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Reactions and electrochemical behaviour of dithiocarbene complexes of platinum(II) ☆

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Abstract

The dithiocarbene complex trans-[(PPh₃)₂PtH{C(SMe)₂}][BF₄] (1) was obtained from the reaction of trans-[(PPh₃)₂PtH(CF₃)] with CH₃SH in the presence of ethereal HBF₄. The reactions of 1 with different nucleophiles, such as Cl⁻, H⁻ and CN⁻ ions, P-donor ligands such as Ph₂PCH₂CH₂PPh₂, PPh₃ and PMe₃, have been investigated and these mostly lead to the decomposition of the dithiocarbene ligand with formation of different sulfured products. From the reaction of 1 with Ph₂PCH₂CH₂PPh₂ the complex [Pt{C(H)(SMe)₂}(PPh₃)(Ph₂PCH₂CH₂PPh₂)][BF₄] (2), containing an inserted dithiocarbene ligand, was isolated in low yield. The electrochemical behaviour of trans-[PtH{C(SMe)₂}(PPh₃)₂][BF₄] and the related complexes trans-[(PPh₃)₂PtH{C(SPh)₂}][BF₄], trans-[(PPh₃)₂PtH{CS(CH₂)_nS}][BF₄] (n = 2 or 3) and cis-[(PPh₃)₂Pt{<u>C(H)S(CH₂)₂S</u>}][BF₄] (with an 'inserted dithiocarbene' ligand) was also investigated in 0.2 M [NBu₄][BF₄]/NCMe by cyclic voltammetry and controlled potential electrolysis, and shown to involve cathodic processes (at potentials dependent on the dithio ligand) with partial reduction of the S-containing ligands to hydrocarbons (ethylene or propylene, although detected in low yields), liberation of PPh₃ and dealkylation of the electrolyte, by the reduced metal centre, to give tributylamine, as indicated by GC-MS. The 'inserted dithiocarbene' complex also presents an anodic process which involves proton liberation. Evolution of any sulfur-containing product has not been detected electrochemically or by GC-MS. These behaviours are compared with those exhibited by related dioxy-, diamino- or aminooxy-carbene complexes.

Keywords: Electrochemistry; Platinum complexes; Hydrido complexes; Dithiocarbene complexes

1. Introduction

The synthetic strategies for a wide variety of cyclic and acyclic Fischer-type carbene complexes of Pt(II) are well established [1], but the reactivity of these systems has been much less investigated. Carbene complexes having N and O as heteroatoms have shown a limited reactivity [2], which includes also decomposition processes [3], while those with S atoms appear to be capable of a much broader range of reactivity [4]. In particular, we have recently reported the unprecedented hydride to carbene migration catalysed by CH_3CN or Cl^- ions occurring under mild conditions at the Pt(II) metal centre of the hydrido dithiocarbene complex trans-[(PPh₃)₂PtH($\overline{CSCH_2CH_2S}$)][BF₄] to give almost quantitatively cis-[(PPh₃)₂Pt{C(H)SCH₂CH₂S}][BF₄] [5]. The key aspects of the reaction are the electrophilicity of the carbene carbon in trans-[(PPh₃)₂PtH($\overline{CSCH_2CH_2S}$)]-[BF₄] and the stabilising effect due to the good coordinating properties of the sulfur atoms in the final product. The hydride to carbene migration has been also reported to occur, at least partially, in the reactions of the acyclic dithiocarbene complex trans-[(PPh₃)₂PtH{C(SPh)₂}][BF₄] with Cl⁻ ions, LiAlH-(O-t-Bu)₃ and chelating diphosphines [4].

Such results have prompted us to extend our previous reaction chemistry to the acyclic hydridodithiocarbene complex *trans*-[(PPh₃)₂PtH{C(SMe)₂}][BF₄] (1), in order to compare its reactivity toward different nucleophiles

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with that reported for other complexes in the such as $[Cp(CO)_2Fe\{C(SMe)_2\}]$ literature and $[(CO)_5W{C(SMe)_2}]$ [6], which contain the same type of dithiocarbene ligand. Furthermore, in particular aiming to investigate the susceptibility to reduction or oxidation and the activation, by electron transfer, of the dithiocarbenes and related ligands, we have also studied the electrochemical behaviour of complex 1, of other dithiocarbene complexes, transand [(PPh₃)₂PtH{C(SPh)₂}][BF₄] and trans-[(PPh₃)₂PtH- $\{\overline{CS(CH_2)_n}S\}$][BF₄] (n=2 or 3), as well as of the derived 'inserted carbene' compound [(PPh₃)₂- $Pt{C(H)S(CH_2)_2}{BF_4}$ and compared them with those exhibited by related dioxy-, diamino- or aminooxycarbene complexes.

