The syntheses and vibrational spectra of bis(carbonyl)platinum(II) fluorosulfate, $Pt(CO)_2(SO_3F)_2$, and bis(carbonyl)palladium(II) fluorosulfate, $Pd(CO)_2(SO_3F)_2$

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Abstract

Reductive carbonylation of platinum(IV) tetrakis(fluorosulfate), $Pt(SO_3F)_4$, in fluorosulfuric acid at 80 °C with a CO pressure of 1–2 atm resulted in the quantitative formation of creamy white bis(carbonyl)platinum(II) fluorosulfate, $Pt(CO)_2(SO_3F)_2$. The corresponding bis(carbonyl)palladium(II) fluorosulfate, $Pd(CO)_2(SO_3F)_2$, has been formed from solid $Pd^{II}Pd^{IV}(SO_3F)_6$ at room temperature and a CO pressure of 0.5 atm as a yellow solid that was thermally stable up to 117 °C. Both compounds gave nearly identical IR and Raman spectra, which suggests a *cis*-square-planar configuration. The average CO stretching frequencies were at 2217 and 2201 cm^{-1} for $Pd(CO)_2(SO_3F)_2$ and $Pt(CO)_2(SO_3F)_2$, respectively. They are unusually high and suggest substantially reduced π-back-donation. $Pd(CO)_2(SO_3F)_2$ is the first example of a thermally stable mononuclear bis(carbonyl) derivative of dipositive palladium.

Introduction

Platinum(II) and palladium(II) carbonyl chlorides have a long history as well as an interesting chemistry [1–3]. The platinum chlorides $Pt(CO)_2Cl_2$, $Pt(CO)Cl_2$ and $Pt_2(CO)_3Cl_4$ were first reported by Schützenberger in 1870 [4] and were hence the first metal carbonyl derivatives to be discovered. The synthesis of the three corresponding palladium(II) carbonyl chlorides was claimed subsequently by Fink [5]. However, Manchot and König [6], who confirmed Schützenberger's findings, were not able to establish the existence of palladium compounds of the composition claimed. Evidently Fink's study had involved the use of palladium metal with a substantial platinum content [6]. It appears that only $Pd(CO)Cl_2$, subsequently shown to be *trans*-$Pd_2(CO)_2Cl_4$ [7] with bridging Cl and terminal CO ligands [$\tilde{\nu}(CO) = 2159–2167\ cm^{-1}$], exists out of the three compounds claimed by Fink [5]. There is also evidence for a carbonyl-bridged isomer with $\tilde{\nu}(CO)$ at 1976 cm^{-1} [8]. While $Pd(CO)_2Cl_2$ still remains unknown, platinum(II) carbonyl chloride, $Pt(CO)_2Cl_2$, is well established [1, 2], and both *cis* and *trans* isomers have been obtained [9–11]. The vibrational and ^{13}C NMR spectra for $Pt(CO)_2Cl_2$ and other noble-metal carbonyl derivatives have been reported [12] and the very high CO-stretching frequencies of 2131–2178 cm^{-1} have led to the suggestion that metal-to-carbon π-back-bonding is drastically reduced [9] in these compounds.

In addition to these carbonyl chlorides, the corresponding bromides (and, in the case of Pt^{II}, the iodides) have been reported [9], and a number of anionic complexes of the type $[M(CO)X_3]^-$ (X = Cl, Br or I; M = Pd or Pt) are known. It is also observed that, in any group of compounds of Pd^{II} or Pt^{II}, the chlorides show higher CO stretching frequencies and greater thermal stability; hence most research has in the past concentrated on the chloro compounds.

Our own involvement in this area goes back a few years and started with the isolation of carbonylgold(I) fluorosulfate, $Au(CO)SO_3F$, formed by the reductive carbonylation of $Au(SO_3F)_3$ in solutions of fluorosulfuric acid [13]. In this reaction, the solvated cation $[Au(CO)_2]^+_{(solv.)}$ was formed as an intermediate. Subsequent solvolysis of $Au(CO)SO_3F$ in liquid SbF_5 in a CO atmosphere allowed isolation of $[Au(CO)_2][Sb_2F_{11}]$ and complete characterization of the linear cation $[Au(CO)_2]^+$ [14]. Both $Au(CO)SO_3F$ [$\tilde{\nu}(CO) = 2197\ cm^{-1}$] [13] and $[Au(CO)_2]^+$ [$\tilde{\nu}(CO)_{av.} = 2235.5\ cm^{-1}$] [14] have unusually high CO-stretching frequencies.

