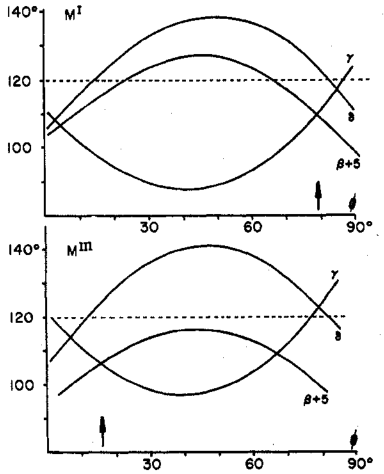

Figure 6. Calculated variations in the angles β, γ, and δ (Figure 5) with changing angle ϕ for the Rh(I) and M(III) (M = Rh, Ir) complexes. The arrows mark the observed values of ϕ for the complexes.

The calculations show that for both M(I) and M(III) complexes the distortions in β, γ, and δ[35] are smaller at the HPM than at the LPM, so that in principle there is, in each case, a geometric preference for the HPM. Therefore[36] we conclude that the observed LPM in the d^6 M(III) complex is electronically preferred.[37]

Variations in α and ϵ are also important[38] because in the M(I) complex these angles are smaller and in the M(III) complexes larger than their ideal values (180 and ca. 120°, respectively). Further calculations performed by varying the parameters α and ϵ about their observed values show that an increase in either or both reduces distortions in β, γ, and δ at both the HPM and LPM. There is also a concomitant change in the ϕ value of the HPM and LPM. Since the effect of increasing α and/or ϵ in the M(I) complex[39] is to relieve chelate ring strain it is pertinent to ask why this does not occur. A likely reason is that the resultant ϕ value at the HPM is then still smaller than the observed value (78.9°). Therefore we conclude that as well as the previously discussed geometric preference for a HPM there is an electronic preference for a ϕ value approaching 90° in the d^8 M(I) complex.

Acknowledgment. We thank Drs. M. A. Bennett, P. W. Clark, and I. B. Tomkins for providing crystals of the complexes and The Australian National University Computer Services Centre for the use of its facilities.

Registry No. **1**, 38904-91-5; **2**, 61300-52-5; **3**, 59706-98-8.

Supplementary Material Available: Listings of anisotropic atomic thermal parameters, structure factor amplitudes, and data collection details (37 pages). Ordering information is given on any current masthead page.

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(35) The HPM and LPM have been calculated as being at the minimum of the sums of the squares of β, γ, and δ from their ideal values. These were assumed to be 120° for γ and δ and 115° for β. The latter value is somewhat arbitrary. Furthermore, we feel intuitively that distortions in β are less energetically unfavorable than those in γ and δ. Nevertheless, variations in the assumed "ideal" for β and differing modes of calculating the minimum do not alter the qualitative conclusions we have drawn.

(36) Clearly the phosphine conformation observed in the M(III) complexes would introduce no extra nonbonded interactions in a M(I) complex. The reverse situation is less certain, but placement of two mutually trans chlorine atoms 2.34 Å from the metal along a vector perpendicular to the mean coordination plane of the metal does not introduce severe nonbonded interactions between the phosphine phenyl groups and the extra chlorine atoms.

(37) A recent LCAO–MO–SCF calculation (Bachmann, C.; Demuynck, J.; Veillard, A. *J. Am. Chem. Soc.* **1978**, *100*, 2366) on the model d^6 metal complex *trans*-$Mo(PH_3)_4(C_2H_4)_2$ suggest that the most stable configuration has the olefinic bond parallel to the P–P vector. This is analogous to the LPM observed in the d^6 M(III) complexes of this work.

(38) Distortions in β, γ, and δ are relatively insensitive to the variation of a (Figure 5) by ca. 0.1 Å.

(39) In the M(III) complexes distortions in α and ϵ are balanced against distortions in β, γ, and δ.

Contribution from the Department of Chemistry,
University of Kentucky, Lexington, Kentucky 40506

Crystal Structure and Solution Dynamics of the Cyclopropylplatinum(II) Complex (2,3-Bis(methoxycarbonyl)-1-methylcyclopropyl)bis(triphenylphosphine)platinum(II) Tetrafluoroborate

THOMAS G. ATTIG,* RUTH J. ZIEGLER, and CAROLYN P. BROCK*

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The crystal structure and dynamic behavior in solution of one of the products of the reaction of *trans*-$PtH(acetone)(PPh_3)_2BF_4$ and *cis*-dimethyl 1-methylenecyclopropane-2,3-dicarboxylate have been determined. The cyclopropylplatinum(II) complex (2,3-bis(methoxycarbonyl)-1-methylcyclopropyl)bis(triphenylphosphine)platinum(II) tetrafluoroborate crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.513$ (1) Å, $b = 19.247$ (3) Å, $c = 19.874(4)$ Å, $\beta = 92.02$ (1)°, and $Z = 4$. The structure was refined with 5382 observations and 224 variables to an R index on F_o of 0.035. The structure confirms the integrity of the cyclopropane ring and shows that the fourth coordination site on the Pt is occupied by one of the ester carbonyls. The compound exhibits dynamic ^1H and ^{13}C NMR spectra that are attributed to the rapid dissociation of the coordinated carbonyl.

Introduction

The reactions of methylenecyclopropane derivatives with zero- and divalent complexes of platinum and palladium generally give either (1) η^2-olefin complexes in which the methylenecyclopropane framework remains intact or (2) η^3-allyl or but-3-enyl complexes resulting from metal-induced cyclopropane ring opening.[1-5] Both of these reaction types have been observed in the reactions of platinum(II) hydrides

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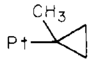
(1) Green, M.; Howard, J. A. K.; Hughes, R. P.; Kellett, S. C.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1975**, 2007–2014.

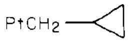
(2) Noyori, R.; Takaya, H. *Chem. Commun.* **1969**, 525.

