

Metal Complexes of Buckminsterfullerene (C₆₀)

PAUL J. FAGAN,* JOSEPH C. CALABRESE, and BRIAN MALONE

Central Research and Development Department, E. I. du Pont de Nemours & Co., Inc.,[†] Experimental Station, P.O. Box 80328, Wilmington, Delaware 19880-0328

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Introduction

Since the initial discovery and subsequent development of the large-scale synthesis of fullerenes,¹ the interaction of these molecules with metals has been of fundamental interest. Initially detected in the gas phase, there are ongoing attempts to prepare, isolate, and characterize fullerenes with metals contained in the interior.^{2,3} To our knowledge, no fullerene is known which has a metal atom as part of the cage, although the report of C₅₉B suggests that this may be possible.^{2c,3} A number of gas-phase species have been produced where it is proposed that the metals are bound to the exterior of the C₆₀ cage.²⁻⁴ Buckminsterfullerene (C₆₀) has been doped with combinations of alkali and other metals to produce high-temperature superconductors.⁵ Interaction of C₆₀ with metal surfaces in various forms has been detected.⁶ The first structurally characterized C₆₀ derivative, (t-BuC₅H₅N)₂OsO₄(C₆₀), contained a metal atom in which osmium was connected through a pair of oxygen atoms to the C₆₀ core.⁷ This Account describes our work on the attachment of metal complexes directly to the exterior of the C₆₀ framework via solution chemistry forming metal-C₆₀ bonds.

The Chemical Nature of C₆₀

As inorganic/organometallic chemists, our interest in C₆₀ was piqued because of all the potential bonding modes this carbon cluster offered to a metal. For a number of years, we had been attaching the organometallic fragment Cp*Ru⁺ (Cp* = η⁵-C₅(CH₃)₅) to aromatic hydrocarbons to produce molecules with a precise geometric array of positive charge for use in the rational crystallization of molecular solids.⁸ Buckminsterfullerene seemed a natural fit for this chemistry. Much of the lore in the literature at the time we started our work was that C₆₀ was basically a relatively unreactive sphere covered with benzene rings.⁹ The only reactivity of which we were aware early on was the osmium tetroxide chemistry of Hawkins et al.⁷ and the Birch reduction attempted by Smalley and co-workers.^{14a} The true chemical nature of C₆₀, however, was

still generally unknown. From a combination of the above ruthenium chemistry and the other metal chem-

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Paul J. Fagan received his B.S. in chemistry from Rutgers University in 1976. He obtained a Ph.D. in inorganic chemistry from Northwestern University in 1980. He went on to do postdoctoral work at the University of Wisconsin, Madison. Since 1982, he has been in the Central Research and Development Department of E. I. du Pont de Nemours & Co. His professional interests are in the general fields of inorganic and organometallic chemistry, including homogeneous catalysis, rational synthesis of molecular solids, and polysilane chemistry.

Joseph C. Calabrese graduated with a B.S. from Allegheny College in 1964 and received a Ph.D. from the University of Wisconsin, Madison, in 1971. He is currently a Staff Scientist at Du Pont and has used crystallography for over 25 years to study a variety of organic, organometallic, and inorganic chemistry problems.

Brian Malone was born in London, England, and attended London University (B.Sc. 1958, Ph.D. 1963). After a postdoctoral fellowship at the California Institute of Technology, he joined Du Pont in 1966, where he has worked mainly on heterogeneous catalysis and plasma chemistry.

istry described in this Account, we were able to conclude that C_{60} behaves chemically more like an electron-deficient alkene (or arene) such as tetracyanoethylene than like relatively electron-rich species such as ethylene or benzene.¹⁵ In retrospect, this may not be too surprising since C_{60} was determined to have a high electron affinity in the gas phase^{10a} and was easily reduced electrochemically in solution.^{1h,11,14a} The unusual long/short bond alternation in the six-membered rings of C_{60} suggested that each double bond is somewhat electronically localized,²¹ and possibly related to this,

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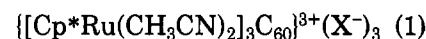
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only relatively small ring currents are detectable in C_{60} .¹² At the same time, each double bond is surrounded by four other electron-withdrawing groups. Add the fact that the double bonds of C_{60} are strained (i.e., nonplanar), and C_{60} is expected to exhibit a rich chemistry. Others have independently come to related conclusions.^{1i,13}

Only a few C_{60} derivatives and products derived from solution reaction chemistry have been rigorously structurally characterized at this point. However, our work¹⁵ and that of many others has definitely established C_{60} as a very reactive molecule.^{13,14,16} It was this reactivity which allowed us to prepare and characterize by X-ray crystallography the first fullerene transition-metal complex which has the metal attached directly to the carbons of the C_{60} cluster, namely, $[(C_6H_5)_3P]_2Pt(\eta^2-C_{60})$.^{15a} Recently, iridium complexes of both C_{60} and C_{70} have also been structurally characterized.^{15,16} An inorganic charge-transfer salt, (tetraphenylporphyrinato)chromium(III)⁺(C_{60})⁻, has been prepared.¹⁷ The metal chemistry of fullerenes is expected to be extensive. In the long term, there is the chance that the metal chemistry of C_{60} will lead to the preparation of new high surface area catalysts, or compounds with new physical properties.

Ruthenium Chemistry

The reaction of C_{60} with excess $Cp^*Ru(CH_3CN)_3^+X^-$ ($X^- = O_3SCF_3^-$)^{8a} proceeds as in eq 1.^{15a} The product $Cp^*Ru(CH_3CN)_3^+X^- + C_{60} \rightarrow$ (excess)



is a brown-red solid which precipitates after several days from dichloromethane solution. The compound appears crystalline, but does not diffract X-rays. Analysis suggested that three ruthenium atoms were attached to each C_{60} molecule, yielding the formulation $\{[Cp^*Ru(CH_3CN)_2]_3C_{60}\}^{3+}(X^-)_3$. The observation that two acetonitriles remained coordinated to the ruthenium atom was unusual if C_{60} behaved like a typical electron-rich aromatic hydrocarbon. Without exception, all other planar six-membered aromatic rings displace the three coordinated acetonitriles to form the sandwich complexes $Cp^*Ru(\eta^6-C_6R_6)^+$ in good yield. The binding of this ruthenium fragment to planar arenes is very strong,^{8a} which makes the C_{60} result all the more striking. This result combined with the knowledge that $Cp^*Ru(CH_3CN)_3^+X^-$ will lose one acetonitrile and bind electron-deficient alkenes, forming the alkene complexes¹⁸ $Cp^*Ru(CH_3CN)_2(\eta^2-alkene)^+X^-$, was the key to our understanding of the reactivity of C_{60} . Displacement of only one acetonitrile from ruthenium indicated that C_{60} was chemically related to electron-poor alkenes. This led us to try chemistry with organometallic compounds that bond strongly to this class of alkene, such as the zero-valent platinum complex $[(C_6H_5)_3P]_2Pt(\eta^2-C_2H_4)$ ^{19a} and other low-valent metal compounds.

