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Voltammetric and Spectroscopic Studies Related to Platinum(II) and Platinum(IV) Dithiocarbamate Redox Chemistry: Electrochemical, ESR, and Electrospray Mass Spectrometric Identification of a Moderately Stable Platinum(III) Cation: $[Pt(S_2CNEt_2)(\eta^3\text{-}P_2P')]^{2+}$ ($P_2P' = Ph_2P(CH_2)_2P(Ph)(CH_2)_2PPh_2$)

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Cyclic voltammetric oxidation of $Pt(R_2dtc)_2$ ($R_2dtc = S_2CNR_2$ = dithiocarbamate) and reduction of $[Pt(R_2dtc)_3]^+$ both failed to show evidence of a Pt(III) intermediate, even at −70 °C and using scan rates up to 10 000 V s^{-1}. Under similar conditions, cyclic voltammetric reduction of a range of *cis*- or *trans*-$Pt(R_2dtc)_2X_2$ complexes (X = Cl, Br, I) showed loss of halide but no evidence for Pt(III) intermediates. In contrast, cyclic voltammetric oxidation of the Pt(II) compound $[Pt(\eta^1\text{-}S_2CNEt_2)(\eta^3\text{-}P_2P')]PF_6$ ($P_2P' = Ph_2P(CH_2)_2P(Ph)(CH_2)_2PPh_2$) occurs at room temperature via two well-resolved one-electron-transfer processes in dichloromethane and acetone at platinum, glassy carbon, and gold electrodes. The first oxidation process is chemically and electrochemically reversible under conditions of cyclic voltammetry (scan rate = 20−1000 mV s^{-1}). This result suggests that the combination of a bulky tridentate phosphine ligand and a monodentate dithiocarbamate ligand enables a relatively stable monomeric Pt(III) complex $[Pt(S_2CNEt_2)(\eta^3\text{-}P_2P')]^{2+}$ to be formed on the voltammetric time scale. Bulk electrolysis experiments demonstrate that the dication is moderately stable on the longer synthetic time scale. An ESR spectrum obtained in frozen dichloromethane after bulk oxidative electrolysis confirms the presence of paramagnetic Pt(III). Additionally, chemical oxidation of $[Pt(\eta^1\text{-}S_2CNEt_2)(\eta^3\text{-}P_2P')]^+$ with $[N(C_6H_4Br)_3]SbCl_6$ allowed direct observation of $[Pt(S_2CNEt_2)(\eta^3\text{-}P_2P')]^{2+}$ in solution by electrospray mass spectrometry (ESMS). However, data obtained by ESMS and ^{31}P NMR spectroscopy demonstrated that diamagnetic Pt(II) and Pt(IV) are the major products of the oxidation, indicating that disproportionation of $[Pt(S_2CNEt_2)(\eta^3\text{-}P_2P')]^{2+}$ occurs on the synthetic, but not voltammetric, time scale. The new data, combined with that from other studies, suggest that bulky ligands are required to enhance the lifetime of monomeric Pt(III) species, which are presumably present only as short-lived intermediates in the commonly observed overall two-electron Pt(IV)/Pt(II) redox reactions.

Introduction

Inorganic platinum chemistry is dominated by four-coordinate Pt(II) and six-coordinate Pt(IV) compounds.[1,2] Not surprisingly therefore, chemical and electrochemical reductions of Pt(IV) compounds, such as $[PtX_6]^{2-}$ (X = halide), normally involve the transfer of two electrons and loss of two ligands in a reductive elimination reaction

$$[PtX_6]^{2-} + 2e^- \rightarrow [PtX_4]^{2-} + 2X^- \qquad (1)$$

and conversely, oxidation of Pt(II) with halogens involves a two-electron oxidative addition reaction

$$[PtX_4]^{2-} + X_2 \rightarrow [PtX_6]^{2-} \qquad (2)$$

Consequently, examples of reductive elimination and oxidative addition abound in platinum redox chemistry.[1,2]

In principle, monomeric Pt(III) compounds could be expected to be formed as one-electron reduction or oxidation products in the overall Pt(IV)/Pt(II) redox process. However, examples of monomeric, paramagnetic Pt(III) compounds are rather rare,[3−6] and in many cases they have been detected only through

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observation of their ESR signals.[4] Diamagnetic dimeric or polymeric Pt(III) compounds are considerably more common.[1,7-15]

Perhaps the most stable and best characterized monomeric Pt(III) complex is $NBu_4[Pt(C_6Cl_5)_4]$, containing square planar Pt(III), which was prepared by oxidation of $(NBu_4)_2[Pt(C_6Cl_5)_4]$ by $TiCl_3$ or halogens. The magnetic and spectral properties and crystallographic characterization of this complex have been reported in a series of papers.[3,16,17] Certain sulfur macrocycles such as 1,4,7-trithiacyclononane (L) can also stabilize Pt(III), as demonstrated by oxidation of $[PtL_2]^{2+}$ (square pyramidal with a nonbonded sulfur atom) to give a paramagnetic compound with a characteristic Pt(III) ESR spectrum.[6]

