Bis(carbonyl)platinum(II) Derivatives: Molecular Structure of *cis*-$Pt(CO)_2(SO_3F)_2$, Complete Vibrational Analysis of *cis*-$Pt(CO)_2Cl_2$, and Attempted Synthesis of *cis*-$Pt(CO)_2F_2$

Britta von Ahsen,[†] Rudolf Wartchow,[‡] Helge Willner,*[,†] Volker Jonas,[§] and Friedhelm Aubke*[,||]

Fachbereich 6, Anorganische Chemie, Gerhard Mercator Universität-GH-Duisburg, Lotharstrasse 1,
D-47048 Duisburg, Germany, Institut für Anorganische Chemie der Universität Hannover,
Callinstrasse 9, D-30167 Hannover, Germany, San Diego Super Computer Centre, MC 0505,
9500 Gilman Drive, San Diego, California 92093-0505, and Department of Chemistry,
The University of British Columbia, 2036 Main Mall, Vancouver, British Columbia V6T1Z1, Canada

Received March 13, 2000

As part of a comprehensive study of square planar palladium(II) and platinum(II) carbonyl derivatives, the molecular structure of *cis*-$Pt(CO)_2(SO_3F)_2$, the complete vibrational spectra of *cis*-$Pt(CO)_2Cl_2$, and the attempted synthesis of *cis*-$Pt(CO)_2F_2$ are reported. *cis*-$Pt(CO)_2(SO_3F)_2$ is isostructural with *cis*-$Pd(CO)_2(SO_3F)_2$ and crystallizes in the monoclinic space group $P2_1/n$ (no. 14). Crystal data: $a = 7.419(1)$ Å; $b = 14.751(2)$ Å; $c = 8.634(1)$ Å; $\beta = 89.95(1)°$; $V = 944.9(2)$ Å^3; $Z = 4$; $T = 300$ K; $R\ [F_o > 4\sigma(F_o)] = 0.0447$ and wR2 = 0.1097. The internal bond parameters of the *cis*-$Pt(CO)_2(SO_3F)_2$ are compared to those of *cis*-$Pd(CO)_2(SO_3F)_2$, *cis*-$Pt(CO)_2Cl_2$, and $[M(CO)_4]^{2+}$, M = Pd, Pt. Solid *cis*-$Pt(CO)_2Cl_2$ is studied by IR and Raman spectroscopy, and the data are compared to those of the matrix-isolated complex by IR spectroscopy. Vibrational assignments are supported by DFT calculations, which provide, in addition to vibrational wavenumbers, estimates of IR and Raman band intensities. The positions of 12 of the expected 15 fundamentals of *cis*-$Pt(CO)_2Cl_2$ are obtained experimentally. Attempts to synthesize *cis*-$Pt(CO)_2F_2$, using, in addition to *cis*-$Pt(CO)_2X_2$, X = Cl or SO_3F, $[Pt(CO)_4][Sb_2F_{11}]_2$ or PtF_6 as starting material and toluene or anhydrous hydrogen fluoride as the reaction medium, are unsuccessful. There are however two interesting results: The reductive carbonylation of PtF_6 in HF produces with $[Pt(CO)_4][PtF_6]$ the first carbonyl fluoride of platinum, and the reaction of $[Pt(CO)_4][Sb_2F_{11}]_2$ and CsF in HF results in the formation of the previously reported anionic cluster complex $Cs_2[Pt_3(CO)_6]_{n\approx 10}$. The inclusion of $[M(CO)_4]^{2+}$, M = Pd, Pt, provides new insights into the nature of the Pd(II)−CO and Pt(II)−CO bonds.

Introduction

The platinum(II) carbonyl chloro complex, *cis*-$Pt(CO)_2Cl_2$, has been known since 1868. Its accidental formation and subsequent isolation by Schützenberger[1,2] predates the discovery of the first homoleptic transition metal carbonyl, $Ni(CO)_4$, by 22 years.[3] There are a number of features that set *cis*-$Pt(CO)_2Cl_2$ clearly apart from other transition metal carbonyl complexes: (i) Its square planar coordination geometry, recently confirmed by a molecular structure determination,[7] is found neither for homoleptic typical transition metal carbonyl complexes,[4−7] nor for highly reduced metal carbonylates.[8] (ii) Its vibrational spectra[9] have in the CO-stretching region $\bar{\nu}_{av}(CO)$ values of about 2165 cm^{-1}, slightly above the $\bar{\nu}(CO)$ of 2143 cm^{-1} [10] in gaseous CO and well outside the range of 2125−1850 cm^{-1}, commonly quoted[4,10−14] for terminal CO groups in typical metal carbonyls. (iii) With only 16 valence electrons associated with platinum in *cis*-$Pt(CO)_2Cl_2$, the EAN or 18-electron rule is not observed. This rule is, with very few exceptions, such as $V(CO)_6$,[4−6] generally valid for transition metal carbonyls.[4−6,8] (iv) The related 18-electron molecules $Pt(CO)_4$ and $Pd(CO)_4$, which are expected to be isostructural with $Ni(CO)_4$, are claimed to exist only in inert gas matrixes together with their molecular fragments.[15]

It hence appears that synergetic M−CO bonding according to the Dewar−Chatt−Duncanson model,[16−18] does not result in thermodynamically stable carbonyl compounds for zerovalent

---

* To whom correspondence should be addressed. F.A.: phone, (604) 822−3817; fax, (604) 822-2847; e-mail, aubke@chem.ubc.ca. H.W.: phone, (49)203-379-3309; fax, (49)203-379-2231; e-mail, willner@uni-duisburg.de.

[†] Gerhard Mercator Universität-GH-Duisburg.

[‡] Universität Hannover.

[§] San Diego Super Computer Center.

[||] The University of British Columbia.

(1) Schützenberger, P. *Bull. Soc. Chim. Fr.* **1868**, *10*, 188.
(2) Schützenberger, P. *C. R. Hebd. Acad. Sci.* **1870**, *10*, 134.
(3) Mond, L.; Langer C.; Quincke, F. *J. Chem. Soc.* **1890**, *57*, 749.
(4) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; Wiley: New York, 1988; pp 58, 1021.
(5) Pruchnick, F. P. *Organometallic Chemistry of Transition Elements*; Plenum: New York, 1990.
(6) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 2nd ed.; Wiley: New York, 1994.
(7) Bagnoli, F.; Belli Dell'Amico, D.; Calderazzo, F.; Englert, U.; Marchetti, F.; Herberich, G. E.; Pasqualetti, N.; Ramello, S. *J. Chem. Soc, Dalton Trans.* **1996**, 4317.
(8) Ellis, J. E. *Adv. Organomet. Chem.* **1990**, *31*, 1.
(9) Browning, J.; Goggin, P.; Goodfellow, R. J.; Norton, M. J.; Rattray, A. J. M.; Taylor, B. F.; Mink, J. *J. Chem. Soc., Dalton Trans.* **1977**, 2061.
(10) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1986.
(11) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: New York, 1975.
(12) Adams, D. M. *Metal−Ligand and Related Vibrations*; Arnold: London, 1967.
(13) Haines, L. M.; Stiddard, M. H. B. *Adv. Inorg. Chem. Radiochem.* **1969**, *12*, 83.
(14) De La Cruz, C.; Sheppard, N. *J. Mol. Struct.* **1990**, *224*, 141.
(15) Moskovits, M.; Ozin, G. A. *Cryochemistry*; Wiley: New York, 1976; p 261.

10.1021/ic000280j CCC: $19.00

Pt and Pd. For *cis*-$Pt(CO)_2Cl_2$ predominantly σ-bonding with significantly reduced π-back-bonding is in harmony with the known spectroscopic[9,19] and structural[7] properties. The square planar geometry of *cis*-$Pt(CO)_2Cl_2$,[7] while uncommon in metal−carbonyl chemistry,[4−6,8] is observed in numerous coordination complexes of divalent platinum and palladium with a d^8 valence electron configuration.[4,20]

The difference in M−CO bonding between typical[4−6] or highly reduced[8] transition metal carbonyl complexes with significant contributions from π-back-bonding[16−18,21,22] on one hand and a small group of predominantly σ-bonded halocarbonyl complexes of Pt(II), Pd(II), Pd(I), and Au(I)[19,23−25] on the other hand is reflected in different chemical behavior.[19,23,24] Of relevance to our study are halogen exchange reactions of the type

$$cis\text{-}Pt(CO)_2Cl_2 + 2HX \rightarrow cis\text{-}Pt(CO)_2X_2 + 2HCl \qquad X = Br, I \quad (1)$$

For the resulting complexes as well as their *trans*-isomers,[19,23,24] the thermal stability of $Pt(CO)_2X_2$, X = Cl, Br, I, with respect to thermal decomposition to the dimers $Pt_2X_4(CO)_2$ increases in the order I < Br < Cl.[19,26] The inverse order of thermal stability is generally found for typical metal carbonyl halides.[4−6] The observed order of stability[19,23,24,26] suggests that $Pt(CO)_2F_2$ will show even higher thermal stability than the chloride; however, this compound has not been synthesized so far, and transition metal carbonyl fluorides of group 10 metals are rather uncommon.[27a,b]

The formal substitution of Cl^- by a more electronegative ligand, the SO_3F^- anion, is achieved by the reductive carbonylation of $Pt(SO_3F)_4$[28] in the Brønsted superacid HSO_3F,[29−32] where *cis*-$Pt(CO)_2(SO_3F)_2$ forms[33] via the mixed-valency intermediate $[Pt(CO)_4][Pt(SO_3F)_6]$.[34] In an analogous manner *cis*-$Pd(CO)_2(SO_3F)_2$ is obtained[33] by the reductive carbonylation of the mixed-valency compound $Pd[Pd(SO_3F)_6]$[35] in HSO_3F. While there is an early, erroneous report,[36] it is generally agreed[19,23−25,37−39] that *cis*-$Pd(CO)_2Cl_2$ is nonexisting. The molecular structure of *cis*-$Pd(CO)_2(SO_3F)_2$ has been reported in the meantime,[40] and the continued use of superacids[41,42] as reaction media in carbonylation reactions has resulted in the synthesis of a substantial number of homoleptic metal carbonyl cations and their derivatives[25,43] with metals from groups 6−12. Most of them have previously been thought to be incapable of existence.

