Structures of 1,2-Dimethyl- and 3-Methyl-cyclopropenebis(triphenylphosphine)platinum(0)

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The crystal and molecular structures of the title compounds (I) 1,2-dimethyl- and (II) 3-methyl-cyclopropenebis(triphenylphosphine)platinum(0) have been each determined from *X*-ray data collected by counter methods. The structures were determined by the heavy-atom method and refined by least-squares techniques to *R* 0·032 [(I), 2390 independent reflections] and 0·051 [(II), 905 independent reflections]. The parameters of the cyclopropene ring in (II) are inaccurate owing to disorder in the crystal used.

The compounds have the same overall molecular structure. On complex formation the cyclopropene ring remains intact, with C=C 1·50 Å, and is co-ordinated to the platinum *via* a metal–olefin interaction with Pt–C 2·28 Å. In (II), the methyl group and the metal lie on opposite sides of the cyclopropene-ring plane.

Crystals are orthorhombic, space group $P2_1/c$ with $Z = 4$ in unit cells of dimensions: (I), $a = 12{\cdot}49(1)$, $b = 17{\cdot}77(7)$, $c = 16{\cdot}38(7)$ Å, $\beta = 109{\cdot}42(5)°$; (II), $a = 11{\cdot}28(3)$, $b = 20{\cdot}74(4)$, $c = 17{\cdot}23(4)$ Å, $\beta = 124{\cdot}5(2)°$.

CYCLOPROPENES, particularly the lower homologues, polymerise rapidly even when stored at low temperatures. The search[1,2] for a cyclopropene carrier complex by means of which cyclopropenes could be stored for indefinite periods resulted in the preparation of a series of complexes of general formula $[LPt(PPh_3)_2]$ (L = cyclopropene derivative). These compounds are prepared by the action of the appropriate cyclopropene on $[(C_2H_4)Pt(PPh_3)_2]$ and the cyclopropenes may be recovered in stoicheiometric quantities from the complexes by the action of carbon disulphide.

The reversibility of these reactions might suggest that the cyclopropene species remains intact on complex formation; it has been shown that similar reactions with cyclopropane result in insertion of the metal into the ring,[3] yet the cyclopropane may still be recovered from the complex, albeit with the use of stronger reagents than carbon disulphide.

In order to resolve this point and to investigate the geometry of the bonded cyclopropene ring we have investigated the structures of two members of the series, *viz.* (I) 1,2-dimethyl- and (II) 3-methyl-cyclopropenebis(triphenylphosphine)platinum.

EXPERIMENTAL

Preliminary examination of the samples showed that (I) is monoclinic, and that (II) occurs in both a monoclinic and an orthorhombic modification. The cell dimensions given below for (I) were obtained by least-squares refinement of θ, −θ values measured on the diffractometer; those for (II) were calculated from precession-photograph measurements.

Crystal Data.—(*a*) *Complex* (I). $C_{41}H_{38}PtP_2$, $M = 787{\cdot}4$, Monoclinic, $a = 12{\cdot}49(1)$, $b = 17{\cdot}77(1)$, $c = 16{\cdot}38(1)$ Å, $\beta = 109{\cdot}42(5)°$, $U = 3488$ Å^3, $D_c = 1{\cdot}52$ g cm^{-3}, $Z = 4$, $F(000) = 1568$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 4·4 mm^{-1}.

(*b*) *Complex* (II). $C_{40}H_{36}PtP_2$, $M = 773{\cdot}4$, $F(000) = 1536$. (i) Monoclinic: $a = 11{\cdot}28(3)$, $b = 20{\cdot}74(4)$, $c = 17{\cdot}23(4)$ Å, $\beta = 124{\cdot}5(2)°$, $U = 3332$ Å^3, $D_c = 1{\cdot}54$ g cm^{-3}, $Z = 4$. μ(Mo-K_α) = 4·6 mm^{-1}. Space group $P2_1/c$. (ii) Orthorhombic: $a = 9{\cdot}57(3)$, $b = 19{\cdot}66(4)$, $c = 18{\cdot}10(4)$ Å, $U = 3405$ Å^3, $D_c = 1{\cdot}50$, $Z = 4$. μ(Mo-K_α) = 4·5 mm^{-1}. Space group $P2_12_12_1$. As we expected a centric to present less problems than a non-centric structure, we chose to carry out the structure determination on the monoclinic form of (II). D_m Was not obtained for either compound.

