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The Chemical Nature of Buckminsterfullerene (C_{60}) and the Characterization of a Platinum Derivative

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Little is known about the chemical nature of the recently isolated carbon clusters (C_{60}, C_{70}, C_{84}, and so forth). One potential application of these materials is as highly dispersed supports for metal catalysts, and therefore the question of how metal atoms bind to C_{60} is of interest. Reaction of C_{60} with organometallic ruthenium and platinum reagents has shown that metals can be attached directly to the carbon framework. The native geometry of C_{60} is almost ideally constructed for dihapto-bonding to a transition metal, and an x-ray diffraction analysis of the platinum complex $[(C_6H_5)_3P]_2Pt(\eta^2\text{-}C_{60})\cdot C_4H_8O$ revealed a structure similar to that known for $[(C_6H_5)_3P]_2Pt(\eta^2\text{-ethylene})$. The reactivity of C_{60} is not like that of relatively electron-rich planar aromatic molecules such as benzene. The carbon-carbon double bonds of C_{60} react like those of very electron-deficient arenes and alkenes.

THE PROPERTIES OF THE RECENTLY isolated carbon clusters (*1*) have attracted considerable attention with regard to theoretical and physical properties (*2–4*), but there are few reports concerning the chemistry of these species (*3–4*). One well-defined derivative has been reported, namely, the osmium tetroxide adduct structurally characterized by Hawkins *et al.* (*3*). We investigated organometallic derivatives of C_{60} to ascertain its chemical nature and report the reactions of C_{60} with the reagents $[(C_6H_5)_3P]_2Pt(\eta^2\text{-}C_2H_4)$ (*5*) and $[Cp^*Ru(CH_3CN)_3]^+O_3SCF_3^-$ [$Cp^* = \eta^5\text{-}C_5(CH_3)_5$] (*6*). Zero-valent Pt compounds are well known to react with electron-poor alkenes and arenes bonding in a dihapto-fashion, but are unreactive toward relatively electron-rich aromatic molecules such as benzene (*5*). In contrast, when $[Cp^*Ru(CH_3CN)_3]^+\text{-}O_3SCF_3^-$ is reacted with relatively electron-rich planar arenes, the three coordinated acetonitriles are displaced resulting in strong, hexahapto-binding of ruthenium to the six-membered ring of the arene (*6*).

Addition of $[(C_6H_5)_3P]_2Pt(\eta^2\text{-}C_2H_4)$ (31 mg) to C_{60} (30 mg) in toluene (2 ml) under a dinitrogen atmosphere resulted in formation of an emerald-green solution from which black microcrystals precipitated over the course of 2 hours. This precipitate was collected by filtration, washed twice with 2-ml portions of toluene and then with 10 ml of hexane, and dried by pulling N_2 through the filter cake. It was recrystallized by first dissolving in tetrahydrofuran (THF), filtering, concentrating, and precipitating with hexane. The isolated yield of this compound was 85% based on the formulation $[(C_6H_5)_3P]_2Pt(\eta^2\text{-}C_{60})$ (THF of crystallization is removed upon drying under vacuum). Elemental analytical data supported this formulation (*7*). The ^{31}P nuclear magnetic resonance (NMR) spectrum (121.7 MHz, external standard H_3PO_4) of this compound in THF-d_8 displayed a singlet at δ 27.0 ppm with satellites due to coupling of ^{31}P to the spin-1/2 isotope ^{195}Pt (33.8 % abundance) ($J_{P\text{-}Pt}$ = 3936 Hz). For comparison, the shift observed for $[(C_6H_5)_3P]_2Pt(\eta^2\text{-}C_2H_4)$ is δ 34.8 with a coupling constant $J_{P\text{-}Pt}$ = 3738 Hz. Since these coupling constants and chemical shifts were similar, it suggested that the coordination sphere about Pt was nearly identical in both the ethylene and C_{60} complexes.

