106. Electrochemistry of Mono- through Hexakis-adducts of C_{60}

by **Corinne Boudon, Jean-Paul Gisselbrecht**, and **Maurice Gross***

Laboratoire d'Electrochimie et de Chimie Physique du Corps Solide, U.R.A. au C.N.R.S. n° 405,
Faculté de Chimie, Université Louis Pasteur, 1 et 4, rue Blaise Pascal, F-67008 Strasbourg Cedex

and **Lyle Isaacs, Harry L. Anderson, Rüdiger Faust**, and **François Diederich***

Laboratorium für Organische Chemie, ETH-Zentrum, Universitätstrasse 16, CH-8092 Zürich

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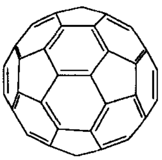
The first systematic electrochemical study by cyclic voltammetry (CV) and rotating-disk electrode (RDE) of the changes in redox properties of covalent fullerene derivatives (**2**–**11**) as a function of increasing number of addends is reported. Dialkynylmethanofullerenes **2**–**4** undergo multiple, fullerene-centered reduction steps at slightly more negative potentials than C_{60} (**1**; see *Table* and *Fig. 1*). The two C-spheres in the dumbbell-shaped dimeric fullerene derivative **4** show independent, identical redox characteristics. This highlights the insulating character of the sp^3-C-atoms in methanofullerenes which prevent through-bond communication of substituent effects from the methano bridge to the fullerene sphere. In the series of mono- through hexakis-adducts **5**–**11**, formed by tether-directed remote functionalization, reductions become increasingly difficult and more irreversible with increasing number of addends (see *Table* and *Fig. 2*). Whereas, in 0.1M Bu_4NPF_6/CH_2Cl_2, the first reduction of mono-adduct **5** occurs reversibly at −1.06 V *vs.* the ferrocene/ferricinium couple (Fc/Fc$^+$), hexakis-adduct **11** is reduced irreversibly only at −1.87 V. Hence, with incremental functionalization of the fullerene, the LUMO of the remaining conjugated framework is raised in energy. Reduction potentials are also dependent on the relative spatial disposition of the addends on the surface of the fullerene sphere. Observed UV/VIS spectral changes and changes in the chemical reactivity along the series **5**–**11** are in accord with the results of electrochemical measurements. Further, with increasing number of addends, the oxidation of derivatives **5**–**11** becomes more reversible. Whereas oxidations are increasingly facilitated upon going from mono-adduct **5** (+1.22 V) to tris-adduct **7** (+0.90 V), they occur at nearly the same potential (+0.95 to +0.99 V) in the higher adducts **8**–**11**. This indicates that the oxidations occur in these compounds at a common sub-structural element, for which a 'cubic' cyclophane is proposed (see *Fig. 3*). This sub-structure is fully developed in hexakis-adduct **11**.

1. Introduction. – Following the initial development of methods for the preparation of covalent mono-adducts of C_{60} (**1**) [1], the formation of multiple adducts of the spherical molecular carbon allotrope rapidly became a central topic in synthetic fullerene chemistry [2–6]. Important targets of this research are the exploration of the regioselectivity patterns in multiple-addition reactions and the investigation of the changes in chemical reactivity and physical properties which occur, when the conjugated π-electron chromophore of the fullerene is reduced as a result of increasing functionalization.

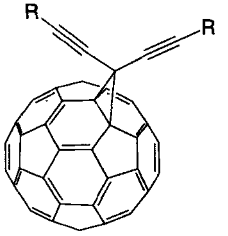
Among the most intriguing properties of C_{60} is its facile electrochemical reducibility in multiple one-electron reduction steps yielding reversibly mono- through hexa-anions [7]. Up to four or five reversible one-electron reduction steps were observed at room temperature in solvents such a benzonitrile, CH_2Cl_2, THF, benzene, or toluene with the first reduction occurring at potentials between −0.3 and −0.5 V (*vs.* the standard calomel electrode (SCE); between *ca.* −0.8 and *ca.* −1.0 V *vs.* the ferrocene/ferricinium couple (Fc/Fc$^+$)). In MeCN/toluene at −10°, the reversible formation of the hexa-anion could be observed by cyclic voltammetry (CV) and differential pulse voltammetry [7e] with the potentials for the six one-electron waves changing from −0.98 for the first to −3.26 V for the sixth reduction step [7f, g, j]. In contrast, electrochemical oxidation of the fullerene is difficult, and only one chemically reversible one-electron oxidation wave was observed at the very positive potential of +1.26 V *vs.* Fc/Fc^+ in 0.1M Bu_4NPF_6/1,1,2,2-tetrachloroethane [8].

