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Reinvestigation of the Electrochemical Behavior of the $Co_2(CO)_6$(ethynylestradiol) Complex. Evidence of Efficient Recombination of the Electrogenerated Fragments

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The electrochemical behavior of $Co_2(CO)_6$(ethynylestradiol) complexes has been reinvestigated by means of electrochemical and spectroscopic techniques. The electrogenerated $[Co_2(CO)_6(\text{ethynylestradiol})]^-$ monoanion is very unstable and undergoes fast cleavage of the Co–Co bond, producing $Co(CO)_4^-$. An efficient recombination $Co(CO)_4^\bullet$ radical (produced from reoxidation of $Co(CO)_4^-$) with the $[Co(CO)_2(\text{ethynylestradiol})]^\bullet$ radical, adsorbed on the electrode, regenerates almost qualitatively the parent complex, in the chemical time scale.

Introduction

The electrochemical behavior of $Co_2(CO)_6$(alkyne) complexes has been investigated in detail by Robinson, Rieger, and co-workers using electrochemical techniques[1] and EPR spectroscopy.[2] Efficient electron-transfer-chain (ETC) reactions have been obtained on such a substrate.[3] The electrochemical scenario consists of a 1e reduction followed by a more or less rapid (depending upon the nature of the alkyne substituents) decomposition of the electrogenerated $[Co_2(CO)_6(\text{alkyne})]^-$ radical anion[1] ($E_{REV}C_{IRR}$ mechanism). Several fragments are produced, $Co(CO)_4^-$, free alkyne, and metallic Co being the only substances positively identified.[1,2] Severe fouling of the solid electrodes accompanies such a process and hinders the mechanistic investigations. The presence of CO simplifies the decomposition pattern of $[Co_2(CO)_6(\text{alkyne})]^-$, $Co(CO)_4^-$ and$[Co(CO)_3(\text{alkyne})]^-$ being produced up to 70% yield.[1,2]

We have been interested in the use of organometallic fragments as electrochemical markers for steroids.[4] In (17α-ethynyl-1,3,5-estratriene-3,17β-diol)dicobalt hexacarbonyl, hereafter $Co_2(CO)_6(HC_2E)$ (1) (Figure 1), the two costituent units, i.e. "$Co_2(CO)_6C{\equiv}C$" and the estradiol frame, undergo relatively independent electrochemical processes. The addition of the bimetallic fragment (having an accessible LUMO) to the steroid makes the resulting bioorganometallic molecule cathodically detectable. Since the spectroelectrochemical results on 1 reported here indicate an unexpected reversibility of the overall electrochemical reduction/reoxidation cycle, we reinvestigate the electrochemical behavior of $Co_2(CO)_6(HC_2E)$ (1) (Figure 1) and those of some homologues, namely $Co_2(CO)_6$(1-ethynyl-1-cyclohexanol), hereafter $Co_2(CO)_6(HC_2C_6H_{10}OH)$ (2), $Co_2(CO)_6(MeC_2Me)$ (3), and $Co_2(CO)_6(HC_2H)$ (4) by means of dc and ac polarography and cyclic voltammetry (CV) in order to better understand the fragment generation/recombination mechanism.

Results and Discussion

Previous CV studies on 1 in CH_2Cl_2 at a Pt electrode showed a rapid poisoning due to adsorption of electroactive species; this fouling was reduced by using polar solvents.[4] Accordingly, we employed acetonitrile as solvent throughout this work. Multiple scan CV tests showed no features attributable to CH_3CN adducts of 1. In the $Co_2(CO)_6$(alkyne) series, diffusion currents due to the $[Co_2(CO)_5(CH_3CN)(\text{alkyne})]^{0/-}$ couple (generated by ETC substitution) are important only if the lifetime of the primarily electrogenerated $[Co_2(CO)_6(\text{alkyne})]^-$ is reasonably high[1] and this is not the case.

dc polarography of an acetonitrile solution of 1 shows a well-defined cathodic wave A at $E_{1/2} = -1.03$ V (Figure 2). The E vs log $[(i_d - i)/i]$ plot slopes 60 mV, indicating the Nernstian character of the 1e reduction.[5] Coulometry at the Hg pool ($E = -1.10$ V) confirms the 1e/molecule character of the reduction[1,4] and indicates that $Co(CO)_4^-$ (exhibiting an anodic wave B at $E_{1/2} = -0.08$ V in the polarographic response and an almost reversible system in the corresponding CV response at a mercury drop) is the only electrochemically active product of the electrolysis (Figure 2). No EPR signal could be detected in the electrolyzed solution even at liquid nitrogen temperature.

