Contribution from the Department of Chemistry, University of Western Ontario, London, Ontario, Canada

Crystal and Molecular Structure of Tetramethylcyclobutadienetrifluoromethylbis(dimethylphenylphosphine)platinum(II) Hexafluoroantimonate

D. B. CRUMP and N. C. PAYNE*

Received January 3, 1973

A single-crystal X-ray diffraction study of the compound $[(C_4(CH_3)_4)CF_3Pt(P(CH_3)_2C_6H_5)_2]SbF_6$, tetramethylcyclobutadienetrifluoromethylbis(dimethylphenylphosphine)platinum(II) hexafluoroantimonate, shows that it crystallizes in the monoclinic space group $P2_1/c$, with unit cell dimensions $a = 8.622$ (6), $b = 18.359$ (13), $c = 20.323$ (13) Å, and $\beta = 102.97$ (8)°; d(measd) = 1.871 (1) g cm^{-3} and d(calcd) = 1.869 g cm^{-3} for $Z = 4$. A three-dimensional structure determination was based upon 2866 observed reflections measured on a four-circle diffractometer. Refinement by full-matrix least-squares methods on F gave a conventional R factor of 0.049. Assuming tetramethylcyclobutadiene to be a monodentate ligand, the angles P–Pt–P = 95.2 (1)° and P–Pt–C = 98.7 (5) and 93.0 (5)° would indicate a distorted tetrahedral geometry about the platinum atom. This is an unusual geometry for a tetracoordinate Pt(II) complex, and the ambiguity in assigning a formal oxidation state to platinum in this compound is discussed. The cyclobutadiene ring is square planar, within the accuracy of the experiment, with a mean C–C bond length of 1.47 (2) Å. The fourfold axis of the cyclobutadiene ring is approximately coincident with the pseudo-threefold axis of the platinum atom. The substituent methyl carbon atoms are bent out of the plane of the cyclobutadiene ring away from the platinum atom an average of 14 (1)°, and the mean distance between the Pt atom and the four carbon atoms in the substituted cyclobutadiene ring is 2.220 (48) Å. The hexafluoroantimonate anion is disordered about two positions and has been refined as two rigid groups with octahedral symmetry and antimony–fluorine bond lengths of 1.83 Å.

Introduction

The chemistry of Pt(II) is characterized by the formation of four-coordinate square-planar complexes, with the metal atom having 16 electrons in the valence shell. Chisholm and Clark,[1] in a series of experiments on cationic Pt(II) complexes, found that the trifluoromethylbis(dimethylphenylphosphine)platinum(II) cation reacted with 2 mol of dimethylacetylene to give a tetramethylcyclobutadiene complex. Their evidence for the formation of a cyclobutadiene complex is based upon elemental analysis, ^{1}H and ^{19}F nmr spectra, and the ir spectrum. The last showed peaks corresponding to those assigned to the tetramethylcyclobutadiene ligand in the complex $[C_4(CH_3)_4NiCl_2]_2$.[2]

Tetramethylcyclobutadiene, which has not been prepared as a free molecule, has a triplet ground state containing four electrons in π-type orbitals: two in an orbital of a_1 symmetry and one in each of two degenerate orbitals of e_g symmetry. The possibility of removing the inherent instability of this triplet ground state by bonding cyclobutadiene to a suitable metal led Longuet-Higgins and Orgel[3] to predict the existence of such complexes before any were prepared. All four electrons are usually regarded as being important in the synergic bonding between a cyclobutadiene moiety and a metal atom. Thus, regarding tetramethylcyclobutadiene as a four-electron neutral ligand, tetramethylcyclobutadienetrifluoromethylbis(dimethylphenylphosphine)platinum(II) hexafluoroantimonate is a Pt(II) complex with formally 18 electrons in the valence shell. Simple molecular orbital theory predicts that an 18-electron transition metal complex will not be square planar and that a pseudotetrahedral geometry is required to allow stable metal–ligand bonding.[4] The chemical evidence for the cyclobutadiene Pt(II) complex described before[1] confirms this prediction; in particular the ^{1}H and ^{19}F nmr parameters are in distinct contrast to the values normally associated with square-planar cationic Pt(II) complexes.[5]

In order to establish the geometry of this new Pt(II) complex and to examine the mode of attachment of the substituted cyclobutadiene ligand to the metal atom, a single-crystal X-ray study was undertaken, the preliminary results of which have appeared elsewhere.[6]

Experimental Section

A crystalline sample of $[(C_4(CH_3)_4)CF_3Pt(P(CH_3)_2C_6H_5)_2]SbF_6$ was prepared by Chisholm according to the published preparation.[1] The compound crystallizes as transparent yellow needles, elongated along [100]. Precession photographs of the hk(0–1) and h(0–1)l planes and Weissenberg photographs of the (0–2)kl planes, using Cu Kα radiation, showed that the systematic absences are $h0l$, l odd, and $0k0$, k odd. The unit cell parameters, $a = 8.622$ (6), $b = 18.359$ (13), $c = 20.323$ (13) Å, and $\beta = 102.97$ (8)°, were found by a least-squares refinement of the angular settings of 14 reflections with $14.5 < 2\theta < 26.6$, measured on a Picker four-circle diffractometer using Mo Kα_1 radiation (λ(Mo Kα_1) = 0.70926 Å). These results demonstrate unambiguously that the space group is $P2_1/c$ (No. 14; $C_{2h}{}^5$).[7] The density of the crystals, determined by flotation in a mixture of carbon tetrachloride and ethyl iodide, is 1.871 (1) g cm^{-3}. This is in good agreement with the value of 1.869 g cm^{-3} calculated on the basis of four molecular units per cell. There are no crystallographic symmetry conditions imposed upon the ions.