Of particular relevance to this study are the synthesis[44] and the molecular structures[45] of salts of the composition $[M(CO)_4][Sb_2F_{11}]_2$, M = Pd, Pt, with square planar tetracarbonyl cations. The synthesis of these species involves the bis(carbonyl)fluorosulfates *cis*-$M(CO)_2(SO_3F)_2$, M = Pd, Pt, as precursors and liquid SbF_5 or the conjugate superacid HF−SbF_5 as the reaction medium.[44,45]

There are three objectives of this study: (i) We will probe the possible existence of *cis*-$Pt(CO)_2F_2$ by using *cis*-$Pt(CO)_2X_2$, X = Cl, SO_3F,[33,34] $[Pt(CO)_4][Sb_2F_{11}]_2$,[44] and PtF_6[46] as starting materials. As reaction media, both conventional solvents such as toluene and the Brønsted superacid HF[41,42,47] are employed. (ii) To complete the structural characterization of the three known *cis*-$M(CO)_2X_2$ complexes, with M = Pd or Pt and X = Cl or SO_3F, we report the molecular structure of *cis*-$Pt(CO)_2(SO_3F)_2$, which permits a comparison of internal bond parameters to those of *cis*-$Pt(CO)_2Cl_2$,[7] *cis*-$Pd(CO)_2(SO_3F)_2$,[40] and $[M(CO)_4]^{2+}$ M = Pd, Pt. (iii) We will present a complete vibrational characterization in the range of 4000−100 cm^{-1} of *cis*-$Pt(CO)_2Cl_2$ by IR spectroscopy of both the solid and the complex isolated in an argon matrix complimented by the Raman spectrum of solid *cis*-$Pt(CO)Cl_2$ between 3000 and 100 cm^{-1}. The vibrational assignments are supported by density functional calculations,[48] which provide, in addition to band positions, estimates of the intensities of IR and Raman bands, as reported recently.[48] For homoleptic metal carbonyl cations and their derivatives,[43] vibrational spectra provide in the CO-stretching range a more precise estimate of the bond strength of the CO bond than do molecular structures. An earlier vibrational study[9] is incomplete and reports largely data for benzene solutions of *cis*-$Pt(CO)_2Cl_2$, which makes a comparison to vibrational data for *cis*-$Pt(CO)_2Cl_2$ and *cis*-$M(CO)_2(SO_3F)_2$, M = Pd, Pt, obtained by us on solid samples, somewhat difficult.

Experimental Section

(a) Chemicals. The metal fluorides MF, M = Na, K, Cs, were obtained as anhydrous salts from commercial sources and stored inside a drybox. HgF_2 was synthesized by fluorination of $HgCl_2$, and AgF was formed from Ag_2CO_3 and 40% aqueous HF. AgF precipitated from the saturated AgF solution by adding acetone. The solid AgF was

---

(16) Dewar, J. S. *Bull. Soc. Chem. Fr.* **1951**, 671.

(17) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

(18) Chatt, J.; Wilkins, R. G. *J. Chem. Soc.* **1952**, 2622.

(19) Calderazzo, F. *J. Organomet. Chem.* **1990**, *400*, 303.

(20) Roundhill, M. *Comprehensive Coordination Chemistry*; Pergamon Press: Oxford, 1987; Vol. 5, p 351.

(21) Pearson, R. G. *Inorg. Chem.* **1984**, *23*, 4675.

(22) Parr, R. G.; Donelly, R. A.; Levy, M.; Palke, W. E. *J. Chem. Phys.* **1978**, *68*, 3801.

(23) Calderazzo, F. *Pure Appl. Chem.* **1978**, *50*, 49.

(24) Calderazzo, F.; Belli Dell'Amico, D. *Pure Appl. Chem.* **1986**, *58*, 561.

(25) Aubke, F.; Wang, C. *Coord. Chem. Rev.* **1994**, *137*, 483.

(26) Andreini, B. P.; Belli Dell'Amico, D.; Calderazzo, F.; Venturi, M. G.; Pelizzi, G.; Segre, A. *J. Organomet. Chem.* **1988**, *354*, 357.

(27) (a) Doherty, N. M.; Hoffman, N. W. *Chem. Rev.* **1991**, *91*, 553. (b) Murphy, E. F.; Murugavel, R.; Roesky, H. W. *Chem. Res.* **1997**, *97*, 3425.

(28) Lee, K. C.; Aubke, F. *Inorg. Chem.* **1984**, *23*, 2124.

(29) Gillespie, R. J. *Acc. Chem. Res.* **1968**, *1*, 202.

(30) Thompson, R. C. In *Inorganic Sulphur Chemistry*; Nickless, G., Ed.; Elsevier: Amsterdam, 1968; p 587.

(31) Jache, A. W. *Adv. Inorg. Radiochem.* **1974**, *16*, 177.

(32) Barr, J.; Gillespie, R. J.; Thompson, R. C. *Inorg. Chem.* **1964**, *3*, 1149.

(33) Hwang, G.; Wang, C.; Bodenbinder, M.; Willner, H.; Aubke, F. *J. Fluorine Chem.* **1994**, *66*, 159.

(34) Hwang, G.; Bodenbinder, M.; Willner, H.; Aubke, F. *Inorg. Chem.* **1993**, *32*, 4667.

(35) Lee K. C.; Aubke, F. *Can. J. Chem.* **1979**, *57*, 2058.

(36) Fink, E. *Compt. Rend.* **1898**, *126*, 646.

(37) Tripathi, S. C.; Srivastava, S. C.; Mani, R. P.; Shrimal, A. K. *Inorg Chim. Acta* **1976**, *17*, 257.

(38) Veergaftik, M. N.; Stromnova, T. A.; Moiseev, I. I. *Russ. J. Inorg. Chem.* **1980**, *25*, 127.

(39) Stromnova, T. A.; Moiseev, I. I. *Russ. Chem. Rev.* **1998**, *67*, 485.

(40) Wang, C.; Willner, H.; Bodenbinder, M.; Batchelor, R. J.; Einstein, F. W. B.; Aubke, F. *Inorg. Chem.* **1994**, *33*, 3521.

(41) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids*; Wiley: New York, 1985.

(42) O'Donnell, T. A. *Superacids and Acidic Melts as Inorganic Reaction Media*; VCH: Weinheim, Germany, 1993.

(43) Willner, H.; Aubke, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2402.

(44) Hwang, G.; Wang, C.; Aubke, F.; Willner, H.; Bodenbinder, M. *Can. J. Chem.* **1993**, *71*, 1532.

(45) Willmer, H.; Bodenbinder, M.; Bröchler, R.; Hwang, G.; Rettig, S. J.; Trotter, J.; v. Ahsen, B.; Jonas, V.; Thiel, W.; Aubke, F. *J. Am. Chem. Soc.*, submitted for publication.

(46) (a) Weinstock, B.; Classen, H. H.; Malm, J. G. *J. Am. Chem. Soc.* **1957**, *79*, 5832. (b) Weinstock, B.; Malm, J. G.; Weaver, E. E. *J. Am. Chem. Soc.* **1961**, *83*, 4310.

(47) Dove, M. F. A.; Clifford, A. F. In *Chemistry in Non-Aqueous Ionizing Solvents*; Jander, J., Spandau, H., Addison, C. C., Eds.; Vieweg: Wiesbaden, 1971; Vols. 1 and 2.

(48) Willner, H.; Bach, C.; Wartchow, R.; Wang, C.; Rettig, S. J.; Trotter, J.; Jonas, V.; Thiel, W.; Aubke, F. *Inorg. Chem.* **2000**, *39*, 1933.

