

Structure and Mechanism of Formation of the Metallooxacyclobutane Complex $\text{Pt}[\text{C}_2(\text{CN})_4\text{O}][\text{As}(\text{C}_6\text{H}_5)_3]_2$, the Product of the Reaction between Tetracyanooxirane and $\text{Pt}[\text{As}(\text{C}_6\text{H}_5)_3]_4$

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Abstract: Metallooxacyclobutane complexes, $\text{Pt}[\text{C}_2(\text{CN})_4\text{O}]\text{L}_2$ ($\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$, $\text{As}(\text{C}_6\text{H}_5)_3$), were prepared from the reaction between tetracyanooxirane (2,2,3,3-tetracyanooxacyclop propane, $\text{C}_2(\text{CN})_4\text{O}$) and PtL_4 . The crystal and molecular structure of the complex where $\text{L} = \text{As}(\text{C}_6\text{H}_5)_3$ has been determined from three-dimensional X-ray diffraction data. The crystal has symmetry consistent with the space group $P2_1/c [C_{2h}^5]$ with four molecules of the complex in a unit cell of dimensions $a = 9.933(2) \text{ \AA}$, $b = 20.477(3) \text{ \AA}$, $c = 18.634(3) \text{ \AA}$, and $\beta = 95.42(1)^\circ$. The structure was refined by least-squares techniques to a conventional R index of 0.039 based on 4819 reflections above background collected using a four-circle diffractometer. The structure determination shows that $\text{Pt}[\text{As}(\text{C}_6\text{H}_5)_3]_2$ has inserted into the carbon-oxygen bond of the oxirane. Such a metallooxacyclobutane ring has recently been suggested as an intermediate in the catalytic formation of ethylene carbonate from Ni^0 complexes, ethylene oxide, and CO_2 . Comparisons are made between the structural parameters of the present complex, the closely related metallocyclobutane complex $\text{Pt}[\text{C}_2(\text{CN})_4\text{CH}_2][\text{P}(\text{C}_6\text{H}_5)_3]_2$, and the small rings tetracyanooxirane and 1,1,2,2-tetracyanocyclopropane. Spectroscopic data and chemical behavior of the metallooxacyclobutane complexes are reported.

Considerable interest has been shown in the reaction of transition metal compounds and systems containing cyclopropane rings.²⁻⁵ Thus it has been demonstrated that a variety of transition metals promote ring opening and a skeletal rearrangement of highly strained ring systems such as bicyclo[1.1.0]butane,^{2a,4} quadricyclene,³ semibullvalene,⁵ and many others. These reactions are often catalytic.^{2a,3,4} A concerted pathway,⁴ interaction of appropriate d orbitals of the metal with the orbitals of the carbocycle, and oxidative addition,^{2,3,5} involving the initial rupture of only one carbon-carbon bond in the first step, have both been proposed for these reactions. Simple insertion reactions of transition metals into the carbon-carbon bond of substituted cyclopropanes and the isolation of the metallocyclobutane complexes,⁶⁻¹⁰ for some of which structural details are known,^{5,7,11,12} support the oxidative addition pathway. Nevertheless there is the question of whether the first step involves overlap of metal d orbitals and Walsh orbitals of the cyclopropane,

followed by ring opening,^{8,11} or if the reaction occurs by an attack of the metal at one carbon atom of the ring,¹⁰ followed by fission of a carbon-carbon bond, forming an ionic intermediate.

Recently we have reported the reaction¹⁰ of the electron deficient 1,1,2,2-tetracyanocyclopropane molecule with zerovalent platinum and palladium complexes and the structure of the metallocyclobutane complex $\text{Pt}[\text{C}_2(\text{CN})_4\text{CH}_2][\text{P}(\text{C}_6\text{H}_5)_3]_2$.¹² Below we describe the reaction of zerovalent platinum compounds of the type PtL_4 [$\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$, $\text{P}(p\text{-CH}_3\text{C}_6\text{H}_4)_3$, $\text{As}(\text{C}_6\text{H}_5)_3$] and the electron deficient tetracyanooxirane molecule (2,2,3,3-tetracyanooxacyclop propane). We report first the result of a structural investigation of the metallooxacyclobutane complex $\text{Pt}[\text{C}_2(\text{CN})_4\text{O}][\text{As}(\text{C}_6\text{H}_5)_3]_2$.

Description and Discussion of the Structure

Figure 1 presents a drawing of the $\text{Pt}[\text{C}_2(\text{CN})_4\text{O}][\text{As}(\text{C}_6\text{H}_5)_3]_2$ molecule (I) and indicates the numbering scheme. The vibrational thermal ellipsoids at their 50% probability level are also displayed in the figure and the root-mean-square amplitudes of vibration are presented in Table I. These vibrational data appear to be reasonable; as expected, the greatest thermal motion is shown by the cyano nitrogen atoms. From the positional parameters in Table II and the correlation matrix, the relevant interatomic distances, bond angles, and their standard deviations were calculated and are presented in Table III.

The crystal structure consists of individual monomeric molecules, each of which is one asymmetric unit. The stereo drawing of four complete molecules in a unit cell (Figure 2) represents a view along the x axis. All intermolecular contacts are normal, the shortest distance being an $\text{H}(33) \cdots \text{H}(33)$ interaction of 2.42 Å in adjacent molecules. In the description of the present

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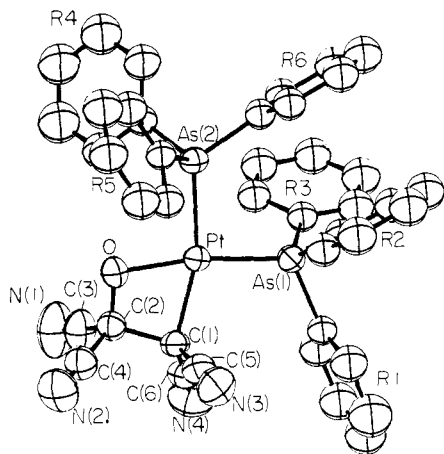


Figure 1. A drawing of the $\text{Pt}[\text{C}_2(\text{CN})_2\text{O}][\text{As}(\text{C}_6\text{H}_5)_3]_2$ molecule. Hydrogen atoms of the phenyl rings have been omitted. The 50% probability vibrational ellipsoids are shown.

Table I. Root-Mean-Square Amplitudes of Vibration (\AA)

| Atom | Min | Intermed | Max |
|-------|------------|------------|------------|
| Pt | 0.1945 (5) | 0.2068 (4) | 0.2190 (4) |
| As(1) | 0.207 (1) | 0.212 (1) | 0.228 (1) |
| As(2) | 0.197 (1) | 0.223 (1) | 0.228 (1) |
| O | 0.195 (7) | 0.241 (7) | 0.333 (7) |
| N(1) | 0.22 (1) | 0.32 (1) | 0.37 (1) |
| N(2) | 0.24 (1) | 0.31 (1) | 0.44 (1) |
| N(3) | 0.25 (1) | 0.31 (1) | 0.36 (1) |
| N(4) | 0.22 (1) | 0.31 (1) | 0.36 (1) |
| C(1) | 0.20 (1) | 0.21 (1) | 0.25 (1) |
| C(2) | 0.21 (1) | 0.22 (1) | 0.25 (1) |
| C(3) | 0.23 (1) | 0.25 (1) | 0.27 (1) |
| C(4) | 0.22 (1) | 0.25 (1) | 0.33 (1) |
| C(5) | 0.21 (1) | 0.26 (1) | 0.28 (1) |
| C(6) | 0.23 (1) | 0.26 (1) | 0.27 (1) |

structure we will compare structural details with those of the closely related complex $\text{Pt}[\text{C}_2(\text{CN})_2\text{CH}_2][\text{P}(\text{C}_6\text{H}_5)_3]_2$ (II)¹² and those of the parent rings 1,1,2,2-tetracyanocyclopropane (III)¹³ and tetracyanooxirane (IV).¹⁴ These molecules and the atom nomenclature in I, II, III, and IV are illustrated in Figure 3. Table IV compares the geometries of these four molecules.