It is interesting to note that the initial intentions leading to the gold(I) carbonyl derivatives were to

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protonate CO in the superacid system $HSO_3F/Au(SO_3F)_3$. However, reductive carbonylation of $Au(SO_3F)_3$ was observed instead [15, 16]. In the present study, we have extended our synthetic approach to the superacid system $HSO_3F/Pt(SO_3F)_4$ [17], and since the corresponding $Pd(SO_3F)_4$ has not been obtained so far, a suspension of palladium(III) fluorosulfate in HSO_3F was used instead. This material was found to be a mixed oxidation state compound, best formulated as $Pd^{II}[Pd^{IV}(SO_3F)_6]$ [18, 19].

The motivation for the present study was three-fold: (i) the expected products, $M(CO)_2(SO_3F)_2$ (M = Pd or Pt), should provide further examples of unusual metal–CO bonding with reduced π-back-bonding; (ii) the non-existence of thermally stable $Pd(CO)_2X_2$-type compounds, or of neutral mononuclear $Pd^{II}CO$ derivatives, presents a challenge to the synthetic chemist; and (iii) both $Pt(CO)_2(SO_3F)_2$ and $Pd(CO)_2(SO_3F)_2$ should, by analogy to the conversion of $Au(CO)SO_3F$ into an $[Au(CO)_2]^+$ salt [14], allow the synthesis of salts containing the square-planar cations $[M(CO)_4]^{2+}$ with M = Pd or Pt. This last objective has in the meantime been realized, and salts of the composition $[M(CO)_4][Sb_2F_{11}]_2$ have been obtained and characterized by us [20].

Experimental

Chemicals

Platinum and palladium powder were obtained from the Ventron Corporation (Alfa Inorganics). Fluorosulfuric acid, HSO_3F (technical grade), was obtained from Orange County Chemicals and purified by double distillation [21]. Bis(fluorosulfuryl) peroxide, $S_2O_6F_2$, was prepared by fluorination of SO_3 using AgF_2 as a catalyst [22]. Antimony pentafluoride, SbF_5, was obtained from Ato Chem North America, and purified first by distillation and then by pumping *in vacuo* at 0 °C. Carbon monoxide (C.P. grade, 99.5% purity) was obtained from Linde Gases and dried by condensing in a trap cooled to −196 °C and partial evaporation. Sulfur dioxide, SO_2 (99.5% purity), was obtained from Matheson Gases and dried by storing over P_4O_{10}. Platinum tetrakis(fluorosulfate), $Pt(SO_3F)_4$ [17], and $Pd(SO_3F)_3$ [19], were prepared as described previously by us.

Instrumentation

Infrared (IR) spectra were recorded on three instruments: a Perkin-Elmer 598 grating spectrometer, a Bomem MB 102 Fourier-transform infrared spectrometer (FT-IR) and a Bomem DA3 series FT-IR. Solid samples were finely ground and pressed as thin films between AgBr or AgCl windows (Harshaw Chemicals). Liquid samples were pipetted onto silicon windows and pressed to form a thin film. Gaseous samples were contained in a 10-cm cell fitted with AgBr windows and a 4-mm Kontes Teflon stopcock. FT-Raman spectra were obtained with a Bruker FRA 106 FT-Raman accessory mounted on an IFS 66v FT-IR optical bench.

Volatile materials and gases were measured in a vacuum line of known volume. A Setra 280E pressure transducer with digital output was used to measure the pressure. Standard vacuum line techniques were employed to manipulate air- and moisture-sensitive samples. Synthetic reactions were carried out inside Pyrex round-bottom flasks (50 or 100 ml) fitted with 4-mm Kontes stopcocks and B10 ground-glass cones. A filtration apparatus similar to that described by Shriver [23] was used. Teflon-coated stir-bars were used for mixing the reactants. Since all the products were hygroscopic, they were manipulated and stored inside a Vacuum Atmosphere Corp. Dri-Lab, model HE 493, filled with dry nitrogen and equipped with an HE 493 Dri-Train.

