w)	364	-11	0.7	3.3	
A ₁ ν_6 $\nu(\text{RhCl})$		340 (w)	320	-20	4.2	7.6	
A ₁ ν_7 $\delta(\text{RhC})$			108		0.4	0.0	
A ₂ ν_8 $\delta(\text{RhCO})$			320				
B ₁ ν_9 $\nu(\text{CO})$		2257 (s)	2221	-36		151.8	
B ₁ ν_{10} $\delta(\text{RhCO})$			445			0.0	
B ₁ ν_{11} $\nu(\text{RhC})$		375 (w)	367	-8		2.3	
B ₁ ν_{12} $\delta(\text{CRhC})$			70			0.0	
B ₂ ν_{13} $\delta(\text{RhCO})$			448			0.0	
B ₂ ν_{14} $\delta(\text{CRhC})$			93			5.8	
E ν_{15} $\nu(\text{CO})$	2237 (vs)		2204	-29	419.1	0.1	
E ν_{16} $\delta(\text{RhCO})$	508 (s)		513		89.8	0.5	
E ν_{17} $\delta(\text{RhCO})$			436		5.5	0.0	
E ν_{18} $\nu(\text{RhC})$			356		5.5	0.5	
E ν_{19} $\delta(\text{RhCO})$			314		5.9	0.0	
E ν_{20} $\delta(\text{CRhCl})$			106		1.8	0.1	
E ν_{21} $\delta(\text{CRhC})$		85 (s)	83		3.2	10.0	
E ν_{22} $\delta(\text{CRhC})$			80		1.6	0.4	

^a $\Delta\nu = \nu(\text{calcd}) - \nu(\text{exptl})$. ^b IR intensities (km mol^{-1}). ^c Raman intensities ($\text{\AA}^4 \text{amu}^{-1}$).

involving the C atom of the carbonyl group. In $[\text{Ir}(\text{CO})_5\text{Cl}]^{2+}$, the Ir-C-O angles range from 176(1) to 179(1)°. However, in $[\text{Rh}(\text{CO})_5\text{Cl}]^{2+}$, where fewer and weaker secondary contacts are found, all but one Rh-C-O group are linear within the quoted error limits.

In summary, the molecular structures of $[\text{Rh}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$ and $[\text{Ir}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$ discussed here allow the structural characterization of the first rhodium(III) carbonyl derivative as well as the first superelectrophilic,²⁵ monochloro carbonyl cations. Further characterization by vibrational spectroscopy aided by DFT calculations will be discussed in the following section.

(c) Vibrational Spectra and Force Constants of the Cations $[\text{Rh}(\text{CO})_5\text{Cl}]^{2+}$ and $[\text{Ir}(\text{CO})_5\text{Cl}]^{2+}$. The experimentally determined vibrational wavenumbers of some of the fundamental vibrations of the cations $[\text{Rh}(\text{CO})_5\text{Cl}]^{2+}$ and $[\text{Ir}(\text{CO})_5\text{Cl}]^{2+}$ are listed in Tables 5 and 6 together with estimated intensities and a vibrational assignment. The experimentally determined band positions are compared to a complete list of calculated band positions as well as IR and Raman intensities, obtained by gradient corrected DFT calculations. Details on the theoretical methods and a listing of vibrational bands due to the $[\text{Sb}_2\text{F}_{11}]^-$ anion or the byproduct $6\text{SbF}_3 \cdot 5\text{SbF}_5$ are found in the Experimental Section.

For a 12-atom molecular cation of point group C_{4v} , the vibrational irreducible representations and their activities are

$$\Gamma_{\text{vib}} = 7A_1 (\text{IR, Ra}) + A_2 (-) + 4B_1 (\text{Ra}) + 2B_2 (\text{Ra}) + 8E (\text{IR, Ra})$$

As can be seen from Tables 5 and 6, of the expected 21 fundamentals for $[\text{Rh}(\text{CO})_5\text{Cl}]^{2+}$ and $[\text{Ir}(\text{CO})_5\text{Cl}]^{2+}$, only 8 and 6, respectively are clearly identified. Among them are all four

