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# Communications

## Observation of Five-Coordinated Platinum(II) Complexes by Mass Spectrometry

*Sir:*

Extensive studies of platinum(II) compounds have shown that ligand displacement reactions of square-planar complexes in solution generally occur by an associative mechanism. Therefore, nucleophilic substitutions of the type

$$PtL_2X_2 + Y^- \rightarrow PtL_2XY + X^- \tag{1}$$

are believed to involve a "five-coordinate" transition state. It still remains uncertain whether this transition state possesses sufficient stability to be regarded as an actual intermediate, $[PtL_2X_2Y]^-$, rather than merely as a phase of the activated complex. Dissociative mechanisms are less preferred and may be expected when the associative process is hindered by the bulkiness of the ligands or when the Pt–X bond is weakened.[1]

The purpose of this work is to provide evidence for the existence of "genuine" intermediates of the type $[PtL_2X_2Y]^-$. These five-coordinate complexes are expected to be extremely labile, both kinetically and thermodynamically. To create and detect them we have used mass spectrometric techniques, which allow detection and identification of species surviving for lifetimes of $10^{-5}$–$10^{-7}$ s.

The reagents were either introduced (e.g., the substrate, $[PtCl_2(PEt_3)_2]$, Et = $C_2H_5$) or generated ($Cl^-$ or $I^-$ ions) in the ion source thermostated at 200 °C. The experiments were carried out by means of a VG ZAB 2F mass spectrometer operating in the negative ion detection mode at 8 kV acceleration voltage. An electron energy of 100 eV (2 mA) was employed in all the experiments reported here.

In a series of experiments, the complex $[PtCl_2(PEt_3)_2]$ was introduced into the ion source via a direct-inlet probe heated at a temperature of 160 °C. At this temperature the vapor pressure of the compound ($10^{-6}$ mbar, monitored in the ion source housing) was high enough to produce a good ion current. Methyl iodide was simultaneously introduced through the septum inlet to a pressure of $10^{-4}$ mbar, i.e. under negative chemical ionization (NCI) conditions,[2] giving rise to a large number of $I^-$ ions. Figure 1 shows the mass spectrum of the negative ions obtained. The spectrum shows a peak at *m/z* 627 corresponding to the five-coordinate species $[PtCl_2I(PEt_3)_2]^-$, in addition to the four-coordinate $[PtClI(PEt_3)_2]^-$ ion at *m/z* 592.[3] This result provides direct experimental evidence for the existence of a five-coordinate adduct with a lifetime longer than $10^{-5}$ s.

The spectrum also shows an abundance of $Cl^-$ ions and a strong peak at *m/z* 535 corresponding to the unexpected five-coordinate species $[PtCl_3(PEt_3)_2]^-$. The $Cl^-$ ions may well arise from the fragmentation of species generated from the $[PtCl_2(PEt_3)_2]$ substrate. It is tempting to attribute the formation of the five-coordinate complex $[PtCl_3(PEt_3)_2]^-$ to the addition of $Cl^-$ to substrate molecules:

$$[PtCl_2(PEt_3)_2] + Cl^- \rightarrow [PtCl_3(PEt_3)_2]^- \tag{2}$$

To establish the existence of reaction 2, the experiments were repeated with use of the same experimental conditions (NCI source configuration[4]) but omitting the addition of $CH_3I$. The mass spectra of $[PtCl_2(PEt_3)_2]$ showed peaks of the following ions (relative abundances, calculated by adding the contributions of all isotopes, are given in parentheses):[3] $[PtCl_3(PEt_3)_2]^-$, *m/z* 535 (100); $[PtCl_2(PEt_3)_2]^-$, *m/z* 500 (62); $[PtCl_3(PEt_3)]^-$, *m/z* 417 (3); $[PtCl_2(PEt_3)]^-$, *m/z* 382 (95); $[PtCl_2]^-$, *m/z* 264 (26); $Cl^-$, *m/z* 35 (300). These data appear to substantiate the hypothesis that $Cl^-$ ions can add to the substrate $[PtCl_2(PEt_3)_2]$ to yield the true five-coordinate intermediate $[PtCl_3(PEt_3)_2]^-$.

