An overview of fullerene chemistry

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Abstract. Fullerenes which were thought to be 'superaromatics' are actually 'super-alkenes'. Reactions in fullerenes are varied, ranging from the addition of simple molecules like H_2 to large molecules like dendrimers. The synthesis, structure, characterization, along with simple reactions like halogenation, oxygenation, metalation, cycloaddition, polymerization and dendrimer addition are discussed.

Keywords. Fullerenes; C_{60}; C_{70}; characterization; reactions.

1. Introduction

Fullerenes and their derivatives possess a number of potentially useful physical, biological and chemical properties. Our interest in the chemistry of fullerenes led us to present this review in which we have attempted to furnish an overall picture of the properties of these novel molecules. The scope of the review is however limited. The conclusion of the authors contributing to this rapidly growing field of research are accepted and presented in a concise manner highlighting the salient features of the original work.

The technique developed by Krätschmer *et al* (1990) for preparing and isolating macroscopic quantities of C_{60}, 'a new form of carbon', opened the way for exploring the molecular and bulk properties of these novel species. Kroto *et al* (1985) reported the nature and chemical reactivity of C_{60} species produced during the nucleation of carbon plasma. C_{60}, which was found to be stable, was named buckminsterfullerene after Buckminster Fuller, American architect, engineer and constructor of geodesic dome. After the report of species up to 33 carbon atoms in the carbon arc (Hintenberger and Dorenburg 1959; Hintenberger *et al* 1961, 1963), Rohfling *et al* (1984) reported that much larger carbon clusters i.e. even numbered C_n with $n = 30-190$ could be produced by vapourization of graphite, among which C_{60} is the most stable one. C_{60} (buckminsterfullerene) **1** and C_{70} (falmarene) **2** and to some extent C_{84} are most accessible members of the family of closed cage molecules known as fullerenes (figure 1) formed entirely of carbon in sp^2-hybridized state. The fullerenes are considered as the third allotrope of carbon after diamond and graphite.
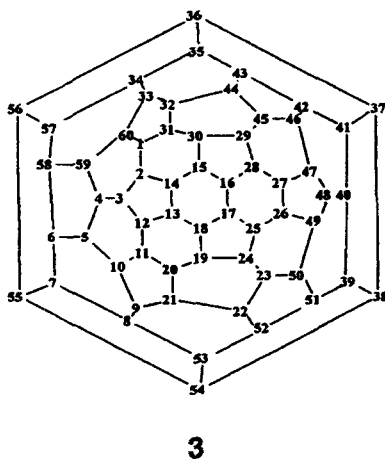
The stability of C_{60} molecule is due to the structure in which the carbon atoms are arranged at the 60 vertices of a truncated icosahedron composed of 32 faces, a

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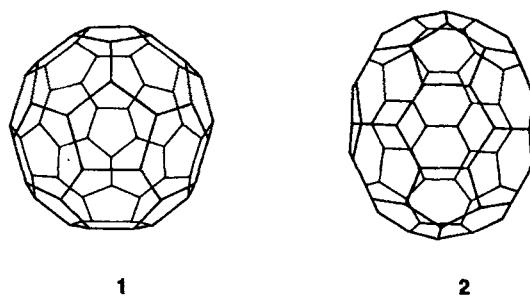
Figure 1. Buckminsterfullerene, C_{60} (12 pentagons and 20 hexagons) and falmarene, C_{70} (12 pentagons and 25 hexagons) (Fowler 1991).

Figure 2. IUPAC numbering of carbon positions in C_{60} shown in Schegel diagram (Kroto *et al* 1991).

structure analogous to a soccer ball. Each molecule of fullerene family (C_n) consists of 12 pentagons and m number of hexagons (other than one), conforming to the relation $m = (n - 20)/2$ (Euler's theorem). Therefore C_{60} is composed of 32 faces of which 12 are pentagons and 20 are hexagons. The position of the different carbon atoms in C_{60} is described by IUPAC nomenclature as shown in figure 2 using Schegel diagram. Accordingly, C_{70} consists of 12 pentagons and 25 hexagons.

By the laser vaporization technique, C_{60} was first produced from a graphite target (Dietz *et al* 1981). It was initially thought that the graphitic sheet fragments might have been ablated from graphite target and rearranged to C_{60}. Subsequent considerations suggested that C_{60} was more likely to have formed by nucleation from carbon vapour consisting at least initially of carbon atoms and very small carbon molecules (Heath *et al* 1987). Krätschmer *et al* (1990) reported the presence

of C_{60} in soot condensed from graphite in argon atmosphere which was identified by the observed isotope shifts of IR absorptions of ^{12}C and ^{13}C. Large variety of carbonaceous materials such as carbon films (Creasy and Breena 1990), polyamides (Creasy and Breena 1988; Campbell *et al* 1990), coal (Greenwood *et al* 1990), polycyclic aromatic hydrocarbons (Lineman *et al* 1989) etc yield predominant C_{60} peak on laser vapourization.

Charged species (positive and negative) are also formed along with neutral C_{60}, and the nucleation rate order was neutrals > cations > anions (O'Brien *et al* 1986). C_{60}^+ was also detected by Homann *et al* (1987) in a sooting flame. Electrochemistry studies showed that at least three anionic forms of C_{60} (C_{60}^{-1}, C_{60}^{-2} and C_{60}^{-3}) and three anionic forms of C_{70} can be produced in solution (Cox *et al* 1991). Studies by Bard *et al* (1992) supported the strong dependence of the redox chemistry of C_{60} on both solvent and cation of supporting electrolyte and demonstrated that electrochemical reduction to the -6 state can be accomplished in liquid ammonia in the presence of K^+. The development of a general method capable of generating stable C_{60}^{n-} species where $n = 1-6$, was reported by Xie *et al* (1992). Using a suitably chosen optimal solvent composition, C_{60} and C_{70} were reduced to C_{60}^{6-} and C_{70}^{6-}. Though earlier reports predicted C_{60} to be extremely stable, it was later reported by Bloomfield *et al* (1985) that C_{60} was susceptible to multiphoton fragmentation, and Bowers *et al* (1988, 1990) showed that C_{60} undergoes metastable fragmentation and small carbon fragments C_n ($n = 2, 4, 6, ...$) are eliminated in the fragmentation process (O'Brien *et al* 1988).

STM studies of thin films of solid solutions showed the presence of C_{60} along with C_{70} (Rao *et al* 1994). The distance between the two C_{60} molecules is 1·47 nm while the distance between two C_{70} molecules in the absence of C_{60} in the vicinity is 1·19 nm and in the presence of C_{60} it is 1·8 nm. Haddon *et al* (1991) reported the excited state paramagnetic contributions to the π-electron ring current magnetic susceptibility. In case of fullerene there are 30 π-bonds, which means that 60 electrons can move about freely and contribute to the magnetic susceptibility. Pauling ring current model predicts a ring current diamagnetic susceptibility 41 times that of π-electron ring current magnetic susceptibility of benzene. The diamagnetism of C_{60} was found to be small, which, according to Haddon *et al* (1991), was attributed to the excited state paramagnetic contributions to the π-electron ring current magnetic susceptibility.

Cast films of C_{60} on noble metal electrodes behave as *n*-type semiconductors in liquid junction cells (Miller *et al* 1991). Haddon *et al* (1991) reported alkali metal doped conducting films of C_{60} and C_{70}, which was attributed to the formation of energy bands from the π-orbitals of C_{60} and C_{70}, and is partially filled with carriers on doping and is an example of three dimensional organic conductors. The highest conductivities observed in the doped films are 4 S/cm (Cs/C_{60}), 100(Rb/C_{60}), 500(K/C_{60}), 20(Na/C_{60}), 10 (Li/C_{60}), and 2(K/C_{70}). Yamada *et al* (1994) reported solar cells from fullerenes. The solar cells of doped-C_{60} as semiconducting material used the *n*- or *p*-layers to form homo- or hetero-junctions. The cells have long life time. Haddon (1996) reported C_{70} thin film transistors made out of thin films of conductivity 2×10^{-9} S/cm. Photoconducting films of poly(vinyl carbazole) doped with fullerenes have been reported (Wang 1992), and quantum yield for primary

charge separation and initial ion pair distance are 0·9 and 19 Å respectively. Transition metal complexes containing fullerene derivatized ligands might be interesting in solar energy studies (Maggini *et al* 1995).

A novel synthetic route to the formation of less air-sensitive fullerene superconductors by mixing oxygen-containing alkaline compounds with C_{60} is reported by Hwang *et al* (1994). The observed stability enhancement and the off-stoichiometry of K content may originate from the presence of oxygen which serves as an oxidative agent. Khairullin *et al* (1994) have systematically studied a new Na-doped C_{60} superconductor prepared from NaN_3. The authors present the experimental results of the low field signal of microwave adsorption and ESR. Hirozawa (1995) reported superconductor thin films comprising a C_{60} layer and a group II element layer alternatively grown on a (100) plane of a substrate selected from RbI, RbBr, RbCl, RbF, KI, KBr, KCl, KF, NaBr, NaCl or· NaF and containing Na or Li. The superconductive materials have a high superconductive transition temperature.

There are reports of interfacial electron transfer to both ground state and excited state triplet C_{60} and C_{70} in self organized planar lipid bilayers (Mauzerall and Huang 1992). The increase of positive photovoltage is due to the presence of C_{60} in lipid bilayers. Because of their electron accepting properties and chemical stability, fullerenes could be used to accomplish photochemical charge separation in the supramolecular systems, initiating the first step of artificial photosynthesis.

There are several practical applications of fullerenes. Antifriction, antiwear and antiseize properties of lubricating oil are improved in the presence of C_{60} (Ginzburg *et al* 1995). The use of dissolved fullerene catalyst as inhibitor of coking reactions, thereby inhibiting formation of coke on a catalyst or catalyst support by eliminating nucleating points or growth regions for such coke formation is reported by Malhotra *et al* (1994). In petrochemical and refining industries, efficient production of many hydrocarbon products are often hindered by fouling, resulting from unwitting polymerization of reactive olefins like 1, 3-butadiene, isoprene or styrene. It is shown that (McClaim 1995) ppm levels of fullerenes inhibit the thermal polymerization of activated olefins like styrene and butyl methacrylate. The extent of polymerization and the molecular weight of the recovered polymer are strongly dependent on fullerene concentration. Fullerenes apparently inhibit polymerization by scavenging monomer species that propagate chain growth. Fullerene antifoulants would offer several advantages over existing technologies since they contain no hetero atoms.

One of the most promising practical applications of the fullerenes involve their optical limiting properties (Maggini *et al* 1995). The preparation of glassy thin films containing fullerenes would offer the possibility of producing filters against optical damage in a number of applications such as protection from high energy laser light. The authors report the successful embedding of fulleropyrrolidines, which are prepared employing the 1, 3-dipolar cycloaddition reaction of azomethine ylides to C_{60}, in sol–gel SiO_2 films and monoliths. Mixtures of cyclofluoroalkylated fullerenes are prepared by the thermal [2 + 2] cycloaddition of fluoroalkenes to a solution or slurry of a fullerene. The cyclofluoro alkylated fullerene mixtures are useful as lubricants or additives to lubricants; in fluorocarbon and/or CFC based cooling systems; in adhesives for fluorocarbon based polymers and in gas separation membranes (Bekiarian *et al* 1995).

The frictional behaviour of fullerenes have been studied by Zhao *et al* (1995). For the sublimated pure C_{60} films on Si (001), a high friction coefficient is observed under different loads and pin materials. For the C_{70} film, the friction coefficient shows pin dependence which changes from 0·5 with Al_2O_3 pin to about 0·9 with 440SS pin. The relatively high friction coefficient of C_{60} and C_{70} films is due to high friction coefficient of C_{60} and C_{70} particles to clump and compress into a high shear strength layer.

2. Synthesis and extraction

First Krätschmer *et al* (1990) and later Haufler *et al* (1990) gave the procedure for the production of macroscopic quantities of fullerenes. Krätschmer *et al* (1990), reported the evaporation of graphite electrodes in an atmosphere of ~ 100 torr of helium, the soot deposited as a film inside the evaporation chamber was collected and dispersed in benzene, CS_2 or CCl_4. The solution was then separated from the soot and dried by gentle heating which left a residue of dark brown to black crystalline material. Haufler *et al* (1990) used a 6 mm (O.D.) graphite rod kept in contact with graphite disk at $\sim 10^{-6}$ torr initially, and thereafter maintained the pressure of helium at 100 torr. The evaporation was accomplished by the contact arc process by 100–200 A current and an rms voltage of 10–20 V. The material was extracted from boiling toluene in a soxhlet extractor. A black powder, with a yield of 8–12% of the original graphite soot was obtained. Thin films and powder samples of the new material could be handled without special precautions. It was found to be stable in air for at least several weeks. Mass spectrometry and IR spectroscopy results suggest that C_{60} and C_{70} are the most dominant pure carbon species present in these samples.

Optical microscopic studies of the material after evaporation show a variety of crystals mainly rods, platelets and starlike flakes. All crystals exhibit a 6-fold symmetry. In transmitted light they appear red to brown, and in reflected light the larger crystals have a metallic appearance whereas platelets show interference colours.

A study by McElvany *et al* (1993) demonstrated the possibility of fullerene formation by coalescence of large cyclic species controlling reaction output by the size of the precursors. In an attempt towards the total synthesis of buckminster-fullerene, Abdourazak *et al* (1995) reported the synthesis of semibuckminster-fullerene 4 (a 'buckybowl'), the symmetrical half of buckminsterfullerene ('bucky-ball'). A number of such buckybowls ($C_{30}H_n$) can result from 'halving' buckminster-fullerene (4–8) to produce two isometric bowl-shaped units (figure 3), followed by addition of hydrogens to the dangling bonds. While the possible dimerization of 4 to C_{60} remains to be explored, these buckybowls represent an exciting new class of compounds and will likely show some unique chemistry associated with its concave as well as convex surfaces. Rubin *et al* (1996) propose an unconventional approach to the rational synthesis of stable endohedral metal fullerene complexes from polyalkynyl precursors on the basis of their remarkable property of cyclo[*n*]carbons to rearrange to fullerene in gas phase. The polyalkynyl precursor
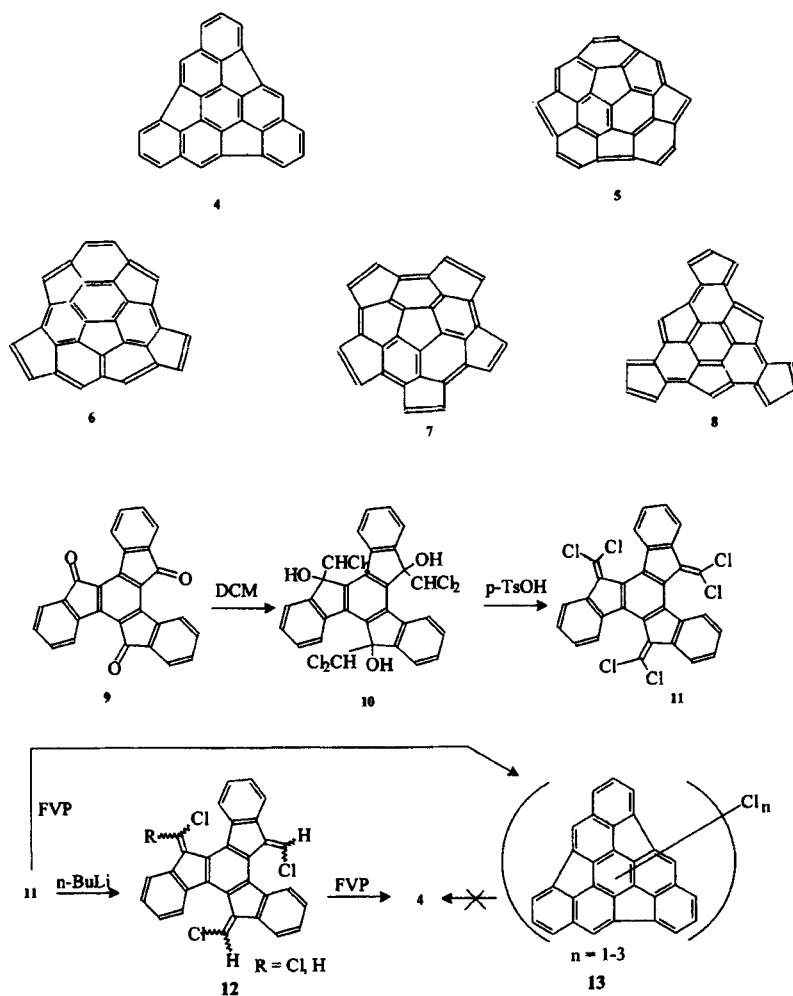
Figure 3. Synthesis of 'Buckybowl', the symmetrical half of C_{60} (DCM, lithium di-chlorohexylamine; FVP, flash vacuum pyrolysis (Abdourazak *et al* 1995)).

cyclophane ($C_{60}H_{18}$) is prepared from 1,3,5-triethynylbenzene. MALDI, FTMS and APCI negative ion mass spectroscopic studies on cyclophane show the formation of clusters of peaks ranging from $C_{60}H_{14}$ to $C_{60}H_{18}$, with $C_{60}H_{18}$ as a prominent ion.

Lamparth *et al* (1995) for the first time reported the formation of nitrogen hetero-fullerenes, $C_{59}N^+$ and $C_{69}N^+$, which are formed by the fragmentation of re-gioselectively synthesized iminofullerene derivatives. The specific arrangement of the nitrogen addends facilitates the removal of a carbon atom from the fullerene core and the incorporation of a nitrogen atom.

3. Characterization of fullerene clusters

Krätschmer *et al* (1990) characterized the new material by mass spectrometry, IR and UV absorption spectroscopy, X-ray and electron diffraction. Later Cox *et al* (1991) characterized the samples by using thermal desorption mass spectrometry with both electron impact ionization and chemical ionization detection, IR absorption, ESR, HPLC, electrochemistry and transmission electron microscopy.

Mass spectral studies indicated a very intense peak for C_{60} at 720 amu. It was evident from MS studies that air stable C_n ($n = 62, 64, 66, 68, 70$) species are present in the sample. The signal for C_{60} starts at about $300°C$ whereas the initial signal for C_{70} starts at about $350°C$. In CI–MS, the intensity ratio between the molecular anion and protonated ion is 15:1, which indicated that electron capture was much more favourable than protonation, for both C_{60} and C_{70}. Normal phase HPLC separation and FAB-MS indicated the ratio of C_{60} and C_{70} in the sample as 3:1. A 60 atom planar carbon cluster was estimated to be thermodynamically less stable than spherical C_{60}.

HPLC purified samples of C_{60} and C_{70}, dissolved in toluene and deposited onto KBr pellet showed four intense absorptions in the FTIR spectra at 1429, 1181, 576 and $527 \, cm^{-1}$ which are in accordance with icosahedral symmetry of C_{60}. A number of additional weak signals are also present in the spectrum, which according to Krätschmer *et al* (1990a,b) might be absorption by the C_{70} molecule or symmetry breaking produced by isotopes other than ^{12}C in C_{60} molecule or by mutual interaction of the C_{60} molecules in the material. Of these four dipole active vibrational modes, three at 1429, 576 and $527 \, cm^{-1}$ lie very close to C_{70} absorptions while the absorption at $1181 \, cm^{-1}$ corresponds to C_{60} only. The FTIR absorptions for C_{70} appear at 1132, 795, 674, 642 and $458 \, cm^{-1}$. Picosecond time-resolved near-IR spectra obtained by pump-probe measurement showed singlet and triplet excited state absorption for C_{60} in the region 700–1300 nm (Watanabe *et al* 1996).

Solution NMR spectra showed that C_{60} molecule had icosahedral point group symmetry (Johnson *et al* 1990; Taylor *et al* 1990). ^{13}C NMR spectra of C_{60} showed only one peak at 143 ppm, in accordance with 60 equivalent carbon atoms, while C_{70} gave five weak peaks at 150·4, 147·9, 147·2, 145·2 and 130·9 ppm in the intensity ratio of 10:20:10:20:10 corresponding to five types of carbons present (Ajie *et al* 1990; Cox *et al* 1991). Yannoni *et al* (1991) reported that in the solid state, lowering the ambient temperature down to 77 K, the rotation of C_{60} ceases to an extent such that the carbon chemical shift anisotropy can be measured.

ESR spectra of C_{60} sample recovered by a toluene rinse of the KBr pellet showed no evidence of the presence of any free radicals at room temperature (Cox *et al* 1991). Singlet atom attachment to each symmetry-equivalent carbon site should result in the formation of a unique fulleryl radical for C_{60}. Lappas *et al* (1994) reported the muon spectra of C_{70} and identified all the five isomers, resulting from Mu (the light isotope of hydrogen) addition to the five inequivalent sites of C_{70}.

D-term or nonadiabatic scattering in a resonance Raman spectrum for C_{60} indicated the presence of substantial nonadiabatic vibrionic coupling through D-term scattering between certain excited electronic states of C_{60} (Armstrong and Lay 1994).

Cyclic voltametry and differential pulse polarographic studies showed that three electrons could be added reversibly to C_n cluster. First reduction wave potential for both C_{60} and C_{70} were same even in different solvents (Wudl *et al* 1991). Theoretical calculations also indicated a triply degenerate LUMO, which suggested that at least 3 electrons could be added relatively easily.

C_{60} also possesses very high electron affinity and ionization potential, electron capture produces more sp^3 character, which decreases the strain energy, while electron loss increases the sp^2 character increasing the strain energy.

X-ray and electron diffraction studies indicated that C_{60} molecules form a regular lattice with a d-spacing of 8·7Å corresponding to the (100) reciprocal lattice vector of hexagonal lattice (Krätschmer *et al* 1990). These studies further suggest that the C_{60} molecules seem to assemble themselves into a somewhat ordered array as if they are effectively spherical, possessing partial crystallinity and shaped like soccer balls. C_{60} molecule has ∼ 7 Å diameter cavity and the nearest neighbour distance is 10·02 Å. The difference represents the effective van der Waals diameter set by repulsion of the π-electron clouds extending outward from each carbon atom.

Thermodynamic properties reported by Mathews *et al* (1992) showed the enthalpy of sublimation to be 181·4 ± 2·3 kJ/mol at 700 K and the vapour pressure as a function of temperature represented by the empirical relation:

$$\log (P/P_a) = -9777 \pm 138/T(K) + 11\cdot582 \pm 0\cdot126.$$

The STM studies for C_{60} and C_{70} layers on ordered Au(111) and Au(110) surfaces were reported by Weaver *et al* (1992) and the results showed the hexagonal close packed layer for both C_{60} and C_{70} on Au(111). On the Au(110) surface the molecules are less ordered but are held more rigidly.

Garrell *et al* (1991) used surface-enhanced Raman (SER) spectroscopy to obtain a clear picture of the surface interactions and the structure of C_{60} on gold. In the SER spectrum of pure C_{60} on gold, with no applied potential, 22 bands were clearly identified. The differences between the SER and Raman spectra provide evidence for, both C_{60} and C_{70}, a loss of symmetry and a change in the electronic structure of C_{60} upon adsorption.

Simulation studies showed C_{60} to be stable against spontaneous disintegration up to 5000 K (Wang *et al* 1992). Intersystem crossing to produce triplet state C_{60} and C_{70} are efficient in this case and triplet state energy is found to be ∼ 33 Kcal/mol (Foote *et al* 1991). Both are very potent generators of singlet oxygen and are inert towards photooxidative damage to biological systems. But the production of singlet oxygen is useful for photobiological or photopolymerization applications. A strong paramagnetic current for five-membered rings and a mild diamagnetic current for six-membered rings are reported. Due to the overall neutrality of C_{60}, the 'current per ring effect' must be larger in the five membered rings.

The successful preparation of a solid solution of C_{60} in a SiO_2 glass matrix by means of sol-gel chemistry was reported by McBranch *et al* (1994). Raman spectroscopy and X-ray diffraction were used to verify that the synthetic route produces glasses with a homogeneous dispersion of intact fullerenes. The vibration spectrum of C_{60} is preserved in C_{60}/SiO_2 gel glass.

70 nm thick SiC films were fabricated on Si (100) wafers under ultrahigh vacuum conditions by depositing C_{60} molecules on substrates held at 900°C (Chen *et al* 1994). The composition and morphology of the films are measured using IR spectroscopy and atom force microscopy.

Oxygen-induced changes in optical properties, structure and conductivity of buckminsterfullerene films have been studied by Makrarova *et al* (1995). O-exposure leads to surface layer formation on the fullerene film. A small amount of oxygen molecules penetrate into the bulk film causing depth-variation of the film-optical parameters, refractive index and extinction coefficient which is attributed to the electronic states in the HOMO and LUMO bands.

C_{60} films up to 1000 Å thick were grown by sublimation at room temperature onto Si(100) and Si(111) substrates that were prepared with surface passivation against dangling bonds. X-ray diffraction measurements reveal that films deposited on such substrates have a high degree of (111)-textured crystallinity which is absent in films deposited on untreated Si, Implications for possible device applications are also discussed (Hebard *et al* 1995).

Stable Langmuir monolayers of monosubstituted C_{60}–malonic acid were formed on pure water and on solutions containing Ca^{2+} or Cd^{2+} ions (Patel *et al* 1996). The results of surface pressure–area isotherm studies for C_{60} $[C(COOH)_2]$ suggested that the divalent cations intercalate between monolayers to give expanded films that can be compressed to solid phases, but on further compression revert back to close-packed monolayers depleted of metal ions.

C_{60} molecules were incorporated into the interlayer of a layered Mg/Al double hydroxide compound and the physicochemical properties of these spherical molecules arranged in two dimensional arrays were examined (Wen-Yi *et al* 1996). To identify the C_{60} environment solid state ^{13}C NMR was employed. The results indicate that C_{60} molecules do not rotate as freely as in the pure solid form and experience rather intimate interactions with either the interlayer proton-containing species or the lattice atoms.

Endo *et al* (1996) adopted electrochemical methods to obtain A_xC_{60} (A = Rb) film from an organic electrolyte solution including C_{60} molecules. The used solution was a mixture of 0·3 mM-C_{60}, 0·1N-$RbClO_4$ and DMF. The particles in the obtained film had a spindle like shape and grew up to the size of ~ 1 μm depending on the reaction temperature. Raman spectra of the film showed the existence of solid C_{60} and revealed the features of polymeric RbC_{60}.

A novel complex thin film of 2,6-*bis*(2,2-bicyanovinyl)pyridine (BDCP) and C_{60} have been fabricated by vacuum co-evaporation of BDCP and C_{60} from different evaporation sources (Ouyang *et al* 1996). The C_{60}-BDCP thin films have shown totally different optical and electronic properties from the films of both the BDCP and C_{60}. Stable and reproducible electronic bistable properties have been observed in sandwich like devices Ag/C_{60}-BDCP/Ag.

Fullerenes, due to their strong electron accepting ability can be hole generators in conducting polymers sensitizing photoinduced charge transfer. The photoconductivity of poly(2,5-dialkoxy-*p*-phenylene-vinylene) is enhanced by several orders of magnitude upon introduction of several mole % of C_{60} (Yoshino *et al* 1993). Positive polarons photogenerated with increased efficiency due to automization of

excitons and/or photopumping from fullerene are considered to be responsible for enhanced photoconductivity. Photoluminescence of polymer is strongly quenched upon C_{60} doping due to dissociations of excitons accompanied by electron transfer to fullerene. The resonant nonlinear optical (NLO) properties and excited dynamics of pristine, chemically and photochemically modified C_{60} are studied at 590·5 nm by time-resolved degenerate four wave mixing and nonlinear transmission (Kafafi *et al* 1994). The chemically modified fullerene consists of (i) composite films of C_{60} with meso-tetraphenyl porphine (TPP) prepared by vacuum vapour deposition and (ii) spin-coated films of solutions C_{60} mixed with the conjugate polymer, poly-[2-methoxy,5-(2'-ethylhexyloxy)-*p*-phenylene vinylene] (MEH–PPV). Photopolymerization of C_{60} leads to an enhancement of its physical properties without substantial alteration of its NLO properties. C_{60} and TPP form a ground state charge-transfer complex with an enhanced NLO response. C_{60} and MEH–PPV form a charge-transfer complex in the excited state, which gives rise to more than an order of magnitude increase in the NLO response for C_{60}, poly-C_{60}, C_{60}: TPP and C_{60}: MEH–PPV films. Lee *et al* (1994) reported the results of comprehensive measurements of photoconductivity in films of MEH–PPV and MEH-PPV/C_{60} composites. The peak transient photoconductivity of MEH–PPV is proportional to the light intensity and electric field, and independent of temperature. The transient photoconductivity (life time and magnitude) of MEH–PPV increases substantially on increasing the concentration of C_{60} in MEH-PPV/C_{60} composite films. To account for the observed photoinduced absorption, Conwell *et al* (1995) determined the position of C_{60} relative to MEH–PPV chains. With the use of Monte-Carlo cooling algorithm, the most probable position of C_{60} is in channel formed by the alkoxide chains, its center ~ 10 Å from that of the MEH–PPV backbone. Photoexcitations in MEH–PPV and MEH-PPV/C_{60} composites were also studied by photoinduced absorption and absorption detected magnetic resonance spectroscopy (Wei *et al* 1996). The authors provide direct evidence that the prominent triplet photoexcitations in pristine MEH–PPV are effectively quenched in MEH-PPV/C_{60}.

The introduction of 1% of fullerenes into polystyrene matrix leads to a significant increase in the electrical conductivity of the system (Aleshin *et al* 1995). Films of fullerene containing PS are prepared by mixing toluene solutions of PS and C_{60} and developed on Si, GaAs and glass substrates. The general features of charge transfer processes in fullerene/conducting polymers (CP) systems, such as energetics of photoinduced charge transfer (PCT) between C_{60} and CP π-electronic states, geometry of π–π overlapping and the role of self trapping effects to polaronic states on C_{60} and CP chains on the PCT dynamics are analysed (Yoshino *et al* 1995).

4. Reactivity of fullerenes

Stability of fullerenes is a balance between strain and aromaticity. Although previously C_{60} was predicted to be stable, later it was found to be much more reactive. Stability of this molecule was attributed to it being the smallest fullerene in which all the 12 pentagons are isolated from each other. Schmalz *et al* (1986), Hosoya (1986), Brendsdal and Cyvin (1989), and Klein *et al* (1986) (counting the Kekule structure of

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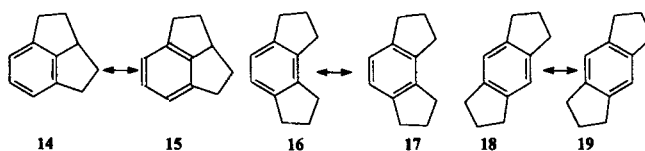
Figure 4. A hexagon fused to two pentagons is shown as three resonating pairs. In structure **16** a double bond does not exist on a five-membered ring.

buckminsterfullerene) reported that 12,500 resonance structures are possible in C_{60}. Let us consider a situation where a six-membered ring containing three alternate π-bonds is fused to two five-membered rings. Three possibilities would arise, each existing as a resonating pair (figure 4). Of the six possible structures, in one structure (**16**) there is no double bond at the [5,6]-ring junction. A double bond in a five-membered ring increases strain and therefore decreases stability. For fullerene to be structurally stable, all the double bonds should be placed in such a manner that there would be no double bonds at the [5,6]-ring junction. Hence out of the 12,500 possible resonating structures of fullerene, there is only one structure in which the double bonds are localized, no double bonds being present at the [5,6]-ring junction making fullerene a reactive molecule containing 60 π-bonds. Thus C_{60} exhibits less aromaticity than benzene. Due to the lack of delocalization, the bond length of $C=C$ bonds in fullerene are less than that in benzene. The reactivity of C_{60} is not like that of electron rich planar aromatic molecules. The C–C double bonds of C_{60} react like those of very electron deficient arenes and alkenes. Therefore C_{60} behaves as an electron deficient 'superalkene' rather than as a 'superaromatic'. Due to electron attracting nature, it readily reacts with nucleophiles.

