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Multilevel Molecular Electronic Species: Electrochemical Reduction of a [2 × 2] Co^{II} Grid-Type Complex by 11 Electrons in 10 Reversible Steps**

Mario Ruben, Esther Breuning, Jean-Paul Gisselbrecht,* and Jean-Marie Lehn*

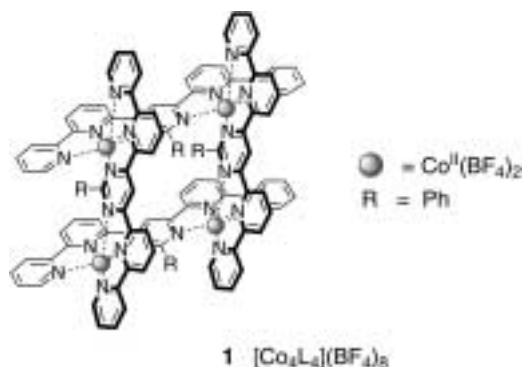
The search for high-density information storage devices has stimulated an increasing interest in molecules exhibiting multistable behavior.^[1] Multistability can be achieved by several means by exploiting changes in intrinsic molecular properties such as spin state,^[2] conformation,^[3] or redox state.^[4] For instance, fullerenes and nanotubes have attracted wide interest in view of their potential in the design of new materials and electronic devices based on their unusual electrochemical behavior (reversible single-electron reductions and semiconducting properties).^[5] Multicenter transition metal complexes with different redox states are very attractive candidates for the design of multilevel electronic systems. Thus, for instance, polynuclear metal complexes of polypyridine ligands present several reversible multielectron steps.^[6]

We have described recently a new class of polypyridine-derived, multinuclear metal complexes of the [2 × 2] M₄^{II} grid-type (M = transition metal),^[7, 8] which have been found to present a range of interesting structural^[7] and physicochem-

[*] Prof. Dr. J.-M. Lehn, Dr. M. Ruben, E. Breuning
Laboratoire de Chimie Supramoléculaire
ISIS-Université Louis Pasteur
4, rue Blaise Pascal, 67000 Strasbourg (France)
Fax: (+33)388-411 020
E-mail: lehn@chimie.u-strasbg.fr
Dr. J.-P. Gisselbrecht
Laboratoire d'Electrochimie et de Chimie-Physique du Corps Solide
UMR 7512,CNRS-Université Louis Pasteur
4, rue Blaise Pascal, 67000 Strasbourg (France)
Fax: (+33)388-611 553
E-mail: gissel@chimie.u-strasbg.fr

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ical (electrochemical,^[7a] magnetic^[9]) properties. Here we report on the exceptional electrochemical and spectroelectrochemical properties of one specific member of this family, complex **1**, [Co₄L₄](BF₄)₈, which was synthesized from ligand



L (L = 4,6-bis(2',2''-bipyrid-6'-yl)-2-phenylpyrimidine^[10]) and Co(BF₄)₂ · 6H₂O as described before.^[7b] The redox behavior of **1** has been investigated in solution (DMF) by cyclic and steady-state voltammetry (Table 1).

Cyclic voltammetry carried out at –20 °C gives rise to a cyclic voltammogram (CV) consisting of ten well-resolved, completely reversible reduction steps on the available potential window (Figures 1a and b). Nine reduction steps are still

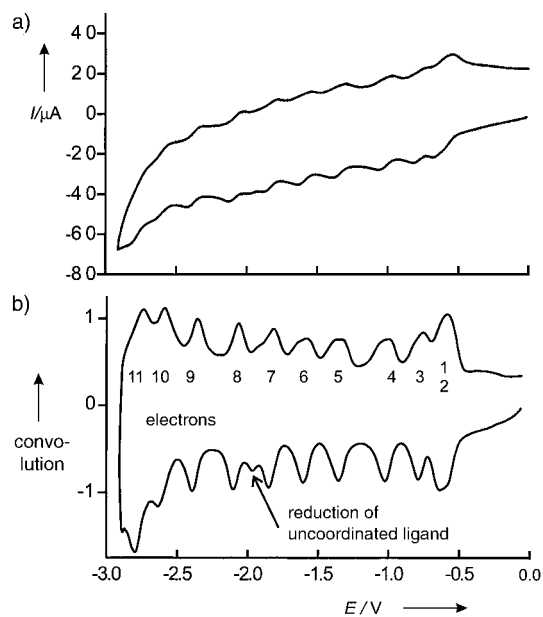


Figure 1. CV (a) and semidifferential convolution of one CV curve (b) of **1** in a 0.1 M solution of Bu₄NPF₆ in DMF at –20 °C on a glassy carbon working electrode at a sweep rate of 1 V s^{–1}.