The CV responses at a Pt working electrode inserted into a coulometric cell, before (a) and after (b) the exhaustive reduction at a mercury pool ($E_w = -1.10$ V) are reported in Figure 3. On passing from Hg to the Pt working electrode there is a slight shift of the potential of peak A, while peak B moves toward positive potentials ($E_p = +0.20$ V) and appears as chemically irreversible.[1,6] The second scan responses are identical (apart from the absolute magnitude of the peak currents) in both the experiments

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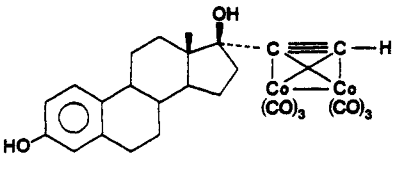

[1]

Figure 1. Sketch of structure of $Co_2(CO)_6$(ethynylestradiol) (1) complex.

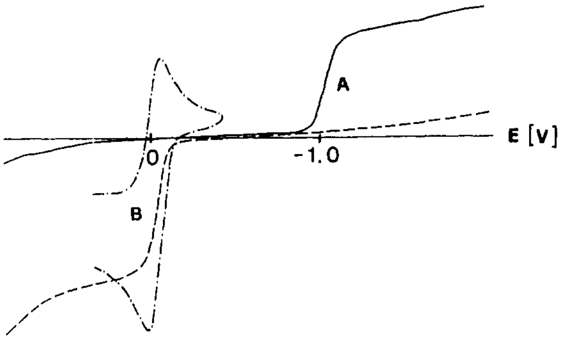

Figure 2. dc electrochemical responses of an acetonitrile solution of 1 (10^{-3} M) containing $[Bu_4N][PF_6]$ as supporting electrolyte (0.1 M) at a mercury electrode, drop time 2 s: (—) polarogram of the initial solution; (---) polarogram after 1e/molecule reduction at $E_w = -1.20$ V; (-·-) cyclic voltammogram at a mercury drop of the reduced solution at 0.5 V s^{-1}.

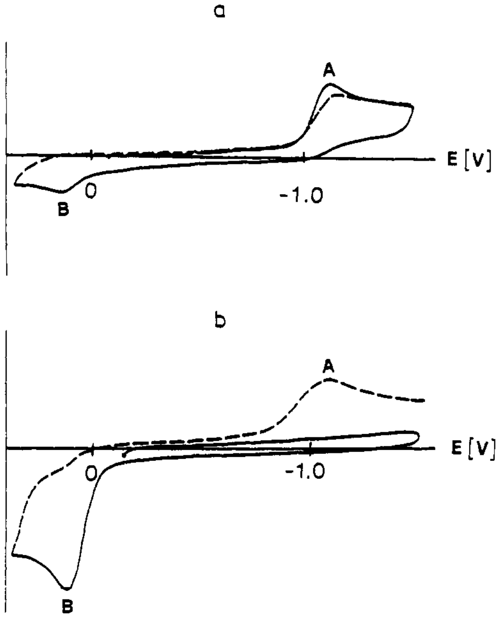

Figure 3. Cyclic voltammograms of an acetonitrile solution of 1 at a Pt electrode, scan rate 0.2 V s^{-1}: (a) initial solution; (b) after exhaustive reduction at a Hg pool with $E_w = -1.10$ V; (—) first scan; (---) second scan.