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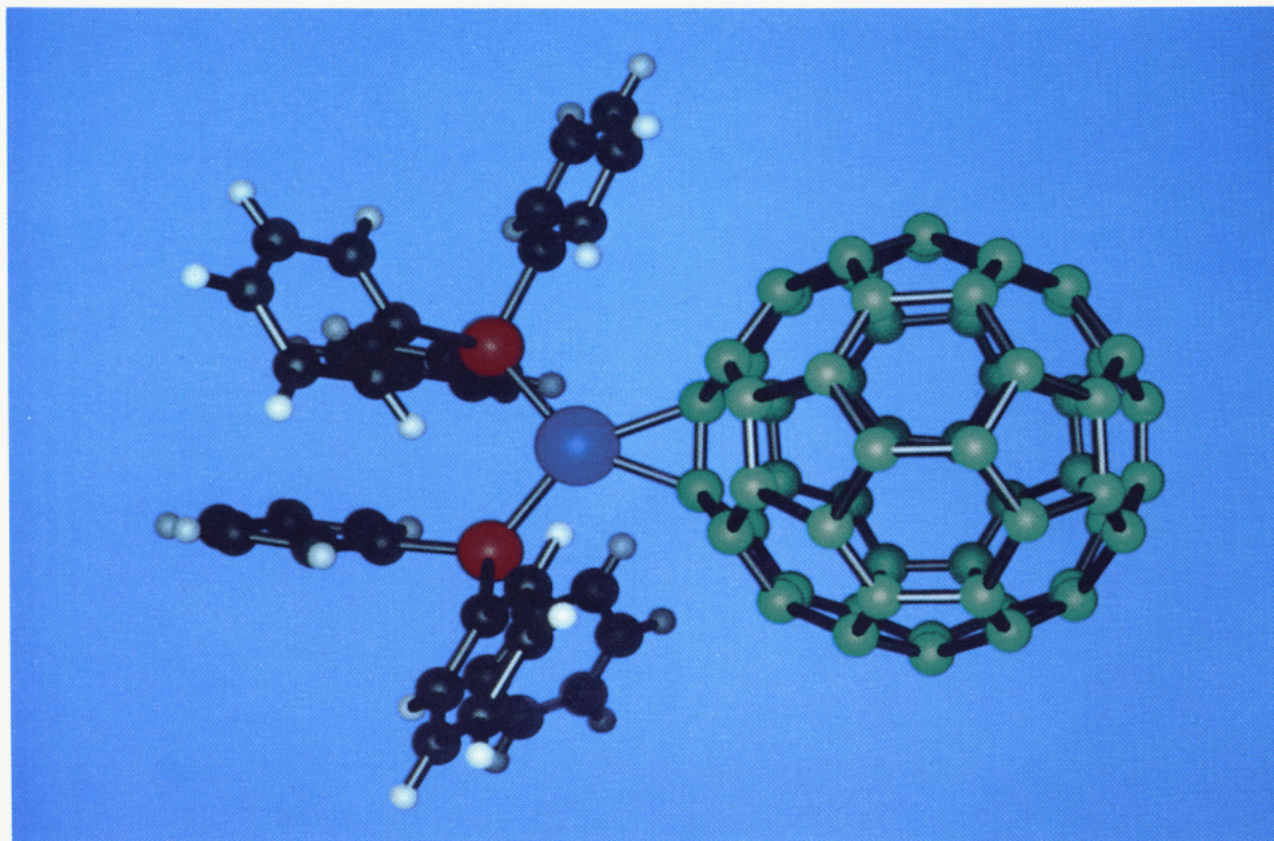
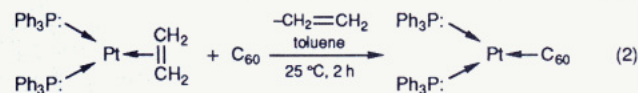


Figure 1. Structure of $[(C_6H_5)_3P]_2Pt(\eta^2-C_{60})$ from X-ray crystallography of the complex $[(C_6H_5)_3P]_2Pt(\eta^2-C_{60})\cdot C_4H_8O$. Carbons of C_{60} are in green; all other carbons are black. Platinum is blue, phosphorus is red, and hydrogens are white.

Platinum, Palladium, and Nickel Chemistry

Low-valent transition-metal complexes are well-known to bind to electron-deficient alkenes and arenes.^{19,20} When the complex $[(C_6H_5)_3P]_2Pt(\eta^2-C_2H_4)$ ^{19a} was reacted with a magenta toluene solution of C_{60} , the solution color changed instantly to a dark emerald green. A black crystalline compound precipitated from this solution. Recrystallization from tetrahydrofuran yielded a compound of formulation $[(C_6H_5)_3P]_2Pt(\eta^2-C_{60})$ in 75% isolated yield (eq 2).¹⁵ From spectroscopy,

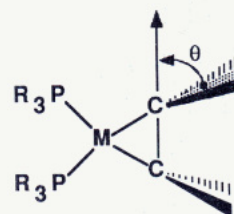


we were able to tell we had a single well-defined compound; however, it was only slightly soluble in tetrahydrofuran, and further characterization was difficult. We made various attempts to grow crystals of the compound and eventually grew one by the tried and true method of leaving an NMR tube around the lab for a few weeks. Although the crystal was weakly diffracting, enough data could be collected to solve the structure. The result we obtained is shown in Figure 1. As we expected, the platinum atom was bound to just two carbon atoms of the C_{60} cage.

