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Redox behavior of the molybdenum and tungsten metallafullerenes $Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$ (dppe = bis-(1,2-diphenylphosphino)ethane) and $W(CO)_3(dppb)(\eta^2\text{-}C_{60})$ (dppb = bis-(1,2-diphenylphosphino)benzene)

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Dedicated to Professor Fausto Calderazzo on the occasion of his 70th birthday

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Abstract

Electrochemistry of $M(CO)_3(\text{diphosphine})(\eta^2\text{-}C_{60})$ (M = W, diphosphine = 1,2-bis(diphenylphosphino)benzene (**1**); Mo, diphosphine = 1,2-bis(diphenylphosphino)ethane (**2**)) shows that they undergo reversibly three fullerene-centred reductions at potential values which are more negative by about 0.2 V with respect to the corresponding steps in free C_{60}. EPR measurements on the electro-generated monoanions $[\mathbf{1}]^-$ and $[\mathbf{2}]^-$ seem to support that the unpaired electron, although delocalized on the fullerene moiety, assumes a non-negligible metallic character, thus suggesting that the LUMOs of the two complexes might be significantly contributed to by the metallic fragments. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Electrochemistry; EPR spectroscopy; Metallafullerenes

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1. Introduction

The multiple electron-transfer ability of free fullerenes [1] do not seem to have given the expected impulse to electrochemical investigations on their transition metal adducts. As a matter of fact, the number of studies concerned with the electrochemical behaviour of C_{60}-metal complexes is still rather limited [2], and aside from one brief report [2e], there are no reports on the C_{70}-analogs.

From the electrochemical viewpoint the coordination of a metal fragment to fullerenes commonly induces shifts of the redox potentials of the well known sequence of one-electron reductions towards more negative values with respect to free fullerene. Only in a few cases was the reductive process facilitated [2e,h].

In a previous paper dealing with the redox behaviour of $M(\eta^2\text{-}C_{60})(CO)_2(\text{phen})(\text{dbm})$ (M = W, Mo; phen = 1,10-phenanthroline; dbm = dibutyl maleate) we gained evidence from EPR measurements that in spite of the fact that the sequential one-electron reductions are centred on the fullerene moiety, the corresponding monoanions might possess significant metallic character [2i]. We present here a spectroelectrochemical investigation performed on the two complexes $M(CO)_3(\text{diphosphine})(\eta^2\text{-}C_{60})$ (M = W, diphosphine = dppb = 1,2-bis-(diphenylphosphino)benzene (**1**); Mo, diphosphine = dppe = 1,2-bis(diphenylphosphino)ethane (**2**)) illustrated in Scheme 1, which further supports such a behaviour. The present complexes have been previously characterized by elemental analysis and spectroscopic techniques [3]. The X-ray structure of complex **2** has been recently published [4].

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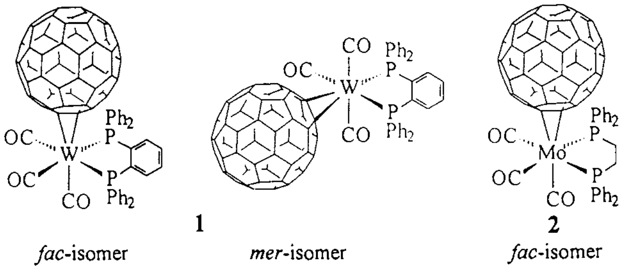

Scheme 1.

2. Experimental

2.1. General procedures

The *fac*/*mer* isomeric mixtures of complexes **1** and **2** [3a,b], the *fac* isomer of **2** [3b], $W(CO)_3(MeCN)(dppb)$ (**3**) [3a], $Mo(CO)_4(dppe)$ (**4**) [5] and *fac*-$Mo(CO)_3$-$(MeCN)(dppe)$ (**5**) [6] were prepared according to the reported procedures.

