Synthesis and Crystal Structure of the Metallacyclopentane Complex 2,2,5,5-Tetracyano-3-ethoxy-1,1-bis(triphenylphosphine)-1-platinacyclopentane

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Reaction of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] with 1,1,2,2-tetracyano-3-ethoxycyclobutane and 1,1,2,2-tetracyano-3-(*p*-methoxyphenyl)cyclobutane gives the platinum-cyclopentane complexes (1) [Pt(PPh$_3$)$_2${C$_4$H$_3$(CN)$_4$OEt}] and (2) [Pt(PPh$_3$)$_2${C$_4$H$_3$(CN)$_4$C$_6$H$_4$OMe}]. The crystal structure of (1) was determined from diffractometer data. Crystals are monoclinic, space group $P2_1/c$, with cell parameters a = 10.586(6), b = 20.422(10), c = 23.234(10) Å, β = 115.23(10)°. *The structure was solved by the heavy-atom method and final least-squares refinement gave R* 0.092 for 2 636 reflections. The platinum atom has been inserted into a carbon–carbon bond. Three- and four-membered carbocycles are compared.

THE presence of a fractional positive charge on the carbon atom of an electronegatively substituted cyclopropane or oxirane such as 1,1,2,2-tetracyanocyclopropane (tccp) and 2,2,3,3-tetracyano-oxacyclopropane (tcneo) has been suggested on the basis of ESCA measurements and theoretical calculations.[1] It is thus at variance with cyclopropane and its aryl or alkyl derivatives, where electrophilic attack by a PtCl$_2$ moiety has been suggested,[2] since tetracyanocyclopropane derivatives and tetracyano-oxacyclopropane are expected to be susceptible to nucleophilic attack by complexes of the type [ML$_n$] (M = Ni, Pd, and Pt; L = tertiary phosphine or arsine). Under very mild conditions, platinum and palladium complexes of the type [ML$_2$(tccp)] or [ML$_2$(tcneo)] have been synthesized.[3-5] As for the reaction mechanism, these complexes are best described as products of an oxidative addition of the intermediate species [ML$_2$] [6-8] with strained electronegatively-activated carbocycles [3] or oxiranes.[5] [ML$_2$] Then acts as a nucleophile, attacking the ring at the centre of lowest electron density. The products of these reactions are ' metalla-oxacyclobutane ' complexes and their formation relieves the strain within the three-membered rings. Nevertheless, the question remains as to whether the driving force of this insertion reaction is the strain energy of the ring, or the positive charge on the carbon atoms of the carbocycle bearing the cyano-substituents. In order to clarify this point the four-membered carbocycle 1,1,2,2-tetracyano-3-substituted-cyclobutane, having a lower strain energy than, and a similar partial positive charge to, tetracyanocyclopropane,[1] was treated with [Pt(PPh$_3$)$_2$(C$_2$H$_4$)]. The structure of the platinum-cyclopentane complex (1) obtained from this reaction was determined from three-dimensional *X*-ray data.

EXPERIMENTAL

The complex [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] was prepared as described in ref. 9, and 1,1,2,2-tetracyano-3-ethoxycyclobutane and 1,1,2,2-tetracyano-3-(*p*-methoxyphenyl)cyclobutane as described in ref. 10. I.r. spectra were recorded on a Perkin-Elmer 457, and ^{1}H n.m.r. spectra on a Varian NV 14 spectrometer.

[Pt(PPh$_3$)$_2${C$_4$H$_3$(CN)$_4$OEt}], *Complex* (1).—To a suspension of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] (0.746 g, 1.0 mmol) in anhydrous diethyl ether (80 ml), was added 1,1,2,2-tetracyano-3-ethoxycyclobutane (0.2 g, 1.0 mmol) in the minimum anhydrous tetrahydrofuran, and the mixture stirred under nitrogen overnight. The light yellow solid was dried, and recrystallized from dichloromethane–diethyl ether as white crystals (0.6 g) of (1); m.p. 193—194 °C (decomp.) (Found: C, 60.05; H, 4.2; N, 6.00; P, 6.80. $C_{46}H_{38}N_4OP_2Pt$ requires C, 60.05; H, 4.15; N, 6.10; P, 6.75%); i.r. (Nujol mull) ν(CN) 2 220 cm^{-1}; ^{1}H n.m.r. (CDCl$_3$, tetramethylsilane as internal standard); τ values: CH$_2$CH$_3$ 8.69 (t), 6.54 (q), cyclic protons (br, m) 5.5—7.84, Ph protons (br, m) 2.2—3.1.

