

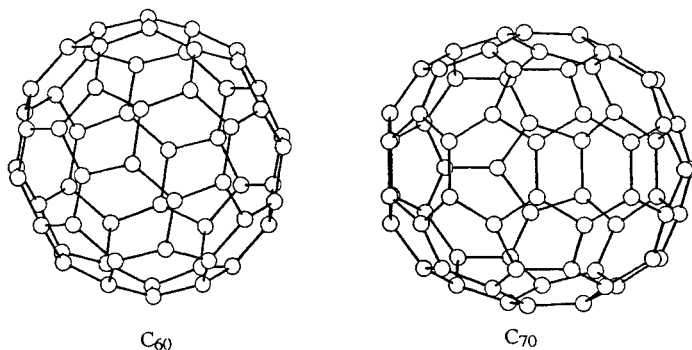
## The structure and reactivity of C<sub>60</sub>

Harold W Kroto, Roger Taylor and David R M Walton

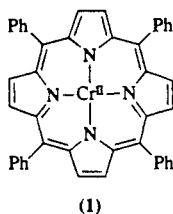
School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ UK

Abstract: C<sub>60</sub> contains thirty double bonds endocyclic to the twenty adjacent hexagons and exocyclic to the twelve isolated pentagons which comprise the highly symmetric, I<sub>h</sub>, structure. As a result the cage exhibits chemical properties commensurate with those of an electron-deficient polyene.

Evidence for the existence of C<sub>60</sub> (Buckminsterfullerene) was first obtained in 1985 (1) and macroscopic quantities of this all-carbon molecule, together with small amounts of the higher fullerene C<sub>70</sub>, became available five years later by solvent extraction and chromatographic separation (2) of the sooty deposit resulting from the resistive heating and vaporisation of graphite (3). All carbons in C<sub>60</sub> are chemically equivalent, as revealed by <sup>13</sup>C n.m.r. spectroscopy (2), however the structure contains thirty localised 'double' (*ca.* 1.39 Å) and sixty 'single' (*ca.* 1.44 Å) bonds; the double bonds are arranged exocyclic to the pentagons (4).

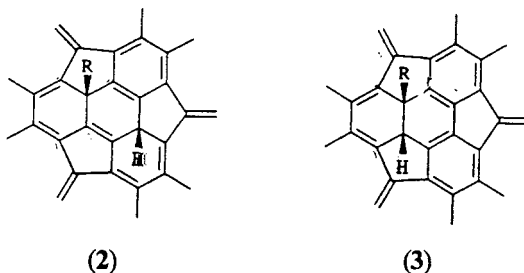


C<sub>60</sub> displays typical electron acceptor properties. For example, it exhibits six reversible one electron reductions in solution (5), commensurate with the filling of a triply degenerate low lying *t<sub>1h</sub>* LUMO. Group 1 and 2 metal salts of C<sub>60</sub> are superconducting with transition temperatures (*T<sub>c</sub>*) 33 K for RbCs<sub>2</sub>C<sub>60</sub> (6) and 8.4 K for Ca<sub>5</sub>C<sub>60</sub> (7). Electroreduction of C<sub>60</sub> in the presence of [Ph<sub>4</sub>P<sup>+</sup>][Cl<sup>-</sup>] yields the mixed salt [Ph<sub>4</sub>P<sup>+</sup>]<sub>3</sub>[C<sub>60</sub>]<sup>-</sup>[Cl<sup>-</sup>]<sub>2</sub> (8), whilst the one-electron reductant, Cr<sup>II</sup>(tpp) (1), gives [(1)<sup>+</sup>][C<sub>60</sub>]<sup>-</sup>[THF]<sub>3</sub>. In the latter, THF stabilises the Cr<sup>III</sup> oxidation state through solvation, whereas the Cr<sup>II</sup>-containing neutral salt is favoured in toluene (9).

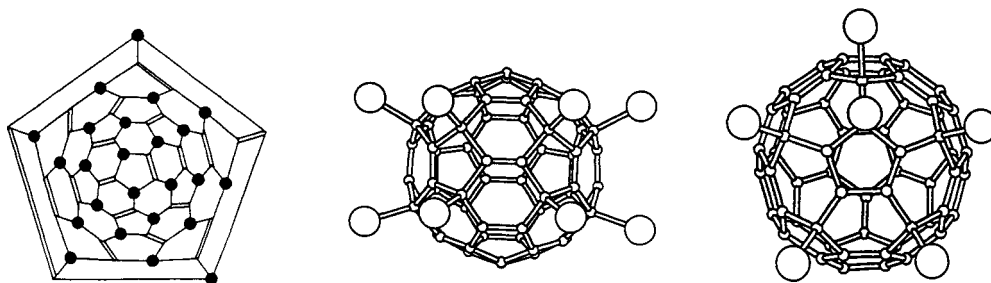


(1)