Material and apparatus for electrochemistry and coupled ESR measurements have been previously described [2i]. All the potential values are referred to the saturated calomel electrode (SCE). Under the present experimental conditions the one-electron oxidation of ferrocene occurs at $E^{\circ\prime} = +0.34$ V in the temperature range from -10 to $+10$°C, and at $E^{\circ\prime} = +0.35$ V at $+20$°C. The external magnetic field H_0 for ESR spectroscopy was calibrated by using a DPPH powder sample ($g_{DPPH} = 2.0036$). A computer simulation of the ESR spectra was carried out by using the SIM14 A program [7].

3. Results and discussion

3.1. Electrochemistry

Fig. 1 compares the cyclic voltammetric response of C_{60} (part a) and that of the *fac*/*mer* isomeric mixture of the adduct $W(CO)_3(dppb)(\eta^2\text{-}C_{60})$ (**1**), (part b).

As seen, the metal complex exhibits three subsequent reduction processes having features of chemical reversibility in cyclic voltammetry, which are shifted towards more negative potentials by ca. 0.2 V with respect to the sequential one-electron reductions of free C_{60}. Cyclic voltammetric tests up to -2.1 V show that the fourth C_{60}-centred reduction, which in free C_{60} is localized close to the solvent discharge [2i], is now shifted beyond the solvent discharge.

A few comments must be devoted to the electronic effects played by the coordination of the metal fragment to the fullerene ligand, as measured by the extent of the above cathodic shift with respect to free C_{60}. Limiting to related tungsten complexes, in the case of $W(\eta^2\text{-}C_{60})(CO)_2(phen)(dbm)$, such a shift was ca. 0.15 V [2i], whereas in the strictly related $W(\eta^2\text{-}C_{60})(CO)_3(dppe)$ it was ca. 0.2 V (in MeCN–toluene solution) [2c]. This means that, in spite of the presence of different ligands, the shifts are essentially constant. These data confirm that the two not easily separable effects responsible for the shifts, namely: the extent of interruption of double-bond conjugation in fullerene caused by η^2-coordination, and the inductive effect exerted by the metal fragment, compensate each other.

Provided that the starred peak-systems shown in Fig. 1 are due to traces of uncoordinated C_{60}, it has to be concluded that the isomeric mixture does not give rise

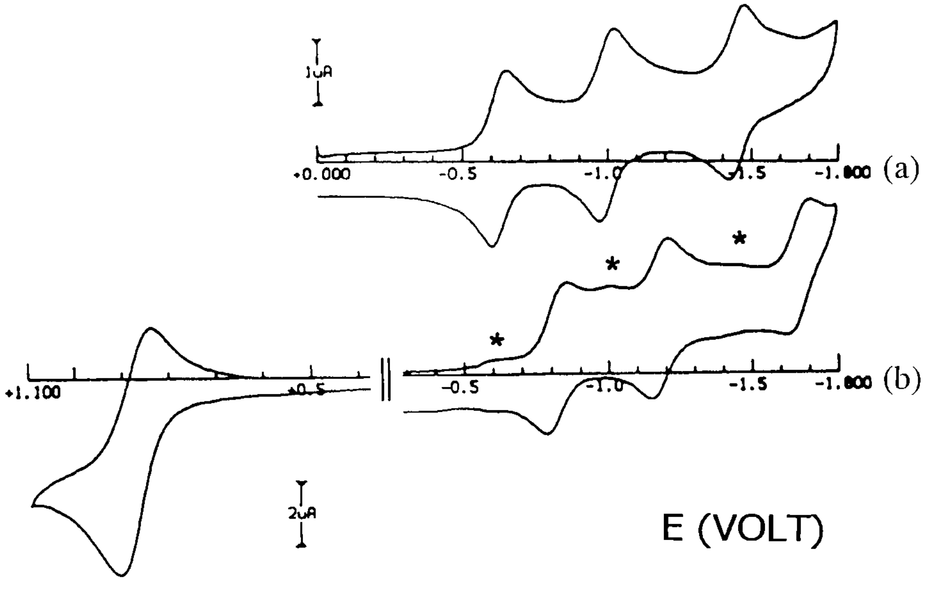

Fig. 1. Cyclic voltammetric responses recorded at a platinum electrode on CH_2Cl_2 solutions containing $[NBu_4][PF_6]$ (0.2 mol dm^{-3}) and: (a) C_{60} (saturated solution); (b) **1** (7×10^{-4} mol dm^{-3}). Scan rate 0.2 V s^{-1}. $T = -10$°C.