Over the last 20 years or so, electrochemical and chemical studies of the redox properties of dithiocarbamate ($[R_2dtc]^- = [S_2CNR_2]^-$) compounds have demonstrated the ability of this ligand to stabilize a wide range of oxidation states.[18-21] In the case of platinum, well-characterized $Pt(R_2dtc)_2$ and $[Pt(R_2dtc)_3]^+$ compounds exist and conventional reductive elimination and oxidative addition reactions occur[21,22]

$$[Pt(R_2dtc)_3]^+ + 2e^- \rightarrow Pt(R_2dtc)_2 + [R_2dtc]^- \quad (3)$$

$$Pt(R_2dtc)_2 + tds \rightarrow [Pt(R_2dtc)_3]^+ + [R_2dtc]^- \quad (4)$$

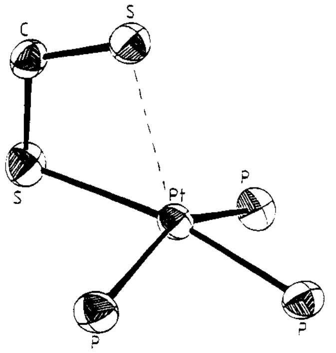
where tds is thiuram disulfide, $(R_2dtc)_2$, the oxidized form of the ligand. Voltammetric studies[23] on the reduction of $[Pt(R_2dtc)_3]^+$ using conventional time domains are consistent with eq 3. Voltammetric oxidation of $Pt(R_2dtc)_2$ is less well characterized, although a small yield of $[Pt(R_2dtc)_3]^+$ has been observed in bulk electrolysis experiments,[23] but no evidence for any Pt(III) intermediates was reported in these studies. Interestingly, some evidence for the formation of Ni(III) intermediates is obtained on reduction of $[Ni(R_2dtc)_3]^+$,[24,25] but the overall reaction is analogous to eq 3.

In contrast, voltammetric oxidation of $[Pt(C_6Cl_5)_4]^{2-}$ gives a well-defined reversible one-electron oxidation response with conventional time scale voltammetry,[3,16,17] reflecting the stability of the Pt(III) species in this system.

More recently, Rieger et al.[26] reported that although voltammetric oxidations of *cis*-$PtR_2(PEt_3)_2$, *trans*-$PtR_2(PEt_3)_2$, *trans*-$PtR(PEt_3)_2Br$ (R = *o*-tolyl), and *trans*-Pt(mesityl)$(PEt_3)_2Br$ are chemically irreversible, oxidation of *trans*-Pt(mesityl)$(PEt_3)_2Cl$ does give a short-lived monomeric Pt(III) species. Consequently, the use of very short time domain methods and the correct ligands, coordination number, stereochemistry, and solvent may be expected to lead to a far wider observation of at least transient Pt(III) intermediates in the oxidations of Pt(II) or the reductions of Pt(IV). Available data indicate that subtle changes in the metal environment lead to significant changes in the ability, or otherwise, to detect Pt(III) intermediates in Pt(II)/Pt(III)/Pt(IV) redox chemistry.

From the above discussion, it is apparent that a general account of the chemistry required to achieve stable, or at least detectable, monomeric Pt(III) intermediates via oxidation of Pt(II) or reduction of Pt(IV) has yet to be reported. Oxidation of Pt(II) in the absence of ligands that could form an octahedral complex and oxidation of a sterically crowded Pt(II) complex appear to be likely methods to achieve this objective. In approaches involving oxidation, electrochemical methods in a noncoordinating solvent, rather than a chemical oxidation which uses oxidative addition, would be expected to increase the prospect of stabilizing Pt(III). While oxidation of $Pt(R_2dtc)_2$ using conventional time domain voltammetric techniques did not achieve this objective,[23] extremely short time domain methods are now available with microelectrodes.[27] These new methods were therefore considered worth applying to oxidation of $Pt(R_2dtc)_2$ as well as to reduction of $[Pt(R_2dtc)_3]^+$ and the related $Pt(R_2dtc)_2X_2$ (X = Br, I) compounds.

Finally, the substituted Pt(II) dithiocarbamate cation $[Pt(\eta^1\text{-}Et_2dtc)(\eta^3\text{-}P_2P')]^+$ ($P_2P' = Ph_2P(CH_2)_2P(Ph)(CH_2)_2PPh_2$) was recently characterized.[28-30] Structure **1** shows the stereochemistry about the metal atom, and although the geometry is square planar, the pendant sulfur atom is quite close to the metal. It was thought possible the significant steric crowding around the metal atom might slow down the rate of reaction of any Pt(III) one-electron-oxidation product. Obviously chelation of the pendant sulfur to give a five-coordinate complex after oxidation is likely, and the five-coordinate geometry intermediate between the four-coordination of Pt(II) and the six-coordination of Pt(IV) provides the possibility of structural compromise, which



structure 1: atomic environment about platinum in solid $[Pt(\eta^1\text{-}Et_2dtc)(\eta^3\text{-}P_2P')]BPh_4$

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may also stabilize Pt(III). Accordingly, electrochemical oxidation studies of this compound have been undertaken.

Experimental Section

Chemicals and Syntheses. [Pt(Et$_2$dtc)(P$_2$P')]PF$_6$,[28] [Pt(R$_2$dtc)$_3$]$^+$,[31] Pt(R$_2$dtc)$_2$,[32] and *cis*- and *trans*-Pt(R$_2$dtc)$_2$X$_2$ (R = Et, ^{n}Pr, ^{n}Bu; X = Br, I)[31] were prepared by literature methods. *Cis/trans*-Pt(R$_2$dtc)$_2$X$_2$ (R = ^{c}Hx; X = Br, I) were prepared similarly. The Bu$_4$NPF$_6$ supporting electrolyte was also prepared by a literature method[33] except for an extra recrystallization from ethanol. Electrochemical grade Bu$_4$NClO$_4$ was obtained from South Western Analytical and used as supplied. [N(4-C$_6$H$_4$Br)$_3$]SbCl$_6$ (Aldrich Chemical Co.) was used as purchased. The dichloromethane and acetone solvents were HPLC grade and were used without further purification.