Table 1. Crystallographic Data for *cis*-$Pt(CO)_2(SO_3F)_2$ in Comparison with *cis*-$Pd(CO)_2(SO_3F)_2$[40]

	cis-$Pt(CO)_2(SO_3F)_2$	*cis*-$Pd(CO)_2(SO_3F)_2$		*cis*-$Pt(CO)_2(SO_3F)_2$	*cis*-$Pd(CO)_2(SO_3F)_2$
empirical formula	$C_2O_8F_2S_2Pt$	$C_2O_8F_2S_2Pd$	ρ_{calcd} (g cm^{-3})	3.158	2.642
fw	449.23	360.53	cryst dimens (mm)	0.26 × 0.20 × 0.07	0.15 × 0.17 × 0.22
cryst syst	monoclinic	monoclinic	temp (K)	300	220
space group	$P2_1/n$ (no.14)	$P2_1/n$ (no.14)	λ(Mo Kα) (Å)	0.710 73	0.710 73
a (Å)	7.419(1)	7.3697(11)	μ (Mo Kα)	153.5	25.2
b (Å)	14.751(2)	14.7742(35)	min−max 2θ (deg)	5.4−56.4	4−54
c (Å)	8.634(1)	8.3237(21)	R	0.0447[a]	0.027[b]
β (deg)	89.95(1)	90.52(2)	wR2	0.1097	
V (Å^3)	944.9(2)	906.3(2)	R_{wF}		0.034[b]
Z	4	4			

[a] $F_0 > 4\sigma(F_0)$. [b] $I_0 \geq 2.5\sigma(I_0.)$

washed with dry acetone and dried in vacuo. Platinum powder (>99% pure) was donated to us by Degussa-Hüls AG, Germany. *cis*-$Pt(CO)_2Cl_2$ was obtained by the reductive carbonylation of $PtCl_4$, generated in situ from hexachloroplatinic acid, $H_2PtCl_6{\cdot}6H_2O$ (Chem Pur, Karlsruhe) in thionyl chloride as described previously.[26,49,50] *cis*-$Pt(CO)_2(SO_3F)_2$ was synthesized by the reductive carbonylation of $Pt(SO_3F)_4$[28] in HSO_3F as reported.[33] $Pt(SO_3F)_4$ was prepared by oxidation of platinum with $S_2O_6F_2$ in HSO_3F as solvent.[51] $[Pt(CO)_4][Sb_2F_{11}]_2$[44] and PtF_6[52,53] were prepared according to published methods. HSO_3F (Bayer AG, Leverkusen) and SbF_5 (Scientific Industrial Association, Moscow) were purified by repeated distillation. Toluene was dried over sodium metal by refluxing. Anhydrous hydrogen fluoride (99% Riedel de Haen) was handled in a stainless steel vacuum line and stored over small amounts of SbF_5 to remove traces of moisture. Carbon monoxide (99%, Linde) was dried by cooling to −196 °C during vacuum transfer.

(b) Instrumentation and Apparatus. (i) General Information. The equipment and reaction vessels for reactions in anhydrous HF or in liquid SbF_5 as well as instrumentation and methods to record IR and Raman spectra have been described very recently.[54]

(ii) Matrix Isolation of *cis*-$Pt(CO)_2Cl_2$. About 50 mg of freshly sublimed *cis*-$Pt(CO)_2Cl_2$ was introduced inside a drybox (M. Braun, Uni-Lab 1200/18) into a small U-shaped trap, which was then incorporated into the matrix isolation apparatus[55] in front of the matrix support (metal mirror). With the sample held at 21 °C and a flow rate of argon of about 3 mmol h^{-1} passed over the sample, a sufficient amount of *cis*-$Pt(CO)_2Cl_2$ could be sublimed and gave a satisfactory argon matrix at 12 K on the matrix support. To record an IR spectrum in the range from 5000 to 400 cm^{-1}, a matrix was prepared with 2 mmol of argon with an extinction maximum of 1.4 at 2171.1 cm^{-1}. A second matrix was prepared from 4 mmol of argon for recording the spectral region from 650 to 100 cm^{-1} with an extinction maximum of 0.44 at 468.3 cm^{-1}. Matrix IR spectra were recorded with a Bruker IFS 66v FT spectrometer operating in the reflectance mode with the help of a transfer optic. A DTGS detector together with a KBr/Ge beam splitter operated in the region of 5000−400 cm^{-1}. Far-IR spectra in the range of 650−100 cm^{-1} were recorded with a DTGS detector together with a Ge coated Mylar beam splitter. Thirty-two scans were co-added for each spectrum, using an apodized resolution of 1.0 cm^{-1}.

(iii) Crystal Growth and X-ray Diffraction of *cis*-$Pt(CO)_2(SO_3F)_2$. To produce a sufficiently large sample for all measurements, 1 g of platinum powder was first oxidized with $S_2O_6F_2$ in HSO_3F to give $Pt(SO_3F)_4$,[28] which was than converted to *cis*-$Pt(CO)_2(SO_3F)_2$ as described before.[33] During evaporation of excess HSO_3F in vacuo, the formation of small droplets was noted at the reactor wall. The droplets appeared to contain small crystals. The reactor was closed, without removing all HSO_3F. In an atmosphere saturated with gaseous HSO_3F, small crystals formed within a few days, which grew after a further week to platelike rectangular crystals with an edge length of about 1−3 mm. The crystals were isolated after removal of all HSO_3F and cleaved with a metal needle. The fragments were wedged into Lindemann glass capillaries of 0.2 mm o.d. Since two attempts indicated disorder and twinning, a small batch of the crystalline sample was recrystallized from about 2 mL of anhydrous HF. After 2 h of standing at 25 °C, all HF was removed in vacuo, to yield in addition to crystalline *cis*-$Pt(CO)_2(SO_3F)_2$ small amounts of a black impurity. Single crystals were selected with a polarizing microscope in a glovebox, and wedged into capillaries. Data were recorded at room temperature with a Stoe IPDS diffractometer using graphite-monochromatized Mo Kα radiation. Crystallographic data and details of the structure solution are summarized in Table 1 and compared to data for *cis*-$Pd(CO)_2(SO_3F)_2$.[40] The structure of *cis*-$Pt(CO)_2(SO_3F)_2$ was solved in $P2_1/n$ by direct methods (SHELXS-86)[56] and refined (SHELXL-93).[57] The programs MOPLO[58] and PLATON[59] were used for the plots and tables.

Results and Discussion

(a) Synthetic Aspects. For the synthesis of *cis*-$Pt(CO)_2Cl_2$ and *cis*-$Pt(CO)_2(SO_3F)_2$ a common general method is used, the reductive carbonylation of platinum(IV) chloride or fluorosulfate in nonaqueous solvents according to the general equation

$$PtX_4 + 3CO \xrightarrow[SOCl_2 \text{ or } HSO_3F]{40-80\ °C,\ 1\ atm} cis\text{-}Pt(CO)_2X_2 + COX_2 \qquad X = Cl, SO_3F \quad (2)$$

There are however considerable differences between both synthetic approaches. For the synthesis of *cis*-$Pt(CO)_2Cl_2$, there are in addition to the reductive carbonylation of $PtCl_4$[26,49,50] in thionyl chloride a number of alternative routes available[7,19,26] including the original method of Schützenberger.[1,2] The method chosen here, originally reported by Calderazzo et al.,[26,49] is very convenient and involves only commercially available reagents or solvents. Thionyl chloride is used both as a reagent in the synthesis of anhydrous $PtCl_4$ from $H_2PtCl_6{\cdot}6H_2O$[26,49] and as the reaction medium in the subsequent reductive carbonylation of $PtCl_4$.[26,49,50]

---

(49) Belli Dell'Amico, D.; Calderazzo, F.; Dell'Amico, G. *Gazz. Chim. Ital.* **1977**, *107*, 101.

(50) Belli Dell'Amico, D.; Calderazzo, F.; Veracini, C. A.; Zandona, N. *Inorg. Chem.* **1984**, *23*, 3030.

(51) (a) Cady, G. H.; Shreeve, J. M. *Inorg. Synth.* **1963**, *7*, 124. (b) Zhang, D.; Wang, C.; Mistry, F.; Powell, B.; Aubke, F. *J. Fluorine Chem.* **1996**, *76*, 83.

(52) (a) Weinstock, B.; Classen, M. H.; Malm, J. G. *J. Am. Chem. Soc.* **1957**, *79*, 5832. (b) Weinstock, B.; Malm, J. G.; Weaver, E. E. *J. Am. Chem. Soc.* **1961**, *83*, 4310.

(53) Ahsen, B. v.; Bach, C.; Pernice, H.; Willner, H.; Aubke, F. *J. Fluorine Chem.* **2000**, *102*, 243.

(54) Bernhardt, E.; Bley, B.; Wartchow, R.; Willner, H.; Bill, E.; Kuhn, P.; Sham, I. H. T.; Bodenbinder, M.; Bröchler, R.; Aubke, F. *J. Am. Chem. Soc.* **1999**, *121*, 7188.

(55) Arguello, G. A.; Grothe, H.; Kronberg, M.; Willner, H.; Mack, H.-G. *J. Phys. Chem.* **1995**, *99*, 17525.

(56) Sheldrick, G. M. SHELXS-86. Program for crystal structure determination, University of Göttingen, 1986.

(57) Sheldrick, G. M. SHELXL-93. Program for crystal structure refinement, University of Göttingen, 1993.

(58) Spek, A. L. PLATON, an integrated tool for the analysis of the results of a single crystal structure determination. *Acta Crystallogr.* **1990**, *A46* (*Suppl.*), C-34.

(59) Thiele, G. MOPLO, ein elektronischer Molekülbaukasten auf dem PC, VCH software, Verlag Chemie.

Conclusions regarding the formation of *cis*-$Pt(CO)_2Cl_2$ by the reductive carbonylation in $SOCl_2$ have been reported.[50] When the dimer $Pt_2(CO)_2(\mu\text{-}Cl)_2Cl_2$ is employed as starting material, the reaction produces at −80 °C only *trans*-$Pt(CO)_2Cl_2$:

$$Pt_2(CO)_2(\mu\text{-}Cl)_2Cl_2 + 2CO \xrightleftharpoons{-80\ ^\circ C} 2\ trans\text{-}Pt(CO)_2Cl_2 \quad (3)$$

At room temperature, *trans*-$Pt(CO)_2Cl_2$ will convert spontaneously to the *cis*-isomer, which appears to be thermodynamically the more stable isomer of the two.[50] In the case of *cis*-$Pt(CO)_2(SO_3F)_2$, there is no evidence for a *trans*-isomer and the corresponding μ-SO_3F dimer is so far unknown as well.

