Inorg. Chem. **1993**, *32*, 1039–1040 **1039**

Crystal Structure and Study of the Volatility of $((PF_3)_2RhCl)_2$

Pascal Doppelt,[*,†] **Louis Ricard,**[‡] **and Valérie Weigel**[†]

ESPCI-CNRS, 10 Rue Vauquelin, 75231 Paris Cedex 05,
France, and Ecole Polytechnique-CNRS, 91128 Palaiseau
Cedex, France

Received July 29, 1992

Introduction

There has been much interest in the formation of thin films of metal using chemical vapor deposition (CVD).[1-3] These films have been used in microelectronics, optical devices, wear protection, and catalysis.[4] We used $((PF_3)_2RhCl)_2$ as a precursor for CVD Rh films;[5] this contain no carbon or oxygen so these atoms cannot be present in the film as impurities. We determined the structure of the complex, which, to our knowledge, had not been reported. We report also a study of the vapor pressure of the complex by means of FT-IR in the gas phase.

Experimental Section and Results

Preparation of the Complex. All reactions were carried out under a nitrogen atmosphere. All solvents were distilled just before reactions were carried out. PF_3 is commercially available. Caution: *Owing to the toxicity of PF_3, this reaction should be carried out in a well-ventilated hood*! The precursor was synthesized by a procedure described previously[6] adapted to a smaller scale of compound (typically 0.2 g), and chloro(1,5-hexadiene)rhodium dimer was used as a starting complex (Aldrich). The precursor was purified by two sublimations, giving large red crystals that were easy to handle and not too air-sensitive. Mp: 66 °C (in a sealed tube under 1 atm of N_2).

Single-Crystal X-ray Diffraction. X-ray single crystals of the precursor were grown slowly (during 2 weeks) in a sealed tube with an internal pressure of 3 Torr. Due to its volatility and sensitivity to air, the crystal was rapidly attached to the tip of a glass fiber with grease and quickly transferred into a cold nitrogen jet. Data were collected at -150 ± 0.5 °C on a Enraf-Nonius CAD4 diffractometer. The crystal structure was solved and refined using the Enraf-Nonius MoLEN package. The compound crystallizes in space group $P2_1/n$, with $a = 10.447(2)$ Å, $b = 9.869(2)$ Å, $c = 14.237(2)$ Å, $\beta = 109.07(1)°$, $V = 1387.2(8)$ Å^3, $Z = 4$, and $d_{calc} = 3.010$ g/cm^3. Mo Kα radiation was used ($\lambda = 0.710\,73$ Å; graphite monochromator) with $\mu = 33.1$ cm^{-1} and $F(000) = 1168$ Å. A total of 4048 unique reflections were recorded in the range $2° \leq 2\theta \leq 60.0°$ of which 1371 were considered as unobserved ($F^2 < 3.0\sigma(F^2)$), leaving 2677 reflections for solution and refinement. The positions of the two rhodium atoms were obtained from a Patterson map. All atoms were given anisotropic temperature factors in the final cycles of least-squares refinement. A non-Poisson weighting scheme was applied with a *p* factor equal to 0.05. The final agreement factors were $R = 0.032$, $R_w = 0.041$, and GOF = 1.05. The crystallographic data are given in Table I. The molecular structure and labeling of the atoms in $((PF_3)_2RhCl)_2$ are shown in Figure 1.

FT-IR in the Gas Phase and Vapor Pressure Measurement. The IR instrument used was a Perkin-Elmer 1600 Series FT-IR. The gas-phase spectra of the precursor were recorded by use of a heated 12-cm gas cell fitted with NaCl windows. The IR spectrum of the precursor in the vapor phase is quite similar to the spectrum obtained in hexane.[6] The vapor pressure measurements were determined by measurement of the IR absorbance at 951 cm^{-1} of a known mass of the complex in the IR cell as a function of temperature as described in ref 7. The vapor pressure of the precursor at 25 °C is 3×10^{-4} Torr.

