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# Reactions with nucleophiles and cathodic electrochemical behaviour of some neutral and cationic diamino-, dioxy- and aminooxycarbene complexes of palladium(II) and platinum(II)

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## Abstract

The bis-diaminocarbene complexes *cis*-$[Cl_2M\{\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2NH}\}_2]$ (M = Pt or Pd) react with one mole of the diphosphine *cis*-$Ph_2PCH{=}CHPPh_2$ (diphoe) in tetrahydrofuran at room temperature or in 1,2-dichloroethane at reflux for 8 h to form cationic derivatives *cis*-$[(diphoe)M\{\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2NH}\}_2]Cl_2$ (M = Pt, **1**; Pd, **2**) with chloride displacement. The cationic hydridocarbene complex *trans*-$[(PPh_3)_2Pt(H)\{\overline{COCH_2CH_2O}\}][BF_4]$ reacts with one mole of diphoe in $CH_2Cl_2$ at room temperature to cleave the ring of the dioxycarbene, generate $CO_2$ and $C_2H_4$, and form the cationic complex $[(diphoe)Pt(H)(PPh_3)][BF_4]$. The reaction of *trans*-$[(PPh_3)_2$-$Pt(H)\{\overline{COCH_2CH_2O}\}][BF_4]$ with $Cl^-$ ions in $CH_2Cl_2$ gives the ring-opened alkoxycarbonyl complex *trans*-$[(PPh_3)_2Pt(H)\{C(O)OCH_2CH_2C\}]$, *trans*-$[(PPh_3)_2Pt(H)(Cl)]$, $ClCH_2CH_2OH$ and $Pt^0$ species. The cathodic behaviour of the diaminocarbene complexes *cis*-$[Cl_2Pd\{\overline{CN(R)CH_2CH_2NH}\}(L)]$ (L = $PPh_3$, R = $C_6H_4OMe$-*p* or $^tBu$; L = $CN\,^tBu$, R = $^tBu$; L = $PPhMe_2$, R = $C_6H_4CH_2Cl$-*o*), as well as of the aminooxy- and dioxy-carbene compounds *trans*-$[(PPh_3)_2Pt(X)(\overline{COCH_2CH_2N}CH_2CH{=}CH_2)][BF_4]$ (X = Cl or Br) and *trans*-$[(PPh_3)_2Pt(H)(\overline{COCH_2CH_2O})][BF_4]$, has been studied by cyclic voltammetry (CV) and controlled potential electrolysis (CPE) in aprotic media. They exhibit an irreversible reduction wave ($E_p^{red}$ in the range $-1.50$ to $-2.0$ V *vs.* SCE), corresponding to two-electron and single-electron cathodic processes for the dichloro-complexes and the other species, respectively. Evidence for the

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formation of low-coordination number zerovalent palladium species is presented, and, in the case of the electrochemical reduction of the dioxycarbenehydrido-complex, quantitative fragmentation of the cyclic carbene to $CO_2$ and ethylene and liberation of dihydrogen were proved by gas chromatography.

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## Introduction

Palladium(II) and platinum(II) carbene complexes, in which the carbene contains one or two heteroatoms (N, O or S) directly bonded to the carbene carbon, have been reported to be fairly unreactive in comparison with carbene complexes of the early transition metals, particularly those of chromium, molybdenum and tungsten [1]. However, several interesting examples of reactions at the carbene moiety in complexes of $Pt^{II}$ have been described. For instance, modification of the carbene in cationic [2] and neutral [3] alkyl(alkoxy)carbene complexes may be achieved by reactions with amines or halide ions. The carbene ligands in cationic derivatives are, however, inert towards neutral reagents ($PR_3$, CO, RNC, pyridine) and $EtO_2CCH{=}CHCO_2Et$, $MeO_2CC{\equiv}CCO_2Me$, and $MeC{\equiv}CMe$ (even under UV irradiation for the last three). More recently, we have reported some deprotonation reactions of $Pt^{II}$ aminocarbenes [4,5] and reactions of phosphonium-substituted carbene complexes [6] to give platinaheterocycles [7]. The cleavage of the metal–carbene bond in certain hydridoalkyldiaminocarbene complexes of platinum(II) by reaction with chelating diphosphines has been recently reported [8].

In contrast to the extensive chemistry developed for complexes with metal–carbon multiple bonds [1,9,10], only a small number of electrochemical studies has been reported [11]. We have previously outlined [12] the redox behaviour of some rhenium phosphine complexes with a variety of metal–carbon multiply bonded ligands, particularly amino-carbyne-type complexes. The results were interpreted in terms of anodically or cathodically induced $\beta$-dehydrogenation to give the corresponding unprotonated complexes.

The present work will focus on the following aspects: (i) structure-reactivity relationships for $Pd^{II}$ and $Pt^{II}$ carbene complexes; (ii) the extension of the cathodic electrochemical study to carbene complexes of $Pd^{II}$ and $Pt^{II}$ derived from nucleophilic (rather than electrophilic) attack at ligating isocyanides.