Electrochemical Measurements. Voltammetric data with conventionally sized electrodes were obtained with 0.5−2 mM solutions of compound in dichloromethane or acetone (with either 0.1 M Bu$_4$NClO$_4$ or 0.1 M Bu$_4$NPF$_6$ as electrolyte) using a Model 174A EG&G Princeton Applied Research (PAR) polarographic analyzer or a Cypress (Lawrence, KS) Model CYSY-1 computer-controlled electroanalysis system. A standard three-electrode experimental arrangement was used. The working electrode for cyclic voltammetry was a polished Pt disk (1.8 mm diameter), a glassy carbon disk (1 mm), or a Au disk (1 mm). For steady state measurements the microelectrodes used were Pt and glassy carbon (both 5 μm diameter). For the rotating disk electrode experiments, the working electrode was a polished Pt disk (2.5 mm) rotated by a variable-speed Metrohm (Herisau) 628-10 electrode rotation assembly. For fast-scan voltammetry, a 5 μm radius Pt disk microelectrode was used with the electrochemical instrumentation described in ref 34. This system was used in a two-electrode (working microdisk electrode and reference electrode) format. The reference electrodes used for all voltammetric work were Ag/AgCl (saturated LiCl in dichloromethane or acetone) separated from the test solution by a salt bridge containing dichloromethane or acetone (0.1 M Bu$_4$NPF$_6$). The auxiliary electrode, when required, was a Pt wire. The reversible voltammetry of an approximately 0.5 mM ferrocene (Fc) solution in the same solvent as the compound under investigation was used as a reference redox couple and all potentials are quoted relative to Fc$^+$/Fc. Solutions were purged with solvent-saturated nitrogen before voltammetric measurements and then maintained under an atmosphere of nitrogen during measurements. Unless otherwise specified, voltammetric data are reported at 22 ± 1 °C.

Bulk electrolysis experiments were performed with 5−10 mL solutions containing approximately 1 mM compound in dichloromethane (0.1 M Bu$_4$NPF$_6$ or 0.5 M Bu$_4$NPF$_6$) or acetone (0.1 M Bu$_4$NPF$_6$) using a Bioanalytical Systems (West Lafayette, IN) BAS 100A electrochemical analyzer. The auxiliary electrode was a Pt gauze basket separated from the solution by a salt bridge with a Vycor plug, the working electrode was also a Pt gauze basket, and the same Ag/AgCl reference electrode used in voltammetric measurements was again employed. The solution was purged with argon prior to the experiment. In the case of bulk oxidation of [Pt(Et$_2$dtc)(P$_2$P')]PF$_6$, when the red brown color of the electrolyzed solution was most intense (~25 min), the solution was transferred to an ESR tube, which had been previously flushed with argon, wrapped in black paper (to avoid possible photochemical decomposition), and transported as quickly as possible to the ESR spectrometer, where it was placed in the probe at 110 K.

ESR and NMR Spectroscopies. ESR spectra were obtained on a Bruker ECS 106 ESR spectrometer working in the X-band (9.35−9.83 GHz) equipped with a rectangular TE$_{102}$ cavity. The spectra were calibrated against diphenylpicrylhydrazyl. A Eurotherm B-VT2000 temperature controller was employed for low-temperature measurements.

^{31}P NMR spectra were recorded in dichloromethane on a Bruker AM-300 spectrometer operating at 121.49 MHz, while ^{195}Pt NMR spectra were recorded in dichloromethane on a JEOL FX 100 instrument at 21.31 MHz. High frequency positive convention is used for all chemical shifts.

Table 1. Cyclic Voltammetric Data for Oxidation of Pt(II) and Reduction of Pt(IV) Compounds in Dichloromethane (0.1 M Bu$_4$NClO$_4$) at a Pt Electrode (Scan Rate 200 mV s^{-1}, Temperature 22 °C)

compd	E^p_{ox} (V^a)	E^p_{red}(trans) (V^a)	E^p_{red}(cis) (V^a)
Pt(Et$_2$dtc)$_2$	0.58		
Pt(*n*-Pr$_2$dtc)$_2$	0.58		
Pt(*n*-Bu$_2$dtc)$_2$	0.60		
Pt(c-Hx$_2$dtc)$_2$	0.55		
Pt(Et$_2$dtc)$_2$I$_2$		−1.08	−1.22
Pt(Et$_2$dtc)$_2$Br$_2$		−1.16	−1.10
Pt(*n*-Pr$_2$dtc)$_2$I$_2$		−1.07	−1.23
Pt(*n*-Pr$_2$dtc)$_2$Br$_2$		−1.12^b	
Pt(*n*-Bu$_2$dtc)$_2$I$_2$		−1.08	−1.20
Pt(*n*-Bu$_2$dtc)$_2$Br$_2$		−1.40^b	
Pt(c-Hx$_2$dtc)$_2$I$_2$		−1.30	−1.36
Pt(c-Hx$_2$dtc)$_2$Br$_2$		−1.22^b	

^{a} V vs Fc$^+$/Fc. ^{b} Responses for the two isomers not resolved.

