Ferrocenyl Fulleropyrrolidines: a Cyclic Voltammetry Study

Michele Maggini,[a] Annika Karlsson,[a] Gianfranco Scorrano,[a] Giancarlo Sandonà,[b] Giuseppe Farnia[b] and Maurizio Prato*[c]

[a] *Centro Meccanismi di Reazioni Organiche del CNR, Dipartimento di Chimica Organica, Università di Padova, Via Marzolo 1, 35131 Padova, Italy*

[b] *Dipartimento di Chimica Fisica, Università di Padova, via Loredan 2, 35131 Padova, Italy*

[c] *Dipartimento di Scienze Farmaceutiche, Università di Trieste, Piazzale Europa 1, 34127 Trieste, Italy*

The cyclic voltammetry of some fullerene–ferrocene derivatives shows that these compounds possess very interesting electrochemical properties.

A key feature which dominates the chemical reactivity of the fullerenes[1] is their high electron affinity.[2] Accordingly, C_{60} acts as an electron acceptor in the presence of strong electron donors to form relatively stable charge-transfer salts which show very interesting solid-state properties.[3] In addition, the discovery that alkali metal doped thin films of C_{60} become superconductors at low temperatures[4] has provided a powerful driving force for the study of the electronic properties of the fullerenes. On the other hand, the experimental demonstration that C_{60} possesses three (degenerate) LUMO levels[2,5] has recently been achieved: in solution, this fullerene can accept reversibly up to six electrons.[6]

This rich electronic and electrochemical behaviour has generated great expectations in the field of materials science. It is expected that chemically modified fullerenes may play a relevant role in the design of novel molecular electronic devices.[7,8] In this context, the combination of the electrochemical properties of C_{60} with those of other electroactive species may lead to new promising materials.[9] We report here the synthesis and the electrochemical properties of some novel fullerene derivatives where C_{60} and ferrocene are covalently bound.

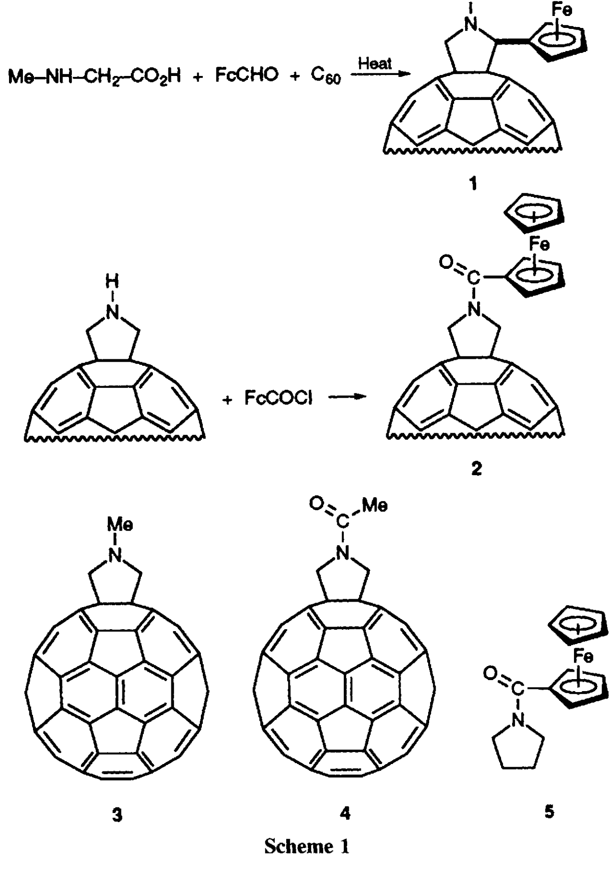
Compounds **1** and **2** were synthesized according to Scheme 1. The general procedure for the preparation of substituted fulleropyrrolidines is based on 1,3-dipolar cycloaddition of azomethine ylides to C_{60} and has been reported elsewhere.[10] All new compounds show correct analytical and spectroscopic data.

