VOLTAMMETRIC BEHAVIOUR OF
cis-DIARYLBIS(TRIETHYLPHOSPHINE)PLATINUM(II)
COMPLEXES

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Summary

The voltammetric behaviour of *cis*-$[Pt(PEt_3)_2(YC_6H_4)_2]$ complexes in acetonitrile has been investigated by cyclic voltammetry and controlled potential coulometry. The oxidation potential increases linearly with increasing electron-withdrawing ability of the Y substituent in the platinum-bonded aryl ligand. The data are related to studies of electrophilic Pt—C bond cleavage.

Introduction

There have been several attempts to correlate structural features of transition metal complexes with kinetic or extra-kinetic parameters. Thus, following the development of semi-empirical equations for structure—reactivity relationships in nucleophilic organic substitution [1], a systematic series of nucleophilic reactivity constants was proposed for displacements in platinum(II) and palladium(II) complexes [2]. More recently, the rates of oxidative addition to platinum(II) derivatives have been correlated with electronic charge transfer band energies [3]. With the increasing interest in oxidative addition reactions, with its accompanying redox change, there has been an increase in the number of studies of structure-redox properties correlations [4] and also of electrochemical approaches to novel syntheses of organic transition metal compounds [5—9]. A primary aim of those investigations was to shed light on the electron transfer process at the electrode and on the factors affecting the electrochemical behav-

iour, such as solvent effects, electronic and steric characteristics of substituents on the ancillary ligands, the nature of the central metal, etc. This is also relevant to the more general topic of electron transfer mechanisms of redox reactions in solution.

As far as Pt—C σ-bonded complexes are concerned, a feature which is subject of current debate is the site of attack of electrophiles which cleave the platinum—carbon bond; the electrophilic attack may involve the metal (via oxidative addition of the electrophile) or the carbon atom of the breaking Pt—C bond:
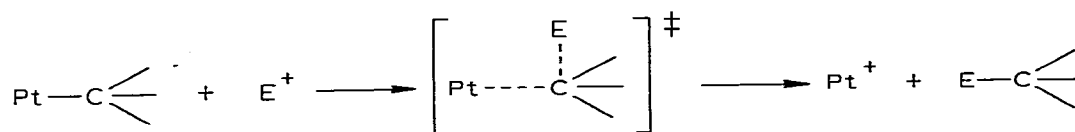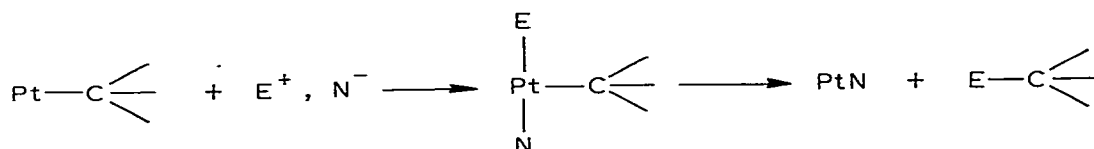
In this connection we found that the rate of cleavage of the first Pt—aryl bond in cis-[Pt(PEt$_3$)$_2$(YC$_6$H$_4$)$_2$] by attack of protons increases with increasing electron release by the Y substituents; a good LFER * was observed between the rate data and the Hammett σ constants of Y [10]. Thus, we thought it worthwhile to seek an independent, extra-kinetic parameter to assess the electron density on platinum in these complexes, as reflected by the ease of metal oxidation. We therefore measured the voltammetric oxidation potentials in acetonitrile of the substrates cis-[Pt(PEt$_3$)$_2$(YC$_6$H$_4$)$_2$] with Y = H, p-Me, p-OMe, o-Me, o-Et, p-Cl, p-F, m-CF$_3$.

Experimental

Materials and complexes

The complexes cis-[Pt(PEt$_3$)$_2$(YC$_6$H$_4$)$_2$] (Y = H [11]; p-Me [11]; o-Et [12]; o-Me [11]; p-OMe [13]; p-F [14]) were prepared by literature methods. The preparation of compounds with Y = m-CF$_3$, p-Cl, is described elsewhere [10].

The solvent acetonitrile was purified by repeated distillation over phosphorus pentoxide and stored over molecular sieves (3 Å). The supporting electrolyte, tetrabutylammonium perchlorate (TBAP), was prepared by neutralization of perchloric acid with tetrabutylammonium hydroxide, recrystallized from methanol and dried under vacuum at 50°C.