Table 6. Experimental and Calculated Vibrational Wavenumbers (cm^{-1}) for $[\text{Ir}(\text{CO})_5\text{Cl}]^{2+}$

vib mode	exptl		calcd BP86/ECP2				
	IR	Raman	ν	$\Delta\nu^a$	IR int ^b	Raman int ^c	
A ₁ ν_1 $\nu(\text{CO})$	2279 (w)	2279 (s)	2251	-28	5.2	197.9	
A ₁ ν_2 $\nu(\text{CO})$	2227 (s)	2228 (s)	2180	-48	223.1	196.4	
A ₁ ν_3 $\delta(\text{IrCO})$			542		81.1	1.7	
A ₁ ν_4 $\nu(\text{IrC})$		430 (m)	425	-5	0.4	17.2	
A ₁ ν_5 $\nu(\text{IrC})$			379		5.0	0.0	
A ₁ ν_6 $\nu(\text{IrCl})$		370 (m)	341	-29	5.7	9.5	
A ₁ ν_7 $\delta(\text{IrC})$			104		1.3	0.0	
A ₂ ν_8 $\delta(\text{IrCO})$			334				
B ₁ ν_9 $\nu(\text{CO})$		2257 (s)	2223	-34		171.8	
B ₁ ν_{10} $\delta(\text{IrCO})$			476			0.0	
B ₁ ν_{11} $\nu(\text{IrC})$			400			1.6	
B ₁ ν_{12} $\delta(\text{ClrC})$			73			0.0	
B ₂ ν_{13} $\delta(\text{IrCO})$			463			0.0	
B ₂ ν_{14} $\delta(\text{ClrC})$			96			6.0	
E ν_{15} $\nu(\text{CO})$	2232 (vs)		2202	-30	553.3	1.1	
E ν_{16} $\delta(\text{IrCO})$			532		94.6	0.2	
E ν_{17} $\delta(\text{IrCO})$			468		10.0	0.2	
E ν_{18} $\nu(\text{IrC})$			370		4.0	0.8	
E ν_{19} $\delta(\text{IrCO})$			326		42.3	0.3	
E ν_{20} $\delta(\text{ClrCl})$			106		0.1	0.1	
E ν_{21} $\delta(\text{ClrC})$			88		2.6	8.6	
E ν_{22} $\delta(\text{ClrC})$			85		0.5	1.8	

^a $\Delta\nu = \nu(\text{calcd}) - \nu(\text{exptl})$. ^b IR intensities (km mol^{-1}). ^c Raman intensities ($\text{\AA}^4 \text{amu}^{-1}$).

CO stretching vibrations, which are found well above 2200 cm^{-1} , in an uncluttered spectral region.

There are four reasons for the low number of fundamentals identified for either cation: (i) Due to separation problems, discussed in the section on synthesis, pure samples of $[\text{M}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$ ($\text{M} = \text{Rh, Ir}$) are not available for a vibrational study. Interference, mainly in the region of 710–400 and 300–270 cm^{-1} , is due to bands of the byproduct $6\text{SbF}_3 \cdot 5\text{SbF}_5$ ^{56,57} or the $[\text{Sb}_2\text{F}_{11}]^-$ anions, which have low symmetry (C_i) in both salts according to their molecular structures. (ii) The very high sensitivity toward moisture of both salts has severely limited the use of IR spectroscopy. In addition we have not been able to record far-IR spectra of the two salts, which leaves IR bands below 450 cm^{-1} undetected. (iii) In oxidative carbonylations the synthesis of the ¹³C isotopomeric salts requires in addition to ¹³CO isotopically pure or enriched starting materials such as $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ or $[\text{Ir}(\text{CO})_3\text{Cl}]_n$, which are not available to us. Therefore only band positions and band intensities can be used as assignment aides. (iv) As the calculated IR and Raman intensities listed in Tables 5 and 6 indicate, many fundamentals appear to be of very low intensity, so that they will be difficult to detect even under ideal conditions. Note: It has recently been possible^{81a} to obtain $[\text{Rh}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$ free of the byproduct $6\text{SbF}_3 \cdot 5\text{SbF}_5$. This has allowed us to record the Ir spectrum, and the wavenumbers found (at 2273 (vw), 240 (m, sh), 528 (m), 2237 (vs), and 508 (s)) are added to Table 5 with a Raman band at 85 (s).

