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Electrochemical and spectroelectrochemical study of cyclometallated platinum derivatives with nitrogen ligands. Electrogeneration of monomeric reduced platinum species

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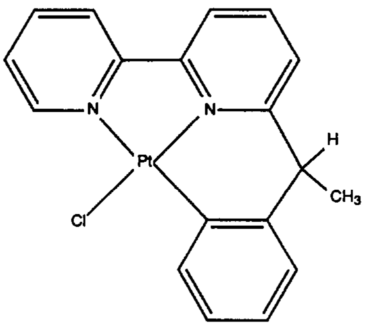
Abstract

The cathodic reduction of the complexes [LPtCl] and $[\mathrm{LPtL'}](\mathrm{BF_4})$ [HL = 6-(1-methylbenzyl)-2,2′-bipyridine and L′ = triphenylphosphine, pyridine, or acetonitrile] has been studied in acetonitrile and dichloromethane solvents. The main goal has been that of defining the nature and reactivity of the corresponding relatively stable one-electron reduced forms. In particular, X-band EPR spectrometry has allowed us to get information about the character (metal- or ligand-based) of the unpaired extra electron of the reduced species.

1. Introduction

After being extensively used for many years in organic chemistry [1,2], in the past decade electrochemical methods have also been widely applied in the field of inorganic chemistry. In recent years, the characterization of new compounds or classes of compounds, in addition to spectroscopic and structural analyses, has often included the definition of the electrochemical properties. More specifically, the electrochemistry of platinum has attracted considerable attention, due to the versatility of this metal, particularly in low oxidation states. In this field, an example of significant studies in electrosynthesis, *viz.* in electrogeneration of species capable of activating chemical bonds, can be found in recent publications of Davies *et al.* [3–5]. Cyclometallated complexes of platinum(II) and palladium(II) supported by nitrogen ligands have been of interest for many years [6]. Besides those with bidentate C–N systems, many species with terdentate ligands are currently under investigation; most of them have N–C–N [7] or C–N–C [8] donor atoms. The complex [LPtCl] (HL = 6-(1-methylbenzyl)-2,2′-bipyridine) **(1)** and related molecules have been previously described by some of us [9,10].



(1)

The deprotonated bipyridine is a terdentate ligand through the two nitrogen atoms and a carbon atom of the phenyl. The compounds are rather peculiar, owing to the simultaneous presence in the ligand of an N–N–C set and of a [5,6]-fused system; the latter feature,

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although not unprecedented, is still rare in platinum chemistry [11]. Aspects of the reactivity of complex **1**, as well as of cationic species $[LPt(L')]^+$, obtained by removing the chloride ion with silver tetrafluoroborate and reaction of the resulting solvate derivative with two-electron donors, have also been reported [12]. Bipyridine complexes are of interest both for fundamental reasons and for applications, so we deemed it worthwhile to investigate the electrochemical behaviour of these molecules, in order to evaluate their stability and reactivity in unusual formal oxidation states. We report here the results obtained in an electrochemical study of the cathodic behaviour of compound **1** and of the related species, $[LPt(PPh_3)]^+$ (**2**), $[LPt(py)]^+$ (**3**), and $[LPt(CH_3CN)]^+$ (**4**). Particular attention has been devoted to the intriguing and important character of the reduction (ligand- or metal-based) [13–19].

2. Experimental section

The synthesis of the compounds has been described elsewhere [9,12]. Acetonitrile (AN) and dichloromethane (Aldrich, anhydrous, 99 + %, Gold Label, water < 0.005%, packaged under dinitrogen) were used without any further purification. Tetraethylammonium tetrafluoroborate (Fluka) supporting electrolyte was dried overnight at 50°C under reduced pressure before use.

All electrochemical experiments were performed using an Amel System 5000 computerized instrument. Cyclic voltammograms were recorded with an Amel Model 863 XY recorder. Cyclic voltammetric and coulometric tests were performed in a conventional H-shaped cell, working and auxiliary electrode compartments being separated by a sintered glass disk. The working electrode was a platinum disk with a diameter of *ca.* 2 mm in the voltammetric tests and a large area platinum gauze in the electrolysis experiments. The reference electrode was an aqueous saturated calomel electrode (SCE), connected to the working electrode compartment through a salt bridge containing the same solvent-supporting electrolyte system. The auxiliary electrode was a mercury pool. Owing to the slowness of the homogeneous chemical reactions coupled to the charge transfer, we did not carry out voltammetric experiments at scan rates higher than 0.5 V s^{-1} or at low temperature, and we did not use a cell different from that used for coulometry [20]. The measurements were carried out at room temperature. The solutions were carefully de-aerated by bubbling 99.999% pure argon through the electrochemical cell; the same gas flowed over the solution during the experiments. The reported potential values are referred to SCE. $E^{r}_{1/2}$, a good approximation to the standard potential of the redox couple, was computed as half the sum of forward and directly associated backward peak potentials of the relevant cyclic voltammetric response [21].