## Experimental

### *General*

All reactions were carried out under a dinitrogen atmosphere. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. 1,2-Dichloroethane (DCE) was distilled from $Na_2CO_3$. All other solvents were of reagent grade and used without further purification. IR spectra were taken on a Perkin Elmer 983 spectrophotometer (abbreviations used: s = strong, m = medium). $^1H$ NMR spectra were recorded on a Bruker AM-400 spectrometer in $CD_2Cl_2$ solution; proton chemical shifts are reported relative to $Me_4Si$, taking the chemical shift of dichloromethane-$d_2$ as +5.32 ppm (abbreviations used: s = singlet, t = triplet, m = multiplet, br = broad; $J$ in Hz). $^{31}P$ NMR spectra at 32 MHz were recorded on a Varian FT 80A spectrometer in $CD_2Cl_2$ solution; phosphorus chemical shifts are from external $H_3PO_4$ 85%; positive chemical shifts are downfield from the reference (s = singlet;

*J* in Hz). The elemental analyses were performed by the Department of Inorganic, Organometallic and Analytical Chemistry of the University of Padova. The melting points were taken on a hot plate apparatus and are uncorrected. GC/Mass spectra were recorded on a QMD 1000 instrument.

### *Electrochemistry*

The electrochemical experiments were carried out either on an EG&G PAR 173 potentiostat/galvanostat and an EG&G PARC 175 Universal programmer, or on an HI-TEK DT 2101 potentiostat/galvanostat and an HI-TEK PP RI waveform generator. Cyclic voltammetry was undertaken in a two-compartment three-electrode cell at a platinum-wire working electrode, probed by a Luggin capillary connected to a silver wire pseudo-reference electrode; a platinum or tungsten auxiliary electrode was employed. Controlled-potential electrolyses were carried out in a three-electrode H-type cell with a mercury pool working electrode and a platinum gauze counter electrode in compartments separated by a glass frit; a Luggin capillary, probing the working electrode, was connected to a silver wire pseudo-reference electrode. Prior to the addition of the complex (for the CPE experiments), each electrolyte solution was pre-electrolyzed at the appropriate potential until a constant background current was observed. The peak potentials of the complexes were measured by cyclic voltammetry in 0.2 mol dm$^{-3}$ [$\mathrm{NBu_4}$][$\mathrm{BF_4}$]/NCMe and are quoted relative to the SCE by using as internal reference the [$\mathrm{Fe(\eta^5\text{-}C_5H_5)_2}$]$^{0/+}$ couple ($E^{\mathrm{ox}}_{1/2} = 0.42$ V *vs.* SCE). All the experiments were done under dinitrogen or argon.

The gas chromatographic analyses were performed with a Carlo Erba GC 6000 Vega series 2 gas chromatograph equipped with a SP 4290 integrator, a Porapak Q 80/100-packed column and a TCD detector. Helium was used as the carrier gas with a flow of 30 cm$^3$/min, and the temperature was programmed to increase, 2 min after each injection, from 50 to 150°C at a rate of 20°C/min; under these conditions, the retention times (sec) were as follows: dihydrogen (0.97), dinitrogen (1.17), argon (1.24), carbon dioxide (3.47) and ethylene (5.31). For quantification of the gaseous products of the cathodic CPE, carried out under argon, argon was used as the internal standard.

### *Starting complexes*

The complexes *cis*-[$\mathrm{Cl_2Pt\{\overline{CN(C_6H_4\text{-}\mathit{p}\text{-}OMe)CH_2CH_2N}H\}_2}$] [13], *cis*-[$\mathrm{Cl_2Pd\{\overline{CN(C_6H_4\text{-}\mathit{p}\text{-}OMe)CH_2CH_2N}H\}_2}$] [14], and *trans*-[$\mathrm{(PPh_3)_2Pt(H)(\overline{COCH_2CH_2O})}$]$\mathrm{BF_4}$ [15] were prepared according to published procedures.

### *Reactions of* cis-*bis(1,2-diphenylphosphino)ethylene (diphoe) with carbene complexes*

*(a) With* cis-*[$\mathrm{Cl_2M\{\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2N}H\}_2}$] (M = Pt or Pd): Synthesis of [(diphoe)$\mathrm{M\{\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2N}H\}_2}$] $\mathrm{Cl_2}$ (M = Pt, 1; M = Pd, 2).* To a solution of *cis*-[$\mathrm{Cl_2Pt\{\overline{CN(C_6H_4\text{-}\mathit{p}\text{-}OMe)CH_2CH_2N}H\}_2}$] (0.247 g, 0.40 mmol) in THF (30 ml) was added solid diphoe (0.160 g, 0.40 mmol) at room temperature. The reaction mixture was stirred for 20 h and then concentrated to small volume (5 ml). Addition of $\mathrm{Et_2O}$ (20 ml) precipitated **1** as a white solid. It was filtered off, washed with $\mathrm{Et_2O}$ (3 × 5 ml) and dried under vacuum. Yield 0.340 g (88%), m.p. 168–169°C. Anal. Found: C, 52.5, H, 4.50; N, 5.70; Cl, 7.70. $\mathrm{C_{42}H_{46}N_4Cl_2O_2P_2Pt}$

calcd.: C, 52.12; H, 4.79; N, 5.79; Cl, 7.32%. Complex **1** was obtained also in 80% yield when the reaction was performed in refluxing DCE for 8 h. IR (Nujol mull, cm$^{-1}$): $\nu(C{=}N)$ 1512 s; $\nu(NH)$ 3189 m. $^1H$ NMR ($CD_2Cl_2$): $\delta(NCH_2)$ 3.88 m, 3.36 m, 3.72 m; $\delta(OCH_3)$ 3.67 s; $\delta(NH)$ 10.78 br. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 48.4 s, $^1J(PPt)$ 2210.