Synthetic reactions

$Pt(CO)_2(SO_3F)_2$

$Pt(CO)_2(SO_3F)_2$ was prepared by admitting 1–2 atm CO onto $Pt(SO_3F)_4$ dissolved in HSO_3F (0.621 mg, 1.05 mmol) in a 50-ml round-bottom flask and heating the solution, while stirring, at 80 °C in an oil bath overnight. The color of the solution was initially red–brown, but a mixture of a yellow solid and a clear, yellow solution quickly formed. Further heating with a heat gun resulted in a clear colorless solution. The CO uptake measured was 3.32 mmol, and all volatile products were measured and identified as $S_2O_5F_2$ and CO_2. Excess HSO_3F was removed slowly *in vacuo*. Cooling to 0 °C was necessary to prevent spraying of the powdery solid. The initial product was found to contain small amounts of residual HSO_3F, which could be removed by drying *in vacuo*. Analysis: Calc. for $C_2O_8S_2F_2Pt$: C, 5.34; S, 14.27%. Found: C, 5.41; S, 14.17%. $Pt(CO)_2(SO_3F)_2$ melted at 100 °C to a translucent, creamy liquid.

$Pd(CO)_2(SO_3F)_2$

Initially 109 mg (1.024 mmol) of palladium powder was converted quantitatively to 415.5 mg (1.029 mmol) of $Pd(SO_3F)_3$ by reaction with $S_2O_6F_2$ in a solution of HSO_3F, as reported previously [19]. After removal of all volatiles (HSO_3F and excess $S_2O_6F_2$) and checking the course of the reaction by weighing, purified CO at an initial pressure of 580 Torr was admitted to the reactor. The dark-brown color of the starting material, distributed as a thin film on the reactor wall, changed immediately to pale yellow. To ensure complete reaction, the reactor was kept under CO pressure for an additional 2 d. After removal of all volatiles, 370.1 mg (1.027

mmol) of $Pd(CO)_2(SO_3F)_2$ was obtained. When $Pd(CO)_2(SO_3F)_2$ was heated to 117 °C, there was a slight color change from yellow to orange, and the compound decomposed with evolution of gas at 120 °C. Analysis: Calc. for $C_2O_8S_2F_2Pd$: C, 6.66; S, 17.78%. Found: C, 6.24; S, 17.1%.

Results and discussion

Synthesis

The synthesis of both bis(carbonyl)platinum(II) fluorosulfate, $Pt(CO)_2(SO_3F)_2$, and bis(carbonyl)palladium(II) fluorosulfate, $Pd(CO)_2(SO_3F)_2$, has been accomplished, initially at room temperature, by reductive carbonylation of either platinum(IV) fluorosulfate or the mixed oxidation state $Pd^{II}Pd^{IV}$ fluorosulfate of the composition $Pd(SO_3F)_3$ with CO at low pressures of ~0.5 atm. While the reactions followed the overall course of the previously reported reductive carbonylation of gold(III) fluorosulfate [13] according to:

$$Au(SO_3F)_3 + 3CO \xrightarrow[HSO_3F]{25\ °C} [Au(CO)_2]^+_{(solv.)} + CO_2 + S_2O_5F_2 + SO_3F^- \quad (1)$$

$$[Au(CO)_2]^+ + SO_3F^- \xrightarrow{70\ °C} Au(CO)SO_3F + CO \quad (2)$$

there were some interesting discrepancies that required modifications in both bases.

The reductive carbonylation of $Pt(SO_3F)_4$ proceeded rather slowly and passed through an intermediate of composition $Pt(CO)_2(SO_3F)_3$. This material precipitated as a yellow, diamagnetic solid from the acid solution and has been identified by us as $[Pt(CO)_4][Pt(SO_3F)_6]$ [24]. There have been previous reports on the preparation and vibrational characterization of salts containing the $[Pt(SO_3F)_6]^{2-}$ anion [17, 25] and the formation reaction, according to:

$$2Pt(SO_3F)_4 + 5CO \xrightarrow[HSO_3F]{25\ °C} [Pt(CO)_4][Pt(SO_3F)_6] + CO_2 + S_2O_5F_2 \quad (3)$$

represents a partial reduction of Pt^{IV} by CO. A corresponding intermediate $[Au(CO)_2][Au(SO_3F)_4]$ has not been obtained so far, even though the constituent ions exist [13–16]. There are two reasons for this: (i) the reduction of Au^{III} proceeds far more rapidly and goes directly to $[Au(CO)_2]^+_{(solv.)}$, even at room temperature; and (ii) salts containing the anion $[Au(SO_3F)_4]^-$ [13, 14] are far more soluble in HSO_3F than those with $[Pt(SO_3F)_6]^{2-}$ as counterion [17, 25], so that a partly reduced intermediate during reductive carbonylation of $Au(SO_3F)_3$ may have escaped detection.

