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# Preparation, Characterization and Reactivity of a Series of Diethylenetriamine (dien) and Substituted dien Complexes of Platinum(II)

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## Abstract

The preparation and characterization of chloro, aquo and hydroxo complexes of diethylenetriamine (dien) and methyl and ethyl substituted dien Pt(II) species are reported. Evidence for the isolation of ring-opened dien complexes from acidic medium is presented, and the difficulties in isolating pure species are discussed. The possibility of producing carbonato complexes via $CO_2$ uptake by the hydroxo species, or via anation of the aquo complexes by bicarbonate was investigated. No evidence for the formation of a complex of the type $Pt(R_5dien)OCO_2$ could be found. These results are discussed in reference to similar work performed on the corresponding Pd(II) species and the nature of the metal–hydroxy bond.

## Introduction

Our earlier interest [1] in the formation and reactivity of octahedral transition metal carbonato complexes revealed a number of areas in need of detailed investigations. One of these concerns the formation and reactivity of square planar monodentate carbonato complexes. We recently studied the formation, aquation and base hydrolysis reactions of a series of carbonato diethylenetriamine (dien) and substituted dien complexes of Pd(II) [2]. Surprisingly, the kinetic data clearly demonstrate that these complexes are not formed via $CO_2$ uptake by the metal hydroxo species as generally found for non-labile octahedral complexes [1], but rather via anation of the metal aquo species by bicarbonate ion. Two possible reasons for this difference were offered [2]. Firstly, the metal aquo species are significantly more labile in the case of the Pd(II) complexes [3], which could favour a substitution route. Secondly, the nature of the Pd–OH bond could be such that $CO_2$ addition is not possible, which is perhaps in line with the peculiar substitution inertness of such Pd–OH complexes notwithstanding the weak nucleophilicity of hydroxide [4, 5].

In this study we selected a similar series of aquo Pt(II) complexes of which three coordination sites are occupied by dien, 1,1,7,7-$Me_4$dien or 1,1,7,7-$Et_4$dien, and investigated their reactivity with $CO_2(aq)$ and $HCO_3^-$. It is well-known that the $Pt-OH_2$ species is significantly less labile than the $Pd-OH_2$ species, so that these species should closely resemble the situation for non-labile octahedral complexes. Therefore, such complexes present a realistic possibility to observe $CO_2$ uptake in case the lability of the M–O bond is the determining factor [1, 2]. The preparation and characterization of this series of Pt(II) complexes revealed unexpected difficulties, of which a brief account is also given since such complexes are of general interest as model compounds in anti-tumor related studies.

## Experimental

Various methods, based on our previous experience with the synthesis of Pd(II) dien and substituted dien complexes, were employed to prepare a series of complexes of the type $[Pt(R_5dien)Cl]X$, where $R_5$dien = dien, 1,1,7,7-$Me_4$dien, 1,1,7,7-dien, and X = Cl, $PF_6$. The isolation and purification of these complexes turned out to be more complicated than expected and forms an important part of this report. Some relevant information is therefore given.

### *$Pt(dien)Cl_2 \cdot HCl$*

2 g $PtCl_2$ and 3.3 ml HCl(c) in 50 ml $H_2O$ were refluxed overnight. The dark red clear solution of $PtCl_4^{2-}$ was filtered and treated with 3 g dien·3HCl. The pH of the solution was adjusted to *ca.* 3 by the addition of LiOH, which was followed by further refluxing for three days. The yellow solution was filtered, concentrated to 15 ml and cooled in ice. A yellow product separated, which was recrystallized from 1 M HCl. *Anal.* (theoretical values): Pt, 49 (48.1); Cl, 26.2 (25.6); C, 12.1 (11.6); N, 10.4 (10.4); H, 3.3 (3.4)%.

