

THE STRUCTURES OF SOME BIS(TRIPHENYLPHOSPHINE)- (HALOGEN-SUBSTITUTED ETHYLENE)PLATINUM(0) COMPLEXES

JAMES N. FRANCIS, ALEXANDER McADAM AND JAMES A. IBERS

Department of Chemistry, Northwestern University, Evanston, Illinois 60201 (U.S.A.)

(Received November 27th, 1970)

SUMMARY

The mixtures of three Pt(olefin) $[P(C_6H_5)_3]_2$ complexes have been determined from X-ray data collected by counter methods. The three olefins are $ClFC=CF_2$, $Cl_2C=CF_2$, and $Cl_2C=CCl_2$. All three complexes crystallize in space group $C_{2h}^5 - P2_1/c$ with four molecules in the cell. The structures of the complexes are similar in overall detail. In each the Pt atom has trigonal coordination, if one counts the olefin as a monodentate ligand. Generally the Pt, the two P atoms, and the central C atoms of the olefin are nearly coplanar. In complex (I) there is disorder among the halogen atoms and little can be determined about the metal olefin geometry; in complex (II) there is a clear indication of *rotational* disorder of the CF_2 group about the C-C central bond. On the basis of the results for complexes (II) and (III) there is an indication that the Pt-C (of Cl) bond is shorter than the Pt-C (of F) bond, and it seems certain that the Pt-C (of Cl) bond is shorter than the Pt-C bonds in the analogous tetracyanoethylene and ethylene complexes.

INTRODUCTION

Over the last few years there have been prepared a number of complexes of general formula bis(triphenylphosphine)(olefin)platinum(0)¹⁻⁴. In a considerable proportion of such complexes the olefin is an ethylene molecule substituted with electron-withdrawing atoms such as Cl or F, or groups such as CF_3 or CN. However, there is an almost complete lack of precise structural information on such complexes⁵, the only published structure being that of the complex of the symmetrical olefin tetracyanoethylene (TCNE)⁶. In view of this lack of structural data, and because of the importance of these complexes in relation to homogeneous catalysis, we felt it would be instructive to study several such complexes. In particular, in order to learn more about the nature of transition-metal-olefin bonding, we set out to determine the geometrical consequences of substituting atoms or groups of different electron-withdrawing power, such as Cl and F, onto the ethylene. To this end we have prepared and examined structurally the complexes of the olefins $ClFC=CF_2$, $Cl_2C=CF_2$, and $Cl_2C=CCl_2$. Since hydrogen atoms are rather difficult to locate in the presence of a metal as heavy as platinum, we did not consider studying the complexes of any hydrogen-containing ethylenes.

EXPERIMENTAL

Preparation

The tetrachloroethylene² and 1,1-dichloro-2,2-difluoroethylene¹ complexes were synthesized by published methods. We are grateful to Professor F.G.A. Stone for a sample of the complex of 1-chloro-1,2,2-trifluoroethylene. The products may be recrystallized from a variety of solvents, the resulting cell dimensions and space groups being a function of the solvent used. The crystal data obtained in a search for suitable crystals are listed below. Generally speaking the crystals are colorless and air stable, but tend to turn slightly yellow on prolonged exposure to X-rays.

Crystal data

(i). $\text{Pt}(\text{ClFC}=\text{CF}_2)[\text{P}(\text{C}_6\text{H}_5)_3]_2$, $\text{C}_{38}\text{ClF}_3\text{H}_{30}\text{Pt}$, (I), mol.wt. = 836.1, monoclinic, $a = 10.927(3)$, $b = 34.369(8)$, $c = 10.892(4)$ Å, $\beta = 123.92(2)^\circ$, temp. = 22.4° , $\lambda(\text{Cu-K}\alpha_1) = 1.5406$ Å, $U = 3395$ Å³, $d_c = 1.636$ g·cm⁻³ for $Z = 4$, $d_o = 1.69(2)$ g·cm⁻³ (by flotation in $\text{CHCl}_3/\text{CH}_3\text{I}$). Systematic absences $h0l:l \neq 2n$, $0k0:k \neq 2n$. Space group C_{2h}^5 - $P2_1/c$. Linear absorption coefficient for Cu-K α X-rays, $\mu = 98.9$ cm⁻¹.

(ii). $\text{Pt}(\text{Cl}_2\text{C}=\text{CF}_2)[\text{P}(\text{C}_6\text{H}_5)_3]_2$ crystallized from 1/1 benzene/heptane, $\text{C}_{38}\text{Cl}_2\text{F}_2\text{H}_{30}\text{P}_2\text{Pt}$, (IIa), mol.wt. = 852.5, monoclinic, $a = 11.876(5)$, $b = 18.101(7)$, $c = 16.768(8)$ Å, $\beta = 108.80(2)^\circ$, temp. = 22.0° , $\lambda(\text{Cu-K}\alpha_1) = 1.5406$ Å, $U = 3419$ Å³, $d_c = 1.656$ g·cm⁻³ for $Z = 4$, $d_o = 1.66(2)$ g·cm⁻³ (by flotation in ZnCl_2 solution). Systematic absences $h0l:l \neq 2n$, $0k0:k \neq 2n$. Space group C_{2h}^5 - $P2_1/c$. Linear absorption coefficient for Cu-K α X-rays, $\mu = 104.6$ cm⁻¹.

(iii). $\text{Pt}(\text{Cl}_2\text{C}=\text{CF}_2)[\text{P}(\text{C}_6\text{H}_5)_3]_2$ crystallized from CH_2Cl_2 , $\text{C}_{38}\text{Cl}_2\text{F}_2\text{H}_{30}\text{P}_2\text{Pt} \cdot \frac{1}{2}\text{CCl}_2\text{H}_2$, (IIb), formula wt. = 895.0, monoclinic, $a = 21.39(3)$, $b = 16.02(2)$, $c = 23.18(3)$ Å, $\beta = 114.0(5)^\circ$, $U = 7258$ Å³, $d_c = 1.64$ g·cm⁻³ for $Z = 8$, $d_o = 1.64(2)$ g·cm⁻³ (by flotation in $\text{CH}_3\text{I}/\text{CCl}_4$). Systematic absences $h0l:l \neq 2n$, $0k0:k \neq 2n$. Space group C_{2h}^5 - $P2_1/c$. Linear absorption coefficient for Cu-K α X-rays, $\mu = 105.5$ cm⁻¹.

(iv). $\text{Pt}(\text{Cl}_2\text{C}=\text{CCl}_2)[\text{P}(\text{C}_6\text{H}_5)_3]_2$ crystallized from 1/1 benzene/heptane, $\text{C}_{38}\text{Cl}_4\text{H}_{30}\text{P}_2\text{Pt}$, (III), mol.wt. = 885.5, monoclinic, $a = 10.685(8)$, $b = 19.868(14)$, $c = 20.156(14)$ Å, $\beta = 124.75(2)^\circ$, temp. = 21.5° , $\lambda(\text{Mo-K}\alpha_1) = 0.7093$ Å, $U = 3516$ Å³, $d_c = 1.673$ g·cm⁻³ for $Z = 4$, $d_o = 1.66(2)$ g·cm⁻³ (by flotation in ZnCl_2 solution). Systematic absences $h0l:l \neq 2n$, $0k0:k \neq 2n$. Space group C_{2h}^5 - $P2_1/c$. Linear absorption coefficient for Mo-K α X-rays, $\mu = 49.7$ cm⁻¹.

