Journal of Organometallic Chemistry, 235 (1982) 375—381
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE LOW TEMPERATURE X-RAY DIFFRACTION STUDY OF A TRIGONAL PLANAR, MIXED OLEFIN, COMPLEX OF PLATINUM(0): $[\mathrm{Pt}\{\mathrm{P(C_6H_{11})_3}\}(\mathrm{C_2H_4})(\mathrm{C_2F_4})]$

JUDITH A.K. HOWARD, PACHANEE MITRPRACHACHON and ARNO ROY
Department of Inorganic Chemistry, The University, Bristol, BS8 1TS (Great Britain)

(Received April 5th, 1982)

Summary

The structure of the title compound has been solved from 5342 corrected intensities, R (R') 0.067 (0.068), and confirms the trigonal planar coordination of the three ligands to platinum, with mean Pt—C(H) and Pt—C(F) separations of 2.027(10) and 2.173(9) Å. The crystals belong to the monoclinic space group $P2_1/a$ with $Z = 4$ in a unit cell, a 11.634(3), b 17.684(7), c 12.137(5) Å; β 108.59(3)° at 200 K. The variations in Pt—C and C═C distances are discussed with reference to related compounds.

Introduction

The discovery of trisethylene platinum [1,2] has led to a rapid expansion of platinum(0) chemistry [3]. Our investigations of the simple olefin complexes, namely, $[\mathrm{Ft(C_2H_4)_3}]$ [1,2], $[\mathrm{Pt(C_7H_{10})_3}]$ [5], and $[\mathrm{Pt(C_2H_4)_2(C_2F_4)}]$ [1,4] were extended to consider the effects of introducing ligands with increased electron donating capacity, such as tertiary phosphines. The title compound provides an excellent combination of three different ligands, of which two are non-equivalent olefins. The synthesis and chemistry of these 16 e platinum(0) complexes $[\mathrm{PPtL_2}]$ have been discussed previously [6]. The compounds show dynamic behaviour in solution with rotation of the olefin ligands, the barrier to which has been shown to be lowered for the remaining ethylene when tetrafluoroethylene replaces one ethylene ligand in $[\mathrm{PPt(C_2H_4)_2}]$ [*]. Thus, in this study the structural changes which accompany an exchange of olefin ligands are investigated in detail.

---

[*] P ≡ tertiary phosphine.

0022-328X/82/0000—0000/$02.75 © 1982 Elsevier Sequoia S.A.

Experimental

The air stable, yellowish-white crystals grown from hexane/CH_2Cl_2 for the X-ray study were prepared [6] by the reaction of tetrafluoroethylene with $[(PCy_3)Pt(C_2H_4)_2]$. The crystal quality was unfortunately poor and some positional disorder has been observed in the solid state. The resultant molecular parameters, therefore, do not show the increased precision we had hoped to obtain by reducing the temperature of the sample to 200 K.

Crystal data are given in Table 1. Diffracted intensities (7643) were collected as described previously [7] using a Syntex P2$_1$ automated four-circle diffractometer and the parameters in Table 1. Corrections were applied for Lorentz, polarisation and X-ray absorption effects and the structure solved by Patterson and Fourier methods. Full matrix least squares refinement was carried out using anisotropic thermal parameters for the Pt, P, F and C atoms of the olefin ligands, isotropic temperature factors for all cyclohexyl carbon atoms, and a common, fixed, isotropic parameter for all hydrogen atoms. Scattering factors were taken from ref. 8 for Pt, ref. 9 for P, C and F, and ref. 10 for H, with the corrections for anomalous dispersion effects from Volume IV [8].

Rather high temperature factors for some of the cyclohexyl carbon atoms led to the trial of various disordered models, but reliable resolution of this positional disorder and subsequent refinement was possible for only one ring [C(6*n*)]. It also seemed likely, from a consideration of the thermal and molecular parameters, that the tetrafluoroethylene ligand could be disordered, through a librational motion about the midpoint C=C to Pt axis, but again alternative C, or F sites were not resolvable.

