Synthesis and Crystal Structure of 3,3,4-Tricyano-2,2-bis(triphenylphosphine)-1-oxa-2-platinacyclobutane

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The title complex has been prepared from the reaction of $[Pt(PPh_3)_2(C_2H_4)]$ with 2,2,3-tricyano-oxacyclopropane, and the crystal structure has been determined by *X*-ray single-crystal analysis. Crystals are monoclinic, space group $P2_1/n$, with $a = 10.820(7)$, $b = 18.827(9)$, $c = 18.581(9)$ Å, and $\beta = 105.4(1)^\circ$. The structure has been solved by the heavy-atom method and refined to R 0.048 for 1 780 reflections. The structural results confirm that platinum is inserted into the carbon–oxygen bond. *X*-Ray and n.m.r. data of this and similar metallacycles are compared and discussed on the basis of a simple bonding model.

METALLAOXACYCLOBUTANE complexes have been proposed as intermediates in the formation of ethylene carbonate in the system carbon dioxide–ethylene oxide catalyzed by nickel(0) complexes.[1] By reaction of 2,2,3,3-tetracyano-oxacyclopropane (L) with low-valent platinum and palladium complexes,[2] oxaplatinacyclobutane complexes were prepared and the structure of $[Pt(AsPh_3)_2L]$ was also determined.[3] It seems clear that the driving force in the ring-opening reaction of three-[4] and four-membered[5] electronegatively substituted carbocycles is the extent of positive charge on the carbon atoms, rather than the strain energy of the carbocycle.[4,5] Several factors appear to be involved in the ring-opening reactions of electronegatively activated

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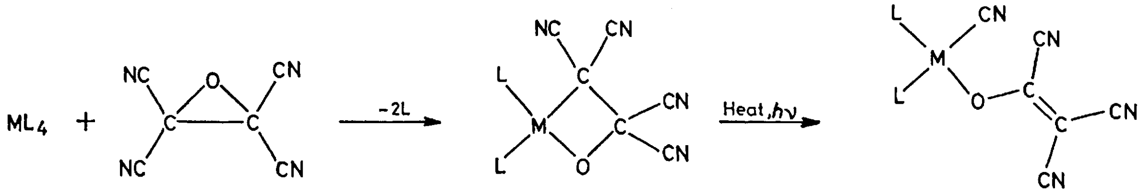
epoxides, where an isomerization reaction follows the insertion (Scheme 1); the ease of these reactions depends on various parameters such as the nature of the metal and basicity of the phosphine.[2] We now report the crystal-structure determination of a complex formed in the reaction of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] with 2,2,3-tricyano-oxacyclopropane.



Scheme 1

EXPERIMENTAL

3,3,4-Tricyano-2,2-bis(triphenylphosphine)-1-oxa-2-platinacyclobutane, [Pt(PPh$_3$)$_2${C(CN)$_2$·CH(CN)·O}].—To a suspension of [Pt(PPh$_3$)$_2$(C$_2$H$_4$)] [6] (1.49 g, 2 mmol) in dry diethyl ether was added an equimolar amount of solid 2,3,3-tricyano-oxacyclopropane.[7,8] A pale yellow solid formed in a few minutes, and was filtered off, dried *in vacuo*, and crystallized from CHCl$_3$–MeOH to give white crystals (1 g), m.p. 218—220 °C (Found: C, 59.2; H, 3.45; N, 4.95. C$_{41}$H$_{31}$N$_3$OP$_2$Pt requires C, 58.7; H, 3.70; N, 5.00%); i.r. spectrum (Nujol mull), ν(CN) at 2 210 cm^{-1}; ^{1}H n.m.r. spectrum (in CDCl$_3$; tetramethylsilane as internal standard), τ 4.25(d) [^3J(Pt–H) 32, J(P–H) 2 Hz]. The coupling constants are in the same range as those observed for [PtL$_2$L′] complexes (L = substituted phosphine; L′ = 1,1,2,2-tetracyanocyclopropane).[4,9]