As eq 2 suggests, the synthesis of *cis*-$Pt(CO)_2(SO_3F)_2$[33] by reductive carbonylation of $Pt(SO_3F)_4$[28] in fluorosulfuric acid[29−31] appears to proceed in a manner similar to that of *cis*-$Pt(CO)_2Cl_2$. HSO_3F is used both in the synthesis of $Pt(SO_3F)_4$ from Pt powder and bis(fluorosulfuryl)peroxide, $S_2O_6F_2$,[51] and as the reaction medium for the subsequent reductive carbonylation, which no longer involves only commercially available reagents. Also the byproduct of the reduction, $CO(SO_3F)_2$, is thermally unstable at room temperature[60] and will decompose quantitatively to CO_2 and $S_2O_5F_2$. Both are separated easily from the main product because of their volatilities. There are to our knowledge no alternative routes to *cis*-$Pt(CO)_2(SO_3F)_2$, and our attempts at a conversion of *cis*-$Pt(CO)_2Cl_2$ into the fluorosulfate by dissolution in HSO_3F are unsuccessful and result in the formation of a brown-colored oily mass, with very little evolution of HCl.

A more substantial difference in the formation reactions (eq 2) of *cis*-$Pt(CO)_2Cl_2$ and *cis*-$Pt(CO)_2(SO_3F)_2$ is due to the reaction medium used, the aprotic solvent $SOCl_2$,[61] and the strongly ionizing Brønsted superacid HSO_3F.[29−32] In HSO_3F the starting material $Pt(SO_3F)_4$ will dissolve[28] to give rise to a diprotonic conjugate Brønsted−Lewis superacid,[41,42] with $[Pt(SO_3F)_6]^{2-}$ as a self-ionization ion.[28] Consequently, in the initial stages of the reductive carbonylation, an intermediate, formulated as the mixed-valency complex $[Pt(CO)_4][Pt(SO_3F)_6]$, is isolated and characterized by vibrational spectroscopy.[34] In the meantime both constituent ions are structurally characterized by us as $[Pt(CO)_4][Sb_2F_{11}]_2$[45] and $Cs_2[Pt(SO_3F)_6]$,[62] respectively. As the reductive carbonylation of $Pt(SO_3F)_4$ in HSO_3F progresses, the intermediate $[Pt(CO)_4][Pt(SO_3F)_6]$ redissolves and is quantitatively converted into *cis*-$Pt(CO)_2(SO_3F)_2$.[33] This suggests that the initial product of the reduction is the solvated cation $[Pt(CO)_4]^{2+}{}_{(solv)}$:

$$Pt(SO_3F)_{4(solv)} + 5CO_{(g)} \xrightarrow[HSO_3F]{40-80\ ^\circ C,\ 1\ atm\ of\ CO} [Pt(CO)_4]^{2+}{}_{(solv)} + CO_{2(g)} + S_2O_5F_{2(1)} + 2SO_3F^-{}_{(solv)} \quad (4)$$

In the initial phase of the reaction with unreacted $[Pt(SO_3F)_6]^{2-}$ still present, $[Pt(CO)_4][Pt(SO_3F)_6]$ forms as intermediate.[34] With increasing SO_3F^- concentration, after all the Pt(IV) species has been reduced and converted to $[Pt(CO)_4]^{2+}$, nucleophilic substitution by SO_3F^- occurs according to

$$[Pt(CO)_4]^{2+}{}_{(solv)} + 2SO_3F^-{}_{(solv)} \xrightarrow[HSO_3F]{80\ ^\circ C} cis\text{-}Pt(CO)_2(SO_3F)_{2(s)} + 2CO_{(g)} \quad (5)$$

These findings are supported by Raman and IR spectra in HSO_3F solution, ^{13}C NMR studies, and the solution behavior of $[Pt(CO)_4][Sb_2F_{11}]_2$[44] in fluorosulfuric acid. The exclusive formation of the *cis*-isomer during the substitution reaction reflects the greater *trans*-directing ability of CO in substitution reactions of square planar complexes.[63] A very similar course of the reductive carbonylation of $Au(SO_3F)_3$[64] in HSO_3F is reported where linear $[Au(CO)_2]^+{}_{(solv)}$ is initially formed and then converted into $Au(CO)SO_3F$.[65,66]

The synthesis of *cis*-$Pd(CO)_2(SO_3F)_2$ is best accomplished by the reductive carbonylation of the mixed-valency compound $Pd[Pd(SO_3F)_6]$[67] in a solid−gas reaction according to

$$Pd[Pd(SO_3F)_6]_{(s)} + 5CO_{(g)} \xrightarrow[1\ h]{25\ ^\circ C,\ 550\ Torr\ of\ CO} 2\ cis\text{-}Pd(CO)_2(SO_3F)_{2(s)} + CO_{2(g)} + S_2O_5F_{2(1)} \quad (6)$$

while in HSO_3F the reaction appears to be rather complex.[33,40]

The carbonylation of *cis*-$M(CO)_2(SO_3F)_2$, M = Pd, Pt, in liquid SbF_5 to give cleanly and quantitatively $[M(CO)_4][Sb_2F_{11}]_2$, M = Pd, Pt, is reported.[44] We have now found that *cis*-$Pt(CO)_2Cl_2$ can also be converted into $[Pt(CO)_4][Sb_2F_{11}]_2$ by carbonylation in SbF_5; however, the reaction is rather slow, and the byproduct, formulated as SbF_4Cl,[43] is more difficult to remove from the product mixture than is the rather volatile $Sb_2F_9(SO_3F)$[67] in the originally reported synthesis of $[M(CO)_4][Sb_2F_{11}]$, M = Pd, Pt.[44] Hence, the conversion of *cis*-$Pt(CO)_2Cl_2$ into $[Pt(CO)_4][Sb_2F_{11}]_2$ is not a useful synthetic route.

A rather elegant synthesis of $[Pt(CO)_4][Sb_2F_{11}]_2$, the reductive carbonylation of PtF_6[52] in SbF_5, has been reported by us very recently.[53] In anhydrous HF the reductive carbonylation of PtF_6 produces quantitatively $[Pt(CO)_4][PtF_6]$, the first example of a platinum carbonyl fluoride of the net composition $Pt(CO)_2F_3$.[53] However, all attempts to convert this compound into *cis*-$Pt(CO)_2F_2$ under more forcing conditions (higher temperatures and CO pressures) in analogy to the conversion of $[Pt(CO)_4][Pt(SO_3F)_6]$ into *cis*-$Pt(CO)_2(SO_3F)_2$[33,34] are unsuccessful. Equally unsuccessful are a number of additional attempts at the synthesis of *cis*-$Pt(CO)_2F_2$: The solvolysis of *cis*-$Pt(CO)_2Cl_2$ in HF does not take place, and the reagent is recovered unchanged. This approach with HX, X = Br, I, leads reportedly[19,26] to *cis*-$Pt(CO)_2X_2$, X = Br, I (see eq 1); however the high enthalpy of formation for HF[68a] makes solvolysis in anhydrous HF thermodynamically unfeasible. As discussed in the Experimental Section, *cis*-$Pt(CO)_2(SO_3F)_2$ can be recrystallized from anhydrous HF. Addition of NaF to the solution results in a complete loss of CO and a rather complex product mixture. Attempted methatetical reactions of *cis*-$Pt(CO)_2Cl_2$ with AgF or HgF_2 in toluene or HF give rise to redox reactions and the formation of

---

(60) (a) Belli Dell'Amico, D.; Calderazzo, F.; Veracini, C. A.; Zandona, N. *Inorg. Chem.* **1984**, *23*, 3030. (b) Lustig, M. *Inorg. Chem.* **1965**, *4*, 1828.

(61) Paul, R. C.; Singh, G. In *The Chemistry of non-Aqueous Solvents*; Lagowskii, J. J., Ed.; Academic Press: New York, 1978; Vol. V B, p 251.

(62) Zhang, D.; Rettig, S. J.; Trotter, J.; Aubke, F. *Inorg. Chem.* **1996**, *35*, 6113.

(63) Wilkins, R. G. *Kinetics and Mechanism. of Reactions of Transition metal Complexes*, 2nd ed.; VCH: Weinheim, 1991.

(64) (a) Lee, K. C.; Aubke, F. *Inorg. Chem.* **1979**, *18*, 389. (b) Lee, K. C.; Aubke, F. *Inorg. Chem.* **1980**, *19*, 119.

(65) Willner, H.; Aubke, F. *Inorg. Chem.* **1990**, *29*, 2195.

(66) Willner, H.; Schaebs, J.; Hwang, G.; Mistry, F.; Jones, R.; Trotter, J.; Aubke, F. *J. Am. Chem. Soc.* **1992**, *114*, 8972.

(67) Wilson, W. W.; Aubke, F. *J. Fluorine Chem.* **1979**, *13*, 431.

(68) (a) Johnson, D. A. *Some Thermodynamic Aspects of Inorganic Chemistry*; Cambridge University Press: Cambridge, U.K., 1968. (b) Clark, H. C. S.; Fawcett, J.; Holloway, J. A.; Hope, E. G.; Peck, L. A.; Russell, D. R. *J. Chem. Soc., Dalton Trans.* **1998**, 1249.

