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# Electrochemical Monitoring of Valence Bond Isomers Interconversion in Bipyridyl-$C_{61}$[⊥] Anions

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**Abstract:** Electrochemical, quantum chemical, and spectroscopic techniques are used to study the dynamics of the reduction of bpy-$C_{61}$. A thorough investigation of the temperature and scan rate dependence of the cyclic voltammetry peaks coupled with numerical simulations clearly reveals that the trianion and the tetraanion undergo two chemical reactions according to the same parallel ECE mechanism. Quantum chemical calculations show that three isomers are quasi equienergetic in the charged states and support the hypothesis that triply and quadruply reduced bpy-$C_{61}$ undergoes facile conversion among three of its structural isomers, i.e., [5,6]-closed bpy-$C_{61}$, [5,6]-open bpy-$C_{61}$, and [6,6]-closed bpy-$C_{61}$. Substituent and/or solvent effects may effectively reverse the roles of [5,6]-closed bpy-$C_{61}$ and [6,6]-closed bpy-$C_{61}$. As for [5,6]-closed isomer, it is the first time that its existence is proposed on the basis of the observation of a redox process. The six reduction peaks of $C_{60}$ have been observed for the first time in a pure solvent (THF, −60 °C), and the cyclic voltammetry peaks of the fullerene moiety and the bpy fragment have been assigned.

## Introduction

The discovery of facile methods for the preparation and purification of gram-quantities of fullerenes has generated a growing interest in the chemical and physical properties of these systems.[1] The study of their electrochemical properties has provided abundant and important information for a number of fundamental aspects which range from the electronic structure of pristine molecules and their derivatives to their chemical reactivity and their redox behavior in homogeneous solutions.[2] In general, electrochemical studies have potentially useful implications for the application of these molecules as semiconductors, superconductors, components of nonlinear optical devices, and biologically active species.[2]

In principle, because of their electron accepting properties and their great chemical stability, fullerenes could be used to accomplish photoinduced charge separation in supramolecular systems, igniting the first step of artificial photosynthesis.[3] In particular, transition metal complexes containing fullerene-derivatized ligands might be potentially interesting for the conversion of solar energy. Toward such a functionalization, the preparation of a compound containing $C_{60}$ and a 2,2′-bipyridine (bpy) group has been pursued in our laboratories. In this respect, fulleroids and methanofullerenes, amongst the various derivatives, have proven to be particularly versatile.[4] These compounds are obtained by addition of aliphatic or aromatic diazoderivatives to one of the 30 equivalent double bonds of $C_{60}$. The resulting pyrazoline then loses nitrogen leaving a carbon bridge either on the junction between a five- and a six-membered ring, [5,6]-isomer, or on that between two adjacent six-membered rings, [6,6]-isomer.[4] Four isomers are, in principle, possible depending on whether the bridgehead

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[⊥] The term bipyridyl-$C_{61}$ (bpy-$C_{61}$) indicates the compounds **1** and **2** of Scheme 1. The suggested IUPAC nomenclature for the fullerene with substituted methylene groups inserted into bonds (compound **1**) is 61-[5-yl-5′-(1-*tert*-butyldimethylsilyloxy)ethyl-2,2′-bipyridyl]-61-methyl-1,6-homofullerene-$C_{60}$. Compounds of this type have also been described as fulleroids. The suggested IUPAC nomenclature for the fullerene with substituted methylene groups added accross adjacent carbon atoms (compound **2**) is 61-[5-yl-5′-((1-*tert*-butyldimethylsilyloxy)ethyl)-2,2′-bipyridyl]-61-methyl-1,2-methanofullerene-$C_{60}$.

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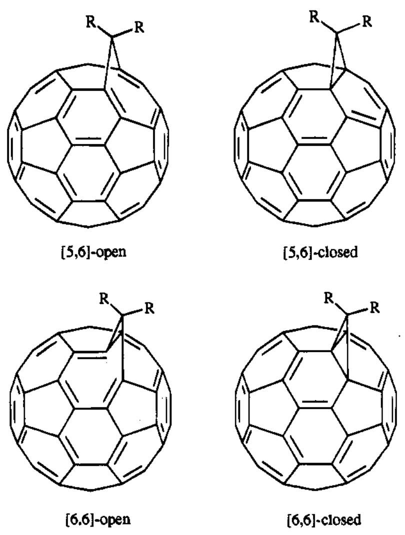
carbon atoms are bonded (cyclopropane) or not (annulene-type), see Chart 1.

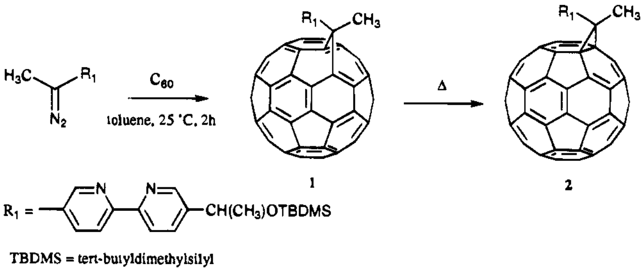
If it contains a cyclopropane ring, the molecule is called methanofullerene ([5,6-]-closed, or [6,6]-closed). In the other case, the fullerene moiety maintains the original $C_{60}$ electronic configuration and is denoted as fulleroid ([5,6]-open and [6,6]-open).[4] Regardless of the nature of the substituents on the bridging carbon atom, synthesis only provides [5,6]-open and [6,6]-closed isomers.[4] The [5,6]-open isomer prevails under kinetically controlled conditions. The [6,6]-closed isomer is the thermodynamically favored isomer which is usually (except for $C_{61}H_2$) obtained by heating the reaction mixture in refluxing conditions.[4] The isomerization can also be brought about via electrochemical reduction of [5,6]-open species.[2z] Recently, it has been shown that, at room temperature, after the third reduction process of [5,6]-open 4-(methoxycarbonyl)phenylfulleroid, an irreversible chemical reaction occurs which gives the [6,6]-closed isomer.[2z] It was also suggested that [5,6]-open–[6,6]-closed isomerization can play a role in the observed homogeneous chemical kinetic complications associated with the electrochemical reduction of some methanofullerene.[2y]

The thermal isomerization in the neutral molecules has received some attention both experimentally and theoretically.[4] Details about the mechanism of electroinduced isomerization are, however, so far not available. The present work is therefore focused on the electroinduced isomerization of the species shown in Scheme 1. Although the major role is played by electrochemical measurements, also spectroscopic measurements and quantum chemical calculations have been performed in order to support the electrochemical mechanisms proposed. For the electrochemical measurements, tetrahydrofuran (THF) was chosen as the solvent since it is rather suitable for voltammetric studies because of its wide potential window and its temperature range in the liquid phase. Moreover, THF dissolves fullerenes and their derivatives, including some metal derivatives of buckminsterfullerene, to an extent which makes them detectable in cyclic voltammetry and in differential pulse polarography.[2f–i] The use of this solvent together with experimental conditions which entailed the careful exclusion of water from the electrochemical cell during the experiments by employing high vacuum techniques and chemical pretreatment of the solvent and the use of low temperatures allowed to observe, for the first time in a pure solvent, six successive reversible one-electron reductions of $C_{60}$. As a matter of fact, the six reductions of $C_{60}$ have long been observed in mixed solvents.[2j,v] Electrochemical studies in pure solvents such as dichloromethane,[2k,m] *N,N*-dimethylformamide,[2d,e] acetonitrile,[2d,e] dichlorobenzene,[2e] benzonitrile,[2d,e,m,n] benzene,[2d,e,n] and THF[2d–g,m] have, however, been so far restricted to the first three or four reductions.