Electrospray Mass Spectrometry. Electrospray mass spectra were obtained on a VG Bio-Q (VG Bio Tech, Altrincham, Cheshire, U.K.) triple-quadrupole electrospray mass spectrometer using a water/methanol/acetic acid (50:50:1%) mobile phase. [Pt(η^1-Et$_2$dtc)(η^3-P$_2$P')]$^+$ was dissolved in dichloromethane (2 mM), and after reaction with [N(C$_6$H$_4$Br)$_3$]SbCl$_6$, this solution was then diluted 1:10 with dichloromethane. The diluted solution was directly injected into the spectrometer via a Rheodyne injector with a 10 μL loop. A Phoenix 20 micro LC syringe pump delivered the solution to the vaporization nozzle of the electrospray ion source at a flow rate of 3 μL min^{-1}. Nitrogen was used both as a drying gas and for nebulization with flow rates of approximately 3 and 100 mL min^{-1}, respectively.

Results and Discussion

Electrochemical Studies. (i) Oxidation of Pt(R$_2$dtc)$_2$. The irreversible oxidation of Pt(R$_2$dtc)$_2$ has been reported to occur at 1.1−1.3 V vs SCE in conventional cyclic voltammetric studies[23] at a platinum disk electrode using moderate scan rates. Data obtained in the present study are consistent with these reports, and indeed even when scan rates up to 10 000 V s^{-1} are used for dichloromethane or acetone solutions, no evidence of chemical reversibilty was obtained, as expected for formation the square planar Pt(III) complex [Pt(R$_2$dtc)$_2$]$^+$. Additionally, use of low temperatures to −70 °C did not achieve any evidence of chemically reversible voltammetric behavior. Apparently, [Pt(R$_2$dtc)$_2$]$^+$ is an extremely short-lived moiety and is too labile to be observed even under short time domain transient voltammetric conditions. Potentials for the irreversible processes obtained at a scan rate of 200 mV s^{-1} are given in Table 1.

In the absence of chemical reversibilty, no further studies on the Pt(R$_2$dtc)$_2$ compounds were attempted.

(ii) Reduction of [Pt(R$_2$dtc)$_3$]$^+$. Cyclic voltammetric reduction of [Pt(R$_2$dtc)$_3$]$^+$ under all conditions of scan rate (up to 10 000 V s^{-1}) and temperature range (down to −70 °C) was always associated with an irreversible overall two-electron process consistent with eq 3, and no evidence for Pt(III) intermediates was detected.

(iii) Reduction of Pt(R$_2$dtc)$_2$X$_2$. The voltammetric reduction at platinum electrodes of several Pt(R$_2$dtc)$_2$X$_2$ (X = Br, I) complexes was investigated, but since all gave similar behavior, only that of Pt(Et$_2$dtc)$_2$I$_2$ will be discussed in detail. A reductive cyclic voltammogram for a freshly prepared solution of *trans*-Pt(Et$_2$dtc)$_2$I$_2$ in dichloromethane (0.1 M Bu$_4$NClO$_4$) is shown in Figure 1a. The first scan reveals two irreversible reduction processes with peak potentials (E^p_{red}) of −1.08 V (major process) and −1.22 V vs Fc$^+$/Fc (minor process), while after reversal of the scan direction, three oxidation processes are

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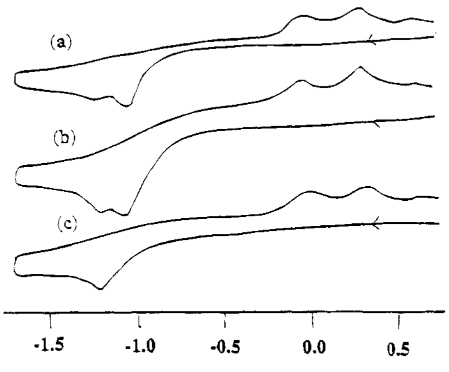

Figure 1. Reductive cyclic voltammograms of a dichloromethane (0.1 M Bu_4NClO_4) solution of *trans*-$Pt(Et_2dtc)_2I_2$ (intially containing a little *cis*-$Pt(Et_2dtc)_2I_2$) at a platinum electrode as a function of time: (a) fresh solution; (b) solution part way through isomerization; (c) solution after complete isomerization. The scan rate was 200 mV s^{-1}.

observed with oxidation potentials (E^{p}_{ox}) of −0.10, 0.26, and 1.10 V vs Fc^+/Fc. The oxidation processes at −0.10 and 0.26 V vs Fc^+/Fc are assigned to the oxidation of iodide, which was released during the course of reduction of $Pt(Et_2dtc)_2I_2$, and this was confirmed by comparison with the oxidation of a solution of iodide derived from NBu_4I. The voltammetry of iodide has been extensively studied in other solvents[35,36] and the processes correspond to

$$6I^- \rightleftharpoons 2I_3^- + 4e^- \tag{5}$$

$$2I_3^- \rightleftharpoons 3I_2 + 2e^- \tag{6}$$

which this work shows to be also operative in dichloromethane. The oxidation process at 0.58 V vs Fc^+/Fc is identified as the oxidation of $Pt(Et_2dtc)_2$ by comparison with the oxidation of an authentic sample. The voltammetric oxidation of $[Et_2dtc]^-$ gives an irreversible response at 0.09 V vs Ag/AgCl[37] (approximately −0.4 V vs Fc^+/Fc) corresponding to the reaction

$$2[Et_2dtc]^- \rightarrow (Et_2dtc)_2 + 2e^- \tag{7}$$

but this response is not observed on the reverse scan in the voltammogram shown in Figure 1, thus indicating that this ligand is not released in the reduction of $Pt(Et_2dtc)_2I_2$.