### *[Pt(dien)Cl]Cl*

The above prepared complex was dissolved in water and the pH adjusted to 10 with the aid of

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LiOH. The solution was heated at 80 °C for 30 min during which the pH was kept at 10 with the addition of more LiOH. The decoloured solution was cooled, the pH reduced to 4 with HCl and concentrated to 15 ml. White crystals separate during cooling in ice, which were washed with ethanol and ether. *Anal.* (theoretical values): Pt, 52.2 (52.8); Cl, 19.2 (19.2); C, 13.0 (13.0); N, 11.6 (11.4); H, 3.5 (3.5)%.

*[Pt(Me₄dien)Cl]PF₆*

2 g $PtCl_2$ and 3.6 ml HCl(c) in 50 ml $H_2O$ were refluxed overnight. The solution of $PtCl_4^{2-}$ was filtered and treated with 1.8 g $Me_4dien{\cdot}3HCl$. LiOH was added to adjust the pH to 1.8, the mixture was refluxed for 2 h and then concentrated to the point where a precipitate started to form. The solution was filtered and $NH_4PF_6$ was added until precipitation was complete. The product was filtered, and washed with ethanol and ether. Subsequent addition of 0.5 g $NH_4PF_6$ to the filtrate and further concentration to 20 ml produced a second fraction of the product. *Anal.* (theoretical values): first fraction – Pt, 37.0 (36.5); F, 19.5 (21.3); C, 17.8 (18.0); N, 7.8 (7.8); Cl, 7.7 (6.6); H, 4.0 (3.9); second fraction – Pt, 35.6 (36.5); F, 19.9 (21.3); C, 18.0 (18.0); N, 7.5 (7.8); Cl, 9.8 (6.6); H, 3.8 (3.9)%. A different complex with the formula $Pt(Me_4dien)Cl_2{\cdot}HCl$ could be isolated when the pH of the solution was adjusted to zero instead of 1.8 and followed by refluxing for two days. The yellow product was isolated by concentrating the solution on a water bath. *Anal.* (theoretical values): Pt, 42 (42.3); Cl, 25.2 (23.0); C, 19.4 (20.8); N, 8.4 (9.1); H, 4.8 (4.8)%.

*[Pt(Et₄dien)Cl]PF₆*

2 g $PtCl_2$ and 4 ml HCl(c) in 20 ml $H_2O$ were refluxed for one day after which the solution was filtered and $Et_4dien$ was added dropwise to the warm filtrate. The solution changed colour from dark red to orange yellow within a couple of minutes. $Et_4dien$ was added until a grey yellow precipitate (not the wanted product) was formed, thus requiring a total of 3 to 4 ml. The solution was refluxed for a couple of minutes, filtered and $NH_4PF_6$ was added to precipitate the complex. The solution was allowed to stand for 30 min after which it was filtered and the precipitate washed with ethanol and ether. Chemical analyses were not in agreement with the expected theoretical values, but do fit the composition $[Pt(Et_4dien)Cl]PF_6{\cdot}HCl$: Pt, 30.8 (31.1); C, 22.8 (23.0); H, 4.8 (4.8); N, 6.4 (6.7); Cl, 13.4 (11.3); F, 17.1 (18.2)%. The deviations for Cl and F are most probably due to the presence of a small fraction of the chloride salt of the complex.

Two procedures were adopted to convert the synthesized chloro complexes *in situ* to the corresponding aquo species. In the first, the chloro complex was treated in solution with the appropriate amount of $AgClO_4$ to precipitate all chloride as AgCl. This aquation process is relatively slow and mixtures of the complex and $AgClO_4$ were stirred at room temperature in the dark for up to 7 days depending on the reactivity, *i.e.* degree of steric hindrance, of the chloro complex. The AgCl precipitate was filtered, and a few drops of 0.1 M $AgClO_4$ solution was added to the filtrate to test for complete precipitation of all released chloride ions. The excess $Ag^+$ in solution was removed by adjusting the pH to 11 and removing the $Ag_2O$ precipitate with the aid of a 0.1 μm filter. The pH of the solution was then adjusted to 4 through the addition of $HClO_4$. In the second, a solution of the chloro complex was adjusted to pH 10 with NaOH and enough time was allowed for the base hydrolysis reaction to go to completion (once again depending on the reactivity of the chloro species). The pH of the solution was monitored and readjusted to 10 during the base hydrolysis reaction. An ion exchanger (Merck MP 7080) in the $OH^-$ form was used to remove the released chloride ions. The pH of the solution containing the hydroxo complex was adjusted to 4 to obtain the aquo complex.