In contrast to the situation encountered here, we have recently been able to determine experimentally the position of all 13 fundamentals of $[\text{Fe}(\text{CO})_6]^{2+}$ in the two structurally character-

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Table 7. Average CO–Stretching Wavenumbers $\bar{\nu}(\text{CO}_{\text{avg}})$ and Approximate CO–Stretching Force Constants f_{CO} for Selected 4d and 5d Metal Carbonyl Derivatives

metal carbonyl species	$\bar{\nu}(\text{CO}_{\text{avg}})$ (cm ⁻¹)	f_{CO} (10 ² N m ⁻¹)	method of f_{CO} determinatn	ref
[Pd(CO) ₄] ²⁺ ^a	2259	20.63	CK ^b	27, 81
[Pt(CO) ₄] ²⁺ ^a	2261	20.64	CK ^b	27, 81
[Ir(CO) ₆] ³⁺ ^a	2268	20.78	CK ^b	34
[Rh(CO) ₅ Cl] ²⁺ ^a	2247	20.41	two mass meth	this work
[Ir(CO) ₅ Cl] ²⁺ ^a	2246	20.39	two mass meth	this work
<i>mer</i> -Ir(CO) ₃ (SO ₃ F) ₃	2217	19.87	two mass meth	33
<i>fac</i> -Ir(CO) ₃ (SO ₃ F) ₃	2182	19.25	two mass meth	this work, 33
[Ru(CO) ₆] ²⁺ ^a	2216	19.82	CK ^b	82
[Os(CO) ₆] ²⁺ ^a	2211	19.76	CK ^b	82

^a Counteranion is [Sb₂F₁₁]⁻. ^b Approximation according to: Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432.

ized salts [Fe(CO)₆][Sb₂F₁₁]₂ and [Fe(CO)₆][SbF₆]₂.²⁸ Here both salts are obtained in very high purity together with their ¹³C isotopomers. IR and Raman spectra are available over the entire spectral range down to 100 cm⁻¹. The overtones observed in the IR spectrum are useful in locating inactive fundamentals or those of low intensity, and vibrational spectra of [Fe(CO)₆]-[Sb₂F₁₁]₂ are very simple. DFT calculations for [Fe(CO)₆]²⁺ ⁴⁸ are again very useful in band assignments, and a normal coordinate analysis is possible.

For both [Rh(CO)₅Cl]²⁺ and [Ir(CO)₅Cl]²⁺, the band positions of all fundamentals are calculated by DFT methods and provide a complete picture. As noted previously for [Fe(CO)₆]²⁺,^{28,48} the calculated CO stretching wavenumbers for [Fe(CO)₆]²⁺ are generally too low by 30–45 cm⁻¹.

The measured average CO stretching wavenumbers and approximated CO stretching force constants for [M(CO)₅Cl]²⁺ (M = Rh, Ir) are collected in Table 7, where they are compared to data for related 4d and 5d metal carbonyl cations. As can be seen, differences in $\bar{\nu}(\text{CO}_{\text{avg}})$ and f_{CO} for pairs of isostructural salts such as [M(CO)₄][SbF₁₁]₂ (M = Pd, Pt^{27,81}), [M(CO)₆]-[Sb₂F₁₁]₂ (M = Ru, Os⁸²) reported previously, and [M(CO)₅Cl]-[Sb₂F₁₁]₂ (M = Rh, Ir) reported here are very small and frequently within error limits. The observed similarity in the strength of the CO bonds in the pairs is attributed to relativistic effects.^{72,73} Differences in $\bar{\nu}(\text{CO}_{\text{avg}})$ and f_{CO} for the homolytic metal carbonyl cations [M(CO)₄]²⁺ (M = Pd, Pt) and [M(CO)₆]²⁺ (M = Ru, Os) in their [Sb₂F₁₁]⁻ salts reflect the different coordination geometries (square planar and octahedral).

For the octahedrally coordinated iridium(III) carbonyl derivatives listed in Table 7, the effect of partial substitution of CO by either Cl⁻ or SO₃F⁻ anion on the overall CO bond strength of the remaining CO ligands is obvious. Of all octahedral homoleptic metal carbonyl cations known,²² the highest $\bar{\nu}(\text{CO}_{\text{avg}})$ and f_{CO} values are observed for the strongest superelectrophile²⁵ [Ir(CO)₆]³⁺. The partial replacement of a single CO ligand by Cl⁻ to give [Ir(CO)₅Cl]²⁺ reduces the complex charge from +3 to +2, which will diminish the Lewis acidity of the iridium(III) center. We note a slight reduction in CO bond strength, due to a modest increase in π -back-donation from iridium to the remaining five CO ligands. A larger decrease in $\bar{\nu}(\text{CO}_{\text{avg}})$ and f_{CO} is observed, when three CO ligands of [Ir(CO)₆]³⁺ are replaced by three SO₃F⁻ anions, to produce the two geometric isomers of Ir(CO)₃(SO₃F)₃. For the *mer*-isomer, which is structurally characterized,³³ both $\bar{\nu}(\text{CO}_{\text{avg}})$ and f_{CO} decrease by 51 cm⁻¹ or 0.91 × 10² N m⁻¹, while for *fac*-Ir(CO)₃(SO₃F)₃ a further reduction of 35 cm⁻¹ or 0.62 × 10² N m⁻¹ is observed.