Buckminsterfullerene has two different types of bonds in the cluster, one at the fusion of two six-membered rings (6-6) and the other at the fusion of a five-membered and a six-membered ring (6-5). In the first structurally-characterized derivative, $(t\text{-BuC}_5\text{H}_5\text{N})_2\text{OsO}_4(C_{60})$, the two oxygen atoms were bound at a 6-6 ring bond.⁷ Likewise, platinum was bound at a 6-6 ring junction.¹⁵ More recently, Balch

et al. have structurally characterized the complex $[(C_6H_5)_3P]_2(CO)ClIr(\eta^2-C_{60})$, in which iridium is again observed to bind at this same position.^{16a} The related iridium complex $(\eta^5\text{-indenyl})(CO)Ir(\eta^2-C_{60})$ prepared by Shapley et al. is undoubtedly coordinated in a similar fashion.^{16c} That reactivity occurs at the 6-6 bond is easily rationalized since it is now well-established that the 6-6 bonds of C_{60} are shorter than the 6-5 bonds and have the most double-bond character.^{7,8,21}

In terms of the platinum coordination sphere, it was found that this C_{60} complex closely resembles the structures seen for other platinum alkene complexes.^{15a} Buckminsterfullerene has many low-lying antibonding orbitals which could accept metal electron density.^{10b} One well-known consequence of metal coordination to an alkene is that the four groups attached to the alkene bend back away from the metal owing to d-orbital back-bonding into the alkene π^* orbital.^{20a} Although various measures of this bending have been proposed,^{20a} the simplest²² is described by the angle θ in the diagram.



This angle is a measure of the deviation of the groups

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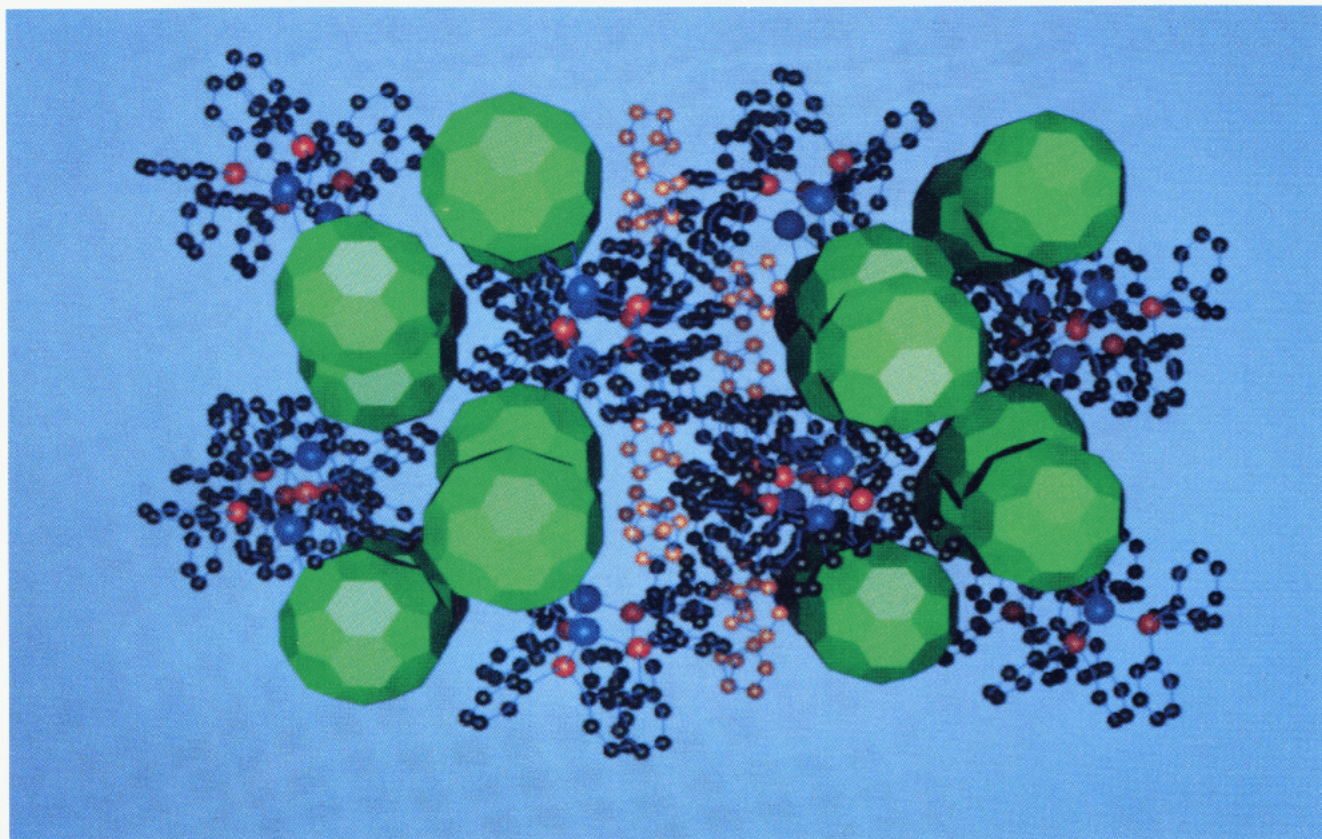
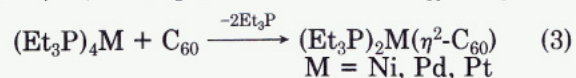


Figure 2. Packing diagram for $[(C_6H_5)_3P]_2Pt(\eta^2-C_{60}) \cdot C_4H_8O$. Atom color code is the same as in Figure 1, except for the disordered tetrahydrofuran molecules, which are shown in orange. The C_{60} clusters are shown as green polyhedra.

attached to the carbon-carbon double bond from the original alkene plane. For platinum alkene complexes, such angles are typically in the range $22-35^\circ$.^{20,22} The carbon-carbon double bonds of C_{60} are already ideally disposed to binding in a η^2 manner to a transition metal since the angle θ in C_{60} is 31° . Upon binding to Pt, θ for the carbon-carbon double bond attached to platinum is increased slightly (average $\theta = 41(2)^\circ$) with the two carbons being pulled away from the C_{60} surface. The propensity of strained alkenes to bind to low-valent metals has been discussed previously in the literature.²² In the C_{70} complex $[(C_6H_5)_3P]_2(CO)ClIr(\eta^2-C_{70})$, the Ir atom binds to the end of the oblong C_{70} that has the most curvature and presumably the most strained double bonds.^{16b} We conclude that the combination of both strain and the electron deficiency of the fullerene carbon-carbon double bonds promotes η^2 binding to these metals (although the relative contribution of each of these factors is not known).

