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Electronic and Electrochemical Properties of Platinum(II) and Platinum-mercury-carboxylato Complexes Containing 2-$Me_2NCH_2C_6H_4$-, 2,6-$(Me_2NCH_2)_2$-C_6H_3- and 2-$Me_2NC_6H_4CH_2$ Ligands

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The organoplatinum(II) compounds $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}PtBr]$ *and* cis-$[(C\text{-}N)_2Pt]$ *(C-N =* 2-$Me_2NCH_2C_6H_4$, 2-$Me_2NC_6H_4CH_2$*) can be chemically irreversibly oxidized in the potential range 1.00 to 1.35 V* vs. *an Ag/AgCl electrode, whereas the organoplatinum–mercury complexes* $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(RCO_2)PtHg(O_2CR)Br]$ *and* $[(C\text{-}N)_2(\mu\text{-}O,O'\text{-}RCO_2)PtHg(O_2CR)]$ *(R = Me) could only be reduced, in the potential range –0.20 to –0.70 V, resulting in deposition of metallic mercury on the electrode. Reoxidation of the mercury occurred in the potential range +1.00 to +1.20 V.*

Both the organoplatinum(II) and organoplatinum–mercury complexes (R = i-Pr) showed strong U.V. absorptions below 320 nm, which are assigned to Metal-to-Ligand Charge Transfer transitions. The bis-benzyl platinum–mercury compound $[(2\text{-}Me_2NC_6H_4CH_2)_2(\mu\text{-}O,O'\text{-}i\text{-}PrCO_2)PtHg(O_2C\text{-}i\text{-}Pr)]$ *showed an additional strong absorption, assigned to a* σ–σ^* *transition, at 335 nm.*

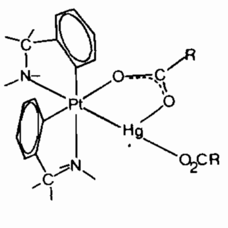
The results have been interpreted as indicating the presence for the Pt–Hg complexes of a metal–metal bond, either covalent or donative, involving interaction of an initially filled, high energy orbital on Pt and an empty orbital on Hg.

Introduction

In a previous paper we reported the synthesis of the organoplatinum–mercury complexes $[(C\text{-}N)_2(RCO_2)PtHg(O_2CR)]$ (I) (C-N = 2-$Me_2NCH_2C_6H_4$, 2-$Me_2NC_6H_4CH_2$) and $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(RCO_2)PtHg(O_2CR)Br]$ (II) starting from the organoplatinum(II) compounds *cis*-$[(C\text{-}N)_2Pt]$ and $[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}PtBr]$ [1, 2]. Their formation has been rationalized by initial nucleophilic attack of the Pt atom on Hg. For the final product I a structure containing a covalent Pt–Hg bond has been established by X-ray diffraction. Compounds of type II have been proposed to contain a Pt-to-Hg donor bond which is stable (see ref. 2). By contrast, the platinum–mercury complex, isolated from the reaction of $Hg(O_2CR)_2$ and *trans*-$[(Me_2NCH_2C_6H_4)_2Pt]$, was unstable and the mononuclear compound $[(2\text{-}Me_2NCH_2C_6H_4)_2Pt^{IV}(O_2CR)_2]$ was formed upon elimination of mercury(0).

In order to obtain a better insight into the electronic properties of the organoplatinum and organoplatinum–mercury compounds we have investigated both the electrochemical behaviour and electronic absorption spectra of these and related compounds. The present work has the limited aim of describing how the individual units constituting the complexes behave in solution.

In this paper we report the results of this investigation and show that the high energy electrons in the organoplatinum(II) compounds occupy a bonding orbital in the Pt–Hg complexes.



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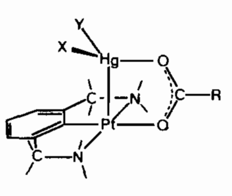

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TABLE I. Electrochemical Data.[a]