(a) and (b). The reduction/reoxidation cycle is thus almost reversible. The parent complex 1 is reformed by an efficient reaction, which follows the oxidation of the electrogenerated $Co(CO)_4^-$ to $Co(CO)_4^•$ (at the potential of peak B). The broadening of peak A in the second scan indicates some fouling of the Pt electrode during the reduction/reoxidation cycle. A more quantitative picture of such a redox cycle can be obtained from spectroelectrochemical experiments using an optically transparent thin-layer electrochemical (OTTLE) IR cell.[7] During the exhaustive reduction of an acetonitrile solution of 1 at $E_w = -1.20$ V (Pt minigrid electrode), the original ν_{CO} bands of 1 gradually disappear (Figure 4) and a new band at 1893 cm^{-1}, easily assigned[8] to $Co(CO)_4^-$ grows. Several weak bands between 2000 and 1950 cm^{-1} are also observed. The reoxidation at $E_w = +0.30$ V, corresponding to the process $Co(CO)_4^- \rightarrow Co(CO)_4^• + 1e^-$, regenerates 1 in almost quantitative yield (90% on the basis of ν_{CO} intensities).[9] Thus $Co(CO)_4^•$ must react with an appropriate radical, likely $[Co(CO)_2(HC_2E)]^•$, which can exist in solution (i) as a solvent-stabilized adduct, i.e. $[Co(CO)_2(CH_3CN)(HC_2E)]^•$, (ii) as a liable dimeric species, i.e. $[Co(CO)_2(HC_2E)]_2$, or (iii) chemisorbed onto the electrode (Figure 5). The lack of prominent IR bands in the OTTLE experiments, the absence of EPR resonances in the frozen solution, the absence of oxidation peaks due to electroactive species in addition to that of $Co(CO)_4^-$, and the poisoning of the Pt electrode in multisweep CV experiments support hypothesis iii. If CO is bubbled in place of Ar into an acetonitrile solution of 1 during the exhaustive electrolysis at a mercury pool ($E_w = -1.10$ V), ca. 2 faradays/mol are consumed and only trace amounts of 1 are obtained after the reduction/reoxidation cycle. The radical $[Co(CO)_3(HC_2E)]^•$, easily formed under CO atmosphere,[1] is reduced at the working potential to $[Co(CO)_3(HC_2E)]^-$, which no longer participates in the redox cycle (Figure 5). The IR-OTTLE experiment on an acetonitrile solution of 1 saturated with CO indicates the generation of larger amounts of $Co(CO)_4^-$ on reduction (peak at 1893 cm^{-1}) and confirms the lack of reversibility on reoxidation.

Table I. Standard Heterogeneous Rate Constants, *k*°, of the Electron-Transfer Process and Homogeneous Rate Constants, *k*, of the Following Chemical Reaction Evaluated by ac Polarography of Complexes 1–4, Along with the Relative Electrode Potentials, *E*°

compd		$k°$ (cm^2 s^{-1})	$E°$ (V)	k (s^{-1})
$Co_2(CO)_6(HC_2E)$	(1)	>1[a]	-1.08	380
$Co_2(CO)_6(HC_2C_6H_{10}OH)$	(2)	>1[a]	-1.02	85
$Co_2(CO)_6(MeC_2Me)$	(3)	>1[a]	-1.18	285[b]
$Co_2(CO)_6(HC_2H)$	(4)	0.27	-1.04	125

[a] Estimated from cot φ experimentally obtained at 1000 Hz. [b] Value uncertain due to the strong contribution of adsorption.

The IR-OTTLE experiments on complexes 2–4 show that their redox reversibility in the chemical time scale is largely incomplete. For 2 the reversibility approaches 50%, for 3 and 4 only traces of parent complexes could be observed after the reduction/reoxidation cycle.

ac Polarography and Voltammetry

The ac measurement provides a complementary view on the reduction mechanism of complexes 1–4. In addition, the high sensitivity and the wide range of time constants (typical of the ac methods) give a more quantitative picture of the overall electrode mechanism.[10] ac phase-selective polarography was used for the determination of the first-order rate constant (k) of the chemical reaction which follows the electrochemical generation of the unstable radical anion $[Co_2(CO)_6(alkyne)]^-$. The electrochemical reversibility of the reduction of complexes 1–4 was checked

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(9) We checked the identity of complex 1 by ^1H NMR spectroscopy before and after the reduction/oxidation cycle using a Pt basket working electrode (reduction at -1.20 V, reoxidation at +0.30 V vs SCE).

