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ELECTROCHEMISTRY OF PLATINUM(II) COORDINATION COMPOUNDS

I. ELECTROREDUCTION OF DIHALOGENOBIS(ISOCYANIDE)-PLATINUM(II) COMPLEXES

P. LEMOINE, A. GIRAUDEAU, M. GROSS,

Laboratoire d'Electrochimie et Chimie Physique du Corps Solide, E.R.A. au C.N.R.S., No. 468, Université Louis Pasteur, 4, rue Blaise Pascal, 67000 Strasbourg (France)

and P. BRAUNSTEIN

Laboratoire de Chimie de Coordination, E.R.A. au C.N.R.S., No. 670, Université Louis Pasteur, 4, rue Blaise Pascal, 67000 Strasbourg (France)

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Summary

Electroreduction of *cis* and *trans* dihalogeobis(isocyanide)platinum(II) complexes PtL_2X_2 (X = Cl, Br, I; L = cyclohexyl isocyanide or tert-butyl isocyanide) on gold and platinum electrodes has been studied in propylene carbonate and acetonitrile containing tetraethylammonium perchlorate as supporting electrolyte. The first, monoelectronic, reduction step is irreversible, the half-wave potential being critically dependent on the chemical nature of X in PtL_2X_2. Potentiostatic reductive coulometry of PtX_2L_2 in the cavity of an ESR spectrometer produces a signal attributed to a monomeric paramagnetic Pt^I complex. It is also shown that one halide anion is liberated per PtX_2L_2 in this first reduction step. A second monoelectronic reduction step is observed, which results in the decomposition of the complex to form a solid deposit containing platinum on the electrode. A reduction scheme is proposed for PtX_2L_2, on the basis of these results.

Introduction

Several studies [1—13] have been made of the electrochemical reduction of square planar coordination complexes of platinum. Table 1 summarizes the main results obtained by polarography in non-aqueous solvents. It is seen that two types of behaviour are observed: examples 1 through 6, Table 1, show that the reduction can occur by reversible monoelectronic transfer, whereas exam-

TABLE 1

POLAROGRAPHIC CHARACTERISTICS OF TETRACOORDINATED Pt^{II} COMPOUNDS IN NON-AQUEOUS SOLVENTS

No.	Electroactive species	First step electroreduction product	Number of e^- exchanged	Reversibility of the reduction	Ref.
1	$Pt(S_2C_2R_2)_2$ [a]	$Pt(S_2C_2R_2)_2^-$	1	rev.	1 2
2	$Pt(o\text{-}C_6H_4(NH)_2)_2$	$Pt(o\text{-}C_6H_4(NH)_2)_2^-$	1	rev.	3
3	$Pt(NH_3)_2Cl_2$	Pt	—	irrev.	4
4	$Pt(S_2C_2(CN)_2)_2$	$Pt(S_2C_2(CN)_2)_2^-$	1	rev.	6
5	$Pt((NH)_2C_2(CN)_2)_2$	$Pt((NH)_2C_2(CN)_2)_2^-$	1	rev.	6
6	Pt(sac sac)$_2$ [b]	Pt(sac sac)$_2^-$	1	rev.	7
	Pt(sac sac)$_2$ [b]	Pt^I	1	$E_{3/4} - E_{1/4} = 52$ mV	8
7	$(Pt(DPPE)_2)^{2+}$ [c]	$Pt(DPPE)_2$	2	rev.	9
8	$(PtCl_2(PR'_3)_2)$ [d]	$Pt(PR_3)_2 + 2Cl^-$	2	irrev.	10, 11
9	$(Pt(M'S_4)_2)^{2-}$ [e]	—	2	—	12
10 [f]	$NiCl_2(PPh_3)_2$	$(NiCl_2(PPh_3)_2)^-$	1	rev. in the presence of Cl^-	13

[a] R = CN, CF_3, C_6H_5, $p\text{-}C_6H_4CH_3$, CH_3. [b] sac sac = dithioacetylacetonate. [c] DPPE = $Ph_2PCH_2CH_2PPh_2$. [d] $R' = Me_xPh_{3-x}$, C_2H_5. [e] M' = Mo or W. [f] Added for comparison with 8 (see text).