0020-1669/80/1319-2315$01.00/0

and methylenecyclopropanes.[3,5,6] The Pt–H bond may add across the exocyclic double bond of the methylenecyclopropane to give initially either (1-methylcyclopropyl)- or (cyclopropylmethyl)platinum, **1** or **2**, respectively. The direction

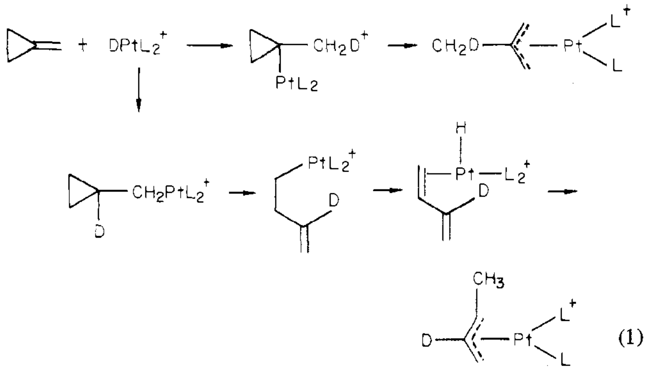


1

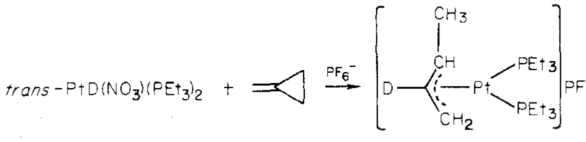


2

of the addition depends on the identity of the stabilizing ligands on the hydride. The 1-methylcyclopropyl species is formed only when PPh_3 is present while the cyclopropylmethyl species is formed for both triaryl- and trialkylphosphines. Thus the reaction of methylenecyclopropane and *trans*-$PtH(NO_3)(PPh_3)_2$ gives a mixture of (η^3-1-methylallyl)- and (η^3-2-methylallyl)platinum(II) complexes while the corresponding reaction of *trans*-$PtH(NO_3)(PEt_3)_2$ affords only the η^3-1-methylallyl isomer.[3] (In the reactions of methylenecyclopropane both the 1-methylcyclopropyl and cyclopropylmethyl species rapidly undergo ring opening to afford isomeric η^3-methylallyl complexes. See, e.g., eq 1 and 2.)

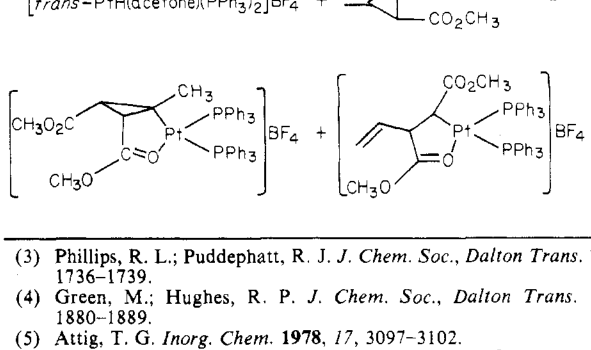


(1)



(2)

We have recently reported that the corresponding reactions of a diester derivative of methylenecyclopropane (*cis*-dimethyl 1-methylenecyclopropane-2,3-dicarboxylate; the dimethyl ester of Feist's acid) do not afford η^3-allyl products but rather but-3-enyl complexes when PEt_3 is the hydride-stabilizing ligand.[5] The coordination of one of the ester carbonyls to the metal prevents further rearrangement to η^3-allyl complexes. We now find that the reaction of [*trans*-PtH(acetone)$(PPh_3)_2]BF_4$ with this ester gives a mixture of a (1-methylcyclopropyl)platinum(II) complex and the but-3-enylplatinum(II) complex. The methylcyclopropyl product is also trapped toward further rearrangement (here, ring opening) by carbonyl coordination to the metal (eq 3).



(3)

Table I. Summary of Crystal Data and Details of Intensity Collection and Refinement

formula	$C_{44}H_{41}BF_4O_4P_2Pt$
fw	977.6
space group	$P2_1/c$
a	10.513 (1) Å
b	19.247 (3) Å
c	19.874 (4) Å
β	92.02 (1)°
V	4018.9 Å^3
Z	4
D(calcd)	1.616 g cm^{-3}
D(obsd)	1.58 (1) g cm^{-3}
cryst dimens	0.22 × 0.38 × 0.38 mm
bounding planes	{100}, {011}
temp	24 ± 1 °C
radiation	Mo Kα (graphite monochromator)
μ	35.84 cm^{-1}
transmission factors	0.261–0.475
takeoff angle	2.20°
scan rate	10–1°/min (θ) depending on prescan (target signal-to-noise ratio 50:1)
scan range	0.8° (2θ) below Kα_1 to 0.8° above Kα_2 extended by 25% on each side for background
2θ limits	2–50°
observations	$+h, +k, \pm l$
p factor	0.03
unique data	7075
unique data with $F_o^2 \geq 3\sigma(F_o^2)$	5382
final no. of variables	224
R on F ($\geq 3\sigma$)	3.5%
R on F^2 (all data)	6.7%
R_w on F ($\geq 3\sigma$)	4.4%
error in observn of unit weight	1.91 e

The transition metal–cyclopropyl σ bond is a relatively rare linkage. The preparation of the iron complex η^5-$C_5H_5Fe(CO)_2(C_3H_5)$ and its ring-expansion reactions with electrophiles such as sulfur dioxide and tetracyanoethylene and its ring-opening reactions with HBF_4 and H^- have been reported.[7,8] The preparation and reactions with acids of the nickel complex η^5-$C_5H_5Ni(PPh_3)(C_3H_5)$ have also been described.[9] Puddephatt et al.[10] have recently prepared a series of platinum(II)– and platinum(IV)–cyclopropyl complexes and have studied their thermal decomposition and cyclopropyl-to-η^3-allyl rearrangements. Herein we report the first crystal structure of a transition-metal–cyclopropyl complex and its dynamic behavior in solution. A preliminary communication of this work has already been published.[6]