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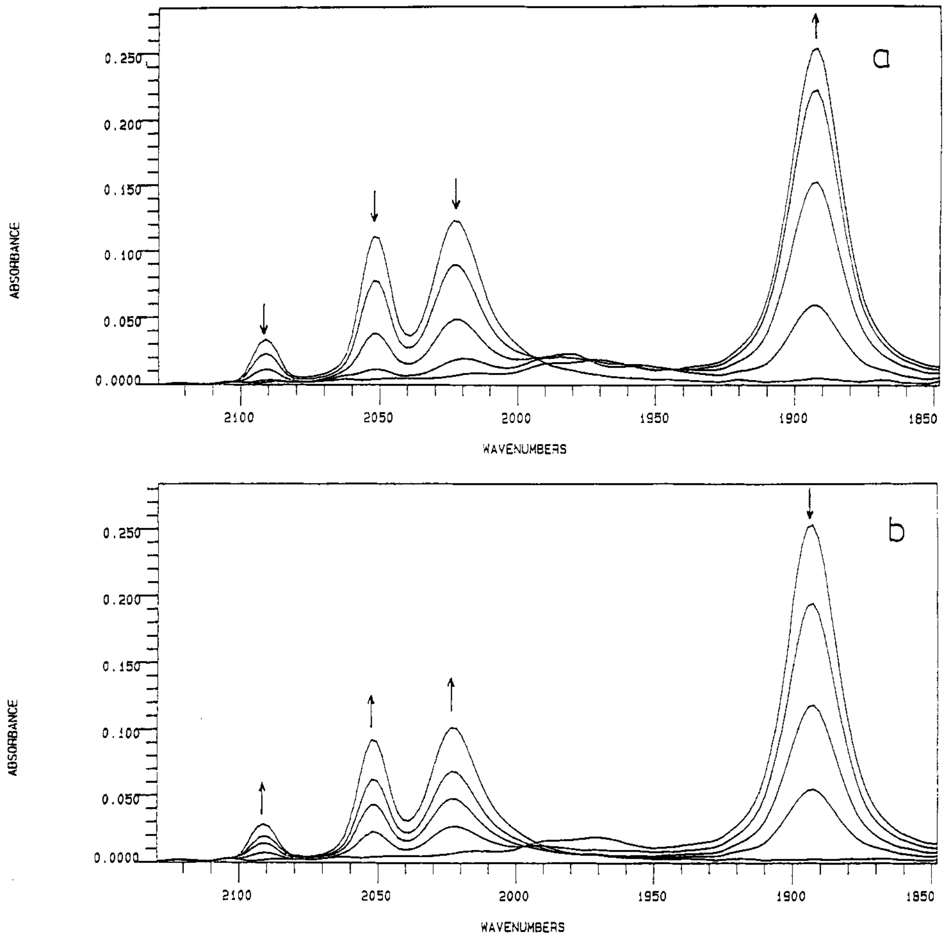

Figure 4. IR-OTTLE spectra of an acetonitrile solution of 1: (a) during the exhaustive reduction at E_w = −1.20 V; (b) during the reoxidation at E_w = 0.30 V.

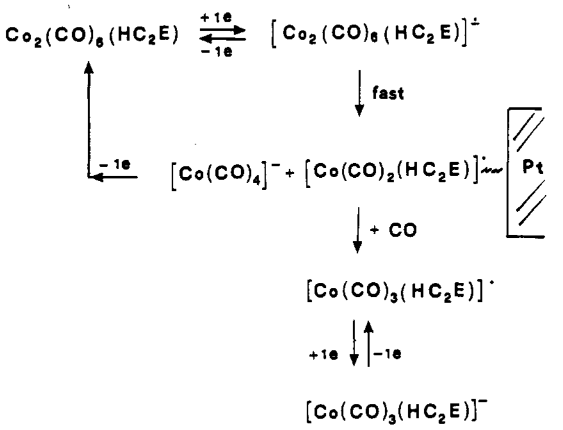

Figure 5. Proposed electrochemical mechanism for the reduction of $Co_2(CO)_6(HC_2E)$ (1). It represents an extension of that previously proposed by Robinson, Rieger, and co-workers.[1,2]