ples 7, 8 and 9, correspond to irreversible bielectronic transfer. Among these systems, the complexes involving four Pt—S or Pt—N bonds are reduced reversibly to give the corresponding anions, while the reduction of some complexes with Pt—P or Pt—S bonds takes place with an irreversible transfer of two electrons in one step (examples 8 and 9). Complexes obtained by the electrochemical reduction of Pt^{II} in non-aqueous solvent are therefore complexes of either Pt^{I} or Pt^0.

The electrochemical reduction mechanisms for the closely related Ni^{II}, Pd^{II}, Pt^{II} compounds show a convergent behaviour from Ni to Pt. Thus, comparing the reduction of $NiCl_2(PPh_3)_2$ with that of $PtCl_2(PPh_3)_2$, we observe that the Ni^{II} complex is reduced to Ni^I in the first step, then further to Ni^0 in a second step, while the Pt^{II} complex is reduced in a single step to Pt^0 (examples 8 and 10, Table 1, ref. 13). In addition to the electrochemical pathway, numerous chemical pathways exist for producing monovalent coordination compounds of Ni, Pd and Pt [14—21]. Most of these compounds are dinuclear complexes either with one metal—metal bond, or with bridging ligands between the two metals: such complexes are diamagnetic. The only paramagnetic, and therefore presumably mononuclear, complexes of Pt^1 known were obtained in two ways a) by the electrochemical reduction of dithiolates complexes of Pt^{II} [6,7], and b) by γ irradiation of Pt^{II} salts [22].

The aim of the present study was to investigate the electrochemical reduction of Pt^{II} compounds. The starting complexes were PtX_2L_2 (X = Cl, Br, I; L = t-BuNC, cyclo-$C_6H_{11}NC$) [25]. The compounds are soluble in CH_3CN or in propylene carbonate, but react spontaneously with mercury. Therefore, we have used a Pt or Au electrode for stationary voltammetry (S.V.), cyclic voltammetry (C.V.) and potentiostatic coulometry. The dia- or para-magnetism of the electrochemical reduction products was determined in situ in an ESR cavity. The initial results obtained for these compounds were recently presented in preliminary note [23].

Experimental

PtL_2X_2 complexes are dissolved in known volumes of propylene carbonate or acetonitrile purified by established procedures [24]. The solutions are colourless at the studied concentrations (10^{-3}—10^{-4} *M*). The solution is degassed under argon in a three-electrode cell. The working electrode is a platinum or gold disc electrode of 3.14 mm^2 area. Potentials are measured against an aqueous saturated calomel electrode (SCE) separated from the non-aqueous solution by a salt bridge containing the same solvent and supporting electrolyte (0.1 *M* $(C_2H_5)_4NClO_4$) as the studied solution in order to prevent water diffusion in the medium. The auxiliary electrode is a platinum wire separated from the solution by a glass fritt (porosity 4). The electrochemical techniques used were stationary voltammetry (SV) (rotating disc electrode 2000 rpm), cyclic voltammetry (CV) and potentiostatic coulometry followed by stationary voltammetry. After each potential scan, the working electrode was polished on an abrasive disc, then washed with distilled water, and dried.

In situ ESR experiments were carried out on an X band Brucker spectrometer on the platinum electrode in continuously degassed solutions (the obtained radicals being air sensitive). It was confirmed that no ESR signal appears when the solvent and supporting electrolyte are reduced at the same potential as the product.

It was also confirmed that the ESR signal increased during the course of the electrolysis and rapidly disappeared upon interruption of polarization. Under our experimental conditions the accessible range of potential in PC and AN was from +2 to −2.3 V/SCE on a solid electrode (Pt—Au).