Fullerenes do not undergo any substitution reaction because of nonattachment of any hydrogen or other groups to the carbon framework. But, these molecules undergo various types of addition reactions with polyconjugated and electron deficient alkenes, and also polymerization reaction with various reagents are known. The derivatives of fullerene show a wide range of solubility and differ in many respects from parent molecule.

C_{60} appears to be more electrophilic than C_{70} evidenced from ^{1}H NMR of hydrogenated fullerene. Fullerenes undergo halogenation, oxygenation, metalation and methylation via either thermal, photochemical, electrophilic, nucleophilic or radical path. There are twelve pentagons in C_{60} arranged in the form of six pyracylene units (**20**) (figure 5). Six electrons can be reversibly added to both C_{60} and C_{70} across the pyracylene unit present in fullerene. Addition of one electron to each pyracylene unit creates aromaticity in one of the pentagonal rings (figure 6). This is the driving force for octahedral addition.

C_{60}, with icosahedral (I_h) symmetry, has only one type of carbon atom and two types of C–C bonds i.e. at the [6,6]- and [5,6]-ring fusion sites. But C_{70} has D_{5h} symmetry and it consists of 5 types of carbon atoms (figure 7), i.e. a–e and eight types of C–C bonds (Balch *et al* 1991). Thus 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.
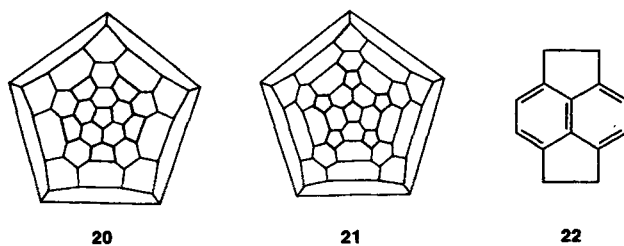
Figure 5. Schegel diagram of C_{60} (20) and C_{70} (21) showing the arrangement of the pentagons and the hexagons forming the pyracylene units (22) (Taylor and Walton 1993).
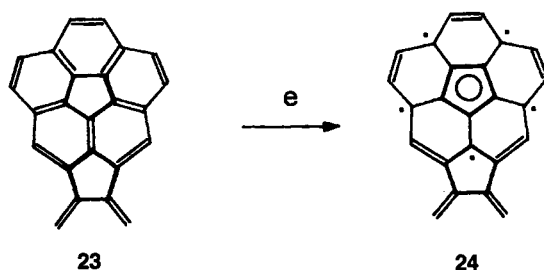
Figure 6. Addition of electron to a pyracylene unit creates aromaticity in the pentagonal rings (Taylor *et al* 1993).
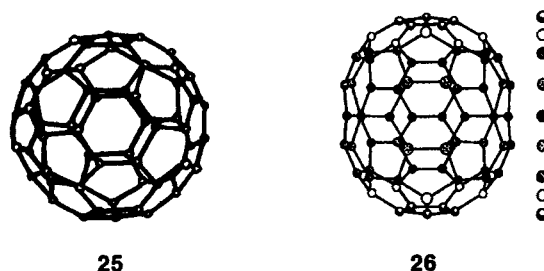
Figure 7. C_{60} has one type of carbon atom and two types of C–C bonds whereas C_{70} has five types of carbon atoms and eight types of C–C bonds (Balch *et al* 1991a).

C_{60} and C_{70} are decomposed by light, with oxygen and ozone playing the crucial role. Mass spectroscopy studies indicate that the molecules undergo complete fragmentation. Fragmentation is less if carried out under nitrogen. Films of C_{60} degrade on storage because of the ability of C_{60} to chemisorb oxygen and on heating in oxygen, C_{60} gradually gets oxidized. IR and NMR spectra of the degraded products (Taylor *et al* 1991) indicate that C–H (including aromatic C–H), C=O, C–O, C=C, substituted aromatic or alkene, C=C, C_2H_5, CH_2, alkyl-O, $\sim CH_2$–O groups are

present. Ozonolysis of fullerene C_{60} generated a mixture of oxidized products having ketone, ester and epoxide functionalities (Malhotra *et al* 1994).

C_{60} acts as both oxidizing and reducing agent. The oxidizing properties of C_{60} are evident from the oxidation of H_2S to sulphur in the presence of C_{60}. Similarly, C_{60} also undergoes reduction under Birch reduction conditions by hydrogen with Pt catalyst, diimide, hydrogen transfer reagents such as dihydrophenanthrene and diborane in THF to give hydrofullerene i.e. $C_{60}H_{18}$, $C_{60}H_{36}$ and $C_{60}H_2$ (Taylor and Walton 1993). C_{70} also undergoes reduction, and hexaanion formed is more stable in case of C_{70} and the addition across each pyracylene unit yields $C_{70}H_{12}$.

5. Exo- and endohedral complex chemistry

The structure of C_{60} is comprised of rigid spheres of radius 4·98 Å with fcc packing ($a = 14·1$ Å), leaving two vacant tetrahedral sites and one octahedral site per C_{60} molecule. These sites are of sufficient size to accommodate spheres of radius 1·12 Å and 2·06 Å respectively. Due to the ~ 7Å diameter of C_{60} cavity, other elements and small molecules can be encapsulated into the cavity, which alters its physical and chemical properties (Freiser *et al* 1991).

McElvany and Callahan (1991) reported the protonation of C_{60}, C_{70}, C_{76}, C_{80} and C_{84}, which were detected by triple quadruple and FT mass spectrometry and the proton affinity lies between that of ammonia and hexamethyl benzene, being close to NH_3, and proton affinity of C_{70} is greater than that of C_{60}. Proton transfer could occur between CH_5^+, H_3O^+, $CH_3 OH_2^+$ and NH_4^+ and the fullerene nucleus.

$C_{60}H^+$ can also be generated by the reaction of C_{60}^+ ions with atomic hydrogen and this can react with another hydrogen atom giving rise to fullerene ion and molecular hydrogen. This reaction is thermodynamically allowed. The molecular hydrogen is responsible for surface recombination of instellar dust grains. C_{60}^+, C_{60}^{2+}, C_{70}^+ and C_{70}^{2+}, all can react with atomic hydrogen (Petrie *et al* 1992) and finally $C_{60}H_n^+$, n up to 3 and $C_{60}H_n^{2+}$, n up to 4 are formed. A slow hydride transfer between C_{60}^{2+} and the saturated hydrocarbon molecules such as C_3H_8, n-C_4H_{10} and i-C_4H_{10} has been observed in SIFT experiments (Bohme *et al* 1992):

$$C_{60}^{2+} + RH \longrightarrow C_{60}H^+ + R^+$$
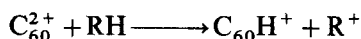
Endohedral complex with heliu ɪn be formed by the high energy collision of C_{60} and C_{70} radical cations with helium target to form C_nHe^+ ($n = 48-58$) (Gross 1991). This group of workers also studied (Gross *et al* 1992) high energy collisions of C_nHe^+ with D_2, N_2, NO or O_2. A four sector tandem mass spectrometer was used to study the collision reactions. It was observed that the small target gases got incorporated into the intact fullerene radical cations resulting in endohedral complexes.

C_{60} under single collision conditions over the energy range from 2 to 78 eV (Anderson *et al* 1992) reacts with C^+ giving rise to C_{61}^+, which decays to C_{60}^+ and C resulting from charge transfer. The exchange has been demonstrated by ^{13}C labelling, the ^{13}C projectile undergoing exchange with C atoms in the C_{60} target.

Green *et al* (1994) reported the incorporation of elemental phosphorous into hexagonal packed C_{60} to give $[(P_4)_2C_{60}]$, and solid state NMR shows that P_4
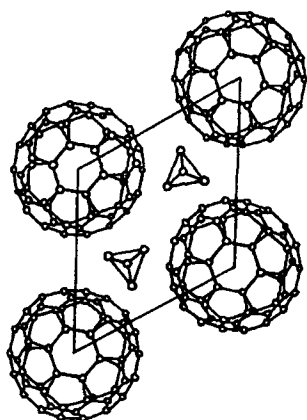
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Figure 8. Incorporation of P_4 tetrahedra to the trigonal prismatic sites of C_{60} (Green *et al* 1994).

tetrahedra occupy trigonal prismatic sites and confirm the retention of molecular nature of the P_4 guest (figure 8). Intercalation of Li into solid C_{60} is reported and the electrochemical formation of $[(C_6H_5)_4P]_3(C_{60})Cl_2$ as microcrystalline powder is obtained. $Na_xC_{60}(THF)_y$ is the first metallic single crystal of C_{60} grown by an electrocrystalline process (Kobayashi *et al* 1994). The formation of single crystal $\{N[P(C_6H_5)_3]^{2+}\}C_{60}$ is reported (Kobayashi *et al* 1993). A phosphine or phosphinite bearing fullerene was synthesized by the reaction of a lithiated phosphine borax or a phosphinite borane with C_{60} followed by removal of the BH_3 group, the substituent undergoing complexation with BH_3 and $PtCl_2$ selectively on the phosphorous atom (Nakamura *et al* 1994).

The formation of $C_{60} S_{16}$ and $C_{70} S_{48}$ has been reported by the addition of S_8 rings to C_{60} and C_{70} respectively (Roth and Adelmann 1992). A $C_{60}2S_8$ complex was produced by reaction of C_{60} with S in trichloroethylene and its single crystal X-ray surface was studied at room temperature (Buravov *et al* 1994). The crystal structure of the $C_{60}2S_8$ complex is a packing of fullerene molecules which form hexagonal channels along the c-axis with eight-membered cyclic molecules of S_8 with the crown conformation inside the channels. The mean value of the C_{60} sphere radius is $3\cdot49(2)$ Å. Each C_{60} molecule is linked to eight S_8 molecules with the shortened intermolecular contacts C......S $3\cdot41(3)$ Å which testifies to a significant extent of localization of electron density in the C_{60} molecule.

C_{60} undergoes hydrosilylation in the presence of Pt or Co catalyst. With HSiMe $(OEt)_2$ hydrosilylation is accompanied by some condensation of the silicon moiety producing H_nC_{60}-$[SiMe(OEt)OR]_{n+m}$ where R = Et or SiMe(OEt)H (West *et al* 1994). Hydrolysis of the product with Si$(OEt)_4$ gave a yellow–orange sol-gel glass with average composition $H_{12}C_{60}$ $[(SiMe_2O)_3 SiMe_2H]_{12}$. Hydrosilylation of C_{60} with a linear siloxane polymer containing Si–H bonds along the chain led to

multiple substitution onto the C_{60} framework with the siloxane effectively 'wrapping up' the fullerene.

The discovery of superconductivity and ferromagnetism in salts of C_{60} has focussed attention on the electronic and structural properties of fulleride ion C_{60}^{n-}. Both C_{60}^{2-} and C_{60}^{3-} salts have been isolated and their electronic ground state disobey Hund's rule and as in the case of C_{60}^{-}, the Jahn-Teller theorem predicts a distortion from icosahedral symmetry to remove orbital degeneracy in the $(t_{1u})^n$ LUMO (Paul *et al* 1994).

The metal fullerene complexes were produced by laser vapourization of the metal–graphite mixture under high temperature/argon flow conditions (Smalley *et al* 1985, 1988). MC_{60}^{+}, the formation of which was detected by FTMS and is found to be very stable and can be fragmented only under extreme activation conditions of multiphoton absorptions at high ArF excimer laser and then by sequential loss of the C_2 species (Smalley *et al* 1988). Exohedral MC_{60}^{+}, M = Li-Cs, Fe, Co, Ni, Cu, Rh, La, U and VO were formed by the direct attachment of M^{+} with C_{60} and varying the amount of C_{60}^{+} by charge transfer. In all the above cases the metals are attached externally to the fullerene cage (Freiser and Huang 1991; Freiser *et al* 1994).

The synthesis of alkali metal intercalated fullerite superconductors (M_xC_{60}, x = 3) are reported by Fischer and Smith (1991). Wudl *et al* (1992) reported the superconductivity for K_3C_{60} at 18 K. Broderick (1994) reported the solution phase synthesis of superconducting M_3C_{60} via soluble alkali metal fulleride precursors. Intercalation of alkali metals by reduction of fullerene to give fullerides M_nC_{60}(M = Li–Cs and n = 0·5–6) is reported (Murphy *et al* 1993). The synthesis of intercalated compounds of fullerenes using thermal decomposition of azides of K and Na was reported by Okotrub *et al* (1994). The preparation of K_3C_{60} and K_2NaC_{60} is by reacting KN_3, NaN_3 and C_{60}–C_{70} mixtures at ~ 390°C. The presence of C_{70} affects the amount of superconducting phase formed and lowers the T_c. Henry *et al* (1995) reported the reaction of face-centered cubic Na_3C_{60} with ammonia at room temperature. The product $(NH_3)_6Na_3C_{60}$ in which both octahedral and tetrahedral interstices in the fulleride array are occupied, despite the similarity in C_{60}^{3-} packing to that in CsC_{60}, shows no superconductivity above 6 K. M_6C_{60} and M_6C_{70} (M = Cs, K, Na) exhibit remarkable catalytic activities in H_2–D_2 exchange and olefin hydrogenation at low temperature. The catalytic activities of M_6C_{60} in H_2–D_2 exchange are strongly dependent on metal size, reactivity decreasing in the order $Cs \gg K \gg Na$. The synthesis of a new ternary fulleride Ba_2CsC_{60} was reported by Duggan *et al* (1996) by reduction of C_{60} by metals in liquid ammonia followed by crystallization at high temperature. The fulleride adopts a novel orientation ordering of the anions in which the Ba cations occupy the tetrahedral sites and Cs the octahedral sites.

Fe^{+} undergoes ligand exchange reactions with preformed C_{60} and C_{70} to generate FeC_{60}^{+} and FeC_{70}^{+} (Freiser *et al* 1991). Freiser *et al* (1992) reported the direct attachment reaction of CoC_{60}^{+} with C_{60} to form $Co(C_{60})^{2+}$. It also pulsed in ethylene, propene, 1-butene and isobutene to form $C_nH_{2n}CoC_{60}^{+}$ (n = 2 – 4), which undergoes ligand displacement reaction with C_{60} to form $Co(C_{60})^{2+}$:

$$CoC_{60}^{+} + C_nH_{2n} \longrightarrow C_nH_{2n}CoC_{60}^{+}$$

$$C_nH_{2n}CoC_{60}^{+} + C_{60} \longrightarrow Co(C_{60})^{2+} + C_nH_{2n}$$
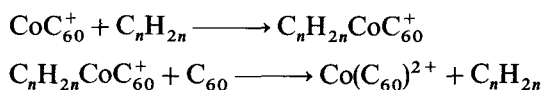
Fe (benzyne)$^+$ and Fe (biphenylene)$^+$ react with C_{60} to form Fe C_{60} $(C_6H_4)^+$ and FeC_{60} $(C_6H_4)^{2+}$. The former also undergoes charge transfer reaction with C_{60} to form C_{60}^+ (Freiser *et al* 1995). Here C_{60} behaves like a highly polarizable alkene and an electron deficient arene.

$$Fe^+ + C_6H_5Cl \longrightarrow Fe\,C_6H_4^+ + HCl$$

$$FeC_6H_4^+ + C_6H_5Cl \longrightarrow Fe(C_6H_4)^{2+} + HCl$$

$$Fe(C_6H_4)^{n+} + C_{60} \xrightarrow{n=1,2} C_{60}Fe(C_6H_4)^{n+}$$

$$\xrightarrow{n=1} C_{60}^+ + Fe(C_6H_4)$$

$$C_{60}Fe(C_6H_4)^{n+} + C_6H_5Cl \xrightarrow{n=1,2} C_{60}(C_6H_4)^{n+} + C_6H_5FeCl$$
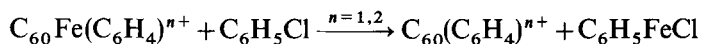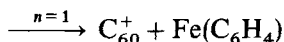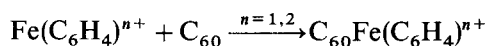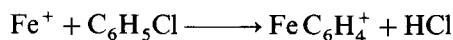
C_{60}^+ reacts with $Fe(CO)_5$ in gas phase to give $Fe(CO)_4C_{60}^+$ and $Fe(CO)_3\,C_{60}^+$ by the elimination of CO and 2CO respectively in equal amounts. C_{60} acts like two electron donor species similar to an alkene ligand, exhibiting a rich exo-coordination chemistry (Freiser *et al* 1992; Kellogg *et al* 1992). Chromium coordinated C_{60}^- has been identified from ESR measurements (Wudl *et al* 1991).

Chai *et al* (1991) found that lanthanum fullerene complex LaC_{82} is soluble in toluene and can be extracted by this solvent. ESR spectra indicated charge-transfer complex of the form $La^{3+}C_{82}^{3-}$ (Johnson *et al* 1992). Similarly Shinohara *et al* (1992) reported the presence of metallofullerenes such as YC_{60}, YC_{70}, YC_{82} and Y_2C_{82}. ESR spectra of these complexes also indicate charge separation state of $Y^{3+}C_{82}^{3-}$. Reactions of excimer laser vapourized and excited fullerene C_{60} with La, Y, Eu and Gd were carried out in the mixtures of C_{60}/La_2O_3, C_{60}/Y_2O_3, C_{60}/Eu_2O_3 and C_{60}/Gd_2O_3 (Huang *et al* 1995). The reaction products MC_{60}, MC_{60-2n} and MC_{60+2n} (M = La, Y, Eu, Gd) were identified by a reflection type time-of-flight mass spectrometer. The products were subjected to reactions with H_2O, O_2 and N_2O. The metallofullerenes are nonreactive toward these molecules due to the endohedral nature of the materials.

Fullerenes with a metal inside the cage have long attracted attention as new chemical entities with novel properties as summarized in a recent review on endohedral complex (Bethune *et al* 1993). Endohedral complex M @ C_{60}^+(M = La, K, Cs, He, Ne, Ar, Y, H_2) have been formed in the gas phase and M @ C_{70}^+ can be formed by the reaction of $M@C_{60}^+$ and C_{70} (Gross 1991; Ross and Callahan 1991; Gross *et al* 1992; Freiser *et al* 1995). Cosmic ray interactions may also lead to the formation of endohedral complexes of H, D and He trapped in fullerene cages.

La, radioactive ^{159}Gd and ^{161}Tb can be encapsulated into the fullerene cage by neutron irradiation. The radioactive endohedral metallofullerenes were found to be stable and separable as normal metal complexes. By means of density functional calculations, the ionization energies and electron affinities of Sc @ C_{82}, Y @ C_{82} and La @ C_{82} are predicted by Nagase and Kobayashi (1994). The results are compared with those of typical empty fullerenes such as C_{60} and C_{70}. The endohedral metallofullerenes are regarded as a sort of 'super atom'. The charges on the metal is little changed even when M @ C_{82} loses or accepts an electron. This allows the formal view that electron removal or gain takes place on the C_{82} cage, with the metals acting as a positive core. The first derivatization of an endohedral metallofullerene

La @ C_{82} yielding an exohedral adduct was reported by Akasaka *et al* (1995). These workers also studied the variation of chemical properties of the endohedral complex with different encapsulated metal atoms. Gd @ C_{82} was derivatized with 1, 1, 2, 2-tetramesityl-1,2-disilirane by photoirradiation and thermal reaction. Though the disilirane did not add thermally to empty fullerenes such as C_{60}, C_{70} and C_{82}, a facile thermal addition to Gd @ C_{82} took place. This is because Gd @ C_{82} is a stronger electron acceptor than empty fullerenes.

Edelmann (1995) in a recent review discussed several endohedral metallofullerenes Ln @ C_{2n} (Ln = Sc, Y, La, Ce, Gd; $n = 37$–45), Ln_2 @ C_{80} (Ln = Sc, La), Sc_2 @ C_{2n} ($n = 37$, 41, 42) and Sc_3 @ C_{82}. Scandium preferably forms endohedral fullerene complexes with two atoms trapped inside the fullerene cage (Sc_2 @ C_{74}, Sc_2 @ C_{82} and Sc_2 @ C_{84}). Other major species that form during the course of reaction are Sc @ C_{82} and Sc_3 @ C_{84}. In Sc_3 @ C_{82}, the three Sc atoms form an equatorial triangle. Metallofullerenes of Sc, Y and La are produced by arc-vapouring mixtures of graphite and lanthanide oxide rods in helium atmosphere. The yield is however only 0·1% of the product soot. A 10-fold increase in the yield of La @ C_{82} is achieved by adopting graphite rod with lanthanum carbide instead of lanthanum oxide rods in helium atmosphere. The metal-filled complex is associated with empty fullerenes, which are separated by silica-packed HPLC column in which tetraphenylporphyrin moieties are anchored to silica surface through carboxyl groups.

Nagashima *et al* (1992) reported an organometallic polymer $C_{60}Pd_n$, which was prepared from C_{60} and a Pd° and the ratio can be varied by thermal disproportionation. In this case palladium atom acts as a binder of C_{60} by coordination to the π-electron on the aromatic surface and two C_{60} atoms are bound to one palladium atom. This polymeric species are neutral, amorphous and stable to air. $(R_3P)_2$ PdC_{60} (toluene) (R = Ph, cyclohexyl) were prepared in high yields by treating $Pd_2(dba)_3$ (dba = dibenzylideneacetone) with R_3P in toluene followed by treating with C_{60} (Anon 1994). Pt complexes of C_{60} and C_{70} were synthesized and characterized by using spectroscopic analysis (Iyoda *et al* 1995). The X-ray data of $(Ph_3P)_2Pt(\eta^2-C_{60})$ containing no solvent of crystallization affords definite bond lengths and angles. Organopalladium or platinum complexes $(\eta^2-C_{60})M(CNR)_2$ (M = Pt, Pd; R = ^{t}Bu, 2,6-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, cyclohexyl) were synthesized from $C_{60}M_n$ (M = Pd, Pt) and from the corresponding isonitriles (Nagashima *et al* 1996).

Treatment of C_{60} with stoichiometric amounts of both $[Cp^*Ru(\mu-H)_2]$ ($Cp^* = C_5H_5$) and $(Cp^*RuCl_2)_2$ produced $Cp^*Ru_2(\mu-H)(\mu-Cl)(C_{60})$, which contains a Ru fragment bound to two conjugated C–C π-bonds (Mavunkal *et al* 1995). The related C_{60} derivative $Cp^*_2Ru_2(\mu-Cl)_2$ (C_{60}) was obtained by using two equivalent of $(Cp^*RuCl_2)_2$. Formation of a transient cationic species $(Cp^*RuC_{60})^+$ is suggested from FAB mass analysis. Ru-C_{60} compounds were prepared by reaction of $Ru_3(CO)_{12}$ with C_{60} in refluxing toluene (Wohlers *et al* 1996). The resulting air-stable solid consists of an amorphous matrix in which we embedded small Ru metal particles of an average size of 2·5 nm. The catalytic activity of Ru-C_{60} compounds at different temperatures is shown in prototype reactions like the liquid phase hydrogenation of cyclohexene at 300 K or the hydrogenation of CO in the Fischer–Tropsch synthesis at 500 K. Photolysis of a 2:1 mixture of $Mo(CO)_4$ (diphos)
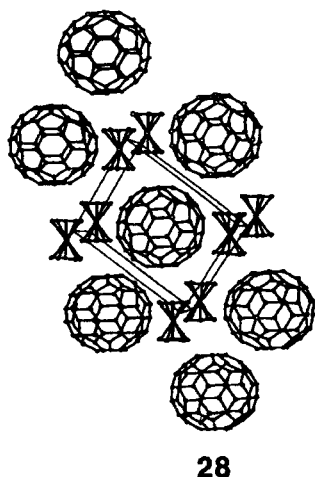
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Figure 9. Cocrystallization of C_{60} with ferrocene (Taylor and Walton 1993).
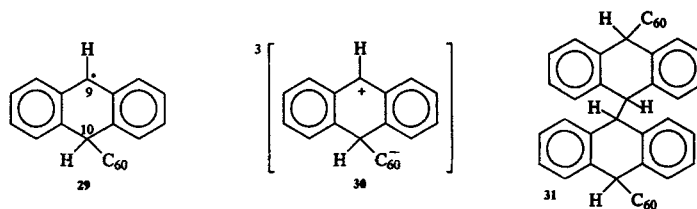

**Figure 10.** EPR-active adduct of $^3C_{60}$ to anthracene: biradicals and zwitterions (Klemt *et al* 1995).

(diphos = 1,2-diphenyl phosphinatoethane) and activated alumina with toluene provides the derivatives $C_{60}[Mo(CO)_3(diphos)]_n$ in varying yields depending on the value of n (Hsu and Shapley 1995).

Fullerenes show a marked tendency to crystallize with solvent molecules trapped in the lattice to form host–guest complexes such as $[C_{60}(\gamma\text{-cyclodextrin})_2]$ (Anderson *et al* 1992; Kuthner *et al* 1992) and $[C_{60}(1,4\text{-hydroquinone})_3]$ (Ermer 1991). C_{60} also formed charge-transfer complex with $[bis(\text{ethylenedithio}) \text{tetrathiafulvene}]$ (Izuoka *et al* 1992).

C_{60} co-crystallized with ferrocene to give black C_{60} (ferrocene)$_2$ and this species is stabilized by weak intermolecular charge transfer interactions (figure 9) (Kroto *et al* 1992). There are reports of various inclusion complexes such as $[Fe(\eta\text{-}C_5H_5)_2]_2C_{60}$ (Kroto *et al* 1992), $[(I_2)_2C_{60}]$ (Cox *et al* 1992) and benzene solvated species, $[C_{60}\cdot4C_6H_6]$ (Kroto *et al* 1992; Balch *et al* 1993). C_{60} reacts with anthracene thermally and photochemically. From EPR studies Klemt *et al* (1995) proposed that the EPR-active intermediates are triplet zwitterions or biradicals (figure 10). A covalently functionalized fullerene comprising an electron donating aniline group coupled to
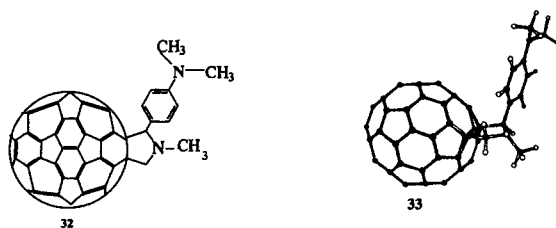
Figure 11. Bridged C_{60}-aniline system: the first active fullerene diad and AM1 structure of the compound (Williams *et al* 1995).
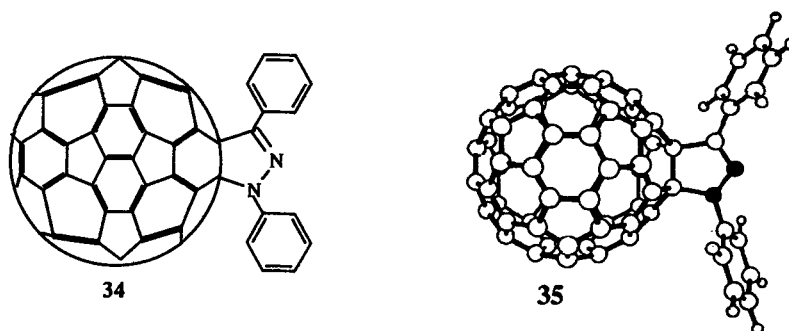
Figure 12. Intramolecular charge-transfer interaction in 1,3-diphenyl-2-pyrazoline ring-fused C_{60} with AM1 structure of the cycloadduct (Matsubara *et al* 1995).

fullerene unit by a saturated heterocyclic bridge (figure 11) is shown to undergo a photoinduced electron transfer process (Williams *et al* 1995). Charge-transfer interaction between benzene ring and a C_{60} sphere is studied in 1,3-diphenyl-2-pyrazoline ring fused C_{60} (figure 12) (Matsubara *et al* 1995). It is observed that the N-phenyl group interacts with C_{60} more strongly than the C-phenyl groups. Electron-transfer reaction between C_{60} radical ion and carbazole cation (Car^+) to produce an excited state of C_{60} has been studied by Gupta and Santhanam (1994):

$$C_{60}^{-} + Car^+ \longrightarrow C_{60}^* + Car$$

$$C_{60}^* \longrightarrow C_{60} + h\nu.$$
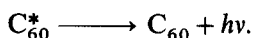
Polar neutrals featuring electronegative atoms such as O or N can also form adducts with C_{60}^{2+} in the gas phase (Bohme *et al* 1992, 1993). The various polar neutrals are NH_3, CH_3NH_2, $C_2H_5NH_2$, $RCN(R = CH_3$, C_2H_5, C_3H_5, n-C_3H_7 and i-C_3H_7), CH_3COCH_3, $CH_3COCH_2CH_3$, HCOOH and CH_3COOH. In some of the cases the formation of secondary adducts is observed. But in case of C_{60}^+ and C_{60}^{3+} only mono and tertiary adducts are formed. So it is possible by gas phase ion
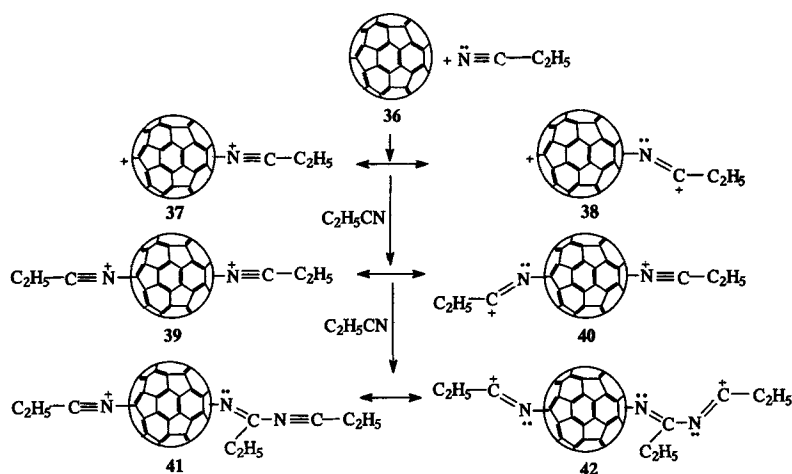
Figure 13. Attachment of C_2H_5CN as 'handles' to C_{60} (Bohme *et al* 1993).

molecule reaction to add one 'handle' to $C_{60}^{\cdot+}$, two to C_{60}^{2+} (figure 13) and three to $C_{60}^{\cdot 3+}$. Charge transfer reactions have also been reported for two fullerene dications (C_{60}^{2+} and C_{70}^{2+}) reacting with benzene, naphthalene, anthracene, C_{60} and C_{70} under SIFT conditions. Solutions of C_{60} and a substituted naphthalene give rise to a new adsorption band that is not observed from solutions containing only C_{60} or the naphthalene (Scurlock and Ogilby 1995). The absorption maximum of this new band successively shifts to a longer wavelength as the ionization potential of the naphthalene decreases. These data reflect a C_{60}-naphthalene cooperative adsorption from a ground state contact complex to form an excited-state complex with charge-transfer character. A 1:1 inclusion complex has been synthesized by the reaction of *p*-tert-butyl-calix[8] arene with C_{60} in toluene solution, and identified with IR spectra, elemental analysis, X-ray powder diffraction and solid state ^{13}C NMR studies (Cai *et al* 1995) which led to the conclusion that C_{60} is encapsulated in hydrophobic cavity of *p*-tert-butyl calix[8]arene. This implies that the interaction between C_{60} and *p*-tert-butyl-calix[8]arene is weak.