Preliminary data on the above four compounds were obtained from precession and Weissenberg photographs taken with Mo-K α and Cu-K α radiations, respectively. The space group for each compound was uniquely determined to be $P2_1/c$. For compounds (I), (IIa), and (III) there are four formula units in the cell, so no crystallographic symmetry conditions need be imposed on any of the molecules. Solution of structure (IIb) was not contemplated as it would require one to find and refine the positions of two independent molecules of complex and one molecule of solvent, and in principle would provide no new information beyond the solution of the structure of compound (IIa).

Data collection

Intensity measurements for all three complexes [(I), (IIa), and (III)] were made

on a Picker Four Circle Diffractometer using procedures which have been described elsewhere⁷. All information pertinent to the collection of the data sets is recorded in Table 1.

Generally speaking, a crystal of suitable size was mounted, and a number of narrow-source, open-counter ω scans examined to ensure that the mosaicity of the crystal was acceptably small. Thereafter the setting angles of about 15 reflections were determined manually through a narrow vertical slit at a small takeoff angle. From these observations the crystal orientation and refined unit cell parameters were derived by a least-squares procedure⁷. The cell dimensions listed in the section on crystal data were obtained in such a manner. Peak intensities were measured using the θ - 2θ scan technique, the scan rate in all cases being 1° per min. The scan information given in Table 1 indicates the scan range: the figures shown indicate the angular distance below the α_1 peak and the distance above the α_2 peak at which the scan limits were set. Background counts were measured at each scan limit.

TABLE 1

SUMMARY OF EXPERIMENTAL CONDITIONS EMPLOYED IN DATA COLLECTION

Complex (olefin)	<i>p</i>	Radiation	Crystal shape	Crystal size (mm)	Mounting	Temp. (°C)
CIFC=CF ₂	0.04	Cu-K α (Ni post filter)	Acicular	0.32 × 0.12 × 0.10	In capillary	22.4
Cl ₂ C=CF ₂	0.04	Cu-K α (Ni post filter)	Prismatic	0.20 × 0.19 × 0.14	Glass fiber	22.0
Cl ₂ C=CCl ₂	0.03	Mo-K α (Nb post filter)	Prismatic	0.20 × 0.17 × 0.11 ^a 0.27 × 0.23 × 0.13 ^b	Glass fiber	21.5
Cl ₂ C=CCl ₂	0.04	Pre-monochrom. Mo-K α	Prismatic	0.34 × 0.27 × 0.17	In capillary (under dry N ₂)	23.0

Complex (olefin)	Crystal-counter distance (cm)	Size of counter aperture (cm)	Take-off angle (°)	Average ω scan (°) ^c	<i>t_b</i> (sec)	Scan speed (°/min)	Shell I	Scan range (°)
CIFC=CF ₂	35	0.4 × 0.4	3.0	0.24	10	1	0.0 < 2 θ ≤ 76.0	-0.8-+1.2
Cl ₂ C=CF ₂	34	0.4 × 0.4	2.0	0.18	20	1	0.0 < 2 θ ≤ 56.0	-0.65-+0.75
Cl ₂ C=CCl ₂	33	0.4 × 0.4	1.3	0.04 ^a 0.10 ^b	20	1	0.0 < 2 θ ≤ 26.5 ^a	-0.35-+0.40 ^a
Cl ₂ C=CCl ₂ ^c	23	0.7 × 0.7	1.5	0.15	10	1	0.0 < 2 θ ≤ 33.0	-0.4-+0.6

Complex (olefin)	Shell II	Scan range (°)	Shell III	Scan range (°)	Reflections		Transmission factors
					Total no.	No. with $F_o^2 > 3\sigma(F_o^2)$	
CIFC=CF ₂	76.0 < 2 θ ≤ 80.0	-0.8-+1.2	80.0 < 2 θ ≤ 85.0	-0.8-+1.2	2388	1862	0.32-0.43
Cl ₂ C=CF ₂	56.0 < 2 θ ≤ 84.0	-0.65+0.75	84.0 < 2 θ ≤ 90.0	-0.65+0.75	2768	2122	0.19-0.32
Cl ₂ C=CCl ₂	26.5 < 2 θ ≤ 32.5	-0.50-+0.65 ^b			1884	1606	0.48-0.67 ^a
Cl ₂ C=CCl ₂ ^c					1926	1326	0.36-0.56

^a Crystal 1. ^b Crystal 2. ^c Peak width at $\frac{1}{2}$ height.

The observed peak counts were corrected for background to yield the net integrated intensity I . The standard deviation of I was estimated by:

$$\sigma(I) = [C_T + (t_c^2/4t_b^2) \cdot (B_1 + B_2) + (p \cdot I)^2]^{\frac{1}{2}}$$

where C_T is the total peak count obtained in t_c seconds, B_1 and B_2 are the background counts, each obtained in t_b seconds, and where $I = C_T - (t_c/2t_b) \cdot (B_1 + B_2)$. The factor p was taken as 0.03 or 0.04 (see Table 1). Only the reflections for which $I \geq 3\sigma(I)$ were used in subsequent calculations. The intensities were corrected for Lorentz-polarization and absorption effects. The calculated transmission factors are listed in Table 1.

Two data sets were collected for the tetrachloroethylene compound. Initially data were collected in our laboratory using our normal procedures⁷. Since crystal decomposition was rapid, a second crystal was mounted after the collection of about 1000 reflections. The structure was solved in the manner described in the next section, and refined to completion. However, it was felt that the results obtained might be highly dependent on the manner in which we corrected the intensities for crystal decomposition, whether by refining two polynomial scale factors (one for each crystal)⁸ or by correcting the data before refinement. Consequently a second data set less subject to crystal decomposition effects was obtained by sealing a crystal in a capillary under dry N_2 gas, and by employing a Picker Four Circle Diffractometer fitted with a graphite monochromator*. Monochromatic Mo- $K\alpha$ radiation was obtained by Bragg reflection from the (002) plane of a highly oriented graphite crystal.

Structure solution and refinement

In all instances once the structure had been solved, refinement was by the method of full-matrix least-squares**. The function minimized was $\Sigma w \cdot \Delta^2$ where $w = 4F_0^2/\sigma^2(F_0^2)$ and $\Delta = |F_0| - |F_c|$, where $|F_0|$ and $|F_c|$ are the observed and calculated structure amplitudes. Throughout the refinements the phenyl rings were constrained to D_{6h} symmetry, and the C-C bond length was fixed at 1.394 Å⁹. The atomic scattering factors used in all calculations were from the usual tabulation¹⁰, with the exceptions of those for Pt¹¹ and H¹². The anomalous corrections of Cromer¹³ for Pt, P, and Cl were applied to the calculated structure factors¹⁴.

