Chiral derivatives of *exo*-metallofullerenes: synthesis and X-ray study of solvate of platinumfullerene cluster with cyclooctene, $\eta^2 - C_{60}Pt[(+)-DIOP] \cdot C_8H_{14}$

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A novel optically active *exo*-metallofullerene derivative, $\eta^2 - C_{60} Pt[(+) - DIOP]$ (1) (DIOP is 2,3-*o*,*o*'-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphinobutane)), is formed as a result of the cleavage of the chelate metallocycle in Pt[(+)-DIOP]₂ and the substitution of the bidentate (+)-DIOP ligand with C_{60} . Cluster 1 was also obtained by replacement of the phosphine ligands in $\eta^2 - C_{60} Pt(PPh_3)_2$ by (+)-DIOP. Compound 1 was identified by its electronic absorption spectra, ³¹P NMR spectra, and the elemental analysis data. A single-crystal X-ray study of the 1 cyclooctene solvate, $\eta^2 - C_{60} Pt[(+)-DIOP] \cdot C_8 H_{14}$ was performed. Packing of the fullerene cores in a crystal of $1 \cdot C_8 H_{14}$ corresponds to the diamond structure subjected to the significant orthorhombic distortions.

Key words: metallofullerenes, synthesis, chirality; platinum, cluster; electronic absorption spectra; ³¹P NMR spectra; X-ray analysis.

One of the important chemical properties of the polyhedron carbon cluster – fullerene C_{60} – is its ability to add coordinate unsaturated complexes of zero-valent metals of the VIII group (Pt, Pd) to form exo-metallofullerenes.¹⁻⁴ It was found that metallocomplexes, containing monodentate phosphine or olefin ligands, and mixed metallocomplexes, containing a bidentate diphosphine ligand were involved in the reaction. Earlier we used the reaction of C₆₀ with Pd complexes containing bidentate optically active ligand (+)-DIOP to introduce a chiral group into metallofullerene molecule.³ As a result the optically active cluster η^2 -C₆₀Pd[(+)-DIOP] was obtained, which is of interest for studying electron structure of fullerenes by chiroptical methods. In this work we report the synthesis and full characterization of cluster η^2 -C₆₀Pt[(+)-DIOP]. This cluster is the first chiral derivative of exo-metallofullerene C₆₀ for which the X-ray study was performed; it is a representative of enantiomerically pure C_{60} derivatives, which are not numerous yet (see Refs. 3 and 5-7).

We have studied the reaction of fullerene C_{60} with stable bischelate complex Pt[(+)-DIOP]₂, synthesized earlier.⁸ The cleavage of the chelate metallocycle followed by the exchange of one of the two ligands results in a cluster, (η^2 -[60]fullerene)-[(+)-2,3-o,o'-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphinobutane-*P*,*P*')]platinum, η^2 -C₆₀Pt[(+)-DIOP] (1) (Scheme 1).

⁺ Deceased in 1995.

Scheme 1



Substitution of (+)-DIOP occurs much more slowly compared to monodentate triphenylphosphine, and its rate is comparable with the rate of *retro-insertion* under the action of C_{60} , in which the sources of platinum carbenoid are mercury platinum compounds.⁹ We used the possibility of ligand exchange in the compound η^2 - C_{60} Pt(PPh₃)₂ to introduce an optically active ligand (Scheme 2) as in the synthesis of the isostructural palladium complex.

Scheme 2

$$C_{60}Pt(PPh_3)_2 + (+)-DIOP \longrightarrow C_{60}Pt[(+)-DIOP]$$

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Table 1. Characteristic maxima in electronic absorption spectra of $C_{60}Pt[(+)-DIOP]$, its analogs, and C_{60} solutions (in toluene)

Compound	λ _{max} /nm				
$\eta^2 - C_{60} Pt[(+) - DIOP]$	337.7, 443.4, 610.7, 645.2 (sh)				
$\eta^2 - C_{60} Pd[(+) - DIOP]$	337.2, 450, 615, 660 (sh)				
η^2 -C ₆₀ Pt(PPh ₃) ₂	337, 442, 605, 641 (sh)				
η^2 -C ₆₀ Pd(PPh ₃) ₂	337, 439, 613, 662 (sh)				
C ₆₀	336.7, 420, 540, 599, 628 (sh)				

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The ³¹P NMR spectrum of compound 1 contains a narrow singlet at δ +11.4 from the two equivalent phosphorus nuclei of the ligand (+)-DIOP (*cf.* Ref. 3), which are linked to platinum. The presence of the direct Pt-P bond is revealed in the form of a doublet due to coupling of ³¹P to the second isotopomer with HFCC $J_{195pt-31P} =$ 3755 Hz. The electronic absorption spectrum (EAS) of cluster 1 contains four main fullerene bands in the region of 330-700 nm (Table 1) like the spectra of other isostructural *exo*-metallofullerenes. The formulation of compound 1 is supported by the elemental analysis data for its crystal *cis*-cyclooctene and toluene solvates: $C_{60}Pt[(+)-DIOP] \cdot C_{7}H_{8}$.



