

The bonding of the cyclopentadienyl ring to the cobalt atom is essentially symmetrical. Given the relatively large thermal parameters of the carbon atoms in the cyclopentadienyl ring, the variation in the cobalt–carbon bond lengths is not significant. Two of the butadiene carbon atoms [C(11), C(16)] are about 0.05 Å closer to the cobalt atom than are the other two [C(17), C(20)]. The four atoms are coplanar and the bond lengths between them indicate a delocalized π system. There is also a plane consisting of these four carbon atoms plus C(12) and C(15), and all six atoms are within 0.040 (2) Å of the plane. The atoms C(17) to C(20) are also coplanar to within 0.030 (3) Å. The adjacent six-membered ring [C(11) to C(16)] is twisted with C(14) and C(13) approximately equidistant [0.310 (4) and 0.49 (4) Å] above and below the plane of the other four atoms. The five-membered ring [C(19)–C(23)] is in an envelope conformation with C(19) 0.573 (3) Å out of the plane defined by the other four carbon atoms.

The disposition of the methoxy group [O–C(24)] relative to the rest of the tricyclic ligand was the reason for this study. In this compound, the oxygen and cobalt atoms are on opposite sides of the tricycle (*i.e. exo* with respect to each other) as in structure (1) in the scheme. In a related structure (Clinet, Duñach & Vollhardt, 1983) where the methoxy group is replaced by a benzyloxy substituent (OCH₂C₆H₅), the oxygen and cobalt atoms are on the same side of the tricycle, as in structure (2) in the scheme. This structure provides a piece of the puzzle regarding the mechanism of cobalt-mediated enediyne cyclizations, and shows that stereochemical control of such cyclizations can be obtained by changing the alkyl substituent of the alkoxy group.

Fig. 2 shows the unit-cell packing.

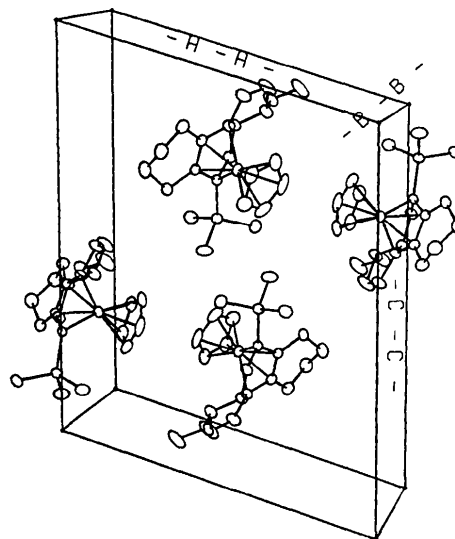


Fig. 2. Arrangement of the molecules in the unit cell.

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Structure of *trans*-Dichloro[dimethyl(phenyl)phosphine] (*trans*-2,3-dimethylpyrrolidine)platinum(II), [PtCl₂(C₆H₁₃N)(C₈H₁₁P)]

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Abstract. $M_r = 503.3$, orthorhombic, $P2_12_1$, $a = 11.295$ (4), $b = 11.964$ (3), $c = 13.200$ (4) Å, $V = 1783.8$ (9) Å³, $Z = 4$, $D_x = 1.874$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 83.3$ cm⁻¹, $F(000) = 968$, room tem-

perature, $R = 0.036$ for 2213 observed counter reflections. The coordination sphere of the Pt^{II} atom is square-planar with a geometry very similar to that of the studied complexes of the type [PtCl₂(R₃P)L] where L is

either one of the eight possible isomers *C,C'*-dimethylpyrrolidine or the unsubstituted pyrrolidine. In the present complex the puckered five-membered ring of the dimethyl-substituted pyrrolidine ligand assumes an envelope-type conformation with C(2) at the flap-tip.

