Formation of *cis*-Bis(carbonyl)palladium(II) Fluorosulfate, *cis*-$Pd(CO)_2(SO_3F)_2$, and Its Crystal and Molecular Structure

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An isomeric mixture of bis(carbonyl)palladium(II) fluorosulfate, $Pd(CO)_2(SO_3F)_2$, is recrystallized from fluorosulfuric acid, HSO_3F, and yields after short, intermittent heating of the solution to 60 °C a single crystal of *cis*-bis(carbonyl)palladium(II) fluorosulfate, *cis*-$Pd(CO)_2(SO_3F)_2$, which crystallizes in a monoclinic unit cell, space group $P2_1/n$, with $Z = 4$, $a = 7.3697(11)$ Å, $b = 14.7742(35)$ Å, $c = 8.3237(21)$ Å, $\beta = 90.52(2)°$, $V = 906.3$ Å^3, and $T = 220$ K. The refinement converges at $R_f = 0.027$ and $R_{wf} = 0.034$. The molecular structure reveals square planar coordination of palladium with terminal CO groups and monodentate fluorosulfates in a cis-geometry. Consistent with the unusually high CO-stretching frequencies ($\bar{\nu}_{av} = 2218$ cm^{-1}), the CO bond lengths are short—1.106(6) and 1.114(6) Å. This suggests substantially reduced π-back-donation, with CO functioning predominantly as a σ-donor. In addition there are weak C···O contacts in the range 2.819(6)–3.172(6) Å, which involve the two noncoordinated oxygens of the fluorosulfate groups. In the absence of significant Pd to CO π-back-donation, secondary contacts involving the electrophilic carbon atom of the CO group as acceptor appear to provide for some degree of charge compensation and to exert a stabilizing influence on the structure. The importance of such secondary contacts to the bonding in nonclassical carbonyls appears not to have been recognized previously.

Introduction

While mononuclear bis(carbonyl)platinum(II) chloride, *cis*-$Pt(CO)_2Cl_2$, first prepared by Schützenberger in 1868,[1] is one of the longest known metal carbonyl derivatives, the corresponding palladium compound, $Pd(CO)_2Cl_2$, has remained elusive. An early claim of its synthesis by Fink[2] could not be confirmed by Manchot and König,[3] who argued that the palladium metal used by Fink had contained substantial amounts of platinum. Subsequent attempts at the synthesis of $Pd(CO)_2Cl_2$ have met with no success, and it is hence accepted in appropriate reviews[4–6] that mononuclear bis(carbonyl)palladium(II) compounds are either nonexistent like the chloride or thermally unstable like two organometallic derivatives of the type *cis*-$Pd(CO)_2R_2$, R = C_6F_5 or C_6Cl_5, in this case even at −30 °C in a CO atmosphere.[7]

Our own work, first on gold(I)[8,9] and more recently on platinum(II) and palladium(II)[10,11] carbonyl derivatives had allowed three conclusions: (i) Thermally stable noble metal carbonyl cations or cationic derivatives may be generated in, or isolated from, solutions in fluorosulfuric acid, HSO_3F, the strongest simple protonic acid.[12] (ii) In the solid state, noble metal carbonyl cations or cationic moieties are stabilized by extremely weakly nucleophilic fluoro anions or anionic groups,[13] such as SO_3F^- [8,10] or $Sb_2F_{11}^-$.[9,11] The thermal stability of the resulting derivatives increases with decreasing nucleophilicity of the counter anion.[8–11] (iii) In contrast to classical π-acid complexes of CO,[14] the CO stretching frequency is in all noble metal carbonyl derivatives not lowered but raised relative to $\bar{\nu}$(CO) in carbon monoxide at 2143 cm^{-1}.[15] With decreasing anion nucleophilicity $\bar{\nu}$(CO) will increase.[8–11] Similar contrasting behavior is found for the chemical shift in ^{13}C NMR spectra of these carbonyls.[9]

To illustrate these observations, *cis*-$Pd(CO)_2(SO_3F)_2$ has recently been obtained together with the isostructural compound *cis*-$Pt(CO)_2(SO_3F)_2$.[10] The palladium(II) compound is thermally stable up to 117 °C and $\bar{\nu}$(CO) is at 2218 cm^{-1}, about 75 cm^{-1} higher than in CO itself.[15] Similar observations are made for carbonyl cations like linear $[Au(CO)_2]^+$ [8,9] or square planar $[M(CO)_4]^{2+}$ (M = Pd, Pt), where $\bar{\nu}(CO)_{av}$ is at 2235.5[9] or 2260 cm^{-1},[11] respectively, and the term "nonclassical metal carbonyls" may be suggested for this unusual group of compounds.