A point of interest is how the compound $[(C_6H_5)_3P]_2Pt(\eta^2-C_{60})$ packs in the solid state. A packing diagram is shown in Figure 2. Basically the lattice is composed of adjacent zigzagging rows of C_{60} with the rest of the atoms and a tetrahydrofuran of crystallization filling in the space between these rows.

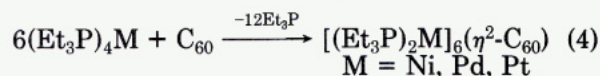
The chemistry discussed above can be extended to prepare related nickel, palladium, and platinum complexes of C_{60} using the metal reagents $M[P(C_2H_5)_3]_4$ ($M = Ni, Pd, Pt$)^{19c,d} (eq 3).¹⁸ All of these C_{60} complexes



form emerald-green solutions. Raman spectroscopy has

proven to be an indispensable tool in providing support for the structure of these compounds.²³ These new metal derivatives have very intense C_{60} -based Raman modes which are almost identical to those of the structurally-characterized compound $[(C_6H_5)_3P]_2Pt(\eta^2-C_{60})$.²³

A question arose as to how many metals could be attached to the C_{60} core. Attempts by others to make multiple additions to C_{60} with a variety of reagents have generally produced extremely complex mixtures, making structural determinations difficult.^{7,13,14} Because many of these compounds have been characterized only by mass spectral analysis or incomplete spectroscopy, it is not even known if the C_{60} spherical core remains intact. We have been able to prepare the first well-characterized products of multiple addition, namely, $[(Et_3P)_2M]_6C_{60}$ ($M = Ni, Pd, Pt$) (eq 4), which have six metal atoms attached to the C_{60} molecule.^{15c} The Ni



and Pd compounds dissolve to give dark red solutions while the Pt is orange in color. From spectroscopic properties, it was found that each of these compounds exists as a single structural isomer, and the structure could be assigned on the basis of the spectroscopy alone.^{15c} However, we were able to obtain crystals of both the platinum and palladium derivatives, and the X-ray crystal structures were determined.^{15c,18} These are the most accurate structures known to date for C_{60} derivatives. The Raman spectra of the Ni, Pd, and Pt com-

(23) Chase, D. B.; Fagan, P. J. *J. Am. Chem. Soc.*, in press.

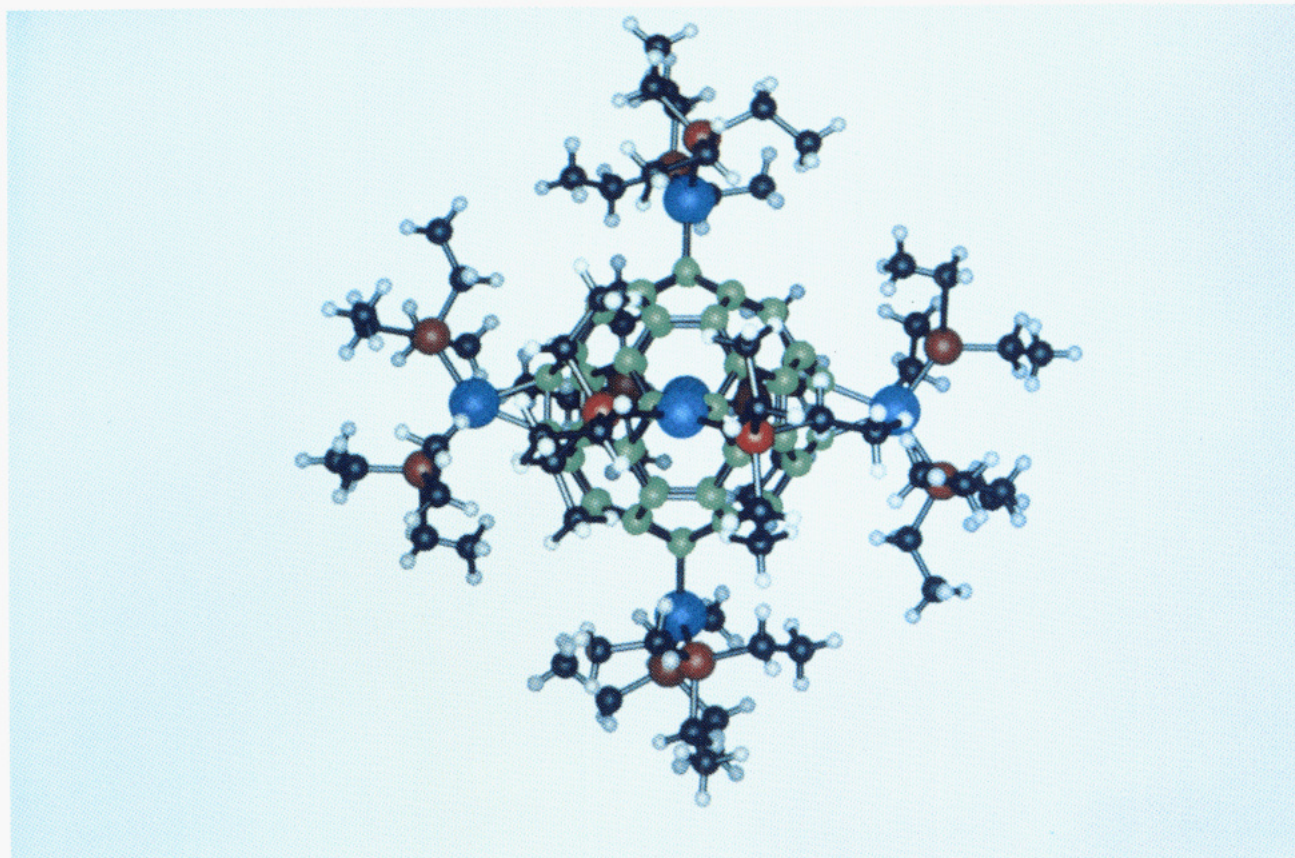


Figure 3. Structure of $[(\text{Et}_3\text{P})_2\text{Pt}]_6\text{C}_{60}$ from X-ray crystallography showing the entire molecule. See Figure 1 for atom color code.