With the development of the covalent chemistry of C_{60}, it became of interest to investigate how electrochemical properties would be influenced by structure, number, and arrangement of addends on the fullerene sphere. A variety of covalent mono-adducts of C_{60} such as methanofullerenes or hydrogenated and alkylated derivatives were found to maintain the characteristic redox properties of the unsubstituted C-sphere [9–14]: they underwent up to four reversible one-electron reduction steps at potentials slightly (*ca.* 0.1 V) more negative than observed with C_{60}. The reductive electron transfers were centered on the C_{60} sphere rather than on the addends, while reversible oxidations were not observed. The electrochemistry of some organic [15] and organometallic [16] multiple adducts of C_{60} was also investigated. Unfortunately, the exact structures of the compounds used in these studies were only known for the organic mono-adduct and the organometallic mono- and hexakis-adducts. The other compounds existed as isomeric mixtures and, in case of the organometallic derivatives (exohedral platinum complexes), were kinetically labile.

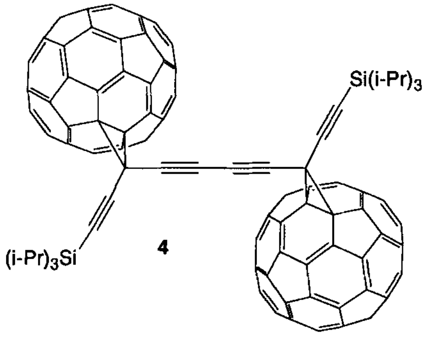
We recently described a versatile strategy for the preparation of mono- through hexakis-adducts of C_{60} based on the concept of *tether-directed remote functionalization* [5]. This synthetic development opened the way for the first systematic cyclic-voltammetry and rotating-disk-electrode (RDE) study of the changes in electrochemical properties of covalent fullerene derivatives, *i.e.*, of **2**–**11**, as a function of increasing number of addends.



1 C_{60}



2 R = $(i\text{-}Pr)_3Si$
3 R = $SiMe_3{-}C{\equiv}C$



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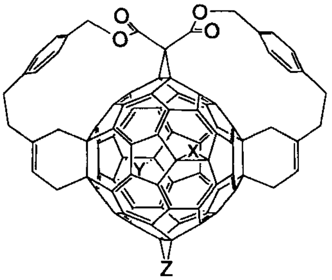
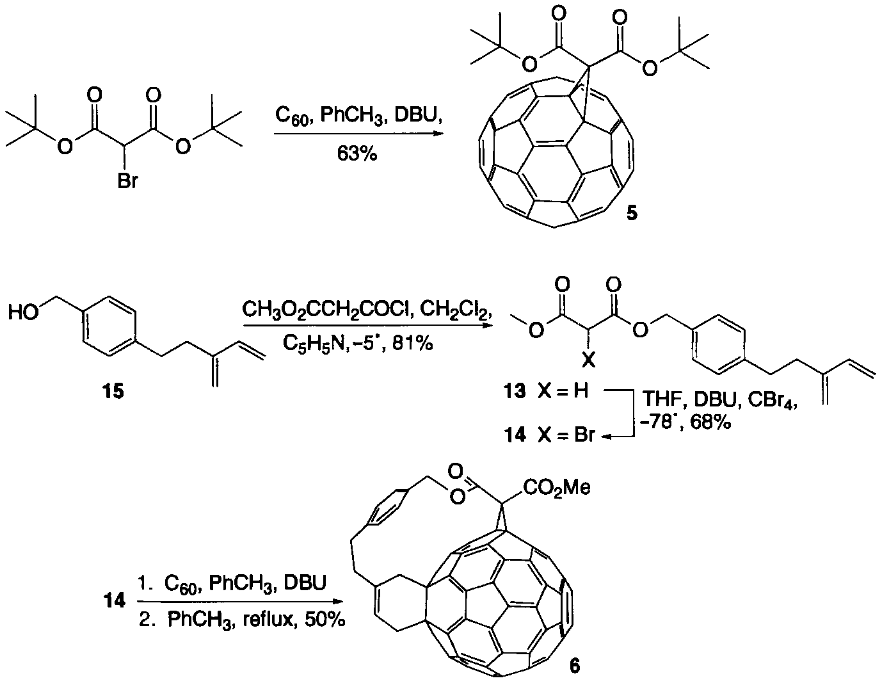