Complete reduction to $Pt(CO)_2(SO_3F)_2$ was observed when the reaction temperature was raised from 25 °C to 80 °C. The yellow intermediate, identified as $[Pt(CO)_4][Pt(SO_3F)_6]$ [24], redissolved and the color of the solution faded gradually. The overall reaction may be formulated as:

$$Pt(SO_3F)_4 + 3CO \xrightarrow[HSO_3F]{80\ °C} Pt(CO)_2(SO_3F)_2 + CO_2 + S_2O_5F_2 \quad (4)$$

The course of the reductive carbonylation reaction was monitored by measuring the CO uptake in an apparatus of known volume. The total uptake of 3.16 mol of CO per mol of $Pt(SO_3F)_4$ was in slight excess of the 3 mol required according to eqn. (4), and it is assumed that small, residual amounts of $S_2O_6F_2$ may be responsible for the discrepancy. As observed previously [13], $S_2O_6F_2$ oxidized CO to CO_2 with $S_2O_5F_2$ being formed as a by-product.

Again, as reported previously [13], CO_2 and $S_2O_5F_2$ were separated by trap-to-trap condensation of the volatile products and identified by their IR spectra [26, 27]. The amounts of both by-products were determined by gas volumetric measurements. The main product, an ivory colored solid of composition $Pt(CO)_2(SO_3F)_2$, was isolated like $Au(CO)SO_3F$ by evaporation of the volatiles in quantitative yield, but unlike $Au(CO)SO_3F$ [13], the material would not sublime *in vacuo* and could not be purified in this manner. The compound was thermally stable up to 100 °C. $Pt(CO)_2(SO_3F)_2$ is very soluble in liquid SO_2, while $[Pt(CO)_4][Pt(SO_3F)_6]$ is not, which permits their separation.

As mentioned in the Introduction, there are a limited number of precedents of the type $Pt(CO)_2X_2$ known, where X = Cl, Br or I [1, 2, 4, 6, 9], but bis(carbonyl)platinum(II) fluorosulfate appears to be the only oxyacid derivative reported to date.

The formation of $Pd(CO)_2(SO_3F)_2$ was anticipated to proceed in a very similar manner, except for the fact that $Pd(SO_3F)_4$ is not known. Hence the mixed oxidation state compound $Pd^{II}Pd^{IV}(SO_3F)_6$ [19] was used instead, even though it has limited solubility in HSO_3F. However, while reductive carbonylation of $Pt(SO_3F)_4$ proceeded slowly and required elevated temperatures to avoid formation of the partly reduced $Pt(CO)_2(SO_3F)_3$, the reaction of CO with Pd^{II}-$Pd^{IV}(SO_3F)_6$ in HSO_3F was fast and usually complete within 30 min. The brown, solid starting material dissolved rapidly in the presence of CO and a pale yellow solution resulted. The yellow solid obtained after solvent removal had the approximate overall composition $Pd(CO)_2(SO_3F)_2$ according to product weight and microanalysis, but the vibrational spectrum suggested a mixture of possibly several carbonyl-containing species. One of these components has been isolated by recrystallization from HSO_3F solution in the form of long needles suitable for an X-ray diffraction study. Details on the molecular structure will be reported shortly [28]. The composition established for this compound by microanalysis was $Pd(CO)SO_3F$, and the vibrational spectra suggested the presence of bridging CO[$\tilde{\nu}$(CO) 1977 cm^{-1} (IR) and 2027 cm^{-1} (Raman)] and bidentate bridging fluorosulfate groups. There is a precedent for the structural type $[Pd(CO)Cl]_n$ [3, 29], where a polymeric chain structure with alternating CO and Cl bridges has been suggested. It appears that reduction to Pd^I occurred, at least in part. Again there are several precedents for the reduction of Pd^{II} compounds to Pd^I carbonyl derivatives [3, 30].

To avoid difficult separation problems, a different synthetic approach was chosen: the reductive carbonylation of solid $Pd^{II}Pd^{IV}(SO_3F)_6$ at room temperature. To facilitate the reaction, it was found useful to deposit a fine film of the freshly prepared brown starting material on the walls of the reactor by the slow removal of excess solvent acid. The reaction again proceeded very rapidly at room temperature and at a CO pressure of ~0.5 atm. The color of the solid changed from brown to yellow within minutes. This time a single main product formed, which was identified as $Pd(CO)_2(SO_3F)_2$ by product weight and microanalysis; however, two impurities, present in very small amounts, were detected by vibrational spectroscopy and identified as $[Pd(CO)SO_3F]_n$ (a weak band in the IR region of 1966 cm^{-1}) and as $Pd(SO_3F)_2$ (very weak shoulders at 1240, 1090, 860 and 611 cm^{-1} [18]. The latter was found only occasionally and identified as tiny purple spots in the sample. The former, $[Pd(CO)SO_3F]_n$, may be responsible for the slightly low C and S contents of the sample analyzed.