The solutions for voltammetric and coulometric tests were deaerated by purging with 99.99% nitrogen which had been previously saturated with acetonitrile.

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* LFER = linear free energy relationship.

Apparatus and procedure

All the electrochemical experiments were carried out at 20 ± 0.1°C.

The potential values are referred to an aqueous SCE. In the voltammetric tests a cell of suitable geometry was employed [15]. For large-scale electrolyses an H-shaped cell with anodic and cathodic compartments separated by a sintered glass disk was used. The working electrodes were a platinum sphere (~1 mm diameter) for voltammetry and a platinum gauze (~10 cm² apparent area) for coulometry.

The polarizing unit for voltammetry has been already described [16]. The recording devices were a Hewlett—Packard Model 7004 B XY pen recorder or a Hewlett—Packard Model 1201 A XY storage oscilloscope. An Amel Model 557/SU potentiostat with an associated Amel Integrator Model 558 was used in the controlled potential electrolyses.

Results and discussion

Figure 1 shows a typical cyclic voltammetric curve for *cis*-[Pt(PEt₃)₂Ph₂] in acetonitrile at a platinum microelectrode. It displays a well defined oxidation peak (A; E_p = +1.08 V) and a smaller associated cathodic peak (B; E_p = —1.43 V). Similar cyclic voltammetric curves were obtained for all the *cis* complexes investigated. The peak potential values for both anodic and cathodic processes are listed in Table 1.

Cyclic voltammetric curves recorded at potential scan rates of up to 100 V s⁻¹ did not show any cathodic peak associated to A in a potential region less cathodic than that at which the peak B is recorded. The $E_p - E_{p/2}$ values for the oxidation peaks, listed in Table 2, suggest an irreversible character of the
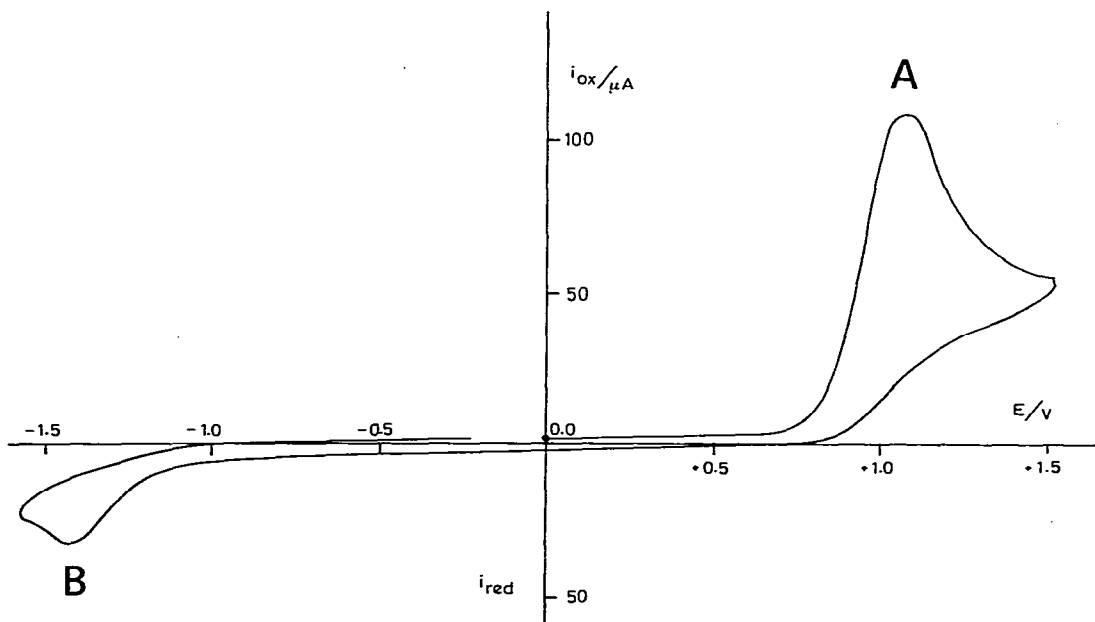

Fig. 1. Cyclic voltammetric curve recorded at a Pt microelectrode on a 5 × 10⁻³ *M cis*-[Pt(PEt₃)₂Ph₂] 0.1 *M* TBAP/CH₃CN solution. Scan rate 0.2 V s⁻¹; ● starting potential; anodic scan.