The corresponding Pd complex **2** was prepared similarly starting from a solution of *cis*-$[Cl_2Pd\{\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2NH}\}_2]$ (0.220 g, 0.40 mmol) in THF (30 ml) and diphoe (0.160 g, 0.40 mmol) at room temperature. The reaction mixture was stirred for 20 h and then concentrated to 5 ml. The white solid obtained by adding $Et_2O$ (20 ml) was filtered off, washed with $Et_2O$ (3 × 5 ml) and dried under vacuum. Yield 0.315 g (85%), m.p. 121–122°C. Anal. Found: C, 59.7; H, 4.95; N, 6.00; Cl, 7.80. $C_{46}H_{48}N_4Cl_2O_2P_2Pd$ calcd.: C, 59.52; H, 5.21; N, 6.04; Cl, 7.64%. IR (Nujol mull, cm$^{-1}$): $\nu(C{=}N)$ 1510 s; $\nu(NH)$ 3179 m. $^1H$ NMR ($CD_2Cl_2$): $\delta(NCH_2)$ 3.67 m, 3.82 m; $\delta(OCH_3)$ 3.73 s; $\delta(NH)$ 10.81 br. $^{31}P$ $\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 46.69 s.

*(b) With* trans-*$[(PPh_3)_2Pt(H)(\overline{COCH_2CH_2O})][BF_4]$ (3).* A solution of *trans*-$[(PPh_3)_2Pt(H)(\overline{COCH_2CH_2O})][BF_4]$ (0.150 g, 0.17 mmol) in $CH_2Cl_2$ (20 ml) was treated with diphoe (0.075 g, 0.19 mmol) at room temperature. The solution immediately turned yellow. An IR spectrum showed the absence of the $\nu(Pt{-}H)$ at 2090 cm$^{-1}$ and the presence of an intense absorption at 2337 cm$^{-1}$ due to $CO_2$. After 1 h a white solid began to precipitate. Stirring was continued for 2 h and then the solution was reduced to 5 ml. On addition of $Et_2O$ (10 ml) a white solid precipitated, which was filtered off, washed with $Et_2O$ (10 ml) and dried under vacuum. It was identified as $[(diphoe)Pt(H)(PPh_3)][BF_4]$ (**3**). Yield 0.110 g (71%), m.p. 219–220°C. Anal. Found: C, 54.85; H, 4.05. $C_{42}H_{38}P_3BF_4Pt$ calcd.: C, 54.96; H, 4.17%.

The reaction described above was followed also by IR spectroscopy at room temperature ($CH_2Cl_2$ solution) and $^1H$ NMR, either at −73°C or at room temperature, for a $10^{-2}$ *M* $CD_2Cl_2$ solution of equimolar amounts of *trans*-$[(PPh_3)_2Pt(H)(\overline{COCH_2CH_2O})][BF_4]$ and diphoe. The results are reported in the Results and Discussion.

### *Reaction of $HBF_4$ with 1*

*Synthesis of $[(diphoe)Pt\{\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2NH}\}_2][BF_4]_2$ (1′).* A solution of **1** (0.322 g, 0.33 mmol) in THF (20 ml) was treated with $HBF_4$ (0.35 mmol, 3.5 ml of 0.1 M $Et_2O$ solution). A white solid immediately precipitated. It was filtered off, washed with $Et_2O$ (3 × 5 ml) and dried under vacuum. Yield 0.310 g (83%), m.p. 184–185°C. Anal. Found: C, 49.0; H, 5.05; N, 4.95. $C_{46}H_{46}N_4B_2F_8O_2P_2Pt$ calcd.: C, 49.42; H, 4.15; N, 5.01%. Complex **1′** was obtained also by reaction of **1** with an excess of $NaBF_4$ in acetone. IR (Nujol mull, cm$^{-1}$): $\nu(C{=}N)$ 1512 s; $\nu(NH)$ 3433 m. $^1H$ NMR ($CD_2Cl_2$): $\delta(NCH_2)$ 3.86 m, 3.67 m, 3.35 m; $\delta(OCH_3)$ 3.61 s; $\delta(NH)$ 8.40 br. $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$): $\delta$ 47.43 s, $^1J(PPt)$ 2209.

### *Reaction of $Cl^-$ ions with* trans-*$[(PPh_3)_2Pt(H)(\overline{COCH_2CH_2O})][BF_4]$*

A solution of *trans*-$[(PPh_3)_2Pt(H)(\overline{COCH_2CH_2O})]BF_4$ (0.293 g, 0.33 mmol) in THF (20 ml) was treated with bis(triphenylphosphine)iminium chloride (PPNCl) (0.190 g, 0.33 mmol). The reaction was followed by IR at room temperature and by

$^1H$ NMR at low temperature (see Results and discussion). After 10 h the solution was concentrated. On addition of $Et_2O$ (10 ml), a white solid precipitated. It was filtered off, washed with $Et_2O$ ($2 \times 2$ ml) and identified as *trans*-$[(PPh_3)_2Pt(H)Cl]$ [yield 0.190 g (60%)], whose $^1H$ NMR data [$CD_2Cl_2$ solution: $\delta$ – 16.22(t), $^2J(HP)$ 12.2, $^1J(HPt)$ 1192] are in agreement with those previously reported [16].