A series of experiments were performed to determine the effect of the pressure in the ion source upon the formation of the individual species. Under high-vacuum conditions[5] (EI mode), the species $[PtCl_3(PEt_3)_2]^-$ and $[PtCl_2(PEt_3)_2]^-$ were no longer present in the spectrum, which showed only the peaks corresponding to $[PtCl_2(PEt_3)]^-$ (4) and $Cl^-$ (100) ions. Thus the spectra show that no stable molecular ions $[PtCl_2(PEt_3)_2]^-$ form by impact of the substrate with the high-energy electrons (100 eV). As for the $[PtCl_3(PEt_3)_2]^-$ species, it is not formed either because the probability of the reagents associating is exceedingly small under the high-vacuum conditions of the EI mode or, if we consider that reactions 3 and 4 (see below) may be involved in the formation of five-coordinate ions, because the high energy of the electrons prevents the molecular ions from forming through an electron capture process.[2]

The peak of the molecular ion $[PtCl_2(PEt_3)_2]^-$ (100) reappeared in the spectrum in addition to the peaks of the $[PtCl_2(PEt_3)]^-$ (69) and $Cl^-$ (72) ions, when a 1:1 mixture of methane and nitrogen was introduced into the ion source (in the same EI configuration) to produce a high yield of slow electrons (electron attachment conditions).[6] It is important to note that no significant formation of $[PtCl_3(PEt_3)_2]^-$ was observed under these conditions, despite the abundance of $[PtCl_2(PEt_3)_2]^-$ ions. This result suggests that the molecular ion may not be involved in the formation of the five-coordinate species (see discussion below).

Mass analyzed ion kinetic energy spectra (MIKES) and collisionally activated dissociation (CAD) spectra[7] were carried out

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[1] Lanza, S.; Minniti, D.; Romeo, R.; Moore, P.; Sachinidis, J.; Tobe, M. L. *J. Chem. Soc., Chem. Commun.* **1984**, 542.

[2] Budzikiewicz, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 624.

[3] Mass numbers relate to $^{194}Pt$ and $^{35}Cl$ isotopes.

[4] With the ion source arranged in the CI configuration (low exhausting speed) the concentration of the sample in the vapor phase is sufficiently high to give rise to a number of collisions among the various species. Such a collisional condition is not verified at the flow pressures characteristic of the electron impact (EI) mode.[5]

[5] The EI conditions are achieved by employing a high exhausting speed in the ion source.

[6] Dougherty, R. C.; Dalton, J.; Biros, F. J. *Org. Mass Spectrom.* **1972**, *6*, 1171. Tannenbaum, H. P.; Roberts, J. D.; Dougherty, R. C. *Anal. Chem.* **1975**, *47*, 49.

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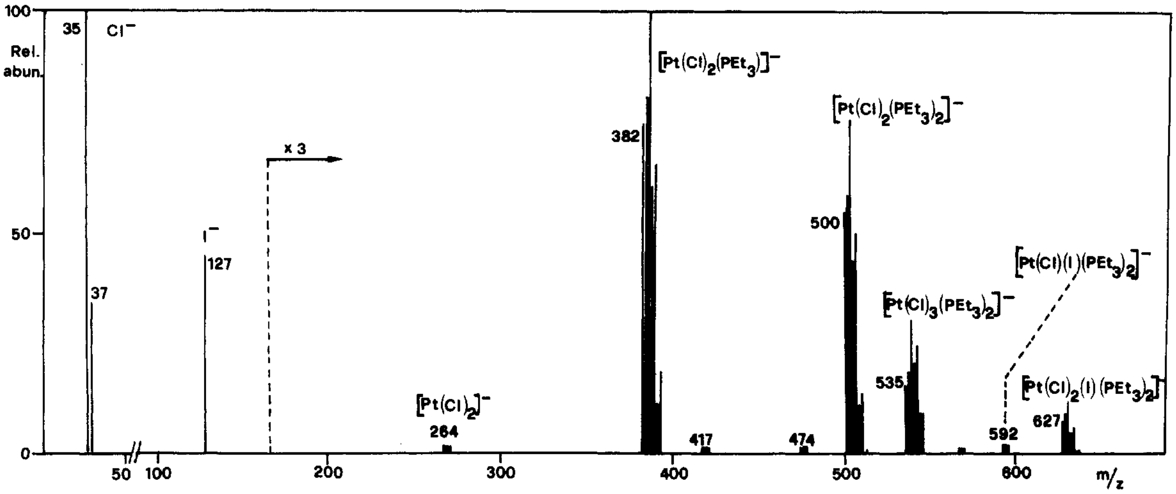