For data collection, a centric prismatic crystal of approximate dimensions 0.30 × 0.26 × 0.16 mm was chosen and mounted with the long dimension [100] nearly parallel to the diffractometer ϕ axis. An optical examination identified the crystal faces as (120) and ($\bar{1}$20) and the forms {001} and {011}. The crystal was measured with a micrometer eyepiece in preparation for an absorption correction, for which μ(Mo Kα) = 54.4 cm^{-1}. ω scans of a number of intense reflections showed an average width at half-height of 0.075°, indicative of a reasonable crystal mosaicity.[8]

Intensities were measured on a Picker four-circle automatic diffractometer, using Nb-filtered Mo radiation. The takeoff angle of 1.2° provided 80% of the maximum Bragg peak intensity. The counter was placed 32 cm from the crystal, and the aperture was 4 × 4 mm. All reflections in the octants hkl and $hk\bar{l}$ with $2.5 < 2\theta < 45.0°$ were collected using the θ–2θ method with a sym-

---

(1) M. H. Chisholm and H. C. Clark, *J. Amer. Chem. Soc.*, 94, 1532 (1972).

(2) H. P. Fritz, *Advan. Organometal. Chem.*, 26, 285 (1971).

(3) H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1969 (1956).

(4) F. A. Cotton in "Chemical Applications of Group Theory," 2nd ed, Wiley, New York, N. Y., 1968.

(5) T. G. Appleton, M. H. Chisholm, H. C. Clark, and L. E. Manzer, *Inorg. Chem.*, 11, 1786 (1972).

(6) M. H. Chisholm, H. C. Clark, D. B. Crump, and N. C. Payne, *Can. J. Chem.*, in press.

(7) "International Tables for X-Ray Crystallography," Kynoch Press, Birmingham, England, 1969.

(8) T. C. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1957.

Table I. Final Atomic Positional and Thermal Parameters[a]

Atom	x	y	z	U_{11}[b]	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	0.18861 (6)	0.23297 (3)	0.01714 (3)	388 (3)	518 (3)	406 (3)	32 (2)	82 (2)	14 (1)
Sb	0.21278 (14)	−0.02404 (6)	0.33890 (6)	817 (6)	611 (4)	832 (8)	−29 (4)	305 (6)	39 (5)
P(1)	0.3528 (5)	0.1307 (2)	0.0164 (2)	547 (20)	566 (18)	528 (20)	86 (16)	111 (16)	33 (16)
P(2)	0.1873 (5)	0.2242 (2)	0.1337 (2)	607 (21)	739 (28)	495 (20)	77 (20)	187 (20)	57 (19)
F(1)	−0.1493 (10)	0.2132 (6)	0.0121 (6)	394 (54)	1316 (85)	1189 (84)	49 (53)	297 (56)	40 (67)
F(2)	−0.0412 (11)	0.1093 (6)	0.0054 (6)	690 (66)	991 (75)	1327 (93)	−276 (55)	−59 (60)	103 (65)
F(3)	−0.0899 (11)	0.1792 (6)	−0.0803 (5)	809 (72)	1628 (103)	726 (71)	−435 (68)	−167 (57)	−70 (66)
C(1)	−0.0340 (20)	0.1815 (10)	−0.0131 (9)	605 (120)	827 (128)	746 (128)	−127 (94)	−118 (99)	62 (97)
C(2)	0.3378 (17)	0.3135 (8)	−0.0254 (7)	637 (116)	659 (96)	437 (88)	84 (77)	105 (80)	98 (71)
C(3)	0.2444 (18)	0.3570 (7)	0.0120 (8)	715 (112)	461 (85)	762 (111)	63 (75)	279 (98)	68 (77)
C(4)	0.0989 (15)	0.3330 (8)	−0.0349 (7)	328 (87)	738 (95)	597 (94)	−16 (75)	157 (75)	−80 (75)
C(5)	0.1907 (17)	0.2895 (7)	−0.0733 (7)	590 (99)	620 (92)	517 (91)	116 (74)	75 (83)	62 (71)
C(6)	0.5088 (18)	0.3164 (9)	−0.0258 (8)	532 (114)	872 (132)	872 (125)	69 (80)	193 (89)	134 (92)
C(7)	0.2804 (18)	0.4153 (8)	0.0604 (8)	732 (112)	553 (91)	757 (110)	7 (81)	47 (84)	−15 (78)
C(8)	−0.0670 (17)	0.3636 (8)	−0.0480 (8)	557 (107)	834 (114)	659 (105)	223 (82)	59 (81)	68 (82)
C(9)	0.1647 (21)	0.2622 (8)	−0.1436 (8)	995 (134)	723 (101)	583 (101)	228 (90)	111 (92)	−15 (81)
C(10)	0.2930 (21)	0.0474 (8)	0.0522 (9)	921 (120)	570 (80)	996 (134)	57 (88)	194 (96)	106 (90)
C(11)	0.5572 (16)	0.1404 (9)	0.0628 (7)	361 (84)	1127 (125)	535 (95)	260 (79)	85 (74)	5 (83)
C(12)	0.1098 (25)	0.3036 (11)	0.1686 (9)	1336 (175)	1213 (152)	624 (115)	410 (132)	372 (118)	4 (116)
C(13)	0.0568 (19)	0.1535 (10)	0.1560 (8)	716 (112)	1086 (129)	645 (107)	−207 (96)	183 (90)	121 (92)
Group	x_g[c]	y_g	z_g	δ	ϵ	η	B, Å^2	α	
$F_6(1)$	0.21278 (14)	−0.02404 (6)	0.33890 (6)	1.616 (7)	−2.484 (6)	−0.553 (8)	12.06 (40)	0.73 (18)	
$F_6(2)$	0.21278 (14)	−0.02404 (6)	0.33890 (6)	3.990 (96)	−1.759 (18)	2.452 (94)	13.70 (120)	0.27 (6)	
Phenyl 1	0.3701 (9)	0.0831 (4)	−0.1332 (4)	2.005 (7)	−3.058 (7)	−1.835 (7)			
Phenyl 2	0.5340 (9)	0.1993 (4)	0.2281 (4)	−0.323 (7)	2.725 (7)	0.403 (8)			

[a] Estimated standard deviations in this and other tables are given in parentheses and correspond to the least significant digits. [b] $U_{ij} = B_{ij}/2\pi^2 a_i^* a_j^*$ (Å). The values have been multiplied by 10^4. The thermal ellipsoid is given by $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. [c] x_g, y_g, and z_g are the fractional coordinates of the group origin, defined in the case of the F_6 groups as the center of the octahedron formed by the fluorine atoms and for the phenyl groups as the center of the hexagon formed by the carbon atoms. δ, ϵ, and η (radians) are the group orientation angles: R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965). α is the multiplicity factor.

metric scan of 0.75°, corrected for dispersion, at a scan rate of 0.5°/min. Stationary 20-sec background counts were taken at the extremes of the 2θ scan. Coincidence losses were minimized for strong reflections by employing copper foil attenuators. Three standard reflections (200), (040), and (006) were recorded after every 100 observations to monitor the stability of the crystal and generator. Since no time-dependent trend was observed, all intensity measurements were put on a common scale without further correction.