[Pt(PPh$_3$)$_2${C$_4$H$_3$(CN)$_4$C$_6$H$_4$OMe}], *Complex* (2).—To a suspension of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] (0.746 g, 1.0 mmol) in anhydrous diethyl ether (100 ml), was added 1,1,2,2-tetracyano-3-(*p*-methoxyphenyl)cyclobutane (0.262 g, 1.0 mmol) in the minimum of anhydrous tetrahydrofuran, and the mixture stirred overnight. The solid obtained was recrystallized as before to give white crystals of (2) (0.380 g), m.p. 245—248 °C (decomp.) (Found: C, 62.20; H, 4.05; N, 5.5; P, 6.20. $C_{51}H_{40}N_4OP_2Pt$ requires C, 62.40; H, 4.10; N, 5.70; P, 6.30%); i.r. (Nujol mull) ν(CN) 2 218 cm^{-1}; ^{1}H n.m.r. (τ values, as before): CH$_3$ 6.25 (s), phenylene protons (4 line system partially overlapped by phosphine protons) centre at 3.45; cyclic protons (br, m) 8.59—5.5.

Crystal Data.—$C_{46}H_{38}N_4OP_2Pt$, Complex (1), M = 919.9, Monoclinic, a = 10.586(6), b = 20.422(10), c = 23.234(10) Å, β = 115.23(10)°, U = 4 543.7 Å^3, D_m (flotation) = 1.40, Z = 4, D_c = 1.35. Mo-K_α radiation, λ = 0.7107 Å; μ(Mo-K_α) = 33.6 cm^{-1}. Space group $P2_1/c$.

Cell parameters were determined from Weissenberg

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photographs taken with Co-K_α radiation and refined with an on-line Siemens diffractometer.

Intensity Measurements.—Three-dimensional intensity data were collected on a Siemens diffractometer by the θ—2θ scan technique with Mo-K_α radiation up to $2\theta_{max.}$ 54° from a crystal of mean dimensions 0.53 mm. All reflections having $I_0 < 3\sigma(I_0)$ were rejected, the remainder (2 636) being corrected for Lorentz-polarization effects and used in the subsequent calculations. No correction for absorption (μR 0.89) was applied.

TABLE 1

Fractional co-ordinates (× 10^4), with estimated standard deviations in parentheses

