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Electrochemical reduction of ligated species 2,2′-bipyridine and 4,4′-diphenyl-2,2′-bipyridine *

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Abstract

Unligated 2,2′-bipyridine and 4,4′-diphenyl-2,2′-bipyridine are reduced at low temperatures in two and three waves, respectively, with formation of the mono- and di-anion, as well as the trianion in case of Ph_2-bpy. The corresponding $M(CO)_4$bpy complexes exhibit two reversible waves at low temperature, increase in the temperature results in loss of the chemical reversibility of the second wave. $M(CO)_4Ph_2$-bpy complexes are reduced in four one-electron steps at low temperatures with formation of a series of anions ranging from the mono- to the tretra-anion. These four waves correspond to the acceptance of the electrons into two redox orbitals. The second redox orbital exhibits a rather small shift upon ligation and no dependence upon the nature of the metal. This is explained in terms of a shielding effect of the electrons already accepted.

Ligand-based redox series having more than two members have been described and analyzed mainly for systems with interacting multiple redox centers [1,2,3 and ref. therein]. Even if the simple theory of these systems [1,2] applies in respect of the number of redox steps and their spacings, more detailed study of the properties of products indicates that the behaviour of these redox series is determined by the operation factors other than those considered in the development of the simple theory [3,4]. These features are mainly connected with the most negative waves [3,4]. From this point of view it would seem to be of interest to study those ligand-based redox series in which a single ligand itself carries two or more redox orbitals and to compare the results obtained with the predictions made on the basis of the theory.

Ligands carrying two redox orbitals are mainly of the porphyrin type (cf. ref. 2 for some typical examples). In these species, however, the difference between the

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* Dedicated to Prof. Luigi Sacconi in recognition of his important contributions to organometallic chemistry.

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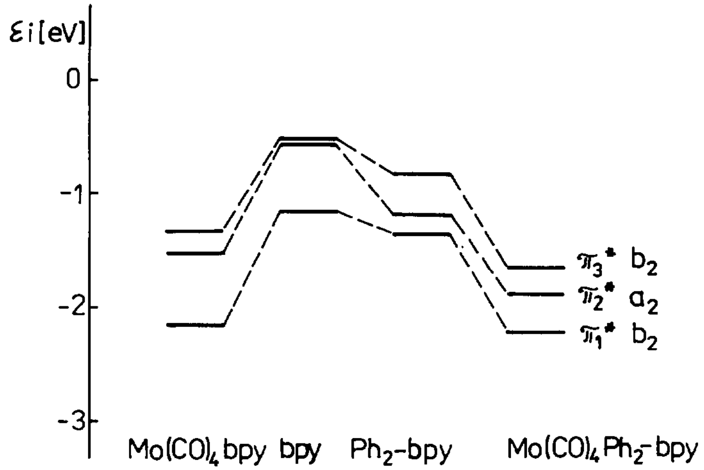

Fig. 1. Diagram of lowest LUMO's for bipyridine, diphenylbipyridine, and their complexes.

orbital energies of the two redox orbitals amounts to 2 or more volts, so that fully independent occupation is to be expected. We chose for our study 4,4′-diphenyl-2,2′-bipyridine, whose behaviour is similar to that of unsubstituted bipyridine with a third reduction wave at more negative potentials. The appearance of this reduction step is due to the conjugation of phenyl substituents with the bipyridine, which lowers considerably the energy of the second LUMO so that its electron affinity reaches a value accessible within the reduction range in nonaqueous solvents. The ligation of 4,4′-diphenyl-2,2′-bipyridine lowers the energies of LUMO's even more, so that a complete set of four reduction waves is to be expected in the accessible range of potentials (cf. Fig. 1).

To investigate the influence of ligation we used a series of complexes ($M(CO)_4$(4,4′-diphenyl-2,2′-bipyridine) ($\equiv M(CO)_4Ph_2bpy$) with $M = Cr$, Mo, W, and compared the results with those for an analogous series of unsubstituted bipyridine complexes. As substitution lability was previously observed for $M(CO)_4bpy$ species [5], we did not expect to establish the identity of the products of all the reduction steps for the ligated species.