A series of side products were isolated during the described preparation of the chloro complexes, and more information on their nature and reactivity will be given in the next section. Chemicals of analytical reagent grade and doubly-distilled, deionized water were used throughout this study. UV–Vis spectra were recorded on Perkin-Elmer Lambda 5 and Shimadzu UV 250 spectrophotometers. IR spectra were recorded on a Beckman 424 D instrument, and NMR spectra on Varian XL 100 and Bruker AM 300 spectrometers. Chemical analyses were performed by the Analytical Laboratory, Hoechst AG, Frankfurt/Main.

## Results and Discussion

### Dien Complexes of Pt(II)

Mann [6] described a procedure for the synthesis of [Pt(dien)X]X, where X = Br or I, and isolated a different species in the case of X = Cl. In a later detailed study Watt and Cude [7] demonstrated that the isolated complex was in fact $Pt_3C_8H_{30}ON_6Cl_8$ and suggested the following structure.

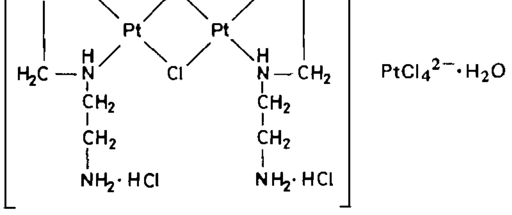

TABLE I. UV–Vis Absorption Spectra of a Series of dien and Substituted dien Complexes of Pt(II)

| Complex | $\lambda_{max}$ (nm) | $\epsilon$ ($M^{-1}$ $cm^{-1}$) |
|---|---|---|
| $Pt(dien)Cl_2 \cdot HCl$ | 270(sh), 303 | ~140, 188 |
| $[Pt(dien)Cl]Cl$ | 268 | 270 |
| $Pt(dien)OH_2^{2+}$ | 247 | 323 |
| $Pt(dien)OH^+$ | 255 | 253 |
| $[Pt(Me_4dien)Cl]PF_6$ Fraction 1 | 268 | 588 |
| Fraction 2 | 274 | 446 |
| $Pt(Me_4dien)OH_2^{2+}$ | 252 | 546 |
| $Pt(Me_4dien)OH^+$ | 258 | 395 |
| $[Pt(Et_4dien)Cl]PF_6 \cdot HCl$ | 280 | 165 |
| $Pt(Et_4dien)Cl^+$ | 278 | 280 |
| $Pt(Et_4dien)OH_2^{2+}$ | 259 | 171 |
| $Pt(Et_4dien)OH^+$ | 268 | 131 |

This species was isolated [7] as orange crystals, which on recrystallization from 1 M HCl changed to dark red. It is quite reasonable to expect the dien ligand to act as a bidentate group in acidic medium, and a closely related ring-opened Pd(II) complex was recently isolated in this laboratory [8].