## Results and discussion

### *Reactions with diphoe*

The bis-diaminocarbene complexes *cis*-$[Cl_2M\{\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2N}H\}_2]$ (M=Pt or Pd) react with 1 equiv. of diphoe according to eq. 1.

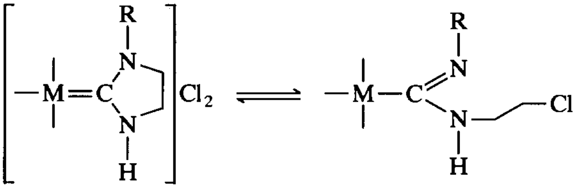
$$cis\text{-}[Cl_2M(carbene)_2] + \overset{\frown}{P\quad P} \xrightarrow[\text{RT or reflux}]{\text{THF or DCE}} [(\overset{\frown}{P\quad P})M(carbene)_2]Cl_2 \qquad (1)$$

M = Pt **1**

Pd **2**

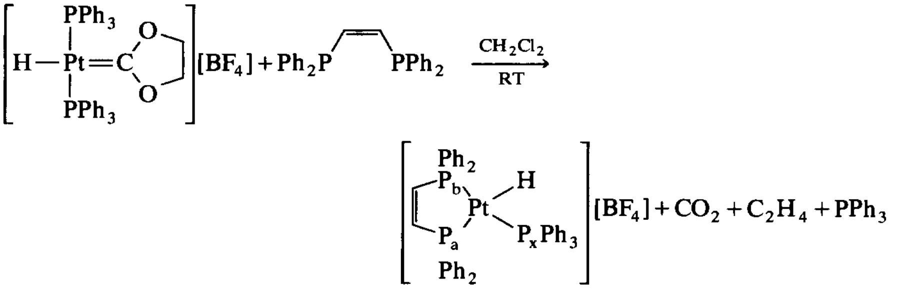
$\overset{\frown}{P\quad P} = Ph_2PCH{=}CHPPh_2$, carbene = $\overline{CN(C_6H_4\text{-}p\text{-}OMe)CH_2CH_2N}H$

These reactions, that have been carried out either in THF at ambient temperature for 1 h or in DCE at reflux for several hours, lead in all cases to the displacement of the $Cl^-$ ligands with the formation of the cationic complexes **1** and **2** in high yield. Even using a molar excess of diphoe, there is no evidence that these reactions proceed with carbene displacement, though this does happen in similar reactions with the hydrido-carbene complexes $[Pt(H)(CF_3)\text{-}\{C[\overline{N(CH_2)_nC}H_2]NHR\}(PPh_3)]$ ($n = 2$ or 4; R=$p$-$MeOC_6H_4$) which lead to the formation of the formamidine $HC[\overline{N(CH_2)_nC}H_2]{=}N(R)$ and $[(P\text{–}P)Pt(H)CF_3)]$ (P–P=$Ph_2PCH{=}CHPPh_2$ or $Ph_2PCH_2CH_2PPh_2$) [8]. Furthermore, there is no evidence of external $Cl^-$ attack on the carbene ring with consequent ring opening and formation of the amidino species II (reaction 2)



I II (2)

Intermediates of type II have been proposed in the formation of cyclic carbenes by nucleophilic attack of $H_2NCH_2CH_2X$ (X=Cl or Br) on coordinated isocyanides [4]. It was hoped that an electrophile such as $H^+$ would shift the equilibrium (2) to the right by reaction with the imino nitrogen of II, thus producing the acyclic carbene moiety $M{=}C(NHR)NHCH_2CH_2Cl$. However, the reaction of **1** proceeds differently, causing only $Cl^-$ exchange by $BF_4^-$ ions (see Experimental section). In order to explore the influence of the $\sigma$-electron donor ability of the ligand *trans* to the carbene in the reactions with diphosphines, we have examined the reactions of the hydrido-carbene complex *trans*-$[(PPh_3)_2Pt(H)(\overline{COCH_2CH_2O})][BF_4]$ with diphoe (eq. 3).



(3)

**3**

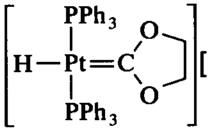
Reaction 3 was followed by IR and $^1H$ NMR spectroscopies at room temperature and also by $^1H$ NMR at low temperature. The IR spectra in $CH_2Cl_2$ of equimolar amounts of the hydrido-carbene *trans*-$[(PPh_3)_2Pt(H)(\overline{COCH_2CH_2O})]$-$[BF_4]$ and diphoe show the immediate formation of $CO_2[\nu(CO_2\}$ 2337 $cm^{-1}]$ and the presence of a broad absorption around 2055 $cm^{-1}$, $\nu$(Pt–H). Similarly, the $^1H$ NMR spectra of an equimolar solution of *trans*-$[(PPh_3)_2Pt(H)(\overline{COCH_2CH_2O})][BF_4]$ and diphoe (*ca.* $10^{-2}$ *M*) at −73°C show the immediate disappearance of the starting hydride resonance at $\delta$ −6.33 and the presence of ethylene (singlet at $\delta$ 5.39) together with a quintet at $\delta$ −10.28. This latter resonance disappears after 3 h at room temperature, being accompanied by the progressive appearance of the signals due to complex **3** (eq. 3).