The most interesting feature of the present structure is that the platinum atom is inserted into the carbon-oxygen bond of the three-membered heterocycle tetracyanooxirane. The inner coordination sphere of complex I is shown in Figure 4.

The platinum atom and the four equatorial atoms, C(1), O, As(1), and As(2), are essentially coplanar. The dihedral angle between the planes C(1)-Pt-O and As(1)-Pt-As(2) is $4.5 (2)^\circ$. The distortion from the square-planar arrangement is much greater in the related four-coordinated complex (II) and in $\text{Pt}[(\text{NC})_2\text{C}=\text{C}(\text{CN})_2][\text{P}(\text{C}_6\text{H}_5)_3]_2$.¹⁵ The analogous dihedral angles are $18.0 (2)$ and 8.3° , respectively. As in the metallocyclobutane compounds,^{7,11,12} the present complex possesses a puckered four-membered ring. The degree of puckering is least in compound I. This may be an effect of the oxygen in the four-membered ring. For example the puckering in cyclobutane is much

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higher than in oxetane,¹⁶ which is essentially planar. The present distortion from planarity can be simply understood in terms of minimization of the nonbonding interactions between the cyano groups attached to C(1) and C(2). An approximate measure for the twisting around the C(1)-C(2) bond is the torsion angles for the carbon chains C(6)-C(1)-C(2)-C(3) and C(5)-C(1)-C(2)-C(4) of $-31.9 (9)$ and $-17.7 (9)^\circ$, respectively. Table V lists calculated least-squares planes through various atoms of the inner coordination sphere and displacements of atoms from these planes. Dihedral angles, torsion angles, and vector-plane normal angles are presented in Table III.

The two independent platinum-arsine distances (2.341 (1) and 2.402 (1) \AA) are in the expected range and are near to the Pt-As bond lengths observed in other complexes, for example *trans*- $\text{PtCl}_2(\text{As}(\text{CH}_3)_3)_2$, Pt-As = 2.308 (2) \AA ,¹⁷ $\text{Pt}[o\text{-phenylenebis}(\text{dimethylarsine})]_2^{2+}$, Pt-As = 2.375 (4) \AA ,¹⁸ and $\text{Pt}(\text{F}_3\text{CC}_2\text{CF}_3)\text{Cl}(\text{CH}_3)_2[\text{As}(\text{CH}_3)_3]_2$, Pt-As = 2.434 (4) \AA .¹⁹ The significantly longer Pt-As bond trans to the carbon atom C(1) reflects the stronger trans influence of carbon compared with oxygen.²⁰ The platinum-carbon bond is 2.103 (7) \AA , slightly shorter than in complex II (2.138 (6) \AA) and the same as in the related complex $\text{Pt}[(\text{NC})_2\text{C}=\text{C}(\text{CN})_2][\text{P}(\text{C}_6\text{H}_5)_3]_2$ ¹⁵ (2.11 (3) \AA) or the Pt- sp^2 C bond in the

bis(acetylacetonato)chloroplatinate anion $\text{PtOC}(\text{CH}_3)_2$

$\text{CHC}(\text{CH}_3)\text{O}[\text{CH}(\text{COCH}_3)_2]\text{Cl}$ of 2.106 (7) \AA .²¹ The platinum-oxygen bond (2.050 (5) \AA) is normal. In the complex $\text{Pt}[\text{CO}_3][\text{P}(\text{C}_6\text{H}_5)_3]_2$ Pt-O is 2.07 \AA ;²² in the dioxygen complex $\text{Pt}(\text{O}_2)[\text{P}(\text{C}_6\text{H}_5)_3]_2$ it is 2.006 (7) \AA .²³

The O-Pt-As(2) angle is $93.2 (2)^\circ$ compared with $102.8 (2)^\circ$ for the C(1)-Pt-As(1) angle. In complex II the analogous angles P(1)-Pt-C(1) and P(2)-Pt-C(2) are, as expected, approximately the same ($97.1 (2)$ and $99.8 (2)^\circ$, respectively). We think this difference in the present complex may arise from the steric requirement of the bulky C(CN)₂ group relative to oxygen. The same effect is seen in the complex $\text{Pt}[\text{Cl}_2\text{C}_2(\text{CN})_2][\text{P}(\text{C}_6\text{H}_5)_3]_2$.²⁴ The angles are $103.1 (7)^\circ$ for $\text{Cl}_2\text{C}-\text{Pt}-\text{P}$ and $114.3 (8)^\circ$ for $(\text{NC})_2\text{C}-\text{Pt}-\text{P}$.

The C(1)-C(2) bond length of 1.58 (1) \AA in I is appreciably greater than the analogous bond distance in tetracyanooxirane (1.496 (2) \AA) (Table IV). It is also longer than the C-C distance in an open carbon chain between sp^3 and sp^2 carbon atoms where electron withdrawing groups are attached (1.521 (3) \AA in the anion $[(\text{NC})_2\text{C}]_2\text{C}-\text{CH}_2\text{CN}^-$ ²⁵ and 1.511 (12) \AA in the $(\text{NC})_2\text{C}-\text{C}(\text{CN})_2\text{H}$ moiety of $\text{Ir}((\text{CN})_2\text{CCH}(\text{CN})_2)((\text{CN})_2\text{CC}(\text{CN})_2)(\text{CO})(\text{P}(\text{C}_6\text{H}_5)_3)_2$.²⁶

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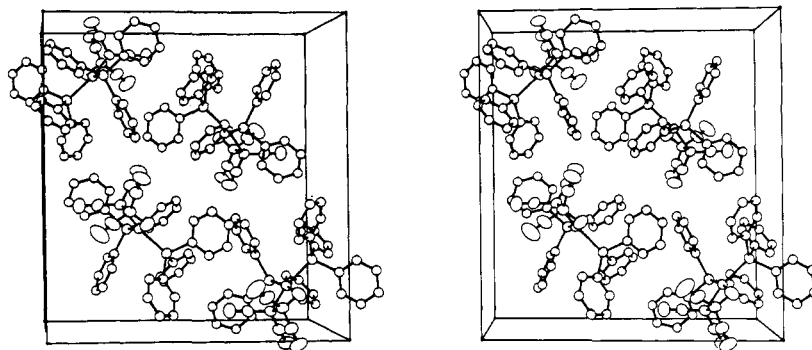


Figure 2. A stereoscopic drawing of four molecules of $\text{Pt}[\text{C}_2(\text{CN})_4\text{O}][\text{As}(\text{C}_6\text{H}_5)_3]_2$ whose central metal atoms all lie within the same unit cell.