Table 1. Redox potentials *E* and redox potential separations ΔE of **1** observed in a 0.1 M solution of Bu₄NPF₆ in DMF on a glassy carbon working electrode at –20 °C (all potentials given versus ferrocene).

Red. step	1	2	3	4	5	6	7	8	9	10	11
<i>E</i> [V]	–0.59	–0.63	–0.78	–1.02	–1.35	–1.60	–1.85	–2.11	–2.40	–2.61	–2.73
ΔE [V]		0.04	0.15	0.24	0.33	0.35	0.25	0.26	0.29	0.21	0.12

observed at room temperature, one less than at low temperature because of the restricted potential window at that temperature.

Analysis of the peak characteristics shows that the peak potentials are independent of the scan rates (10–1000 mV s^{–1}) and that the cathodic and anodic peak current ratio (I_{pc}/I_{pa}) for each step is unity. Each peak current is also proportional to the square root of the scan rate, as expected for a reversible process. Thus, subsequent chemical reactions can be excluded. The shape and amplitude of the first reduction peak are indicative of the overlap of two one-electron transfers.

Steady-state voltammetry at the rotating disc electrode gives rise to seven well-resolved reduction waves, further ones being less well defined. The wave amplitudes indicate that the first reduction step involves two electrons, whereas the remaining steps present one electron each. Careful examination of the first reduction step, which presents a log-plot slope of 90 mV ($\lg[(I/I_d - I)] = f(E)$; I_d = diffusion current) and twice the amplitude of a one-electron reduction, results in the assignment of two overlapping one-electron steps separated by about 40 mV.^[11]

Based on these results, we can conclude that ten well-resolved, reversible reduction steps involving eleven electrons are observable in **1** at –20 °C. As far as we are aware, this represents the highest reported number of well-characterized, resolved and reversible one-electron reductions on a molecular compound. For example, the fullerenes C₆₀ and C₇₀ exhibit only six reversible single-electron reductions spread over a larger potential window and located at much more negative potentials (from –0.98 V to –3.26 V).^[5]

At –1.95 V, we observe a small additional signal which can be attributed, by comparison, to the reduction of some uncoordinated ligand. This additional signal already appears during the first scan and does not increase on continued scanning. Even the use of pure crystalline material of **1** could not prevent the presence of the additional signal. However, exhaustive electrolysis as carried out by spectroelectrochemical investigations (see below) only slightly increases this signal. Thus, we attribute it to a trace of the uncoordinated ligand present in solution in equilibrium with compound **1** independent of the electrochemical studies. Indeed, investigations concerning the stability of the reduced species indicate that even after 20 repeated scans to –2.73 V, the obtained CV remained superimposable with the first scan. In comparison, the homologous Fe₄^{II} and Zn₄^{II} grid-type compounds as well as the mononuclear [Co(terpy)₂]²⁺ (after threefold reduction; terpy = 2,2':6',2''-terpyridine) showed fast decomposition under identical conditions.^[12]

Basically the same voltammetric pattern is observed in acetonitrile, but with a limited number of observable waves due to the lower solubility of the reduced species of **1** in this solvent. However, an oxidation wave corresponding to the

transfer of four electrons at +1.0 V could be detected only by steady-state voltammetry in acetonitrile. This wave is widely spread out and has a log-plot slope of 300 mV. Such behavior is indicative of a kinetically slow process of the $\text{Co}^{\text{II}}/\text{Co}^{\text{III}}$ redox couple, occurring stepwise on the four metal centers of the complex. Slow electron transfer rates have been observed on encapsulated metal ions in bulky and dendrimeric structures.^[13]

Spectroelectrochemical studies were carried out on **1** up to the seventh reduction step (Figure 2). The evolution of the spectrum during the first four steps is in agreement with ligand-centered reductions: the initial $\pi-\pi^*$ band of the

