New Cages and Unusual Guests: Fullerene Chemistry Continues To Excite

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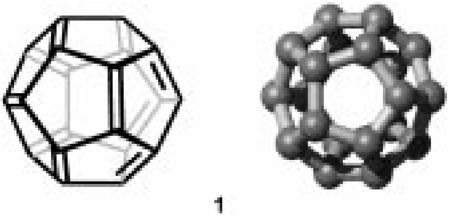
Since Krätschmer, Huffman et al. discovered[1] the synthetic route to fullerenes[2] in macroscopic quantities over ten years ago, ever-expanding research into the chemistry of these molecular allotropes of carbon has developed. Alongside the isolation of numerous higher fullerenes[3] and endohedral derivatives,[4] the specific synthesis of exohedral fullerene adducts[5] is particularly prominent. With the development of several exohedral addition reactions and the ability to exert close control over the regioselectivity of multiple additions,[6] made-to-measure fullerene derivatives have become accessible. Because of the unique properties of fullerenes, such as their spherical, rigid form, the ability to incorporate endohedral guests,[4] easily reversible electron transfer properties,[7] minimal reorganization energy leading to exceptional photophysical properties[8] and remarkable free-radical scavenging properties, interesting materials such as superconductors[10] and derivatives with noteworthy biological activity[11] such as HIV-protease inhibition[12] and high potential for neuroprotection[13] have been produced. From the beginning, fullerene chemistry has also been shaped by the sometimes unexpected discovery of exceptionally attractive structures derived from the parent systems. Examples include heterofullerenes,[14] open clusters[15] and supramolecular aggregates.[16] The sequence of startling developments continues.

To illustrate this, here a selective gallery of new fullerenes distinguished by their unusual structural properties will be presented. For example, Prinzbach et al. recently detected unambiguously the smallest fullerene, C_{20} (**1**), in the gas phase.[17] This is so remarkable because this fullerene consists only of condensed, unsaturated five-membered rings and thus exhibits an enormously high strain energy. The smallest fullerene that can be isolated as a stable compound is C_{60}, in which all of the five-membered rings are surrounded by six-membered rings and so the isolated pentagon rule (IPR) is satisfied. A well-known phenomenon that one observes in the mass spectra of "normal" fullerenes is *shrink wrapping*, in which successive C_2 fragments are "spat out", leading to the formation of smaller fullerenes.[5a] However, the smallest fullerene that can be produced in the gas phase in this manner is C_{32}.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The production of C_{20} was made possible by the use of dodecahedrane, $C_{20}H_{20}$, as the starting material by Prinzbach et al., which is the stable, perhydrogenated form of C_{20}. This was exhaustively brominated with preservation of the carbon framework, then subjected to a gas-phase debromination. The fullerene structure of the C_{20} thus formed was confirmed by photoelectron spectroscopy. These spectra leave open the possibility that C_{20} exhibits Jahn–Teller distortion. These results were recently supported by calculations showing that, in neutral C_{20}, not all of the π orbitals are fully occupied.[18] On the other hand, it was predicted that the closed-shell $C_{20}{}^{2+}$ system is undistorted and highly diatropic and that the recently described $2(N+1)^2$ rule for spherical aromaticity is satisfied.[18] Indeed, the intensities of the $C_{20}{}^{2+}$ signals imply remarkable kinetic stability of the minifullerene. *Note added in proof* (February 20, 2001): the photoelectron spectra of $C_{20}{}^{2-}$ have recently been confirmed by theoretical calculations, M. Saito, Y. Miyamoto, *Phys. Rev. Lett.*, in press.

The production of fullerene derivatives with highly unusual forms is possible in principle by the exohedral addition of multiple addends to the C_{60} parent molecule. This was recently strikingly shown in the crystal structure analysis of $C_{60}F_{18}$ (**2**), originally synthesized in 1996 (Figure 1).[19] Following the specific addition of the fluorine atoms in the form of a