The signal at $\delta$ −10.28 may be attributed to pentacoordinate intermediate of the type $[(\overset{\frown}{P\quad P})Pt(H)(PPh_3)_2]^+$ (**A**). Since only one $^2J$(HP) is observed [$^2J$(HP) 34 Hz, $^1J$(HPt) 646 Hz] it is possible that species **A** is involved in a fast equilibrium with free $PPh_3$, which makes the four phosphorus atoms equivalent on the NMR time scale. It is noteworthy that a series of five-coordinate $Pt^{II}$ hydrides of the type $[(P_4)PtH]^+$ ($P_4$ = 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane, which is a tetradentate ligand) have been recently reported [17a] to show hydride resonance in the range from $\delta$ −9.7 to −10.8 with $^1J$(HPt) to *ca.* 700 Hz. Furthermore, the pentacoordinate hydrido-compound $[HNi\{P(OMe)_3\}_4]$ [17b], which is a catalyst for olefin isomerization, is reported to show a quintet for the hydride resonance at $\delta$ −12.0 [$^2J$(HP) 29.5 Hz] in $CDCl_3$ at −25°C.

Compound **3** [IR Nujol mull: $\nu$(Pt–H) 2050 $cm^{-1}$] shows a hydride resonance at $\delta$ −2.76 as a doublet of doublets of doublets [$^2J(HP_x)$ 6 Hz, $^2J(HP_b)$ 20 Hz, $^2J(HP_a)$ 170 Hz, $^1J$(HPt) 953 Hz, see labelling scheme in reaction (3)], with coupling constants values which agree well with those reported for other hydrido-complexes of $Pt^{II}$ [18]. The $^{31}P$ NMR spectrum shows an ABX system, whose analysis gave the following results: $\delta(P_a)$ 62.80 [$^2J(P_aP_b)$ 8.2 Hz, $^2J(P_bP_x)$ 15 Hz, $^2J(P_xP_b)$ 346 Hz, $^1J$(PtP) 1916 Hz], $\delta(P_b)$ 60.39 [$^1J$(PtP) 2506 Hz], $\delta(P_x)$ 25.53 [$^1J$(PtP) 3400 Hz].

### *Reactions with $Cl^-$ ions*

The cationic hydrido-dioxycarbene *trans*-$[(PPh_3)_2Pt(H)(\overline{COCH_2CH_2O})][BF_4]$ rapidly reacts with equimolar amounts of $Cl^-$ ions to give a complex mixture of products according to eq. 4.



$$[\mathrm{BF_4}] + \mathrm{Cl^-} \longrightarrow trans\text{-}[(\mathrm{PPh_3})_2\mathrm{Pt(H)}\{[\mathrm{C(O)OCH_2CH_2Cl}]\}]$$

III

$$+ [(\mathrm{PPh_3})_2\mathrm{Pt(CO)_2}] + \mathrm{ClCH_2CH_2OH}$$
$$+\ trans\text{-}[(\mathrm{PPh_3})_2\mathrm{Pt(H)Cl}] \qquad (4)$$
$$+ [(\mathrm{PPh_3})_4\mathrm{Pt_3(CO)_3}]$$