2. Experimental

2.1. General procedures and materials

All reactions were carried out under a dinitrogen atmosphere, but work up of the reaction products was performed in air. Diethyl ether and dichloromethane were distilled from sodium benzophenone ketyl and acetonitrile from calcium hydride. All other solvents were of reagent grade and used without further purification. HBF₄ (54% solution in Et_2O), diphos (1,2bis(diphenylphosphino)ethane), LiBHEt₃ (lithiumtriethylborohydride, 1.0 M solution in THF) and PPNCl (bis(triphenylphosphine)iminium chloride) were commercially available products and used as received. IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer (abbreviation: m = medium). ³¹P, ¹H and ¹³C NMR spectra were run on a Bruker AC-200 spectrometer in CD₂Cl₂ or CDCl₃ solutions; proton chemical shifts are reported from Me₄Si by taking the chemical shift of dichloromethane- d_2 as +5.32 ppm, dimethyl sulfoxide-d₆ as +2.50 and chloroform-d as +7.21 ppm; phosphorus chemical shifts are from external H₃PO₄ 85%; positive chemical shifts are downfield from the reference (abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad; J are given in Hz). The fast atom bombardment (FAB) [7] mass spectra were obtained using *m*-nitrobenzyl alcohol as a matrix on a VG ZAB 2F [8] instrument operating with a Xe atom beam energy of 8 keV. Metastable transitions were detected by mass analysed ion kinetic energy (MIKE) spectrometry [9]. The GC-MS analyses were performed on a QMD 1000 instrument (using a PS 264 column, 30 m×0.25 mm×0.3 μ m; 1 min at 100 °C and from 100 to 280 °C, 10°/min; He flux 1 ml/min) or on a Trio 2000 (model 1140 VG) mass spectrometer with a Carlo Erba HRGC (Mega series) chromatograph (using a DB1 column, 30 m×0.25mm×0.25 μ m; 1 min at 30 °C and from 30 to 250 °C, 30°/min; He flux 2 ml/min).

The elemental analyses were performed by the Department of Analytical Chemistry of the University of Padua. The melting points were taken on a hot plate apparatus and are uncorrected. The complexes <u>trans-[(PPh_3)_2PtH(CF_3)]</u> [10], trans-[(PPh_3)_2PtH(<u>CSCH_2CH_2S)]</u>[BF₄][11], trans-[(PPh_3)_2PtH(<u>CSCH_2CH_2S)]</u>[BF₄][4] and trans-[(PPh_3)_2PtH{C(SPh)_2}][BF₄][4] were prepared as previously reported.

2.2. Electrochemical studies

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 threeelectrode cell, at a platinum-wire or disc (0.5 or 1 mm diameter) 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 Pt gauze (anodic processes) or an Hg-pool (cathodic processes) working electrode, and a Pt-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. The reduction or oxidation potentials of the complexes were measured by cyclic voltammetry in 0.2 mol dm⁻³ $[NBu_4][BF_4]/NCMe$ and the $E_{1/2}^{red}$ (reversible processes), $E_{p/2}^{red}$ or $E_{p/2}^{ox}$ (irreversible processes) values, measured at 200 mV s⁻¹, are quoted relative to the SCE by using as internal reference the $[Fe(\eta^5-C_5H_5)_2]^{0/+}$ couple $(E_{1/2}^{ox} = 0.45 \text{ V versus SCE}, \text{ in } 0.2 \text{ mol } \text{dm}^{-3} [\text{NBu}_4][\text{BF}_4]/$ NCMe).

The acid-base potentiometric titration of the electrochemically oxidized solution of [(PPh₃)₂- $Pt{C(H)SCH_2CH_2S}$ [BF₄] [4] was carried out by using a solution of NaOH in CH₃OH which was standardized by titration against benzoic acid in NCMe. The result presented has been corrected for background effects by performing also the titration of the blank solution of 0.2 mol dm⁻³ [NBu₄][BF₄] which was electrolysed under identical conditions to those used for the corresponding complex solution. Moreover, prior to the addition of the complex the electrolyte solution was pre-electrolysed at the appropriate potential until a constant and close to zero current, thus conceivably eliminating the interference of eventual traces of residual moisture during the subsequent controlled-potential electrolysis of the complex solution.

The cathodically electrolysed solutions and their gaseous atmospheres were analysed by GC-MS using a Carlo Erba HRGC (Mega series) chromatograph and a Trio 2000 (model 1140 VG) mass spectrometer (see above). Blanks were also done by GC-MS analyses of electrolysed solutions and their gaseous atmospheres (obtained under identical experimental conditions but in the absence of the complexes) as well as of nonelectrolysed solutions of the corresponding complexes.

2.3. Synthesis of trans- $[(PPh_3)_2PtH\{C(SCH_3)_2\}]BF_4$ (1)

A suspension of trans-[(PPh₃)₂PtH(CF₃)] (0.30 g, 0.38 mmol) in anhydrous Et₂O (50 ml) was reacted with an excess of gaseous CH₃SH at 0 °C and immediately treated with HBF_4 (2 drops). The reaction mixture immediately turned to a yellow solution from which a whitish product started to precipitate in a few minutes. The reaction mixture was stirred for 30 min at 0 °C and then for an additional 30 min at room temperature. The white precipitate was filtered off, washed with Et₂O (10 ml) and then recrystallized from CH₂Cl₂/ Et₂O. Yield 0.300 g (87%). M.p. 217-219 °C (dec.). Anal. Calc. for C₃₉H₃₇P₂PtS₂BF₄: C, 51.27; H, 4.08. Found: C, 50.19; H, 4.03%. IR (Nujol mull; cm⁻¹): v(PtH) 2055 (m), v(CS) 999, 939 and 843. ¹H NMR (room temperature, CD_2Cl_2): $\delta(H) - 7.66$ (t, ²J(HP) 12.77, ¹J(HPt) 706); δ(SCH₃, anti) 2.67 (t, ⁴J(HPt) 4.36), δ (SCH₃, syn) 2.03 (s). ¹³C NMR (CD₂Cl₂): δ (C)_{carbene} 305.8 (t, ²J(CP) 9.76, ¹J(CPt) 710.0); δ(SCH₃, anti) 28.62 (s, ${}^{3}J(CPt)$ 68.50), $\delta(SCH_{3}, syn)$ 26.03 (s, ${}^{3}J(CPt)$ 55.20). ³¹P{¹H} NMR (CD₂Cl₂): δ (P) 26.86 (s, ¹J(PPt) 2823). FAB mass spectrum (m-nitrobenzyl alcohol as matrix): m/e 826 (30%, M^+ of the cation), 810 (15%, $[M - CH_4]^+$, 718 (100%, $[M - CH(SCH_3)_2]^{+}$). The MIKE spectra show the loss of CH_4 and CH_3HS from ions at m/z826.