A total of 4064 reflections with $(\sin\theta)/\lambda < 0.54$ were measured and the recorded intensities were corrected for background, Lorentz, and polarization effects. A standard deviation (σ) was calculated for each intensity from the formula

$$(\sigma(I))^2 = \text{count} + \tfrac{1}{4}(t_c/t_b)^2(b_1 + b_2) + (pI)^2$$

where $I = \text{count} - \tfrac{1}{2}(b_1 + b_2)(t_c/t_b)$ and "count" is the total count measured in time t_c. b_1 and b_2 are the background counts each measured in time t_b. The constant p was selected as 0.04.[9] Equivalent reflections were averaged to give a total of 3593 reflections of which the 2866 that had $I > 3\sigma(I)$ were used in the structure determination and refinement. Absorption correction trials using $\mu = 54.4$ cm^{-1} for Mo Kα radiation showed transmission factors varying from 0.28 to 0.49, so an absorption correction was applied during the course of the structure refinement.[10]

Structure Solution and Refinement

The position of the platinum atom was located from a three-dimensional Patterson synthesis. One cycle of full-matrix least-squares refinement on F, varying positional parameters, and an isotropic temperature factor, minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, led to agreement factors $R_1 = 0.45$ and $R_2 = 0.53$. The weight w is defined as $w = 4F_o^2/\sigma^2(F_o^2)$, $R_1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_2 = w(|F_o| - |F_c|)^2/\Sigma wF_o^2$. The atomic scattering factors for Pt, Sb, P, F, and C were taken from Cromer and Waber;[11] that of H was taken from Stewart, *et al.*[12] The values of F_c were corrected for the real and imaginary anomalous dispersion contributions of Pt, Sb, and P; the values are those of Cromer, *et al.*[13] A series of least-squares refinements and difference Fourier syntheses located all the 38 nonhydrogen atoms. The two phenyl rings and the fluorine atoms of the anion were treated as rigid groups, with D_{6h} and O_h symmetry, respectively. The phenyl ring C-C bond length was taken as 1.392 Å, and the Sb-F bond length in the anion as 1.83 Å.[14]

A refinement of the 20 individual atoms with isotropic temperature factors applied to all atoms except platinum and phosphorus, for which anisotropic temperature factors were used, and the 18 group atoms, including an overall thermal parameter for each group, gave residuals of $R_1 = 0.085$ and $R_2 = 0.107$. At this stage, anisotropic temperature factors were applied to all nongroup atoms except antimony. Individual isotropic temperature factors were included for all the group atoms, and one cycle of refinement of the atomic positional parameters of all atoms reduced R_1 to 0.06 and R_2 to 0.079. Difference Fourier syntheses calculated in the regions of the 24 methyl hydrogen atoms showed peaks in chemically reasonable positions, so the hydrogen atoms were included in the model. Idealized coordinates were used, assuming tetrahedral coordination about the carbon atoms and a C-H bond length of 1.09 Å. The contribution to F_c of the ten phenyl hydrogen atoms was also included, assuming idealized calculated positions (d(C-H) = 1.0 Å). One cycle of least-squares refinement including the contributions of the 34 hydrogen atoms lowered R_1 to 0.058 and R_2 to 0.077.

A total difference Fourier synthesis at this stage showed the principal residual peaks to be in the region of the SbF_6 anion. The antimony atom had been refined with an isotropic temperature factor up to this point, as it was considered to be in a spherically symmetric environment. However, two large peaks (~2.1 e Å^{-3}) in the vicinity of the antimony atom suggested than an anisotropic temperature factor would be more suitable. In addition, six peaks at the apices of an octahedron around the antimony atom were

---

(9) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

(10) The absorption correction was performed using the analytical method of de Meulewoer and Tompa in the program AGNOST as modified by D. Cahen and J. A. Ibers, *J. Appl. Crystallogr.*, 5, 298 (1972). Various local programs were used in the structure determination, but Patterson functions and Fourier syntheses were calculated using a version of Zalkin's FORDAP. Refinement and structure factor calculations were made with WOCLS, a version of Ibers' NUCLS. Errors in derived quantities were obtained from the Busing-Martin-Levy ORFFE, and drawings were made using Johnson's ORTEP.

(11) D. T. Cromer and J. H. Waber, *Acta Crystallogr.*, 18, 104 (1965).

(12) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

(13) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, 53, 1891 (1970).

(14) A. J. Edwards and G. R. Jones, *Chem. Commun.*, 1304 (1967).