Reductive controlled-potential electrolysis of $Pt(Et_2dtc)_2I_2$ in dichloromethane (0.5 M Bu_4NClO_4) at −1.3 V vs Fc^+/Fc was monitored by coulometry and confirms that two electrons per molecule are transferred on the longer synthetic time scale. At the conclusion of the electrolysis, there was no voltammetric evidence for any remaining $Pt(Et_2dtc)_2I_2$. The iodide and triiodide oxidation waves and the oxidation wave for $Pt(Et_2dtc)_2$ were the only responses in the voltammogram. A comparison of the current produced at a platinum rotating disk electrode for the reduction of $Pt(Et_2dtc)_2I_2$ with that for the known[38] one-electron oxidation of $Co(Et_2dtc)_3$ was also consistent with a two-electron reduction process.

Thus, all the data for the voltammetric reduction of $Pt(Et_2dtc)_2I_2$ are consistent with the overall reaction

$$trans\text{-}Pt(Et_2dtc)_2I_2 + 2e^- \rightarrow Pt(Et_2dtc)_2 + 2I^- \tag{8a}$$

The shape of the cyclic voltammograms for the reduction of *trans*-$Pt(Et_2dtc)_2I_2$ changes with time. The reduction peak at −1.08 V vs Fc^+/Fc becomes smaller and is replaced by another one at −1.22 V vs Fc^+/Fc as shown in Figure 1b. The cyclic voltammograms show that iodide and triiodide oxidation waves are still present on the reverse scans. The new process is assigned to reduction of *cis*-$Pt(Et_2dtc)_2I_2$ formed by slow isomerization of the trans isomer in solution, and this was confirmed by comparison with the cyclic voltammogram of an authentic sample of *cis*-$Pt(Et_2dtc)_2I_2$, but the overall chemistry of the system is unchanged (eq 8b).

$$cis\text{-}Pt(Et_2dtc)_2I_2 + 2e^- \rightarrow Pt(Et_2dtc)_2 + 2I^- \tag{8b}$$

Generally similar voltammetric behavior was observed for *trans*-$Pt(Et_2dtc)_2Br_2$, with two oxidation responses on the reverse scan due to the presence of released bromide ion, and slow isomerization to the cis isomer was also noted. Data for these and several other analogous compounds are given in Table 1. Even at fast scan rates (up to 10 000 V s^{-1}), the overall two-electron irreversible response associated with eqs 8a and 8b is still observed with no evidence for Pt(III) intermediates in the reduction.

The rates of trans → cis isomerization are difficult to quantify by voltammetry because of poor resolution. However, monitoring of this first-order reaction by ^{195}Pt NMR spectroscopy is straightforward and leads to the data contained in Table 2. Activation parameters contained in the table are consistent with the bond-breaking mechanism previously proposed.[39]

The overall conclusion to be drawn from the above studies is that Pt(III) complexes cannot be observed, even as short-lived species, as intermediates in the oxidation of conventional square planar Pt(II) complexes or in the reduction of conventional octahedral Pt(IV) species. The remainder of this paper is concerned with the oxidation of the sterically hindered Pt(II) cation $[Pt(\eta^1\text{-}Et_2dtc)(\eta^3\text{-}P_2P')]^+$.

(iv) Oxidation of $[Pt(\eta^1\text{-}Et_2dtc)(\eta^3\text{-}P_2P')]^+$. Figure 2a shows a cyclic voltammogram obtained at a 1.8 mm diameter Pt disk electrode for a 0.5 mM solution of $[Pt(\eta^1\text{-}Et_2dtc)(\eta^3\text{-}P_2P')]PF_6$ in dichloromethane (0.1 M Bu_4NPF_6). Three oxidative processes and one reductive process are observed, which are denoted as 1 (reversible), 2 (irreversible), 3 (irreversible), and 4 (irreversible) in Figure 2a. However, in acetone at a glassy carbon electrode, process 3 has a small degree of reversibilty at a scan rate of 500 mV s^{-1}. Data for these processes obtained at a scan rate of 500 mV s^{-1} in dichloromethane and acetone at platinum, glassy carbon, and gold electrodes are summarized in Table 3. Because of the close proximity of processes 1 and 2 at platinum, it is difficult to study process 1 alone. However, if the potential scan is switched just beyond process 1 ($(E^{p}_{ox})_1$), then as shown in Figure 2b, process 1 is completely chemically reversible. Thus, unlike the oxidation of $Pt(R_2dtc)_2$, oxidation of the sterically crowded $[Pt(\eta^1\text{-}Et_2dtc)(\eta^3\text{-}P_2P')]^+$ gives a well-defined reversible one-electron process under conventional cyclic voltammetric conditions at room temperature. Similar voltammetric responses are observed under similar conditions at glassy carbon and gold electrodes, and Figure 2c shows details of the oxidative responses at glassy carbon.