2.4. Reaction of 1 with diphos. Synthesis of $[Pt{C(H)(SCH_3)_2}(PPh_3)(diphos)][BF_4]$ (2)

The hydrido dithiocarbene complex 1 (0.100 g, 0.109 mmol) was dissolved in CH₂Cl₂ (10 ml) at 0 °C and Ph₂PCH₂CH₂PPh₂ (diphos) (0.045 g, 0.113 mmol) was added. The uncoloured solution turned yellow. After 5 h a white precipitate formed and an IR spectrum of the reaction mixture showed that the Pt–H absorption at 2059 cm⁻¹ had disappeared. The solid product was filtered off and washed with Et₂O (10 ml). Yield 0.012 g, 10%. M.p. 126–129 °C (dec.). Anal. Calc. for C₄₇H₄₆P₃S₂PtBF₄: C, 53.81; H, 4.41. Found: C, 51.95; H, 4.22%. ¹H NMR (DMSO-d₆): δ 2.62 (m, CH, ³J(HPt) 27.9), 2.09 (s, SCH₃). ³¹P{¹H} NMR (DMSO-d₆): 47.97 (s, ¹J(PPt) 2322.7), 25.63 (s, ¹J(PPt) 2826).

3. Results and discussion

3.1. Synthesis and reactions of trans-[(PPh₃)₂PtH{C(SCH₃)₂}][BF₄]

The reaction of $trans-[(PPh_3)_2PtH(CF_3)]$ in the presence of ethereal HBF₄ with CH₃SH affords the hydrido dithiocarbene complex $trans-[(PPh_3)_2PtH-{C(SCH_3)_2}][BF_4]$ (1) in high yield according to Eq. (1).

$$\begin{array}{c} \begin{array}{c} PPh_{3} \\ PPh_{3} \end{array} \xrightarrow{PPh_{3}} SCH_{3} \end{array} \xrightarrow{P}Ph_{3} SCH_{3} \xrightarrow{+} BF_{4}(Et_{2}O) \\ PPh_{3} \end{array} \xrightarrow{P}Ph_{3} SCH_{3} \xrightarrow{+} BF_{4}(Et_{2}O) \end{array}$$

Complex 1 is a white solid, stable in the solid state and soluble in chlorinated solvents. It has been spectroscopically characterized by IR, ³¹P, ¹H and ¹³C NMR techniques (see Section 2). In particular, the room temperature ¹H and ¹³C NMR spectra show two distinct resonances of the SMe groups which likely adopt *anti* and *syn* conformations determined by a restricted rotation about the S–C(carbene) bond due to π bonding between the two atoms, as previously observed for other complexes containing the same dithiocarbene ligand [6].



This behaviour has been previously described for the complexes *trans*-[(PPh₃)₂PtX{C(SCH₃)₂}] (X = Cl, I) [12], while the room temperature NMR spectra of $[Cp(CO)_2Fe{C(SMe)_2}]$ [13] and $[(CO)_5W{C(SMe)_2}]$ [14] show only a singlet for the methyl protons.

Line-shape analysis of the SMe resonances in the ¹H NMR spectrum of 1 in the temperature range 298-335 K established a barrier of $\Delta G_{335 \text{ K}}^{\pm}=16.3$ kcal mol⁻¹ for complete rotation about the S-C(carbene) bond. This barrier is similar to those observed in other dimethylthiocarbenes. For example, the barrier of rotation of the SMe group for a series of [Cp(CO)LFe{C(SMe)₂)}] (L=CO, RNC, N-, P-donor ligand) complexes was $\Delta G^{\pm}=10-13$ kcal mol⁻¹ [6], for which the coalescence temperature was found in the range 200-270 K.

The signals of the *anti* SMe group in the ¹H and ¹³C NMR spectra may be readily assigned on the basis of the ⁴J(HPt) and ³J(CPt) values (see Section 2), which are higher than those observed for the *syn* SMe group [15]. These assignments are supported by the fact that the methyl groups *trans* to Pt in carbamoyl [15a] and carbene [15b] complexes have been previously observed to exhibit larger coupling constants than *cis* methyl

groups and also with the higher field resonance of the $syn CH_3$ group in a position *cis* to the Pt, where there is greater shielding from the phosphine phenyl groups [12].