The procedure used for the data collections was similar for both compounds. The crystal of (I) had dimensions 0·1 × 0·25 × 0·3 mm^3, and 2390 independent reflections were obtained with intensities significantly above background and $\sin\theta/\lambda \leqslant 0{\cdot}59$. The crystal of (II) was 0·07 × 0·25 × 0·6 mm^3, and 905 independent intensities above background were obtained out to $\sin\theta/\lambda$ 0·36.

The crystals were mounted with the c^* axis coinciding with the ϕ axis of a Nonius automatic three-circle diffractometer equipped with a scintillation counter and pulse-height discriminator. Zr-Filtered Mo-K_α radiation was used with a θ, 2θ scan and background counts were measured for half the scan time at each end of the scan range. A control reflection, monitored regularly, showed no significant variation of intensity.

An azimuth-dependent absorption correction (according to the method of Furnas[4]) and the normal Lorentz and polarization corrections were applied to the data sets. Data were obtained on a common arbitrary scale. The estimated standard deviation, σ, of a net intensity, *I*, was derived from $\sigma^2(I) = [C + B_1 + B_2 + (0{\cdot}035I)^2]$, in which *C* is the total integrated count, B_1 and B_2 are the background counts and $I = C - B_1 - B_2$. A reflection was considered observed if $I \geqslant 2\sigma(I)$. Further, we assumed that $\sigma(I)/I = \sigma(F_o^2)/F_o^2 = 2\sigma(F_o)/F_o$.

Structure Determination and Refinement.—The function minimized during the refinements was $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$ is the weight of a reflection. For both compounds the platinum and phosphorus positions were readily obtained from a three-dimensional Patterson function.

For (I) all carbon atoms could be located from a three-dimensional difference electron-density map, calculated after least-squares refinement of the platinum and phosphorus parameters. The phenyl rings were introduced in the next cycles of refinement as rigid groups (C–C 1·39 Å, C–C–C 120°) with individual isotropic parameters for the carbon atoms. Refinement of the co-ordinates of platinum, of phosphorus, and of the carbons of the 1,2-dimethylcyclo-

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[1] J. P. Visser, A. J. Schipperijn, J. Lukas, D. Bright, and J. J. de Boer, *Chem. Comm.*, 1971, 1266.

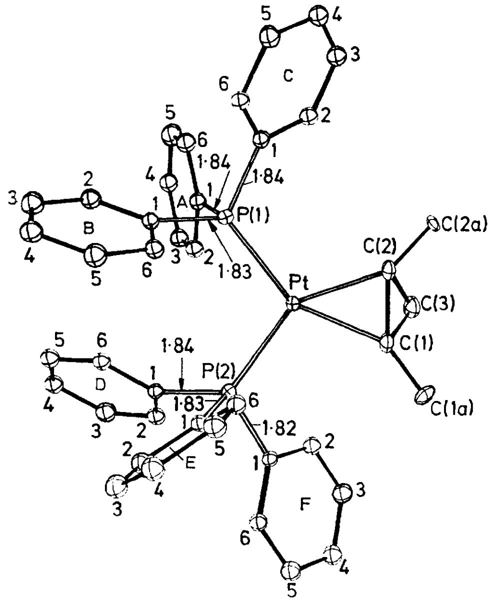
[2] J. P. Visser, A. J. Schipperijn, and J. Lukas, *J. Organometallic Chem.*, 1973, **47**, 433.

[3] N. A. Baily, R. D. Gillard, M. Keaton, R. Mason, and D. R. Russell, *Chem. Comm.*, 1966, 396.

[4] Th. C. Furnas, ' Single Crystal Orienter Instruction Manual,' *X*-Ray Department, General Electric Company, Milwaukee, U.S.A.

propene group, together with anisotropic vibration parameters for the non-carbon atoms and isotropic ones for the carbon atoms resulted in R 0·045 and R' 0·076 {where $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$}.