Evidence for the positions of the ethylene hydrogen atoms was surprisingly strong, and their contributions, together with those for the calculated positions of the cyclohexyl hydrogen atoms, were included in subsequent structure factor calculations, but neither their positional nor thermal parameters were

TABLE 1

CRYSTAL DATA FOR $[Pt\{P(C_6H_{11})_3\}(C_2H_4)(C_2F_4)]$

Molecular weight	599.6
Space group	$P2_1/a$
a (Å)	11.634(3)
b	17.684(7)
c	12.137(5)
β°	108.59(3)
U (Å^3)	2367(2)
Z	4
F(000)	1192
λ(Mo-K_α)	0.710 69
μ (cm^{-1})	61.3
Independent data used	5342
2θ |max|°	60
Temperature (K)	200
D_c (ambient) g cm^{-3}	1.58
$I > n\sigma(I)$; n	2

TABLE 2

FINAL ATOMIC POSITIONAL (FRACTIONAL COORDINATES) PARAMETERS FOR $[\mathrm{Pt}\{\mathrm{P}(\mathrm{C_6H_{11}})_3\}(\mathrm{C_2H_4})(\mathrm{C_2F_4})]$ WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z
Pt	0.02871(3)	0.01633(2)	0.29549(3)
P	0.1654(2)	0.1041(1)	0.2631(2)
F(11)	−0.1643(5)	0.1278(4)	0.2717(6)
F(12)	−0.1795(5)	0.0805(4)	0.1023(5)
F(21)	−0.1995(7)	−0.0082(4)	0.3519(5)
F(22)	−0.2062(6)	−0.0591(4)	0.1848(6)
C(1)	−0.1344(9)	0.0672(5)	0.2252(8)
C(2)	−0.1490(10)	−0.0081(6)	0.2659(9)
C(3)	0.0725(10)	−0.0873(5)	0.3948(9)
C(4)	0.1777(10)	−0.0574(5)	0.3908(8)
C(51)	0.0878(9)	0.1634(5)	0.1344(8)
C(52)	0.0408(11)	0.1173(7)	0.0179(10)
C(53)	−0.0448(12)	0.1660(7)	−0.0749(12)
C(54)	0.044(2)	0.237(1)	−0.099(2)
C(55)	0.065(2)	0.285(1)	0.026(2)
C(56)	0.159(1)	0.2346(9)	0.117(1)
C(61)	0.3070(9)	0.0611(6)	0.2555(9)
C(62)	0.2838(11)	0.0022(6)	0.1516(11)
C(63)	0.399(2)	−0.046(1)	0.181(1)
C(641) [a]	0.503(2)	0.000(1)	0.171(1)
C(642) [a]	0.493(5)	0.035(3)	0.133(4)
C(651) [a]	0.532(2)	0.063(1)	0.278(2)
C(652) [a]	0.522(3)	0.096(1)	0.232(3)
C(66)	0.4081(13)	0.1160(8)	0.2493(12)
C(71)	0.2164(8)	0.1745(5)	0.3841(7)
C(72)	0.2952(9)	0.1367(6)	0.4951(9)
C(73)	0.3359(10)	0.1961(6)	0.5948(9)
C(74)	0.2302(10)	0.2356(6)	0.6139(9)
C(75)	0.1495(10)	0.2735(6)	0.4998(10)
C(76)	0.1099(10)	0.2141(6)	0.4011(9)
H(31) [b]	0.0608	−0.0784	0.4723
H(32)	0.0177	−0.1283	0.3601
H(41)	0.2279	−0.0467	0.4691
H(42)	0.2214	−0.0507	0.3274

[a] Atom disordered between two sites (C(*nm*1) and C(*nm*2)) in the ratio (%) 65/35. [b] Ethylene hydrogen atomic positional parameters only are given. Those for all other hydrogen atoms are deposited.

refined. A weighting scheme of the form $W = [\sigma^2(F_o)]^{-1}$, was employed to give a reasonable weight analysis. $\sigma(F_o)$ is the estimated standard deviation in $[F_{obs}]$ based only on counting statistics. Final atomic positional parameters are given in Table 2 *, associated bond lengths and inter-bond angles in Table 3, with selected least squares planes in Table 4.