Table I. Crystallographic Data for $((PF_3)_2RhCl)_2$

chem formula $Cl_2F_{12}P_4Rh_2$	fw 628.59
$a = 10.447(2)$ Å	space group $P2_1/n$
$b = 9.869(2)$ Å	Mo Kα, $\lambda = 0.710\,73$ Å
$c = 14.237(2)$ Å	$\rho_{calc} = 3.010$ g cm^{-3}
$\beta = 109.09(1)°$	$\mu = 33.1$ cm^{-1}
$V = 1387.2(8)$ Å^3	$R = 0.032^a$
$Z = 4$	$R_w = 0.041$
$T = -150 \pm 0.5$ °C	

[a] The agreement factors are defined as $R = \sum\|F_o| - |F_c\|/\sum|F_o|$ and $R_w = (\sum(w|F_o| - |F_c|)^2/\sum|F_o|^2)^{1/2}$.

Table II. Positional Parameters for $((PF_3)_2RhCl)_2$

atom	*x*	*y*	*z*	B,[a] Å^2
Rh1	0.35959(4)	0.07835(4)	0.42679(3)	1.700(6)
Rh2	0.07832(4)	0.08933(4)	0.43310(3)	1.636(6)
Cl1	0.1943(1)	−0.0990(1)	0.3935(1)	2.27(2)
Cl2	0.2858(1)	0.1233(1)	0.56571(9)	2.37(2)
P1	0.3920(1)	0.0370(2)	0.2899(1)	2.23(3)
P2	0.4724(2)	0.2610(2)	0.4516(1)	2.84(3)
P3	0.0082(2)	0.2787(2)	0.4677(1)	2.49(3)
P4	−0.0837(1)	0.0605(2)	0.2983(1)	2.13(2)
F1	0.2807(4)	0.0814(4)	0.1956(3)	3.79(9)
F2	0.4017(4)	−0.1118(4)	0.2624(3)	3.65(8)
F3	0.5134(4)	0.0929(5)	0.2646(3)	4.49(9)
F4	0.5859(5)	0.2855(6)	0.4076(4)	7.6(1)
F5	0.5523(4)	0.3029(4)	0.5560(3)	3.73(8)
F6	0.3919(6)	0.3872(5)	0.4208(6)	11.6(2)
F7	0.0812(5)	0.4033(4)	0.4462(3)	5.74(9)
F8	0.0271(4)	0.3110(4)	0.5153(3)	3.48(8)
F9	−0.1368(4)	0.3254(5)	0.4228(4)	6.6(1)
F10	−0.1377(4)	−0.0823(4)	0.2702(3)	3.44(8)
F11	−0.0528(4)	0.0928(5)	0.2025(3)	4.20(9)
F12	−0.2182(4)	0.1358(5)	0.2750(3)	4.6(1)

[a] B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

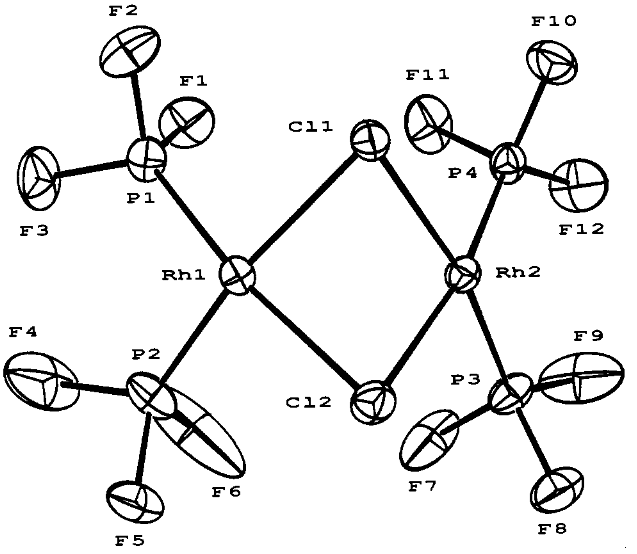

Figure 1. Molecular structure of $((PF_3)_2RhCl)_2$.

Discussion and Conclusion

Crystallographic Study. The molecular structure of the complex is given in Figure 1. Selected bond angles and bond

---

[†] ESPCI, Laboratoire de chimie et d'électrochimie des matériaux moléculaires, CNRS (URA 429).

[‡] Ecole Polytechnique, Laboratoire de chimie du phosphore et des métaux de transition, CNRS (UMR 13).