**Chart 1**



**Scheme 1**



## Results and Discussion

**I. $C_{60}$.** Figure 1 shows the differential pulse polarographic (a, c) and the cyclic voltammetric (b, d) curves for a $C_{60}$ saturated solution of THF at 25 and −60 °C.

Upon reduction, five or six successive reversible processes are observed at the two temperatures respectively. The corresponding $E_{1/2}$ values are reported in Table 1.

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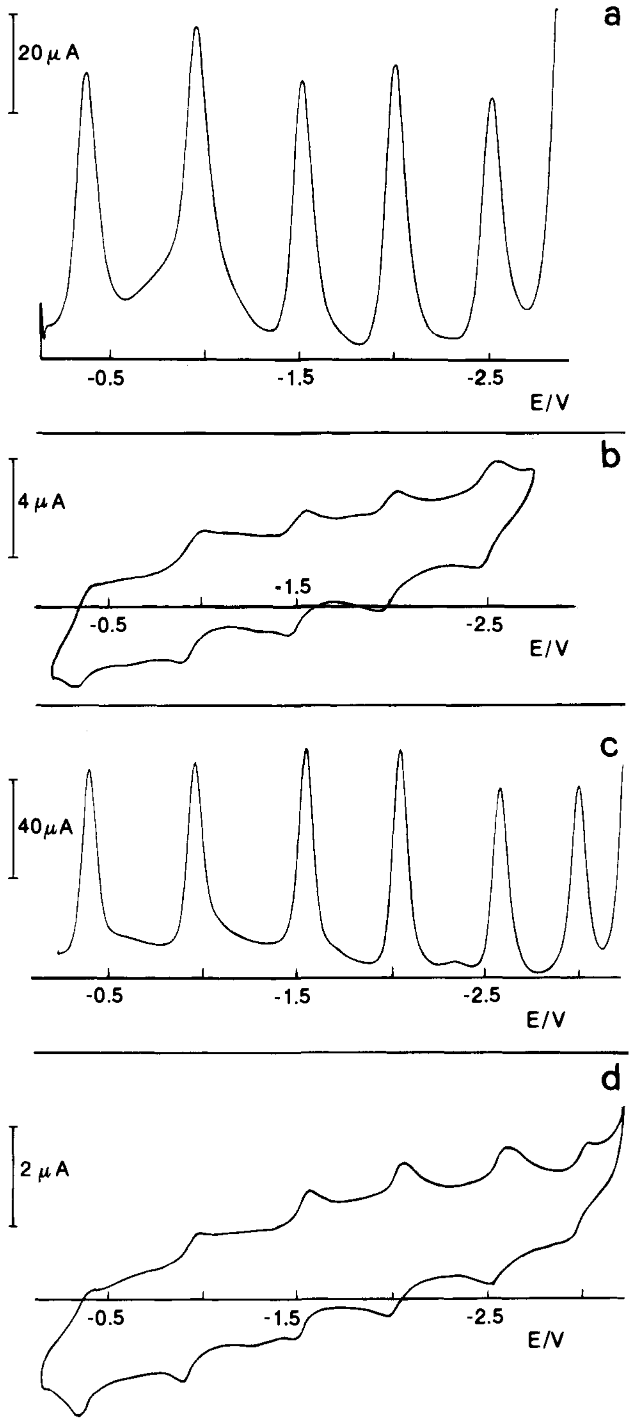

**Figure 1.** (a) Differential pulse voltammetic curve for a saturated $C_{60}$, 0.05 M $(C_4H_9)_4NPF_6$ THF solution: sweep rate = 0.02 V/s, pulse height = 20 mV; $T$ = 25 °C. (b) Steady-state cyclic voltammetric curve for the same solution: sweep rate = 0.2 V/s; $T$ = 25 °C. (c) As in (a), $T$ = −60 °C. (d) As in (b), $T$ = −60 °C. Working electrode = Pt.

**Table 1.** $E_{1/2}$ (V vs SCE) in THF/TBAH[a]

| | | | | | | |
|---|---|---|---|---|---|---|
| **1** | −0.42 | −0.98 | −1.53 | −1.99 | −2.37 | −2.58 |
| **2** | −0.43 | −0.97 | −1.58 | −2.05 | −2.37 | −2.58 |
| $C_{60}$ (25 °C) | −0.35 | −0.94 | −1.50 | −1.99 | −2.50 | |
| $C_{60}$ (−60 °C) | −0.38 | −0.95 | −1.53 | −2.02 | −2.55 | −3.01 |

[a] Working electrode = Pt, $E_{1/2}^{Fc+/0}$ = 0.58 V (25 °C), 0.52 V (−60 °C).

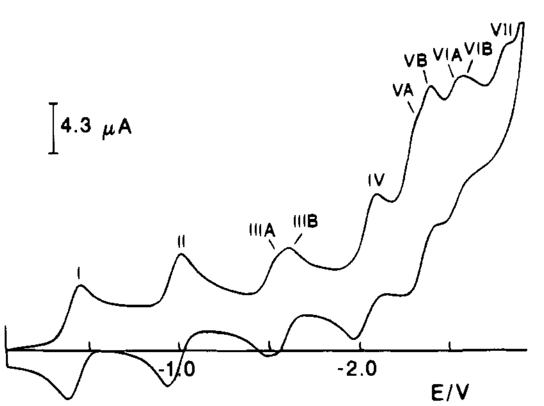

**Figure 2.** Cyclic voltammetric curve for a 0.5 mM compound **1**, 0.05 M $(C_4H_9)_4NPF_6$ THF solution: sweep rate = 0.1 V/s; working electrode = Pt: temperature = 25 °C.

The observed processes can be described as successive one-electron, reversible, diffusion-controlled reductions of the fullerene. The $E_{1/2}$ values measured at room temperature, for the first four reductions, are in agreement with those reported in literature.[2d,e] It is worth noticing that $E_{1/2}$ of the reductions depends linearly on the charge of the oxidized form of each redox couple, $n$. According to a treatment based on Born's solvation model,[2w] this indicates that the energetics of electron addition to $C_{60}$ is dominated by solvation effects both at room and low temperature. Moreover, at both temperatures, the slope of $E_{1/2}$ plotted versus ($n$ − 0.5) is 0.53 V which coincides with the value reported for $C_{60}$ reduction in a large family of different media.[2w]

No oxidation process was observed at low or room temperature within the available potential window (25 °C: +1.20 V; −60 °C: +1.30V).

**II. bpy-$C_{61}$ 1 and 2.** Compound **1** was prepared, according to Wudl's methodology,[4] by reaction between $C_{60}$ and the corresponding substituted diazomethane (Scheme 1).

The structural determination of **1** was carried out, in analogy to our previous work,[4d] by means of $^1H$, $^{13}C$ NMR, and UV−vis spectroscopy (see Experimental Section and Supplementary material). Conversion to **2** was achieved by heating to 150 °C a dilute solution of **1** in *o*-dichlorobenzene for 24 h.

The cyclic voltammetric curve (cvc) recorded for a 0.5 mM solution of **1** in THF at $v$ = 0.1 V/s and 25 °C is shown in Figure 2.

The curve shows seven main reduction processes. The corresponding peaks are denoted by progressive Roman numbers with increasingly more negative potentials. Peaks III, V, and VI result from the overlapping of two peaks indicated by letters A and B. As far as peaks IIIA and IIIB are concerned, their overall charge is equal to that of single peaks and correspond to a charge transfer of a single electron.