7 X = Y = Z = —
8 X = $(EtO_2C)_2C$, Y = Z = —
9 X = Y = $(EtO_2CCH_2O_2C)_2C$, Z = —
10 X = Z = $(EtO_2CCH_2O_2C)_2C$, Y = —
11 X = Y = Z = $(EtO_2C)_2C$
12 X = $(EtO_2CCH_2O_2C)_2C$, Y = Z = —

These studies showed dramatic changes in reducibility and oxidizability with increasing attenuation of the conjugated fullerene π-electron chromophore. They also allowed correlation of the changes in redox behavior of fullerene multiple adducts with experimentally observed changes in chemical reactivity and spectroscopic properties.

2. Results and Discussion. – 2.1. *Synthesis.* Compounds **2** [17], **3** and **4** [18], and **7**–**12** [5] were obtained by following published procedures. The alkynylated methanofullerenes were prepared as part of our ongoing program on novel fullerene-acetylene hybrid carbon allotropes [5b] [18]. Diester **5** [19] was obtained by addition of di(*tert*-butyl) 2-bromomalonate to C_{60} in a *Bingel* reaction (*Scheme 1*) [20]. For the synthesis of bis-adduct **6** by tether-directed remote functionalization, 2-bromomalonate **14** was prepared by esterification of benzyl alcohol **15** [5a] with 'methyl malonyl chloride' ($MeOOCCH_2COCl$) to give **13**, followed by bromination. Attachment of **14** to C_{60} was accomplished under *Bingel* conditions in toluene with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as base, and the resulting wine-red methanofullerene intermediate was heated in refluxing toluene for 39 h to complete the *Diels-Alder* reaction leading to **6** [5a]. This compound was isolated as a brown solid by flash chromatography. All spectroscopic data conclusively support the C_s-symmetrical structure of **6**. Details of the synthesis and characterization of all fullerene adducts obtained by tether-directed remote functionalization will be reported in a separate full account [21].

Scheme 1. *Synthesis of Mono-adduct* **5** *and Bis-adduct* **6** *of* C_{60}



2.2. *Electrochemical Studies.* 2.2.1. *Alkynylated Methanofullerenes.* As an initial calibration, the reduction potentials for C_{60} (**1**) were determined by CV in CH_2Cl_2 with 0.1M Bu_4NPF_6 as electrolyte (*Table*). The values for the observed three reversible one-reduction waves are in good agreement with those reported previously [7a–c] [7h–j]. Next, the cyclic voltammograms of the alkynylated methanofullerenes **2**–**4** were investigated

Table. *Reduction and Oxidation Characteristics* (*vs.* Fc/Fc$^+$) *of* **1**–**11** *on Pt or Glassy C Electrodes in* CH_2Cl_2 + *0.1*M Bu_4NPF_6

	Cyclic voltammetry				Rotating-disk electrode			
	Reduction a)			Oxidation a)	Reduction b)			Oxidation b)
	E_1	E_2	E_3	E_1	E_1	E_2	E_3	E_1
1 c)	–0.98 (59)	–1.37 (61)	–1.83 (60)					
2 c)	–1.02 (70)	–1.40 (70)	–1.92 d) e)					
3 c)	–1.00 (71) f)	–1.38 d)			–0.99 (54)	–1.38 (58)	–1.52 (71)	
4	–0.99 d) e)	–1.43 (52)	–1.56 (63)					
5	–1.06 (70)	–1.45 (70)	–1.94 (80)	+1.22 d)	–1.08 (63)	–1.47 (60)	–1.98 (51)	+1.23 (98)
6	–1.18 (75)	–1.56 (75)	–2.20 d)	+1.04 (120)	–1.19 (80)	–1.56 (80)	–2.25 (90)	+1.04 (76)
7	–1.29 (78)	–1.67 (84)	–2.33 d)	+0.90 (92)	–1.30 (68)	–1.70 (67)		+0.90 (70)
8	–1.53 (90)	–1.63 (70)		+0.98 (170)	–1.57 (119)			+0.98 (62)
9	–1.66 d)	–2.20 d)		+0.95 (100)	–1.66 (63)	–2.23 (84)		+0.94 (61)
10	–1.57 d)	–2.27 d)		+0.99 (75)	–1.59 (98)	–2.30 (79)		+0.97 (60)
11	–1.87 d)			+0.99 (81)	–1.85 (131)			+0.98 (71)