Introduction. The structures of the complexes *trans*-[PtCl₂(Et₃P)(*cis*-2,3-dimethylpyrrolidine)], (IV), and *trans*-[PtCl₂(Et₃P)(*cis*-2,4-dimethylpyrrolidine)], (V), were determined by X-ray analysis in order to assign *cis* or *trans* configuration to the products of the platinum-promoted cyclization of the unsaturated amines CH₂=CH-CH(CH₃)-CH₂CH₂-NH₂ and CH₂=CH-CH₂-CH(CH₃)-CH₂-NH₂ respectively (Ambuehl, Pregosin, Venanzi, Consiglio, Bachechi & Zambonelli, 1979). The two structures revealed different conformations for the puckered five-membered rings of the coordinated pyrrolidines.

The structural study was then continued to determine the conformations assumed by the five-membered ring of other derivatives of pyrrolidine.

Among the complexes of the type *trans*-[PtCl₂(R₃P)L], besides (IV) and (V) already mentioned, the following complexes have been studied: *trans*-[PtCl₂(Et₃P)(pyrrolidine)], (II), and *trans*-[PtCl₂(Et₃P)(*trans*-2,5-dimethylpyrrolidine)], (III), (Bachechi, Mura & Zambonelli, 1980).

In the present paper the structure of another member of the series, the complex *trans*-[PtCl₂(Me₂PhP)(*trans*-2,3-dimethylpyrrolidine)], (I), is reported.

Experimental. The compound was prepared by reacting the amine with *sym-trans*-[Pt₂Cl₄(R₃P)₂] (Chatt & Venanzi, 1955). In the first preparation the phosphine ligand was triethylphosphine as in the complexes already studied. Since no crystals suitable for X-ray analysis were obtained, the phosphine ligand was changed and Me₂PhP was tried successfully. The *trans*-2,3-dimethylpyrrolidine was prepared together with the *cis* isomer by the cyclization reaction described by Cottin (1966). The *trans* isomer was then isolated by preparative gas chromatography.

Crystals of the complex grown from petroleum ether (333–353 K), space group from Weissenberg photographs; prismatic crystal 0.2 × 0.3 × 0.4 mm, Syntex P₂ computer-controlled four-circle diffractometer, graphite monochromator, cell parameters by least squares from setting angles of 15 reflections with 22 ≤ 2θ ≤ 32°. Total of 2948 reflections collected in scan range 2θ = 3–58° (h = 0 to 15, k = 0 to 16, l = 0 to 18); ω-scan mode, with scan rate depending on intensity; three standards measured every 100 reflections, no significant change; data processed to yield values of I and σ(I) (Bachechi, Zambonelli & Macrotrigiano, 1977); in the estimation of σ(I) the uncertainty factor was p = 0.0062, as calculated from the variance of the standard reflections (McCandlish, Stout &

Andrews, 1975). Corrections for Lorentz, polarization and shape-anisotropy effects applied (North, Phillips & Mathews, 1968; Spagna & Zambonelli, 1971). Of 2796 independent reflections (R_{int} = 0.0137), 2213 with I > 3σ(I) (583 non-observed) used for structure determination. Structure solved by Patterson and Fourier methods and refined by full-matrix least-squares procedure, function ∑w(|F_o| - |F_c|)², with w = 4F_o²/σ(F_o²), minimized. Heavier atoms with anisotropic thermal parameters and H atoms with fixed coordinates and isotropic thermal parameters (173 parameters refined). Convergence at R = 0.036 (wR = 0.043). The enantiomeric structure, refined separately, converged at R = 0.050 (wR = 0.059) and could be rejected. (Δ/σ)_{max} = 0.05; final difference map with no peaks exceeding 0.30 e Å⁻³. All calculations performed on an HP 2100 MX minicomputer of the CNR Research Area of Rome using local programs (Cerrini & Spagna, 1977). Scattering factors and anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974).

Discussion. The final positional parameters of the non-H atoms are given in Table 1.* A perspective view of the molecule is shown in Fig. 1. Interatomic bond lengths and angles are given in Table 2.

The coordination around the Pt atom is square-planar with the two Cl atoms in *trans* positions, and the P atom of the dimethyl(phenyl)phosphine ligand and the N atom of the pyrrolidine ligand as donor atoms.

Bond lengths and angles appear to be normal and compare well with those observed in the analogous complexes (II), (III), (IV) and (V).