No oxidation process is observed by scanning the potential up to the anodic limit for this medium.

A comparison of the cvc's obtained for $C_{60}$ and **1** under the same conditions shows that the relative positions of the first four peaks of **1** and $C_{60}$ occur at similar potentials. The only difference is a slightly negative shift of 30−70 mV for **1** with respect to $C_{60}$. The remaining part of the curves, instead, present very different characteristics. The similarity of the regions in which the peaks of the first four reductions develop suggests that the reductions are largely localized on the fullerene moiety of **1**. Notice that the observed shift is analogous to that observed in other fullerene derivatives with electron-donating substituents.[21] Interestingly, peak III is split into two components in the cvc of **1**. A lowering of the scan rate decreases the height of peak IIIA and increases the height of peak IIIB, Figure 3a.

If a second scan is carried out without renewing the diffusion layer, peak IIIA is virtually absent, and only peak IIIB is observed. Already at scan rates as low as 0.4 V/s, see Figure

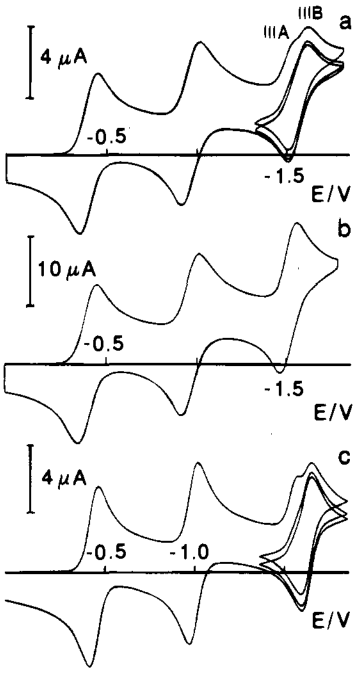

**Figure 3.** Cyclic voltammetric curves for a 0.5 mM compound **1**, 0.05 M $(C_4H_9)_4NPF_6$ THF solution: (a) sweep rate = 0.05 V/s and (b) sweep rate 0.4 V/s; working electrode = Pt; temperature = 25 °C. (c) Simulated cyclic voltammetric curve according to the mechanism of Scheme 2 (case a) in the conditions of Figure 3a.

**Scheme 2**

$$[A]^n + e \Leftrightarrow [A]^{n-1} \qquad E_{1/2,1}$$

$$[A]^{n-1} \xrightarrow{k} [B]^{n-1}$$

$$[B]^n + e \Leftrightarrow [B]^{n-1} \qquad E_{1/2,2}$$

**$E_{1/2,1} > E_{1/2,2}$; case a: n = -2; case b: n = -3**
A represents [5,6]-open isomer and **B** [6,6]-closed isomer (see text)

3b, only peak IIIA is detected. An analogous effect on the cvc is observed by lowering the temperature and maintaining constant the scan rate. In particular, at temperatures as low as −5 °C and at 0.05 V/s, a single peak coincident with peak IIIA of Figure 3a is observed. Such a behavior suggests that chemical reactions are present in the electrode process. The parallel ECE ($\vec{E}\vec{C}\vec{E}$) mechanism shown in Scheme 2 (case a) permits to rationalize the experimental results. In this mechanism, an irreversible homogeneous chemical reaction follows the third electron transfer to give a product whose $E_{1/2}$ is more negative than that of the parent species. In Scheme 2 (case a), A represents the parent compound **1** and B represents the product of the chemical reaction.

The mechanism has been confirmed by a numerical simulation of the cvc's, see Figure 3c. The simulation was performed over a 10-fold range of scan rates which permitted the obtaining unambiguously of both the rate constant, $k$ (2.5 ± 0.5 $s^{-1}$ at 25 °C), and the $E_{1/2}$ of the $B^{2-}/B^{3-}$ redox couple (−1.58 V). From the slope of the linear Arrhenius plot, obtained by utilizing the $k$ values from the simulations of cvc's recorded at different temperatures, the activation energy relative to the chemical reaction was 9 ± 2 kcal/mol (38 ± 8 kJ/mol). A first indication of the nature of the product of the chemical reaction can be obtained by the similarity of behavior of **1** and [5,6]-open $p$-(methoxycarbonyl)phenylfulleroid in dichlorobenzene or acetonitrile/toluene solution. This compound was shown to isomerize irreversibly to the [6,6]-closed species after the third reduction.[2z]

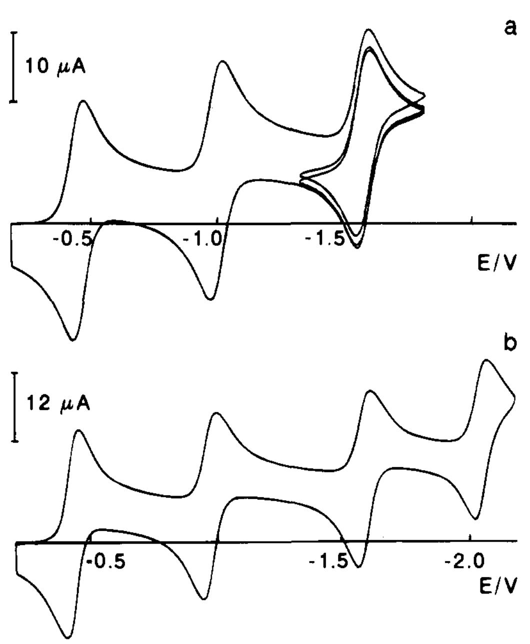

**Figure 4.** Cyclic voltammetric curve for a 1.0 mM compound **2**, 0.05 M $(C_4H_9)_4NPF_6$ THF solution: working electrode = Pt; temperature = 25 °C; sweep rate (a) 0.05 V/s and (b) 0.1 V/s.

Corroboration to the hypothesis that the [5,6] to [6,6] isomerization constitutes the chemical step coupled to the electron transfer can be obtained by performing directly a cvc on [6,6]-closed bpy-$C_{61}$ (compound **2**). In Figure 4a such a cvc is shown. The experiment was run in the same conditions of those reported for Figure 3a.

The coincidence of $E_{1/2}$ of the third reduction of this species (see Table 1) with the value, obtained via simulation, of the product of the chemical reaction lends strong support to the hypothesis. On the basis of this mechanism, the first and second cathodic peaks would correspond to the reductions of the [5,6]-isomer, while the relative anodic peaks correspond to the oxidations of the [6,6]-closed isomer (or of a mixtures of the two isomers). An effect of the isomerization, on these peaks, could therefore be expected. However, they practically occur at the same potentials for both isomers, see Table 1, and no effect is therefore observed. Further evidence for the presence of the reaction mechanism proposed was obtained through a spectroelectrochemical experiment in which a 0.5 mM solution of **1** was electrolyzed at −1.70 V. This corresponds to the three-electron reduction of the species. The UV−vis spectra of the electrolyzed solution was taken in-situ and recorded periodically. As the electrolysis proceeds, the narrow absorption peak at 424 nm, typical of the [5,6]-open isomer, decreases, and a shoulder corresponding to the absorption peak at 430 nm, typical of the [6,6]-closed isomer, increases. Unfortunately, the isolation and further characterization of the electrolysis product was prevented by its instability on the long time-scale.

As to peak IV, experiments were carried out in order to investigate the effects of both temperature and scan rate. Figure 5 shows the influence of temperature on cvc's.