TABLE 1

VOLTAMMETRIC PEAK POTENTIAL VALUES FOR THE INVESTIGATED COMPLEXES [a]

cis-Platinum(II) compound	$(E_p)_A$ (V)	$(E_p)_B$ (V)
$Pt(PEt_3)_2Ph_2$	+1.08	−1.43
$Pt(PEt_3)_2(p\text{-}MeC_6H_4)_2$	+1.05	−1.42
$Pt(PEt_3)_2(o\text{-}MeC_6H_4)_2$	+1.11	−1.42
$Pt(PEt_3)_2(o\text{-}EtC_6H_4)_2$	+1.11	−1.42
$Pt(PEt_3)_2(p\text{-}MeOC_6H_4)_2$	+0.83	−1.41
$Pt(PEt_3)_2(p\text{-}FC_6H_4)_2$	+1.29	−1.44
$Pt(PEt_3)_2(m\text{-}CF_3C_6H_4)_2$	+1.55	−1.32
$Pt(PEt_3)_2(p\text{-}ClC_6H_4)_2$	+1.27	−1.48

[a] The peak potential values refer to cyclic voltammetric curves recorded at a potential scan rate of 200 mV s^{-1}.

anodic process. Accordingly, the oxidation peaks shifted towards more positive potentials on increasing the scan rate. The anodic shift of $(E_p)_A$ ($\delta E_p/\delta \log v$, reported in Table 2) was almost constant over the tested range 0.05—10 V s^{-1} for all complexes under study and equal to about 100 mV for the ten-fold increase in scan rate.

Furthermore, the ratios $(i_p)_A/C v^{1/2}$ (v in the range 0.05—10 V s^{-1} and depolarizer concentration C in the range 3.9×10^{-4}—7.3×10^{-3} M) were constant for all the compounds. This means that adsorption complications, preceding chemical reactions, and also e.c.e. type mechanisms can be disregarded.

All these results are consistent with a charge transfer step irreversible in character; in fact, for a quasi-reversible charge transfer process the slope of a plot of E_p vs. $\log v$ can be expected to change on varying the scan rate, i.e. as

TABLE 2

VOLTAMMETRIC QUANTITIES OF THE cis-$Pt(PEt_3)_2(C_6H_4Y)_2$ COMPLEXES

cis-Platinum(II) compound	$(E_p)_A - (E_{p/2})_A$ (mV) [a]	αn_a [b]	$\dfrac{\delta (E_p)_A}{\delta \log v}$ (mV) [c]	αn_a [d]
$Pt(PEt_3)_2Ph_2$	155	0.31	100	0.30
$Pt(PEt_3)_2(p\text{-}MeC_6H_4)_2$	155	0.31	99	0.30
$Pt(PEt_3)_2(o\text{-}MeC_6H_4)_2$	150	0.32	92	0.32
$Pt(PEt_3)_2(o\text{-}EtC_6H_4)_2$	145	0.33	94	0.31
$Pt(PEt_3)_2(p\text{-}MeOC_6H_4)_2$	145	0.33	99	0.30
$Pt(PEt_3)_2(p\text{-}FC_6H_4)_2$	150	0.32	93	0.32
$Pt(PEt_3)_2(m\text{-}CF_3C_6H_4)_2$	160	0.30	103	0.29
$Pt(PEt_3)_2(p\text{-}ClC_6H_4)_2$	160	0.30	101	0.29

[a] Calculated from voltammetric curves recorded at a scan rate of 200 mV s^{-1}. [b] Calculated from the equation $\alpha n_a = \dfrac{0.048}{(E_p)_A - (E_{p/2})_A}$. [c] Calculated at potential scan rate ranging from 0.05 to 10 V s^{-1}.
[d] Calculated from the equation $\alpha n_a = \dfrac{0.0295}{\delta E_p/\delta \log v}$.

the reversible character of the charge transfer step changes [17]. If a subsequent chemical reaction is coupled, it will affect the response to an extent variable as a function of the scan rate [18]; in any case a non-linear trend in the plot of E_p vs. log v might be observed.