	Compound	E_p (V)	E_p (V)
		Oxidation	Product Reduction
A	$Me_2NCH_2C_6H_5$	1.40	–0.77
B	$2\text{-}Me_2NC_6H_4CH_3$	1.45	–0.50, 0.41
C	$1,3\text{-}(Me_2NCH_2)C_6H_4$	1.42	–0.20, –0.77
	Hg[b]	1.09	
1	*trans*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pt]$	0.87, 1.17, 1.31	
2	*cis*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pt]$	1.23	0.22
3	*cis*-$[(2\text{-}Me_2NC_6H_4CH_2)_2Pt]$	1.05	
4	$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}PtBr]$	1.32	0.10
5	*cis*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pd]$	1.30	
		Reduction	Product Oxidation
6	$[(2\text{-}Me_2NCH_2C_6H_4)_2(\mu\text{-}O,O'\text{-}MeCO_2)PtHg(O_2CMe)]$[c]	–0.37	1.32
7	$[(2\text{-}Me_2NC_6H_4CH_2)_2(\mu\text{-}O,O'\text{-}MeCO_2)PtHg(O_2CMe)]$	–0.38, –0.59	1.04, 1.09
8	$[\{2,6\text{-}(Me_2NCH_2)_2C_6H_3\}(MeCO_2)PtHg(O_2CMe)Br]$	–0.24, –0.70	1.09
	$[Hg(O_2C\text{-}i\text{-}Pr)_2]$	–0.25	1.02, 1.18

[a] From cyclic voltammetry; scan rate 200 mV/sec, measured in CH_2Cl_2. [b] Liquid mercury in combination with a platinum electrode. [c] Measured in acetone.

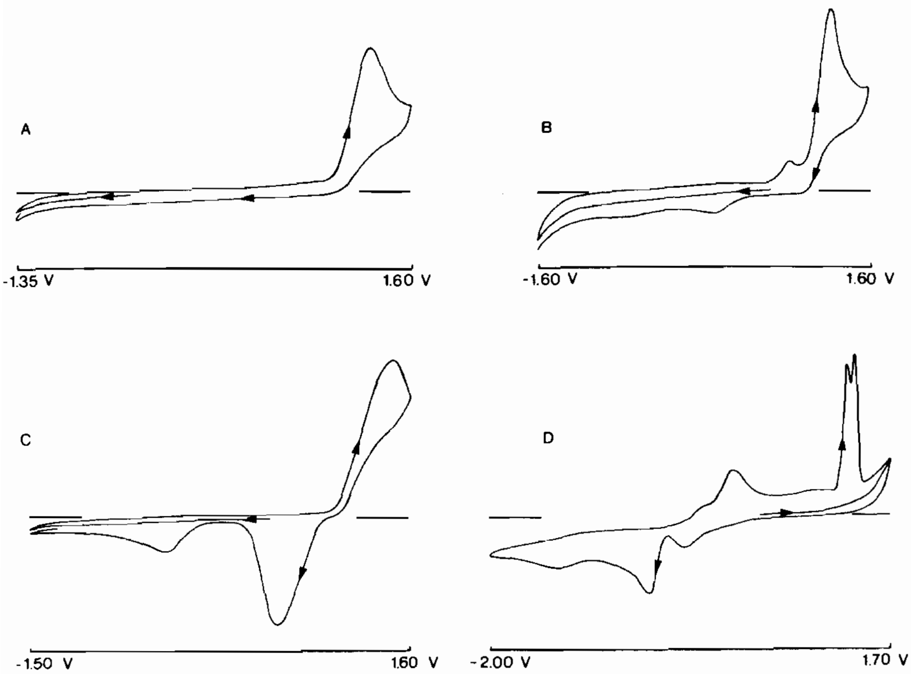

Fig. 1. Cyclic voltammograms of the oxidation of A: *cis*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pd]$ (5), B: *cis*-$[(2\text{-}Me_2NCH_2C_6H_4)_2Pt]$ (2), and C: $2\text{-}Me_2NC_6H_4Me$ and the reduction of D: $[(2\text{-}Me_2NCH_2C_6H_4)_2(\mu\text{-}O,O'\text{-}MeCO_2)PtHg(O_2CMe)]$ (6).

Experimental

The electrochemical measurements were made with three electrode Bruker E310 or PAR 174 A instruments with platinum working and auxiliary electrodes. Measurements were made on *ca.* 10^{-3} mol dm^{-3} complex solution in acetone or dichloromethane (0.1 mol dm^{-3} Bu_4NClO_4), with potentials referred to an Ag/AgCl (0.1 mol dm^{-3} LiCl–acetone) reference electrode [3]. Cyclic voltammograms were taken with a scan rate of 200 mV s^{-1}. All values reported in this paper are measured on the first and second scan voltammograms. UV–visible spectra were obtained with a Cary 14 spectrophotometer. Experiments involving low temperature measurements were done in EPA solution (5:5:2 ethanol/pentane/acetone). The compounds were prepared according to literature methods [2, 4, 5].