Table II. Derived Atom Parameters

Group 1	x	y	z	Phenyl 1[a]	x	y	z	B, Å^2
F(1)	0.2909 (12)	−0.1074 (3)	0.3838 (5)	C(14)	0.3641 (13)	0.1036 (5)	−0.0679 (4)	4.8 (3)
F(2)	0.1346 (12)	0.0593 (3)	0.2940 (5)	C(15)	0.4969 (10)	0.1208 (6)	−0.0933 (5)	5.9 (4)
F(3)	0.0406 (8)	−0.0276 (5)	0.3775 (5)	C(16)	0.5028 (12)	0.1004 (7)	−0.1583 (6)	7.5 (4)
F(4)	0.3850 (8)	−0.0205 (5)	0.3003 (5)	C(17)	0.3761 (15)	0.0626 (7)	−0.1985 (4)	7.9 (5)
F(5)	0.1047 (10)	−0.0787 (5)	0.2680 (4)	C(18)	0.2433 (12)	0.0453 (6)	−0.1730 (5)	8.3 (5)
F(6)	0.3208 (10)	0.0306 (5)	0.4098 (4)	C(19)	0.2374 (11)	0.0657 (6)	−0.1081 (6)	6.9 (4)

Group 2	x	y	z	Phenyl 2	x	y	z	B, Å^2
F(1)	0.2040 (39)	−0.1229 (2)	0.3273 (17)	C(20)	0.3811 (10)	0.2099 (5)	0.1889 (5)	4.6 (3)
F(2)	0.2216 (39)	0.0749 (2)	0.3505 (17)	C(21)	0.4164 (12)	0.1476 (5)	0.2287 (6)	5.8 (4)
F(3)	0.2434 (38)	−0.0364 (18)	0.4302 (3)	C(22)	0.5684 (14)	0.1370 (5)	0.2676 (5)	7.7 (5)
F(4)	0.1821 (38)	−0.0117 (18)	0.2475 (3)	C(23)	0.6868 (10)	0.1886 (7)	0.2673 (6)	8.2 (5)
F(5)	−0.0027 (6)	−0.0218 (17)	0.3314 (16)	C(24)	0.6516 (11)	0.2510 (6)	0.2276 (6)	7.4 (4)
F(6)	0.4282 (6)	−0.0263 (17)	0.3464 (16)	C(25)	0.4996 (13)	0.2616 (4)	0.1886 (5)	5.8 (4)

Atom	x	y	z	Atom	x	y	z
H(6,1)[b]	0.541	0.273	−0.057	H(12,1)	0.185	0.354	0.161
H(6,2)	0.540	0.369	−0.045	H(12,2)	−0.011	0.317	0.142
H(6,3)	0.583	0.310	0.026	H(12,3)	0.120	0.300	0.222
H(7,1)	0.311	0.393	0.112	H(13,1)	−0.065	0.158	0.122
H(7,2)	0.376	0.448	0.051	H(13,2)	0.101	0.099	0.147
H(7,3)	0.173	0.450	0.056	H(13,3)	0.048	0.158	0.208
H(8,1)	−0.151	0.325	−0.081	H(15)	0.591	0.151	−0.064
H(8,2)	−0.104	0.368	0.000	H(16)	0.604	0.115	−0.178
H(8,3)	−0.073	0.415	−0.073	H(17)	0.384	0.047	−0.248
H(9,1)	0.049	0.232	−0.156	H(18)	0.151	0.015	−0.204
H(9,2)	0.154	0.308	−0.179	H(19)	0.139	0.051	−0.090
H(9,3)	0.258	0.226	−0.149	H(21)	0.327	0.108	0.227
H(10,1)	0.175	0.029	0.028	H(22)	0.594	0.089	0.297
H(10,2)	0.286	0.058	0.108	H(23)	0.800	0.181	0.298
H(10,3)	0.379	0.003	0.055	H(24)	0.739	0.291	0.230
H(11,1)	0.637	0.108	0.040	H(25)	0.472	0.309	0.161
H(11,2)	0.593	0.197	0.066				
H(11,3)	0.568	0.120	0.116				

[a] Phenyl 1 is bonded to P(1) through C(14), and phenyl 2 is bonded to P(2) through C(20). Carbon atoms are numbered sequentially around the ring. [b] A hydrogen atom is numbered by specifying the carbon atom to which it is bonded. If more than one hydrogen atom is bonded to a given atom, it is distinguished by a second number in parentheses. Thus H(10,2) is the second hydrogen atom bonded to C(10). For each hydrogen atom $B = 5$ Å^2.

clearly indicative of disorder in the fluorine positions of the anion. A second F_6 group was defined, and the subsequent least-squares cycles included a disorder parameter which refined the multiplicities of the two F_6 groups. The center of each group was constrained to be coincident with the position of the antimony atom and the appropriate constraints on the parameters and their derivatives were made. Refining the two F_6 groups with group temperature factors and with anisotropic temperature factors applied to all nongroup atoms, R_1 converged to 0.049 and R_2 to 0.063. The final value of the disorder parameter was 0.75 (1). A comparison of F_o and F_c values showed that secondary extinction was not significant. A difference Fourier synthesis computed from structure factors based on the final model contained eight peaks of electron density exceeding 1 e Å^{-3}; the two largest of these 1.7 (1) and 1.3 (1) e Å^{-3} at (0.0315, 0.2323, 0.0213) and (0.3280, 0.2319, 0.0), respectively, are associated with the Pt atom. The remaining six peaks are all in the vicinity of the anion fluorine atoms, suggesting that the disorder model used in the refinement is not a completely adequate description of the anion. A statistical analysis of the weighted R values of all reflections showed no unusual trends with $|F_o|$, indices, or $\lambda^{-1} \sin \theta$. The standard deviation of an observation of unit weight is 2.32 electrons.

The final positional and thermal parameters of the nongroup atoms are given in Table I, along with the positional and thermal parameters for the four rigid groups. The derived hydrogen atom positional parameters, the derived positional parameters and isotropic temperature factors for the phenyl carbon atoms, and the derived parameters of the anion fluorine atoms are given in Table II. The final values of $10|F_o|$ and $10|F_c|$ (in electrons) for those reflections used in the refinements are given in Table III.[15]

Table IV. Selected Bond Distances (Å) and Bond Angles (deg)