Cyclic voltammetry (CV) was employed to study the electrochemical properties of these species in solution. The results are reported in Fig. 1, where the cyclic voltammograms of **1** and **2** are reported, together with those of C_{60} and the *N*-methylpyrrolidine derivative **3**[10] for comparison. All the experiments were performed at −45 °C in 3 : 1 toluene–acetonitrile solutions, containing tetra-*n*-butylammonium perchlorate (TBAP, 0.1 mol dm^{-3}) as supporting electrolyte, with Pt or glassy carbon (GC) as the working electrode, a Pt counter electrode and a silver wire as a quasi-reference electrode. To each solution dry neutral alumina (0.2 g for 10 ml of solution) was added under nitrogen. The voltammetric behaviour of C_{60} and substrates **1**–**3** (0.1–0.3 mmol dm^{-3}) is basically the same on either Pt or GC electrode. Potential data, reported in Table 1, are referenced to the potential of the Fc^+/Fc redox couple (Fc = ferrocene) utilised as an internal standard. Errors are estimates at ±5 mV.

Several features of the CVs reported in Fig. 1 can be considered. First of all, lowering the temperature to −45 °C together with the help of dry alumina makes it easy to obtain satisfactory results. Commercial spectrophotometric grade solvents do not need to be distilled into the cell and only a nitrogen flow is required. In these conditions we were able to reproduce the outstanding results reported by Echegoyen *et al.* for C_{60}.[6]

As can be seen from Fig. 1 and from Table 1, the observed reduction potentials of **1**–**3** are shifted to more negative values when compared to those of unsubstituted C_{60}. This is expected as the saturation of a double bond in C_{60} causes a partial loss of conjugation. Even though conjugation is still an elusive concept while speaking of C_{60},[7] undoubtedly saturation[11] or metal coordination[12] of a double bond in C_{60} causes a shift, toward more negative values, in the reduction potentials. Owing to this effect, only five reduction peaks for the C_{60} moiety in **1**–**3** are detected in the accessible potential range (see below for comment on the sixth reduction peak in the CV of **2**).

A comparison of the values of the $E_{1/2}$ potentials† of **1** and **2** with those of **3** shows two different trends. In the case of **1** the reduction peaks are all shifted, though slightly, to more negative values ($\Delta E_{1/2}$ – 20–30 mV) and the shift can be attributed to interactions between the donating ferrocene moiety and the accepting C_{60} spheroid. This interpretation is in agreement with the shift to more positive values of the fullerene-attached ferrocene potential in **1** as compared with the standard Fc^+/Fc couple ($\Delta E_{1/2}$ = + 50 mV). This result compares favourably with the observation that C_{60} and ferrocene form a complex which crystallizes from the solution.[13] In the solid state, ferrocene occupies the holes between C_{60} spheres and the result is close packing of the two species. In our case, both ferrocene and C_{60} belong to the same molecule and are sufficiently close to give an intramolecular interaction. The geometry, however, is not correct, and this is reflected by the small values of the potential changes.



Scheme 1

On the other hand, the potentials in the voltammogram of **2** are all shifted to less negative values with respect to those of **3** ($\Delta E_{1/2}$ = + 50–70 mV). Since C_{60} and ferrocene are now too distant for intramolecular interactions, one would have expected to find no difference in the behaviour of **2** and **3**. We have attributed this anodic shift to the presence of the amide group. In fact, the *N*-acetyl derivative **4**, prepared by acetylation of the NH parent compound (Scheme 1), shows negative $E_{1/2}$ values at exactly the same potentials as **2** (Table 1). The influence of the amide group on the potentials of **2** and **4** is not clear, and is currently under investigation. The same ferrocenyl amide group is responsible for the sixth peak observed at $E_{1/2}$ − 3.22 V in the CV of **2**: the model compound **5** exhibits a reversible reduction peak at the same potential ($E_{1/2}$ − 3.22 V). On the oxidation side, the occurrence of adsorption phenomena in the experiments with **2** [*cf.* the shape of peak couple at + 0.16 V in Fig. 1(*d*)] has prevented a comparison of this potential value with that of **5** ($E_{1/2}$ + 0.12 V).