Results and Discussion

Electrochemistry

The electrochemical redox behaviour of the organometal(II) compounds, organoplatinum–mercury complexes and related compounds, summarized in Table I, have been studied at a platinum electrode *vs.* an Ag/AgCl electrode in dichloromethane solution with the cyclic voltammetric technique.

In the first cycle of the cyclic voltammograms of the organometal complexes 1–5, only oxidation waves are observed. Compounds 2–5 could be oxidized in a single step in the potential range 1.05–1.40 V (Table I; Figure 1a, b). For compound 1 three oxidation waves were observed (0.87, 1.17 and 1.31 V), the relative intensity varied with the number of cycles (*vide infra*). All the oxidations are chemically irreversible as evidenced by the cyclic voltammograms, which showed only very small or no new cathodic waves after the first oxidation (Table I). No attempt has been performed to identify the oxidation products.

The easy oxidation of the organoplatinum complexes is in line with their ability, found earlier, to donate electrons to post-transition metal complexes [1]. The instability of the oxidation products may be related to the generally found instability of mononuclear platinum(III) complexes. Vlček reported irreversible one-electron oxidation of the d^8-square planar complexes [L_2(CO)IrX] and proposed the formation of metal–metal bonded species resulting from dimerization of the so produced iridium(II) species [6]. Whether a similar reaction occurs for the present platinum complexes is not known.

It is noteworthy that reversible oxidation, and even complete oxidation series, have been reported for various platinum(II) complexes but these always contain ligand systems, like thiosemicarbazides, which are stable in several oxidation states [7].

The present results indicate that oxidation is the only electrochemical process occurring for the organoplatinum compounds within the potential limits of the solvent and, as the oxidation is irreversible, the products formed are seemingly unstable under experimental conditions.

The complexes studied show some influence of the coordination sphere upon the E_p value (see Table I). We see a lower E_p value for the benzylic compound 3 compared with the aryl compounds 2 and 4. The oxidation potential of the *cis*-palladium compound 5 is higher than the value of the corresponding *cis*-platinum compound 2, in line with the lower basicity for Pd. For the *trans*-platinum compound 1 a somewhat different behaviour was observed, it showed several oxidation waves, one at a much lower E_p (0.87 V) and till now we have no explanation for this.

Chemical oxidations of d^8-square planar complexes, which are very common for Ir and Rh and, somewhat less so for Pt metal complexes, normally proceed via an oxidative addition process, involving the initially filled high energy d_{z^2} orbital, and in which the coordination sphere of the metal centre is extended. It cannot be deduced whether the electrochemical oxidation process also involves the electrons in the high energy d_{z^2} orbital, but this seems to be very likely.

The proposal that the oxidation occurs at the metal centre and not at the ligand system is supported by the following facts: *i* the free ligands in their protonated forms (A–C) showed oxidation at higher E_p values (Table I); *ii* their products are electrochemically active (Fig. 1c) and *iii* the organoplatinum–mercury compounds did not show such oxidation waves.

The organoplatinum–mercury complexes 6–8 and [Hg(O_2C-i-Pr)$_2$] did not produce oxidation waves in the first cycle of the cyclic voltammogram. However, the compounds could be reduced in the potential range –0.20 to –0.70 V (Table I). In a few cases, more than one reduction wave was observed, probably to assign to a sequence of reduction steps involving either only the starting complex or also the decomposition products. In either case, all these reductions are chemically irreversible and result in deposition of mercury on the platinum electrode and formation of new electrochemically active species [8]† as deduced from new anodic waves in the second and further cycles. Furthermore, the potentials of the various oxidation and reduction waves change drastically within the first five cycles. This behaviour must be attributed to instability of the electrode system resulting from deposition of mercury on the platinum working electrode. This coating of the electrode is deduced from oxidation spikes observed around +1.10 V after the first cycle (Fig. 1d and Table I), which can be explained by the oxidation of pure mercury and mercury which has

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†Elimination of mercury has also been observed upon reduction of mercury–metal carbonyl complexes, resulting in metal carbonyl anions [8].