a) Values quoted: (E_pa + E_pc)/2 in V and, in parenthesis, ΔE_pc in mV at 0.1 V s^{-1}. For irreversible processes, E_pc in V is quoted. b) Values quoted: $E_{1/2}$ in V and, in parenthesis, the slope log $(I/(I_d-I))$ in mV. c) Reduction on Pt electrode in CH_2Cl_2 + 0.1M Bu_4NPF_6. d) Irreversible process. e) Reversible for $v > 1$ V s^{-1}. f) $v = 10$ V s^{-1}.

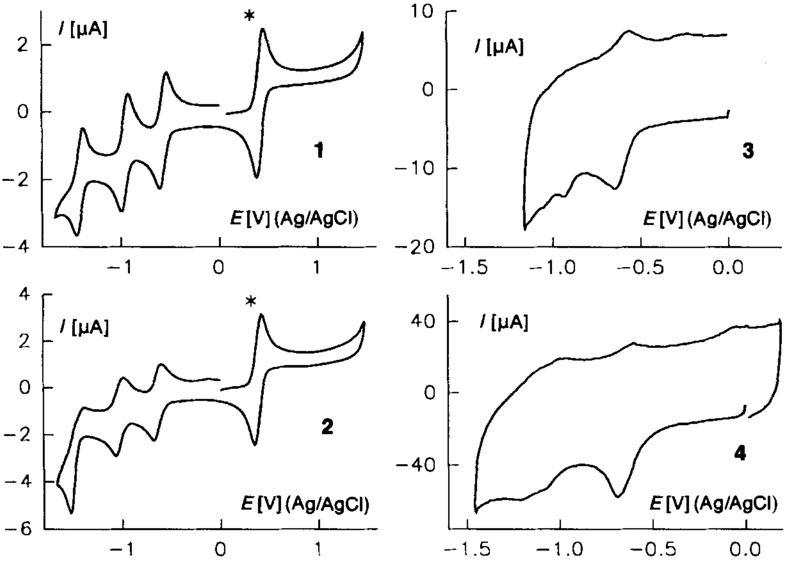
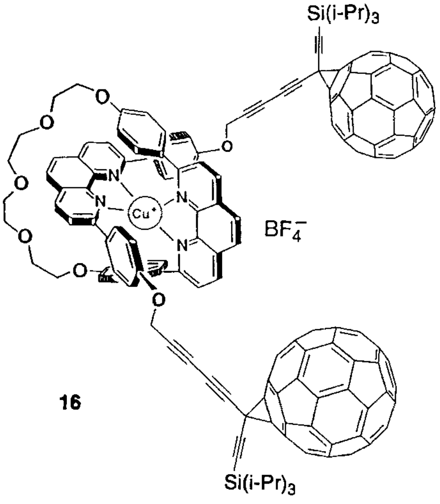


Fig. 1. *Cyclic voltammetry of* C_{60} (**1**) *and of the methanofullerenes* **2**–**4**. Solvent, CH_2Cl_2 + 0.1M Bu_4NPF_6; working electrode, Pt disk (2 mm diameter); scan rates, 0.1 V s^{-1} (**1** and **2**) and 10 V s^{-1} (**3** and **4**). * = Fc/Fc$^+$ couple.