Table 2. Bond lengths (d) in structure of $1 \cdot C_8 H_{14}$

Bond	d/Å	Bond	d/Å
$\overline{Pt(1)} - C(1)$	2.09(2)	C(51) - C(52)	1.37(2)
Pt(1) - C(2)	2.12(2)	C(51) - C(60)	1.50(3)
Pt(1) - P(2)	2.262(4)	C(52)-C(53)	1.41(2)
Pt(1) - P(1)	2.279(4)	C(53)-C(54)	1.39(3)
P(1) - C(61)	1.821(13)	C(54)-C(55)	1.37(3)
P(1) - C(68)	1.826(8)	C(12) - C(11)	1.43(2)
P(1) - C(74)	1.846(8)	C(12) - C(13)	1.44(2)
P(2) - C(86)	1.812(9)	C(11) - C(10)	1.45(2)
P(2) - C(80)	1.832(8)	C(11) - C(28)	1.49(2)
P(2) - C(64)	1.86(2)	C(10) - C(9)	1.34(2)
O(1) - C(65)	1.41(2)	C(10) - C(26)	1.41(2)
O(1) - C(62)	1.45(2)	C(9)-C(8)	1.47(2)
O(2) - C(65)	1.43(2)	C(8) - C(24)	1.39(2)
O(2)-C(63)	1.435(14)	C(13) - C(30)	1.45(2)
C(1) - C(6)	1.44(2)	C(30)-C(29)	1.43(3)
C(1) - C(2)	1.51(2)	C(30)-C(31)	1.48(2)
C(1) - C(9)	1.57(2)	C(29)-C(28)	1.35(3)
C(2)-C(12)	1.43(2)	C(29)-C(47)	1.48(2)
C(2)-C(3)	1.47(2)	C(28)C(27)	1.41(3)
C(3)-C(4)	1.41(2)	C(27)-C(26)	1.40(3)
C(3)-C(14)	1.43(2)	C(27)-C(45)	1.44(2)
C(4)-C(5)	1.44(2)	C(26)-C(25)	1.40(3)
C(4)-C(17)	1.49(2)	C(25)C(24)	1.47(3)
C(5)-C(6)	1.34(2)	C(25)-C(43)	1.47(2)
C(5)-C(19)	1.41(2)	C(24)-C(23)	1.42(2)
C(6)-C(7)	1.46(2)	C(23)-C(42)	1.46(2)
C(7)-C(21)	1.39(2)	C(31)C(48)	1.44(2)
C(7)—C(8)	1.40(3)	C(48)—C(49)	1.40(2)
C(14)C(15)	1.45(2)	C(48)—C(47)	1.46(3)
C(14) - C(13)	1.46(3)	C(47) - C(46)	1.41(3)
C(15)—C(16)	1.42(3)	C(46)—C(58)	1.41(3)
C(15) - C(32)	1.48(2)	C(46) - C(45)	1.43(3)
C(16) - C(17)	1.34(3)	C(45)—C(44)	1.37(3)
C(16) - C(34)	1.50(2)	C(44) - C(43)	1.35(3)
C(17) - C(18)	1.43(3)	C(44) - C(57)	1.48(2)
C(18) - C(19)	1.40(3)	C(43) - C(42)	1.48(3)
C(18) - C(36)	1.44(2)	C(42) = C(41)	1.41(3)
C(19) - C(20)	1.40(3)	C(41) - C(50)	1.44(2)
C(20) - C(21)	1.40(3)	C(49) - C(39)	1.46(2)
C(20) - C(38)	1.49(2)	C(59) - C(58)	1.30(2)
C(21) = C(22)	1.42(2)	C(59) - C(00)	1.41(2)
C(22) = C(23)	1.39(4)	C(58) = C(57)	1.41(2)
C(22) = C(39)	1.40(2)	C(57) = C(50)	1.30(3)
C(32) = C(31)	1.33(3)	C(55) = C(50)	1.37(2)
C(33) = C(50)	1.43(2)	C(5) = C(60)	1.53(2)
C(33) - C(34)	1.46(3)	C(67) = C(63)	1.53(2) 1.52(2)
C(34) - C(35)	1 42(3)	C(63) - C(64)	1.50(2)
C(35) - C(52)	1.41(3)	C(65) - C(66)	1.46(2)
C(35) - C(36)	1.43(3)	C(65) - C(67)	1.52(2)
C(36) - C(37)	1.37(3)	C(92)-C(99)	1.22(4)
C(37) - C(38)	1.36(3)	C(92)-C(93)	1.43(5)
C(37)-C(53)	1.49(3)	C(93)-C(94)	1.41(3)
C(38)-C(39)	1.46(3)	C(94)-C(95)	1.56(3)
C(39)-C(40)	1.42(3)	C(95)-C(96)	1.57(4)
C(40)-C(41)	1.33(4)	C(96)-C(97)	1.58(4)
C(40)-C(54)	1.43(2)	C(97)-C(98)	1.67(4)
C(50)-C(51)	1.45(2)	C(98)-C(99)	1.41(4)
C(50)-C(49)	1.48(3)		

