

In Fig. 3 is given the methanol electrooxidation at Ag/GC which illustrates the quite different behaviour of alcohol on non-noble electrode surface. Methanol is active only very deeply in the oxide region at Ag/GC electrode. The similar behaviour exhibits isopropanol. That pointed out the advantage of the utilization of noble-metal electrodes in electrooxidation of mono-hydroxyl alcohols taking into account the area of the potential before the oxide formation. Another kind of the modification of GC probably can be more promising.

The electrooxidation of CH<sub>2</sub>O is observed in the area before the oxide formation at Ag/GC electrode in 0.1 M NaOH (5). The advantage of that reaction on noble metal surfaces is appearance of much higher anodic currents at Au and Pt (~ 20 mA/cm<sup>2</sup>) (4).

The examination of the electrooxidation of polyhydroxyl alcohols at Ag/GC electrodes is in progress and comparative study with Pt(1) and Au(2) electrodes should be given separately. The preliminary results promise the different behaviour that has been obtained with mono-hydroxyl alcohol and CH<sub>2</sub>O.

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#### REDOX PROPERTIES OF HYDRIDE COMPLEXES OF Pt(II) WITH A METAL-CARBON SINGLE BOND

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#### Abstract

The electrochemical investigation, by cyclic voltammetry and controlled potential electrolysis at Pt electrodes, is reported for complexes trans- or cis-[PtHRL<sub>2</sub>] [R = cyano- or trifluoro-alkyl, phenyl or cyano-phenyl; L = tertiary phosphine or 1/2 diphosphine] in acetonitrile, and they are shown to undergo Pt-H bond cleavage (with proton extrusion) upon anodic oxidation at ca. 0.8 ~ 1.7 V vs. SCE.

#### Introduction

We have been investigating [1-3] the activation of chemical bonds by electron transfer in palladium and platinum complexes with metal-carbon double bonds, in particular the monocarbenes cis-[MCl<sub>2</sub>{CN(R)CH<sub>2</sub>CH<sub>2</sub>X} (L)] (M = Pd or Pt; L = isocyanide or organophosphine, R = alkyl or aryl, X = NH or O), the dicarbenes cis-[MCl<sub>2</sub>{CN(R)CH<sub>2</sub>CH<sub>2</sub>X} ]<sub>2</sub> and the dinuclear diaminecarbenes {MCl[μ-CNCH<sub>2</sub>CH<sub>2</sub>Y] (PPh<sub>3</sub>) }<sub>2</sub> (Y = NR or O). These species undergo anodic processes involving electroinduced proton extrusion upon heterolytic N-H or C-H bond cleavage [1,2].

In the present study, we have extended this type of investigation to various hydride complexes with Pt(II)-carbon single bonds and observed that proton loss results from metal-hydride bond cleavage induced by electron transfer.

Results and discussion

The complexes investigated are of the types trans- or cis-[PtHRL<sub>2</sub>] [R = C<sub>3</sub>H<sub>6</sub>CN, CH<sub>2</sub>CF<sub>3</sub>, CF<sub>3</sub>, Ph or C<sub>6</sub>H<sub>4</sub>CN-2; L = PPh<sub>3</sub>, PEtPh<sub>2</sub>, PMe<sub>2</sub>Ph, P(CH<sub>2</sub>Ph)Ph<sub>2</sub> or 1/2 diphosphine] and the studies were performed by cyclic voltammetry (CV) and controlled potential electrolysis (CPE), in 0.2 M [Bu<sub>4</sub>N][BF<sub>4</sub>]/NCMe, at a Pt disc or a Pt gauze electrode, respectively.

Commonly the electrochemical studies were hampered by fast electrode deactivation. Therefore, in order to get reproducibility, polishing of the disc electrode was required after running each cyclic voltammogram; moreover, along each electrolysis, the Pt-gauze electrode had also to be frequently cleaned.

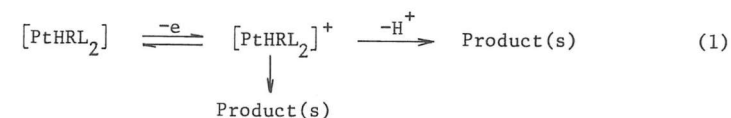
A further difficulty resulted from the recognized low stability of some of these complexes in solution, namely cis-[PtH(CH<sub>2</sub>CF<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>] which is known [4] to undergo reductive elimination of CH<sub>3</sub>CF<sub>3</sub> (under our experimental conditions, however, we did not detect appreciable decomposition of this complex along the CV study).