pounds are quite similar, and it can be concluded that all are isostructural.²³

The X-ray result for the platinum derivative is depicted in Figure 3 with all of the atoms included. Stripping away the ethyl groups reveals the inner core of these molecules as shown in Figures 4 (Pd) and 5 (Pt). The metals are in an octahedral array surrounding the exterior of the C_{60} core. Excluding the ethyl groups, the molecules have almost ideal T_h point group symmetry, which is relatively rarely observed. Each platinum is bound across a 6–6 ring junction, as in $[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{Pt}(\eta^2\text{-C}_{60})$.

A comparison of the C_{60} bond lengths for both the platinum and palladium derivatives is shown in Figure 6 along with the most favored resonance structure based on these bond lengths. Each platinum pulls out two carbons from the C_{60} framework and greatly lengthens the carbon–carbon bond to which it is attached. Relative to C_{60} , bonds B and D (Figure 6) are also lengthened significantly. In the palladium derivative, similar distortions of the sphere are seen although they are less pronounced.

Excluding the carbons bound to platinum, the rest of the C_{60} structure is described by eight six-membered rings arranged in a cubic array on the C_{60} surface. Each of these rings retains some of the short/long bond alternation observed in C_{60} (bonds C and E in Figure 6). The difference between C and E (ca. 0.036 Å) is much less than the corresponding difference in C_{60} itself (ca. 0.06 Å²¹). We conclude that these rings are becoming more benzene-like or “aromatic” in these derivatives. Because the metals pull the carbons to which they are attached out of the C_{60} framework (by about 0.15 Å),

there are three carbons in each of the six-membered rings that are less pyramidal. This would explain the tendency of bonds C and E to equalize in length and both approach the typical value for arenes (ca. 1.395 Å).

The packing diagram of the complex $[(\text{Et}_3\text{P})_2\text{Pt}]_6\text{C}_{60}$ is shown in Figure 7. This packing arrangement corresponds to a simple hexagonal packing of spheres (...AAA... stacking of close-packed layers).²⁴ In contrast, C_{60} occurs with primarily face-centered-cubic packing (ABAB...) or hexagonal close-packing (ABCABC...).^{1a,25} The addition of six bis(triethylphosphine)platinum units essentially coats C_{60} with a hydrocarbon/metal shell, and although these nearly spherical objects are close-packed within each layer in a fashion similar to C_{60} itself, the stacking of these layers relative to each other differs.

Both the monosubstituted metal derivatives and the hexasubstituted derivatives can be isolated and structurally characterized. What happens in between, and why do only six metals attach themselves to the C_{60} sphere? The latter question is easily answered by examination of the space-filling model in Figure 8. Although there are small pockets in the molecule directly over the six-membered rings that form the cubic array

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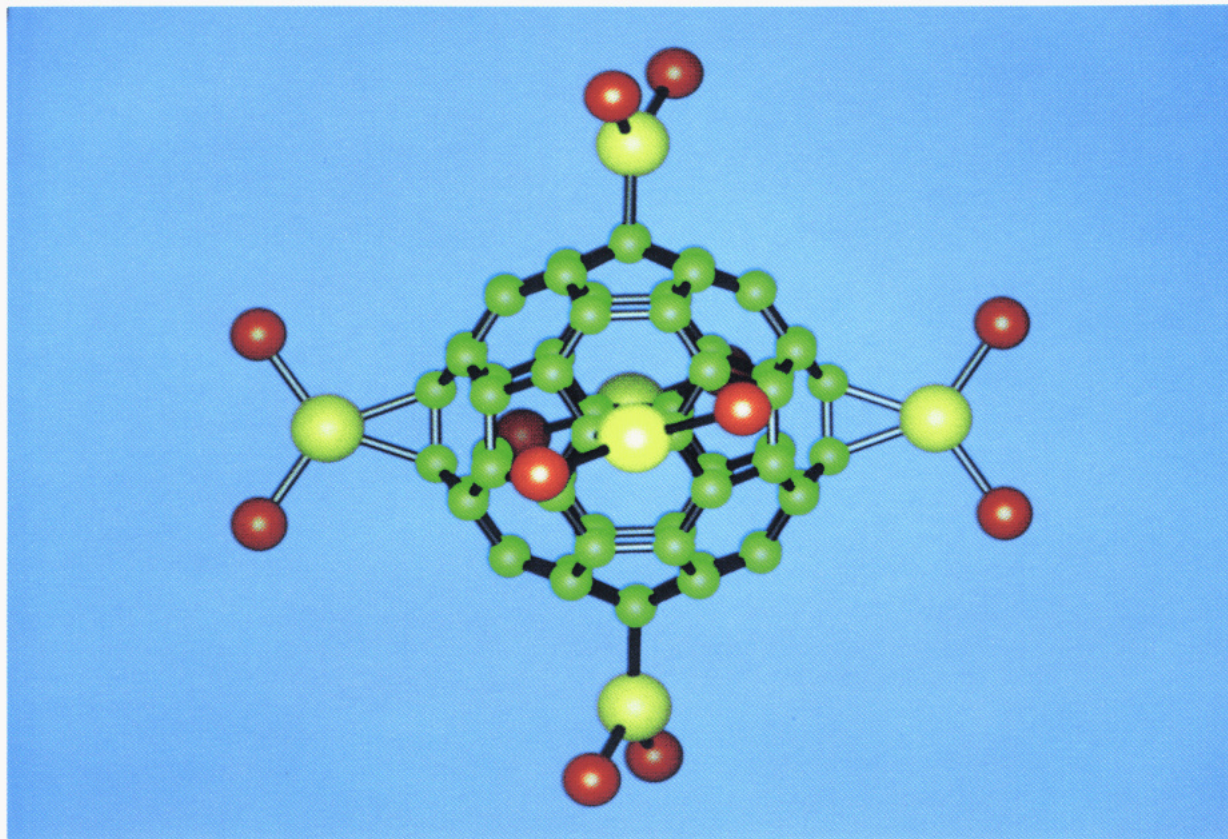


Figure 4. Structure of $[(Et_3P)_2Pd]_6C_{60}$ with ethyl groups removed. View shown is looking down a 2-fold symmetry axis under idealized T_h point group symmetry. Atom color code: Pd, yellow; P, red; C, green.