(1) Kompa, K. L. *Angew. Chem., Int. Ed. Engl.* **1988**, *27* 1311–1325.

(2) Westwood, W. *Gmelin Handbook of Inorganic Chemistry*, 8th ed.; Verlag Chemie: Weinheim, Germany, 1986; Supplement Vol. A1, Technology of Platinum-Group Metals, pp 43–50.

(3) Herman, I. P. *Chem. Rev*, **1989**, *89*, 1323–1357.

(4) Powell, C. F.; Oxley, J. H.; Blocher, J. M. *Vapor Deposition*; John Wiley: New York, 1966.

(5) Doppelt, P.; Weigel, V.; Guinot, P. Presented at the E-MRS Meeting, ICEM, Symposium C, Strasbourg, France, 1992.

(6) Bennett, M. A.; Patmore, D. J. *Inorg. Chem.* **1971**, *10*, 2387–2395.

(7) Dryden, N. H.; Kumar, R.; Ou, E.; Rashidi, M.; Roy, S.; Norton, P. R.; Puddephatt, R. J.; Scott, J. D. *Chem. Mater.* **1991**, *3*, 677–685.

0020-1669/93/1332-1039$04.00/0

Table III. Selected Bond Distances (Å) and Angles (deg) for $((PF_3)_2RhCl)_2$

	Bond Distances		
Rh1–Rh2	2.9709(5)	Rh1–Cl1	2.394(1)
Rh1–Cl2	2.387(1)	Rh1–P1	2.123(2)
Rh1–P2	2.119(2)	Rh2–Cl1	2.384(1)
Rh2–Cl2	2.388(1)	Rh2–P3	2.123(1)
Rh2–OP4	2.123(1)	P1–F1	2.525(4)
	Bond Angles		
Rh2–Rh1–Cl1	51.41(3)	Rh2–Rh1–Cl2	51.53(3)
Rh2–Rh1–P1	119.37(4)	Rh2–Rh1–P2	117.74(5)
Cl1–Rh1–Cl2	83.84(5)	Cl1–Rh1–P1	89.93(6)
Cl1–Rh1–P2	168.64(6)	Cl2–Rh1–P1	170.89(6)
Cl2–Rh1–P2	90.92(6)	P1–Rh1–P2	94.01(7)
Rh1–Rh2–Cl1	51.71(3)	Rh1–Rh2–Cl2	51.52(3)
Rh1–Rh2–P3	117.30(5)	Rh1–Rh2–OP4	118.17(4)
Cl1–Rh2–Cl2	84.04(5)	Cl1–Rh2–P3	168.91(6)
Cl1–Rh2–P4	89.92(6)	Cl2–Rh2–P3	89.18(6)
Cl2–Rh2–P4	169.54(6)	P3–Rh2–P4	95.40(6)
Rh1–Cl1–Rh2	76.88(4)	Rh1–Cl2–Rh2	76.95(4)
Rh1–P1–F1	116.6(2)	Rh1–P1–F2	117.6(2)
Rh1–P1–F3	122.7(2)	F1–P1–F2	98.4(2)
F1–P1–F3	98.1(2)	F2–P1–F3	99.0(3)

lengths are shown in Table III. The molecule basically consists of two $(PF_3)_2RhCl_2$ planes with a dihedral angle of 113.54°. The intramolecular Rh–Rh distance of 2.9709(5) Å is very short[8] compared with equivalent distances in other compounds of the same family at 25 °C: 3.12 Å in $((CO)_2RhCl)_2$;[9] 3.50 Å in (RhCl-(1,5-cyclooctadiene))$_2$.[10]

The PF_3 ligands are oriented toward the central axis of the dimer so that P–F contacts are minimized. As a consequence, the Rh atom is 0.14 Å out of the main plane formed by the four ligands. The Rh–P distance (PF_3), average 2.12 Å, is shorter than the corresponding Rh–P distances in other Rh complexes containing phosphine ligands (2.37 Å in $RhCl(C_2F_4)(PPh_3)_2$,[11] for example). This is not surprising since the Rh–P bond is likely to be strengthened by strong back-bonding to the PF_3 ligand.[12]

Intermolecular Rh–Rh interactions are present, as can be seen in Figure 2. The intermolecular Rh–Rh distances (average 3.375 Å) are comparable to those found in other Rh dimers. The resultant "zigzag" structure exists in other structurally related complexes such as $((CO)_2RhCl)_2$[9] or $((PF_3)_2IrCl)_2$.[13] Intermolecular interactions must be weak because of the high volatility of the complex.