A difference electron-density map calculated at this stage with low-order data ($\sin\theta/\lambda \leqslant 0{\cdot}35$ Å^{-1}) only, did not show the hydrogen atom positions unambiguously. Therefore we introduced hydrogen atoms on the phenyl rings and on C(3) (see Figure) in calculated positions, assuming the usual geometries with C–H 0·95 Å. The hydrogen positions were not refined, but adjusted with the carbon shifts. A hydrogen temperature factor was taken to be 1 Å^2 greater than that of the carbon atom to which that hydrogen atom was attached. In the following cycles we also allowed for anisotropic vibration of the dimethylcyclopropene carbon atoms, which resulted in a final value for R of 0·032 and for R' of 0·036. Final atomic parameters are listed in Table 1. Final F_o and F_c values for both compounds are deposited in the National Lending Library as Supplementary Publication No. 21227 (4 pp., 1 microfiche).†



The molecule of (I), showing the atom and ring numbering system used

In the case of (II), the phenyl rings were located by means of several cycles of difference-Fourier syntheses followed by least-squares refinement. The rings were included as rigid groups each with an overall isotropic vibration parameter. When all six rings had been included, the residuals were R 0·097 and R' 0·138. A difference synthesis at this stage showed one well resolved peak at the expected position of the methyl carbon, but where the three cyclopropene carbon atoms were expected there was only a diffuse banana-shaped blob. Since we could not assign definite positions to the ring carbons from this map, we next included the ring as a seventh rigid group using the parameters observed for (I). Refinement of this model, with individual isotropic vibration parameters for all carbon atoms and anisotropic parameters for the platinum and phosphorus atoms, gave the final values R 0·051 and R' 0·062. Final atomic parameters are listed in Table 2.

TABLE 1

Final atomic ($\times 10^4$; Pt $\times 10^5$) and thermal parameters for (I), with estimated standard deviations in parentheses

	x	y	z	B/Å^2
Pt	9735(4)	10295(2)	19080(3)	*
P(1)	2313(2)	397(2)	2980(2)	*
P(2)	1966(2)	1781(2)	1278(2)	*
C(1a)	−1432(9)	2001(6)	928(7)	*
C(1)	−745(9)	1274(7)	1199(8)	*
C(2)	−657(9)	709(6)	1900(8)	*
C(3)	−1203(10)	469(7)	943(8)	*
C(2a)	−1298(8)	695(6)	2556(6)	*
C(A1)	2887(15)	−442(5)	2610(6)	4·0(2)
C(A2)	2908(11)	−446(4)	1767(5)	5·1(3)
C(A3)	3268(7)	−1084(5)	1442(4)	6·1(4)
C(A4)	3608(15)	−1719(5)	1960(7)	5·9(3)
C(A5)	3587(12)	−1715(4)	2804(6)	6·7(3)
C(A6)	3227(7)	−1076(5)	3129(4)	5·5(3)
C(B1)	3554(5)	939(4)	3614(4)	3·7(2)
C(B2)	4652(6)	651(3)	3890(5)	5·3(3)
C(B3)	5557(5)	1104(5)	4353(5)	6·5(3)
C(B4)	5366(6)	1845(5)	4541(5)	6·5(3)
C(B5)	4268(7)	2133(3)	4265(5)	6·1(3)
C(B6)	3362(5)	1680(4)	3801(5)	4·5(2)
C(C1)	1802(7)	11(4)	3822(4)	4·0(2)
C(C2)	1007(6)	−566(4)	3585(3)	5·0(3)
C(C3)	609(7)	−893(4)	4201(5)	5·5(3)
C(C4)	1007(8)	−642(5)	5053(4)	5·4(3)
C(C5)	1802(6)	−65(4)	5290(3)	5·6(3)
C(C6)	2200(7)	262(4)	4674(5)	4·7(3)
C(D1)	3294(6)	1450(9)	1136(5)	3·8(2)
C(D2)	3306(5)	1166(7)	348(4)	5·1(3)
C(D3)	4310(7)	890(4)	272(4)	6·4(3)
C(D4)	5302(6)	897(9)	984(5)	5·9(3)
C(D5)	5289(5)	1181(7)	1772(4)	5·4(3)
C(D6)	4285(7)	1457(4)	1848(3)	4·7(2)
C(E1)	2374(9)	2701(4)	1795(5)	3·9(2)
C(E2)	3271(7)	3125(4)	1719(5)	5·3(3)
C(E3)	3558(7)	3804(5)	2159(6)	6·4(3)
C(E4)	2947(10)	4059(4)	2675(6)	6·5(3)
C(E5)	2049(7)	3635(4)	2752(5)	6·2(3)
C(E6)	1763(6)	2956(5)	2312(5)	4·9(3)
C(F1)	1116(6)	2022(4)	169(4)	3·7(2)
C(F2)	354(6)	1488(3)	−314(5)	5·2(3)
C(F3)	−312(6)	1647(4)	−1162(5)	6·0(3)
C(F4)	−217(6)	2339(5)	−1526(4)	6·1(3)
C(F5)	546(7)	2873(3)	−1042(5)	6·0(3)
C(F6)	1212(6)	2715(4)	−195(5)	4·5(2)