TABLE II. Electronic Absorption Data.[a]

Compound	ν (nm)	$\epsilon \times 10^{-3}$
1 *trans*-$[(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_2\text{Pt}]$	307	18.6
	265	25.4
2 *cis*-$[(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_2\text{Pt}]$	305	14.5
	260	19.0
3 *cis*-$[(2\text{-Me}_2\text{NC}_6\text{H}_4\text{CH}_2)_2\text{Pt}]$	273	17.4
4 $[\{2,6\text{-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}\text{PtBr}]$	281	17.0
5 *cis*-$[(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_2\text{Pd}]$	262	24.5
6 $[(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_2(\mu\text{-}O,O'\text{-i-PrCO}_2)\text{PtHg(O}_2\text{C-i-Pr)}]$	298	25.4
7 $[(2\text{-Me}_2\text{NC}_6\text{H}_4\text{CH}_2)_2(\mu\text{-}O,O'\text{-i-PrCO}_2)\text{PtHg(O}_2\text{C-i-Pr)}]$	283	23.4
8 $[\{2,6\text{-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}(\text{i-PrCO}_2)\text{PtHg(O}_2\text{C-i-Pr)Br}]$	260	36.0

[a] Measured in $CHCl_3$.

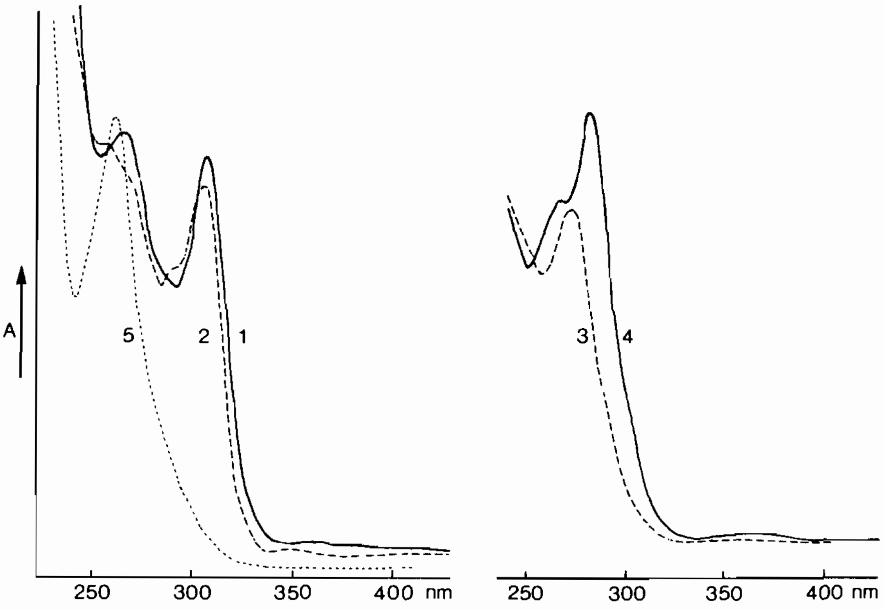

Fig. 2. Electronic absorption spectra of the organometal(II) complexes 1–5 (see Table II) in $CHCl_3$.

undergone a reaction with platinum [9]*. The electrode could be regenerated by stripping off the mercury by repeated scanning (5X) through the potential region 1.0 to 1.6 V.

Electronic Absorption Spectra

The electronic absorption spectra of the cyclometallated metal(II) complexes, as recorded in $CHCl_3$ solution, are presented in Fig. 2. Above 330 nm only very weak absorption bands are observed which are assigned to d–d transitions. Strong absorption bands are observed only between 330 and 250 nm (Table II), which agrees with the white colour of the compounds (below 250 nm the solvent starts to absorb).

The absorptions fulfil the criteria mentioned by Gray *et al.* [10] for the assignment of metal-to-ligand charge transfer transitions (MLCT) in square planar Rh and Ir complexes; *i.e.*, a high molar extinc-

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*Brubaker [9] has reported that mercury-coated platinum electrodes contain mercury in two different forms: one form exhibiting the electrochemical surface properties of pure mercury and a second which has undergone a reaction with platinum. The dissolution reactions were represented by the following equations: $2\ Hg \rightarrow Hg_2^{2+} + 2e^-$ and $PtHg_x \rightarrow Pt(black) + xHg^{2+} + 2x\ e^-$.