$Pt(ClFC=CF_2)[P(C_6H_5)_3]_2$. The first structure to be solved was that of the complex of $ClFC=CF_2$. It was solved by conventional Patterson, least-squares, and Fourier methods, and refined to a conventional R -factor (on F) of 0.06. The structure¹⁵, as expected, showed a planar environment for the Pt atom with the two olefinic C atoms lying in the plane of the Pt and two P atoms. The olefinic substituents are pushed back from the Pt atom. However, during the refinement of the isotropic thermal parameters of the olefinic substituents, it became clear that the Cl atom must be disordered about all four substituent positions, since whichever position was refined as a chlorine atom showed much larger thermal motion than the three atoms considered to be fluorine atoms. Since the positions of the olefinic carbon atoms are a

* We are most grateful to Professor J. H. Enemark of the Chemistry Department, University of Arizona, Tucson, for putting his laboratory at our disposal for the collection of these data.

** In addition to local programs for the CDC 6400, the following computer programs were used in this work: Zalkin's FORDAP Fourier program, Hamilton's GONO9 absorption program, the Busing-Levy ORFFE error function program, and Johnson's ORTEP plotting program. Our least-squares program NUCLS, in its nongroup form, closely resembles the Busing-Levy ORFLS program.

sensitive function of the treatment of the disorder, little of interest concerning the mode of metal-olefin bonding results. Suffice it to say that the two Pt-P distance of 2.320(6) and 2.304(6) Å and the P(1)-Pt-P(2) angle of 104.7(2), which remained virtually constant during the various refinements of the atoms of the olefin, are in the range for such complexes (see later). The overall geometry of the complex is also the same as in the TCNE complex⁶. There was the interesting observation that the Pt-C (of ClF) distance was shorter than that of Pt-C (of F₂), an unexpected result. For this reason studies on related structures were undertaken.

$Pt(Cl_2C=CF_2)[P(C_6H_5)_3]_2$. Since disorder had occurred in the above structure, we felt that an olefin complex in which the possibilities of disorder might be less should be examined. Consequently we turned our attention to the complex of Cl₂C=CF₂. This was again solved by conventional techniques.

A Patterson synthesis carried out on data for which $2\theta \leq 56.0^\circ$ (743 reflections) revealed the Pt atom, but gave several possible positions for the P and Cl atoms. One cycle of refinement of the positional and isotropic thermal parameters associated with the Pt atom reduced the agreement factors $R(\Sigma|\Delta|/\Sigma|F_o|)$ and $R_w[(\Sigma w \cdot \Delta^2/\Sigma w \cdot F_o^2)^{1/2}]$ to values of 0.344 and 0.390, respectively. A difference Fourier synthesis then revealed the positions of all other non-hydrogen atoms with the exception of the two olefinic C atoms. The positions of these atoms were inferred. A further cycle of refinement of a polynomial scale factor together with all positional isotropic thermal parameters reduced R and R_w to 0.204 and 0.294. This form of the scale factor was necessary to correct for the severe crystal decomposition encountered during data collection. All data with $F_o^2 > 3\sigma(F_o^2)$ were then corrected for absorption and four cycles of refinement varying positional and isotropic thermal parameters converged to R and R_w values of 0.112 and 0.141, respectively. At this point it was clear that disorder was again a problem, but the nature of the disorder was most unexpected. The thermal parameters associated with the two F atoms were much too high, and the positional parameters of C(1), attached to the F's, were such that the C-C distance was an impossible 1.99 Å. It was clear that there is some rotational disorder

TABLE 2

POSITIONAL AND THERMAL PARAMETERS FOR $Pt(Cl_2C=CF_2)[P(C_6H_5)_3]_2$

Atom	x	y	z	$B_{iso}(\text{\AA}^2)$ or β_{11}^a	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.08659(8)	0.10368(5)	0.20687(5)	128.1(1.6)	34.9(6)	43.5(7)	-0.7(5)	5.0(6)	1.5(4)
P(1)	0.1949(5)	0.1687(3)	0.1381(3)	140(7)	37(2)	49(3)	10(3)	13(4)	2(2)
P(2)	0.2303(5)	0.0417(3)	0.3115(3)	142(7)	33(2)	51(3)	-1(3)	11(4)	1(2)
Cl(1)	-0.1630(8)	0.0863(6)	0.0501(5)	214(11)	181(7)	68(4)	-49(7)	13(6)	-26(5)
Cl(2)	-0.1316(8)	0.2234(5)	0.1506(5)	251(12)	84(4)	122(5)	43(6)	16(7)	6(4)
C(1)	-0.0785(23)	0.1402(15)	0.1363(16)	8.8(7)					
C(2)	-0.0780	0.0860	0.2100	10.0					
F(11)	-0.1591	0.0227	0.1609	12.0					
F(12)	-0.1110	0.0035	0.2038	7.7					
F(21)	-0.0632	0.0619	0.2834	5.1					
F(22)	-0.0971	0.1051	0.2704	6.6					

^a The form of the anisotropic temperature factor is $\exp[-(\beta_{11} \cdot h^2 + \beta_{22} \cdot k^2 + \beta_{33} \cdot l^2 + 2\beta_{12} \cdot h \cdot k + 2\beta_{13} \cdot h \cdot l + 2\beta_{23} \cdot k \cdot l)]$. The values of β_{ij} have been multiplied by 10^4 .

TABLE 3

GROUP POSITIONAL PARAMETERS FOR $\text{Pt}(\text{Cl}_2\text{C}=\text{CF}_2)[\text{P}(\text{C}_6\text{H}_5)_3]_2$

Group	x_c^a	y_c	z_c	δ	ϵ	η
R _{1A}	0.0340(8)	0.1776(6)	-0.0586(7)	-0.067(10)	3.095(11)	0.973(10)
R _{1B}	0.2552(8)	0.3341(5)	0.2114(6)	1.789(15)	-2.238(9)	-2.588(15)
R _{1C}	0.4549(10)	0.1184(5)	0.1311(8)	-0.934(21)	-2.091(10)	2.420(20)
R _{2A}	0.3396(8)	-0.1007(6)	0.2464(7)	-2.823(19)	-2.065(10)	1.504(19)
R _{2B}	0.4409(9)	0.1478(5)	0.4163(5)	0.783(10)	-2.937(9)	-2.844(9)
R _{2C}	0.1347(8)	-0.0367(6)	0.4514(7)	2.375(11)	2.538(10)	-1.484(11)

^a These group parameters have been defined previously (see ref. 9).

about the C-C bond such that each F atom must be considered as partitioned into several groups covering an angular range of rotation of about 20° around the C-C bond. Many refinements were carried out to try to describe the nature of the disorder in a quantitative way. Unfortunately these attempts were not successful and we have been forced to position C(1) and four half-fluorine atoms as indicated in Table 2. These atoms were given reasonable isotropic thermal parameters, but neither the positional nor thermal parameters were varied during the final refinement.

Three further cycles of refinement of the anisotropic thermal parameters associated with the heavy atoms, an isotropic thermal parameter for C(2), and overall group thermal parameters for the phenyl rings converged to $R=0.067$ and $R_w=0.090$. In the final cycle no parameter shifted by more than $\frac{2}{3}$ of an estimated standard deviation.