Experimental

Chemicals

Tetrahydrofuran (Merck) (THF) was used after refluxing over metallic sodium and potassium and benzophenone [6]. *N*-Dimethylformamide (DMF) was purified by by Aoyagui's procedure [7]. In the final operating step the solvents were distilled in a closed system into the electrochemical cell containing supporting electrolyte and depolarizer.

Tetrabutylammonium hexafluorophosphate (Fluka) twice recrystallized from ethanol and dried for 12 h under argon at 150 °C was used as the supporting electrolyte.

2,2′-Bipyridine and 4,4′-diphenyl-2,2′-bipyridine (GFS Chem. Comp.) were used without further purification. Complexes, $M(CO)_4bpy$ and $M(CO)_4Ph_2bpy$ with

M = Cr, Mo, W, were prepared by a modification of Wrighton's method [8], as described previously [5].

Apparatus and procedure

All voltammetric measurements were made in the one-compartment cell with a platinum working electrode, sealed platinum wire counter electrode, and silver wire quasireference electrode, as described previously [4]. The cell with the supporting electrolyte was dried in an argon atmosphere at 140 °C for 24 h before use. Voltammograms were recorded with a PA-3 polarograph (Laboratorní přístroje, Praha).

The resulting curves obtained in THF showed, in spite of the use of a three electrode system, a distortion involving uncompensated $i \cdot R$ drop at the electrode surface. A correction was made for this $i \cdot R$ drop by a computer program.

Absorption spectra of reduction products were measured in the optically transparent thin layer electrolytic cell by the procedure described previously [4]. ESR measurements were carried out as previously described [4].

Quantum chemical calculations on the starting complexes and free ligands were made by the the CNDO method using Tondelo's parametrization [9] and standard CNDO/S [10] parameters for main group elements. Systems were treated as having C_{2v} symmetry. The variation of the dihedral angle between the phenyl group and bipyridine unit does not change the character of the redox orbitals, and so only the planar configuration was considered.

Results

Ligands

Literature reports are not wholly consistent as regards the behaviour of bipyridine and its analogues. We showed a few years ago that the first reduction wave of bipyridine and of some of its derivatives is fully reversible both electrochemically and chemically [11]. With the improvement of experimental techniques we were able to carry out the analysis for the second bipyridine waves and the third wave of Ph_2bpy.

2,2′-Bipyridine. As described previously, under conditions involving exclusion of traces of water the first bipyridine wave is fully reversible both electrochemically and chemically at normal temperature. Addition of even traces of water, however, causes the anodic current to decrease and eventually to disappear [1].

The second reduction step (see Fig. 2) shows a reversible shape at normal temperatures in solutions scrupulously free from water or any other proton-donor, but even under these conditions no anodic response is observed. When the temperature is lowered the anodic response starts to appear, and at about −60 °C in tetrahydrofuran almost full chemical reversibility, i.e. full reoxidation of the product, is observed. At the same time the difference between the half-wave potentials increases from about 590 to 670 mV.

This observation can be explained only in terms of deactivation of the primary product (evidently the dianion of bipyridine) at normal temperatures, the rate of which decreases as the temperature is lowered. The question arises as to the nature of this deactivation; since the concentration of water or any direct proton-donor is much lower than that of bipyridine, it has to be assumed that the source of protons