Results

a) Stationary voltammetry (SV)

The PtL_2X_2 compounds studied by SV showed a well defined reduction wave whose characteristics are given in Table 2. As the limiting currents I_1 are proportional to *C* and as the $1/I_1$ vs $1/\omega^{1/2}$ ($500 < \omega < 5000$ rpm) plots are straight lines intersecting the origin, all of the cathodic limiting currents are diffusion controlled (*C* range 10^{-4} to 2×10^{-3} *M*). Levitch's relationship was found to apply. Successive potential scans gave reproducible *I-V* curves, indicating the absence of electrode passivation. Logarithmic analysis of the reduction waves (SV) indicated an irreversible reduction process. The measured half-wave potentials became more cathodic as the halide (X) ligand became more electronegative and did not depend on the nature of the ligand L (L = t-BuNC or cyclo-$C_6H_{11}NC$) nor on the *cis-trans* configuration of the electroactive complex.

b) Cyclic voltammetry (CV)

The cyclic voltammograms of the PtX_2L_2 complexes are presented in Fig-

TABLE 2

ELECTROREDUCTION OF PtX_2L_2 IN PROPYLENE CARBONATE AND 0.1 *M* TEAP

Stationary voltammetry and cyclic voltammetry on gold electrode (Electrode area = 3.14 mm^2, 20°C)

Electroactive species	Stationary voltammetry (rotating disc electrode)			fir	Cyclic voltammetry first step	
	$E_{1/2}$ (V/SCE)	I_l (μA)	c (mole/l)	$\log \frac{I}{I_d - I}$ (mV/log)	E_p^c (V/SCE)	I_p^c (μA)
$PtCl_2(t\text{-}BuNC)_2$	−1.80	12	2×10^{-3}	142	−1.90	6.0
$PtCl_2(cyclo\text{-}C_6H_{11}NC)_2$	−1.80	14	1.2×10^{-3}	116	−1.85	7.4
$PtBr_2(cyclo\text{-}C_6H_{11}NC)_2$	−1.65	18	1.6×10^{-3}	145	−1.75	8.0
$PtI_2(cyclo\text{-}C_6H_{11}NC)_2$	−1.18	6.4	9×10^{-4}	145	−1.20	1.36

ure 1. Two reduction steps are observed in the potential range explored.

First reduction step. For a triangular scan from 0 to −2.3 V/SCE, we observe a reduction peak E_p^c corresponding to the first reduction step; the E_p^c and I_p^c characteristics are gathered in Table 2. No corresponding anodic peak is observed for the potential scan rate range explored (0.01 to 10 v/S). This result is in agreement with an irreversible electronic transfer as already observed in SV. Dependence of I_p and E_p^c on the potential scan rate v is characteristic of a slow electrochemical process controlled by diffusion (Table 3).

Second reduction step. The second reduction step shows only a cathodic peak (without a corresponding anodic peak) at the limit of the potential range available in our experimental conditions (Figure 1). Therefore, a detailed analy-