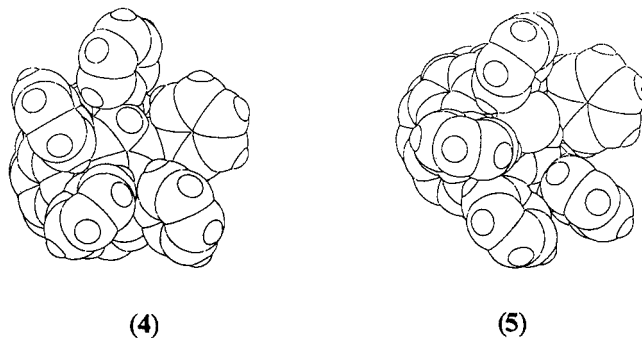
The  $C_{60}$  cage is susceptible to nucleophilic attack, but the degree of addition is difficult to control. For example the mass spectrum of  $C_{60}Me_n$ , obtained by quenching  $C_{60}^{6-}$  with MeI, reveals the presence of species up to  $n = 24$ , with  $C_{60}Me_6$  and  $C_{60}Me_8$  dominant (9). By contrast, careful treatment of  $C_{60}$  with one equivalent of *eg.* *t*-BuLi (10) followed by protonation yields two mono-adducts,  $C_{60}RH$  [ $R = t$ -Bu, (2) and (3)]; (2) slowly rearranges to the thermodynamically favoured isomer (3) which contains no pentagonal double bond (11).



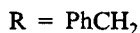
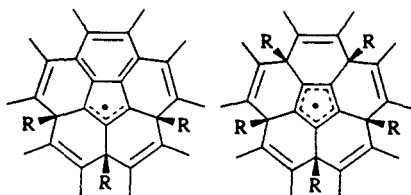
Liquid bromine reacts with  $C_{60}$  to give  $C_{60}Br_{24}$  in which all bromines are equivalent (12) (Schlegl diagram: 24 is the maximum number of bromines which can be attached to the cage so as to avoid occupation of adjacent sites). Bromination in  $CS_2$  yields  $C_{60}Br_8$ , whereas in benzene or  $CCl_4$   $C_{60}Br_6$  is formed (13). Treatment of  $C_{60}$  with ICl gives  $C_{60}Cl_6$  which is isostructural with the bromine analogue (14).



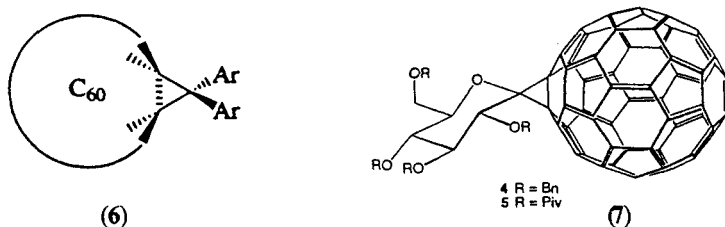
$C_{60}$  reacts with benzene in the presence of  $Br_2$  and  $FeCl_3$  to give mixed products including  $C_{60}Ph_6$  (15),  $C_{60}Ph_5H$  (4) and  $C_{60}Ph_{12}$  (16), based upon mass spectral evidence. Reaction of  $C_{60}Cl_6$  with benzene and  $FeCl_3$  gives  $C_{60}Ph_5Cl$  (5) which is readily reduced to (4) (17).



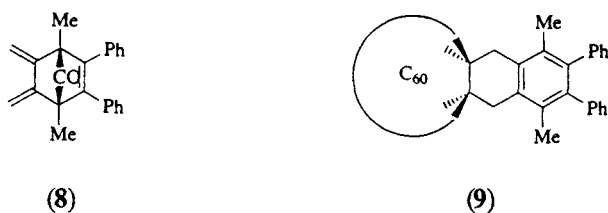
Benzyl radicals react with  $C_{60}$  to give  $C_{60}(CH_2Ph)_n$  ( $n \leq 15$ ) (18). E.s.r. spectra reveal the presence of allyl and cyclopentadienyl sites on the cage, a result which may have a bearing on possible intermediates in the bromination of  $C_{60}$ .