The curves were obtained at 0.1 V/s by reversing the potential scan after peak IV. At 25 °C, peak III shows the two components due to the reduction of the two isomers. Peak IV corresponds to the reduction of a single species. Such a behavior might be rationalized considering that, on the present time scale, the isomerization of the [5,6]-open trianion to the

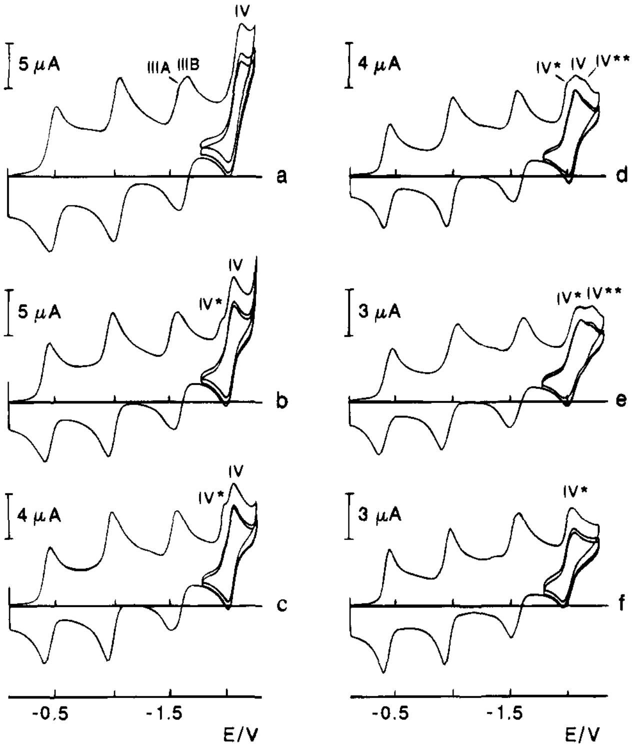

**Figure 5.** Cyclic voltammetric curves of a 0.5 mM compound **1**, 0.05 M $(C_4H_9)_4NPF_6$ THF solution: sweep rate = 0.1 V/s; working electrode = Pt; temperature (a) 25 °C, (b) 4 °C, (c) −18 °C, (d) −38 °C, (e) −58 °C, and (f) −78 °C.

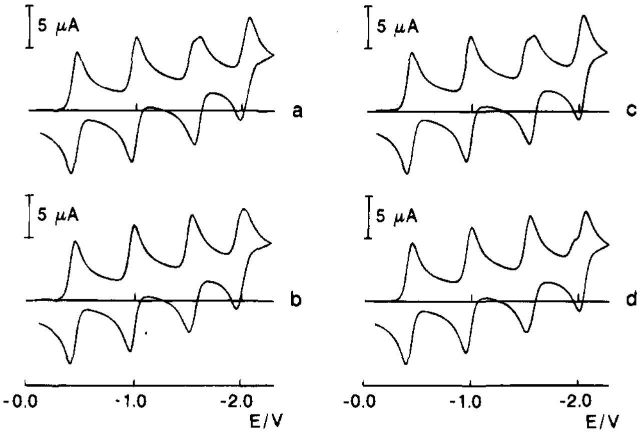

**Figure 6.** Simulated cyclic voltammetric curves corresponding to Figure 5a,b. The simulations were performed: (a) and (b) according to Scheme 2 (case a) and (c) and (d) according to Scheme 2 (case b) (see text).

[6,6]-closed trianion is quantitative. Peak IV therefore corresponds to the fourth one-electron reversible reduction of [6,6]-closed bpy-$C_{61}$. Its $E_{1/2}$, in fact, coincides with that of the fourth peak of the pristine species (Figure 4b). This assignment is confirmed by digital simulation (see Figure 6a) carried out extending the mechanism of Scheme 2 (case a) to include a fourth electron transfer.

The parameters used were the same of Figure 3c for the first three reduction processes and the experimental $E_{1/2}$ value of the pristine [6,6]-closed species for the fourth redox process. The agreement between the simulated and the experimental curves is very good.

At 4 °C, Figure 5b, the two-component pattern on the cathodic peak III is not present. This corresponds to a one-electron reversible reduction of [5,6]-open dianion. By contrast, a new component is observed at slightly less negative potentials than peak IV. This is indicated as IV*. Peak IV* becomes more evident as the temperature is further lowered, Figure 5c. On the basis of what was discussed above for the assignment of peak IV, peak IV* might be attributed to the reduction of parent [5,6]-open species which has not been able to isomerize on the time scale of the CV experiments. The subsequent simulation, based on this working hypothesis is not in agreement with the experimental curve, compare Figures 6b and 5b. This is hardly surprising. In fact, at this temperature, the isomerization reaction of the [5,6]-open trianion does not proceed to a sufficient extent on the time scale of the CV experiment to give a sufficient amount of the [6,6]-closed trianion. The fourth peak, in the simulation, corresponds to the fourth reduction of basically unreacted [5,6]-open bpy-$C_{61}$. Interestingly, the disagreement between experiment and simulation may easily be explained if also the tetraanion is involved in a chemical reaction. In particular, the evolution of CV pattern with either temperature or scan rate strongly suggests that an $\overline{E}C\overline{E}$ mechanism, similar to that occurring in third reduction but with a faster chemical step, is operative. Such a mechanism is shown in Scheme 2 (case b), where species A represents compound **1** ([5,6]-open isomer) and species B compound **2** ([6,6]-closed isomer). This hypothesis has been confirmed by numerical simulations. Figure 6c,d show the simulated cvc's, calculated according to the mechanism of Scheme 2 (case b) and the same parameters of Figure 6a,b. The agreement, in this case, is excellent. From the simulation, the values relative to the fourth reduction of [5,6]-open isomer for $k$ (15 ± 3 $s^{-1}$ at 4 °C) and $E_{1/2}$ (−2.05 V) were obtained. The temperature dependence of the rate constant gave an Arrhenius activation energy of 7 ± 2 kcal/mol (29 ± 8 kJ/mol).

If the temperature is further lowered, however, a further reversible peak, indicated by IV**, at slightly more negative potentials than peaks IV and IV*, is observed, Figure 5d. Its height increases as the temperature is further lowered, Figure 5e, at the expense of the height of peak IV. Since the overall charge associated with peaks IV, IV*, and IV** corresponds to a one-electron charge transfer, these peaks should represent globally the fourth reduction of three different forms of bpy-$C_{61}$. On the basis of the CV behavior, the species responsible for peak IV** can be identified as an intermediate in [5,6]-open/[6,6]-closed isomerization.

The overall mechanism for peak IV can be summarized as follows: at high temperatures, the irreversible conversion of the intermediate to the [6,6]-closed isomer is fast, and peak IV* and IV** cannot be observed, Figure 5a. Lowering the temperature increasingly inhibits the formation of **2** at the level of the third reduction and both **1** and **2** ([5,6]-open and [6,6]-closed isomers) are reduced, Figure 5b,c (appearance of peak IV*). Further lowering of the temperature allows the observation of the transient intermediate for the [5,6]-open to [6,6]-closed isomerization, Figure 5d,e. Eventually, **1** cannot isomerize any more, and only the starting material [5,6]-open is observed, peak IV*, Figure 5f.

Confirmation of this mechanism, shown in Scheme 3, has again been obtained by simulations which were able to reproduce the whole variety of patterns observed in Figure 5.