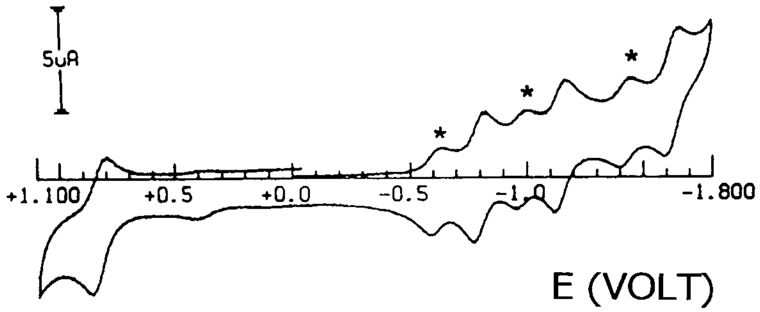

Fig. 2. Cyclic voltammetric response recorded at a platinum electrode on a CH_2Cl_2 solution containing $[NBu_4][PF_6]$ (0.2 mol dm^{-3}) and *fac*-**2** (9×10^{-4} mol dm^{-3}). Scan rate 0.2 V s^{-1}. $T = -10$°C.

to separate waves, thus indicating that the two isomers cannot be distinguished by electrochemical techniques.

Complex **1** also undergoes an anodic process confidently assigned to the oxidation of the W(0) fragment, the peak-current of which is about twice that of each reduction step. Such an oxidation process is complicated by chemical reactions in that the i_{pc}/i_{pa} ratio at slow scan rates is about 0.5. As a matter of fact, after the consumption of two electrons/molecule in controlled potential coulometry ($E_w = +0.9$ V), the electrolysis current abruptly slows down, but it remains slightly higher than the background current up to the consumption of about four electrons per molecule, indicating that the degradation likely involves releasing of redox active fragments of the type $W(X)(CO)_3(dppe)$, X being speculatively some coordinating molecule occasionally present in solution (such as traces of water).

It seems noteworthy to point out that, even at the slow scan rate of 0.02 V s^{-1}, the cathodic cyclic voltammetric profile of **1** does not put in evidence any of the chemical complications observed for the reductions of $M(\eta^2\text{-}C_{60})(PR_3)_2$ (M = Ni, Pd, Pt) (which afforded a cathodic shift of ca. 0.4 V with respect to free C_{60}) [2a], thus pointing out that in the present case the bonding of the metal fragment to the fullerene is much stronger. In confirmation of the chemical reversibility of the first cathodic step, cyclic voltammetry performed on exhaustively one-electron reduced solutions ($E_w = -1.0$ V) displays a voltammetric profile quite complementary to that shown in Fig. 1.

The same electrochemical behavior is exhibited by either the *fac*/*mer* isomeric mixture, or the *fac* isomer of complex $Mo(CO)_3(dppe)(\eta^2\text{-}C_{60})$ (**2**). In these cases however, as illustrated in Fig. 2, which refers to *fac*-**2**, the amount of free C_{60} is notably higher. Although repeated attempts to further purify these products were unsuccessful, the role played by the presence of the metal fragments remains well detectable.

It is useful to note that the metal fragment precursors $W(CO)_3(MeCN)(dppb)$ (**3**) and *fac*-$Mo(CO)_3(MeCN)(dppe)$ (**5**) undergo a one-electron oxidation at potentials less positive by about 0.5 V than the anodic processes observed for their C_{60}-adducts, whereas, $Mo(CO)_4(dppe)$ (**4**) just undergoes a two-electron oxidation at potential values essentially coincident with the latter. This result seems to indicate that substitution of MeCN ligands in **3** or **5** for CO or for C_{60} causes substantially similar electronic effects as far as the oxidation of the metal fragment is concerned.

The formal electrode potentials of the above discussed redox changes are compiled in Table 1.