---

* All supplementary material viz. calculated and observed structure factors, hydrogen atom coordinates and associated parameters can be obtained from the author upon request.

TABLE 3

BOND LENGTHS (Å) AND INTERBOND ANGLES (°) FOR $[Pt\{P(C_6H_{11})_3\}(C_2H_4)(C_2F_4)]$: (200 K) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Distances		Angles	
Pt—P	2.343(2)	P—Pt—C(1)	103.3(3)
		P—Pt—C(2)	145.0(3)
Pt—C(1)	2.026(9)	P—Pt—C(3)	127.1(3)
Pt—C(2)	2.029(12)	P—Pt—C(4)	91.0(3)
C(1)—C(2)	1.45(2)	P—Pt—C(1,2) [a]	124.2
Pt—C(3)	2.163(9)	P—Pt—C(3,4) [a]	109.0
Pt—C(4)	2.183(9)	C(1)—Pt—C(2)	41.9(4)
C(3)—C(4)	1.35(2)	C(3)—Pt—C(4)	36.1(4)
Pt—C(1,2) [a]	1.894		
Pt—C(3,4) [a]	2.065	C(1,2)—Pt—C(3,4) [a]	126.8
C(1)—F(11)	1.31(1)	F(11)—C(1)—F(12)	104.8(7)
C(1)—F(12)	1.43(1)	F(11)—C(1)—C(2)	122.0(10)
		F(12)—C(1)—C(2)	117.5(8)
C(2)—F(21)	1.35(1)	F(21)—C(2)—F(22)	109.2(9)
C(2)—F(22)	1.34(1)	F(21)—C(2)—C(1)	113.1(10)
		F(22)—C(2)—C(1)	116.8(9)
C(3)—H(31) [b]	1.00		
C(3)—H(32) [b]	0.97		
C(4)—H(41) [b]	0.96		
C(4)—H(42) [b]	1.05		
P—C(51)	1.859(9)	C(51)—P—C(61)	113.1(8)
P—C(61)	1.843(12)	C(51)—P—C(71)	103.4(8)
P—C(71)	1.872(9)	C(61)—P—C(71)	104.4(8)
		Pt—P—C(51)	109.9(3)
		Pt—P—C(61)	113.6(3)
		Pt—P—C(71)	111.8(3)
C(51)—C(52)	1.57(1)	C(56)—C(51)—C(52)	110(1)
C(52)—C(53)	1.51(2)	C(51)—C(52)—C(53)	109(1)
C(53)—C(54)	1.61(3)	C(52)—C(53)—C(54)	105(1)
C(54)—C(55)	1.69(3)	C(53)—C(54)—C(55)	98(1)
C(55)—C(56)	1.56(2)	C(54)—C(55)—C(56)	103(1)
C(56)—C(51)	1.56(2)	C(55)—C(56)—C(51)	106(1)
C(61)—C(62)	1.59(2)	C(66)—C(61)—C(62)	108(1)
C(62)—C(63)	1.53(3)	C(61)—C(62)—C(63)	105(1)
C(63)—C(641) [c]	1.49(3)	C(62)—C(63)—C(641)	110(2)
C(63)—C(542) [c]	1.99(3)	C(62)—C(63)—C(642)	93(2)
C(641)—C(651) [c]	1.66(3)	C(63)—C(641)—C(651)	105(2)
C(642)—C(652) [c]	1.57(6)	C(63)—C(642)—C(652)	105(4)
C(651)—C(66) [c]	1.66(3)	C(642)—C(652)—C(66)	108(3)
C(652)—C(66) [c]	1.45(4)	C(641)—C(651)—C(66)	106(1)
C(66)—C(61)	1.55(2)	C(651)—C(66)—C(61)	105(1)

[a] Midpoint C(*n*,*m*) of line joining C(*n*) to C(*m*): positional parameter not refined. [b] No e.s.d. given for hydrogen atom parameters. Fixed contribution. [c] Partially disordered cyclohexyl C atoms.