The formation of $Pd(SO_3F)_2$ as a by-product is not surprising since it is possible to reduce $Au(SO_3F)_3$ to polymeric $Au(SO_3F)_2$ with CO under certain conditions [31]. The failure to convert $Pd(SO_3F)_2$ to $Pd(CO)_2(SO_3F)_2$ by CO addition was surprising because $PdCl_2$ adds CO under more forcing conditions (120 °C and 50 atm CO) to give $Pd_2(CO)_2Cl_4$ [32]; this could, however, be due to a structural difference. Thus, $Pd(SO_3F)_2$ is a paramagnetic three-dimensional polymer with Pd^{2+} in an octahedral environment [18, 19], while $PdCl_2$ is a diamagnetic chain polymer with Pd in a square-planar environment [33].

The method of synthesis by a solid–gas reaction according to:

$$Pd(SO_3F)_3(s) + 3CO(g) \xrightarrow[0.5\ \text{atm}]{25\ °C} Pd(CO)_2(SO_3F)_2(s) + CO_2(g) + S_2O_5F_2(l) \quad (5)$$

requires that only small amounts of reactants (~500 mg) are used, to assure complete reaction within a short period of time. On the other hand, product isolation is very easy and nearly quantitative conversion is generally found.

Bis(carbonyl)palladium(II) fluorosulfate, $Pd(CO)_2(SO_3F)_2$, is a yellow solid which was thermally stable up to 117 °C before decomposition was noted. This is comparable to the thermal stability of $Pt(CO)_2(SO_3F)_2$. In contrast to the platinum(II) analogue, $Pd(CO)_2(SO_3F)_2$ is the first reported neutral, monomeric palladium(II) carbonyl derivative. It is also the first example of a compound where two monodentate CO ligands are coordinated to Pd^{II} exhibiting reasonable thermal stability. Evidently the strongly electron-withdrawing fluorosulfate groups enhance the acceptor ability of the Pd metal center.

Two reports of related compounds merit further mention here. The molecular structure of a dinuclear complex, the μ-chlorobis(carbonyl)palladium(I) dimer, $[PdCl(CO)_2]_2$, has been reported [34], but there are some inconsistencies. The Pd–C distances are unusually short (1.852 Å), which could imply extensive π-back-bonding, while the average CO bond length was again very short (1.089 Å), much shorter than in CO itself (1.121 Å) [35], which would suggest the complete absence of back-donation. Finally, $\tilde{\nu}$(CO) values ranged between 2103 and 1997 cm^{-1}, which again suggests substantial π-back-donation. It is also disturbing that in all structures of Pd^I carbonyl derivatives reported so far [36–38], including $Pd(CO)SO_3F$ [28], either strong and short Pd–Pd bonds, compared with the 3.317 Å distance found here, and/or bridging or semibridging CO groups exist, while here terminal CO and bridging chloro groups are found.

While the compound discussed above is a Pd^I derivative, there are two monomeric Pd^{II} compounds of the type $Pd(CO)_2R_2$ ($R = C_6F_5$ or C_6Cl_5) [39], but both decompose below 30 °C with CO evolution.

The similar thermal stability of the two Pd^{II} and Pt^{II} carbonyl derivatives is surprising for another reason. Both $Au(CO)SO_3F$ [13] and $[Au(CO)_2][Sb_2F_{11}]$ [14] are stable thermally well above 140 °C and, when finally decomposed, form gold metal. The silver(I) carbonyl compounds $Ag(CO)B(OTeF_5)_4$ [40] and $Ag(CO)_2B(OTeF_5)_4$ [41] decompose well below room temperature with reversable CO release and the formation of $Ag[B(OTeF_5)_4]$. It is concluded that this situation is not observed in Group 10 and that the use of very weakly basic anions should lead to further examples of palladium carbonyl derivatives.