**Figure 1.** Mass spectrum of $[PtCl_2(PEt_3)_2]$ complex under negative chemical ionization $(CH_3I)$ conditions.

Table I. Relative Abundances[b] of the $[PtCl_2(PEt_3)_2]^-$ and $[PtCl_3(PEt_3)_2]^-$ Ions at Different Potentials of the Repeller Electrode

| repeller potential,[a] V | rel abundance $[PtCl_3(PEt_3)_2]^-$ |
|---|---|
| 0 | 51 |
| −1.0 | 37 |
| −1.5 | 16 |

[a] Potential of the repeller relative to the ion source. [b] The relative abundance of the $[PtCl_2(PEt_3)_2]^-$ ion is 100 in all cases.

in order to investigate the stability of the five-coordinate adduct. The absence of peaks due to fragment ions in the MIKE spectra of $[PtCl_3(PEt_3)_2]^-$ ions shows that this species is definitely stable in the time scale of the mass spectrometric measurements (lifetimes $\simeq 10^{-5}$ s). Under collisional conditions[8] (CAD), abundant losses of $PEt_3$, $PEt_3Cl$, $(PEt_3)_2Cl$, and Et, accompanied by minor losses of Cl· atoms,, as well as by the formation of $Cl^-$ ions, became observable.

The data of Table I show that the ratio of $[PtCl_3(PEt_3)_2]^-$ complex to molecular anion decreases on decreasing the residence times of the negative species in the ion source (i.e. by applying more negative potentials to a repeller electrode in the ion source). This result shows that the five-coordinate species can be formed by a mechanism involving ionic reagents, namely, through an ion/molecule process.

In summary, the following three mechanisms of the formation of the five-coordinate adduct can account for the experimental data presented here:

$$[PtCl_2(PEt_3)_2] + Cl^- \rightarrow [PtCl_3(PEt_3)_2]^- \quad (2)$$

$$[PtCl_2(PEt_3)_2]^- + Cl\cdot \rightarrow [PtCl_3(PEt_3)_2]^- \quad (3)$$

$$[PtCl_2(PEt_3)_2]^- + [PtCl_2(PEt_3)_2] \rightarrow [PtCl(PEt_3)_2] + [PtCl_3(PEt_3)_2]^- \quad (4)$$

The following considerations are of interest in trying to evaluate the relative importance of pathways 2 and 3: (i) The initial substrate molecule $[PtCl_2(PEt_3)_2]$ is present in the gas phase in the ion source at a concentration several orders of magnitude greater than that of the ionic species $[PtCl_2(PEt_3)_2]^-$ and $Cl^-$. (ii) Free chlorine radicals are certainly present in the ion source, although their concentration is unknown. (iii) The concentration of $Cl^-$ ions is about 5 times greater than that of $[PtCl_2(PEt_3)_2]^-$.