Fig. 1. Structure of complex 1.

Angle	ω/deg	Angle	ω/deg
C(1) - Pt(1) - C(2)	42.0(4)	C(12)-C(2)-C(3)	103(2)
C(1) - Pt(1) - P(2)	146.3(4)	C(12) - C(2) - C(1)	120(2)
C(2) - Pt(1) - P(2)	104.4(4)	C(3) - C(2) - C(1)	115(2)
C(1) - Pt(1) - P(1)	104.2(4)	C(12)-C(2)-Pt(1)	125.7(13)
C(2) - Pt(1) - P(1)	146.2(4)	C(3) - C(2) - Pt(1)	122.1(11)
P(2) - Pt(1) - P(1)	109.47(13)	C(1)-C(2)-Pt(1)	68.1(10)
C(61)-P(1)-C(68) 105.8(6)	O(1)-C(62)-C(63)	104.1(11)
C(61)-P(1)-C(74) 102.0(6)	O(1)-C(62)-C(61)	105.2(11)
C(68)-P(1)-C(74) 103.0(4)	C(63)-C(62)-C(61)	117.7(12)
C(61) - P(1) - Pt(1)	118.2(5)	O(2)-C(63)-C(64)	109.7(11)
C(68) - P(1) - Pt(1)	113.0(3)	O(2)-C(63)-C(62)	104.0(11)
C(74) - P(1) - Pt(1)	113.2(3)	C(64)-C(63)-C(62)	118.7(13)
C(86)-P(2)-C(80) 102.9(5)	C(63)—C(64)—P(2)	117.2(11)
C(86) - P(2) - C(64)) 101.6(7)	O(1)-C(65)-O(2)	103.1(9)
C(80)-P(2)-C(64) 102.5(6)	O(1)-C(65)-C(66)	110.1(13)
C(86) - P(2) - Pt(1)	116.1(4)	O(2)-C(65)-C(66)	107.2(12)
C(80) - P(2) - Pt(1)	111.1(4)	O(1)—C(65)—C(67)	112.8(12)
C(64) - P(2) - Pt(1)	120.4(5)	O(2)-C(65)-C(67)	110.1(13)
C(65) - O(1) - C(62)	107.5(11)	C(66)—C(65)—C(67)	113.0(12)
C(65)—O(2)—C(63) 109.4(10)	C(99)—C(92)—C(93)	128(5)
C(6) - C(1) - C(2)	118(2)	C(94)-C(93)-C(92)	114(3)
C(6) - C(1) - C(9)	107(2)	C(93)-C(94)-C(95)	112(3)
C(2) - C(1) - C(9)	112(2)	C(94)-C(95)-C(96)	107(2)
C(6) - C(1) - Pt(1)	124.3(12)	C(95)—C(96)—C(97)	125(2)
C(2)-C(1)-Pt(1)	69.9(11)	C(96)-C(97)-C(98)	112(2)
C(9) - C(1) - Pt(1)	120.2(12)	C(99)—C(98)—C(97)	115(2)
		C(92)-C(99)-C(98)	136(3)

Table 3. Main bond angles (ω) in structure of $1 \cdot C_8 H_{14}$

The molecular structure of crystal cyclooctene solvate of complex $(\eta^2-[60]$ fullerene)-[(+)-2, 3-o, o'-isopropylidene-2, 3-dihydroxy-1, 4-bis(diphenylphosphinobutane-P, P')]platinum, $\eta^2-C_{60}Pt[(+)-DIOP] \cdot C_8H_{14}$ $(1 \cdot C_8H_{14})$, was unambiguously established by a singlecrystal X-ray study. The bond lengths and the main bond angles in the structure $1 \cdot C_8H_{14}$ are presented in Tables 2 and 3. Figure 1 demonstrates the molecular structure of the complex.