6. Addition reactions

6.1 *Addition of hydrogen*

C_{60} may catalyze autooxidation of hydrides. Under Birch reduction conditions, $C_{60}H_{18}$, $C_{60}H_{36}$ and $C_{60}H_2$ have been isolated and found to be strongly acidic (Haufler *et al* 1990). $C_{60}H_2$ is unstable in the presence of C_{60}. A T_h symmetry has been inferred for $C_{60}H_{36}$. The proposed structure of $C_{60}H_{36}$ consists of only iso- lated double bonds and not conjugated or aromatic double bonds. This is due to the

ability of the latter to undergo Birch reduction. Transfer hydrogenation of C_{60} with dihydroanthracene produces $C_{60}H_{18}$ or $C_{60}H_{36}$ depending on the reaction conditions (Buhl *et al* 1995). Hydrogen radical induced hydrogenation of fullerite (a mixture of crude C_{60} and C_{70}) was also reported to produce $C_{60}H_{36}$ at elevated temperature. The computed endohedral ^3He NMR chemical shifts of the $C_{60}H_{36}$ isomers can be related semiquantitatively to the ring current and anisotropic effects of benzene and ethylene moieties present.

The direct solid state synthesis of $C_{60}H_2$ was carried out by controlling the amount of hydrogen introduced into the reaction with C_{60} (Morosin *et al* 1994). Palladium hydride has been used as the source of hydrogen. In addition to $C_{60}H_2$, small amounts of $C_{60}H_4$ have been obtained. Electrochemical behaviour of $C_{60}H_2$ is very similar to the parent fullerene i.e. C_{60}, with $C_{60}H_2$ being only slightly difficult to reduce (Guarr *et al* 1993). The addition of a single electron is sufficient to induce conversion of $C_{60}H_2$ to C_{60}. $C_{60}H_2$ undergoes a net oxidation under 'reducing' conditions.

Darwish *et al* (1996) reviewed the previous work on polyhydrogenation of fullerenes. The most probable structure of the hydrides, based on their aromaticity is presented.

Zinc/conc. HCl is an excellent and rapid reducing agent for benzene or toluene solutions of fullerenes at room temperature. The polyhydrogenated species are unstable towards light and undergo oxidative degradation. In absence of light and oxygen, $C_{60}H_{36}$ exhibits high thermal stability. Further reduction of $C_{60}H_{34}$ gives trimethylene adducts.

6.2 *Addition of halogens*

Halogens can add to the carbon framework of C_{60} clusters. A maximum of twentyfour groups can be added to C_{60} without any two groups being adjacent. Figure 14 shows 24 nonadjacent sites in the C_{60} framework.

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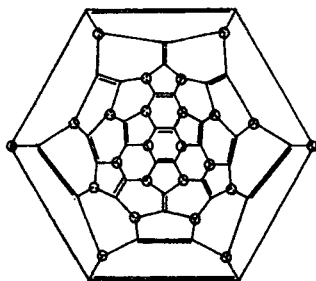
Figure 14. Schegel diagram showing twentyfour nonadjacent sites in C_{60} (Taylor and Walton 1993).

Halogens such as fluorine, chlorine, bromine and iodine can add to the fullerene framework in different proportions giving varieties of products. In the stabilities of the various isomers generated by the addition of halogens to the conjugated double bonds of C_{60} to form $C_{60}X_n$ have indicated a strong preference for 1, 2 addition with X = F and Cl, while preference for 1, 4 addition with X = Br and I (figure 15) due to large size of Br and I in comparison to other. The 1, 2-isomers will be clearly destabilized by steric interaction as X becomes larger.

Mass spectrometric results provide evidence that the reaction of C_{60} with bromine and $FeCl_3$ in benzene produces the species $C_{60}Ph_n$ ($n = 6, 8, 12$ and 16), indicating that Friedel-Crafts reaction of benzene by brominated C_{60} intermediates had occurred.

Bromination of C_{60} in neat bromine gives evidence for the uptake of 28 bromines to give a quantitative yield of yellow bromine soluble microcrystals, which is believed to be $C_{60}Br_{24}$ along with some $C_{60}Br_8$ and $C_{60}Br_6$ (figure 16) as determined from X-ray diffraction analysis (Tebbe *et al* 1992). The product $C_{60}Br_{24}$ displays T_h symmetry, only slightly distorted from the parent I_h symmetry. The bromo compound decomposes to C_{60} on heating and the stability order is fluoro > chloro > bromo and $C_{60}Br_{24} > C_{60} Br_8 > C_{60} Br_6$. The instability of $C_{60}Br_8$ and $C_{60}Br_6$ may reflect
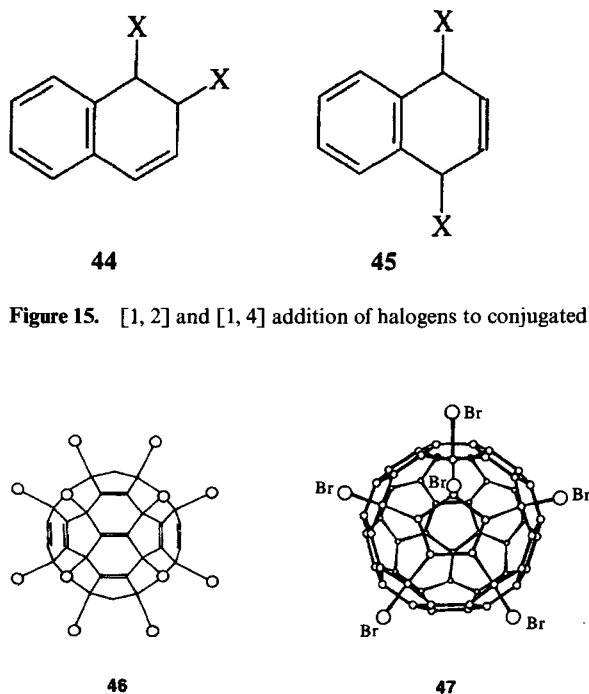
Figure 15. [1, 2] and [1, 4] addition of halogens to conjugated system of C_{60}.

Figure 16. Brominated C_{60} as $C_{60} Br_{24}$ alongwith some $C_{60} Br_6$ (Tebbe *et al* 1992; Taylor *et al* 1992).

the presence of four and two double bonds in pentagonal rings in their respective structures and $C_{60}Br_6$ contains an eclipsing steric interaction (Taylor *et al* 1992). The bromine adds to the carbon framework by 1,4-addition to fused pairs of six-membered rings with the closest Br, Br placement being 1,3. The composition of the crystal determined by elemental analysis showed that 25 to 28 bromine atoms were present in each C_{60}. Vibrational spectra indicate that the product contains a centre of symmetry and maximum symmetry possible is T_h. This structure has well defined pattern of 72 C–C bonds and 18 C=C bonds. Spectral data of 'free Br_2' suggest that the composition of molecular structure as C_{60} Br_{24} $(Br_2)_{0.5-2}$. (Average value of C–Br, C–C and C=C bond distances are 1·993(6), 1·500(19) and 1·339(6) Å respectively with the estimated standard deviations). Bromine attached to carbon at the 1 and 4 positions causes 12 of the 20 six-membered rings to adopt to boat conformation and the remaining eight six-membered rings with bromine at the 1,3- and 1,5-positions adopt to chair conformations.

The treatment of C_{60} with chlorine in chloroorganic solvents at various temperatures did not result in any detectable reaction, but in a hot glass tube under a slow stream of chlorine gas, the reaction takes place readily. On the average, twenty-four chlorine atoms are added to the skeleton which is confirmed by elemental analysis (Olah *et al* 1991).

The FTIR spectrum shows a strong C–Cl stretch ($848·5\ cm^{-1}$) and is distinct from IR spectrum of the parent molecule. The $22·4$ MHz solid state ^{13}C NMR spectrum showed broad absorptions at 50–150 ppm. In FAB and FIMS mass spectrometry under mild ionization conditions, polychlorofullerenes lose chlorine to give only peak at C_{60} (M^+, 720) and C_{70} (M^+, 840). There are reports of addition of ICl to C_{60} in toluene at room temperature to give a polychloro derivative $C_{60}Cl_6$. The ^{13}C NMR spectra suggest $C_{60}Cl_6$ to be isostructural with $C_{60}Br_6$. Reaction of iodine monochloride with a benzene solution of C_{70} produced $C_{70}Cl_{10}$ (Birkett *et al* 1995). The compound decomposes slowly in air, which was attributed to instability arising from the adjacent and eclipsed chlorines. The proposed structure is unique for a halogenated fullerene in having no double bonds in pentagons (figure 17).
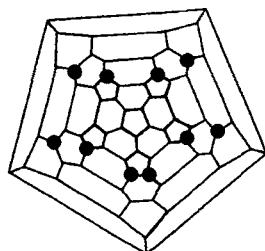
48

Figure 17. Structure of $C_{70}Cl_{10}$ showing possible positions of chlorine atoms (Birkett *et al* 1995a).

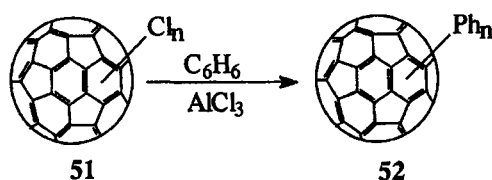**Figure 18.** Replacement of chlorine atoms by methoxy groups.

Figure 19. Friedel-Crafts reaction with benzene.

Methoxy groups can replace all chlorine atoms from polychlorinated derivative to give polymethoxy derivative (figure 18), which is confirmed by mass spectrometry (polymethoxylation up to 26 methoxy groups M^+, 1526) and ^1H NMR (a broad envelope of methoxy group centered at δ 3·7). Further, there is a sequential loss of methoxy group from $C_{60}(OMe)_{26}$ to finally produce $C_{60}(OMe)$. This observation of addition of 26 methoxy groups confirms that there are more than 24 chlorine atoms in the polychlorinated derivative.

Polychlorinated fullerene also undergoes Friedel-Crafts reaction with benzene to produce polyphenylated product (figure 19), containing up to 22 phenyl groups. ^{13}C NMR spectrum shows a broad absorption at δ 128 ppm, indicating phenylation. FAB mass spectrometry indicates substitution by at least 22 phenyl groups (M^+, 2414) with no residual chlorine remaining in the product.

In contrast to the polybrominated and polychlorinated product, addition of 60 fluorines to C_{60} has been reported (Taylor *et al* 1991). But stability decreases beyond $C_{60}F_{48}$ making subsequent addition of fluorine very slow. Fluoro compounds are much more soluble and reactive but their formation is difficult to control. Fluorinated C_{70} seems to be less stable than fluorinated C_{60}. Fluorination is very slow and steric crowding is predicted to increase the C–C bond length by about 0·05 Å and decrease the C–F bond strength by 15% relative to that in CF_4. Fluorinated C_{60} undergoes nucleophilic substitution by hydroxide ion and the rate of the reaction decreases as the fluorine content reduces (figure 20). Higher fluoro-fullerenes are strong oxidizing and fluorinating agents. The double charged anions of $C_{60}F_x$ ($x = 48$ and 46) can be generated in the gas phase by sequential electron capture (Zhou and Gary 1994). The reaction of C_{60} and C_{70} with MnF_3 under vacuum at elevated temperatures resulted in high purity $C_{60}F_{36}$ and $C_{70}F_{36/38/40}$. $C_{60}F_{36}$ has been characterized by mass spectra showing an intense peak at 1404 amu. 2D
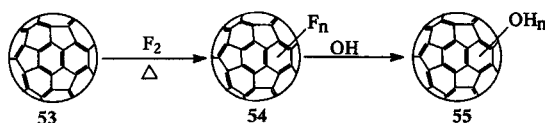
Figure 20. Nucleophilic substitution of fluorine by hydroxide ion in polyfluorinated C_{60}.
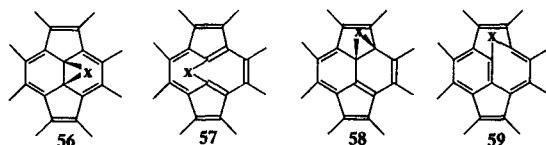

Figure 21. Four possible additions: [6,6]-closed, [6,6]-open, [5,6]-closed, [5,6]-open.

(COSY) ^{19}F NMR study indicated that the product consists of four isomers. Fluorination of C_{70} was carried out and the mass spectra showed main peaks at 1524, 1562 and 1600 amu, indicating that the product is a mixture of $C_{70}F_{36/38/40}$ with $C_{70}F_{38}$ as the major component.

7. Addition leading to ring expansion and bridging

Fullerenes undergo addition reaction with various types of reagents forming oxygen, carbon, nitrogen and metallic bridges. Addition may take place across either [6,6]-ring junction or [5,6]-ring junction and the rings are either open fulleroid or closed fullerene structures. Thus a total of four configurations are possible i.e. [6,6]-open, [6,6]-closed, [5,6]-open and [5,6]-closed (figure 21). If the derivative of fullerene contains cyclopropane rings ([5,6]-closed and [6,6]-closed), the molecule is called methanofullerene, otherwise it is called fulleroid ([5,6]-open and [6,6]-open).

7.1 *Carbon bridging*

C_{60} undergoes 1,3-dipolar addition reaction with ethyl diazoacetate and diphenyl diazomethane followed by elimination to introduce R_2C (R = H, Ar) groups into carbon framework (Suzuki *et al* 1991) (figure 22). In the reaction of diphenyl diazomethane with C_{60}, the addition takes place across one of the [6,6]-ring junctions. These reactions proceed by the elimination of N_2 to produce Ph_2C_{61}. Six molecules of diphenyl diazomethane can add to C_{60} to give $Ph_{12}C_{66}$. Suzuki *et al* (1992) prepared the pyrazoline **64** by addition of diazomethane to C_{60}. Thermolysis of the pyrazoline furnished the rearranged product $C_{61}H_2$ (**69**) (figure 23) with methylene insertion into a 5,6 'long' bond of C_{60} ([5,6]-open). Smith and co-workers (1993)
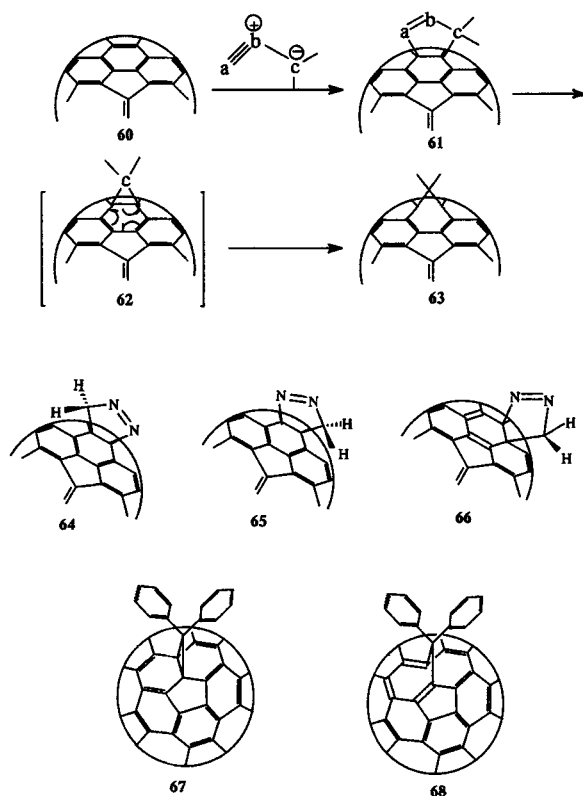
Figure 22. Addition–elimination reactions in fullerene leading to the synthesis of H_2C_{61} and Ph_2C_{61}, both closed and open isomers (Suzuki *et al* 1991).
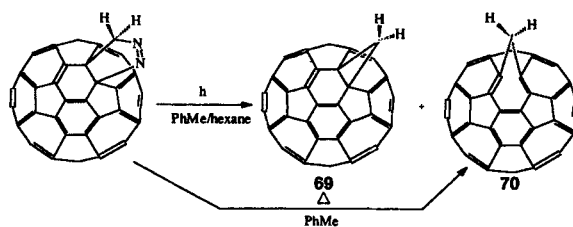

Figure 23. Thermolysis and photolysis of the pyrazoline to give isomeric annulene and methanofullerene (Smith *et al* 1993).

explored the photolysis of **64** and obtained a mixture of annulene **69** alongwith the isomeric methanofullerene **70** derived from methylene insertion into a 6,6 'short' bond ([6,6]-closed).

Although it was previously suggested [6,6]-open structure to be most stable one, the later report by Prato *et al* (1993) showed from spectroscopic studies and MNDO

calculations the addition to lead to a mixture of methanofullerene and methano-annulene. Among all the isomers possible, lowest energy product is **70**. The energetic preference for structure **70** of fullerene derivatives is due to most number of double bonded [6,6]-ring junctions and greatest number of 5-radialene rings in these structures. The [5,6]-open isomer is stable under kinetically controlled conditions while the [6,6]-closed isomer is stable under thermodynamically controlled conditions. Osterodt *et al* (1994) reported the first X-ray crystal structure of a methanofullerene (figure 24), confirming the cyclopropane structure for [6,6]-ring-methano-bridged fullerenes.

There are four 6,6- and four 6,5-ring junctions in C_{70} (figure 25). Like C_{60}, C_{70} was expected to react with diazomethane involving one or more of the four types of 6,6-ring fusions. The X-ray crystal structure (Roth and Adelmann 1992) of the clathrates $C_{70} \cdot 6S_8$, in agreement with earlier *ab initio* calculations on the isolated fullerenes (Scuseria 1991; McKenzie *et al* 1992), revealed that the bonds **i** and **ii** are
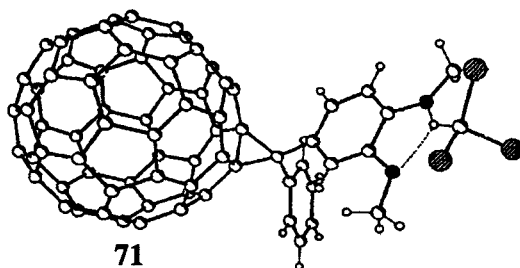
Figure 24. X-ray crystal structure of [(3,4-dimethoxyphenyl)phenylmethano][60]fullerene confirming the cyclopropane structure for [6,6]-ring-methano-bridged fullerenes. A chloroform molecule is shown as hydrogen bonded to the methoxy group (Osterodt *et al* 1994).
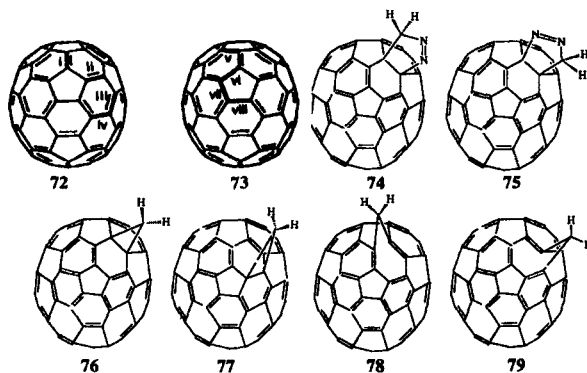
Figure 25. The eight different bonding sites in C_{70}, two isomeric pyrazolines and their thermal and photochemical decomposition products (Smith *et al* 1995).
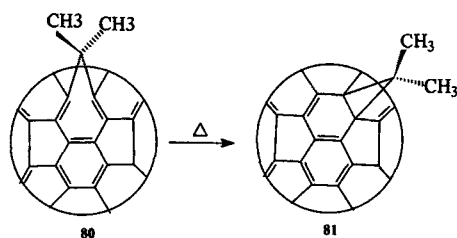
Figure 26. Thermal isomerization of annulene to cyclopropane (Smith *et al* 1995).
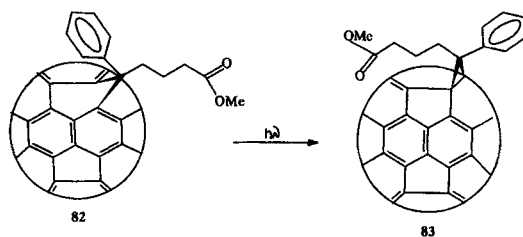
Figure 27. Zimmerman rearrangement of a fulleroid to methanofullerene (Wudl *et al* 1995).

by far the shortest bonds in C_{70}, suggesting that they would prove to be most reactive. Hawkins *et al* (1993) observed that bond **i** is more reactive than **ii**, which they attributed to greater local curvature. Thus toluene solution of C_{70} reacts with etherial diazomethane at 0°C to produce a mixture of isomeric pyrazolines derivative (**74, 75**) (figure 25), which, upon photolysis, gives two isomeric $C_{71}H_2$ cyclopropanes (**76, 77**). Thermolysis of the pyrazolines produces two isomeric annulenes (**78, 79**), which is confirmed by NMR and UV spectroscopy (Smith *et al* 1994, 1995). Smith *et al* (1995) also studied the reaction of dimethyldiazomethane with C_{60}, which led to $C_{63}H_6$ annulene **80** (figure 26), the latter upon heating is converted to the cyclopropane isomer **81** with an activation energy of ~ 25 kcal mol^{-1}. Wudl *et al* (1995) reported photochemical conversion of a fulleroid (**82**) carrying phenyl and methyl butyrate substituents on the methane carbon to its methanofullerene isomer via di-π-methane (Zimmerman) rearrangement (figure 27). The ^{13}C NMR spectral peak of C(61) at 50·7 ppm and bridgehead carbons at 79·3 ppm are in accordance with the methanofullerene structure. The sp^3 carbon formally carrying two vinyl groups represents the basic structural moiety required for a photochemical di-π-methane rearrangement and the mechanism of rearrangement is a free radical one (figure 28). The reaction takes place from the triplet state due to the efficient intersystem crossing in C_{60}. The diradical formed is stable due to the attachment of phenyl groups. This photochemical reaction is of great synthetic interest, because the thermal rearrangement of fullerene is not feasible otherwise due to product instability.
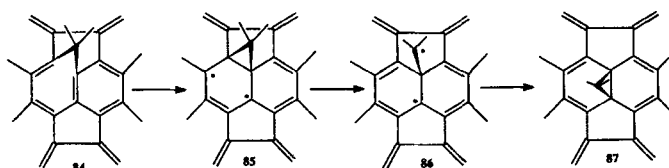
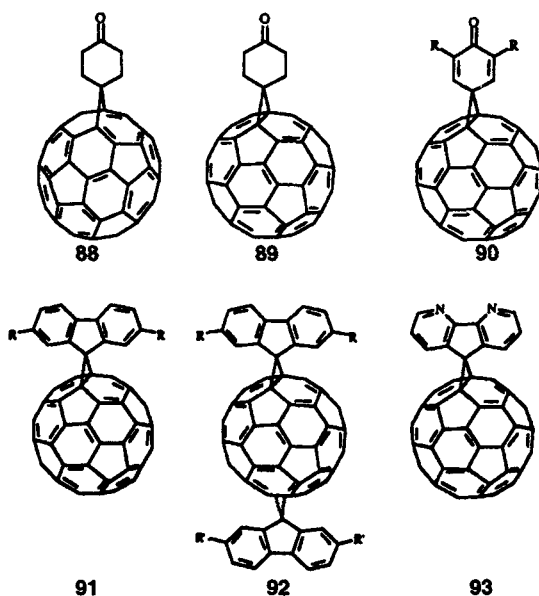**Figure 28.** Photochemical di-π-methane rearrangement (Zimmerman) mechanism.

Figure 29. The influence of addends on the electronic properties of C_{60} (Eiermann *et al* 1995).

The 5,6- and 6,6-isomers of 1,1-(4-oxocyclohexano)-fullerene, **88** and **89** respectively (figure 29) are characterized by cyclic voltametry (CV) (Eiermann *et al* 1995), which is the most direct method for studying the influence of addends on the electronic properties of fullerenes. In **90**, which has two double bonds in the cyclohexane ring, the reduction is facilitated by more than 70 mV as compared to **89**. For a number of fluorenofullerenes (**91**–**93**) isolated exclusively as adducts on [6,6]-ring junctions, the CV spectra clearly demonstrate striking influence of electron-donating and electron-withdrawing groups of the fluorenyl group on the C_{60} moiety. Ohno *et al* (1996b), reported the synthesis and electrochemistry of quinone-type methanofullerene derivatives in which, depending upon the substitution pattern on the cyclohexanedienone moiety, the reduction potential could be tuned, leading to novel

fullerene derivatives exhibiting better acceptor properties than C_{60}. In addition to the monoadduct (95) (figure 30), the *bis-* as well as the *tris*-adducts of the corresponding 1,4-diazoanthrone are separated by chromatography. The methanofullerene structure is ascertained by the observation of bridgehead carbon in the 74–85 ppm of ^{13}C NMR. The FTIR and FABMS results were also consistent with the assigned structure, and the ^1H NMR spectra show the typical resonance signals of the cyclohexanedione moiety. No evidence of the fulleroid ([5,6]) isomer is observed. The better acceptor ability of the compounds (95–97) could be rationalized by the periconjugation of the p_z–π orbitals of the cyclohexadienone moiety and the orbitals of the fullerene carbon atoms adjacent to the cyclopropane ring. The more negative reduction potential value found for the anthrone derivative (97) is attributed to the steric interaction of the aromatic peri-hydrogens with the spheroid, leading to a significant deviation from orthogonality, and, hence, the loss of periconjugation.

Ishida *et al* (1995) reported the synthesis of a [60]fullerene substituted TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl) radical (figure 31). The UV-VIS absorption spectra of 101 is very similar to that of C_{60}. The electronic structure of C_{60} moiety is only slightly perturbed, strongly suggesting that [60]fullerene-TEMPO has an open [5,6]-structure with C_{60} conjugation retained. To confirm this structure, these
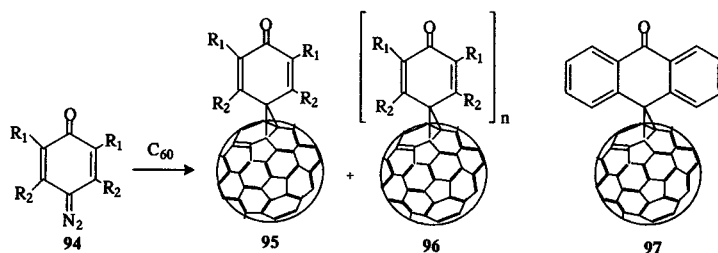
Figure 30. Quinone-type methanofullerenes in which, depending upon the substitution pattern on the cyclohexanedienone moiety, the reduction potential can be tuned (Ohno *et al* 1996b).
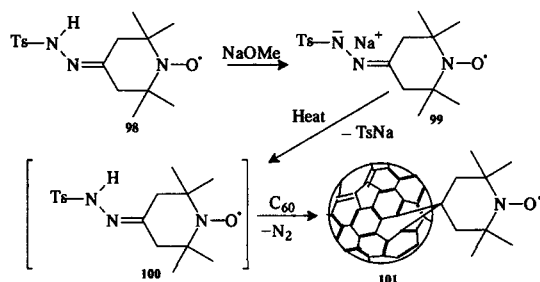
Figure 31. A [60]fullerene-substituted[2,2,6,6-tetramethylpiperidin-1-oxyl] radical (Ishida *et al* 1995).
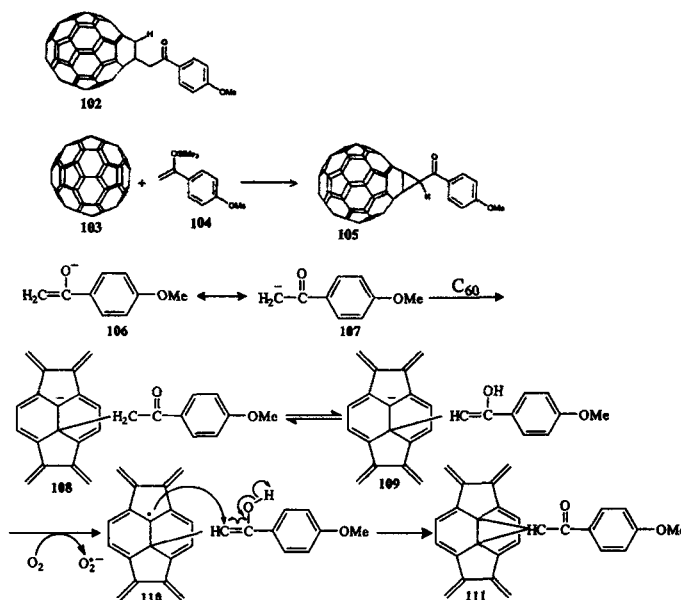
Figure 32. Reaction of [60]fullerene with 1-(4-methoxyphenyl)-1-(trimethylsilyloxy) ethylene and the reaction mechanism (Shu *et al* 1995).

workers synthesized $C_{60}(CEt)_2$. The ^1H NMR analysis revealed that the two ethyl groups are inequivalent with a very large difference in chemical shifts. The synthetic method involved a 1,3-dipolar cycloaddition of diazocompounds to C_{60}, followed by elimination of N_2 is quite similar to the synthesis of C_{60} (CH_2) by Suzuki *et al* (1991).

Aiming at the synthesis of **102**, Shu *et al* (1995), identified the product to be **105** (figure 32). The mechanism was suggested to involve a free radical intermediate, oxygen available in the reaction atmosphere taking part in the reaction course. [60]Fullerene reacts with 1-(4-methoxyphenyl)-1-(trimethylsiloxy)ethylene in the presence of the complex of KF and 18-crown-6 to form a cyclopropane ring containing monoadduct (Shu *et al* 1995).

Tether-directed remote functionalization of C_{60}, followed by a further addition step and subsequent removal of the tether-reactive group conjugate, led to the synthesis of the first regiospecific tetrakis-adduct (**115**) (figure 33) (Cardullo *et al* 1996). In the tetrakis adducts, all four methano-bridges lie on an equatorial belt and the array of cyclopropane rings divides the fullerene core into two equivalent tetrabenzopyracylene structures linked together by four biphenyl-type bonds (**116**).