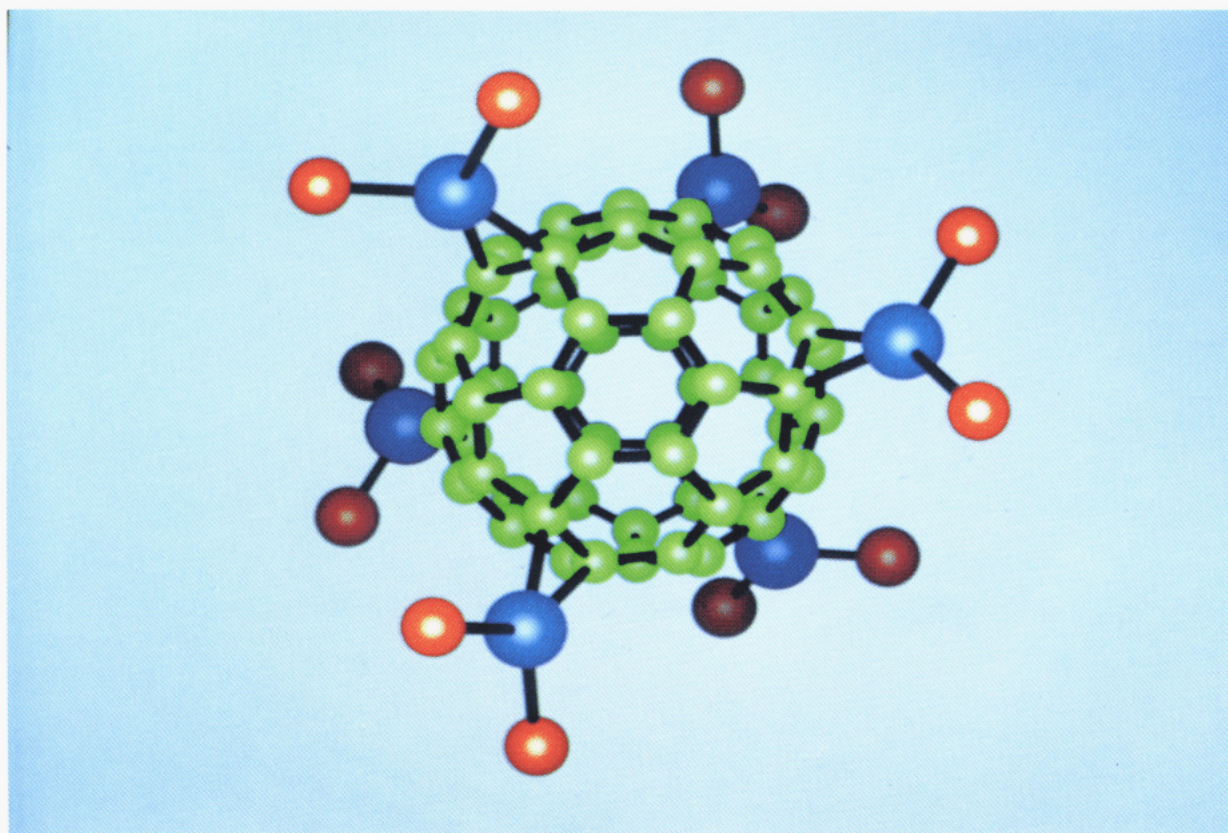


Figure 5. Structure of $[(Et_3P)_2Pt]_6C_{60}$ looking down a 3-fold symmetry axis under idealized T_h point group symmetry. See Figure 1 for atom color code.

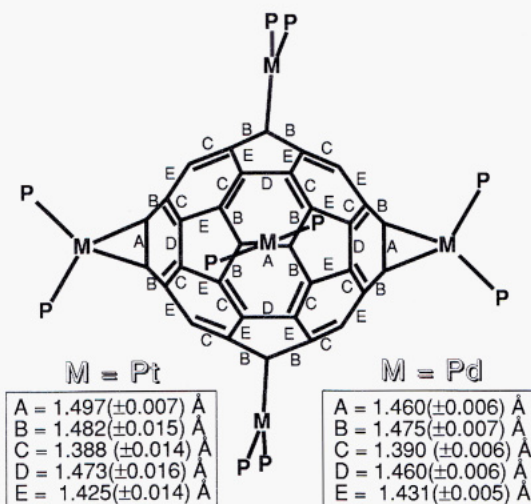
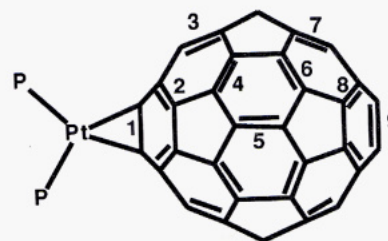


Figure 6. Bond distances and favored electronic resonance structure for the compounds $[(\text{Et}_3\text{P})_2\text{M}]_6\text{C}_{60}$ ($\text{M} = \text{Pd}, \text{Pt}$). With T_h symmetry, there are five unique symmetry-related sets of C-C bonds (A,B,C,D,E).

discussed earlier, there is clearly no room for a seventh $(\text{Et}_3\text{P})_2\text{Pt}$ fragment. Thus the octahedral array of metal fragments is sterically the optimum situation. There may be electronic factors which also stabilize this arrangement (for example, the previously discussed tendency for some of the rings to become more aromatic), but this conclusion awaits detailed theoretical calculations on these molecules. Wudl and co-workers have reported that six morpholines can add to C_{60} ,¹⁴ⁱ as well as six diphenylcarbene units.^{14j} Because the structures of these molecules have not been determined,

their relation to the above hexasubstituted metal derivatives is unknown.