Within experimental accuracy the positional parameters of the fullerene C_{60} core, coordinating the Pt atom by C(1)-C(2) bond coincide with the corresponding characteristics of the crystal structure of complex η^2 -C₆₀Pt(PPh₃)₂·THF (2)¹⁰ (henceforth the values of positional parameters of complex 2 are given in braces). As in structure 2, the fullerene core in the cluster 1 undergoes minor deformations due to coordination by the metal atom. All the five- and six-membered rings of the fullerene core (except for the four rings containing C(1)) and C(2) atoms, linked to platinum) are planar within 0.02 Å. Five-membered cycles C(1)C(6)C(7)C(8)C(9) and C(2)C(3)C(14)C(13)C(12) have conformation of a "planar envelope". Deviations of C(1) and C(2) atoms from the average planes of the other four atoms of these cycles towards the metal atom are 0.18 and 0. 15 Å, respectively. Deviations of C(1) and C(2) atoms from the centroid of the fullerene core to Pt(1) atom also affect conformations of six-membered cycles C(1)C(2)C(3)C(4)C(5)C(6) and

C(1)C(2)C(12)C(11)C(10)C(9); the first of them attains the form of a very flattened "boat", and the latter — the form of a "sofa" (atoms C(3), C(6) and C(12) are displaced from C(1)C(2)C(4)C(5) and C(1)C(2)C(9)C(10)C(11)planes by 0.09, 0.07 and 0.13 Å, respectively).

Ninety C-C bonds of the fullerene core C_{60} belong to two chemically non-equivalent types: 60 of them are involved concurrently in five- and six-membered rings (such bonds are usually named 5,6-bonds), and the other 30 bonds — in two six-membered rings (6.6-bonds). In spite of very effective delocalization of π -electron density throughout the entire surface of the fullerene core, its the only possible «classical» structural formula considers all 5,6-bonds as single and all 6,6-bonds as double bonds. In accordance with these ideas we observed that cluster 1 (like the other most accurately structurally studied fullerene C_{60} derivatives^{2,10}) contains two types of distances: the average values of the bond length of 5,6- and 6,6-bonds in structure 1 (except for the bonds involving C(1) and C(2) atoms linked to the metal atom) are 1.44 {1.45} Å and 1.40 {1.39} Å, respectively. Such a distribution of bond lengths is in a good agreement with the fact that η^2 -coordination of a transition metal atom in all structurally studied fullerenes occurs exclusively at the more electron-rich 6,6-bonds of fullerene core.

As could be expected the C(1)-C(2) bond length is markedly elongated [1.51(2) {1.50} Å] compared to the lengths of the other 6,6-bonds, although in this case the



Fig. 2. Coordination tetrahedron of the fullerene core centroid packing of a $1 \cdot C_8 H_{14}$ crystal. Both symmetrically independent distances between the centroids of the cores and the largest and the smallest angles in the tetrahedron are presented (other angles are within the range $105-110^\circ$).

experimental accuracy achieved allows us to judge the particular C—C distances only with great care. For this reason the best parameter for evaluating the deformation of the fullerene core in the case of metal coordination is the distance from the centroid of the C_{60} core to all of the carbon atoms (the coordinates of the centroid of fullerene core were calculated with no consideration for the C(1) and C(2) atoms and the directly opposite to them C(55) and C(60)). The value of this parameter averaged for all

atoms of the C_{60} core is equal to 3.53 {3.53} Å, whereas the centroid—C(1) and centroid—C(2) distances in molecule 1 are in fact identical and elongated to 3.72 [3.68 and 3.73] Å.

Unsubstituted fullerene C_{60} is crystallized in a facecentered cubic cell;¹¹ this packing pattern is one of the closest packings. Each fullerene molecule in this crystal has twelve nearest neighbors in a cubooctahedral environment (positioned in a cubooctahedron vertex) at the equal distances 9.943 Å from the central molecule (henceforth the distances between fullerene cores mean the distances between the centroids of the fullerene cores).