Ag or Hg, respectively. The nucleophilic substitution of $[Pt(CO)_4]^{2+}$ in HF does not occur: $[Pt(CO)_4][PtF_6]$ remains unchanged, and $[Pt(CO)_4][Sb_2F_{11}]_2$ can be recrystallized from HF.[45]

The lack of success in obtaining *cis*-$Pt(CO)F_2$ should not be surprising. As relevant reviews in ref 27a,b indicate, fluoro complexes of Pt(II) with better stabilizing ligands (phosphines or chelating phosphines) are thermally unstable. A case in point is a recent study by E. G. Hope et al.[68b] on $[(PR_3)_3PtF]^+$ and related complexes.

A rather unexpected product is observed when $[Pt(CO)_4][Sb_2F_{11}]_2$ is reacted with a solution of CsF in anhydrous HF. The evolution of gas is noted, and a black solid is formed. The gas phase contains a mixture of CO and COF_2. The IR spectrum shows in addition to bands due to $Cs[SbF_6]$[69] strong absorptions in the CO-stretching region at 2074, 1885, and 1830 cm^{-1}. The intense color and the observed band positions suggest the presence of an anionic platinum carbonyl cluster species[70] of the type $[Pt_3(CO)_6]_n{}^{2-}$ with $n \approx 10$. These cluster anions are obtained by the reductive carbonylation of $Na_2[PtCl_6]\cdot 6H_2O$ in aqueous alkaline solution or of *cis*-$Pt(CO)_2Cl_2$ in THF or methanol.[70] According to the molecular structures,[71] trinuclear $[Pt_3(CO)_3(\mu\text{-}CO)_3]$ moieties of point group D_{3h} are stacked into columns of the type $[Pt_3(CO)_3(\mu\text{-}CO)_3]_n{}^{2-}$ with $n = 1-6 \sim 10$. The formation of anionic clusters of this type in basic HF solution is rather unusual, and no clear explanation for the formation reaction can be offered at this time.

As discussed earlier for *cis*-$Pd(CO)_2(SO_3F)_2$,[40] the growth of single crystals is difficult and tedious as well for *cis*-$Pt(CO)_2(SO_3F)_2$ because of the high solubility of both salts in fluorosulfuric acid (see the Experimental Section). To obtain single crystals, suitable for a molecular structure determination, recrystallization from anhydrous HF is needed. The molecular structure of *cis*-$Pt(CO)_2(SO_3F)_2$ will be discussed in the next section.

In summary, even though *cis*-$Pt(CO)_2(SO_3F)_2$ has been known since 1994,[33] the exact pathway of its formation in HSO_3F has only recently become known and is reported here. Interestingly, *cis*-$M(CO)_2(SO_3F)_2$, M = Pd, Pt, is both a convenient starting material for the synthesis of $[M(CO)_4][Sb_2F_{11}]_2$ in liquid SbF_5 and a reaction product of the nucleophilic substitution of $[M(CO)_4]^{2+}$ by SO_3F^- in HSO_3F. The related platinum(II) carbonyl fluoride, *cis*-$Pt(CO)_2F_2$, remains unknown, and dinuclear $[Pt(CO)_4][PtF_6]$, reported by us very recently,[53] is so far the only stable, isolated metal carbonyl fluoride formed by a group 10 element. The material is characterized by vibrational methods.[53]

(b) Structural Aspects. Crystallographic data for *cis*-$Pt(CO)_2(SO_3F)_2$ are listed in Table 1 and are compared to the previously reported data for *cis*-$Pd(CO)_2(SO_3F)_2$.[40]

As can be seen, both compounds are isostructural and the lattice parameters are very similar. The unit cell volume of *cis*-$Pt(CO)_2(SO_3F)_2$ is about 4.1% larger than that of the palladium compound. This is due in part to the data collection for the Pt compound at higher temperature, but this larger volume is in contrast to observations for the isostructural pairs $[M(CO)_4][Sb_2F_{11}]_2$, M = Pd, Pt,[45] $[M(CO)_5Cl][Sb_2F_{11}]_2$, M = Rh, Ir,[48] $[M(CO)_6][Sb_2F_{11}]_2$, M = Ru, Os,[72] and $[M(CO)_6][SbF_6]_2$, M = Ru, Os,[72] where for the 5d complex very slightly smaller unit cell volumes (between 0.3% and 0.9%) are observed than for the corresponding 4d complex. It has been concluded that in addition to relativistic effects[73,74] stronger interionic secondary contacts[75] between the C atoms of the dipositive cations and F atoms of the fluoroantimonate anions are found for the Pt(II),[45] Ir(III),[48] and Os(II)[72] salts than are observed for the corresponding Pd(II),[45] Rh(III),[48] and Ru(II)[72] complexes in the four isostructural pairs, and that these stronger interionic contacts are largely responsible for the observed contractions in unit cell volumes of the 5d metal complexes.

In the neutral molecules *cis*-$Pt(CO)_2(SO_3F)_2$ and *cis*-$Pd(CO)_2(SO_3F)_2$,[40] weaker inter- and intramolecular secondary contacts (about four per CO group) are observed. These contacts involve terminal oxygen atoms of the fluorosulfate ligands and the carbon atoms of the CO ligands. Because the strengths of intermolecular contacts in *cis*-$Pt(CO)_2(SO_3F)_2$ are comparable with those in *cis*-$Pd(CO)_2(SO_3F)_2$, the higher cell volume of the platinum compound is understandable. Judging by the sums of the van der Waals radii,[76] there are no significant secondary contacts involving the metal atoms in the two isostructural pairs *cis*-$M(CO)_2(SO_3F)_2$[40] and $[M(CO)_4][Sb_2F_{11}]_2$, M = Pd, Pt.[45] This is surprising, since with square planar coordination geometries for the metals in both pairs, the central atom should be equally well accessible. It hence appears that a higher partial positive charge resides on the C atoms of the predominantly σ-bonded and strongly polarized CO ligands.[77]

As discussed in some detail for *cis*-$Pd(CO)_2(SO_3F)_2$[40] and illustrated by the packing of four molecules in the unit cell, as a consequence of the significant intermolecular OC- - -OS contacts, the molecular structure is expanded into a 3-dimensional, supramolecular network.[40] A similar packing arrangement is found for the *cis*-$Pt(CO)_2(SO_3F)_2$ molecule, but this will not be discussed here, to avoid repetition.

A slightly different packing arrangement is reported for *cis*-$Pt(CO)_2Cl_2$,[7] which crystallizes in the same monoclinic space group as *cis*-$M(CO)_2(SO_3F)_2$, M = Pd, Pt. Here the essentially square planar molecules are stacked along the *c*-axis parallel to each other but are rotated in such a manner as to allow secondary C- - -Cl contacts between adjacent molecules. As a consequence of the stacking, rather short Pt- - -Pt contacts of 3.378(1) Å[7] form. A similar packing arrangement due to C- - -Cl contacts is present in linear Au(CO)Cl in the solid state.[78] It appears the more complicated, 3-dimensional packing arrangement observed for *cis*-$M(CO)_2(SO_3F)_2$, M = Pd,[40] Pt, is a consequence of the molecular nature of the $-OSO_2F$ ligand, where more significant and varied secondary intermolecular contacts[40] are possible than is the case for the chloro ligand in *cis*-$Pt(CO)_2Cl_2$.[7]

The noted similarity in the packing of molecules within the unit cells (see Figure 2 in ref 40) for *cis*-$Pt(CO)_2(SO_3F)_2$ and *cis*-$Pd(CO)_2(SO_3F)_2$ extends also to the molecular structure which is shown for *cis*-$Pt(CO)_2(SO_3F)_2$ in Figure 1. Selected interatomic distances, bond angles for the immediate coordination environment of M(II), and torsion angles for both molecules are listed in Table 2. The two fluorosulfate groups both fall below the molecular plane formed by the $M(CO)_2O_2$ moiety, M = Pd, Pt. A similar pairwise arrangement of fluorosulfate

---

(69) Weidlein, J.; Müller, U.; Dehnicke, K. *Schwingungsfrequenzen*; Thieme Verlag: Stuttgart, 1981.

(70) Longoni, G.; Chini, P. *J. Am. Chem. Soc.* **1976**, *98*, 7225.

(71) Calabrese, J. C.; Dahl, L. F.; Chini, P.; Longoni, G.; Martinengo, S. *J. Am. Chem. Soc.* **1974**, *96*, 2614.

(72) Bernhardt, E.; Bach, C.; Wartchow, R.; Willner, H.; Aubke, F. *Inorg. Chem.*, to be submitted for publication.

(73) Pyykkö, P.; Desclaux, J. P. *Acc. Chem. Res.* **1979**, *12*, 276.

(74) Pyykkö, P. *Chem. Rev.* **1988**, *88*, 563.

(75) Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 1.

(76) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(77) Goldman, A. S.; Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1996**, *118*, 12159.

(78) Jones, P. G. *Z. Naturforsch.* **1982**, *37 B*, 823.