The reaction was monitored by IR spectroscopy at room temperature and by $^1$H NMR at room and at low temperature. The IR spectra of the reacting mixture (*ca.* $5 \times 10^{-2}$ *M* in $CH_2Cl_2$ solution) show the progressive decrease over 60 min of the Pt–H band at 2090 cm$^{-1}$ with concomitant formation of strong absorptions at 1985 and 1942 cm$^{-1}$ due to $\nu$(CO) of the $Pt^0$ species $[(PPh_3)_2Pt(CO)_2]$ [19]. Carbonyl bands are also observed at 1900, 1807 and 1776 cm$^{-1}$, which ascribed to the trinuclear platinum cluster $[(PPh_3)_4Pt_3(CO)_3]$ derived from $[(PPh_3)_2Pt(CO)_2]$ [20]. Other absorptions are a low intensity band at 2337 cm$^{-1}$ due to $\nu(CO_2)$, indicating a side reaction involving rupture of the carbene ring, a band at 2234 cm$^{-1}$, due to $\nu$(Pt–H) of *trans*-$[(PPh_3)_2Pt(H)Cl]$ [16] the intensity of which increases over 2 h, and a very strong band at 1624 cm$^{-1}$, which appears at the beginning of the reaction, but which diminishes gradually after 1 h. This last absorption is attributed to the alkoxycarbonyl species III (eq. 4), identified by $^1$H NMR (*vide infra*). The $^1$H NMR spectrum of the reacting mixture in $CD_2Cl_2$ at −70°C shows successive diminution of the hydride resonance of the starting complex at $\delta$ −6.40 and the immediate formation of another hydride resonance [triplet at $\delta$ −7.21, $^2J$(HP) 17.5 Hz, $^1J$(HPt) 653 Hz], which starts to decrease after 1 h. This last signal is attributed to the hydridoalkoxycarbonyl species III (eq. 4), which is not stable in solution, but reacts with adventitious $H_2O$ to give free $ClCH_2CH_2OH$ and, presumably, the unstable hydroxycarbonyl moiety Pt–COOH, which rapidly decomposes to give $Pt^0$ species [21]. In the $^1$H NMR spectrum at low temperature there are also two triplets at $\delta$ 3.23 and $\delta$ 2.90 [$^3J$(HH) 6.3 Hz] due to $-CH_2Cl$ and $-OCH_2$ protons of III, respectively. These resonances slowly disappear, giving rise to signals at $\delta$ 3.77 (triplet) and 3.63 (triplet) [$^3J$(HH) 6.9 Hz] due to free 2-chloroethanol. Thus, the behaviour of the dioxycarbene ligand in *trans*-$[(PPh_3)_2Pt(H)(\overline{COCH_2CH_2O})][BF_4]$ toward $Cl^-$ ions is similar to that described for $[CpFe(CO)_2\{\overline{COCH_2CH_2O}\}]$ [22a]. Furthermore, coupling of the cyclic dioxycarbene unit to give the alkoxyolefin $\overline{OCH_2CH_2OC}{=}\overline{COCH_2CH_2O}$ has not been observed, presumably because the fragmentation of the cyclic dioxycarbene to give $CO_2$/ethylene and the intermediate III are faster. However, it is worth noting that the coupling of two carbene units was observed previously in the formation of tetrathiafulvalene derivative from the reactions of cyclic 1,3-dithiol-2-ylidene $Ni^0$ complexes with CO [22b] or from $Fe^0$ complexes by electrochemical or chemical oxidation [22c].

### *Electrochemical studies*

*(a) Neutral diaminocarbene palladium complexes.* By cyclic voltammetry (CV), the diaminocarbenedichlorocomplexes *cis*-$[Cl_2Pd\{\overline{CN(R)CH_2CH_2NH}\}(L)]$ ($L = PPh_3$, $R = C_6H_4OMe$-*p* or $^tBu$; $L = CN^tBu$, $R = {}^tBu$; $L = PPhMe_2$, $R = C_6H_4$-

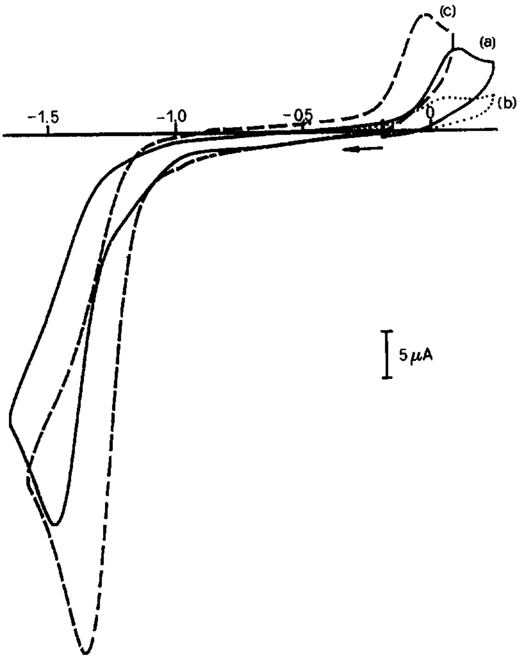


Fig. 1. Cyclic voltammograms for *cis*-$[\mathrm{Cl_2Pd(PPh_3)\{\overline{CN(C_6H_4OMe\text{-}\mathit{p})CH_2CH_2NH}\}}]$ 1.0 m*M*, in 0.2 M$[\mathrm{Bu_4N}][\mathrm{BF_4}]$/NCMe, at a Pt electrode ($v = 100$ mV $\mathrm{s^{-1}}$). (a) Complex alone (solid line). (b) In the presence of PhI (25 equiv.) (dotted line). (c) In the presence of $[\mathrm{Et_4N}]\mathrm{Cl}$ (10 equiv.) (dashed line).

$\mathrm{CH_2Cl}$-*o*), in 0.2 mol $\mathrm{dm^{-3}}$ $[\mathrm{Bu_4N}][\mathrm{BF_4}]$/NCMe and at a Pt electrode, undergo an irreversible cathodic process with peak potential ($E_p^{red}$, measured at 100 mV $\mathrm{s^{-1}}$) in the range −1.5 to −1.8 V *vs.* SCE (Table 1). By controlled potential electrolysis (CPE), this cathodic wave was shown to involve *ca.* two electrons (1.7–1.9).

The product of the CV reduction is electrooxidable at an anodic wave ($E_p^{ox} = 0.12$ to 0.26 V) observed during the subsequent CV anodic sweep (Fig. 1); however, this wave is repressed [Fig. 1 (b)] by addition of an excess of PhI.