The ¹³C NMR resonance of the carbene carbon atom in 1 shows up at 305.8 ppm, which is similar to those of the electrophilic dithiocarbenes $[(CO)_5W{C(SMe)_2}]$ (300.0 ppm) and $[Cp(CO)_2Fe{C(SMe)_2}]$ (303.1 ppm) [6], but markedly shifted downfield (~80–100 ppm) with respect to other Pt(II) hydridocarbenes such as the diaminocarbene $[PtH(CF_3)(PPh_3){C-(NCH_2CH_2CH_2)NHR}]$ (206.8 ppm) [16] or the dioxocarbene *trans*-[(PPh_3)_2PtH(COCH_2CH_2O)][BF_4] (233.9 ppm) [4], thus suggesting that the carbene carbon in dithiocarbene complexes would be more susceptible to nucleophilic attack.

Previous studies on the reactivity of transition metal dithiocarbenes have evidenced the involvement of a direct attack of the nucleophile at the carbon atom [6], which may result in the formation of a stable carbene carbon-nucleophile bond or it may promote the cleavage of a mercapto group or other types of rearrangements. On the other hand, as mentioned earlier, for Pt(II) hydridodithiocarbene complexes experimental evidence showed that initial attack of the nucleophile (Cl⁻, H⁻, diphosphine) at the metal centre is preferential and this then leads to hydride to carbene migration or to the dithiocarbene decomposition [4,5a]. In order to explore the generality of these reactions we have investigated the reactivity of trans- $[(PPh_3)_2PtH{C(SCH_3)_2}][BF_4]$ with different nucleophiles.

By reacting compound 1 in CD_2Cl_2 with an equivalent amount of PPN⁺Cl⁻ a very slow reaction took place, which was followed by ¹H NMR. No reaction intermediates were observed, but only a slow decrease of the starting hydride signal at -7.64 ppm. After 4 days the hydride resonance of *trans*-[(PPh₃)₂Pt(H)Cl] [17] was observed to grow up at -16.33 ppm (triplet, ²J(HP) 13.4, ¹J(HPt) 1197.5). The GC-MS analysis of the reaction mixture indicated the presence of CH₃SH (at 2.38 min) and of CH₃SCH₂SCH₃ (at 11.68 min).

The reactions of 1 with the chelating diphosphine $Ph_2PCH_2CH_2PPh_2$ (diphos) and monodentate phosphines also were investigated. The reaction of 1 with diphos (Eq. (2)) afforded in very low yield (~10%) $[Pt{C(H)(SCH_3)_2}(PPh_3)(diphos)][BF_4]$ (2), containing the 'inserted' dithiocarbene ligand which is likely derived by the hydride to carbene migration, promoted by the entering diphosphine ligand. This reaction was followed by ¹H and ³¹P NMR spectroscopies at room temperature. The ¹H NMR spectrum showed the immediate appearance of a hydride signal at -10.31 ppm (quintet, ²J(HP) 33.78, ¹J(HPt) 659) and signals at 46.60 ppm (¹J(PPt) 2345) and at 20.57 ppm (¹J(PPt) 2359) in the ³¹P NMR spectrum, which may be attributed to a six-

coordinated species with four exchanging metal P bonds similar to that observed [3] in the analogous reactions of diphosphines with trans-[(PPh₃)₂PtH(CSCH₂CH₂S)]-[BF₄], trans-[(PPh₃)₂PtH{C(SPh)₂}][BF₄] and trans- $[(PPh_3)_2PtH(COCH_2CH_2O)][BF_4]$. The resonance at -10.31 ppm in the ¹H NMR was then observed to slowly disappear with time (12 h), while a new hydride resonance appeared at -2.69 ppm (doublet of doublets, ²J(HP) 65.36 and 3.0, ¹J(HPt) 882.5). The ¹H NMR spectrum showed also a CH proton at 3.33 ppm (doublet of doublets, ³J(HP) 11.78 and 6.23, ²J(HPt) 56.4), likely corresponding to a species of the type [Pt{C(H)SCH₃SCH₃}(diphos)] containing the inserted thiocarbene ligand S-bonded to Pt, due to the similarity of these data with those found for the complex cis- $[(PPh_3)_2Pt{C(H)S(CH_2)_2}][BF_4]$ [5]. The ³¹P NMR of the solution showed also the slow appearance of the signals of compound 2 at 47.97 and 25.63 ppm, which then started to precipitate after some hours. The GC-MS analysis of the reaction mixture revealed the presence of CH₃SH and CH₃SCH₂SCH₃. After 24 h, no hydride resonance was observed but only a doublet at 4.74 ppm $(^{2}J(HP) 9.1)$, which disappears upon addition of a base such as NEt, and thus it was tentatively attributed to the phosphonium salt [Ph₃P⁺CH- $(SMe)_2$ [BF₄⁻] [18], possibly derived by attack of free PPh₃ (formed by substitution at the metal centre of the entering diphosphine and well detected as a broad signal in the ³¹P NMR spectrum of the solution at -3.98 ppm) at the carbone carbon as reported for other dithiocarbene systems [19].