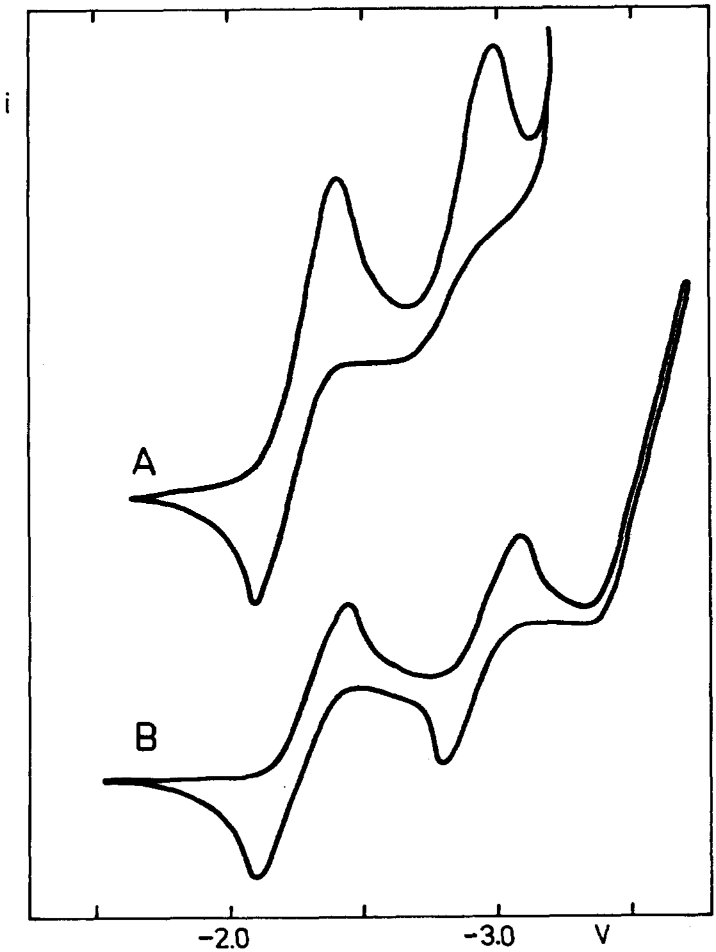

Fig. 2. Cyclic voltammogram of 2,2′-bipyridine (10^{-3} *M*) in THF (0.1 TBAH). Scan rate 100 mV/s. Curve A: 20 ° C; curve B: − 62 ° C; original recording without correction for residual *i* · *R*-drop.

is probably the solvent or the cation of the supporting electrolyte. The nature of this deactivation process is under study.

4,4′-Diphenyl-2,2′-bipyridine exhibits three reduction waves at normal temperatures, and four at low temperatures (− 60 ° C).

The first reduction wave when recorded in isolation (cf. Fig. 3) is fully reversible electrochemically as well as chemically at all temperatures studied.

The two more negative steps, located at − 2.40 and − 2.60 V, respectively, are interrelated, and correspond to a one electron reduction of the ligand: at normal temperatures the wave at − 2.40 is rather small and shows no reoxidation in the anodic part, whereas that at − 2.60 V dominates and is to a large degree chemically reversible. At the same time the anodic part of the first reduction step at − 2.00, is lowered when the potential is reversed at values at or more negative than those of the wave at − 2.40 V, and two new fully irreversible anodic peaks appear (see Fig. 3). With decresing temperature the peak at − 2.40 V increases at the expense of that