Results and discussion

The structure consists of discrete molecules (Fig. 1) in which the platinum atom is essentially coplanar with the four olefinic carbon atoms and with the

TABLE 4

SELECTED LEAST SQUARE PLANES FOR $[Pt\{P(C_6H_{11})_3\}(C_2H_4)(C_2F_4)]$ IN THE FORM $px + qx + rz = s$ (where x, y and z are fractional co-ordinates)

Plane descriptions	p	q	r	s
(1) Pt, C(1), C(2)	−2.779	6.611	11.234	3.348
(2) Pt, C(3), C(4)	−2.171	9.028	10.378	3.152
(3) Pt, P, C(1), C(2), C(3), C(4)	−2.653	8.308	10.693	3.248
(4) C(1), F(11), F(12)	10.518	7.626	−3.045	−1.594
(5) C(2), F(21), F(22)	6.063	−12.438	3.545	0.140
(6) C(3), H(31), H(32)	7.219	−11.708	2.434	2.506
(7) C(4), H(41), H(42)	−3.083	16.923	−0.336	−1.651

Maximum deviation from plane (3) observed for C(1) and C(2) ±0.07 Å

Angles between planes |1|—|2| 9°
|4|—|5| 79°
|6|—|7| 32°

phosphorus atom of the phosphine ligand (Table 4), thus providing a further example of this predicted geometry [11].

The Pt—C separations (2.027 and 2.173 Å) can be compared with the equivalent ones of $[Pt(C_2H_4)_2(C_2F_4)]$ where the mean Pt—C(F) and Pt—C(H) are 2.031 Å and 2.229 Å respectively. In the aforementioned compound and also in $[Pt(C_2H_4)(PCy_3)$ (Duroquinone)] [12], the olefin has been observed to be asymmetrically bound to Pt, with significant differences in Pt—C separations. The parameters from the more recent study of $[Pt(C_2H_4)(PCy_3)$(Duroquinone)],

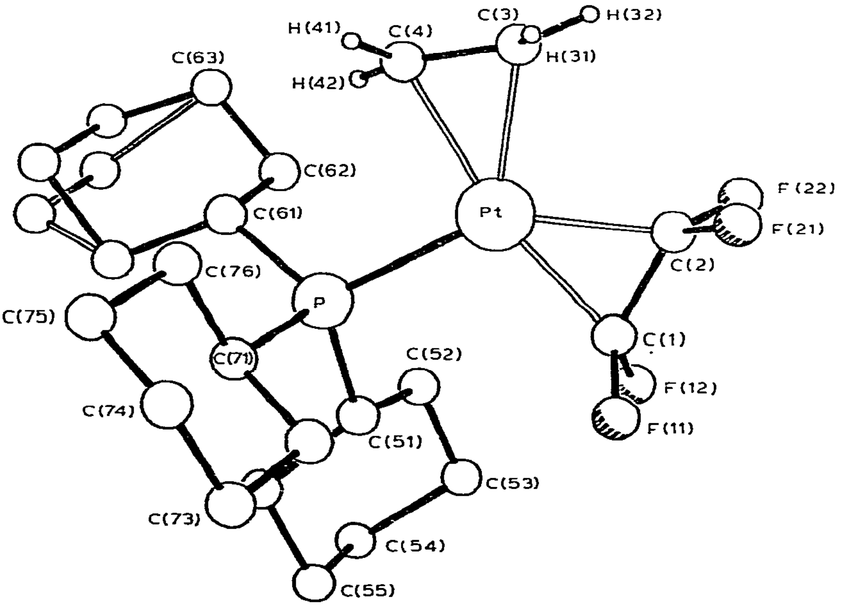
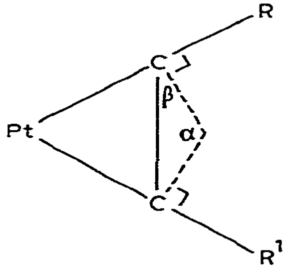


Fig. 1. The structure of $[Pt\{P(C_6H_{11})_3\}(C_2H_4)(C_2F_4)]$.

another example of three different ligands attached to platinum with the same trigonal planar geometry, suggests that perhaps such an arrangement might be observed herein, the inequivalence of the Pt—C distances arising from the positions of the olefinic carbon atoms relative to phosphine and the CF_2 moiety of the tetrafluoroethylene, each of which has different π donor/acceptor characteristics from ethylene itself. Unfortunately the quality of the data and the resultant accuracy of the molecular parameters, means that the difference in the Pt—C distances observed for the title compound (Δ = 0.002 Å) is not significant (e.s.d. 0.009 Å).