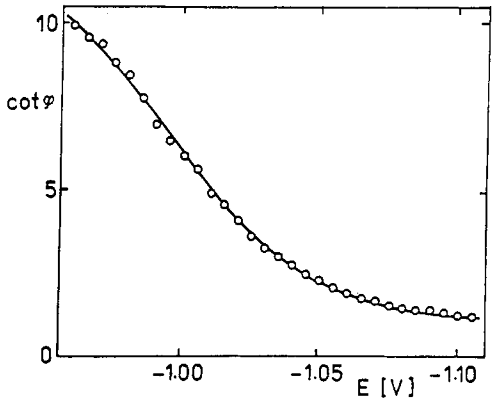

Figure 6. Potential dependence of cot $\varphi = Z_F'/Z_F''$ for 1 in acetonitrile: (○) experimental values calculated from the electrode admittance data. The regression curve (—) corresponds to the parameters k = 380 s^{-1}, $E°$ = −1.08 V.

at sufficiently high frequency (500–1000 Hz), where the character of electrode admittance is not influenced by the relatively slow (in comparison with the range of frequency employed) electroinactivating chemical reaction. The same faradaic summit current[11] was obtained for the in-phase and quadrature components, which indicates a diffusion-controlled process. Only for compound 4 was a moderately slow electron-transfer process detected at highest frequencies. The determination of the rate constant of the following chemical reaction was then calculated from experiments at low frequency (10 Hz) by using the theoretical approach for the $E_{REV}C_{IRR}$ mechanism. The numerical results are summarized in Table I, and the regression curve of the potential dependence of phase angle φ of faradaic impedance obtained from ac polarograms of 1 is depicted in Figure 6. Such a regression analysis provides the values of the first-order rate constant, k, and of the standard electrode potential $E°$.

Noteworthy, 1 exhibits the highest k value of the series, in other words the $[Co_2(CO)_6(HC_2E)]^-$ anion is the shortest lived. The comparison of lifetimes (at room temperature) of 1^-, ca. 3 ms, with those reported[1] for other $Co_2(CO)_6(RC_2R)$ (R = Ph, 17 ms, R = Bu^t, 70 ms, R = CF_3, several

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[11] The term summit current has been suggested for ac polarography by the IUPAC Commission on Electroanalytical Chemistry: Meites, L.; Zuman, P.; Nurnberg, H. W. *Pure Appl. Chem.* **1985**, *57*, 1491.

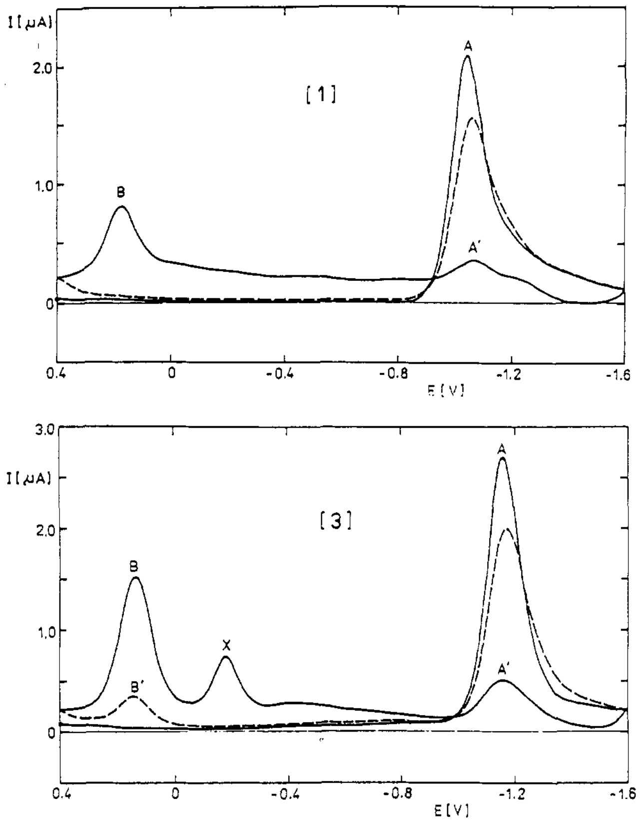

Figure 7. ac CV responses of acetonitrile solutions of 1 and 3 at a Pt electrode, frequency 100 Hz, scan rate 200 m V s^{-1}: (—) first scan, (- - -) second scan.