	x	*y*	*z*	B/Å^2
Pt	814(1)	2 537(1)	1 409(0)	*
P(1)	307(9)	3 513(5)	835(4)	*
P(2)	2 635(8)	3 008(4)	2 281(4)	*
O	677(38)	489(21)	1 525(17)	*
N(1)	−3 280(28)	2 484(18)	549(14)	*
N(2)	−461(32)	1 940(26)	−372(16)	*
N(3)	3 616(29)	1 218(15)	2 639(14)	*
N(4)	−530(31)	1 516(16)	2 426(15)	*
C(1)	−455(31)	4 108(16)	1 201(14)	4.3(7)
C(2)	−414(44)	4 833(24)	1 118(19)	7.4(12)
C(3)	−1 227(52)	5 220(25)	1 387(23)	8.9(14)
C(4)	−1 817(50)	4 927(27)	1 683(23)	9.1(14)
C(5)	−1 969(39)	4 235(50)	1 802(18)	6.2(10)
C(6)	−1 222(44)	3 888(21)	1 518(20)	7.0(11)
C(7)	−986(34)	3 532(17)	10(15)	4.4(8)
C(8)	−2 360(34)	3 646(16)	−122(15)	4.2(8)
C(9)	−3 535(35)	3 626(17)	−773(16)	5.2(8)
C(10)	−2 995(38)	3 581(19)	−1 252(17)	5.2(9)
C(11)	−1 505(35)	3 536(17)	−1 123(16)	4.7(8)
C(12)	−454(32)	3 558(16)	− 475(15)	4.3(7)
C(13)	1 881(32)	3 827(16)	719(15)	4.3(7)
C(14)	2 776(32)	3 316(15)	759(15)	4.2(7)
C(15)	3 917(39)	3 483(19)	617(18)	5.8(9)
C(16)	4 345(45)	4 129(22)	571(21)	6.8(12)
C(17)	3 283(46)	4 598(23)	507(21)	8.1(12)
C(18)	2 040(34)	4 431(17)	544(15)	4.9(8)
C(19)	4 494(35)	2 830(17)	2 418(15)	4.4(8)
C(20)	5 568(34)	3 127(16)	2 823(15)	4.2(7)
C(21)	6 849(92)	2 940(48)	2 795(41)	19.5(34)
C(22)	7 056(40)	2 485(23)	2 429(17)	7.1(9)
C(23)	5 903(42)	2 181(20)	1 983(18)	6.3(9)
C(24)	4 519(33)	2 378(15)	1 982(15)	4.2(8)
C(25)	2 572(35)	2 777(17)	3 042(15)	4.2(7)
C(26)	3 691(34)	2 469(20)	3 521(14)	5.4(7)
C(27)	3 586(47)	2 387(23)	4 166(21)	7.7(12)
C(28)	2 088(40)	2 413(20)	4 130(18)	6.3(9)
C(29)	1 031(41)	2 621(19)	3 634(19)	6.4(10)
C(30)	1 117(35)	2 769(17)	3 041(15)	4.6(7)
C(31)	2 764(37)	3 895(19)	2 422(17)	5.2(9)
C(32)	3 599(33)	4 282(17)	2 167(15)	4.5(8)
C(33)	3 746(36)	4 946(18)	2 231(16)	4.9(8)
C(34)	2 929(40)	5.256(20)	2 534(18)	6.2(10)
C(35)	2 087(38)	4 915(19)	2 716(17)	5.8(9)
C(36)	2 004(36)	4 197(18)	2 706(16)	5.1(8)
C(37)	1 033(30)	1 589(15)	1 843(14)	
C(38)	775(41)	1 047(14)	1 261(15)	
C(39)	−747(36)	1 191(17)	821(20)	
C(40)	−819(28)	1 991(14)	688(11)	
C(41)	−493(43)	1 933(23)	134(17)	
C(42)	−2 144(34)	2 253(19)	595(10)	
C(43)	114(37)	1 580(19)	2 169(17)	
C(44)	2 620(35)	1 367(19)	2 309(17)	
C(45)	1 173(58)	−146(20)	1 200(23)	
C(46)	1 368(109)	−453(30)	1 561(30)	

Structure Determination and Refinement.—The structure was solved by conventional Patterson and Fourier methods. With anisotropic temperature factors assigned to all atoms except the phenyl carbon atoms, final least-squares refinement gave R 0.092. The final weighting scheme was $w = 1/(A + B|F_o| + C|F_o|^2)$ where $A = 27.0$, $B = 1.0$, and $C = 0.002$ were chosen so as to maintain $w(|F_o| - |F_c|^2)$ essentially constant over all ranges of $|F_o|$ and $(\sin\theta/\lambda)$. Final atomic parameters are listed in Table 1 together with their estimated standard deviations. Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21707 (10 pp., 1 microfiche).* Atomic scattering factors were taken from ref. 11.

DISCUSSION

Description of the Structure.—The crystal structure consists of discrete molecules as shown in Figure 1, together with the atom numbering scheme used. The co-ordination around platinum is square planar with no significant tetrahedral distortion. The four donor atoms are coplanar within 0.01 Å, the Pt atom being displaced *ca.* 0.2 Å above this plane. The dihedral