We were also able to isolate orange–red crystals during the reaction of $PtCl_4^{2-}$ with dien·3HCl by following the procedure described for $Pt(dien)Cl_2 \cdot HCl$ but not adjusting the pH through the addition of LiOH. Our analyses favour a species similar to that above but with composition* $[(dien \cdot HCl)Pt(\mu\text{-}Cl)_2Pt(dien \cdot HCl)]PtCl_4 \cdot HCl \cdot 3H_2O$. When this complex is dissolved in aqueous solution an immediate drop in pH is observed which corresponds to the instantaneous release of one mole of HCl. Furthermore, the UV–Vis spectra indicate some similarity with that reported for $Pt(dien)Cl_2 \cdot HCl$ (see further discussion). The IR spectrum of our isolated complex is in very close agreement with that published by Watt and Cude [7]. Important is the strong band at 1510 $cm^{-1}$ which was assigned to the presence of the $NH_3Cl$ group [7].

The recrystallized $Pt(dien)Cl_2 \cdot HCl$ species is most likely a monomeric ring-opened species similar to the $Pd(Me_3dien)Cl_2 \cdot HCl$ species isolated before [8]. This complex exhibits a characteristic absorption at 303 nm, which slowly decreases with time (see Fig. 1) accompanied by an increasing absorbance at 268 nm and a decrease in pH of the solution. This is ascribed to a spontaneous ring-closing reaction during which $H^+$ is released and the $Pt(dien)Cl^+$ species is produced. A $1.1 \times 10^{-3}$ M solution (pH 6.5) exhibits a drop in pH to 2.95 during this reaction, indicating the release of protons in the ratio 1:1. Furthermore, the final spectrum (Fig. 1) exhibits a maximum absorption at 268 nm with $\epsilon = 262$ $M^{-1}$ $cm^{-1}$, which is in excellent agreement with that for the $Pt(dien)Cl^+$ species reported in Table I. Addition of base to this species results in the rapid formation of $Pt(dien)OH^+$, which on acidification with HCl produces $Pt(dien)OH_2^{2+}$ and anates to $Pt(dien)Cl^+$. The IR spectrum of the isolated complex is in close agreement with that found for the chloro-bridged ring-opened species and exhibits a strong band at 1490 $cm^{-1}$ due to the presence of $NH_3Cl$.

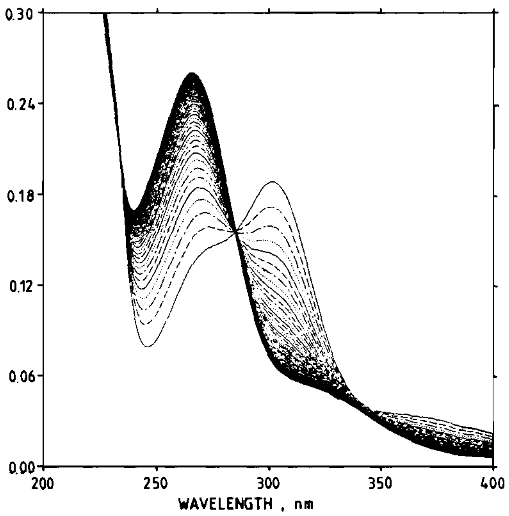

Fig. 1. Repetitive scan spectra for the ring-closure reaction of $Pt(dien)Cl_2 \cdot HCl$ in aqueous solution. [Pt] = $9.1 \times 10^{-4}$ M, $\Delta t$ = 10 min, temperature = 310 K, optical pathlength = 1 cm.

The UV-Vis spectrum of the isolated [Pt(dien)Cl]-Cl species (see Table I) is in close agreement with that reported by Alcock *et al.* [9], *viz.* $\lambda_{max} = 264$ nm and $\epsilon = 261$ $M^{-1}$ $cm^{-1}$, and those previously found in this laboratory [10, 11]. The IR spectrum of our complex is identical to that reported before [7], and as expected does not show a band around 1500 $cm^{-1}$. Significant differences exist for the aquo