(*Fig. 1*). The electrochemistry of methanofullerenes containing substituents other than alkynyl groups was previously extensively studied by *Wudl* and coworkers [9] [15]. The results obtained with **2**–**4** are in general agreement with these data: up to three reversible one-electron reduction steps occur at more negative potentials than those measured for C_{60}, and no oxidation is observed at potentials below +1.0 V (*vs.* Fc/Fc^+; *Table*). The first two one-electron reductions of **2**–**4** occur at very similar potential. Previous studies [9] [15] showed that the reduction potentials of methanofullerenes are not very sensitive to the nature of the substituents at the methano bridge, since the sp^3-C-atom of this bridge acts as an insulator. However, the reductions of methanofullerenes **3** and **4** with butadiynyl groups are significantly less reversible than those of the simple ethynyl derivative **2**. This is consistent with the observed tendency of **3** to polymerize and form an insoluble conducting film on the cathode, as was reported previously [22]. Interestingly, dumbbell-shaped **4** was found inert toward such polymerization.

The electrochemical properties of the dumbbell-shaped dimeric methanofullerene **4** were of particular interest, since information about the extent of electronic communication between the two linked C-spheres was expected. A single potential value (−0.99 V) is assigned to the transfer of one electron to each of the two C_{60} moieties in **4**, and two very close potentials (−1.43 and −1.56 V) for their second reduction step. The comparison with the reduction potentials for the monomeric analogs **2** (−1.02 and −1.40 V) and **3** (−1.00 and −1.38 V) suggests that both through-bond and through-space electronic communication between the two fullerene moieties in **4** must not be very efficient. Clearly, the sp^3-C-atoms in the two butadiynediyl-linked methano bridges of **4** act as insulators. If electronic communication would be effective, the strongly electron-attracting character of the two C_{60} moieties presumably would significantly change their individual redox potentials as compared to those of the monomeric analogs. The absence of electronic communication between the two fullerene moieties in **4** is also apparent from UV/VIS-spectral comparisons [18a] and from X-ray structural data [18b]. Similar conclusions were derived by *Wudl* and coworkers [9] for a dumbbell-shaped methanofullerene in



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which the connector between the methano bridges of the C-spheres was a 1,3- or 1,4-phenylene moiety. Redox measurements on this system demonstrated that the two fullerene components were redox-independent centers for the first four electron transfers.

These findings contrast with the results of recent electrochemical studies on rotaxane **16** with two fullerene stoppers [23]. In **16**, the redox potential of the Cu^{II}/Cu^{I} couple appeared significantly more anodic ($\Delta E^\circ \approx 0.2$ V) than for other similar mononuclear complexes, and this observation was explained by a substantial destabilization of the highest oxidation state of the copper center by the strong electron-withdrawing effect of the fullerene [23]. Interestingly, although the fullerene stoppers in **16** apparently influence the redox properties of the metal center, the latter does not seem to change the redox properties of the fullerene moieties which were irreversibly reduced at *ca.* –0.6 V *vs.* SCE in MeCN (*ca.* –1.1 V *vs.* Fc/Fc^+).

2.2.2. *Comparative Studies in a Series of Mono- through Hexakis-adducts of C_{60}.* The insensitivity of the fullerene redox properties to the nature of the substituents on the bridging sp^3-C-atoms in methanofullerenes was advantageous for a comparative study of the electrochemical properties in the series of mono- through hexakis-adducts **5**–**11**. Differences in the nature of the ester groups at the methano bridges were expected to have only very small effects on the redox properties. Reduction and oxidation potentials for **5**–**11** were measured on Pt or glassy C electrodes; the measured values were the same as long as ΔE_p did not exceed 90 mV at 0.1 V s^{-1} in cyclic voltammetry. Similar results were obtained using the rotating disk electrode technique (*Table*). The cyclic voltammograms for **5**–**11** are shown in *Fig. 2*.

As observed with the alkynylmethanofullerenes, the first reduction of **5** is slightly more difficult than for C_{60} itself (–1.06 *vs.* –0.98 V). Two additional reversible one-electron reductions are observed at –1.45 and –1.94 V, again at slightly more negative potentials compared to C_{60}. Addition of a second addend in form of the cyclohexene ring in **6** makes the first two one-electron transfers more difficult by *ca.* 0.1–0.15 V, whereas the third reduction becomes more difficult by 0.26 V as well as irreversible. Addition of the third addend in **7** in the form of a second cyclohexene ring once again shifts the two reversible and the third irreversible reduction to more negative potentials by *ca.* 0.1–0.15 V (as compared to bis-adduct **6**). This general trend is followed across the entire series **5**–**11**: the reduction potentials become more negative with each additional addend, and they become increasingly irreversible. There are, however, several interesting discontinuities in this general trend.