Although we did not observe any redox wave in the -2.0 to +2.0 V (vs. SCE) range for a number of these compounds — e.g., trans-[PtH(CF<sub>3</sub>)L<sub>2</sub>] (L = PMe<sub>2</sub>Ph, PEtPh<sub>2</sub>, P(CH<sub>2</sub>Ph)Ph<sub>2</sub> or PPh<sub>3</sub>) and [PtH(CH<sub>2</sub>CF<sub>3</sub>)(CNC<sub>6</sub>H<sub>4</sub>OMe-4)(PPh<sub>3</sub>)<sub>2</sub>] —, others (Table) exhibit by cyclic voltammetry an irreversible anodic wave at E<sub>p</sub><sup>ox</sup> from ca. 0.8 V, for trans-[PtH(C<sub>3</sub>H<sub>6</sub>CN)(PPh<sub>3</sub>)<sub>2</sub>] (Fig.) or trans-[PtH(C<sub>6</sub>H<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (which also presents a second irreversible oxidation wave at 1.9 V), up to ca. 1.7 V, for cis-[PtH(CH<sub>2</sub>CF<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>].

The current-function for that wave does not vary significantly with the scan rate, indicating the involvement of a constant number of electrons\*. By controlled potential electrolysis, the transfer of a maximum of one electron (experimental values, which should be taken cautiously — see above —, lie usually between ca. 0.6 and 1.0

\* Values of ca. 0.35 and ca. 0.3 for the transfer coefficient (α) have been estimated for the anodic waves of trans-[PtH(C<sub>3</sub>H<sub>6</sub>CN)(PPh<sub>3</sub>)<sub>2</sub>] and trans-[PtH(C<sub>6</sub>H<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>], respectively, from the slope of the plot of E<sub>p</sub><sup>ox</sup> vs. log v, i.e., ΔE<sub>p</sub>/Δlog v = 30/αn (mV) [5], where v is the scan rate (mV s<sup>-1</sup>) and n is the number of electrons involved (measured by CPE).

electron) appears to occur, thus suggesting the formation of Pt(III) species. However, such products of oxidation are not stable and proton loss at an appreciable extent (ca. 0.1-0.7 H<sup>+</sup>) seems to result from the anodic heterolytic cleavage of the Pt-H bond (eq.1); this proton liberation has been measured by potentiometric titration of the electrolyzed solution.



Therefore, the complexes of the present study present quite a distinct electrochemical behaviour from that quoted [6] for other Pt(II) species

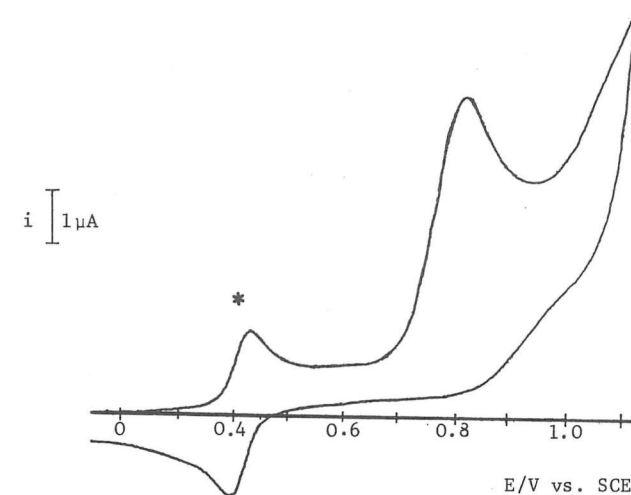


Fig. Cyclic voltammogram of trans-[PtH(C<sub>3</sub>H<sub>6</sub>CN)(PPh<sub>3</sub>)<sub>2</sub>] in 0.2 M [Bu<sub>4</sub>N][BF<sub>4</sub>]/NCMe, at a Pt disc electrode (100 mV s<sup>-1</sup>).

\* Ferrocene (internal standard).

Table. Summary of electrochemical <sup>a</sup> and potentiometric titration data for hydride complexes of platinum(II).

Complex	$E_p^{ox}/V$ <sup>b</sup>	$n(e^-)$ <sup>c</sup>	$n(H^+)$ <sup>d</sup>
<i>trans</i> -[PtH(C <sub>3</sub> H <sub>6</sub> CN)(PPh <sub>3</sub> ) <sub>2</sub> ]	0.84	0.8	0.6
<i>trans</i> -[PtH(C <sub>6</sub> H <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>e</sup>	0.77	0.6	0.3
<i>trans</i> -[PtH(C <sub>6</sub> H <sub>4</sub> CN-2)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>f</sup>	1.24	0.8	0.1
<i>cis</i> -[PtH(CH <sub>2</sub> CF <sub>3</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>g</sup>	1.65	0.8	0.7
[PtH(CH <sub>2</sub> CF <sub>3</sub> )(Ph <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> )]	1.29	— <sup>h</sup>	—
[PtH(CF <sub>3</sub> )(Ph <sub>2</sub> PCH <sub>2</sub> CH <sub>2</sub> PPh <sub>2</sub> )] <sup>i</sup>	1.45	0.5	0.2
[PtH(CF <sub>3</sub> )(Ph <sub>2</sub> PCH=CHPPh <sub>2</sub> )]	1.27	1.0	0.5