Owing to the poor stability of the reduced species, essentially due to their high reducing power, X-band EPR spectra of the labile forms were in most cases obtained by using a suitable cell for *in situ* electrogeneration (*i.e.* inside the cavity of the instrument) [22]. However, in some cases, small volumes of previously electrolyzed solutions were transferred from the electrolysis cell into the spectrometer probe; the electrochemical cell and the probe were inside a glove-box under argon. A Bruker ER2200 SRL spectrometer operating at 9.38 GHz was used. The microwave frequency was calibrated against powdered dpph samples.

^1H- and ^{31}P-NMR spectra were recorded on a Varian VXR 300 spectrometer, operating at 300 (^1H) and 121.4 (^{31}P) MHz. ^{31}P chemical shifts are relative to 85% H_3PO_4 external standard, with positive shifts to high frequency.

3. Results and discussion

3.1. Electrochemistry

Typical cyclic voltammetric curves recorded on a solution of 2.5×10^{-3} M compound **2** and 0.1 M tetraethylammonium tetrafluoroborate in AN are reported in Fig. 1; two consecutive cathodic processes are evident. Qualitatively similar responses were obtained with all the compounds examined. Our attention has been focused on the first (less cathodic) process (the A–B peak system). For all the complexes studied, the ratio between anodic (backward) and cathodic (forward) peak currents was equal to one, even at a potential scan rate as low as 50 mV s^{-1}. The peak separation

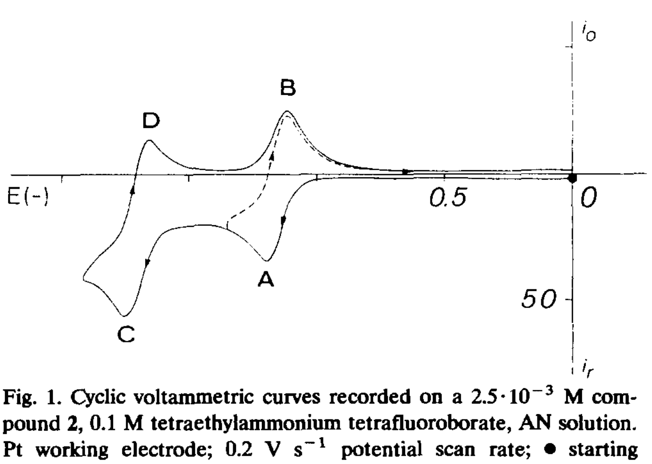

Fig. 1. Cyclic voltammetric curves recorded on a $2.5 \cdot 10^{-3}$ M compound **2**, 0.1 M tetraethylammonium tetrafluoroborate, AN solution. Pt working electrode; 0.2 V s^{-1} potential scan rate; ● starting potential for the initially cathodic scans. *E*, in V, is referred to SCE; *i* in μA.

TABLE 1. Reduction potentials

Compound	$E^{r}_{1/2}$ /V *vs.* SCE
1	-1.355 [a]; -1.340 [b]
2	-1.150 [a]; -1.145 [b]
3	-1.160 [a]; -1.165 [b]
4	-1.215 [a]; -1.20 [b,c]

[a] AN solvent. [b] CH_2Cl_2 solvent. [c] $(E_p)_c$ value at 0.2 V s^{-1}; the associated backward peak is undetectable.

was in all cases within the range 80 to 100 mV, in the absence of any IR drop compensation, and one electron was involved (*vide infra*) in the redox process. Hence, we concluded that a one-electron reversible simple electrode reduction is operative, any irreversible chemical reaction following the charge transfer being slow enough not to be significant on the relatively short voltammetric time scale. Table 1 summarizes the $E^{r}_{1/2}$ values for compounds **1**–**4**.

