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Synthesis, Crystal, and Molecular Structure of the Palladium(0)–Fullerene Derivative (η^2-C_{60})Pd(PPh_3)$_2$

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Summary: Buckminsterfullerene, C_{60}, reacts with Pd(PPh_3)$_4$ in solution to give in high yield a palladium(0) complex, (C_{60})Pd(PPh_3)$_2$, in which fullerene is ligated in a η^2 fashion. The molecular structure of this compound has been established by the X-ray study of a single crystal.

After the discovery of the existence of polyhedral carbon clusters, fullerenes,[1] and the development of preparative methods for their production,[2] the chemical properties of these uncommon molecules began to be investigated. Hawkins et al.[3] first demonstrated the ability of a double bond in C_{60} to react selectively as an isolated moiety. Shortly afterwards it was shown that the same bond could serve as a ligand site in η^2 complexes of platinum(0)[4] and iridium(I).[5] As is known, low-valent transition-metal complexes have been recognized as carbenoid-like reagents.[6] However, an important difference has been observed in the reactivity of fullerenes vs the reagents mentioned above or genuine carbenes. The latter have afforded "fulleroids", wherein the integrity of the fullerene core is not completely preserved.[7] This provokes an interest in the detailed structure of other products of carbenoid-type reactions with fullerenes.

In a continuation of our studies in the fullerene area,[8] we report the synthesis and molecular structure of (η^2-C_{60})bis(triphenylphosphine)palladium (I). This compound is one of the palladium–fullerene derivatives[9] that can relate, inter alia, to the active sites in the catalysts of the Pd/C type. The structure of I, established by X-ray single-crystal analysis, is compared to that of the platinum analogue previously described by Fagan, Calabrese, and Malone.[4a]

When C_{60}[10] (36.2 mg, 0.05 mmol) and Pd(PPh_3)$_4$ (59.2 mg, 0.051 mmol) were dissolved in 5 mL of oxygen-free toluene, a chlorophyll-green solution was formed.[12] This solution was diluted with hexane (55 mL) and left to crystallize. After 5 days the crystals which formed were isolated, washed with hexane, and dried in a stream of argon. A yield of 60.6 mg (89%) of I was obtained as nearly black crystals with shiny faces that were brown in transmitting light: dec 278–282 °C.[13]

The molecular structure of unsolvated I was unambiguously established by a single-crystal X-ray study[15] (Figure 1). Within experimental accuracy, it essentially coincides with the previously determined structure of (Ph_3P)$_2$Pt(η^2-C_{60}) (II) as a crystal of its mono-THF solvate[4a] (cf. values in brackets). The Pd atom coordination is square planar (Figure 2), the Pd, P_1, P_2, C_1, and C_2 atoms being coplanar within 0.06 Å [0.02 Å]. Due to coordination by the Pd(PPh_3)$_2$ unit the fullerene core is slightly distorted, similar to what was found for II.

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(2) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990,** *347,* 354.

(3) Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Loren, S. D.; Hollander, F. J. *Science* **1991,** *252,* 312.

(4) (a) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Science* **1991,** *252,* 1160. (b) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Acc. Chem. Res.* **1992,** *25,* 134.

(5) (a) Balch, A. L.; Catalano, V. J.; Lee, J. W.; Olmstead, M. M.; Parkin, S. R. *J. Am. Chem. Soc.* **1991,** *113,* 8953. (b) Koefod, R. S.; Hudgens, M. F.; Shapley, J. R. *J. Am. Chem. Soc.* **1991,** *113,* 8957. This is the first X-ray structure for a C_{70}–metal complex.

(6) Sokolov, V. I.; Reutov, O. A. *Coord. Chem. Rev.* **1978,** *27,* 89.

(7) Wudl, F. *Acc. Chem. Res.* **1992,** *25,* 134.

(8) (a) Tumanski, B. L.; Bashilov, V. V.; Bubnov, N. N.; Solodovnikov, S. P.; Sokolov, V. I. *Izv. Akad. Nauk, Ser. Khim.* **1992,** 1938 and references therein. (b) For an analysis of the various kinds of ligation of buckminsterfullerene and occurrence of chirality in some exohedral metal complexes, see: Sokolov, V. I. *Dokl. Akad. Nauk* **1992,** *326,* 647.

(9) (a) Workers at E. I. du Pont de Nemours and Co. have reported the existence and Raman spectrum of (Ph_3P)$_2$Pd(η^2-C_{60}), but no details of preparation and characterization were provided: Chase, B.; Fagan, P. J. *J. Am. Chem. Soc.* **1992,** *114,* 2252. Also electrochemical studies of (Ph_3P)$_2$Pt(η^2-C_{60}), (Et_3P)$_2$M(η^2-C_{60}), [(Et_3P)$_2$M]$_6$(C_{60}) (M = Ni, Pd, Pt), and [(Et_3P)$_2$Pt]$_n$(C_{60})(n = 2–4) have been reported (Lerke, S. A.; Parkinson, B. A.; Evans, D. H.; Fagan, P. J. *J. Am. Chem. Soc.* **1992,** *114,* 7807), and the X-ray crystal structures of (Et_3P)$_2$Pt(η^2-C_{60}) and (Et_3P)$_2$Pd(η^2-C_{60}) have been compared.[4b] See also: Fagan, P. J.; Calabrese, J. C.; Malone, B. In *Fullerenes*; Hammond, G. S., Kuck, V. J., Eds.; ACS Symposium Series 481; American Chemical Society: Washington, DC, 1992; pp 177–186. (b) The oligomeric compounds $C_{60}Pd_x$ have been independently prepared by two groups starting from $Pd_2(dba)_3$: Nagashima, H.; Nakaoka, A.; Saito, Y.; Kato, M.; Kawanishi, T. *J. Chem. Soc., Chem. Commun.* **1992,** 377. Sokolov, V. I., unpublished results.