Experimental Section

Preparation. To a rapidly stirred solution of 480 mg (0.635 mmol) of *trans*-$PtHCl(PPh_3)_2$ in 10 mL of CH_2Cl_2 was added 120 mg (0.615 mmol) of $AgBF_4$ in 10 mL of freshly distilled acetone. After removal of the AgCl by centrifugation, the resulting solution was concentrated to approximately 10 mL and was treated with 108 mg (0.635 mmol) of *cis*-dimethyl 1-methylenecyclopropane-2,3-dicarboxylate. After being stirred for 4 h, the solution was concentrated to give colorless crystals of the title compound with a small impurity of the other isomer $\{\overline{Pt[CH(COOCH_3)CH(COOCH_3)(CH{=}CH_2)]}(PPh_3)_2\}BF_4$. Recrystallization from a CH_2Cl_2/CH_3OH solution gave 246 mg (41%) of the title compound in high purity; mp 194–199 °C. Anal. Calcd for $C_{44}H_{41}BF_4O_4P_2Pt$: C, 54.06; H, 4.23. Found: C, 53.86; H, 4.29.

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(3) Phillips, R. L.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1736–1739.

(4) Green, M.; Hughes, R. P. *J. Chem. Soc., Dalton Trans.* **1976**, 1880–1889.

(5) Attig, T. G. *Inorg. Chem.* **1978**, *17*, 3097–3102.

(6) Attig, T. G. *J. Organomet. Chem.* **1978**, *145*, C13–C17.

(7) Cutler, A.; Fish, R. W.; Giering, W. P.; Rosenblum, M. *J. Am. Chem. Soc.* **1972**, *94*, 4354–4355.

(8) Cohen, L.; Giering, W. P.; Kenedy, D.; Magatti, C. V.; Sanders, A. *J. Organomet. Chem.* **1974**, *65*, C57–C60.

(9) Brown, J. M.; Mertis, K. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1993–2001.

(10) Phillips, R. L.; Puddephatt, R. J. *J. Chem. Soc., Dalton Trans.* **1978**, 1732–1735.

Table II. Positional and Thermal Parameters for Nongroup Atoms

	x^a	y	z	$\beta_{11}{}^b$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	0.067950 (20)	0.115546 (12)	0.258775 (12)	49.79 (22)	16.14 (7)	15.70 (7)	2.42 (11)	3.06 (8)	−2.22 (6)
P(1)	0.01438 (14)	0.06634 (8)	0.16068 (8)	53.2 (13)	16.7 (5)	15.8 (4)	−0.5 (6)	1.2 (6)	−0.5 (4)
P(2)	0.24195 (14)	0.04352 (9)	0.28770 (8)	59.0 (14)	18.7 (5)	17.3 (4)	1.8 (6)	1.3 (6)	0.2 (4)
O(1)	−0.1414 (6)	0.1003 (4)	0.3856 (3)	118 (6)	58 (3)	30 (2)	−9 (3)	−2 (3)	9 (2)
O(2)	−0.2888 (5)	0.0801 (3)	0.3054 (3)	107 (6)	33 (2)	35 (2)	−6 (3)	−4 (3)	4 (2)
O(3)	0.1070 (4)	0.1579 (3)	0.3552 (2)	84 (5)	25 (2)	21 (1)	6 (2)	−1 (2)	−7 (1)
O(4)	0.0330 (5)	0.2290 (3)	0.4327 (2)	119 (6)	33 (2)	23 (2)	8 (3)	3 (2)	−11 (1)
C(1)	−0.1776 (6)	0.1845 (4)	0.2986 (4)	72 (6)	30 (3)	28 (2)	3 (3)	9 (3)	−3 (2)
C(2)	−0.0684 (6)	0.2292 (4)	0.3246 (4)	71 (6)	21 (2)	30 (2)	9 (3)	3 (3)	−9 (2)
C(3)	−0.0663 (6)	0.1957 (3)	0.2532 (3)	66 (6)	17 (2)	27 (2)	6 (3)	3 (3)	3 (2)
C(4)	−0.0834 (7)	0.2478 (4)	0.1979 (4)	108 (8)	23 (2)	26 (2)	−2 (3)	−4 (3)	−5 (2)
C(5)	−0.1998 (6)	0.1179 (4)	0.3358 (4)	61 (6)	32 (3)	30 (2)	2 (3)	13 (3)	−6 (2)
C(6)	−0.3156 (9)	0.0133 (5)	0.3390 (5)	142 (11)	30 (3)	50 (4)	−7 (5)	14 (5)	9 (3)
C(7)	0.0271 (6)	0.2017 (4)	0.3726 (4)	85 (7)	24 (2)	22 (2)	−4 (3)	10 (3)	−3 (2)
C(8)	0.1347 (9)	0.2049 (5)	0.4795 (5)	160 (11)	39 (3)	32 (3)	4 (5)	−9 (5)	−8 (3)

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses in this and all subsequent tables. [b] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The quantities given are the thermal coefficients × 10^4.

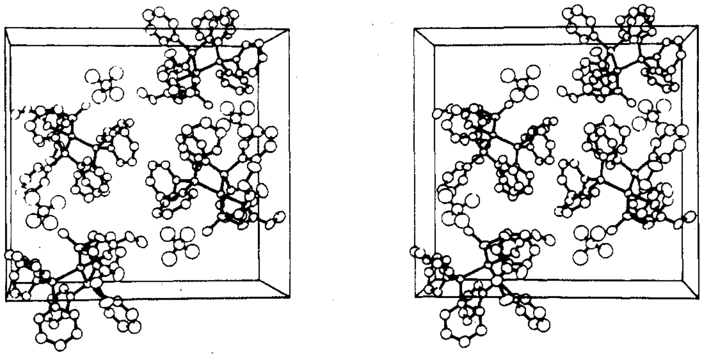

Figure 1. Stereoscopic view of the contents of the unit cell. Only one of the orientations of the BF_4^- ion is shown. In this and the following drawings the shapes of the atoms correspond to 50% probability contours of thermal motion and H atoms have been omitted for the sake of clarity. The *a* axis points into the paper, the *b* axis points vertically upward, and the *c* axis runs horizontally from left to right.