The reactions of 1 with monodentate phosphines take a different course according to the nature of the P ligands. While PPh₃ only gave rise to exchange processes with the coordinated phosphines, as evidenced by the broad signal of free PPh₃ in the ³¹P NMR spectrum of the reaction mixture, PMe₃ (3 equiv.) reacted immediately in CDCl₃ as shown by the immediate disappearance of the starting hydride resonance in the ¹H NMR spectrum. The ³¹P NMR spectrum showed the presence of free PPh₃ ligands, which then promote the decomposition of the carbene complex with formation of CH₃SCH₂SCH₃, found in the GC-MS analysis together with CH₃SH and CH₃SCH₃ (3.88 min). In the ¹H NMR spectrum a signal at 5.10 ppm (²J(HP) 8.43) was tentatively attributed to the phosphonium salt $[PMe_3^+CH(SMe)_2][BF_4^-]$. This signal disappears on

addition of a base due to the formation of the corresponding ylide. The phosphonium salt also in this case can originate by the expected direct attack of PMe_3 on the carbene carbon.

It is noteworthy that in the reactions of 1 with monodentate phosphines there is no evidence of the formation of the dimercapto phosphorane product $\{Pt-S(Me)C(=PR_3)SMe\}$ as reported, for instance, in the reactions of $[W(CO)_5 \{C(SMe)_2\}]$ with PR_3 (R = alkyl, aryl, OMe) ligands. These latter reactions proceed by an initial phosphine attack at the carbone carbon to intermediate adduct of the type form an $[W(CO)_{5}[C(SMe)_{2}](PR_{3})]$, which then rearranges to the dimercapto phosphorane product [(CO)₅W{S(Me)C-(PR₃)SMe}] [19].

The reaction of 1 with $LiB(C_2H_5)_3H$ (Eq. (3)) was followed by ¹H and ³¹P NMR in CD₂Cl₂ at room temperature. The immediate formation (in about 10%) yield with respect to the hydride signal of the starting compound) of a new hydride species was detected in the ¹H NMR spectrum at -4.68 ppm (doublet of doublets, ²J(HP) 42.4 and 198.8, ¹J(HPt) 1150) together with a doublet of doublets at 3.01 ppm (${}^{3}J(HP)$ 14.0 and 7.3, ¹J(HPt) masked), while the ³¹P NMR spectrum showed two doublets at 22.00 and 20.0 ppm with ${}^{2}J(PP)$ 20.8 Hz (¹⁹⁵Pt satellites were too low to be observed). These signals have been attributed to a cis-hydridoalkyl species of the type cis-[PtH{CH(SMe)SMe}- $(PPh_3)_2$, which is observed to slowly undergo reductive elimination at room temperature to give CH₃SCH₂SCH₃ (detected in the GC-MS spectrum), free PPh₃ and Pt metal. The cis-hydrido-alkyl species may be likely formed by migration of the hydride to the carbon promoted by the entering H^- ion as found for similar reactions with CH₃CN or Cl⁻ ion with other hydrido dithiocarbene complexes of Pt(II) [4,5a].



Finally compound I was reacted with 1 equiv. of $NEt_4^+CN^-$ and the reaction was followed by ¹H NMR. An immediate disappearance of the starting hydride resonance was observed with the concomitant appearance of a new hydride signal at -9.02 ppm (singlet, ¹J(HPt) 888.0), while a broad signal centred at 2.50 ppm suggested the presence of a five-coordinated species of the type [PtH(CN){C(SMe)SMe}(PPh_3)_2] with a non-rigid geometry. The initial hydrido intermediate slowly decomposed to give a new species showing in the ¹H NMR spectrum a hydride resonance at -7.99 ppm (doublet, ²J(HP) 136.7, ¹J(HPt) 713.5) and a broad singlet centred at 2.68 ppm (attributed to the SMe group) and in the ³¹P NMR spectrum a singlet at 23.43 ppm likely corresponding to a species of the type $[PtH(CN){C(SMe)_2}(PPh_3)]$, while free PPh₃ was well evidenced in the ³¹P NMR spectrum. After one day a whitish precipitate formed, quite insoluble in common organic solvents, and the GC-MS analysis of the reaction mixture revealed the presence of CH₃SH, CH₃SCH₂SCH₃, CH₃SCH₃ and the tetrathio derivative $(CH_3S)_2C = C(SCH_3)_2$, albeit in a small amount. This latter species is likely originated by the coupling of two carbene units previously reported for the iron dithiocarbene complex $[(CO)_2Fe(L)_2(CSCHR =$ CHRS)] [6], but its formation has never been observed with Pt(II) dithiocarbene complexes.

In conclusion also for compound 1, as well as for other Pt(II) dithiocarbene complexes previously mentioned, no evidence for a direct attack of an entering nucleophile on the carbene carbon as the main reaction is obtained, in contrast with similar reactions with octahedral dithiocarbene complexes of Fe and W [6]. This behaviour may be likely explained by the square planar geometry of the Pt(II) hydrido dithiocarbene complexes under study, having the metal centre less hindered. In particular no evidence of a direct attack of H⁻ on the carbene carbon is obtained, suggesting that the observed electrochemical reduction processes (see below) are not simply localized at the carbene carbon.

3.2. Electrochemical studies. Cyclic voltammetry

By cyclic voltammetry (CV), the dithiocarbene complexes, in 0.2 mol dm⁻³ [NBu₄][BF₄]/NCMe and at a Pt wire or disc electrode undergo a single electron reversible (or partially reversible) and diffusion controlled cathodic process at $E_{1/2}^{red}$ in the range of -1.1to -1.3 V versus SCE (Table 1), that with the aromatic carbene ligand being reduced at a higher potential (-1.1 V) than the others which exhibit alkyl thiocarbenes (-1.3 V), in accord with the stronger electron donor ability of the alkyl relative to the phenyl group. Typical cyclic voltammograms are shown in Figs. 1 and 2 for trans-[(PPh₃)₂PtH{=C(SMe)₂}][BF₄] and trans-[(PPh₃)₂PtH(CSCH₂CH₂S)][BF₄], respectively.