Whereas most of the changes to more negative reduction potentials with the incremental addition of addends amount to *ca.* 0.1–0.15 V, the shift to more negative potential is substantially larger (*ca.* 0.2–0.3 V) between **7** and **8** and between **9** or **10** and **11**. These discontinuities in electrochemical properties correlate with the observed reactivity of these compounds. The *Bingel* reaction [20], *i.e.*, the nucleophilic attack of the anion of diethyl 2-bromomalonate at the C-sphere, should be favored by the electrophilicity of the fullerene adduct. In return, the more electrophilic derivatives should be more readily reduced; therefore, the ease of nucleophilic attack should parallel that of electrochemical reduction. Experimentally one found that tris-adduct **7** was transformed into tetrakis-adduct **8** by its reaction with diethyl 2-bromomalonate (5 equiv.) and DBU in chlorobenzene in 72% yield (*Scheme 2*) [5a]. Despite the large excess of nucleophilic reagent, the transformation of **7** to **8** was very clean, not producing higher adducts. In view of the

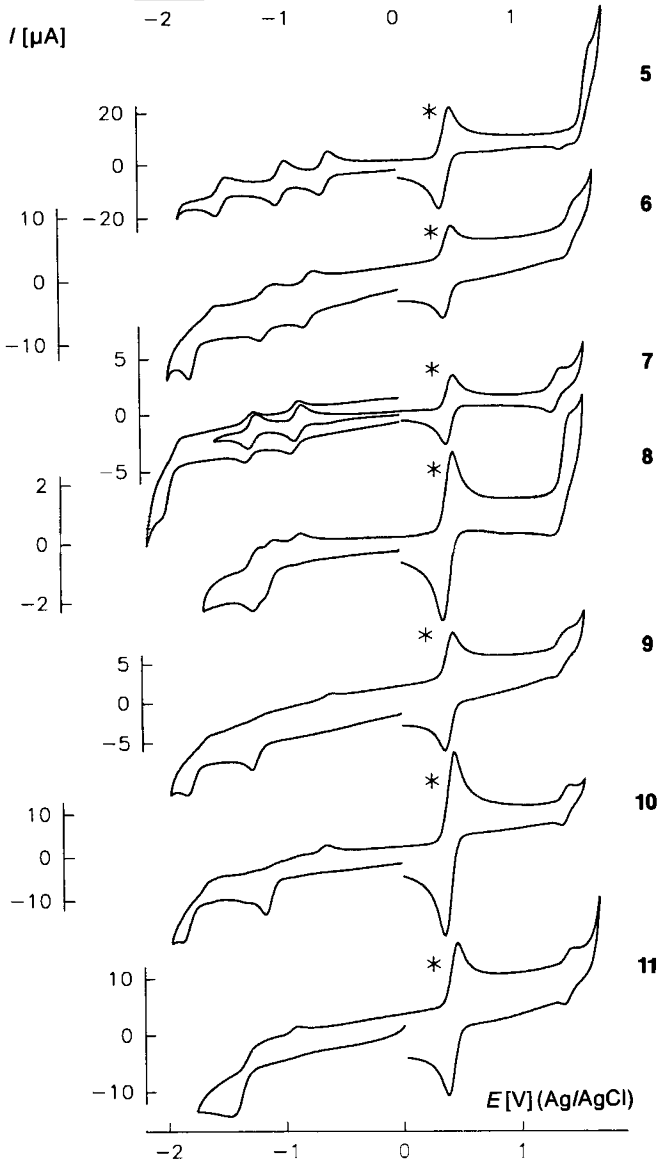
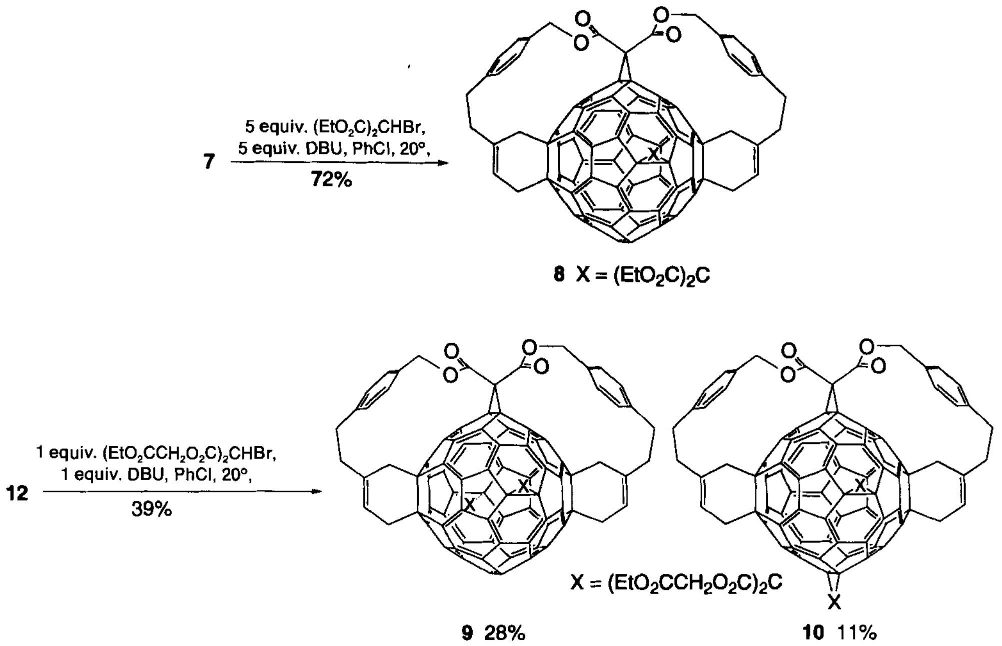