Lamparth *et al* (1995) reported regioselective synthesis of $C_{66}(COOEt)_{12}$ by successive cyclopropanation of equatorial 6–6 double bonds. Other hexaadducts with an analogous addition pattern were synthesized by Isaacs *et al* (1994) and by Kräutler *et al* (1995). Lamparth *et al* (1995) found that the reaction of C_{60} and 9,10-dimethylanthracene (DMA) is reversible at room temperature (figure 34). The adduct $C_{60}(DMA)_n$ being mixtures of regioisomers and the reaction shifting equili-
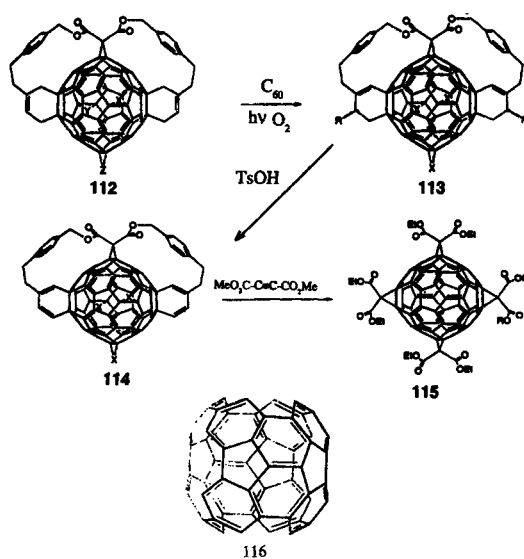
Figure 33. Regiospecific synthesis of a tetrakis adduct. **116** describes the adducts as composed of two biphenyl-type connected tetrabenzopyracylene substructures (Cardullo *et al* 1996).
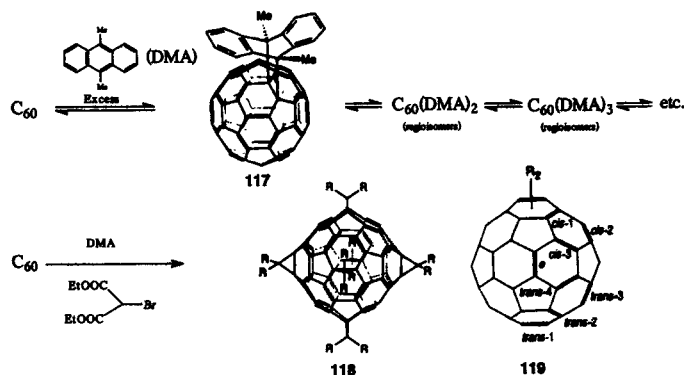
Figure 34. Reversible template-directed activation of equatorial double bonds of C_{60}: Regioselective direct synthesis of C_{66} $(COOEt)_{12}$. Positional relationship of the eight different double bonds in a C_{60} monoadduct relative to the 6–6 bond carrying the first addend is shown in **119** (Lamparth *et al* 1995).

brium towards unmodified C_{60}. This reversibility is the basis of template activation for irreversible regioselective addition at 6–6 equatorial bonds by addend-substitution reaction. The synthesis of $C_{66}(COOEt)_{12}$ after template activation with DMA was successful as a one-step process and as the only regiomeric hexaadduct.
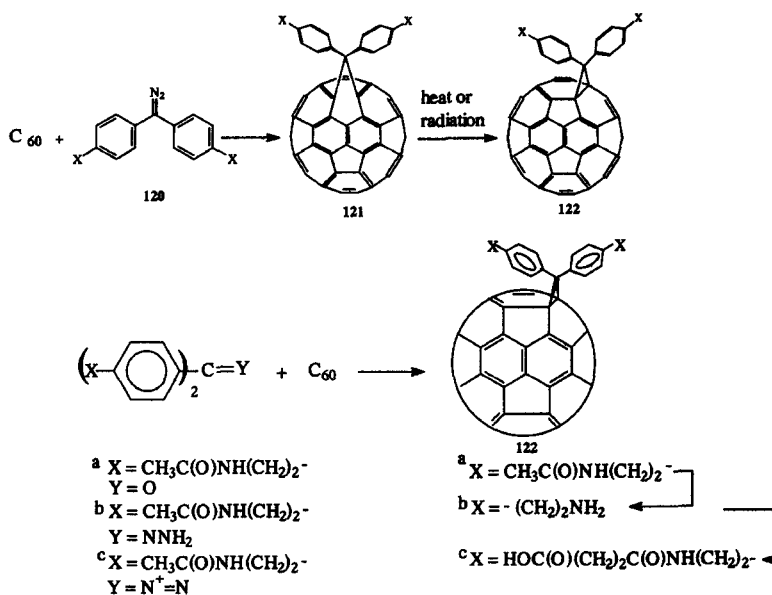
Figure 35. Synthesis of substituted diphenyl diazomethane derivative of C_{60} (Wudl *et al* 1993; Tomioka and Yamamoto 1995).

Two new methanofullerenes, $C_{60}(CHCN)$ and $C_{60}(CBr)_2$ were prepared by treating a mixture of C_{60} with either CH_2BrCN or $CHBr_3$, respectively (Benito *et al* 1996). The products were characterized by EI–MS and IR and shown by ^{13}C NMR to consist solely of [6,6]-ring junction adduct.

Synthesis of C_{60} derivatives bearing carboxy groups was reported by Tomioka and Yamamoto (1995). *Bis*(4-tert-butoxycarbonylphenyl) diazomethanes is treated with C_{60} to give the corresponding 1,2-methano derivatives, which upon hydrolysis with CF_3COOH gave the carboxy bearing fullerene derivatives (figure 35). An important application of inflation of fullerene nucleus is the ability of C_{60} fullerene derivatives to interact with the active site of HIV -1 protease (HIVP) to inhibit an HIV enzyme (Friedman *et al* 1993). A diamido diacid diphenyl fulleroid derivative was designed to inhibit HIV enzyme. This compound was prepared in three steps from C_{60} via a suitably substituted diphenyldiazomethane. Compound **122** is soluble in water at pH $\geqslant 7$, making it an ideal substrate for evaluation of physiological and pharmaceutical properties of methanofullerene. It was suggested that since C_{60} molecule has approximately the same radius as the cylinder that describes the active sites of HIVP and since C_{60} (and its derivatives) is primarily hydrophobic, there is an opportunity for strong hydrophobic interaction between the C_{60} derivative and the active site surfaces. This interaction makes C_{60} derivatives as inhibitors of HIVP. Kinetic analysis of HIVP in the presence of water soluble C_{60} derivatives suggests a competitive mode of inhibition. It was suggested through modelling that C_{60} derivatives should be inhibitors of HIVP due to their steric and chemical complementarity with the active sites.

7.2   *Nitrogen bridging*

Two types of addition of organic azides to C_{60} are known. When alkyl azide is used, the addition reaction occurs at the $[5,6]$-ring junction to give an azafulleroid. On the other hand, when N_3COR is employed, the adduct formed at the $[6,6]$-ring junction becomes the predominant product.

[(Trimethylsilyl)-ethoxy] methyl azide (SEM N_3) and substituted benzyl azides add to C_{60} to give the corresponding fulleroids by the elimination of N_2 upon heating (Prato *et al* 1993a) (figure 36). The addition is reported to take place across the 5,6-ring junction (i.e. open annulene structure), which is confirmed by the appearance of all the fullerene carbons in the sp^2 region of the spectrum. The azaful-leroids (123) formed are found to be more electronegative than their carbon analogs.

The first example of a photochemical reaction between C_{60} and an N-hydroxy-succinimide functionalized perfluorophenyl azide was reported by Yan *et al* (1994). The reaction is believed to take place via the addition of the photogenerated, highly reactive nitrene intermediate to a $[6,6]$ double bond of C_{60}. Only the aziridine monoadduct (125) (figure 37) is formed. There are sixteen peaks in the region
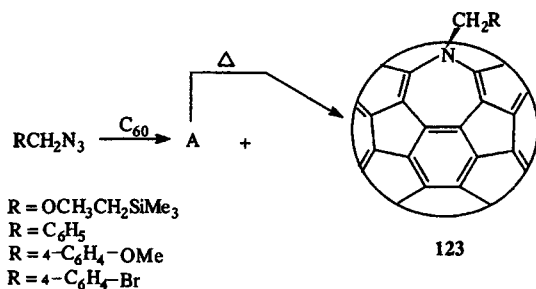
Figure 36.   Synthesis of azafulleroids (Prato *et al* 1993a).
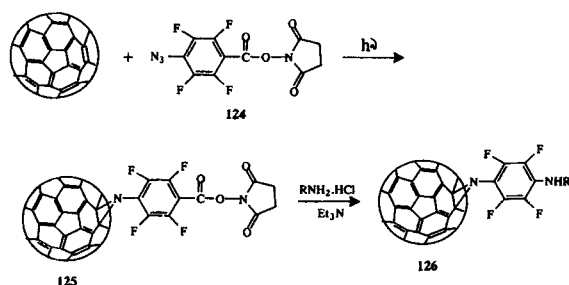
Figure 37.   Photochemical reaction between C_{60} and N-hydroxysuccinimide-functiona-lized perfluorophenyl azide (Yan *et al* 1994).
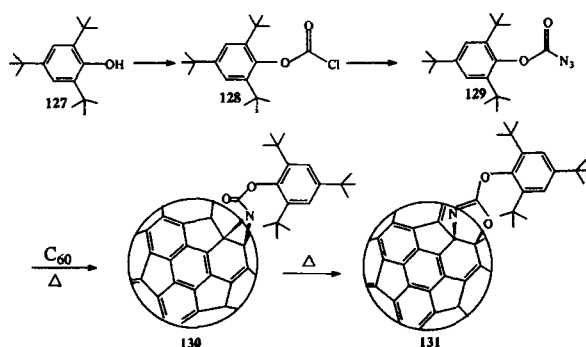
Figure 38. Reaction of C_{60} with azidoformate to form fullero aziridine (Banks *et al* 1994a).

$\delta 140$–146 in the ^{13}C NMR spectrum. The carbon atoms attached to a fluorine atom are not observed due to strong ^{13}C–^{19}F coupling. The C_{60} skeleton of the product is thus of C_{2v} symmetry. Hence the azamethanofullerene and azamethanoannulene [5,6]-ring structures are eliminated. The ^{13}C NMR spectra also showed a peak at $\delta 80\cdot37$ which corresponds to a bridgehead carbon. These data indicated that **125** is an aziridine at [6,6]-ring junction of C_{60}.

The isolation of nitrogen bridged fulleroaziridine (figure 38) with a σ-homoaromatic closed [6,6]-structure from the reaction of C_{60} with an azido formate (at elevated temperature) was reported by Banks *et al* (1994a). The fulleroaziridine rearranges on the fullerene surface upon further heating to fullerene having O and N heteroatoms vicinally bound to the [6,6]-ring fusion sites. Fulleroaziridines are formed in excellent yield by trapping of the appropriate nitrene at a [6,6]-ring junction of C_{60}. Such compounds are thermally unstable and on heating result in an irreversible rearrangement to fullerooxazoles. Base-induced α-elimination from substituted O-4-nitrophenyl sulphonylhydroxamic acid has been used as a mild source of nitrene for capture by [60]fullerene. Rearrangement of the resulting [60]fullereno [1′,2′:2,3]aziridine bearing a N-ethoxy carbonyl grouping under the influence of chloromethylsilane results in the quantitative formation of [60]fullereno[1′,2′:4,5] oxazolidin-2-one, which can be cleaved to yield 1-hydroxy-2-N-methylamino [60]fullerene. Isolation of closed [6,6]-bridged aziridinofullerenes (C_{60} NCOOR) by reaction of C_{60} with singlet oxycarbonylnitrenes is accompanied by small amount of previously undetected closed [5,6]-adducts, thought to arise by trapping of triplet nitrenes (Banks *et al* 1996). Isomerization of the [6,6]-bridged adducts to the corresponding oxazalo-[4′,5′:1,2] [60]fullerene derivatives occurs upon heating with the exception of the tert-butoxycarbonyl adducts, which eliminates isobutene and carbon dioxide to yield the parent aziridinofullerene $C_{60}NH$. Addition of nitrenes to C_{60} furnished the fullerene derivative, the detailed spectroscopic analysis revealed that these products are [5,6]-open azaannulenes rather than the reportedly [6,5]-closed aziridines (Smith *et al* 1996).

The reaction of C_{60} with aryl azides (PhN_3, $4-NC-C_6Hl_4N_3$) in dichlorobenzene at room temperature leads to isolable triazolinobenzene derivatives (Averdung and Mattay 1996) (figure 39). Photolysis of this derivative selectively yields aziridinofullerenes. Thermolysis, on the other hand, affords azafulleroids as main product next to C_{60}. The first photochemical induced rearrangement of azafulleroid (1,6-aza-bridged isomers) to aziridinofullerenes (1,2-aza-bridged isomers) is described. Besides aziridines, the photochemical reaction of aryl azides with C_{60} predominantly yields one novel bisadduct. The synthesis of 1,2-(3,4-dihydro-2H-pyrralo)-[60]fullerenes by [3 + 2] cycloaddition of nitrile ylides are reported.

The first example of [6,6]-open-bridged compounds by selective reduction of C–C bond of [6,6]-closed-bridged aziridofullerene was reported by Banks *et al* (1996). The [6,6]-closed-bridged aziridofullerene (**136**) is reduced in acid medium to give the dihydroderivative (**137**) having a bridged ten-membered ring (figure 40). FAB–MS analysis of product confirmed that **136** has undergone reduction with
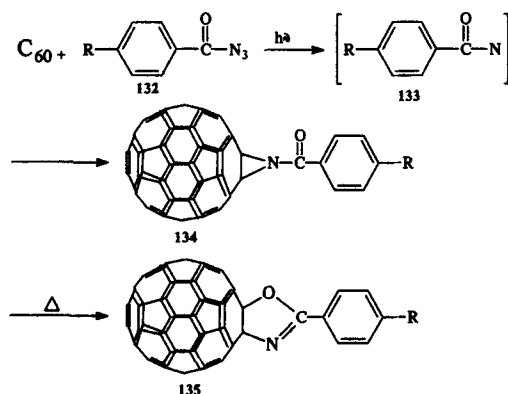
Figure 39. Formation of fulleroaziridine and thermal rearrangement to fullerooxazole (Averdung and Mattay 1995).
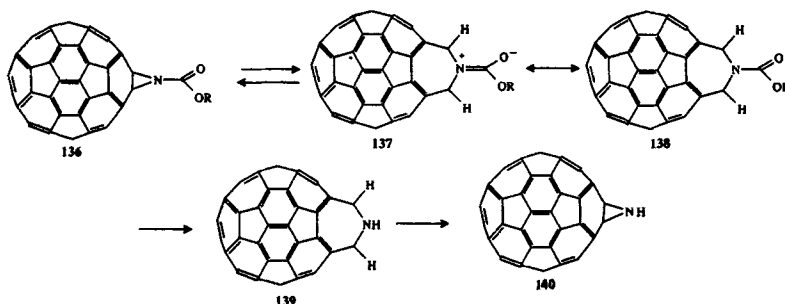
Figure 40. Incorporation of nitrogen at an open [6,6]-ring juncture (Banks *et al* 1996).

incorporation of two hydrogen atoms. Evidence of addition of hydrogen atoms symmetrically across the aziridine moiety with ring expansion was provided by ^{13}C NMR data. Reaction of 2-azidobenzothiazole and 1-azido-4-(3′,5′-dimethyl-1′-pyra-zalyl)tetrafluorobenzene with [60]fullerene was reported by Jagerovic *et al* (1996). By FAB–MS and ^{13}C NMR spectroscopy the structure of three new imino[60]fullerenes were established. Two monoadducts, a [6,6]-closed σ-aziridinofullerene and a [5,6]-open π-azafulleroid and one π-bisazafulleroid were identified.

Grösser *et al* (1995) found that treatment of C_{60} with methyl azidoacetate yields triazoline **141** (figure 41), which when heated results in a mixture of nitrogen bridged monoadducts with [5,6]-open (**142**) and a [6,6]-closed (**143**) structures. In addition a bisadduct (**144**) is also formed, in which two neighbouring [5,6]-open bonds are imino bridged. The reaction of C_{60} with $N_3(CH_2)_n N_3$ ($n = 2$ or 3) gives the corresponding bisazafulleroids (figure 42). The addition at the two [5,6]-ring junctions of the same five-membered ring (**145**) or at the two five-membered ring junctions of different five-membered rings (**146**) is possible. From the ^{13}C NMR and UV-VIS
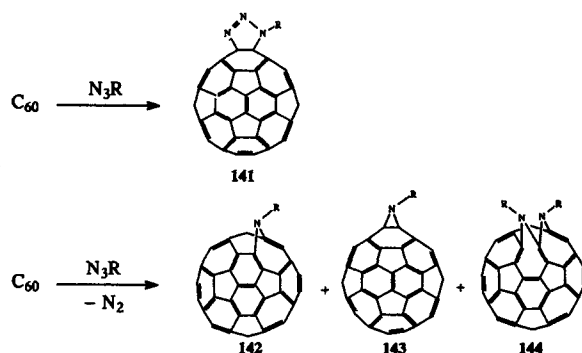

Figure 41. Ring expansion of the fullerene core by highly regioselective formation of diazafulleroids (Grösser *et al* 1995).
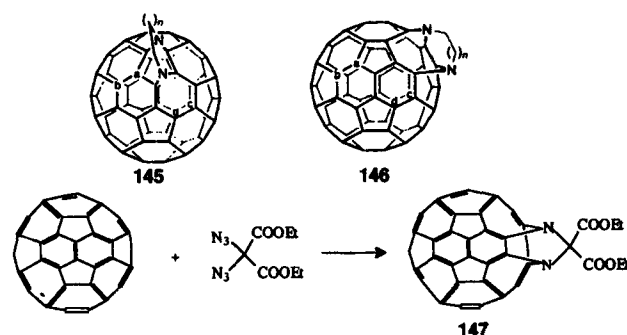

Figure 42. Bisazafulleroids (Shiu *et al* 1995; Dong *et al* 1995).

studies the bisazafulleroid was assigned the structure **145** in which the addition is shown at the two [5,6]-ring junctions of the same five-membered ring. Dong *et al* (1995) reported a doubly bridged fulleroid **147** by reacting C_{60} with diethyl-diazidomalonate. Three structures corresponding to a double 5,6-insertion, a double 6,6-insertion and a 5,6/6,6-insertion were considered. The ^1H NMR study of **147** showed two sets of ethoxy groups. From this observation and that addition of mono-azido compounds to C_{60} is established to be 5,6-insertion, the authors proposed the double bridged fulleroid as a double 5,6-insertion.

The first report of the synthesis and characterization of a C_{60} bearing triple-chain lipid (**148**) (figure 43) was reported by Murakami *et al* (1996). Spectral evidence suggested the lipid to exist as a closed aziridine structure at a [6,6]-ring junction of C_{60}.

7.3 Oxygen bridging

Ultraviolet irradiation of C_{60} in presence of oxygen in hexane gives rise to the corresponding epoxides (Taylor *et al* 1991) (figure 44). When these epoxides are heated the corresponding ethers are formed. Ethers are also formed by the UV irradiation of fullerene. Extensive irradiation degrades the epoxides to the carbonyl containing compounds. The addition of oxygen takes place across the [6,6]-central bond of pyracylene unit of C_{60}. The electrochemical oxidation of C_{60} led to the generation of $C_{60}O_n$ ($n = 1$–4) (Kalsbeck and Thorp 1991). The photooxidation of C_{60} in benzene furnished a single mono oxide $C_{60}O$ as the sole isolable product. Spectroscopic analysis strongly supports the epoxide structure (**150**) and not the
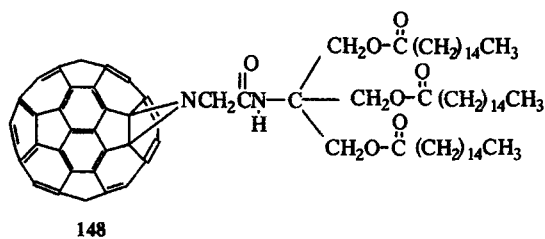

148

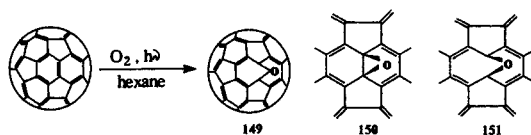**Figure 43.** A C_{60} bearing lipid (Murakami *et al* 1996).

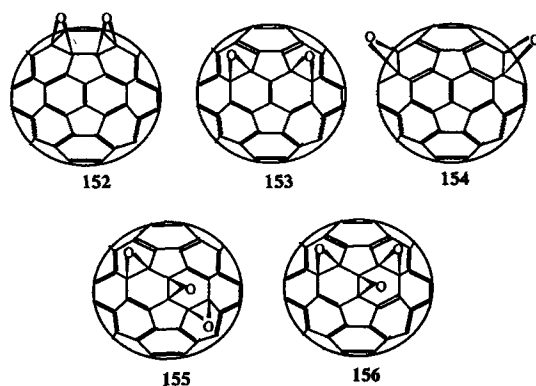**Figure 44.** Epoxide formation at the [6,6]-bond of pyracylene unit.

Figure 45. Diepoxy- and triepoxy[60]fullerenes (Hamano *et al* 1995).

isomeric 1,6-oxido [10] annulene (**151**) (Creegan *et al* 1992). Juha *et al* (1994) observed that C_{60} in its ground state does not react with excited molecular oxygen, chemically generated externally. It is suggested that the fullerene cage must itself be excited to be able to react with singlet oxygen.

In applying cytochrome P450 chemical model to studies on drug metabolism, Hamano *et al* (1995) synthesized 1,2-diepoxy[60]fullerene as a step in the analysis of the metabolic transformation of C_{60}. From the spectroscopic data, out of the three possible symmetrical structures (**152–154**) the diepoxide was identified as the 1,2,3,4-diepoxy[60]fullerene (figure 45). In addition to the diepoxide, two triepoxides (**155,156**) were also isolated and identified as 1,2;3,4;9,10-triepoxy[60]fullerene and 1,2;3,4;11,12-triepoxy[60]fullerene.

The eight symmetry non-equivalent bonds in C_{70} would yield as many as eight isomeric epoxides and an equal number of oxidoannulenes. Diederich *et al* (1991) reported the isolation of $C_{70}O$ and based on UV and mass spectra, the compound was formulated as an annulene with the oxygen atom bridging an unspecified [6,6]-ring fusion. Smith *et al* (1996) reported the synthesis of two isomeric epoxides and confirmed the structure to be [6,6]-closed (**157, 158**) (figure 46).

C_{60} contains 30 formal double bonds. Its spherical nature places stringent steric constraints on the conversion of the molozonide intermediate (**161**) to the ozonide. In presence of toluene **161** rearranges to 1,2-diketone (**163**) accompanied by formation of isomeric cresols (figure 47). The products are 2,5-xylol and 2,4-xylol. The oxidation occurs at the various double bonds of C_{60} ball, generating a mixture of oxidized product having ketonic, ester and epoxide functionalities.

7.4 Other nonmetal and metal bridging

Wudl *et al* (1993) reported the addition of *bis*(2,6-diisopropylphenyl)silylene with C_{60} to give an adduct by the addition across the [6,6]-ring fusion to give silirane
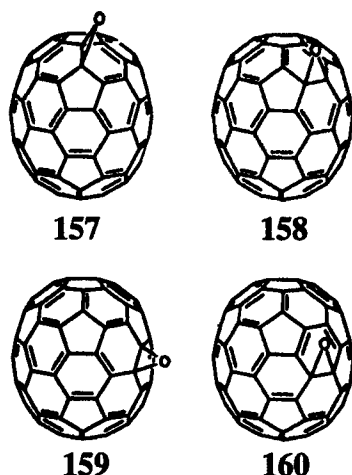
157   **158**

159   **160**

Figure 46. Four possible [6,6] $C_{70}O$ epoxides (Smith *et al* 1996).
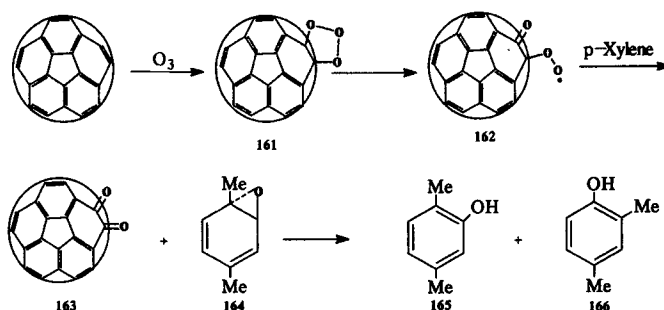

Figure 47. Steric constraints prevent conversion of molozonide intermediate to the ozonide (Malhotra *et al* 1994b).

(figure 48) with exothermicity of 61·3 kcal/mol. The ^{13}C NMR signal at $\delta = 71·12$ supports the structure **167** for the above adduct rather than **168**.

In reaction with metal derivatives, C_{60} also behaves as an alkene (giving η^2-coordination) rather than an aromatic (η^6-coordination). The first structurally characterized C_{60} derivative is an osmate ester with C–O–Os bonds, $(t\text{-Bu } C_5H_5N_2)_2$ $Os(=O)_2O_2C_{60}$ (Hawkins *et al* 1990). Two of the above adducts can be added to C_{60}. Hawkins *et al* (1993) reported the formation of adducts of C_{60} with OsO_4(4-t-Bu Py) and its analogs. The X-ray analysis of the crystals of osmium complex indicated the elimination of free rotation of C_{60} spheroids in the solid state. Osmylation of C_{60} yields 1:1 and 2:1 adducts with cup and band shaped π-systems respectively (figure 49). Five regioisomers of 2:1 adduct C_{60} $(OsO_4L_2)_2$ are formed including two chiral isomers, which are formed due to the substitution pattern in the
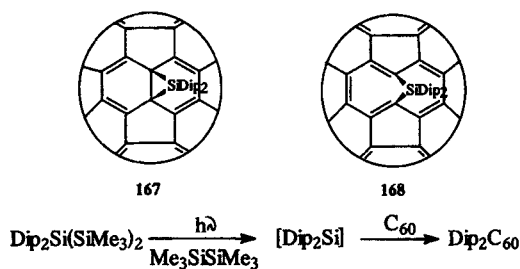
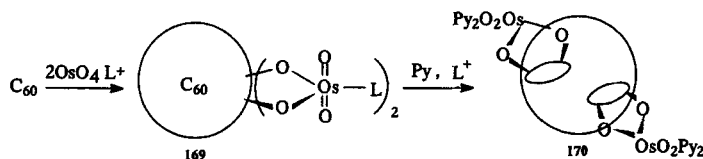**Figure 48.** Synthesis of siliranes (Wudl *et al* 1995).

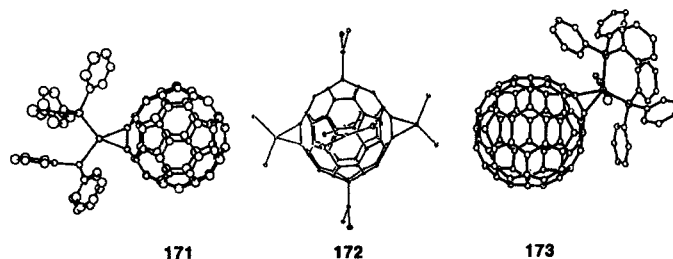**Figure 49.** Osmylation of C_{60} (Hawkins *et al* 1993).

Figure 50. Platinum and iridium functionalized complexes of C_{60} (Balch *et al* 1991a; Fagan *et al* 1991a).

icosahedral carbon cluster (Hawkins *et al* 1993). Osmylation of C_{70} with 0·75 equiv. of OsO_4 in pyridine/toluene at 0° C yielded two isomers of C_{70} (OsO_4 Py_2). Osmylation occurs at the double bonds and not at the single or intermediate (aromatic) bonds. Greater reactivity at more pyramidalized carbons corresponds to greater strain relief as the fullerene carbons become four coordinate.

The synthesis of the first optically active organometallic fullerene derivative by η^2-functionalization of C_{60} by Pd^0 complex was reported by Bashilov *et al* (1993). Reactions of C_{60} with organometallic ruthenium and platinum reagents were thoroughly studied in which metals can be directly attached to the carbon framework by dihapto bonding and X-ray diffraction analysis of platinum complex $[Ph_3P]_2$ Pt (η^2-C_{60})-C_4H_8O showed that the structure is similar to the $[Ph_3P]_2$ Pt (η^2-ethylene) (Fagan *et al* 1991).

$[Ph_3P]_2$ Pt(η^2-C_{60}) can be prepared by the addition of C_{60} with $[Ph_3P]_2$ Pt(η^2-ethylene) in toluene under nitrogen atmosphere. From the ^{31}P NMR spectral data of the above compound (**171**) (figure 50) it was indicated that, coupling constants

and chemical shifts were similar for both C_{60} and ethylene complex. From this it was suggested that coordination sphere about platinum was nearly identical in both the cases i.e. addition takes place across two fused six-membered rings rather than at the junction of five- and six-membered rings. Spectroscopic data also reveals that the organometallic derivative in contrast to diazomethane adduct has a open ring (i.e. fulleroid) structure. Fagan *et al* (1992) in another report showed that either one, two or six groups can be added, the latter giving an octahedral array. In this process only one isomer was obtained and in hexasubstituted platinum derivative $\{[(C_2H_5)_3P]_2Pt\}_6C_{60}$, (172), the phosphorous, platinum and C_{60} atoms exhibit T_h point group symmetry. Monoadducts of C_{60} have also been formed with nickel and palladium. Iridium complex-alkene adduct can also add to C_{60} across 6,6-ring fusion in dihapto fashion to form a crystalline derivative (Balch *et al* 1991). Two iridium adducts can be added to C_{60}. Shapley *et al* (1992) reported the addition of complex $(\eta^5\text{-}C_9H_7)$ Ir(CO) to C_{60} in dihapto fashion to form $(\eta^5\text{-}C_9H_7)$ Ir(CO) $(\eta^2\text{-}C_{60})$. The complex formed is air stable. Ir (CO)Cl(PPh$_3$)$_2$ can also add to C_{70} to give $(\eta^2\text{-}C_{70})$ Ir(CO)Cl(PPh$_3$)$_2$(173) by addition across one of the high order π-bonds adjacent to the pentagonal cap (Balch *et al* 1991). Iridium ion is bound to an a–b edge of C_{70}. The symmetry around the iridium atom is similar to that of $(\eta^2\text{-}C_{60})$Ir(CO) Cl(PPh$_3$)$_2$ and two iridium adducts can be added. Ir(CO)Cl(PMe$_2$Ph)$_2$ can also form diadduct with C_{70}[Ir(CO)Cl(PMe$_2$Ph)$_2$]$_2$ (Balch *et al* 1992).

8. Cycloaddition reaction

Fullerenes undergo various types of cycloaddition reactions such as [2+2], [2+3], [2+4], [4+4], [2+2+2] and other higher electron count reactions. These reactions provide efficient means of attaching functional groups, imparting useful properties to the parent molecule.

In [2+4] cycloaddition reaction, fullerene nucleus acts as a dienophile (Wudl 1992). This is due to the fact that inter five-membered ring bonds are fulvenoid and also electrophilic in nature. In case of both C_{60} and C_{70}, up to six molecules of diene can be added to C_{60} nucleus across the six pyracylene units.