Vibrational spectra

The IR and Raman spectra for $Pd(CO)_2(SO_3F)_2$, $Pt(CO)_2(SO_3F)_2$ and $Au(CO)SO_3F$ as reported previously are listed in Table 1, together with an approximate assignment for the Pd^{II} and Pt^{II} derivatives. The IR spectrum of $Pd(CO)_2(SO_3F)_2$ and the $\tilde{\nu}$(CO)

TABLE 1. The vibrational wavenumbers (cm^{-1}) for $Pd(CO)_2(SO_3F)_2$, $Pt(CO)_2(SO_3F)_2$ and $Au(CO)SO_3F$ and estimated band intensities

$Pd(CO)_2(SO_3F)_2$		$Pt(CO)_2(SO_3F)_2$		$Au(CO)SO_3F$[a]		Approx. assignment
IR	Raman	IR	Raman	IR	Raman	
2228 (ms)[b]	2228 (vs)	2219 (s)	2218 (vs)			$\nu_{sym}(^{12}CO)$
	2212 (w, sh)		2191 (m)			ν_{sym}(*trans*)[c]
2208 (s)	2207 (ms)	2185 (vs)	2181 (s)	2195 (s)	2198 (vs)	$\nu_{asym}(^{12}CO)$
2166 (w, sh)		2145 (vw)				ν_{asym}(*trans*)
		1397 (s)	1395 (s)			$\nu_{asym}SO$
1380 (s)	1382 (s)	1389 (s, sh)				
1360 (s)	1358 (ms)	1378 (vs)	1376 (m)	1360 (vs)	1368 (w)	
		1362 (w, sh)				
1229 (s, sh)		1230 (m, sh)				$\nu_{sym}(SO_2)$
1206 (vs)	1208 (s)	1209 (vs)	1212 (s)	1198 (vs)	1200 (m)	
		1034 (m, sh)				$\nu(SO\cdots M)$
1038 (s)	1031 (vs)	1026 (s)	1019 (s)			
1019 (vs)	1003 (s)	1009 (vs)	993 (m)	1020 (vs)	1020(s)	
935 (vw)						
794 (vs)	808 (m)	799 (s)	815 (w)	810 (s)	792 (w, br)	$\nu(SF)$
	789 (mw)		792 (w)	768 (s)		
648 (s)	649 (vs)	657 (ms)	656 (s)	641 (m)	640 (m)	$\nu(MO)+\delta(SO_2)$
638 (ms)		648 (m, sh)				
586 (vs)	586 (m)	589 (s, sh)	588 (mw)			$\delta_{asym}(SO_3)$
	579 (m)	584 (s)	580 (m)	577 (s)	578 (m)	
554 (s)	559 (m)	557 (ms)	565 (w)			$\delta_{sym}(SO_3)$
	552 (mw)	551 (s)	554 (w)	554 (s)	553 (w)	
514 (ms)		476, 472 (ms)	475 (w, sh)			δ(M–CO)?
440 (ms)	455 (mw)	436 (w)	462 (ms)	445 (w)	456 (w)	$\nu(MO)+\delta(SO_3)$
417 (vw)	405 (w)	411 (vw)	412 (w)	411 (w)	400 (w)	$\rho(SO_3F)$
406 (ms)	388 (s)			390 (w)		
	290 (vs)		291 (m)	251 (m)	268 (m)	unassigned torsion and deformation modes
			276 (vw)			
	167 (m, sh)		175 (w)			
	147 (ms)		151 (m)			
	134 (m)		138 (vw)		115 (w)	

[a] Ref. 13.

[b] Abbreviations: s = strong, m = medium, w = weak, v = very, br = broad, sh = shoulder, ν = stretching mode, δ = bonding mode, ρ = rocking, sym = symmetric, asym = asymmetrical.

[c] (*trans*) assigned to *trans*-$M(CO)_2(SO_3F)_2$, see text.

region of the Raman spectrum are shown in Fig. 1. The similarity, in particular in the vibrational spectra of $Pd(CO)_2(SO_3F)_2$ and $Pt(CO)_2(SO_3F)_2$, is readily recognized from the listing in Table 1. The greater complexity of the two sets of spectra for both compounds compared to the rather simple spectra for $Au(CO)SO_3F$ [13] is not unexpected on account of vibrational coupling primarily between the two fluorosulfates, which appear to be weakly coordinated to the two respective metal centers. A similar band distribution and a similar coordination mode has been observed previously for $M(CO)_5SO_3F$ (M = Mn or Re) [42]. The low position of $\tilde{\nu}(SF)$ at ~800 cm^{-1} and the position of $\tilde{\nu}(SO\cdots M)$ at ~1000–1040 cm^{-1} are consistent with a high ionic character for the metal–OSO_2F bonds in all instances.