TABLE 4

DERIVED PARAMETERS OF GROUP CARBON ATOMS IN $\text{Pt}(\text{Cl}_2\text{C}=\text{CF}_2)[\text{P}(\text{C}_6\text{H}_5)_3]_2$

Atom	x	y	z	B group (\AA^2)
R _{1A} C1	0.1038(12)	0.1776(11)	0.0257(7)	8.4(3)
C2	0.0760(14)	0.2441(8)	-0.0182(11)	
C3	0.0062(15)	0.2440(8)	-0.1025(11)	
C4	-0.0358(13)	0.1775(11)	-0.1429(7)	
C5	-0.0081(15)	0.1111(8)	-0.0990(11)	
C6	0.0617(15)	0.1111(8)	-0.0147(11)	
R _{1B} C1	0.2281(13)	0.2633(6)	0.1783(9)	7.1(3)
C2	0.1770(11)	0.2898(8)	0.2369(9)	
C3	0.2041(13)	0.3606(9)	0.2700(8)	
C4	0.2823(14)	0.4050(6)	0.2445(10)	
C5	0.3335(12)	0.3785(8)	0.1859(10)	
C6	0.3064(13)	0.3076(9)	0.1528(8)	
R _{1C} C1	0.3427(12)	0.1387(9)	0.1332(12)	8.6(3)
C2	0.4416(17)	0.1483(9)	0.2042(9)	
C3	0.5539(13)	0.1280(9)	0.2021(9)	
C4	0.5672(12)	0.0982(9)	0.1290(12)	
C5	0.2683(17)	0.0886(8)	0.0580(9)	
C6	0.3560(13)	0.1088(9)	0.0601(9)	

TABLE 4 (continued)

Atom	x	y	z	B group (Å ²)
R _{2A} Cl	0.2977(13)	-0.0380(7)	0.2763(11)	7.8(3)
C2	0.3346(14)	-0.0994(10)	0.3283(7)	
C3	0.3764(13)	-0.1620(7)	0.2983(10)	
C4	0.3814(13)	-0.1633(7)	0.2164(11)	
C5	0.3446(14)	-0.1019(10)	0.1644(7)	
C6	0.3027(13)	-0.0393(7)	0.1944(10)	
R _{2B} Cl	0.3518(12)	0.0991(8)	0.3725(9)	7.2(3)
C2	0.3224(10)	0.1698(9)	0.3925(9)	
C3	0.4115(15)	0.2184(6)	0.4363(9)	
C4	0.5300(12)	0.1965(8)	0.4602(8)	
C5	0.5595(10)	0.1258(9)	0.4402(9)	
C6	0.4704(15)	0.0772(6)	0.3964(10)	
R _{2C} C1	0.1755(14)	-0.0007(9)	0.3923(9)	7.9(3)
C2	0.0939(14)	-0.0583(9)	0.3673(7)	
C3	0.0531(12)	-0.0943(7)	0.4263(11)	
C4	0.0939(13)	-0.0728(8)	0.5104(9)	
C5	0.1755(13)	-0.0152(9)	0.5355(7)	
C6	0.2162(11)	0.0208(7)	0.4764(11)	

The positional and thermal parameters for all nongroup atoms are listed in Table 2, together with the associated standard deviations as estimated from the inverse matrix. In Table 3 are listed the orientation and positional parameters associated with the groups and in Table 4 are given the derived positional parameters of the carbon atoms of the phenyl groups.

An examination of $\Sigma w \cdot \Delta^2$ as a function of $|F_o|$ and $\lambda^{-1} \sin \theta$ revealed no unexpected trends. The values of $|F_c|$ for those weak reflections omitted from the refinement were in the expected range. Accordingly these data are omitted from the final tabulation of $10|F_o|$ and $10|F_c|$ (in electrons)*.

$Pt(Cl_2C=CCl_2)[P(C_6H_5)_3]_2$. The structure of this complex was solved using the original data set. A Patterson map based on low-order data ($2\theta < 26.5^\circ$) revealed the position of the Pt atom and trial positions for the two P atoms. One cycle of least-squares refinement led to a value of R of 0.32. On a subsequent difference map again all non-hydrogen atoms with the exception of the two olefinic carbon atoms were located. A cycle of refinement (in which all nongroup atoms were assigned isotropic thermal parameters, and the phenyl rings overall group thermal parameters) reduced R and R_w to 0.102 and 0.137, respectively. A difference synthesis revealed residual electron density in the region associated with the two C atoms, but the atoms themselves were not resolved. However the positions of the two C atoms were inferred, and were

* The Tables for the $Cl_2C=CF_2$ and $CCl_2=CCl_2$ complexes have been deposited as NAPS Document No. 01317 with the ASIS National Auxiliary Publication Service, c/o CCM Information Corp., 909 Third Avenue, New York, N.Y. 10022. A copy may be secured by citing the document number and by remitting \$2.00 for a microfiche or \$5.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

TABLE 5
POSITIONAL AND THERMAL PARAMETERS FOR $\text{Pt}(\text{Cl}_2\text{C}=\text{CCl}_2)_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$

Atom	x	y	z	$B_{\text{iso}}(\text{\AA}^2)$ or β_{11}^a	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.35574(13)	0.07770(5)	0.24376(6)	262.5(2.8)	27.9(4)	54.7(6)	11.1(8)	55.1(1.0)	1.6(4)
P(1)	0.3561(9)	-0.0363(3)	0.2267(4)	260(16)	33(3)	55(4)	10(5)	48(7)	3(2)
P(2)	0.5921(9)	0.1050(3)	0.2771(4)	311(18)	27(3)	40(4)	0(5)	53(6)	-1(2)
Cl(1)	0.0944(14)	0.0652(4)	0.2795(8)	649(32)	62(4)	202(9)	-22(8)	285(16)	4(5)
Cl(2)	0.0027(11)	0.1123(5)	0.1203(6)	379(23)	69(4)	114(7)	13(7)	-26(10)	1(4)
Cl(3)	0.3259(12)	0.1811(5)	0.3615(5)	519(27)	74(4)	96(6)	11(7)	127(10)	-6(4)
Cl(4)	0.2222(11)	0.2380(4)	0.2099(5)	527(26)	48(3)	110(6)	-2(7)	120(10)	6(4)
C(1)	0.1473(36)	0.0986(15)	0.2176(19)	10.5(9)					
C(2)	0.2642(30)	0.1614(13)	0.2596(16)	7.9(7)					

^a The form of the anisotropic temperature factor is $\exp[-(\beta_{11} \cdot h^2 + \beta_{22} \cdot k^2 + \beta_{33} \cdot l^2 + 2\beta_{12} \cdot h \cdot k + 2\beta_{13} \cdot h \cdot l + 2\beta_{23} \cdot k \cdot l)]$. The values of β_{ij} have been multiplied by 10^4 .

successfully refined using isotropic thermal parameters. At the end of three cycles of such refinement R and R_w had values of 0.072 and 0.095.

Next all data were corrected for absorption. Thereafter three cycles of refinement of all positional parameters, and anisotropic temperature factors for all nongroup atoms, converged to R and R_w values of 0.060 and 0.078, respectively.

At this point a new data set was obtained using Mo- $K\alpha$ radiation made monochromatic by means of a graphite crystal. The use of the monochromator severely curtailed crystal decomposition. The intensities of three standard reflections were monitored during data collection, and at the end of the experiment these had decayed uniformly by about 10.0(2.3)%. The data were corrected for this decomposition during processing. Before refinement began an absorption correction was applied.