We have performed some preliminary studies to ascertain the mechanistic pathway that leads to formation of the hexasubstituted platinum derivative. We prepared the disubstituted compound $\{[(\text{C}_2\text{H}_5)_3\text{P}]_2\text{Pt}\}_2\text{C}_{60}$.¹⁸ Referring to the diagram, there are a total of eight



different disubstituted isomers possible if we limit Pt to binding to the 6-6 ring junctions. By ^{31}P NMR, we observe the formation of only three isomers.¹⁸ One can be assigned to the 1,9-“trans” isomer (a singlet in the ^{31}P NMR). The 1,2 and 1,3 isomers are not expected to form on steric grounds. The 1,5 isomer is not observed (this should display a phosphorus singlet and an AB quartet in a 1:1 intensity ratio), so this leaves either the 1,4, 1,6, 1,7, or 1,8 isomers as the remaining structural possibilities for the other two isomers. These should be observed as patterns of AB quartets in the ^{31}P NMR spectrum, and this is what is seen. Clearly, except for the “trans” isomer, none of these correspond to the final substitution positions in the hexasubstituted derivatives. Therefore, we conclude that as the substitution on the C_{60} core increases, the $(\text{Et}_3\text{P})_2\text{Pt}$ fragments become labile and equilibrate on and off the C_{60}

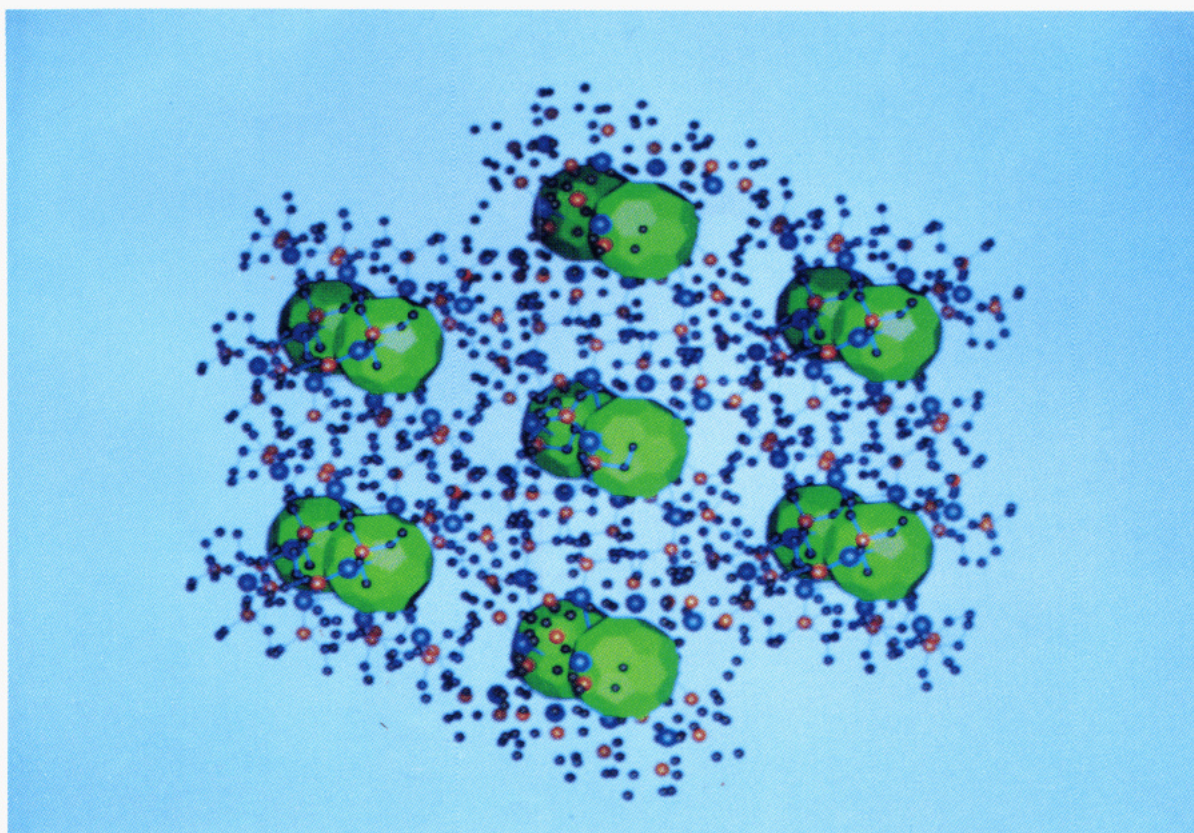


Figure 7. Solid-state packing diagram for $[(\text{Et}_3\text{P})_2\text{Pt}]_6\text{C}_{60}$. The C_{60} clusters are shown as green polyhedra. Although the compound crystallizes in the primitive space group $P\bar{1}$, the relation to a simple hexagonal lattice of close-packed objects²⁴ is apparent.

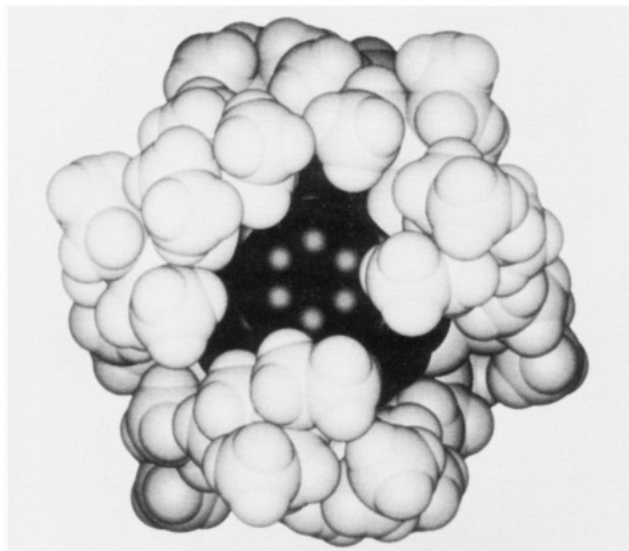


Figure 8. Van der Waals space-filling model for $[(Et_3P)_2M]_6C_{60}$ looking down the 3-fold symmetry axis under idealized T_h point group symmetry. C_{60} is in black, and $(Et_3P)_2Pt$ groups are in white.