Table 2. Selected Internal Bond Parameters for *cis*-$M(CO)_2(SO_3F)_2$, M = Pd, Pt

	cis-$Pt(CO)_2(SO_3F)_2$	*cis*-$Pd(CO)_2(SO_3F)_2$[40]		*cis*-$Pt(CO)_2(SO_3F)_2$	*cis*-$Pd(CO)_2(SO_3F)_2$[40]
		(a) Bond Lengths (Å)			
M−C(1)	1.868(13)	1.919(5)	S(1)−F(1)	1.535(8)	1.557(3)
M−C(2)	1.897(13)	1.945(5)	S(2)−O(21)	1.474(8)	1.480(3)
M−O(11)	2.024(9)	2.016(3)	S(2)−O(22)	1.426(11)	1.402(4)
M−O(21)	2.022(9)	2.006(3)	S(2)−O(23)	1.346(18)	1.394(4)
S(1)−O(11)	1.482(12)	1.479(3)	S(2)−F(2)	1.565(15)	1.565(4)
S(1)−O(12)	1.399(10)	1.422(4)	C(1)−O(1)	1.130(17)	1.114(6)
S(1)−O(13)	1.401(10)	1.413(4)	C(2)−O(2)	1.103(16)	1.102(6)
		(b) Bond Angles (deg)			
O(11)−M−O(21)	84.5(4)	86.0(1)	C(2)−M−C(1)	91.5(5)	91.8(2)
O(11)−M−C(2)	92.7(5)	91.7(2)	M−C(2)−O(2)	178.3(11)	178.9(4)
O(11)−M−C(1)	175.3(5)	176.2(2)	M−C(1)−O(1)	176.6(12)	177.5(4)
O(21)−M−C(2)	176.1(5)	176.3(2)	M−O(11)−S(1)	125.1(6)	123.5(2)
O(21)−M−C(1)	91.1(5)	90.4(2)	M−O(21)−S(2)	124.7(6)	124.7(2)
		(c) Torsion Angles (deg)			
O(21)−M−O(11)−S(1)	−122.8(7)	−122.0(2)	F(1)−S(1)−O(11)−M	72.3(7)	73.8(2)
O(11)−M−O(21)−S(2)	105.3(7)	106.5(2)	F(2)−S(2)−O(21)−M	81.1(8)	83.0(2)

Table 3. Selected Structural and Vibrational Data for Cationic Palladium(II) and Platinum(II) Carbonyl Complexes

compound	d_{av}(M−C) (Å)	d_{av}(C−O) (Å)	$\bar{\nu}_{av}$(CO) (cm^{-1})	$f_{CO} \times 10^{2\,d}$ (N m^{-1})	ref[a]
$[Pd(CO)_4][Sb_2F_{11}]_2$	1.992(2)	1.106(6)	2259	20.63	45, 44
$[Pt(CO)_4][Sb_2F_{11}]_2$	1.982(9)	1.110(9)	2261	20.64	45, 44
cis-$Pd(CO)_2(SO_3F)_2$	1.932(5)	1.108(6)	2217.5	19.87	40, 33
cis-$Pt(CO)_2(SO_3F)_2$	1.882(3)	1.116(6)	2202	19.56	*b*, 34
cis-$Pt(CO)_2Cl_2$	1.897(5)	1.115(6)	2171[e]	18.67	7, *b*
trans-$Pt_2(CO)_2I_2(\mu\text{-}I)_2$	1.88(3)	1.06(4)	2106[c]	17.93	26, 26

[a] The first reference listed refers to structural data; the second reference refers to vibrational data. [b] This work. [c] Solution in *n*-heptane. [d] Approximation according to Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* **1962**, *84*, 4432. [e] IR data of solid *cis*-$Pt(CO)_2Cl_2$ at room temperature (see Table 4).

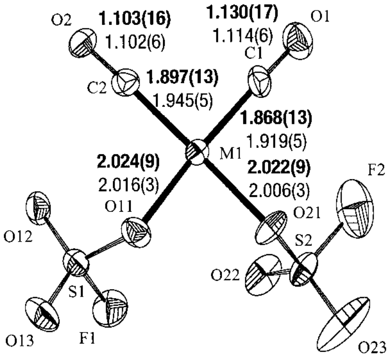

Figure 1. Molecular structures of *cis*-$M(CO)_2(SO_3F)_2$, M = Pd, Pt, with 50% probability thermal ellipsoids shown. Bond distances for *cis*-$Pt(CO)_2(SO_3F)_2$ are in bold.

ligands is found in the square planar structures of $[Au(SO_3F)_4]^-$ [62] and for the terminal fluorosulfate groups in dimeric $[Au(SO_3F)_3]_2$.[79]

Both $M(CO)_2(SO_3F)_2$, M = Pd, Pt, molecules have no crystallographic symmetry. This is in particular apparent from the two torsion angles F(1)−S(1)−O(11)−M and F(2)−S(2)−O(21)−M, M = Pd,[40] Pt, listed in Table 2, which have comparable but different magnitudes in both molecules (see Table 2). Mirror symmetry would require an opposite sense of rotation for both sets of angles. This is again similar to findings for $[Au(SO_3F)_4]^-$ [62] and $[Au(SO_3F)_3]_2$.[79] There is also in all instances[40,62,79] a small displacement of the metal out of the principal molecular plane.

The distances of chemically equivalent bonds are generally not significantly different in both $M(CO)_2(SO_3F)_2$, M = Pd,[40] Pt, molecules with the exception of terminal S−O and M−C bonds. The variation in bond lengths is attributed to the participation of O(S) and C(O) atoms in intermolecular and intramolecular, secondary interactions of variable strength.[40] Likewise the observed slight deviation from linearity for the M−C−O groups with bond angles between 176.6(12)° and178.9(4)° is attributed to the involvement of carbon in inter- and intramolecular contacts. These deviations from linearity for the M−C−O groups are observed for all other structurally characterized metal carbonyl cations,[45,48,59,72,80−82] with fluoroantimonate(V) anions, where in all instances significant interionic C- - -F contacts are found.

When interatomic distances for *cis*-$Pt(CO)_2(SO_3F)_2$ and its palladium(II) analogue are compared, it is noted that the Pt−C distances are significantly shorter than the corresponding Pd−C bond lengths, while M−O and C−O distances show small differences, usually within error limits.

To allow a broader comparison, we have summarized in Table 3 average M−C and C−O distances for all six structurally characterized cationic or neutral Pt(II) and Pd(II) derivatives, including so far unpublished structural data for $[M(CO)_4][Sb_2F_{11}]_2$, M = Pd, Pt.[45] As can be seen in Table 3 there are generally significant differences in metal−carbon distances, while *d*(C−O) values vary little. It is commonly observed that, for cationic carbonyl compounds,[19,25,43] the C−O distances are at the shorter end of bond lengths listed in the Cambridge data index[83] with a mean distance of 1.143 Å and a lower quartile value of 1.132 Å based on 10 022 examples. However, C−O

---

(79) Willner, H.; Rettig, S. J.; Trotter, J.; Aubke, F. *Can. J. Chem.* **1991**, *69*, 391.

(80) Bodenbinder, M.; Balzer-Jöllenbeck, G.; Willner, H.; Batchelor, R. J.; Einstein, F. W. B.; Wang, C.; Aubke, F. *Inorg. Chem.* **1996**, *35*, 82.

(81) Bröchler, R.; Freidank, D.; Bodenbinder, M.; Sham, I. H. T.; Willner, H.; Rettig, S. J.; Trotter, J.; Aubke, F. *Inorg. Chem.* **1999**, *38*, 3684.

(82) Bröchler, R.; Sham, I. H. T.; Bodenbinder, M.; Schmitz, V.; Rettig, S. J.; Trotter, J.; Aubke, F. *Inorg. Chem.* **2000**, *39*, 2172.

(83) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, Suppl., 1.

bond distances are apparently insensitive to small changes in the high CO bond order in metal carbonyl cations and their derivatives.[43,44] Therefore, average CO-stretching wavenumbers $\bar{\nu}_{av}$(CO) and CO-stretching force constants, f_{CO}, are included in Table 3. They provide a more accurate and sensitive estimation of the strength of the CO bond.

As can be seen in Table 3, structural and vibrational data for the isostructural pair $[M(CO)_4][Sb_2F_{11}]_2$, M = Pd, Pt,[44,45] are essentially identical within esd values. Due to relativistic effects,[73,74] the effective radii of Pt(II) and Pd(II) appear to be the same in both cations. The metal−carbon distances are the longest so far observed in metal carbonyls of Pd(II) and Pt(II) and for the latter well in excess of q_u, the upper quartile values of 29 data sets in the Cambridge data compilation.[83] The observed ν_{av}(CO) and f_{CO} values of about 2260 cm^{-1} and 20.6 × 10^2 N m are the highest for square planar metal carbonyl derivatives.[44] They are surpassed only by data for linear $[Hg(CO)_2]^{2+}$ [80] (2280 cm^{-1} and 21.0 × 10^2 N m^{-1}) or tripositive, octahedral $[Ir(CO)_6]^{3+}$ [53,84] (2268 cm^{-1} and 20.8 × 10^2 N m^{-1}). The three sets of data from $[Sb_2F_{11}]^-$ salts in all instances represent the closest approach for "σ-only" M−CO bonding for linear,[80] square planar,[44,45] and octahedral[53,84] geometries.

The substitution of two *trans*-CO ligands of the $[M(CO)_4]^{2+}$ cations, M = Pd, Pt, by anions (SO_3F^- or Cl^-) to produce the neutral molecules *cis*-$Pt(CO)_2Cl_2$ and *cis*-$M(CO)_2(SO_3F)_2$, M = Pd, Pt, is expected to reduce the Lewis acidity of the metal center. As can be seen from the data in Table 3, the M−CO bonds to the remaining carbonyl ligands, *trans* to the anionic ligands, shorten, while $\bar{\nu}_{av}$(CO) and f_{CO} decrease, suggestive of a reduction in C−O bond strength. For the two fluorosulfate derivatives, the decrease in d_{av}(M−C), $\bar{\nu}_{av}$(CO), and f_{CO} is larger for *cis*-$Pt(CO)_2(SO_3F)_2$ than for its Pd analogue, with ν_{av}(CO) 15 cm^{-1} higher in *cis*-$Pd(CO)_2(SO_3F)_2$. This is not uncommon, because in palladium(II) and platinum(II) halo carbonyls of comparable composition and identical structures, $\bar{\nu}_{av}$(CO) is usually about 30 cm^{-1} higher in the palladium compound.[19,26,85−87] In two structurally characterized $[n\text{-}Bu_4N][MCl_3(CO)]$ salts with M = Pd[85] or Pt,[88] d(Pd−C) and d(Pt−C) are 1.87(1) and 1.82(1) Å, respectively, while the $\bar{\nu}$(CO) values are 2132 and 2098 cm^{-1}. It appears that Pt(II) is both a better π-acceptor toward the anionic ligand and a better π-donor toward CO than is Pd(II), resulting in a higher π-contribution for the Pt−CO bonds, *trans* to the anion and a slight reduction in C−O bond strength.