It is evident from these data that, for compounds **2**, **3** and **4**, the nature of the ligand in the fourth position has only a minor effect on the reduction potential. There is a small cathodic shift on passing from triphenylphosphine to pyridine and finally to acetonitrile. A more marked difference is noted for the chloro-derivative (**1**). Conductivity measurements proved that this complex dissociates only to an extent of *ca.* 10% in AN, and dissociation is negligible in dichloromethane. The basically neutral character of the electroactive species accounts for the shift of the reduction potential towards more negative values. The closeness of the values found in the two different solvents suggests that solvation effects play only a minor role.

Controlled potential electrolyses were performed at the potentials of peak A (150 mV cathodic to the peak potential) on AN solutions of the **1**, **2**, **3** and **4** derivatives. One electron per molecule of electrolyzed species was used, and in all cases except for compound **4**, the same peak system was recorded at the end of the electrolysis. Of course, the anodic peak was now recorded on a direct anodic scan starting at the electrolysis potential and the cathodic peak was detected on the reverse scan as a directly associated backward response. In the case of complex **4** a slow rearrangement seems to take place during the long time (*ca.* 1 h) of the exhaustive electrolysis, since an additional anodic-cathodic peak system, shifted cathodically by about 250 mV, was recorded at the end of these experiments.

Within two to five hours after completion of the electrolyses, all reduced platinum species had undergone spontaneous reoxidation, though the solutions were kept under an argon flow. The voltammetric peaks recorded at the end of this process indicate that the chloro-derivative reoxidizes to the initial neutral compound, that the acetonitrile adduct changes to the oxidized form of the second redox couple monitored at the end of the exhaustive reduction, and the phosphine complex reoxidizes, mainly to the starting oxidized form [^{31}P NMR (CD_3CN): δ 19.9 ppm, $J(Pt{-}P) = 4439$ Hz] and, to a minor extent, to the same product as the acetonitrile complex. The pyridine adduct also does this. The species the acetonitrile adduct give rise to is being identified.

The ^{31}P-NMR spectra on the spontaneously reoxidized solutions of the phosphine derivative revealed that a considerable amount of phosphorus was present in the solution as triphenylphosphine oxide. We have also reduced complex **2** in the presence of various amounts of phosphine (up to a 10:1 excess). The ^{31}P NMR spectra show that in the reoxidized solutions, various amounts of triphenylphosphine oxide are present as well as complex **2**. Significant spontaneous oxidation of triphenylphosphine to triphenylphosphine oxide can be ruled out, as shown by suitable blanks. We cannot explain these results at the moment but we are currently trying to identify the species responsible for this oxidation.

3.2. *Spectroelectrochemistry*

We recorded the EPR spectra of exhaustively reduced solutions of the different compounds, in pure AN and in AN–CH_2Cl_2 (9:1 or 8:2) mixed solutions, both at liquid nitrogen and at room temperatures. The complexity of the heterocyclic ligand, containing different nuclei (some of which nearly equivalent) capable of coupling to the unpaired electron, makes an exhaustive analysis of the spectra rather difficult. However, some information can be extracted. In particular, the presence or absence of hyperfine ^{195}Pt nuclear splitting ($I_{^{195}Pt} = 1/2$; natural abundance *ca.* 34%) can be used to determine the degree of interaction with the metal centre [13,14,18,19]. For this reason spectra were recorded on the different compounds under comparable experimental conditions of solvent, temperature, and resonance frequency.

Figure 2a shows the X-band EPR spectrum of electrogenerated $[LPt(PPh_3)]$, in AN solution, at liquid nitrogen temperature (100 K). The intense signal is broad ($g_{av} = 1.996$) and no hyperfine ^{195}Pt nuclear splitting is evident. Any magnetic coupling of nitrogen nuclei in the ligand is also undetectable, due to the linewidth (ΔH (100 K) $> a(N)_{aniso}$). Upon raising the temperature of the AN solution above the glass–fluid phase transition, the EPR lineshape becomes isotropic and at room temperature it displays a well-resolved hyperfine pattern. Figure 2b shows the 300 K X-band EPR spectrum. The observed g_{iso} value (1.995) is quite close to the g_{av} calculated from the glassy solution spectrum.

The resolution of the complex hyperfine pattern strongly suggests that the lineshape is due mainly to the strong magnetic interaction of the unpaired electron with the nuclei of L. Further, there is no suggestion of ^{195}Pt satellites in the room temperature spectrum. Minor interaction of the unpaired electron with the metal cannot be excluded, because the satellites may be hidden by the ligand hyperfine structure.