The starting point of this refinement was the set of parameters obtained from the refinement of the first data set. One cycle, in which only the positional parameters and a scale factor were refined, reduced R to 0.099. Two cycles of refinement, in which all nongroup atoms were assigned anisotropic thermal parameters and each of the phenyl rings an overall group thermal parameter, converged to R and R_w values of 0.051 and 0.064, respectively, for the 1326 observations with $F_o^2 > 3\sigma(F_o^2)$. However, the thermal ellipsoid associated with C(2) was non-positive definite. As a consequence of this we decided to refine isotropic thermal parameters for C(1) and C(2). After two further cycles, the refinement converged to R of 0.053 and R_w of 0.068. A difference Fourier map then revealed peaks corresponding to some of the phenyl hydrogen atoms. Therefore fixed contributions for the ring hydrogen atoms were included in all further structure factor calculations; the C-H distance was taken as 1.0 Å, and the temperature factor of each hydrogen atom was set equal to that of the overall temperature factor of the group to which it belonged. Two final cycles of least-squares refinement, in which individual isotropic thermal parameters were assigned to each carbon atom of the phenyl rings, reduced R and R_w to 0.050 and 0.062. In the final cycle no parameter shifted by more than $\frac{1}{2}$ of its estimated standard deviation. The standard deviation of an observation of unit weight is 2.42. However, the relative correctness of the weighting scheme, judged by the variation of mean $\Sigma w \cdot \Delta^2$ with $\lambda^{-1} \cdot \sin\theta$ and $|F_o|$, is satisfactory. No extinction corrections were applied.

The positional and thermal parameters for all nongroup atoms are listed in Table 5, together with the associated standard deviations as estimated from the inverse matrix. In Table 6 are listed the positional and orientation parameters associated with the groups, and in Table 7 are given the derived positions for each of the group carbon

TABLE 6

GROUP POSITIONAL PARAMETERS FOR $\text{Pt}(\text{Cl}_2\text{C}=\text{CCl}_2)[\text{P}(\text{C}_6\text{H}_5)_3]_2$

Group	x_c^a	y_c	z_c	δ	ϵ	η
R _{1A}	0.3996(11)	-0.0935(6)	0.0910(7)	-2.857(10)	-2.861(14)	1.540(12)
R _{1B}	0.6164(13)	-0.0877(5)	0.4049(8)	-2.238(15)	2.325(14)	-1.335(15)
R _{1C}	0.0492(14)	-0.1209(6)	0.1639(7)	-2.430(19)	-2.363(10)	-2.919(17)
R _{2A}	0.5675(14)	0.1972(5)	0.1389(7)	1.444(11)	-2.946(13)	2.172(10)
R _{2B}	0.7747(11)	0.1881(5)	0.4431(7)	-0.564(14)	2.398(13)	-1.770(12)
R _{2C}	0.8404(12)	-0.0068(5)	0.3094(7)	-1.257(19)	-2.173(9)	2.651(18)

^a These group parameters have been defined previously (see ref. 9).

TABLE 7

DERIVED PARAMETERS OF GROUP CARBON ATOMS IN $\text{Pt}(\text{Cl}_2\text{C}=\text{CCl}_2)[\text{P}(\text{C}_6\text{H}_5)_3]_2$

Atom	x	y	z	$B_{\text{iso}}(\text{\AA}^2)$
R _{1A} C1	0.3826(21)	-0.0655(11)	0.1523(10)	7.4(7)
C2	0.4282(20)	-0.1305(9)	0.1494(11)	9.5(8)
C3	0.4452(20)	-0.1486(7)	0.0881(14)	9.9(8)
C4	0.4166(22)	-0.1016(12)	0.0297(11)	10.7(9)
C5	0.3711(20)	-0.0365(10)	0.0325(10)	9.7(8)
C6	0.3540(18)	-0.0185(7)	0.0938(13)	7.7(7)
R _{1B} C1	0.5050(19)	-0.0699(9)	0.3252(8)	7.2(7)
C2	0.6346(24)	-0.1045(9)	0.3438(11)	8.8(8)
C3	0.7460(17)	-0.1224(8)	0.4235(14)	7.7(7)
C4	0.7277(19)	-0.1056(9)	0.4846(8)	9.5(8)
C5	0.5981(25)	-0.0710(8)	0.4661(11)	10.0(8)
C6	0.4868(17)	-0.0531(8)	0.3864(14)	9.0(8)
R _{1C} C1	0.1825(18)	-0.0845(9)	0.1934(12)	6.3(6)
C2	0.1797(18)	-0.1355(10)	0.2400(8)	7.8(7)
C3	0.0464(26)	-0.1719(8)	0.2106(12)	9.2(8)
C4	-0.0842(18)	-0.1574(9)	0.1345(13)	9.6(8)
C5	-0.0814(18)	-0.1064(10)	0.0878(8)	10.0(8)
C6	0.0520(25)	-0.0700(8)	0.1173(11)	9.7(8)
R _{2A} C1	0.5814(25)	0.1564(7)	0.1990(10)	6.4(6)
C2	0.4407(18)	0.1843(9)	0.1402(12)	7.5(7)
C3	0.4267(17)	0.2251(8)	0.0801(10)	8.7(7)
C4	0.5535(26)	0.2380(8)	0.0788(10)	8.0(7)
C5	0.6943(19)	0.2101(9)	0.1375(13)	9.3(8)
C6	0.7082(16)	0.1693(9)	0.1977(10)	8.2(7)
R _{2B} C1	0.6917(17)	0.1562(9)	0.3681(8)	6.7(6)
C2	0.7873(21)	0.2100(9)	0.3814(11)	9.2(8)
C3	0.8703(17)	0.2419(7)	0.4564(13)	9.7(8)
C4	0.8576(18)	0.2201(9)	0.5180(9)	8.0(8)
C5	0.7620(21)	0.1663(9)	0.5048(10)	8.5(7)
C6	0.6791(17)	0.1344(7)	0.4298(12)	7.0(6)
R _{2C} C1	0.7386(18)	0.0437(7)	0.2971(11)	5.6(6)
C2	0.8636(21)	0.0291(8)	0.3750(9)	6.7(6)
C3	0.9655(15)	-0.0214(9)	0.3873(8)	7.6(7)
C4	0.9423(18)	-0.0573(7)	0.3218(12)	8.3(7)
C5	0.8172(21)	-0.0426(8)	0.2439(10)	8.1(7)
C6	0.7154(16)	0.0078(8)	0.2316(8)	7.3(7)

atoms, together with the associated isotropic temperature factors.

A comparison of $|F_o|$ and $|F_c|$ for the 404 reflections omitted from the refinement [$F_o^2 < 3\sigma(F_o^2)$] revealed six for which $|F_o^2 - F_c^2|$ lay between 3- and $5\sigma(F_o^2)$, all the others having $|F_o^2 - F_c^2| < 3\sigma(F_o^2)$. Thus these data are omitted from the final tabulation of structure amplitudes where we present the values of $10|F_o|$ and $10|F_c|$ (in electrons) for those reflections used in the refinements*.

* See footnote p. 137.

RESULTS AND DISCUSSION

The complexes of $(Cl_2C=CF_2)$ and $(Cl_2C=CCl_2)$ both exist as discrete molecules.