Table 3 reports the relevant torsion angles defining the arrangement of the phosphine ligand. The dimethyl(phenyl)phosphine assumes an arrangement similar to those of the triethylphosphine in the already-mentioned complexes.

In contrast, the pyrrolidine ligand assumes a different arrangement with respect to the PtCl₂(R₃P) moiety in each of the complexes so far studied. In (I) the PtCl₂(Me₂PhP) moiety is bisectonal in the planar part of the pyrrolidine ring. Me(1) and Me(2) are equatorially oriented in the puckered part of the ring. Me(1) is in a *trans* and Me(2) in a *cis* position with respect to the PtCl₂(Me₂PhP) moiety.

The *trans*-2,3-pyrrolidine ligand has an envelope-like conformation with C(2) at the flap-tip. The atoms C(1), N, C(4), C(3) are almost exactly coplanar while C(2) is 0.61 (2) Å out of their best plane. This plane makes a dihedral angle of 39 (1)° with the plane through C(1),

* Lists of structure factors, anisotropic thermal parameters and torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39954 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

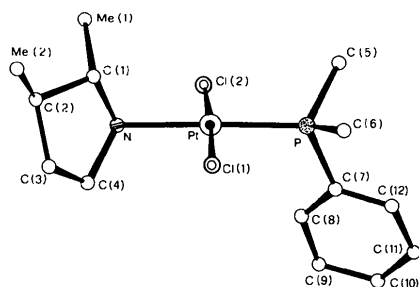
Table 1. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters (\AA^2)

$$B_{\text{eq}} = \frac{1}{3}(B_{11} + B_{22} + B_{33}).$$

	x	y	z	B_{eq}
Pt	2236.9 (1)	1410.3 (5)	1063.0 (5)	3.02 (2)
Cl(1)	466 (4)	2333 (3)	1211 (4)	4.2 (2)
Cl(2)	4040 (5)	583 (4)	871 (6)	7.1 (3)
N	3024 (19)	2871 (15)	362 (16)	3.5 (10)
P	1470 (4)	-139 (3)	1719 (4)	3.5 (2)
C(1)	3239 (17)	3787 (13)	1169 (13)	4.4 (7)
C(2)	3172 (16)	4871 (14)	572 (14)	4.6 (7)
C(3)	2155 (19)	4604 (14)	-197 (14)	5.8 (8)
C(4)	2343 (16)	3403 (13)	-513 (13)	4.1 (7)
C(5)	2479 (16)	-929 (15)	2549 (13)	5.2 (8)
C(6)	80 (18)	78 (15)	2481 (17)	6.5 (8)
C(7)	1008 (16)	-1150 (14)	774 (13)	3.5 (7)
C(8)	1506 (19)	-1104 (16)	-148 (19)	5.4 (10)
C(9)	1242 (17)	-1842 (14)	-935 (13)	5.3 (7)
C(10)	443 (18)	-2711 (16)	-685 (14)	5.0 (8)
C(11)	-53 (20)	-2798 (16)	260 (14)	5.9 (8)
C(12)	226 (16)	-1994 (14)	994 (15)	5.1 (7)
Me(1)	4506 (17)	3644 (17)	1627 (14)	6.2 (8)
Me(2)	2883 (18)	5881 (17)	1285 (15)	7.6 (9)

 Table 2. Interatomic bond lengths (\AA) and angles ($^\circ$), with e.s.d.'s in parentheses