The solvent markedly affects the overall lineshape of the spectrum, both at liquid nitrogen and room temperatures. The spectrum recorded in AN–CH_2Cl_2 solution at liquid nitrogen temperature has a rhombic structure; the lineshape resembles those reported in refs. 13 and 18 for the $[(bpy)PtCl_2]^-$ and in ref. 19 for the $[(bpym)PtPh_2]^-$ species, also showing two satellites, hence suggesting partial metal character for the unpaired electron. The corresponding room temperature spectrum is less resolved than that of pure AN solution, probably as a consequence of a large linewidth.

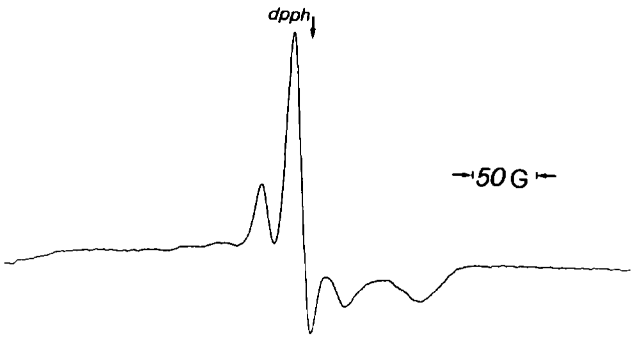

Fig. 3. EPR spectrum of $[LPt(CH_3CN)]$, 8:2 AN:CH_2Cl_2 solution, at liquid nitrogen temperature.

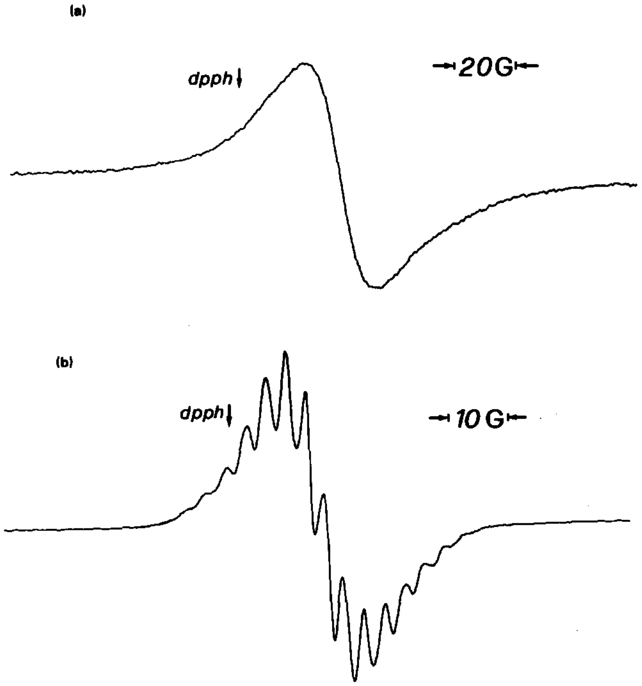

Fig. 2. EPR spectra of $[LPt(PPh_3)]$, AN solution, at liquid nitrogen (a) and room (b) temperature.

There are differences in the X-band EPR spectra of the electrogenerated $[LPt(CH_3CN)]$ in pure AN and in AN–CH_2Cl_2 solutions. Though spectra at liquid nitrogen temperature in AN solvent show a single broad signal ($g_{iso} = 1.993$) with a poorly resolved hyperfine pattern, in room temperature spectra there is a broad main absorption with ill-defined hyperfine structure and two platinum satellite peaks. As in the case of compound **2**, the liquid nitrogen spectrum in AN–CH_2Cl_2 mixed solution (see Fig. 3) displays a rhombic structure [18,19], while the room temperature spectrum in this solvent medium consists of a single line and two less intense platinum satellites. In AN, chloride and pyridine ligands lead to broad-band, unresolved glass spectra, but the corresponding room temperature absorption patterns suggest partial metal character, hyperfine interaction with N and H nuclei being undetectable, and well resolved satellite peaks due to interaction with ^{195}Pt being evident.

Thus the X-band EPR spectra are useful indications of the electronic distribution in paramagnetic species containing platinum in the formal oxidation state I. The hyperfine ^{195}Pt coupling constants are in all cases rather small, 20 to 30 G, comparable to those found for the $[(bpy)PtCl_2]^-$ [13] and $[(bpym)PtPh_2]^-$ [19], suggesting only minor metal-based character for the extra electron. From the line shapes, we conclude that the metal character of the unpaired electron in triphenylphosphine derivative is lower than in the other complexes. The degree of metal character of the electron in similar compounds may be a useful element for predicting relative reactivities in the series of compounds.

Acknowledgments

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