 $Pt(Cl_2C=CCl_2)[P(C_6H_5)_3]_2$

All intermolecular contacts are normal, the shortest being 2.53 Å between $R_{1C}H_3$ and $R_{2A}H_5$ atoms in adjacent molecules. Fig. 1 presents a drawing of the inner coordination sphere of the molecule, and Fig. 2 shows an overall view of the molecule, showing the numbering of all atoms. The 50% probability ellipsoids for thermal motion are displayed in both diagrams and listed in Table 8. Note that the chlorine atoms display considerably higher vibrational amplitudes than do the other atoms in the molecule. In Tables 9 and 10 we present relevant interatomic distances and angles.

The platinum atom has a planar coordination as in the TCNE complex. If one views the olefin as a monodentate ligand then the platinum is three-coordinate.

As in the TCNE and $ClFC=CF_2$ complexes, the olefin has lost its planar geometry on coordination to the metal, the chlorine atoms being bent back from the central metal atom. This is shown in Figs. 1 and 2.

The two central C atoms of the olefin are, within experimental error, equidis-

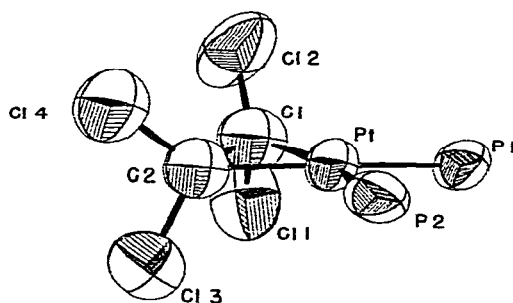


Fig. 1. The inner coordination about the Pt atom in $Pt(Cl_2C=CCl_2)[P(C_6H_5)_3]_2$. The 50% probability vibrational ellipsoids are shown.

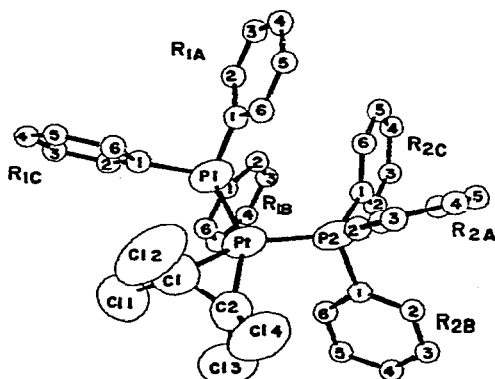


Fig. 2. The overall coordination in $Pt(Cl_2C=CCl_2)[P(C_6H_5)_3]_2$

TABLE 8

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å) FOR $\text{Pt}(\text{Cl}_2\text{C}=\text{CCl}_2)[\text{P}(\text{C}_6\text{H}_5)_3]_2$

Atom	Minimum	Intermediate	Maximum
Pt	0.232(2)	0.276(2)	0.349(2)
P(1)	0.249(10)	0.280(10)	0.360(10)
P(2)	0.230(10)	0.237(10)	0.377(10)
Cl(1)	0.315(11)	0.395(11)	0.553(13)
Cl(2)	0.290(12)	0.373(11)	0.633(14)
Cl(3)	0.346(11)	0.391(11)	0.465(12)
Cl(4)	0.306(11)	0.392(10)	0.479(11)

TABLE 9

SELECTED DISTANCES (Å) IN $\text{Pt}(\text{Cl}_2\text{C}=\text{CCl}_2)[\text{P}(\text{C}_6\text{H}_5)_3]_2$

<i>Bond distances</i>			
Pt-P(1)	2.292(7)	C(1)-Cl(1)	1.77(3)
Pt-P(2)	2.278(8)	C(1)-Cl(2)	1.69(3)
Pt-C(1)	2.02(3)	C(2)-Cl(3)	1.81(3)
Pt-C(2)	2.05(3)	C(2)-Cl(4)	1.73(3)
C(1)-C(2)	1.62(3)		
P(1)-R _{1A} Cl	1.78(1)	P(2)-R _{2A} Cl	1.82(1)
P(1)-R _{1B} Cl	1.82(2)	P(2)-R _{2B} Cl	1.82(1)
P(1)-R _{1C} Cl	1.84(2)	P(2)-R _{2C} Cl	1.84(2)
<i>Nonbonded distances</i>			
Pt...Cl(1)	3.267(10)	P(1)...P(2)	3.516(10)
Pt...Cl(2)	3.193(9)	P(1)...C(1)	3.43(3)
Pt...Cl(3)	3.289(9)	P(1)...C(2)	3.50(3)
Pt...Cl(4)	3.396(9)		

TABLE 10

SELECTED INTRAMOLECULAR ANGLES (°) IN $\text{Pt}(\text{Cl}_2\text{C}=\text{CCl}_2)[\text{P}(\text{C}_6\text{H}_5)_3]_2$

P(1)-Pt-P(2)	100.6(2)	Pt-C(1)-C(2)	67.4(1.5)
C(1)-Pt-C(2)	47.1(1.0)	Pt-C(2)-C(1)	65.6(1.5)
P(1)-Pt-C(1)	105.1(8)		
P(2)-Pt-C(2)	108.0(8)		
Pt-C(1)-Cl(1)	119.2(7)	Pt-C(2)-Cl(3)	117.2(1.4)
Pt-C(1)-Cl(2)	118.7(1.8)	Pt-C(2)-Cl(4)	127.8(1.6)
Cl(1)-C(1)-Cl(2)	115.6(1.9)	Cl(3)-C(2)-Cl(4)	105.9(1.9)
Cl(1)-C(1)-C(2)	112.4(2.1)	Cl(3)-C(2)-C(1)	115.8(1.9)
Cl(2)-C(1)-C(2)	113.9(2.1)	Cl(4)-C(2)-C(1)	120.3(2.0)
Pt-P(1)-R _{1A} Cl	117.6(7)	Pt-P(2)-R _{2A} Cl	111.5(8)
Pt-P(1)-R _{1B} Cl	105.9(6)	Pt-P(2)-R _{2B} Cl	110.1(4)
Pt-P(1)-R _{1C} Cl	118.8(6)	Pt-P(2)-R _{2C} Cl	124.7(6)
R _{1A} Cl-P(1)-R _{1B} Cl	109.9(8)	R _{2A} Cl-P(2)-R _{2B} Cl	105.7(7)
R _{1A} Cl-P(1)-R _{1C} Cl	97.8(8)	R _{2A} Cl-P(2)-R _{2C} Cl	100.7(7)
R _{1B} Cl-P(1)-R _{1C} Cl	106.2(7)	R _{2B} Cl-P(2)-R _{2C} Cl	102.4(7)

tant from the Pt atom. The mean Pt-C_{olefin} distance of 2.03(3) Å in this complex appears to be distinctly shorter than the mean Pt-C_{olefin} distance of 2.11(3) Å found in the analogous TCNE⁶ and ethylene¹⁷ complexes. Although taken by itself this result is below the level of significance, the evidence presented in this and the next paper will indicate that this phenomenon of short Pt-C(Cl) distances is a general feature.