* Anisotropic, in the form, $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, with parameters (Pt and P $\times 10^5$, C $\times 10^4$):

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	569(5)	269(2)	343(3)	11(3)	151(3)	32(2)
P(1)	716(27)	277(11)	329(15)	38(14)	135(16)	27(10)
P(2)	602(26)	276(11)	389(15)	−6(13)	173(16)	22(10)
C(1a)	84(12)	33(5)	55(6)	26(6)	15(7)	9(5)
C(1)	50(10)	54(7)	55(7)	−6(6)	12(7)	1(5)
C(2)	54(10)	42(5)	61(7)	−10(6)	12(7)	−5(5)
C(3)	83(13)	51(6)	77(8)	−14(7)	16(8)	−6(6)
C(2a)	54(9)	39(4)	32(5)	−12(5)	25(6)	0(4)

Attempts to refine the cyclopropene carbons as individual atoms did indeed produce lower R values, but the interatomic distances became unreasonable, as did the temperature factors of these atoms.

We next re-examined the elemental analysis of our sample, and it was found to contain a small but significant trace of chlorine. Further research showed that when the compound is prepared in hydrocarbon solvents, the only product appears to be the orthorhombic modification, but if chloroform is used as the solvent, a mixture of the orthorhombic and monoclinic forms is obtained. This evidence

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† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

suggests co-crystallisation of the cyclopropene complex with a chloro-compound. However, attempts to interpret the difference map in terms of a partial occupancy of the most likely chloro-compound, $[Cl(CHCl_2)Pt(PPh_3)_2]$, were unsuccessful and the refinement was abandoned at this stage.

TABLE 2

Final atomic (Pt × 10^5, P × 10^4, C × 10^3) and thermal parameters for (II), with estimated standard deviations in parentheses