While vibrational spectroscopy is extremely useful in this area, a number of these nonclassical carbonyl derivatives have also been characterized by single-crystal X-ray diffraction. The molecular structures of Au(CO)Cl[16] and Cu(CO)Cl[17] are known. More recently X-ray diffraction studies of the thermally unstable Ag(I) derivatives $Ag(CO)B(OTeF_5)_4$[18] and $[Ag(CO)_2][B(OTeF_5)_4]$[19] at −100 and −125 °C, respectively, have been reported.

In group 10 very few thermally stable carbonyl derivatives of divalent palladium or platinum appear to be structurally characterized. We have recently[20] reported the molecular structure of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$, which contains a cyclic,

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completely planar $[Pd_2(\mu\text{-}CO)_2]^{2+}$ cation, point group D_{2h}, with symmetrically bridging carbonyl ligands. The unusually high $\bar{\nu}(CO)_{av}$ of 2002 cm^{-1}, about 200 cm^{-1} higher than usually observed for bridging carbonyl ligands,[14,21] again suggests substantially reduced metal to CO π-back-donation. In addition, the structures of two salts of the type $[n\text{-}Bu_4N][Pd(CO)X_3]$, X = Cl or Br, with square planar $[Pd(CO)X_3]^-$ anions are known.[22]

We now want to report the molecular structure of *cis*-bis(carbonyl)palladium(II) fluorosulfate, *cis*-$Pd(CO)_2(SO_3F)_2$, which is determined by single-crystal X-ray diffraction at 220 K. Single crystals of both *cis*-$Pd(CO)_2(SO_3F)_2$ and of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$[20] are obtained by recrystallization of an isomeric mixture of the composition $Pd(CO)_2(SO_3F)_2$ from fluorosulfuric acid under slightly different conditions. These experimental conditions will be discussed here as well, and an explanation for these unusual findings will be advanced.

Experimental Section

Chemicals. Palladium powder was obtained from the Ventron Corp. Palladium tris(fluorosulfate), $Pd(SO_3F)_3$, was synthesized by following a published method,[23] and its reductive carbonylation with CO in fluorosulfuric acid as a solvent to give $Pd(CO)_2(SO_3F)_2$ as an isomeric mixture has been reported recently.[10] Fluorosulfuric acid (technical grade) was obtained from Orange County Chemicals and purified by double distillation at atmospheric pressure.[24]

Preparation of Single Crystals of *cis*-$Pd(CO)_2(SO_3F)_2$. About 150 mg of pale yellow, freshly prepared $Pd(CO)_2(SO_3F)_2$ was dissolved in approximately 5 mL of fluorosulfuric acid. The color of the solution changed gradually to orange-red, and after about 1 week, a very small amount of tiny orange needles of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ had formed. In order to obtain larger crystals, the mixture was heated in a water bath to 60 °C for 3 h, whereupon the orange red solid redissolved. On cooling of the solution to room temperature and reducing its volume by removing some of the acid in vacuo, a single yellow crystal plate formed, which grew over a period of 3 weeks into a relatively large crystal with dimensions of about 2.2 × 1.5 × 1.5 mm. The remaining orange liquid had *cis*-$Pd(CO)_2(SO_3F)_2$ and small amounts of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ dissolved according to its IR spectrum.

The crystal was isolated by pipetting off the remaining solution inside the drybox and washing the crystal 3 times with small quantities of HSO_3F. The crystal was dried by removing all volatiles in vacuo.

X-ray Crystallography. Under a dry nitrogen atmosphere, a fragment was cleaved from the pale yellow colored crystal and was gently wedged in a capillary tube with a trace of fluorocarbon grease as an adhesive. The tube was hot-wire sealed in the glovebox. Data were recorded at 220 K with an Enraf-Nonius CAD4F diffractometer equipped with an in-house modified low-temperature attachment using graphite-monochromatized Mo Kα radiation. Intensity standards (2 every 1 h) showed no decay until near the end of the data acquisition, when there was a systematic decline in intensity by 13% over a period of about 7 h. The data were corrected for the effects of absorption by the Gaussian integration method, and corrections were carefully checked against measured ψ-scans. Data reduction included corrections for intensity scale variation and for Lorentz and polarization effects.

The structure was solved from the Patterson map by the heavy atom method. The final full-matrix least squares refinement of 136 parameters, using 1464 data ($I_o \geq 2.5\sigma(I_o)$), included coordinates and anisotropic thermal parameters for all atoms. A weighting scheme based on counting statistics was applied such that $\langle w(|F_o| - |F_c|)^2\rangle$ was near constant as a function of both $|F_o|$ and $(\sin\theta)/\lambda$. The refinement converged at R_F = 0.027 and R_{wF} = 0.034.