Concomitant with the shorter Pt-C(Cl) distances, the chlorine atoms are pushed back further from the olefinic C atoms than are the CN groups in the TCNE complex⁶. A measure of this bending back is the mean value of (90° - β) where the angle β¹⁶ is defined in Table 11. The relevant values for the Cl₂C=CCl₂ and TCNE complexes are 40.6(3.0)° and 31.8°.

The value of 1.62(3) Å found for the length of the C(1)-C(2) bond seems suspiciously long, primarily because it exceeds that found for the central C-C bond length in either the Cl₂C=C(CN)₂ or the TCNE complex. This in some way may be connected with the observation that we could not successfully refine anisotropic thermal parameters for C(1) and C(2). Yet on a statistical basis the value of 1.62(3) Å is only marginally larger than that of 1.49(5) Å found in the TCNE complex⁶. However, the C-C bond is significantly longer than the value of 1.339(2)¹⁸ Å, found in the ethylene molecule and its derivatives.

The Pt-P distances of 2.292(7) Å and 2.278(8) Å are comparable with the corresponding values [2.291(9) and 2.288(8) Å] found in the TCNE complex⁶ and those (2.270 and 2.265 Å) found in the ethylene complex¹⁷.

TABLE 11

MISCELLANEOUS INTRA-PLANAR AND VECTOR-PLANE-NORMAL ANGLES (°) IN Pt(Cl₂C=CCl₂)[P(C₆H₅)₃]₂

Dihedral angles ^a		Vector-plane-normal angles ^b	
Pt...P(1)...P(2) } Pt...C(2)...C(1) }	12.3(1.5)	C(1)...C(2) } Pt...P(2)...P(1) }	78.1(1.5)
C(1)...Cl(1)...Cl(2) } C(2)-Cl(1)-Cl(3) }	81.3(2.2) ≡ α ^c	C(1)...C(2) } C(1)...Cl(1)...Cl(2) }	47.5(3.0) ≡ β ₁ ^c
Pt...C(1)...C(2) } C(1)...C(2)...Cl(1) }	113.5(2.0)	C(2)...C(1) } C(2)...Cl(4)...Cl(3) }	51.3(2.5) ≡ β ₂ ^c
Pt...C(1)...C(2) } C(1)...C(2)...Cl(2) }	112.6(2.1)		β _{av} = 49.4(3.0)}
Pt...C(1)...C(2) } C(1)...C(2)...Cl(3) }	109.8(1.7)		
Pt...C(1)...C(2) } C(1)...C(2)...Cl(4) }	120.9(2.0)		

^a Let the two groups of atoms be A(1)...A(2)...A(3) and B(1)...B(2)...B(3). Form vector V(1) from A(1) to A(2). Form vector V(2) from A(1) to A(3). Then normal to the plane of A(1)...A(2)...A(3) is parallel to V(1) × V(2). Form a similar normal to the plane of B(1)...B(2)...B(3). Then the dihedral angle is defined as the angle between the two normals. ^b Let the two groups of atoms be A(1)...A(2) and B(1)...B(2)...B(3). Form the vector V(1) from A(1) to A(2). Form the normal V(2) to B(1)...B(2)...B(3) as for the dihedral angles. Then the angle given here is between V(1) and V(2). ^c The angles α and β are defined as shown. They are measures of the bending back of the CX₂ planes from their "original" planar configuration. See ref. 16 for more details.

There appears, as in the TCNE complex, to be a slight twist in the coordination of the olefin to the metal. As shown in Table 11 the dihedral angle between the planes defined by Pt-P(1)-P(2) and Pt-C(2)-C(1) is $12.3(1.5)^\circ$. The deviations of the atoms from the weighted least-squares plane through atoms Pt, P(1), P(2), C(1), and C(2) are indicative of the same effect. The equation of this plane is $-2.262x - 2.880y + 18.439z - 3.468 \text{ \AA} = 0$. The displacements of these atoms from this plane are, respectively, $-0.001(1)$, $+0.012(7)$, $+0.001(7)$, $-0.073(33)$, and $+0.257(28) \text{ \AA}$. Thus C(2) is tilted considerably below the mean plane, and C(1), to a much lesser extent, is tilted above the plane. In this connection note that the Pt atom is not equidistant from all four chlorine atoms (see Table 9). Atom Cl(2) is displaced slightly towards Pt, while Cl(4) is displaced away from Pt. Thus there is a slight rotation about C(1)-C(2), perhaps as a result of nonbonded interactions between the eclipsed Cl atoms.

The P(1)-Pt-P(2) angles of $100.6(2)$ and $101.4(3)^\circ$ in the complexes of $\text{Cl}_2\text{C}=\text{CCl}_2$ and TCNE⁶ are strictly comparable, though the C(1)-Pt-C(2) angles are not comparable [$47.1(1.0)^\circ$ in C_2Cl_4 vs. $41.5(1.3)^\circ$ in TCNE].

The C-Cl bond lengths lie in the expected range¹⁹.

Pt(Cl₂C=CF₂)[P(C₆H₅)₃]₂

The results from this structural determination are dependent on the assumed position of the CF₂ group. For instance, in earlier refinements, when atom C(1) was allowed to refine away from the position in which it was finally fixed, then atom C(2) generally moved slightly nearer to the Pt atom, so that the Pt-C(2) distance was about 2.00 \AA . However, despite this dependence we consider the results merit discussion for several reasons:

(a). In all the previous refinements we have undertaken the five heavy atoms have varied very little from their final refined positions. This is also true of the phenyl groups, and, to a lesser degree, of the position of C(1). Moreover, the final *R* value of 0.061 for 2122 observed reflections is not unreasonable.

(b). This is the first complex in which rotational disorder about the C-C bond has been observed, although the evidence for rotation of an alkene about the



bond in solution²⁰ is well documented.

The overall geometry of this complex is the same as that of the $\text{Cl}_2\text{C}=\text{CCl}_2$ and other such complexes, the substituents attached to the olefinic C atoms being pushed away from the central metal atom. Selected interatomic distances and angles are listed in Table 13 and the root-mean-square amplitudes of vibration of the heavy atoms in Table 12. As appears to be typical in such complexes the Cl atoms exhibit the largest vibrations.

As shown in Table 13 the Pt-P distances of $2.303(6)$ and $2.314(5) \text{ \AA}$ and the P(1)-Pt-P(2) angle of $103.4(2)^\circ$ are very similar to those found in the TCNE complex and C_2Cl_4 complexes. The Pt-C(1) distance of $2.05(3) \text{ \AA}$ does not differ from the mean value of $2.03(3) \text{ \AA}$ found in the $\text{Cl}_2\text{C}=\text{CCl}_2$ complex. The Pt...Cl distances of $3.296(8)$ and $3.279(8)$ are also comparable with those found in the $\text{Cl}_2\text{C}=\text{CCl}_2$ compound.