The cyclic voltammogram at platinum showing the three oxidative steps was studied as a function of both scan rate and concentration. At faster scan rates and higher concentrations, process 2 becomes relatively more pronounced. These features, together with its symmetrical shape, suggest that this is a

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Table 2. ^{195}Pt NMR Data and Kinetic Data for Trans → Cis Isomerization in Chloroform Solution

compd	$\delta(^{195}\mathrm{Pt})$(trans) (ppm)[a]	$\delta(^{195}\mathrm{Pt})$(cis) (ppm)[a]	T (°C)	rate const ($\mathrm{s^{-1}}$)
$\mathrm{Pt(Et_2dtc)_2I_2}$	−3585			
$\mathrm{Pt(Et_2dtc)_2Br_2}$	−2310	−2420	23.3	$(2.5 \pm 0.4) \times 10^{-5}$
$\mathrm{Pt(}n\mathrm{\text{-}Pr_2dtc)_2I_2}$[b]	−3525	−3675	9.5	$(7.2 \pm 0.5) \times 10^{-6}$
			23.3	$(4.6 \pm 0.5) \times 10^{-5}$
			29.0	$(6.7 \pm 0.6) \times 10^{-5}$
			35.0	$(1.5 \pm 0.3) \times 10^{-4}$
			40.0	$(2.4 \pm 0.4) \times 10^{-4}$
$\mathrm{Pt(}n\mathrm{\text{-}Pr_2dtc)_2Br_2}$[c]	−2350	−2450	30.0	$(1.2 \pm 0.3) \times 10^{-6}$
			45.0	$(3.1 \pm 0.6) \times 10^{-5}$
			50.0	$(1.1 \pm 0.4) \times 10^{-4}$
$\mathrm{Pt(}n\mathrm{\text{-}Bu_2dtc)_2I_2}$	−3515	−3675	23.3	$(2.8 \pm 0.3) \times 10^{-5}$
$\mathrm{Pt(}n\mathrm{\text{-}Bu_2dtc)_2Br_2}$	−2345	−2540	23.3	$(4.4 \pm 0.3) \times 10^{-5}$

[a] Referenced against 1 M $\mathrm{H_2PtCl_6}$ in concentrated HCl. [b] $\Delta H^* = 81 \pm 6$ kJ mol^{-1}, $k_{298} = (4.3 \pm 0.4) \times 10^{-5}$ s^{-1}, $\Delta S^* = -57 \pm 5$ J K^{-1} mol^{-1}, $E_a = 86 \pm 8$ kJ mol^{-1}. [c] $\Delta H^* = 172 \pm 12$ kJ mol^{-1}, $k_{298} = (4.1 \pm 0.4) \times 10^{-7}$ s^{-1}, $\Delta S^* = -210 \pm 16$ J K^{-1} mol^{-1}, $E_a = 177 \pm 15$ kJ mol^{-1}.

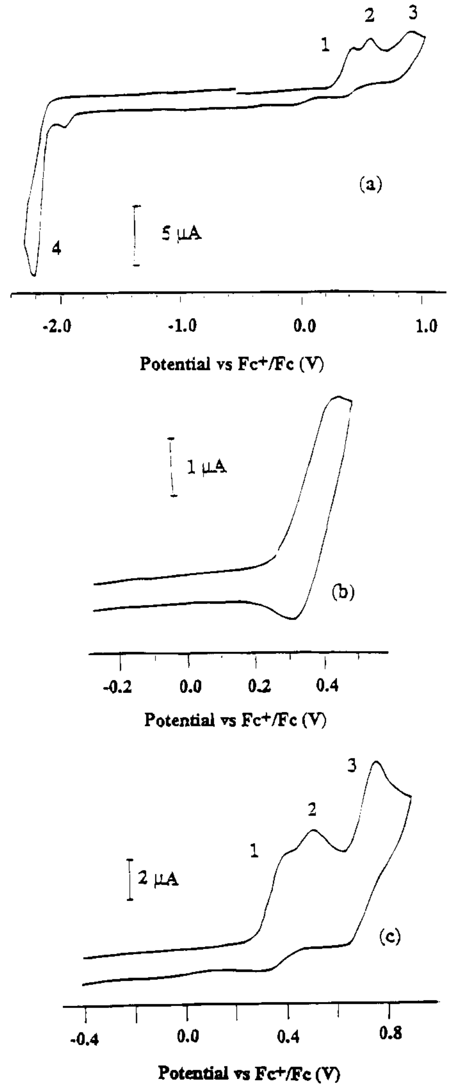

Figure 2. Oxidative cyclic voltammograms of a dichloromethane (0.1 M $\mathrm{Bu_4NPF_6}$) solution of $[\mathrm{Pt}(\eta^1\text{-}\mathrm{Et_2dtc})(\eta^3\text{-}\mathrm{P_2P'})]\mathrm{PF_6}$ (scan rate 500 mV s^{-1}): (a) complete potential range showing all processes at platinum; (b) potential switched immediately after process 1 at platinum; (c) details of the oxidative processes at a glassy carbon electrode.

surface-confined process, corresponding to oxidation of an adsorbed material. In contrast, processes 1 and 3 always have the asymmetrical diffusion-controlled shape, with process 1 exhibiting a high degree of chemical reversibility.

Process 4 is always irreversible and occurs at very negative potentials. Its peak height suggests a two-electron reduction, that is Pt(II) to Pt(0), but due to its proximity to the solvent limit, bulk electrolysis experiments could not be undertaken.

Since the one-electron oxidation of $[\mathrm{Pt}(\eta^1\text{-}\mathrm{Et_2dtc})(\eta^3\text{-}\mathrm{P_2P'})]^+$ (process 1) is the major interest of this work, emphasis is given to this step in subsequent discussion.