Study of the Volatility of the Precursor. The melting point of the precursor has been given, but there is no information about its volatility. We studied the volatility of the CVD precursor by FT-IR spectroscopy in the gas phase. The diagram given in Figure 3 was obtained; it shows that the complex is quite volatile. The complex is stable up to 150 °C. Above this temperature, decomposition takes place as shown by the appearance in the IR spectrum of ν(P–F) vibrations due to free PF_3.[12] The continuity of the vapor pressure curve suggests that the compound does not melt under the conditions of the measurement as we have confirmed visually. This is in contrast with the behavior of $PtMe_2(CNMe)_2$ described in ref 7.

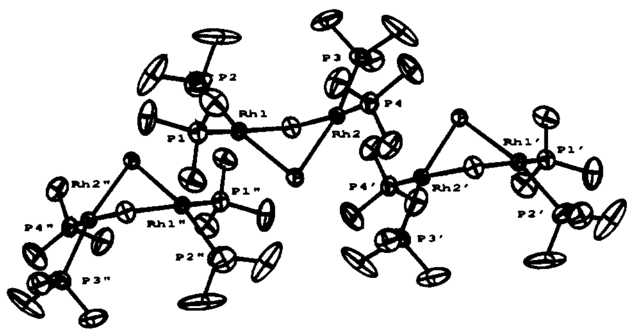

Figure 2. Packing arrangement of $((PF_3)_2RhCl)_2$, showing intermolecular Rh–Rh interactions.

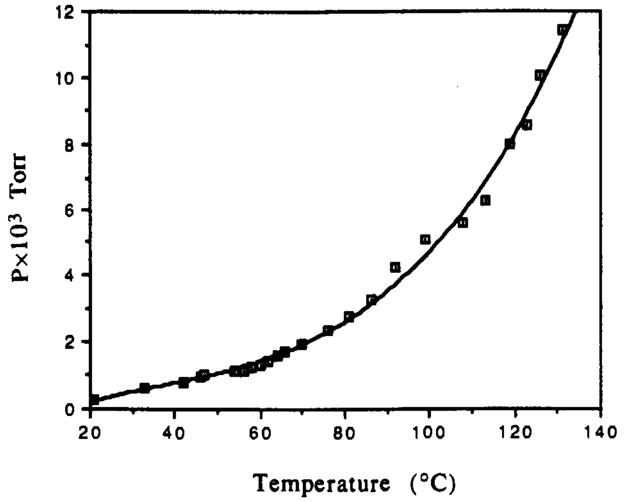

Figure 3. Vapor pressure of $((PF_3)_2RhCl)_2$ as a function of temperature.

In conclusion, the volatile Rh complex $((PF_3)_2RhCl)_2$ has been completely characterized by an X-ray structure. Studies of its volatility and temperature of decomposition show that it is a suitable precursor for CVD Rh films.

Supplementary Material Available: A full length table of crystallographic data (Table A), a table of distances, angles, and thermal parameters (Table B), and a table of least-squares planes (Table C) (6 pages). Ordering information is given on any current masthead page.

---

(8) The question of the existence of a Rh–Rh metal bond will be studied separately.

(9) Dahl, L. F.; Martell, C.; Wampler, D. L. *J. Am. Chem. Soc.* **1961**, *83*, 1761–1762.

(10) Ibers, J. A.; Snyder, R. G. *J. Am. Chem. Soc.* **1962**, *84*, 495–496.

(11) Hitchcock, P. B.; Mc Partlin, M.; Mason, R. *J. Chem. Soc., Chem. Commun.* **1969**, 1367–1368.

(12) Nixon, J. F. *Adv. Inorg. Radiochem.* **1985**, *29*, 41–141.

(13) Hitchcock, P. B.; Morton, S.; Nixon, J. F. *J. Chem. Soc., Dalton Trans.* **1985**, 1295–1301.