Table II. Positional, Thermal, and Group Parameters for $\text{Pt}[\text{C}_2(\text{CN})_4\text{O}][\text{As}(\text{C}_6\text{H}_5)_3]_2$

| Atom | x | y | z | $10^4\beta_{11}^a$ | $10^4\beta_{22}$ | $10^4\beta_{33}$ | $10^4\beta_{12}$ | $10^4\beta_{13}$ | $10^4\beta_{23}$ |
|-------|--------------------------|-------------|--------------|--------------------|------------------|------------------|------------------|------------------|------------------|
| Pt | 0.21870 (3) ^b | 0.15904 (1) | -0.18291 (1) | 86.4 (3) | 20.02 (8) | 24.8 (1) | -2.2 (1) | 4.5 (1) | -2.46 (7) |
| As(1) | 0.44121 (7) | 0.16497 (4) | -0.21417 (4) | 91.8 (8) | 23.4 (2) | 25.8 (2) | -1.7 (3) | 6.5 (3) | -1.5 (2) |
| As(2) | 0.24724 (8) | 0.23954 (4) | -0.08898 (4) | 103.7 (9) | 21.5 (2) | 24.7 (2) | -0.2 (3) | 3.3 (4) | -2.8 (2) |
| O | 0.0205 (5) | 0.1420 (3) | -0.1664 (3) | 89 (6) | 36 (2) | 50 (2) | -13 (3) | 20 (3) | -13 (2) |
| N(1) | -0.1510 (8) | 0.0006 (4) | -0.1922 (5) | 193 (13) | 34 (3) | 70 (4) | -19 (5) | 16 (6) | 15 (3) |
| N(2) | -0.1444 (10) | 0.1668 (5) | -0.3288 (6) | 170 (13) | 60 (4) | 78 (5) | 25 (6) | 7 (6) | 33 (4) |
| N(3) | 0.1508 (9) | 0.0857 (4) | -0.3851 (4) | 248 (15) | 48 (3) | 36 (3) | -14 (5) | 5 (5) | -3 (3) |
| N(4) | 0.2229 (8) | -0.0220 (4) | -0.1824 (5) | 179 (12) | 28 (2) | 68 (4) | 19 (4) | -7 (6) | 8 (3) |
| C(1) | 0.1357 (7) | 0.0828 (3) | -0.2486 (4) | 103 (9) | 21 (2) | 29 (2) | 4 (3) | -3 (4) | -4 (2) |
| C(2) | -0.0068 (7) | 0.1025 (3) | -0.2246 (4) | 97 (9) | 22 (2) | 36 (3) | -1 (3) | 4 (4) | 1 (2) |
| C(3) | -0.0902 (8) | 0.0446 (4) | -0.2071 (5) | 126 (11) | 27 (2) | 41 (3) | -2 (4) | 7 (5) | 3 (2) |
| C(4) | -0.0854 (9) | 0.1376 (4) | -0.2852 (5) | 125 (11) | 33 (3) | 51 (4) | 8 (4) | 10 (5) | 13 (3) |
| C(5) | 0.1455 (9) | 0.0839 (4) | -0.3240 (5) | 141 (11) | 29 (2) | 33 (3) | -9 (4) | 5 (5) | -6 (2) |
| C(6) | 0.1853 (9) | 0.0226 (4) | -0.2129 (5) | 135 (11) | 25 (2) | 41 (3) | 1 (4) | 5 (5) | -2 (2) |

| Group ^c | x_c | y_c | z_c | δ | ϵ | η |
|--------------------|------------|------------|-------------|------------|------------|------------|
| 1 | 0.5185 (4) | 0.0603 (2) | -0.3399 (2) | -2.717 (5) | -2.396 (3) | -1.513 (5) |
| 2 | 0.4990 (4) | 0.3080 (2) | -0.2901 (2) | -1.799 (3) | 3.010 (3) | -2.678 (3) |
| 3 | 0.6550 (4) | 0.1226 (2) | -0.0743 (2) | -0.855 (4) | 2.795 (3) | 0.883 (4) |
| 4 | 0.1163 (4) | 0.1721 (2) | 0.0508 (2) | -2.885 (4) | 2.766 (3) | 1.028 (4) |
| 5 | 0.0474 (4) | 0.3671 (2) | -0.1218 (2) | 2.349 (5) | 2.418 (4) | -0.132 (5) |
| 6 | 0.5519 (4) | 0.2974 (2) | -0.0359 (2) | -3.017 (5) | -2.261 (3) | 2.867 (5) |

^a The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. ^b Numbers in parentheses given here and in other tables are estimated standard deviations in the least significant figures. ^c x_c , y_c , z_c are the fractional coordinates of the ring center; δ , ϵ , and η (in radians) have been defined in R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **4**, 773 (1965). The groups 1-6 are phenyl rings.

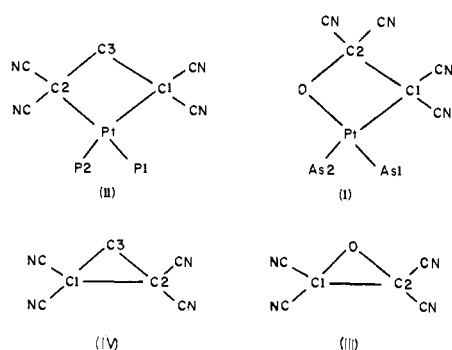


Figure 3. Numbering scheme in the four molecules $\text{Pt}[\text{C}_2(\text{CN})_4\text{O}][\text{As}(\text{C}_6\text{H}_5)_3]_2$ (I), $\text{Pt}[\text{C}_2(\text{CN})_4\text{CH}_2][\text{P}(\text{C}_6\text{H}_5)_3]_2$ (II), tetracyanooxirane (III), and 1,1,2,2-tetracyanocyclopropane (IV).

Such lengthening of the carbon-carbon bond is not surprising, as bond distances may be expected to increase with relief of strain within the three-membered ring. For example the carbon-carbon bond distances in oxetane¹⁶ and oxirane²⁷ are 1.549 (3) and 1.472 (2) Å, respectively, and a similar trend is shown in the bond

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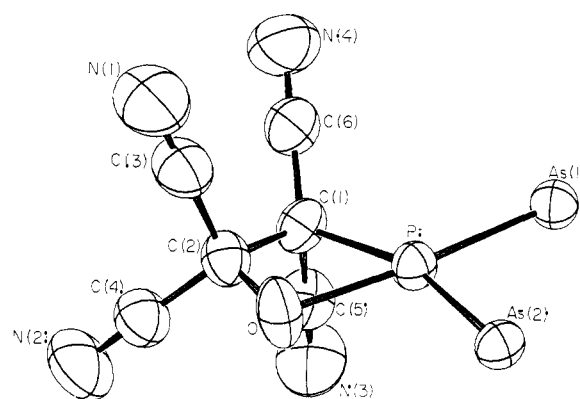


Figure 4. The conformation of the metallooxacyclobutane ring in the molecule $\text{Pt}[\text{C}_2(\text{CN})_4\text{O}][\text{As}(\text{C}_6\text{H}_5)_3]_2$.

lengths of 1,2,3,4-tetracyanocyclobutane²⁸ and 1,2,3-tricyanocyclopropane²⁹ (1.561 (3) and 1.518 (3) Å). The average value 1.565 (9) Å of the C-C bond distance,