Pt-P(1)	2.354 (4)	P(1)-Pt-P(2)	95.2 (1)
Pt-P(2)	2.376 (4)	P(1)-Pt-C(1)	98.7 (5)
Pt-C(1)	2.103 (16)	P(2)-Pt-C(1)	93.0 (5)
Pt-C(2)	2.256 (14)	Pt-P(1)-C(10)	116.3 (6)
Pt-C(3)	2.335 (14)	Pt-P(1)-C(11)	115.8 (5)
Pt-C(4)	2.173 (14)	Pt-P(1)-C(14)	112.7 (4)
Pt-C(5)	2.114 (14)	C(10)-P(1)-C(11)	101.8 (8)
P(1)-C(10)	1.817 (16)	C(10)-P(1)-C(14)	103.2 (7)
P(1)-C(11)	1.811 (15)	C(11)-P(1)-C(14)	105.5 (7)
P(1)-C(14)	1.807 (10)	Pt-P(2)-C(12)	114.9 (6)
P(2)-C(12)	1.812 (18)	Pt-P(2)-C(13)	115.7 (5)
P(2)-C(13)	1.840 (16)	Pt-P(2)-C(20)	114.7 (4)
P(2)-C(20)	1.811 (10)	C(12)-P(2)-C(13)	99.8 (9)
C(1)-F(1)	1.35 (2)	C(12)-P(2)-C(20)	104.1 (7)
C(1)-F(2)	1.38 (2)	C(13)-P(2)-C(20)	106.0 (8)
C(1)-F(3)	1.34 (2)	Pt-C(1)-F(1)	113.4 (1.1)
C(2)-C(3)	1.46 (2)	Pt-C(1)-F(2)	116.4 (1.1)
C(3)-C(4)	1.46 (2)	Pt-C(1)-F(3)	113.4 (1.2)
C(4)-C(5)	1.47 (2)	F(1)-C(1)-F(2)	103.2 (1.4)
C(5)-C(2)	1.48 (2)	F(1)-C(1)-F(3)	105.8 (1.3)
C(2)-C(6)	1.48 (2)	F(2)-C(1)-F(3)	102.6 (1.3)
C(3)-C(7)	1.44 (2)	C(5)-C(2)-C(3)	90.7 (1.2)
C(4)-C(8)	1.50 (2)	C(2)-C(3)-C(4)	89.4 (1.1)
C(5)-C(9)	1.48 (2)	C(3)-C(4)-C(5)	91.4 (1.1)
		C(4)-C(5)-C(2)	88.5 (1.1)
		C(6)-C(2)-C(3)	130.5 (1.4)
		C(6)-C(2)-C(5)	135.7 (1.3)
		C(7)-C(3)-C(2)	134.6 (1.4)
		C(7)-C(3)-C(4)	133.7 (1.3)
		C(8)-C(4)-C(3)	130.1 (1.3)
		C(8)-C(4)-C(5)	135.7 (1.3)
		C(9)-C(5)-C(4)	135.5 (1.3)
		C(9)-C(5)-C(2)	130.9 (1.4)

Description of the Structure

The crystal structure can be considered as built up from

---

[15] Table III, a listing of structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 photocopy or \$2.00 for microfiche, referring to code number INORG-73-1663.

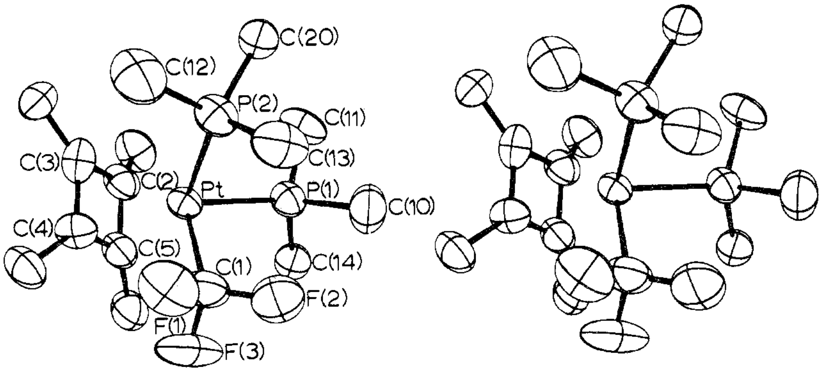


Figure 1. A stereoscopic view of the coordination environment of Pt in the molecule Pt(CF$_3$)(P(CH$_3$)$_2$C$_6$H$_5$)$_2$(C$_4$(CH$_3$)$_4$)SbF$_6$. For the sake of clarity only the phenyl α carbon atoms are included, and all hydrogen atoms have been omitted.

the packing of discrete ions, since the closest anion–cation interaction is 3.1 Å, between F(1,6) and C(3). The principal intramolecular bond lengths and angles are given in Table IV.

The inner coordination sphere of the platinum atom is shown in the stereo projection, Figure 1. If the cyclobutadiene fragment is assumed to be a monodentate ligand, with a formal bond between the platinum atom and the center of the ring, the overall geometry about the platinum can be regarded as distorted tetrahedral. This interpretation is supported by the pseudopyramidal arrangement of the three other ligands bonded to platinum, with angles P(1)-Pt-P(2) = 95.2 (1)°, P(1)-Pt-C(1) = 98.7 (5)°, and P(2)-Pt-C(1) = 93.0 (5)°.

The mean Pt-P bond length of 2.365 (4) Å is longer than the bonds usually found in Pt(II) square-planar phosphine complexes. However, the remainder of the phosphine geometry is as expected with mean P-C bond lengths of 1.816 (4) Å and the carbon atoms being somewhat compressed from tetrahedral geometry. The mean C-P-C bond angle is 103.4 (8)° compared with the mean Pt-P-C bond angle of 115.0 (5)°. A similar compression of substituents is observed in the CF$_3$ group, for which the mean F-C-F bond angle is 103.9 (1.2)° compared with the mean Pt-C-F bond angle of 114.4 (1.1)°. The mean C-F bond length is 1.36 (2) Å, and the Pt-CF$_3$ bond distance is 2.103 (16) Å.