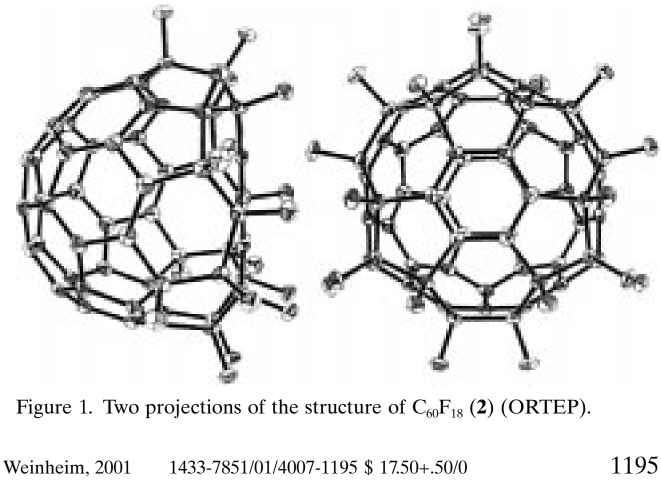
Figure 1. Two projections of the structure of $C_{60}F_{18}$ (**2**) (ORTEP).

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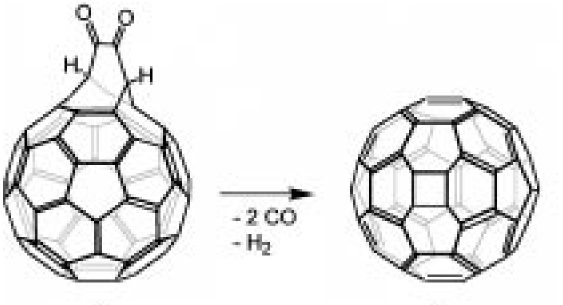
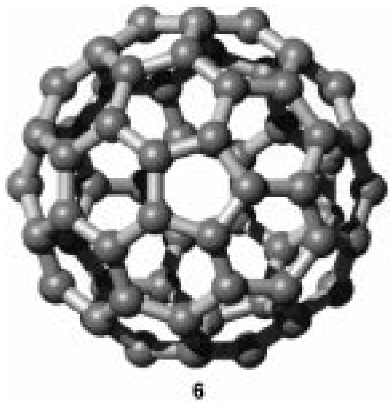
belt and the consequent formation of 18 sp^3-hybridized C atoms, a half-flattened molecule in the shape of a tortoise results. The most striking feature of the bonding is the presence of an isolated benzene ring on the belly of the tortoise. In contrast with C_{60} itself, all of the bond lengths within this six-membered ring are identical. It is possible that the potential formation of this aromatic substructure is a driving force behind the regioselectivity of the 18-fold fluorination of C_{60}. Recently, the same group isolated a highly symmetrical isomer of $C_{60}F_{20}$, which exhibits a Saturn-like conformation, containing two independent corannulene subunits connected by a $(CF)_{20}$ chain.[20] Other π-electron substructures within the fullerene core were recently generated by Rubin et al.[21] and Diederich et al.,[22] with the synthesis of new hexaadducts exhibiting novel D_3- and D_2-symmetrical addition patterns.

C_{70} is the second IPR fullerene after C_{60}. Therefore, no stable fullerenes are to be expected between C_{60} and C_{70}. Besides normal fullerenes, however, conceptual and nonclassical fullerenes may be envisaged. Nonclassical fullerenes include rings of other sizes together with the five- and six-membered rings. As an example of a nonclassical fullerene, Rubin et al. recently identified C_{62} (**3**) in the gas phase, arising from the inclusion of an additional four-membered ring into C_{60}.[23] The instability of **3** is indicated by a very small HOMO–LUMO gap of 1.84 eV, compared with 2.76 eV in C_{60}. Compound **3** was synthesized by the fragmentation of diketone **4** [Eq. (1)], made by a series of cycloadditions. Laser desorption Fourier transform mass spectrometry resulted in a very effective fragmentation to the radical anion by stepwise removal of two CO groups and two H atoms from **4**.