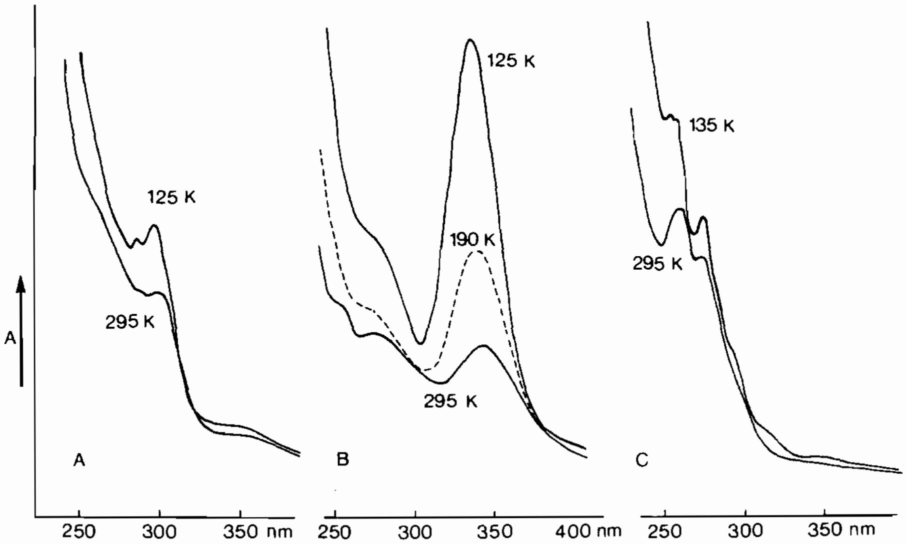

Fig. 3. The electronic absorption spectra of the organplatinum–mercury complexes 6 (A), 7 (B) and 8 (C) in EPA solutions at different temperatures.

tion coefficient (Table II), lack of intensity-decrease upon cooling, and an energy ordering third row metal < second row metal. The latter is shown by the compounds *cis*-[(2-$Me_2NCH_2C_6H_4)_2M$], M = Pt (2), M = Pd (5). The spectra of the *cis* and *trans* isomer of the aryl compound [(2-$Me_2NCH_2C_6H_4)_2Pt$] are quite similar, while for the benzyl compound *cis*-[(2-$Me_2NC_6H_4CH_2)_2Pt$] (3) MLCT absorptions are observed at shorter wavelengths when compared with the aryl compounds. This indicates that in the aryl compounds the MLCT transitions involve a ligand orbital which directly overlaps with the metal d-orbitals.

For the organoplatinum–mercury compounds 6–8 similar absorptions are observed in the 250–310 nm wavelength region with comparable extinction coefficients, and these can likewise be assigned to MLCT transitions (Table II and Fig. 3). The intensities of these bands increase somewhat upon lowering the temperature as a result of solvent contraction. For 6 an additional absorption is observed at 350 nm which is weak and only slightly temperature dependent, and thus likely to be due to a ligand-field transition. Compound 8 shows almost no absorption above 320 nm.

By contrast, compound 7 shows, besides the metal-to-ligand transitions, an intense absorption at 335 nm with a very strong temperature effect (Fig. 3b). Such an intense near-UV band that sharpens and intensifies upon cooling has been observed for several di- and poly-nuclear metal carbonyl complexes and the generally accepted assignment involves a σ–σ^* transition [11]. A common feature of those complexes is that all are known to have a two-electron metal–metal σ bond.

The present platinum–mercury complex 7 can also be thought of as containing a metal–metal σ bond [2] and, although the ligand system is completely different from those of the carbonyl complexes, the observed behaviour makes a σ–σ^* assignment for complex 7 appropriate.

While in some cases the observation of such strongly temperature dependent absorptions has been used as evidence for the presence of a direct metal–metal bond, the reverse is not necessarily true. Such absorptions are absent for the platinum–mercury complexes 6 and 8 (Fig. 3). Nevertheless, a direct platinum–mercury bond has been evidenced for the acetato analogue of 6 by a crystal structure determination [1]. In a way, the difference between 6 and 8 on the one hand and 7 on the other, might be related to the type of cyclometallated ligand, containing an aryl–Pt and an alkyl–Pt bond respectively.

Unfortunately, the present results do not give information about the ordening of the various energy levels and the relative position of the metal–metal bond in the platinum–mercury complexes.

Conclusions

The present results indicate that oxidation of organoplatinum(II) compounds is easily performed, though certain differences in oxidation potentials for the structurally related compounds remain unexplained. A similar oxidation of the organoplatinum–mercury complexes is not possible, which suggests that no high energy electrons are available. This can be explained by the presence of a direct platinum–mercury interaction, being either covalent or donative in nature, and as a result a reduced electron density at the platinum centre in the platinum–mercury compounds as compared with the organoplatinum(II) complexes. The presence of covalent M–M′ bond is supported for the platinum–mercury compound 7 by its UV spectrum showing, besides the normal MLCT transitions, an absorption which is very likely due to a σ–σ^* transition.

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