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Table III. Distances (Å) and Angles (deg)

| Distances | | Bond angles | |
|--------------------------------------|------------|---|------------|
| Pt-As(1) | 2.341 (1) | As(1)-Pt-As(2) | 95.54 (3) |
| Pt-As(2) | 2.402 (1) | O-Pt-C(1) | 68.4 (3) |
| Pt-C(1) | 2.103 (7) | O-Pt-As(2) | 93.2 (2) |
| Pt-O | 2.050 (5) | C(1)-Pt-As(1) | 102.8 (2) |
| Pt...C(2) | 2.576 (7) | O-Pt-As(1) | 171.2 (2) |
| C(1)-C(2) | 1.58 (1) | C(1)-Pt-As(2) | 161.1 (2) |
| O-C(2) | 1.361 (9) | C(2)-O-Pt | 96.0 (4) |
| O...C(1) | 2.335 (9) | C(2)-C(1)-Pt | 87.7 (4) |
| C(1)-C(5) | 1.42 (1) | O-C(2)-C(1) | 105.1 (5) |
| C(1)-C(6) | 1.46 (1) | C(5)-C(1)-C(6) | 114.3 (7) |
| C(2)-C(3) | 1.50 (1) | C(4)-C(2)-C(3) | 106.5 (6) |
| C(2)-C(4) | 1.49 (1) | C(5)-C(1)-Pt | 120.4 (6) |
| C(3)-N(1) | 1.13 (1) | C(5)-C(1)-C(2) | 115.1 (6) |
| C(4)-N(2) | 1.13 (1) | C(6)-C(1)-Pt | 105.4 (5) |
| C(5)-N(3) | 1.14 (1) | C(6)-C(1)-C(2) | 111.1 (7) |
| C(6)-N(4) | 1.12 (1) | O-C(2)-C(4) | 111.5 (7) |
| As(1)-C(11) | 1.922 (5) | C(4)-C(2)-C(1) | 109.2 (7) |
| As(1)-C(21) | 1.930 (5) | O-C(2)-C(3) | 111.7 (7) |
| As(1)-C(31) | 1.923 (5) | C(3)-C(2)-C(1) | 112.9 (6) |
| As(2)-C(41) | 1.925 (5) | N(1)-C(3)-C(2) | 178.1 (9) |
| As(2)-C(51) | 1.910 (5) | N(2)-C(4)-C(2) | 176.7 (12) |
| As(2)-C(61) | 1.919 (4) | N(3)-C(5)-C(1) | 178.4 (10) |
| | | N(4)-C(6)-C(1) | 176.5 (10) |
| | | C(11)-As(1)-C(31) | 102.8 (2) |
| | | C(11)-As(1)-C(21) | 102.0 (2) |
| | | C(31)-As(1)-C(21) | 113.2 (2) |
| | | C(51)-As(2)-C(61) | 103.9 (2) |
| | | C(51)-As(2)-C(41) | 103.9 (2) |
| | | C(61)-As(2)-C(41) | 106.2 (2) |
| | | | 177.4 (10) |
| | | | 105.3 (41) |
| Dihedral angles ^b | | Vector-plane normal angles ^b | |
| O-Pt-C(1) | -4.5 (2) | Pt-O | -89.0 (2) |
| As(1)-Pt-As(2) | | | |
| C(1)-Pt-C | -18.2 (7) | As(2)-Pt-As(1) | -93.0 (2) |
| O-C(2)-C(1) | | | |
| As(1)-Pt-As(2) | 15.2 (6) | Pt-C(1) | 85.6 (2) |
| C(1)-C(2)-O | | | |
| | | As(2)-Pt-As(1) | 46.3 (9) |
| | | C(2)-C(1) | |
| | | C(1)-C(6)-C(5) ≡ β | |
| | | C(1)-C(2) | 37.0 (9) |
| | | C(2)-C(4)-C(3) | |
| Torsion angles ^c | | | |
| C(6)-C(1)-C(2)-C(3) | -31.2 (9) | | |
| C(5)-C(1)-C(2)-C(4) | -17.7 (9) | | |
| Pt-C(1)-C(2)-O | -14.8 (5) | | |
| C(1)-C(2)-O-Pt | 15.2 (5) | | |
| C(2)-O-Pt-C(1) | -11.8 (4) | | |
| O-Pt-C(1)-C(2) | 10.1 (4) | | |
| Displacement of an atom from a plane | | | |
| C(1) | | | |
| As(1)-Pt-As(2) | -0.163 (7) | | |
| C(2) | | | |
| As(1)-Pt-As(2) | 0.136 (7) | | |
| O | | | |
| As(1)-Pt-As(2) | -0.037 (6) | | |
| C(1) | | | |
| C(6)-C(5)-C(2) | 0.386 (8) | | |
| C(2) | | | |
| C(3)-C(4)-C(1) | -0.505 (9) | | |
| C(2) | | | |
| C(1)-O-Pt | 0.276 (10) | | |

^a These are average quantities. The estimated standard deviation in parentheses is the larger of an individual standard deviation or of the standard deviation of a single observation as calculated from the mean. ^b The sense of these angles is defined in J. K. Stalick and J. A. Ibers, *J. Amer. Chem. Soc.*, **92**, 5333 (1970). ^c The sense of these angles is defined in W. R. Busing, K. O. Martin, and H. A. Levy, ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., March, 1964.

observed in the isoelectronic platinum complex II, does not differ from the C-C bond length found here.

On the other hand, the C(2)-O bond distance (1.361 (9) Å) in I is significantly shorter than in tetra-cyanooxirane (mean value 1.424 (1) Å). This change is in contrast to the effect of a normal ring expansion. As for the carbon-carbon bonds, the carbon-oxygen bond length usually increases slightly with relief of ring strain. For example the C-O bond distance in oxirane²⁷ is 1.436 (2) Å and in oxetane¹⁶ 1.449 (2) Å. Values of the C-O bond length similar to that found here are observed in the aromatic systems 3,4-furandicarboxylic acid (1.356 (3) Å)³⁰ and salicylic acid³¹ (distance

(30) D. E. Williams and R. E. Rundle, *J. Amer. Chem. Soc.*, **86**, 1660 (1964).

(31) W. Cochran, *Acta Crystallogr.*, **6**, 260 (1953).

between the ring carbon and the hydroxyl group 1.361 (5) Å) and also in the platinum complex $\text{PtOOC}(\text{CH}_3)_2\text{O}-[\text{P}(\text{C}_6\text{H}_5)_3]_2$ (C-O 1.32 (4) and 1.40 (4) Å).³²

The exocyclic C-C and C≡N bonds are normal, the average bond distances being 1.47 (4) and 1.13 (1) Å, respectively. The average C-C≡N bond angle of 177.4 (10)° is not significantly different from 180°.

The exocyclic NC-C-CN bond angles of 114.3 (7)° (around C(1)) and 106.5 (6)° (around C(2)) are significantly different. The analogous bond angles in tetra-cyanooxirane are 116.9 (2) and 117.2 (2)° and suggest sp² hybridization at both ring carbon atoms, in ac-

(32) R. Ugo, F. Conti, S. Cenini, R. Mason, and G. B. Robertson, *Chem. Commun.*, 1498 (1968).

Table IV. Comparison of Intramolecular Distances and Bond Angles

| | Compound | | | |
|-------------------|------------------------------|------------------------|------------------------|-----------------|
| | I | II | III | IV ^a |
| | Intramolecular Distances (Å) | | | |
| Pt-C(1) | 2.103 (7) | 2.137 (6) | | |
| C(1)-C(2) | 1.58 (1) | | 1.496 (2) | 1.561 (4) |
| C(1)-C(3) | | 1.545 (9) | | 1.501 (4) |
| C(2)-C(3) | | 1.584 (9) | | 1.506 (4) |
| C(2)-O | 1.361 (9) | | 1.424 (1) ^b | |
| C-CN ^b | 1.47 (4) | 1.441 (10) | 1.450 (1) | 1.449 (3) |
| C-N ^b | 1.13 (1) | 1.147 (14) | 1.129 (1) | 1.138 (3) |
| | Bond Angles (deg) | | | |
| α^c | 68.4 (3) | 68.4 (2) | | |
| β | 105.1 (5) | 100.4 (5) | | |
| γ | 87.7 (4) | 93.5 (4) | | |
| δ | 96.0 (4) | 92.3 (4) | | |
| NC-C(1)-CN | 114.3 (7) | | 117.1 (1) | 114.7 (3) |
| NC-C(2)-CN | 106.5 (6) | 111.4 (6) ^b | | 116.2 (2) |
| H-C(3)-H | | 104 (5) | | |

^a See Figure 3 for the numbering scheme. ^b These are average quantities. See footnote *a* in Table III. ^c With reference to I and II shown in Figure 3, α is the angle at Pt and the other angles proceed clockwise in the order δ , β , and γ .