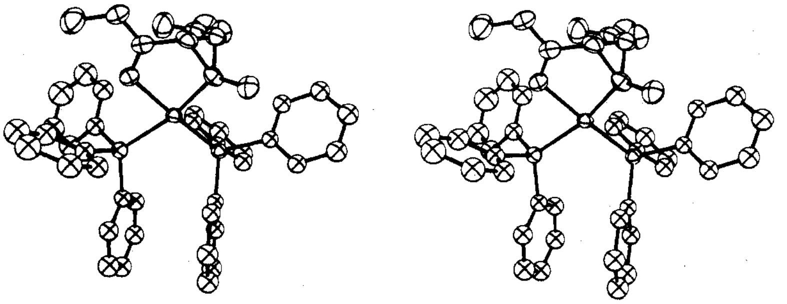

Figure 2. Stereoscopic drawing of the cation.

The second isomer was isolated in 38% yield as the PF_6^- salt by addition of NH_4PF_6 (55 mg) to the mother liquor.

Crystal Structure Determination. Crystals of the title compound were grown by slow evaporation of a CH_2Cl_2/CH_3OH solution and were mounted in capillaries to prevent decomposition. Data were collected with an Enraf-Nonius CAD-4/F diffractometer; details are summarized in Table I. Unit cell data were determined as part of a least-squares fit to the setting angles of 22 reflections having $2\theta > 22°$. The space group was determined by photographic methods. After the Pt and P atoms were located from a Patterson map,[11] difference Fourier syntheses and full-matrix least-squares refinements revealed the positions of the other nonhydrogen atoms and the mode of coordination of the cyclopropyl ligand. Scattering factors were taken from the usual tabulation[12] and anomalous terms for the Pt and P atoms were included. The BF_4^- ion was found to be disordered with respect to both position (a nonpositive definite thermal ellipsoid results if a single B atom is included) and orientation. The most successful model included two rigid BF_4^- groups with bond lengths of 1.39 Å as found in structures of the Na^+, K^+, and Ca^{2+} salts.[13] Three isotropic factors were refined, one for the two B atoms and one for each set of four F atoms. The six C_6H_5 rings were also treated as rigid groups (C–C = 1.397 Å). The hydrogen atoms were all located from difference Fourier maps after anisotropic refinement and were included as fixed contributions after idealization (C–H = 1.00 Å; *B* values are 1 $Å^2$ higher than those of the attached C atoms). The four highest peaks in a final difference map are 1.0–1.2 $e/Å^3$ in height (about one-eighth of a C atom peak) and are associated with the BF_4^-

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(11) In addition to various local programs for the IBM 370/165 computer, local versions of the following programs were employed: Zalkin's Fourier program FORDAP; the Busing–Levy ORFFE error function program; the absorption correction program AGNOST; Johnson's thermal ellipsoid plotting program ORTEP. Our version of Ibers's least-squares program NUCLS, which in its nongroup form closely resembles the Busing–Levy ORFLS program, was also used.

(12) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(13) (a) Brunton, G. *Acta Crystallogr., Sect. B* **1968**, *24*, 1703–1704. (b) Brunton, G. *Ibid.* **1969**, *25*, 2161–2162. (c) Jordan, T. H.; Dickens, B.; Schroeder, L. W.; Brown, W. E. *Ibid.* **1975**, *31*, 669–672.