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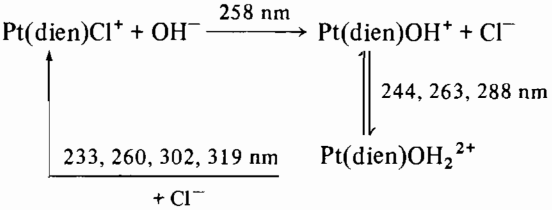
**Anal.* (theoretical value): Pt, 50.5 (50.4); Cl, 27.8 (27.5); C, 8.2 (8.2); N, 7.1 (7.2); H, 2.9 (2.2)%.

and hydroxo complexes prepared *in situ*, for which Alcock *et al.* [9] report $\lambda_{max}$ = 240 and 238 nm, and $\epsilon$ = 410 and 438 $M^{-1}$ $cm^{-1}$, respectively. Nevertheless, their isosbestic points observed at 290, 264 and 244 nm for the hydrolysis of $Pt(dien)OH_2^{2+}$ to $Pt(dien)OH^+$ are almost identical to those (288, 263 and 244 nm) observed in this study. In addition, the p$K_a$ value of 6.13 reported [9] for the aquo complex in 0.1 M $NaClO_4$ is close to that found in this study, *viz.* 6.3 and 6.4 in dilute and 1.0 M ionic strength medium, respectively. The reactions in Scheme 1 outline the usual reactivity of such complexes, and the observed isobestic points are also included.



Scheme 1.

Preliminary $^1H$ NMR measurements clearly indicated that the $Pt(dien)Cl^+$ species is significantly more symmetrical than the other two dien complexes isolated. This complex exhibits a clear triplet at 3.58 ppm and an overlap of triplets for the other $CH_2$ groups between 2.8 and 3.5 ppm. The $Pt(dien)Cl_2 \cdot HCl$ and chloro-bridged species exhibit similar, but more complex, spectra than for $Pt(dien)Cl^+$, and a detailed assignment of the resonances could not be made.

### *$Me_4$dien Complexes of Pt(II)*

The two isolated fractions of $[Pt(Me_4dien)Cl]PF_6$ exhibit significantly different absorption spectra (Table I). The deviations in the chemical analyses from the theoretically expected values are most probably due to the presence of small quantities of the chloride salt. Treatment of both fractions with $AgClO_4$ resulted in the same aquo complex with $\lambda_{max}$ at 252 nm. A spectrophotometric pH titration resulted in a p$K_a$ value of 6.1 in dilute solution. Isosbestic points observed during these reactions are included in Scheme 2. The chloro complex prepared *in situ* via anation of the aquo complex by chloride, exhibited a maximum absorption at 274 nm, *i.e.* similar to that for the second isolated fraction. The isolated chloro complex with $\lambda_{max}$ at 268 nm (fraction 1) is probably contaminated with some $Pt(Me_4dien)Cl_2 \cdot HCl$, since the latter species exhibits a structureless absorption in the UV region which will cause the 274 nm band of the chloro complex to shift to a lower wavelength. The $Pt(Me_4dien)Cl_2 \cdot HCl$ complex is most likely also a protonated ring-opened species, similar to the corresponding dien species, since it undergoes a slow change in solution which is accompanied by a decrease in pH (*i.e.* release of $H^+$) and the formation of a band at 274 nm for the ring-closed species. In the presence of base, the chloro complex undergoes hydrolysis to the $Pt(Me_4dien)OH^+$ species (clean isosbestic points at 267, 306 and 322 nm), followed by a slow subsequent irreversible decomposition reaction which is accompanied by a significant increase in absorbance and the formation of a band at 253 nm (see Fig. 2). This product is most probably a hydroxy-bridged species and subsequent acidification results in the partial formation of the chloro complex only.