Concerning the possibility that five-coordinate ions $[PtCl_3(PEt_3)_2]^-$ are formed according to pathway 4, its must be noted that this reaction appears unlikely if we look at the abundant production of $[PtCl_3(PEt_3)_2]^-$ species in the experiment performed in presence of $CH_3I$ (see Figure 1). In these experimental conditions reaction 4 should be, in fact, strongly depressed by the occurrence of the competitive reaction

Table II. Dependence of the Abundances of the Ions $Cl^-$, $[PtCl_2(PEt_3)_2]^-$, and $[PtCl_3(PEt_3)_2]^-$ on the Total Current Intensity

| total ion current[b] | ion current (abundance)[a] | | |
|---|---|---|---|
| | $Cl^-$ | $[PtCl_2(PEt_3)_2]^-$ | $[PtCl_3(PEt_3)_2]^-$ |
| $1.3 \times 10^{-3}$ | $1.1 \times 10^{-3}$ (85) | $0.2 \times 10^{-3}$ (15) | |
| $3.2 \times 10^{-2}$ | $1.9 \times 10^{-2}$ (60) | $0.9 \times 10^{-2}$ (29) | $0.4 \times 10^{-2}$ (11) |
| $1.0 \times 10^{-1}$ | $0.78 \times 10^{-1}$ (78) | $0.14 \times 10^{-1}$ (14) | $0.08 \times 10^{-1}$ (8) |
| $9.5 \times 10^{-1}$ | $7.5 \times 10^{-1}$ (79) | $1.1 \times 10^{-1}$ (12) | $0.9 \times 10^{-1}$ (9) |
| 2.0 | 1.5 (75) | 0.26 (13) | 0.24 (12) |
| 4.3 | 2.6 (60) | 0.60 (14) | 1.10 (26) |
| 6.6 | 3.2 (48) | 0.65 (10) | 2.75 (42) |

[a] Intensity of the current (μA) transported by the single ionic species and, in parentheses, their relative abundances (%). [b] Sum of the intensities of the current transported by the three ions (μA).

$$[PtCl_2(PEt_3)_2]^- + CH_3I \rightarrow [PtCl_2I(PEt_3)_2]^- + CH_3\cdot \quad (5)$$

The collisions with $CH_3I$ are in fact the most probable events occurring to the molecular ions of the complex because methyl iodide is the predominant neutral species present in the ion source. Furthermore, if the molecular ions $[PtCl_2(PEt_3)_2]^-$ show the tendency of capturing halogen atoms according to reactions 3, 4, and 5, it should be reasonable to expect that the other platinum-containing ions, such as $[PtCl_2]^-$ ($m/z$ 264) and $[PtCl_2(PEt_3)]^-$ ($m/z$ 382), behave similarly, giving rise to the ions $[PtCl_3]^-$ ($m/z$ 299), $[PtCl_2I]^-$ ($m/z$ 391), $[PtCl_2I(PEt_3)]^-$ ($m/z$ 509), and $[PtCl_3(PEt_3)]^-$ ($m/z$ 417). On the contrary, they are absent (Figure 1) with the exception of a little amount of the last ($m/z$ 417), which may however rise from $[PtCl_3(PEt_3)_2]^-$ ions by $PEt_3$ loss.

A series of experiments at increasing temperatures (140–220 °C) of the insertion probe was performed to determine the effect of increased concentration (vapor pressure) of the substrate on the relative abundances of the ionic species. Table II shows the correlation between the abundances of the relevant ions (in terms of current intensities) and the total ion current. These data show that the abundance of the five-coordinate ion increases with the intensity of the total ion current (i.e. with the vapor pressure of the starting complex) at a rate greater than that of the molecular ion $[PtCl_2(PEt_3)_2]^-$. Furthermore, Table II confirms that the abundance of the $Cl^-$ ions is consistently greater than that of the molecular ions.

In summary, the experimental evidence strongly suggests that the five-coordinate adduct is formed by mechanism 2, although it does not rule out that paths 3 and/or 4 may be of importance.

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(7) Cooks, R. G.; Beynon, J. H.; Caprioli, R. M.; Lester, G. R. "Metastable Ions"; Elsevier: Amsterdam, 1973. Levsen, K.; Schwarz, H. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 509.

(8) Collisional experiments were performed in the second field free region with air as collision gas at a pressure of $10^{-5}$ mbar.

