carbonyl ligand was added to Mn(1), and the Mn(1)···O(1) distance was lengthened to a nonbonding value, 3.278 (3) Å. The ketonic C(3)–O(1) distance is slightly shorter than that in **3**, 1.282 (6) Å, and the C=O absorption frequency is increased to 1553 cm^{-1}.[16] The CO addition to **2** is fully reversible, and when solutions of **4** were purged with nitrogen for 24 h at 25 °C, compound **2** was regenerated in essentially a quantitative yield.[18] The results of this study are summarized in Scheme I. Studies of the reactivity of the ketonic grouping are in progress.

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Supplementary Material Available: Tables of crystal data, positional parameters, bond distances and angles, and anisotropic thermal parameters for **3** and **4** (18 pages); tables of structure factors for **3** and **4** (20 pages). Ordering information is given on any current masthead page.

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(18) A solution of 10.0 mg of **4** in 50 mL of hexane was purged with nitrogen at 25 °C for 24 h. **2**, 9.0 mg, 96% yield, was isolated after workup by TLC.

A Multiply-Substituted Buckminsterfullerene (C_{60}) with an Octahedral Array of Platinum Atoms

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Fundamental questions concerning the chemistry of the recently isolated carbon clusters (C_{60}, C_{70}, C_{84}, etc.)[1] include how many substituents can be attached and what, if any, geometrical preferences or electronic directing effects guide the substitution chemistry of these molecules. Several structurally-characterized derivatives of C_{60} have been reported, including $(t\text{-}BuC_5H_4N)_2OsO_4C_{60}$[2] and $[(C_6H_5)_3P]_2Pt(\eta^2\text{-}C_{60})$.[3] In these cases only two of the C_{60} carbon atoms are derivatized. There is evidence that multiply-substituted compounds exist, but these usually occur as mixtures and have not been structurally defined.[2,4] Here we describe the characterization of the hexa-substituted platinum derivative $\{[(C_2H_5)_3P]_2Pt\}_6C_{60}$. This is the first example of a reaction that selectively forms a *single isomer* of a highly-substituted C_{60} derivative in high yield. The phosphorus, platinum, and C_{60} atoms have nearly ideal and rarely observed T_h point group symmetry.

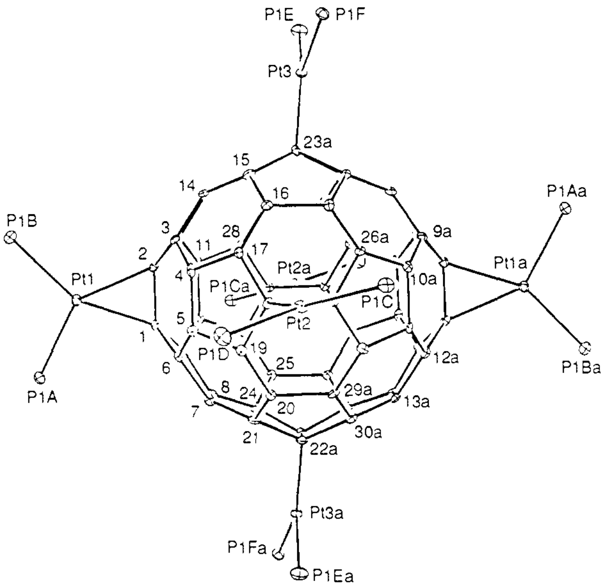

Figure 1. Diagram of one of the two independent molecules of $\{[(C_2H_5)_3P]_2Pt\}_6C_{60}$. For clarity, phosphine ethyl groups are not shown. As in $[(C_6H_5)_3P]_2Pt(\eta^2\text{-}C_{60})$,[3] carbons attached to Pt are pulled out from the original C_{60} frame with their average distance to the C_{60} centroid being 3.687 (±0.009) Å (range 3.663–3.697 Å). Under idealized T_h symmetry, there are two other unique symmetry related sets of carbon atoms in the C_{60} frame, i.e. those two bonds from Pt and those three bonds from Pt (average distance to centroid = 3.538 (±0.013) and 3.526 (±0.010) Å, respectively). The twists of the P–Pt–P planes relative to the C–Pt–C planes are 13.2° (Pt1), 15.8° (Pt2), and 9.6° (Pt3). (Values of 12.5°, 2.6°, and 17.0° are found for the other molecule.) The Pt atoms bend away to different extents from the normal to the C_{60} surface. For example, the Pt3–midpoint (C22,C23a)–centroid (C_{60}) angle is 175.1° whereas for Pt1 and Pt2 these angles are 177.8° and 179.4°, respectively (values of 173.8, 178.5, and 178.8° are observed for the other molecule). Bond distances and angles about the Pt atoms are as follows: average Pt–C (bonds G, Figure 2) = 2.115 (±0.017) Å, range 2.084 (8)–2.137 (9) Å; average Pt–P (bonds F, Figure 2) = 2.261 (±0.007) Å, range 2.251 (3)–2.272 (3) Å; average P–Pt–P = 111.8 (±1.2)°, range 110.5 (1)–114.0 (1)°; average C–Pt–C = 41.4 (±0.2)°, range 41.3 (3)°–41.8 (3)°; average P–Pt–C (smaller angle) = 103.7 (±3.6)°, range 98.0 (3)°–110.9 (2)°.