The platinum atom is dissymmetrically bonded with respect to the carbon atoms of the cyclobutadiene ring. The Pt-C bond lengths vary from Pt-C(5) = 2.114 (14) Å to Pt-C(3) = 2.335 (14) Å, an overall difference of 0.22 (2) Å or 10σ. One explanation for this difference could involve a weak intramolecular hydrogen-bonding mechanism between the fluorine atoms of the trifluoromethyl group and the methyl hydrogen atoms bonded to C(4) and C(5). The distances C(8)-F(1) = 3.16 Å and C(9)-F(3) = 3.17 Å are both significantly less than the sum of the van der Waals radii[16] for a fluorine atom (1.35 Å) and a methyl group (2.0 Å) supporting at least a weak interaction. Alternatively, crystal packing forces may be responsible for the inequivalence of the Pt-ring C bonds. This interpretation is consistent with the observation that the angles subtended at the Pt atom by the center of the cyclobutadiene ring and P(1), P(2), and C(1) are 122 (1), 125 (1), and 116 (1)°, respectively. That is, the cyclobutadiene group is tilted closer to the trifluoromethyl group rather than the bulkier dimethylphenylphosphine ligands.

The dimensions of the cyclobutadiene fragment are shown in Figure 2. The mean C-C bond length of 1.47 (2) Å agrees with the values determined by other workers[17-21] for both the tetramethyl- and tetraphenylcyclobutadiene ligands (see Table V). The average ring C-C-C angle is 90.0 (1.1)° showing that the ring is planar within the precision of the experiment. The equation of the plane and the mean displacements of the ring and substituent methyl carbon atoms from the plane are given in Table VI. The methyl carbon atoms are bent out of the plane of the ring, away from the platinum atom, an average of 14.0 (1)°, and define a second plane whose equation is also given in Table VI.

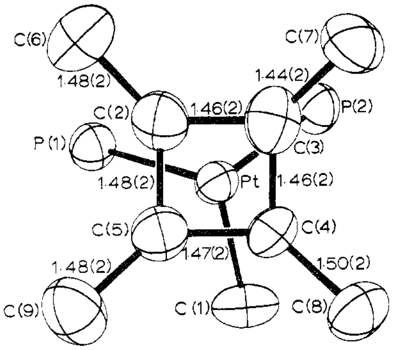


Figure 2. View down the cyclobutadiene C$_4$ axis. For the sake of clarity only the immediate coordination environment of Pt is included.

During the refinements, the SbF$_6$ anion was constrained to O_h symmetry, with the origin of each of the two groups constrained to be coincident with the antimony atom positional parameters. Thus all Sb-F bond lengths are 1.83 Å.

Discussion

The geometry about the platinum atom in this complex is unusual and as predicted is not square planar. In order to discuss the geometry, it is necessary to assign a formal coordination number to tetramethylcyclobutadiene. Two principal models are available. First, we regard the cyclobutadiene fragment as a monodentate ligand, in which case the structure can be described as distorted tetrahedral. This model is consistent with the large a$_1$ contribution to the metal-ligand bond which is suggested by the nmr results.[6] Second, cyclobutadiene could be regarded as three-coordinate, by analogy with cyclopentadienyl complexes, in which case the structure can be described as distorted octahedral.

(16) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 2nd ed, Interscience, New York, N. Y., 1967.

(17) I. D. Dunitz, H. C. Mez, O. S. Mills, and H. M. M. Shearer, *Helv. Chim. Acta*, 45, 647 (1962).

(18) E. F. Epstein and L. F. Dahl, *J. Amer. Chem. Soc.*, 92, 502 (1970).

(19) R. P. Dodge and V. Schomaker, *Acta Crystallogr.*, 18, 614 (1965).

(20) M. Mathew and G. J. Palenik, *Can. J. Chem.*, 47, 705 (1969).

(21) M. I. Davis and C. S. Speed, *J. Organometal. Chem.*, 21, 401 (1970).

Table V. Geometries of Cyclobutadiene Rings

Compd	Mean bond length, Å	Mean bond angle, deg	Bend-back angle, deg	Ref
$[Ni\{C_4(CH_3)_4\}Cl_2]_2 \cdot C_6H_6$	1.44 (2)	90	6.5	17
$[Fe(CO)_3(CH_3C_2CH_3)_2]Ni[C_4(CH_3)_4]$	1.463 (20)	90.0 (6)	7.3	18
$Fe(CO)_3(C_6H_5C_2C_6H_5)_2$	1.459 (17)	90.0 (1.0)	10.4	19
$[(Ph_4C_4)Mo(CO)_2Br]_2$ [a]	1.461 (13)	90.0		20
$(C_4H_4)Fe(CO)_3$ [a]	1.456 (15)	90.0		21
This work	1.47 (2)	90.0 (1.0)	14 (1)	

[a] Insufficient information to calculate bend-back angles.

Table VI

Plane of the Cyclobutadiene Ring and Displacement of the Methyl Carbons

Plane: C(2), C(3), C(4), C(5)

Equation: $1.677x + 14.44y - 12.50z = -5.413$

Plane atoms	Dist from plane, Å	Methyl carbons	Dist from plane, Å
C(2)	−0.002 (13)	C(6)	0.33
C(3)	0.002 (14)	C(7)	0.30
C(4)	−0.002 (14)	C(8)	0.33
C(5)	0.002 (14)	C(9)	0.44

Plane of the Methyl Carbons

Plane: C(6), C(7), C(8), C(9)

Equation: $1.672x + 14.76y - 12.02z = -5.851$

Plane atoms	Dist from plane, Å	Plane atoms	Dist from plane, Å
C(6)	−0.020 (16)	C(8)	−0.019 (15)
C(7)	0.021 (16)	C(9)	0.020 (16)

It is to be anticipated that the e-orbital contribution to the metal-ligand bond is sufficient to resolve the triplet ground state of cyclobutadiene. Invoking this π-type bonding is not inconsistent with the nmr observation that in solution above 60° the C_4Me_4 ring rotates about its local C_4 symmetry axis. The e orbitals are symmetric with respect to the metal-C_4Me_4 axis and so the barrier to rotation would be very low.