C_{60} undergoes [2+4] cycloaddition reaction with various reagents such as anthracene, furan, cyclopentadiene, nitrile oxide, isobenzofuran, *o*-quinodimethanes etc to give the corresponding cycloadduct. In all the reactions, the addition takes place across the junction of two six-membered rings rather than at the junction of five- and six-membered rings. Rubin *et al* (1993) reported the reaction between anthracene and C_{60}, but the adducts could not be isolated and characterized. A C_{60}-cyclopentadiene adduct was isolated from a low pressure benzene flame by Rotello *et al* (1993). The ^{1}H and ^{13}C NMR spectra of the cycloadduct correspond to the expected Cs symmetry of the molecule formed by addition across the C_6–C_6 ring fusion. Wudl *et al* (1993) reported the multiple addition product formed by the addition of excess cyclopentadiene or anthracene to C_{60} and obtained the poly-adduct (figure 51). In this reaction, up to six molecules of cyclopentadiene or anthracene could be added to C_{60} moiety. Komatsu *et al* (1993) used naphthalene as
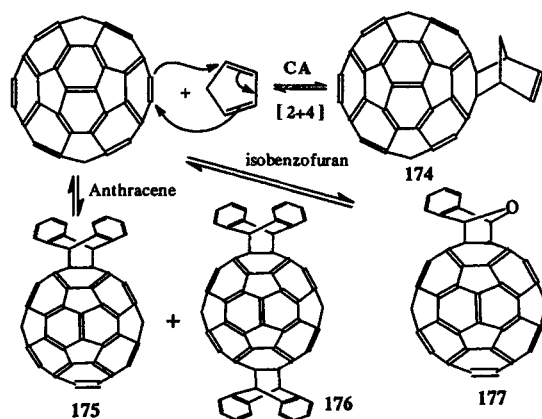
Figure 51. [2 + 4] cycloaddition reaction. Up to six molecules of diene add at the [6,6]-ring junction.

a high boiling solvent and isolated selectively the 1:1 adduct. Tsuda *et al* (1993) reported the synthesis of several cycloadducts of C_{60} with anthracene, cyclopentadiene, 1,3-diphenylisobenzofuran and 1,3-dimethyl butadiene. The adducts are characterized by means of negative ion FAB mass and ^{1}H and ^{13}C NMR spectroscopy. For anthracene, both mono- and di-adducts (**175,176**) are isolated and characterized. Schlueter *et al* (1993) characterized the C_{60}-anthracene 1:1 adduct by NMR, UV-vis, IR, mass spectroscopies and thermogravimetric analysis. The TGA indicated a 19·97% weight loss, the onset of transition occurring at 120°C, which is expected for the removal of a single anthracene unit. Klemt *et al* (1995) studied the reaction between C_{60} and anthracene and observed EPR-active adducts of $^3C_{60}$ to anthracene.

In all the above reactions, the cycloadduct formed revert back to C_{60}, which was detected by X-ray crystallographic studies and mass spectral analysis. To overcome this difficulty, Prato *et al* (1993) reported that when C_{60} reacts with isobenzofuran generated *in situ* from 1,4-dihydro-1,4-epoxy-3-phenylisoquinoline in refluxing benzene, the corresponding cycloadduct obtained by fusion at the [6,6]-ring junction did not undergo cycloreversion. Rubin *et al* (1993) synthesized the adduct (**178**) by [2 + 4] cycloaddition of C_{60} with 5,6-dimethylene-1,4-dimethyl-2,3-diphenyl norboran-2-en-7-one, which by elimination of CO finally gave a stable adduct (**179**) (figure 52). This adduct does not undergo *retro*-Diels-Alder reaction due to the stability imparted by the aromatic ring, and this must be overcome to give cycloreversion product C_{60} and *o*-quinodimethane intermediate. The reaction of C_{60} with *in situ* generated 6b, 10a-dihydrofluoranthene affords a stable [4 + 2] cycloadduct (Averdung and Mattay 1994). Diels-Alder reaction of 4-amino-*o*-quinodimethane with C_{60} affords a thermally stable and chemically reactive adduct (Walter *et al* 1996). The nucleophilic amino group is well suited for the covalent attachment of different molecules to the [60]fullerene core by further chemical reaction.
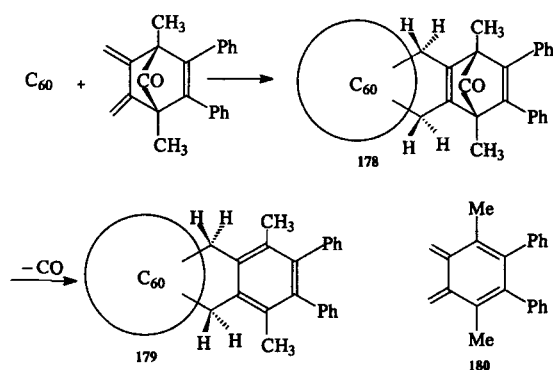
Figure 52. Synthesis of stable cycloadducts by [2 + 4] cycloaddition followed by elimination (Rubin *et al* 1993).
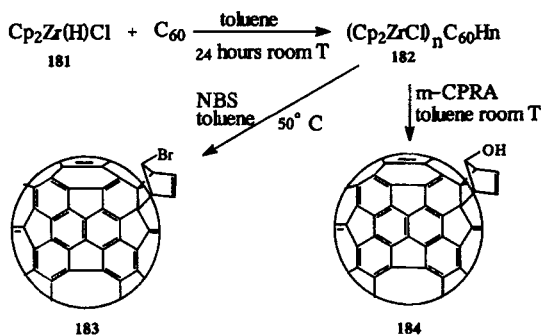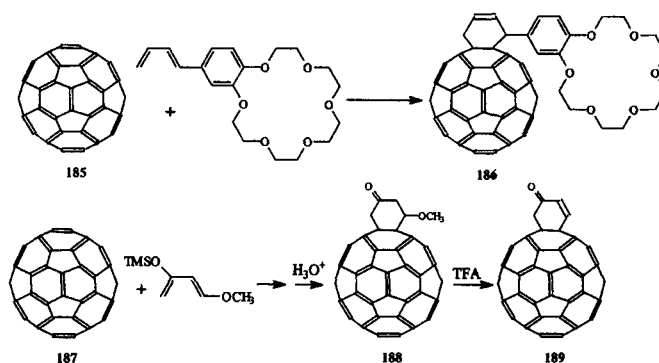

Figure 53. Cycloaddition of metallofullerene (Ballenweg *et al* 1994).

Metallofullerene undergoes cycloaddition reaction with various reagents. C_{60} hydrozirconation adduct (182) reacts with NBS and *m*-chloroperbenzoic acid, leading to Diels-Alder adduct with bromo- and hydroxycyclopentadiene respectively (figure 53) (Ballenweg *et al* 1994). Both exo- and endo-isomers are possible. Endo isomer is more stable with respect to the double bond in the norbornene position. A three-step mechanism to explain this unusual reaction is proposed (Ballenweg *et al* 1996).

Wilson and Lu (1993) reported the results of C_{60} – Diels-Alder reaction with a relatively unreactive crown ether diene 185 (figure 54), and followed the reaction course by electrospray MS method. The reaction is not reversible. C_{60} also reacts with 'Danishefsky Diene' (187) to produce annealed ketone 188, which could be useful for preparation of the functionalized fullerenes. The synthesis of the fullerene derivatives of quinones was first reported by Iyoda *et al* (1994). The compound 190 (figure 54a) was of interest because of a potential donor–acceptor interaction between fullerene and *p*-benzoquinone parts, and because of the opposite acceptor–donor interaction between C_{60} semiquinone radical or hydroquinone dianion 191

Figure 54. Cycloaddition of a crown ether diene and Danishefsky diene (1-methoxy-3-(trimethylsiloxyl)-1,3-butadiene) to [60]fullerene (Wilson and Lu 1993).
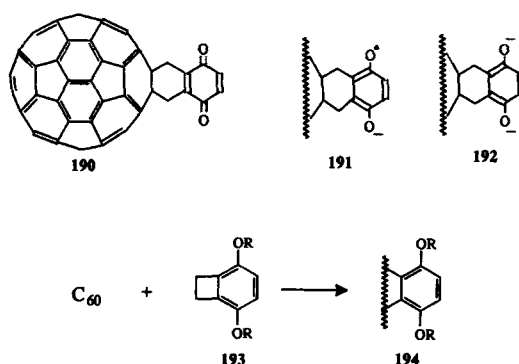
Figure 54a. Redox system containing fullerene and *p*-benzoquinone (Iyoda *et al* 1994).

and **192**. To construct the novel redox system, C_{60} was allowed to react with 3,6-dimethoxybenzocyclobutane **193** to give the monoadduct **194**. The removal of methyl group resulted in the desired compound. In order to estimate the $\pi-\pi$ interaction between fullerene and quinone parts, the redox potential of **190**, **194** and C_{60} were measured by cyclic voltametry.

The high-pressure Diels-Alder reaction of C_{60} with substituted tropone derivatives gives stable [2 + 4] cycloadducts (Liu *et al* 1995). The selectivity is controlled by the steric environment. The Diels-Alder reaction between C_{60} and 2,3-dimethylene-1,4-dioxane or 4,5-dimethylene-2,2-dimethyldioxolane are reported by Torres-Garicia and Mattay (1996). The regioselective functionalization of C_{60} by way of [2 + 4] cycloaddition reactions give synthetic access to exohedrally derivatized fullerenes, with either flexible or rigidly bound addends. The binding of the addends to the central carbon sphere is made effectively irreversible by subsequent addition reactions at the double bond of the addends (Kräeutler and Maynollo 1996).

An *et al* (1995) reported the reaction of C_{60} with 1,3-dienes to afford substituted 1,2-(4′-cyclohexeno)buckminsterfullerenes. These cyclohexenones are sensitive to

ambient light and air, easily undergoing $^1O_2$ ene reaction to form the corresponding hydroperoxides. The reaction is used advantageously in the preparation of allylic alcohols. Kräutler and Maynollo (1995b) reported a remarkably regioselective six-fold [2 + 4] cycloaddition of C_{60} with 2,3-dimethyl-1,3-butadiene. The six-fold Diels-Alder reaction of 1,3-diene takes place at the six symmetry-equivalent '6-6 bonds' located between the six-membered rings of fullerene. The Diels-Alder strategy was found suitable for the functionalization of C_{60} using 1,3-butadienes substituted with an electron withdrawing group as well as an electron donating group. This gives cyclohexene-fused C_{60} derivatives (Ohno *et al* 1996a), having ethoxycarbonyl, acetyl, cyano, phenylsulphonyl and nitro substituents. These cycloadducts are stabilized by conjugation with the substituent and no cycloreversion takes place.
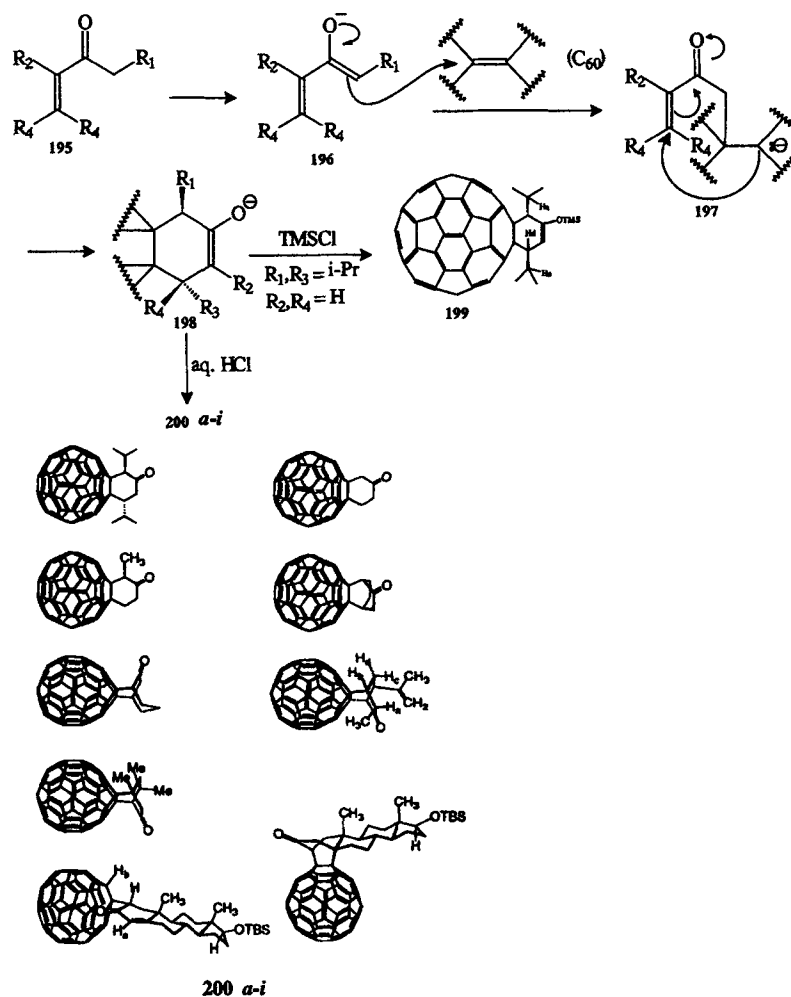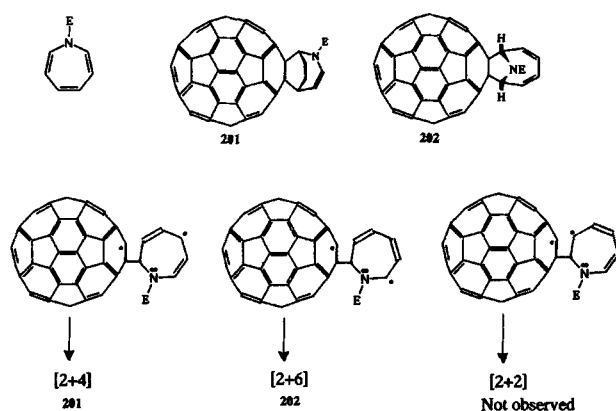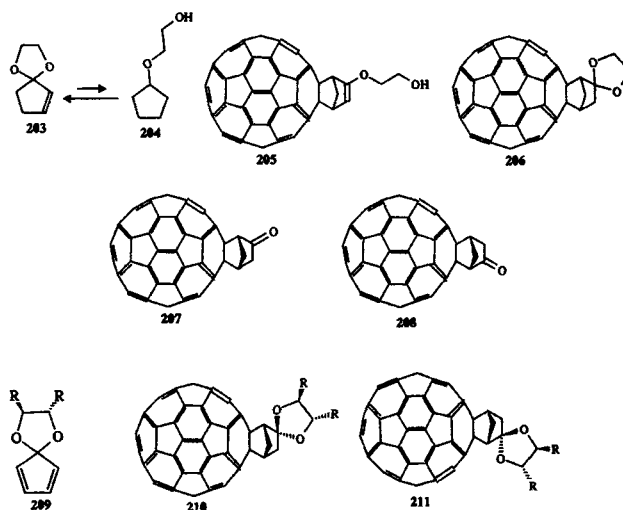

Figure 55. Synthesis of sterically congested C_{60} derivatives with defined stereochemistry (Ganapathi *et al* 1995).

Figure 56. Competing pathways in the photolytic cycloaddition reactions of N-ethoxycarbonylazepine to [60] fullerene (Banks *et al* 1995).

Figure 57. Reaction of C_{60} with cyclopent-2-enone acetals: a convenient access to chiral C_{60} derivatives (Ohkita *et al* 1995).

Attaching a cyclohexane ring with a sterically crowded 1,4-position to C_{60} was accomplished by Ganapathi *et al* (1995). The reaction involved a 'double Michael' addition of a dienolate anion to C_{60} (figure 55). Protonation of **198** resulted in the desired cyclohexyl moiety attached to C_{60} (**200** *a–i*). Either of the two diasteromers might be formed and both were predicted to show significant increase in apolar binding to HIV-protease. HIV-1 protease is an important target for antiviral therapy since it has vital function in the maturation of the AIDS-inducing virus. Banks *et al* (1995) in a course of further investigation of their reported work on synthesis of closed [6,6]fulleroaziridines observed the formation of **201** and **202** (figure 56).
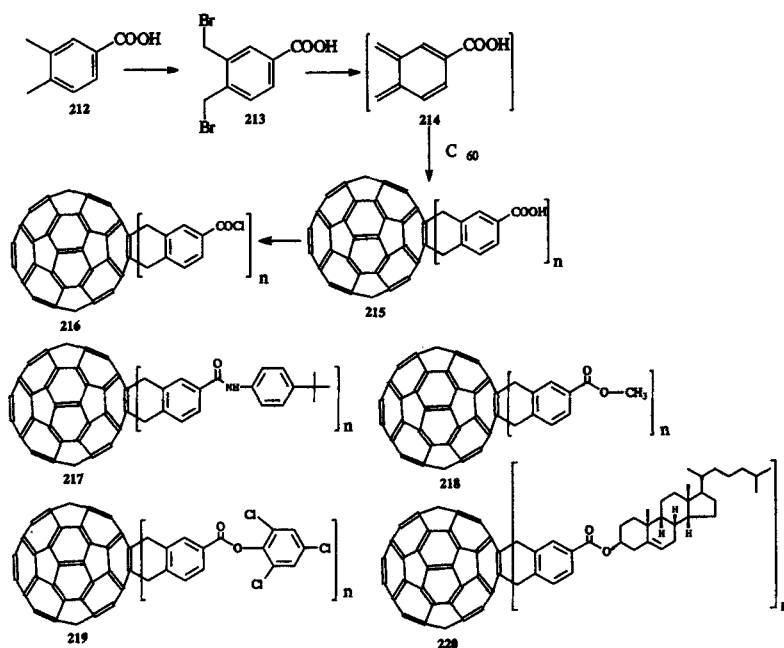
Figure 58. Diels-Alder adduct of C_{60} and 4-carboxy-*o*-quinodimethane: Synthesis and chemical transformation (Belik *et al* 1995).

Benzene, used as the solvent, captured the photolytically generated nitrene to produce *N*-ethoxycarbonylazepine, which then underwent further photoreaction with C_{60} giving [2 + 4] and [2 + 6] cycloadducts. Formation of [2 + 2] photoadduct was not detected. Reaction of cyclopent-2-enone acetal **204** with C_{60} at [6,6] ring junction via its ring opened form **205** is reported by Ohkita *et al* (1995). The primary cycloadduct **205** (figure 57) is promptly converted to the acetal **206**, thereby effectively preventing the reversion of the adduct to the reactants. Hydrolysis of **206** afforded the corresponding ($\pm$) ketone **207, 208** in quantitative yields. The authors also investigated the reaction of C_{60} with acetal **209**, bearing a chiral auxillary and derived from L-tartaric acid. Two diastereomeric monoadducts **210** and **211** were isolated in nearly equal amounts, indicating insignificant asymmetric induction in the process.

C_{60} undergoes a smooth irreversible *hetero*-Diels-Alder reaction with an α, β-unsaturated thiocarbonyl compound, prepared *in situ* from thioacrylamide and acyl chloride, to give dihydrothiopyran-fused C_{60} cycloadducts (Ohno *et al* 1995). This is the first example of a sulphur-bonded C_{60} derivative.

The [2 + 4]cycloaddition reaction of *o*-quinodimethane with C_{60} is a method of choice for the synthesis of physically stable and chemically reactive C_{60} adducts. A multitude of reactive functional groups can be introduced in the process. Belik *et al* (1995) reported the synthesis of carboxy-substituted adducts of C_{60} and *o*-quinodimethane, and subsequent reaction of the adducts with alcohols and amines. The chlorides (**216**) are transformed to amides and esters with 4-*tert*-butylaniline, methanol, 2,4,6-trichlorophenol and chloresterol (**217–220**) (figure 58).
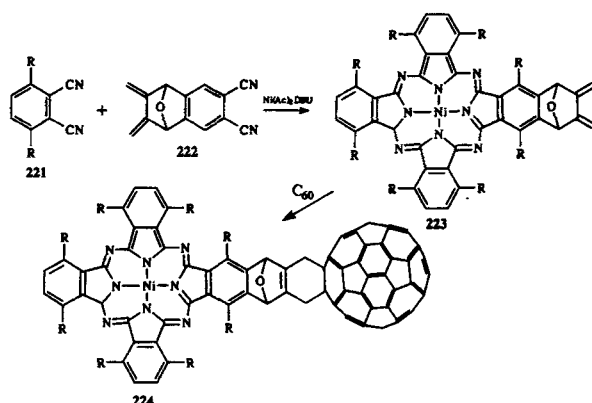
Figure 59. A Diels-Alder adduct of [60] fullerene with a phthalocyanine—a green fullerene (Linssen *et al* 1995).
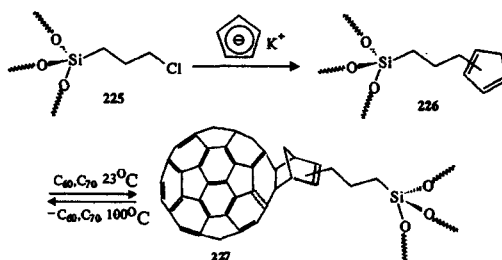

Figure 60. Nonchromatographic purification of fullerenes via reversible addition to silica-supported dienes (Nie and Rotello 1996).

The synthesis and electrochemistry of a Diels-Alder adduct of C_{60} with nickel phthalocyanine (**223**) resulted in a 'green fullerene' (**224**) (figure 59). The nickel phthalocyanine was synthesized from 3,6-diheptylphthalodinitrile (**221**) and 1,2,3,4-tetrahydro-2,3-dimethylene-1,4-epoxynaphthalene-6,7-dicarbonitrile (**222**) to react with nickel acetate in the presence of a catalytic amount of 1,8-diaza-bicyclo[5·4·0]undec-7-ene (DBU). The C_{60} adduct of **223** was formed at the [6,6]-ring junction providing the 'green fullerene'.

The property of reversible cycloaddition of free (Rotello *et al* 1993) and polymer supported (Guhr *et al* 1995) dienes to C_{60} led Nie and Rotello (1996) to devise a simple method for the purification of fullerenes. Reaction of chloropropyl functionalized silica gel **225** with potassium cyclopentadienylide provided the cyclopentadiene-functionalized silica gel **226** (figure 60). This material reacted readily with C_{60} and C_{70} to yield mixed C_{60}/C_{70} conjugate **227**, which on heating released 93·7% of bound C_{60} and 41·1% of bound C_{70}. The process was fully reproducible, with fullerenes being completely reabsorbed upon cooling. The difference in release provided fullerenes significantly enriched in C_{60}: the initial C_{60}/C_{70} ratio was 90:10, the final ratio was 96:4.

Paquette and Trego (1996) condensed bifunctional dienes with C_{60}, the products were dumbbell-like systems **230** and **231** (figure 61). When hericene (**232**), a trifunctional diene (2, 3, 5, 6, 7, 8-hexamethylidene bicyclo [2·2·2] octane) was treated with C_{60}, cycloaddition takes place in a three-dimensional format, resulting in the adduct **233**. This is the first example of a 'radiafullerene' with three carbon spheres radiating out symmetrically from the staging framework.

Exceptions to the dienophilic character to C_{60} are known. Cooks *et al* (1992) reported both 1, 4- and 1, 2-type addition of C_{60} to benzene giving a mixture of two products. In the 1, 4-addition reaction, addition preferentially takes place across the
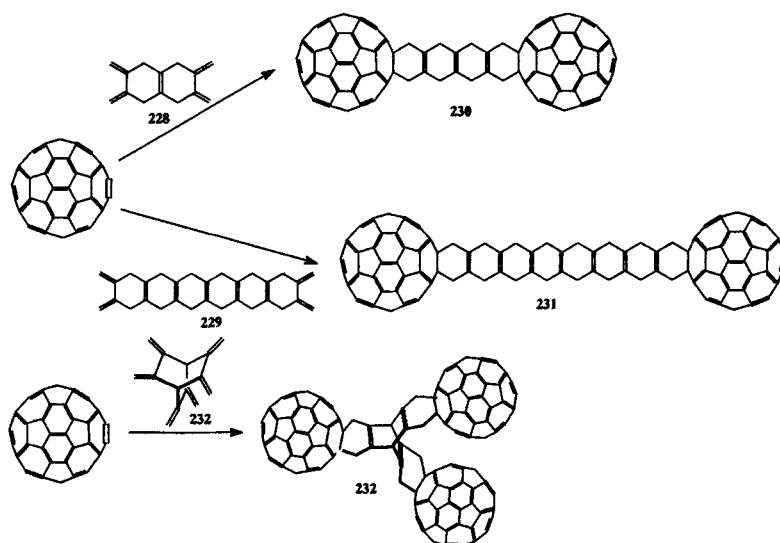
Figure 61. Extended projection of C_{60} spheres into three dimensional space-three-fold cycloaddition of [60] fullerene to hericene (Paquette and Trego 1996).
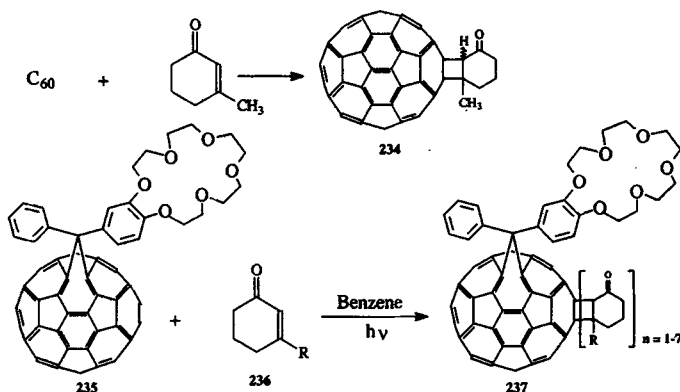
Figure 62. C_{60}–enone [2 + 2] photoadducts. Addition of enones to crown ether fulleroid is followed by ESI–MS studies (Wilson *et al* 1993b).
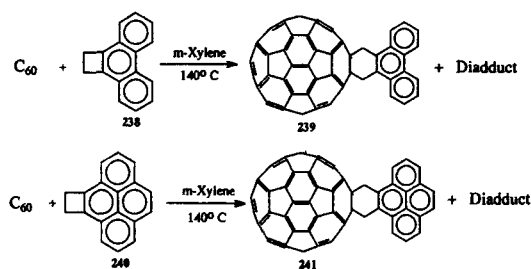
Figure 63. Reaction of fullerene with benzocyclobutene homologs (Tago *et al* 1993).
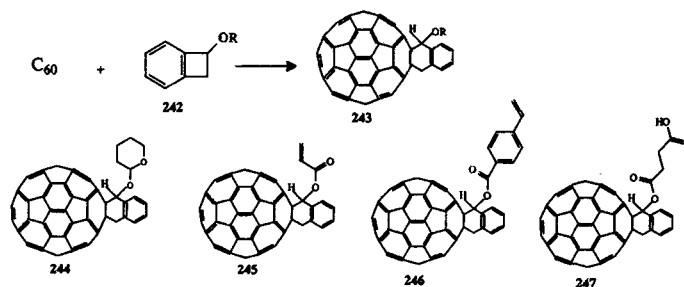

Figure 64. An expeditious route to fullerene adducts by reaction of [60] fullerene with benzocyclobutenol (Zhang and Foote 1994).

1,4-position within a ring and not between two. Up to four molecules of benzene can add to C_{60} from which monoaddition product is preferentially formed which is characterized by ^{1}H and ^{13}C NMR spectroscopy. C_{70} also reacts with benzene in a similar fashion as C_{60} and the probable addition site is along 1,9-bonds (Darwish *et al* 1994). Addition along 7,8-bonds is also possible, but less probable. C_{70} can add up to 10 benzene molecules, which was confirmed by mass spectroscopy.

C_{60} is readily functionalized by photocycloaddition with cyclohexenones in a reaction that involves the attack of enone triplet excited states on the fullerene. Wilson *et al* (1993b) reported the preparation of [2+2] photocycloadducts of C_{60} and cyclic enones (figure 62). Photocycloaddition of 3-methylcyclohexenone to C_{60} formed chiral *cis*- and *trans*-fused adducts which are separated by HPLC. A variety of substituted cyclohexenones as well as cycloheptenones are used (Schuster *et al* 1994). The course of reaction upon UV-irradiation of crown ether fulleroid **235** and 3-methylcyclohexene-2-one in benzene solution was followed by ESI–MS, which was seen as a uniquely suitable tool for studying such reactions.

C_{60} was easily converted to its derivatives by treatment with benzocyclobutene homologs using the thermally allowed conrotatory $[\sigma_2 + \pi_2]$ electrocyclic ring opening of the benzocyclobutene homologs (figure 63) (Tago *et al* 1993). Reaction of C_{60} with benzocyclobutenol **242** and its methoxy ether gave 1,9-dihydrofullerene cycloadduct **243** in high yields (figure 64). The alcohol was converted to pyranyl ether **244**, acrylate **245**, *p*-vinyl benzoate **246** and acid succinate esters **247** (Zhang and Foote 1994).
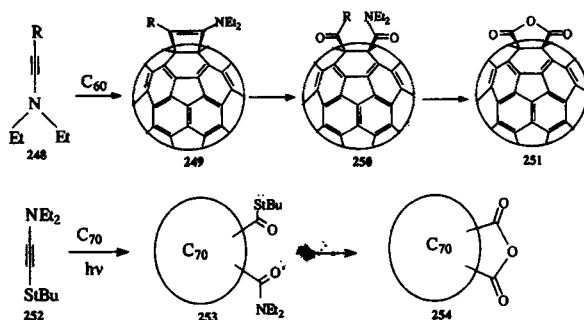
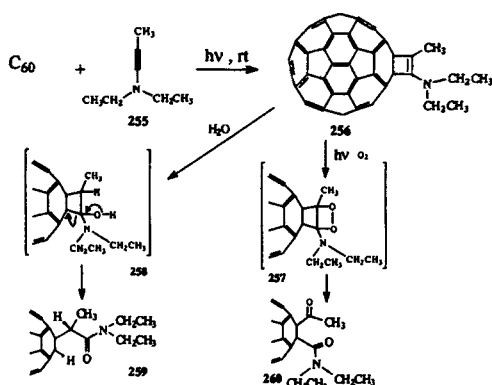**Figure 65.** Synthesis of $C_{62}O_3$ and $C_{72}O_3$ (Zhang and Foote 1995).

Figure 66. Photochemical [2 + 2] cycloaddition of N,N'-diethylpropynyl amine to C_{60} (Zhang *et al* 1993a).

Zhang and Foote (1995) synthesized the first fullerene anhydrides, $C_{62}O_3$ and $C_{72}O_3$ by [2 + 2] photochemical addition of C_{60} and C_{70} to both yndiamine and thioynamines and latter upon self-sensitized photooxidation of the adducts (figure 65). C_{60} reacts with both N, N, N', N'-tetraethylene diamine and N, N-diethyl-2-ethyl thioethyne diamine to give the corresponding cyclobutene intermediate (249), which upon self-sensitized photooxygenation in toluene gives diamide (250). This on treatment with *p*-toluene sulphonic acid gives finally 1,2-dihydrofullerene [60]-1,2-dicarboxylic acid anhydride (251). C_{70} reacts ~ 4 times faster than C_{60} in which addition takes place across the 1,9-bond of C_{70}, while in the case of C_{60} the addition site is [6, 6]-ring junction. Due to the electron rich characteristic of ynamine and the electron deficient characteristic of fullerenes, it was suggested that ground state electron-transfer or charge-transfer mechanism takes place during the addition process.