Table 1. Crystallographic Data for the Structure Determination of $Pd(CO)_2(SO_3F)_2$ at 220 K

formula	$PdS_2F_2O_8C_2$	cryst system	Monoclinic
fw	360.53	space group	$P2_1/n$
a (Å)[a]	7.3697(11)	ρ_c (g cm^{-3})	2.642
b (Å)	14.7742(35)	λ(Mo Kα_1) (Å)	0.709 30
c (Å)	8.3237(21)	μ(Mo Kα) (cm^{-1})	25.2
β (deg)	90.52(2)	min–max 2θ (deg)	4–54
V (Å^3)	906.3	transm[b]	0.620–0.719
Z	4	crystal dimens (mm)	0.15 × 0.17 × 0.22
R_F[c]	0.027	R_{wF}[d]	0.034

[a] Cell dimensions were determined from 25 reflections (36° ≤ 2θ ≤ 42°). [b] The data were corrected for the effects of absorption, by the Gaussian integration method. [c] $R_F = \sum|(|F_o| - |F_c|)|/\sum|F_o|$, for 1464 data ($I_o \geq 2.5\sigma(I_o)$). [d] $R_{wF} = [\sum(w(|F_o| - |F_c|)^2)/\sum(wF_o^2)]^{1/2}$ for 1464 data ($I_o \geq 2.5\sigma(I_o)$); $w = [\sigma(F_o)^2 + 0.0002F_o^2]^{-1}$.

Table 2. Atomic Coordinates[a] and Equivalent Isotropic Temperature Factors (Å^2) for $Pd(CO)_2(SO_3F)_2$ at 220 K

atom	x	y	z	U_{eq}
Pd	0.46944(4)	0.140596(22)	0.19753(4)	0.0229
S(1)	0.12649(15)	0.18335(8)	–0.00469(14)	0.0288
S(2)	0.36929(18)	–0.05813(8)	0.27490(14)	0.0319
F(1)	0.1073(5)	0.08221(19)	–0.0545(4)	0.0474
F(2)	0.5670(5)	–0.0855(3)	0.3249(4)	0.0661
O(11)	0.2084(4)	0.17541(24)	0.1576(4)	0.0328
O(12)	0.2456(5)	0.22102(22)	–0.1204(4)	0.0362
O(13)	–0.0527(5)	0.2170(3)	0.0023(5)	0.0448
O(21)	0.3703(5)	0.03764(22)	0.3269(4)	0.0325
O(22)	0.3688(6)	–0.0692(3)	0.1076(4)	0.0482
O(23)	0.2593(8)	–0.1108(3)	0.3732(6)	0.0597
O(1)	0.8518(5)	0.0775(3)	0.2755(4)	0.0438
O(2)	0.6031(4)	0.30614(24)	0.0153(4)	0.0387
C(1)	0.7126(7)	0.1026(3)	0.2471(5)	0.0312
C(2)	0.5559(6)	0.2458(3)	0.0803(6)	0.0284

[a] The general equivalent positions in the space group $P2_1/n$ are as follows: x, y, z; $-x, -y, -z$; $^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$; $^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$.

The programs used for the structure determination were from the NRCVAX Crystal Structure System[25] and CRYSTALS.[26] Complex scattering factors for neutral atoms[27] were used in the calculation of structure factors. Computations were carried out on a MicroVAX-II and on 80486-processor-based personal computers. Crystallographic details are summarized in Table 1. Final fractional atomic coordinates are listed in Table 2.

Rigid body analysis[28] of the anisotropic thermal parameters of the molecule yielded R = 0.27 for the agreement between observed and calculated U_{ij} and, as expected, underestimated the thermal motion of many of the outer atoms while overestimating that for the palladium atom. Analysis of the internal motion of the molecule in terms of a segmented rigid body[29] in which each OSO_2F group was allowed internal libration about the S(1)–O(11) and S(2)–O(21) bond axes gave R = 0.17 but showed similar discrepancies between calculated and observed thermal parameters as did the simple rigid body model. Models in which different internal librational axes for the OSO_2F groups (such as the Pd–O bond axes) were specified either produced no significant improvement over this model or were ill-conditioned. Each OSO_2F group, when independently modeled as a rigid body, gave R = 0.015, 0.031 for the groups containing S(1) and S(2), respectively, and no significant residual motion. These analyses, along with independently determined riding motion corrections for selected pairs of atoms, were used to estimate the probable ranges of corrections (always positive) for the bond lengths given in the footnote to Table 3.