	x	y	z	B
Pt	1990(16)	9077(3)	22185(10)	*
P(1)	1845(10)	1174(4)	1914(6)	*
P(2)	777(10)	−70(5)	2915(6)	*
C(4)	−380(3)	180(2)	137(2)	7·6(10)
C(1)	−153(4)	104(2)	223(3)	11·1(13)
C(2)	−122(5)	171(2)	205(4)	16·9(18)
C(3)	−266(4)	139(3)	130(3)	14·8(16)
C(A1)	119(3)	174(1)	94(2)	4·0(8)
C(A2)	167(3)	169(1)	35(2)	7·2(10)
C(A3)	122(3)	214(1)	−36(2)	9·5(12)
C(A4)	29(4)	264(1)	−48(2)	7·9(10)
C(A5)	−19(3)	268(1)	10(2)	7·6(10)
C(A6)	26(2)	223(1)	81(2)	6·4(9)
C(B1)	341(3)	160(2)	289(1)	4·6(8)
C(B2)	425(2)	200(1)	274(1)	4·5(8)
C(B3)	546(3)	230(1)	349(2)	4·8(8)
C(B4)	583(3)	220(2)	440(1)	5·1(8)
C(B5)	500(2)	180(1)	456(1)	5·8(9)
C(B6)	379(3)	150(1)	380(2)	4·9(8)
C(C1)	258(3)	53(1)	158(1)	4·3(8)
C(C2)	167(2)	4(1)	102(2)	5·9(9)
C(C3)	216(3)	−45(1)	73(1)	6·3(9)
C(C4)	358(3)	−44(1)	99(2)	7·1(10)
C(C5)	449(2)	5(1)	155(2)	6·0(9)
C(C6)	400(2)	54(1)	185(1)	5·0(8)
C(D1)	139(2)	−5(1)	416(1)	5·1(9)
C(D2)	204(2)	−57(1)	475(2)	5·2(8)
C(D3)	241(2)	−55(1)	567(1)	5·6(9)
C(D4)	213(2)	1(1)	599(1)	4·9(9)
C(D5)	149(2)	54(1)	540(2)	5·4(9)
C(D6)	112(2)	51(1)	448(2)	5·4(9)
C(E1)	223(2)	−59(1)	305(2)	4·7(8)
C(E2)	365(3)	−38(1)	360(1)	6·3(9)
C(E3)	472(2)	−74(2)	364(2)	7·9(10)
C(E4)	437(3)	−131(1)	312(2)	8·1(10)
C(E5)	294(3)	−151(1)	256(2)	9·1(11)
C(E6)	188(2)	−115(1)	253(2)	7·1(10)
C(F1)	−76(3)	−60(2)	235(2)	4·7(8)
C(F2)	−89(2)	−112(2)	281(1)	6·3(9)
C(F3)	−210(4)	−151(1)	233(2)	7·1(10)
C(F4)	−319(3)	−138(2)	139(2)	7·9(10)
C(F5)	−307(2)	−85(2)	94(1)	7·6(10)
C(F6)	−185(4)	−46(1)	142(2)	7·2(10)

* Anisotropic parameters (see footnote to Table 1); for Pt × 10^5, for P × 10^4:

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	1526(30)	330(6)	711(12)	86(13)	651(14)	156(9)
P(1)	164(17)	24(4)	51(7)	9(6)	53(9)	−4(4)
P(2)	147(17)	34(4)	54(7)	−14(7)	66(9)	−9(4)

Throughout the refinements neutral atomic scattering factors and the correction terms for anomalous scattering of platinum and phosphorus from ref. 5 were used. For the actual refinement we employed NUCLS, Ibers' version of the Martin, Busing, and Levy OR FLS[6] least-squares program. Their OR FFE[7] program was used for the calculation of estimated standard deviations (σ values) on bond length and angles of non-group atoms. The σ on the molecular parameters involving one or more atoms refined as a member of a rigid group were calculated by Templeton's method.[8]

DISCUSSION AND DESCRIPTION OF THE STRUCTURE

Both structures are built up *via* the packing of monomeric units of $LPt(PPh_3)_2$ ($L = C_5H_8$ or C_4H_6) and excluding hydrogen contacts the shortest intermolecular contacts are C(C4) · · · C(C4′) 3·36(2) for (I), and C(C2) · · · C(C2′) 3·40(7) Å for (II).

TABLE 3

Molecular parameters for (I), with estimated standard deviations in parentheses

(*a*) Bond distances (Å)

Pt–P(1)	2·278(4)	C(1)–C(1a)	1·53(1)
Pt–P(2)	2·288(4)	C(1)–C(2)	1·50(1)
Pt–C(1)	2·12(1)	C(1)–C(3)	1·54(1)
Pt–C(2)	2·11(1)	C(2)–C(2a)	1·54(1)
Pt–C(3)	2·83(1)	C(2)–C(3)	1·55(2)
P(1)–C(A1)	1·84(1)	P(2)–C(D1)	1·84(1)
P(1)–C(B1)	1·83(1)	P(2)–C(E1)	1·83(1)
P(1)–C(C1)	1·84(1)	P(2)–C(F1)	1·82(1)

C–C in Ph rings A–F 1·39

(*b*) Bond angles (°)