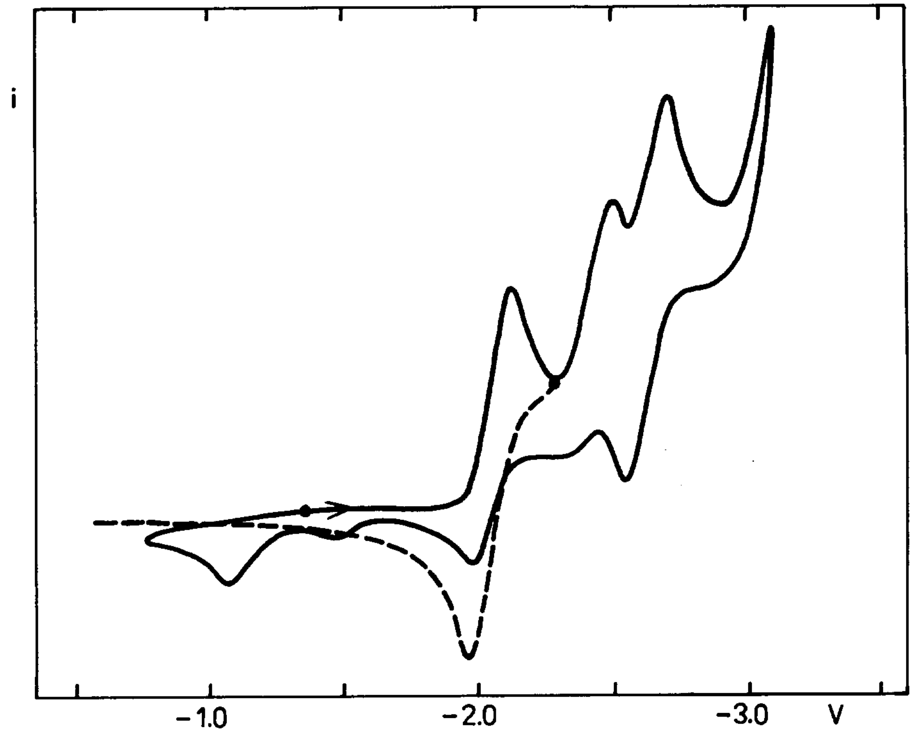

Fig. 3. Cyclic voltammogram of 4,4′-diphenyl-2,2′-bipyridine (10^{-3} *M*) in THF; scan rate 100 mV/s; 20 °C. Solid line: scan reversed at −3.1 V dashed line: scan reversed at −2.28 V; original recording without correction for residual $i \cdot R$-drop.

at −2.60 V, both still adding up approximately to a one electron reduction per particle. At −60 °C the wave at −2.40 V becomes dominant and fully reversible, both electrochemically and chemically (Fig. 4). With decreasing scan rate the wave at −2.60 slighly increases at the expense of that at −2.40 even at these low temperatures. At even lower temperatures (ca. −80 °C) the wave at −2.60 V almost disappears. The latter step is chemically reversible in the whole range of temperatures studied.

At low temperatures, owing to the opening of the accessible potential window, the wave corresponding to the third reduction step appears; this is fully reversible chemically and slightly irreversible electrochemically (the difference between peak potentials is increased to 56 mV compared with 44 mV for the first wave after correction for uncompensated $i \cdot R$ drop at −70 °C).

From the above we conclude that in the limiting case of low temperatures and fast scan rate, Ph_2bpy is reduced in three steps, at −2.00, −2.40 and −2.98 V, with formation of monoanion, dianion, and eventually trianion. However, the monoanion, as the primary product of first reduction undergoes a rather fast chemical reaction resulting in two separate reductions in the second step. Although we have not examined the nature of this chemical change in detail, we conclude that it results in a reversible blockage of active sites in the dianion form, as can be deduced from the full chemical reversibility of the reduction at −2.60 V at all temperatures.

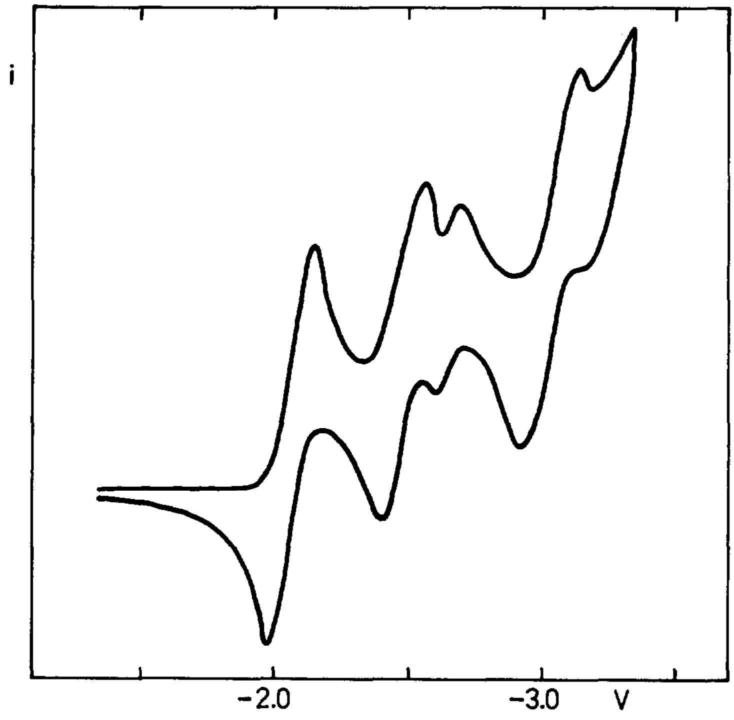

Fig. 4. Cyclic voltammogram of 4,4′-diphenyl-2,2′-bipyridine (10^{-3} *M*) in THF; scan rate 100 mV/s; −62° C. Original recording without correction for residual *i*·*R*-drop.