Results and Discussion

A. Synthetic Aspects. Bis(carbonyl)palladium(II) fluorosulfate, $Pd(CO)_2(SO_3F)_2$, is synthesized[10] by reductive carbonylation of the mixed valency compound $Pd^{II}Pd^{IV}(SO_3F)_6$[23] according to

$$Pd^{II}Pd^{IV}(SO_3F)_6 + 5CO \xrightarrow[\sim 550\ \text{Torr, 1h}]{25\ ^\circ C} 2Pd(CO)_2(SO_3F)_2 + CO_2 + S_2O_5F_2 \quad (1)$$

Depending on the reaction conditions, the solid reaction

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Table 3. Selected Intramolecular Distances (Å) and Angles (deg) for $Pd(CO)_2(SO_3F)_2$ at 220 K

	Bond Distances		
Pd–O(11)	2.016(3)[a]	S(1)–F(1)	1.557(3)[f]
Pd–O(21)	2.006(3)[a]	S(2)–O(21)	1.480(3)[c]
Pd–C(2)	1.945(5)[b]	S(2)–O(22)	1.402(4)[g]
Pd–C(1)	1.919(5)[b]	S(2)–O(23)	1.394(4)[h]
S(1)–O(11)	1.479(3)[c]	S(2)–F(2)	1.565(4)[i]
S(1)–O(12)	1.422(4)[d]	C(2)–O(2)	1.102(6)[j]
S(1)–O(13)	1.413(4)[e]	C(1)–O(1)	1.114(6)[j]
	Bond Angles		
O(11)–Pd–O(21)	86.00(13)	F(1)–S(1)–O(13)	105.43(22)
O(11)–Pd–C(2)	91.71(16)	O(21)–S(2)–O(22)	113.70(22)
O(11)–Pd–C(1)	176.23(17)	O(21)–S(2)–F(2)	99.62(21)
O(21)–Pd–C(2)	176.25(16)	O(21)–S(2)–O(23)	111.30(23)
O(21)–Pd–C(1)	90.39(17)	O(22)–S(2)–F(2)	103.19(24)
C(2)–Pd–C(1)	91.83(19)	O(22)–S(2)–O(23)	121.4(3)
O(11)–S(1)–O(12)	113.58(19)	F(2)–S(2)–O(23)	104.2(3)
O(11)–S(1)–F(1)	101.68(19)	Pd–O(11)–S(1)	123.48(19)
O(11)–S(1)–O(13)	111.35(22)	Od–O(21)–S(2)	124.68(19)
O(12)–S(1)–F(1)	104.50(20)	Pd–C(2)–O(2)	178.9(4)
O(12)–S(1)–O(13)	118.24(23)	Pd–C(1)–O(1)	177.5(4)

[a–j] Thermal motion corrections using rigid body, segmented rigid body, or riding models indicate that the actual bond lengths should be greater by the following: [a]0.004–0.009 Å; [b]0.001–0.004 Å; [c]0.001–0.019 Å; [d]0.008–0.014 Å; [e]0.009–0.022 Å; [f]0.010–0.024 Å; [g]0.018–0.020 Å; [h]0.020–0.049 Å; [i]0.024–0.033 Å; [j]0.002–0.023 Å.

products differ. A solid–gas reaction results in a product which is exclusively *cis*-$Pd(CO)_2(SO_3F)_2$. If the reaction is carried out in fluorosulfuric acid, in analogy to the reductive carbonylation of $Au(SO_3F)_3$,[8] the composition of the product established by microanalysis is $Pd(CO)_2(SO_3F)_2$, but the cis-isomer is now only a minor constituent according to the infrared spectrum. Two additional IR bands of equally high intensity are observed at 2179 and 1967 cm^{-1}. These bands are attributed to terminal and bridging CO ligands, respectively, and the presence of a CO-bridged oligomer is suggested. This oligomer, which has so far not been obtained in pure form, is tentatively formulated as $[Pd_2(\mu\text{-}CO)_2(CO)_2(SO_3F)_2](SO_3F)_2$ on the basis of microanalysis and vibrational spectra. The position of the band due to bridging CO (1967 cm^{-1}) differs measurably from the band position in $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ at 1977 cm^{-1}. On long standing at 25 °C the intensity of the two bands at 2179 and 1967 cm^{-1} gradually decreases, while the CO bands due to the cis-isomer at 2228 and 2208 cm^{-1} increase concomitantly in intensity. After about 2 months complete conversion in the solid state to *cis*-$Pd(CO)_2(SO_3F)_2$ has occurred. When the isomer mixture is redissolved immediately after synthesis to effect separation by crystallization and the solution is kept at room temperature for 2 weeks, orange-red crystal needles of the composition $Pd(CO)SO_3F$ form and reductive decomposition has apparently occurred. The molecular structure obtained is that of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$[20] described in the Introduction.

If, on the other hand, the solution of $Pd(CO)_2(SO_3F)_2$ in HSO_3F is heated intermittently for 3 h to 60 °C, initially formed small crystals of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ will redissolve. According to the IR spectrum primarily *cis*-$Pd(CO)_2(SO_3F)_2$ is now present in solution with $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$ only a minor constituent. At room temperature and after gradual, slow removal of HSO_3F in vacuo, crystallization of *cis*-$Pd(CO)_2(SO_3F)_2$ starts. The identity of the crystalline material is ascertained by vibrational spectroscopy.