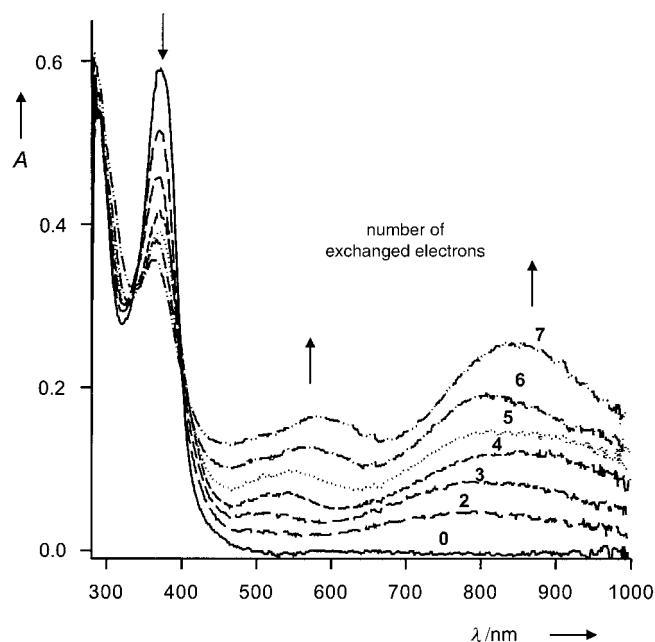


Figure 2. Electronic spectra of **1** and its electrochemically generated reduced forms in a 0.1M solution of Bu_4NPF_6 in DMF at 298 K.

unreduced ligand at 370 nm decreases subsequently and two broad bands appear at 550 nm and around 800 nm. These low-energy bands can be attributed to intraligand $\pi-\pi^*$ transitions from the new SOMOs (monoanion) to the first and the second new LUMOs (monoanion) of the reduced ligands.^[14] The initial spectrum could be recovered by stepwise oxidation of the generated heptaanion, indicative of the high stability of the reduced species.

Semiempirical PM3 molecular orbital calculations^[15] showed that the LUMO of the uncoordinated, neutral ligand is mainly centered on the pyrimidine ring. The double coordination of the pyrimidine in **1** strongly stabilizes this molecular orbital. Thus, the first four reducing electrons should be mainly localized on the bridging pyrimidine rings of the ligands. One notes that, starting with the fifth reduction, the two low-energy bands increase further, but are shifted remarkably to lower energies. Thus, the second series of four electrons is also localized on the ligand (at least up to the observable seventh electron). The red shift of the new intraligand bands can be attributed to an electronic destabilization of the corresponding HOMOs of the ligands, as a

consequence of the two electrons introduced onto the pyrimidine orbital.

In general, the gradual evolution of the intensities of the new bands expresses a proportionality with the number of reducing electrons (only the seventh step is slightly larger because of the involvement of some uncoordinated ligand). The shift of the bands to lower energies in the course of reduction is also an indication for an electronic coupling of the reduced ligands. This is also confirmed by the increasing differences between the values of the first four reduction waves in the CV ($\Delta E(1-2)=0.04$ V; $\Delta E(2-3)=0.15$ V; $\Delta E(3-4)=0.24$ V). Because of the small separation between the first and the second reduction, it can be concluded that the first two reductions concern two parallel ligands and that these electrons are coupled only to a very small extent. The next two reductions occur at the remaining two ligands and the negative charge on the ligands is increasingly delocalized over the complex. We assume that up to twelve electrons could be introduced into compound **1**, but the last one is probably taken up at a potential too negative to be observed.

As far as we are aware, this study presents the highest number of well-resolved, completely reversible reductions of a molecular compound. Additionally, the ten successive reduced species derived from **1** exhibit a remarkable stability in solution. Investigations concerning the reduction behavior of $[2 \times 2]$ Co_4^{I} grid-type compounds deposited as monolayers^[16] on graphite are in progress. They should in particular allow one to examine the potential use of the reported extraordinary electrochemical behavior of this class of compounds in future information storage devices.^[17]