Addition of 0.724 g (1.08 mmol) of $[(C_2H_5)_3P]_4Pt$[5] to a solution of 75 mg (0.10 mmol) of C_{60} in 5 mL of benzene produced a dark orange-brown solution. After 10 min, solvent and released triethylphosphine were removed in vacuo. Benzene was added until the compound all dissolved, and the solution was filtered. After removal of solvent, hexane (ca. 6–10 mL) was added to the flask; the air-sensitive, orange, crystalline solid was collected by filtration, washed three times with 1–2-mL portions of hexane, and dried in vacuo to obtain an 88% yield of $\{[(C_2H_5)_3P]_2Pt\}_6C_{60}$.[6]

The simplicity of the ^{31}P NMR spectrum (one resonance) and the ^{13}C NMR spectrum (three resonances for C_{60} in a 2:2:1 ratio) as well as the observed couplings among the spin $^1/_2$ nuclei allowed unambiguous assignment of the structure.[6] The molecule has a C_{60} core bearing six octahedrally-disposed $[(C_2H_5)_3P]_2Pt$ groups

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(6) Anal. Calcd for $C_{132}H_{180}P_{12}Pt_6$: C, 47.91; H, 5.48. Found: C, 47.13; H, 5.18. ^{31}P NMR (121.7 MHz, external standard H_3PO_4, C_6D_6) δ 16.6 (s, $J_{P\text{-}Pt} = 3.777$ Hz). ^1H NMR (C_6D_6, 300 MHz): δ 1.10 (multiplet, CH_3) and 1.81 (multiplet, CH_2). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.6 MHz): δ 9.0 (singlet with ^{195}Pt satellites, $J_{C\text{-}Pt} = 12.0$ Hz, PCH_2CH_3), 20.6 (multiplet, AXX′ spin system with overlapping ^{195}Pt satellites, $J^2_{Pt\text{-}C} \approx 38$ Hz, $J_{P\text{-}C}(av) = 12$ Hz, PCH_2CH_3), 79.2 (multiplet, AXX′ spin system with ^{195}Pt satellites, $J_{Pt\text{-}C} \approx 203$ Hz, $J^2_{P\text{-}C}(av) = 17$ Hz, Pt–C), 142.1 (singlet, Pt–C–C–C), 153.8 (singlet with ^{195}Pt satellites, $J^2_{Pt\text{-}C} = 26$ Hz, Pt–C–C–C).

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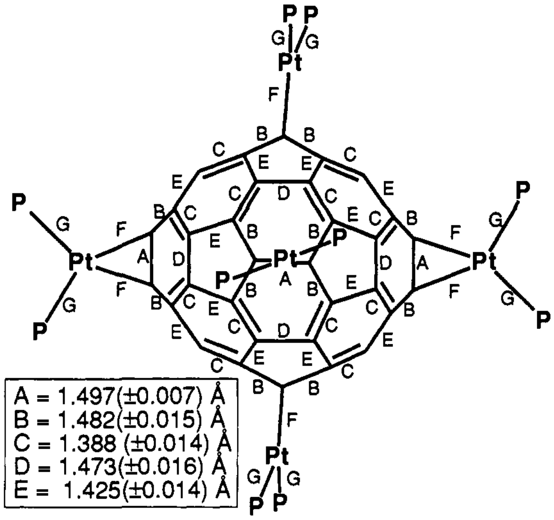

Figure 2. With T_h symmetry there are five unique symmetry-related sets of C–C bonds in the C_{60} framework (A, B, C, D, E). The average values of these bonds are shown and were determined using distances obtained for both independent molecules. These bonds had the following ranges of values (Å): A, 1.490 (11)–1.508 (12); B, 1.446 (13)–1.511 (13); C, 1.366 (13)–1.427 (11); D, 1.453 (12)–1.503 (11); E, 1.392 (13)–1.455 (11). There are eight unique angles subtended by bonds A, B, C, D, and E (deg): AB = 117.5 (±0.9), range 115.3 (8)–119.1 (7); BB = 104.5 (±0.9), range 102.9 (8)–106.0 (8); BC = 122.1 (±0.9), range 119.1 (9)–123.4 (9); BE = 109.6 (±0.8), range 107.8 (9)–110.8 (8); CD = 120.2 (±0.8), range 118.2 (8)–120.9 (8); CE (attached to B) = 119.2 (±0.8), range 117.7 (9)–121.0 (10); CE (attached to D) = 120.7 (±0.8), range 119.1 (9)–122.1 (8); DE = 107.8 (±0.7), range 106.5 (8)–109.1 (9).