The complex with the 'inserted carbene' ligand, *cis*-[(PPh₃)₂Pt{ $\overline{C(H)S(CH_2)_2}$ }][BF₄], presents, by CV, a single electron irreversible cathodic process (Fig. 3(a)) at a somewhat lower reduction potential ($E_{p/2}^{red} = -1.55$ V). Moreover, an irreversible anodic wave (Fig. 3(b)) is observed at $E_{p/2}^{ox} = 1.31$ V which, by controlled potential electrolysis (CPE) (see below), corresponds to a twoelectron process (Table 1). The current-functions of both waves are independent of the scan rate (ν in the 20–20 000 mV s⁻¹ range) and from the slopes (-30/ α n mV) of the corresponding linear plots of E_p versus

Table 1
Electrochemical data * for dithiocarbene-Pt(II) complexes and related
species

Compound	$E_{1/2}^{ox} (E_{p/2}^{red})$ (V)	$n(e^{-})^{\mathrm{red}}$
$[(PPh_3)_2PtH{=C(SPh)_2}][BF_4]^{\circ}$	- 1.10	2.1
$[(PPh_3)_2PtH{=C(SMe)_2}][BF_4]^{d}$	-1.33	1.9
$[(PPh_3)_2PtH{=\overline{CS(CH_2)_2S}}][BF_4]^{\circ}$	-1.32	1.1
$[(PPh_3)_2PtH{=\overline{CS(CH_2)_3}}][BF_4]'$	- 1.34	1.2
[(PPh ₃) ₂ Pt{C(H)S(CH ₂) ₂ S}][BF ₄] ^g	(-1.55)	1.1
$[(PPh_3)_2PtH{=\overline{CO(CH_2)_2O}}][BF_4]^{h,i}$	(-2.00)	1.0
CS ₂ ^h	(-1.77) ⁱ	0.8 ^k
HSPh ^h	(-1.37) ¹	

^a In NCMe/0.2 mol dm⁻³ [Bu₄N][BF₄], unless stated otherwise. CV studies performed at a Pt wire or disc (ϕ =0.5 or 1 mm) electrode, and CPE studies at a Hg pool (cathodic processes) or Pt gauze (anodic processes) electrode. Redox potential values in V, quoted relative to SCE (those in brackets correspond to irreversible processes) by using as internal reference the [Fe(η^5 -C₅H₅)₂]⁰⁺ couple ($E_{1/2}^{ox}$ =0.45 V vs. SCE in NCMe/[Bu₄N][BF₄]), and measured by CV at 200 mV s⁻¹.

^b Value measured by CPE.

^c A new weak reversible cathodic wave at $E_{1/2}^{rec} = -1.27$ V and a new broad and irreversible anodic wave at $E_p^{ox} \sim 0.67$ V are detected after cathodic CPE at the cathodic wave (-1.10 V).

^d Upon CV scan reversal, irreversible anodic waves are detected at $E_p^{ox} = 0.41$ and 0.59 V; a broad and irreversible anodic wave at $E_p^{ox} \sim 0.6$ V (involving a charge transfer of only ~0.03 electrons measured by CPE at a Pt gauze electrode) is detected after cathodic CPE. GC-MS analyses of the cathodically electrolysed solution indicated ~0.6 mol of free PPh₃ (also detected by ³¹P NMR) and ~0.3 mol of NBu₃ per mol of complex.

^c GC-MS analyses of the cathodically electrolysed solution indicated ~ 0.5 mol of free PPh₃ (also detected by ³¹P NMR) per mol of complex, as well as, in the gaseous atmosphere, ethylene.

^f GC-MS analyses of the cathodically electrolysed solution indicated ~ 0.4 mol of free PPh₃ and ~ 0.1 mol of NBu₃ per mol of complex and, in the gaseous atmosphere, propylene.

⁸ Upon CV scan reversal, an irreversible anodic wave is detected at $E_p^{\text{ox}} = -0.30$ V; GC-MS analyses of the cathodically electrolysed solution indicated ~1.3 mol of free PPh₃ per mol of complex, as well as non-quantified amounts of NBu₃ and ethylene. The complex presents also an irreversible anodic wave at $E_{p2}^{\text{ox}} = 1.31$ V, with $n(e^-) = 1.8$ as measured by CPE, which leads to proton loss (0.9 H⁺, as measured by potentiometric acid-base titration of the electrolyzed solution and corrected for background effects).

^h Included for comparative purposes.

ⁱ Ref. [3].

 ${}^{j}E_{\rm p}^{\rm red} = -1.91$ V; upon CV scan reversal, an irreversible anodic wave is observed at $E_{\rm p}^{\rm ox} \sim 0.35$ V.

^k In NCMe/0.2 mol dm⁻³ [Et₄N]Cl.

 $^{1}E_{p}^{red} = -1.53$ V; irreversible anodic waves are detected at $E_{p}^{rex} \sim 1.29$, 1.58 and 1.67 V.

log ν , the values of 0.73 and 0.59 were estimated for the transfer coefficient (α) for the cathodic and the anodic process, respectively.