As expected, substituted fullerene cores in a crystal of cluster $1 \cdot C_8 H_{14}$ are packed essentially less closely. It is most convenient to describe this packing as the diamond structure subjected to significant orthorhombic distortions, i.e., elongated along the diagonal of one of faces in cubic diamond cell and contracted along the second diagonal of the same face. (In this pattern instead of diamond carbon atoms we consider the centroids of fullerene cores in a crystal of $1 \cdot C_8 H_{14}$.) As a result each fullerene core has four nearest neighbors positioned in the vertices of the distorted tetrahedron (Fig. 2), in which one of the angles is significantly increased (to 128°), and the opposite angle is substantially decreased (to 94°). Both symmetrically nonequivalent shortest distances between neighboring cores (10.103 and 10.295 Å) are markedly greater than those in a crystal of unsubstituted fullerene.

To date the packing of fullerene cores in a crystal of $1 \cdot C_8 H_{14}$ has not been observed, as follows from consideration of packings of fullerene derivatives using Cambridge Structural Data Bank (CSDB) (at least in crystals of those C_{60} derivatives for which CSDB has complete structural data available).



Fig. 3. Crystal packing of $1 \cdot C_8 H_{14}$ solvate: views along the axes x (a), y (b), and z (c); fullerene – centroids of C_{60} cores, COE – centroids of cyclooctene solvate molecules.

The views of the fullerene cores packing along the axes x and z in a crystal of $1 \cdot C_8 H_{14}$ (which correspond to the views of the diamond structure along two mutually perpendicular diagonals of one face in a cubic cell) are presented in the form of hexagonal nets (Fig. 3, a and c), where solvate cyclooctene molecules are positioned in the centroids of six-membered cycles observed along axis x, and corresponding cavities on the view along axis z are occupied with Pt(DIOP) moieties.

We have not found any specific interactions between solvate cyclooctene molecule and the fullerene core in structure $1 \cdot C_8 H_{14}$: all the distances between them surpass 3.6 Å (this value corresponds to the usual van der Waals contacts).

The geometry of the organometallic moiety in molecule 1 is in good agreement with the parameters of Pt complexes containing DIOP ligand, for example, MeClPt[(S,S)-DIOP]¹³ (3) and $(\eta^2-C_2H_4)Pt[(R,R)-DIOP]^{14}$ (4). The coordination of the platinum atom in structure 1 is square-planar; its deviation from the average P(1)P(2)C(1)C(2) plane is 0.006 Å. Within experimental accuracy the distances Pt(1)-C(1) [2.09(2) Å] and Pt(1)-C(2) [2.12(2) Å] do not differ from the similar bond distances in molecules of the fullerene complex 2 (2.145 and 2.115 Å) and in the ethylene analog of 1, compound 4 (2.110 and 2.100 Å); the distances Pt(1)-P(1) [2.279(4) Å and Pt(1)-P(2) [2.262(4) Å] are also consistent with the corresponding distances in structures 2 (2.303 and 2.253 Å) and 4 (2.261 and 2.254 Å).

As was reported earlier,¹³ ligand (S,S)-DIOP is very conformationally flexible. Actually, conformation of the seven-membered metallocycle in cluster 1 substantially differs from the conformation of the chelate ring in compound 3 (described as "twist chair" ¹³) and can be characterized by the deviations of atoms Pt(1), C(62), and C(63) (+0.64, -0.46 and +0.37 Å, respectively) from the P(1)P(2)C(61)C(64) plane within 0.13 Å. The conformation of the five-membered ring in molecule 1 also differs from that found for complex 3. This ring in molecule 1 has an "envelope" conformation with the C(65) atom deviating by 0.47 Å from the average plane of other atoms of this ring within 0.04 Å.

Unlike structure 3, the orientation of pairs of phenyl moieties at both P atoms is identical: in each case one of the P-C(Ph) bonds ("axial") forms an angle with the P(1)Pt(1)P(2) plane, which is substantially closer to 90° (65 and 63° for P(1)-C(68) and P(2)-C(86) bonds, respectively) than the second ("equatorial") P-C(Ph) bond at the same P atom (15° and 32° for P(1)-C(74) and P(2)-C(80) bonds, respectively).

Experimental

All the reactions were carried out in argon atmosphere. The solvents were dried, degassed, and distilled under Ar. Complex $Pt[(+)-DIOP]_2$ was obtained using a well known procedure.⁸ Compound $\eta^{2-}C_{60}Pt(PPh_3)_2$ was synthesized by a "retro-insertion" method using *trans*-bromo(2,2-diphenylethylmercur)-

bis(triphenylphosphine)platinum.⁹ The ${}^{31}P{}^{1}H$ NMR spectra were recorded on a Bruker WP-200 SY instrument; 1 % H₃PO₄ was used as the standard. The electronic absorption spectra were recorded on a Specord UV-Vis spectrophotometer.