Hence solutions of similar concentrations of the yellow isomeric mixture with the composition $Pd(CO)_2(SO_3F)_2$ will produce, depending on the experimental conditions, two different products: orange-red needles of $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$[20] or yellow plates of *cis*-$Pd(CO)_2(SO_3F)_2$, both as single crystals. Since yellow solutions of pure *cis*-$Pd(CO)_2(SO_3F)_2$, which appears to be the thermodynamically stable isomer, remain unchanged at 25 °C over a period of 1 month, it appears that only the oligomeric form of $Pd(CO)_2(SO_3F)_2$, thought to be $[Pd_2(CO)_2(\mu\text{-}CO)_2(SO_3F)_2](SO_3F)_2$, will rearrange in a solution of HSO_3F. At 60 °C primarily *cis*-$Pd(CO)_2(SO_3F)_2$ is formed which slowly crystallizes from solution as described here. This isomerization reaction occurs also in the solid state but much more slowly.

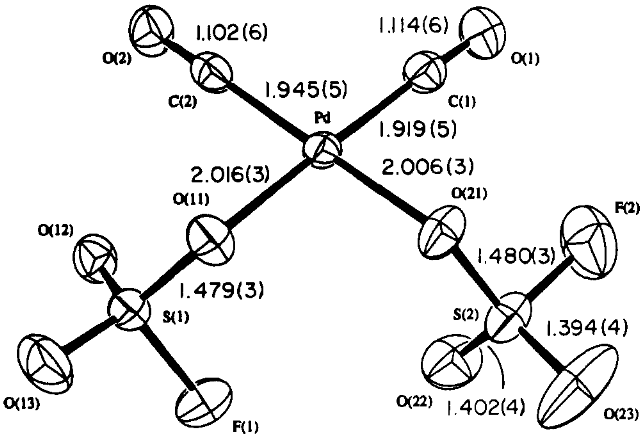

Figure 1. Molecular structure of $Pd(CO)_2(SO_3F)_2$ with 50% enclosure thermal ellipsoids shown. Selected bond lengths are given in Å.

At room temperature the preferred pathway appears to be the reductive decomposition of the CO-bridged oligomer, to $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$, which proceeds slowly to precipitate in crystalline form.

It is fortuitous that the two types of crystals obtained from nearly identical solutions allow determination of two highly unusual structures, one featuring the first example of a cyclic $[Pd_2(\mu\text{-}CO)_2]^{2+}$ ion[20] and the other representing the first thermally stable bis(carbonyl)palladium(II) derivative, *cis*-$Pd(CO)_2(SO_3F)_2$. Both compounds are examples of nonclassical carbonyl bonding.

A final comment may be made: The presence of weak shoulders at 2166 cm^{-1} in the IR spectrum and at 2212 cm^{-1} in the Raman spectrum of *cis*-$Pd(CO)_2(SO_3F)_2$ had been interpreted as being due to a small amount of *trans*-$Pd(CO)_2(SO_3F)_2$.[10] Vibrational spectra obtained on single crystal fragments are completely identical to those reported previously[10] and include the two weak bands. It hence appears that our interpretation of both bands is in error, and we suggest that the weak shoulder in the IR spectrum is the $\bar{\nu}(^{13}CO)$ satellite band and that the Raman band at 2212 cm^{-1} is produced by factor group splitting of the principal band at 2207 cm^{-1}. It is noted that $Z = 4$, which implies that factor group splitting is possible.

B. Discussion of the Molecular Structure of *cis*-$Pd(CO)_2(SO_3F)_2$. The molecular structure, shown in Figure 1, shows the coordination about the palladium atom to be square planar with *cis* stereochemistry. Bond distances and angles are given in Table 3. The molecule has no crystallographic symmetry and deviates from molecular mirror symmetry in the torsion angles about the Pd–O bonds (*cf.* O(21)–Pd–O(11)–S(1), −122.0(2)°; O(11)–Pd–O(21)–S(2), 106.5(2)°) and, more markedly, in the torsion angles about the O–S bonds (*cf.* F(1)–S(1)–O(11)–Pd, 73.8(2)°; F(2)–S(2)–O(21)–Pd, 83.0(2)°. Note that mirror symmetry would require the opposite sense of rotation, which is not the case, for the latter pair of torsion angles. The lengths of chemically equivalent bonds are generally not significantly different with the notable exceptions of the terminal S–O bonds and also the Pd–C bonds. The variations in both the S–O and Pd–C bond lengths appear to reflect the degree to which the oxygen and carbon atoms concerned are involved in weakly attractive intermolecular and intramolecular interactions (see below). The bond lengths fall within the expected ranges. The lengths of the C–O bonds lie at the lower end of the range exhibited for transition metal carbonyls, in keeping with the spectroscopic results.[10]