Moreover, an increase of the chloride concentration, by addition of $[\mathrm{Et_4N}]\mathrm{Cl}$, leads to an enhancement of the current peaks and to shifts to less cathodic and to less anodic peak potentials for the cathodic and the anodic waves, respectively [Fig. 1 (c)], and hence to a decrease of the peak separation $|E_p^{red} - E_p^{ox}|$. These observations are consistent with a promotion of the electron-transfer by the chloride ions, as known [23] to occur for some $\mathrm{Pt^{II}}$ or $\mathrm{Pt^{IV}}$ compounds, whereas the cathodic shift of the anodic wave can also indicate [24] that the electrogenerated reduced species still involve chloride anions as ligands. Those effects were not observed upon deliberate addition of water (up to twenty fold molar excess), instead of the chloride salt, thus ruling out effects of possible traces of moisture in that salt. Furthermore, this behaviour is consistent with that reported [24,25] for $[\mathrm{Cl_2Pd(PPh_3)_2}]$ and, therefore, conceivably can also be interpreted on the basis of the electrogeneration of low-coordinate zerovalent palladium compounds, possibly of the types $[\mathrm{Cl_2PdL(diaminocarbene)}]^{2-}$, $[\mathrm{ClPdL(diaminocarbene)}]^{-}$ or derived species, which, in a simplified way, can be denoted as "$Pd^0L$(diaminocarbene)" formed according to the overal process 5 [$x = 0$–2].

$$[Cl_2Pd^{II}L(\text{diaminocarbene})] \xrightarrow[-xCl^-]{2e^-} \text{“}Pd^0L(\text{diaminocarbene})\text{”} \qquad (5)$$

The restraint of the oxidation wave for the electrogenerated zerovalent Pd species upon addition of PhI may be due to oxidative addition, just as $[PhPdI(PPh_3)_2]$ is obtained [24] from the electrochemical reduction of $[Cl_2Pd(PPh_3)_2]$ in the presence of PhI.

However, in contrast to $[Cl_2Pd(PPh_3)_2]$ [24], addition of chloride to our systems (at least up to 20 equivalents) does not result in an appreciable stabilization of the monovalent palladium electrogenerated species (relative to the zerovalent ones) at the cathodic wave, since this wave does not split into two.

The cathodic processes observed in our complexes also relate to those reported [26,27] for *cis*- or *trans*-$[Cl_2Pt(PR_3)_2]$ (R = alkyl or aryl) which show cyclic voltammograms exhibiting a single cathodic peak in a range of potentials ($E_p^{red} \approx -1.6$ to $-2.2$ V, at a Hg electrode, in NCMe or NCMe/$C_6H_6$ containing $[Bu_4N][ClO_4]$). Moreover, the reactive zerovalent platinum species $[Pt(PR_3)_2]$ appears to be generated upon two-electron cathodic reduction of the corresponding dichloroplatinum(II) complexes.

The peak potential values of the cathodic processes ($E_p^{red}$) of our complexes (Table 1) appear to reflect the expected order of the net electron-donor character of the ligands, an increase of the $\sigma$-donor ability and/or a decrease of the $\pi$-acceptor character resulting in a destabilizing influence on the metal(0) species. Hence, the t-butylaminocarbene complexes show $E_p^{red}$ values ($-1.84$ or $-1.66$ V for the $PPh_3$ or the $CN^tBu$ compound, respectively) which are lower than those observed ($-1.50$ and $-1.56$ V) for related arylaminocarbene species. Moreover, our diaminocarbene complexes are reduced at a considerably more cathodic potential ($E_p^{red} \approx -1.5$ to $-1.8$ V) than that quoted [24] for the triphenylphosphine compound $[Cl_2Pd(PPh_3)_2]$ ($E_p^{red} = -1.0$ V), because the carbene is a stronger electron releaser than $PPh_3$ [12,28]. In addition, no cathodic reduction was detected above the potential of the electrolyte solution reduction for comparable dicarbene complexes, such as *cis*-$[Cl_2Pt\{CN(C_6H_4OMe\text{-}p)CH_2CH_2NH\}_2]$, *cis*-$[Cl_2Pt\{CN(C_6H_4OMe\text{-}p)CH_2CH_2O\}_2]$ and *trans*-$[Cl_2Pd\{CN(C_6H_4OMe\text{-}p)CH_2CH_2NH\}_2]$.

These observations are in overall agreement with relationships between $E_p^{red}$ and thermodynamic parameters such as the Hammett's $\sigma_p$ substituent constant [29].

*(b) Cationic aminooxy- or dioxycarbene platinum complexes.* The cationic complexes *trans*-$[(PPh_3)_2Pt(X)(COCH_2CH_2NCH_2CH{=}CH_2)][BF_4]$ (X = Cl or Br) and *trans*-$[(PPh_3)_2Pt(H)(COCH_2CH_2O)][BF_4]$, with a single anionic ligand, in 0.2 mol $dm^{-3}$ $[Bu_4N][BF_4]$/NCMe (and, for the latter complex, also in 0.2 mol $dm^{-3}$ $LiClO_4$/THF) and at a Pt electrode, undergo, by CV, an irreversible cathodic process ($E_p^{red} = -1.75$ and $-2.0$ V, respectively) which, by CPE, involves a single electron transfer (Table 1).