We now address the question of how the species $[PtCl_2(PEt_3)_2]^-$ and $Cl^-$, which according to eq 2, 3, and 4 should be responsible for the formation of $[PtCl_3(PEt_3)_2]^-$, are generated in the ion source. The chloride ions can arise, but to a minor extent, from the fragmentation of the negative ions because their abundance is not proportional to that of the molecular and fragment ions and indeed are abundant even in their absence, as can be seen by comparing the abundance of $Cl^-$ under electron impact (100) and electron attachment conditions (72). This behavior suggests that the chloride ions are mainly produced through an ion-pair mechanism:

$$e^* + [PtCl_2(PEt_3)_2] \rightarrow e + [PtCl_2(PEt_3)_2]^* \rightarrow [PtCl(PEt_3)_2]^+ + Cl^-$$

As for $[PtCl_2(PEt_3)_2]^-$ ions, they are abundant when the vapor pressure of the substrate $[PtCl_2(PEt_3)_2]$ is relatively high (CI source configuration) and also under electron attachment conditions ($CH_4 + N_2$). These results are indicative of the mechanism of formation

$$e_{slow} + [PtCl_2(PEt_3)_2] \rightarrow [PtCl_2(PEt_3)_2]^-$$

The overall results may be summarized as follows. Under EI conditions abundant $Cl^-$ ions are formed through an ion-pair mechanism. When the pressure of the ion source is relatively high, a five-coordinate adduct is easily produced either by addition of $Cl^-$ to substrate molecule $[PtCl_2(PEt_3)_2]$ or, although less likely, by reaction of molecular ions $[PtCl_2(PEt_3)_2]^-$ alternatively with Cl· radicals or complex molecules. The five-coordinate adduct is stable on the time scale of the sector mass spectrometric measurements and does not reveal appreciable decomposition after having left the ion source. An analogous five-coordinate complex, $[PtCl_2I(PEt_3)_2]^-$, is produced in the presence of methyl iodide.

The conclusions of the present work, being obtained under mass spectrometric conditions, do not permit a straightforward extension to reactions in solution. Thus, although we have been able to show that $[PtCl_3(PEt_3)_2]^-$ and $[PtCl_2I(PEt_3)_2]^-$ ions are genuine intermediates, a distinction between transition states and five-coordinate intermediates in substitutions of the type depicted by eq 1 is still to be proven.

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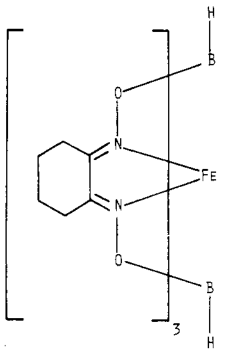
## Synthesis and Characterization of an Iron Clathrochelate Containing an Unreactive Boron–Hydrogen Bond

*Sir:*

The anion $BH(OR)_3^-$ has been shown to be a powerful reducing agent.[1] We have incorporated this functionality into a rigid clathrochelate ligand and have found it to be remarkably unreactive. The compound, $[Fe(NOX)_3(BH)_2]$ (**1**),[2] is prepared by reacting a mixture of cyclohexanedione dioxime ($NOXH_2$) and anhydrous ferrous bromide in dry acetonitrile with sodium borohydride. The red-orange solid that precipitates is purified by column chromatography (neutral alumina, methylene chloride solvent) and recrystallized from chloroform/methanol.[3] Infrared studies reveal a strong terminal B–H stretch at 2490 cm$^{-1}$ along with other bands common to this family of clathrochelates ($\nu_{C=N}$ = 1578 and 1492 cm$^{-1}$; $\nu_{N-O}$ = 1232 and 1060 cm$^{-1}$; $\nu_{B-O}$ = 1203 cm$^{-1}$).[4,5] The $^{11}$B nuclear magnetic resonance spectrum (Bruker WM 500; 160.47 MHz) consists of a broad symmetrical doublet ($J_{B-H}$ = 120 Hz) centered at −31.9 ppm ($BF_3 \cdot O(C_2H_5)_2$ reference), which collapses to a singlet when broad-band proton decoupling is used (See Figure 1). No other $^{11}$B resonance is observed, indicating that both boron atoms are in equivalent environments. The $^1$H NMR spectrum (Varian T60) in $CDCl_3$ is dominated by the two broad methylene resonances at 2.90 ppm ($\beta$ to the oxime nitrogen) and 1.80 ppm ($\gamma$ to the oxime nitrogen) vs. $Me_4Si$ (internal standard). The hydridic proton's resonance is ill resolved because of the quadrupole broadening of the adjacent boron atom and the interfering overlap of the methylene resonances. UV-visible spectroscopy produces a spectrum reminiscent of other examples of this class of compound[4,5] with an intense charge-transfer band centered at 22.3 × 10$^3$ cm$^{-1}$ ($\epsilon$ = 18 000 L/mol·cm; $CH_3CN$).