A digital simulation of the process

$$\mathrm{A^+} \rightleftharpoons \mathrm{A^{2+}} + \mathrm{e^-} \tag{9}$$

(corresponding to process 1) with the switching potential near $(E^{\mathrm{p}}{}_{\mathrm{ox}})_1$ was undertaken and confirms the chemical reversibility of the process. The peak to peak separation of 120 mV at a scan rate of 500 mV s^{-1} may be compared to a value of 105 mV for the oxidation of ferrocene (Fc) under identical conditions. It is therefore concluded that process 1 is a reversible one-electron step that produces a Pt(III) compound which is stable on the voltammetric time scale:

$$[\mathrm{Pt}(\eta^1\text{-}\mathrm{Et_2dtc})(\eta^3\text{-}\mathrm{P_2P'})]^+ \rightleftharpoons [\mathrm{Pt}(\mathrm{Et_2dtc})(\eta^3\text{-}\mathrm{P_2P'})]^{2+} + \mathrm{e^-} \tag{10}$$

The coordination mode of the dithiocarbamate in the Pt(III) complex cannot be determined from these measurements, since it is possible that the $\eta^1 \rightleftharpoons \eta^2$ processes occur so rapidly that equilibrium conditions are achieved on the electrochemical time scale so that electrochemical and chemical reversibility is observed in cyclic voltammograms.

Simulation of the diffusion-controlled current that would have been observed in the absence of process 2 and the use of this extrapolated response as the base line for process 3 lead to the conclusion that process 3 also corresponds to a one-electron oxidation step. It is likely that in the Pt(IV) complex the dithiocarbamate ligand becomes chelated and that a sixth ligand (Y) is acquired from the solvent or electrolyte; thus the overall process is likely to be

$$[\mathrm{Pt}(\eta^1\text{-}\mathrm{Et_2dtc})(\eta^3\text{-}\mathrm{P_2P'})]^+ \xrightleftharpoons{-\mathrm{e^-}} [\mathrm{Pt}(\mathrm{Et_2dtc})(\eta^3\text{-}\mathrm{P_2P'})]^{2+} \xrightleftharpoons{-\mathrm{e^-}} [\mathrm{Pt}(\eta^2\text{-}\mathrm{Et_2dtc})(\eta^3\text{-}\mathrm{P_2P'})]^{3+} \xrightarrow{+\mathrm{Y}} [\mathrm{Pt}(\eta^2\text{-}\mathrm{Et_2dtc})(\eta^3\text{-}\mathrm{P_2P'})\mathrm{Y}]^{3+} \tag{11}$$

While the origin of surface-confined process 2 has not been identified, the monodentate dithiocarbamate ligand contains a pendant sulfur atom which may be expected to adsorb onto the surface. This would give rise to a surface-controlled, rather than a diffusion-controlled, process at a potential different from that of the diffusion-controlled process 1. Reduction processes on the reverse scan of the cyclic voltammogram, Figure 2a, also indicate the reduction of surface-attached species.

The surface activity made it impossible to undertake steady state measurements at Pt and glassy carbon microelectrodes because it induced severe electrode fouling. However, at a rotating Pt disk electrode a well-defined sigmoidal shaped curve

Table 3. Cyclic Voltammetric Data at 500 mV s^{-1} for 0.5 mM [Pt(η^1-Et$_2$dtc)(η^3-P$_2$P$'$)]PF$_6$ at 20 °C

	solvent CH$_2$Cl$_2$ (0.1 M Bu$_4$NPF$_6$)[a]			solvent Me$_2$CO (0.1 M Bu$_4$NPF$_6$)[a]	
peak potential	Pt electrode	GC[b] electrode	Au electrode	Pt electrode	GC[b] electrode
$(E^{p}_{ox})_1$	0.445	0.435	0.385	0.460	0.410
$(E^{p}_{ox})_2$	0.570	0.620	0.500	0.620	0.510
$(E^{p}_{ox})_3$	0.910	0.770	0.975	1.030	0.780
$(\Delta E^{p})_1$[c]	0.120	0.110	0.150	0.120	0.110
$(E^{p}_{red})_4$	−2.210	−2.190	−2.325	−2.290	−2.250

[a] Potentials vs Fc$^+$/Fc (V). [b] GC = glassy carbon. [c] Separation (V) between E^{p}_{ox} and E^{p}_{red}.

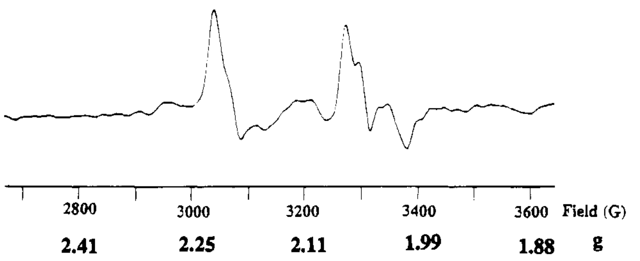

Figure 3. ESR spectrum of a partially electrolyzed 1.0 mM [Pt(η^1-Et$_2$dtc)(η^3-P$_2$P$'$)]PF$_6$ dichloromethane solution (0.5 M Bu$_4$NPF$_6$) which has been frozen at 90 K. The spectrum was recorded at a microwave frequency of 9.45 GHz and a microwave power of 20 mW.

was obtained for process 1 at potentials prior to the onset of process 2. The ratio of the limiting current per unit concentration for process 1 under these conditions to that for the two-electron reduction process

$$\mathrm{Pt(Et_2dtc)_2Br_2} + 2e^- \rightarrow \mathrm{Pt(Et_2dtc)_2} + 2\mathrm{Br}^- \qquad (12)$$

was almost exactly 0.5 at a scan rate of 10 mV s^{-1} and electrode rotation rates up to 1500 rpm. On the basis of the assumption that Pt(Et$_2$dtc)$_2$Br$_2$ and [Pt(η^1-Et$_2$dtc)(η^3-P$_2$P$'$)]$^+$ have similar diffusion coefficients, this result again leads to the conclusion that process 1 is a one-electron charge transfer step.