Cycloadditions of dipoles and dienes (Diels Alder reaction) to  $C_{60}$  have proved to be a particularly fruitful area of research and offer what is arguably the best way to date of developing the organofunctional chemistry of  $C_{60}$ . For example, one or more (up to six) diaryldiazomethane units add across the interpentagonal bonds to give pyrazolines which spontaneously lose  $N_2$  to generate the diarylhomofullerene,  $C_{60}CAR_2$  (6) (19). This strategy has been employed to prepare  $C_{60}$  containing polymers (20) and, using a diazirine (carbene precursor) to attach a protected glycoside residue indirectly to the cage (7) (21).

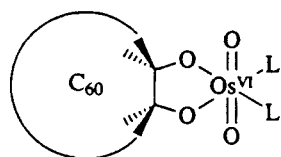


Retro-Diels Alder processes can often be troublesome. For example, the cyclopentadiene adduct of  $C_{60}$  decomposes upon heating unless the double bond in the addend is saturated (22). With diene (8), subsequent CO loss from the initial product of cycloaddition leads to formation of a stable aromatic ring (9) (23).

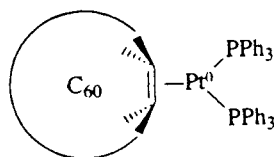


Transition metals have played an important role in the development of  $C_{60}$  chemistry. Reaction with  $OsO_4$  in the presence of 4-*t*-butylpyridine (L) gave the osmyl ester  $C_{60}[OsO_4L_2]$  (10), the first  $C_{60}$  derivative to be fully characterised (24). The structures of five isomeric bis-osmyl esters have been deduced from their n.m.r. spectra (25). The platinum complex

$C_{60}Pt(PPh_3)_2$  (**11**) exhibits the properties commonly associated with eta-2 compounds (26); hexa-adducts,  $C_{60}[M(PEt_3)_2]_6$  ( $M = Ni, Pd$  and  $Pt$ ), with the metals disposed octahedrally around the cage, have been prepared (27).



(10)



(11)

## REFERENCES

1. H.W. Kroto *et al.* *Nature (London)* **318**, 162-163 (1985).
2. R. Taylor *et al.* *J.Chem.Soc.,Chem.Comm.* 1423-1425 (1990).
3. W. Krätschmer *et al.* *Nature (London)* **347**, 354-358 (1990).
4. W.I.F. David *et al.* *Nature (London)* **353**, 147-150 (1991).
5. Q. Xie *et al.* *J.Am.Chem.Soc.* **114**, 3978-3980 (1992).
6. T. Tanigaki *et al.* *Nature (London)* **352**, 222-223 (1991).
7. A.R. Kortan *et al.* *Nature (London)* **355**, 529-530 (1992).
8. P.-M. Allemand *et al.* *J.Am.Chem.Soc.* **113**, 1780-2781 (1991).
9. H. Schwarz *Angew.Chem.Int.Ed.Engl.* **31**, 293-297 (1992).
10. A. Hirsch *et al.* *Angew.Chem.Int.Ed.Engl.* **31**, 766-768 (1992).
11. P.J. Fagan *et al.* *J.Am.Chem.Soc.* **114**, 9697-9699 (1992).
12. F.N. Tebbe *et al.* *Science* **256**, 822-825 (1992).
13. P.R. Birkett *et al.* *Nature (London)* **357**, 479-481 (1992).
14. P.R. Birkett *et al.* *J.Chem.Soc.,Chem.Comm.* 1230-1232 (1993).
15. S.H. Hoke *et al.* *Rapid Commun.Mass Spectrosc.* **36**, 1309-1310 (1992).
16. R. Taylor *J.Chem.Soc.,Chem.Comm.* 667-668 (1992).
17. A.G. Avent *et al.* *J.Chem.Soc.,Chem.Comm.* in press.
18. P.J. Krusic *Science* **254**, 1183-1185 (1991).
19. F. Wudl *Acc.Chem.Res.* **25**, 157-161 (1992).
20. S. Shi *et al.* *J.Am.Chem.Soc.* **114**, 656-657 (1992).
21. A. Vasella *et al.* *Angew.Chem.Int.Ed.Engl.* **31**, 1388-1390 (1992).
22. M.F. Meidine *et al.* *J.Chem.Soc.,Chem Commun.* 1342-1344 (1993).
23. Y. Rubin *et al.* *J.Am.Chem.Soc.* **115**, 344-345 (1993).
24. J.M. Hawkins *et al.* *Science* **252**, 312-314 (1991); J.M. Hawkins *Acc.Chem.Res.* **25**, 150-156 (1992).
25. J.M. Hawkins *et al.* *J.Am.Chem.Soc.* **114**, 7954-7955 (1992).
26. P.J. Fagan *et al.* *Science* **252**, 1160-1161 (1991).
27. P.J. Fagan *et al.* *J.Am.Chem.Soc.* **113**, 9408-9409 (1991).