The cathodic wave of trans-[(PPh₃)₂PtH{C-(SMe)₂}][BF₄] (at $E_{1/2}^{red} = -1.33$ V) appears to corre-



Fig. 1. Cyclic voltammogram for *trans*-[(PPh₃)₂PtH{=C(SMe)₂}][BF₄] (2.4 mM) in 0.2 M [NBu₄][BF₄]/NCMe, at a Pt disc (ϕ =1 mm) electrode (scan rate=200 mV s⁻¹; potential in V vs. SCE).



Fig. 2. Cyclic voltammogram for $trans-[(PPh_3)_2PtH_{=CS(CH_2)_2S}][BF_4]$ (1.2 mM) in 0.2 M [NBu₄][BF₄]/NCMe, at a Pt disc ($\phi = 1$ mm) electrode (scan rate = 200 mV s⁻¹; potential in V vs. SCE).



Fig. 3. Cyclic voltammogram for $[(PPh_3)_2 Pt[C(H)S(CH_2)_2]][BF_4]$ (1.1 mM) in 0.2 M [NBu₄][BF₄]/NCMe, at a Pt disc ($\phi = 1$ mm) electrode (scan rate = 200 mV s⁻¹; potential in V vs. SCE). (a) Cathodic sweep; (b) anodic sweep. *Internal reference, $[Fe(\eta^5-C_3H_3)_2]^{0'+}$.

spond to an EC process and, upon scan reversal, irreversible anodic waves are detected at $E_{p/2}^{ox} =$ 0.41 and 0.59 V, with relatively weak peak currents (Fig. 1). Moreover, an anodic wave at $E_{p/2}^{ox} = -0.34$ V (Fig. 3(a)) is detected upon scan reversal following the irreversible cathodic process of *cis*-[(PPh₃)₂Pt{C(H)S(CH₂)₂S}][BF₄] at $E_{p/2}^{red} = -1.55$ V. The species responsible for such anodic waves, generated in the cathodic processes, have not been identified (see below). All the above-mentioned dithiocarbene or derived complexes are reduced at a cathodic potential (~ -1.1 to -1.6 V) which is significantly higher than that exhibited by free carbon disulfide ($E_{p/2}^{red} = -1.77$ V, as measured in this study under identical experimental conditions). Moreover, they are reduced also at a less cathodic potential than that, -2.0 V [3], of the related dioxocarbene complex trans-[(PPh₃)₂PtH-(COCH₂CH₂O)][BF₄] which similarly displays a more accessible reduction potential than that required by the direct reduction of carbon dioxide (-3.0 V in similar experimental conditions [20]).

In addition, the reduction potentials of the dithiocarbene complexes are substantially less cathodic than that $(E_{p/2}^{red} = -2.0 \text{ V})$, also measured in this work, of the reduction of *trans*-[(PPh₃)₂PtH(NCMe)][BF₄], with an acetonitrile ligand which is expected not to be redox active in the studied range of potential.

These observations indicate that the reduction potential of Pt(II) complexes of the type *trans*- $[(PPh_3)_2PtH(L)][BF_4]$ (L=two-electron donor ligand) is quite sensitive to the nature of the ligand L, and the cathodic process should involve the metal, the LUMO presenting a significant metal character, in accord with the above-mentioned electrophilic character of this atom.

3.3. Electrochemical studies. Controlled potential electrolysis

Although for all the dithiocarbene complexes of this study the CV current-functions for the single-electron cathodic process do not vary significantly with the scan rate (in the range 20–20 000 mV s⁻¹), by CPE at an Hg-pool electrode, in NCMe/0.2 M [NBu₄][BF₄], a two-electron process is observed for the acyclic carbene compounds, whereas a single-electron transfer is involved in the cyclic carbene species.

In the case of the acyclic carbene compounds, broad and irreversible anodic waves at $E_p^{ox} \sim 0.6-0.7$ V are observed by cyclic voltammetry upon exhaustive CPE at their cathodic waves. Such anodic waves present weak peak currents in comparison with those of the cathodic waves of their parent complexes and involve a low charge transfer as measured by CPE at a Pt-gauze electrode (e.g. ~ 0.03 electrons for the di(methylthio)carbene complex). They correspond to unidentified products possibly formed in low yields.

Neither CS_2 or thiol (HSPh or HSMe), in principle possible products of the reduction of the dithiocarbene ligands, have been detected by CV (their redox waves – see Table 1 – have not been observed) upon exhaustive cathodic CPE of any of the complexes. This was also confirmed by GC-MS of the electrolysed solution which did not detect the formation of those species or of any other possible [4,6] S-containing organic products such as the dithiols, $HS(CH_2)_nSH$ (n = 2 or 3), the disulfides PhSSPh or MeSSMe, the dithiolanes $H_2CS(CH_2)_nS$ (n=2 or 3) or the olefins $\overline{S(CH_2)_nSC}=CS(CH_2)_nS$, depending on the dithiocarbene complex.

Tetrathiooxalate, $C_2S_4^{2-}$, is a known [21] product of carbon disulfide reduction which in solution further converts into other sulfur products. It can be isolated from the electrolytic medium by precipitation of its K⁺ or Et₄N⁺ salt when using an adequate electrolyte such as [Et₄N]X (X⁻ = halide) or KI [21], but we failed to obtain such a precipitate upon cathodic CPE of our complexes using [Et₄N]Cl as the electrolyte; hence, either such a species was not formed in our cases or the low concentration of its salt precluded precipitation.