The simulations also provided the kinetic parameters of the chemical reactions which take place during the CV together with the halfwave potential corresponding to fourth reduction of the intermediate ($E_{1/2} = -2.16$ V). It is important to notice that the simulation results suggest that, *for both trianion and tetraanion*, the first step of the isomerization reaction may be considered a reversible process. This reaction occurs rapidly on the time scale of the experiment. The successive irreversible

**Scheme 3**

$$\begin{tikzcd}
{[A]} \arrow[r, Leftrightarrow] & {[A]^{-}} \arrow[r, Leftrightarrow] & {[A]^{2-}} \arrow[r, Leftrightarrow] & {[A]^{3-}} \arrow[r, Leftrightarrow] \arrow[d, shift right] & {[A]^{4-}} \arrow[d, shift right] \\
 & & & {[C]^{3-}} \arrow[u, shift right] \arrow[r, Leftrightarrow] \arrow[d] & {[C]^{4-}} \arrow[u, shift right] \arrow[d] \\
{[B]} \arrow[r, Leftrightarrow] & {[B]^{-}} \arrow[r, Leftrightarrow] & {[B]^{2-}} \arrow[r, Leftrightarrow] & {[B]^{3-}} \arrow[r, Leftrightarrow] & {[B]^{4-}}
\end{tikzcd}$$

**A** represents [5,6]-open isomer, **B** [6,6]-closed isomer and **C** [5,6]-closed isomer (see text)

step is the rate determining step. Since in our initial simulations, the presence of an intermediate was not taken into account, the rate constants obtained according to the models of Scheme 2 (case a and case b) must be considered as apparent rate constants. Analogously, the activation energies given above are the sum of two terms, namely the reaction enthalpy relative to the first step (equilibrium) and the activation energy of the second step. For both the trianion and the tetraanion, the reaction enthalpy of the first step, calculated according to Scheme 3, was 1−2 kcal/mol. Consistently, the Arrhenius activation energy values relative to the second step were close to those obtained according to Scheme 2 (cases a and b).

As expected, the same modifications of cvc obtained by varying the temperature are observed by increasing the scan rate. At 25 °C, for instance, the changes of the morphologies of the cvc's observed in Figure 5 are obtained increasing the scan rate from 0.1 to 50 V/s. A comparison between curves obtained at different scan rates and at a single temperature is, however, less immediate than that between curves obtained at different temperatures and at a single scan rate because of the capacitive and ohmic effects.

It is important now to consider the chemical identity of the intermediate which appears in the processes associated to peaks III and IV. In Chart 1, the structures of the four possible isomeric methanofullerenes are shown. It is evident that the most favorite candidate for the role of intermediate in the stepwise [5,6]-open/[6,6]-closed isomerization is [5,6]-closed species. Participation of this isomer to the thermal isomerization of neutral fulleroids has already been proposed.[4e] Involvement of [5,6]-closed intermediate in the electroinduced, room temperature, [5,6]-open/[6,6]-closed isomerization of 4-(methoxycarbonyl)phenylfulleroid trianion was also suggested on the basis of purely mechanistic reasonings.[2z] On the basis of the above considerations and of the experimental evidences, we propose the [5,6]-closed isomer as the intermediate C in the mechanism illustrated in Scheme 3. Unfortunately, the unavailability of a sample of stable [5,6]-closed bpy-$C_{61}$ has prevented the further experimental confirmation of the proposed identity of intermediate.

Support can, however, be obtained by quantum chemical calculations. Because of the size of the system, we were forced to resort to semiempirical quantum chemistry. As it has already been discussed,[4e] MNDO-PM3, is well suited to study [5,6]-fulleroids and [6,6]-methanofullerenes in their neutral state. A systematic study of five derivatives[4e] showed that, with the exception of $C_{61}H_2$, all the $C_{61}R_2$ compounds are more stable in the [6,6]-closed configuration, where R= −OMe, −COOEt, −COO$^t$Bu, −Ph. The energy difference between the [5,6]-open and the [6,6]-closed isomers of these neutral compounds was found to range from 4.70 kcal/mol (19.66 kJ/mol) to 7.31 kcal/mol (30.58 kJ/mol). The largest gap was found for phenyl substitution. Again apart for $C_{61}H_2$, the energy difference between the [6,6]-closed configuration and the [5,6]-closed structure was found to be constantly slightly larger than 20 kcal/mol (83.68 kJ/mol).[4e] No minima were found for the [6,6]-open geometry. Based on this report, we decided to use the MNDO-PM3 model[5] to study the neutral molecule, its trianion, and its tetraanion of the three isomers of $C_{61}$Hpy, where py is a pyridine ring. Our system is therefore somewhat different from those studied in ref 4e, where two identical substituents were present and contains only a significant part of that studied experimentally. The calculations for the trianion were carried out using the restricted open shell Hartree−Fock method to avoid problems of spin contamination that may arise from the use of the unrestricted Hartree−Fock method. For the even electron systems restricted Hartree−Fock calculations were performed. All the calculations were run with the Gaussian92 program.[6] In the study, we were able to locate the stationary points corresponding to the [5,6]-open, [5,6]-closed, and [6,6]-closed species for the three molecular states. In practice, this amounts to nine stationary points. Two types of bonds undergo strong variation upon reduction. The first is the bond between the bridging atom and the carbon atoms in the fullerene frame. In the [5,6]-closed species these bond lengths are 1.508 and 1.509 Å in the neutral molecule, 1.524 and 1.529 Å in the trianion, and 1.526 and 1.537 Å in the tetraanion. For the [5,6]-open isomer all the distances range between 1.496 and 1.499 Å. For the [6,6]-closed species, the bond lengths are 1.506 and 1.506 Å in the neutral molecule, 1.511 and 1.512 Å in the trianion, and 1.516 and 1.520 Å in the tetraanion. The second and most relevant distance is the so called [5,6] or [6,6] bond distance. For the [5,6]-closed species this is 1.654 Å in the neutral molecule, 1.555 Å in the trianion, and 1.548 Å in the tetraanion. In the [6,6]-closed species the bond distance ranges from 1.555 Å in the neutral molecule, to 1.538 Å in the trianion, to 1.528 Å in the tetraanion. It is therefore apparent that, in the closed isomers, electronic reductions leads to similar bond lengths. This agrees with what is observed for reduced $C_{60}$: in $C_{60}{}^{6-}$, the two symmetry inequivalent bond lengths become nearly identical.[7] While the carbon−carbon bond length decreases upon successive reductions for the closed isomers, the opposite occurs for the [5,6]-open species. In this molecule, the bond distance goes from 2.206 Å in the neutral molecule, to 2.269 Å in the trianion, to 2.291 Å in the tetraanion.

The energetics of the nine stationary points calculated by the PM3 model is of consequence for the reaction mechanism proposed to assign the peaks of the cvc. Comparison of the energies for the three charges, namely 0, −3, and −4, within the same isomer would require modeling of the solvent effect and is outside the scope of this work. It is of interest, instead, to compare the heats of formation for the same charge of the different isomers. In the neutral system, the [6,6]-closed isomer has the lowest energy, the [5,6]-open structure is 3.41 kcal/mol (14.27 kJ/mol) higher, while the [5,6]-closed configuration is 20.99 kcal/mol (87.82 kJ/mol) above. This result is in keeping with that of reference 4e. Perhaps not totally surprisingly in view of the analysis of the cvc, for both the trianion and the tetraanion, the [5,6]-closed form becomes the most stable form. One should also notice that for both anions, the energy span of

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(5) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (b) Stewart, J. J. P. *J. Comp. Chem.* **1989**, *10*, 209.