Zhang *et al* (1993a) studied the photochemical [2 + 2] cycloaddition of N, N-diethylpropynylamine (255) to C_{60} (figure 66). The cyclobutanamine 256 is unique in that it has a photosensitizer (the dihydrofullerene) and a photooxidizable group (the enamine) in the same molecule. Brief exposure to air at room light cleaves the enamine double bond producing the ketoamide 260. Tokuyama *et al* (1994) reported
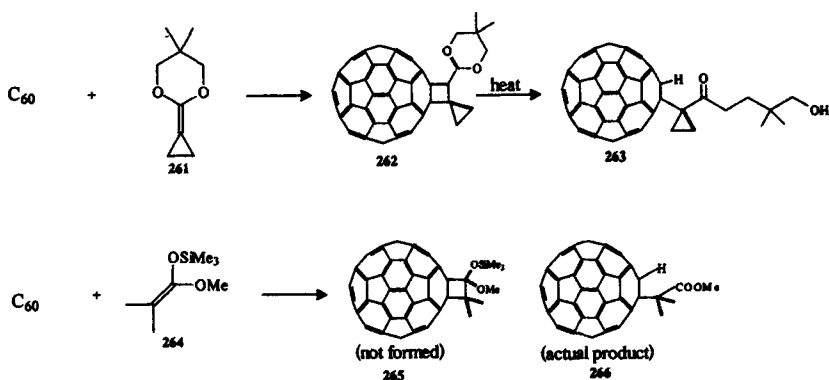
Figure 67. Photoaddition of silyl ketene acetal to [60] fullerene (Tokuyama *et al* 1994).
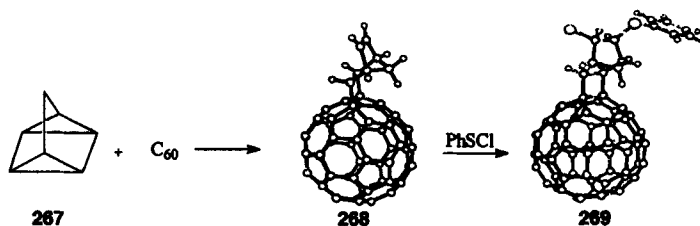

Figure 68. Addition of quadricyclane to C_{60}: Easy access to fullerene derivatives bearing a reactive double bond in the side chain (Prato *et al* 1993d).

that a highly strained ketene acetal (**261**) (figure 67) undergoes stepwise [2 + 2] cycloaddition to give **262**, whose C–C bond was cleaved upon heating in aqueous H_2SO_4 to give the ester **263**. Photoaddition of an unstrained silyl ketene acetal (**264**) to C_{60} took place at room temperature in wet toluene to afford a fullerene sub- stituted carboxylic ester (**266**) instead of the expected [2 + 2] cycloadduct. The· mechanism was suggested to involve a zwitterion formed through a radical ion-pair (Tokuyama *et al* 1994).

Reaction of C_{60} with quadricylene gives a stable [6, 6] adduct (**268**) (figure 68), a derivative of C_{60} bearing a reactive double bond in the side chain (Prato *et al* 1993). The double bond reacts readily with electrophiles such as PhSCl. Single cycloaddi- tion reactions have been utilized to attach prefunctionalized dienes to C_{60}, the 'ball and chain' adduct (**270**) (figure 69), reported by Khan *et al* (1993), is an example of the complex product available by this approach. The chemistry of cycloaddition onto π-centres already attached by σ-bonds to C_{60} is little explored. Warrener *et al* (1995) reported the cycloaddition of norbornene-containing enes (**271** and **274**) with 3,6-di(2'-pyridyl) pyridazine providing powerful chelating sites.

Prato *et al* (1993b) reported [2 + 3] cycloaddition of C_{60} with trimethylene methane (TMM), the latter reacting as a nonpolar or polar intermediate (figure 70). The TMM precursor, which gave the best results in terms of isolation and characteri- zation, was the methylenecyclopropanone ketal **277** which was heated overnight at 70°C in the presence of equimolar C_{60}. The reaction resulted in the isolation of two
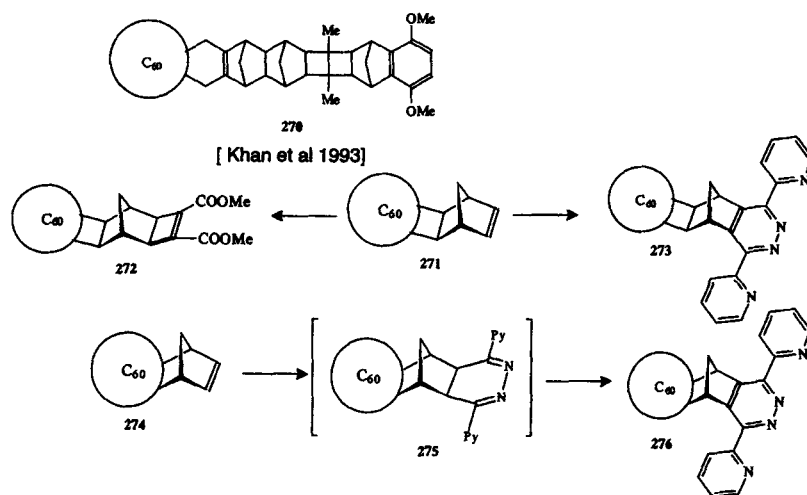
Figure 69. Attaching chelating capacity to [60] fullerene via short rigid rods (Warrener *et al* 1995).
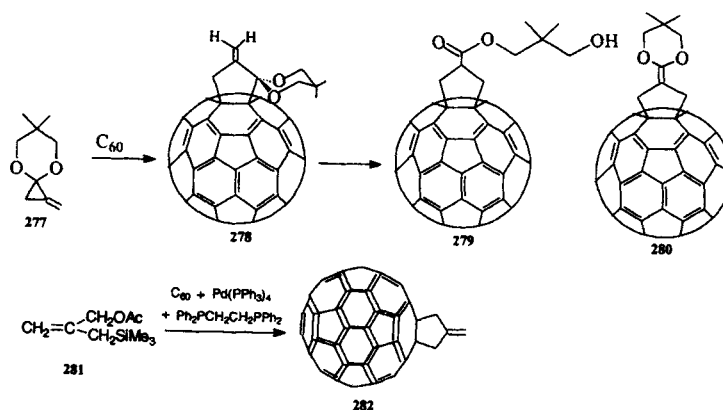
Figure 70. [3 + 2] cycloaddition of C_{60} with trimethylene methane (Prato *et al* 1993). Synthesis of parent TMM-C_{60} (282) (Shiu *et al* 1994).

products 278 and 279, the ester 279 could be the silica gel catalyzed hydrolysis of the ketene acetal 280. The product is stabilized by the irreversible addition of TMM. The first synthesis of the parent TMM-C_{60} adduct 282 was achieved by means of palladium-catalyzed [2 + 3] cycloaddition (Shiu *et al* 1994). C_{60} was first mixed with a stoichiometric amount of [Pd(PPh$_3$)$_4$] and Ph$_2$PCH$_2$CH$_2$PPh$_2$ in benzene, which resulted in the palladium-C_{60} complex. Addition of a benzene solution of the TMM precursor 281 resulted in the adduct 282.

C_{60} can add in 1,3-dipolar fashion to azomethine ylides such as $H_2C=N^+(CH_3)-CH_2^-$ (283) (Maggini *et al* 1993) giving the substituted pyrrolidines (284) in which the ring opening of the azomethine ylides takes place (figure 71). Azomethine ylide is conveniently generated from a mixture of N-methylglycine
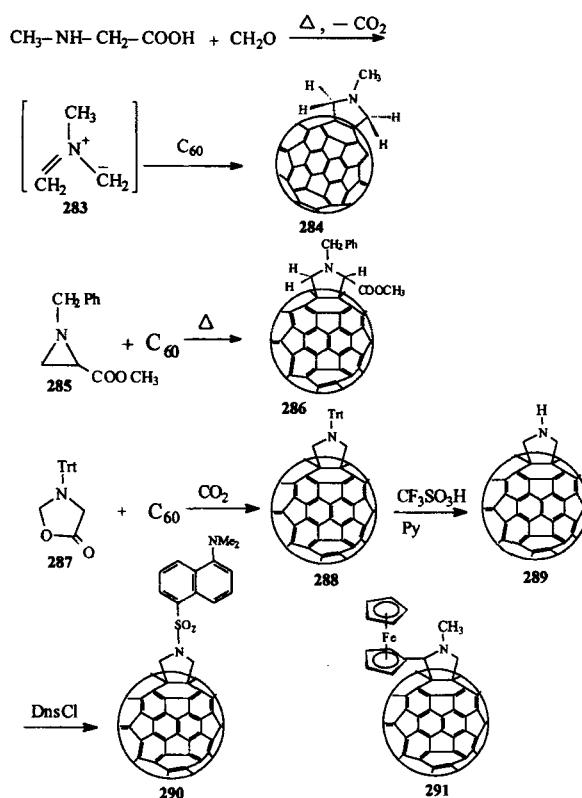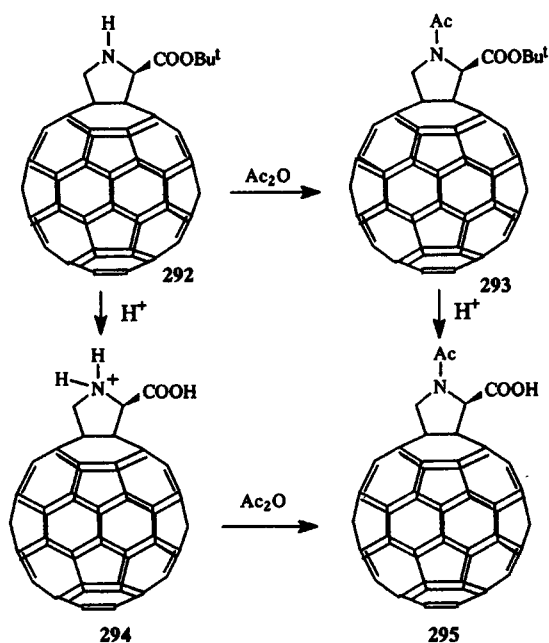
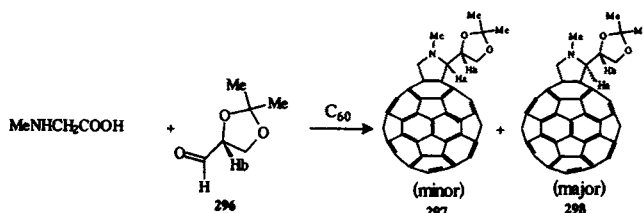Figure 71. 1,3-Dipolar addition of azomethine ylides (Maggini *et al* 1993).

and paraformaldehyde. From the spectroscopic data it was concluded that the symmetry of the substituted pyrrolidine is C_{2v} which accounts for the addition at [6,6]-ring fusion. Another approach to azomethine ylides is the thermal ring opening of the aziridines. Thus heating 285 with C_{60} in toluene, led to the pyrrolidine 286. Yet another method involves heating 3-triphenylmethyl-5-oxazolidinone with C_{60} which provides 288. Addition of pyridine and dansyl chloride to 288 brought about the isolation of dansyl pyrrolidine derivative 290. The possibility of further reacting 289 with a series of electrophiles provides an extremely versatile approach to many functionalized fullerenes. The combination of two electroactive species, ferrocene and C_{60}, could be achieved by this method. By heating a mixture of ferrocene aldehyde, sarcosine, and C_{60} in toluene at reflux, compound 291 was isolated, exhibiting the reduction and oxidation pattern of both C_{60} and ferrocene moieties.

Maggini *et al* (1994) described the preparation of N-acetyl derivatives of fullero-3,4-prolines. Fulleroproline *tert*-butyl ester 292, prepared by reacting glycine *tert*-butyl ester, paraformaldehyde and C_{60} in refluxing toluene was found to be unstable, probably owing to the reactivity of amines with fullerenes (figure 72). Functionalization of nitrogen by treating the reaction mixture directly with acetic anhydride resulted in stable acetamido derivative 293. When 292 was treated with

trifluoromethanosulphonic acid, the protonated amino acid was obtained, which reacts with acetic anhydride to give the N-acetyl derivative **295**. This water-soluble compound is a potential candidate for synthesis of peptides containing C_{60} that may have HIV protease inhibitory properties. 1,3-Dipolar cycloaddition of chiral azomethine ylides to C_{60} afforded a mixture of diastereomeric fulleropyrrolidines which could be separated by flash chromatography (Novello *et al* 1996). The stereoselectivity is most probably due to steric reasons. In all the three cases of addition of azomethine ylides (figure 73 showing one such case) to C_{60}, the chiral 1,3-dipole has a bulky group that directs the addition, the hindered bulkier site being oriented away from the C_{60} frame. N-benzyl azomethine ylide was generated *in situ* by desilylation of N-benzyl-N-(methoxymethyl)-N-[(trimethylsilyl)methyl]-amine catalyzed by trifluoroacetic acid (Laborde 1992). Zhang *et al* (1993b) used this method to synthesize a C_{60}-fused N-benzylpyrrolidine (figure 74). New cycloadducts
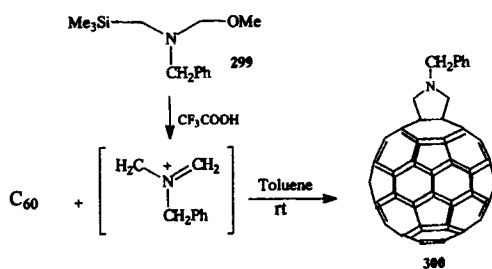

Figure 72. Synthesis of fulleroproline with an amino acid directly linked to fullerene (Maggini *et al* 1994).
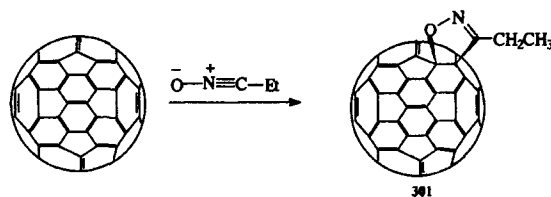

Figure 73. Stereoselective addition to [60] fullerene (Novello *et al* 1996).
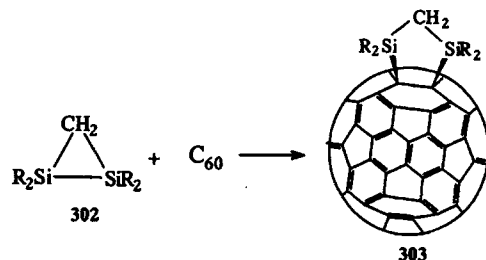
Figure 74. Generation of azomethine ylide by desilylation and formation of C_{60}-fused N-benzylpyrrolidine (Zhang *et al* 1993b).

Figure 75. 1,3-Dipolar addition to fullerene with nitrile oxide (Meier and Poplawska 1993).

Figure 76. [2 + 3] photoadduct formation of C_{60} with disilirane (Akasaka *et al* 1993).

are obtained by the reaction of C_{60} with pyrazalidinium ylides and 4-aryl-5-arylimino-2-pheynyl-1,2,4-thiadiazolidin-3-ones respectively (Bartoszek *et al* 1996).

1,3-Dipolar addition of C_{60} with nitrile oxide reported by Meier and Poplawska (1993) giving the corresponding cycloadduct of C_s symmetry, which was confirmed by ^{13}C NMR spectroscopy, resulting from addition across [6,6]-ring junction (figure 75). The addition of acetonitrile oxide to C_{60} also takes place in similar 1,3-dipolar fashion to give the corresponding isoxazoline of C_s symmetry.

Akasaka *et al* (1993) reported the first photochemical [2 + 3] cycloaddition of C_{60} with disilirane (figure 76). The reaction proceeds via a charge-transfer interaction. The addition of disilirane to C_{70} also leads to the formation of a photoadduct with the addition occurring at the equatorial belt (e-e) (Akasaka *et al* 1994).
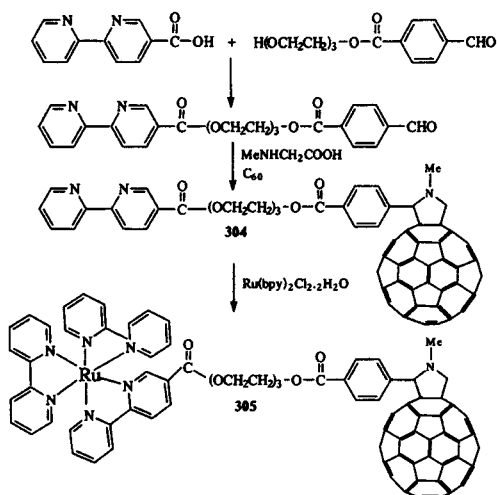
Figure 77. A C_{60} derivative covalently linked to a ruthenium(II)tris(bipyridine) complex (Maggini *et al* 1995b).

Ru$(bpy)_3^{2+}$ complexes constitute a class of photoactive compounds, known to give energy transfers in the excited states. C_{60} is known to accept reversibly up to six electrons. The coupling of the two was reported by Maggini *et al* (1995b). Such compounds are appealing as on–off components in molecular switches. C_{60} was functionalized via azomethine ylide cycloaddition (Maggini *et al* 1993) to give fullero-pyrrolidine **304** (figure 77), which has a bipyridyl group. It was then allowed to react with Ru$(bpy)_2Cl_2 \cdot 2H_2O$ to yield a C_{60} derivative covalently linked to Ru(II) *tris*(bi-pyridine) complex (**305**). A fullerene–porphyrin conjugate, covalently linked via a pyrrolidine linkage was prepared by treating *b*-formyltetraphenyl porphyrin with fullerene C_{60} and MeNHCH$_2$COOH (Drovetskaya *et al* 1995). The Ni(II) complex was similarly prepared from the Ni(II) complex of the porphyrin. A por-phyrin-linked fullerene where a C_{60} moiety is covalently linked to the meso position of 5,15-diarylporphyrin with a pyrrolidine spacer was prepared (Imahori and Sukata 1996). N-Methyl glycine, 10,20-*bis* (3,5-di-*tert*-butylphenyl)-5-formyl por-phyrinatonickel(II) and C_{60} were refluxed in toluene to give the porphyrin-linked fullerene.

Gan *et al* (1996) reported the direct reaction between amino acid esters and C_{60}. A novel air-assisted radical reaction mechanism is proposed. Thermal reaction between glycine ethyl ester and C_{60} resulted in an unexpected product **306** (figure 78). It was suggested that acetone present in ethanol solvent reacts with glycine ester to form a 1,3-dipolar intermediate, which adds on to C_{60} giving **306**. When the same reaction was carried out through a photochemical route, the isolated product was **307**. Photochemical addition of sarcosine provided **308**, the reaction is twice as fast as the glycine ester reaction. So the methyl group on the nitrogen had a more positive than a negative effect on the reaction rate. The hydrolysis of **307** and **308** to result in the corresponding carboxylic acids is not possible as C_{60} reacts with
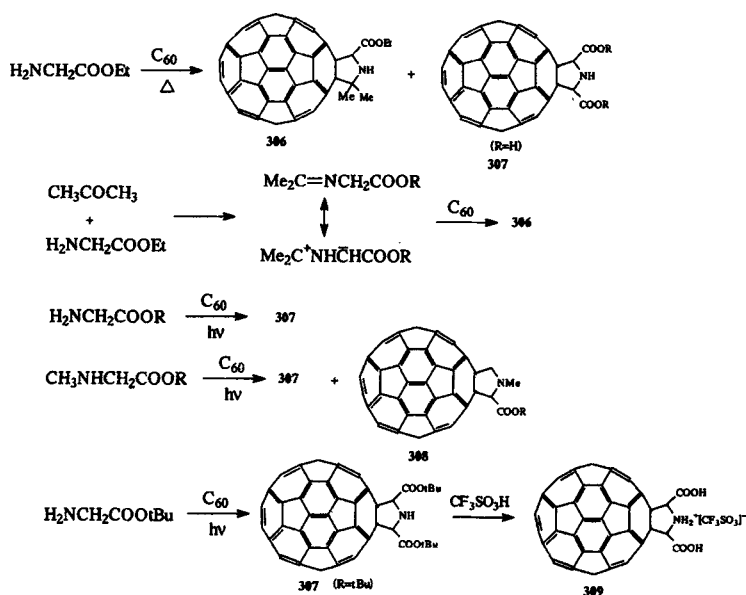
Figure 78. Fullerene amino acid derivatives (Gan *et al* 1996).

hydroxides to give fullerols. The *t*-butyl ester analog of **307** is hydrolysed by tri-fluoromethane sulphonic acid to yield the dicarboxylic acid **309**, which are of great interest in the investigation of the biologically active fullerenes.

The reversible cycloaddition of Rh(II) catalyzed diazoimides to C_{60} was studied by Gonzalez *et al* (1994). The adducts were found to undergo ready thermal cycloreversion. To generate and determine if the isomunchone (**312**) (figure 79) dipole remained intact in the process, the adduct **311** was heated in toluene in the presence of N-phenylmaleimide. Besides C_{60}, the reaction mixture contained the known adduct **313**.

Arce *et al* (1996) reported the synthesis of a stable bridged bisfulleroid **315**, which originated from a facile photochemically promoted rearrangement of **314** (figure 80). The bridged bisfulleroid formed a Co(III) complex readily. An alternate route to synthesis of **315** in higher yields was reported by these workers. Addition of a 2-fold excess of 1-(trimethylsilyl)-1,3-butadiene to C_{60} afforded the silyl ether, which on acidification furnished the allylic alcohol in up to gram quantities. Photolysis of the latter afforded good yields of the bisfulleroid.

Slow addition of ethyl propiolate to a toluene solution of C_{60} in tricyclohexyl-phosphine [$P(Cy)_3$] at ambient temperature afforded a $[2+2+2]$ cycloaddition product **320** (figure 81). In the absence of $P(Cy)_3$, no product was formed (Liou and Cheng 1995). The spectral data strongly support a head-to-tail addition of two propiolate units to C_{60}. $P(Cy)_3$ acts as a nucleophile and a leaving group. The mechanism of the reaction is discussed.

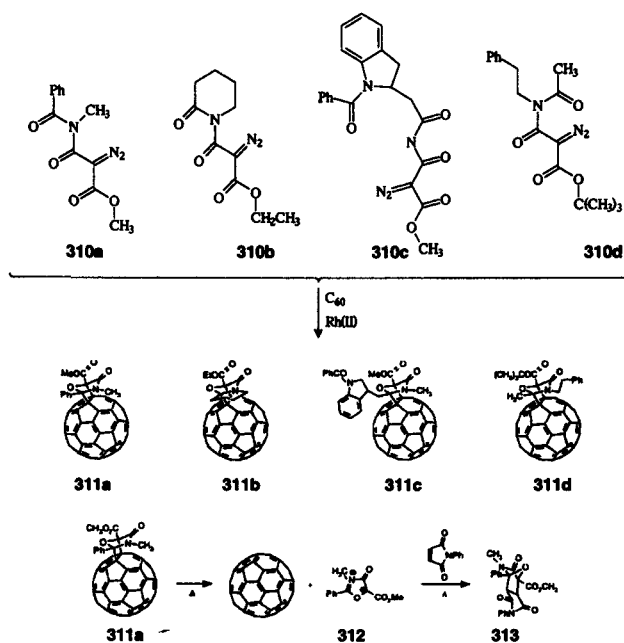**Figure 79.** The reversible cycloaddition of isomünchones to C_{60} (González *et al* 1994).

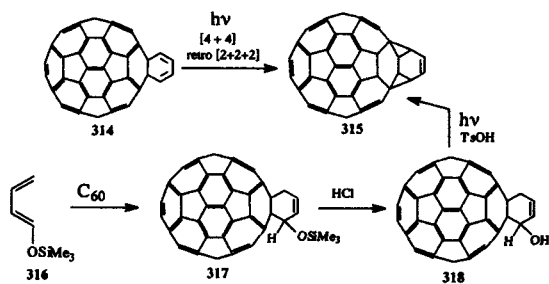**Figure 80.** Triple scission of a six-membered ring on the surface of C_{60} via consecutive pericyclic reactions (Arce *et al* 1996).

$$C_{60} \quad + \quad 2\,HC{\equiv}CCOOR \xrightarrow{\ P(Cy)_3\ }$$
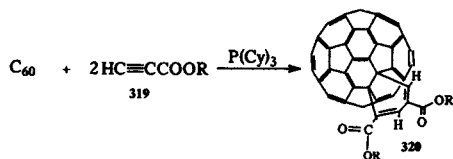
319

320

Figure 81. Cyclotrimerization of alkynes with [60] fullerene (Liou and Cheng 1995).

9. Nucleophilic addition reactions

The observed high electron affinity of C_{60} to its electron donating ability leads to the prediction that this class of materials are susceptible to nucleophilic addition. C_{60} reacts with both neutral and charged nucleophiles to give a variety of adducts. Neutral nucleophiles such as amines can be added to C_{60} (Wudl *et al* 1991c) to form the corresponding adduct. In this process a maximum of 12 amine molecules can be added to C_{60} nucleus but the most stable one is the adduct which contains six amino groups. The addition takes place across the 6, 6-ring junction of the pyracylene unit, resulting in an octahedral array. Six morpholine units can add to C_{60} to give $C_{60}H_6$ (morpholine)$_6$. The reaction of C_{60} with an excess of morpholine or piperidine in benzene in the presence of oxygen led to the isolation of hydrogenated aminoadducts **321, 322** (figure 82) with a preferred 1, 4-addition (Schick *et al* 1995). The first aminated fullerene dimer (**323**) with a single inter-fullerene connection was also a major reaction product. The dimer is insoluble in most organic solvents and only slightly soluble in *o*-dichlorobenzene.

C_{60} adds on to 1, 2-diamines, the addition proceeds with an apparent loss of two hydrogen atoms to form a variety of products (Kampe *et al* 1993; Kampe and Egger 1995; Maggini *et al* 1995c). Balch *et al* (1995, 1996) carried out X-ray studies of $C_{60}N_2(C_2H_4)_2$ **324** and one isomer of $C_{60}[N_2(C_2H_4)_2]_2$ (**325**). The structure of **325** (figure 83) reveals that the diamine has added across a [6, 6]-ring junction as ex-
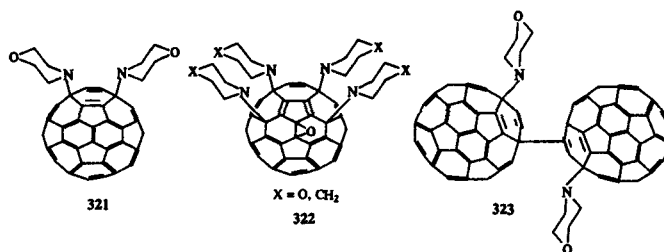

Figure 82. Reaction of C_{60} with morpholine and piperidine: preferred 1,4-addition and fullerene dimer formation (Schick *et al* 1995).
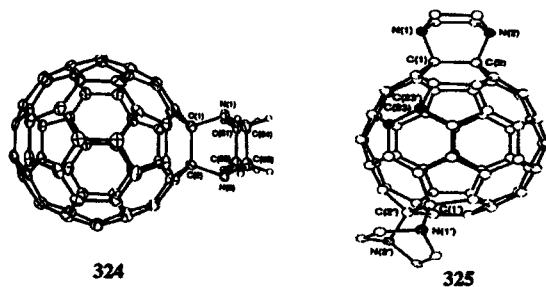

Figure 83. Prospective views of $C_{60}N_2(C_2H_4)_2$ and $C_{60}[N_2(C_2H_4)_2]_2$ (Balch *et al* 1995).

pected and a local distortion of the fullerene is produced. This distortion is manifest in the displacement of C(1) and C(2) away from their normal positions as the fullerene surface, and an elongation of C(1)–C(2) bond, the length of which is 1·624(8) Å. In comparison, the length of a normal C–C bond at a [6, 6]ring junction of an undistorted fullerene is 1·383(4) Å. The double addition product has C_2 symmetry, with the C_2 axis bisecting the bond between C(23) and C(23′), and, hence, is chiral. However each individual crystal is achiral and contains a racemic mixture of the double addition product. C_{60} and triethylamine (TEA) undergo characteristic photoinduced electron transfer–proton transfer reaction at a room temperature toluene solution (Lawson *et al* 1995). The C_{60}-TEA ion-pair intermediate in a non-polar but polarizable solvent is formed, which gets transformed to the cycloadduct **326** (figure 84). However, it is not clear how the two methine hydrogens on the cage are eliminated for the final product. Leigh *et al* (1992) reported that the family of fullerene azacrown ethers (**327**) (figure 85) formed by the addition of azacrown ethers in toluene to C_{60} at room temperature, resulted in the monoamine derivative of fullerenes. Both 1, 2- and 1, 4-addition products are possible, but the 1, 2-addition product is most stable.

Charged nucleophiles can add to C_{60} as alkylation by either Grignard or organolithium reagents followed by reaction with alkyl iodide. In this process many mono and polyadduct of C_{60} are formed e.g. $C_{60}H$ *t*-Bu, $C_{60}HEt$, $C_{60}Me_{10}Ph_{10}$,
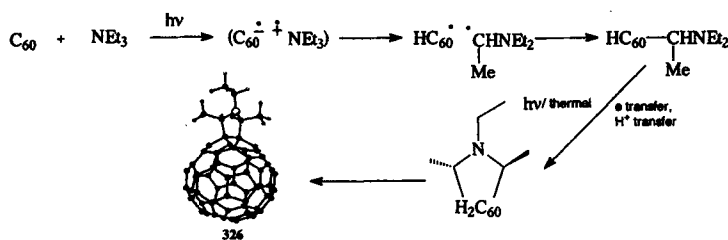
Figure 84. Photochemical inter- and intra-molecular electron transfer reactions of C_{60} and a tertiary amine (Lawson *et al* 1995).


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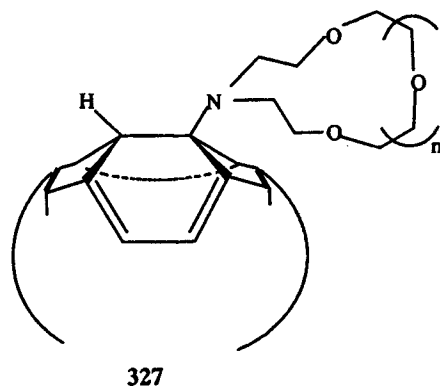
Figure 85. Addition of azacrown ethers to fullerene (Leigh *et al* 1992).

$C_{60}Me_3Ph_2$ and $C_{60}Me$ *t*-Bu. Nucleophilic reactions led to the synthesis of $C_{60}H(CH_2CMe:CH_2)$, $C_{60}H\backslash(CH_2CMe:CH_2)_8$, $C_{60}H_8(C_9H_7)_8$ by treating C_{60} with 2-methylallyl magnesium chloride and sodium indenide in THF (Huang *et al* 1994). Addition of ortho-quinodimethanes to C_{60} leads to stable easily soluble derivatives (Belik *et al* 1994). Substituents like carboxy, hydroxy and amino groups have been in positions more or less close to C_{60} and these groups allow further reactions. The adduct of 4-fluoro-3-nitrobenzoyl benzocyclobutene and C_{60} shows a high affinity for nucleophilic substitution by amines. Dodecylated C_{60}-$[(Do)_nC_{60}(H)_n]$ and butylated C_{60}-$[(Bu)_nC_{60}(H)_n]$ were synthesized by Levon *et al* (1994). XRD results reveal that the structure of C_{60} expands to a primitive hexagonal structure upon butylation and to a layered structure upon dodecylation.