P(1)–Pt–P(2)	105·5(1)	C(1a)–C(1)–C(3)	125·5(9)
P(1)–Pt–C(2)	109·4(4)	C(2)–C(1)–C(3)	61·0(8)
P(2)–Pt–C(1)	103·6(4)	C(2)–C(1)–Pt	68·9(6)
C(2)–Pt–C(1)	41·6(4)	C(2a)–C(2)–C(3)	123·2(9)
		C(1)–C(2)–C(3)	60·9(8)
		C(1)–C(2)–Pt	69·5(6)
		C(1)–C(3)–C(2)	58·1(7)
Pt–P(1)–C(A1)	114·3(5)	Pt–P(2)–C(D1)	121·0(5)
Pt–P(1)–C(B1)	116·4(3)	P–P(2)–C(E1)	114·8(4)
Pt–P(1)–C(C1)	114·5(3)	Pt–P(2)–C(F1)	113·3(3)
C(A1)–P(1)–C(B1)	105·3(6)	C(D1)–P(2)–C(E1)	102·7(6)
C(A1)–P(1)–C(C1)	102·4(5)	C(D1)–P(2)–D(F1)	101·5(4)
C(B1)–P(1)–C(C1)	102·2(4)	C(E1)–P(2)–C(F1)	103·4(4)

C–C–C in Ph rings A–F 120

TABLE 4

Molecular parameters for (II), with estimated standard deviations in parentheses

(*a*) Bond distances (Å)

Pt–P(1)	2·26(2)	P(1)–C(A1)	1·82(4)
Pt–P(2)	2·26(1)	P(1)–C(B1)	1·84(4)
Pt–C(1)	1·98(5)	P(1)–C(C1)	1·82(3)
Pt–C(2)	2·21(5)	P(2)–C(D1)	1·84(3)
Pt–C(3)	2·85(3)	P(2)–C(E1)	1·86(3)
C(4)–C(3)	1·61(7)	P(2)–C(F1)	1·80(4)

C–C in Ph rings A–F 1·39

(*b*) Bond angles (°)

P(1)–Pt–P(2)	108·3(4)	C(1)–C(3)–C(4)	113(5)
P(1)–Pt–C(2)	115(2)	C(2)–C(3)–C(4)	103(4)
P(2)–Pt–C(1)	96(2)		
C(2)–Pt–C(1)	42(2)		
Pt–P(1)–C(A1)	114(1)	Pt–P(2)–C(D1)	114(1)
Pt–P(1)–C(B1)	113(1)	Pt–P(2)–C(E1)	123(1)
Pt–P(1)–C(C1)	118(1)	Pt–P(2)–C(F1)	111(1)
C(A1)–P(1)–C(B1)	102(2)	C(D1)–P(2)–C(E1)	98(1)
C(A1)–P(1)–C(C1)	102(2)	C(D1)–P(2)–D(F1)	105(2)
C(B1)–P(1)–C(C1)	105(2)	C(E1)–P(2)–C(F1)	103(2)

C–C–C in Ph rings A–F 120

Both structures have the same overall molecular geometry. A general view of (I) is given in the Figure together with the atomic numbering scheme. A selection of bond lengths and angles for the two compounds is given in Tables 3 and 4. Unfortunately we

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[5] 'International Tables for *X*-ray Crystallography,' volume III, Kynoch Press, Birmingham, 1962.

[6] W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory, Report TM 305.

[7] W. R. Busing, K. O. Martin, and H. A. Levy, Oak Ridge National Laboratory, Report TM 306.

[8] D. H. Templeton, *Acta Cryst.*, 1959, **12**, 771.

failed to obtain a precise determination of the cyclopropene ring parameters for (II) and are unable to comment on the details of the ring geometry in this compound. Nevertheless, it is clear from the difference electron-density maps that the methyl group, C(4), in (II) lies on the opposite side of the ring plane to the platinum atom, and that the co-ordination of the cyclopropene ring to the metal is essentially the same as in (I). In the discussion which follows we refer only to the parameters found for (I), unless otherwise stated.

The co-ordination of the platinum is distorted square-planar (Tables 4 and 5), one side of the square is formed by two atoms of the cyclopropene ring, the other by the phosphorus atoms. The angle between the Pt, C(1), C(2) plane and the C(1)—(3) plane is 115·8(6)°, comparable with that found in π-allyl complexes. However, C(3) is too far away from the metal atom for a significant bonding interaction to occur. Therefore any suggestion of deprotonation of the cyclopropene molecule followed by an allylic or anti-aromatic co-ordination to the platinum may be rejected. The C–C distances in the cyclopropene ring are all *ca.* 1·50 Å. Thus the ring remains intact on complex formation. This contrasts with the results for a cyclopropane–platinum derivative, $[(C_3H_6)PtCl_2(py)_2]$,[2] in which the platinum atom is inserted into the cyclopropane ring, and where the distance between the co-ordinated carbons is 2·54 Å.