The formal oxidation state of the platinum atom is also uncertain. Although some chemical evidence has been reported demonstrating the existence of a salt of C_4^{2+},[22] and C_4^{2-} [23] as an intermediate, we prefer to regard cyclobutadiene as a neutral ligand. It is interesting to note that if the cyclobutadiene ligand were ionically bound as C_4^{2-}, the e orbitals would be filled, and if the local site symmetry of the ring were lower than C_{2v} the degeneracy of the e orbitals would be removed. In this situation a Jahn-Teller distortion of the square-planar ring would be expected, but there is no evidence for such a distortion either in this cyclobutadiene complex or in the structures reported by other workers.[17-21]

The free tetramethylcyclobutadiene molecule would be expected to be planar, and the loss of planarity observed when it is bonded to a metal atom can be explained in terms of the lessening of nonbonding intramolecular interactions. Alternatively, Kettle[24] has shown that the loss of overall planarity for substituted cyclic π-bonding ligands upon coordination to a transition metal is the logical outcome of the distortion of the σ-bonding framework of the ring. The large bend-back angles observed in this complex, 14 (1)°, are perhaps indicative of a large contribution of the a_1 ligand orbital to the overall metal-ligand bond.

The Pt-P bond lengths are long (2.365 (4) Å) in comparison with the values normally observed for Pt(II) square-planar complexes. Values found in these laboratories for Pt-P bond lengths in platinum-acetylene, -alkoxycarbene, and -alkylaminocarbene complexes are typically about 2.30 Å.[25-27] The average bond length is comparable with the mean value of 2.340 (8) Å determined by Albano, *et al.*,[28] in $[Pt(P(C_6H_5)_3)_3CO]$, formally a Pt(0) complex. Unfortunately, metal-phosphine phosphorus bond lengths appear very sensitive to the other coordinated ligands and are not necessarily indicative of the oxidation state of the metal.

Albano[28] described Pt-P bonding as a synergic process involving σ donation of electrons from the P atom to the Pt atom, and a d_π-d_π back-donation of electrons from the metal to the P atom. He suggested that the Pt-P bond lengths reflect the σ- and π-bonding properties of the remaining ligands. Tolman,[29] in studies of complexes of the type $[Ni(CO)_3X]$, where X is a triply connected phosphorus ligand, proposed that π back-bonding may not be a significant contribution to the Ni-P bond. Using this approach, tetramethylcyclobutadiene must be a very good σ donor, better than CO in *trans*-$[Cl(CO)Pt(P(C_2H_5)_3)_2]^+$ where the average Pt-P bond length is 2.34 Å[30] and considerably better than the substituents in *trans*-$[HClPt(P(C_6H_5)_2(C_2H_5))_2]$ and *trans*-$[HBrPt(P(C_2H_5)_3)_2]$ for which the Pt-P bond lengths are in the range 2.26-2.27 Å.[31,32]

However, we feel that a synergic bonding scheme, as proposed by Albano, is more consistent with the Pt-P bond length data presented here. For example, when the other ligands bonded to Pt are poor π acceptors, *e.g.*, H, Cl, and Br, the Pt-P bond may have a considerable π component accounting for the short bond lengths observed. The introduction of a substituent with both σ-donor and π-acceptor capabilities should therefore increase the Pt-P bond lengths. Thus, in a structural examination of *trans*-$[CH_3(CH_3C{\equiv}CCH_3)Pt(P(CH_3)_2(C_6H_5))_2]PF_6$ a mean Pt–P bond length of 2.302 (3) Å[25] was found. The geometry of the coordinated acetylene showed an 11 (3)° distortion from linearity and no significant increase in the C≡C bond length. This is consistent with the acetylene behaving as a poor yet significant π acceptor and as a σ donor. By contrast, the CO group can behave both as a good σ donor and as a good π acceptor, and the Pt-P bond lengths are significantly longer. The nmr evidence is consistent with tetramethylcyclobutadiene being a good σ donor and, moreover, it must behave as a π acceptor to resolve the triplet ground state and to remain uncharged. Thus long Pt-P bond lengths might be expected.

In summary, we feel that the molecule described herein is best considered as a complex of Pt(II), with a distorted tetrahedral geometry at the Pt atom. The bond between the substituted cyclobutadiene ligand and the Pt atom contains both an a_1 and an e component, but the structural and chemical evidences are consistent with a stronger a_1 compo-

---

[22] H. H. Freedman and A. E. Young, *J. Amer. Chem. Soc.*, 86, 734 (1964).

[23] J. S. McKennis, L. Brener, J. R. Schweiger, and R. Pettit, *Chem. Commun.*, 365 (1972).

[24] S. F. A. Kettle, *Inorg. Chim. Acta*, 1, 303 (1967).

[25] B. W. Davies and N. C. Payne, unpublished results.

[26] R. F. Stepaniak and N. C. Payne, *J. Organometal. Chem.*, in press.

[27] R. F. Stepaniak and N. C. Payne, unpublished results.

[28] V. G. Albano, G. M. B. Ricci, and P. L. Bellon, *Inorg. Chem.*, 8, 2109 (1969).

[29] C. A. Tolman, *J. Amer. Chem. Soc.*, 92, 2950 (1970).

[30] H. C. Clark, P. W. R. Corfield, K. R. Dixon, and J. A. Ibers, *J. Amer. Chem. Soc.*, 89, 3360 (1967).

[31] R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, 4, 773 (1965).

[32] P. G. Owston, J. M. Partridge, and J. M. Rowe, *Acta Crystallogr.*, 13, 246 (1960).

nent. However, such a description of this molecule and of other π-cyclic organometallic complexes is of dubious value, because of the limitations of the formal concepts of coordination number and oxidation state.

Registry No. $[(C_4(CH_3)_4)CF_3Pt(P(CH_3)_2C_6H_5)_2]SbF_6$, 39526-70-0.

Acknowledgment. We thank the National Research Council of Canada for financial support of this work.