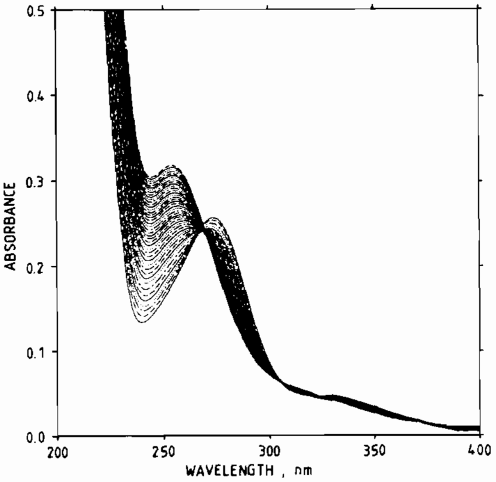
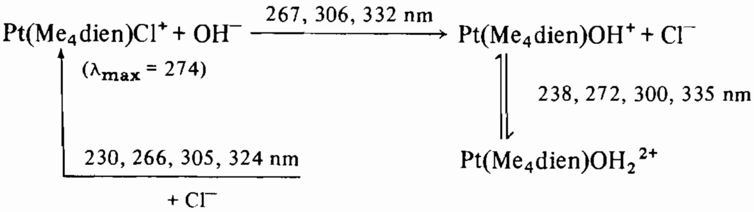


Fig. 2. Repetitive scan spectra for the base hydrolysis of $Pt(Me_4dien)Cl^+$. [Pt] = 5.7 × $10^{-4}$ M, $\Delta t$ = 60 min, temperature = 310 K, pH = 10, optical pathlength = 1 cm.

### *$Et_4$dien Complexes of Pt(II)*

According to the experimental conditions employed, it seems as if the most sterically hindered complex of the series is produced significantly faster



Scheme 2.

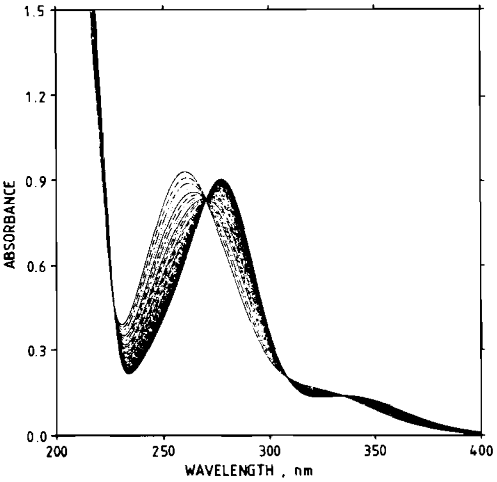


Fig. 3. Repetitive scan spectra for the anation of Pt(Et$_4$dien)-OH$_2^{2+}$ by chloride in acidic aqueous solution. [Pt] = 6 × 10$^{-3}$ M, [Cl$^-$] = 5.6 × 10$^{-2}$ M, $\Delta t$ = 45 min, temperature = 310 K, optical pathlength = 0.88 cm.

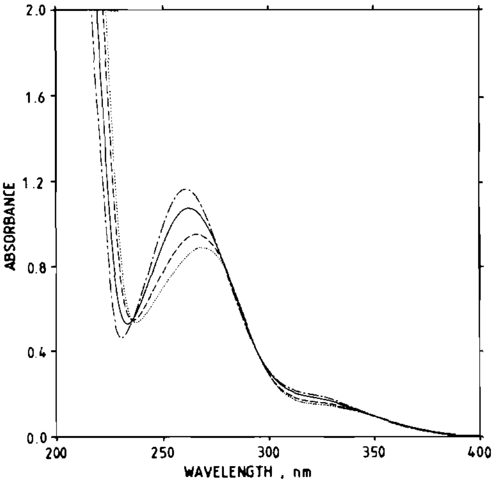


Fig. 4. Spectrophotometric determination of the acid dissociation constant of Pt(Et$_4$dien)OH$_2^{2+}$. [Pt] = 6.7 × 10$^{-3}$ M, temperature = 298 K, optical pathlength = 1 cm, ionic strength = 0.01 M. —·— pH = 3.7, —— pH = 6.0, – – – pH = 6.8, - - - -·pH = 11.4.