Fig. 2. *Cyclic voltammetry of mono- through hexakis-adducts* **5–11** *of* C_{60}. Solvent, $CH_2Cl_2 + 0.1$ M Bu_4NPF_6; working electrode, Pt disk (2 mm diameter); scan rates, 0.1 V s^{-1}. * = Fc/Fc^+ couple.

electrochemical data, this is no longer surprising, since the reduction of **8** (−1.53 V) is 0.24 V more difficult than the reduction of **7** (−1.29 V), and correspondingly **7** should show greatly enhanced reactivity over **8** toward nucleophilic attack.

A similar effect is seen in the conversion of **12** (a close analog of **8**) to a mixture of the pentakis-adducts **9** and **10**. When **12** was reacted with the appropriate 2-bromomalonate

Scheme 2



anion, a mixture of **9** and **10**, along with hexakis-adduct was produced (*Scheme 2*) [5b]. Recovered **12** amounted to 31%, and the combined pentakis-adducts **9** (28%) and **10** (11%) were obtained in 39% yield, while the corresponding hexakis-adduct probably accounted for *ca.* 20–25% of the remaining 30% of the total mass balance [5b]. Clearly, there is only a small difference in reactivity between the tetrakis- and the pentakis-adducts. In agreement with this data, the difference in the reduction potentials between **8** (and similarly for **12**) and **9** or **10** is small (−1.53 V *vs.* −1.66 or −1.57 V).

The potential difference (0.09 V) between the irreversible reductions of **9** (−1.66 V) and **10** (−1.57 V) shows that the redox properties are dependent on the pattern of the addends on the surface of the fullerene. The more negative potential for **9** indicates a higher stability of this pentakis-adduct, and this might be the reason why **9** was preferentially formed (71:29 selectivity) over **10** in the *Bingel* reaction of tetrakis-adduct **8**.

A very large jump towards more negative potentials is observed for the second one-electron reduction step (0.57 and 0.64 V, resp.) upon passing from tetrakis-adduct **8** to the pentakis-adducts **9** and **10**. Both first and second reductions of the pentakis-adducts become irreversible on the CV time scale. Hexakis-adduct **11** is the most difficult compound in the series to be reduced; an irreversible reduction is observed at −1.87 V. In **11**, the conjugated fullerene chromophore is reduced to that of a strained 'cubic' cyclophane (*Fig. 3*), and the LUMO should be correspondingly raised in its energy, making it more difficult to accept electrons in the electrochemical reduction. X-Ray crystal structures show that the 'cubic' cyclophane chromophore in hexakis-adduct **11** and in a related hexakis-adduct containing six bis(ethoxycarbonyl)methano bridges has become more benzenoid [4c] [5b]. Bond-length alternation typically observed in C_{60} and mono-