<sup>a</sup> Studies performed at a Pt disc (CV) or gauze (CPE) electrode, in 0.2 M [Bu<sub>4</sub>N][BF<sub>4</sub>]/NCMe. <sup>b</sup> Values in V vs. SCE, measured by CV at 100 mV s<sup>-1</sup>, by using as internal reference the couple [Fe(η<sup>2</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sup>0/+</sup> [E<sub>1/2</sub><sup>ox</sup> = 0.45 V vs. SCE]. <sup>c</sup> Values measured by CPE at the anodic wave; they should be taken cautiously (see the text). <sup>d</sup> Measured by potentiometric titration of the electrolyzed solution (by using a solution of NaOH which was standardized by titration against benzoic acid in NCMe) and corrected for background effects. <sup>e</sup> A second and irreversible wave is observed at E<sub>p</sub><sup>ox</sup> = 1.90 V. <sup>f</sup> An irreversible cathodic wave at E<sub>p</sub><sup>red</sup> = -1.76 V is observed after CPE at the anodic wave. <sup>g</sup> An irreversible cathodic wave at E<sub>p</sub><sup>red</sup> = -1.66 V is observed after CPE at the anodic wave. <sup>h</sup> Not possible to measure on account of the strong adsorption at the electrode surface. <sup>i</sup> An irreversible cathodic wave at E<sub>p</sub><sup>red</sup> = -1.62 V is observed after CPE at the anodic wave.

of the type *cis*- or *trans*-[PtCl<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] which undergo a two-electron oxidation to Pt(IV) at a higher potential (ca. 1.8-2.0 V range).

However, a related example of anodically induced deprotonation of a hydride-Pt(II) complex has been reported [7] for *trans*-[PtHCl(PEt<sub>3</sub>)<sub>2</sub>], but it involves an overall two-electron process with formation of a product with the metal in the initial oxidation state (II).

Apart from H<sup>+</sup>, the other products of the anodic oxidation of our complexes have not been identified. Nevertheless, in some cases, upon controlled potential electrolysis at the abovementioned anodic wave, a cathodic wave is observed at E<sub>p</sub><sup>red</sup> = -1.76, -1.66 or -1.62 V, for the species anodically derived from *trans*-[PtH(C<sub>6</sub>H<sub>4</sub>CN-2)(PPh<sub>3</sub>)<sub>2</sub>], *cis*-[PtH(CH<sub>2</sub>CF<sub>3</sub>)(PPh<sub>3</sub>)<sub>2</sub>] or [PtH(CF<sub>3</sub>)(Ph<sub>2</sub>PCH=CHPPh<sub>2</sub>)], respectively.

#### Final Comments

This study indicates that a number of hydride complexes of the type [PtHRL<sub>2</sub>] undergoes an anodic process which partially involves proton loss upon Pt-H bond cleavage, in agreement with the expected increase of the acidic character as a result of the metal oxidation. The final complex products have not yet been characterized but, in some cases, they appear to be redox active, undergoing an irreversible cathodic reduction.

The possibility of electroactivation of the platinum-carbon bond in these processes is under investigation.

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#### REDOX PROPERTIES OF SOME TRYPTAMINE-DERIVED SALICYLALDIMINES AND OF THEIR TETRA-COORDINATE COBALT(II), NICKEL(II) OR COPPER(II) COMPLEXES

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#### Summary

The redox properties of various Schiff bases (HL, derived from condensation of tryptamine with salicylaldehyde derivatives) and of some of their complexes  $[ML_2]$  ( $M = Co, Ni$  or  $Cu$ ) have been studied by cyclic voltammetry and cathodic controlled potential electrolysis, in aprotic media. They present both anodic and cathodic processes which, in the case of the complexes, can be either ligand or metal centred, the redox potentials of the latter, for both the  $M(II/III)$  and  $M(I/II)$  redox pairs, following the order:  $Co < Ni < Cu$ .

#### Introduction

Although complexes with Schiff bases presenting a bulky group can exhibit unusual properties, only a limited number of them have been reported [1] to contain an indole group in particular within a derivative of tryptamine (a species with a recognized biological activity). Therefore, in pursuit of our interest on the redox properties of complexes with biological significance [2], we have embarked upon the investigation of the electrochemical behaviour of complexes with such a type of Schiff bases, and we now report the preliminary results we have obtained.