than the other complexes. This is mainly due to the free base of the ligand being employed, since the pH is then significantly higher than for the dien ligands in the acidic form and the deprotonated amine groups can coordinate more effectively. The isolated [Pt(Et$_4$dien)Cl]PF$_6$·HCl complex has a maximum at 280 nm and exhibits a slow ring-closure reaction accompanied by an increase in absorption and a decrease in pH. Anation of the aquo complex by Cl$^-$ produced a similar spectrum for the Pt(Et$_4$dien)Cl$^+$ species with clean isosbestic points at 229, 272, 310 and 337 nm (see Fig. 3). Deprotonation of the Pt(Et$_4$dien)OH$_2^{2+}$ species is accompanied by isosbestic points at 235, 280, 295 and 351 nm and a p$K_a$ value of 6.1 in dilute solution (see Fig. 4).

It follows from the previous sections in which the preparation and behaviour of the investigated chloro, aquo and hydroxo complexes of Pt(II) were described, that the systems are significantly more complicated than for the corresponding Pd(II) complexes. This must be related to the inertness of the PtCl$_4^{2-}$ species enabling the formation of various intermediate species. In general it is possible to isolate ring-opened species, most probably of dimeric nature, *i.e.* chloro bridged, of which the isolation strongly depends on the acidity of the medium. Although complexes of the type [Pt(dien)X]X are widely used by investigators in different fields, details on their preparation are only given in a few papers [6, 7, 9, 12, 13] and hardly any UV–Vis spectral data have been reported. This is a dangerous situation in the light of our present findings since the different isolated species exhibit very different kinetic behaviour. The stabilization of ring-opened species can be associated with the stability of the Pt–Cl bond. Similarly, the lability of the Pd–Cl bond accounts for the fact that ring-closed species are usually isolated, with the exception of the one complex referred to above [8]. The strength of the metal–ligand bond in the case of the Pt(II) complexes is also reflected in the p$K_a$ values for the aquo complexes reported in this paper, which are on the average *ca.* one unit lower than for the corresponding Pd(II) complexes [3].

### *Formation of Carbonato Complexes*

Various procedures were adopted in an effort to synthesize carbonato complexes of the type Pt(R$_5$dien)OCO$_2$ similar to those of the corresponding Pd complexes [2]. The procedures included reactions with CO$_2$(g) or HCO$_3^-$ in various pH and concentration ranges, under mild and extreme conditions (*viz.* boiling under reflux), and in the presence of carbonic anhydrase, a biochemical catalyst. Our earlier experience with the corresponding Pd complexes demonstrated that a pH of between 8 and 10 was very favourable for such complexation reactions. Our very extensive efforts [14] indicated that no carbonato complexes are produced under all conditions employed, neither via CO$_2$ uptake, nor via HCO$_3^-$ anation.

The absence of CO$_2$ uptake by Pd–OH complexes was interpreted in terms of a presumably peculiar nature of the metal–hydroxy bond. Furthermore, this process has to compete with substitution reactions of the corresponding aquo complexes, which are known to be fairly labile. The less labile platinum aquo complexes exhibit similar characteristics, indicating that CO$_2$ uptake definitely does not occur to a detectable extent. It follows that square planar hydroxo species cannot take up CO$_2$ in the way octahedral species do [1]. A possible reason may be the ability of the hydroxy ligand to form an additional bond with the vacant $P_z$ orbital on the metal atom, *i.e.* a semi-five-coordinate species. In such a case the decrease in electron density on the oxygen atom will restrict the binding with $CO_2$, and account for the inertness of such species. The absence of any observable substitution reaction (water for bicarbonate) can either be due to the stability of the $Pt-OH_2$ bond or the weak nucleophilicity of the $HCO_3^-$ ligand [2]. Substitution by $CO_3^{2-}$ is not considered since under such conditions the complex will be present in solution as the inert hydroxo species [4, 5].

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