**1**

Cyclic voltammetric studies[6] at a platinum electrode in $CH_3CN$ (0.1 M in tetra-*n*-butylammonium fluoroborate) show a quasi-reversible oxidation wave centered at +0.72 V (65 mV peak to peak separation, scan rate 100 mV/s) vs. the $Ag^0/Ag^+$ (0.1 M in $CH_3CN$) reference electrode. This oxidation is assigned to the Fe(II)/Fe(III) couple; however, attempts to synthesize the Fe(III) clathrochelate electrolytically have failed to produce a stable product. Evidence supporting a metal-centered redox process instead of a ligand-centered process arises from the facts that (1) variations in the ligand system of the iron clathrochelates do not greatly affect the position or the reversibility of the cyclic voltammetric waves[5] and (2) electrochemical studies of cobalt complexes with identical ligand systems do not produce redox couples other than those that are well established (through electrolytic studies) as being metal centered.[7]

**Chemical Reactivity.** Brown and co-workers[8] have shown that the reaction of acetone with sodium triisopropoxyborohydride in diglyme at 0 °C is complete in seconds. Attempts to react $[Fe(NOX)_3(BH)_2]$ with acetone have yielded no reaction after 16 h of reflux. The acid stability of the complex is even more noteworthy. Material isolated from glacial acetic acid after 67 h of reflux still exhibited a strong $\nu_{B-H}$ band at 2485 cm$^{-1}$; however, some acetate ester formation did occur gradually as evidenced by the appearance of infrared bands typical of esters ($\nu_{C=O}$ = 1730 cm$^{-1}$; $\nu_{C-O}$ = 1270 cm$^{-1}$)[9] in the isolated materials. Studies in concentrated hydrochloric acid indicate that the complex

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(1) Brown, H. C.; Mead, E. J. *J. Am. Chem. Soc.* **1953**, *75*, 6263.

(2) IUPAC name: [Tris($\mu$-(1,2-cyclohexanedione dioximato)-*O*:*O*′)dihydrodiborato(2−)]-*N*,*N*′,*N*″,*N*‴,*N*⁗,*N*⁗′]iron(II).

(3) Anal. Calcd for $C_{18}H_{26}B_2FeN_6O_6$: C, 43.24; H, 5.24; N, 16.81. Found: C, 43.04; H, 5.44; N, 16.53.

(4) Jackels, S. C.; Rose, N. J. *Inorg. Chem.* **1973**, *12*, 1232.

(5) Robbins, M. K.; Naser, D. W.; Heiland, J. L.; Grzybowski, J. J. *Inorg. Chem.*, in press.

(6) A Bioanalytical Systems CV-1V cyclic voltammetry instrument was used in conjunction with an H-type cell with a glass frit separating the reference electrode from the working electrode compartment.

(7) Holbert, J. W.; Roche, J. J.; Grzybowski, J. J., manuscript in preparation.

(8) Brown, H. C.; Mead, E. J.; Shoaf, C. J. *J. Am. Chem. Soc.* **1956**, *78*, 3616.

(9) The compound had been dried in vacuo at 110 °C to remove any unreacted acetic acid.

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