The electrochemical properties of compounds **1–3** reported in the present work confirm[14] that the outstanding reduction pattern of C_{60} is retained in many of its derivatives. In the fulleropyrrolidines containing ferrocene covalently bound, the relative reversible oxidation peak is observed. Whenever an interaction is possible between the electroactive moieties, the corresponding potentials may vary in both cathodic and anodic directions. These interactions, however, are extremely labile, and the overall effect is very small, certainly not comparable to the periconjugation phenomenon reported by Wudl and coworkers.[15]

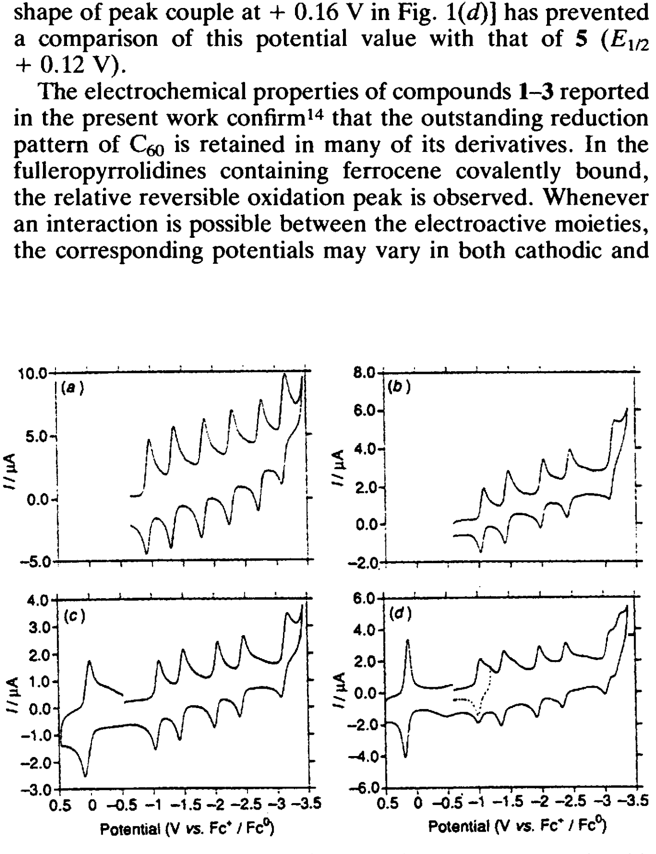


Fig. 1 CVs (sweep rate 0.1 V s^{-1}) of C_{60} (*a*) and substrates **3** (*b*), **1** (*c*) and **2** (*d*) on GC electrode in 3:1 toluene–acetonitrile solutions (0.1 mol dm^{-3} TBAP), at −45 °C

Table 1 $E_{1/2}$ values (V *vs.* Fc^+/Fc) of the redox couples of C_{60} and compounds **1–4**, detected by CV (sweep rate 0.1 V s^{-1}) in 3:1 toluene–acetonitrile solutions (0.1 mol dm^{-3} TBAP), at −45 °C. Errors are estimated at ± 5 mV.

	$E^{0/1-}$	$E^{1-/2-}$	$E^{2-/3-}$	$E^{3-/4-}$	$E^{4-/5-}$	$E^{5-/6-}$	$E^{1+/0}$
C_{60}	−0.94	−1.33	−1.83	−2.28	−2.74	−3.14	
1	−1.08	−1.47	−2.03	−2.44	−3.14		+0.05
2	−1.00	−1.38	−1.95	−2.36	−3.05	−3.22	+0.16
3	−1.05	−1.44	−2.01	−2.42	−3.12		
4	−1.00	−1.38	−1.95	−2.36	−3.05		

We thank Professor Fred Wudl (University of California, Santa Barbara) for his help in the preparation of this manuscript.