By analogy with the behaviour of the neutral aminocarbene complexes, the cathodic process can also lead to low valent carbene compounds. However, in the case of *trans*-$[(PPh_3)_2Pt(H)(COCH_2CH_2O)][BF_4]$, complete fragmentation of the

Table 1

Summary of electrochemical cathodic data [a] for diamino-, oxyamino- and dioxy-carbene complexes of $Pd^{II}$ and $Pt^{II}$

| Complex | $E_p^{red}$ (V) [b] | $n$ ($e^-$) [c] | $E_p^{ox}$ (V) [d] |
|---|---|---|---|
| *cis*-$[Cl_2Pd(PPh_3)\{\overline{CN(C_6H_4OMe\text{-}p)CH_2CH_2NH}\}]$ | −1.50 | 1.68 | 0.12 |
| *cis*-$[Cl_2Pd(PPh_3)\{\overline{CN(^tBu)CH_2CH_2NH}\}]$ | −1.84 | 1.71 | 0.22 |
| *cis*-$[Cl_2Pd(CN^tBu)\{\overline{CN(^tBu)CH_2CH_2NH}\}]$ | −1.66 | 1.74 | 0.18 |
| *cis*-$[Cl_2Pd(PPhMe_2)\{\overline{CN(C_6H_4CH_2Cl\text{-}o)CH_2CH_2NH}\}]$ | −1.56 | 1.87 | 0.26 [e] |
| *trans*-$[(PPh_3)_2Pt(X)(\overline{COCH_2CH_2N}CH_2CH{=}CH_2)][BF_4]$ [f] | −1.75 | 0.99 | - |
| *trans*-$[(PPh_3)_2Pt(H)(\overline{COCH_2CH_2O})][BF_4]$ | −2.0 | 0.98 [g] | - |

[a] Studies performed at a Pt wire (CV) or at a Hg-pool electrode (CPE) in NCMe/0.2 mol $dm^{-3}$ $[Bu_4N][BF_4]$. [b] Values in volt *vs.* SCE, for the cathodic wave, measured by CV at 100 mV $s^{-1}$, by using as internal reference the couple $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ [$E_{1/2}^{ox} = 0.42$ V *vs.* SCE, in NCMe]. [c] Number of electrons transferred in the cathodic process, as measured by CPE at the corresponding wave. [d] Values in volts *vs.* SCE (measured as in *b*, unless stated otherwise), for the anodic wave of the electrogenerated species at the cathodic wave with quoted $E_p^{red}$. [e] Measured at 500 mV $s^{-1}$ (wave only clearly observed for $\nu \geq 200$ mV $s^{-1}$). [f] X = Cl or Br. [g] Leading to quantitative evolution of $CO_2 + C_2H_4$ and to loss of $H_2$ (measured by gas chromatography), also observed in THF/0.2 mol $dm^{-3}$ $LiClO_4$.

dioxycarbene ligand occurs upon exhaustive cathodic CPE, to give $CO_2$ and ethylene in a quantitative yield, as measured by gas chromatography which also detected $H_2$. The formation of these gases was not detected upon cathodic CPE for any of the other complexes of this study, or in blank experiments.

The cathodically induced cleavage of the dioxycarbene ligand to $CO_2$ and $C_2H_4$ is consistent with a related conversion [22a] of this ligand as a result of the chemical reduction (*e.g.*: by sodium amalgam or sodium naphthalenide) of $[(\eta^5\text{-}C_5H_5)Fe(CO)_2(\overline{COCH_2CH_2O})]$.

Moreover, since extensive dihydrogen evolution also results from the cathodic CPE of the hydride complex, zerovalent platinum species, such as $Pt(PPh_3)_2$ known [26] also to be cathodically generated from *cis*-$[Cl_2Pt(PPh_3)_2]$, can be products of the reduction (eq. 6).

$$[(PPh_3)_2Pt^{II}(H)(\overline{COCH_2CH_2O})]^+ \xrightarrow{+e^-} \text{“}Pt^0(PPh_3)_2\text{”} + CO_2 + C_2H_4 + 1/2H_2 \qquad (6)$$

The occurrence of cathodically induced metal dehydrogenation has also been quoted for other cationic hydride complexes, such as $[(\eta^5\text{-}C_5H_5)CoH(PR_3)_2]^+$ (R = Et, Ph, or OMe) [30] and $[ReClH(NCR)(Ph_2PCH_2CH_2PPh_2)_2]^+$ [31], giving the corresponding reduced neutral compounds, $[(\eta^5\text{-}C_5H_5)Co(PR_3)_2]$ and $[ReCl(NCR)(Ph_2PCH_2CH_2PPh_2)_2]$, respectively.

## Final comments

The cathodic processes displayed by the cyclic carbene complexes of $Pd^{II}$ or $Pt^{II}$ (except for the dioxycarbene species in which the carbene ligand undergoes fragmentation reactions) appear to lead to synthesis of zerovalent carbene compounds. This attractive hypothesis (which conceivably involves heterolytic cathodic cleavage of metal–halide bonds or homolytic cathodic rupture of a metal-hydride bond) will be tested by attempting the isolation and full characterization of the final products.

Low-coordination-number zerovalent complexes of Pd or Pt are believed to play a key role in various catalytic processes, but convenient synthetic methods are still unknown, except in restricted cases [25,26]. Therefore, their synthesis by electrochemical generation is of much interest. To our knowledge, the studies we report here are the first attempts to apply electrochemical (cathodic) methods to carbene complexes of Pd or Pt.

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