Crystal Data.—C$_{41}$H$_{31}$N$_3$OP$_2$Pt, M = 838.8, Monoclinic, a = 10.820(7), b = 18.827(9), c = 18.581(9) Å, β = 105.4(1)°, U = 3.649.7 Å^3, D_c = 1.53 g cm^{-3}, Z = 4, D_m = 1.54 g cm^{-3}, F(000) = 1 656. Mo-K_α radiation, λ = 0.710 7 Å, μ(Mo-K_α) 41.7 cm^{-1}, space group $P2_1/n$. Cell parameters were determined from Weissenberg and precession photographs taken with Co-K_α radiation and refined with an on-line automatic 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 for a maximum 2θ angle of 44°. Reflections having $I_o < 3\sigma(I_o)$ were rejected, the remainder being corrected for Lorentz and polarization factors. A total of 1 780 independent reflections was used in the subsequent calculations. No correction for absorption was applied (μR 0.31).

Structure Determination and Refinement.—The structure was solved by conventional Patterson and Fourier methods. Least-squares isotropic refinement reduced R to 0.061. When anisotropic temperature factors were assigned to all the atoms, except the phenyl carbon atoms, the final least-squares refinement gave R 0.048. No attempt was made to locate the hydrogen atoms. The final weighting scheme was $w = 1/(A + B|F_o| + C|F_o|^2)$ where A = 48.0, B = 1.0, and C = 0.003 4 were chosen so as to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and (sin θ)/λ. Final atomic parameters are listed in Table 1 together with their estimated standard deviations.

TABLE 1

Fractional co-ordinates (× 10^4) and isotropic temperature factors, with estimated standard deviations in parentheses; asterisks indicate anisotropic temperature factors

	x	y	z	B/Å^2
Pt	−76(1)	473(0)	1 967(1)	*
P(1)	1 399(5)	570(3)	3 117(4)	*
P(2)	−779(6)	−630(3)	2 098(4)	*
O	489(16)	1 439(8)	1 644(9)	*
N(1)	−659(23)	2 601(12)	211(15)	*
N(2)	−1 634(26)	69(13)	−381(15)	*
N(3)	−3 182(26)	1 393(15)	1 162(17)	*
C(1)	−1 169(21)	832(10)	902(12)	*
C(2)	−68(25)	1 365(12)	891(13)	*
C(3)	−453(24)	2 063(14)	497(16)	*
C(4)	−1 441(22)	408(14)	211(14)	*
C(5)	−2 287(23)	1 140(14)	1 004(16)	*
C(6)	915(20)	1 265(12)	3 672(12)	2.9(5)
C(7)	−19(23)	1 752(13)	3 291(14)	4.1(6)
C(8)	−264(32)	2 322(19)	3 789(19)	7.2(9)
C(9)	456(29)	2 407(17)	4 512(18)	6.3(8)
C(10)	1 363(25)	1 932(14)	4 850(15)	4.6(6)
C(11)	1 623(23)	1 368(14)	4 440(14)	4.0(5)
C(12)	1 850(22)	−136(13)	3 823(14)	3.5(5)
C(13)	1 001(19)	−313(11)	4 223(12)	3.0(4)
C(14)	1 269(28)	−855(17)	4 777(17)	5.9(7)
C(15)	2 438(29)	−1 221(17)	4 870(18)	6.2(7)
C(16)	3 276(29)	−1 070(17)	4 450(18)	5.8(7)
C(17)	3 006(23)	−479(16)	3 929(14)	4.6(5)
C(18)	2 900(23)	838(14)	2 945(15)	4.0(5)
C(19)	3 231(23)	542(15)	2 305(14)	4.6(5)
C(20)	4 439(30)	768(17)	2 154(18)	6.4(8)
C(21)	5 258(28)	1 227(16)	2 615(17)	5.8(7)
C(22)	4 941(30)	1 513(18)	3 249(18)	6.9(8)
C(23)	3 754(24)	1 316(14)	3 438(15)	4.3(6)
C(24)	547(23)	−1 275(13)	2 321(14)	3.8(5)
C(25)	1 431(22)	−1 204(13)	1 883(14)	3.7(5)
C(26)	2 548(28)	−1 645(17)	2 051(18)	6.2(7)
C(27)	2 675(34)	−2 154(18)	2 629(20)	7.1(9)
C(28)	1 757(29)	−2 222(17)	3 047(18)	6.0(7)
C(29)	631(25)	−1 775(14)	2 936(15)	4.3(6)
C(30)	−1 787(23)	−750(13)	2 723(14)	4.0(5)
C(31)	−2 407(28)	−1 441(17)	2 763(17)	5.8(7)
C(32)	−3 287(31)	−1 542(19)	3 249(19)	7.3(9)
C(33)	−3 600(29)	−961(17)	3 573(18)	6.1(7)
C(34)	−3 053(28)	−295(15)	3 551(17)	5.8(7)
C(35)	−2 143(26)	−181(15)	3 130(16)	5.1(6)
C(36)	−1 828(23)	−956(13)	1 187(14)	3.9(5)
C(37)	−3 102(24)	−669(13)	951(14)	4.3(6)
C(38)	−3 957(25)	−851(15)	247(16)	4.8(6)
C(39)	−3 529(26)	−1 385(15)	−146(16)	5.2(6)
C(40)	−2 306(27)	−1 704(16)	84(17)	5.4(7)
C(41)	−1 458(25)	−1 486(15)	769(15)	4.6(6)

Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication

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No. SUP 22152 (8 pp.).[*] Atomic scattering factors were taken from ref. 10.

RESULTS AND DISCUSSION

Description and Discussion of the Structure.—The crystal structure (Figure 1) consists of monomeric $[Pt(PPh_3)_2\{C(CN)_2{\cdot}CH(CN){\cdot}O\}]$ [(1) in Figure 2] molecules. The most interesting feature is that the platinum atom is inserted into the carbon–oxygen bond of the three-membered heterocycle tricyano-oxirane, the carbon atom bearing two cyano-substituents being involved in the insertion process. The same kind of insertion has been found in the complex $[Pt(AsPh_3)_2\{C(CN)_2{\cdot}C(CN)_2{\cdot}O\}]$ [(2), Figure 2].

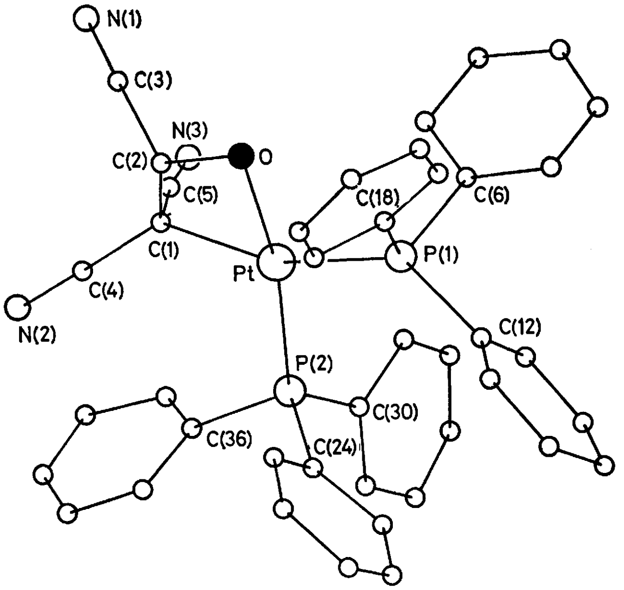

FIGURE 1 A view of the molecule (1) with the atom-numbering scheme

The platinum atom and the four equatorial atoms, P(1), P(2), O, and C(1), are nearly coplanar with a slight tetrahedral distortion. The dihedral angle between the planes C(1)–Pt–O and P(1)–Pt–P(2) is 6.8°. Such a distortion is similar to that found in complex (2) (4.5°), but smaller than that (18.0°) found[11] in $[Pt(PPh_3)_2\{C(CN)_2{\cdot}CH_2{\cdot}C(CN)_2\}]$ [(3), Figure 2]. It seems likely that the greater deviation from planarity observed in complex (3) is due to the larger steric interactions deriving from substitution of the oxygen atom by the bulkier $C(CN)_2$ group.