Table III. Thermal Parameters and Derived Positional Parameters

Rigid Group Atoms

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
R1C1	−0.0516 (4)	−0.0203 (2)	0.1701 (2)	2.86 (11)	R4C1	0.3277 (4)	−0.0088 (2)	0.2273 (2)	2.84 (11)
R1C2	−0.0663 (4)	−0.0472 (2)	0.2346 (2)	3.53 (12)	R4C2	0.2770 (3)	−0.0734 (2)	0.2087 (2)	3.49 (13)
R1C3	−0.1278 (5)	−0.1108 (2)	0.2430 (2)	4.55 (15)	R4C3	0.3446 (4)	−0.1175 (2)	0.1671 (2)	3.82 (13)
R1C4	−0.1747 (5)	−0.1475 (2)	0.1867 (2)	4.86 (16)	R4C4	0.4628 (4)	−0.0970 (2)	0.1439 (2)	4.08 (14)
R1C5	−0.1600 (4)	−0.1206 (2)	0.1222 (2)	4.74 (16)	R4C5	0.5134 (3)	−0.0324 (2)	0.1624 (2)	4.44 (15)
R1C6	−0.0985 (4)	−0.0570 (2)	0.1139 (2)	3.83 (14)	R4C6	0.4459 (4)	0.0117 (2)	0.2041 (2)	3.56 (13)
R2C1	−0.1136 (3)	0.1071 (2)	0.1104 (2)	2.63 (10)	R5C1	0.3557 (4)	0.1053 (2)	0.3232 (2)	3.17 (12)
R2C2	−0.2340 (3)	0.1076 (2)	0.3179 (2)	3.20 (12)	R5C2	0.3866 (4)	0.1635 (2)	0.2850 (2)	3.62 (13)
R2C3	−0.3342 (3)	0.1430 (2)	0.1050 (2)	3.74 (13)	R5C3	0.4645 (4)	0.2154 (2)	0.3131 (2)	4.59 (16)
R2C4	−0.3140 (3)	0.1779 (2)	0.0447 (2)	4.04 (14)	R5C4	0.5116 (4)	0.2092 (2)	0.3794 (2)	5.06 (17)
R2C5	−0.1935 (4)	0.1773 (2)	0.0172 (2)	3.93 (14)	R5C5	0.4808 (5)	0.1510 (3)	0.4176 (2)	5.44 (18)
R2C6	−0.0933 (3)	0.1419 (2)	0.0500 (2)	3.22 (12)	R5C6	0.4028 (4)	0.0991 (2)	0.3895 (2)	4.36 (15)
R3C1	0.1482 (3)	0.0640 (2)	0.1052 (2)	2.59 (10)	R6C1	0.2141 (4)	−0.0194 (2)	0.3540 (2)	3.32 (12)
R3C2	0.1834 (4)	0.0050 (2)	0.0693 (2)	3.23 (12)	R6C2	0.3009 (4)	−0.0730 (3)	0.3671 (2)	4.55 (16)
R3C3	0.2879 (4)	0.0075 (2)	0.0279 (2)	3.94 (14)	R6C3	0.2781 (5)	−0.1215 (2)	0.4176 (3)	5.60 (19)
R3C4	0.3572 (3)	0.0690 (2)	0.0223 (2)	4.07 (14)	R6C4	0.1683 (5)	−0.1164 (3)	0.4549 (2)	7.04 (23)
R3C5	0.3220 (4)	0.1280 (2)	0.0582 (2)	3.84 (14)	R6C5	0.0815 (4)	−0.0627 (3)	0.4418 (3)	6.09 (20)
R3C6	0.2175 (4)	0.1255 (2)	0.0996 (2)	3.06 (12)	R6C6	0.1043 (4)	−0.0142 (2)	0.3913 (2)	4.23 (15)
B(1)	0.3696 (5)	0.3173 (3)	0.1302 (3)	5.71 (24)	B(2)	0.3817 (9)	0.3066 (6)	0.1264 (5)	5.71
F(11)	0.2748 (7)	0.2743 (5)	0.1539 (5)	9.91 (24)	F(21)	0.4093 (16)	0.3025 (9)	0.0586 (6)	10.45 (40)
F(12)	0.4355 (8)	0.3479 (5)	0.1844 (4)	9.91	F(22)	0.4514 (13)	0.2567 (7)	0.1622 (8)	10.45
F(13)	0.4533 (8)	0.2783 (5)	0.0930 (5)	9.91	F(23)	0.4138 (16)	0.3722 (6)	0.1507 (8)	10.45
F(14)	0.3148 (8)	0.3688 (4)	0.0896 (4)	9.91	F(24)	0.2525 (10)	0.2950 (9)	0.1339 (9)	10.45

Rigid Groups

group	x_c[a]	y_c	z_c	δ[b]	ϵ	η
ring 1	−0.113 16 (27)	−0.083 92 (16)	0.178 41 (16)	2.656 (3)	−3.006 (2)	1.658 (3)
ring 2	−0.213 76 (25)	0.142 47 (14)	0.077 52 (14)	−1.151 (3)	2.304 (2)	0.719 (4)
ring 3	0.252 70 (24)	0.066 50 (15)	0.063 75 (13)	−0.153 (2)	−2.896 (2)	2.452 (3)
ring 4	0.395 24 (26)	−0.052 89 (16)	0.185 59 (14)	−0.825 (2)	3.078 (2)	2.483 (3)
ring 5	0.433 69 (27)	0.157 26 (17)	0.351 31 (17)	−3.005 (5)	−2.114 (3)	−0.825 (5)
ring 6	0.191 20 (32)	−0.067 86 (18)	0.404 46 (17)	1.070 (3)	−2.911 (3)	−0.838 (3)
BF4(1)[c]	0.369 6 (5)	0.317 3 (3)	0.130 2 (3)	−0.903 (23)	1.814 (6)	1.600 (23)
BF4(2)	0.381 7 (9)	0.306 6 (6)	0.126 4 (5)	0.776 (11)	−2.711 (10)	1.705 (10)

[a] x_c, y_c, and z_c are the fractional coordinates of the origin of the rigid group. [b] The rigid-group orientation angles δ, ϵ, and η (radians) are those defined previously (La Placa, S. J.; Ibers, J. A. *Acta Crystallogr.* **1965**, *18*, 511). [c] Occupancy factor 0.620 (10).

ion. An analysis of $\sum w(|F_o| - |F_c|)^2$ [where $w = 4F_o^2/\sigma^2(F_o^2)$] as a function of F_o, $(\sin\theta)/\lambda$, and the Miller indices revealed relatively poorer agreement at low scattering angles. This trend is not surprising considering the difficulty in modeling the BF_4^- disorder. No corrections for extinction or decomposition appeared necessary. The final parameters for the nongroup atoms are given in Table II; rigid-body parameters and derived positions of the group atoms are listed in Table III. Tabulations of $10|F_o|$ vs. $10|F_c|$, principal root-mean-square amplitudes of vibration, and hydrogen atom parameters are available.[14]

Spectra. ^1H and ^{13}C NMR spectra were recorded on a Varian CFT-20 spectrometer with Me_4Si or known solvent as an internal standard. The ^{31}P NMR spectra were recorded on a Bruker HX-90 spectrometer at 36.4 MHz with 85% H_3PO_4 as an external reference. Infrared spectra were recorded on a Perkin-Elmer 621 spectrophotometer as Nujol mulls or in dichloromethane solution and were calibrated with a polystyrene film.

Results and Discussion

Description of the Crystal Structure. The solution and refinement of this structure confirms the presence of the platinum–cyclopropyl linkage postulated previously.[6] Stereoviews of the unit cell and the cation are shown in Figures 1 and 2; Figure 3 displays the inner coordination sphere and the organic ligand. Selected distances, angles, and least-squares planes can be found in Figure 3 and Table IV. The unit cell diagram shows that the BF_4^- ions approach the square-planar Pt complexes along an axial direction; however, all Pt···F distances are greater than 4.3 Å, and there is no evidence for bond formation.