Table V. Weighted Least-Squares Planes

| Plane Equation: $Ax + By + Cz - D = 0$, with x, y, z in Monoclinic Coordinates | | | | |
|--|-------|---------|--------|--------|
| Plane | A | B | C | D |
| 1 | 2.284 | -14.370 | 12.104 | -3.955 |
| 2 | 2.078 | -14.679 | 11.970 | -4.069 |
| 3 | 2.070 | -14.690 | 11.966 | -4.072 |

| Deviations from the Planes, Å | | | |
|-------------------------------|----------------------|-------------|-------------|
| Atom | 1 | 2 | 3 |
| Pt | -0.0450 ^a | -0.0005 (3) | 0.0000 (3) |
| As(1) | -0.0002 (7) | 0.0008 (7) | -0.0006 (7) |
| As(2) | 0.0004 (7) | 0.0014 (7) | 0.0004 (7) |
| C(1) | 0.066 (7) | 0.160 (7) | 0.162 (7) |
| C(2) | -0.252 | -0.135 (7) | -0.135 (7) |
| O | -0.053 (6) | 0.035 (6) | 0.037 (6) |

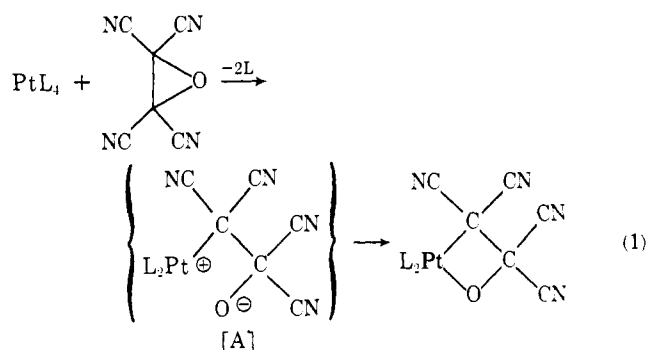
^a If the deviation of an atom from the plane is not assigned a standard deviation, the atom was not used in the calculation of the plane.

cordance with the Walsh³³ bonding scheme for cyclopropane rings. The significant decrease of the exocyclic bond angle around C(2) indicates a strong increase in p-orbital contribution to the hybrid orbitals interacting with the adjacent cyano carbon atoms. A similar trend in the exocyclic bond angles may be observed in the molecules oxirane and oxetane. The former compound possesses a H-C-H bond angle of 116.7°,²⁷ while the average exocyclic bond angle in oxetane is 110.5 (2)°.¹⁶ The exocyclic NC-C-CN bond angle around the carbon C(1) has not changed upon metalation. The average value of the comparable exocyclic NC-C-CN bond angles of the platinum complex II is 111.4 (6)°. The remarkably different hybridization of both ring carbon atoms is also shown by their displacement out of the plane formed by C(3), C(4), C(1) for C(2) and by C(6), C(5), C(2) for C(1). The distance from the plane is 0.505 (9) for C(2) and 0.386 (8) Å for C(1). The last value, which would be zero for an sp² C atom, reflects also the bending back from the metal of the two cyanide groups attached to C(1). This effect may be steric, as well as electronic. The angle β , which has been used to describe the nonplanarity of coordinated olefins, is 46.3 (9)°.²⁴ In the related complex Pt[(NC)₂C=C(CN)₂][P(C₆H₅)₃]₂, β is 56.6°.^{16,24}

(33) A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).

Reactions and Discussion

Some new platinum complexes of the type Pt[C₂(CN)₄O]L₂ (L = P(C₆H₅)₃, P(*p*-CH₃C₆H₄)₃, As(C₆H₅)₃) have been synthesized under very mild conditions by the reaction represented in eq 1. Originally these



complexes were formulated as the insertion product of PtL₂ into the C-C bond of the three-membered tetracyanooxirane ring^{9,34} by analogy with the reaction of PtL₄ and 1,1,2,2-tetracyanocyclopropane.^{10,12} Ir data of the new complexes are presented in Table VI. The

Table VI. Infrared Spectra (in cm⁻¹)

| Compounds | ν_{CN}^a | $\nu_{\text{C-O}}^b$ |
|--|---------------------|----------------------|
| Pt[C ₂ (CN) ₄ O][As(C ₆ H ₅) ₃] ₂ (I) | 2220 m | (1070) ^c |
| Pt[C ₂ (CN) ₄ O][P(C ₆ H ₅) ₃] ₂ (V) | 2220 m | 1070 m |
| Pt[C ₂ (CN) ₄ O][P(<i>p</i> -CH ₃ C ₆ H ₄) ₃] ₂ (VI) | 2220 m | 1075 m |

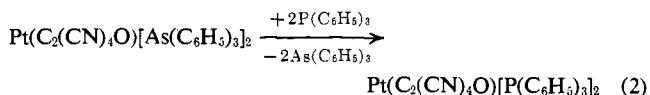
^a Measured in Nujol or CHCl₃ solution. ^b Nujol mull. ^c At the same frequency a band attributable to As(C₆H₅)₃ is present.

sharp single $\nu(\text{CN})$ stretching frequency at 2220 cm⁻¹ is independent of the ligand L. The medium absorption band at 1070 cm⁻¹, originally attributed to $\nu(\text{C-O-C})$,⁹ can also be assigned to a metal-oxygen-carbon linkage in an alkoxy type complex.³⁵ The present example shows once more how difficult it may be to determine the structure of a new compound only on the basis of non-

(34) W. H. Baddley and W. D. Pitts, Jr., Abstracts, 165th National Meeting of the American Chemical Society, Dallas, Tex., 1973, No. INOR 73.

(35) R. C. Mehrotra, *Inorg. Chim. Acta Rev.*, **1**, 99 (1967).

characteristic ir absorption bands. By the exchange reaction presented in eq 2, the same product is obtained



as by reaction 1 ($\text{L} = \text{P}(\text{C}_6\text{H}_5)_3$). Under the mild reaction conditions a rearrangement of the metallocyclobutane ring is very unlikely, so that the same structure for all tetracyanooxirane adducts is most probable.

Recently metallocyclobutane complexes have been proposed as intermediates in the catalytic formation of ethylene carbonate in the system Ni^0 , ethylene oxide, and CO_2 .³⁶ The present compound shows no reactivity with CO or CO_2 at room temperature.