In order to substantiate this proposal, we performed a single-crystal x-ray structural analysis of the complex $[(C_6H_5)_3P]_2Pt(\eta^2\text{-}C_{60})\cdot C_4H_8O$. Small multiple needles were grown by slow evaporation from THF. A thin needle was cut in half to obtain a weakly diffracting single crystal from which x-ray data were successfully collected and analyzed (*8*). Accuracy of the structure was limited because of the small size of the crystal and disorder associated with THF molecules contained in the lattice (Fig. 1). The bonding parameters within the C_{60} framework agree closely with those obtained for the osmium tetroxide derivative of Hawkins *et al.* (*3*). In this case, Pt serves to anchor the molecule and reduce disorder problems. Rotation of alkenes about the platinum-alkene bond has a substantial energy barrier (*9*). The bis(triphenylphosphine)platinum moiety bonds to two carbon atoms of the C_{60} molecule at the junction of two fused six-membered rings rather than at the junction of the five- and six-membered rings. The bonding pattern is reminiscent of other structurally characterized transition metal–alkene complexes (*9, 10*). Bond distances and bond angles about Pt are shown in Fig. 2. The metrical data agree with those previously established for $[(C_6H_5)_3P]_2Pt(\eta^2\text{-}C_2H_4)$ (*10*).

It is well known that upon coordination of a transition metal such as Pt to an alkene, the four groups attached to the carbon-carbon double bond splay back away from the metal center (*11*). One measure of this distortion is to determine the degree to which two groups attached to one end of a double bond bend back relative to remaining planar. This can be defined as the angle between the vector described by the two doubly bonded carbons and the plane defined by one of these carbons and the two groups attached to it. Typical angles in Pt complexes with unconstrained carbon-substituted alkenes range from approximately 22° to 35° (*12*). In this regard, the natural curvature of C_{60} should permit bonding to a

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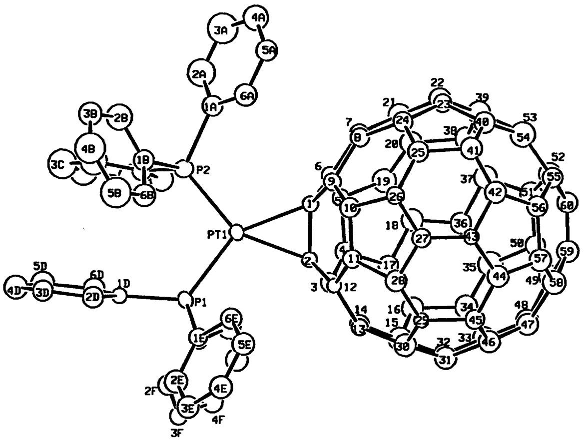

Fig. 1. View of the $[(C_6H_5)_3P]_2Pt(\eta^2\text{-}C_{60})$ molecule as revealed by the x-ray crystallographic analysis of $[(C_6H_5)_3P]_2Pt(\eta^2\text{-}C_{60})\cdot C_4H_8O$. The accuracy of the C–C bonds is limited to ~0.03 Å. The C_{60} distances range from 1.318(29) to 1.534(39) Å. Each of the five-membered and six-membered rings of the C_{60} fragment are planar to within 0.03 to 0.05 Å except for those containing C1 and C2. These atoms are pulled out from the rest of the C_{60} framework. The distances from the centroid of the C_{60} to all of the carbon atoms except C1 and C2 range from 3.48 to 3.60 Å with the average being 3.53 Å; the centroid-C1 and centroid-C2 distances are 3.68 and 3.73 Å, respectively. For the bonds not directly associated with platinum binding (that is, excluding carbon bonds, C1–C2, C1–C6, C1–C9, C2–C3, and C2–C12), the average C–C bond length at the junctions of two six-membered rings was 1.388(30) Å. At the junction of fused five- and six-membered rings the average was 1.445(30) Å. These average values for the two types of bonds in C_{60} are similar to those found in the osmium tetroxide derivative (*3*).

low-valent transition metal with relatively little deformation of the C_{60} skeleton. For example, examining the geometry about the bond C59–C60 directly opposite where Pt is coordinated, the planes defined by C60–C52–C55 and C59–C49–C58 are tilted away from the C59–C60 axis by 31(2)° and 30(2)°, respectively (numbers in parentheses are the standard error in the last digit or digits). The corresponding angles between the C1–C2 axis (attached to Pt) and the planes described by C2–C3–C12 and C1–C6–C9 are 44(2)° and 38(2)°, respectively.