Complex (1) possesses a puckered four-membered metallacycle like the related (2) and (3). However, the data in Table 2 show that the degree of puckering (30°) is significantly higher than in (2) (18.2°), while it is closer to that in (3) (24.4°). Again, this is attributable to the different steric situations in the three complexes. The conformation of the four-membered ring appears to be essentially determined by the non-bonding interactions among the side groups and the ring atoms. Thus, the smaller extent of puckering of complex (2) may be explained in terms of a compromise between the interactions of the cyano-groups at C(1) and C(2) and those between the platinum atom and the CN group at C(2).

TABLE 2

Comparison of dihedral angles (°), torsion angles (°), and out-of-plane displacements (Å) for complexes (1)—(3)

	(1)	(2)	(3)
α [a,b]	30.0	18.2	24.4
Torsion angles			
Pt–C(1)–C(2)–X [b]	24.4	14.8	20.1
C(1)–C(2)–X–Pt	25.5	15.2	20.0
C(2)–X–Pt–C(1)	20.0	11.8	15.2
X–Pt–C(1)–C(2)	17.4	10.1	15.6
Displacement of C(2) from the planes defined by C(1), X, Pt	0.47	0.28	0.41

[a] The dihedral angle between the planes X,Pt,C(1) and X,C(1),C(2). [b] X = O for (1) and (2) and $C(CN)_2$ for (3).

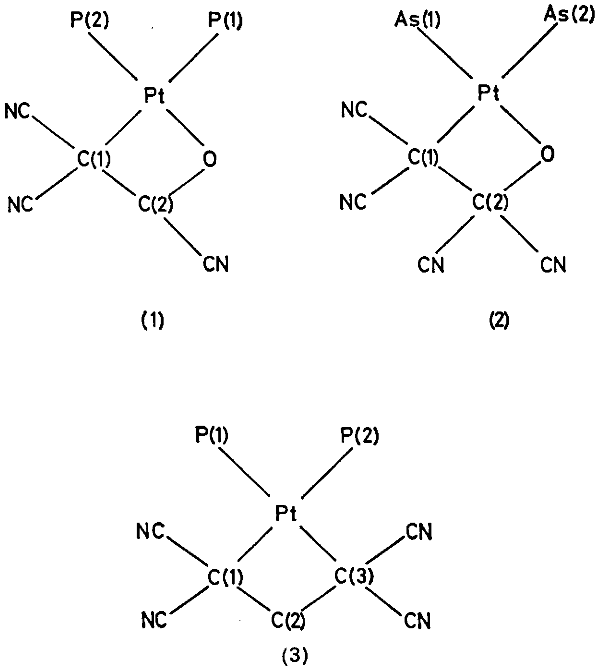

FIGURE 2 Simplified sketches and atom numbering for molecules (1)—(3)

Replacement of a cyano-group by a less bulky hydrogen atom as in (1) allows a greater twisting around the C(1)–C(2) bond and a larger amount of puckering. This results in the hydrogen atom pointing towards the metal atom while the CN group at C(2) is bent as far as possible from Pt.

Bond lengths and angles are given in Table 3. The two platinum–phosphorus distances are 2.311(6) and 2.247(6) Å. The significantly longer Pt–P bond *trans* to C(1) indicates the stronger *trans* influence of carbon compared with oxygen. The platinum–carbon bond [2.13(2) Å] is

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[*] For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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very close to the values found in complexes (2) and (3) [2.103(7) and 2.138(6) Å respectively] and in the related $[\mathrm{Pt(PPh_3)_2(tcne)}]$ (tcne = tetracyanoethylene) [12] [2.11(3) Å], and $[\mathrm{Pt(PPh_3)_2\{C_2(CN)_4C_2H_3(OEt)\}}]$ [2.15(3) Å].[5] The other bond lengths of the metallacycle are similar to those found in complex (2). Within the accuracy of the analysis, the exocyclic C–C and C–N bond distances are quite normal.