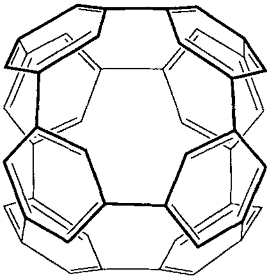


Fig. 3. *Illustration of the benzenoid 'cubic' cyclophane sub-structure formed upon sixfold pseudo-octahedral addition to the fullerene sphere*

adducts (6-6 bonds *ca.* 0.07 Å shorter than 6-5 bonds) is significantly reduced (to *ca.* 0.04 Å) in the eight aromatic rings of the 'cubic' cyclophane chromophore. In agreement with the electrochemical and structural data, the UV/VIS spectrum of **11** shows almost no absorption in the VIS region of the spectrum. Its absorption tails to *ca.* 460 nm with the first bands appearing below 400 nm [5a]. In contrast, pentakis-adducts **9** and **10** still show their first absorption bands above 550 nm [5b].

Whereas the first reductions change from reversible to irreversible in the series **5**–**11**, the converse is observed for the electrochemical oxidation: the oxidation of mono-adduct **5** is irreversible (at +1.22 V), while it becomes more reversible in tris-adduct **7** and beyond. Bis- and tris-adducts **6** and **7** are oxidized more readily (+1.04 and +0.90 V) than mono-adduct **5**. Interestingly, the oxidation potentials no longer change significantly beyond the tetrakis-adduct **8**. In the CV's of **8**–**11**, the reversible oxidation potentials are +0.98, +0.95, +0.99, and +0.99 V, respectively. This strongly suggests that a common structural element of the functionalized C-sphere is undergoing oxidation in each instance. We propose that the benzenoid rings in the 'cubic' cyclophane sub-structure shown in *Fig. 3*, are the sites of oxidation leading to the observed relatively constant oxidation potential.

3. Conclusions. – The electrochemical studies described herein revealed very significant effects of the number and pattern of the addends in fullerene derivatives on their reduction and oxidation characteristics. The sp^3-C-atoms in the methano bridges of methanofullerenes such as the alkynyl derivatives **2**–**4** act as insulators, which greatly reduce the effects of the nature of substituents at the bridge on the C-sphere-centered redox processes. The first reduction potential in the series of mono- through hexakis-adduct **5**–**11** is highly dependent on the number of addends; with each additional addend, the reduction potential shifts between 0.1 to 0.3 V to more negative values. Whereas the first reduction of mono-adduct **5** occurs reversibly at −1.06 V, hexakis-adduct **11** is reduced irreversibly at −1.87 V. This is clearly a consequence of the restriction of the conjugated fullerene chromophore in this series and a corresponding energetic raise of the LUMO. The reduction is also dependent on the regiochemistry of the addends on the surface of the fullerene sphere as seen in the comparative behavior of **9** and **10**. Further, as more addends are added in the series **5**–**11**, the number of observable reduction steps as well as their reversibility is decreased. Preliminary analysis shows that UV/VIS-spectral changes and changes in the reactivity towards nucleophiles in the series correlate with the ease of electrochemical reduction. Whereas the reductions become more irreversible with increasing number of addends, oxidations become more reversible. Oxidations only become increasingly facilitated up to the stage of tris-adduct **7** and remain almost constant in the higher adducts **8**–**11**. This indicates that, in the oxidative processes, the same common structural sub-structures are involved for which the benzenoid rings of a 'cubic' cyclophane is proposed, a sub-structure that becomes fully formed in hexakis-adduct **11**.

Experimental Part

The electrochemical measurements were made in CH_2Cl_2 with 0.1M Bu_4NPF_6 as electrolyte, on Pt or glassy C working electrodes, at r.t. (22 ± 2°). Ag/AgCl was the reference electrode; the ferrocene/ferricinium couple was used throughout as internal redox standard. The three-electrode cell was connected to a computerized multipurpose electrochemical device *Dacfamov* (*Microtec – CNRS*, Toulouse, France) interfaced with an *Apple II* microcomputer. The working electrode was a Pt disk (diameter 2 mm) or a glassy C disk (diameter 2 mm) which remained motionless for cyclic voltammetry from 10 mV s^{-1} to 10 V s^{-1} or was a rotating-disk electrode (RDE) for stationary voltammetric measurements.

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