There is a very small displacement (0.036(3) Å) of the palladium atom out of the least-squares plane of the coordinating

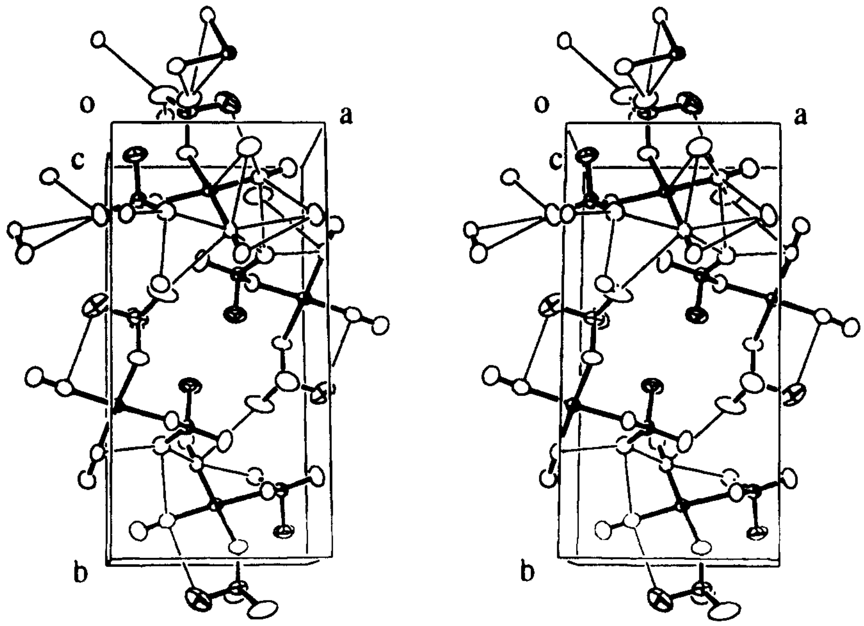

Figure 2. Stereo diagram of the crystal structure of $Pd(CO)_2(SO_3F)_2$, showing four complete molecules whose palladium atoms lie within the unit cell plus additional atoms adjacent to one molecule (top) to allow the depiction of the significant nonbonded and secondary interactions (thin lines). For clarity not all atoms within the unit cell are included. The 50% enclosure thermal ellipsoids are shown.

atoms toward an oxygen atom of a fluorosulfate group on a neighboring molecule (Pd···O(22)′, 3.007(4) Å, where ′ indicates $1 - x, -y, -z$). The sum of accepted van der Waals radii for palladium and oxygen is 3.22 Å.[30] There are no other intermolecular distances to palladium which are less than the sums of the corresponding pairs of van der Waals radii. On the opposite side of the coordination plane the nearest interatomic distances from a neighboring molecule to the palladium atom are as follows: Pd···O(23)″, 3.250(3) Å, and Pd···O(13)″, 3.301(4) Å (where ″ indicates $^1/_2 + x, ^1/_2 - y, ^1/_2 + z$).

There are a number of intermolecular C···O contacts (four for each carbon atom) to the terminal oxygen atoms of the fluorosulfate groups in the range 2.839(6)–3.172(6) Å which may provide a stabilizing influence on the structure. In a complementary fashion, each of the terminal oxygen atoms of the fluorosulfate groups has two intermolecular contacts to carbon atoms. There is also an intermolecular contact between O(2) and O(13) ″ of 2.861(5) Å (where ″ indicates $1 + x, y, z$). In light of the numerous C···O contacts it is of interest that this latter distance represents the only significant nonbonded contact involving a carbonyl oxygen atom. The above mentioned Pd···O-(22)′, C···O, and O···O distances are the only intermolecular separations significantly less than the sums of appropriate pairs of van der Waals radii. These nonbonded contacts as well as the "unimposed" intramolecular contacts C(1)···F(2) (3.051(6) Å) and C(2)···O(12) (2.843(6) Å) are shown in Figure 2. This figure includes the four complete molecules whose palladium atoms lie within the unit cell plus additional atoms to show the significant intermolecular contacts to one molecule, the atomic coordinates of which are given in Table 2. The unit cell is shown for reference. For clarity, not all of the molecular fragments which protrude into the cell are depicted.

The weak C···O (and C···F) interactions discussed above allow another comment. In previous discussions of thermally stable noble metal carbonyl salts and cationic derivatives like $[Au(CO)_2][Sb_2F_{11}]$,[8,9] $Au(CO)SO_3F$,[8] *cis*-$Pt(CO)_2(SO_3F)_2$,[10] and $[M(CO)_4][Sb_2F_{11}]_2$[11] (M = Pt or Pd), we had advanced the view that thermal stability as well as the extent to which $\bar{\nu}$(CO) was raised above the value of $\bar{\nu}$(CO) in gaseous CO was strictly a function of the weak nucleophilicity of the counteranion or the anionic moiety, resulting in strong polar contributions to the metal–CO bond. It appears now that the molecular nature of the anions may allow for additional stabilization of the coordinated carbonyl ligands via C···O or C···F contacts.