(6) Gaussian 92, Revision B; Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1992.

(7) (a) Andreoni, W.; Gygi, F.; Parrinello, M. *Phys. Rev. Lett.* **1992**, *68*, 823. (b) Negri, F.; Orlandi, G.; Zerbetto, F.; *Chem. Phys. Lett.* **1992**, *196*, 303.

the three isomers is less than 5 kcal/mol (20.92 kJ/mol). As such, their stabilities can be reversed by solvent or substituent effects. More in detail, for the trianion the [5,6]-open species is 3.54 kcal/mol (14.81 kJ/mol) more energetic than the [5,6]-closed isomer, while the [6,6]-closed structure is 4.01 kcal/mol (16.78 kJ/mol) higher. In the tetraanion, the [5,6]-open isomer is 4.67 kcal/mol (19.54 kJ/mol) above the ground state configuration, while the [6,6]-closed isomer is 3.80 kcal/mol (15.90 kJ/mol) more energetic.

On the basis of the spectroscopic and quantum chemical results, it is highly plausible to identify species C in Scheme 3 as [5,6]-closed bpy-$C_{61}$. The quantum chemical calculations also suggest that different solvents or different substituents might affect the energy ordering of the three quasi degenerate reduced species and lead to a different reaction scheme in which the role of the [6,6]-closed and [5,6]-closed molecules are reversed.

As far as the redox processes beyond the fourth electron transfer are concerned, Figures 2 and 7a−d show the evolution of the cvc's with temperature at a scan rate of 0.1 V/s.

The whole potential window was probed. Such a window obviously increases with lowering the temperature. Besides the observations reported above, a relatively strong temperature effect is also observed on the redox processes occurring at more negative potentials.

Peak V, consists, at room temperature, of two overlapping redox processes corresponding to peaks VA and VB. Lowering the temperature, it gradually converts to a single one-electron charge transfer, peak VB.

Peak VI also shows, at room temperature, two components, VIA and VIB. Again, at lower temperatures, it turns into a single one-electron reversible peak, peak VIB.

The processes associated with the following peaks are more difficult to describe because they occur at potentials close to the base solution discharge which itself changes with temperature. In general, however, one can affirm that, depending on the available potential window, one or two redox processes are observed. They seem to correspond to a charge transfer of less than one electron and their relative heights change with temperature. Overall their chemical reversibility is difficult to ascertain.

Recently, the CV behavior of some methanofullerenes/fulleroids containing phenyl groups at the bridging carbon was studied in quite similar experimental conditions.[2y] In particular, the behavior at very negative potentials was decribed together with the effect of temperature and/or scan rate on the CV pattern. Decreasing the temperature and increasing the scan rate, six reversible and evenly spaced reduction peaks were observed. They were assigned to sequential reductions of the fullerene moiety in analogy to what observed, in the same medium, for $C_{60}$. The cvc's for **1**, however, are strikingly different from those reported in ref 2y. In particular, the relatively simple two-peak pattern previously observed beyond the fourth electron transfer is replaced by a complex four-peak pattern. Such a different behavior is certainly due to the different redox properties of the substituents: it is well-known that bpy is electroactive. The cvc for the model molecule (**5**) in which the saturated bridging carbon carrying the fullerene moiety is replaced by a −CO− group shows in fact a reversible one-electron peak with $E_{1/2} = -1.59$ V followed by two irreversible peaks each corresponding to less than one-electron charge transfers. Such peaks match well peaks VB, VII, and VIII in Figures 2 and 7 for both their relative positions and their heights. On the basis of such a comparison, the processes can therefore be attributed to successive reductions of bpy moiety of **1**. The cathodic shift, with respect to the model molecule, of the peaks of **1** is probably due to either the electron-withdrawing effect of −CO− group (an analogous effect is observed, for instance, in 5,5′-dicarboxyethyl-bpy[8]) or to the electrostatic repulsion of the bpy fragment with the already four times reduced fullerene moiety.

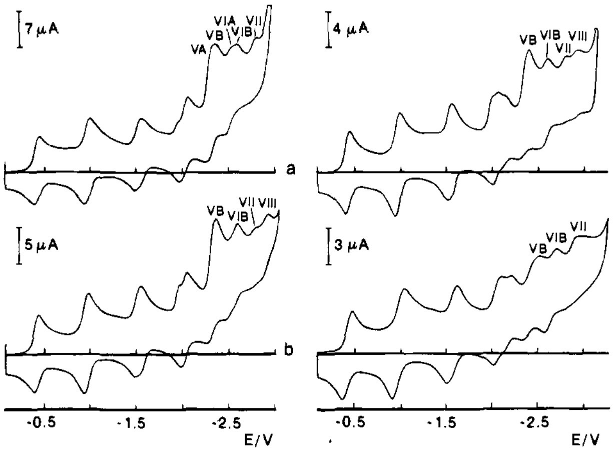
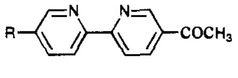


**Figure 7.** Cyclic voltammetric curves of a 0.5 mM compound **1**, 0.05 M $(C_4H_9)_4NPF_6$ THF solution: sweep rate = 0.1 V/s; working electrode = Pt; temperature (a) 4 °C, (b) −18 °C, (c) −38 °C, and (d) −58 °C.



**3**: R = $COCH_3$
**4**: R = $CH(CH_3)OH$
**5**: R = $CH(CH_3)OTBDMS$
TBDMS = tert-butyldimethylsilyl

This assignment, however, can only be tentative because of the chemical complications associated with these redox processes. In this regard, the cvc for 5,5′-diacetyl-bpy (**3**), that is the model molecule where the $-CH(CH_3)OTBDMS$ group has been replaced by another $-COCH_3$ group, recorded in the same conditions of that of the above model molecule (**5**), shows two reversible one-electron charge transfers with $E_{1/2} = -1.17$ and −1.48 V, respectively. This points out that the irreversible behavior in the model molecule is likely due to the presence of the −OTBDMS group. It is evident that, in view of its possible application in photochemical molecular devices, chemical instability of the anions should be avoided for it may reduce the lifetime of the charge-separation excited state. Therefore, although stabilization of anions might follow from coordination to metal, −OTBDMS group should be replaced by a different, stable protective group. Notice, however, that, at −58 °C (Figure 7d), the cvc simplifies and peaks V and VII seem to correspond to single one-electron reversible charge transfers. According to the above tentative assignment, peak VIB in Figures 2 and 7 would therefore represent the fifth (reversible) one-electron reduction of the fullerene moiety. This reduction process is also observed, with the same $E_{1/2}$, in the cvc for **2** (Table 1). This suggests that such reduction is not influenced by [5,6]-open/[6,6]-closed isomerism.

The overall cvc pattern would therefore result from the superposition of the redox behavior of the nearly independent methanofullerene/fulleroid and bpy moieties. Interactions between these fragments may, however, occur. The occurrence of bond breakage in **1**, which, in turn, gives rise to a carbanionic open structure stabilized by a delocalization of the negative charge on the pyridine rings may in fact be responsible for peaks VA and VIA in Figures 2 and 7, in analogy to what suggested in ref 2y. However, since, in contrast to ref 2y, temperature and scan rate changes have only minor effects on this part of the cvc, one infers that some additional stabilization of the cyclopropane ring is brought about by bpy substituents.

## Conclusions

The study of the reduction processes of $C_{60}$ in THF at −60 °C has allowed the observance of, for the first time in a pure solvent, six successive reversible one electron reductions.