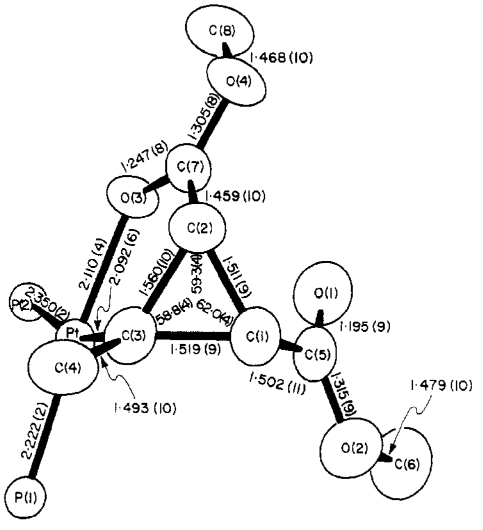
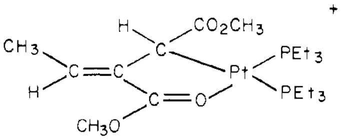


Figure 3. Organic ligand and coordination sphere of the cation.

The structure of the cation is the first reported of a transition-metal–cyclopropyl complex. In many respects, however, it is very similar to the structure of the $\{\mathrm{Pt}[\eta^1\text{-}\mathrm{CH(COOCH_3)C(COOCH_3){=}CHCH_3}](\mathrm{PEt_3})_2\}^+$ cation:[15]



Both cations contain a quaternary carbon atom coordinated

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[14] See paragraph at end of paper regarding supplementary material.

[15] Brock, C. P.; Attig, T. G. *J. Am. Chem. Soc.* **1980**, *102*, 1319–1326.

Table IV. Distances, Angles, and Least-Squares Planes for the Cation

Distances, Å			
P(1)–R1C1	1.819 (4)	P(2)–R4C1	1.829 (4)
P(1)–R2C1	1.824 (4)	P(2)–R5C1	1.812 (4)
P(1)–R3C1	1.818 (4)	P(2)–R6C1	1.821 (4)
Pt···B(1)	5.678 (6)	Pt···B(2)	5.652 (11)
Bond Angles, Deg			
P(1)–Pt–P(2)	97.7 (1)	Pt–C(3)–C(4)	126.7 (5)
P(1)–Pt–C(3)	96.8 (2)	C(1)–C(3)–C(4)	117.2 (6)
P(1)–Pt–O(3)	175.5 (1)	C(2)–C(3)–C(4)	112.8 (6)
P(2)–Pt–C(3)	165.0 (2)	C(1)–C(5)–O(1)	124.4 (7)
P(2)–Pt–O(3)	83.1 (1)	C(1)–C(5)–O(2)	111.6 (7)
C(3)–Pt–O(3)	82.7 (2)	O(1)–C(5)–O(2)	124.0 (8)
C(2)–C(1)–C(5)	116.6 (6)	C(2)–C(7)–O(3)	121.3 (6)
C(3)–C(1)–C(5)	123.4 (6)	C(2)–C(7)–O(4)	117.4 (6)
C(1)–C(2)–C(7)	120.9 (6)	O(3)–C(7)–O(4)	121.0 (6)
C(3)–C(2)–C(7)	114.4 (5)	C(5)–O(2)–C(6)	114.7 (7)
Pt–C(3)–C(1)	113.3 (5)	Pt–O(3)–C(7)	113.6 (4)
Pt–C(3)–C(2)	106.7 (4)	C(7)–O(4)–C(8)	117.5 (6)
Displacements from Plane, Å			
Plane Defined by Pt, P(1), P(2)			
C(2)	0.164 (8)	C(7)	0.329 (7)
C(3)	−0.136 (7)	O(3)	0.162 (5)
Dihedral Angles, Deg			
Pt, P(1), P(2) C(1), C(2), C(3)	65.6 (4)	ring 2 ring 6	22.1 (5)
ring 1 ring 5	15.7 (3)	ring 3 ring 4	11.6 (3)
Conformation Angles, Deg			
O(1)–C(5)–C(1)–C(2)	3.9 (10)	O(3)–C(7)–C(2)–C(3)	3.8 (10)

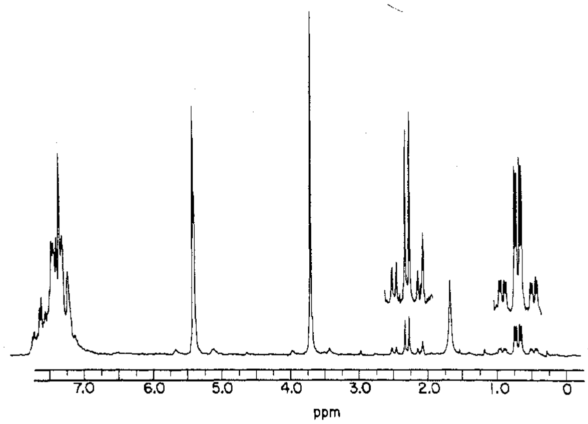

Figure 4. Room-temperature ^{1}H NMR spectra of the title compound. The multiplet at δ 5.4 is due to CH_2Cl_2; the broad singlet at δ 1.8 is due to water.