Secondary interactions involving the carbon atom of the CO ligand have seemingly not been noticed for other noble metal carbonyl derivatives.[16-19] It is however interesting to note that, in the structure of linear Au(CO)Cl,[16] individual molecules are packed in such a manner that, in addition to Au···Au contacts of 3.38 Å, each carbon has four contacts to Cl of adjacent molecules of ~3.35 Å, slightly less than the sum of the van der Waals radii of 3.45 Å.[30]

C. Structural Comparison to Related Compounds. As stated in the Introduction, *cis*-$Pd(CO)_2(SO_3F)_2$ is the first thermally stable, bis(carbonyl) palladium(II) derivative which is synthesized[10] and now structurally characterized. There is a report on the synthesis and the molecular structure of a dinuclear complex of the formula $[Pd(\mu\text{-Cl})(CO)_2]_2$,[31] where palladium has the formal oxidation state +1. The central atom appears to be in a distorted square planar environment, the CO ligands are terminal, and asymmetric chloride bridges are claimed.[31] Both the composition and the structure are uncharacteristic and unprecedented for a palladium(I) carbonyl derivative.[4,6] In all reported Pd(I) structures,[32-36] including $[Pd_2(\mu\text{-CO})_2](SO_3F)_2$,[20] bridging CO ligands are observed while chloride, where present,[32,36] is a monodentate, terminal ligand.

Since the reported unit cell parameters, all reported internuclear distances and bond angles, and the IR band positions and relative intensities reported are within accepted error limits identical to those published previously for $[Rh(\mu\text{-Cl})(CO)_2]_2$,[37,38] a reinvestigation is suggested.

The two anions $[Pd(CO)Cl_3]^-$ and $[Pd(CO)Br_3]^-$[22] have the square planar structure in common with *cis*-$Pd(CO)_2(SO_3F)_2$.

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While the C–O distances reported are not significantly different, the Pd–C distance for $[Pd(CO)Cl_3]^-$ is at 1.87(1) Å significantly shorter than 1.945(5) and 1.919(5) Å found for *cis*-$Pd(CO)_2(SO_3F)_2$, which would suggest more π-back-donation for the Pd–CO moiety in this anion consistent with $\bar{\nu}(CO)$ of 2132 cm^{-1} vs $\bar{\nu}(CO)_{av}$ of 2218 cm^{-1} for the *cis*-$Pd(CO)_2(SO_3F)_2$.[10] The structure of $[Pd(CO)Br_3]^-$ is of too low precision (Pd–C = 1.87(3) Å) to make a useful comparison; however, the $\bar{\nu}(CO)$ value of 2120 cm^{-1} allows a similar conclusion as reached for the chloro anion.

Structural features for $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$,[20] where the CO groups and the fluorosulfate anions are both bridging may be constrasted with those of *cis*-$Pd(CO)_2(SO_3F)_2$. Pd–C (1.984(4), 1.966(4) Å) and C–O (1.133(6) Å) distances within the cyclic $[Pd_2(\mu\text{-}CO)_2]^{2+}$ cation are respectively longer than those in *cis*-$Pd(CO)_2(SO_3F)_2$. For the anion in $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$, the difference in *d*(S–O) between coordinated and noncoordinated O atoms is ~0.025 Å, consistent with weakly coordinated fluorosulfate ions. For the monodentate covalent fluorosulfate groups in *cis*-$Pd(CO)_2(SO_3F)_2$ this difference is ~0.072 Å. Finally, stronger Pd–O bonds are found for *cis*-$Pd(CO)_2(SO_3F)_2$ (d(Pd–O_{av}) = 2.011 Å) compared to 2.156 Å for $[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$.

Even though both molecular structures differ drastically, the long Pd–C bonds found and the vibrational spectra in the $\bar{\nu}(CO)$ region suggest that in both palladium carbonyl fluorosulfates nonclassical Pd–CO bonding with reduced π-back-donation is encountered.

Covalent monodentate fluorosulfate groups bound to a noble metal are also found in dimeric $[Au(SO_3F)_3]_2$.[39] The higher positive formal charge on the central metal and the noted[40,41] ability of gold to form strong covalent bonds results in a longer S–O_b bond of 1.501(8) Å and correspondingly in shorter S–F and S–O_t bonds, where t denotes a terminal and b a bridging oxygen atom. A more detailed comparison between both OSO_2F groups is perhaps inappropriate on account of the thermal motion of the terminal O and F atoms observed in the structure of $[Au(SO_3F)_3]_2$.[39]

Consistent with vibrational data for *cis*-$Pd(CO)_2(SO_3F)_2$, $Au(CO)SO_3F$,[8] and the previously reported $M(CO)_5SO_3F$ (M = Mn or Re),[42] the fluorosulfate group may be termed semi-ionic. This is best reflected in the difference in SO bond lengths between coordinating and terminal oxygen atoms. For *cis*-$Pd(CO)_2(SO_3F)_2$, the average differences are 0.063 and 0.082 Å for the slightly nonequivalent fluorosulfate groups. For $[Au(SO_3F)_3]_2$[39] the difference is about 0.11 Å.