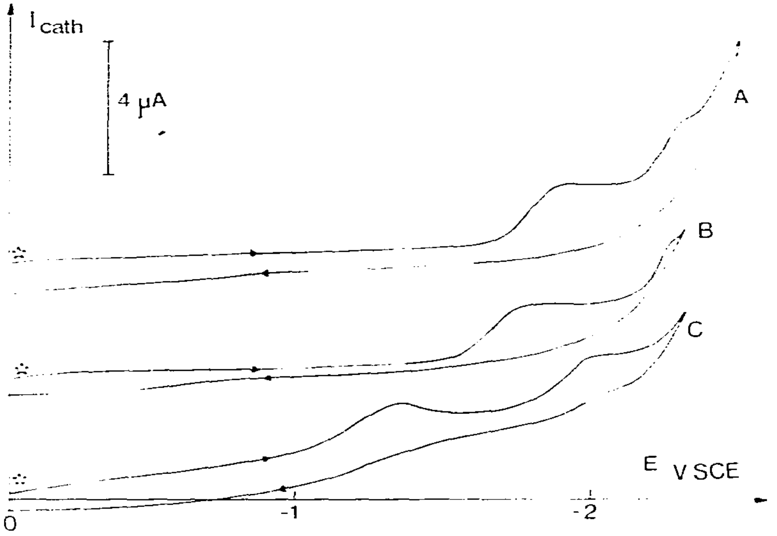

Fig. 1. Cyclic voltammetry of PtL_2X_2 on gold electrode in propylene carbonate containing 0.1 *M* TEAP. Potential scan 0.1 V/s. curve A, $PtCl_2(t\text{-}BuNC)_2$ 2×10^{-3} *M*; curve B, $PtBr_2(cyclo\text{-}C_6H_{11}NC)_2$ 1.6×10^{-3} *M*; curve C, $PtI_2(cyclo\text{-}C_6H_{11}NC)_2$ 1×10^{-3} *M*.

TABLE 3

CYCLIC VOLTAMMETRY OF THE FIRST REDUCTION STEP OF $PtI_2(cyclo\text{-}C_6H_{11}NC)_2$ (9×10^{-4} *M*, in propylene carbonate + 0.1 *M* TEAP on gold electrode)

v ($V\ s^{-1}$)	$-E_p^c$ (V/SCE)	i_p^c (μA)	$-E_{p/2}^c$ (V/SCE)	$\lvert E_p^c - E_{p/2}^c \rvert$ (V)
1.00	1.48	9.2	1.33	0.15
0.50	1.43	6.5	1.30	0.13
0.20	1.39	4.0	1.25	0.14
0.14	1.37	3.1	1.23	0.14
0.10	1.35	2.8	1.20	0.15
0.04	1.33	1.8	1.20	0.13
0.01	1.30	1.1	1.15	0.15

sis of this peak was not possible. The identical heights of this recorded cathodic peak and preceeding peak demonstrated that this reduction step is also monoelectronic. The potential peak value is shifted cathodically as the potential scan rate increases. In connection with this second reduction step, we observed a deposit on the working electrode studied after potentiostatic coulometry.

c) Potentiostatic coulometry

Potentiostatic coulometry confirmed that the first reduction step is monoelectronic. The same result is obtained by comparing the wave heights (SV) of the complexes $PtCl_2L_2$ (L = t-BuNC, cyclo-$C_6H_{11}NC$) with the corresponding $PtCl_2(PPh_3)_2$ wave height, which is reduced via a well known bielectronic process [10,11], assuming that $PtCl_2L_2$ and $PtCl_2(PPh_3)_2$ have similar diffusion coefficients. In the course of the first reduction step, all the solutions turned yellow. The reduction of the mononuclear complexes PtX_2L_2 of Pt^{II} leads to a Pt^I compound, which is further reduced to Pt^0 in a second reduction step. The gold electrode becomes thereby covered with a solid deposit, which electron probe X-Rays microanalysis has shown to contain platinum; it is clear from this experiment that the Pt^I complex is destroyed after the second reduction step.

If, during the exhausitive reduction of $PtCl_2(cyclo\text{-}C_6H_{11}NC)_2$ at a potential corresponding to the first reduction step the polarization is interrupted and the electrolyzed solution checked by SV, two new polarographic waves appear ($E_{1/2} = -1.15$ V and $E_{1/2} = -1.65$ V/SCE), the limiting currents of which increase with time: the reduction products react chemically and give new electroreducible species. The mechanism of the first reduction step is therefore an electrochemical-chemical process, of which the chemical step is slow.

After exhaustive electrolysis at the first step potential, we determined by SV the concentration of the X^- ions liberated during the reduction by comparison of the X^- oxidation wave height with that of a calibrated solution containing Et_4NX. The results showed that one mole of X^- was liberated per mole of PtX_2L_2 reduced.