4 **3** (1)

The recent preparation of complexes such as $Sc_3N@C_{80}$ (**5**) has caused a great sensation in the field of endohedral fullerenes.[24] It has emerged that the presence of small quantities of N_2 in a fullerene reactor allows the synthesis of new endohedral fullerenes, such as the trigonal-planar Sc_3N unit encased in the high-symmetry, icosahedral C_{80} cage **6**. The exact structure of **5** was determined by X-ray crystal structure analysis. ^{13}C NMR spectroscopic investigations have shown that, at room temperature, the Sc_3N unit is free to move in the C_{80} cage and so only two signals for the C atoms in C_{80} are observed. This C_{80} isomer is a third icosahedral fullerene alongside C_{20} and C_{60} and has an unstable and antiaromatic, ground-state, open-shell structure as an empty cage and has not yet been isolated. In the case of **5**, the cage is stabilized by six negative charges which result in aromaticity.[18]



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Another striking development with endohedral fullerenes was the synthesis of $N@C_{60}$ (**7**), which was the first example of encapsulation of a nonmetal atom.[25] It is particularly surprising that the enclosed nitrogen exists as a single atom and no bonding to the fullerene framework is apparent. The fullerene therefore represents a trap for extremely reactive atomic nitrogen. This phenomenon is due to the fact that curvature results in the inner surface of the fullerene cage being inert, whilst the outer surface is distinguished by high reactivity.[26] The formation of a covalent bond with the enclosed N atom, which has a half-filled p-shell (three unpaired electrons) and so displays minimal electron affinity, would lead to a distinct rise in the strain energy of the total system. Thanks to the absence of relaxation mechanisms, the lowest ESR linewidths yet observed occur in the spectra of **7**.[27] The wavefunction of the enclosed N atom is influenced by subsequent exohedral adduct formation with one or more addends. This is caused by the altered cage structure of the adducts. The analogous complexes $N@C_{70}$ and $P@C_{60}$ are made in a similar way to $N@C_{60}$, by bombarding a thin layer of fullerene on a cathode with energy-rich N^+ or P^+ ions, respectively.[25]

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These selected examples from more recent fullerene chemistry truly emphasize what high potential for unusual structures with novel properties is associated with this class of substances. It remains clear that fullerene chemistry is still at an early stage and one may anticipate future surprises.

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Highly Enantioselective or Not?—Chiral Monodentate Monophosphorus Ligands in the Asymmetric Hydrogenation

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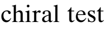
The development was over before it had really begun—this was certainly true for the use of monodentate chiral monophosphorus ligands in rhodium(I) catalysts for enantioselective hydrogenation reactions. Initially everything seemed very promising. In 1965 Wilkinson and co-workers discovered that $[RhCl(PPh_3)_3]$ catalyzes the hydrogenation of olefins.[1] Only a few months later Vaska and Rhodes reported the use of *trans*-coordinated bis(monophosphane) iridium complexes in the reduction of alkenes.[2] Monophosphane ligands were also prominent in other newly discovered metal catalysts, whereas *cis*-chelating diphosphanes, such as bis(diphenylphosphanyl)ethane greatly reduced the rate of hydrogenation. Mechanistic studies showed that the dissociation of a phosphane from Wilkinson's complex is essential for the initiation of the catalytic cycle. For this reason bidentate diphosphane ligands were regarded as unsuitable since the chelate effect enhances their binding to the metal center.[3]

In 1968, the suggestion from Horner and co-workers to employ chiral monophosphanes for the enantioselective hydrogenation of prochiral olefins was both timely and logical.[4] Two Monsanto chemists, Knowles and Sabacky, realized this idea only a few months later through the use of a rhodium complex with the P-chiral ligands PAMP (*o*-anisylmethylphenylphosphane **1a**) and CAMP (*o*-anisylcyclohexylmethylphosphane **1b**) for the hydrogenation of atropic acid.[5] They generated hydratropic acid in a 15% optical yield. With this report itaconic acid (ItH_2) began its career as a prochiral test substrate, it was reduced with a 3% optical yield.

1a: R^1 = *o*-$MeOC_6H_4$, R^2 = Ph (PAMP)
1b: R^1 = *o*-$MeOC_6H_4$, R^2 = *cyc*-C_6H_{11} (CAMP)
1c: R^1 = Ph, R^2 = *n*-C_3H_7



Still in the same year Horner et al., now showed that prochiral styrene could be hydrogenated in up to 8% optical yield by using an in situ formed Rh^I complex of methylphenyl-*n*-propylphosphane (**1c**).[6] Clearly the disappointingly low enantioselectivities were a deciding factor that greatly hindered the rapid adoption of the new hydrogenation method.

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