TABLE 5

Distances to the Pt, P(1), P(2), C(1), C(2) plane in (I) (Å)

Pt	−0·0001(4)	C(2)	0·024(12)
P(1)	0·001(3)	C(1a)	0·84(1)
P(2)	0·001(3)	C(2a)	−1·20(1)
C(1)	0·002(12)	C(3)	0·92(1)

The compound is therefore an olefin complex of platinum(0) analogous to $[\{(CN)_2C{:}C(CN)_2\}Pt(PPh_3)_2]$.[9] Metal–olefin bonding may be visualized as occurring either through two σ bonds from the olefinic carbons to the metal or through interaction of an empty orbital in the metal with the olefinic π-orbital. The second model may be further refined by postulating a back-bonding interaction between two filled metal orbitals with an empty olefinic π* orbital. This back-bonding effect is exactly equivalent to the σ bonding model, so that a better overall picture may be obtained if the metal–olefinic interaction is viewed as a competition between the metal–π and metal–π* orbital interaction. If the former prevails, then the configuration in the co-ordinated ligand should remain virtually identical with that in the free molecule. If the latter (and hence the σ bonding model) is more important, then the olefinic bond should be longer, and the configuration about the bonded carbons closer to tetrahedral than in the free ligand.

In (I) the cyclopropene double bond [1·50(1) Å] is considerably longer than in the free ligand (1·30 Å).[10] However, the value in (I) compares very well with that (1·52 Å) found for $[\{(CN)_2C{:}C(CN)_2\}Pt(PPh_3)_2]$,[9] and both these values are considerably higher than the mean (1·40 Å) for the olefinic iron complexes: $[(CH_2{:}CH{\cdot}CN)Fe(CO)_4]$ (ref. 11) and $[\{(HCO_2)CH{:}CH(CO_2H)\}Fe(CO)_4]$.[12] Moreover, the methyl groups in the cyclopropene ring (which are expected to be coplanar with the ring in the free molecule) are bent away from the platinum atom, such that the angle between the planes through C(1)—(3) and C(1a),C(1),C(2),C(2a) is 112° *cf.* corresponding value (150°) for $[\{(HCO_2)CH{:}CH(CO_2H)\}Fe(CO)_4]$.[12] These parameters suggest that the contribution from the σ form is greater in the platinum compounds than in the iron compounds, which is not surprising when we consider the relatively large number of σ bonded platinum–alkyl complexes. There still remains considerable π interaction, however, as shown by the Pt–C distances of 2·12 Å, considerably longer than for the pure σ bond, *e.g.* 2·02 Å in $[\{Me_3Pt(OH)\}_4]$.[13]

The grouping P(1),P(2),Pt,C(1),C(2) is planar; the Pt–P distances [2·278(4) and 2·288(4) Å] for (I) are in excellent agreement with those [2·26(2) and 2·26(1) Å] for (II) and for $[(PhC{:}CPh)Pt(PPh_3)_2]$ (2·28 and 2·27 Å)[14] and for $[\{(CN)_2C{:}C(CN)_2\}Pt(PPh_3)_2]$ [2·29(1) and 2·30(1) Å].[9] However, in these compounds the dihedral angles between the planes Pt,P(1),P(2) and Pt,C(1),C(2) are 14 and 6°, respectively, resulting in a non-planar grouping. This variance has been ascribed to a low-energy barrier to rotation about the platinum–olefin linkage coupled with packing forces.

The reasons for the observed disorder of the cyclopropene ring atoms are rather obscure, and we have no reasonable explanation for its origin. Possibly a study of the orthorhombic modification of (II) would be more fruitful.

We thank Dr. J. P. Visser for supplying suitable crystals.

[4/1626 *Received*, 5*th August*, 1974]

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