surface. This provides a means for the metals to adjust to the T_h symmetry structure. Indeed, if 1 equiv of diphenylacetylene is added to a solution of $[(Et_3P)_2Pt]_6C_{60}$ in benzene, an instantaneous reaction occurs to produce the complexes $(Et_3P)_2Pt[\eta^2-C_2-(C_6H_5)_2]$ and $[(Et_3P)_2Pt]_5C_{60}$ as the major products. For steric reasons, it is unlikely that this is an associative reaction, and therefore we conclude that $[(Et_3P)_2Pt]_6C_{60}$ is in equilibrium with a small amount of the metal fragment $(Et_3P)_2Pt^{26}$ even in nonpolar solvents. This suggests that increasing metal substitution steadily decreases the electron affinity of the C_{60} cluster, making subsequent coordination of electron-rich metals less favorable. Shapley and co-workers have found that in the complex $(\eta^5\text{-indenyl})(CO)Ir(\eta^2-C_{60})$ iridium can be cleaved from C_{60} by addition of other ligands, although this is believed to be an associative reaction.^{16c}

Effect of Metal Substitution on C_{60}

The lability of the hexasubstituted derivatives suggests that the electron affinity of the C_{60} cluster has been drastically reduced. To address this point, we have performed electrochemical studies on the metal complexes in tetrahydrofuran. It is found that the monosubstituted derivatives $(Et_3P)_2MC_{60}$ ($M = Ni, Pd, Pt$) are 0.34 V harder to reduce than C_{60} itself!²⁷ Shapley et al. have also observed that an iridium complex is more difficult to reduce electrochemically.^{16c} (A number of derivatives of unknown structure show similar effects.)^{13,14i,j} With increasing amounts of metal substitution, the complexes become increasingly harder to reduce. The hexasubstituted derivatives are only reduced at very negative potentials (ca. 2.7–3.0 V harder to reduce than C_{60}). Furthermore, upon reduction the complexes become unstable and release the metal moieties into solution, producing free C_{60} anions. The rate of this release increases with the degree of reduction, i.e., the rate of decomposition follows the order

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$(R_3P)_2PtC_{60}^{3-} > (R_3P)_2PtC_{60}^{2-} > (R_3P)_2PtC_{60}^{-}$.²⁷ Raman studies support π -back-bonding from the metal to C_{60} as the primary means of transferring electron density onto the carbon cluster, as is also evident from the X-ray structural parameters. We conclude that reducing these complexes then adds additional electron density into the π^* orbitals of the cluster, which drives the metals off since the metals cannot back-bond as effectively.

We propose that the addition of a metal has two effects on C_{60} electronic structure. The major effect is to remove one double bond from conjugation with the remaining 29 double bonds because of metal back-bonding (lengthening the bond to 1.50 Å in the case of platinum). Removal of a double bond in any conjugated polyene system is expected to raise the energy of the lowest unoccupied orbital, or in other words decrease the electron affinity of the molecule. The other possible effect is to “leak” some d-orbital back-bonding electron density into the π^* orbitals of the remaining double bonds on the cluster. However, the extent of this latter effect is probably small. Otherwise, it is hard to explain the observation that the monosubstituted Ni, Pd, and Pt complexes $(Et_3P)_2M(\eta^2-C_{60})$ are reduced at *exactly the same potential* despite the fact that the three different metals back-bond to different extents. Donation of electrons from the metal via back-bonding is thus a relatively localized effect on the sphere. Upon addition of a radical to C_{60} , there is evidence that the unpaired spin does not wander far from the initial point of attack and is not delocalized over the entire sphere.^{14e,f} Thus one would not expect metal back-bonding electron density to extend too far from the site of metal binding. As long as metal back-bonding is not weak, the net effect of metal coordination is to electronically decouple one carbon–carbon double bond from the other 29 conjugated double bonds. This remaining system of 29 double bonds is what primarily determines the electron affinity of the molecule.

The decreased electron affinity of C_{60} upon binding of a metal also explains why the monosubstituted complex can be formed selectively in reaction with the low-valent-metal reagents. The tendency of a second metal to add is significantly reduced, and even if some disubstituted metal complex does form, there is a substantial driving force for the disubstituted derivative to react with free C_{60} in solution and form the monosubstituted derivative. The number of metals on each C_{60} can thus be controlled simply by stoichiometry. Since the electron affinity of C_{60} can be tuned by the number of metal groups on the cluster, this suggests that one could use the metals as protecting groups to modify the reactivity of C_{60} and make it more manageable.

Concluding Remarks

A host of low-valent, electron-rich transition metal, lanthanide, actinide, and main-group metal compounds are known which should react and bind the metals to fullerenes and their derivatives. A number of metal vapors should also react, the superconducting compounds being the first examples formed by this route.⁵ Catalytic addition of other reagents to C_{60} (even something as simple as hydrogenation) is worthy of pursuit. Add to this the large number of compounds that have reactive organic fragments (metal alkyls,

carbenes, carbynes, amides, etc.), and the possibilities become infinite. The anions of C_{60} should also produce interesting metal chemistry. For example, there are hints that these can be used to form ferrocene-like bis(buckminsterfullerene) complexes.^{4a} Inorganic charge-transfer salts as well as solid-state metal/ C_{60} compounds with unique properties should also arise from these anions. More synthetically challenging will be to open a fullerene, insert a metal atom inside, and reclose to produce (M@fullerenes).^{3b}

There are several aspects of fullerenes that make them chemically and physically unique, and time will tell if these have any industrially significant applications. (Hyperbole tends to be rampant with any new discovery.) It may be anachronistic to maintain that

exploratory metal chemistry of fullerenes will lead to discovery of new catalysts or useful materials. But if nothing else, perhaps new ideas (the most precious scientific commodities) in organometallic/inorganic/solid-state chemistry and other fields will emerge from this venture.

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Registry No. C_{60} , 99685-96-8.