The Pt—P bond length of 2.343(2) Å is slightly longer than that in the duroquinone complex, viz.: 2.327(1) Å, whereas we might have predicted the reverse result, given that tetrafluoroethylene is a stronger π acceptor than duroquinone, an assumption supported by the closer Pt—C interaction and longer C═C distances, 2.027(10), 1.45(2) Å and 2.151(4), 1.432(6) Å respectively. The difference between the Pt—C(H) in both compounds is less significant, 2.173(9) cf. 2.169(6) Å, similarly for the corresponding C═C values of 1.35(2) and 1.398(8) Å.

The degree of bend back at the coordinated carbon atom of the substituent atoms, given by the parameters α and β, as designated by Ibers [13] (I) are 32°, 77.5° for the ethylene and 79° and 50.6° for the tetrafluoroethylene ligands respectively. The corresponding values in $[Pt(C_2H_4)_2(C_2F_4)]$ are 32°, 74° and 70.4, 54.8°. α which increases from zero on coordination, whilst β decreases from 90°, does so with an increase in the electronegativity of the substituent atoms and hence the ligated carbon atoms approach a more tetrahedral geometry for the CF_2 moiety.



(I)

The reduction in the barrier to rotation of the remaining ethylene ligand when one (C_2H_4) in $[Pt(C_2H_4)_2(P)]$ was replaced by (C_2F_4), calculated to be approximately 3 kcal mol^{-1} from the NMR data [6], is supported by the molecular geometry observed herein. The shorter Pt—C(F) and longer C═C(F) distances reflect a higher π donor and π^* acceptor capacity of (C_2F_4) relative to (C_2H_4), hence a higher barrier to rotation of the former. In the title compound, two environmentally distinct (CF_2) groups are observed in the ^{19}F NMR spectrum. A similar difference in rotational ability of (C_2F_4) versus (C_2H_4) has been reported previously for $[(C_5H_5)Rh(C_2H_4)(C_2F_4)]$ [14].

Acknowledgments

The authors wish to acknowledge The Amilia Earhart Foundation for a grant to P. Mitrprachachon and Dr. J.L. Spencer for a crystalline sample.

References

1 M. Green, J.A.K. Howard, J.L. Spencer and F.G.A. Stone, J. Chem. Soc., Chem. Commun., (1975) 449.
2 J.L. Spencer, Inorganic Synthesis Vol. XIX, 213.
3 F.G.A. Stone, Inorg. Chim. Acta, (1981) 33.
4 J.A.K. Howard, Abstracts XIth I.U. Cr. (Warsaw), 1978.
5 M. Green, J.A.K. Howard, J.L. Spencer and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1977) 271.
6 N.C. Harrison, M. Murray, J.L. Spencer and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1978) 1337.
7 A. Modinos and P. Woodward, J. Chem. Soc., Dalton Trans., (1974) 2065.
8 Volume IV. International Tables for X-ray Crystallography (1975). Kynoch Press, Birmingham, U.K.
9 D.T. Cromer and J.B. Mann, Acta Crystallogr. A24, (1968) 321.
10 R.F. Stewart, E. Davidson and W. Simpson, J. Chem. Phys., 42 (1965) 3175.
11 R. Hoffmann and N. Rösch, Inorg. Chem., 13 (1974) 2656.
12 M. Chetcuti, J.A. Herbert, J.A.K. Howard, M. Pfeffer, J.L. Spencer and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1981) 284.
13 J.A. Ibers and J.K. Stalick, J. Am. Chem. Soc., 92 (1970) 5333.
14 L.J. Guggenberger and R. Cramer, J. Am. Chem. Soc., 94 (1972) 3779.