Pt—Cl(1)	2.293 (4)	C(2)—Me(2)	1.566 (27)
Pt—Cl(2)	2.278 (5)	P—C(5)	1.842 (18)
Pt—P	2.222 (4)	P—C(6)	1.882 (22)
Pt—N	2.168 (19)	P—C(7)	1.814 (17)
N—C(1)	1.547 (26)	C(7)—C(8)	1.341 (30)
C(1)—C(2)	1.519 (24)	C(8)—C(9)	1.396 (29)
C(2)—C(3)	1.565 (27)	C(9)—C(10)	1.416 (27)
C(3)—C(4)	1.512 (23)	C(10)—C(11)	1.372 (27)
C(4)—N	1.526 (27)	C(11)—C(12)	1.401 (26)
C(1)—Me(1)	1.563 (27)	C(12)—C(7)	1.373 (24)
Cl(1)—Pt—Cl(2)	176.7 (2)	C(7)—C(8)—C(9)	124.0 (19)
Cl(1)—Pt—P	91.6 (2)	C(8)—C(9)—C(10)	115.3 (17)
Cl(1)—Pt—N	90.4 (6)	C(9)—C(10)—C(11)	121.9 (17)
Cl(2)—Pt—P	91.7 (2)	C(10)—C(11)—C(12)	119.0 (18)
Cl(2)—Pt—N	86.3 (6)	C(11)—C(12)—C(7)	120.2 (18)
P—Pt—N	177.1 (6)	C(12)—C(7)—C(8)	119.5 (17)
Pt—N—C(1)	109.9 (13)	N—C(1)—C(2)	103.9 (14)
Pt—N—C(4)	116.9 (13)	C(1)—C(2)—C(3)	101.5 (14)
Pt—P—C(5)	114.7 (6)	C(2)—C(3)—C(4)	105.6 (15)
Pt—P—C(6)	114.7 (6)	C(3)—C(4)—N	105.0 (14)
Pt—P—C(7)	113.6 (6)	C(4)—N—C(1)	107.7 (14)
C(5)—P—C(6)	105.6 (9)	N—C(1)—Me(1)	109.4 (15)
C(5)—P—C(7)	104.2 (8)	C(2)—C(1)—Me(1)	109.8 (15)
C(6)—P—C(7)	102.7 (9)	C(1)—C(2)—Me(2)	110.9 (15)
P—C(7)—C(8)	118.4 (14)	C(3)—C(2)—Me(2)	113.2 (15)
P—C(7)—C(12)	122.0 (14)		


 Fig. 1. A perspective representation of the molecule *trans*-[PtCl₂(Me₂PhP)(*trans*-2,3-dimethylpyrrolidine)].

C(2), C(3). The conformation of the *cis*-2,3-pyrrolidine ligand in (IV) is also of the envelope type but the maximum puckering occurs at C(4).

The complex has three chiral atoms N, C(1) and C(2) with configuration N(*S*):C(1)(*S*):C(2)(*R*).

Schematic representations of the pyrrolidine rings in the five complexes so far studied are drawn in Fig. 2 with the configurations which maintain the same arrangement of the PtCl₂(R₃P) moiety with respect to the rings for the chosen numbering of atoms.

 Table 3. Relevant torsion angles ($^\circ$) defining the arrangements of the ligands in (I), with e.s.d.'s in parentheses

	(I)	(II)–(V)*
Cl(1)—Pt—P—C(5)	-143 (1)	-140
Cl(1)—Pt—P—C(6)	-20 (1)	-17
Cl(1)—Pt—P—C(7)	97 (1)	104
Cl(2)—Pt—P—C(5)	37 (1)	43
Cl(2)—Pt—P—C(6)	160 (1)	165
Cl(2)—Pt—P—C(7)	-82 (1)	73
Cl(1)—Pt—N—C(1)	74 (1)	
Cl(1)—Pt—N—C(4)	-50 (1)	
Cl(2)—Pt—N—C(1)	-106 (1)	
Cl(2)—Pt—N—C(4)	130 (1)	

* Averaged values of the torsion angles defining the arrangement of the phosphino ligand in the related complexes, (II) to (V).