C_{60} reacts with $PhCH_2ONa$ —$PhCH_2OH$ in the presence of air to afford a 1,3-dioxolane derivative of C_{60} (**328**) (Wang *et al* 1995). The mechanism of the reaction is discussed (figure 86). Komatsu *et al* (1994b) reported the first alkyne C_{60} derivatives, which would be a versatile precursor to a variety of new molecules. The ethynyl handle was provided by [(trimethylsilyl)-ethynyl]lithium. Both *mono*- and *bis*-adducts (figure 87) were isolated. The product yields were highly dependent on reaction conditions.

Schneider *et al* (1994) reported that hydroxy groups can be added to C_{60} by reaction with BH_3-THF complex followed by hydrolysis with either glacial acetic acid, $NaOH/H_2O_2$ or NaOH. This gives water soluble fullerols. A very convenient
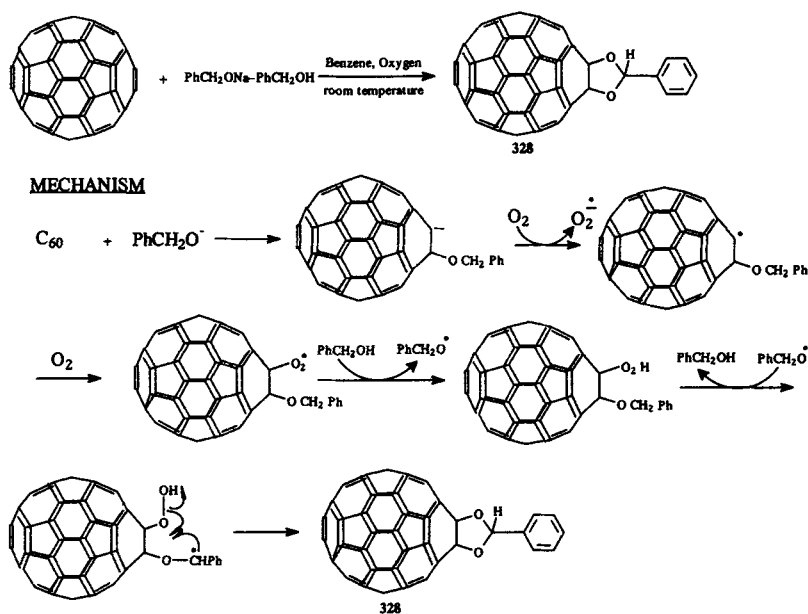
Figure 86. Formation of a 1,3-dioxane derivative and involvement of oxygen in a nucleophilic addition reaction of C_{60} with sodium alkoxide (Wang *et al* 1995).

method for the synthesis of $C_{60}(OH)_x$ was reported by Sun *et al* (1996). C_{60} in toluene is reacted with potassium and hydrolysis of the product provides fullerols.

Di-addended and tetra-addended C_{60} were synthesized through the use of novel organoborane intermediates. The C_{60}, C_{70} or higher fullerene is reacted with a borane such as BH_3 in toluene to form an organoborane intermediate which on hydrolysis with water or alcohol results in the di-addended or tetra-addended product. The reaction of lithiated phosphine-borane or a phosphinite-borane with C_{60}, followed by removal of the BH_3 group, affords a fullerene substituent, which undergoes complexation with BH_3 and $PtCl_2$ selectively on the phosphorus atom with a 1:1 and 2:1 stoichiometry (Yamago *et al* 1994b). Two types of isopropoxysilyl compounds, $C_{60}(H)[CH_2Si(O^iPr)Me_2]$ **332** and $C_{60}[CH_2Si(O^iPr)Me_2]_2$ **333** are isolated from C_{60} and $ClMgCH_2SiMe_2(O^iPr)$ (Nagashima *et al* 1995). The conversion of the isopropoxy groups of **332** and **333** to the corresponding chlorides and triflates is reported by Nagashima *et al* (1995) (figure 88). The high oxophilicity of the silicon atoms of the chlorides and triflates in turn resulted in an expeditious way to link alcohols, phenols, and even silica to C_{60} moieties.

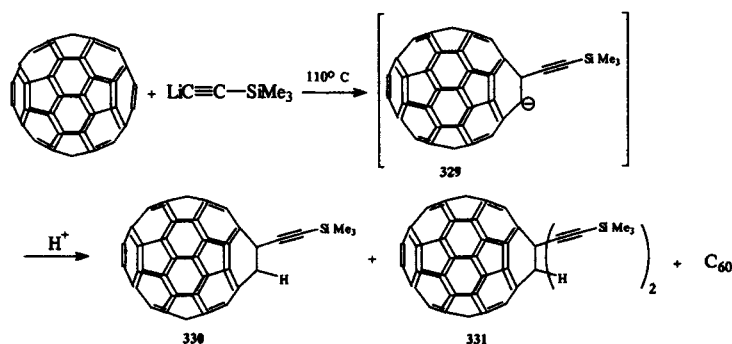**Figure 87.** Acetylene derivatives of C_{60} (Komatsu *et al* 1994).
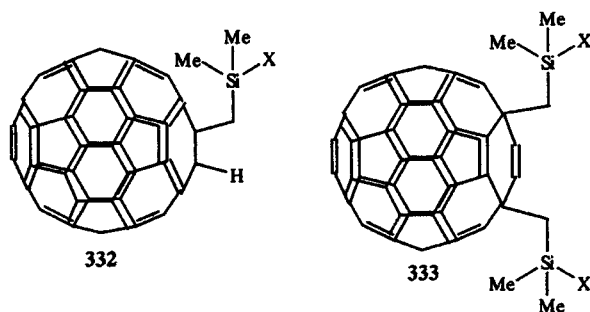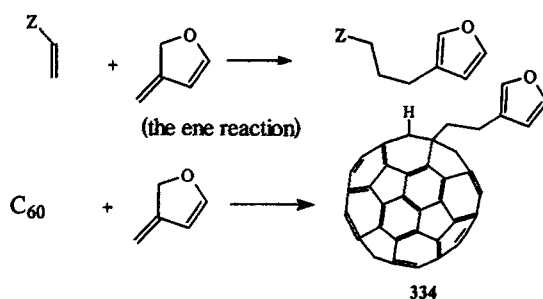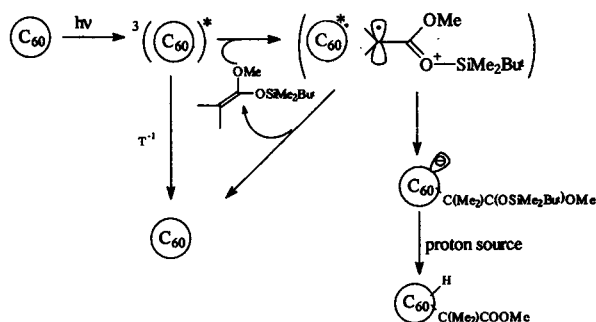

Figure 88. Chlorosilanes and silyl triflates containing C_{60}: a versatile synthetic route linking C_{60} moieties with alcohols, phenols, and silica (Nagashima *et al* 1995).

Figure 89. Ene reaction of C_{60} and 3-methylene-2,3-dihydrofuran (Miles and Smiley 1996).

Figure 90. Photo-induced electron transfer from ketene silyl acetals to the triplet excited state of C_{60} leading to fullerene acetates (Mikami *et al* 1995).

The reaction of C_{60} with 1-heptene and 4-allylanisole (Wu *et al* 1994), and 3,5-di-*t*-butyl-4-[(trimethylsiloxyl)allyl]benzene (Komatsu *et al* 1994) were the first published report of an ene reaction (figure 89) with a fullerene. 4-Alkylanisole reacts with C_{60} at 200–220 °C to form an ene reaction adduct (Wu *et al* 1994). Miles and Smiley (1996) reported the ene reaction of C_{60} and 3-methylene-2,3-dihydrofuran and isolated fullerene addition product **334** in good yields. The chemical manipulation of furan ring provides a means of obtaining a whole host of new fullerene compounds, including water soluble fullerenes. Analogous to 'prototropic ene reaction', Mikami *et al* (1995) reported 'silatropic ene reaction' of C_{60} with esters derived from ketene silyl acetals (KSA), to provide fullerene acetates. The addition of KSAs to the triplet excited state of C_{60} takes place via photoinduced electron transfer (figure 90). The reaction is useful for further elaboration to fullerene amide and peptide of biological importance.

1,9-(4-Hydroxycyclohexano)buckminsterfullerene **338** is a versatile alcohol that permits further functionalization of C_{60} which permits the preparation of a variety of C_{60}-derivatives. An *et al* (1993) reported the preparation of first α-amino acid derivatives (**339, 340**) (figure 91). The de-protected amino acids are water soluble and retain the unusual redox and photophysical properties of C_{60}. The Diels-Alder
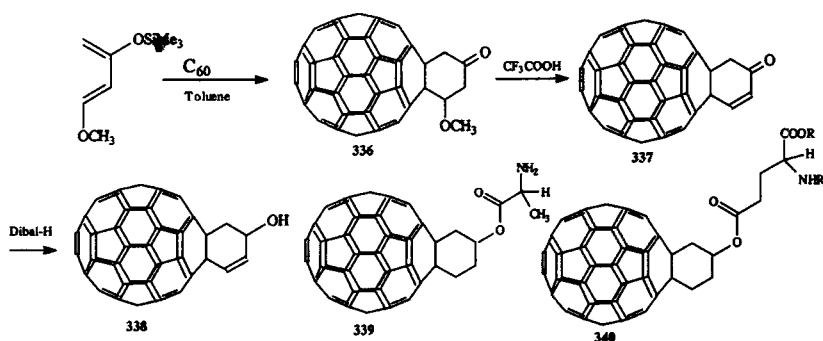
Figure 91. A methodology for the reversible solubilization of fullerenes and synthesis of α-amino acid derivatives (An *et al* 1993, 1995a).
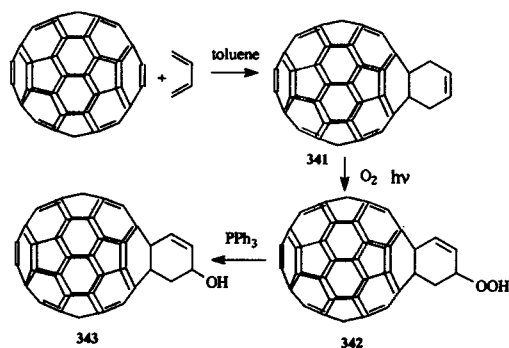
Figure 92. Singlet oxygen ene reaction of cyclohexenobuckminsterfullerene (An *et al* 1995a).

reaction of 1,3-butadiene and C_{60} is noted for its instability towards air and light, affording hydroperoxide **342** (figure 92). Reaction of C_{60} with $^1O_2$ afforded the allylic alcohol **343** after reduction with PPh_3 (An *et al* 1995). The dihydrofullerene moiety plays the role of $^1O_2$-sensitizer, and the cyclohexene moiety that of an unavoidable reaction center. The alcohol **344** available from the [2 + 3] cycloaddition of a dipolar trimethylenemethane was treated with benzoyl chloride and pyridine to yield the benzoate (figure 93) (Yamago *et al* 1993). By this method fullerene bearing olefins, aldehydes, alcohol, sugar and amino acid groups are synthesized by oxidation, reduction and C–O and C–C forming reactions.

10. Electrophilic addition reactions

Fullerene is unreactive towards the electrophilic reagents because of its electron withdrawing nature. This obstacle is overcome by the formation of their anions which act as potent reactant. Methyl iodide reacts with C_{60} to form methylated derivative and this is confirmed by ^1H and ^{13}C NMR spectrum δ (^1H) ~ 0·06,
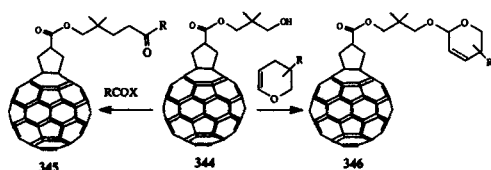
Figure 93. Derivatization of organofullerenes (Yamago *et al* 1993).
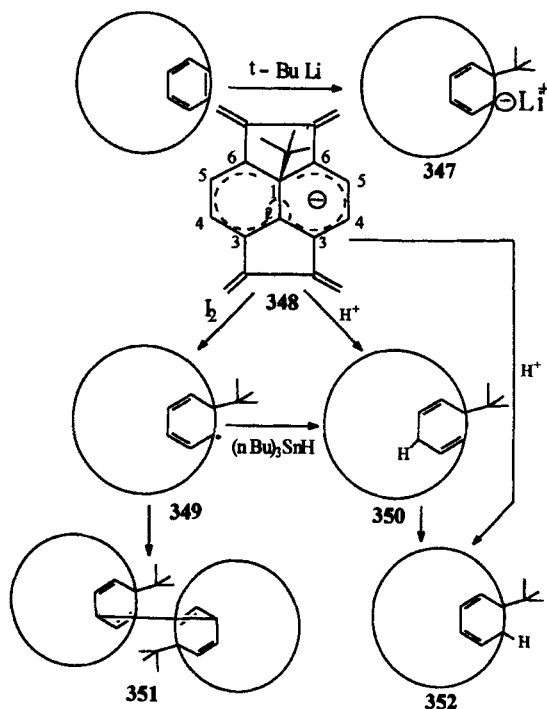
Figure 94. Reaction of C_{60} with *t*-BuLi and synthesis of *t*-BuHC$_{60}$ (Fagan *et al* 1992).

$\delta(^{13}C) \sim 1$. $(CH_3)_6$ and $(CH_3)_8$ fullerene derivatives predominate in the products, which contained up to 24 methyl groups (Bausch *et al* 1991). More controlled anion formation has been achieved in the reaction of C_{60} with *t*-Bu Li (**347**) (figure 94) (Fagan *et al* 1992). It forms *t*-BuC$_{60}$ with small amounts of $(t\text{-Bu})_n C_{60}{}^{n-1}$ $(n = 2\text{-}6)$. *t*-BuHC$_{60}$ exists in two forms with the H and *t*-Bu groups in either 1,2- or 1,11-positions (**350, 352**). The latter rearranges to the former, which is more stable. The high electron withdrawal by the cage makes *t*-BuHC$_{60}$ a strong carbon acid ($pK_a = 5.7$) with a weak C–H bond dissociation energy (71 kcal/mol).

Pure C_{60} and C_{60}/C_{70} mixtures undergo $AlCl_3$ or $FeCl_3$-catalyzed reaction with aromatics such as benzene and toluene to polyarene units by initial protonation of the cage by the $HAlCl_3OH$ super acid (Olah *et al* 1991). Since Ar and H are added across fullerene double bonds, the reaction can be characterized as fullerenation of

aromatics the products $C_{60}H_nAr_n$, the species with $n = 12$ and 16 are especially obtained when aromatic group is Ph. The results support the direct fullerenation of the aromatic ring by initial protonation of fullerene to the corresponding fullerene cation and subsequent Friedel-Crafts alkylation. FAB mass spectrometry indicated a strong mass peak (M^+, 1656), supporting the formation of $C_{60}(C_6H_6)_{12}$ and also formation of $C_{60}(C_6H_6)_{16}$ (M^+, 1968). There is no evidence of phenylation of C_{70} in fullerene mixture.

$C_{60}Cl_6$ can be phenylated and arylated to give derivatives of the type $C_{60}Ar_5Cl$, which may be readily converted to $C_{60}Ar_5H$ (Taylor *et al* 1994). The compounds $C_{60}Ph_5H$ and various other phenylated derivatives are isolated from the product of reaction of C_{60} with bromine, $FeCl_3$/benzene. In the presence of $FeCl_3$, benzene readily undergoes electrophilic substitution by $C_{70}Cl_{10}$ to give both yellow $C_{70}Ph_{10}$ and orange-red $C_{70}Ph_8$ each of which is luminescent (Avent *et al* 1996). $C_{70}Ph_{10}$ is not formed directly from $C_{70}Cl_{10}$, but rather by further phenylation of the intermediate $C_{70}Ph_8$. The adjacent Ph groups of $C_{70}Ph_{10}$ are sterically prevented from rotating at room temperature. $C_{70}Ph_8$ spontaneously oxidizes in air to form a *bis*-lactone $C_{70}Ph_8O_4$, having an eleven-membered whole in the fullerene cage (Birkett *et al* 1995b). The reaction is believed to proceed via insertion of oxygen into [5,6]-bonds followed by oxidative cleavage of the adjacent double bond.

Chiang *et al* (1992) reported initial electrophilic attack of nitronium ion to C_{60} to form an intermediate $C_{60}(NO^{2+})_x$ and nucleophilic 1,3- or 1,5-substitution followed by hydrolysis to finally give polyhydroxy organocarboxylate derivative consisting of average 13–15 hydroxyl substituents and 4–5 *p*-bromobenzoate moieties per C_{60} molecule. This upon hydrolysis gives the corresponding water soluble fullerols consisting of 18–20 hydroxyl groups per C_{60} molecule.

$$NO_2BF_4 + RCOOH \rightarrow RCOO^-NO_2^+ + HBF_4$$

$$C_{60} \xrightarrow[\text{2)H}_2\text{O}]{\text{1)RCOO}^-\text{NO}_2^+} C_{60}(-OCOR)_x(OH)_y$$

$$(R = -C_6H_5, p\text{-}C_6H_4Br, \; x = 13\text{--}15, \; y = 4\text{--}5)$$

$$C_{60}(-OCOR)_x(OH)_y \xrightarrow{\text{NaOH/H}_2\text{O}} C_{60}(OH)_{x+y}, \quad x + y = 18\text{--}20$$
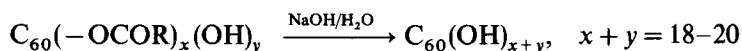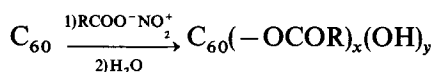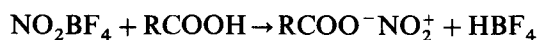
C_{60} nitroderivatives were also prepared by reacting C_{60} in the inert CCl_4 solution with conc. HNO_3 and NO_2 gas (Huang *et al* 1996). The product had the composition $C_{60}(NO_2)_x(OH)_y$. C_{60} is sulphonated in fuming sulphuric acid and chlorinated in chlorosulphonic acid (Miller *et al* 1994). Both reactions involve initial oxidation of C_{60} followed by *in situ* trapping of electrophilic C_{60} cation.

11. Radical (neutral, anion, and cation) addition to C_{60}

The radicals such as Me·, Ph·, PhS·, $PhCH_2$·, CBr_3·, CF_3·, and Me_3CO· react with C_{60} forming either mono or poly or both types of adducts (Krusic *et al* 1991a; Morton *et al* 1992b), although in some cases rapid reversion to C_{60} occurs. There are thirty double bonds in C_{60} to which free radicals can add to give radical
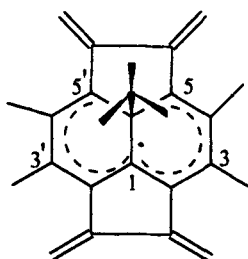
Figure 95. Radical addition of C_{60} and preferred orientation of alkyl substituent (Krusic *et al* 1993).

adducts. Normally the addition takes place across the [6,6]-double bond of pyracylene unit. In case of monoadduct the radical is located on one of the ring fusion site of [6,6]-double bond and substitution on the other side. Each half of the radical structure is of C_s symmetry. As reported by Krusic *et al* (1991) up to 11 phenyl groups, 15 benzyl groups and 35 methyl groups can be added to C_{60} in the course of reaction.

Alkyl radicals can readily add to C_{60} to give the product $R_n C_{60}$, which can be detected by mass spectrometry for even n and by ESR spectroscopy for odd n. The dependence of signal intensity on temperature and dilution (Krusic *et al* 1993) established the fact that the radical adduct of C_{60} exists in equilibrium with their dimers: 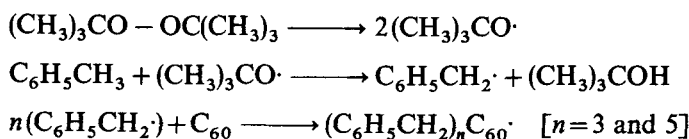$RC_{60}C_{60}R \rightleftharpoons 2RC_{60}$. There exists substantial rotational barrier about $R-C_{60}$ bond (C_6-C_9) (figure 95), so that substituents adopt preferred equilibrium conformation relative to C_{60} framework. For t-Bu-C_{60}, activation energy for internal rotation is 8·2 kcal/mol.

Photochemically generated benzylic radical adds to give $(C_6H_5CH_2)_n C_{60}$ where $n = 1$ to 15 (Krusic *et al* 1991a). Mass and ESR spectra of the above adduct show two intense signals for $n = 3$ and 5 and these two were found to be most stable having allylic and pentadienyl structure respectively (figure 96):

$$(CH_3)_3CO - OC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot$$

$$C_6H_5CH_3 + (CH_3)_3CO\cdot \longrightarrow C_6H_5CH_2\cdot + (CH_3)_3COH$$

$$n(C_6H_5CH_2\cdot) + C_{60} \longrightarrow (C_6H_5CH_2)_n C_{60}\cdot \quad [n = 3 \text{ and } 5]$$

In all the above cases of radical adduct, the radicals formed are not allowed for delocalization because delocalization placed double bond in the pentagonal rings. So the radicals formed are unstable leading to dimerization. ESR spectra confirms that C_{60} t-Bu radical (**349**) forms a dimer (**351**) (figure 94) and steric constraints suggest that dimerization must take place at para position.

Alkoxy radicals (RO·) generated photochemically from peroxides add to C_{60} yielding the RO-$C_{60}\cdot$ radical adduct which is detected by ESR spectroscopy (Cremonini *et al* 1993). A more convenient photolytic source of alkoxy radicals for addition to fullerenes is dialkoxy disulphide ROSSOR. Borghi *et al* (1996) studied the radical adduct RO-$C_{60}\cdot$(R = Me, Et, i-Pr, and t-Bu) obtained by photolysis of the corresponding ROSSOR derivatives in the presence of C_{60}.
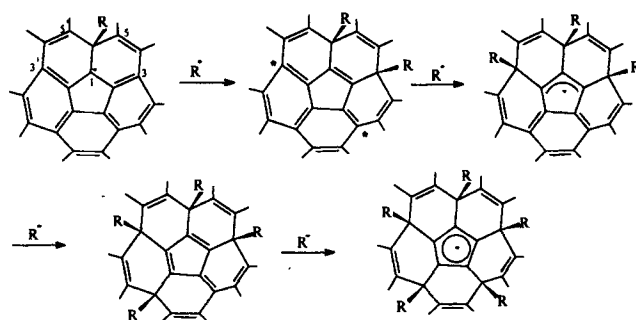
Figure 96. Addition of photochemically generated benzylic radical to C_{60} (Krusic *et al* 1991a).

The rotation about the intercage bond of singly bonded C_{60} dimers $RC_{60}C_{60}R$ (R = H, Me, and *t*-Bu attached at ortho or para positions from pivot carbon atoms) obtained by dimerization of RC_{60}· radicals, has been studied by molecular mechanics (Osawa *et al* 1996). The predicted rotational barriers are high ranging from 15 kcal/mol for the least hindered p,p'-$(HC_{60})_2$ to the almost forbidding values for those carrying *tert*-butyl groups. Contrary to the expectation, rotamers with R groups close to each other like the gauche form are predicted to be consistently more stable than with maximally separated substituents, by as much as 10 kcal/mol in case of R = *tert*-butyl.

The reaction of $(\eta^3$-$Ph_3C)Re(CO)_4$ with CO is known to produce $Re(CO)_5$, via homolysis of a weak Re–C bond in a $(\eta^1$-$Ph_3C)Re(CO)_5$ intermediate. The reaction with C_{60} in the presence of CO results in colour change in the solution with the formation of $C_{60}[Re(CO)_5]_2$ by either thermal or photochemical process (Zhang *et al* 1993). The photolysis of C_{60} in the presence of donor molecules such as dimethyl aniline, tetramethylphenylene diamine, hexamethyl benzene etc in toluene/2-Me THF solutions to produce radical anion of C_{60}. With benzyltrialkyl tin derivative, the photolysis of C_{60} in toluene/2Me THF solution is also reported and confirmed by ESR spectroscopy.

Olah *et al* (1991a) carried out oxidation studies on C_{60} and C_{70} using SbF_5 in SO_2ClF solution, a system found highly efficient for oxidation of polycyclic aromatic to their dications. Green coloured solution is obtained that gave extremely broad ^{13}C NMR spectra at all temperatures employed. The results indicated the generation of diradical cations instead of diamagnetic di- or polycations. A novel synthetic route for the formation of the biphenyl anion from benzene using fullerene anion was reported by Eastman *et al* (1994). 18-Crown-6-assisted potassium metal reduction of C_{60} in benzene at room temperature gave coupling of benzene and ultimately the biphenyl anion, identified by ESR studies. Stable 1-octynyl-C_{60}-carbanion was generated by the reaction of 1-octynyl-C_{60}-H with *t*-BuOK in THF and its structure was confirmed by ^1H and ^{13}C NMR spectra (Murata *et al* 1996). The redox properties are studied by cyclic voltametry and involve a one electron oxidation process affording a dimer of the corresponding radical. The reaction of

dianion species with various carbon electrophiles afforded the 1,2- or 1,4-disubstituted dihydrofullerenes.

12. Polymerization reactions

Zhu *et al* (1994) observed the phenomena of electrical fusion of fullerenes in a laser desorption mass spectrometric study of adduct compounds of R_nC_{60} ($R = C_6H_5CH_2$ or C_9H_7) in the negative ion channel. The nature of R is believed to play a key role in the formation of stable higher mass fullerenes and doubly charged negative ions of C_{60} in the gas phase. Yang and Yuan (1995) treated sublimed C_{60} thin films by direct current discharge plasma. The UV-visible spectra of the treated C_{60} films show the plasma polymerization of C_{60} film surface. Ultraviolet irradiation of C_{60} in the absence of oxygen formed a polymeric product $(C_{60})_n$, where $n \sim 20$ and this again undergoes ring opening reaction to finally give 1,2-addition products (Taylor and Walton 1993).

C_{60} and C_{70} initiate the polymerization of the monomer 1,3-butadiene in the gas phase (Wang *et al* 1992a). While $C_{60}^{\cdot+}$ and $C_{70}^{\cdot+}$ were found to be unreactive towards 1,3-butadiene, both C_{60}^{2+} and C_{70}^{2+} were observed to react readily. In the process of polymerization, the coulombic repulsion between the positive charges is relaxed as more butadiene monomers are added. There are two ways in which a polymer chain can be propagated. One is the propagation of polymer chain on one side of the cage in a tadpole-like fashion and the second is on both sides of the cage in a spindle-like fashion. From the above it was concluded that the fullerene cage may become a pendant on or be blocked in the polybutadiene chain (figure 97). Reaction of C_{60}^+, C_{60}^{2+} and C_{60}^{3+} were investigated with C_2H_2 and C_2H_4 in the gas phase (Wang *et al* 1996a). The C_{60}^+ is unreactive and C_{60}^{2+} reacts only slowly by adduct formation. · However C_{60}^{3+} reacts rapidly with C_2H_2 by adduct formation and electron transfer. A mechanism is proposed for the polymerization without and with hydride shift in the derivatized fullerene cation.
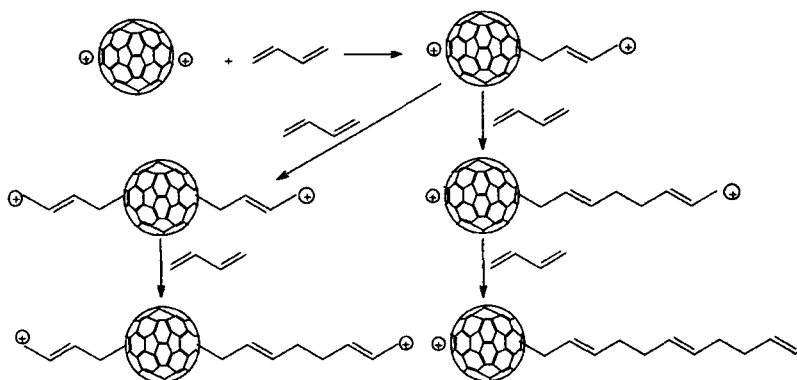

Figure 97. Attachment of polybutadiene chain to fullerene cage (Wang *et al* 1992).
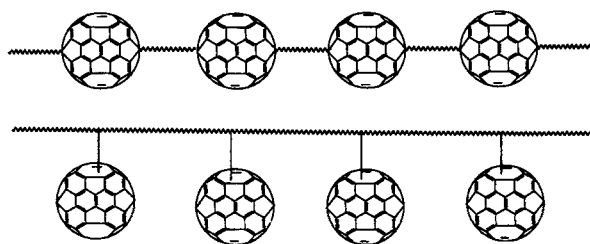
Figure 98. 'Pearl necklace' and 'charm-bracelet' type polymers of fullerene.
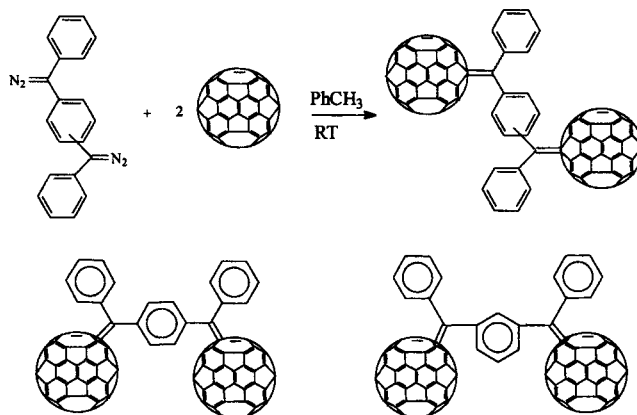
Figure 99. Synthesis of a basic unit for 'pearl necklace' polymers (Suzuki *et al* 1992).