In summary, the previously observed[9,19,26,85−87] differences in metal−carbon distances and/or $\bar{\nu}$(CO) for identical palladium and platinum carbonyl compounds are clearly induced by the anionic ligands. They are not observed for the homoleptic cation $[M(CO)_4]^{2+}$,[45] M = Pd, Pt (see Table 3), and are hence not due to intrinsic differences between the Pt−C and Pd−C bonds.

When *cis*-$Pt(CO)_2(SO_3F)_2$ is compared to *cis*-$Pt(CO)_2Cl_2$, ν_{av}(CO) is lowered even further by 22 cm^{-1}, for the latter, which reflects differences in the electronegativity of the anionic ligands SO_3F^- and Cl^-. Even lower $\bar{\nu}_{av}$(CO) values reported for *cis*-$Pt(CO)_2Br_2$[9,19] and *cis*-$Pt(CO)_2I_2$[19] are consistent with this conclusion; however, the Pt−CO bonds in *cis*-$Pt(CO)_2Cl_2$[7] with an average distance of 1.897(3) Å are longer than in *cis*-$Pt(CO)_2(SO_3F)_2$ (1.882(3) Å) and well above the q_u value of 1.878 Å in the Cambridge data compilation.[83] These facts are contradictory; while the vibrational criteria ($\bar{\nu}_{av}$(CO) and f_{CO}) suggest increased π-back-bonding for *cis*-$Pt(CO)_2Cl_2$ relative to *cis*-$Pt(CO)_2(SO_3F)_2$, the opposite conclusion may be drawn from the structural features d(Pt−CO) in both compounds. The correspondence between long M−C bonds and high CO values in Table 3 commonly observed for homoleptic metal carbonyl cations,[43] in accordance with theoretical studies,[89,90] does not apply to the *cis*-$Pt(CO)_2Cl_2$−*cis*-$Pt(CO)_2(SO_3F)_2$ pair.

A similar situation has been found recently for the *trans*-(O−C)−Ir(III)−X, X = Cl, SO_3F, segments in the molecular structures of $[Ir(CO)_5Cl][Sb_2F_{11}]_2$[48,84] and *mer*-$Ir(CO)_3(SO_3F)_3$,[91] where Cl^- appears to weaken while SO_3F^- strengthens the Ir(III)−CO bonds *trans* to the anionic ligands relative to the remaining $Ir(CO)_n$, n = 4, 2, bonds in the molecules *cis* to Cl^- or SO_3F^-. Due to vibrational mixing of the CO-stretching vibrations in both molecules,[48,84,91] ν_{av}(CO) and f_{CO} for the *trans*-CO groups are not obtainable. For the approximately linear molecules Au(CO)Cl ($\bar{\nu}$(CO) = 2183 cm^{-1})[9] and $Au(CO)SO_3F$ ($\bar{\nu}$(CO) = 2198 cm^{-1}),[65] only the molecular structure of Au(CO)Cl[78] is known, which precludes a comparison.

From the examples cited above, it appears the Cl^- and SO_3F^- affect the *trans*-CO ligand differently. The more electronegative SO_3F^- group reduces the Lewis acidity of the metal center to a lesser degree than the chloro ligands, which is reflected in higher $\bar{\nu}$(CO) values for the fluorosulfates. On the other hand, the $-OSO_2F$ ligand appears to increase π-contributions to the M−C, M = Pt, Ir,[48,84] bond more effectively than the Cl^- ligand, which results in shorter M−C bonds for the former.

(c) Vibrational Analysis of *cis*-$Pt(CO)_2Cl_2$. For the square planar, seven-atom molecule of point group C_{2v}, the irreducible representations of the fundamental vibrations are

$$\Gamma_{vib} = 6A_1\ (\text{IR, Ra p}) + 2A_2\ (\text{Ra dp}) + 2B_1\ (\text{IR, Ra dp}) + 5B_2\ (\text{IR, Ra dp})$$

Hence, there are 15 Raman-active and 13 IR-active fundamentals expected. A complete vibrational analysis of *cis*-$Pt(CO)_2Cl_2$ is of interest for the following reasons: (i) An earlier vibrational analysis[9] is incomplete, and a number of assignments are ambiguous. A Raman spectrum over the entire range is reported,[9] but only 9 of the 15 expected, Raman-active modes are detected. (ii) The previously reported vibrational modes in the CO-stretching region show a dependence on the solvents used[9,26] (benzene, toluene, n-heptane, $C_2H_2Cl_4$) with ν(CO) at higher wavenumbers in the solid state. (iii) There is to our knowledge no vibrational analysis for a square planar, seven-atom molecule. We have recently[92] reported a vibrational analysis of a related species, square planar, cyclic $[Pd_2(\mu\text{-}CO)_2]^{2+}$ of point group D_{2h}. (iv) Of three *cis*-$Pt(CO)_2$ derivatives discussed in this study, only *cis*-$Pt(CO)_2Cl_2$ is sufficiently volatile at room temperature, to allow a matrix isolation−IR study. Band proliferation due to factor group splitting, which may result in misinterpretations, can now be avoided.

In addition to matrix isolation, vibrational assignments are assisted by density functional theoretical calculations. Details

---

(84) Bach, C.; Willner, H.; Wang, C.; Rettig, S. J.; Trotter, J.; Aubke, F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1974.

(85) Andreini, B. P.; Belli Dell'Amico, D.; Calderazzo, F.; Venturi, M. G.; Pelizzi, G. *J. Organomet. Chem.* **1988**, *354*, 369.

(86) Calderazzo, F.; Belli Dell'Amico, D. *Inorg. Chem.* **1981**, *20*, 1310.

(87) Belli Dell'Amico, D.; Calderazzo, F.; Zandona, N. *Inorg. Chem.* **1984**, *23*, 137.

(88) Russel, D. R.; Tucker, P. A.; Wilson, G. *J. Organomet. Chem.* **1976**, *104*, 387.

(89) Sherwood, D. E.; Hall, M. B. *Inorg. Chem.* **1983**, *22*, 93.

(90) Lupinetti, A. J.; Jonas, V.; Thiel, W.; Strauss, S. H.; Frenking, G. *Eur. J. Chem.* **1999**, *5*, 2573.

(91) Wang, C.; Lewis, A. R.; Batchelor, R. J.; Einstein, F. W. B.; Willner, H.; Aubke, F. *Inorg. Chem.* **1996**, *35*, 1279.

(92) Wang, C.; Bodenbinder, M.; Willner, H.; Rettig, S. J.; Trotter, J.; Aubke, F. *Inorg. Chem.* **1994**, *33*, 779.

Table 4. Experimental and Calculated Vibrational Data (cm^{-1}) (Intensities) for *cis*-$Pt(CO)_2Cl_2$ and Assignment and Description of Vibrational Modes

experimental			calculated[a]				assignment according to C_{2v} symmetry		approx description of modes[e]
$IR_{(Ar\ matrix)}$[b]	$IR_{(solid)}$[c]	$Ra_{(solid)}$	ν	$I_{(IR)}$	$I_{(Ra)}$	$\Delta\nu$[d]			
4331.1 (0.9)	4362 (w)						$2\nu_1$	$2A_1$	
4273.1 (0.3)	4311 (w)						$\nu_1 + \nu_{11}$	$A_1 + B_2$	
4239.1 (0.2)	4285 (vw)						$2\nu_{11}$	$2B_2$	
2638.3 (0.5)	2725 (vw)						$\nu_1 + \nu_{12}$	$A_1 + B_2$	
2606.9 (0.8)	2639 (vw)						$\nu_1 + \nu_{13}$	$A_1 + B_2$	
2594.8 (0.4)							$\nu_{11} + \nu_{12}$	$B_2 + B_2$	
	2609 (w)								
2587.3 (0.2)							$\nu_{11} + \nu_7$	$B_2 + A_2$	
2563.8 (0.8)	2577 (vw)						$\nu_{11} + \nu_{13}$	$B_2 + B_2$	
2171.1 (95)	2190 (vs)	2189 (100)	2125	(77)	(100)[f]	−46	ν_1	A_1	$\nu_s(CO)$
2154.3 (3.7)	2175 (sh)	2174	2111				ν_1'	A'	$\nu_s(^{13}CO)$[g]
2126.9 (100)	2152 (vs)	2146 (75)	2082	(100)[h]	(72)	−45	ν_{11}	B_2	$\nu_{as}(CO)$
2088.8 (4.6)	2113 (m)	2114	2046				ν_{11}'	A'	$\nu_{as}(^{13}CO)$[g]
546.9 (16)	537 (s)	541 (0.2)	524	(6.9)	(0.8)	−23	ν_2	A_1	$\delta(PtCO)$
		457 (41)	483	(0.0)	(7.4)	+26	ν_3	A_1	$\nu_s(PtC)$
483.9 (8.3)			478	(3.0)	(0.2)	−6	ν_9	B_1	$\omega(OCPtCO)$
	458 (vs)								
468.3 (12)		434 (0.9)	441	(3.9)	(0.1)	−27	ν_{12}	B_2	$\rho(PtCO)$
			441	(0.0)	(0.2)		ν_7	A_2	$\tau(OCPtCO)$
436.0 (2.8)	424 (w)		461	(0.8)	(2.2)	+25	ν_{13}	B_2	$\nu_{as}(PtC)$
386.6[i] (5.3)	369 (s)	370 (98)	356	(2.0)	(7.3)	−31	ν_4	A_1	$\nu_s(PtCl)$
362.6[i] (9.3)	350 (s)	346 (21)	331	(4.9)	(2.4)	−32	ν_{14}	B_2	$\nu_{as}(PtCl)$
	157 (w)	160 (115)	141	(0.0)	(1.4)	−19	ν_5	A_1	$\delta(ClPtCl)$
116.5 (0.6)	109 (m)		96	(0.2)	(0.0)	−21	ν_{10}	B_1	$\omega(ClPtCl)$
		117 (169)	93	(0.1)	(2.5)	−24	ν_6	A_1	$\delta(CPtC)$
			92	(0.0)	(0.0)		ν_{15}	B_2	ρ (ClPtCl)
			73	(0.0)	(0.0)		ν_8	A_2	$\tau(ClPtCl)$