(10) Purified by column chromatography on Al_2O_3 with hexane–toluene as eluent, as previously described.[11]

(11) Koch, A. S.; Khemani, K. C.; Wudl, F. *J. Org. Chem.* **1991,** *56,* 4543.

(12) After 90 min the ^{31}P NMR spectrum of this solution disclosed the presence of free PPh_3 (δ −4, 8 ppm) and of I having one signal of ligated PPh_3 (δ 25.4 ppm), 1% H_3PO_4 being used as external standard.[14] No exchange between coordinated and free PPh_3 was observed at room temperature. However, both PPh_3 ligands in I have been replaced by a (+)-DIOP ligand to afford the first, to our knowledge, optically active organometallic fullerene derivative, [(+)-DIOP]Pd(η^2-C_{60}) (Bashilov, V. V.; Sokolov, V. I., submitted for publication to *Izv. Akad. Nauk*).

(13) Anal. Calcd for (C_{60})Pd[P(C_6H_5)$_3$]$_2$ (≡$C_{96}H_{30}P_2Pd$): C, 85.31; H, 2.24; P, 4.58. Found: C, 84.78; H, 2.20; P, 4.69. Absorption spectra of the single crystal used for the X-ray study and of the bulk of crystals have been identical, containing a strong characteristic band at 439 mm, close to that found for (η^2-C_{60})–Ir.[5b]

(14) For comparison, δ_P is 27.0 ppm in (PPh_3)$_2$Pt(η^2-C_{60})[4a] and 27.2 ppm in (ma)Pd(PPh_3)$_2$ (ma = maleic anhydride) (this work).

(15) Crystal data for I: $C_{96}H_{30}P_2Pd$, M_r = 1351.5, monoclinic, space group $P2_1/c$, a = 16.280(6) Å, b = 35.121(11) Å, c = 10.248(4) Å, β = 107.54(2)°, V = 5587(3) Å^3, ρ_{calcd} = 1.607 g/cm^3 for Z = 4. Intensities of 4119 independent reflections and cell parameters were measured at 193 K with a Syntex $P2_1$ automated diffractometer using Mo Kα radiation (λ = 0.710 69 Å, graphite monochromator, θ–2θ scan, $\theta \leq 23°$). The structure was solved by the heavy-atom technique and refined by blocked full-matrix least squares. The Pd, P_1, and P_2 atoms were refined in the anisotropic and the carbon atoms in the isotropic approximation. The hydrogen atoms were placed in calculated positions which were recalculated after each least-squares refinement cycle; the H atom common isotropic temperature factor was refined (its final value was 0.083 Å^2). The refinement of 413 variables against 2832 reflections with $I > 2\sigma$ converged to R = 0.100 and R_w = 0.094. All calculations were carried out with an IBM PC AT computer using the SHELXTL PC program package.[16]

(16) Robinson, W.; Sheldrick, G. M. SHELX. In *Crystallographic Computing-Techniques and New Technologies*; Isaacs, N. W., Taylor, M. R., Eds.; Oxford University Press: Oxford, England, 1988; p 366.

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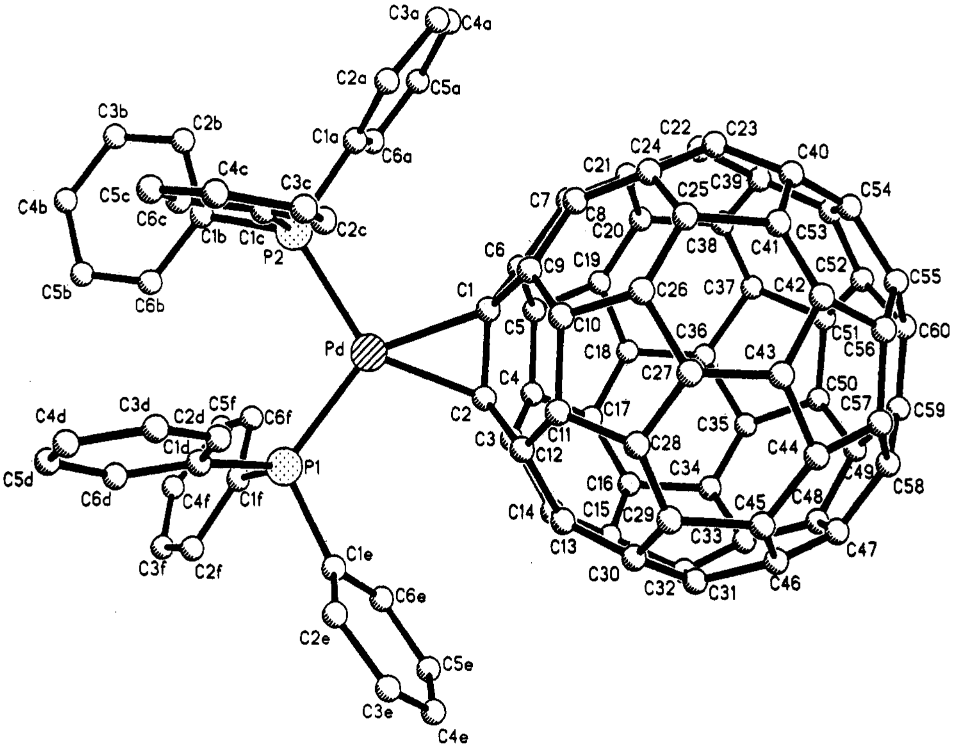