Fulleroid formation has opened the way for the synthesis of two types of polymerization i.e. 'pearl necklace' and 'charm bracelet' (figure 98) (Amato 1991). The former is the hypothetical one in which C_{60} framework is the part of a backbone and the latter is a polymer in which C_{60} is attached to the side chain of a traditional polymer. The third variety of polymer also exists in which a necklace variant with a direct link between the cages is apparently formed on polymerization of C_{60} by UV radiation in the absence of oxygen (Wudl *et al* 1992). A basic unit for 'pearl necklace' polymer is the diphenyl fulleroid (figure 99) (Suzuki *et al* 1992). Fullerene inflation reaction can yield molecules which are the basic unit of pearl necklace polymers in which the fulleroid becomes part of the polymer backbone. Nigam *et al* (1995b) investigated the addition of 2-methylaziridine to C_{60}. The adduct was suggested to have ten aziridine rings per molecule of C_{60}. This C_{60}-methylaziridine reacts readily with phenolic and epoxy monomers via aziridine ring opening to produce polymers with good thermal stability. The first 'charm bracelet' conjugated polymers—an electroconducting polythiophene with covalently bound fullerene was reported by Benincori *et al* (1996). The polymer is prepared by electrochemical polymerization of a cyclopenta[2,1-b:3,4-b'] dithiophen-4-ylidene fullerene-C_{60} adduct. The electrical properties of the polymers are reported.
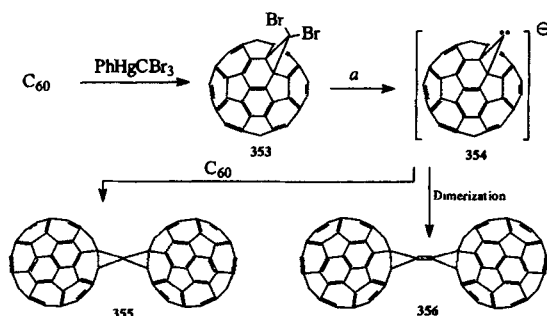
Figure 100. Evidence of the carbon allotropes C_{121} and C_{122} *a-* i. toluene, $Fe(CO)_5$, $0°C$ reflux, ii. toluene, hv, 330 nm, 25° C, iii. toluene, Cu, reflux and iv. toluene or THF, BrLi, $-90°C$, reflux (Osterodt and Vögtle 1996).
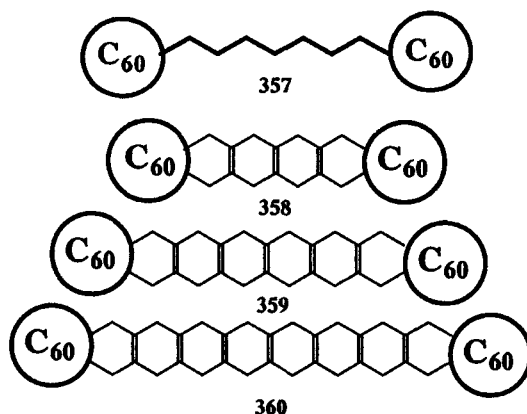
Figure 101. Controlled spacing of C_{60} carbon spheres (Paquette and Graham 1995).

C_{60} dimerizes into various forms, and there are several reports of singly bonded dimers (Morton *et al* 1992a; Keizer *et al* 1993; Yoshida *et al* 1994). The rotation about the intercage bond of singly bonded C_{60} dimers $RC_{60}C_{60}R$ obtained by dimerization of RC_{60}· radicals has been studied by molecular mechanics (Osawa *et al* 1996). The first indication of a double-bonded dimer is reported by Osterodt *et al* (1996). The addition of methanofullerenecarbene, $C_{60}C$:, to C_{60} and its dimerization would provide **355** (C_{121}) and **356** (C_{122}) (figure 100) which have been detected by mass spectroscopy. There is a possibility that **355** and **356** are formed under mass spectrometric conditions. The ^1H NMR spectra of the dimer shows a very broad band, indicating the presence of a number of isomers.

Controlled spacing of C_{60}-carbon spheres with 1,4-cyclohexadienyl ladders by pairwise Diels-Alder cycloaddition to C_{60} was reported by Paquette and Graham (1995) (figure 101). A number of dumbbell-like structures could be designed. Diederich *et al* (1995) reported the synthesis of a rotaxane **363** (figure 102) assembled via the copper(I) templated approach, bearing two C_{60} units as chemical stoppers. The syn-
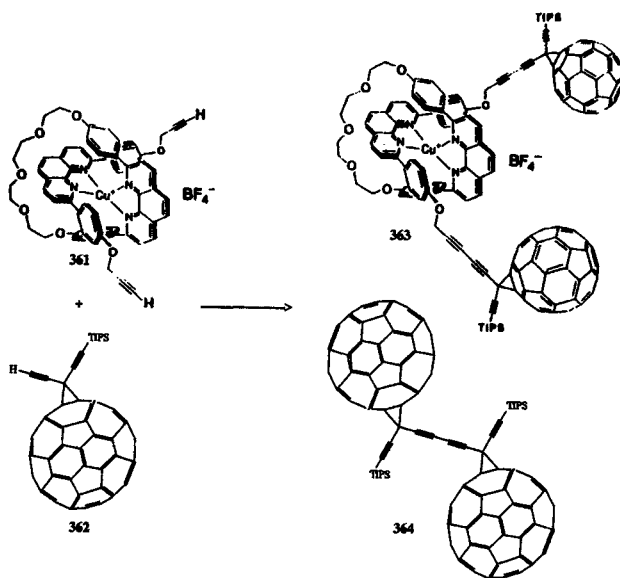
Figure 102. A copper(I)-complexed rotaxane with two fullerene stoppers (Diederich *et al* 1995).
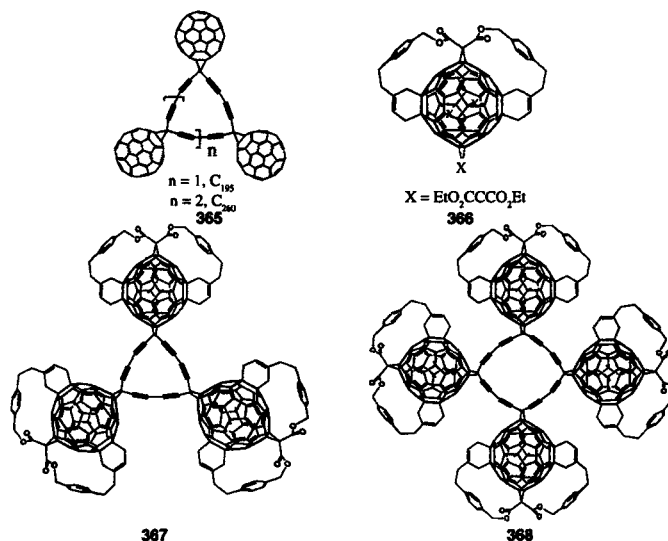
Figure 103. First members of a new class of carbon allotropes $C_{n(60+5)}$: C_{195}, C_{260} and their solubilized derivatives (Isaacs *et al* 1995a).

thesis of **363** is based on the oxidative coupling reaction of terminal alkynes function-alized on C_{60} (**362**) and copper(I) rotaxane **361** in the presence of Hay catalyst [CuCl–TMEDA–O_2(TMEDA = N, N, N', N'-tetramethylethylenediamine)]. A dimeric fullerene derivative resulted from the homocoupling reaction of **362**.
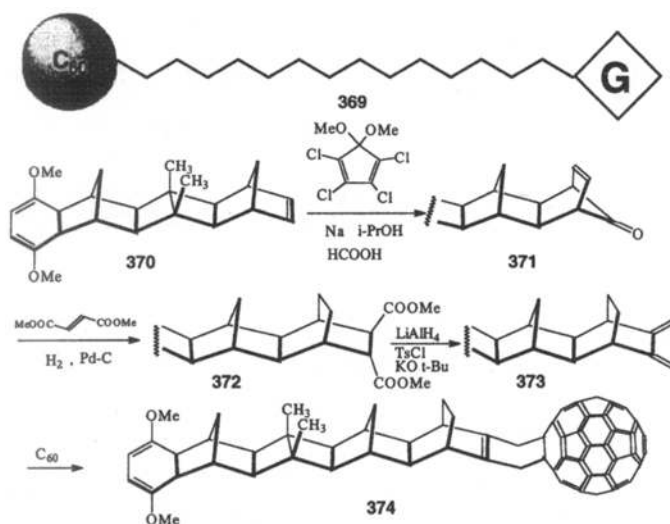
Figure 104. Synthesis of a rigid 'ball-and-chain' system through Diels-Alder functionalization of C_{60} (Khan *et al* 1993).

A number of new carbon allotropes of molecular formula $C_{n(60+5)}$ are synthesized by oxidative cyclization of diethynylmethanofullerene (figure 103). The smallest number of this family C_{195} (**365**) consists of a *cyclo*-C_{15} core surrounded by three peripheral fullerenes, whereas C_{260} is a *cyclo*-C_{20} derivative with four fullerenes. Isaacs *et al* (1995) extended their above work to the synthesis of analogous tri- and tetramers **367** and **368** respectively. The starting material synthesized by the method of template activation (Cardullo *et al* 1996) subjected to nucleophilic addition/elimination of 1,5-*bis* (trimethylsiyl)-3-bromopenta-1,4-diyne so as to introduce diethynylmethano group, leading to dialkynylmethanofullerene hexaadduct **366**. Deprotection and subsequent oxidative cyclization led to two major derivatives of the carbon allotropes C_{195} and C_{260} providing **367** and **368**.

Khan *et al* (1993) reported the ball-chain molecule **374** in which the chain comprises a rigid polynorbornyl-bicyclo [2·20]hexyl bridge (figure 104). The configuration of the novel bridge diene can be systematically altered and a variety of functional groups **G** appended. The application of Diels-Alder cycloaddition to the formation of polymer bound fullerene i.e. synthesis of cyclopentadiene functionalized polymers have been reported (Guhr *et al* 1994). The reaction of merrified peptide resin (**375**) in toluene with excess sodium cyclopentadienylide at $-20°C$ formed functionalized polymers (figure 105) which react with C_{60} at room temperature to give fullerene functionalized polymer (**377**). This reaction has opened the way for the covalent attachment of fullerenes to a polymer support through Diels-Alder cycloaddition and the product formed has shown to be readily reversible, allowing recovery of C_{60} upon heating of the resin.

C_{60} reacts with benzyl radical to form polybenzylated fullerenes. C_{60} can be incorporated in a copolymer with *p*-xylylene, the product is unstable and readily reacts with oxygen. Xylylene (**378**), a diradical analogue of benzylic radical easily
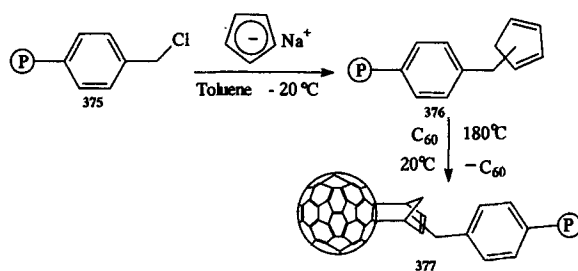
Figure 105. Synthesis of cyclopentadiene functionalized polymers of C_{60} (Guhr *et al* 1994).
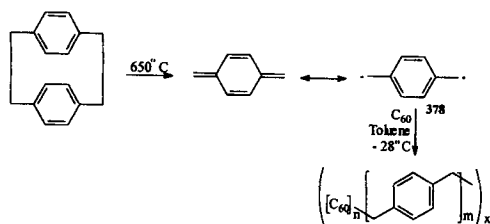
Figure 106. Copolymerization of xylylene with C_{60} (Loy and Asssink 1992).

prepared by flash thermolysis of paracyclophane is known to form poly(*p*-xylylene) by reacting readily with itself (Loy and Asssink 1992). In this reaction the polymerization of C_{60} and *p*-xylene takes place by the free radical pathway (figure 106) and the copolymer formed is insoluble which is due to the cross linking through multiple benzylation on the C_{60} molecule (Tebbe *et al* 1991).

The fullerenation of polystyrene provides a facile method of homogeneously dispersing fullerene molecules into polymer matrices. Anionic co-polymerization of C_{60} with styrene monomer gives a mixture of products known as flagellanes and are highly soluble (Taylor and Walton 1993). This can also be processed in the melt. C_{60} can be incorporated into noncrosslinked polystyrene by reaction with $AlCl_3$. Polystyrene-based fullerene polymers have been of particular interest because of potential technological applications (Cao and Webber 1995; Bunker *et al* 1995; Camp *et al* 1995; Weis *et al* 1995). C_{60} and C_{70} co-polymerize with styrene in a standard free radical polymerization either in bulk or co-dissolved in an aromatic solvent (Cao and Webber 1995). The resulting polymers are soluble and behave like ordinary polystyrene in solution except for the dark brown colour. The adsorption spectrum of the co-polymer is strongly modified from that of the parent fullerene, and the fluorescence is blue-shifted and much stronger. C_{60}-styrene random co-polymers with different C_{60} content are prepared using bulk and solution polymerization techniques (Bunker *et al* 1995). The C_{60}-styrene co-polymers have quite different adsorption and emission properties from both polystyrene and C_{60}. The significantly larger fluorescence yields in the co-polymers are attributed to reduced symmetry of C_{60} molecules upon being incorporated into polymer structures. Liu *et al* (1996) reported preparation of pendant C_{60}-polystyrene polymers **379** (figure 107) by use of Friedel-Crafts type reactions.
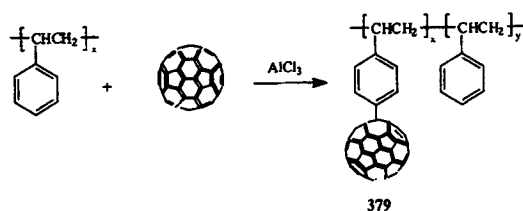
Figure 107. Soluble pendant [60] fullerene-polystyrene polymers (Liu *et al* 1996).
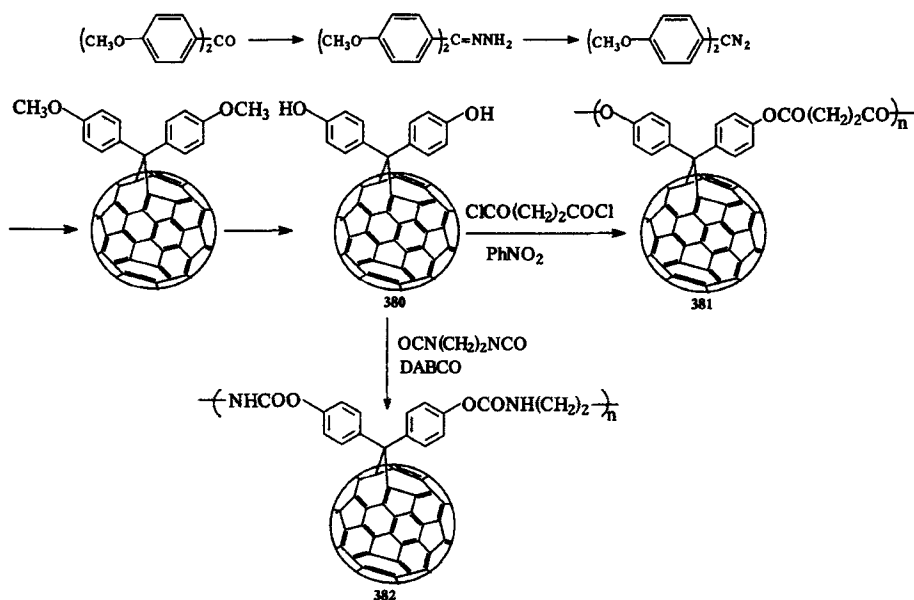
Figure 108. Polyester and polyurethane derivatives of fulleroid (Shi *et al* 1992).

Fullerene-functionalized polymers were prepared by covalently attaching fullerenes to amino-containing flexible hydrocarbon polymers. These materials are soluble in hexane or THF in which the fullerene is essentially insoluble (Patil and Schriver 1995). A series of amino-terminated polystyrenes with relatively narrow molecular weight distribution was synthesized by living anionic polymerization and subsequent end-capping (Weis *et al* 1995). The reaction of the terminal amino function with C_{60} was monitored *in situ* by UV spectroscopy. Hydroxy- and amino-functionalized fullerenes also are the potential reactants for the formation of C_{60} containing polyesters and polyamides (Chiang *et al* 1992a, b). The methanofullerenes can give rise to pendant chain polymers. The fulleroid $(HOC_6H_4)_2 C_{61}$, (**380**), with sebacryl chloride or hexamethylene diisocyanate polymerize to produce two charm bracelet type polymers containing C_{61} molecules dangling from the polymer bone i.e. polyester and polyurethane derivatives of C_{61} (figure 108) (Shi *et al* 1992).
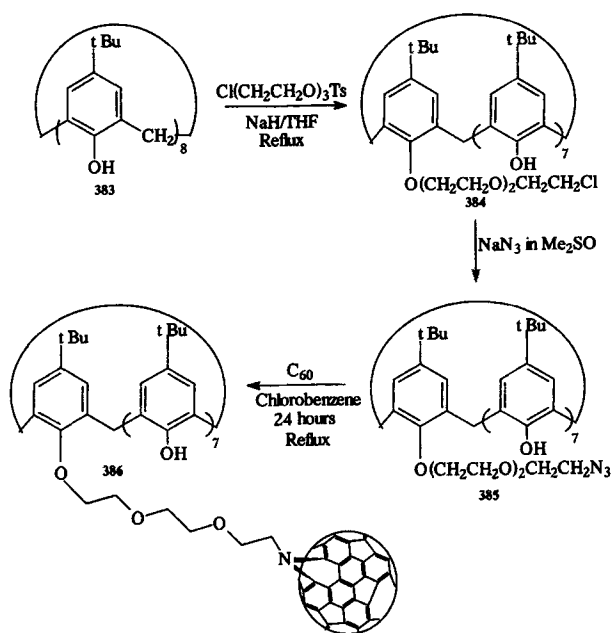
Figure 109. Synthesis of calix fullerene (Shinkai *et al* 1994).

Polyether modified fullerenes were prepared under mild conditions by reacting C_{60} or C_{70} in toluene with a bifunctional amino-terminated poly (oxyethylene) or poly(oxypropylene) (Manalova *et al* 1994). In the early stages of the reaction soluble products are formed. Later cross-linking proceeds between the polyfunctional fullerenes and the bifunctional polyethers. The non-crosslinked fullerene is soluble in toluene and water; on evaporation of toluene, adhesive films are formed. An adduct of C_{60} and 2-methyl aziridine was prepared and co-polymerized with Novolac and Bisphenol A to provide three dimensional polymers containing C_{60} with low coefficients of friction and good wear properties for use as potential solid lubricants (Nigam *et al* 1995b). Co-polymerization of C_{60} with paracyclophane at high temperature was studied (Huang *et al* 1994a). Main chain polymers with the incorporated [60]fullerene units were readily prepared by reaction of buckminsterfullerene with functional bis-*o*-quinodimethanes. Cross-linking was effectively suppressed by carefully directed admixing of a mono-*o*-quinodimethane. A polymer of high molecular weight consisting of eighty [60]fullerene units on the average was prepared (Guegel *et al* 1996). Reactions of C_{60} with the complex Pd_2 (dibenzylidene acetone)$_3$ $CHCl_3$ results in a ligand displacement reaction to give $C_{60}Pd_n$ (Nagashima *et al* 1992). $C_{60}Pd_{3.5}$ catalyzed the hydrogenation of diphenyl acetylene consistent with the presence of palladium atoms on the polymer surface.

C_{60} functionalized calix[8] arene connected by a polyether chain i.e. calix fullerene has been prepared (Shinkai *et al* 1994) (figure 109). There are reports of grafting of C_{60} onto a polyethylene surface. When polyethylene films functionalized
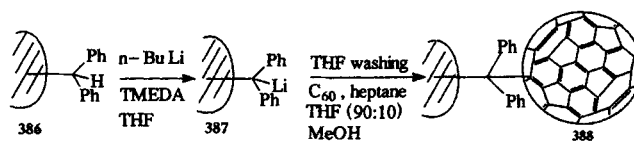
Figure 110. Grafting of C_{60} onto polyethylene surface (Bergbreiter and Gray 1993).

with diphenyl methyl groups react with *n*-BuLi, deprotonated to give a nucleophilic lithiated surface. This surface is used to covalently bind C_{60} to polyethylene (figure 110) (Bergbreiter *et al* 1993). The presence of C_{60} graft was confirmed by XPS, UV-visible and fluorescence spectroscopy.

Starburst dendrimers, which are three dimensional, highly ordered oligomeric and polymeric compounds formed from smaller molecules by reiterative reaction sequences (Tomalia *et al* 1990), can mimic certain properties of micelles, liposomes and even those of biomolecules. A new branch of 'supramolecular chemistry' has sparked new developments in both organic and macromolecular chemistry. Some examples of such class of compounds include iptycenes (**389**), which are a class of all-hydrocarbon dendrimer prototypes (Hart *et al* 1986), dendrimeric macromolecules based on adamantane (**390**) (Newkome *et al* 1992) and dendrimeric polyethers (**391**) (figure 111).

Hawker *et al* (1994) reported the addition of dendrimeric molecules to fullerenes. The fascinating thing about the dendrimeric addition is the polymeric fragment (due to their global three dimensional structure) which lead to greater encapsulation and the ability to prepare monofunctional, monodisperse materials of known molecular mass. It is the one step cycloaddition reaction of a dendritic azide with C_{60} (figure 112). Due to the increase of molecular mass by 3400 for each dendrimer addition, only mono- and di-addition products are observed and no higher addition products. When six dendrimer was added to C_{60}, the mono- and di-addition products are found to be 2:3 with no observable higher addition product and this is exclusively due to steric crowding around the C_{60} molecule. Wooley *et al* (1993) reported the attachment of polyether dendrimers to phenol-functionalized fullerenes (figure 113). The benzylic bromide group at the focal point of a fourth-generation dendrimer (**394**) reacts with the phenolic groups located at the surface of the functionalized fullerene and thus two dendrimers couple with one fullerene to give the fullerene-bound dendrimer **395**.

Fullerenols which contain multiple polar hydroxy functions in a ball-shaped fullerene structure are versatile molecules in the prospective design of three-dimensionally stretched polymers. Chiang *et al* (1994) reported the synthesis of urethane-connected polyether star polymers (**398**) (figure 114) utilizing fullerenol as a molecular core containing six chemically bonded polymer arms per C_{60} on average, with a narrow distribution of arms per molecule and a polydispersity index of 1·45. Fullerenol **396** was treated with polymer of diisocyanated urethane polyether **397** followed by termination reaction with dodecan-1-ol which afforded the corresponding C_{60}-based urethane-connected polyether dendritic polymers.
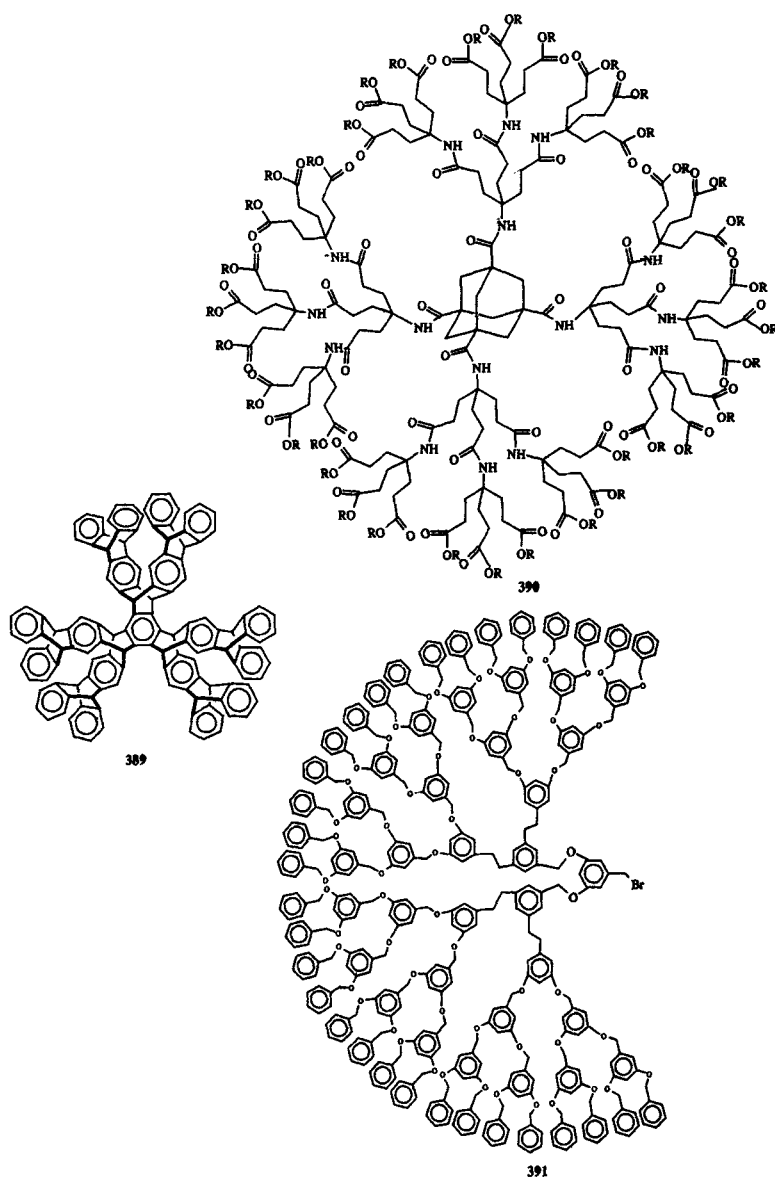
Figure 111. Some examples of dendrimers (Hart *et al* 1986; Newkome *et al* 1992; Hawker *et al* 1993).

The average molecular mass of **398** was obtained as Mn 18000 and Mw 26000, which corresponds to a fullerenol-based dendritic polymer with six linear urethane-connected polymer arms on average. Polyhydroxylated C_{60} is thus used as an efficient hyper-cross-linking agent (Chiang *et al* 1995). These authors (Wang *et al* 1996b) also reported the synthesis of diisocyanate-terminated polyurethane by the
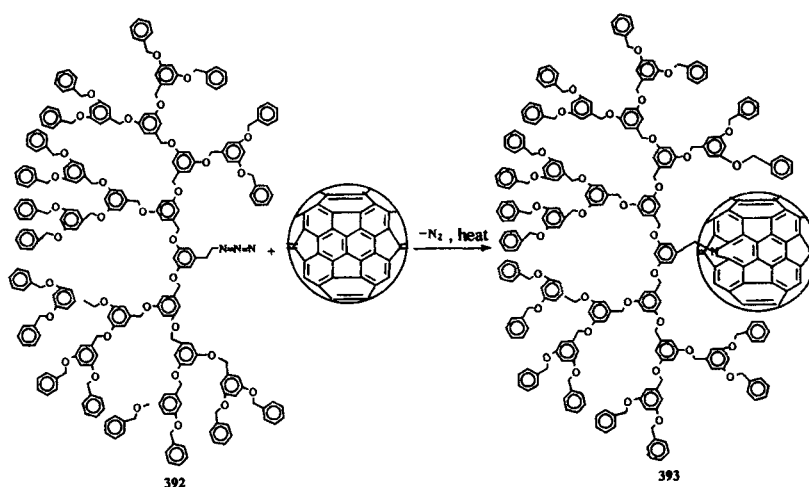
Figure 112. Dendrimer addition to C_{60} (Hawker *et al* 1994).
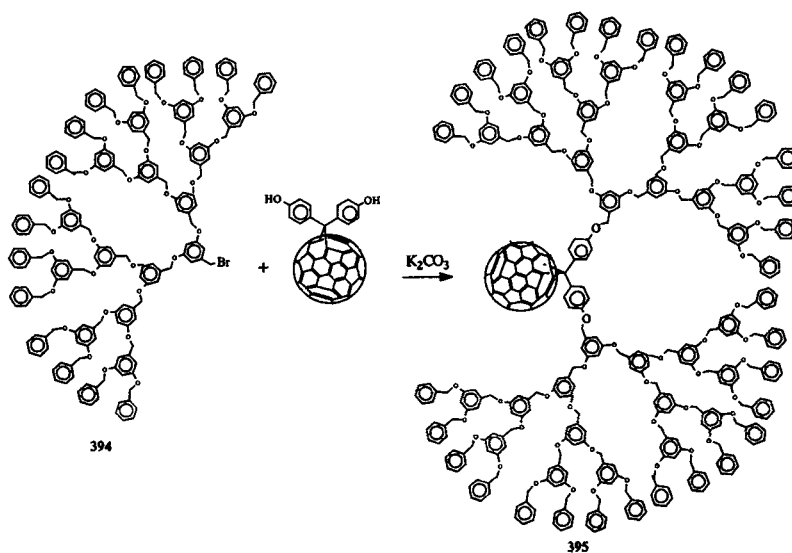
Figure 113. Dendrimer attachment to phenol-functionalized fullerene (Wooley *et al* 1993).

reaction of poly(tetramethylene oxide) glycol and MDI and then allowing to react with fullerenol. The resultant flexible polymers exhibited greatly enhanced thermal stability in comparison with those of the corresponding linear polyurethane and analogous elastomers, which were cross-linked with 1,1,1-*tris*(hydroxymethyl) ethane. A synthetic method leading to the preparation of a thin layer of conductive
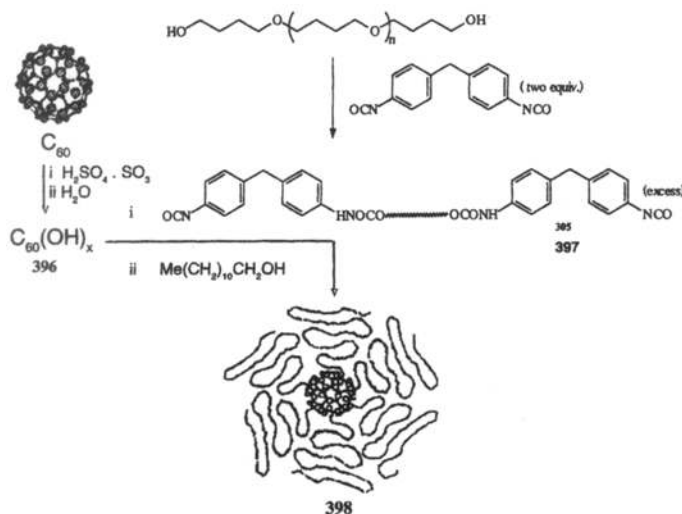
Figure 114. Fullerenol derived urethane-connected polyether dendritic polymers (Chiang *et al* 1994).

polyaniline/polyurethane IPN at the near surface of a fullerenol-based elastomeric substrate was demonstrated by using aqueous ammonium persulphate as an oxidizing agent in presence of HCl. This new material exhibits a conductivity of 2 S/cm at ambient temperature with the retention of most bulk properties of the parent elastomer such as elongation and tensile strength at break.

The fullerene polymers are manufactured from several types of C_n (n is integer of geometrically spherical compound) directly bonded through C at a vacancy of $\geqslant 1$ fullerenes with missing C positions (Ata *et al* 1996). Such polymers are used as membrane materials. Fullerene functionalized amine containing polymers and polymerizable monomers are characterized by high temperature stability capable of withstanding a temperature of at least about 300°C and in some instances as high as 650°C, when in polymerized form. In some cases enhanced mechanical properties also result in case of cross-linked polymers (Narang *et al* 1994). Photoconductive composites for copiers are reported (Yoshino *et al* 1994). The compounds contain substituted poly(*p*-phenylenevinylenes) and fullerenes.

13. Conclusion

The chemistry of C_{60} and C_{70} have made significant progress over the years and within a short span hundreds of papers, along with reviews and monographs have appeared on the subject. The field is full of promise and for chemists in general and organic and polymer chemists in particular it would be an exciting branch of research in the coming decades. The future attention would be on the synthesis and

characterization of many novel molecules. The possible application of such materials in different fields would be the focal point of such activity.

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