It is also apparent that the spectra are dominated by the fluorosulfate bands in the frequency range below 600 cm^{-1}. Hence it is very difficult to assign metal–carbon stretching and C–O deformation modes unambiguously without help from labeled (^{13}C and ^{18}O) isotopomers. Judging from our experience in the case of $[Au(CO)_2]^+$ [14], these bands are very weak and

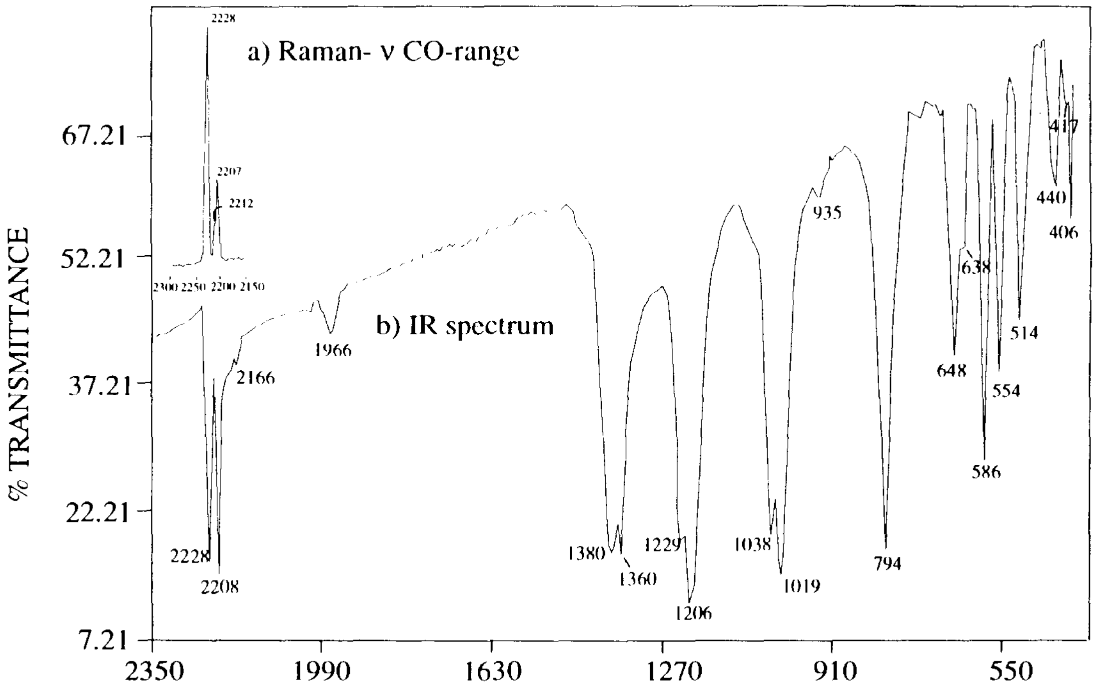

Fig. 1. The vibrational spectra of *cis*-$Pd(CO)_2(SO_3F)_2$.

difficult to recognize. They also coincide partly with deformation modes due to the fluorosulfate group.

On the other hand, the CO-stretching modes are clearly recognizable and allow a number of useful conclusions:

(i) The principal species present appears to be *cis*-$M(CO)_2(SO_3F)_2$ (M = Pd or Pt) as judged by the coincident bands in the Raman and IR spectra. However, there are weak bands present in the Raman and IR spectra of both $Pd(CO)_2(SO_3F)_2$ and $Pt(CO)_2(SO_3F)_2$ at 2212 or 2166 and 2191 or 2145 cm^{-1}, respectively, which follow the mutual exclusion rule and may be tentatively attributed to the *trans* isomer.

(ii) The average stretching frequency is higher for *cis*-$Pd(CO)_2(SO_3F)_2$ (2216.5 cm^{-1} IR and 2217.5 cm^{-1} Raman) than for *cis*-$Pt(CO)_2(SO_3F)_2$ (2202 cm^{-1} IR and 2198.5 cm^{-1} Raman). This has also been noted previously for the binuclear pair $M_2Cl_4(CO)_2$ (M = Pd or Pt) [32], for $Pd(CO)_2R_2$ (R = C_6F_5 or C_6Cl_5) [39] and for the anion pairs $[MX_3(CO)]^-$ (M = Pd or Pt, and X = Cl or Br) [12]. In all these instances terminal rather than bridging CO groups are present.

(iii) The CO average stretching frequency for *cis*-$Pt(CO)_2(SO_3F)_2$, observed in Raman spectra of solid samples at 2198.5 cm^{-1}, is higher than that reported for *cis*-$Pt(CO)_2Cl_2$ (2164.5 cm^{-1}) or *cis*-$Pt(CO)_2Br_2$ (2153 cm^{-1}) [12]. Similar slight shifts are found for $Au(CO)SO_3F$ [13] (2197 cm^{-1}) and $Au(CO)Cl$ (2183 cm^{-1}) [12]. These are consistent with the view that $\tilde{\nu}(CO)$ will increase with decreasing nucleophilicity of the anionic group. As observed previously for *cis*-$Pt(CO)_2Cl_2$ [12] and *cis*-$M(CO)_2R_2$ [39] (M = Pt or Pd, R = C_6F_5 or C_6Cl_5), the symmetric CO stretching frequencies are observed at higher wavenumbers than their asymmetric counterparts. Our assignment is based on the intensities of the IR and Raman bands in this region.