3.2. EPR measurements

Fig. 3 shows the low-temperature ($T = 100$ K) X-band EPR spectrum of the tungsten monoanion $[\mathbf{1}]^-$ obtained by macroelectrolysis of a CH_2Cl_2 solution of **1** at −20°C.

Two partially overlapping paramagnetic species appear. The most intense, low field $S = 1/2$ signal exhibits a broad and resolved axial structure ($g_{\parallel} = g_{\perp} \neq g_e$), the parameters of which are:

$$g_{\parallel} = 2.045(4),\ g_{\perp} = 2.005(4),\ \langle g \rangle = (g_{\parallel} + 2g_{\perp})/3 = 2.020(4)$$

As it happened for the monoanion $[W(\eta^2\text{-}C_{60})(CO)_2(phen)(dbm)]^-$ [2i] these anisotropic parameters, which are significantly different from those typical of organic radicals, might be interpreted assigning a significant metal character to the unpaired electron, in spite of the fact that it is electrochemically well evident that the extra-electron enters the fullerene moiety. Unfortunately, also in this case the lack of the hyperfine W satellite splittings (W-183, I = 5/2; natural abundance = 14.4%), likely due to the actual anisotropic linewidth (which also prevents the detection of the super-hyperfine phosphorus splittings (P-31, I = 1/2; natural abundance = 100%)), does not give definitive evidence to such an interpretation.

As far as the second minor paramagnetic species is concerned, it appears as a narrow and unresolved peak overlapping the perpendicular region of the 'metallic' species, and in agreement with the presence of traces of

Table 1
Formal electrode potentials (V vs. SCE) and peak-to-peak separations (mV) for the redox changes exhibited by the metallafullerenes **1**, **2** and the related species **3**, **4**, in dichloromethane solution, at −10°C [a]

Complex	$E^{o\prime}_{0/-}$	ΔE_p [b]	$E^{o\prime}_{-/2-}$	ΔE_p [b]	$E^{o\prime}_{2-/3-}$	ΔE_p [b]	$E^{o\prime b}_{3-/4-}$	$E^{o\prime}_{0/2+}$ [b,c]
C_{60}	−0.63	59	−1.00	60	−1.45	64	−1.9 [d]	–
1	−0.80	64	−1.14	66	−1.64	78	–	+0.86
2	−0.82	72	−1.17	58	−1.65	74	–	+0.86
3								+0.39
4								+0.86
5								+0.36

[a] No significant difference in redox potentials was obtained at room temperature.
[b] Measured at 0.2 V s^{-1}.
[c] Coupled to slow chemical complications.
[d] Close to the solvent discharge.

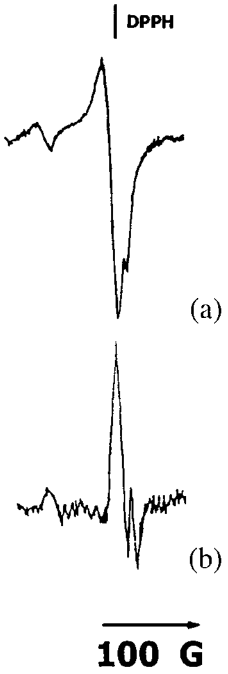

Fig. 3. X-band EPR spectra of a CH_2Cl_2 solution of [**1**]$^-$ at 100 K. (a) First derivative mode; (b) second derivative mode.