Contribution from the Department of Chemistry,
The Ohio State University, Columbus, Ohio 43210

Trigonal-Bipyramidal and Square-Pyramidal Five-Coordinate Cobalt(II). Crystal and Molecular Structures of the Red and Green Isomers of Chlorobis[1,2-bis(diphenylphosphino)ethane]cobalt(II) Trichlorostannate(II)[1]

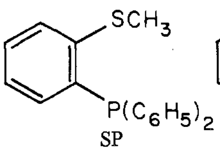
JUDITH K. STALICK,[2] P. W. R. CORFIELD, and DEVON W. MEEK*

Received October 20, 1972

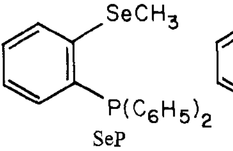
The crystal and molecular structures of two low-spin five-coordinate cobalt(II) complexes containing the same set of donor atoms have been determined from three-dimensional X-ray data collected by counter methods. The red complex $[Co(dpe)_2Cl]SnCl_3$ (dpe = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$) crystallizes in space group $C_{2h}{}^5$-$P2_1/c$ of the monoclinic system, with four formula units in a cell of dimensions $a = 17.727$ (7), $b = 16.431$ (6), and $c = 19.741$ (8) Å; $\beta = 122.13$ (1)°. The observed and calculated densities are 1.51 and 1.520 g/cm^3, respectively. The green complex $[Co(dpe)_2Cl]SnCl_3 \cdot C_6H_5Cl$ crystallizes in space group $C_i{}^1$-$P\bar{1}$ of the triclinic system, with two formula units in a cell of dimensions $a = 11.781$ (11), $b = 12.846$ (12), and $c = 19.893$ (19) Å; $\alpha = 106.38$ (2), $\beta = 93.76$ (2), and $\gamma = 101.81$ (2)°. The observed and calculated densities are 1.47 and 1.456 g/cm^3, respectively. The structures of both the red and the green complexes have been refined by least-squares techniques to final R factors on F of 0.065 for the red complex and 0.101 for the green complex. The structures both consist of discrete five-coordinate cations and pyramidal $SnCl_3^-$ anions. The difference in color can be ascribed to a difference in the stereochemistry of the cation: the red complex is a tetragonal pyramid with an apical Cl atom and four P atoms in the basal plane, whereas the green complex is based on the trigonal-bipyramidal geometry with two P atoms at the axial positions and two P atoms and one Cl atom in the equatorial plane. Distortions from the two idealized geometries can be attributed to the 81-83° bite of the diphosphine ligand. The Co-Cl distance of 2.398 (2) Å in the tetragonal pyramid is 0.15 Å longer than that in the trigonal bipyramid of 2.251 (5) Å. The average Co-P distances are 2.276 and 2.258 Å in the red and green forms, respectively. The $SnCl_3^-$ anion is pyramidal in both complexes. In organic solvents there is an equilibrium between the red and green forms, with the green form predominating. It is suggested that the interconversion of forms takes place through a four-coordinate intermediate involving rupture of a Co-P bond.

Introduction

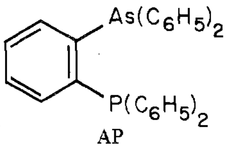
There have been several reports of low-spin five-coordinate cobalt(II) complexes of the type $[CoL_2X]Y$, where L is a neutral bidentate ligand and X a coordinating anion. Dyer and Meek[3] prepared several complexes of this type where L = AP, X = Cl, Br, I, Y = SnX_3, ClO_4; L = SP, SeP, X = Br,



SP



SeP



AP

Y = ClO_4. All these complexes formed by ligands with *o*-phenylene linkages exhibit a deep red color and have been formulated as square-pyramidal Co(II) complexes.[3] When L = *cis*-1,2-bis(diphenylphosphino)ethylene, a ligand which has steric requirements similar to those of SP, SeP, and AP, a series of dark green complexes has been isolated for X = Cl, Br, I, NCS, Y = $B(C_6H_5)_4$; X = Cl, Y = $SnCl_3$; and X = NCS, Y = $Co(NCS)_4$.[4] And when L = 1,2-bis(diphenylphosphino)ethane (dpe), Sacco and Gorieri[5] have reported a series of red or orange compounds where X = NO_3, Y = NO_3, $B(C_6H_5)_4$; X = I, Y = NO_3, I, ClO_4, $B(C_6H_5)_4$; and X = NCS, Y = NCS, ClO_4; and a series of green compounds where X = Br, Y = Br, ClO_4; X = NCS, Y = $Co(NCS)_4$; and X = Cl, Y = $CoCl_4$. The dark green complex $[Co(dpe)_2Br]Br$ had previously been reported by Chatt, *et al.*[6] Horrocks, VanHecke, and Hall also assigned a square-pyramidal geometry to the green series $[Co(dpe)_2X]X$ (X = Cl, Br, I) on the basis of the electronic spectra and detailed esr results.[7]

Several new complexes of empirical composition $Co(dpe)_2 \cdot SnX_4$ (X = Cl, Br, I) have been isolated from nonaqueous solutions containing a mixture of a cobalt(II) halide, the corresponding stannous halide, and the diphosphine ligand.[4] For the bromide and chloride cases, either a deep red or a deep green crystalline material of identical composition can be isolated depending on the solvent, temperature, and isolation procedures. The analytical, conductance, magnetic, and electronic spectral data indicate that both the red and green series are low-spin, five-coordinate cobalt(II) complexes. The magnetic moments (μ_{eff} = 2.03-2.14 BM) of the red series are somewhat higher than those of the green series (μ_{eff} = 1.89-1.97 BM).[4] However, both ranges are consistent with the values reported previously for five-coordinate cobalt(II) complexes.[3,8] The electronic spectra

---

[1] Presented in part at the Symposium on Five-Coordinate Complexes at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971; see Abstracts, No. INORG 96.

[2] Ohio State University Postdoctoral Fellow, July-Dec 1970; Postdoctoral Research Associate, Jan 1971-Sept 1972.

[3] G. Dyer and D. W. Meek, *J. Amer. Chem. Soc.*, 89, 3983 (1967).

[4] J. K. Stalick, G. Dyer, C. A. McAuliffe, and D. W. Meek, to be submitted for publication.

[5] A. Sacco and F. Gorieri, *Gazz. Chim. Ital.*, 687 (1963).

[6] J. Chatt, F. A. Hart, and D. T. Rosevear, *J. Chem. Soc.*, 5504 (1961).

[7] W. D. Horrocks, Jr., G. R. VanHecke, and D. D. Hall, *Inorg. Chem.*, 6, 694 (1967).

[8] L. Sacconi, *J. Chem. Soc. A*, 248 (1970).