To summarize, it appears unambiguously that bipyridine and its substitution derivatives are reduced reversibly with the formation of mono- and di-anions, or trianions, providing the solution is scrupulously pure and the temperature is kept low. However, even under our best experimental conditions inactivation of dianions is observed at normal temperatures. The discrepancies in the literature, i.e. the describtion of the reductions as irreversible or as distorted, are obviously due to imperfect experimental conditions, leading to high rates of deactivation. This process not only causes the anodic response to disappear but leads also to a lower, and thus wrong, difference in the successive half-wave potentials. The correct value of this difference approaches of 0.7 V for bipyridine.

Complexes

M(CO)₄bpy (M = Cr, Mo, W)

The behaviour of these complexes, especially that of their first reduction, has been briefly described previously (cf. ref. 5).

All the complexes $M(CO)_4bpy$ with M = Cr, Mo, W show two reduction steps (for the values of the half-wave potentials see Table 1.). The first reduction step, fully reversible electrochemically, is shifted towards positive potentials compared with that for unligated bipyridine by 0.6 to 0.75 V. The second reduction, 0.68 V more negative, is slightly irreversible electrochemically (the difference in peak

Table 1

Redox Potentials of $M(CO)_4bpy$ and $M(CO)_4Ph_2bpy$ (−65 °C; vs. SCE; Pt-electrode)

Compound	E_1°	E_2°	E_3°	E_4°
bpy	−2.20	−2.86		
$Cr(CO)_4bpy$	−1.61	−2.28		
$Mo(CO)_4bpy$	−1.53	−2.21		
$W(CO)_4bpy$	−1.46	−2.15		
4,4′-Ph_2bpy	−2.00	−2.40 (−2.60)	−2.98	
$Cr(CO)_4Ph_2bpy$	−1.52	−2.03	−2.72	−2.96
$Mo(CO)_4Ph_2bpy$	−1.45	−2.00	−2.72	−2.96
$W(CO)_4Ph_2bpy$	−1.36	−1.93	−2.72	−2.97

potentials is ca. 56 mV at −55 °C). Under our best experimental conditions we have never observed full chemical reversibility even at very low temperatures. At 20 °C there is almost no anodic current corresponding to reoxidation. At −55 °C the anodic response amounts to about 70% of the cathodic one at a scan rate of 100 mV/s. At the same time difference between half-wave potentials is increased, owing to less effective deactivation of the primary product of the second reduction: e.g. for $Mo(CO)_4bpy$ the difference $\Delta E^\circ_{1/2}$ is 610 mV at 20 °C, 640 mV at −15 °C, 670 mV at −40 °C and 680 mV at −55 °C, respectively. The ESR spectrum of the product from the first reduction is that of the ligated monoanion of bipyridine, as described previously [5,12].

We thus conclude that the reduction of $M(CO)_4bpy$ proceeds via the formation of monoanion in the first step and of the dianion in the second. The dianion, however, readily undergoes substitution, and decomposes at higher temperatures without formation of any electrochemically active species. The lability of the complex dianion exceeds that of the unligated dipyridine dianion.

$M(CO)_4Ph_2bpy$ (M = Cr, Mo, W)

All complexes $M(CO)_4Ph_2bpy$ with M = Cr, Mo, W are reduced at low temperatures in four waves. All of these are one-electron steps, and at temperatures around −70 °C are chemically fully reversible (see Fig. 5). The first, second, and fourth waves are also fully reversible electrochemically, whereas the third shows a small degree of electrochemical irreversibility (the difference of peak potentials is 60 mV at −70 °C).

With increase in temperature only the first reduction step remains fully reversible, all the others exhibiting a decrease of the anodic part, indicating subsequent chemical reactions which deactivate the various initial products. The second reduction step is the most sensitive in respect of deactivation.

As the values in Table 1, indicate, the position of the first reduction step depends upon the nature of the central metal atom, moving towards positive potentials in the order Cr < Mo < W. The absolute shift of the reduction of the complex compared with that of unligated Ph_2bpy is considerably smaller than in the case of bipyridine complexes. The influence of the nature of the metal is even smaller in the second reduction and, within the experimental error, is absent for the third and fourth reduction steps.