Received, 24th September 1993; Com. 3/05775E

Footnote

† $E_{1/2} = (E^{an}_{peak} + E^{cat}_{peak})/2$.

References

1 H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature*, 1985, **318**, 162; W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman, *Nature*, 1990, **347**, 354.

2 R. C. Haddon, L. E. Brus and K. Raghavachari, *Chem. Phys. Lett.*, 1986, **125**, 459; R. F. Curl and R. E. Smalley, *Science*, 1988, **242**, 1017. L. S. Wang, J. Conceicao, C. Jin and R. E. Smalley, *Chem. Phys. Lett.*, 1991, **182**, 5.

3 P.-M. Allemand, K. C. Khemani, A. Koch, F. Wudl, K. Holczer, S. Donovan, G. Gruner and J. D. Thompson, *Science*, 1991, **253**, 301; P. W. Stephens, D. Cox, J. W. Lauher, L. Mihali, J. B. Wiley, P.-M. Allemand, A. Hirsch, K. Holczer, Q. Li, J. D. Thompson and F. Wudl, *Nature*, 1992, **355**, 331.

4 R. C. Haddon, A. F. Hebbard, M. J. Rosseinski, D. W. Murphy, S. J. Duclos, K. B. Lyons, B. Miller, J. M. Rosamilia, R. M. Fleming, A. R. Korton, S. H. Glarum, A. V. Makhija, A. J. Muller, R. H. Eick, S. M. Zahurak, R. Tycko, G. Dabbach and F. A. Thiel, *Nature*, 1991, **350**, 320. A. F. Hebbard, M. J. Rosseinski, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez and A. R. Kortan, *Nature*, 1991, **350**, 600.

5 F. Negri, G. Orlandi and F. Zerbetto, *J. Am. Chem. Soc.*, 1992, **114**, 2909.

6 Q. Xie, E. Perez-Cordero and L. Echegoyen, *J. Am. Chem. Soc.*, 1992, **114**, 3978; Y. Ohsawa and T. Saji, *J. Chem. Soc., Chem. Commun.*, 1992, 782.

7 R. Taylor and D. R. M. Walton, *Nature*, 1993, **363**, 685.

8 S. I. Khan, A. M. Oliver, M. N. Paddon-Row and Y. Rubin, *J. Am. Chem. Soc.*, 1993, **115**, 4919.

9 Substrates containing two redox centres are very useful for applications in molecular electronics: J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1304. See also: A. J. Moore, P. J. Skabara, M. R. Bryce, A. S. Batsanov, J. A. K. Howard and S. T. A. K. Daley, *J. Chem. Soc., Chem. Commun.*, 1993, 417.

10 M. Maggini, G. Scorrano and M. Prato, *J. Am. Chem. Soc.*, 1993, **115**, 9798.

11 T. Suzuki, Q. Li, K. C. Khemani, F. Wudl and O. Almarsson, *Science*, 1991, **254**, 1186; P. J. Fagan, P. J. Krusic, D. H. Evans, S. Lerke and E. Johnston, *J. Am. Chem. Soc.*, 1992, **114**, 9697.

12 R. S. Koefod, C. Xu, W. Lu and J. R. Shapley, *J. Phys. Chem.*, 1992, **96**, 2928; S. A. Lerke, B. A. Parkinson, D. H. Evans and P. J. Fagan, *J. Am. Chem. Soc.*, 1992, **114**, 7807.

13 J. D. Crane, P. B. Hichcock, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1992, 1764.

14 F. Wudl, *Acc. Chem. Res.*, 1992, **25**, 157.

15 F. Wudl, T. Suzuki and M. Prato, *Synth. Metals*, 1993, **59**, 297; M. Eiermann, M. Prato, T. Suzuki, Q. Li, F. Wudl, R. C. Haddon and M. Maggini, submitted for publication, *J. Am. Chem. Soc.*