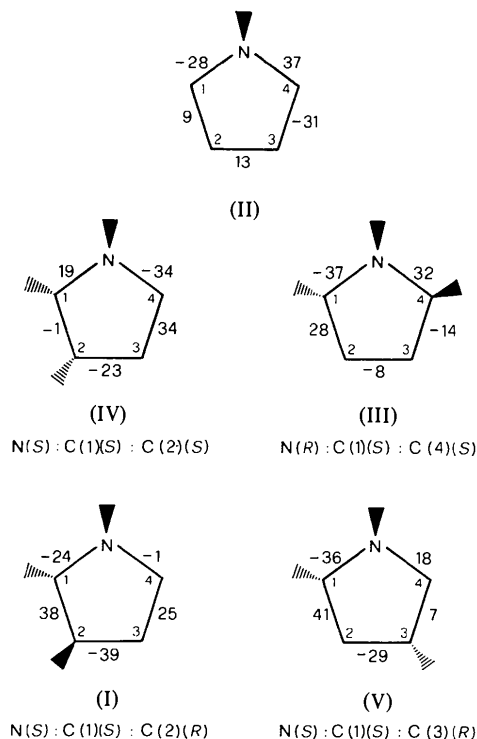


Fig. 2. Torsion angles ($^\circ$) internal to the pyrrolidine ring observed in the five complexes (e.s.d.'s 0.2 $^\circ$), (I), (II), (III), (IV) and (V). The signs refer to those configurations which maintain the same arrangement of the PtCl₂(R₃P) moiety for the given numbering of atoms.

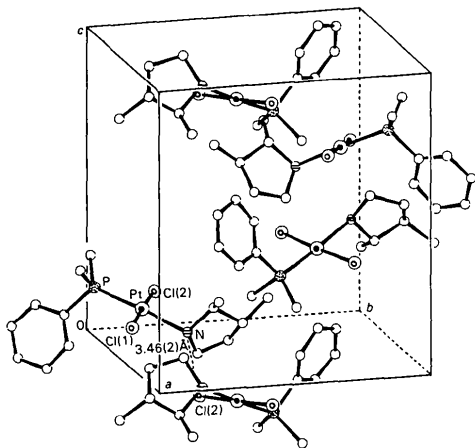


Fig. 3. Packing arrangement of the molecules viewed down *a*.

It can be observed that the conformation of the unsubstituted pyrrolidine ring in (II) may be considered intermediate between the conformation of the ring in (IV) and that in (III), perhaps closer to the conformation in (IV) which has an envelope-like form with C(4) at the flap. Therefore the five structures seem to represent five phases of the pseudorotation of the pyrrolidine ring in the sequence (IV)→(II)→(III)→(V)→(I) or, to stress the influence of the methyl substituents, (IV)←(II)→(III)→(V)→(I).

The shortest intermolecular contact [3.46 (2) Å], observed between N and Cl(2)[$\frac{1}{2}+x$, $\frac{1}{2}-y$, $-z$], is probably due to an N—H...Cl hydrogen bond. The packing arrangement is shown in Fig. 3.

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(Hexafluoroacetylacetonato-*O,O'*)(1-hydroxy-2,2,6,6-tetramethylpiperidinato-*O,N*)palladium(II), [Pd(C₅HF₆O₂)(C₉H₁₈NO)], a Metal Complex Containing a Reduced Nitroxyl Radical

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Abstract. $M_r = 469.7$, monoclinic, $P2_1/n$, $a = 7.875$ (3), $b = 20.511$ (8), $c = 11.655$ (3) Å, $\beta = 105.67$ (3)°, $V = 1812$ (1) Å³, $Z = 4$, $D_x = 1.722$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.08$ mm⁻¹, $F(000) = 936$, $T = 297$ K, final $R = 0.042$ for 2498 observed reflections. The Pd atom is bound to a chelating hexafluoroacetylacetonato ligand and to a reduced nitroxyl radical coordinated in an η^2 fashion through its N and O atoms. Principal bond distances include Pd—O(F₆acac) = 2.058 (4), 2.078 (4), Pd—O(nitroxyl) = 2.009 (4), Pd—N = 1.985 (4), N—O = 1.346 (5) Å.

Introduction. The title compound was prepared in the course of exploratory studies of the reactions of stable nitroxyl radicals with transition-metal complexes containing a strongly Lewis-acidic metal center. Previous studies in this series have yielded examples of various types of interactions of the nitroxyl group, including metal coordination of the nitroxyl radical through O (Dickman & Doedens, 1981; Porter, Dickman & Doedens, 1983; Porter & Doedens, 1985), bidentate N,O binding of the reduced radical (Dickman & Doedens, 1982), hydrogen bonding to coordinated water (Dickman & Doedens, 1983), and formation of a co-crystallized solid with no specific interactions involving the nitroxyl group (Porter & Doedens, 1984). We

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