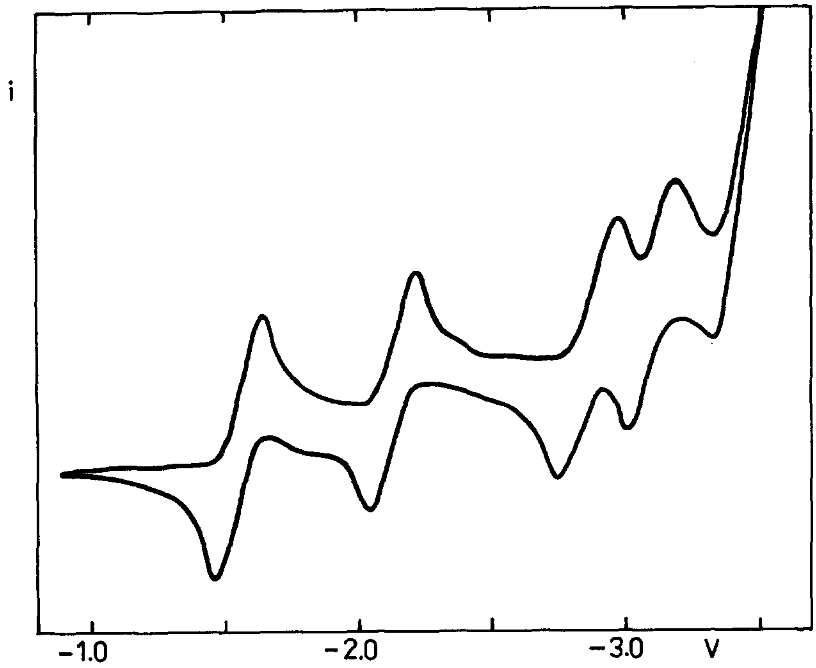

Fig. 5. Cyclic voltammogram of $Mo(CO)_4Ph_2bpy$ (10^{-3} *M*) in THF. Scan rate 100 mV/s; −70 ° C. Original recording without correction for residual *i*·*R*-drop.

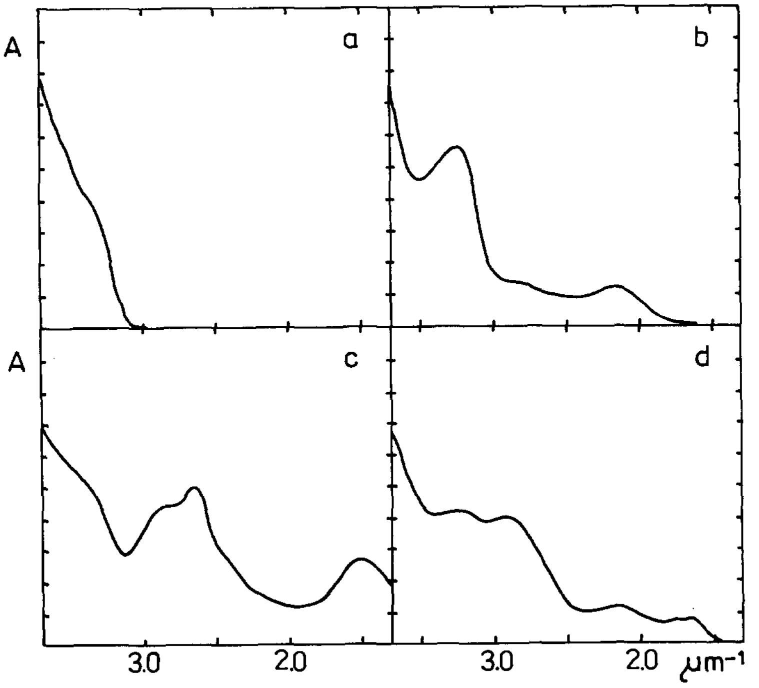

Fig. 6. UV-VIS spectra of Ph_2-bpy (a) and its monoanion (c) compared with those of $Mo(CO)_4$Phbpy (b) and its monoanion (d); 0.1 *M* TBAH in THF solution, OTTLE cell, gold minigrid working electrode, 20 ° C.

Figure 6 compares the UV-VIS spectra of the free ligand with those of the complex in their unreduced forms and in monoanions. The spectra exhibit a blue shift of the ligand based transitions, as in the other complexes of this type. The ESR spectrum was determined only for the monoanion at normal and liquid nitrogen temperatures. It shows a symmetrical signal with unresolved fine structure and a g-value very close to that for a free radical ($g = 2.003$). At normal temperature a partly resolved fine structure is observed.