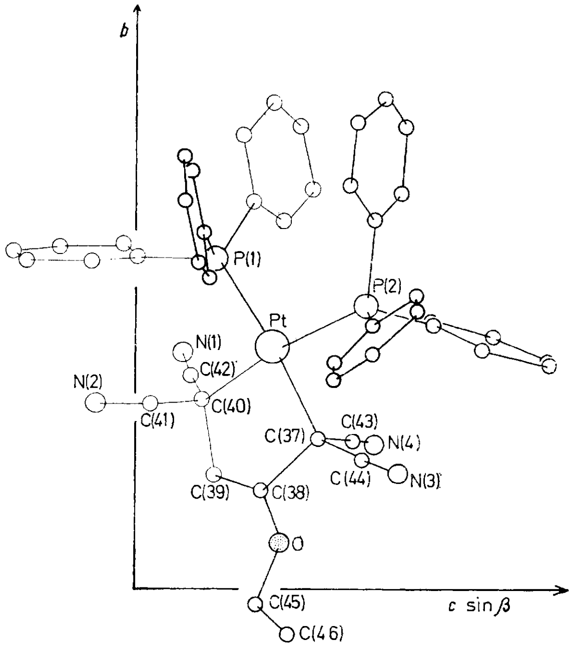
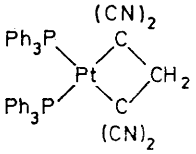
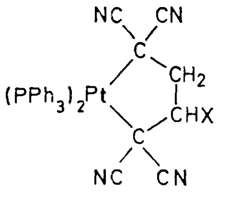


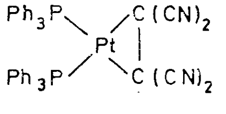
FIGURE 1 A view of the molecule, showing the atom numbering scheme. Phenyl atoms are numbered sequentially with C(1), C(7), and C(13) attached to P(1), and C(19), C(25), and C(31) attached to P(2)

(3)





(4)



(1) X = OEt

(2) X = C_6H_4OMe

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

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angle (ϕ) between the planes P(1),Pt,P(2) and C(37),Pt,C(40) is 1.5°, in contrast with the values of 18.0 and 8.3° in the analogous complexes $[Pt(PPh_3)_2\{C_3H_2(CN)_4\}]$ [complex (3) [4]] and $[Pt(PPh_3)_2\{C_2(CN)_4\}]$ [complex (4) [12]] respectively. The co-ordination parameters of these complexes with five-, four-, and three-membered metallacycles are compared in Table 2. As expected, the C–Pt–C angle increases from 41 to 78° with the increasing size of the ring, while the P–Pt–C angle decreases. There is a relationship between P–Pt–P bond angles and Pt–P bond lengths (Figure 2). The change in the P–Pt–P angle and Pt–P distance from three- to five-membered rings appears to be due to steric interactions caused by the increased size of the cyclic moiety.

TABLE 2

Comparison of geometries of five-, four-, and three-membered ' metallacycles '

Complex	P–Pt–P/°	P–Pt–C/°	C–Pt–C/°	P–Pt/Å	ϕ/°
(1)	92.8(3)	94.9(7)	78(1)	2.330(10)	1.5
		94.6(7)		2.327(7)	
(3)	96.99(6)	99.8(2)	68.4(2)	2.291(2)	18.0
		97.1(2)		2.314(2)	
(4)	101.4(3)	106(1)	41(1)	2.288(8)	8.3
		111(1)		2.291(9)	

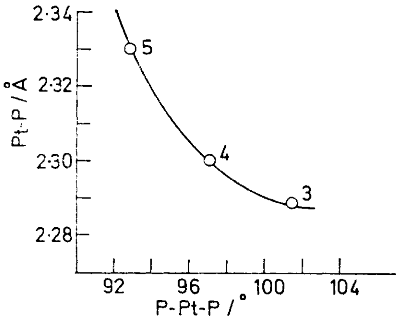


FIGURE 2 Relation between Pt–P bond lengths and P–Pt–P bond angles in three-, four-, and five-membered ' metallacycles '