Figure 1. Molecular structure of (η^2-C_{60})$Pd(PPh_3)_2$ (I).

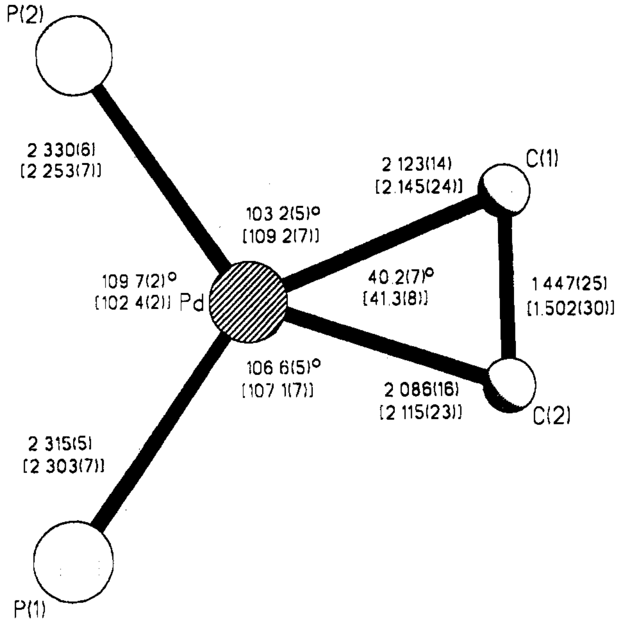

Figure 2. The Pd coordination sphere in I (distances are in angstroms and angles in degrees; comparable values for the platinum analogue[4a] are given in brackets).

The five- and six-membered rings of the C_{60} core are planar within 0.04 Å [0.03–0.05 Å], excluding the rings containing C_1 and C_2. The last four rings deviate from planarity up to 0.05 Å. The average C–C bond length at the junctions of the five- and six-membered rings [(5,6)-bond] is 1.45(3) Å [1.445(30) Å] and that at the junctions of two six-membered rings [(6,6)-bond] is 1.39(3) Å [1.388(30) Å], except for the somewhat elongated bonds involving the C_1 and C_2 atoms directly linked to palladium: C_1–C_2 = 1.45(3), C_1–C_6 = 1.51(2), C_1–C_9 = 1.43(2), C_2–C_3 = 1.52(3), C_2–C_{12} = 1.51(2) Å.

The elongation of the C_1–C_2 bond in I is expectedly less than in its platinum analogue (1.447 vs 1.502 Å compared with 1.39 Å for an unperturbed (6,6)-bond). This fact probably reflects less strong (η^2-C_{60})–metal bonding for palladium as compared to platinum.

The distances from the centroid of the C_{60} core to its carbon atoms are in the range 3.48(3)–3.60(3) Å [3.48–3.60 Å] with an average of 3.55(3) Å [3.53 Å], except for the distances to the C_1 and C_2 atoms (3.69(3) [3.68] and 3.68(3) Å [3.73 Å], respectively). Some deformation of the C_{60} core in the neighborhood of the C_1 and C_2 atoms relative to its natural curvature is evident from a comparison of the angles between the C_1–C_2 line and the C_1–C_6–C_9 and C_2–C_3–C_{12} planes (40(2) [44(2)] and 38(2)° [38(2)°], respectively) and the angles between the opposite C_{59}–C_{60} line and the C_{52}–C_{55}–C_{60} and C_{49}–C_{58}–C_{59} planes (33(2) [31(2)] and 29(2)° [30(2)°], respectively).

Intermolecular distances in the crystal of I are unexceptional and correspond to van der Waals interactions. The packing motive corresponds to somewhat distorted hexagonal close packing with the molecular coordination number equal to 12.

Supplementary Material Available: Tables giving crystal data and data collection and refinement details, positional and thermal parameters, and bond lengths and angles for (η^2-C_{60})-$Pd(PPh_3)_2$ (12 pages). Ordering information is given on any current masthead page.

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