For compound **1**, seven overall reduction processes are observed. The comparison of the voltammetric behavior of the two species has allowed the proposal of a reasonable localization of redox sites. In particular, the first four and the sixth reductions are likely to be localized on the fullerene moiety, while the others are localized on the bpy moiety. Of the reduction peaks observed for **1**, only the first two are reversible in all conditions, while the remaining reductions are complicated by chemical reactions coupled to the electron transfer.

The study conducted at various temperatures and scan rates suggests that the [5,6]-open/[6,6]-closed isomerization occurs according to an $\overrightarrow{E}C\overleftarrow{E}$ mechanism. At temperatures higher than about 5 °C, such reaction occurs concomitantly with the third reduction, while at lower temperatures its onset is located at the fourth reduction.

Numerical simulation techniques confirmed the above $\overrightarrow{E}C\overleftarrow{E}$ mechanism and allowed the determination of the kinetic parameters. Further confirmation also came from the study of a sample of pristine [6,6]-closed isomer (compound **2**), which was supposed to be involved in the reaction mechanism.

Also the [5,6]-closed species appears in the electrode reduction of **1** at the level of the fourth reduction. It should be emphasized that this is the first time that the presence of an intermediate of this type is proposed on the basis of the observation of a redox process.

Quantum chemical calculations have shown that the three structural isomers of a model system, namely [5,6]-open py-$C_{60}$, [5,6]-closed py-$C_{60}$, and [6,6]-closed py-$C_{60}$ become nearly equienergetic in the trianion and the tetraanion. This lends support to the proposed mechanism and suggests that modification of the substituents or different solvents may effectively reverse the role played by the [5,6]-closed and the [6,6]-closed isomers. In principle, this could provide a synthetic way to the elusive [5,6]-closed bpy-$C_{61}$.

## Experimental Section

**Instrumentation.** $^{1}H$ NMR and $^{13}C$ NMR were recorded on a Bruker AC 250 spectrometer. Chemical shifts are given in parts per million ($\delta$) relative to tetramethylsilane. UV−vis spectra were taken on a Perkin-Elmer Lambda 5 spectrophotometer. FT-IR spectra were recorded on a Perkin-Elmer 1720 X spectrophotometer. GC-MS analyses were performed on a Hewlett-Packard electron impact mass spectrometer 5070 coupled with a gas chromatograph 8890 equipped with a 15 m × 0.25 mm column: stationary phase, SE-30; film thickness, 0.25 m. MALDI mass spectra were obtained in positive linear mode at 15 kV acceleration voltage, using 2,5-dihydroxybenzoic acid as matrix. Melting points were determined with a Büchi apparatus and are uncorrected. Reactions were monitored by thin layer chromatography using Merck precoated silica gel 60-$F_{254}$ (0.25 mm thickness) plates. Flash column chromatography was performed employing 230−400 mesh silica gel (ICN Biomedicals).

Voltammograms were recorded with a AMEL Model 552 potentiostat controlled by a AMEL Model 568 function generator, a AMEL Model 865 A/D converter, a Hewlett-Packard 7475A digital plotter, and a Nicolet Model 3091 digital oscilloscope. The minimization of the uncompensated resistance effect in the voltammetric measurements was achieved by the positive-feedback circuit of the potentiostat. Differential pulse voltammetry experiments were carried out by a AMEL Mod 466 Polarographic analyzer. UV−vis spectra were taken using a VARIAN Cary 5E UV−vis-NIR spectrophotometer. Temperature control was accomplished within 0.1 °C by a Lauda Klein-Kryomat thermostat.

**Materials.** All materials were reagent grade chemicals. $C_{60}$ (>99.99%) was purchased from SES Research (Texas) and from Hoechst A. G. (gold grade). Tetrabutylammonium hexafluorophosphate (TBAH, puriss. from Fluka) was used as supporting electrolyte as received. The solvents were distilled prior to use. Dry vacuum-distilled THF was mixed under argon with sodium anthracenide and allowed to stand for 6−7 days in order to remove traces of water and oxygen.[9] The solvent was then distilled into the electrochemical cell soon before performing the experiment.

**5-Acetyl-5′-(1-hydroxyethyl)-2,2′-bipyridine 4.** A tetrahydrofuran solution (300 mL) containing 5,5′-diacetyl-2,2′-bipyridine, prepared from 3-acetylpyridine according to the procedure described in ref 10, (1 g, 4.17 mmol) and sodium borohydride (53 mg, 1.4 mmol) was heated to 50 °C for 6 h and then stirred at ambient temperature overnight. The solvent was then evaporated at reduced pressure, and the resulting raw material was purified by column chromatography ($SiO_2$, eluant: $CH_2Cl_2/CH_3OH$ 98:2): 0.44 g (yield 44%), mp = 105−7 °C; IR (neat) $\nu$ ($cm^{-1}$) 3361, 1682, 1581, 1370, 1277, 838; $^{1}H$ NMR (250 MHz, $CDCl_3$) $\delta$ 1.58 (d, 3H, $J$ = 6.6 Hz), 2.68 (s, 3H), 5.04 (q, 1H, $J$ = 6.6 Hz), 7.89 (dd, 1H, $J$ = 8.0 Hz, $J$ = 2.2 Hz), 8.34 (dd, 1H, $J$ = 8.0 Hz, $J$ = 2.2 Hz), 8.46 (d, 1H, $J$ = 8.0 Hz), 8.52 (d, 1H, $J$ = 8.0 Hz), 8.70 (d, 1H, $J$ = 2.2 Hz); 9.21 (m, 1H). $C_{14}H_{14}N_2O_2$ (MW = 242.3); MS $m/z$ 242 ($M^{+}$, 35), 227 (100), 199 (78).

**5-Acetyl-5′-((1-*tert*-butyldimethylsilyloxy)ethyl)-2,2′-bipyridine (5).** To a stirred solution of alcohol **4** (0.44 g, 1.82 mmol) and imidazole (0.309 g, 4.54 mmol) in dry *N,N*-dimethylformamide (3 mL) was added *tert*-butyldimethylsilyl chloride (0.412 g, 2.73 mmol) at room temperature portionwise under nitrogen. After stirring overnight at ambient temperature, the reaction mixture was diluted with dichloromethane (50 mL) and filtered. The solvent was then evaporated at reduced pressure and the raw material was purified by crystallization from a methanol/water mixture: 0.40 g (yield 62%), mp = 64−6 °C; IR (neat) $\nu$ ($cm^{-1}$) 2931, 1691, 1589, 1260, 830; $^{1}H$ NMR (250 MHz, $CDCl_3$) $\delta$ 0.01 (s, 3H), 0.08 (s, 3H), 0.92 (s, 9H), 1.48 (d, 3H, $J$ = 6.2 Hz), 2.68 (s, 3H), 4.98 (q, 1H, $J$ = 6.2 Hz), 7.83 (dd, 1H, $J$ = 8.0 Hz, $J$ = 2.2 Hz), 8.34 (dd, 1H, $J$ = 8.0 Hz, $J$ = 2.2 Hz), 8.44 (d, 1H, $J$ = 8.0 Hz), 8.52 (d, 1H, $J$ = 8.0 Hz), 8.68 (d, 1H, $J$ = 2.2 Hz), 9.22 (m, 1H); $C_{20}H_{28}N_2O_2Si$ (MW = 356); MS $m/z$ 356 ($M^{\bullet+}$, 1), 299 (49), 225 (100); elemental anal. Calcd: C, 67.38; H, 7.92; N, 7.86. Found: C, 68.32; H, 8.15; N, 7.47.