[a] BP86/ECP2. [b] Bond position of the most intense matrix site. [c] s = strong; m = medium; w = weak; sh = shoulder; v = very. [d] Difference between calculated and IR (matrix) or Raman (solid) wavenumbers. [e] ν = stretching; s = symmetric; as = asymmetric; δ = deformation; ρ = rocking; τ = twisting; ω = wagging. [f] Absolute intensity 184.0 Å^4 amu^{-1}. [g] *cis*-$Pt(^{12}CO)(^{13}CO)Cl_2$. [h] Absolute intensity 605.9 km mol^{-1}. [i] Chlorine isotopic pattern strongly disturbed by matrix splitting.

on the method used and the background to the theoretical approach have been published recently.[48,93] It is, as seen in Table 4, now possible to calculate vibrational wavenumbers, as well as IR and Raman intensities.

The observed IR bands and Raman lines of solid *cis*-$Pt(CO)_2Cl_2$ in the range of 5000−100 cm^{-1} are listed in Table 4 together with their estimated (IR) or measured (Raman) relative intensities. They are compared to the infrared band positions of the most intense matrix sites of *cis*-$Pt(CO)_2Cl_2$ in solid argon at 12 K and their measured intensities. The experimental vibrational wavenumbers and intensities are compared to calculated wavenumbers and IR as well as Raman intensities of gaseous *cis*-$Pt(CO)_2Cl_2$. The differences between the calculated and experimental matrix IR or Raman wavenumbers, $\Delta\nu$, are listed as well. A vibrational assignment based on C_{2v} symmetry of the molecule and an approximate description of the fundamental modes complete the listings in Table 4.

As can be seen in Table 4, 12 of the 15 fundamentals of *cis*-$Pt(CO)_2Cl_2$ are detected experimentally. Of the three remaining fundamentals, ν_7 (A_2) and ν_8 (A_2) are both only Raman active, while ν_{15} (B_2) has a very low calculated intensity, with the last two bands expected below 100 cm^{-1}, outside the experimental range.

As expected for *cis*-$Pt(CO)_2Cl_2$ with C_{2v} symmetry, IR bands and Raman lines of solid samples at room temperature show very good correspondence. There are interesting differences between the observed IR and Raman wavenumbers of the solid and those of matrix-isolated molecules. It is not surprising that $PtCl_2$ stretching modes, identified by the $^{35}Cl/^{37}Cl$ isotope splitting, and the $PtCl_2$ deformation modes are shifted to higher wavenumbers by about 12−18 cm^{-1} in the matrix IR spectrum. According to the reported molecular structure,[7] there are significant Cl- - -C secondary contacts, resulting in an extended, supramolecular structure.[7] These contacts are not possible in an argon matrix, and the platinum−chlorine bonds, which are reported to be very strong, with distances of 2.2863(13) and 2.2972(13) Å[7] relative to the q_l value of 2.297 Å for 293 cases of platinum bonds to terminal chlorine,[83] become even stronger in the isolated molecule because of increased Cl−Pt π-bonding contributions. Increased π-back-bonding to the C−O ligands is also apparent from shifts to higher wavenumbers for ν(Pt−C) as well as the Pt−C−O deformation modes, with shifts of about 10 cm^{-1}. More notable however are shifts of the CO-stretching modes to lower wavenumbers, where in the matrix spectrum ν_s is found at 2171 cm^{-1} and ν_{as} at ~2127 cm^{-1} compared to 2190 and 2152 cm^{-1} in solid *cis*-$Pt(CO)_2Cl_2$. The observed ν(CO) values in the matrix IR spectrum are now very comparable to solution IR data in various aprotic, weakly coordinating solvents,[9,19,26] where any intermolecular association via C- - -Cl contacts should be reduced or even prevented.

The shifts observed for matrix-isolated *cis*-$Pt(CO)_2Cl_2$ are also detected in the overtones and combination bands observed in the infrared spectra listed in Table 4, and the value of providing a complete assignment and vibrational analysis for *cis*-$Pt(CO)_2Cl_2$ now becomes apparent in the detection of small changes in π-bonding within the molecule.

Agreement between calculated and experimental vibrational wavenumbers is only fair. As is commonly observed,[45,48,54,93] calculated CO-stretching wavenumbers for gaseous molecules and ions are in general lower than experimental values. In our case they are even lower by about 45 cm^{-1} than the matrix IR wavenumbers. However, interestingly the ν(Pt−C) values for

---

(93) Jonas, V.; Thiel, W. *J. Chem. Phys.* **1995**, *102*, 8474.

calculated $Pt(CO)_2Cl_2$ are shifted to higher values relative to Raman and matrix IR data by about 25 cm^{-1}. This suggests increased π-back-bonding in the calculated molecule relative to the matrix-isolated species. There are also some discrepancies between calculated and observed intensities of Raman lines. However, the calculated wavenumbers are very useful in arriving at a sound vibrational assignment and at locating unobserved or unobservable fundamentals as discussed above and elsewhere.[48,54]

We have in the past[43] viewed secondary interionic or intermolecular interactions as a means to form extended or supermolecular structures, which provide greater stability toward loss of CO. It seems now that these significant contacts, at least the intermolecular and interionic ones, will strengthen the C−O bonds in solid compounds and may in part be responsible for the high ν(CO) values for *cis*-$M(CO)_2(SO_3F)_2$, M = Pd, Pt,[33] $Au(CO)SO_3F$,[65,66] and $Ir(CO)_3(SO_3F)_3$.[91] Matrix isolation studies on any of these molecules would be interesting but certainly more difficult than in the case of *cis*-$Pt(CO)_2Cl_2$ as described in this study.

It seems improbable to attribute the observed two ν(CO) wavenumbers in matrix-isolated *cis*-$Pt(CO)_2Cl_2$ to temperature shifts, because ν(CO) of the gas-phase CO molecule[10] is reduced in an argon matrix by only 5 cm^{-1} to 2138 cm^{-1}.[94] In addition it would be impossible to attribute the observed positive shifts for Pt−Cl and Pt−C vibrations to temperature effects. The proposed redistribution of π-electron density in *cis*-$Pt(CO)_2Cl_2$ is a more logical choice, consistent with earlier observations.[9,19,26]

Summary and Conclusions

The molecular structure determination of *cis*-$Pt(CO)_2(SO_3F)_2$ reported here completes structural studies of square planar palladium and platinum derivatives synthesized by us. They include $[M(CO)_4][Sb_2F_{11}]_2$[44,45] and *cis*-$M(CO)_2(SO_3F)_2$, M = Pd, Pt,[33,40] and c-$[Pd_2(\mu\text{-}CO)_2](SO_3F)_2$.[90] In all instances extended molecular structures are encountered. Of the so far reported metal carbonyl fluorosulfates,[33,65,89,90] all but $Au(CO)SO_3F$[65] are now structurally characterized. In group 10, the recently reported structure of the longest known metal carbonyl derivative, *cis*-$Pt(CO)_2Cl_2$,[7] and that of *cis*-$Pd(CO)_2(SO_3F)_2$[40] allow a useful structural comparison. The complete vibrational analysis and matrix isolation study of *cis*-$Pt(CO)_2Cl_2$ provides new insights into π-bonding for the extended molecular structure.[7] Despite some efforts, *cis*-$Pt(CO)_2F_2$ remains elusive. Simple mononuclear organometallic fluorides of low-valent metals continue to remain very rare species.[27a,b]

Acknowledgment. Financial support by Deutsche Forschungsgemeinschaft (DFG), Fonds der Chemischen Industrie (FCI), and the Natural Science and Engineering Research Council of Canada (NSERC) is gratefully acknowledged.

Supporting Information Available: X-ray crystallographic file for *cis*-$Pt(CO)_2(SO_3F)_2$ in CIF format. This material is available via the Internet at http://pubs.acs.org.

IC000280J

---

(94) Schatte, G.; Willner, H.; Hoge, D.; Knözinger, E.; Schrems, O. *J. Phys. Chem.* **1989**, *93*, 6025.