Table 8. Calculated Internal Force Constants F_{int} for [Rh(CO)₅Cl]²⁺ and [Ir(CO)₅Cl]²⁺ ^a

internal force constants (10 ² N m ⁻¹)	[Rh(CO) ₅ Cl] ²⁺	[Ir(CO) ₅ Cl] ²⁺
$F_{\text{CO,ax}}$ ^b	19.38	19.09
$F_{\text{CO,eq}}$ ^b	19.61	19.58
$F_{\text{MC,ax}}$	1.60	2.12
$F_{\text{MC,eq}}$	1.79	2.15
F_{MCl}	2.03	2.17
$F_{\text{MCO,ax}}$	0.27	0.32
$F_{\text{MCO,eq-ax}}$	0.34	0.37
$F_{\text{MCO,eq-eq}}$	0.32	0.35
F_{ClMC}	0.70	0.86
$F_{\text{CO,CO,ax-eq}}$	0.03	0.04
$F_{\text{CO,CO,eq-eq,cis}}$	0.03	0.03
$F_{\text{CO,CO,eq-eq,trans}}$	0.01	0.01
$F_{\text{MC,MC,ax-eq}}$	0.05	0.09
$F_{\text{MC,MC,eq-eq,cis}}$	0.06	0.08
$F_{\text{MC,MC,eq-eq,trans}}$	0.61	0.74

^a All data are obtained from the BP86/ECP2 calculations. ^b Average CO stretching force constants: 19.56 for M = Rh, 1948 for M = Ir.

For the pair [M(CO)₅Cl][Sb₂F₁₁]₂ (M = Rh, Ir) slightly stronger C–O bonds are found than for [M(CO)₆][Sb₂F₁₁]₂ (M = Ru, Os). This reflects a higher Lewis acidity of the M^{III}Cl moiety (M = Rh, Ir) than for either Ru(II) or Os(II) in salts with very similar molecular structures.^{28,29} Even though structural data for the two cations [M(CO)₅Cl]²⁺ (M = Rh, Ir) are available, the limited vibrational data for both salts are not sufficient for a normal coordinate analysis. The internal force constants from BP 86/ECP 2 calculations are listed in Table 8 for [M(CO)₅Cl]²⁺ (M = Rh, Ir). The derived average CO-stretching force constants (footnote *b*) are smaller than the corresponding empirical values (Table 7), in analogy to previous results⁸³ for the hexacarbonyl cations (M = Ru, Os, Ir) which show similar deviations of 0.6 to 0.9 × 10² N m⁻¹. Hence, the trends for the average CO-stretching force constants are the same for the experimental results (Table 7) and the BP86/ECP2 results (Table 8, ref 83): The values for [M(CO)₅Cl]²⁺ (M = Rh, Ir) fall between those for [Ir(CO)₆]³⁺ and [M(CO)₆]²⁺ (M = Ru, Os).

Both for [Rh(CO)₅Cl]²⁺ and [Ir(CO)₅Cl]²⁺, the stretching force constant for the axial CO ligand is calculated to be smaller than that for the equatorial CO ligand. This is consistent with the computed bond lengths (Table 4). The experimental CO bond length (Tables 2 and 3) would seem to indicate an opposite trend, but the quoted uncertainties are too large to allow a definite assessment. The calculated force constants for the axial M–C bond are again smaller than those for the equatorial M–C bonds, which is in line with the experimental bond length (Tables 2 and 3) and the computed bond lengths for M = Rh but not for M = Ir (Table 4); in the latter case, the differences between the axial and equatorial positions are rather small (Tables 4 and 8). Judging from the calculated stretching force constants, the Cl⁻ ligand thus appears to weaken the M–C and C–O bonds in trans position to itself, relative to the equatorial positions, whereas the experimental and theoretical bond lengths do not exhibit such a clear-cut trend.