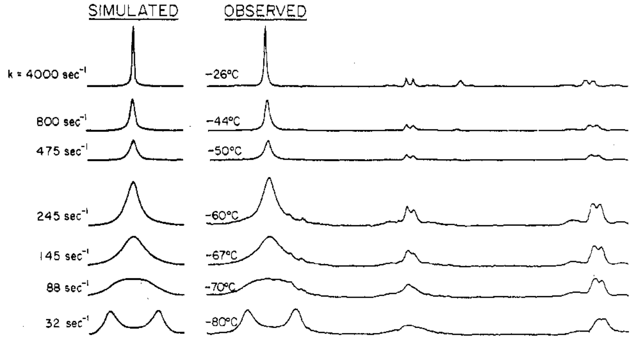

Figure 5. Variable-temperature ^{1}H NMR spectra and simulated spectra for the methyl esters of the cyclopropane ring. The rate constants in the simulated spectra are for $k_{b\to a}$.

to platinum, and they have very similar chelate rings. The Pt–C distances in the two compounds do not differ significantly (2.092 (6) Å in the cyclopropyl, 2.114 (14) Å in the η^1-allyl complex) in spite of the change in hybridization at the carbon atoms. The Pt–C bond in the cyclopropyl complex would be expected to be shorter than in the η^1-allyl complex due to the increased s character of the bonding orbitals, but any such change is obscured by the relatively large standard deviations in the structure of the latter. There are no significant differences in the bond lengths between the chelate rings in the two structures, and the corresponding bond angles differ by at most 5°. Although neither ring is planar, that in the cyclopropyl cation is approximately so (Table IV) while that in the η^1-allyl has a pronounced envelope conformation. The large (0.128 (2) Å) difference between the two Pt–P bond lengths in the cyclopropyl cation reflects the expected[16] large difference in the trans influence of the quaternary carbon and carbonyl oxygen ligands. A similar difference (0.090 (6) Å) was seen in the allyl cation.

The bonding within the cyclopropyl ring is significantly asymmetric. The bond which is part of the chelate ring is longer than the other two (differences: 0.041 (11) and 0.048 (12) Å), and the C–C–C angle at C(1) is correspondingly larger than those at C(2) and C(3) (differences: 2.7 (7) and 3.2 (8)°). The origin of this asymmetry is not clear. Inductive effects resulting from electron-withdrawing substituents tend to lengthen all bonds equally while removal of electrons by π interactions shortens the C–C bond across the ring from the substituent.[17] In this cation neither of the ester groups is in a favorable position for conjugation with the ring; rotations of 50.7 (9) and 49.2 (9)° about C–C bonds are required to bring O(1) and O(3), respectively, into planes perpendicular to the C_3 ring, i.e., the optimum positions for orbital overlap. Donation of electrons *into* the ring through π interaction with the platinum atom might contribute to asymmetry, but the Pt d orbitals do not appear to be in a favorable position for overlap with the π^* orbital in the C_3 ring. Steric strain from the formation of the chelate ring could also explain the lengthening of the C(2)–C(3) bond. Other bond lengths and angles involving C(1), C(2), and C(3) are in the ranges observed for substituted cyclopropanes.[17] The dihedral angle of 65 (1)° between the cyclopropane and five-membered chelate rings is very similar to those seen in two closely related organic systems: 2,5-dimethyl-7,7-dicyanonorcaradiene[18] and 6,6-diphenyl-3,3-diethyl-3-azoniabicyclo[3.1.0]hexane bromide.[19]

Structure and Dynamics in Solution. The ^{1}H NMR spectrum of the title compound at room temperature is shown in Figure 4. Both methyl groups of the ester are equivalent and appear as a singlet of relative intensity 6 at δ 3.59. The two cyclopropyl ring protons are also equivalent and appear as a doublet at δ 2.18 (J(P–H) = 5 Hz) of relative intensity 2 with ^{195}Pt ($I = {}^1/_2$, 34% abundance) satellites (J(Pt–H) = 30 Hz). The methyl group on the cyclopropyl ring appears as a doublet of doublets of relative intensity 3 ($J(P_{cis}$–H) = 2 Hz; $J(P_{trans}$–H) = 5.8 Hz) at δ 0.58 with ^{195}Pt satellites (J(Pt–H) = 36 Hz). This spectrum suggests that the cation has a dynamic structure in solution and is undergoing a process that interchanges the halves of the cyclopropane ring. Both the methyl ester groups and the vicinal protons of the ring would be expected to be nonequivalent if the cation had a static structure in solution the same as is found in the solid state.

The variable-temperature ^{1}H NMR spectra and simulated spectra[20] are shown in Figure 5. Upon lowering of the tem-

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(16) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335–422.

(17) Lauher, J. W.; Ibers, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 561–567.

(18) Fritchie, C. J., Jr. *Acta Crystallogr.* **1966**, *20*, 27–36.

(19) Ahmed, F. R.; Gabe, E. J. *Acta Crystallogr.* **1964**, *17*, 603–608.

(20) Calculated spectra were simulated by the density matrix procedure of Kaplan[21] and Alexander.[22]

(21) Kaplan, J. I. *J. Chem. Phys.* **1958**, *28*, 278–282; **1958**, *29*, 462.

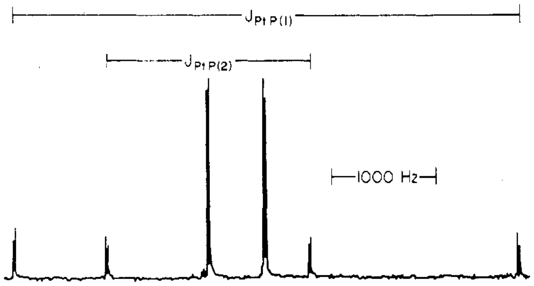
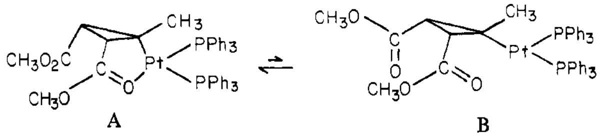


Figure 6. ^{31}P NMR spectrum at 30 °C.

perature the methyl ester peak broadens, coalesces at −70°C, and begins to sharpen into two singlets below −80°. A similar temperature-dependent spectrum should be observed for the cyclopropane ring protons; however, the coalescence temperature is much lower due to the expected small difference in chemical shifts of these protons in the limiting spectrum. The methyl group on the ring does not show any broadening, only a loss of fine structure at low temperature. An activation energy of 8.2 ± 0.5 kcal/mol was calculated from an Arrhenius plot with $\Delta G^{\ddagger} = 10.2 \pm 0.5$ kcal/mol, $\Delta H^{\ddagger} = 7.8 \pm 0.5$ kcal/mol, and $\Delta S^{\ddagger} = -10.3 \pm 1.4$ eu.