As for the reaction mechanism, the present complex is best described as an oxidative addition product from the intermediate species PtL_2 and tetracyanooxirane. PtL_2 acts as a nucleophile, attacking the oxirane ring at the center of lowest electron density. The presence of a positive charge on the two ring carbon atoms has been proposed on the basis of ESCA measurements and theoretical calculations.³⁷ The attack may lead to cleavage of the weakest bond in the strained ring, here the C–O bond, and an intermediate (A) (reaction 1) may be formed. This mechanism is supported by the observation that attack of a simple nucleophile such as I^- or pyridine also promotes cleavage of the C–O bond in tetracyanooxirane.³⁸ In contrast, olefins form substituted furans in a concerted reaction.³⁹ Kinetics from this thermal reaction³⁹ and theoretical considerations⁴⁰ indicate that in solution tetracyanooxirane is in equilibrium with an activated species, probably a 1,3-dipole or a resonating π -biradical $[(\text{NC})_2\text{C}^*-\text{O}-\text{C}^*(\text{CN})_2]$. It seems that PtL_2 cannot react in a concerted manner or at least that a nucleophilic attack is the preferred pathway. On the other hand the reaction of 1,1,2,2-tetracyanocyclopropane and PtL_4 leads to fission of the $(\text{NC})_2\text{C}-\text{C}(\text{CN})_2$ bond. Comparison of the analogous C–C bonds in tetracyanooxirane and 1,1,2,2-tetracyanocyclopropane shows that the substitution of the CH_2 group in the cyclopropane for the isoelectronic oxygen atom in the oxirane strengthens the C–C bond opposite to the oxygen atom. A similar trend is observed in the molecules cyclopropane (C–C = 1.510 (2) Å)⁴¹ and oxirane (C–C = 1.472 (2) Å).²⁷ This effect of the electronegative oxygen has been explained by MO calculations using Walsh orbitals of the cyclopropane.⁴²

Note that potassium cyanide does not liberate tetracyanooxirane from the complex. Such a liberation reaction is observed for alkyl- or aryl-substituted metallocyclobutane compounds, such as $\text{Pt}[\text{C}_3\text{H}_4(\text{C}_6\text{H}_5)_2]_2[\text{P}(\text{C}_6\text{H}_5)_3]_2$.⁸ In the present complexes attack of KCN leads to ring opening at Pt–O to form the anion $[\text{Pt}(\text{CN})[\text{C}(\text{CN})_2-\text{C}(\text{CN})_2-\text{O}][\text{As}(\text{C}_6\text{H}_5)_3]_2]^-$.

(36) R. J. De Pasquale, *J. Chem. Soc., Chem. Commun.*, 157 (1973).

(37) G. D. Stucky, D. A. Matthews, J. Hedman, M. Klason, and C. Nordling, *J. Amer. Chem. Soc.*, **94**, 8009 (1972).

(38) W. J. Linn, O. W. Webster, and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 3651 (1965).

(39) W. J. Linn and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 3657 (1965); W. J. Linn, *ibid.*, **87**, 3665 (1965).

(40) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968); E. F. Hayes and A. K. O. Siu, *ibid.*, **93**, 2090 (1971).

(41) O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, **17**, 538 (1964).

(42) R. Hoffmann and W. D. Stohrer, *J. Amer. Chem. Soc.*, **93**, 6941 (1971); H. Günther, *Tetrahedron Lett.*, 5173 (1970).

The bonding in the metallocyclobutane ring can best be understood in terms of four two-center, two-electron σ -bonds. The σ -bonds between platinum–carbon and platinum–oxygen may be formed by overlap of the 2p orbitals with more or less s-orbital contribution of the light atoms and metal orbitals of the correct symmetry. Such a model explains easily all the observed structural details of the present complex I and also of the tetracyanocyclopropane complex II.

Experimental Section

Collection and Reduction of X-Ray Data. The metallocyclobutane complex (I) was prepared by the method outlined below and recrystallized from dichloromethane–pentane. The air-stable crystals were colorless, transparent, octagonal needles with well-formed faces. Weissenberg and precession photographs taken with $\text{Cu K}\alpha$ radiation indicated that the crystals belong to the monoclinic system. The systematic absence of $0k0$ reflections when $k \neq 2n$ and $h0l$ reflections when $l \neq 2n$ is consistent with the space group $\text{C}_{2h}^5\text{-P}2_1/c$. A crystal of approximate dimensions $0.25 \times 0.35 \times 0.7$ mm, mounted with the needle axis [100] approximately along the spindle axis, was transferred to a Picker FACS-I automatic diffractometer. The lattice parameters were obtained as previously described⁴³ by hand centering of 14 reflections with $\text{Mo K}\alpha_1$ radiation (λ 0.70930 Å) in the range $28^\circ \leq 2\theta \leq 34^\circ$. The cell constants at 22° are $a = 9.933$ (2) Å, $b = 20.477$ (3) Å, $c = 18.634$ (3) Å, and $\beta = 95.42$ (1)°. The calculated density, based on four molecules per unit cell, is 1.675 g/cm³ and agrees well with an observed value of 1.67 (2) g/cm³, as measured by flotation in $\text{CCl}_4\text{-BrF}_2\text{CCF}_2\text{Br}$. Data were collected in shells of 2θ by the θ - 2θ scan method using monochromatic $\text{Mo K}\alpha$ radiation produced by Bragg reflection from the (002) plane of a highly oriented graphite crystal. The scan range in 2θ was from -1.0° below the $\text{K}\alpha_1$ peak to $+1.0^\circ$ above the $\text{K}\alpha_2$ peak. The takeoff angle was 2.4° and a receiving aperture 4.5 mm high and 3.5 mm wide was positioned 32 cm from the crystal. Initially background counts of 10 sec were taken at the end of each scan range. Beyond 2θ of 33° this was increased to 20 sec. A scan rate of 2° in $2\theta/\text{min}$ was used.

Data were collected in the range $2.5 < 2\theta \leq 49^\circ$. During the course of data collection six standard reflections from diverse regions of reciprocal space were measured every 100 reflections. At the end of the data collection, the intensities of all six standard reflections had, on the average, decreased by about 5%. Compensation for this decay was made during the data processing. During the course of data collection the crystal yellowed. The data were processed as previously described^{43,44} using a value of 0.04 for p . Of the 6920 reflections measured, 5125 obey the condition $F_o^2 > 3\sigma(F_o^2)$ and of these 4819 are unique and were used in subsequent refinements.

Solution and Refinement of the Structure. A sharpened, origin-removed Patterson map was calculated⁴⁵ and interpreted to give the coordinates of the platinum and the two arsenic atoms. The remaining nonhydrogen atoms were readily located by the usual combination of Fourier and least-squares techniques. Throughout the refinement the function minimized was $\sum w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, respectively, and where the weight, w , is $4F_o^2/\sigma^2(F_o^2)$. The agreement indices R_1 and R_2 are defined as

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

and

$$R_2 = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum wF_o^2} \right]^{1/2}$$

The atomic scattering factors for all nonhydrogen atoms were taken from the usual tabulation,⁴⁶ while those for H were from the

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

(44) R. J. Doedens and J. A. Ibers, *Inorg. Chem.*, **6**, 204 (1967).

(45) In addition to various local programs for the CDC 6400, local modifications of the following programs were employed: Dewar's FAME program, Zalkin's FORDAP Fourier program, the AGNOST absorption program, Johnson's ORTEP II thermal ellipsoid plotting program, Busing and Levy's ORFFE error function program. Our least-squares program, NUCLS, in its nongroup form, closely resembles the Busing and Levy ORFLS program.

(46) D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography," Vol. 4, Kynoch Press, Birmingham, England, Table 2.2A, in press.