The computed MCO bending and CO, CO interaction force constants for [M(CO)₅Cl]²⁺ (M = Rh, Ir) lie in a range similar to those⁸³ for the hexacarbonyl cations [M(CO)₆]ⁿ⁺ (M = Ru, Os, Ir). As discussed previously,⁸³ these low force constants indicate that π -back-bonding is of minor importance in these systems. With the exception of the CO stretching force constants,

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the calculated internal force constants are generally somewhat smaller in $[\text{Rh}(\text{CO})_5\text{Cl}]^{2+}$ than in $[\text{Ir}(\text{CO})_5\text{Cl}]^{2+}$, which suggests that the metal–ligand bonding is stronger in the latter cation.

Summary and Conclusion

The first rhodium(III) carbonyl cation, $[\text{Rh}(\text{CO})_5\text{Cl}]^{2+}$, has been synthesized as the $[\text{Sb}_2\text{F}_{11}]^-$ salt and is characterized by a crystal structure determination, vibrational spectroscopy in the CO stretching range, where $\bar{\nu}(\text{CO}_{\text{avg}})$ is about 100 cm^{-1} higher than in free CO, and theoretical calculations using gradient corrected DFT methods. In addition, a new synthetic route to $[\text{Ir}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$, whose structure has been reported previously by us,³⁴ is found in the oxidative carbonylation of $[\text{Ir}(\text{CO})_3\text{Cl}]_n$ in $\text{HF}-\text{SbF}_5$. This new approach should be suitable, for the synthesis of other salts with $[\text{M}(\text{CO})_5\text{X}]^{2+}$ cations with $\text{M} = \text{Co}, \text{Rh}, \text{and Ir}$ and $\text{X} = \text{F}, \text{Br}, \text{H}, \text{and CN}$. Density functional studies on $[\text{M}(\text{CO})_5\text{Cl}]^{2+}$ ($\text{M} = \text{Rh}, \text{Ir}$) have provided an excellent insight into the bonding of this new class of superelectrophilic²⁵ metal carbonyl cations.²² All attempts to generate $[\text{Rh}(\text{CO})_6]^{3+}$ in superacid media have been unsuccessful so far, and the only promising route appears to be the reductive carbonylation of RhF_6 ⁵³ in analogy to the conversion of IrF_6 into $[\text{Ir}(\text{CO})_6]^{3+}$.³⁴ Attempts in this direction are currently under way.

In summary, as in the past,²² superacid systems^{19,20} like the conjugate Brønsted–Lewis superacid $\text{HF}-\text{SbF}_5$ ^{19,20} have allowed the generation of the first superelectrophilic, monosubstituted metal carbonyl cations of the composition $[\text{M}(\text{CO})_5\text{Cl}]^{2+}$

($\text{M} = \text{Rh}, \text{Ir}$). Salts are formed with the superacid anion $[\text{Sb}_2\text{F}_{11}]^-$,²³ which are characterized by X-ray diffraction, vibrational spectroscopy, and computational methods based on density functional theory. We are not aware of any other reaction medium or counteranion that has allowed the generation and stabilization of any superelectrophilic²⁵ metal carbonyl cation in the condensed phase.

Acknowledgment. Financial support by the following organizations is gratefully acknowledged: Deutsche Forschungsgemeinschaft (DFG), Fonds der Chemischen Industrie (FCI), Schweizerischer Nationalfonds, Natural Science and Engineering Research Council of Canada (NSERC), and the North Atlantic Treaty Organization (NATO). The calculations were carried out using IBM RS/6000 and Silicon Graphics workstations at the University Zürich and ETH Zürich (C4 Cluster) as well as the NEC SX-4 computer at CSCS Manno.

Supporting Information Available: Tables of supplementary crystallographic data, anisotropic displacement parameters, and selected distances and angles for $[\text{Rh}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$ and $[\text{Ir}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$ as CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>. Crystallographic information for $[\text{Ir}(\text{CO})_5\text{Cl}][\text{Sb}_2\text{F}_{11}]_2$ is also available from Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany. The deposit number is CSD-405106. The complete calculated vibrational data (wavenumbers and IR and Raman intensities) both on the ECP1 and BP86/ECP2 levels are available as Microsoft Word for Windows 97 data files from the authors.

IC9911926