Two mechanisms consistent with the NMR results may be suggested: (1) dissociation of the ester carbonyl followed by a small rotation of the Pt–C bond to place both ester groups equidistant from the vacant coordination site on platinum and (2) dissociation of the ester carbonyl followed by a distortion of the coordination geometry at platinum from a pseudo square-planar geometry to a three-coordinate trigonal geometry in which both ester carbonyls are equivalent. One can differentiate between these two mechanisms by examining the variable-temperature ^{31}P spectra. In mechanism 1 the two phosphorus nuclei remain nonequivalent at all times and a temperature-independent ^{31}P spectrum should be observed. In mechanism 2 the two phosphorus nuclei may be interchanged in the trigonal intermediate, and thus if this mechanism were operative, a temperature-dependent spectrum analogous to that observed for the methyl esters in the ^{1}H NMR spectra should be observed. We have measured the ^{31}P NMR spectrum from +30 to −85 °C and have found no temperature dependence which suggests that mechanism 1 is correct. The predicted coalescence temperature for mechanism 2 of −35 °C (calculated from the rate data obtained from the variable-temperature ^{1}H NMR spectra and the chemical shift differences for the two phosphorus nuclei in the ^{31}P spectra) is well within the temperature range studied. The ^{31}P NMR spectrum at 30 °C is shown in Figure 6. The phosphorus nuclei appear as two doublets (J(P–P) = 20.1 Hz) at 23.30 and 8.47 ppm downfield from external 85% H_3PO_4. The assignments of these doublets can readily be made on the basis of the large difference in J(Pt–P) for the two resonances since the magnitude of the coupling constant is inversely proportional to the strength of the trans influence of the ligands. Consequently the doublet at 23.30 ppm (J(Pt–P) = 1937 Hz) is assigned to the phosphorus trans to the cyclopropyl ring, and the doublet at 8.47 ppm (J(Pt–P) = 4795 Hz) is assigned to the phosphorus trans to the carbonyl. The former coupling constant is in the range expected when phosphorus is trans to an sp^3 carbon ligand; the latter is one of the largest Pt–P coupling constants reported. The very large difference in the Pt–P coupling constants is in accord with the very large difference in the corresponding bond lengths determined in the crystal structure.

We have also examined the infrared spectra of the title compound in the solid state and in solution to study any differences in structure in these phases and to gain some insight into the equilibrium shown in (4). Since we were unable to observe species **B** (the intermediate in mechanism 1) in the NMR experiments, we had hoped to detect its presence in solution by infrared techniques. The solid-state infrared spectrum exhibits carbonyl absorptions at 1712 and 1583 cm^{-1} consistent with structure A which are assigned respectively to uncoordinated and coordinated carbonyls. A similar spectrum is obtained in solution with absorptions at 1723 and 1585 cm^{-1}. We are unable to determine the relative amounts of structure A in equilibrium with structure **B** in solution. The infrared spectrum in solution has approximately the same relative intensities as those found in the solid state. Presumably the absorption of the uncoordinated carbonyl in **B** would be very close to that of structure A and may be hidden under the broad absorption. However, on the basis of the comparison between the solution and solid-state spectra, we feel that structure A is the predominant form in solution and that the equilibrium shown above lies very much to the left.



A B (4)

We have studied a large number of complexes that contain this five-membered chelate ring about Pt with two cis phosphines and have found only one other complex that exhibits dissociation of the carbonyl in solution in the absence of other ligands. The η^1-allyl complex $\{\overline{\mathrm{Pt[CHCOOCH_3C(COO}}\mathrm{CH_3)}{=}\mathrm{CHCH_3](PEt_3)_2}\}\mathrm{PF_6}$ is found to undergo a solution to solid state $\eta^1 \rightarrow \eta^3$ rearrangement upon crystallization. In solution the cation is the η^1-allyl complex with a coordinated carbonyl, while in the solid state the cation exists as the η^3-allyl complex $\{\mathrm{Pt[\eta^3\text{-}CH(CH_3)C(CO_2CH_3)CH(CO_2CH_3)](PEt_3)_2}\}\mathrm{PF_6}$ in which neither carbonyl is coordinated.[15] Therefore there must exist in solution some small concentration of the η^3-allyl species. Interestingly, the corresponding BPh_4^- salt does not exhibit this $\eta^1 \rightarrow \eta^3$ rearrangement. The ready dissociation of the coordinated carbonyl in the cyclopropyl cation presumably is related to the fact that the chelate ring has a three-membered ring fused to it which creates considerable strain and thus makes the Pt–O bond labile.

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Registry No. (2,3-Bis(methoxycarbonyl)-1-methylcyclopropyl)-bis(triphenylphosphine)platinum(II) tetrafluoroborate, 73597-14-5; $\{\overline{\mathrm{Pt[CH(COOCH_3)CH(COOCH_3)}}\mathrm{(CH{=}CH_2)](PPh_3)_2}\}\mathrm{PF_6}$, 659-12-98-3; *trans*-PtH(acetone)$(PPh_3)_2BF_4$, 37036-05-8; *trans*-PtHCl-$(PPh_3)_2$, 16841-99-9; *cis*-dimethyl 1-methylenecyclopropane-2,3-dicarboxylate, 51019-97-7.

Supplementary Material Available: Tables of principal root-mean-square amplitudes of vibration, calculated hydrogen positional parameters, and observed and calculated structure factor amplitudes (35 pages). Ordering information is given on any current masthead page.

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(22) Alexander, S. *J. Chem. Phys.* **1962**, *37*, 967–980; **1963**, *38*, 1787–1788; **1964**, *40*, 2741.