(each bound in a dihapto manner) and having overall T_h point group symmetry (ignoring the ethyl groups). X-ray crystallographic results on $\{[(C_2H_5)_3P]_2Pt\}_6C_{60}$ confirmed this.[7] The accuracy of this structure[7] is much improved compared to previous C_{60} structures.[2,3] The asymmetric unit consists of two half-molecules on different inversion centers that generate two independent molecules (Figure 1). Both molecules are essentially identical with differences in the ethyl group orientations and in the twisting and bending of the $[(C_2H_5)_3P]_2Pt$ groups about the Pt–alkene bonds; because of this twisting, each molecular core deviates slightly from perfect T_h point group symmetry. Relative to free C_{60}, coordination of Pt lengthens the attached and adjacent C–C bonds (bonds A and B in Figure 2) which approach values of typical C–C single bonds. Bonds D are also lengthened, and we propose these are forced to stretch owing to both the lengthening of the A bonds which are parallel to it and the lengthening of the B bonds which could also exert a net strain parallel to D. As in C_{60} itself, bond-length alternation (for which there is evidence experimentally and theoretically)[2,3,8] persists in the eight six-membered rings composed of bonds C and E (planar to within ≤0.019 Å). Bonds C (exo to the five-membered rings) are shortest leading to the favored resonance form depicted in Figure 2. For comparison, in $[(C_6H_5)_3P]_2Pt(\eta^2\text{-}C_{60})$ the two distinct bond types averaged to 1.39 (±0.04) and 1.44 (±0.04) Å.[3]

The octahedral array of platinum atoms in this structure is readily understood. All evidence to date suggests that for metal complexation the bonds between two fused six-membered rings in C_{60} are the most reactive, these bonds being shorter and having the most double bond character.[2,3,8] There are a total of 30 such six–six ring fusions in C_{60}. Binding of a $[(C_2H_5)_3P]_2Pt$ group at one of these bonds sterically protects four of the surrounding six–six ring junctions. Thus, placing six $[(C_2H_5)_3P]_2Pt$ groups on C_{60} essentially blocks all of the remaining 24 six–six ring bonds to further attack by platinum.

In conclusion, C_{60} can be substituted multiple times by electron-rich reagents, and a total of at least 12 carbon atoms of the C_{60} framework can participate in bonding. These results suggest that the geometry of substitution about C_{60} is controlled in this case by the special electronic structure of C_{60} (with localization of double bonds between the six–six ring fusions) and the size of the $[(C_2H_5)_3P]_2Pt$ groups. We are investigating the geometry of the less-substituted C_{60} derivatives which are the intermediates leading up to this novel compound.

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Supplementary Material Available: Details of X-ray crystallographic analysis and tables of atomic coordinates, bond distances and angles, and thermal parameters (14 pages); listings of observed and calculated structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

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(7) Crystal data: $C_{132}H_{180}P_{12}Pt_6$; dark red parallelopiped, ≈0.12 × 0.26 × 0.39 mm; triclinic, $P\bar{1}$ (No. 2); $a = 14.841$ (3) Å, $b = 15.419$ (1) Å, $c = 30.882$ (2) Å, $\alpha = 95.25$ (1)°, $\beta = 98.74$ (1)°, $\gamma = 112.20$ (1)° (from 25 reflections); $Z = 2$; $V = 6380.9$ Å^3; $T = -70$ °C; FW = 3309.12; $D_c = 1.722$ g/cm^3; final $R = 0.043$, $R_w = 0.033$. For bond distances, numbers in parentheses are the estimated standard deviations. An error which contains "±" notation is the standard deviation of the calculated average of a number of bond measurements.

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Amine Photoredox Reactions: A Photoinduced "Methylene Shuttle" Initiated via Two-Electron Oxidation of a Tertiary Amine by Anthraquinone

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The photooxidation of tertiary amines by excited electron acceptors is generally indicated to occur by a sequence of electron-transfer quenching (SET), proton transfer, and electron transfer.[1-10] Although examples of rather clean reactivity to afford net two-electron products such as enamines or iminium ions are known,[4-12] these reactions often give complex mixtures and evidence for a variety of radical intermediates. The formation of oxidation products (enamines and/or secondary amines) which are themselves good donors frequently frustrates utilization of this reaction for preparative purposes. In the present paper we report an example of a tertiary amine photooxidation in which selective net two-electron oxidation of the amine leads to novel products in excellent yield and efficiency via self-condensation of highly reactive two-electron redox intermediates.

Previous investigations have established that irradiation of 9,10-anthraquinone (AQ) in the presence of potential reductants

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