We recall·that the anodic shift of the E_p value for the case of a chemical reaction following a reversible charge trar.sfer step is equal to $30/n$ mV for each ten-fold increase in scan rate [19]. The response relative to an irreversible anodic process exhibits a shift of $30/\alpha n_a$ mV, towards more positive potentials, for a ten-fold increase in scan rate [17,19]; the position of the response along the potential axis is evidently unaffected by the occurrence of a chemical reaction following the charge transfer step. Hence it is impossible to state whether or not the irreversible anodic oxidation of the studied complexes is followed by a chemical reaction.

Controlled potential coulometric experiments corresponding to the anodic process led in all cases to a consumption of two mol of electrons per mol of electrolyzed complex. As expected, the oxidation products are hence platinum-(IV) species. Cyclic voltammetric tests carried out on the exhaustively electrol-yzed solutions revealed the presence in the solution of a species which can be reduced at potential values corresponding to peak B in Fig. 1. Peak A was again recorded after traversing this reduction peak.

Figure 2 shows a plot of the anodic peak potentials vs. the Hammett σ-constants [20]. A good relationship of this sort can only be expected for reversible electrode reactions; in the case of irreversible electrode processes a similar correla-
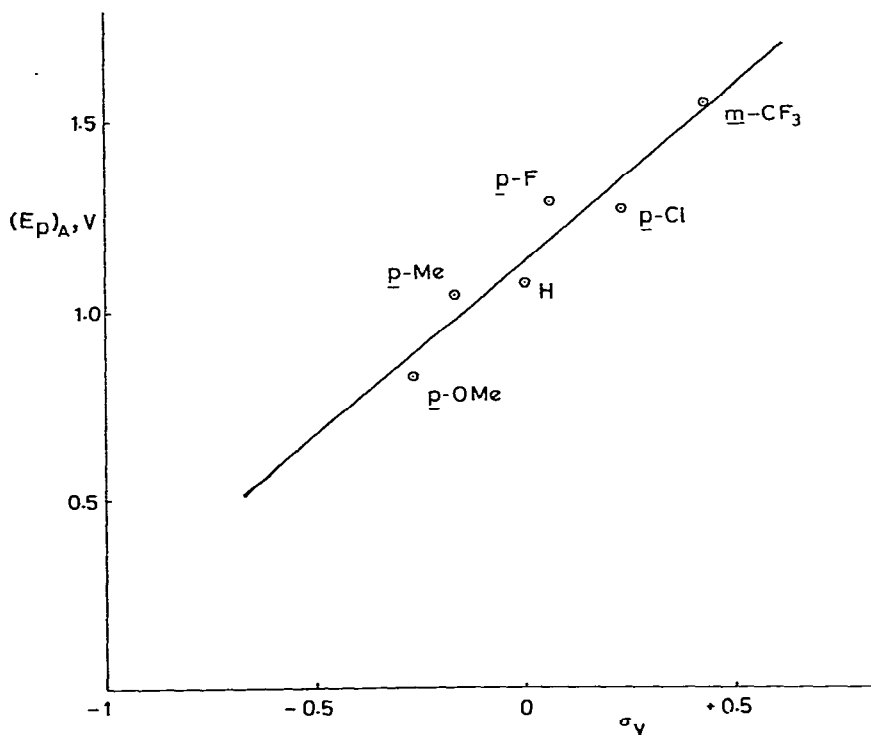

Fig. 2. Plot of the anodic peak potential values vs. the Hammett σ-constants [20].

tion is expected only if the transfer coefficients α are the same for all the studied compounds. Since it is unlikely that these substrates, which are similar in composition and coordination geometry, release differing numbers of electrons in the slow electrode step (n_a), the equality of the α values can be deduced from the very similar αn_a values reported in Table 2. These values were calculated both from each voltammetric curve and from the slopes of the plots of E_p vs. $\log v$ [17,19].

As can be seen from Fig. 2, the anodic peak potential decreases with increasing electron donor ability of the Y substituent, clearly because of increased availability of electron density on the metal. This trend is in agreement with the increase of rate of electrophilic cleavage with increasing electron releasing ability of Y that we observed for these substrates [10], indicating that the activation processes for electrophilic attack and oxidation of the central metal are governed by similar factors. However, this cannot be taken as evidence that electrophilic attack on these substrates takes place via oxidative addition to platinum rather than direct attack on the Pt—C bond, since the substituent may also affect the electronic density in such a bond.

As for the nature of the voltammetric oxidation product, we propose a platinum(IV) octahedral structure with apical positions possibly occupied by solvent molecules.

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