Synthesis of $\eta^2 - C_{60} Pt[(+) - DIOP]$ by substitution of (+) - DIOP in Pt[(+) - DIOP]₂ with C_{60} . *A*. A solution of Pt[(+) - DIOP]₂ (63.94 mg, 0.0536 mmol) was added to a solution of fullerene C_{60} (39.5 mg, 0.0548 mmol) in 18 mL of toluene placed in the Schlenk vessel. ³¹P NMR (toluene), δ : -11.6 (s, $J_{195P_1-31P} = 3751$ Hz). The resulting solution was stirred for 20 min, filtered through a G4 filter, and the filtrate was diluted with hexane (100 mL). After 4 days the crystals were separated from the green mother liquor, washed with pentane, and dried *in vacuo* to yield complex 1 (54.32 mg, 67 %). A sample of 1 for analysis was isolated after recrystallization of the compound from a *cis*-cyclooctene—hexane mixture in the form of the larger-sized crystals of the solvate η^2 -C₆₀Pt[(+)-DIOP] · C₈H₁₄. Found (%): C, 78.08; H, 2.98; P, 4.06. ³¹P NMR (C₈H₁₄), δ : 11.4 (s, $J_{195P_1-31P} = 3755$ Hz). The crystals were used for X-ray studies of the structure 1.

B. Control experiment: fullerene C_{60} (41.60 mg, 0.0577 mmol) and Pt[(+)-DIOP]₂ (68.81 mg, 0.0577 mmol) were suspended in 7 mL of cycloctene and stirred for 48 h. The course of the reaction was monitored from signals in the ³¹P NMR{¹H}, δ : -22 ((+)-DIOP); -11.7 (Pt[(+)-DIOP]₂); +11.4 (η^2 -C₆₀Pt[(+)-DIOP]). Fifty hours later conversion was ~ 99 %.

Synthesis of η^2 -C₆₀Pt[(+)-DIOP] by replacement of PPh₃ with (+)-DIOP in complex η^2 -C₆₀Pt(PPh₃)₂. In 25 mL of toluene C₆₀Pt(PPh₃)₂ (105.9 mg, 0.0735 mmol) and (+)-DIOP (77 mg, 0.154 mmol) were dissolved with stirring. One hour after 70 mL of hexane were added to the reaction mixture, and the resulting solution was allowed to stand at room temperature for 24 h. The needle crystals were separated, washed with hexane, and dried *in vacuo* to yield complex η^2 -C₆₀Pt[(+)-DIOP]₂ · C₇H₈ (78.65 mg, 71 %). Found (%): P, 4.14. C₉₈H₄₀O₂P₂Pt. Calculated (%): P, 4.11. ³¹P NMR (C₈H₁₄), δ : 11.4 (s, J_{195p,-31p} = 3755 Hz). X-ray study. Crystals of $1 \cdot C_8H_{14}$ (C₉₉H₄₆O₂P₂Pt, M = 1524.39) are rhombic, at 148 K a = 18.479(5) Å, b = 22.816(5) Å,

X-ray study. Crystals of $1 \cdot C_8 H_{14}$ ($C_{99} H_{46} O_2 P_2 Pt$, M = 1524.39) are rhombic, at 148 K a = 18.479(5) Å, b = 22.816(5) Å, c = 14.803(3) Å, V = 6241(3) Å³, Z = 4, space group $P2_12_{12}_{1}$, $d_{calc} = 1.622$ g cm⁻³, F(000) = 3056. Cell parameters (determined from 24 reflections in the region of $20 \le 2\theta \le 21^\circ$) and intensities of 6619 independent reflections were measured on a Siemens P3/PC automated diffractometer (148 K, Mo-K α -radiation, graphite monochromator, $\theta/2\theta$ -scanning, $\theta \le 26^\circ$).

The structure was solved by the direct method. All nonhydrogen atoms were solved from successive Fourier difference and refined by a least squares method. Because of the very limited number of experimental structural factors (a slightly reflecting crystal in non-central symmetrical space group) in anisotropic refinement of the fullerene core, limitations were imposed on some bond distances considering the presence of the intrinsic symmetry plane of fullerene passing through C(1), C(2), C(55), and C(60) atoms (Program SHELXTL PLUS, version 5)*. The benzene rings of the DIOP-ligand were considered rigid body in the refinement (C-C, 1.39 Å; C-H, 0.96 Å). The hydrogen atoms in organic ligand were located geometrically (C-H, 0.96 Å) and involved in the final refinement in the riding model approximation with the common isotropic temperature factor refined ($U_{iso} = 0.065(14)$ Å²). Because of sub-

^{*}For obtaining independent characteristics of environment for each of the C(1) and C(2) atoms no limitations were imposed considering the second plane of the fullerene core.