The weighted least-squares plane through atoms P(1), Pt, P(2) and C(1) has

TABLE 12

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (Å) IN Pt(Cl₂C=CF₂)[P(C₆H₅)₃]₂

Atom	Minimum	Intermediate	Maximum
Pt	0.226(2)	0.241(2)	0.315(2)
P(1)	0.236(8)	0.255(8)	0.321(8)
P(2)	0.234(8)	0.249(7)	0.323(8)
Cl(1)	0.271(10)	0.392(10)	0.561(12)
Cl(2)	0.315(9)	0.398(9)	0.473(10)

TABLE 13

SELECTED DISTANCES (Å) AND INTRAMOLECULAR ANGLES (°) IN Pt(Cl₂C=CF₂)[P(C₆H₅)₃]₂

<i>Bond distances</i>			
Pt-P(1)	2.303(6)	C(1)-Cl(1)	1.77(3)
Pt-P(2)	2.314(5)	C(1)-Cl(2)	1.68(3)
Pt-C(1)	2.05(3)		
P(1)-R _{1A} Cl	1.85(1)	P(2)-R _{2A} Cl	1.84(1)
P(1)-R _{1B} Cl	1.84(1)	P(2)-R _{2B} Cl	1.81(1)
P(1)-R _{1C} Cl	1.86(2)	P(2)-R _{2C} Cl	1.85(1)
<i>Nonbonded distances</i>			
Pt...Cl(1)	3.296(8)	P(1)...P(2)	3.625(8)
Pt...Cl(2)	3.279(8)	P(1)...C(1)	3.28(3)
<i>Angles</i>			
P(1)-Pt-P(2)	103.4(2)	Pt-C(1)-C(1)	119.0(1.5)
P(1)-Pt-C(1)	97.5(7)	Pt-C(1)-Cl(2)	122.7(1.5)
		Cl(1)-C(1)-Cl(2)	118.0(1.6)
Pt-P(1)-R _{1A} Cl	108.4(5)	Pt-P(2)-R _{2A} Cl	115.5(5)
Pt-P(1)-R _{1B} Cl	112.4(4)	Pt-P(2)-R _{2B} Cl	114.3(5)
Pt-P(1)-R _{1C} Cl	123.9(6)	Pt-P(2)-R _{2C} Cl	114.2(5)
R _{1A} Cl-P(1)-R _{1B} Cl	106.1(8)	R _{2A} Cl-P(2)-R _{2B} Cl	106.4(7)
R _{1A} Cl-P(1)-R _{1C} Cl	103.3(6)	R _{2A} Cl-P(2)-R _{2C} Cl	101.7(7)
R _{1B} Cl-P(1)-R _{1C} Cl	101.2(7)	R _{2B} Cl-P(2)-R _{2C} Cl	103.3(6)

the equation $-1.664x + 13.988y + 10.589z + 3.497 \text{ Å} = 0$. The displacements of the atoms from this plane are, respectively, $-0.001(5)$, $+0.000(1)$, $-0.001(5)$, and $-0.039(27) \text{ Å}$.

Discussion

The overall Pt-P distances and P-Pt-P angles in the three complexes discussed in this paper are comparable with those in the TCNE⁶ complex. The Pt...Cl distances in the Cl₂C=CCl₂ and Cl₂C=CF₂ structures also agree very closely. The Pt-C(Cl) distances of 2.03(3) and 2.05(3) Å in these two structures do not differ significantly. However there is a distinct suggestion that the Pt-C distance is shorter than in the TCNE⁶ and ethylene¹⁷ complexes [2.11(3) Å]. Consistent with this shortening of the Pt-C(Cl) bond length, the Cl atoms appear to be pushed further back from the Pt atom than do the CN groups in the TCNE complex. This is discussed in the following paper.

It has been fairly well established (certainly in the case of Fe and Co derivatives)²¹ that a metal-perfluoroalkyl bond is significantly shorter (0.06–0.07 Å) than the analogous metal-alkyl linkage. This has been ascribed²² to a combination of strengthened σ -bonding and d_{π} - σ^* back donation enhanced by the greater electron-withdrawing power of the F atoms. As far as we know no one has yet obtained any structural information on a M-CCl₃ bond. However, if one follows the above argument, then this distance is a function of the electron-withdrawing powers of the alkyl substituents, and so the bond lengths should follow the trend M-CF₃ < M-CCl₃ < M-CH₃.

It is interesting that in a recent X-ray analysis of *trans*-Ni(σ -C₆Cl₅)(σ -C₆F₅)(PPh₂Me)₂²³ it was found that the Ni-C₆Cl₅ distance of 1.905(10) Å is significantly shorter than the Ni-C₆F₅ distance of 1.987(9) Å. In view of our results we suggest there is a case for examining the relative effects of CF₃ vs. CCl₃ groups, rather than merely assuming effects for CCl₃ groups intermediate between those of CF₃ and CH₃.

Although we have been unable to refine the disorder of the CF₂ group in the Cl₂C=CF₂ structure there is no question as to the existence of rotational disorder about the C-C bond. This disorder is illustrated approximately in Fig. 3. Such disorder

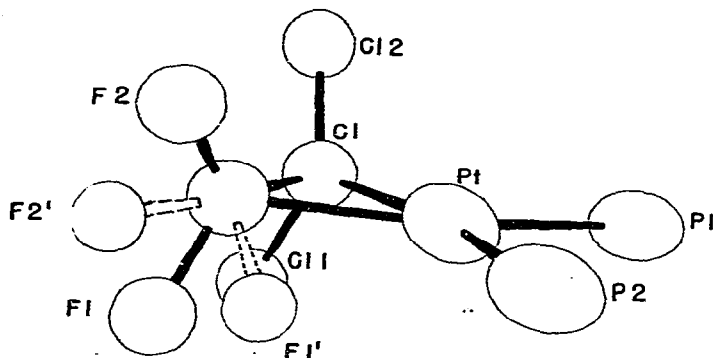
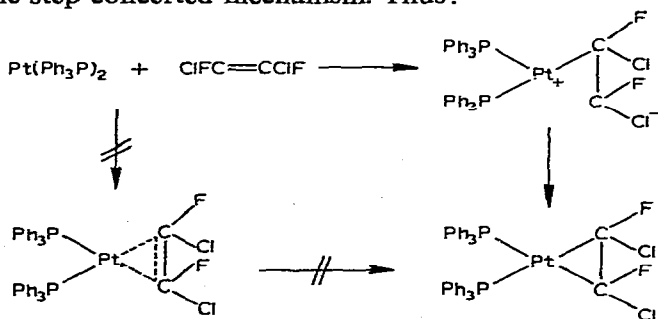


Fig. 3. The inner coordination about the Pt atom in Pt(Cl₂C=CF₂)[P(C₆H₅)₃]₂ illustrating the rotational disorder of the CF₂ group about the C-C bond.

is not inconsistent with the proposed mechanism of formation of such complexes. Ashley-Smith, Green, and Wood²⁴ have suggested that the addition of *cis*/*trans*-ClFC=CClF to bis(triphenylphosphine)stilbeneplatinum proceeds as a polar, two-step, cyclo-addition reaction, with formation of a dipolar intermediate, rather than by a one-step concerted mechanism. Thus:



If such a dipolar intermediate were formed during the addition of $\text{Cl}_2\text{C}=\overset{\ominus}{\text{C}}\text{F}_2$, then one would expect the negative charge to be located on the C atom to which were attached the more electron-withdrawing group, *e.g.*, the CF_2 group. Such an intermediate would then exist for a sufficient time to allow some rotation about the C-C bond before ring closure.

ACKNOWLEDGEMENT

We are indebted to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their support of this research.

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