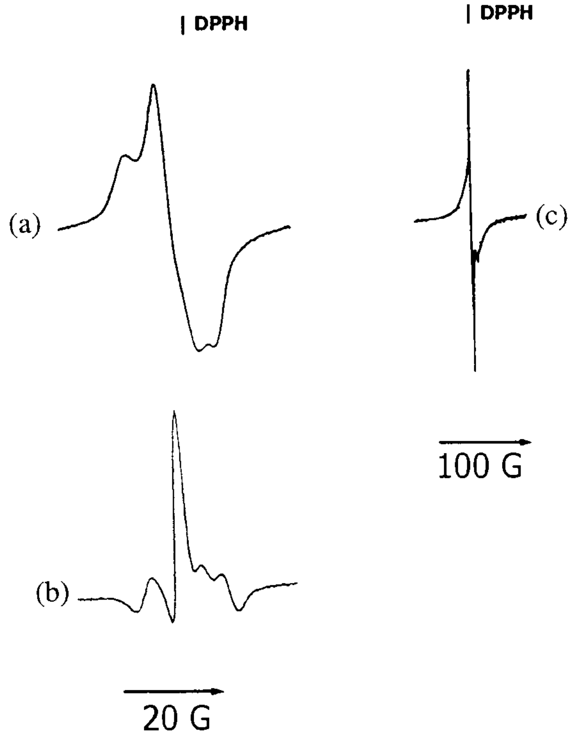

Fig. 4. X-band EPR spectra recorded on a CH_2Cl_2 solution of [**2**]$^-$. First (a) and second (b) derivative mode at $T = 100$ K; (c) first derivative mode at $T = 180$ K.

free C_{60}, its parameters ($g_{\text{averaged}} = 1.999(4)$; $\Delta H_{\text{averaged}} = 7.0(4)$ G) quite well fit those of free $[C_{60}]^-$ monoanion [2i]. In this connection, a rough evaluation of the ratio between the two species from the EPR spectrum ([**1**]$^-$:$[C_{60}]^-$ ca. 15:1) agrees well with that deduced from the relative cyclic voltammetric patterns.

The rising of the temperature to the glassy–fluid transition phase (about 180 K) induces the disappearance of the supposed metallic signal, whereas that of the $[C_{60}]^-$ remains detectable but slightly sharpened ($g_{\text{isotropic}} = 2.000(4)$), as expected in the case of fast motion conditions [8]. As a matter of fact, the disappearance of the isotropic 'metallic' signal might underline the noticeable metal spin-orbit interaction able to induce effective fastening of the electron spin relaxation processes. In agreement with this picture, the refreezing of the fluid solution fully restores the spectroscopic picture illustrated in Fig. 3.

Passing to the EPR features of the species electrogenerated in correspondence of the first reduction process of the molybdenum species **2**, Fig. 4a,b shows the relevant X-band EPR spectrum recorded at $T = 100$ K. Again two different, essentially overlapping, $S = 1/2$ paramagnetic species are detectable. In contrast with the previous situation and in agreement with the higher level of C_{60} impurities, see Fig. 2, now the $[C_{60}]^-$ absorption gives rise to a rather intense signal

($g_{\text{averaged}} = 2.001(2)$; $\Delta H_{\text{averaged}} = 6.0(2)$ G). On the other hand, the anisotropic pattern attributable to [**2**]$^-$ displays a rhombic structure, which appears well resolved in the second derivative mode, whose parameters are:

$$g_1 = 2.006(2);\ g_m = 1.994(2),\ g_h = 1.993/2);\ \langle g \rangle$$
$$= (g_1 + g_m + g_h)/3 = 1.998(2)$$

Also in this case, neither Mo-95 ($I = 5/2$, natural abundance = 15.7%) nor Mo-97 ($I = 5/2$, natural abundance = 9.5%) satellite peaks, nor P-31 splittings are detectable. In comparison with the corresponding tungsten monoanion [**1**]$^-$, a reduced 'metallic' contribution to the LUMO of **2** could be operative. At the glassy–fluid transition, $T = 180$ K, the anisotropic signal collapses in a broad and unresolved signal, Fig. 4c, which overlaps the intense fulleride signal ([**2**]$^-$: $g_{\text{iso}} = 1.998(2)$; $[C_{60}]^-$: $g_{\text{iso}} = 2.001(2)$. Upon refreezing, the original spectral pattern is restored.

4. Conclusions

We have shown that the fullerene moieties of the metallafullerene complexes **1** and **2** undergo the well known sequences of reversible one-electron reductions at potentials more negative (by about 0.2 V) than those of free C_{60}, thus indicating that, as it happens in most metallafullerenes, the metal fragment pushes electron density towards the fullerene ligand. More importantly, we have once again given further support to the previous finding [2i] that the LUMO of metallafullerenes might receive a significant contribution from the appended metal fragments.

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