**61-[5-Yl-5′-((1-*tert*-butyldimethylsilyloxy)ethyl)-2,2′-bipyridyl]-61-methyl-1,6-homofullerene-$C_{60}$ (1).** The hydrazone of **5** was prepared by dissolving compound **5** (0.1 g, 0.28 mmol) in 10 mL of absolute ethanol. Anhydrous hydrazine 0.1 mL was added, and the reaction mixture was heated to reflux temperature for 2 h. The solvent was evaporated at reduced pressure, and the oily residue was dried under vacuum. The crude was dissolved in 10 mL of chloroform, then anhydrous sodium sulfate (0.3 g) and manganese dioxide (0.2 g) were added portionwise at room temperature, and the mixture was stirred for 30 min in the dark. The resulting red-orange solution [IR (neat) $\nu_{N=N}$ 2048 $cm^{-1}$] was filtered by suction on a small pad of Celite in order to remove all solids. Due to the instability to $SiO_2$ and concentration, the diazo compound was added directly to a toluene solution (130 mL) containing $C_{60}$ (0.1 g, 0.14 mmol). The solution was stirred at room temperature for 2 h. Then the solvents were evaporated at reduced pressure and the solid residue was purified by column chromatography ($SiO_2$, eluant/toluene, then toluene/isopropyl alcohol 9:1): 65 mg (yield 44%); $^{1}H$ NMR (250 MHz, $CS_2/CD_2Cl_2$ 1:1) $\delta$ 0.08 (s, 3H), 0.18 (s, 3H), 0.99 (s, 9H), 1.49 (s, 3H), 1.54 (d, 3H, $J$ = 6.2 Hz), 5.02 (q, 1H, $J$ = 6.2 Hz), 7.80 (dd, 1H, $J$ = 8.2 Hz, $J$ = 2.1 Hz), 8.42 (dd, 1H, $J$ = 8.2 Hz, $J$ = 2.1 Hz) 8.48 (d, 1H, $J$ = 7.7 Hz), 8.62 (m, 1H), 8.67 (d, 1H, $J$ = 8.2 Hz), 9.28 (d, 1H, $J$ = 2.1 Hz); $^{13}C$ NMR (62.5 MHz, $CS_2/CD_2Cl_2$ 1:1) $\delta$ −4.53, −4.46, 25.40, 26.02, 27.21, 54.62, 69.06, 120.96, 121.33, 133.62, 135.14, 136.72, 137.07, 137.45, 138.16, 138.86, 139.03, 139.75, 139.91, 140.46, 140.65,

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141.48, 141.57, 142.11, 142.26, 142.31, 142.45, 142.54, 142.96, 143.11, 143.27, 143.32, 143.73, 143.77, 143.89, 143.96, 144.11, 144.34, 144.60, 144.91, 144.97, 145.21, 146.65, 147.52, 149.61, 154.34, 155.23; $C_{80}H_{28}N_2OSi$ (MW = 1061.2); MALDI-MS *m/z* 1061 ($M^+$).

**61-[5-Yl-5′-(1-*tert*-butyldimethylsilyloxy)ethyl-2,2′-bipyridyl]-61-methyl-1,2-methanofullerene-$C_{60}$ (2).** Fulleroid **1** was converted quantitatively to methanofullerene **2** according to literature[2z] by heating to 150 °C for 24 h a 0.5 mM solution of **1** in *o*-dichlorobenzene: $^1H$ NMR (250 MHz, $CDCl_3$) $\delta$ 0.02 (s, 3H), 0.10 (s, 3H), 0.92 (s, 9H), 1.50 (d, 3H, $J = 6.21$ Hz), 2.60 (s, 3H), 5.00 (q, 1H, $J = 6.21$ Hz), 7.88 (m, 1H), 8.46 (m, 2H), 8.62 (m, 1H), 8.69 (m, 1H), 9.30 (m, 1H); $^{13}C$ NMR (62.5 MHz, $CDCl_3$) $\delta$ −4.80, 22.16, 25.81, 27.05, 44.27, 68.78, 79.60, 120.64, 120.91, 134.08, 135.22, 137.52, 138.16, 139.42, 140.93, 141.06, 142.15, 142.24, 142.54, 143.0, 143.03, 143.11, 143.75, 144.11, 144.46, 144.54, 144.62, 144.72, 144.80, 145.01, 145.07, 145.17, 145.22, 145.76, 146.88, 147.56, 148.04, 151.48, 154.34, 155.75; MALDI-MS *m/z* 1062 ($MH^+$).

**Electrochemical Experimental Procedures.** The one-compartment electrochemical cell was of airtight design with high-vacuum glass stopcocks fitted with either Teflon or Kalrez (DuPont) O-rings in order to prevent contamination by grease. The connections to the high-vacuum line and to the Schlenck containing the solvent were obtained by spherical joints also fitted with Kalrez O-rings. The pressure measured in the electrochemical cell prior to perform the trap-to-trap distillation of the solvent was typically $2.0-3.0 \times 10^{-5}$ mbar. The working electrode consisted of a 0.6 mm-diameter platinum wire (electrode area 0.15 $cm^2$ approximately) sealed in glass. The counter electrode consisted of a platinum spiral, and the quasi-reference electrode was a silver spiral. The quasi-reference electrode drift was negligible for the time required by a single experiment. Both the counter and the reference electrode were separated from the working electrode by ~0.5 cm. Potentials were measured with the ferrocene standard[11] and are always referred to SCE.[9] $E_{1/2}$ values, correspond to $(E_{pc} - E_{pa})/2$ (reductions) from CV or were deduced from dpp peak potentials.[12] The temperature-dependent ferrocinium/ferrocene couple standard potential was measured with respect to SCE by a nonisothermal arrangement according to the method outlined in ref 13. In some experiments a SCE reference electrode was used, separated from the working electrode compartment by a sintered glass frit. Ferrocene was also used as internal standard for checking the electrochemical reversibility of one-electron charge transfers.

Potential-controlled bulk electrolysis was carried out in a three-compartment electrochemical cell with both the SCE reference electrode and the platinum spiral counter electrode separated from the working electrode compartment by sintered glass frits. The working electrode was a large area platinum gauze. The electrolized solution was monitored at intervals during the electrolysis by voltammetry with periodical renewal of the diffusion layer,[14] and, at the same time, UV−vis spectra were taken.

**Digital Simulation of Cyclic Voltammetric Experiments.** The CV simulations were carried out by using an explicit finite difference scheme making use of a commercially available software[15] opportunely modified for the simulation of repetitive cycles. All the electrochemical steps were considered fast in the simulation,[2a−c,16] and the simulation parameters were chosen so as to obtain a visual best fit over a 10-fold range of scan rates. This procedure allowed the assignment of the rate constants of the chemical steps with a 20% error.

The effect due to the occurrence of homogeneous or solution electron transfer (SET) between the intermediates produced during the experiment in the layer of solution close to the electrode surface was also taken into account in some simulations. The importance of considering the SET reactions in the simulation of the cyclic voltammetry of systems which involve more than two states of oxidation and/or more than two structural modifications in the time scale of the experiment was pointed out[17] especially in those cases in which the chemical steps are not too fast so that the reactants and products concentrations are appreciable in the proximity to the electrode.

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**Supplementary Material Available:** $^1H$, $^{13}C$ NMR, and UV−vis spectra of fullerene derivatives **1** and **2** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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