Atom	x	у	Ζ	$U_{eq}/Å^2$	_	Atom	x	у	Z	U_{eq}/\dot{A}^2
Pt(1)	5146(1)	5458(1)	4914(1)	25(1)		C(46)	984(12)	5577(10)	5765(16)	83(5)
P(1)	5796(2)	5299(2)	3629(2)	29(1)		C(45)	1251(7)	5293(6)	4972(21)	92(4)
P(2)	5776(2)	5121(2)	6118(3)	35(1)		C(44)	1018(10)	5601(10)	4230(16)	81(5)
O(1)	7923(6)	5161(6)	4125(7)	62(4)		C(43)	1420(9)	5676(11)	3477(15)	92(5)
O(2)	[•] 7909(5)	5466(6)	5554(6)	40(3)		C(42)	1484(10)	6239(12)	2987(11)	97(5)
C(1)	4191(9)	5850(8)	4462(9)	26(3)		C(41)	1115(11)	6733(10)	3326(12)	89(5)
C(2)	4181(9)	5796(8)	5476(9)	27(3)		C(49)	1112(9)	6602(8)	6801(9)	59(4)
C(3)	4162(8)	6357(7)	, 15970(8)	37(3)		C(59)	655(8)	6578(8)	6001(11)	47(3)
C(4)	4230(9)	6895(8)	5506(12)	52(4)		C(58)	608(9)	6086(9)	5488(14)	61(4)
C(5)	4194(8)	6929(7)	4533(12)	44(3)		C(57)	614(10)	6125(10)	4535(14)	68(4)
C(6)	4151(9)	6428(8)	4071(9)	37(3)		C(56)	669(10)	6662(10)	4115(12)	70(4)
C(7)	3681(10)	6385(9)	3279(9)	58(4)		C(55)	725(10)	7209(9)	4644(12)	56(4)
C(14)	3694(10)	6312(9)	6740(9)	63(4)		C(60)	711(9)	7125(9)	5561(12)	44(3)
C(15)	3321(11)	6825(12)	7077(11)	83(5)		C(61)	6759(6)	5467(7)	3643(9)	35(3)
C(16)	3394(11)	7360(11)	6594(16)	92(5)		C(62)	7168(8)	5137(7)	4388(10)	39(4)
C(17)	3790(11)	7398(9)	5835(16)	80(5)		C(63)	7158(7)	5397(7)	5332(8)	35(3)
C(18)	3569(7)	7720(5)	5055(22)	92(4)		C(64)	6780(8)	5067(7)	6072(11)	45(4)
C(19)	3802(10)	7430(9)	4272(17)	76(5)		C(65)	8341(6)	5143(6)	4922(12)	36(3)
C(20)	3348(11)	7411(9)	3518(15)	87(5)		C(66)	9011(7)	5468(7)	4796(12)	66(5)
C(21)	3288(10)	6869(11)	2995(11)	80(5)		C(67)	8464(8)	4524(7)	5263(11)	65(5)
C(22)	2555(9)	6836(10)	2713(10)	95(5)		C(68)	5725(4)	4548(3)	3215(6)	26(3)
C(32)	2568(10)	6718(10)	7387(11)	86(5)		C(69)	6141(4)	4335(4)	2505(6)	44(4)
C(33)	2192(11)	7235(10)	7112(12)	86(5)		C(70)	6077(5)	3753(4)	2238(5)	56(5)
C(34)	2665(12)	7644(10)	6644(16)	95(5)		C(71)	5595(5)	3384(3)	2682(6)	27(3)
C(35)	2405(13)	7955(10)	5884(17)	104(5)		C(72)	5179(4)	3596(3)	3391(6)	41(3)
C(36)	2867(8)	7992(6)	5115(21)	103(5)		C(73)	5243(4)	4178(4)	3658(5)	33(3)
C(37)	2448(12)	7985(10)	4351(18)	105(6)		C(74)	5476(4)	5738(4)	2660(5)	29(3)
C(38)	2630(12)	7701(10)	3578(16)	98(5)		C(75)	5734(4)	6307(4)	2567(6)	47(4)
C(39)	2141(12)	7334(13)	3049(14)	115(6)		C(76)	5470(5)	6664(3)	1880(7)	62(5)
C(40)	1412(10)	7265(12)	3335(13)	98(6)		C(77)	4949(5)	6451(4)	1287(5)	44(4)
C(50)	1472(9)	7181(9)	6813(10)	64(4)		C(78)	4692(4)	5882(4)	1381(5)	40(4)
C(51)	1233(11)	7522(9)	6039(13)	67(4)		C(79)	4955(5)	5525(3)	2067(5)	32(3)
C(52)	1688(11)	7890(8)	5574(16)	78(4)		C(80)	5627(5)	5585(4)	7111(5)	27(3)
C(53)	1675(11)	7904(10)	4621(17)	90(5)		C(81)	6032(5)	6091(5)	7243(7)	63(5)