Owing to the lability of the second reduction product [5], we could not investigate the UV-VIS and ESR-spectra of the dianions and the more reduced species.

We conclude that the complexes $M(CO)_4Ph_2bpy$ are reduced in four one-electron steps, which at low temperatures form a redox series going from the monoanion to the tetraanion. Except for that for the monoanion, these anions readily undergo substitution at higher temperatures.

It has to be noted that all the complexes studied exhibit additional oxidation steps with rather complex behaviour, involving fast substitution of one CO ligand by a solvent molecule. These processes are predominantly metal centred, and will be described later.

Discussion

The results described above show that in the complexes studied the reductions are fully localized on the ligands. This is in accordance with quantum chemical calculations, which indicate a very small contribution of the metal to the LUMO's of the complexes; e.g. for $Mo(CO)_4Ph_2bpy$ the first LUMO (b_2) has about 2% participation by metal orbitals whereas the second (a_2) only 0.3%, i.e. essentially zero. We are thus dealing with a fully ligand-based redox series.

We conclude that the shift of the first reduction of the ligated molecule relative to that of the free ligand towards positive potentials is essentially due to central field effects [1]. This shift is smaller for Ph_2bpy than for bipyridine, probably because of a larger delocalization of the electron over the remote phenyl groups (the b_2-level is 34.5% delocalized over the phenyl group) and thus to a smaller central field influence upon the redox orbital. The difference $\Delta E^{\circ}_{1/2}$ in the bipyridine complex remains almost constant on going from Cr to W, and is very close to that for free bipyridine, as expected for a ligand-based redox series. In Ph_2bpy complexes the difference depends slightly upon the nature of the metal, and is higher than that for the second wave of the unligated Ph_2bpy, approaching the value observed for the wave of the latter at -2.60 which was ascribed to the reduction of a form of Ph_2bpy with blocked sites involved in deactivaton of the free dianion of Ph_2bpy.

The third reduction of Ph_2bpy in its complexes exhibits a shift towards positive potentials considerably smaller than that for the first reduction (0.48 to 0.64 for the latter, compared with 0.26 for the third reduction). Furthermore, the metal has no influence on the third and fourth reductions.

A decrease in the positive shift between the reduction localized in the first and second LUMO, respectively, can be also deduced from Aoyagui's data [13] for the 2,4,6-tri-2-pyridyl-1,3,5-triazin (TPTZ) ligand: e.g. in the complex $Ru(TPTZ)_2^{2+}$ the first localized reduction of the ligand is shifted by 0.73 V with respect to that for the free ligand, whereas the reduction localized in the second LUMO of TPTZ exhibits a shift of only 0.22 V. Similarly, only a very small influence was observed [14] for complexes of the type M(η^2-olefin)(Ph_2-phen) with M = Pt, Pd for their third and fourth reductions, most probably localized on the Ph_2-phen ligand. The authors accounted for this in terms of full localization of the redox change on the ligand but our results point to another explanation. As we have seen, the first redox orbital localized reduction of $M(CO)_4$bpy and of $M(CO)_4Ph_2$bpy is metal dependent even when the metal participation in the redox orbital is very small, and essentially zero. The lack of dependence on the nature of the metal as well as a much smaller shift towards more positive potentials of the third reduction, localized onto the second LUMO (a_2), seem to be due to the shielding effect, which the electrons already accepted in the first LUMO exhibit upon the central field of the metal atom, or more precisely of the $M(CO)_4$ fragment of the complex. This explanation, which is supported by quantum chemical calculations, seems to have a much more general validity.

Finally we take note of the relatively small difference between the third and fourth reduction of $M(CO)_4Ph_2$bpy complexes ($\Delta E_{3/4}$ 0.25V). This lowering of the intraligand electronic repulsion [1] is evidently due to the greater delocalization of the second redox orbital (ca. 45%) over the phenyl groups. The fourth reduction of the free ligand is outside the experimental potential window, but even the difference $\Delta E_{1/2}$ for the free ligand is considerably smaller than that in bipyridine, indicating a higher delocalization of the redox orbital over the phenyl rings.

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