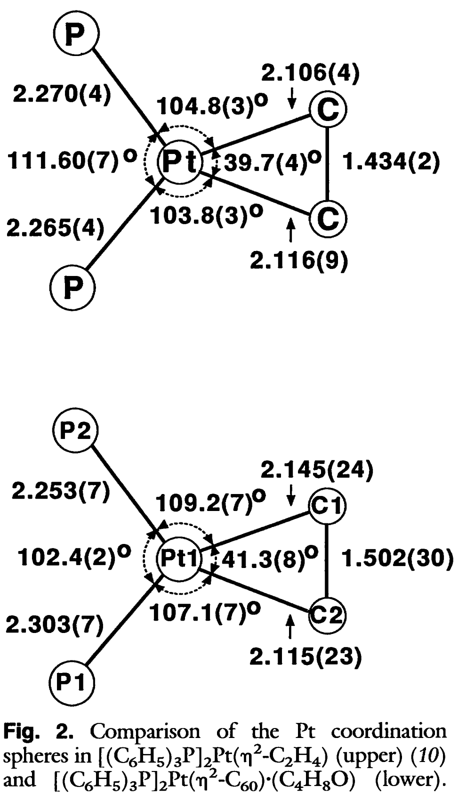

Fig. 2. Comparison of the Pt coordination spheres in $[(C_6H_5)_3P]_2Pt(\eta^2\text{-}C_2H_4)$ (upper) (*10*) and $[(C_6H_5)_3P]_2Pt(\eta^2\text{-}C_{60})\cdot(C_4H_8O)$ (lower). The atoms P1, P2, Pt1, C1, and C2 are coplanar to within 0.02 Å. The phosphine ligands in the C_{60} complex are bent back more than in the ethylene complex, which may reflect the greater steric bulk of C_{60} versus ethylene.

Reaction of C_{60} with a tenfold excess of the reagent $[Cp^*Ru(CH_3CN)_3]^+O_3SCF_3^-$ in CH_2Cl_2 at 25°C for a period of 5 days yielded a brown precipitate, which preliminary data suggests has the formulation $\{[Cp^*Ru(CH_3CN)_2]_x(C_{60})\}^{x+}(O_3SCF_3^-)_x$ (*13*). Although we were not able to obtain an x-ray crystal structure of this complex, the fact that the metal retains two acetonitrile molecules of coordination leads to the conclusion that each ruthenium bonds to just two carbon atoms of the C_{60} cluster. Whether or not this is the case, this observed chemistry is highly unusual if C_{60} were reacting chemically like a typical planar electron-rich aromatic molecule such as benzene.

Although C_{60} may be perfectly suited for bonding in a dihapto-fashion, this is not so for hexahapto-bonding (and to some extent tetrahapto-bonding), since from above the "plane" of a six-membered ring in the molecule, the carbon *p*-orbitals are tilted away from the center of the ring. This tilt may weaken the overlap of the highest occupied and lowest unoccupied molecular orbitals of C_{60} with the ruthenium-centered unfilled and filled *d*-orbitals, respectively. In this case, acetonitrile is apparently a strong enough donor to compete with any such interaction. This is not to say that hexahaptobonding is not possible with a weaker donor than acetonitrile, or with another metal ligand combination.

We note that C_{60} is *not* chemically inert (*14*) but reacts readily with electron-rich reagents. Its double-bond reactivity resembles that of very electron-poor arenes and alkenes. It follows that much of the reaction chemistry of these types of carbon-carbon double bonds might be successfully applied to C_{60}.

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13. ^{1}H NMR (CD_3NO_2; 300 MHz): δ 1.82 (broadened singlet, 15 H, Cp*) and 2.62 (broadened singlet, 6 H, CH_3CN). $^{13}C\{^1H\}$ NMR (CD_3NO_2, 75.6 MHz): δ 4.6 (s, CH_3CN); 9.8 (s, $(CH_3)_5C_5$); 96.4 (s, $(CH_3)_5C_5$); 122.6 (q, $J_{C\text{-}F}$ = 323 Hz, CF_3SO_3); 130.0 (s, CH_3CN); and 160 to 138 (broad asymmetric envelope, C_{60}). (The broadening of the resonances and the decrease of the linewidths with increasing concentration of the compound suggests a process involving exchange of free and bound acetonitrile is occurring concurrent with migration of ruthenium on the C_{60} surface.) By preparing an NMR sample with a known weight of $\{[Cp^*Ru(CH_3CN)_2]_x(C_{60})\}^{x+}(O_3SCF_3^-)_x$ and integrating relative to an internal standard of known amount, the value of x was determined to be 3. Elemental analytical data (C, 54.07; H, 3.04; and N, 4.08) was ambiguous but suggests a value for x of either 3 or 4.
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