Experimental Section

The electrochemical studies were carried out in a 0.1M solution of Bu_4NPF_6 in DMF in a classical three-electrode cell connected to a computerized electrochemical device AUTOLAB (Eco Chemie B.V. Holland). The working electrode was a glassy carbon disc (3 mm diameter), the auxiliary electrode a platinum wire, and the reference electrode an aqueous Ag/AgCl electrode. The measurements were carried out by cyclic and steady-state voltammetry (rotating-disc electrode). Under our experimental conditions, ferrocene, used as internal standard, was oxidized at +0.45 V versus Ag/AgCl. Spectroelectrochemical studies were carried out in a home-made borosilicate glass cell placed in a diode array UV/vis spectrophotometer HP 8453 (Hewlett Packard). A platinum grid (1000 mesh) was placed in the optical pathway (about 0.1 mm) of the OTTE cell (OTTE = optically transparent thin-layer electrode). The auxiliary electrode was a platinum wire and the reference electrode was an aqueous Ag/AgCl electrode.

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Repetitive Application of Perfluoro-Tagged Pd Complexes for Stille Couplings in a Fluorous Biphasic System**

Siegfried Schneider and Willi Bannwarth*

The recovery and reuse of expensive catalysts is an important topic in catalytic processes. Thus, in homogeneous catalysis the use of liquid biphasic systems has attracted a great deal of attention. Examples include the aqueous biphasic Ruhrchemie/Rhône-Poulenc process,^[1] catalytic reactions in supercritical carbon dioxide,^[2] catalysis in molten salts,^[3] and use of fluorous biphasic systems (FBS).^[4]

In the FBS concept, first reported by Horváth and Rábai,^[5] owing to the perfluorinated ligands on the organometallic catalyst it is soluble in a fluorous phase (e.g. $n\text{-C}_6\text{F}_{14}$, C_7F_{16} , $\text{C}_6\text{F}_{13}\text{Br}$, $\text{CF}_3\text{C}_6\text{F}_{11}$). The reaction is carried out in a two-phase mixture consisting of a perfluorinated solvent and an organic solvent (toluene, hexane, acetonitrile). Such a two-phase system often becomes homogeneous at elevated temperature. Lowering the temperature after reaction leads to reformation of the two phases; the organic phase contains the product, the fluorous phase the catalyst to be reused.

This new concept has been applied to a number of catalytic reactions such as hydroformylation of alkenes,^[5] oligomerization of ethylene,^[6] hydroboration of alkenes,^[7] oxidation of aldehydes,^[8] thioethers,^[8] and alkanes,^[9] epoxidations,^[8, 10–12] Wacker oxidation of alkenes,^[13] rhodium-catalyzed carbenoid reaction,^[14] palladium-catalyzed allylic nucleophilic substitution,^[15] cross-coupling of arylzinc bromides with aryl iodides,^[16] and the Heck reaction.^[17]

Here, we report on the synthesis of three new fluoro-tagged bis-triphenylphosphanepalladium complexes and their application to the Stille cross-coupling reaction,^[18] with the goal of reusing the catalyst for subsequent cross-couplings.

Fluoro-tagged phosphanes **1a–c** were synthesized with slight modifications of the original procedures^[16, 19] (Scheme 1 a, b). Replacement of the iodine substituent of *m*- or *p*-iodoaniline by the perfluoro tag followed by bromination of the diazonium intermediate delivered the corresponding bromobenzene with the fluoro tag in the *m*- or *p*-position, respectively. Br–Li exchange and reaction with PCl_3 yielded the desired phosphanes **1a** and **1b**. To the best of our knowledge, **1b** has not been reported in the literature. Phosphane **1c** was prepared starting from 1,4-dibromobenzene (Scheme 1 b). Reaction of the corresponding Grignard compound with $\text{C}_8\text{F}_{17}\text{CH}_2\text{CH}_2\text{I}$ was applied to introduce the perfluoro tag. Br–Li exchange and reaction with PCl_3 led to

[*] Prof. Dr. W. Bannwarth, Dipl.-Chem. S. Schneider^[+]
Universität Freiburg
Institut für Chemie und Biochemie
Albertstrasse 21, 79104 Freiburg (Germany)
Fax: (+49) 761-203-8705
E-mail: willi.bannwarth@organik.chemie.uni-freiburg.de

[+] Present address: Byk-Gulden-Pharmaceuticals
Byk-Gulden-Strasse 2, 78467 Konstanz (Germany)

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