d) Potentiostatic coulometry in the ESR cavity

When potentiostatic coulometry is carried out in the ESR cavity at poten-

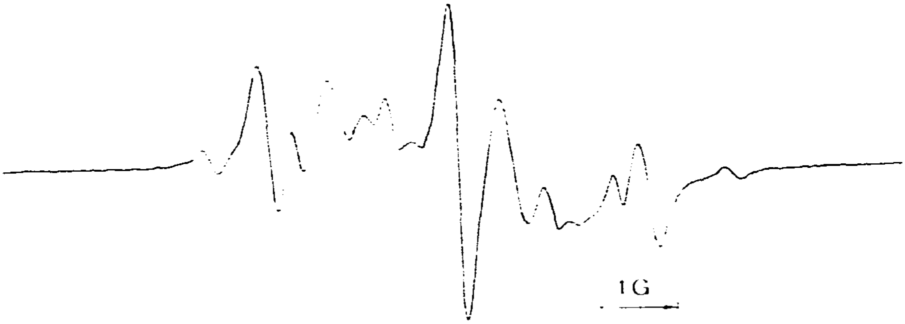

Fig. 2. ESR signal obtained when $PtCl_2(t\text{-}BuNC)_2$ is electrolyzed during 24 h at −2 V/SCE at ambient temperature in the following medium: CH_3CN + 0.1 M TEAP + saturated $PtCl_2(t\text{-}BuNC)_2$. Working electrode: Pt. (X Band Brucker spectrometer). $PtBr_2(cyclo\text{-}C_6H_{11}NC)_2$ and $PtI_2(cyclo\text{-}C_6H_{11}NC)_2$ exhibit broad lines under the same conditions.

tials corresponding to the first reduction step, there appears a signal whose magnitude increases with the duration of the electrolysis (Figure 2). This signal is obtained at room temperature as well as at 77 K, where no hyperfine structure is observable. Upon interruption of the polarisation, the intensity decreases slowly, indicating a moderate stability of the paramagnetic electrochemically generated species. The first reduction step thus leads to a paramagnetic complex of Pt^I, presumably mononuclear.

Discussion

The above results lead us to propose the following reduction scheme for PtX_2L_2:

First electrochemical step:

$Pt^{(II)}X_2L_2 + 1\,e^- \rightarrow Pt^{(I)}XL_2^{\cdot} + X^-$

↓

dimerization or coordination to the solvent

Second electrochemical step:

$Pt^{(I)}XL_2^{\cdot} + 1\,e^- \rightarrow$ decomposition of the complex
(Platinum deposition on gold electrode)

The chemical reactions following the first reduction step may involve dimerization of solvent coordination *. Attempts to isolate the reduction products were unsuccessful. The nature of the electrode (Pt or Au) has little effect on the reduction products or on the reduction potential values. The reduction potential values for the complexes $PtX_2(t\text{-}BuNC)_2$ are close to those for the complexes $PtX_2(cyclo\text{-}C_6H_{11}NC)_2$, while they change by about 0.6 V when going from chlorine to iodine in the same PtL_2X_2 family (Table 2).

Comparing the electrochemical behaviour of $PtCl_2(RNC)_2$ ($E_{1/2} = -1.80$ V/SCE) with that of $PtCl_2(PPh_3)_2$ ($E_{1/2} = -1.43$ V/SCE), it can be seen that the first complex is reduced to Pt^0 through Pt^I while the second is reduced directly to Pt^0. This is probably due to the Pt—isocyanide bond, which stabilizes the

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* Note added in proof: In a recent publication [26] the reduction of cationic Pt^{II} isocyanide complexes has been reported. The first monoelectric step led to a Pt^I dimer.

formed Pt^I radical by back-donation, since this effect is weak in the Pt—PPh_3 bond (it is well known that the PPh_3 ligands are weaker π acceptors than the RNC ligands). The *cis-trans* nature of a $PtCl_2(RNC)_2$ complex does not affect the electrochemical reduction results. A similar conclusion was previously reached for *cis* and *trans* $PtCl_2(PPh_3)_2$ complexes [10].

Conclusion

It is shown that the electrochemical reduction of PtX_2L_2 complexes on a solid electrode in propylene carbonate or acetonitrile solutions occurs in two irreversible monoelectronic steps. During the first step the Pt^{II} complex is reduced to a paramagnetic Pt^I complex, while one halide ion is liberated per reduced PtX_2L_2 molecule. The second reduction step leads to Pt^0, and the complex is destroyed.

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