Bulk oxidative electrolysis of a bright yellow solution of [Pt(η^1-Et$_2$dtc)(η^3-P$_2$P$'$)]PF$_6$ in dichloromethane (0.5 M Bu$_4$NPF$_6$) at 22 °C was performed at a platinum basket electrode held at 0.46 V vs Fc$^+$/Fc, corresponding to a value slightly more positive than $(E^{p}_{ox})_1$. The color gradually changed to red-brown during the course of the experiment and subsequently faded during the final 10 min of the electrolysis to give a colorless solution. In acetone, no red-brown intermediate was observed. Coulometric monitoring during exhaustive electrolysis gave an apparent *n* value of 1.2 ± 0.2 electrons per molecule of [Pt(η^1-Et$_2$dtc)(η^3-P$_2$P$'$)]$^+$. This value and the color change observed during the bulk electrolysis suggest that the product, postulated to be [Pt(Et$_2$dtc)(η^3-P$_2$P$'$)]$^{2+}$ on the basis of the voltammetic studies, is unstable on the longer time scale, especially in acetone. In the presence of another ligand, such as acetate, an *n* value of 2.0 was obtained after exhaustive electrolysis. ^{31}P NMR spectroscopy of the solution after oxidative electrolysis shows a number of signals due to diamagnetic species, probably both Pt(II) and Pt(IV).

Characterization of Pt(III) by Other Techniques. ESR spectroscopy of a partially oxidized (brown) dichloromethane solution does not give a signal at room temperature, but when the sample is cooled to below the freezing point of dichloromethane, the spectrum shown in Figure 3 is observed, which is consistent with the generation of a paramagnetic Pt(III) species. In order to observe this signal, considerable care has to be taken to exclude air and moisture from the sample. No signal is observed after exhaustive electrolysis (colorless solution).

ESMS studies could not be carried out on the electrochemically oxidized solution because of the high concentration of supporting electrolyte present, so chemical oxidation of [Pt(η^1-Et$_2$dtc)(η^3-P$_2$P$'$)]PF$_6$ was investigated. The oxidant chosen was [N(C$_6$H$_4$Br)$_3$]SbCl$_6$ ("magic blue"), since its reversible redox couple in dichloromethane is more positive than that of Pt(III)/Pt(II). The ES mass spectrum of a dichloromethane solution of [Pt(η^1-Et$_2$dtc)(η^3-P$_2$P$'$)]PF$_6$ after oxidation with this reagent gave a base peak due to the Pt(II) complex [Pt(P$_2$P$'$)Cl]$^+$ (*m/z* 765) (confirmed by ^{31}P NMR spectroscopy) and weaker signals due to the Pt(IV) cations [Pt(S$_2$CNEt$_2$)(P$_2$P$'$)(CH$_3$COO)]$^{2+}$ (*m/z* 467) and [Pt(S$_2$CNEt$_2$)(P$_2$P$'$)Cl]$^{2+}$ (*m/z* 456) and the Pt(III) cation [Pt(S$_2$CNEt$_2$)(P$_2$P$'$)]$^{2+}$ (*m/z* 438.5) together with several unidentified signals. The isotopic mass distribution for the peak at *m/z* 438.5 showed it was due to a doubly charged cation, which therefore unambiguously confirms the formation of the Pt(III) cation [Pt(S$_2$CNEt$_2$)(P$_2$P$'$)]$^{2+}$.

All of the above data are consistent with the Pt(III) complex [Pt(S$_2$CNEt$_2$)(P$_2$P$'$)]$^{2+}$ being formed quantitatively on the short voltammetric time scale, and undergoing a complex series of reactions on the synthetic time scale, presumably involving disproportionation to generate Pt(II) and Pt(IV) species. The results of the synthetic time scale experiments therefore resemble those for the oxidation of Pt(S$_2$CNEt$_2$)$_2$, where [Pt(S$_2$CNEt$_2$)$_3$]$^+$ is a minor product after bulk electrolysis[23] and a range of other unidentified products are also formed.

Conclusions

The data obtained in this work, along with other data,[3] suggest that the presence of bulky ligands such as those found in [Pt(S$_2$CNEt$_2$)(P$_2$P$'$)]$^+$ appears to be a requirement for kinetic stabilization of monomeric Pt(III) compounds formed by the oxidation of Pt(II) compounds. This argument is supported by the lack of detection of a reversible one-electron oxidation in the voltammetry of Pt(R$_2$dtc)$_2$ compounds. The bulky ligands appear to slow down the rate of disproportionation reactions which occur on the synthetic time scale. Additionally, the monodentate dithiocarbamate ligand can readily chelate to give a five-coordinate intermediate, and this unusual feature may be important. The steric constraints provided by the P$_2$P$'$ ligand are also probably important in the stabilization of Pt(III), since the presence of dithiocarbamate and bidentate phosphine ligand or dithiocarbamate alone cannot achieve this result. Presumably, analogous arguments apply to reduction of Pt(IV) compounds, where bulky polydentate ligands which are poor leaving groups may be a prerequisite for the formation of detectable Pt(III) complexes.

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