Table VII. Derived Parameters for Ring Atoms

| Ring atom ^a | Carbon | | | | Hydrogen | | | |
|------------------------|-------------------------|-------------|-------------|-------------------|--------------------|--------|--------|-------------------|
| | x | y | z | B, Å ² | x | y | z | B, Å ² |
| 11 | 0.4866 (6) ^b | 0.1040 (2) | -0.2865 (3) | 4.0 (1) | | | | |
| 12 | 0.4655 (6) | 0.1217 (2) | -0.3591 (3) | 5.6 (2) | 0.429 ^c | 0.163 | -0.372 | 6.5 |
| 13 | 0.4975 (7) | 0.0780 (3) | -0.4125 (2) | 6.6 (2) | 0.483 | 0.090 | -0.462 | 7.7 |
| 14 | 0.5505 (7) | 0.0166 (3) | -0.3933 (3) | 7.6 (3) | 0.572 | -0.013 | -0.430 | 8.5 |
| 15 | 0.5715 (7) | -0.0011 (2) | -0.3207 (4) | 8.7 (3) | 0.608 | -0.043 | -0.308 | 9.4 |
| 16 | 0.5396 (6) | 0.0426 (3) | -0.2673 (3) | 6.3 (2) | 0.554 | 0.031 | -0.218 | 7.1 |
| 21 | 0.4785 (5) | 0.2477 (2) | -0.2579 (3) | 4.1 (1) | | | | |
| 22 | 0.3706 (4) | 0.2911 (3) | -0.2714 (3) | 4.9 (2) | 0.283 | 0.280 | -0.259 | 5.6 |
| 23 | 0.3911 (5) | 0.3515 (2) | -0.3036 (3) | 5.9 (2) | 0.318 | 0.381 | -0.313 | 6.7 |
| 24 | 0.5200 (6) | 0.3684 (2) | -0.3223 (3) | 6.0 (2) | 0.533 | 0.409 | -0.344 | 7.1 |
| 25 | 0.6274 (5) | 0.3249 (3) | -0.3088 (3) | 6.7 (2) | 0.715 | 0.336 | -0.322 | 7.6 |
| 26 | 0.6069 (4) | 0.2646 (3) | -0.2766 (3) | 5.7 (2) | 0.680 | 0.235 | -0.267 | 6.8 |
| 31 | 0.5681 (5) | 0.1435 (2) | -0.1332 (2) | 4.2 (1) | | | | |
| 32 | 0.5247 (4) | 0.0966 (3) | -0.0861 (3) | 5.2 (2) | 0.436 | 0.079 | -0.094 | 5.8 |
| 33 | 0.6116 (6) | 0.0757 (3) | -0.0272 (3) | 6.8 (2) | 0.582 | 0.044 | 0.005 | 7.7 |
| 34 | 0.7418 (6) | 0.1017 (3) | -0.0155 (3) | 6.8 (2) | 0.801 | 0.088 | 0.025 | 7.6 |
| 35 | 0.7852 (4) | 0.1487 (3) | -0.0626 (3) | 6.6 (2) | 0.874 | 0.166 | -0.055 | 7.2 |
| 36 | 0.6984 (5) | 0.1695 (2) | -0.1215 (3) | 5.2 (2) | 0.728 | 0.201 | -0.153 | 5.8 |
| 41 | 0.1756 (5) | 0.2018 (2) | -0.0060 (2) | 4.0 (1) | | | | |
| 42 | 0.1171 (6) | 0.2401 (2) | 0.0448 (3) | 5.9 (2) | 0.118 | 0.286 | 0.041 | 6.6 |
| 43 | 0.0578 (6) | 0.2104 (3) | 0.1015 (3) | 7.2 (2) | 0.018 | 0.236 | 0.136 | 8.0 |
| 44 | 0.0570 (6) | 0.1424 (3) | 0.1075 (3) | 6.8 (2) | 0.017 | 0.122 | 0.146 | 7.5 |
| 45 | 0.1156 (6) | 0.1041 (2) | 0.0568 (3) | 6.5 (2) | 0.115 | 0.058 | 0.061 | 7.3 |
| 46 | 0.1749 (6) | 0.1338 (2) | 0.0000 (3) | 5.2 (2) | 0.215 | 0.108 | -0.034 | 5.9 |
| 51 | 0.1370 (5) | 0.3148 (2) | -0.1100 (3) | 4.3 (1) | | | | |
| 52 | 0.1575 (5) | 0.3721 (3) | -0.0696 (3) | 6.1 (2) | 0.232 | 0.375 | -0.034 | 7.3 |
| 53 | 0.0679 (7) | 0.4244 (2) | -0.0815 (4) | 7.7 (3) | 0.082 | 0.463 | -0.054 | 8.7 |
| 54 | -0.0422 (6) | 0.4194 (3) | -0.1338 (4) | 8.0 (3) | -0.103 | 0.455 | -0.142 | 8.9 |
| 55 | -0.0627 (5) | 0.3622 (3) | -0.1741 (3) | 7.9 (3) | -0.138 | 0.359 | -0.210 | 8.9 |
| 56 | 0.0269 (6) | 0.3099 (3) | -0.1622 (3) | 5.9 (2) | 0.013 | 0.271 | -0.190 | 6.7 |
| 61 | 0.4206 (4) | 0.2751 (2) | -0.0555 (3) | 4.2 (1) | | | | |
| 62 | 0.4766 (5) | 0.3236 (2) | -0.0962 (2) | 4.8 (2) | 0.425 | 0.341 | -0.137 | 5.4 |
| 63 | 0.6078 (5) | 0.3459 (2) | -0.0767 (3) | 5.9 (2) | 0.646 | 0.379 | -0.104 | 6.8 |
| 64 | 0.6831 (4) | 0.3197 (3) | -0.0164 (3) | 6.7 (2) | 0.772 | 0.335 | -0.003 | 7.7 |
| 65 | 0.6272 (5) | 0.2712 (3) | 0.0244 (3) | 6.0 (2) | 0.678 | 0.253 | 0.065 | 6.9 |
| 66 | 0.4960 (5) | 0.2490 (2) | 0.0048 (3) | 4.9 (2) | 0.458 | 0.216 | 0.033 | 5.7 |

^a Ring atoms are numbered sequentially with 11, 21, and 31 attached to As(1) and 41, 51, and 61 attached to As(2). ^b The estimated standard deviations are derived from those of the group parameters. ^c The hydrogen atom 12 is attached to carbon atom 12, hydrogen 13 is attached to carbon 13, etc.

calculation of Stewart, *et al.*⁴⁷ The effects of anomalous dispersion were included in F_c .⁴⁸ The trial structure was refined by a least-squares procedure in which the phenyl rings were constrained to D_{6h} symmetry and treated as rigid groups (C-C = 1.390 Å) with overall group thermal parameters. The initial isotropic refinement, based on the inner 2527 data, led to a value of R_1 of 0.060. An absorption correction was now made. The 11 crystal faces were {010}, {001}, {011} and ($\bar{1}0$), (110), ($\bar{1}00$). Based on a calculated linear absorption coefficient of 55.29 cm⁻¹, the transmission factors were found to vary between 0.156 and 0.264. An ensuing cycle of refinement in which all nongroup atoms were allowed to vibrate anisotropically and all group atoms were assigned individual isotropic thermal parameters converged to a value of R_1 of 0.042 for the 4819 observations. The positions of the 30 phenyl hydrogen atoms were idealized (C-H = 0.95 Å), and each was assigned an isotropic thermal parameter 1 Å² larger than that of the carbon atom to which it is attached. The contributions of the hydrogen atoms were included in subsequent structure factor calculations. One further cycle of anisotropic refinement reduced the values of R_1 and R_2 to 0.039 and 0.047, respectively, for the 4817 observations and 200 variables. In the final cycle an isotropic correction for secondary extinction was made.⁴⁹ The extinction parameter converged to the value $2.2 (3) \times 10^{-7} e^{-2}$. The final atomic parameters and their standard deviations, as estimated from the inverse matrix, are listed in Table II. The derived positions for the ring carbon atoms as well as the idealized positions of the phenyl hydrogen atoms are given in Table VII.