Both CO bonds appear to be slightly shorter than in CO itself (1.12822[8,15]), but when thermal motion corrections are employed using rigid body, segmented rigid body, or riding models, the situation becomes less clear, as seen in Table 3. While the vibrational spectra with $\bar{\nu}(CO)_{av}$ at 2218 cm^{-1} vs 2143 cm^{-1} [15,41] for gaseous CO strongly suggest that the CO bond lengths should be shorter in *cis*-$Pd(CO)_2(SO_3F)_2$ than in CO, this is not unambiguously established by the structural data presented here, when these data are carefully analyzed. The same conclusions are reached when CO bond lengths and vibrational CO stretching frequencies for cationic CO derivatives of group 10 and 11 elements,[16–20] summarized in Table 4, are examined. In all instances the sometimes substantial estimated standard deviations should allow no firm conclusions based on C–O bond lengths alone. Furthermore it is unclear whether thermal motion corrections have been applied, since all previous reports are either short communications[16,17] or preliminary accounts with insufficient details.[18,19]

Table 4. CO Bond Distances and CO Stretching Frequencies for Nonclassical Cationic Metal Carbonyl Derivatives

compd	*d*(C–O) (Å)	$\bar{\nu}(CO)_{av}$ (cm^{-1})	ref
$Cu(CO)Cl$	1.11(2)	2120	17
$Ag(CO)B(OTeF_5)_4$	1.077(16)	2204	18
$[Ag(CO)_2][B(OTeF_5)_4]$	1.07(5), 1.09(5), 1.09(6), 1.08(4)	2198[a]	19
$Au(CO)Cl$	1.11(3)	2170	16, 42
$[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$	1.133(6)	2002	20[b]
cis-$Pd(CO)_2(SO_3F)_2$	1.102(6), 1.114(6)	2218	this work and 10
CO	1.12822(7)	2143	15, 41

[a] IR data only are reported. [b] Molecule has a symmetrically bridging CO ligand.

Vibrational data allow firmer conclusions when a comparison to $\bar{\nu}(CO)$ of 2143 cm^{-1} [43] is made. It has been our approach in the past[9,11] to record FT-IR and FT-Raman spectra down to 50 cm^{-1} and to arrive, with the aid of ^{13}C and ^{18}O isotopic substitution, at a complete vibrational assignment for the frequently simple, highly symmetrical cations like $[Au(CO)_2]^+$,[9] $[M(CO)_4]^{2+}$ [11] (M = Pd or Pt), and $[Pd_2(\mu\text{-}CO)_2]^{2+}$.[20] A sound vibrational assignment and a normal coordinate analysis, to eliminate where possible any vibrational mixing, followed by force constant calculations according to Jones[45] or Cotton–Kraihanzel[46,47] as reported by us[9,11] appears more informative than CO bond lengths. This approach has provided a solid basis on which to judge whether and to what extent π-back-donation from metal to CO has been reduced.[9,11]

Summary and Conclusions

The molecular structure of the only presently known, thermally stable bis(carbonyl)palladium(II) derivative, *cis*-$Pd(CO)_2(SO_3F)_2$, confirms the cis-geometry around palladium, suggested by the vibrational spectra.[10] The short C–O bond distances are consistent with the high $\bar{\nu}(CO)_{av}$ values of 2218 cm^{-1} and suggest reduced palladium to CO π-back-donation. It seems reasonable that in the absence of significant π-bonding, which would result in a charge compensation for carbon, the slight positive charge on each carbon atom gives rise to weak interactions with five oxygen (and in one case, fluorine) atoms of the fluorosulfate groups. The importance of such secondary interactions for the stability of the solid-state structure appears not to have been recognized previously for nonclassical carbonyl derivatives, but as the structure of Au(CO)Cl[16] indicates, this observation made for *cis*-$Pd(CO)_2(SO_3F)_2$ here is not a singular case. In solution of HSO_3F, from which the compound is recrystallized and in which all other thermally stable noble metal carbonyls have been found to exist in,[8–11] solvation may well stabilize the cations by similar weak O···C interactions.

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Supplementary Material Available: Tables listing additional crystallographic details, anisotropic thermal parameters, torsion angles, least-squares planes, and intermolecular and selected intramolecular distances (6 pages). Ordering information is given on any current masthead page.

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