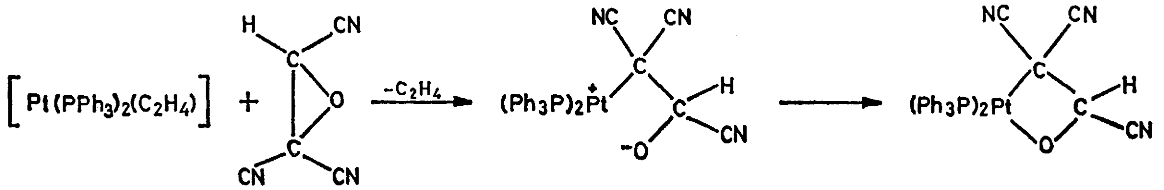
TABLE 3

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

(*a*) Distances			
Pt–P(1)	2.311(6)	C(1)–C(5)	1.40(4)
Pt–P(2)	2.247(6)	C(2)–C(3)	1.51(3)
Pt–O	2.06(2)	N(1)–C(3)	1.14(3)
Pt–C(1)	2.13(2)	N(2)–C(4)	1.24(4)
O–C(2)	1.38(3)	N(3)–C(5)	1.18(4)
C(1)–C(2)	1.56(3)	P–C (mean)	1.83(3)
C(1)–C(4)	1.47(3)	C–C (phenyls)	1.42(4)
(*b*) Angles			
P(1)–Pt–P(2)	98.2(2)	C(2)–C(1)–C(5)	115(2)
P(1)–Pt–O	90.8(4)	C(4)–C(1)–C(5)	111(2)
P(1)–Pt–C(1)	155.8(5)	C(1)–C(4)–N(2)	177(3)
P(2)–Pt–O	169.6(5)	C(1)–C(5)–N(3)	174(3)
P(2)–Pt–C(1)	105.9(5)	C(2)–C(3)–N(1)	175(3)
O–Pt–C(1)	65.4(7)	Pt–P(1)–C(6)	110.3(6)
Pt–O–C(2)	97(1)	Pt–P(1)–C(12)	126.1(8)
Pt–C(1)–C(2)	89(1)	Pt–P(1)–C(18)	106.9(9)
O–C(2)–C(1)	100(2)	Pt–P(2)–C(24)	111.6(8)
Pt–C(1)–C(4)	125(1)	Pt–P(2)–C(30)	117.7(8)
Pt–C(1)–C(5)	107(2)	Pt–P(2)–C(36)	110.3(8)
O–C(2)–C(3)	113(2)	C–P–C (mean)	105(1)
C(1)–C(2)–C(3)	117(2)	C–C–C (phenyls)	120(3)
C(2)–C(1)–C(4)	108(2)		

The C(1)–Pt–P(2) angle is 105.9(5)° while the O–Pt–P(1) angle is 90.8(4)°. A similar difference in these values has been found in complex (2), the corresponding angles [C(1)–Pt–As(1) and O–Pt–As(2)] being 102.8(2) and 93.2(2)° respectively. On the other hand, in complex (3) the P–Pt–C angles are, as expected, approximately the same [97.1(2) and 99.8(2)°]. As already suggested,[3] this effect may be attributed to the steric requirements of the bulky $\mathrm{C(CN)_2}$ group relative to oxygen. Furthermore, in spite of this distortion in complexes (1) and (2), the angles P(As)–Pt–P(As) [98.2(2) and 95.54(3)°] and C–Pt–O [65.4(7) and 68.4(3)°] have values very close to those found in the four-membered metallacycles.[5] Ring-opening reactions in electronegatively activated carbocycles and epoxides have been shown to proceed *via* nucleophilic addition of the $\mathrm{ML_2}$ moiety to the carbon atom bearing the electron-withdrawing substituents,[3,5] where the presence of a positive charge has been demonstrated by *X*-ray photoelectron spectroscopy and theoretical considerations.[13] As predicted, the present reaction proceeds as in Scheme 2.

The bonding between three-membered carbocycles and platinum has been interpreted as involving a synergic interaction [4,14] between available metal orbitals of the correct symmetry and the molecular orbitals of the cyclopropane moiety as obtained from the Walsh description.[15] However, this model does not readily explain the puckering observed in complex (3) where the Pt–C(1) and Pt–C(2) bonds are best described as possessing an effective σ character.[11] The bonding in the metallaoxacyclobutane complexes (1) and (2) [3] can also be best understood in terms of platinum–carbon and –oxygen σ bonds, and the larger puckering observed in complex (1) seems to be attributable to the relief of strain caused by the replacement of a cyano-group by a hydrogen atom.



(4) (1)

SCHEME 2

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