TABLE 3

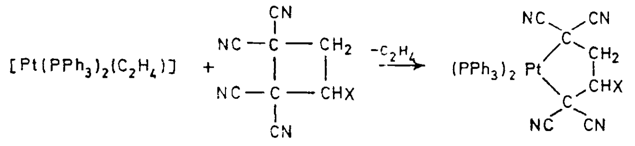
Relevant bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances			
Pt–P(1)	2.33(1)	C(37)–C(43)	1.47(6)
Pt–P(2)	2.33(1)	C(37)–C(44)	1.63(4)
Pt–C(37)	2.15(3)	C(42)–N(1)	1.25(5)
Pt–C(40)	2.14(2)	C(42)–N(2)	1.19(6)
C(37)–C(38)	1.68(5)	C(44)–N(3)	1.05(4)
C(38)–C(39)	1.52(5)	C(43)–N(4)	1.09(6)
C(39)–C(40)	1.66(5)	C(38)–O	1.32(5)
C(40)–C(41)	1.47(6)	O–C(45)	1.69(7)
C(40)–C(42)	1.43(5)	C(45)–C(46)	1.00(8)
(*b*) Angles			
P(1)–Pt–P(2)	92.8(3)	Pt–C(40)–C(41)	108(2)
P(1)–Pt–C(40)	94.9(7)	Pt–C(40)–C(42)	110(2)
P(1)–Pt–C(37)	172.5(7)	C(39)–C(40)–C(41)	94(3)
P(2)–Pt–C(37)	94.6(7)	C(39)–C(40)–C(42)	111(3)
P(2)–Pt–C(40)	172.3(8)	C(37)–C(43)–N(4)	173(4)
C(37)–Pt–C(40)	78(1)	C(37)–C(44)–N(3)	175(5)
Pt–C(37)–C(38)	106(2)	C(40)–C(42)–N(1)	177(3)
Pt–C(40)–C(39)	114(2)	C(40)–C(41)–N(2)	168(4)
C(37)–C(38)–C(39)	100(3)	C(37)–C(38)–O	102(3)
C(38)–C(39)–C(40)	105(2)	C(39)–C(38)–O	102(3)
Pt–C(37)–C(43)	107(2)	C(38)–O–C(45)	111(4)
Pt–C(37)–C(44)	116(2)	O–C(45)–C(46)	96(7)
C(38)–C(37)–C(43)	120(3)		
C(38)–C(37)–C(44)	97(3)		

Finally, the geometry of the metallacyclopentane is close to that of an envelope conformation with the torsion angle around the ethylene bridge being 43°, and atoms C(38) and C(39) displaced 1.02 and 0.27 Å above the co-ordination plane.

Relevant bond lengths and angles are listed in Table 3. Bond lengths in the ethoxy group are not very accurate because of high thermal motion of the relevant atoms.

Conclusions. —1,1,2,2-Tetracyano-3-substituted-cyclobutane [10] reacts at room temperature under nitrogen with an equimolar amount of $[Pt(PPh_3)_2(C_2H_4)]$ according to the following reaction:



(1) X = OEt
(2) X = C_6H_4OMe

The platinum atom has thus been inserted into the cyclobutane ring between the two carbon atoms bearing the cyano-substituents. This leads to the formation of a five-membered ring, giving a ' metallacyclopentane ' compound, which may therefore be formulated as the product of insertion of $[Pt(PPh_3)_2]$ into the C–C bond of the four-membered ring in a way similar to that in the reaction of $[Pt(PPh_3)_4]$ and 1,1,2,2-tetracyanocyclopropane [3] which gives a ' metallacyclobutane ' complex. Under the same experimental conditions platinum(0) complexes do not react with 1,2-dicyanocyclopropane.[3] Our results confirm the suggestion [3] that ring-opening reactions of highly strained carbocycles occur by attack of the metal at the most positively charged carbon atom of the cyclic moiety followed by the cleavage of the weakest bond involving this atom. Moreover they support the hypothesis that the driving force in ring-opening, involving electronegatively substituted three- or four-membered carbocycles, is the positive charge on the carbon atom rather than the strain energy. We found, in fact, the following reactivity sequence: 1,1,2,2-tetracyanocyclopropane > 1,1,2,2-tetracyano-3-substituted-cyclobutane > 1,2-dicyanocyclopropane. This trend may be better interpreted on the basis of the extent of positive charge on the carbon atom bearing the cyano-substituents, rather than in terms of strain energy which is known to be higher in cyclopropane than in cyclobutane. The strain energy, however, must play some role since the tetracyano-substituted three-membered ring is more reactive than is the four-membered one.

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