Nevertheless, we have obtained evidence for reduction of the dithiocarbene ligands in our systems.

In fact, the gaseous atmospheres of the electrolysed solutions, obtained by cathodic CPE in a closed electrochemical cell, of the complexes with the carbene ligand =CSCH₂CH₂S (or with the derived $-C(H)SCH_2CH_2S$ group) or with =CSCH₂CH₂CH₂S contain ethylene or propylene, respectively, although formed in modest or low yields (below ~ 0.2 mol/mol complex), as detected by GC-MS.

These reductions relate to what we have observed [3] for trans-[(PPh₃)₂PtH(COCH₂CH₂O)][BF₄] which leads to the quantitative fragmentation of the dioxycarbene ligand into ethylene and CO₂. However, in the present study of complexes with the cyclic dithiocarbenes or derived $-C(H)SCH_2CH_2S$ ligand, liberation of CS_2 was not detected (see above) corresponding to the possible formation of a complex product with a nonlabile carbon disulfide or derived ligand such as dithioformate (HCS_2^{-}) . This would be in agreement with the higher electrophilic character of the dithiocarbene compared to the dioxycarbene ligand and with the good coordinating ability of the sulfur atoms, which promote, e.g. the hydride migration to the carbon atom and/or the S-ligation to the metal. Hence, the cathodic reduction of such complexes could be tentatively interpreted, in part, by reaction (4) in which Pt denotes $\{(PPh_3)_2Pt\}$ or a derived metal centre.

$$[\underline{Pt}(H) \{= \overline{CS(CH_2)_n}S \}]^+ \xrightarrow{\epsilon}$$

$$\underline{Pt}(S_2CH)' + CH_2CH_2 (n=2)$$

or
$$CH_2 = CHCH_3$$
 $(n=3)$

In contrast with CS₂, liberation of PPh₃ was detected by GC-MS analysis (and by ³¹P NMR spectroscopy) of the cathodically electrolysed solutions of the dithiocarbene complexes (0.4–0.6 mol PPh₃/mol complex) and of the 'inserted carbene' compound (1.3 mol PPh₃/mol complex). Moreover, tributylamine was also detected by GC-MS, mainly upon two-electron cathodic CPE of the di(methylthio)carbene complex (0.3 mol NBu₃/mol complex). The electrolyte is the source of this amine

(4)

(reaction (5)) and these observations suggest that the two-electron reduction of the Pt(II) complex could lead to the coordinatively unsaturated (upon phosphine loss) Pt(0) species which could dealkylate the tetrabutylammonium cation.

$$NBu_{4}^{+} \xrightarrow{[(PPh_{3})_{2}Pt^{II}(H)\{C(SR)_{2}\}]^{+/2e^{-}}}_{-PPh_{3}, -Bu'} NBu_{3}$$
(5)

A similar behaviour towards tetraalkylammonium salts has been reported to occur for $[Pt(PEt_3)_2]$ [22] and other unsaturated low-valent transition metal species such as $[Rh(diphosphine)_2]$ [23], but not for $[Pt(PPh_3)_2]$ which is not basic enough. It is believed [22,23] to involve β -proton abstraction from the NBu₄⁺ cation, by the metal centre, possible via oxidative addition of a C(β)-H bond initiating a Hoffman degradation process. 1-Butene is also an expected [22,23] product of this process but it was not identified in our systems, suggesting that the butyl group (or a derived one) removed from the tetrabutylammonium ion was trapped by the metal site.

As mentioned above, the 'inserted carbene' complex $cis-[(PPh_3)_2Pt{C(H)S(CH_2)_2}][BF_4]$ is the only one which displays, by cyclic voltammetry, an anodic wave (observed at $E_{p/2}^{ox} = 1.31$ V). By controlled potential electrolysis at a Pt-gauze electrode, the anodic process involves ~ 2 electrons; moreover, liberation of one proton also occurs in this process, as measured by potentiometric titration of the electrolysed solution. This anodic behaviour relates to those observed [2] for some aminooxycarbene or diaminocarbene complexes of platinum or palladium, which present irreversible oxidation waves with liberation of protons possibly resulting from anodically induced N-H or C-H bond cleavage, the former at an amino group and the latter at methylene groups adjacent to amino- or oxy-carbene moieties. Examples are given by [PtCl(PPh₃)- $\{\mu \text{-COCH}_2\text{CH}_2\text{N}\text{-}C,N\}\}_2$ or cis-[PtCl₂{CN(C₄H₄OMe-4)- $\overline{CH_2CH_2NH}_2$ which undergo a single electron first anodic process at $E_p^{ox} = 1.67$ or 1.20 V, respectively, with proton loss [2].

The related behaviour of the 'inserted carbene' complex of this study can be tentatively explained by considering the anodically induced proton loss from the ligated carbon atom as indicated in Eq. (6) in which <u>Pt</u> denotes $\{Pt(PPh_3)_2\}$ or a derived metal centre. An increase of the acidity character of this species results from the single-electron oxidation of the complex to form, upon H⁺ loss, an unstable Pt(I)-carbene species which is further oxidized to a Pt(II) product which we did not succeed in isolating and characterising. We consider the proton is not lost from any of the methylene groups since no anodic process (with proton loss) has been detected for any of the dithiocarbene complexes.

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