hours) indicates that the half-lives of the radical anions $[Co_2(CO)_6(RC_2R)]^-$ increase with the electron-withdrawing ability and, to a less extent, with the steric bulk of the substituents, R. However, the reversibility of the redox cycle (in the chemical time scale) is highest for 1, indicating that the estradiol substituent is able to stabilize the "$Co(CO)_2(HC_2E)$" fragment in solution or, more likely, the estradiol favors the reversible adsorption on the electrode. Therefore this radical is ready for an efficient recombination with $Co(CO)_4^{\bullet}$, as far as it is generated at the electrode by reoxidation of $Co(CO)_4^-$. Indeed, among the other $Co_2(CO)_6$(alkyne) complexes tested, only 2 gives a reasonable reversibility in the redox cycle, the -OH functionality could be responsible for the efficient adsorption of electrogenerated radical onto the electrode. This recombination of electrogenerated radical parallels that found for iron "flyover bridge" complexes.[12]

Figure 7 shows the ac CV responses of 1 and 3, the latter being representative of 2–4. Peak A corresponds to the reduction of the complex under investigation, the small height of the associated reoxidation peak A′ in the reverse scan testifies a fast following chemical reaction. At positive potentials, peak B corresponds to the oxidation of the $Co(CO)_4^-$ anion to the $Co(CO)_4^{\bullet}$ radical. In the case of complexes 2–4 as well as other $Co_2(CO)_6$(alkyne) complexes,[1] an additional peak X is observed due to the oxidation of an unidentified electroactive fragment. In the second scan, the reduction peak B′ corresponding to the reverse process $Co(CO)_4^{\bullet} + 1e^- \rightarrow Co(CO)_4^-$ is observed (although with reduced height) for complexes 2–4, but it is totally absent for 1. This indicates that the $Co(CO)_4^{\bullet}$ radical rapidly vanishes in the acetonitrile solution of 1. In principle, three reactions can consume $Co(CO)_4^{\bullet}$ as formed: (i) decomposition to metallic cobalt (ii) dimerization to $Co_2(CO)_8$ (unstable in N-donor solvents, because of its disproportionation[13]), and (iii) recombination with the appropriate $[Co(CO)_2(alkyne)]^{\bullet}$ fragment to give back the parent compound. The absence of peak B′ in the CV response of 1 indicates that reaction iii is faster and predominant in the case of complex 1.

Experimental Section

The $Co_2(CO)_6$(alkyne) (1–4) derivatives were synthesized according to the literature[14] procedures, by reacting $Co_2(CO)_8$ with ethynylestradiol, 1-ethynyl-1-cyclohexanol, but-2-yne, and ethyne, respectively. Their purity was checked by IR and ^1H NMR spectroscopy on Perkin-Elmer 580 B and JEOL EX-400 instruments, respectively.

The EPR spectra were recorded on a Varian E-109 instrument operating in the X-band mode.

Electrochemistry was performed with an EG&G PAR 273 electrochemical analyzer connected to an interfaced IBM microcomputer and to an EG&G PAR Model 5210 lock-in amplifier (for ac measurements). A standard three-electrode cell was designed to allow the tip of the reference electrode (SCE) to closely approach the working electrode. Positive feedback *iR* compensation was applied routinely. All measurements were carried out under Ar in anhydrous deoxygenated solvents; solutions were 1×10^{-3} M with respect to the compounds under study and 1×10^{-1} M with respect to the supporting electrolyte, $[Bu_4N][PF_6]$. The temperature of the solution was kept constant within 1 °C, by circulation of thermostated water–ethanol mixture through the double wall of the cell. The Pt-disk electrode was soaking in nitric acid, rinsed with distilled water, and dried with a paper tissue. Before each set of measurements, it was preconditioned at +0.80 V. Potential data (vs SCE) were checked against the ferrocene (0/1+) couple; under the actual experimental conditions the ferrocene/ferrocenium couple is located at +0.40 V in acetonitrile.[15]

Optically transparent thin-layer electrochemistry (OTTLE) was performed using a cell assembled as previously described.[7] The corresponding IR spectra were measured on a Philips 9800 FT-IR spectrometer.

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