An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, setting angles, and Miller indices indicated no unusual trends. The error

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in an observation of unit weight is 1.61 e. The maximum density on a final difference Fourier map is 1.1 (1) e/Å³, approximately 25% of the height of a carbon atom in this structure. The final values of the structure amplitudes are tabulated as $10|F_o|$ and $10|F_c|$ (in electrons) for those reflections used in the refinement.⁵⁰

Preparations. The complexes Pt[As(C₆H₅)₃]₄,⁵¹ Pt[(C₆H₅)₃]₄,⁵² and Pt[P(*p*-CH₃C₆H₄)₃]₄⁵³ were prepared by methods previously described, as was tetracyanooxirane.³⁸ Infrared spectra were recorded on a Perkin-Elmer Model 457. Molecular weight determinations in CHCl₃ were carried out using a Mechrolab HP-302B. Microanalyses were performed by Dornis and Kolbe, Mülheim, Germany.

Reactions of PtL₄ Complexes with Tetracyanooxirane. Pt[C₂(CN)₄O][As(C₆H₅)₃]₂ (I). C₂(CN)₄O (0.43 g, 3 mmol) was dissolved in 100 ml of anhydrous benzene, and to this solution was added 4.25 g (3 mmol) of [Pt(As(C₆H₅)₃)₄], dissolved in a minimum amount of the same solvent. The resulting solution was stirred under nitrogen, and after 20 min the solvent was evaporated, at reduced pressure, to a small volume and the white air-stable product Pt[C₂(CN)₄O][As(C₆H₅)₃]₂ began to precipitate. The precipitation was completed by addition of CH₃OH. The complex was filtered off, washed with methanol and ethyl ether, dried *in vacuo*, and recrystallized from CHCl₃-CH₃OH: dec pt 190-193°; yield 49%; mol wt calcd 951, found 930. *Anal.* Calcd for C₄₂H₃₀As₂N₄O: C, 52.95; H, 3.15; N, 5.88. Found: C, 52.8; H, 3.2; N, 5.7.

Pt[C₂(CN)₄O][P(C₆H₅)₃]₂ (V). The same procedure using Pt[P(C₆H₅)₃]₄ gave the white air-stable product in 50% yield: dec pt

(50) See paragraph at end of paper regarding supplementary material.

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210–215°; mol wt calcd 864, found 796. *Anal.* Calcd for $C_{42}H_{30}N_4P_2O$: C, 58.29; H, 3.50; N, 6.49. Found: C, 58.3; H, 3.5; N, 6.5.

$Pt[C_2(CN)_4O][P(p-CH_3C_6H_4)_3]_2$ (VI). This complex was obtained similarly as a white solid using $Pt[P(p-CH_3C_6H_4)_3]_3$ as the parent compound: yield 30%; dec pt 207–213°; mol wt calcd 948. *Anal.* Calcd for $C_{48}H_{42}N_4P_2O$: C, 60.82; H, 4.43; N, 5.91. Found: C, 60.6; H, 4.4; N, 5.9.

Reactivity. Carbon Monoxide. The complex $Pt[C_2(CN)_4O][P(C_6H_5)_3]_2$ (V) (0.864 g, 1 mmol) was dissolved in CH_2Cl_2 . The solution was stirred in a CO atmosphere for 4 hr. The solvent was evaporated to a small volume; after addition of CH_3OH only starting material was recovered.

Carbon Dioxide. The complex $Pt[C_2(CN)_4O][As(C_6H_5)_3]_2$ (I) (0.095 g, 0.1 mmol) was dissolved in $CHCl_3$ -benzene. The solution was stirred in a CO_2 atmosphere for 14 hr. Only starting material was recovered.

Potassium Cyanide. $Pt[C_2(CN)_4O][As(C_6H_5)_3]_2$ (I) (0.476 g, 0.5 mmol) was suspended in ethanol (50 ml), and KCN was added (0.032 g, 0.5 mmol). The resulting suspension was stirred for 20 min at 60°. During this time a clear solution was obtained. To this solution $[NET_4]Br$, dissolved in 40 ml of ethanol, was added. After reduction to small volume and addition of a few milliliters of water, an off-white solid was obtained in almost quantitative yield: ir spectrum (Nujol mull) $\nu_{CN} = 2180, 2140\text{ cm}^{-1}$; 1:1 electrolyte in CH_2Cl_2 .

Hydrogen Cyanide. HCN was bubbled through a solution of 0.43 g (0.5 mmol) of $Pt[C_2(CN)_4O][P(C_6H_5)_3]_2$ (V) in anhydrous THF for 10 min. The solution was stirred overnight in an HCN atmosphere and white crystals precipitated. By comparison with an authentic sample the crystals proved to be *cis*- $Pt[CN]_2[P(C_6-$

$H_5)_3]_2$. The organic product was not identified. With the same procedure but using HCl *cis*- $PtCl_2[P(C_6H_5)_3]_2$ was obtained.

Exchange Reactions. $Pt[C_2(CN)_4O][As(C_6H_5)_3]_2$ (I) (0.476 g, 0.5 mmol) was dissolved in a mixture of 40 ml of benzene and 20 ml of $CHCl_3$. $P(C_6H_5)_3$ (0.6 g) was added. The solution was stirred for 1 hr at 60°. The volume was reduced and ethyl ether was added. The resulting white solid was filtered, washed with ether and *n*-hexane, and dried *in vacuo*. The product was identical with $Pt[C_2(CN)_4O][P(C_6H_5)_3]_2$ obtained by the method described above, *e.g.*, $Pt[P(C_6H_5)_3]_4 + C_2(CN)_4O$. The same type of reaction was carried out with $P(p-CH_3C_6H_4)_3$, to yield $Pt[C_2(CN)_4O][P(p-CH_3C_6H_4)_3]_2$.

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Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$6.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-6893.

Molecular Orbital Theory of the Electronic Structure of Organic Compounds. XXI. Rotational Potentials for Geminal Methyl Groups

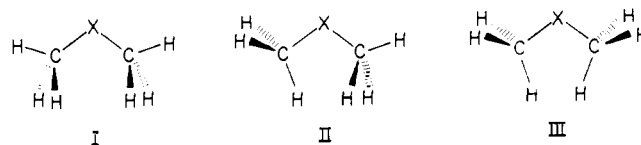
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Abstract: *Ab initio* molecular orbital theory using the 4-31G split valence basis is used to investigate the potential surfaces for the double methyl rotors, propane, dimethylamine, dimethyl ether, dimethylcarbene (singlet), isobutene, acetone, dimethylborane, and isopropyl cation. Experimental results, where available, are reproduced fairly satisfactorily. Qualitatively, the changes of the rotational barriers going from a single rotor to the corresponding double rotor are well explained by an "aromatic" stabilization involving bonding between methyl groups if the central atom is a π donor (as in dimethyl ether) and a corresponding "antiaromatic" destabilization if the central atom is a π acceptor.

The threefold potential barriers for internal rotation of methyl groups have been studied experimentally and theoretically for a wide variety of organic molecules.² In this paper, we shall be concerned with methyl rotation in molecules where two such groups are attached to a common center X so that there may be interaction between them. Among all possible posi-

tions for the two groups, three clearly defined conformations I–III are possible. For propane (X being CH_2)



these may be described as double staggered, staggered eclipsed, and double eclipsed. Conformation I is characterized by one CH bond of each methyl being trans to the XC bond of the other methyl. In III the corresponding CH bonds are cis with regard to the XC bonds and II, finally, exhibits one cis and one trans

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