Finally, an interesting observation deserves some comment. When IR spectra were recorded on solutions of the two carbonyl derivatives in HSO_3F, the two $\tilde{\nu}(CO)$ bands observed were shifted to slightly higher wavenumbers. For $Pd(CO)_2(SO_3F)_2$, both $\tilde{\nu}(CO)$ bands were shifted from 2207 and 2227 cm^{-1} to 2214 and 2233 cm^{-1}, respectively. For $Pt(CO)_2(SO_3F)_2$, $\tilde{\nu}(CO)$ shifts from 2185 and 2219 cm^{-1} to 2191 and 2224 cm^{-1} were noted on dissolution in fluorosulfuric acid. It is suggested that partial ionization according to:

$$M(CO)_2(SO_3F)_2 \underset{HSO_3F}{\overset{25\ °C}{\rightleftharpoons}} [M(CO)_2SO_3F]^+_{(solv.)} + SO_3F^- \qquad (6)$$

may be responsible for the observed upward shifts by about six wavenumbers.

It may also be surmized by analogy to $[Au(CO)_2]^+$ that the solvated cations $[M(CO)_4]^{2+}$ (M = Pd or Pt) may form initially, but no attempt was made to identify them by vibrational spectroscopy because both have been isolated recently as white solids of the composition $[M(CO)_4][Sb_2F_{11}]_2$ [24]. The *cis*-bis(carbonyl)-palladium(II) fluorosulfate is one of few seemingly mono-nuclear bis(carbonyl)palladium(II) derivatives reported so far, and it is surprising that the thermal stability is comparable to that of its Pt^{II} congener. Judging from their vibrational spectra, both *cis*-$Pd(CO)_2(SO_3F)_2$ and *cis*-$Pt(CO)_2(SO_3F)_2$ appear to be isostructural. It may seem surprising that the palladium(II) compound is yellow while *cis*-$Pt(CO)_2(SO_3F)_2$ is nearly colorless. It may be argued that the origin of the color may be $SO_3F \rightarrow Pd^{II}$ charge transfer with Pd^{II} ranking higher in the charge-transfer series than Pt^{II} [43]. Most other Pd(CO)–chloro derivatives are described as yellow–orange [32, 37].

Summary and conclusions

In summary, all observations made are consistent with the presence of *cis*-$M(CO)_2(SO_3F)_2$ (M = Pd or Pt) as the main species in both preparations. This is in agreement with observations made in the case of $Pt(CO)_2Cl_2$, that the *cis* isomer is thermodynamically the more stable isomer of the two [9].

The results presented here show that reductive carbonylation reactions in fluorosulfuric acid may be extended from the reported reduction of $Au(SO_3F)_3$ [13, 14] to $Pt(SO_3F)_4$ and $Pd(SO_3F)_3$, even though the latter is not appreciably soluble in HSO_3F. However, in both cases, complications are noted for opposite reasons. Reduction of $Pt(SO_3F)_4$ proceeded sluggishly and a partly reduced intermediate of composition $Pt(CO)_2(SO_3F)_3$ was isolated as a precipitate and identified as $[Pt(CO)_4][Pt(SO_3F)_6]$ [20]. At elevated temperatures complete reduction to Pt^{II} was observed.

In the case of $Pd(SO_3F)_3$, reductive carbonylation in HSO_3F was facile at 25 °C; however, a mixture of products was formed. Two components of this mixture were isolated and identified: polymeric $[Pd(CO)SO_3F]_n$ [28] and *cis*-$Pd(CO)_2(SO_3F)_2$, which was better obtained in the reduction of solid $Pd(SO_3F)_3$ at 25 °C.

Finally, it is noteworthy that $\bar{\nu}(CO)_{av.}$ for $Pd(CO)_2(SO_3F)_2$ is at 2217 cm^{-1}, the highest for any ternary noble-metal carbonyl derivative reported so far. Only for $[Au(CO)_2]^+$ [13, 14] and for the recently synthesized cations $[M(CO)_4]^{2+}$ (M = Pd or Pt) have higher average stretching frequencies been reported.

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