C(54)	1195(9)	7549(10)	4154(13)	71(4)		C(82)	5869(6)	6465(4)	7956(8)	77(6)
C(12)	3623(8)	5458(9)	5904(10)	46(3)		C(83)	5301(6)	6333(4)	8537(6)	63(5)
C(11)	3149(9)	5083(7)	5408(13)	56(4)		C(84)	4897(5)	5826(5)	8406(6)	54(4)
C(10)	3110(9)	5129(9)	4433(14)	65(4)		C(85)	5060(5)	5452(4)	7693(6)	47(4)
C(9)	3588(8)	5469(10)	3997(9)	46(4)		C(86)	5531(6)	4398(4)	6523(7)	39(4)
C(8)	3344(8)	5838(9)	3244(10)	60(4)		C(87)	5942(5)	4141(5)	7201(7)	70(5)
C(13)	3370(10)	5731(10)	6723(10)	72(5)		C(88)	5810(6)	3565(5)	7458(7)	85(6)
C(30)	2621(11)	5661(10)	6999(11)	85(5)		C(89)	5266(7)	3246(4)	7035(8)	70(5)
C(29)	2152(12)	5293(9)	6482(15)	89(5)		C(90)	4855(6)	3503(4)	6356(7)	75(5)
C(28)	2379(10)	5050(8)	5696(16)	76(4)		C(91)	4987(5)	4079(5)	6100(6)	52(4)
C(27)	1945(7)	5010(6)	4914(22)	93(4)		C(92)	2613(20)	1971(14)	5388(34)	201(25)
C(26)	2388(11)	5064(10)	4151(17)	94(5)		C(93)	1912(17)	1865(9)	5007(39)	150(12)
C(25)	2132(10)	5390(11)	3414(14)	96(5)		C(94)	1412(12)	2320(9)	5165(18)	97(8)
C(24)	2635(10)	5784(11)	2942(11)	90(5)		C(95)	1476(12)	2822(14)	4458(13)	107(10)
C(23)	2234(9)	6288(11)	2683(11)	102(5)		C(96)	1869(17)	3349(9)	4930(42)	204(24)
C(31)	2256(10)	6195(10)	7338(10)	83(4)		C(97)	2686(24)	3353(10)	5243(16)	159(14)
C(48)	1518(11)	6112(10)	7051(12)	81(5)		C(98)	3171(13)	2838(15)	4716(17)	112(10)
C(47)	1429(11)	5573(10)	6536(15)	91(5)		C(99)	3102(13)	2270(15)	5086(31)	150(14)

Table 4. Atomic coordinates (×10⁴) and equivalent isotropic temperature factors (×10⁴) in structure of $1 \cdot C_8 H_{14}$

stantial thermal vibrations of the cyclooctene solvate molecule, we failed to determine unambiguously the position of the double bond in this molecule; the hydrogen atoms in the solvate ligand are not localized. Correction for absorption (μ (Mo-K α) = 23.6 cm⁻¹) was introduced using DIFABS Program.¹⁵ The absolute structure was determined by refinement of the Flack

parameter (x = 0.00(2));¹⁶ configuration of chiral centers C(62) and C(63) coincided with the well known configuration of (S,S)-DIOP ligand (see Ref. 13, for example). The final scattering factors: $R_1 = 0.0649$ for 3726 reflections with $I > 2\sigma(I)$; $wR_2 = 0.1295$ for all reflections measured. Coordinates of nonhydrogen atoms are presented in Table 4. This work was performed within the framework of Russian Program "Fullerenes and Atomic Clusters", and was financially supported by the Russian Foundation for Basic Research (Projects Nos. 93-03-18725 and 94-03-08338), Project 079/B-19, and the International Science Foundation (Grants MNR 300 and MO4 300).

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